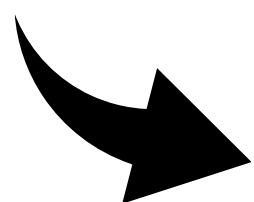


HYDRA BOOKS

KARMA

[Click here to join our](#)
[telegram channel for more](#)
[amzing content](#)





ARJUNA

for

JEE
MAIN & ADVANCED

CHEMISTRY

FULL COURSE STUDY MATERIAL

Class XI

- IUPAC Nomenclature
- Isomerism
- General Organic Chemistry
- Hydrocarbon
- Environmental Chemistry
- Purification, Quantitative and Qualitative Analysis of Organic Compounds

Module-4





CONTENTS

Chemistry Module-4

1-260

12	IUPAC Nomenclature	1-42
13	Isomerism	43-97
14	General Organic Chemistry	98-143
15	Hydrocarbon	144-209
16	Environmental Chemistry	210-233
17	Purification, Quantitative and Qualitative Analysis of Organic Compounds.....	234-260

CHAPTER

12

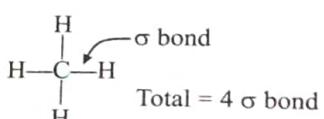
IUPAC Nomenclature

BONDING IN ORGANIC COMPOUNDS

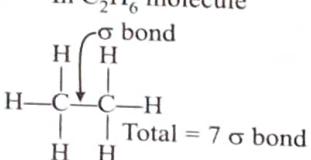
Two types of covalent bond exist in organic compounds.

- (a) **Sigma bond (σ):** The covalent bond formed between 2 atoms by mutual sharing of 1 pair of e^- . It is denoted by (-).

Ex. In CH_4 molecule

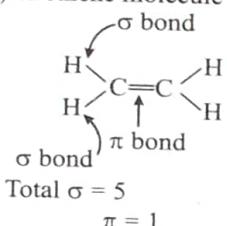


In C_2H_6 molecule

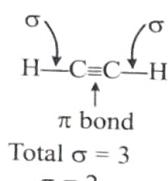


- (b) **Multiple bond (π):** Any other bond with σ bond is π bond.

Ex. (i) In ethene molecule



(ii) In ethyne molecule



Ex. Calculate σ and π bond in following compounds.

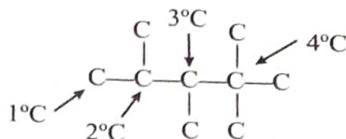
- (a) $\text{HC}\equiv\text{CCH}=\text{CHCH}_3$
 (b) $\text{CH}_2=\text{C}=\text{CHCH}_3$

Sol. (a) $\sigma_{\text{C-C}}: 4$; $\sigma_{\text{C-H}}: 6$; $\pi_{\text{C=C}}: 1$; $\pi_{\text{C}\equiv\text{C}}: 2$
 (b) $\sigma_{\text{C-C}}: 3$; $\sigma_{\text{C-H}}: 6$; $\pi_{\text{C=C}}: 2$

Some Important Definitions

- (i) **Catenation:** The property of atoms of an element to link with one another forming chains of identical atoms is called catenation.
- (ii) **Homologous series:** Homologous series may be defined as a series of similarly constituted compounds in which the members possess the same functional group, have similar chemical characteristics and have a regular gradation in their physical properties. The two consecutive members differ in their molecular formula by CH_2 .
- (iii) **Classification of Carbon:** There are four types of carbon present in organic compounds. The carbon which is directly attached with one, two, three and four carbon atoms are known as primary, secondary, tertiary and quaternary carbon atom respectively.

On the basis of carbon atom, hydrogen atoms bonded with 1°, 2° or 3° are named as primary, secondary or tertiary hydrogen atom respectively.



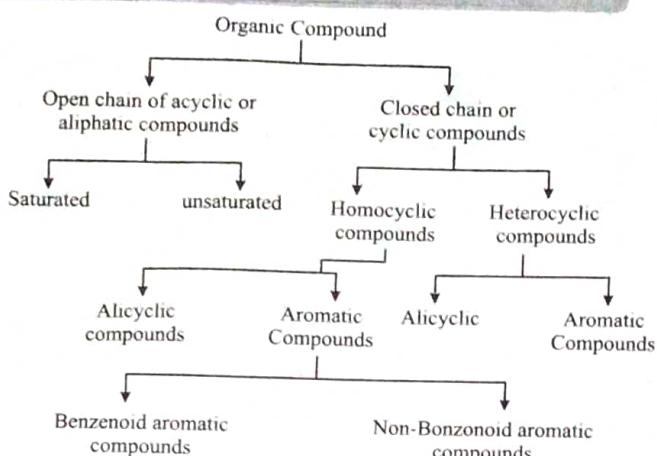
STRUCTURAL REPRESENTATION OF ORGANIC COMPOUNDS

There are three ways for representation of organic compounds:

- (i) **Complete structural formula:** Such a structural formula focuses on the electrons involved in bond formation. A single dash (-) represents a single bond, double dash (=) is used for double bond and a triple dash (\equiv) represents triple bond. Lone-pairs of electrons on heteroatoms (e.g., oxygen, nitrogen, sulphur, halogens etc.) may or may not be shown.
- (ii) **Condensed structural formula:** Structural formulas can be further abbreviated by omitting some or all of the dashes representing covalent bonds and by indicating the number of identical groups attached to an atom by a subscript. The resulting expression of the compound is called a condensed structural formula.
- (iii) **Bond line formula:** In this formula, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are drawn in a zig-zag fashion. The only atoms specifically written are oxygen, chlorine, nitrogen etc.

Condensed form	Expanded form	Bond line form
$\text{C}(\text{CH}_3)_4$	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C} \\ \\ \text{H} \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \\ \\ \text{H} \end{array}$	
$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C} \quad \text{C}-\text{C} \\ \quad \\ \text{H} \quad \text{H} \\ \\ \text{H} \end{array}$	
$\text{H}_2\text{N}(\text{CH}_2)_2\text{OCH}_3$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{N} \quad \text{C} \quad \text{C}-\text{O} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	

CLASSIFICATION OF ORGANIC COMPOUNDS



ORGANIC COMPOUNDS AND FUNCTIONAL GROUPS

Number of known organic compounds is much more than inorganic compounds but, it has been possible to group them into classes or families based on their structural features. This has given organic chemistry a logical and systematic shape. Examples are as follows:

Alkanes [general formula C_nH_{2n+2} where $n = 1, 2, 3, \dots$]

These are open-chain aliphatic saturated hydrocarbon which have no functional groups. These are also called **paraffins**.

$n = 1 \Rightarrow \text{CH}_4$	-	Methane
$n = 3 \Rightarrow \text{CH}_3\text{CH}_2\text{CH}_3$	-	Propane
$n = 5 \Rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	-	Pentane
$n = 2 \Rightarrow \text{C}_2\text{H}_6$	-	Ethane
$n = 4 \Rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	-	Butane
$n = 10 \Rightarrow \text{CH}_3(\text{CH}_2)_8\text{CH}_3$	-	Decane

Alkenes [general formula C_nH_{2n} , where $n = 2, 3, \dots, 10$]

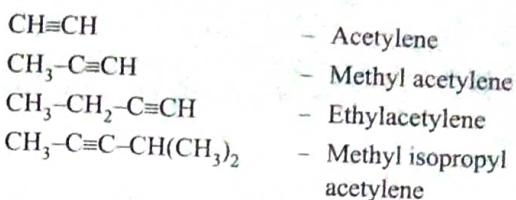
Alkenes are open chain unsaturated hydrocarbons and having carbon–carbon double bonds ($C = C$). These are also called **alkylenes or olefins**. The first three members are generally named by their common names.

Ex.	$\text{CH}_2 = \text{CH}_2$ Ethylene	$\text{CH}_3 - \text{CH} = \text{CH}_2$ Propylene
		CH_3 $\text{CH}_3 - \text{C} = \text{CH}_2$

Alkynes [general formula C_nH_{2n-2} , where $n = 2, 3, \dots$]

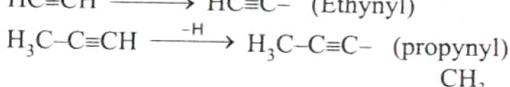
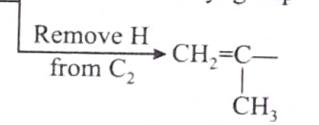
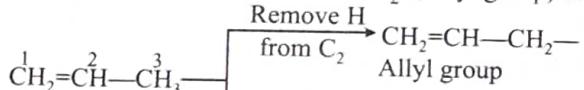
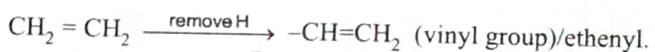
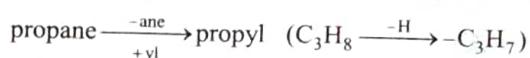
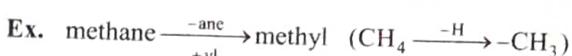
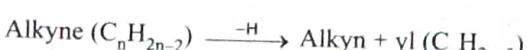
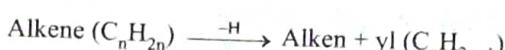
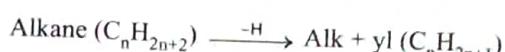
Unsaturated aliphatic hydrocarbons containing a carbon–carbon triple bond are called alkynes.

The common names of a few simple alkynes are given below.



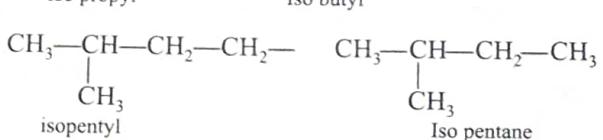
Some Names of Hydrocarbon Groups

(A) Alkyl, Alkenyl & Alkynyl groups



(B) **Iso alkyl group:** A compound having $-\text{CH}_2\text{CH}_3$ group is called iso alkyl group.

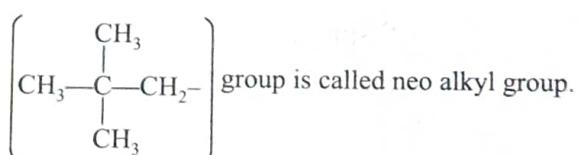
Ex. $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-$ $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-$

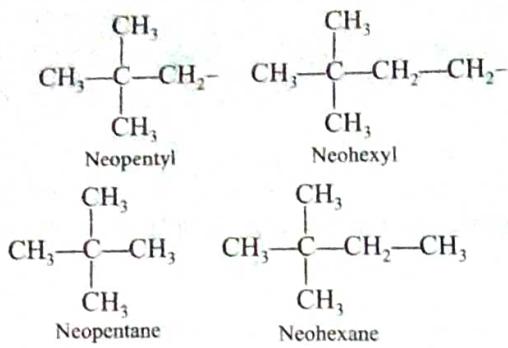


Exception: Isooctane

$$\text{CH}_3 - \underset{\text{CH}_3}{\underset{|}{\text{C}}} - \text{CH}_2 - \underset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH}_3$$

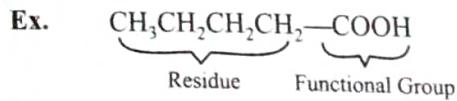
(C) **Neo alkyl group:** Compound having



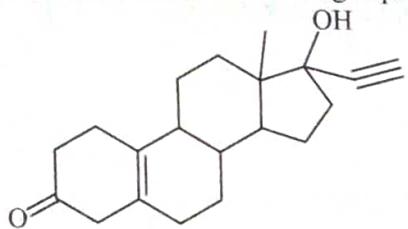
Ex.**Functional Group and Residue**

The characteristic group of atom which decide the physical and chemical properties of an organic molecule is called functional group.

Functional group is that portion of molecule which is highly reactive and takes part in chemical reactions. Rest of the molecule is called Residue.

**Train Your Brain**

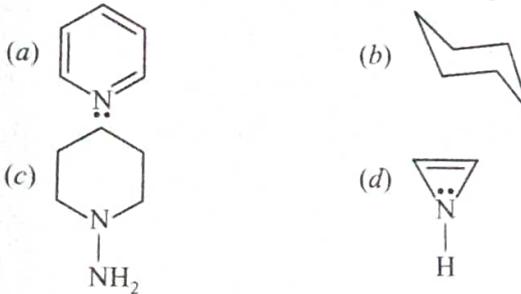
Example 3: How many different functional groups are present?



- (a) 3 (b) 4 (c) 5 (d) 6

Sol. (b) $(-\text{OH}), (-\equiv-), (-=\text{=}), (-\text{C}\text{=O}-)$
Functional groups.

Example 4: The saturated heterocyclic compound is:

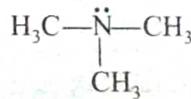


Sol. (c) Saturated heterocyclic compounds do not have any unsaturation & have atleast one hetero atom within the ring.

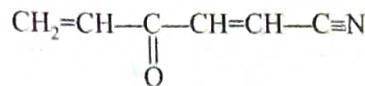
Example 5: The simplest tertiary amine has:

- (a) 2 carbons (b) 3 carbons
(c) 4 carbons (d) 5 carbons

Sol. (b) tertiary amine

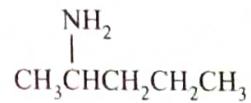
**Concept Application**

4. The number of olefinic bonds in the given compound is/are:



- (a) 2 (b) 3
(c) 1 (d) 4

5. The compound below is classified as a _____.



- (a) Primary amine (b) Secondary amine
(c) Tertiary amine (d) Primary amide

IUPAC SYSTEM OF NOMENCLATURE

The IUPAC name of any organic compound consists of maximum five parts in the following sequence.

Secondary prefix + Primary prefix + Word root + Primary suffix + Secondary suffix

Word Root

It is the basic unit of the name. It denotes the number of carbon atoms present in the principal chain (the longest possible continuous chain of carbon atoms including the functional group and based upon the common names of alkanes) of the organic molecules.

No. of carbon atoms in parent chain	Word root (Alk)	No. of carbon atoms in parent chain	Word root (Alk)	No. of carbon atoms in parent chain	Word root (Alk)
1	Meth	9	Non	20	Icos
2	Eth	10	Dec	30	Triacont
3	Prop	11	Undec	40	Tetracont
4	But	12	Dodec	50	Pentacont
5	Pent	13	Tridec	60	Hexacont
6	Hex	14	Tetradec	70	Heptacont
7	Hept	15	Pentadec	80	Octacont
8	Oct	16	Hexadeca	100	Cent & Hect

Primary Suffix

A primary suffix is always added to the word root to indicate whether the carbon chain is saturated or unsaturated. The three basic primary suffixes are given below:

Type of carbon chain	Primary suffix	General name
(a) Saturated	-ane	Alkane
(b) Unsaturated with one double bond	-ene	Alkene
(c) Unsaturated with one triple bond	-yne	Alkyne

If the parent carbon chain contains two, three or more double or triple bonds, numerical prefix such as di (for two), tri (for three), tetra (for four) etc. are added to the primary suffix.

For example,

Type of carbon chain	Primary suffix	General name
(a) Unsaturated with two double bonds	(a) + diene	Alkadiene
(b) Unsaturated with two triple bonds	(a) + diyne	Alkadiyne
(c) Both double and triple bonds	enyne	Alkenyne

Secondary Suffix

A secondary suffix is then added to the primary suffix to indicate the nature of the functional group present in the organic compounds. Secondary suffix of important functional groups are given below in their decreasing order of seniority.

S.No.	Class	Name	Suffix	Prefix
1.	R - COOH	Alkanoic Acid	-oic acid (carboxylic acid)	Carboxy
2.	R - SO ₃ H	Alkane sulphonic Acid	-sulphonic acid	sulpho
3.	$\begin{array}{c} R-C-O-C-R \\ \quad \\ O \quad O \end{array}$	Alkanonic Anhydride	-oic anhydride (carboxylic anhydride)	-----
4.	R - COOR	Alkyl alkanoate	-oate (carboxylate)	alkoxy carbonyl or alkanoyl oxy
5.	$\begin{array}{c} R-C-X \\ \\ O \end{array}$	Alkanoyl halide	-oyl halide (carbonyl halide)	halo carbonyl
6.	$\begin{array}{c} R-C-NH_2 \\ \\ O \end{array}$	Alkanamide	-amide (carboxamide)	carbamoyl
7.	R - C ≡ N	Alkanenitrile	-nitrile (carbonitrile)	cyano
8.	$\begin{array}{c} R-C-H \\ \\ O \end{array}$	Alkanal	-al (carbaldehyde)	formyl / oxo
9.	$\begin{array}{c} R-C-H \\ \\ O \end{array}$	Alkanone	-one	oxo
10.	R - OH	Alkanol	-ol	hydroxy
11.	R - SH	Alkanethiol	-thiol	mercapto
12.	R - NH ₂	Alkanamine	-amine	amino

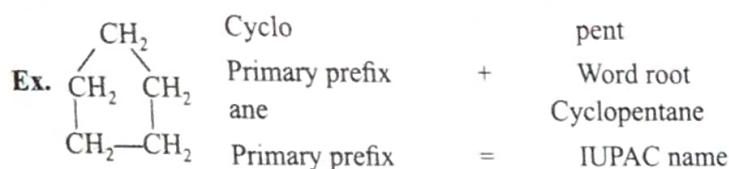
The following examples illustrate the use of word root, primary suffix and secondary suffix in naming of organic compounds.

Organic compounds	Word root	Primary suffix	Secondary suffix	IUPAC name
$\text{CH}_3\text{CH}_2\text{OH}$	Eth	an(e)	ol	Ethanol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	Prop	an(e)	amine	Propanamine
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	But	an(e)	oic acid	Butanoic acid
$\text{CH}_3\text{CH}_2\text{CN}$	Prop	an(e)	nitrile	Propanenitrile
$\text{CH}_2=\text{CHCHO}$	Prop	en(e)	al	Propenal
$\text{HC}=\text{CCOOH}$	Prop	yn(e)	oic acid	Propynoic acid

Primary Prefix

A primary prefix is used simply to distinguish cyclic from acyclic compounds.

For example, in case of carbocyclic compounds, (cyclic compounds containing only carbon atoms in the ring), a primary prefix, **cyclo** is used immediately before the word root. Thus,



If the prefix *cyclo* is not used, it simply indicates that the compound is acyclic or open chain.

Secondary Prefix

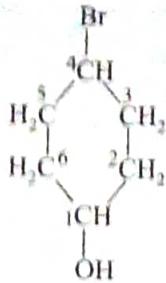
In IUPAC system of nomenclature, certain groups are not considered as functional groups but are treated as substituents. These are called secondary prefixes and are added immediately before the word root (or the primary prefix in case of carbocyclic compounds) in alphabetical order to denote the side chains or substituent groups. The secondary prefixes for some groups which are always treated as substituent groups (regardless of the fact whether the organic compound is monofunctional or polyfunctional) are given below:

Substituent group	Secondary prefix	Substituent group	Secondary prefix
- F	Fluoro	- OCH ₃ (- OMe)	Methoxy
- Cl	Chloro	- OC ₂ H ₅ (- OEt)	Ethoxy
- Br	Bromo	- R	Alkyl
- I	Iodo	- CH ₃ (- Me)	Methyl
- NO ₂	Nitro	- C ₂ H ₅ (- Et)	Ethyl
- NO	Nitroso	- CH ₂ CH ₂ CH ₃ (n-Pr)	n-Propyl
- N [⊕] ≡N	Diazo	- CH(CH ₃) ₂ (- iPr)	Isopropyl
- OR	Alkoxy	- C(CH ₃) ₃ (t-Bu)	t-Butyl

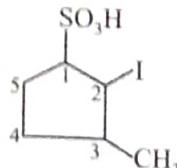
Example:

Organic compounds	"Secondary prefix"	Word root	"Primary suffix"	IUPAC name
$\text{CH}_3\text{CH}_2\text{-Br}$	Bromo	eth	ane	Bromoethane
$\text{CH}_3\text{-NO}_2$	Nitro	meth	ane	Nitromethane
$\text{C}_2\text{H}_5\text{-OC}_2\text{H}_5$	Ethoxy	eth	ane	Ethoxyethane

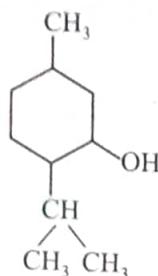
Ex.



4-Bromo
Secondary prefix + cyclo Primary prefix + hex Word root + an(e) Primary prefix + 1-ol Secondary suffix



2-Iodo-3-methyl
Secondary prefix + cyclo Primary prefix + pent Word root + ane Primary suffix + 1-sulphonic acid Secondary suffix

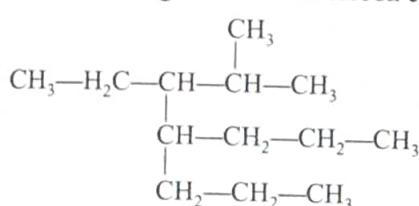


2-Isopropyl-5-methyl
Secondary prefix + cyclo Primary prefix + hex Word root + an(e) Primary suffix + ol Secondary suffix

IUPAC NOMENCLATURE OF BRANCHED/ COMPLEX ALKANES

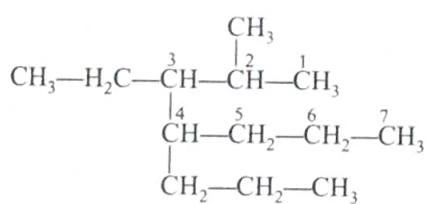
Parent Carbon Chain Selection

(a) Select the longest continuous carbon chain in the molecule.



Longest chain has 7 carbons so word root is "Hept"

(b) When chains of equal lengths are competing for selection then that chain is selected which has more number of substituents/branches.



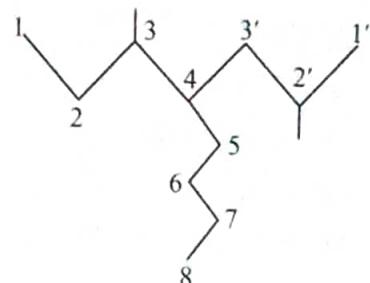
longest chain has 7 carbon & 3 substituents

- (c) When the number of substituents are same then the substituents at the nearest positions from the either end is prefer for parent chain selection.

Ex. Here , 2 choices for longest chain

Chain- (A) 1-2-3-4-5-6-7-8

Chain- (B) 1'-2'-3'-4'-5'-6'-7'-8'



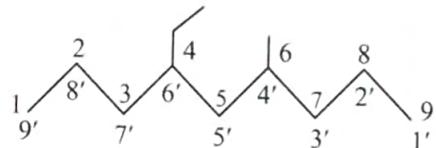
Chain- (A) & Chain- (B) both have 2 substituents but in chain-B substituent is nearer (at 2nd position) than in chain-A (at 3rd position). So, chain-B will be preferred.

- (d) If the two substituents are found in equivalent positions the lower number is given to the one coming first in the alphabetical order.

Ex. Here , 2 choices for longest chain

Chain- (A) 1-2-3-4-5-6-7-8-9

Chain- (B) 1'-2'-3'-4'-5'-6'-7'-8'-9'



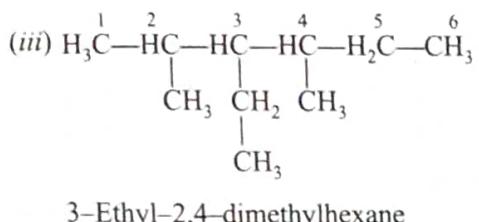
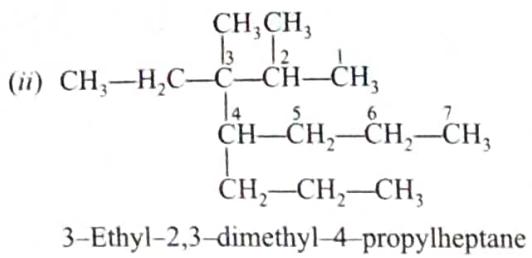
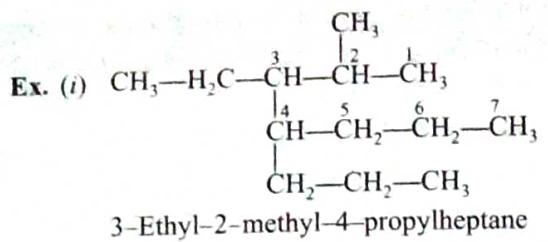
In both chain-A and chain-B, substituents are at same position (4th). In chain-A substituent is ethyl and in chain-B, it is methyl. Alphabetically ethyl will be preferred. So, chain-A is selected.

Numbering of the Parent Carbon Chain

The numbering is done in such a way that the branched carbon atoms get the lowest possible number:

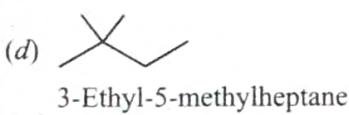
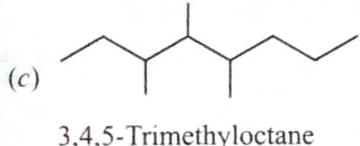
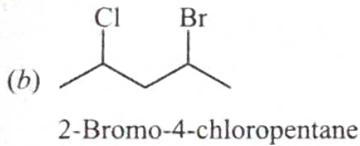
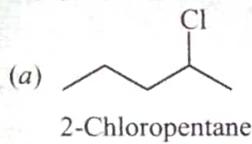
Note:

- (1) Write the substituents in place of secondary prefix with their appropriate locations in alphabetical order.
- (2) If the same substituent occurs more than once in the molecule, the prefix di (for two), tri (for three), etc. are used to indicate how many times it appears.
- (3) Prefixes di, tri, tetra etc. are not considered in deciding alphabetical order for simple substituents but considered for complex substituents.
- (4) Iso & Neo is considered for alphabetical seniority order.
- (5) Numbers are separated from each other by commas(,).
- (6) Numbers are separated from words by hyphens and there is no break between name of substituents and word root.



Train Your Brain

Example 6: Which is incorrect IUPAC name?



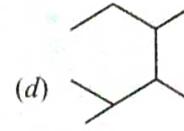
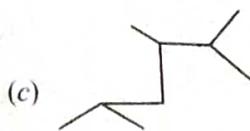
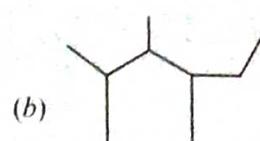
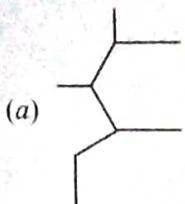
Sol. (d) In (b) IUPAC naming is not in alphabetical order.

Example 7: A student named a certain compound as 2,3-diethylbutane. its correct IUPAC names is:

- (a) 2,3-Dimethylhexane
- (b) 3,4-Dimethylhexane
- (c) 2-Ethyl-3-methylpentane
- (d) 2-Ethylbutane

Sol. (b) Longest chain has 6 carbon and at 3, 4 position ($-\text{CH}_3$) is substituent group.

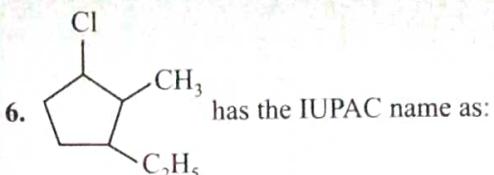
Example 8: Which is the incorrect structure of 2,3,4-Trimethylhexane:



Sol. (c) In (c) methyl is present at 2, 3 and at 5 position of the chain.

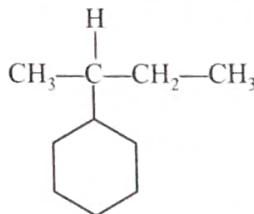


Concept Application



- (a) 3-Chloro-1-ethyl-2-methylcyclopentane
- (b) 1-Chloro-3-ethyl-2-methylcyclopentane
- (c) 4-Chloro-1-ethyl-5-methylcyclopentane
- (d) None of above

7. IUPAC name of the following compound is:



- (a) 2-Cyclohexylbutane
- (b) 2-Phenylbutane
- (c) 3-Cyclohexylbutane
- (d) 1-(Methylpropyl)cyclohexane

IUPAC Nomenclature of Alkenes/Alkynes/Alkenyne Alkenes

Functional group: $-\text{C}=\text{C}-$

- (1) Select the longest carbon chain containing carbon-carbon double bond. This need not be the longest chain in the compound as a whole. Parent name will be alkenes corresponding to number of carbon atoms in the longest chain.

(5) If ring has unsaturation and side chain is saturated then ring is selected as parent chain.

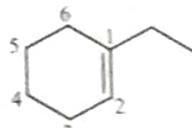
If side chain has unsaturation and ring is saturated then side chain is selected as parent chain.

If both have unsaturation the chain with maximum unsaturation has selected as parent chain.

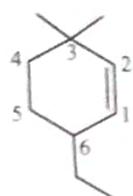
If equal unsaturation then longest chain is selected as parent chain.

If unsaturation and number of carbon atoms both are equal then ring is selected as parent chain.

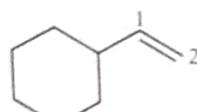
Ex.



1-Ethylcyclohex-1-ene



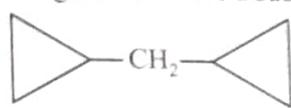
6-Ethyl-3,3-dimethylcyclohex-1-ene



Cyclohexyl ethene

(6) If more than one alicyclic ring is attached to a single chain then the compound is named as a derivative of alkane and the ring are treated as a substituent group.

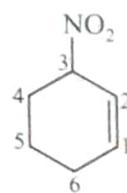
Ex.



Dicyclopropylmethane

(7) If a multiple bond and some other substituents are present in the ring, the numbering is done in such a way that the multiple bond gets the lowest number

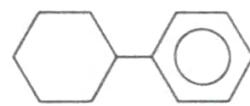
Ex.



3-Nitrocyclohex-1-ene

(8) If a compound contains an alicyclic ring directly linked to the benzene ring. It is named as a derivative of benzene.

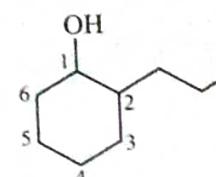
Ex.



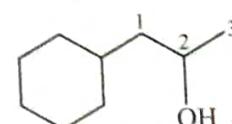
Cyclohexylbenzene

(9) If functional group is present in cyclic compounds then the main chain is taken in which principal functional lie's, if the principal functional group is present in ring also then main chain will be taken for the maximum no. of carbon atoms.

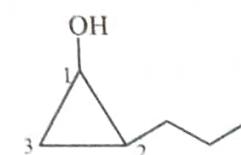
Ex.



2-Propylcyclohexan-1-ol



1-Cyclohexylpropan-2-ol



2-Propyl cyclopropan-1-ol

(10)

When chain terminating functional group is directly attached with ring then ring is taken as parent chain & special suffix is used for this functional group.

Functional Group

Suffix

CHO

Carbaldehyde

COOH

Carboxylic Acid

COX

Carbonyl halide

COOR

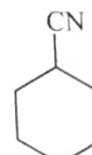
Alkyl Carboxylate

CONH₂

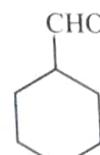
Carboxamide

CN

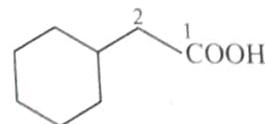
Ex.



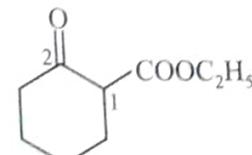
Cyclohexanecarbonitrile



Cyclohexanecarbaldehyde



2-Cyclohexyl ethanoic acid

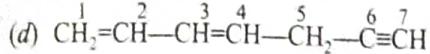
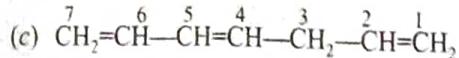
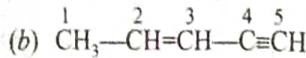
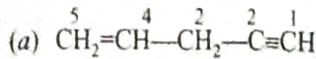


Ethyl 2-oxocyclohexane-1-carboxylate

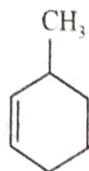


Train Your Brain

Example 9: Select the structure with correct numbering in the chain:



Sol. (d) In (d) lowest sum is $(1 + 3 + 6) = 10$ numbering should be from alkene side (Alphabetical order).



Example 10: The IUPAC name of

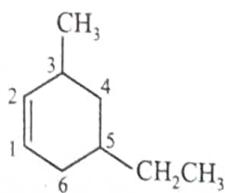
(a) 1-Methyl-5-ethyl cyclohex-2-ene

(b) 5-Ethyl-3-methyl cyclohex-1-ene

(c) 4-Ethyl-6-methyl cyclohex-1-ene

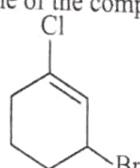
(d) 1-Ethyl-5-methyl cyclohex-3-ene

Sol. (b)



Concept Application

8. The IUPAC name of the compound shown below is:



(a) 2-Bromo-6-chlorocyclohex-1-ene

(b) 6-Bromo-2-chlorocyclohexene

(c) 3-Bromo-1-chlorocyclohexene

(d) 1-Bromo-3-chlorocyclohexene

Sol. (c)

9. IUPAC name of $\text{CH}_3-\text{CH}=\text{C}=\text{CH}-\text{C}\equiv\text{CH}$ is:

(a) 2-Hexen-4-yne

(b) Hexa-2,3-dien-1-yne

(c) Hexa-3,4-dien-1-yne

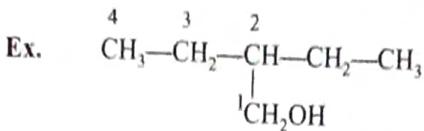
(d) None of these

Sol. (c)

IUPAC Nomenclature of Compounds Containing Functional Groups

Rules for non chain terminating functional groups

(1) **Parent chain:** Select the longest possible chain with maximum functional group and maximum unsaturation without caring whether it also denotes the longest possible chain or not.

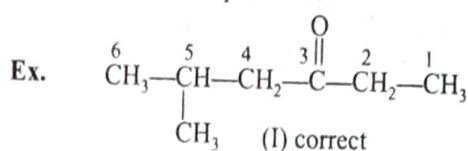


2-Ethyl butan-1-ol

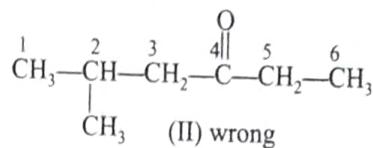
(Parent chain contains four rather than five carbon atoms)

(2) Lowest number for the functional group

Numbering is done from that side of the chain which gives lowest locant to the principle functional group followed by double and triple bonds.



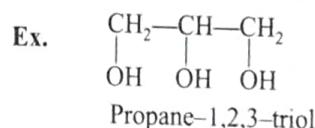
5-Methyl hexan-3-one



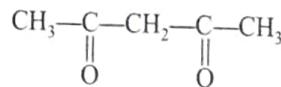
(C=O group gets lowest number 3)

(C=O group gets number 4 which is not lowest)

(3) If a compound contains two or more like groups, the numerical prefixes di, tri, tetra etc. are used.



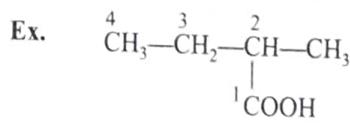
Propane-1,2,3-triol



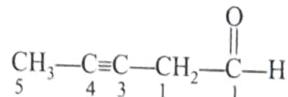
Pentane -2, 4-dione

Rules for Chain Terminating Functional Groups

(1) When a chain terminating functional group such as $-\text{CHO}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{CONH}_2$, $-\text{COCl}$, $-\text{C}\equiv\text{N}$ etc. is present, it is always given number 1 (one.)



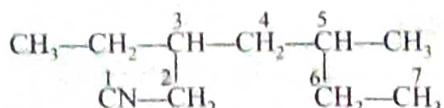
2-Methylbutan-1-oic acid



Pent-3-yn-1-al



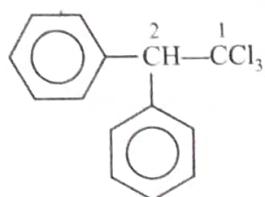
Ex. Write the IUPAC name of the given compound.



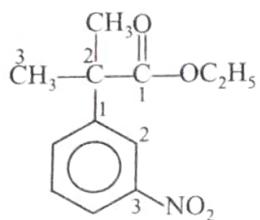
Sol.

- The longest chain containing functional group is of 7 carbon atoms. Therefore, the word root is hept & the chain is numbered as shown.
- There is no multiple bond in it. Hence, the primary suffix is **ane**.
- The functional groups is $-\text{CN}$. Hence, secondary suffix is **nitrile**.
- Moreover, there is a methyl group on carbon 5 and ethyl group on carbon 3.
- The IUPAC name is, therefore, **3-Ethyl-5-methyl heptanenitrile**

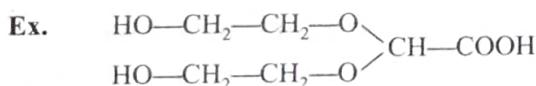
- (2) The name for benzene as substituent is phenyl. In case the phenyl ring is further substituted, the carbon atoms of the ring directly attached to the parent chain in such a ways that the substituent on the ring gets the least possible number. For example:



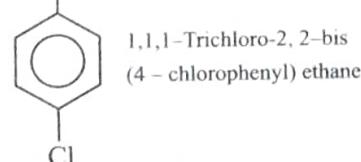
1, 1,1-Trichloro-2,2-diphenylethane



- (3) If the organic molecule contains more than one similar complex substituents, then the numeral prefixes such as di, tri, tetra etc. are replaced by bis, tris, tetrakis etc. respectively.

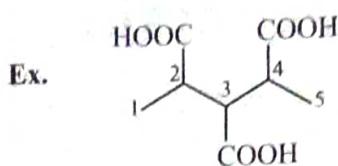


2,2-Bis (2-hydroxyethoxy) ethanoic acid

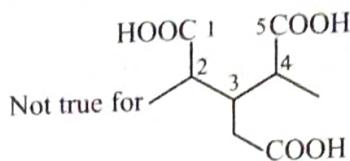


Note: Common name is D.D.T. (Dichloro diphenyl trichloro ethane) and is used as insecticide.

- (4) When 3 or more principle functional groups are directly attached with an open chain, then special suffix is used.



Pentane- 2, 3, 4-tricarboxylic acid.

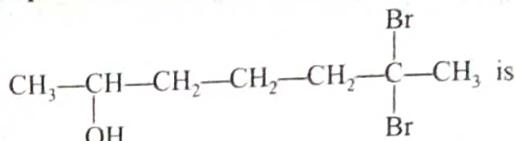


3-Carboxymethyl-2,4- dimethylpentanedioic acid.

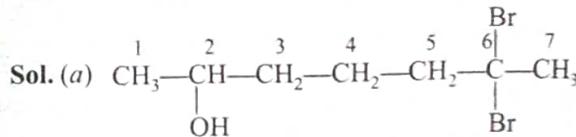


Train Your Brain

Example 11: The IUPAC name of

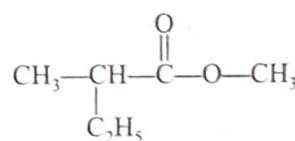


- (a) 6,6-Dibromoheptan-2-ol
- (b) 2,2-Dibromoheptan-6-ol
- (c) 6,6-Dibromoheptan-2-al
- (d) None of these



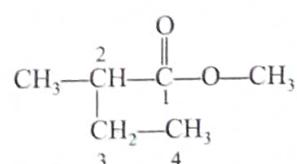
Select the longest chain and alcohol will be in its parent chain.

Example 12: The correct IUPAC name of following compound is:



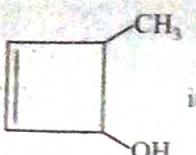
- (a) Methyl-2-ethylpropanoate
- (b) Methylbutane-2-carboxylate
- (c) Methyl-2-methylbutanoate
- (d) Methoxypentanone

Sol. (c)



Priority has given 1 to ester group.

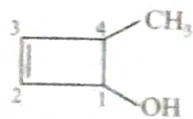
Example 13: The IUPAC name of



is:

- 4-Methylcyclobut-1-en-3-ol
- 2-Methylcyclobut-3-en-1-ol
- 2-Methylcyclobut-1-en-3-ol
- 4-Methylcyclobut-2-en-1-ol

Sol.

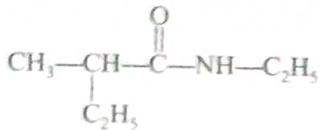


Alcohol has given priority over alkene.



Concept Application

10. The IUPAC name of the compound is:



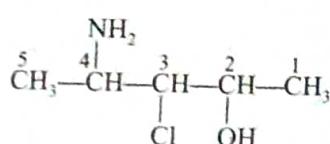
- N-Ethyl-2-ethylpropanamide
- N-Ethyl-2-methylbutanamide
- N-Ethyl-2-methylpropanecarboxamide
- N-Ethyl-2-ethylethanecarboxamide

11. The correct structure for the compound Hept-3-en-5-yn-2-one is:

- $\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_3$
- $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_3$
- $\text{H}_3\text{C}-\text{HC}=\text{CH}-\text{CH}=\text{CH}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_3$
- $\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_3$

(2) Some functional group such as all halo groups (fluoro, bromo, chloro, iodo), nitroso (NO) nitro ($-\text{NO}_2$) and alkoxy ($-\text{OR}$) are always treated as substituent groups.

Ex.

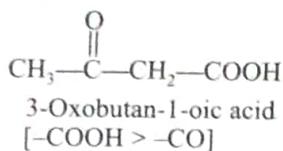


4-Amino-3-chloropentan-2-ol
($-\text{NH}_2$ & $-\text{Cl}$ group treated as substituent)

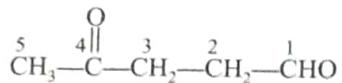
Note: Numbering the principal chain order is:

[Principal functional group > double bond > triple bond > substituents]

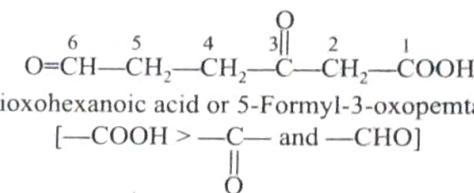
Ex.



3-Oxobutan-1-oic acid
[- COOH > - CO]



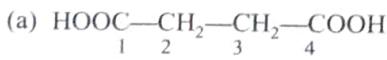
4-Oxopentan-1-al
[- CHO > C=O]



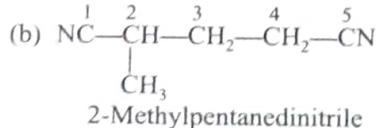
3, 6-Dioxohexanoic acid or 5-Formyl-3-oxopentanoic acid
[- COOH > C=O and $-\text{CHO}$]

(3) If more than one same chain terminating group are present then the principal chain is selected including the functional groups and numbering is done from that side which gives lowest locant to unsaturation and substituents.

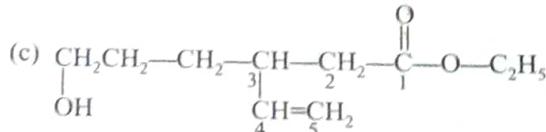
Ex.



Butane-1, 4 dioic acid



2-Methylpentanedinitrile



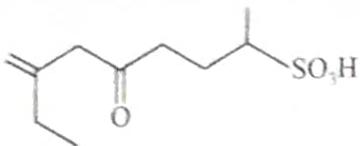
Ethyl-3-(3-hydroxy propyl) pent-4-enoate

Parent chain contains five rather than six carbon atoms.



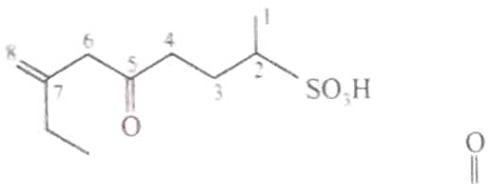
Train Your Brain

Example 14: The correct IUPAC name of the compound is:



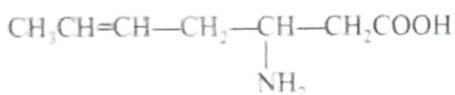
- (a) 6-Ethyl-1-methyl-4-oxohept-6-ene-1-sulphonic acid
- (b) 7-Ethyl-5-oxooct-7-ene-2-sulphonic acid
- (c) 2-Ethyl-7-sulphooct-1-ene-4-one
- (d) 7-Methylene-5-oxononane-2-sulphonic acid

Sol. (b)

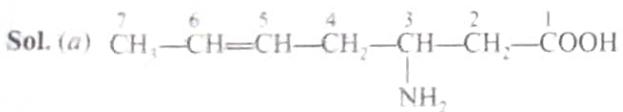


$(-\text{SO}_3\text{H})$ has given priority over $(-\text{C}=\text{C}-)$ and $(-\text{C}=\text{O}-)$.

Example 15: The IUPAC name of the following is:



- (a) 3-Aminohept-5-enoic acid
- (b) 5-Aminohex-2-enecarboxylic acid
- (c) 3-Aminohept-4-enoic acid
- (d) 5-Aminohept-2-enoic acid

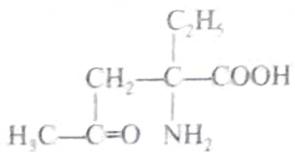


$(-\text{COOH})$ had been given priority over $(-\text{NH}_2)$ and $(-\text{C}=\text{C}-)$ functional group.



Concept Application

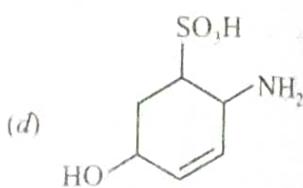
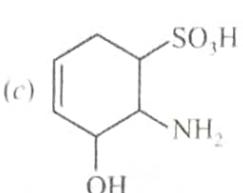
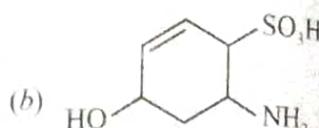
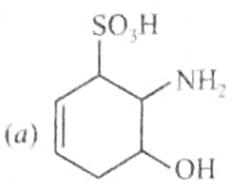
12. The IUPAC name of given compound is:



- (a) 2-Oxo-4-amino-4-ethylpentanoic acid
- (b) 2-Amino-4-oxo-2-ethylpentanoic acid
- (c) 3-Amino-3-carboxy-5-hexanone
- (d) 2-Amino-2-ethyl-4-oxopentanoic acid

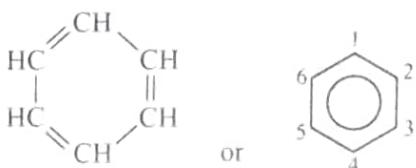
13. The correct structure of 6-Amino-4-hydroxycyclohex-

2-ene-1-sulphonic acid:



NOMENCLATURE OF AROMATIC COMPOUNDS

The aromatic compounds are cyclic compounds which contain one or more benzene type rings. Benzene is the simplest hydrocarbon of aromatic series which has planar cyclic ring of six carbon atoms having three double bonds in alternate positions as shown below.

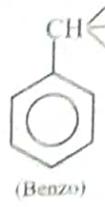


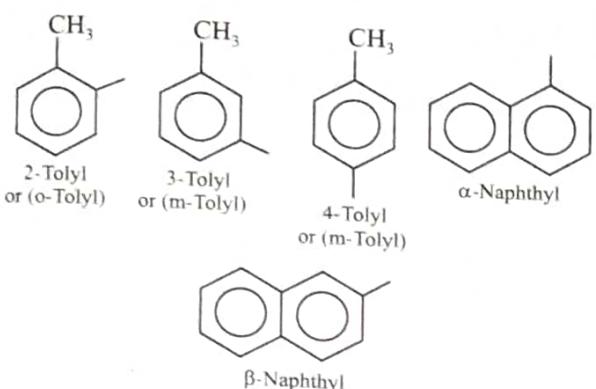
(i) Nuclear substituted: The functional group is directly attached to the benzene ring, in the IUPAC system they are named as derivatives of benzene. The position of the substituents in disubstituted benzenes are indicated either by prefixes such as o-(ortho) for 1,2,m-(meta) for 1,3 and p-(para) for 1,4 position. However, many of their common names have also been adopted by the IUPAC system.

(ii) Side chain substituted: If functional group is present in the side chain of the benzene ring in the IUPAC system, these are usually named as phenyl derivatives of the corresponding aliphatic compounds.

The IUPAC and common names of a few important members of each family are given below.

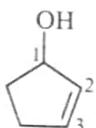
1. Aryl groups:



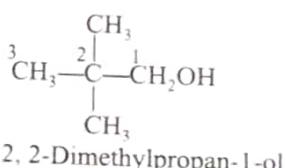
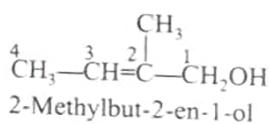


Some important 1993 recommendations for IUPAC nomenclature of organic compounds

- Locants (numerals and / or letters) are placed immediately before the part of the name to which they relate. For example: CH₃CH₂CH = CH₂ should be named as but-1-ene. CH₃CH₂CH₂OH should be named as propan-1-ol. Similarly, a few more examples are given as following:



Cyclopent-2-en-1-ol



- The locant 1 is often omitted when there is no ambiguity. For example.



In all the above examples locant 1 for the functional group is omitted because the position of the functional group is unambiguous. However, in the following cases the position of the functional group must be mentioned.

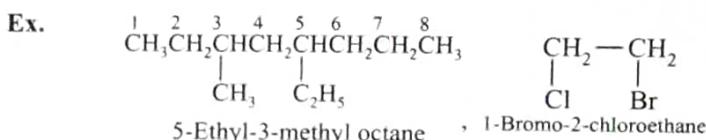


Here, we cannot write simply propanol (or propanamine) because there are two propanols; propan-1-ol and propan-2-ol.

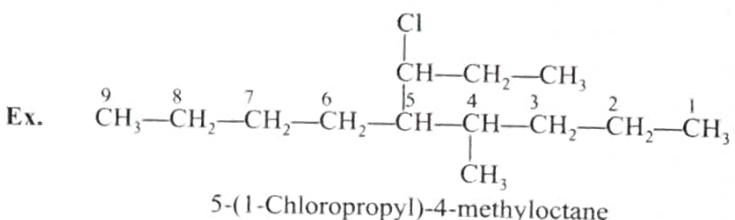
- Arrangement of Prefixes:

- Simple prefixes such as methyl, ethyl, chloro, nitro, hydroxy, etc. are arranged alphabetically.

The prefixes di, tri, etc. are however not considered for comparison.

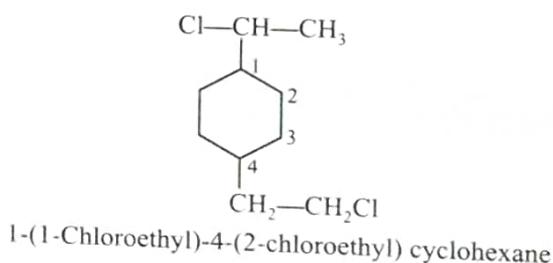


- The name of a prefix for a substituted substituent is considered to begin with the first letter of its complete name.



For the substituted 1-chloropropyl, 'C' is taken as the first letter.

- When two or more prefixes consist of identical roman letters priority for citation is given to the group which contains the lowest locant at the first point of difference. For example,

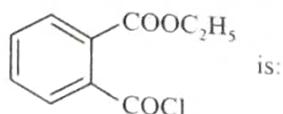


Here, 1-chloroethyl gets priority over 2-chloroethyl.



Train Your Brain

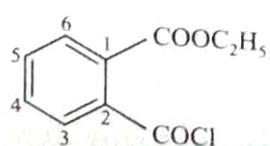
Example 16: IUPAC name of the compound



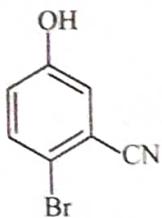
is:

- 2-Chlorocarbonylethylbenzenecarboxylate
- 2-Carboxyethylbenzoylchloride
- Ethyl-2-(chlorocarbonyl)benzoate
- Ethyl-1-chlorocarbonylbenzenecarboxylate

Sol. (c)

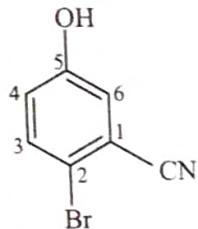


Example 17: The IUPAC name of the following compound is:



- (a) 4-Bromo-3-cyanophenol
- (b) 2-Bromo-5-hydroxybenzonitrile
- (c) 2-Cyano-4-hydroxybromobenzene
- (d) 6-Bromo-3-hydroxybenzonitrile

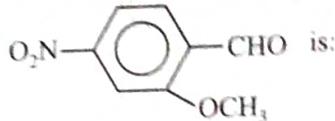
Sol. (b)



(—CN) has been given priority over (—OH) and (—Br).

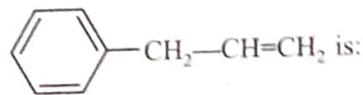
Concept Application

14. The IUPAC name of the compound is:



- (a) 2-Methoxy-4-nitrobenzaldehyde
- (b) 4-Nitroanisaldehyde
- (c) 3-Methoxy-4-formylnitrobenzene
- (d) 2-Formyl-4-nitroanisole

15. IUPAC name of the compound

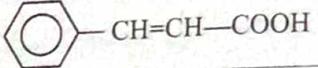
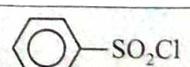


- (a) 1-Phenylprop-2-ene
- (b) 3-Phenylprop-1-ene
- (c) 1-(Prop-1-enyl) benzene
- (d) 1-(Prop-2-enyl) benzene

Some Frequently Used Common Names

S. No.	Common Name	Structure Formula
1.	Isooctane	$\begin{array}{c} \text{CH}_3 & & \text{CH}_3 \\ & \text{CH}-\text{CH}_2-\text{C}-\text{CH}_3 \\ & & \\ \text{CH}_3 & & \text{CH}_3 \end{array}$
2.	Triptane	$\begin{array}{c} \text{CH}_3 & & \\ & \text{CH}-\text{C}-\text{CH}_3 \\ & & \\ \text{CH}_3 & & \text{CH}_3 \end{array}$
3.	Ethylene	$\text{H}_2\text{C}=\text{CH}_2$
4.	Acetylene	$\text{HC}\equiv\text{CH}$
5.	Allylene	$\text{HC}\equiv\text{C}-\text{CH}_3$
6.	Crotonylene	$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$
7.	Allene	$\text{CH}_2=\text{C}=\text{CH}_2$
8.	Ketene	$\text{CH}_2=\text{C}=\text{O}$
9.	Acetone or Dimethyl Ketone	$\text{CH}_3-\text{C}(=\text{O})-\text{CH}_3$
10.	Pivaldehyde	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CHO} \\ \\ \text{CH}_3 \end{array}$
11.	Chloral	$\text{Cl}_3\text{C}-\text{CHO}$
12.	Acrolein or Acryl aldehyde	$\text{CH}_2=\text{CH}-\text{CHO}$

S. No.	Common Name	Structure Formula
13.	Acetophenone or Methyl phenyl Ketone	$\text{CH}_3-\text{C}(=\text{O})-\text{C}_6\text{H}_5$
14.	Benzophenone or Diphenyl Ketone	$\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{C}_6\text{H}_5$
15.	Pinacol	$\begin{matrix} \text{CH}_3\text{CH}_3 \\ \quad \\ \text{CH}_3-\text{C}-\text{C}-\text{CH}_3 \\ \quad \\ \text{OH} \quad \text{OH} \end{matrix}$
16.	Pinacolone	$\begin{matrix} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}(=\text{O})-\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{matrix}$
17.	Mesityl oxide (Dimer of acetone)	$\begin{matrix} \text{CH}_3-\text{C}=\text{CH}-\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{O} \end{matrix}$
18.	Phorone (Trimer of acetone)	$\begin{matrix} \text{CH}_3-\text{C}=\text{CH}-\text{C}=\text{CH}-\text{C}-\text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \quad \text{O} \quad \text{CH}_3 \end{matrix}$
19.	Oxalic acid	HOOC-COOH
20.	Malonic acid	$\text{HOOC-CH}_2\text{-COOH}$
21.	Succinic acid	$\text{HOOC-(CH}_2)_2\text{-COOH}$
22.	Gluteric acid	$\text{HOOC-(CH}_2)_3\text{-COOH}$
23.	Adipic acid	$\text{HOOC-(CH}_2)_4\text{-COOH}$
24.	Pimelic acid	$\text{HOOC-(CH}_2)_5\text{-COOH}$
25.	Maleic acid	$\begin{matrix} \text{H}-\text{C}-\text{COOH} \\ \\ \text{H}-\text{C}-\text{COOH} \end{matrix} \quad (\text{cis})$
26.	Fumaric acid	$\begin{matrix} \text{H}-\text{C}-\text{COOH} \\ \\ \text{HOOC-C-H} \end{matrix} \quad (\text{trans})$
27.	Cyanic acid	$\text{HO-C}\equiv\text{N}$
28.	Isocyanic acid (Tautomer of cyanic acid)	O=C=NH
29.	Isourea (Tautomer of urea)	$\begin{matrix} \text{H}_2\text{N}-\text{C}=\text{NH} \\ \\ \text{OH} \end{matrix}$
30.	Chloroform (Anaesthetic agent)	CHCl_3
31.	Chloropicrin (Nitro Chloroform)	$\text{Cl}_3\text{C-NO}_2$
32.	Chloretone (Chloroform + acetone)	$\begin{matrix} \text{CCl}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ \\ \text{OH} \end{matrix}$
33.	(Fire - extinguisher)	CCl_4
34.	Westrosol or Triclene	$\begin{matrix} \text{Cl} > \text{C}=\text{C} < \text{H} \\ \text{Cl} \end{matrix}$

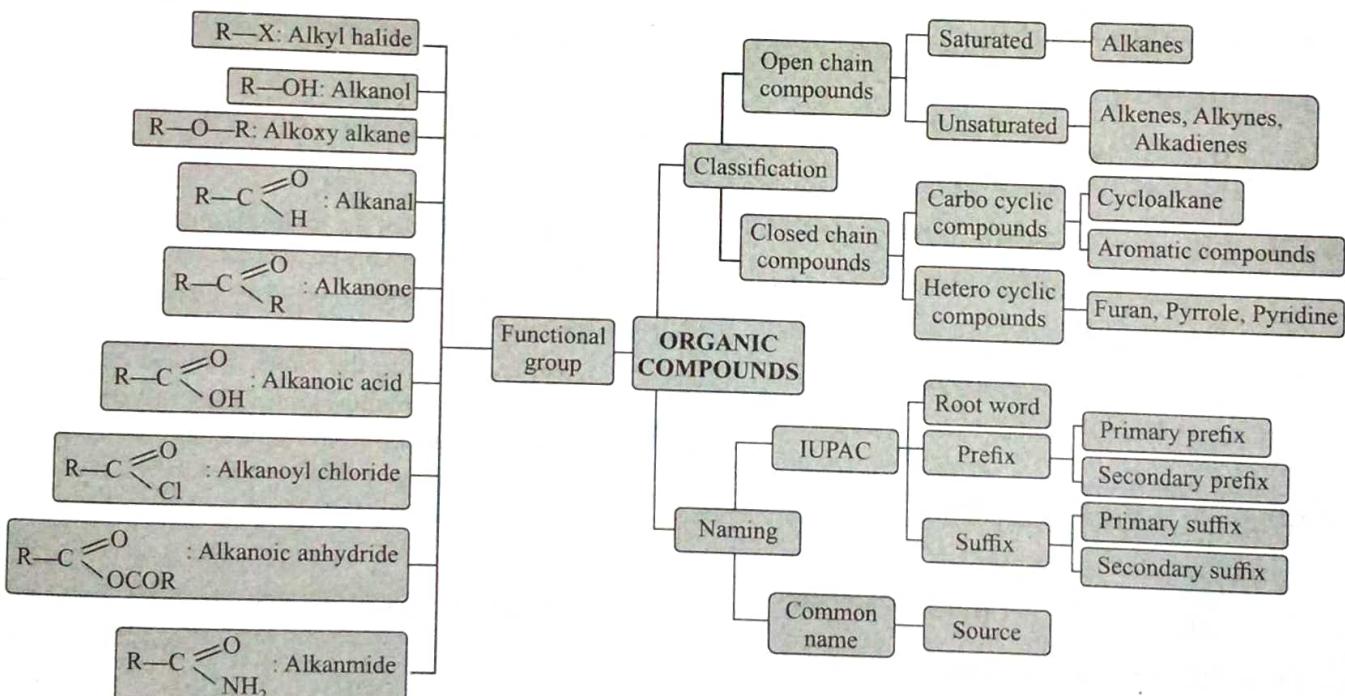
S. No.	Common Name	Structure Formula
35.	Westron	$\text{Cl} > \text{CH} - \text{CH} < \text{Cl}$
36.	Tetraclene or Perclene	$\text{Cl} > \text{C} = \text{C} < \text{Cl}$
37.	Isoprene	$\text{CH}_2 = \underset{\text{CH}_3}{\text{C}} - \text{CH} = \text{CH}_2$
38.	Chloroprene (Monomer of Neoprene Polymer)	$\text{CH}_2 = \underset{\text{Cl}}{\text{C}} - \text{CH} = \text{CH}_2$
39.	AAE (Acetoacetic ester) or EAA (Ethyl acetoacetate)	$\text{CH}_3 - \underset{\text{O}}{\text{C}} - \text{CH}_2 - \underset{\text{O}}{\text{C}} - \text{OC}_2\text{H}_5$
40.	Acrylic acid	$\text{CH}_2 = \text{CH} - \text{COOH}$
41.	Crotonic acid	$\text{CH}_3 - \text{CH} = \text{CH} - \text{COOH}$
42.	Cinnamic acid	
43.	Glycol	$\begin{array}{c} \text{CH}_2 - \text{OH} \\ \\ \text{CH}_2 - \text{OH} \end{array}$
44.	Glycerol	$\begin{array}{c} \text{CH}_2 - \text{OH} \\ \\ \text{CH} - \text{OH} \\ \\ \text{CH}_2 - \text{OH} \end{array}$
45.	Phosgene or Carbonyl chloride	$\text{Cl} - \underset{\text{O}}{\text{C}} - \text{Cl}$
46.	Glyceraldehyde	$\begin{array}{c} \text{CH}_2 - \text{OH} \\ \\ \text{CH} - \text{OH} \\ \\ \text{CHO} \end{array}$
47.	Glyceric acid	$\begin{array}{c} \text{CH}_2 - \text{OH} \\ \\ \text{CH} - \text{OH} \\ \\ \text{COOH} \end{array}$
48.	Glyoxal	$\begin{array}{c} \text{CHO} \\ \\ \text{CHO} \end{array}$
49.	Glycine	$\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$
50.	α -Alanine	$\text{H}_2\text{N}-\underset{\text{CH}_3}{\text{CH}}-\text{COOH}$
51.	Tilden reagent	$\text{Cl}-\text{N}=\text{O}$
52.	Grignard reagent	$\text{R}-\text{MgX}$
53.	Frankland reagent	$\text{R}-\text{Zn}-\text{R}$
54.	Hinsberg reagent (used in N-compounds)	

S. No.	Common Name	Structure Formula
55.	Mustard Gas (Explosive used in I-world war)	Cl—CH ₂ —CH ₂ —S—CH ₂ —CH ₂ —Cl
56.	Lewisite (Explosive used in II-world war)	Cl—CH=CH—AsCl ₂
57.	Semicarbazide	H ₂ N—NH—C(=O)—NH ₂
58.	Schiff's Base or Anil	R—CH=N—R
59.	Methylal	CH ₃ —CH^{OCH ₃}_{OCH ₃}
60.	Ethylal	CH ₃ —CH^{OCH ₂ CH ₃}_{OCH ₂ CH ₃}
61.	Mercaptal	R>C^{SR}_H
62.	Mercaptol	R>C^{SR}_{SR}
63.	Mercaptan	R—SH
64.	Mercaptide	R—S—R
65.	Mesitylene	
66.	Toluene	
67.	Cummene or Isopropyl benzene	
68.	Acetanilide	CH ₃ —C(=O)—NH—
69.	Benzanilide	
70.	Anisole	
71.	Phenetole	
72.	Azo benzene	
73.	Hydrazo benzene	

S. No.	Common Name	Structure Formula
74.	Phthalic acid	
75.	Phthalic anhydride	
76.	Phthalimide	
77.	Anthranilic acid	
78.	Sulphanilic acid (Forms zwitter ion)	
79.	Aspirin (Analgesic) or o-Acetoxy benzoic acid	
80.	Salol (Antiseptic) or Phenyl salicylate	
81.	Oil of wintergreen or Methyl salicylate	
82.	o-Cresol	
83.	o-Toluic acid	
84.	o-Tolidene	
85.	p-Benzoquinone	 (Antiaromatic)
86.	Gammexane or Lindane or BHC (Benzene hexachloride)	 (Alicyclic)
87.	Salicylaldehyde	

S. No.	Common Name	Structure Formula
88.	Salicylic acid	
89.	Picric acid	
90.	Tosyl chloride	
91.	Styrene	
92.	o-Xylene	

Short Notes



If the organic compound contains a functional group, multiple bonds, side chain or substituents, the following order of preference must be followed,

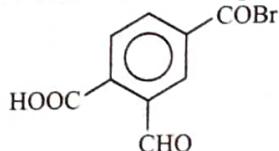
Functional group > Double bond > Triple bond > Side chain

The following order of preference is used for selecting the principal functional group:

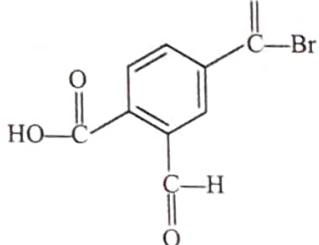
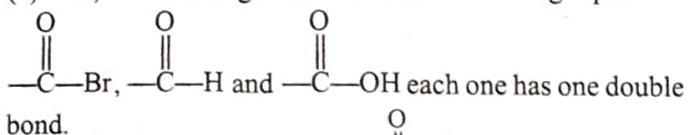
Carboxylic acids > sulphuric acids > acid anhydrides > esters > acid chlorides > amides > nitriles
> aldehydes > ketones > alcohols > amines > imines > ethers > alkenes > alkynes.

Solved Examples

1. Identify degree of unsaturation of given compound:

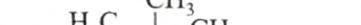


Sol. (c) In, Benzene ring 3 double bond and one ring is present.



2. Which of the following has longest parent carbon chain?

- (a) 

(b) 

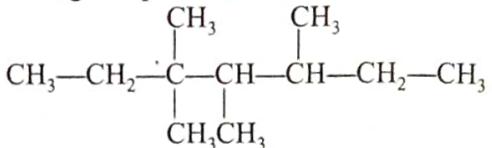
(c) 

(d) 

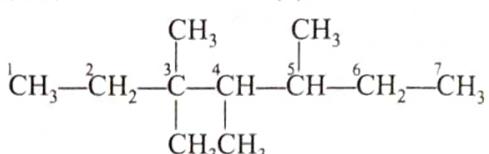
Sol. (c)

$$\begin{array}{ccccccc}
 & & \text{CH}_3 & & & & \\
 & & | & & & & \\
 & & \text{H}_3\text{C} & -\text{C}- & \text{CH}_3 & & \\
 & & | & & & & \\
 & & 2 & & & & \\
 & & & & & & \\
 \text{CH}_3 & -\text{CH} & -\text{CH}_2 & -\text{CH}_2 & -\text{CH} & -\text{CH}_3 & \\
 & | & & & | & & \\
 & \text{H}_3\text{C} & & & \text{CH}_3 & & \\
 & | & & & | & & \\
 & 7 & & & 8 & &
 \end{array}$$

3. In following compound the correct lowest set of locants is



Sol. (a)



4. Ethyl methyl vinyl amine has the structure:

- $$(a) \text{CH}_3\text{CH}_2-\underset{\substack{| \\ \text{CH}_3}}{\text{N}}-\text{CH}_2\text{CH}=\text{CH}_2$$

- $$(b) \text{CH}_3\text{CH}_2-\underset{\text{CH}_3}{\text{N}}-\text{CH}=\text{CH}_2$$

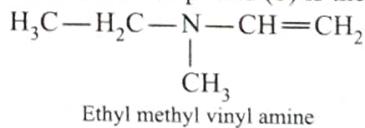
- $$(c) \text{CH}_2=\text{CH}-\underset{\text{CH}_3}{\text{N}}-\text{CH}=\text{CH}_2$$

- $$(d) \text{CH}_3-\underset{\text{CH}_3}{\text{N}}-\text{CH}=\text{CH}_2$$

Sol. (b) $\text{H}_3\text{C}-\text{H}_2\text{C}-\overset{\text{CH}_3}{\underset{|}{\text{N}}}-\text{CH}=\text{CH}_2$

As per the name of the molecule amine group should be in vinyl position. Doubly bonded carbon is the cinylic position. Therefore, compound (a) is wrong because it has amine group in allylic position.

Also according to the name, we have ethyl and methyl substituent to the amine group. Thus only compound (b) has those substituent. Hence compound (b) is the correct one.



5. Which is the structure of Phthalic acid?

- (a) 

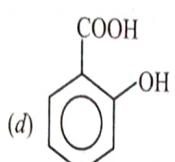
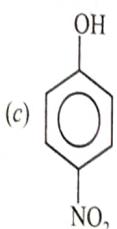
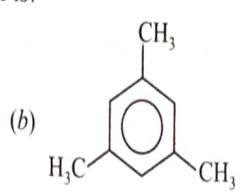
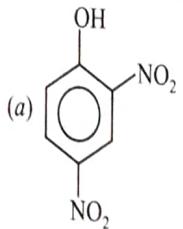
(b) 

(c) 

(d) 

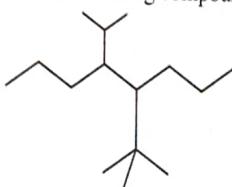
Sol. (a) Phthalic acid is an aromatic dicarboxylic acid (ortho to each other.)

6. The structure of Mesitylene is?



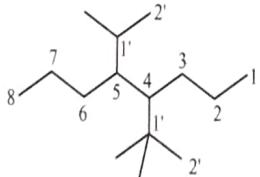
Sol. (b) Mesitylene or 1, 3, 5-trimethyl benzene.

7. IUPAC name of the following compound is:

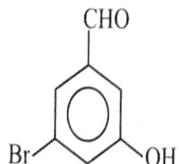


- (a) 4-(1-methylethyl)-5-(1,1-dimethylethyl)octane
- (b) 4-(1,1-dimethylethyl)-5-(1-methylethyl)octane
- (c) 2,2-Trimethyl-4,5-dipropylhexane
- (d) 4-Isopropyl-5-(1,1-dimethylethyl)octane

Sol. (b)

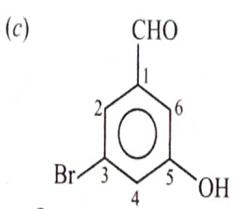


8. The IUPAC name of the following compound is:



- (a) 5-Bromo-3-hydroxybenzenecarbaldehyde
- (b) 3-Bromo-5-formylphenol
- (c) 3-Bromo-5-hydroxybenzenecarbaldehyde
- (d) 1-Bromo-3-formyl-5-hydroxybenzene

Sol. (c)

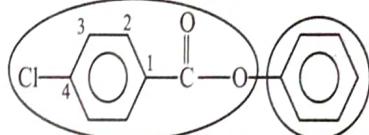


$(-\text{C}-\text{H})$ group has been given out 1st priority over $(-\text{OH})$ and $(-\text{Br})$

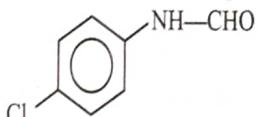
9. IUPAC name of $\text{Cl}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{Cl}$ is:

- (a) 4-Chlorophenyl benzoate.
- (b) Phenyl-4-chlorobenzene carboxylate.
- (c) Benzyl-4-chlorobenzene carboxylate.
- (d) 4-Chloro diphenylcarboxylate.

Sol. (b)

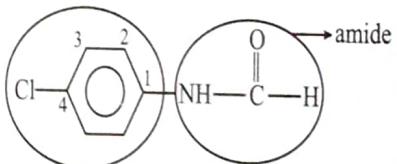


10. The correct IUPAC name of the compound:

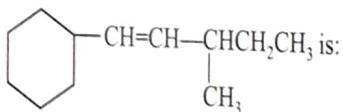


- (a) N-Formyl-4-chlorobenzenamine
- (b) N-Formyl-4-chloroaniline
- (c) N-(4-chlorophenyl)methanamide
- (d) N-(Parachlorophenyl)-N-formylaniline

Sol. (c)

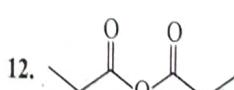
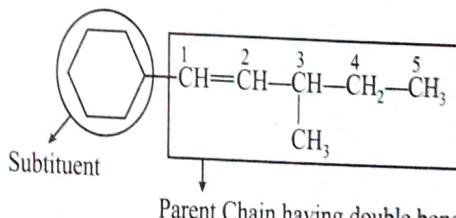


11. The IUPAC name of



- (a) 1-Cyclohexyl-3-methyl-1-pentene
- (b) 3-Methyl-5-cyclohexylpent-1-ene
- (c) 1-Cyclohexyl-3-ethylbut-1-ene
- (d) 1-Cyclohexyl-3,4-dmethylbut-1-ene

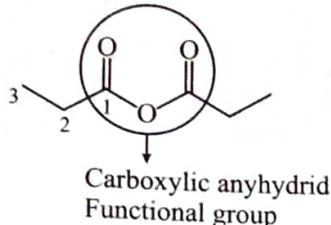
Sol. (a)



The IUPAC name of the compound is:

- (a) Propanoic anhydride
- (b) Dipropanoic anhydride
- (c) Ethoxy propanoic acid
- (d) 1-Oxopropyl propanoate

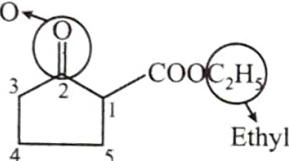
Sol. (a)



13. has the IUPAC name:
 COOC_2H_5

- (a) Ethyl-2-oxocyclopentanecarboxylate
- (b) 2-Cyclopentanone-1-carbethoxy
- (c) 2-Ethylcarbonatecyclopentanone
- (d) 1-Keto-2-carbethoxycyclopentanone

Sol. (a)

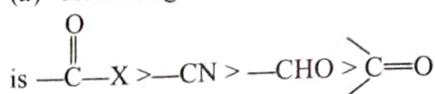


$(-\text{C}=\text{O}-\text{O}-)$ has given priority over $(-\text{C}=\text{O}-)$

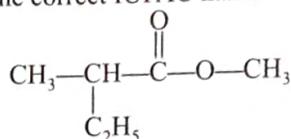
14. Identify correct order of priority of functional groups:

- (a) $-\text{CHO} > \text{C=O} > -\text{COX} > -\text{CN}$
- (b) $-\text{COX} > -\text{CHO} > \text{C=O} > -\text{CN}$
- (c) $-\text{CHO} > -\text{CN} > -\text{COX} > \text{C=O}$
- (d) $-\text{COX} > -\text{CN} > -\text{CHO} > \text{C=O}$

Sol. (d) According to IUPAC: Functional groups priority order

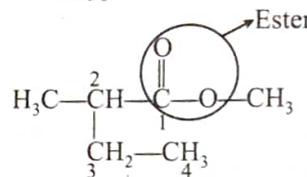


15. The correct IUPAC name of following compound is:



- (a) Methyl-2-ethylpropanoate
- (b) Methylbutane-2-carboxylate
- (c) Methyl-2-methylbutanoate
- (d) Methoxypentanone

Sol. (c)



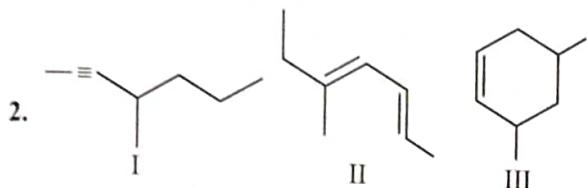
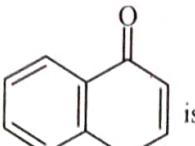
Exercise-1 (Topicwise)

FUNDAMENTAL OF ORGANIC CHEMISTRY

1. Molecular formula of naphthaquinone is:

- (a) $C_{12}H_8O_2$
(c) $C_{10}H_6O_2$

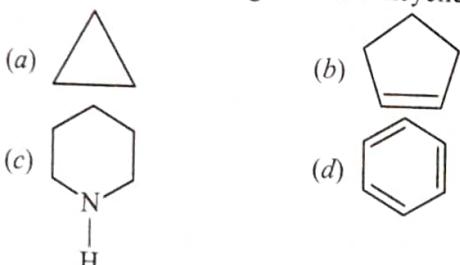
- (b) $C_{11}H_6O_2$
(d) $C_{10}H_8O_2$



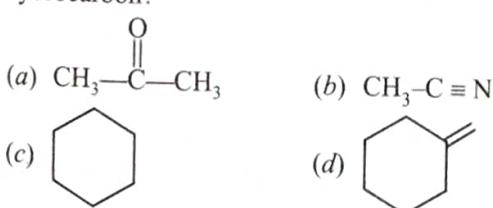
Incorrect statement for the above structure:

- (a) I, II & III have C_nH_{2n-2} general formula.
(b) I, II & III have same empirical formula.
(c) I, II are identical and homologue of compound III.
(d) I, II & III have same molecular formula.

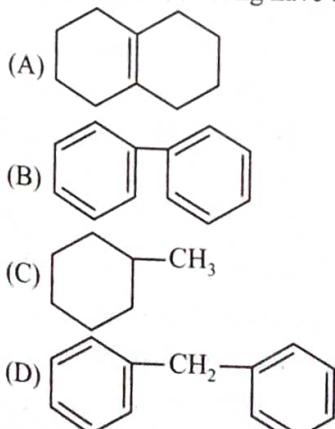
3. Which of the following is not an alicyclic compound?



4. Which of the following compound is unsaturated hydrocarbon?



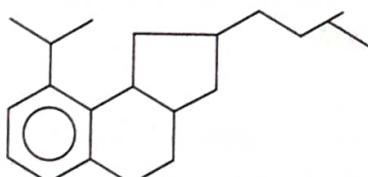
5. Which of the following have only 2° H- atom?



Correct code is:

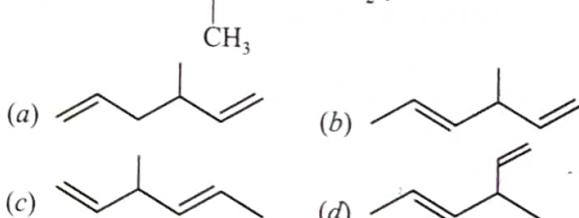
- (a) Only A and B
(c) A,C and D
(b) A,B and D
(d) All of them

6. Number of 3° and 2° carbon atoms in the following compound are:

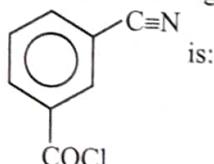


- (a) 7, 8
(c) 6, 8
(b) 6, 9
(d) 8, 9

7. Which of the following is not the bond line structure of $CH_3-CH=CH-CH-CH=CH_2$?

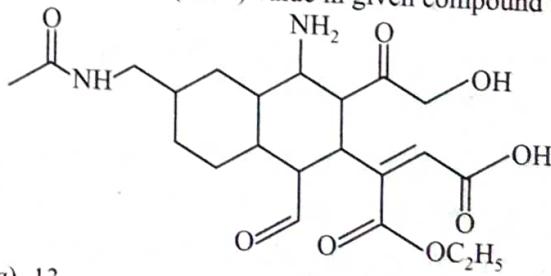


8. Identify degree of unsaturation of given compound



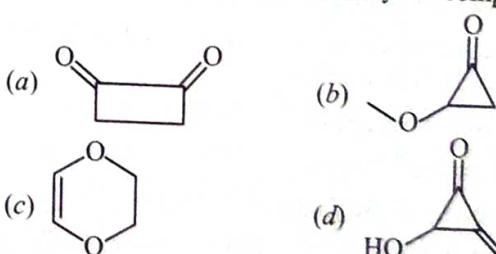
- (a) 5
(c) 7
(b) 6
(d) 8

9. Sum of total number of different functional group and double bond equivalent (DBE) value in given compound is:



- (a) 13
(c) 15
(b) 14
(d) 16

10. Which of the following is heterocyclic compound?



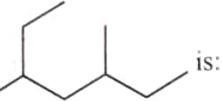
11. Which of the following homologous series has incorrect general formula?

- (a) Alkyne C_nH_{2n-2}
- (b) Alkanol $C_nH_{2n+2}O$
- (c) Alkanal $C_nH_{2n+1}O$
- (d) Carboxylic acid $C_nH_{2n}O_2$

12. The third member of the homologous series of aliphatic aldehydes has the structure:

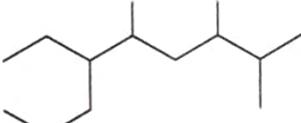
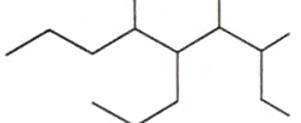
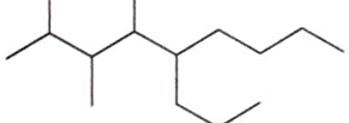
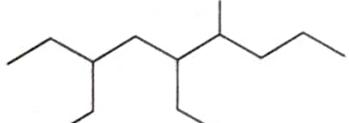
- (a) CH_3CH_2CHO
- (b) $CH_3(CH_2)_2CHO$
- (c) $H_3COCH_2CH_3$
- (d) CH_3COCH_3

IUPAC-NOMENCLATURE OF ALKANE & CYCLO ALKANE

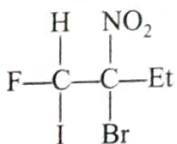
13. The correct IUPAC name of the alkane  is:

- (a) 2-Ethyl-4-methylhexane
- (b) 5-Ethyl-3-methylhexane
- (c) 3,5-Dimethylheptane
- (d) 3,5-Dimethylhexane

14. The correct structure of 6-Ethyl-2,3,5-trimethylnonane is:

- (a) 
- (b) 
- (c) 
- (d) 

15. The correct IUPAC name of the following compound is:

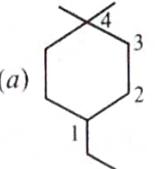
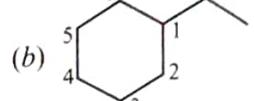
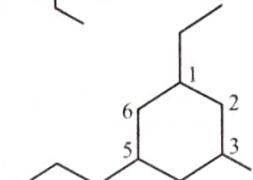
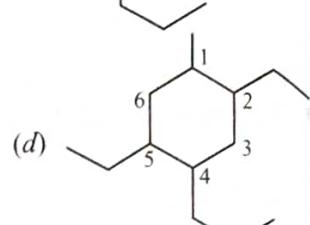


- (a) 1-Bromo-1-ethyl-2-fluoro-2-iodo-1-nitroethane.
- (b) 3-Bromo-4-fluoro-4-iodo-3-nitrobutane.
- (c) 2-Bromo-1-fluoro-1-iodo-2-nitrobutane.
- (d) 1-Fluoro-1-iodo-2-bromo-2-ethyl-2-nitroethane.

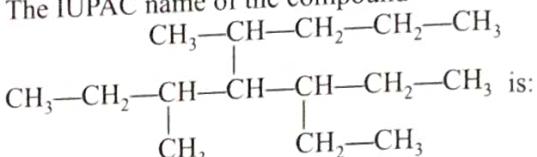
16. A student named a certain compound as 2,3-diethylbutane. Its correct IUPAC names is:

- (a) 2,3-Dimethylhexane
- (b) 3,4-Dimethylhexane
- (c) 2-Ethyl-3-methylpentane
- (d) 2-Ethylbutane

17. In which of the following compound IUPAC numbering is correct?

- (a) 
- (b) 
- (c) 
- (d) 

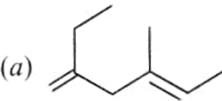
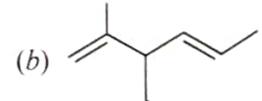
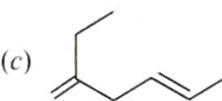
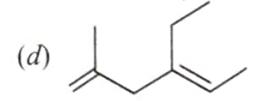
18. The IUPAC name of the compound



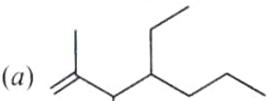
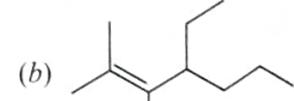
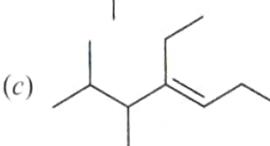
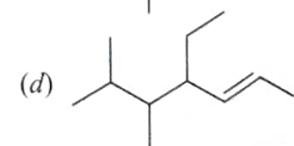
- (a) 5-Ethyl-3-methyl-4-(1-methylpropyl) octane
- (b) 4-Ethyl-6-methyl-5-(1-methylpropyl) octane
- (c) 3-Ethyl-5-methyl-4-(1-methylpropyl) octane
- (d) 4-Sec-butyl-5-ethyl-5-methylheptane

IUPAC-NOMENCLATURE OF ALKENE, ALKYNE, CYCLO ALKENE AND POLYENES

19. The correct structure of 2-Ethyl-3-methyl hexa-1,4-diene:

- (a) 
- (b) 
- (c) 
- (d) 

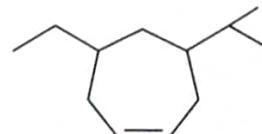
20. Select the structure of 4-ethyl-2,3-dimethyl-2-heptene:

- (a) 
- (b) 
- (c) 
- (d) 

21. The correct IUPAC name of 2-ethyl-3-pentyne is:

- (a) 3-Methylhexyne-4
- (b) 4-Ethylpentyne-2
- (c) 4-Methylhexyne-2
- (d) None of these

22. Correct IUPAC name of the following

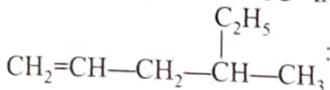


- (a) 4-Ethyl-6-(1-methylethyl)cycloheptene
- (b) 4-(1-Methylethyl)-6-ethylcycloheptene
- (c) 4-Ethyl-6-isopropylcycloheptene
- (d) None of these

23. Select the structure with correct numbering in the chain:

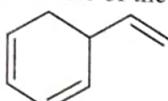
- (a) $\overset{5}{\text{CH}_2}=\overset{4}{\text{CH}}-\overset{3}{\text{CH}_2}-\overset{2}{\text{C}}\equiv\overset{1}{\text{CH}}$
- (b) $\overset{1}{\text{CH}_3}-\overset{2}{\text{CH}}-\overset{3}{\text{CH}}=\overset{4}{\text{CH}}-\overset{5}{\text{CH}_2}-\overset{6}{\text{C}}\equiv\overset{7}{\text{CH}}$
- (c) $\overset{7}{\text{CH}_2}=\overset{6}{\text{CH}}-\overset{5}{\text{CH}}-\overset{4}{\text{CH}}-\overset{3}{\text{CH}}-\overset{2}{\text{CH}_2}-\overset{1}{\text{CH}\equiv\text{CH}_2}$
- (d) $\overset{1}{\text{CH}_2}=\overset{2}{\text{CH}}-\overset{3}{\text{CH}}-\overset{4}{\text{CH}}-\overset{5}{\text{CH}}-\overset{6}{\text{CH}_2}-\overset{7}{\text{C}}\equiv\overset{1}{\text{CH}}$

24. The correct IUPAC name of the compound



- (a) 4-Ethylpent-1-ene
- (b) 2-Ethylpent-4-ene
- (c) 4-Methylhex-1-ene
- (d) 3-Methylhex-1-ene

25. The correct IUPAC name of the compound

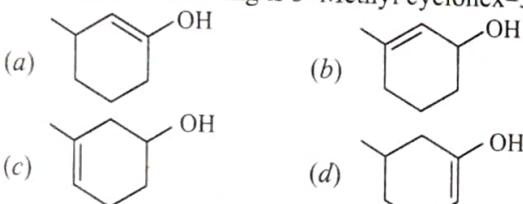


is:

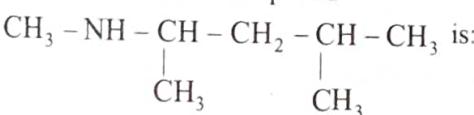
- (a) 1-Ethenylcyclohexa-2,4-diene
- (b) 5-Ethenylcyclohexa-1,3-diene
- (c) 6-Ethenylcyclohexa-1,3-diene
- (d) Cyclohexa-2,4-dienylethene

IUPAC NOMENCLATURE OF NON-CHAIN TERMINATING FUNCTIONAL GROUPS

26. Which of the following is 3-Methyl cyclohex-3-enol?



27. IUPAC name of the compound

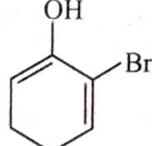


- (a) 2-(N-methylamino)-4-methylpentane
- (b) N-Methyl-4-methylpentan-2-amine
- (c) 2-(N-methylamino)-3-isopropylpropane
- (d) 2-(N-methylamino)-1,4,4-trimethylbutane

28. is named as:

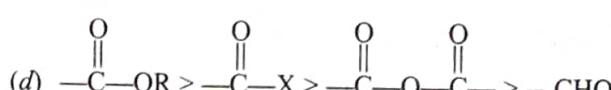
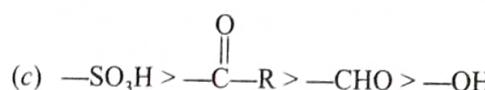
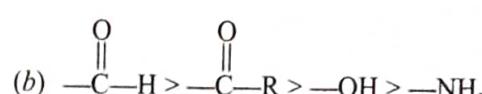
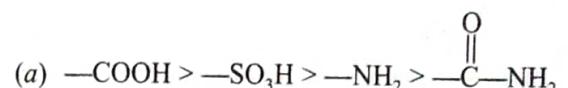
- (a) 2,3-Dimethylenebutanal
- (b) 3-Methyl-2-methylenebut-3-enone
- (c) 3-Methyl-2-methylidenebut-3-enal
- (d) 2,3-Dimethylenebutanone

29. The sum of positions of (-OH) and (-Br) in the above compound is:

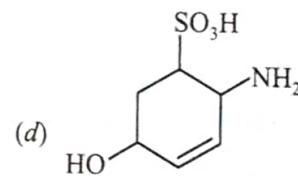
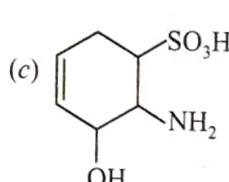
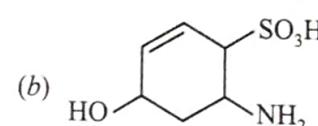
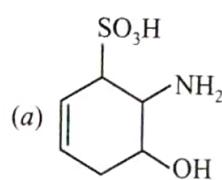


- (a) 3
- (b) 5
- (c) 6
- (d) 7

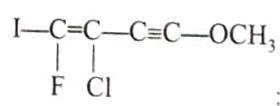
30. Which of the following is a correct priority order of functional groups?



31. The correct structure of 6-Amino-4-hydroxycyclohex-2-ene-1-sulphonic acid.



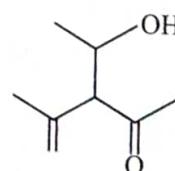
32. The correct IUPAC name of the given compound is



- (a) 3-Chloro-1-fluoro-1-iodo-4-methoxybut-1-en-3-yne
- (b) 4-Methoxy-2-chloro-1-fluoro-1-iodobutene
- (c) 3-Chloro-4-fluoro-4-iodo-1-methoxybutene
- (d) 2-Chloro-1-fluoro-1-ido-4-methoxybutene

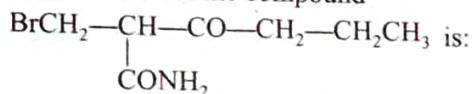
IUPAC-NOMENCLATURE OF CHAIN TERMINATING FUNCTIONAL GROUPS

33. The correct IUPAC name of the compound is:



- (a) 3-(1-Methylethyl)-4-hydroxy pentan-2-one
- (b) 3-(1-Hydroxyethyl)-4-methylpent-4-en-2-one
- (c) 3-(1-Hydroxymethyl)-4-methylene pentan-2-one
- (d) 3-(1-Oxoethyl)-4-methylpent-4-en-2-ol.

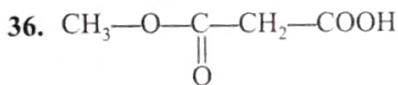
34. IUPAC name of the compound



- (a) 2-(Bromomethyl)-3-oxohexanamide
- (b) 1-Bromo-2-amido-3-oxohexane
- (c) 1-Bromo-2-amido-n-propylketone
- (d) 3-Bromo-2-propanoyl-propanamide

35. Which of the following compounds has wrong IUPAC name?

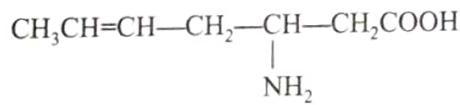
- (a) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COO} - \text{CH}_2\text{CH}_3$
→ ethyl butanoate
- (b) $\text{CH}_3 - \underset{\text{CH}_2-\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{CHO}$ → 3-ethyl-butanal
- (c) $\text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$ → 3-ethyl-2-butanol
- (d) $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \underset{\text{O}}{\overset{||}{\text{C}}} - \text{CH}_2 - \text{CH}_3$ →
2-methyl-3-pentanone



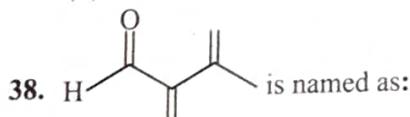
The IUPAC name of the above compound is:

- (a) 2-Acetoxyethanoic acid
- (b) 2-Methoxycarbonylethanoic acid
- (c) 3-Methoxyformylethanoic acid
- (d) 2-Methoxyformylacetic acid

37. The IUPAC name of the following is:

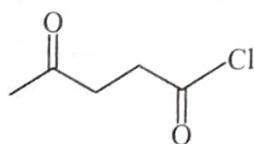


- (a) 3-Aminohept-5-enoic acid
- (b) 5-Aminohex-2-enecarboxylic acid
- (c) 3-Aminohept-4-enoic acid
- (d) 5-Aminohept-2-enoic acid



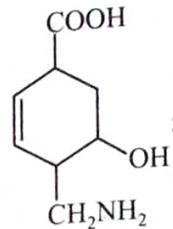
- (a) 2,3-Dimethylenebutanal
- (b) 3-Methyl-2-methylenebut-3-enone
- (c) 3-Methyl-2-methylenebut-3-enal
- (d) 2,3-Dimethylenebutanone

39. The correct IUPAC name of compound is:



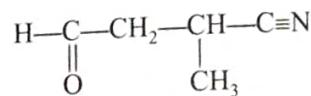
- (a) 1-Chloropentane-1,4-dione
- (b) 4-Chlorocarbonylbutan-2-one
- (c) 4-Oxopentanoyl chloride
- (d) 3-Oxobutanecarbonyl chloride

40. The correct IUPAC name of following compound is



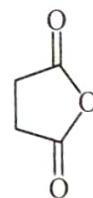
- (a) 4-Aminomethyl-3-hydroxycyclohex-5-ene-1-carboxylic acid
- (b) 2-Aminomethyl-5-carboxycyclohex-3-en-1-ol
- (c) 4-Aminomethyl-5-hydroxycyclohex-2-ene-1-carboxylic acid
- (d) 3-Hydroxy-4-aminomethylcyclohex-5-en-1-oic acid

41. IUPAC name of given compound is:



- (a) 3-Carbonitrile-3-methyl butanal
- (b) 3-Formyl-2-methylpropnenitrile
- (c) 3-Cyanobutanal
- (d) 2-Methyl-4-oxobutanenitrile

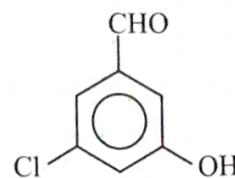
42. The IUPAC name of the compound is:



- (a) Cyclobutanedioic anhydride
- (b) Butanedicarboxylic anhydride
- (c) Cyclobutanedicarboxylic anhydride
- (d) Butanedioic anhydride

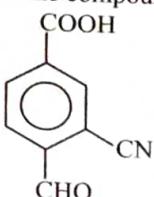
IUPAC-NOMENCLATURE OF AROMATIC COMPOUNDS

43. The IUPAC name of the following compound is:



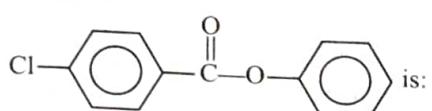
- (a) 5-Chloro-3-hydroxybenzenecarbaldehyde
- (b) 3-Chloro-5-formylphenol
- (c) 3-Chloro-5-hydroxybenzenecarbaldehyde
- (d) 1-Chloro-3-formyl-5-hydroxy benzene

44. The IUPAC name of the compound is:



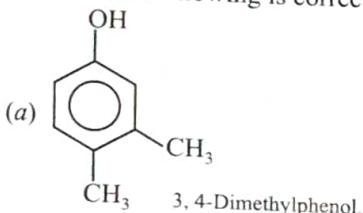
- (a) 2-Cyano-1-formylbenzene-4-carboxylic acid
- (b) 3-Cyano-4-formylbenzoic acid
- (c) 4-Carboxy-2-cyanobenzene-1-carbaldehyde
- (d) 2-Formyl-5-carboxybenzene-1-carbonitrile

45. IUPAC name of

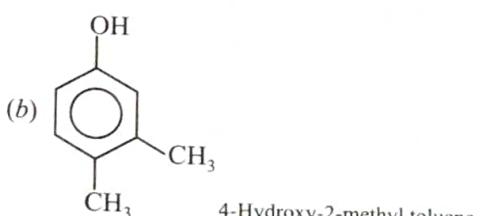


- (a) 4-Chlorophenylbenzoate.
- (b) Phenyl-4-chlorobenzoate.
- (c) Benzyl-4-chlorobenzene carboxylate.
- (d) 4-Chlorodiphenylcarboxylate

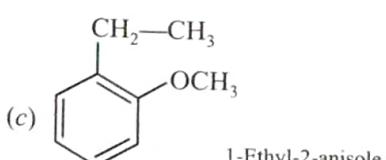
46. Which of the following is correct IUPAC name?



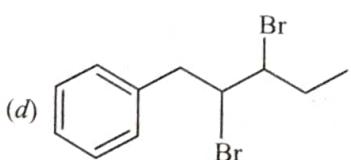
3, 4-Dimethylphenol.



4-Hydroxy-2-methyl toluene.

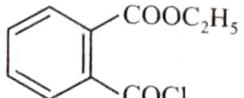


1-Ethyl-2-anisole.



1-(2,3-Dibromopentyl) benzene.

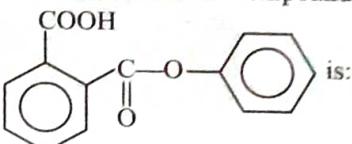
47. IUPAC name of the compound



is:

- (a) 2-Chlorocarbonyl ethylbenzenecarboxylate
- (b) 2-Carboxyethylbenzoyl chloride
- (c) Ethyl-2-(chlorocarbonyl) benzenecarboxylate
- (d) Ethyl-1-(chlorocarbonyl) benzenecarboxylate

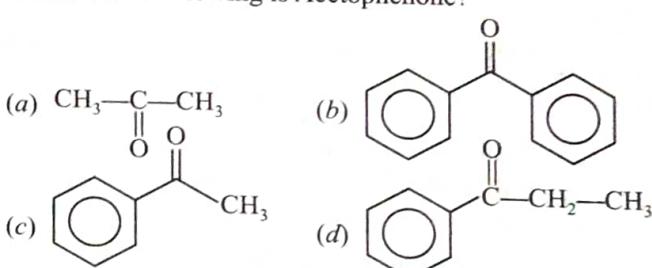
48. The correct IUPAC name of the compound



- (a) 2-Phenoxy carbonylbenzene carboxylic acid
- (b) Phenyl-2-carboxybenzenecarboxylate
- (c) 2-Benzoyloxybenzene carboxylic acid
- (d) 2-Benzoyloxycarbonylbenzene carboxylic acid

Common Names Systems

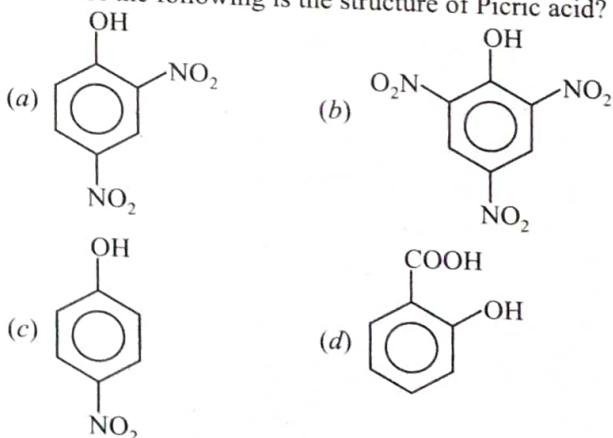
49. Which of the following is Acetophenone?



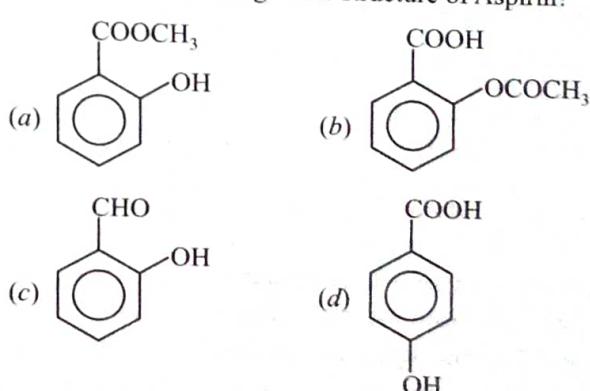
50. Which of the following is crotonic acid?

- (a) CH2=CH-COOH
- (b) C6H5-CH=CH-COOH
- (c) CH3-CH=CH-COOH
- (d) $\begin{array}{c} \text{CH}-\text{COOH} \\ \parallel \\ \text{CH}-\text{COOH} \end{array}$

51. Which of the following is the structure of Picric acid?



52. Which of the following is the structure of Aspirin?

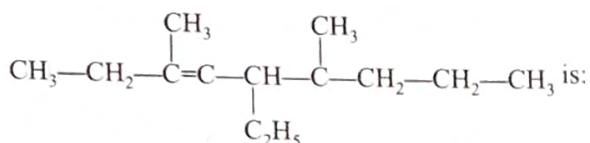


Exercise-2 (Learning Plus)

1. Which among the following is the correct IUPAC name of isoamylene?

- (a) 1-Pentene
- (b) 2-Methyl-2-butene
- (c) 3-Methyl-1-butene
- (d) 2-Methyl-1-butene

2. The correct IUPAC name of the compound

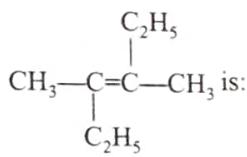


- (a) 5-Ethyl-3,6-dimethylnon-3-ene
- (b) 5-Ethyl-4,7-dimethylnon-3-ene
- (c) 4-Methyl-5,7-diethyloct-2-ene
- (d) 2,4-Ethyl-5-methyloct-2-ene

3. The correct structure of 4-bromo-3-methyl but-1-ene is:

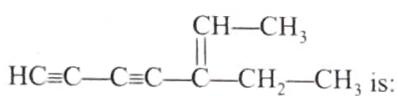
- (a) $\text{BrCH}=\text{C}(\text{CH}_3)_2$
- (b) $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Br}$
- (c) $\text{H}_2\text{C}=\text{C}=\text{CH}(\text{CH}_3)-\text{CH}_2\text{Br}$
- (d) $\text{CH}_3-\text{C}(\text{CH}_3)=\text{CHCH}_2\text{Br}$

4. The correct IUPAC name of



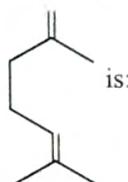
- (a) 1,2-Diethylbutane
- (b) 2-Ethyl-3-methylpentane
- (c) 3,4-Dimethyl-3-hexene
- (d) None is correct

5. The IUPAC name of



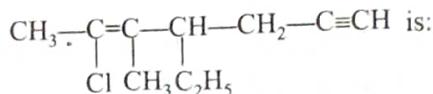
- (a) 5-Ethyl-5-heptene-1,3-diyne
- (b) 3-Ethyl-2-heptene-4,6-diyne
- (c) 5-Ethenyl-1,3-heptatriyne
- (d) 3-Ethenyl-4, 6-heptatriyne

6. IUPAC Name of the compound



- (a) 1,1,5-Tri ethyl-1,6-hexadiene
- (b) 2,6-Dimethyl-2,6-heptadiene
- (c) 2,6-Dimethylhepta-1,5-diene
- (d) None of these

7. The IUPAC name of

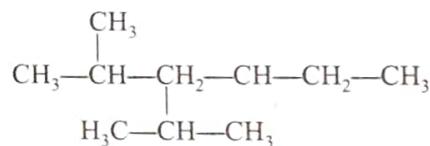


- (a) 6-Chloro-4-ethyl-5-methyl-5-hepten-1-yne
- (b) 5-methyl-4-ethyl-6-chloro-5-hepten-1-yne
- (c) 6-Chloro-4-ethyl-5-methyl-1-hepten-5-yne
- (d) 2-Chloro-4-ethyl-methyl-6-hepten-2-ene

8. The IUPAC name of the compound $\text{Br}(\text{Cl})\text{CHCF}_3$ is:

- (a) Haloethane
- (b) 1,1,1-Trifluoro-2-bromo-2-chloroethane
- (c) 2-Bromo-2-chloro-1,1,1-trifluoroethane
- (d) 1-Bromo-1-chloro-2,2,2-trifluoro ethane

9. The correct IUPAC name for the given structure is:



- (a) 3-Isopropyl-4-methylhexane
- (b) 4-Isopropyl-3-methylhexane
- (c) 3-Ethyl-2,5-dimethylhexane
- (d) 2-Ethyl-3-isopropylpentane

10. The IUPAC name of tert-butyl chloride is:

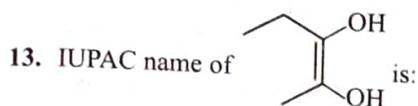
- (a) 4-Chlorobutane
- (b) 2-Ethyl-2-methylpentane
- (c) 3-Ethyl-2-methylpentane
- (d) 2-Chloro-2-Methylpropane

11. The IUPAC name of

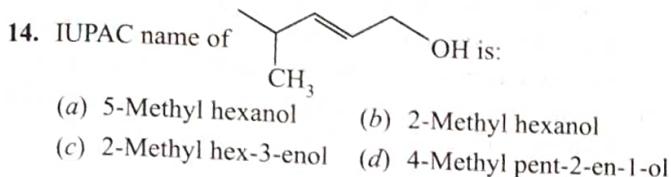
- (a) 1,1-Diethyl-2,2-dimethylpentane
- (b) 4,4-Dimethyl-5,5-diethylpentane
- (c) 5,-5-Diethyl-4,4-dimethylpentane
- (d) 3-Ethyl-4,4-dimethylheptane

12. The IUPAC name of

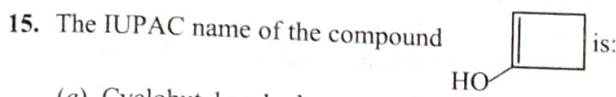
- (a) 2-Ethyl-3-methyl-1-penten-4-yne
- (b) 2-Ethyl-3-methyl-4-pentyn-1-ene
- (c) 4-Ethyl-3-methyl-1-pentyn-4-ene
- (d) 4-Ethyl-3-ethyl-4-penten-1-yne



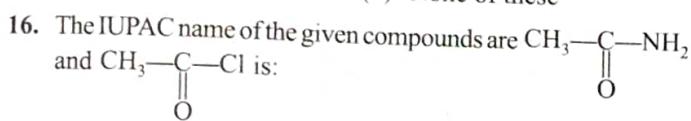
- (a) But-2-ene-2,3-diol
- (b) Pent-2-ene-2,3-diol
- (c) 2-Methylbut-2-ene-2,3-diol
- (d) Pent-3-ene-3,4-diol



- (a) 5-Methyl hexanol
- (b) 2-Methyl hexanol
- (c) 2-Methyl hex-3-enol
- (d) 4-Methyl pent-2-en-1-ol

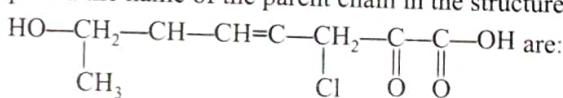


- (a) Cyclobut-1-en-1-ol
- (b) Hydroxy cyclobutene
- (c) Cyclobutanol
- (d) None of these



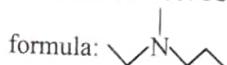
- (a) 1-Amino-1-oxo ethane, 1-chloro ethanal
- (b) 1-Amino ethanal, acetoyl chloride
- (c) 1-Oxoethanamine, ethanoyl chloride
- (d) Ethanamide, Ethanoyl chloride

17. The suffix of the principal group, the prefixes for the other groups and the name of the parent chain in the structure

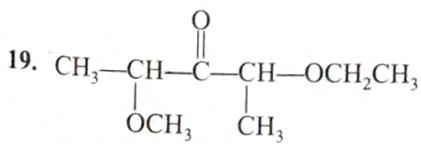


- (a) -oic acid, chloro, hydroxy, oxo, methyl, 4-heptene
- (b) -oic acid, chloro, hydroxy, methyl, oxo, 4-heptene
- (c) -one, carboxy, chloro, methyl, hydroxy, 4-heptene
- (d) -one, carboxy, chloro, methyl, hydroxy, 4-heptene

18. Write the correct IUPAC name of the following bond line formula:



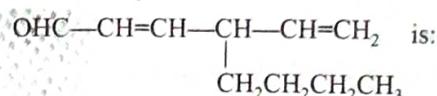
- (a) N-Methyl-N-ethyl propanamine
- (b) N-Ethyl-N-methyl propane-1-amine
- (c) N-Methyl-N-propyl ethan-1-amine
- (d) N-Ethyl-N-propyl-N-methyl-amine



The IUPAC name of this compound is:

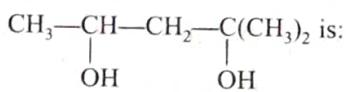
- (a) 2-Ethoxy-4-methoxy pentan-3-one
- (b) 2-Methoxy-4-ethoxy-pentan-3-one
- (c) 2-Ethoxy-4-methoxy pentan-3-one
- (d) None of these

20. IUPAC name of,

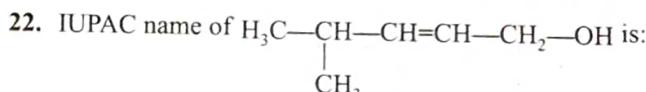


- (a) 4-Butyl-2,5-hexadien-1-al
- (b) 5-Vinyloct-3-en-1-al
- (c) 5-Vinyloct-5-en-8-al
- (d) 3-Butyl-1,4-hexadien-6-al

21. The IUPAC name of



- (a) 2-Methyl-2,4-dihydroxy propane
- (b) 2,2-Dimethyl-4-hydroxy butanol
- (c) 2-Methyl-2,4-pentane diol
- (d) 2-Hydroxy-4,4-dimethyl butanol-4



- (a) 5-Methylhexanol
- (b) 2-Methylhexanol
- (c) 2-Methylhex-3-enol
- (d) 4-Methylpent-2-en-1-ol

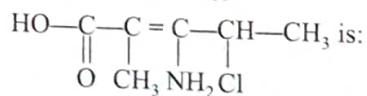
23. The IUPAC name of $\text{C}_6\text{H}_5\text{CH}=\text{CH}-\text{COOH}$ is:

- (a) Cinnamic acid
- (b) 1-Phenyl-2-carboxy ethene
- (c) 3-Phenylprop-2-enoic acid
- (d) Dihydroxy-3-phenylpropionic acid

24. The IUPAC name of $(\text{CH}_3)_2\text{CH}-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_3$ is:

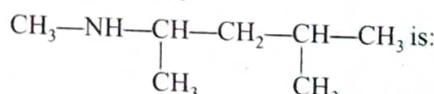
- (a) Ethylbutyrate
- (b) Isopropylpropionate
- (c) Ethyl-2-methylpropanoate
- (d) Isobutylethanoate

25. The systematic name for



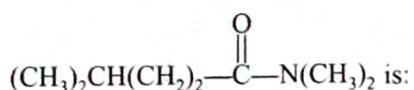
- (a) 2-Methyl-3-amino-4-chloro-2-pentenoic acid
- (b) 1-Hydroxy-1-oxo-2-methyl-3-amino-4-chloro-2-pentene
- (c) 3-Amino-4-chloro-2-methyl-2-pentenoic acid
- (d) 3-Amino-2,4-dimethyl-4-chloro-2-butenoic acid

26. The IUPAC name of



- (a) 2-(N-methyl amino)-4-methyl pentane
- (b) N,4-dimethyl pentan-2-amine
- (c) 2-(N-methyl amino)-3-isopropylpropane
- (d) 2-(N-methyl amino)-1,4,4-trimethylbutane

27. The IUPAC name of

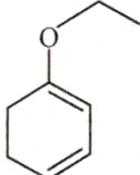


- (a) N, N, 4-trimethylpentanamide
- (b) Dimethylamino-4-methylpentanone
- (c) N, N-dimethylamino-4-methylpentanamide
- (d) 2-Methyl-5-oxodimethylpentanamine

28. A compound of molecular formula $C_6H_{12}O_3$ can never have a functional group:

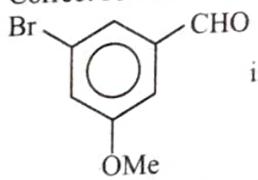
- (a) Carboxylic acid ($\text{---C}(=\text{O})\text{OH}$)
- (b) Aldehyde ($\text{---C}(=\text{O})\text{H}$)
- (c) Ester ($\text{---C}(=\text{O})\text{O---}$)
- (d) Anhydride ($\text{---C}(=\text{O})\text{O---C}(=\text{O})\text{---}$)

29. IUPAC name of the compound is:



- (a) 1-Ethoxycyclohexa-1,3-diene
- (b) 1-Ethoxycyclohexa-1,5-diene
- (c) 2-Ethoxycyclohexa-1,5-diene
- (d) 4-Ethoxycyclohexa-1,3-diene

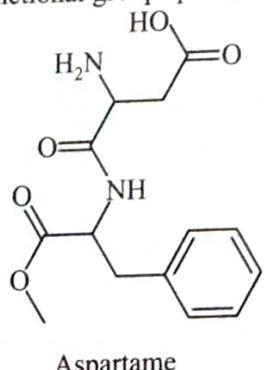
30. Correct IUPAC name for the compound



is:

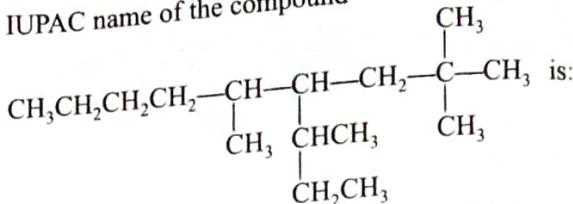
- (a) 3-Methoxy-5-bromobenzencarbaldehyde
- (b) 3-Formyl-5-bromophenylmethylether
- (c) 3-Formyl-5-bromo-1-methoxybenzene
- (d) 3-Bromo-5-methoxybenzenecarbaldehyde

31. Number of functional groups present in Aspartame are:



- (a) 4
- (b) 5
- (c) 7
- (d) 6

32. IUPAC name of the compound

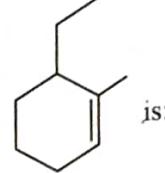


- (a) 2,2,5-Trimethyl-4-(1-methylpropyl)nonane
- (b) 4,8,8-Trimethyl-6-(1-methylpropyl)nonane
- (c) 3,5-Dimethyl-4-(1-methylene tertiary butyl)nonane
- (d) 6,6-Dimethyl-2-propyl-4-(1-methylpropyl)heptane

33. In the structure of 4-Isopropyl-2,4,5-trimethylheptane, number of 1° , 2° and 3° H's are respectively:

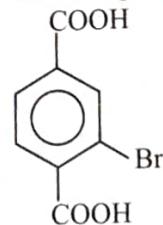
- | | |
|--------------|--------------|
| (a) 18, 5, 4 | (b) 21, 4, 3 |
| (c) 18, 4, 3 | (d) 21, 5, 4 |

34. The correct IUPAC numbering in the compound



- | | | | |
|-----|--|-----|--|
| (a) | | (b) | |
| (c) | | (d) | |

35. IUPAC name of the following molecule is:

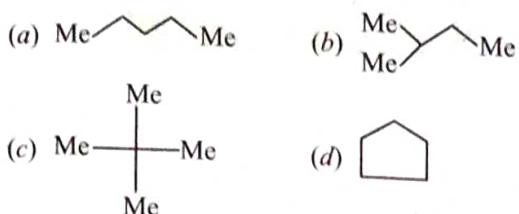


- (a) 2-Bromobenzene-1,4-dioic acid
- (b) 3-Bromobenzene-1,4-dicarboxylic acid
- (c) 2-Bromobenzene-1,4-dicarboxylic acid
- (d) 3-Bromobenzene-1,6-dicarboxylic acid

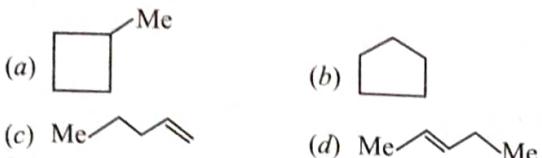
36. Which of the following is correctly named?

- | | | | |
|-----|--|-----|--|
| (a) | | (b) | |
| (c) | | (d) | |

37. An alkane (A) having a molecular mass of 72 produces one monochlorination product. The compound (A) is:



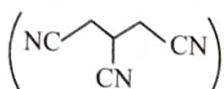
38. A compound (A) with molecular formula C_5H_{10} gives one monochlorination product. The compound (A) is:



39. The IUPAC name of vinyl acetylene is:

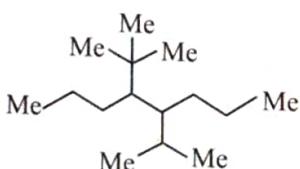
- (a) Pent-1-en-4-yne (b) Pent-4-yn-1-ene
 (c) But-1-en-3-yne (d) But-1-yn-3-ene

40. The IUPAC name of the following compound is:



- (a) Propane-1,2,3-tricarbonitrile
 (b) 3-Cyanopetane-1,5-dinitrile
 (c) Pentane-1,3,5-trinitrile
 (d) All are correct

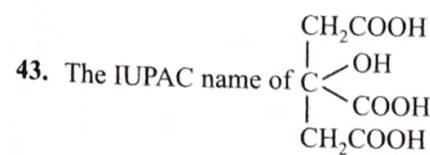
41. Give the IUPAC name of:



- (a) 2,2-Dimethyl-3-propyl-4-isopropyl heptane.
 (b) 4-Isopropyl-5-t-butyl octane.
 (c) 4-t-Butyl-5-isopropyl octane.
 (d) 2-Methyl-3-propyl-4-isopropyl heptane.

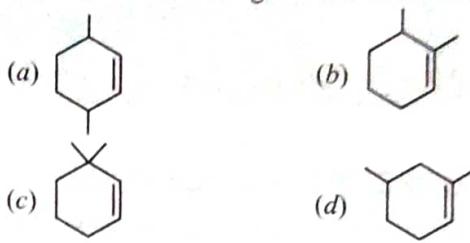
42. Which of the following statements is wrong for a homologous series?

- (a) All members have a general formula.
 (b) All members have the same functional group.
 (c) All members have the same chemical properties.
 (d) All members have the same physical properties.



- (a) 3-Carboxy-3-hydroxypentanedicarboxylic acid.
 (b) 2-Hydroxypropane-1,2,3-tricarboxylic acid.
 (c) 2-Hydroxypropane-1,2,3-trioic acid.
 (d) 3-Hydroxypropane-1,2,3-tricarboxylic acid.

44. Which of the following name will be incorrect?



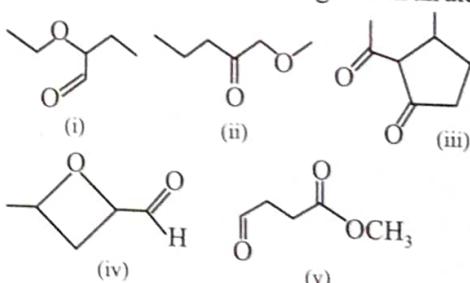
45. Correct IUPAC name of the given compound is:

- (a) Methyl 3-ethylclohexene
 (b) 5-Ethyl-1-methylcyclohexene
 (c) 2-Ethyl-4-methylcyclohexene
 (d) 3-Ethyl-1-methylcyclohexene

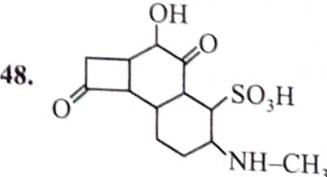
46. The IUPAC name of is:

- (a) 1-Bromo-2-chloro-3-fluoro-6-iodobenzene.
 (b) 2-Bromo-1-chloro-5-fluoro-3-iodobenzene.
 (c) 4-Bromo-2-chloro-5-iodo-1-fluorobenzene.
 (d) 2-Bromo-3-chloro-1-iodo-5-fluorobenzene.

47. Many organic compounds contain more than one functional group. Which of the following is both an aldehyde and ether?



- (a) (i) only (b) (i) and (iv)
 (c) (ii) and (v) (d) (iii) and (iv)



Which functional group is present in the above compound?

- (a) Carboxylic acid
 (b) Aldehyde
 (c) Thiol
 (d) Alcohol

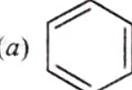
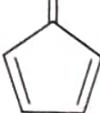
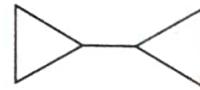
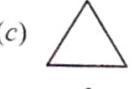
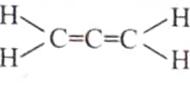
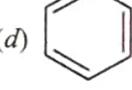
49. IUPAC name of this compound will be

- (a) Hex-5-en-1-yne
 (b) Hex-1-en-5-yne
 (c) Hex-6-en-1-yne
 (d) Hex-1-en-6-yne

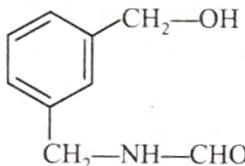
Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

1. Select the pair of compounds having same general formula?

- (a)  and 
- (b)  and 
- (c)  and 
- (d)  and $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$

2. Which functional groups are not present in given compound?

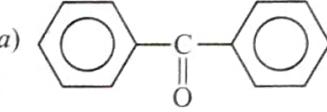
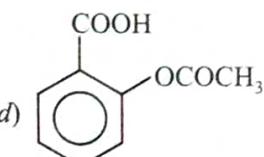


- (a) Amide
- (b) Alcohol
- (c) Amine
- (d) Aldehyde

3. Select the correct IUPAC name:

- (a) Methane-1,1,1,1-tetracarboxylic acid
- (b) 5-Carbonyl-heptane-1,7-dioic acid
- (c) 2-Chloro ethanoylchloride
- (d) 1-Bromo-3-fluoro-4-methylcyclohexane

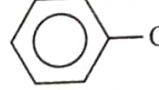
4. Which of the following are correct common names?

- (a)  Acetophenone
- (b) CH_3COCH_3 Acetone
- (c) PhCOCH_3 Benzophenone
- (d)  Aspirin (Acetyl salicylic acid)

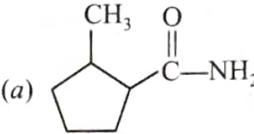
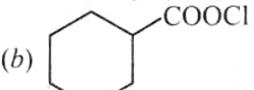
5. Which of the following IUPAC name(s) is/are incorrect?

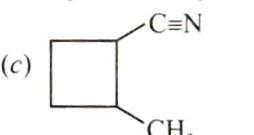
- (a) 4-Chloro-3-methylcyclopentanol
- (b) 1-Amino-3-bromohexan-1-one
- (c) 4-chloro-3-methylcyclohexane carboxylic acid
- (d) 3-Bromo-1-methylhexan-1-ol

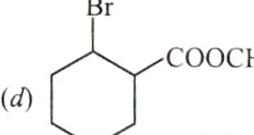
6. Which of the following represent correct pair of homologues?

- (a)  & 
- (b) $\text{Me}-\text{OH}$ & $\text{MeCH}_2\text{CH}_2\text{OH}$
- (c) $\text{H}-\overset{\text{O}}{\underset{\text{C}}{\text{||}}}-\text{O}-\text{CH}_3$ & $\text{CH}_3-\overset{\text{O}}{\underset{\text{C}}{\text{||}}}-\text{O}-\text{CH}_3$
- (d) $\text{CH}_3-\text{CH}_2-\text{NH}_2$ & $\text{CH}_3-\text{CH}_2-\text{N}(\text{H})-\text{CH}_3$

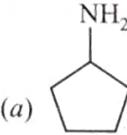
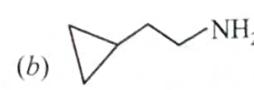
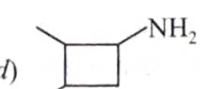
7. Which of the following IUPAC names are correct?

- (a)  2-Methylcyclopentanecarboxamide.
- (b)  Cyclohexanoyl chloride.

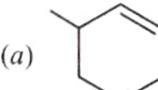
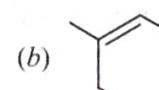
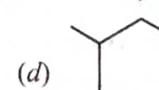
- (c)  2-Methylcyclobutanecarbonitrile

- (d)  Methyl-2-bromocyclohexanecarboxylate

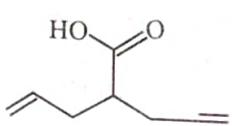
8. Which among the following compound(s) is a primary amine with the molecular formula $\text{C}_5\text{H}_{11}\text{N}$?

- (a) 
- (b) 
- (c) $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_3$
- (d) 

9. Which of the following is/are 3-Methyl cyclohex-3-enol?

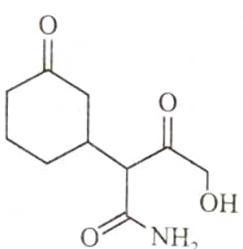
- (a) 
- (b) 
- (c) 
- (d) 

10. Which of the following statement(s) is/are correct?



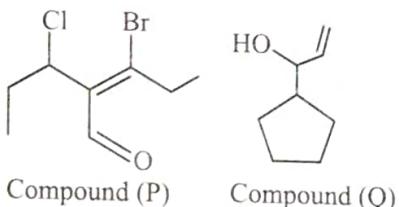
- (a) Double bond equivalent (DBE) value of the compound is 4.
- (b) Total 3 different functional groups are present.
- (c) Correct IUPAC name is 2-(prop-2-ynyl) pent-4-enoic acid.
- (d) Correct IUPAC name is 2-(prop-2-enyl) pent-4-ynoic acid.

11. Functional group present in given compound is/are?



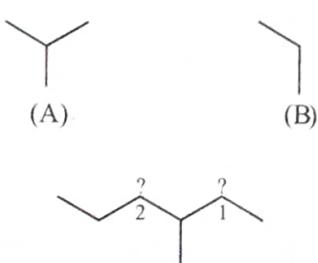
- (a) Alcohol
- (b) Ketone
- (c) Carboxylic acid
- (d) Amide

12. Correct statement about the following compounds (P) and (Q) is:



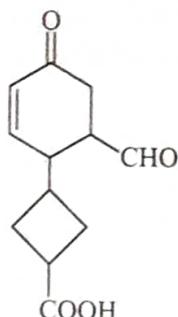
- (a) Total number of substituents in compound (P) is (1).
- (b) Total number of carbon atoms in parent chain of compound (Q) is (3).
- (c) IUPAC name of compound (Q) is 1-Cyclopentyl prop-2-en-1-ol.
- (d) Total number of carbons in parent chain of compound (P) are 5.

13. Build 5-ethyl-2,3,4-trimethylheptane by dragging the groups to the question marks:



- (a) A(1) B(2)
- (b) A(2) B(1)
- (c) A(1) A(2)
- (d) B(1) B(2)

14. Which of the following statements are correct for the given compound?



- (a) Double bond equivalent value is 5.
- (b) Number of carbon in parent chain is 4.
- (c) Correct IUPAC name is 3-(6-formyl-4-oxocyclohex-2-enyl)cyclobutane carboxylic acid.
- (d) Number of 2° carbons are 6.

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 15 to 17): A saturated hydrocarbon (P) has six membered ring. Three alkyl groups attached to the ring are alternate to each other.

- (i) First group has only two carbon atoms.
- (ii) Second group has four carbon atoms and its all hydrogen atoms are chemically same.
- (iii) Third group has total five carbon atoms. Its main chain contains three carbon atoms with ethyl as a substituent.

15. How many 3° hydrogen atoms are present in the hydrocarbon (P)?

- (a) 2
- (b) 3
- (c) 4
- (d) 5

16. How many 2° carbon atoms are present in the compound (P)?

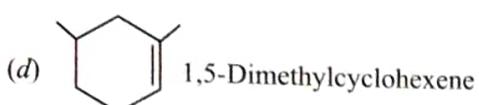
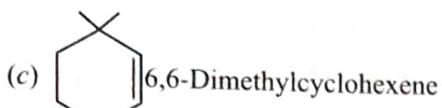
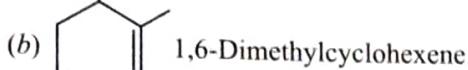
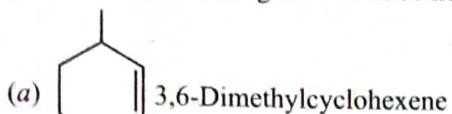
- (a) 10
- (b) 12
- (c) 6
- (d) 8

17. IUPAC name of hydrocarbon (P) is:

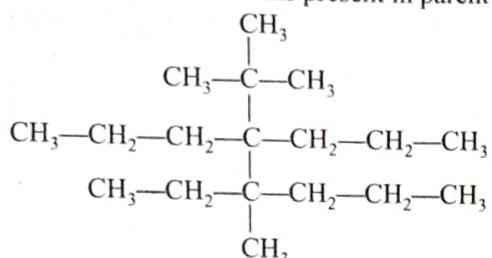
- (a) 1-(1-Ethylpropyl)-3-ethyl-5-(1,1-dimethylethyl)cyclohexane
- (b) 1-Ethyl-3-(1-ethylpropyl)-5-(1,1-dimethylethyl)cyclohexane
- (c) 1-(1,1-Dimethylethyl)-3-ethyl-5-(1-ethylpropyl)cyclohexane
- (d) 1-(1,1-Dimethylethyl)-3-ethyl-5-(2-ethylpropyl)cyclohexane

Comprehension (Q. 18 to 19): To avoid having to memorize the names of thousands of structural units, chemists have devised rules that name compounds on the basis of their structures. That way, only the rules have to be learned because the name is based on the structure, these rules make it possible to deduce the structure of a compound from its name. This method of nomenclature is called systematic nomenclature. It is also called IUPAC nomenclature

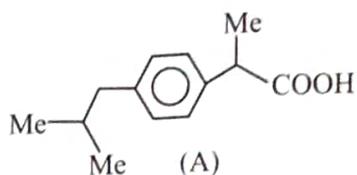
- 18.** Which of the following name will be not correct?



- 19.** Total number of carbon atoms present in parent chain is:



Comprehension (Q. 20 to 23): The analgesic drug ibuprofen (A) is chiral and exists in (+) and (-) forms. One enantiomer is physiologically active, while the other is physiologically inactive. The structure of ibuprofen is given below:



- 20.** The principal functional group in (A) is:

21. The IUPAC name of (A) is:

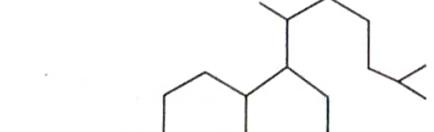
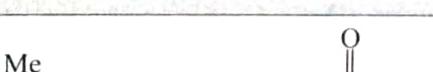
- (a) 3-(p-Isobutyl phenyl) propanoic acid
 - (b) 2-(p-Isobutyl phenyl) propanoic acid
 - (c) 3-(p-sec-Butyl phenyl) propanoic acid
 - (d) 2-(p-sec-Butyl phenyl) propanoic acid

- 22.** The number of π -bonds in (A) is:

23. The number of σ -bonds in (A) is:

MATCH THE COLUMN TYPE QUESTIONS

- 24.** Match the column

Column-I Compound		Column-II Containing all the functional groups	
A.	 <p>Vitamin D₃</p>	p.	1° amine
B.	 <p>Amphetamine</p>	q.	2° alcohol
C.		r.	Triene
		s.	Aldehyde and ene

- (c) A → p; B → q; C → s

- (d) A → s; B → p; C → q

25. Match the column

Column-I Compound		Column-II Containing all the functional groups	
A.	 Aspartame	p.	ene and diester
B.	 Demerol	q.	Carboxylic acid, 1° amine, amide
C.	 A synthetic cockroach repellent	r.	Ester
		s.	3° amine

(a) A → p; B → r,s; C → q,r

(b) A → q,r; B → r,s; C → p

(c) A → q; B → r; C → p

(d) A → p; B → r; C → q

26. Match the column

Column-I Compound		Column-II Containing all the functional groups	
A.	 (Adipic acid)	p.	6 Carbons in parent chain.
B.	 (Muscarine)	q.	3 Carbons in parent chain.
C.	 (Limonene)	r.	D.B.E. (Double bond equivalent) value is 5.
D.	 (IUPAC name: 2-[4-(2-methylpropyl) phenyl] propanoic acid)	s.	Only 1 type of functional group is present.
		t.	IUPAC name is 2-[4-(2-methylpropyl) phenyl] propanoic acid.

(a) A → q,r,t; B → p,s; C → p,s; D → p,s

(b) A → r,s,t; B → p,s; C → p,s; D → q,r,t

(c) A → q,r,t; B → p,q; C → p,s; D → p,s

(d) A → p,s; B → p,s; C → p,s; D → q,r,t

27. Match the column. (Note: Each statement in column I has only one match in column II.)

	Column-I (Group)		Column-II (Name)
A.		p.	sec-Butyl
B.		q.	tert-Butyl
C.		r.	Isopropyl
D.		s.	Neopentyl
E.		t.	Isobutyl

- (a) A → r; B → p; C → t; D → q; E → s
 (b) A → p; B → r; C → t; D → q; E → s
 (c) A → r; B → p; C → q; D → t; E → s
 (d) A → r; B → p; C → t; D → ; E → q
28. Match the column. (Note: Each statement in column I has one or more matches in column II.)

	Column-I (Common name)		Column-II Characteristics (I)		Column-III (Structure)
A.	Piperazine	i.	Cyclic esters	p.	
B.	Lactide	ii.	Cyclic amide	q.	
C.	Lactam	iii.	Cyclic diester	r.	
D.	Lactone	iv.	Cyclic diamide	w.	

- (a) A → iv, q; B → iii, s; C → i, r; D → ii, p
 (b) A → iii, s; B → iv, q; C → i, r; D → ii, p
 (c) A → iv, q; B → ii, p; C → iii, s; D → i, r
 (d) A → iv, q; B → iii, s; C → ii, p; D → i, r

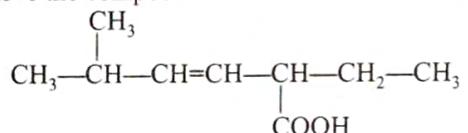
NUMERICAL TYPE QUESTIONS

29. Possible number of compounds with different structures and IUPAC name-bromo-methyl butanoic acid. Where p represents position of side chains/substituents?

30. Number of correct names in the given substituents are:

- | | |
|---------------------------|--------------------|
| (a)
(b)
(c) =CH-CH3 | Ethylmethyl |
| (d) -C≡CH | 2,3-Dimethylpropyl |
| (e) -CH2-C≡CH | Ethyldiene |
| (f) -CH(CH3)CH2-CH3 | Ethynyl |
| (g) -CH2-CH(CH3)CH(CH3)2 | Prop-1-ynyl |
| (h) -CH2=CH-CH3 | 1-Methylpropyl |
| (i) -CH2-CH=CH2 | 2,3-Dimethylbutyl |
| (j) -C=CH2 | 2-Methylethenyl |
| (k) -CH2-CH=CH2 | 2-Propenyl |

31. Observe the compound



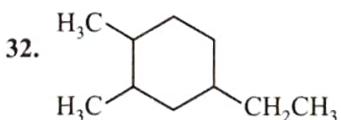
and answer the given question.

x = Number of carbon atoms in principal carbon chain.

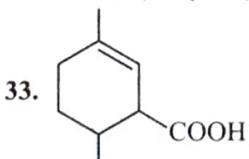
y = locant of methyl group.

z = locant of C = C.

Write your answer as x + y + z.



When IUPAC name to above compound is given, then substituents gets respectively (x, y and z) number, so the sum of (x + y + z) will be.



Number of positional isomers by changing position of -COOH only = X.

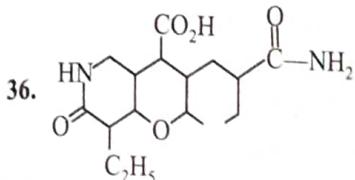
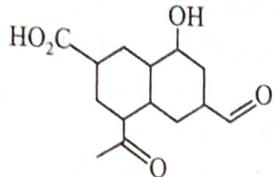
Number of positional isomers by changing position of double bond only = Y.

Include the given compound in both X & Y.

What is the value of |X-Y|?

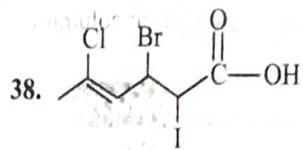
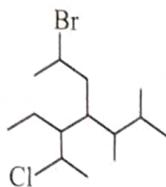
34. A cyclic organic compound containing nitrogen atom and 5 carbon atom with DBE 4 then find the total value of ($\sigma - \pi$) bonds.

35. How many different functional groups are present in the given compound?



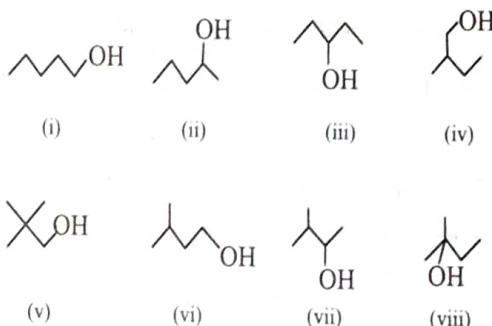
Number of functional groups in the above compound is

37. How many total number of substituents are present in the following compound?



Total number of substituent present in the above compound

39. How many number of compounds, will have same IUPAC name?



Exercise-4 (Past Year Questions)

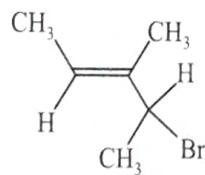
JEE MAIN

1. The distillation technique most suited for separating glycerol from spentlye in the soap industry is: (2016)

- (a) Simple distillation
- (b) Fractional distillation
- (c) Steam distillation
- (d) Distillation under reduced pressure

2. What is the IUPAC name of the following compound?

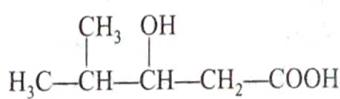
(2019)



- (a) 3-Bromo-1,2-dimethylbut -1-ene
- (b) 3-Bromo-3-methyl-1,2-dimethylprop-1-ene
- (c) 2-Bromo-3-methylpent-3-ene
- (d) 4-Bromo-3-methylpent-2-ene

3. The IUPAC name of the following compound is:

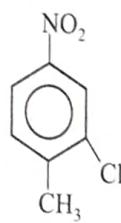
(2019)



- (a) 2-Methyl-3-hydroxypentan-5-oic acid
- (b) 4,4-Dimethyl-3-hydroxy butanoic acid
- (c) 3-Hydroxy-4-methylpentanoic acid
- (d) 4-Methyl-3-hydroxypentanoic acid

4. The correct IUPAC name of the following compound is:

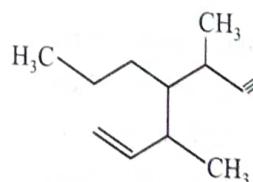
(2019)



- (a) 5-Chloro-4-methyl-1-nitrobenzene
- (b) 2-Methyl-5-nitro-1-chlorobenzene
- (c) 3-Chloro-4-methyl-1-nitrobenzene
- (d) 2-Chloro-1-methyl-4-nitrobenzene

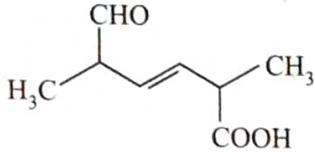
5. The IUPAC name of the following compound is:

(2019)



- (a) 3,5-Dimethyl-4-propylhept-6-en-1-yne
 (b) 3-Methyl-4-(3-methylprop-1-enyl)-1-heptyne
 (c) 3-Methyl-4-(1-methylprop-2-ynyl)-1-heptene
 (d) 3,5-Dimethyl-4-propylhept-1-en-6-yne

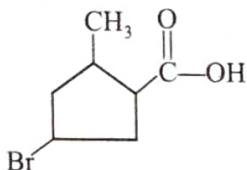
6. The IUPAC name for the following compound is: (2020)



- (a) 6-Formyl-2-methyl-hex-3-enoic acid
 (b) 2,5-Dimethyl-6-carboxy-hex-3-enal
 (c) 2,5-Dimethyl-5-carboxy-hex-3-enal
 (d) 2,5-Dimethyl-6-oxo-hex-3-enoic acid

7. The IUPAC name of the following compound is:

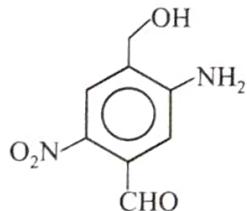
(2020)



- (a) 3-Bromo-5-methylcyclopentane carboxylic acid
 (b) 3-Bromo-5-methylcyclopentanoic acid
 (c) 5-Bromo-3-methylcyclopentanoic acid
 (d) 4-Bromo-2-methylcyclopentane carboxylic acid

8. The IUPAC name of the following compound is:

(2020)



- (a) 4-Amino-2-formyl-5-hydroxymethyl nitrobenzene
 (b) 5-Amino-4-hydroxymethyl-1-2-nitrobenzaldehyde
 (c) 3-Amino-4-hydroxymethyl-1-5-nitrobenzaldehyde
 (d) 2-Nitro-4-hydroxymethyl-5-amino benzaldehyde

9. Choose the correct name for compound given below:

(2021)



- (a) (4E)-5-Bromo-hex-4-en-2-yne
 (b) (2E)-2-Bromo-hex-4-yn-2-ene
 (c) (2E)-2-Bromo-hex-2-en-4-yne
 (d) (4E)-5-Bromo-hex-2-en-4-yne

10. Mesityl oxide is a common name of:
 (a) 2,4-Dimethylpentan-3-one
 (b) 3-Methylcyclohexane carbaldehyde
 (c) 2-Methylcyclohexanone
 (d) 4-Methylpent-3-en-2-one

11. Choose the correct name for compound given below: (2021)

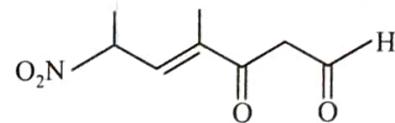
- (a) (4E)-5-Bromo-hex-2-en-4-yne
 (b) (2E)-2-Bromo-hex-4-yn-2-ene
 (c) (2E)-2-Bromo-hex-2-en-4-yne
 (d) (4E)-5-Bromo-hex-4-en-2-yne

12. The IUPAC name of ethylidene chloride is: (2021)

- (a) 1-Chloroethene (b) 1-Chloroethyne
 (c) 1,2-Dichloroethane (d) 1,1-Dichloroethane

13. The correct IUPAC name of the following compound is:

(2022)



- (a) 4-Methyl-2-nitro-5-oxohept-3-enal
 (b) 4-Methyl-5-oxo-2-nitrohept-3-enal
 (c) 4-Methyl-6-nitro-3-oxohept-4-enal
 (d) 6-Formyl-4-methyl-2-nitrohex-3-enal

14. The correct decreasing order of priority of functional groups in naming an organic compound as per IUPAC system of nomenclature is: (2022)

- (a) —COOH > —CONH₂ > —COCl > —CHO
 (b) —SO₃H > —COCl > —CONH₂ > —CN
 (c) —COOR > —COCl > —NH₂ > C=O
 (d) —COOH > —COOR > —CONH₂ > —COCl

15. Match List-I with List-II.

	List-I		List-II
A.		p.	Spiro compound
B.		q.	Aromatic compound
C.		r.	Non-planar Heterocyclic compound
D.		s.	Bicyclo compound

Choose the correct answer from the options given below:

- (a) (A) – q, (B) – p, (C) – s, (D) – r
 (b) (A) – s, (B) – r, (C) – p, (D) – q
 (c) (A) – r, (B) – s, (C) – p, (D) – q
 (d) (A) – s, (B) – r, (C) – q, (D) – p

JEE ADVANCED

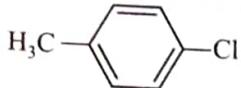
16. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is (are): (2012)

- (a) sp and sp^3
- (b) sp and sp^2
- (c) Only sp^3
- (d) sp^2 and sp^3

17. The carboxyl functional group ($-COOH$) is present in: (2012)

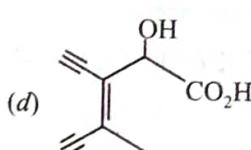
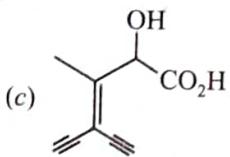
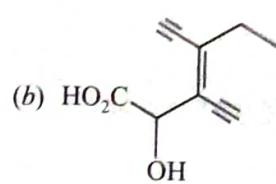
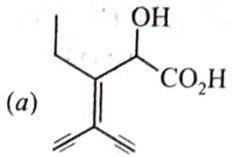
- (a) Picric acid
- (b) Barbituric acid
- (c) Ascorbic acid
- (d) Aspirin

18. The IUPAC name(s) of the following compound is/are: (2017)



- (a) 4-Methylchlorobenzene
- (b) 4-Chlorotoluene
- (c) 1-Chloro-4-methylbenzene
- (d) 1-Methyl-4-chlorobenzene

19. Which one of the following structures has the IUPAC name 3-ethyl-2-hydroxy-4-methylhex-3-en-5-yneoic acid? (2020)



ANSWER KEY

CONCEPT APPLICATION

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|--------|--------|--------|--------|---------|
| 1. (c) | 2. (a) | 3. (d) | 4. (a) | 5. (a) | 6. (b) | 7. (d) | 8. (c) | 9. (c) | 10. (b) |
| 11. (d) | 12. (d) | 13. (b) | 14. (a) | 15. (b) | | | | | |

EXERCISE-1 (TOPICWISE)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (c) | 3. (d) | 4. (d) | 5. (b) | 6. (d) | 7. (a) | 8. (c) | 9. (d) | 10. (c) |
| 11. (c) | 12. (a) | 13. (c) | 14. (a) | 15. (c) | 16. (b) | 17. (c) | 18. (c) | 19. (b) | 20. (c) |
| 21. (a) | 22. (d) | 23. (c) | 24. (b) | 25. (c) | 26. (b) | 27. (c) | 28. (d) | 29. (b) | 30. (b) |
| 31. (d) | 32. (b) | 33. (a) | 34. (b) | 35. (b) | 36. (a) | 37. (c) | 38. (c) | 39. (c) | 40. (d) |
| 41. (a) | 42. (d) | 43. (c) | 44. (b) | 45. (b) | 46. (a) | 47. (c) | 48. (a) | 49. (c) | 50. (c) |
| 51. (b) | 52. (b) | | | | | | | | |

EXERCISE-2 (LEARNING PLUS)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (a) | 3. (c) | 4. (c) | 5. (a) | 6. (c) | 7. (a) | 8. (c) | 9. (a) | 10. (d) |
| 11. (d) | 12. (a) | 13. (b) | 14. (d) | 15. (a) | 16. (d) | 17. (b) | 18. (b) | 19. (a) | 20. (a) |
| 21. (c) | 22. (d) | 23. (c) | 24. (c) | 25. (c) | 26. (b) | 27. (a) | 28. (d) | 29. (a) | 30. (d) |
| 31. (a) | 32. (a) | 33. (b) | 34. (d) | 35. (c) | 36. (c) | 37. (c) | 38. (b) | 39. (c) | 40. (a) |
| 41. (c) | 42. (d) | 43. (b) | 44. (c) | 45. (b) | 46. (b) | 47. (b) | 48. (d) | 49. (b) | |

EXERCISE-3 (JEE ADVANCED LEVEL)

- | | | | | | | | | | |
|-------------|-------------|----------------------|-------------|------------|----------|------------|----------|---------|-------------|
| 1. (a,d) | 2. (c,d) | 3. (a,c) | 4. (b,d) | 5. (a,b,d) | 6. (b,c) | 7. (a,c,d) | 8. (a,b) | 9. (c) | 10. (a,b,c) |
| 11. (a,b,d) | 12. (b,c,d) | 13. (a) | 14. (b,c,d) | 15. (c) | 16. (c) | 17. (c) | 18. (c) | 19. (d) | 20. (b) |
| 21. (b) | 22. (c) | 23. [4] | 24. (a) | 25. (b) | 26. (d) | 27. (a) | 28. (d) | 29. [6] | 30. [5] |
| 31. [14] | 32. [7] | 33. [1] x = 7, y = 8 | | 34. [8] | 35. [4] | 36. [5] | 37. [4] | 38. [3] | 39. [0] |

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|--------|--------|--------|--------|---------|
| 1. (d) | 2. (d) | 3. (c) | 4. (d) | 5. (d) | 6. (d) | 7. (d) | 8. (b) | 9. (c) | 10. (d) |
| 11. (c) | 12. (d) | 13. (c) | 14. (b) | 15. (c) | | | | | |

JEE Advanced

- | | | | | | | | | | |
|---------|---------|-----------|---------|--|--|--|--|--|--|
| 16. (b) | 17. (d) | 18. (b,c) | 19. (d) | | | | | | |
|---------|---------|-----------|---------|--|--|--|--|--|--|

CHAPTER

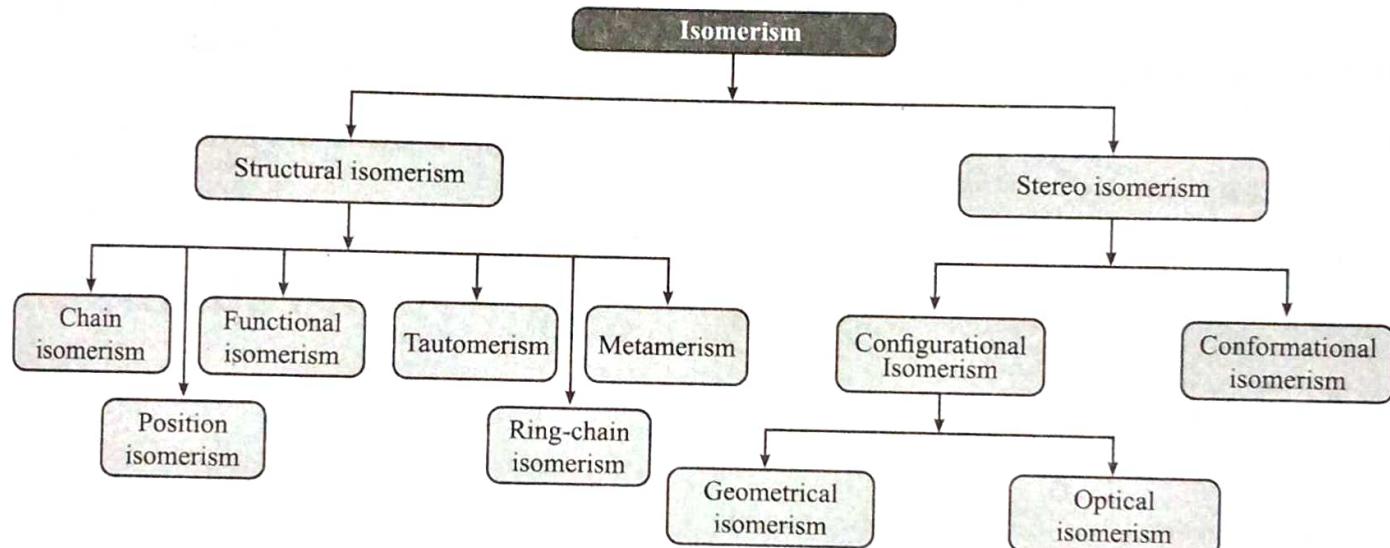
13

Isomerism

INTRODUCTION

- The organic compounds which have same molecular formula but different properties are called as isomers and the phenomenon is called **isomerism**.
- The term "isomerism" is given by **Berzelius**.

Classification of Isomerism



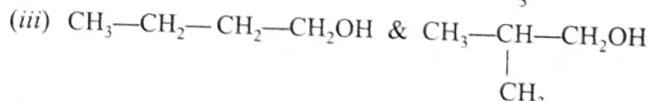
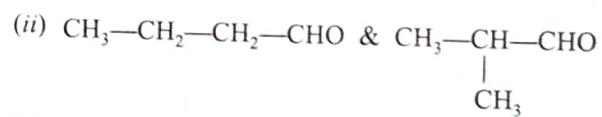
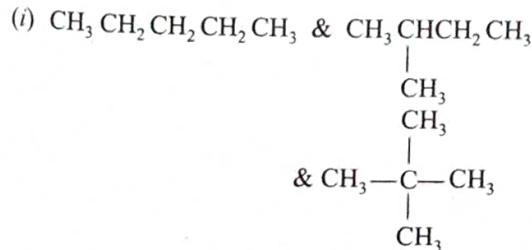
Structural Isomerism

Structural isomers possess the same molecular formula but different structural formula. The term **constitutional isomerism** is a more modern term of structural isomerism. It arises because of the difference in the sequence of covalently bonded atoms in the molecule without reference to space.

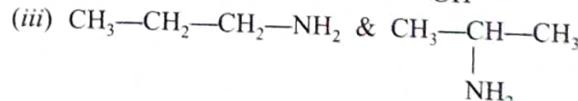
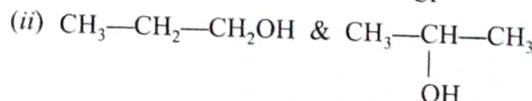
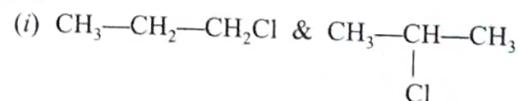
It is sub-classified into following types:

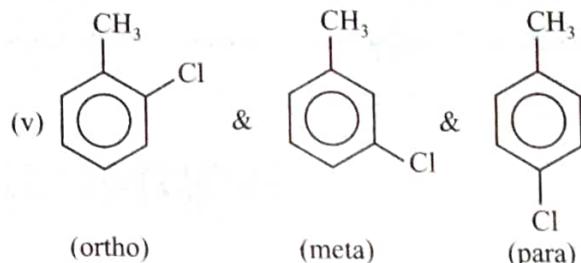
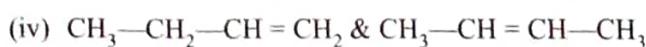
- Chain Isomerism:** Chain isomers possess the same molecular formula, same functional group but different principal carbon chain.

e.g.



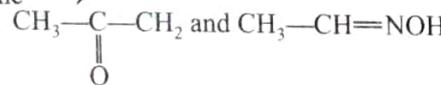
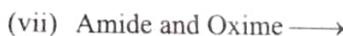
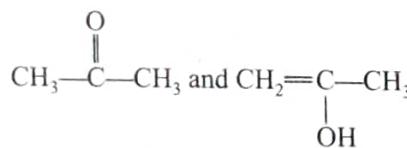
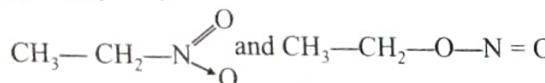
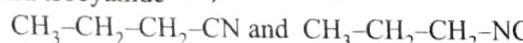
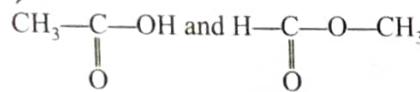
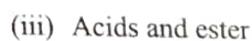
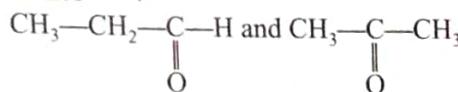
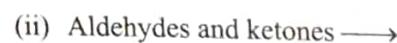
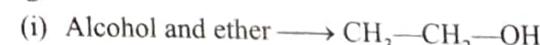
- Position Isomerism:** Position isomers possess the same molecular formula, same functional group but different position of substituent, multiple bond or functional group.





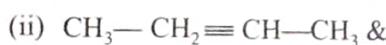
3. Functional Group Isomerism: Compound which have same molecular formula but different functional groups are called functional isomers.

eg.

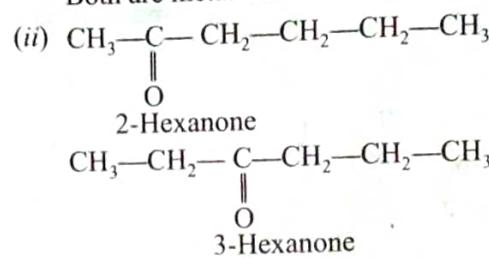
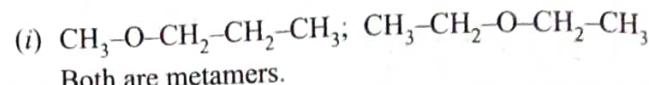
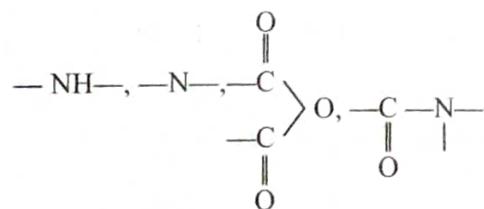
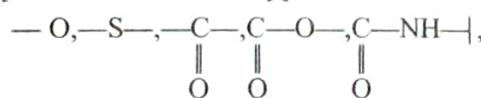


4. Ring chain isomerism: Ring-chain isomers possess the same molecular formula but difference of carbon-chain or ring.

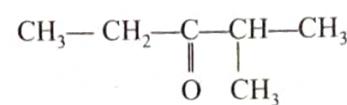
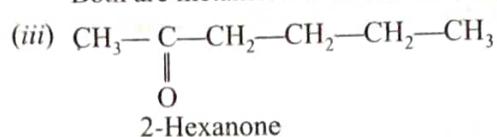
e.g.



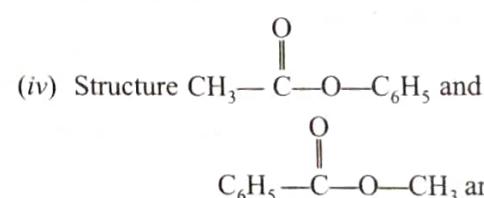
5. Metamerism: Same molecular formula, same polyvalent Functional group but different alkyl groups attached to polyvalent Functional group. Polyvalent Functional group [More than one valency] are:



Both are metamers and Position isomer

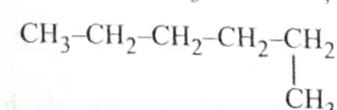
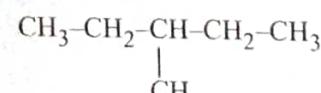


Both are Metamers, Chain isomers



Train Your Brain

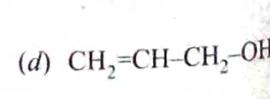
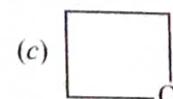
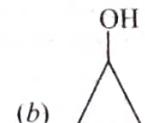
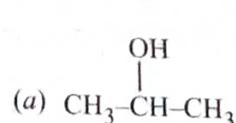
Example 1: What is the correct relationship between the following compounds?



- (a) Chain isomers (b) Position isomers
(c) Functional isomers (d) Identical

Sol. (a) Some molecular formula different principle chain.

Example 2: Which of the following is not an isomer of compound $\text{CH}_3\text{CH}_2\text{CHO}$



Sol. (a) Compound (a) because of different molecular formula.

Example 3: Functional isomer of $\text{CH}_3\text{COOCH}_3$ is –

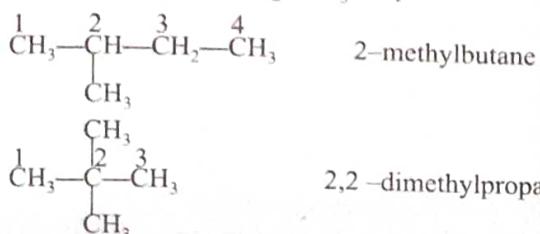
- (a) $\text{CH}_3\text{CH}_2\text{COOH}$ (b) $\text{HOCH}_2-\text{CH}_2\text{CHO}$
 (c) Both of the above (d) None of the above

Sol. (c) Same molecular formula but different functional groups.

Example 4: How many structural isomers possible for C_5H_{12} .

- (a) 2 (b) 3
 (c) 4 (d) 5

Sol. (b) $\text{CH}_3-\overset{5}{\text{CH}_2}-\overset{4}{\text{CH}_2}-\overset{3}{\text{CH}_2}-\overset{2}{\text{CH}_2}-\overset{1}{\text{CH}_3}$ n-pentane



Concept Application

1. and are:

- (a) Chain Isomers (b) Functional isomers
 (c) Position isomers (d) All the above

2. $\text{CH}_3-\text{CH}_2-\text{NH}-\text{CHO}$; $\text{CH}_3-\overset{\text{NH}_2}{\underset{\text{II}}{\text{CH}}}-\text{CHO}$

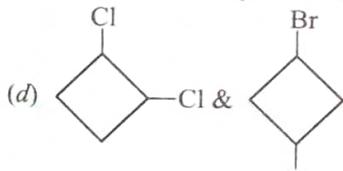
I

Which type of isomerism is observed between I and II.

- (a) Chain isomers (b) Position isomers
 (c) Functional isomers (d) Metamers

3. Which one of the following pairs are called position isomers

- (a) $\text{CH}_2(\text{OH})\text{CH}_2\text{COOH}$ and $\text{CH}_3-\text{CH}(\text{OH})\text{COOH}$
 (b) $\text{C}_2\text{H}_5\text{OH}$ and CH_3OH
 (c) $\text{CH}_3-\text{NH}-\text{CH}_3$ and $\text{CH}_3\text{CH}_2-\text{NH}_2$



4. Which compound is not the isomer of 3-Ethyl-2-methylpentane?

- (a) (b)
 (c) (d)

5. How many structural isomers does C_4H_8 have?

- (a) 3 (b) 4
 (c) 5 (d) 6

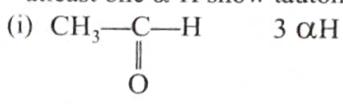
(6) Tautomerism

- ❖ Tautomerism is a special type of functional group isomerism which arises due to the transfer of H- atom as proton from a polyvalent atom to other polyvalent atom.
- ❖ Such isomers are directly and readily inter convertible under ordinary conditions, and the isomers are called tautomers.
- ❖ Tautomers exist in dynamic equilibrium.
- ❖ They have no separate existence under ordinary conditions like other isomers mentioned above.
- ❖ Tautomerism is thus the property shown by certain compounds exhibiting different properties, as if they possess different structures and these constitutional isomers are called tautomers.

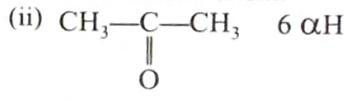
CONDITION FOR TAUTOMERISM

A. Triad System

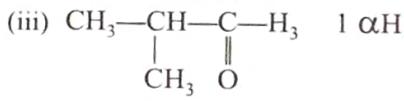
(a) **For carbonyl compounds:** Carbonyl compounds having atleast one α -H show tautomerism.



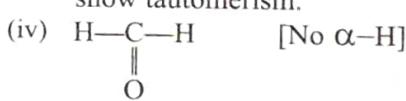
show tautomerism.



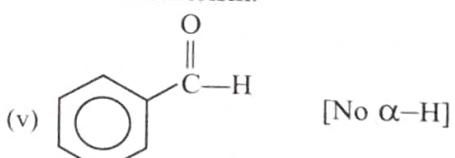
show tautomerism.



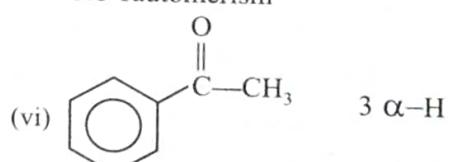
show tautomerism.



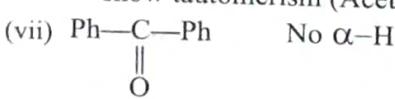
No tautomerism.



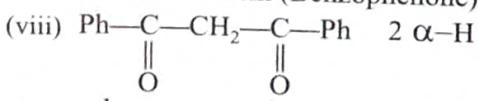
No Tautomerism



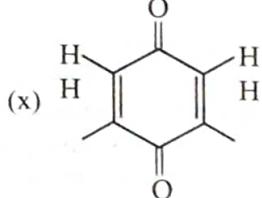
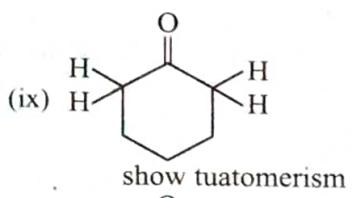
show tautomerism (Aceto phenone)



No tautomerism (Benzophenone)

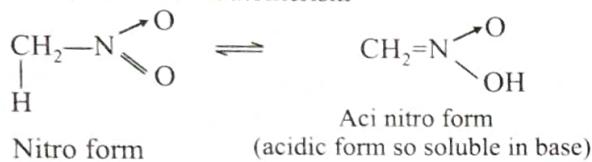


show tautomerism



α -H, attached sp^2 C-carbon does not take part in tautomerism

(b) **For nitro compounds:** Nitro compounds having atleast one α -H show tautomerism



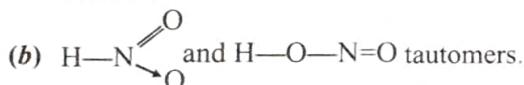
Note: Nitro compounds with atleast one α -H are soluble in NaOH.

B. Diad System

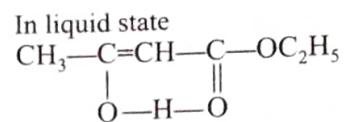
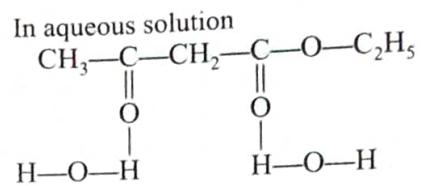
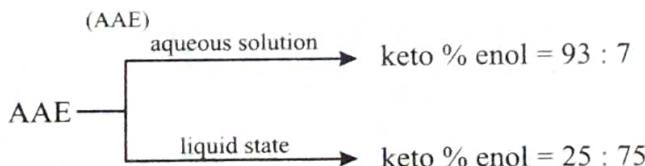
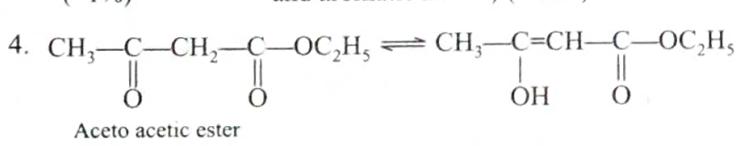
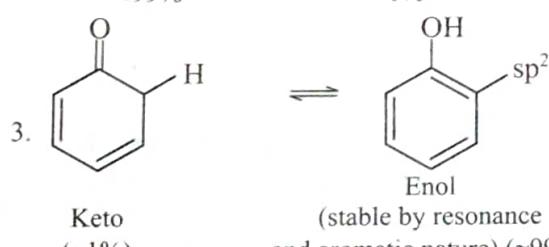
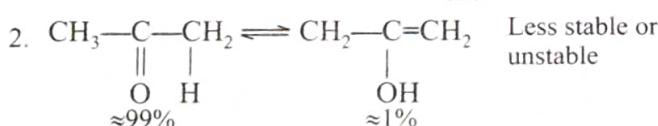
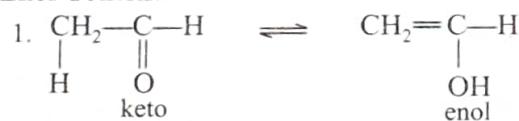
(a) $\text{H}-\text{C}\equiv\text{N}$ and $\text{H}-\text{N}\equiv\text{C}$ are tautomers [also Functional isomers][while $\text{R}-\text{C}\equiv\text{N}$ and $\text{R}-\text{N}\equiv\text{C}$ are only Functional isomers.



Active H



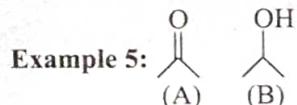
Enol Content



1. Enol content \propto number of $>\text{C}=\text{O}$ group.
2. If number of $>\text{C}=\text{O}$ groups are equal then proportional to number of α -H.
3. Group $-\text{OH}$ attached to sp^2 carbon or double bond is less stable or unstable.
4. More active H, more take part in tautomerism.
5. Stability of enol form depends on
 - (i) Resonance and (ii) H-Bond.



Train Your Brain

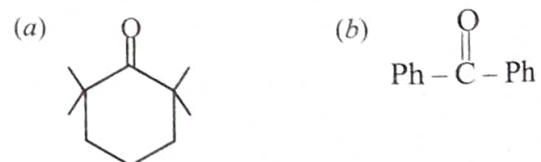


Relationship between (A) & (B) is (other then tautomerism)?

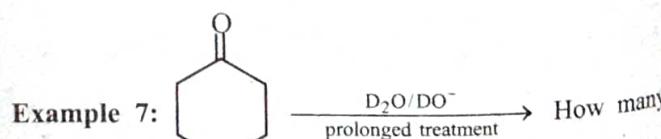
- Functional isomerism
- Metamer
- Chain isomer
- Positional isomer

Sol. (a) As both have different functional group carbonyl & alcohol.

Example 6: Which of the following compound will not undergo Tautomerism?



Sol. (d) Because there is no α -hydrogen in all given compounds.

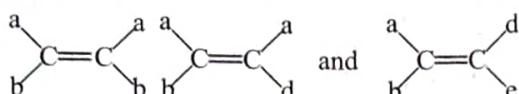


hydrogen is replaced by deuterium during given reaction?

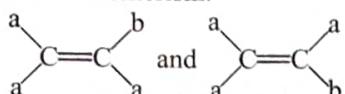
- 2
- 4
- 6
- 8

Sol. (b) There are 4 α -hydrogen, So 4 hydrogen is replaced by deuterium during given reaction.

(II) Different groups should be attached at each doubly bonded atom.



On the other hand, following types of compounds can not show geometrical isomerism.

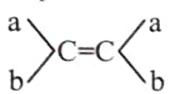


are identical but not geometrical isomers.

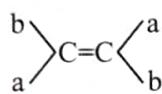
(III) Groups responsible to show geometrical isomerism must be nearly in the same plane.

NOMENCLATURE SYSTEMS GEOMETRICAL ISOMERS

Cis-Trans System: If same groups at same side then cis and if same groups at different side then trans.



[Same groups, same side]
cis

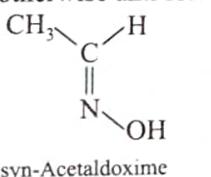


[Same groups different side]
trans

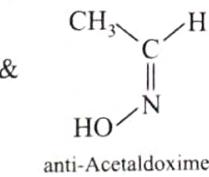
GEOMETRICAL ISOMERISM IN OXIME

Oxime of aldehyde and oxime of unsymmetrical ketone also show Geometrical isomerism.

❖ In Aldoximes if -OH group and H atom is same side then it is syn form otherwise anti form.

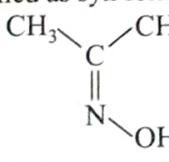


syn-Acetaldoxime

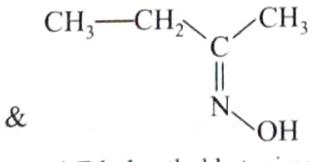


anti-Acetaldoxime

❖ In unsymmetrical Ketoxime, if -OH and the alphabetically alkyl present. On the same side of double bond, then it is called as syn form and other isomer is anti form.



syn-Ethylmethyl ketoxime

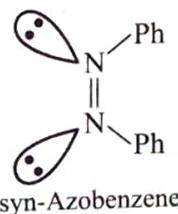


anti-Ethylmethyl ketoxime

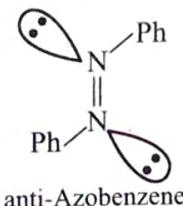
GEOMETRICAL IN AZO COMPOUNDS

All azo compounds shows geometrical isomerism.

e.g. $\text{Ph}-\text{N}=\text{N}-\text{Ph}$



syn-Azobenzene



anti-Azobenzene

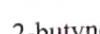


Train Your Brain

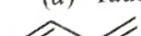
Example 8: 2-butyne and 1,3-butadiene are –

- (a) Chain isomers (b) Position isomers
(c) Functional isomers (d) Tautomers

Sol. (c)



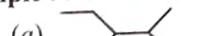
2-butyne
(alkyne)



1,3-butadiene
(diene)

Functional Isomer

Example 9: Cis-trans isomerism is shown by:



(a)



(b)



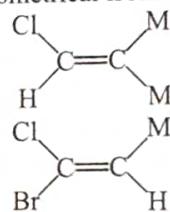
(c)



(d)

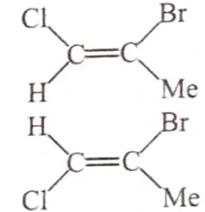
Sol. (a) Different groups are present on both sides.

Example 10: Among the given compounds identify the pair of geometrical isomers:



(a) I & II

(c) II & IV



(b) I & III

(d) III & IV

Sol. (c) cis-trans isomers are pair of geometrical isomers.



Concept Application

9. Which of the following compounds can exhibit geometrical isomerism?

- (a) 2-pentyne (b) 2-pentene
(c) 2-methylpropane (d) 2-methyl-2-butene

10. Which of the following compounds will show geometrical isomerism?

- (a) Propene (b) 2-methyl-2-butene
(c) 1-phenylpropene (d) 2-butyne

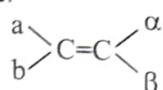
11. Which of the following pairs of compounds are geometrical isomers?

- (a) and
(b) and
(c) and
(d) and

COMPARISON OF PROPERTIES OF CIS OR TRANS-ISOMERS: (REF. \Rightarrow 2-BUTENE)

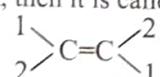
S.No.	Properties	Answer	Reason
1.	Stability	trans > cis	Trans have less mutual repulsion between the group.
2.	Dipole moment	cis > trans	Trans have zero dipole moment.
3.	Polarity	cis > trans	cis have more dipole moment so more polar.
4.	Solubility in water	cis > trans	cis is more polar so more soluble
5.	Boiling Point (BP)	cis > trans	cis is more polar so more Boiling point.
6.	Melting Point (MP)	trans > cis	Trans is symmetrical molecule therefore better packing in crystal lattice, so it has more Melting point.

E-Z Configuration: In such type of compounds Geometrical Isomer is not express by cis-trans nomenclature, thus a better system E-Z, is applicable.

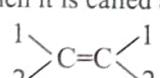


E → Entgegen (opposite),
Z → Zusammen (same)

E-form: When two high priority group attach on the opposite side of double bonded carbon, then it is called as E-form.

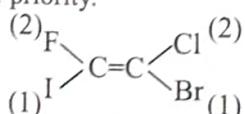


Z-form: When two high priority group attach on the same side of double bonded carbon, then it is called as Z-form.

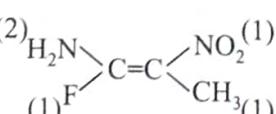


Priority Rule: Kahn, Ingold & Bräuer proposed a so-called "rule of 2".

Rule-1: When atom or group of atom which are directly attached to the stereogenic centre have higher atomic number will have higher priority.

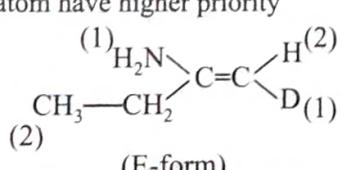


(Z_c-form)

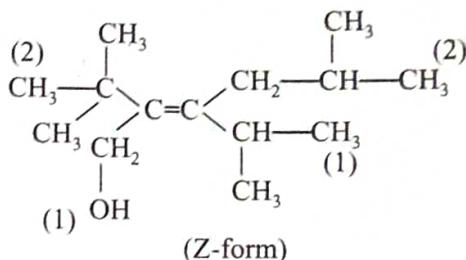


(E-form)

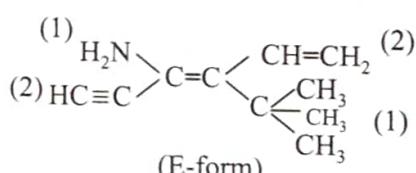
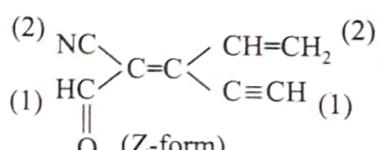
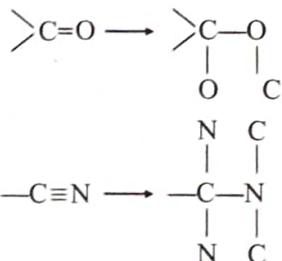
Rule-2: When the atomic number will be same, then higher atomic weight group or atom have higher priority.



Rule-3: When both atomic number and atomic weight are same then priority will be decided by the next joining atom.

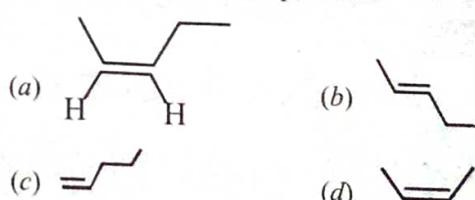


Rule-4: If multiple bonded group attach to the double bonded carbon, then they consider in following manner.



Train Your Brain

Example 11: Identify (Z)-2-pentene:



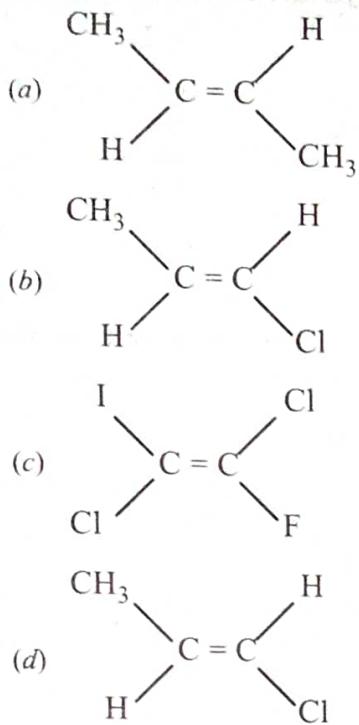
Sol. (a) As it have higher priority groups on same side.

Example 12: Which of the following is correct sequence for priority order based on CIP rule?

- (a) $-\text{C}\equiv\text{CH} < -\text{CH}=\text{CH}_2$
 (b) $-\text{OCH}_3 < -\text{OH} < -\text{NHCH}_3 < -\text{SH}$
 (c) $-\text{H} < -\text{CH}_3 < -\text{O-H} < -\text{F}$
 (d) $-\text{NO}_2 < -\text{NO} < -\text{OH} < -\text{Br}$

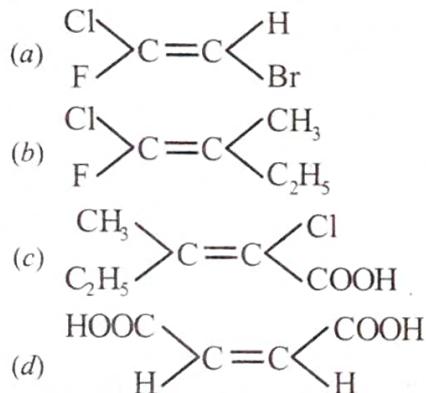
Sol. (c) As it is in order of increasing atomic number

Example 13: Which Trans isomers are also Z-isomer?



Sol. (c) It is following both trans and z-isomer condition.

Example 14: The 'Z'-isomer is:

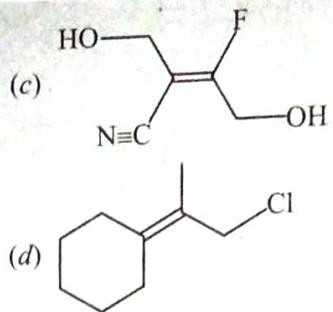
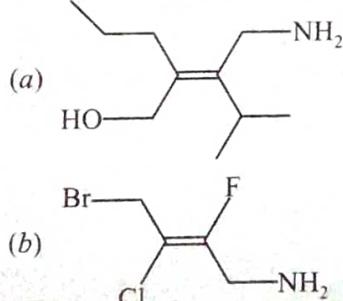


Sol. (d) Higher priority group on same side.

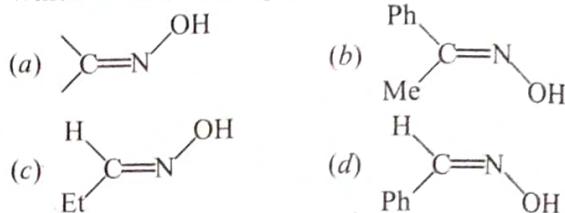


Concept Application

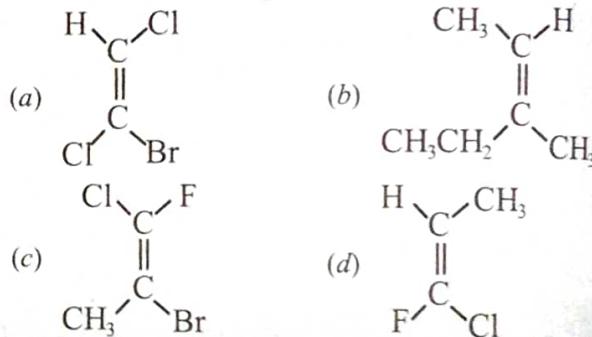
12. Which alkene has the Z configuration along double bond?



13. Which of the following is a Z isomer?

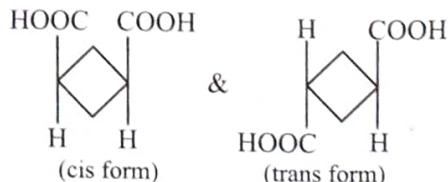
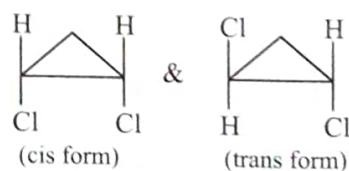


14. Which of the following are E-isomers?



GEOMETRICAL ISOMERISM IN CYCLOALKANE

In cyclic compound the rotation about C—C single bond is not possible because of the rigidity caused by the presence of other carbon of the ring which keep them tightly held, thus a disubstituted cyclic compound (having the two substitution at the separate carbon) will also show Geometrical Isomerism.

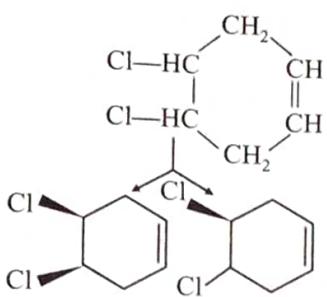


G.I. in Cycloalkenes: Compound can show G.I about two system

- (i) **Ring:** Minimum 2 saturated carbon atoms on ring with different units.
- (ii) **Double bond:** Ring should be composed of minimum eight atoms.

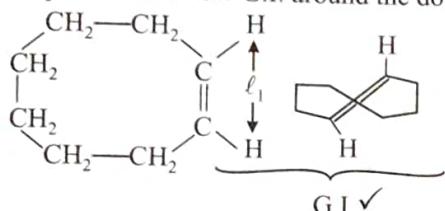
Since its one of the G.I has twisted ring.

Example: (i)



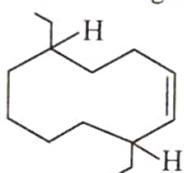
Example: (ii)

This compound will show G.I. around the double bond.



Example: (iii)

It can show G.I. around the ring and double bond.



G.I. in Alkylidene Cycloalkanes and Alkylidene Cycloalkenes

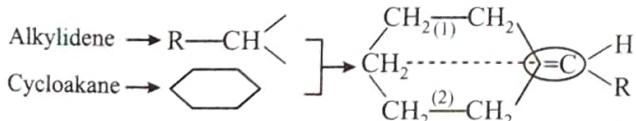
The compounds can show G.I. about 3 systems

(i) Ring:- Min 2 saturated atoms with different units

(ii) Double bond is ring:- Min 8 atoms in ring

(iii) Double bond outside the Ring:

Double bond atoms should individually have different units.
If ring is present on a terminal it is divided into two parts & these parts are considered as two units for that terminal



This compound will not show G.I. around the ring and double bond.

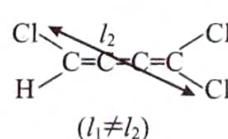
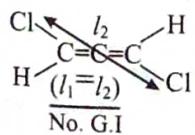
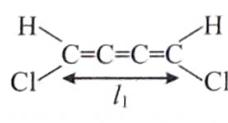
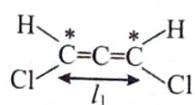
Note: (a) Even π -bond do not show G.I.

(b) Odd π -bonded show G.I.

Cumulated polyene

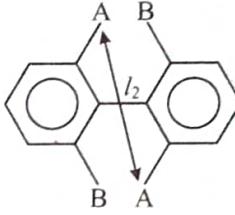
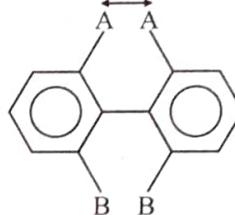
Units in \perp plane
(even no. of D.B.)
No. G.I.

Units in same plane
(odd no. of D.B.)
(G.I.)



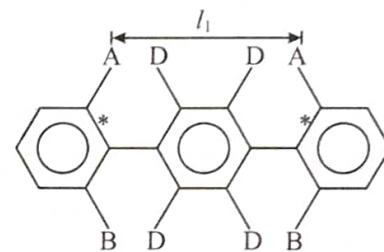
Poly phenyl: Those poly phenyls in which any rings are in same plane unit on rings are individually different none of the repelling unit is Hydrogen show G.I.

l_1



$(l_1 = l_2)$

l_1

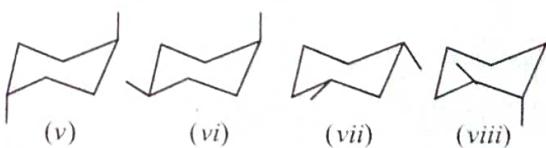
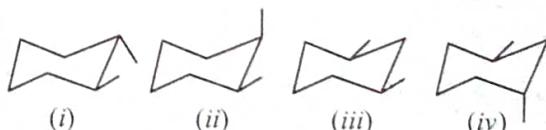


$(l_1 \neq l_2)$



Train Your Brain

Example 15: In the following structures, which conformations are in cis form?



Sol. (ii, iii, vi, vii)

(i) 1, 2 equatorial equatorial = trans

(ii) 1, 2 axial equatorial = cis

(iii) 1, 3 equatorial equatorial = cis

(iv) 1, 3 axial equatorial = trans

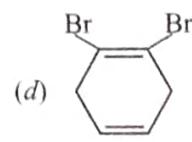
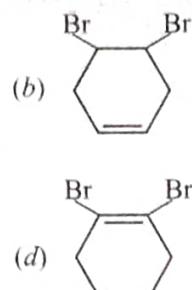
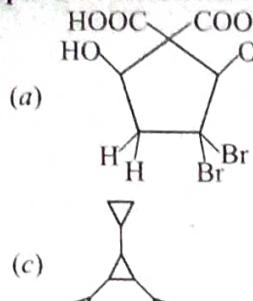
(v) 1, 4 axial axial = trans

(vi) 1, 4 axial equatorial = cis

(vii) 1, 3 equatorial equatorial = cis

(viii) 1, 2 axial axial = trans

Example 16: Which will not show geometrical isomerism?

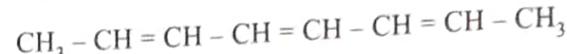


Sol. (d) This not show geometrical isomerism.

if n is even no. then, $p = \frac{n}{2}$;

if n is odd no. then, $p = \frac{n+1}{2}$.

e.g.



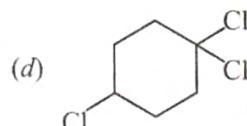
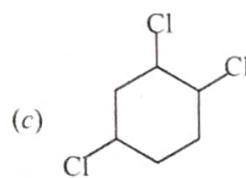
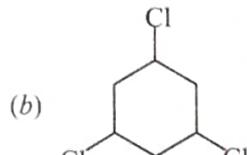
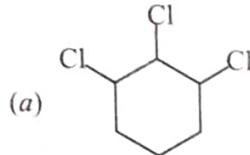
$$\text{here } n = 3 \text{ and } p = \frac{3+1}{2} = 2$$

Total isomers = 6

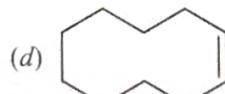
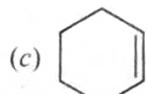
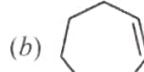


Concept Application

15. Which of the following compounds does not have any geometrical isomer?

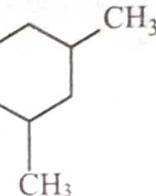


16. Geometrical isomerism is possible in:



Train Your Brain

Example 17:



How many geometrical isomers are possible for the above compound?

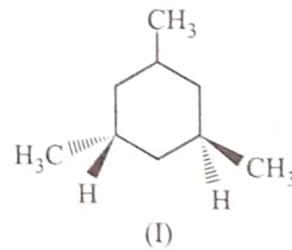
(a) 0

(b) 2

(c) 3

(d) 4

Sol. (b)



Example 18:

How many geometrical isomers are possible for the above compound?

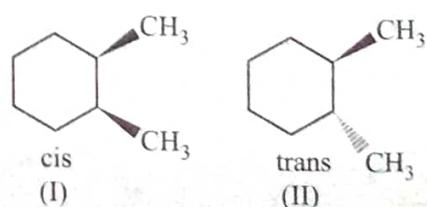
(a) 0

(b) 2

(c) 3

(d) 4

Sol. (b)



CALCULATION OF GEOMETRICAL ISOMER

Number of Geometrical isomers in polyene [N]:

Case-1: When compound is unsymmetrical

If $R_1 \neq R_2$ ($R_1 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - R_2$)

$$\text{No. of G.I.} = 2^n \quad n \rightarrow \text{no of stereogenic centre}$$

e.g. $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{C}_2\text{H}_5$

$$N = 2^n = 2^2 = 4.$$

Case-2: When compound is symmetrical

If $R_1 = R_2$ ($R_1 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - R_2$)

$$\text{No. of G.I.} = 2^{n-1} + 2^{p-1}$$

Example 19: Total number of geometrical isomers possible in given compound is;



Sol. (4) Unsymmetrical $\Rightarrow n = 2$

Total Geometrical Isomers = $2^2 = 4$

Example 20: Total number of geometrical isomers possible in given compound is:

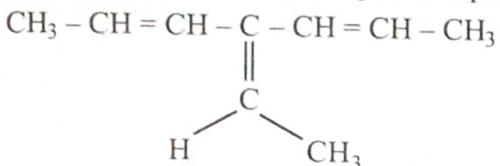


Sol. (4) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2$
 $n = 2$, Unsymmetrical

$$\text{Total Geometrical Isomers} = 2^n$$

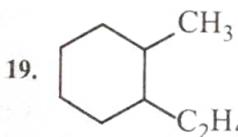
Concept Application

17. Find out geometrical isomers in given compound

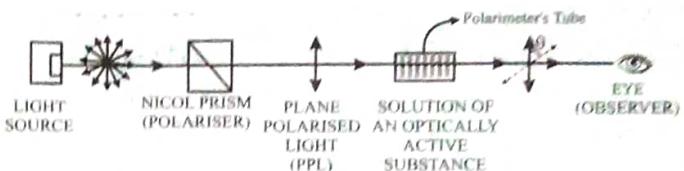


$$18. \text{CH}_3 - \text{CH} = \underset{\text{Br}}{\underset{|}{\text{C}}} - \underset{\text{Cl}}{\underset{|}{\text{C}}} = \text{CH} - \text{CH}_3$$

How many geometrical isomers are possible for this compound?



How many geometrical isomers are possible for the above compound?



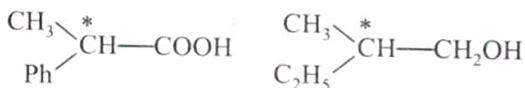
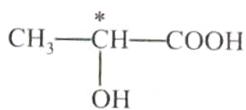
The observed rotation of the plane of polarised light produced by a solution depends upon—

1. The concentration of the substance in tube. (C gm/mol)
 2. The length of the solution column. (l dm) [$1\text{ dm} = 10\text{ cm}$]
 3. The temperature of the experiment ($t^\circ\text{C}$)
 4. The wavelength of the light used. (λ Å)

Definition and examples of optical Isomerism: All these substances are known to exist in three stages.

1. One rotating the plane of polarized light to the right is named **dextrorotatory**
(Latin, Dexter - right) or direction (+) form.
 2. One rotating the plane of polarised light to the left this form is named **laevorotatory**.
(Latin, laevo = left) or direction (-) form
 3. An inactive form which does not rotate the plane polarized light at all this is mixture of equal amounts of (+) and (-) forms and hence it is optical inactive. It is named (\pm) - mixture or **Racemic mixture**.
(Latin, Racemic - mixture of equal compounds)

The simple organic compounds which show optical activity are:



4. Specific rotation (α): Specific rotation is the number of degrees of rotation observed if a 1-dm (10-cm) tube is used and the compound has concentration 1 gm/mL. Thus specific rotation $[\alpha]$ is:

$$[\alpha]_t^\lambda = \frac{\theta}{l \times C}$$

$[\alpha]$ = Specific rotation; θ = observed angle of rotation
(degree)

l = Pathlength (dm); C = concentration (gm/ml)

λ = wavelength (nm); t = temperature (25°C)

Note:

- (i) Specific rotation of a compound is independent of the length of tube and concentration of the solution.
 - (ii) Since optical rotatory power is a property of molecules, if two substances have unequal molecular weights but are alike with respect to the power of rotating the plane of polarized light, the substance of smaller molecular weight has the larger specific rotation, simply because it has more molecules per unit weight.

CAUSE OF OPTICAL ACTIVITY

The foundation of modern theory of stereochemistry was laid by Louis Pasteur when he observed two different kind of crystals, which were mirror images of each other. Aqueous solution of both types of crystals showed optical rotation that was equal in magnitude but opposite in direction. Pasteur believed that this difference in optical activity was associated with the three dimensional arrangement of atoms in the two types of crystals. Later van't Hoff and LeBel proposed that all the four valencies of carbon are directed towards the four corners of regular tetrahedron, and if all the four substituent attached to such a carbon are different the resulting molecule lack symmetry and such a molecule is referred to as asymmetric molecule and asymmetry of the molecule is responsible for optical activity in such organic compounds.

Chirality

A compound which is non-superimposable to its mirror image is called chiral while a compound which is superimposable to its mirror image is called achiral.

Chiral Centre

A compound in which a carbon is attached with four different groups lacks symmetry and is called chiral carbon or asymmetric carbon. It is represented by C*.

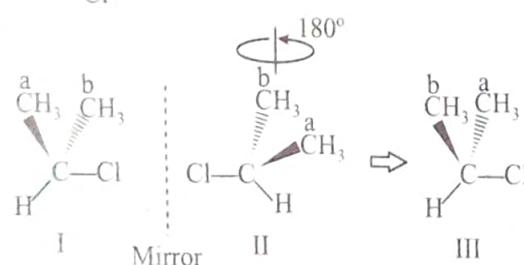
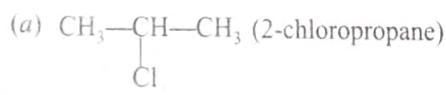
(I) Asymmetric and dissymmetric compounds:

A molecule which does not possess any element of symmetry (there are all 23 elements of symmetry) is called asymmetric. A molecule which does not possess plane of symmetry, centre of symmetry and alternating axis of symmetry is called dissymmetric.

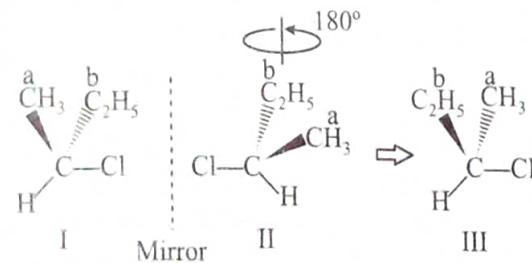
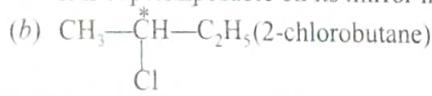
(II) Condition for optical activity:

The minimum condition for a compound to show optical activity is molecular dissymmetry i.e. absence of plane of symmetry, centre of symmetry and alternating axis of symmetry.

For Examples:



I has no chiral centre since two groups (a & b) are identical. It is superimposable on its mirror image II (\equiv III).



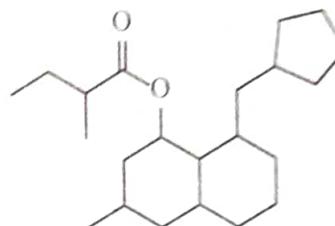
I has one chiral centre it is asymmetric & it is non-superimposable to its mirror image II (\neq III).

The necessary condition for chirality is not just the presence of asymmetric carbon atoms but the dissymmetry of the molecule as a whole.



Train Your Brain

Example 21: How many chiral centers are in the following compound?



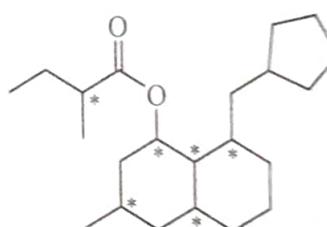
(a) 4

(b) 5

(c) 6

(d) 7

Sol. (c)



Example 22: Choose the correct statement:

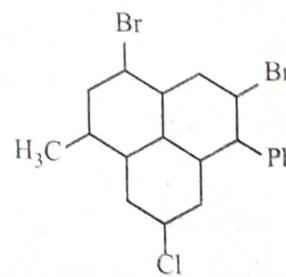
- single chiral carbon containing molecules are optically active.
- More than one chiral carbon containing molecules are always optically active.
- Molecule must be symmetrical for chirality.
- Chiral carbon is sp^2 hybridized.

Sol. (a) Carbon containing one chiral carbon is always optically active.



Concept Application

20. Count the number of chiral carbons in given compound?



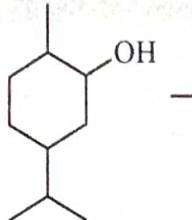
(a) 9

(b) 6

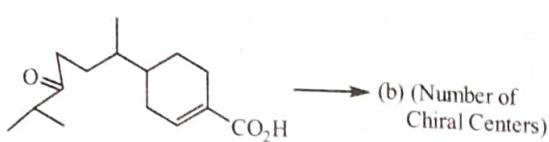
(c) 7

(d) 5

21.



→ (a) (Number of Chiral Centers)



→ (b) (Number of Chiral Centers)

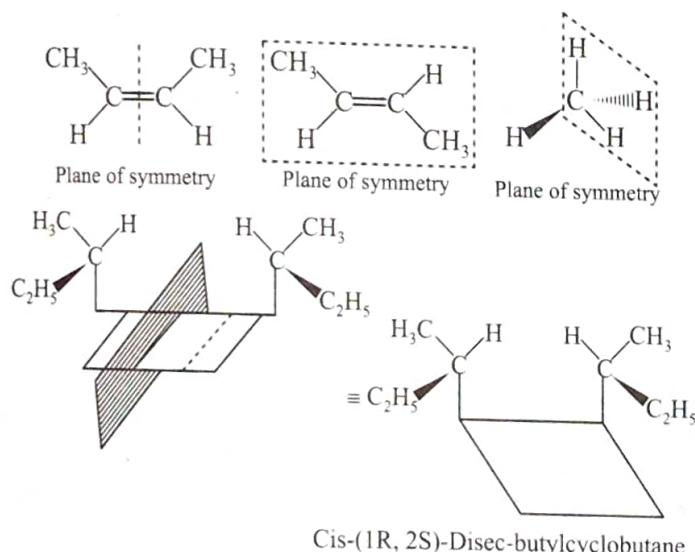
Sum of chiral centers ($a + b = ?$) is:

- (a) 3 (b) 4 (c) 5 (d) 6

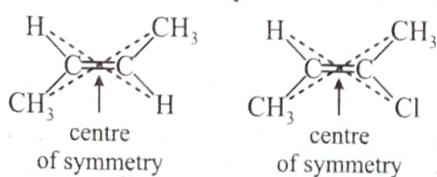
Element of symmetry and concept of molecular dissymmetry/ asymmetry and chirality

Plane of symmetry (σ):

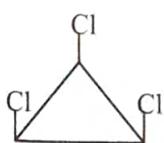
It is an imaginary plane which bisects the molecule in two equal halves in such a way that each half of the molecule is the mirror image of the other half.



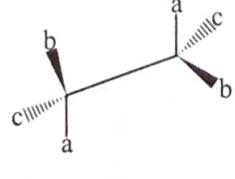
Centre of symmetry (i): A centre of symmetry is a point from which lines, when drawn on one side and produced an equal distance on the other side, will meet identical points in the molecule.



Axis of symmetry (C_n): Axis of symmetry is a line about which the molecule can be rotated by $360^\circ/n$ and thereby produce a molecule indistinguishable from the original molecule.



C_3 axis of symmetry

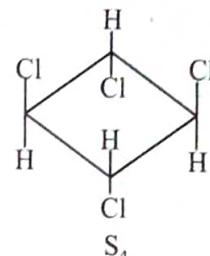
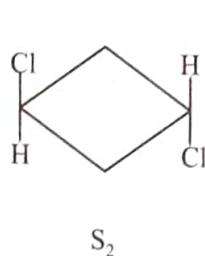


C_2 axis of symmetry

Alternating axis of symmetry (S_n):

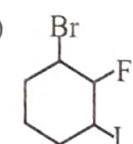
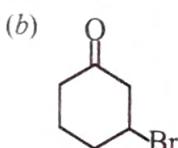
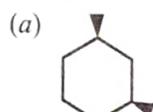
A molecule possess an n -fold alternating axis of symmetry if when rotated through an angle of $360^\circ/n$ about this axis and then followed by reflection in plane perpendicular to the axis; the molecule is indistinguishable from the original molecule.

It is also called Improper axis of symmetry.



Train Your Brain

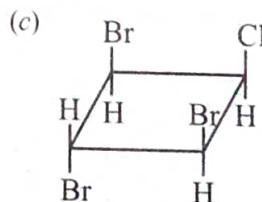
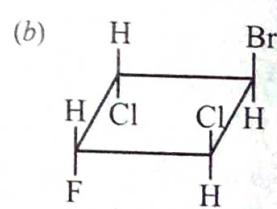
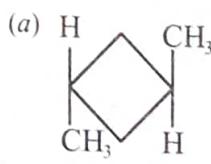
Example 23: Which compound have plane of symmetry?



(d) All the above

Sol. (a) There is an imaginary plane possible which can resets the compound equally.

Example 24: Which of the following compound has plane of symmetry (POS) but not centre of symmetry (COS)?



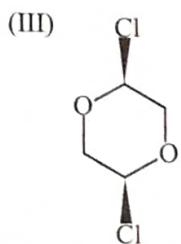
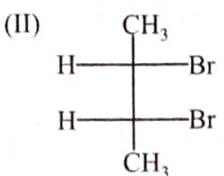
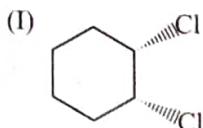
(d) All the above

Sol. (c) There is no centre of symmetry as there is different functional group diagonally.



Concept Application

22. Which of the following compounds have only one POS?



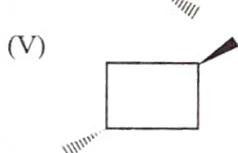
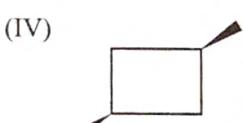
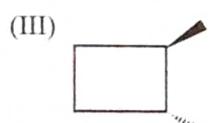
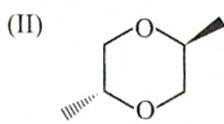
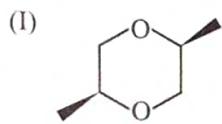
(a) I, IV

(c) II, III

(b) I, II, IV

(d) I, II

23. Identify compounds have centre of symmetry Ci?



(a) II, V

(c) I, III, IV

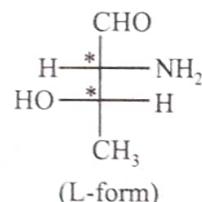
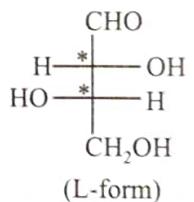
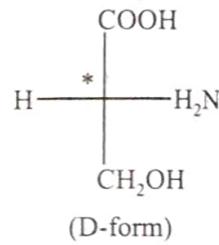
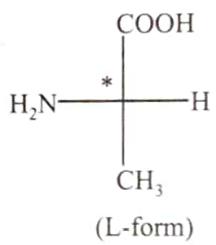
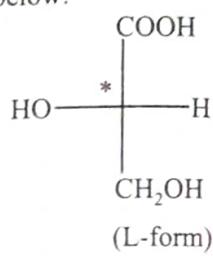
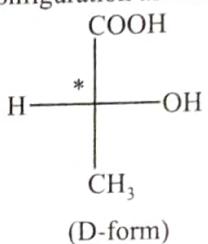
(b) I, IV, V

(d) All of these

Rules for D-L configuration:

- (i) All carbon containing functional Group should be on vertical lines.
- (ii) Maximum no. of carbon atoms should be on vertical lines.
- (iii) Higher priority functional group should be present at the top position.

❖ All molecules which could be chemically related to D-glyceraldehyde are assigned the D-configuration and those related to L-glyceraldehyde are designated L-configuration as illustrated below:



Special Point

- ❖ The method of separating a racemic mixture into its enantiomeric constituents is called as **Resolution**.
- ❖ There is no direct relation between D,L- configuration with d, l or (+), (-) configuration.

R-S SYSTEM (ABSOLUTE CONFIGURATION)

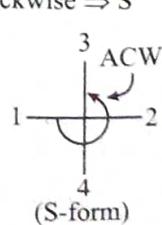
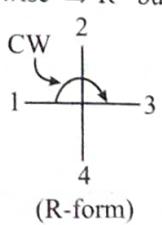
R → Rectus (Right) S → Sinister (Left)

R-S nomenclature is assigned as follow:

Step-I: By the set of sequence rule, we give the priority order of atom or group connected through the chiral carbon.

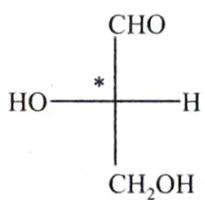
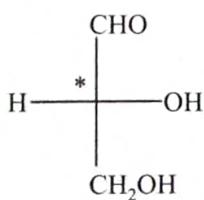
Step-II: If atom/group of minimum priority present on the vertical line, then put arrow 1 → 2 → 3.

If it is clockwise ⇒ R but Anti clockwise ⇒ S



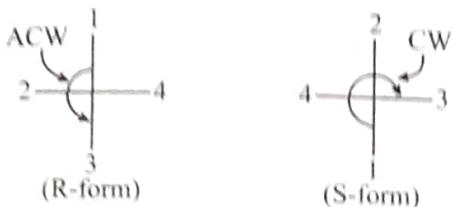
D AND L-SYSTEM (RELATIVE CONFIGURATION)

- ❖ It is applicable for Fischer projection formula.
- ❖ It represents relative configuration with respect to glyceraldehydes.
- ❖ Following configuration of glyceraldehyde is considered as standard configuration.



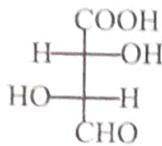
Step-III: If minimum priority group present on the horizontal line, then put arrow 1→2→3.

If it is clockwise \Rightarrow S but anticlockwise \Rightarrow R.



Train Your Brain

Example 25: Configurations of the carbon atoms C₂ and C₃ in the following compound are respectively.

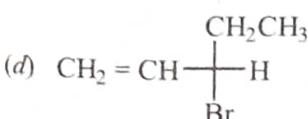
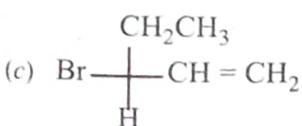
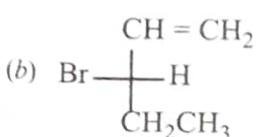
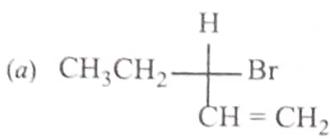


- (a) R, R
(c) R, S

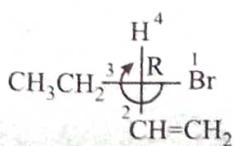
- (b) S, S
(d) S, R

Sol. (a) R,R

Example 26: Which of the following compounds has R configuration?

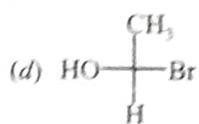
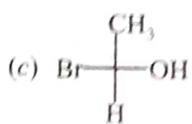
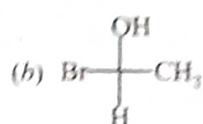
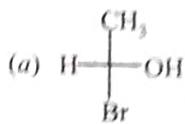


Sol. (a)

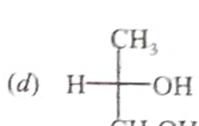
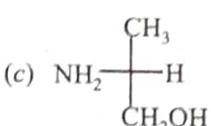
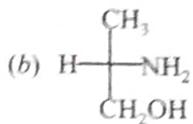
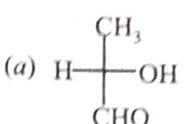


Concept Application

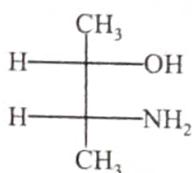
24. Which of the following compound has 'S' configuration?



25. Which of the following compound has 'R' configuration?



26. The correct configuration assigned for given compound:

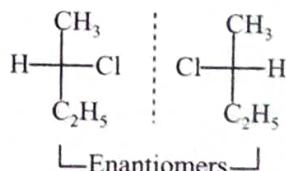


- (a) 2R, 3R
(c) 2R, 3S
(b) 2S, 3S
(d) 2S, 3R

PROPERTIES OF ENANTIOMERS

1. Stereoisomers which are non-superimposable mirror images of each other are called enantiomers.
2. Enantiomers have chiral molecule (optically active).
3. Enantiomers have identical physical properties like BP, MP, refractive index, density etc.
4. They rotate PPL in opposite direction but to the equal extent.

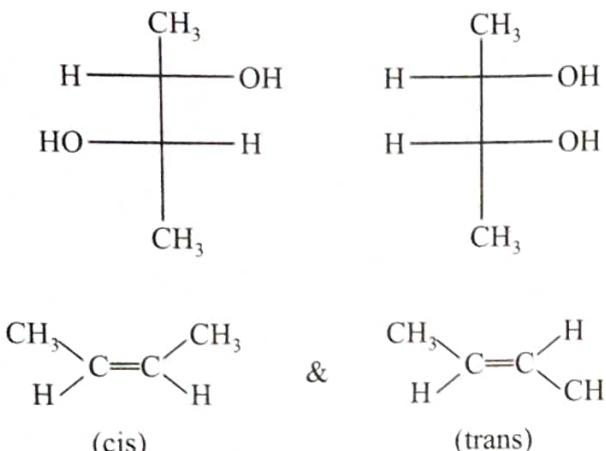
Ex.(a) 2-Chlorobutane:



DIASTEROMERS

Such configurational isomers which are neither be mirror image nor be superimposable on each other, called as diastereoisomer.

e.g.



Cis-trans isomer are geometrical isomer but they are not the mirror image thus, they are said to be diastereomer.

CHARACTERISTICS OF DIASTEREOMERS

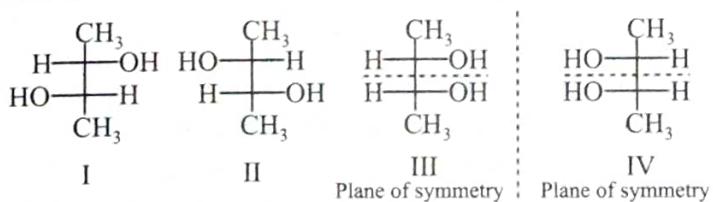
- They are generally optical active, however geometrical isomers are exception.
- They have different physical properties like MP, BP, density, solubilities & value of specific rotation.
- They are separated by fractional distillation, fractional crystallisation & chromatography etc.
- They exhibit similar but not identical chemical behaviour.

MESO COMPOUNDS

An optical inactive molecule whose atleast one diastereomer is optically active.

- Mirror image of meso compound is superimposable over each other & non resolvable.
- Molecule contains chiral centres & symmetry but optically inactive.

Ex. Let us consider the stereoisomers of 2, 3-Butanediol



Racemic Mixture

A mixture of equal amounts of enantiomers is called a racemic mixture or racemic modification. A racemic modification is always optically inactive when enantiomers are mixed together, the rotation caused by a molecule of one enantiomer is exactly cancelled by an equal and opposite rotation caused by a molecule of its enantiomer.

The prefix (\pm) is used to specify the racemic nature of the particular sample.

e.g. (\pm) Lactic acid, or ($d+l$) Lactic acid.

Optical Purity

Sometimes we deal with mixture that is neither optically pure nor racemic mixture. In these cases we specify the optical purity of the mixture. It is defined as the ratio of its rotation to the rotation of pure enantiomer.

$$\text{Optical purity} = \frac{\text{observed optical rotation}}{\text{optical rotation of pure enantiomer}} \times 100$$

Enantiomeric Excess

To compute the enantiomeric excess of amixture we calculate the excess of predominant enantiomer as a percentage of the entire mixture. The calculation of enantiomeric excess gives the same result as the calculation of optical purity.

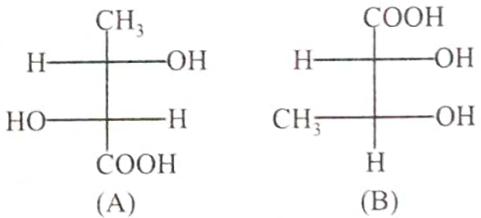
$$\therefore \text{Optical purity} = \text{Enantiomeric excess} = \frac{|d-l|}{d+l} \times 100$$

$$= \frac{\text{excess of one enantiomer over other}}{\text{entire mixture}} \times 100$$



Train Your Brain

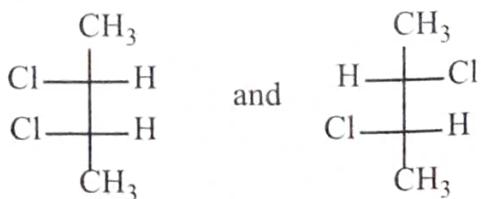
Example 27: Find relation between these two compounds A and B:



- (a) Enantiomers (b) Diastereomers
 (c) Structural Isomers (d) Identical

Sol. (d) First rotate compound be in the plane then interchange CH₃, OH, H valency then we get compound B which is identical to A.

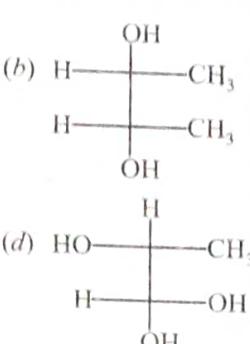
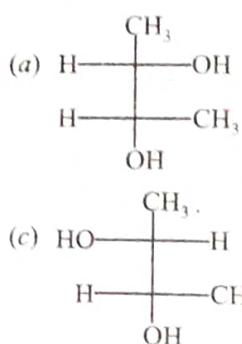
Example 28: What is the relationship between the following molecules?



- (a) Enantiomers
 (b) Diastereomers
 (c) Constitutional isomers
 (d) Geometrical isomers

Sol. (b) As this is not mirror image to each other.

Example 29: Which of the following structure is not meso-2, 3-butanediol?

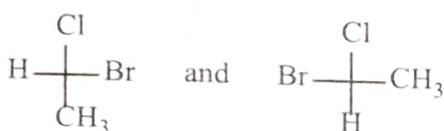


Sol. (a) Meso compounds are achiral compounds having more than one chiral centers. Meso compounds are bisected by an internal plane of symmetry which cause the optical inactivity of the compound.



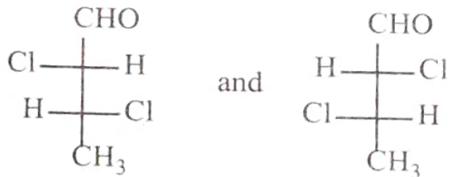
Concept Application

27. What is the relationship between the structures shown below?



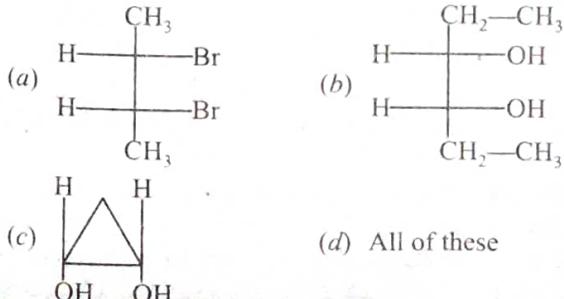
- (a) Enantiomers
- (b) Diastereomers
- (c) Configurational isomers
- (d) Identical compounds

28. What is the relationship between the following molecules?



- (a) Enantiomers
- (b) Diastereomers
- (c) Constitutional isomers
- (d) Conformational isomers

29. Which of the following is a meso compound?



Number of Optical Isomers:

Case-1: When the molecule is unsymmetrical.
(It cannot be divided into two halves)

$$\text{Number of stereoisomers} = 2^n$$

$$\text{Number of meso form} = 0$$

$$\text{Total number of optical isomers} = 2^n$$

Where n is the number of chiral carbon atoms

Case-2: When the molecule is symmetrical and number of chiral carbon = even number

$$\text{Number of stereoisomers} = 2^{(n-1)}$$

$$\text{Number of meso isomers} = 2^{(n/2-1)}$$

$$\text{Total number of optical isomers} = 2^{(n-1)} + 2^{\left(\frac{n}{2}-1\right)}$$

Case-3: When the molecule is symmetrical number of chiral carbon = odd number

$$\text{Number of stereoisomers} = 2^{(n-1)} + 2^{\frac{(n-1)}{2}}$$

$$\text{Number of meso isomers} = 2^{\frac{(n-1)}{2}}$$

$$\text{Total number of optical isomers} = 2^{n-1}$$

Number of Stereoisomers

Number of Stereoisomers (either geometrical or optical or both) can be found by calculating the number of stereocentres in the compound.

Nature of compound	No. of Stereoisomers (n=no. of stereocentres)
(i) Compound with dissimilar ends	2^n
(ii) Compound with similar ends and even stereocentres	$2^{n-1} + 2^{\frac{n-1}{2}}$
(iii) Compound with similar ends and odd stereocentres	$2^{n-1} + 2^{\frac{n-1}{2}}$
(a) If only geometrical stereocentres are present in the molecule	2^{n-1} only
(b) If only optical stereocentres are present in the molecule	



Train Your Brain

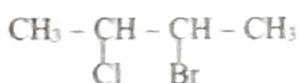
Example 30: How many stereoisomers (geometrical and optical) are possible for the following compound?



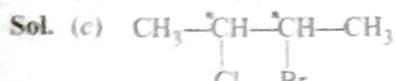
- | | |
|-------|-------|
| (a) 1 | (b) 2 |
| (c) 3 | (d) 4 |

Sol. (d) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}(\text{OH})\text{COOH}$ *^(cis/trans) *^(R/S)

Example 31: Number of stereo isomers possible for given compound 2-bromo-3-chlorobutane:



- (a) 2 (b) 3 (c) 4 (d) 6



$$2^2 = 4$$

Example 32: Total number of stereoisomer of following compound is:



- (a) 2 (b) 4 (c) 6 (d) 8

Sol. (c) Because 3 chiral centres are present so $2^{(n-1)} + \frac{(n-1)}{2} = 2^2 + 2^1 = 6$.

Example 33: The total number of stereoisomer possible for 2, 3-dichloro butane:

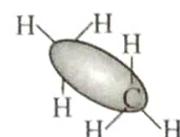
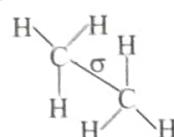
- (a) 2 (b) 3 (c) 4 (d) 5

Sol. (b) Total No. of optical isomers = $2^{(n-1)} + 2^{\left(\frac{n}{2}-1\right)}$
= 3; here n = 2

CONFORMATIONAL (STEREO ISOMERISM)

Conformations

Free rotation: For defining free rotation let us consider the bonding in ethane.



Ethane molecule
carbon-carbon σ -bond

We find that the σ -bond joining the carbon atoms is cylindrically symmetrical about the line joining the two carbon nuclei; if the energy does not differ much in different arrangements the molecule can rotate about this carbon-carbon σ bond, we describe this freedom to change by saying that there is free rotation about the carbon-carbon single bond.

Conformations:

Different arrangements of atoms that can be converted into one another by rotation about single bonds are called conformations.

Conformers:

There are infinite arrangement (conformations) which arise due to free rotation around carbon-carbon σ bond, out of them different conformations corresponding to energy minima are called conformers. The conformational isomerism arises due to free rotation along a bond.

Note: Conformers are also called as rotational isomers or conformational isomers.

Conformational Energy:

The rotational energy barrier is known as conformational energy. It is the potential energy difference between most stable conformation and least stable conformation.

Configuration vs Conformation

Configuration is the spatial arrangement of molecule without considering the internal forces acting on the molecule whereas conformation is the spatial arrangement of the molecule when all the internal forces are taken into account. In this more restricted sense, the term conformation is used to designate different spatial arrangements arising by twisting or rotation of bonds of a given configuration.

Newman projection:

For conformational analysis, a special type of structural formula convenient to use which is called newman projection formula and another type is a saw horse formula.



Newman projection
formula

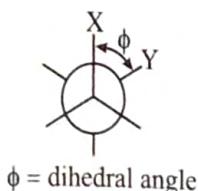


sawhorse formula

To write newman projection formula we imagine ourselves taking a view from one carbon atom directly along the selected bond axis to the next atom. The front carbon and its other bonds are represented as and those of the back carbon as .

Dihedral Angle

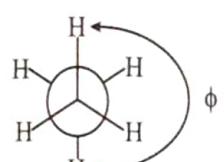
The angle between C-X and C-Y in X-C-C-Y when it is visualised along C-C bond.



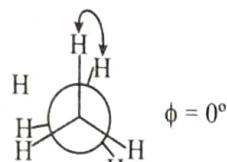
ϕ = dihedral angle

Staggered, Eclipsed and Skew Conformations

- (I) The staggered conformation of a molecule is that conformation where the dihedral angle between the bonds at each atom of carbon-carbon bond is 60° , 180° , 300° .
- (II) In the eclipsed conformation the atoms bonded to carbons at each end of carbon-carbon bond are directly opposite to one another. The dihedral angle between them is 0° , 120° , 240° .



staggered conformation of ethane



Eclipsed conformation of ethane

- (III) Skew conformation: All conformations other than staggered or eclipsed are skew conformations.

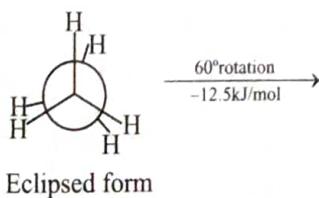
Factors Affecting Stability of Conformations

- (I) Angle strain: Any deviation from "normal" bond angles are accompanied by angle strain. It is normally present in the cyclic structures but absent in the acyclic structures.
- (II) Torsional strain: Any pair of tetrahedral carbons attached to each other tend to have their bonds staggered for minimum repulsion between their bonds. Any deviation from the staggered conformation are accompanied by torsional strain. It is also known as Pitzer strain or Eclipsing strain.
- (III) Van der Waals strain: Non bonded atoms or groups that just touch each other i.e. they are about as far apart as the sum of their van der Waals radii, if brought any closer together they repel each other. Such crowding together is accompanied by van der Waals strain.

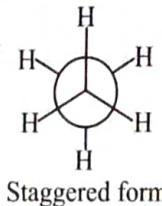
Conformational Analysis of Ethane

Ethane molecule contains a carbon-carbon σ bond and each carbon is further attached to 3 H-atoms. It exists in two extreme conformations i.e.

(i) Eclipsed conformation



(ii) Staggered conformation

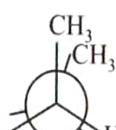


Staggered form

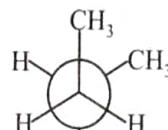
The potential energy barrier between the two conformations of ethane is about 12.5 kJ/mol. The potential energy of ethane molecule is at a minimum for the staggered conformation, increase with rotation and reaches a maximum at the eclipsed conformation. Most ethane molecules naturally exist in the most stable staggered conformation. There are only three energy minima, that is ethane has only three conformers. Since they are indistinguishable and degenerate.

Conformational Analysis of Butane

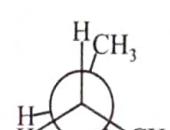
If we consider rotation about the C_2-C_3 bond of butane, we find that there are six important conformations shown as I - VI below:



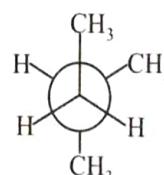
I
Eclipsed conformation



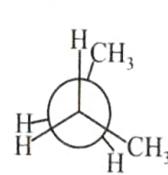
II
Gauche conformation



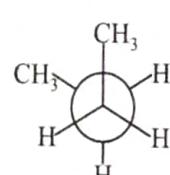
III
partially eclipsed conformation



IV
Anti conformation

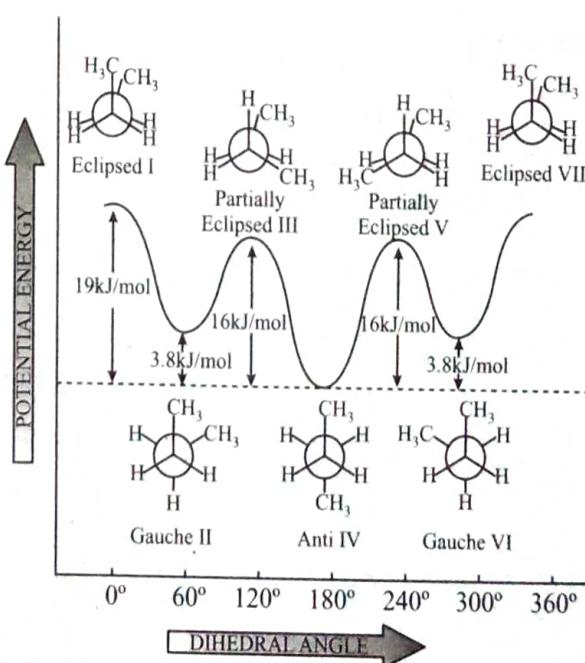


V
Partially eclipsed conformation



VI
gauche conformation

Energy profile of conformations of butane:





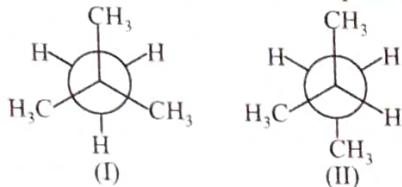
Train Your Brain

Example 34: The eclipsed and staggered conformation of ethane is due to

- (a) Free rotation about C–C single bond
- (b) Restricted rotation about C–C single bond
- (c) Absence of rotation about C–C bond
- (d) None of the above

Sol. (a) Due to σ bond rotation.

Example 35: The two structures I & II represents:



- (a) Conformational isomers
- (b) Optical isomers
- (c) Constitutional isomers
- (d) Identical isomers

Sol. (c) Connectivity of carbon atoms are not same so these are constitutional isomers.

Example 36: In the complete rotation of butane from 0° to 360° the gauche conformation appears:

- (a) Once
- (b) Twice
- (c) Thrice
- (d) Four times

Sol. (b) 0° (Eclipsed); 60° (Gauche); 120° (Partially eclipsed); 180° (Anti); 240° (Partially eclipsed), 300° (Gauche); 360° (Eclipsed).

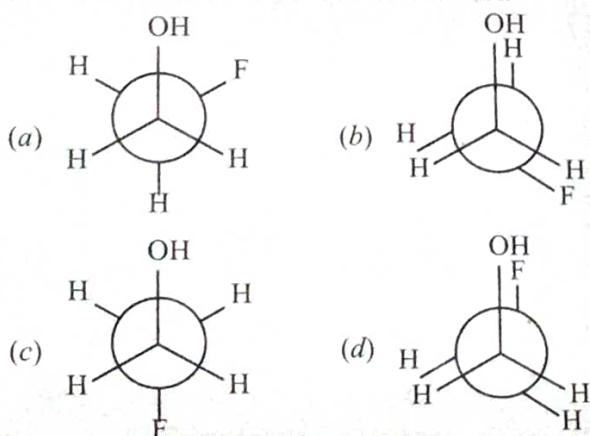
Example 37: Which of the following is associated with Torsional strain?

- (a) Repulsion between bond pair of electrons
- (b) Inductive effect
- (c) Bond angle strain
- (d) Attraction of opposite charges

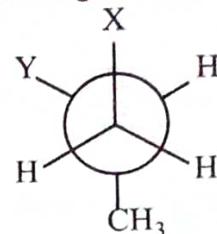
Sol. (a) Repulsion between bond pairs electrons is defined as torsional strain.

Concept Application

33. Most stable conformer of 2-Fluoro ethanol:

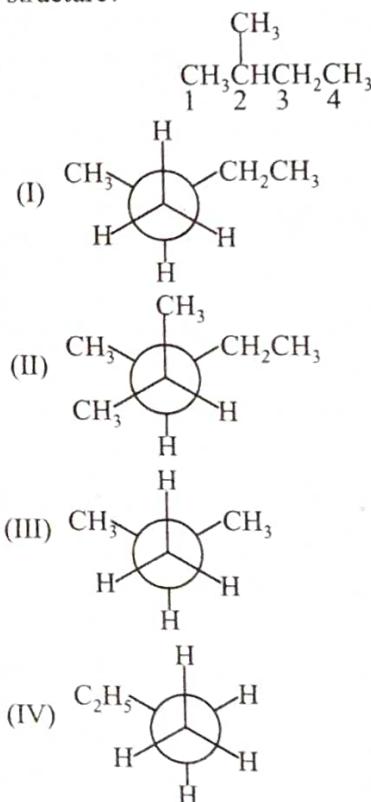


34. For conformation 2-methyl-propane which pair in correctly match for given compound:



- (a) X = H, Y = H
- (b) X = CH₃, Y = CH₃
- (c) X = H, Y = CH₃
- (d) X = CH₃, Y = H

35. Which of the following is the staggered conformation for rotation about the C₁–C₂ bond in the following structure?

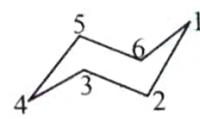


- (a) I
- (b) II
- (c) III
- (d) IV

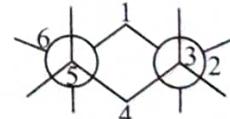
CONFORMATIONAL ANALYSIS OF CYCLOHEXANE

Conformational analysis of cyclohexane

(I) Chair form: The most stable conformation of cyclohexane ring is the chair conformation. It is the staggered form of cyclohexane. In this non-planar structure the C–C bond angles are close to 109.5° . This conformation is free from all the strains (like angle strain and torsional strain.)

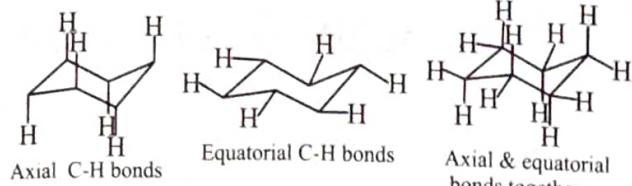


Chair Conformation



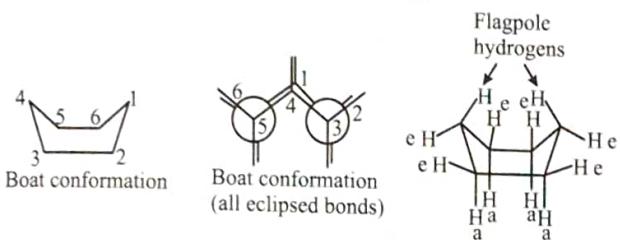
Chair form(all staggered bonds)

Axial and equatorial bonds in chair form of cyclohexane:



The 12 hydrogen atoms of chair conformation of cyclohexane can be divided into two groups. Six of the hydrogens called axial hydrogens, hence their bonds parallel to a vertical axis that passes through the rings centre. These axial bonds are directed up & down on adjacent carbons. The second set of six hydrogens called equatorial hydrogens which are located approximately along the equator of the molecule.

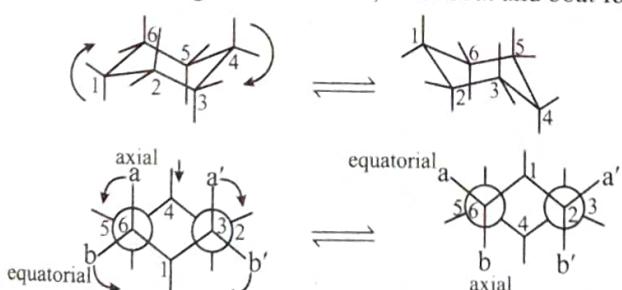
(II) Boat form: Another conformation which is known as boat conformation has exactly eclipsed conformations. Boat form is the transition state of two chair form.



In boat form of cyclohexane 6 hydrogens are equatorial, 4 hydrogens are axial and two hydrogens are flagpoles. It is an unstable conformation of cyclohexane due to torsional strain among axial hydrogens and due to van der waals strain caused by crowding between the "flagpole" hydrogens.

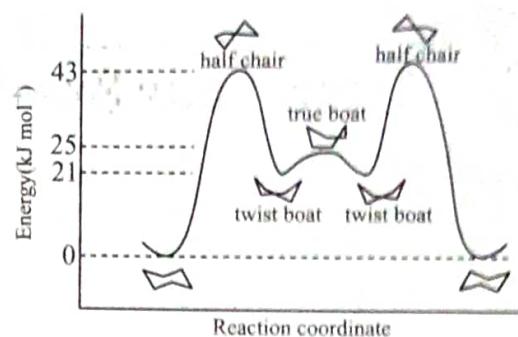
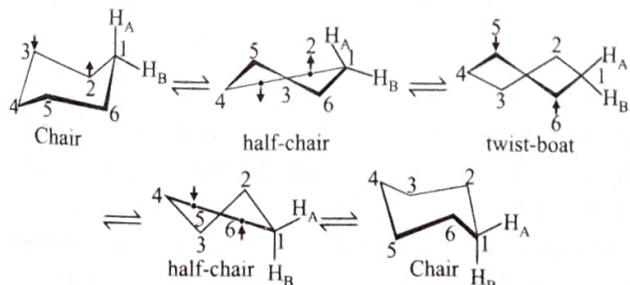
Conformational inversion (Ring flipping) in cyclohexane:

Like alkanes cyclohexane too is conformationally mobile. Through a process known as ring inversion, chair-chair interconversion, or more simply ring flipping one chair conformation is converted to another chair through the half chair, twist boat and boat form.



By ring flipping all axial bonds convert to equatorial and vice-versa. The activation energy for cyclohexane ring inversion is 45 kJ/mol. It is a very rapid process with a half-life of about 10^{-5} sec. at 25°C.

The relative energy profile of various conformations of cyclohexane

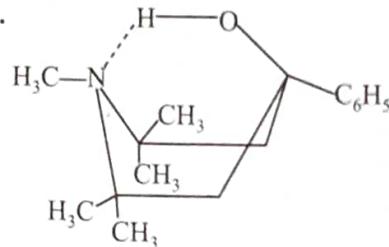


Because of the greater stability of the chair form, more than 99% of the molecules are estimated to be in a chair conformation of any given moment.

Note:

- Twist boat form of cyclohexane is chiral.
- Some molecules due to intramolecular hydrogen bond stabilization exist in boat form rather than chair form.

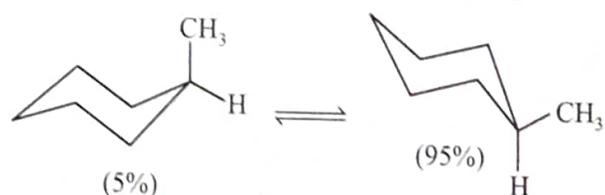
Ex.



1, 2, 2, 6,6- Pentamethyl-4-hydroxyl-4-phenyl piperidine

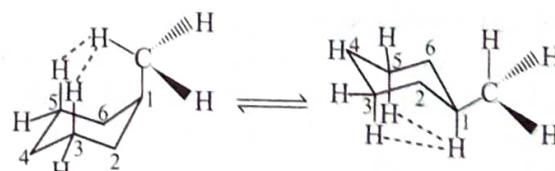
Conformational Analysis of Monosubstituted Cyclohexanes

In ring inversion in methyl cyclohexane the two chair conformations are not equivalent. In one chair the methyl group is axial ; in the other it is equatorial. At room temperature 95% of the methylcyclohexane exist in equatorial methyl group whereas only 5% of the molecule have an axial methyl group.



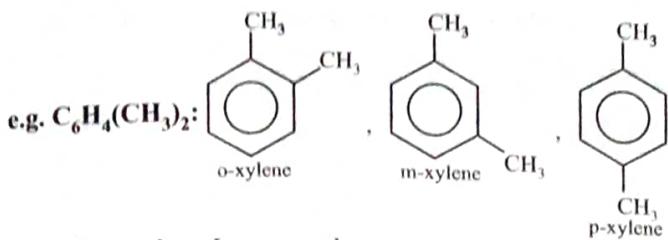
1, 3-diaxial repulsion:

A methyl group is less crowded when it is equatorial than when it is axial. The distance between the axial methyl groups at C-1 and two hydrogens at C-3 & C-5 is less than the sum of their vander waal radii which causes vander waal strain in the axial conformation. This type of crowding is called 1, 3-diaxial repulsions. When the methyl group is equatorial, it experience no significant crowding.



Vander waals strain between hydrogen of axial CH₃ and axial hydrogens at C-3 and C-5

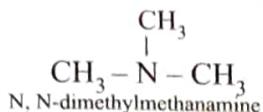
No vander waals strain between axial hydrogen at C-1 and axial hydrogens at C-3 & C-5



Functional isomerism: It occurs when compounds have the same molecular formula but different functional groups.

e.g. C_3H_9N : $CH_3 - CH_2 - CH_2 - NH_2$, 1-propanamine

$CH_3 - CH_2 - NH - CH_3$, N-methylethanamine



Metamerism: This type of isomerism occurs when the isomers differ with respect to the nature of alkyl groups around the same polyvalent functional group.

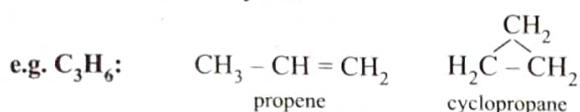
e.g. $C_4H_{10}O$: $CH_3 - O - CH_2 - CH_2 - CH_3$

n-propyl methylether

$CH_3 - CH_2 - O - CH_2 - CH_3$

diethyl ether

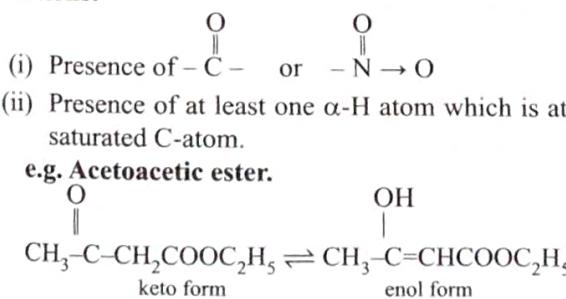
Ring-Chain isomerism: In this type of isomerism, one isomer is open chain but another is cyclic.



- ❖ For chain, positional and metamerism, functional group must be same.
- ❖ Metamerism may also show chain and position isomerism but priority is given to metamerism.

Tautomerism: This type of isomerism is due to spontaneous interconversion of two isomeric forms into each other with different functional groups in dynamic equilibrium.

Conditions:



Enol content enhance by:

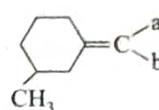
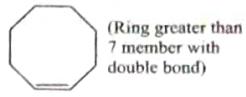
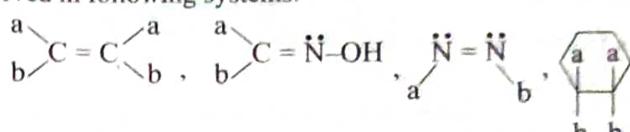
- ❖ Acidity of α -H of keto form.
- ❖ Intra molecular H-Bonding in enol form.
- ❖ Resonance in enol form.
- ❖ Aromatisation in enol form.

(B) Stereoisomerism

Compounds with the same molecular formula and structural formula but having difference in the spatial arrangement of atoms or groups in 3D space are called stereoisomers and the phenomenon is called stereoisomerism.

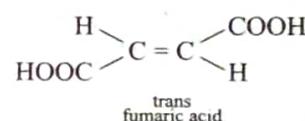
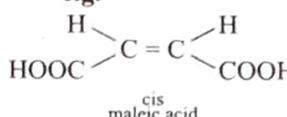
Types of Stereoisomerism

Geometrical isomerism: It is due to restricted rotation and is observed in following systems.



- ❖ **Cis-trans isomerism:** The cis compound is the one with the same groups on the same side of the bond, and the trans has the same groups on the opposite sides. Both isomers have different physical and chemical properties.

e.g.



- ❖ General physical properties of geometrical isomer of but-2-ene

- | | |
|---------------------|-------------|
| (i) Stability | trans > cis |
| (ii) Dipole moment | cis > trans |
| (iii) Boiling point | cis > trans |
| (iv) Melting point | trans > cis |

Calculation of number of geometrical isomers:

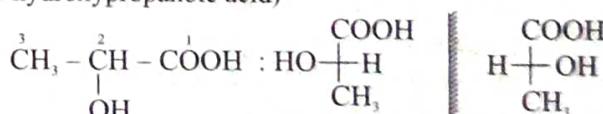
Unsymmetrical	2^n
Symmetrical	$2^{n-1} + 2^{m-1}$ $m = \frac{n}{2}$ (If n is even) $m = \frac{n+1}{2}$ (If n is odd)

❖ Where n = number of sites where GI is possible.

Optical isomerism: Compounds having similar molecular and structural formula but differing in the stereochemical formula and behaviour towards plane polarised light are called optical isomers and this phenomenon is called optical isomerism.

Types of optical isomers

- (1) Optically active
 - ❖ Dextrorotatory (d)
 - ❖ Laevorotatory (l)
- (2) Optically inactive
 - ❖ Meso
 - ❖ **Condition** Molecule should be asymmetric or chiral i.e. symmetry elements (POS & COS) should be absent.
 - ❖ The carbon atom linked to four different groups is called **chiral carbon**.
 - ❖ **Fischer projection** An optical isomer can be represented by Fischer projection which is planar representation of three dimensional structure.
Fischer projection representation of lactic acid (2-hydroxypropanoic acid)



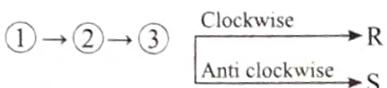
❖ Configuration of optical isomer

- (a) Absolute configuration (R/S system)
- (b) Relative configuration (D/L system)

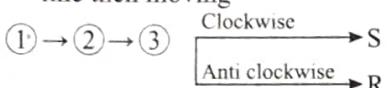
❖ Determination of R/S configuration

Rule-1 Assign the priority to the four groups attached to the chiral carbon according to priority rule.

Rule-2 If lowest priority ④ is bonded to vertical line then moving



Rule-3 If lowest priority ④ is bonded to horizontal line then moving



Determination of D/L system

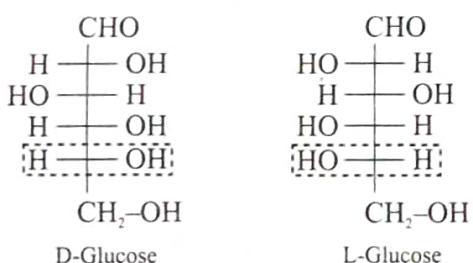
- ❖ Reference molecule glyceraldehyde
- ❖ It is used to assign configuration in carbohydrate amino acid and similar compounds.

Rule: Arrange parent carbon chain the vertical line

- ❖ Placed most oxidised carbon on the top or nearest to top.
- ❖ On highest IUPAC numbered chiral carbon

If OH group on RHS → D

If OH group on LHS → L



CIP Sequence Rule

The following rules are followed for deciding the precedence order of the atoms or groups:-

- (i) Highest priority is assigned to the atoms of higher atomic number attached to asymmetric carbon atom.
 - (ii) In case of isotopes, isotopes having higher atomic mass is given priority.
 - (iii) If the first atom of a group attached to asymmetric carbon atom is same then we consider the atomic number of 2nd atom or subsequent atoms in group.
 - (iv) If there is a double bond or triple bond, both atoms are considered to the duplicated for triplicated.
- ❖ Non-superimposable mirror images are called **enantiomers** which rotate the plane polarised light up to same extent but in opposite direction.
 - ❖ **Diastereomers** are stereoisomers which are not mirror images of each other. They have different physical and chemical properties.

❖ **Meso compounds** are those compounds whose molecules are superimposable on their mirror images inspite of the presence of asymmetric carbon atom.

❖ An equimolar mixture of the enantiomers (d & l) is called **racemic mixture**. The process of converting d- or l- form of an optically active compound into racemic form is called **racemisation**.

❖ The process by which d/l mixture is separated into d and l forms with the help of chiral reagents or chiral catalyst is known as **resolution**.

❖ Compound containing chiral carbon may or may not be optically active but show optical isomerism.

❖ For optical isomer chiral carbon is not the necessary condition.

Calculation of number of optical isomers

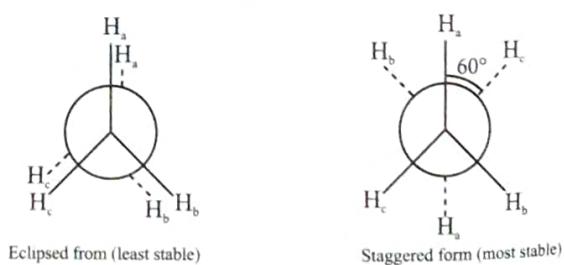
The compound	Optically active forms	Optically inactive forms (meso)
Unsymmetrical	2^n	Zero
Symmetrical If n = even	$2^{(n-1)}$	$2^{\frac{n-1}{2}}$
Symmetrical If n = odd	$2^{(n-1)} - 2^{\frac{(n-1)}{2}}$	$2^{\frac{(n-1)}{2}}$

* Where n = no. of chiral carbon

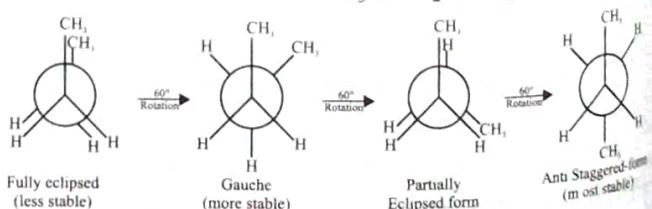
The different arrangement of atoms in space that results from the carbon-carbon single bond free rotation by 0-360° are called conformations or conformational isomers or rotational isomers and this phenomenon is called conformational isomers.

Conformational Isomerism

Newman projection: Here two carbon atoms forming the σ bond are represented one by circle and other by centre of the circle. Circle represents rear side C and its centre represents front side carbon. The C-H bonds of front carbon are depicted from the centre of the circle while C-H bond of the back carbon are drawn from the circumference of the circle.



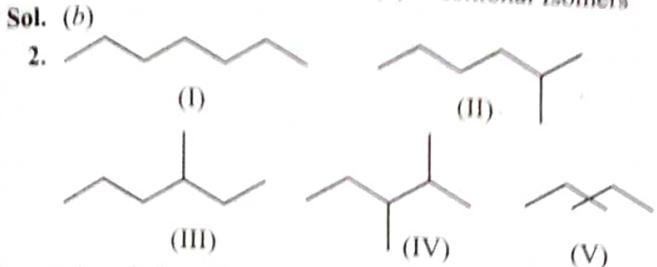
❖ Conformations of butane: $\text{CH}_3 - \overset{4}{\text{CH}_2} - \overset{3}{\text{CH}_2} - \overset{2}{\text{CH}_2} - \overset{1}{\text{CH}_3}$



- ❖ The order of stability of conformations of n-butane. Anti staggered > Gauche > Partially eclipsed > Fully eclipsed
- ❖ Relative stability of various conformation of cyclohexane is Chair > twist boat > boat > half chair.

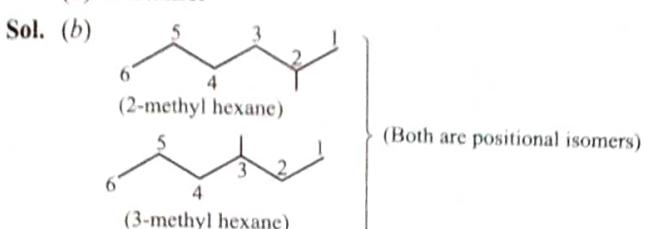
Solved Examples

1. 1° Amide, 2° Amide and 3° Amide having same M.F are:
 (a) Metamers
 (c) Chain Isomers
 (b) Functional Isomers
 (d) Positional Isomers

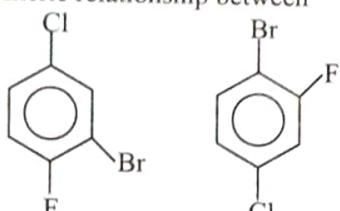


The relationship between (II & III) is

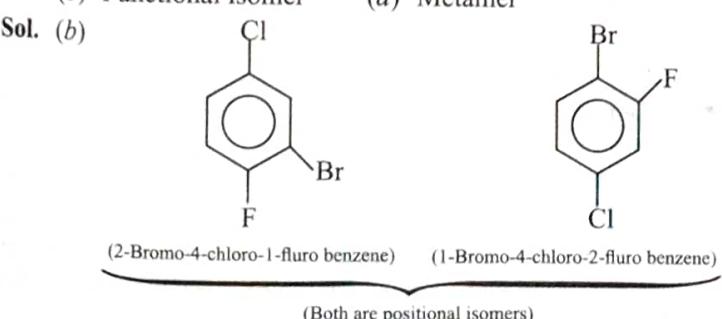
- (a) Chain isomer
 (b) Positional isomer
 (c) Functional group isomer
 (d) Metamer



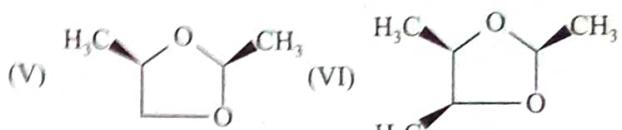
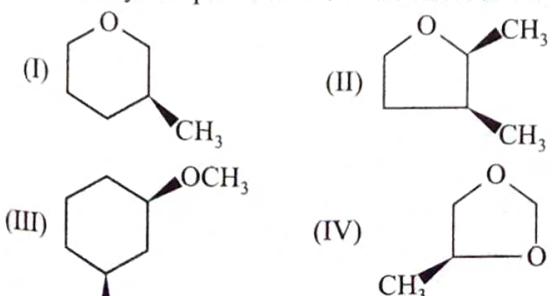
3. Correct isomeric relationship between



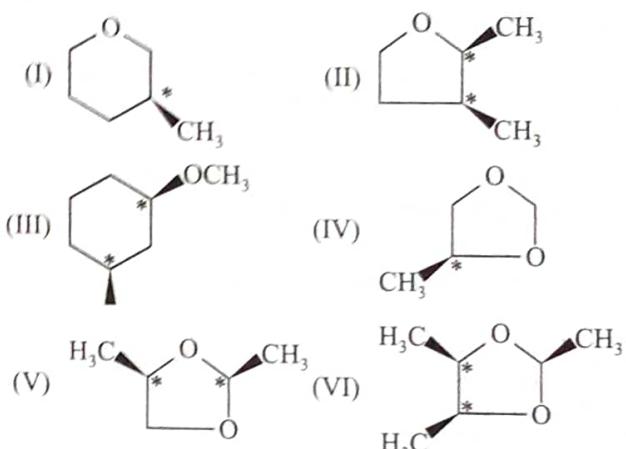
- (a) Chain isomer
 (c) Functional isomer
 (b) Positional isomer
 (d) Metamer



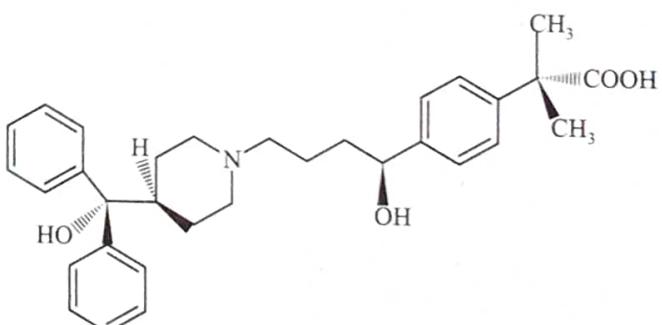
4. How many compounds have two chiral center?



Sol. (3)

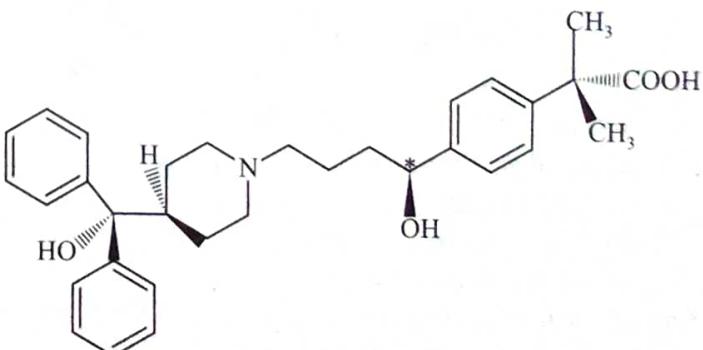


5. Allegra, a common prescription drug with the structure shown below, is given for the treatment of seasonal allergies. How many stereogenic carbon does allegra possess?

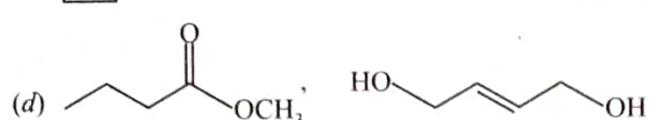
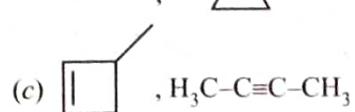
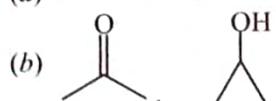
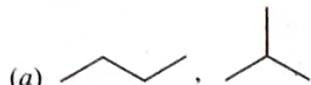


- (a) 4
 (b) 2
 (c) 3
 (d) 1

Sol. (d) 1 stereogenic carbon does Allegra posses because as it is clearly visible in the above molecular structure that at the extreme right c is not attached to 4 different group (there are 2CH₃) but there is carbon in middle with an OH, H and 2 different sides.



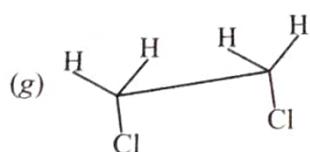
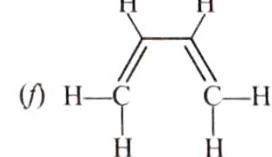
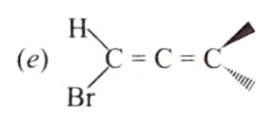
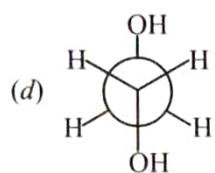
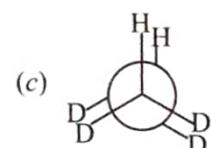
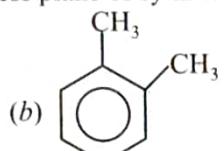
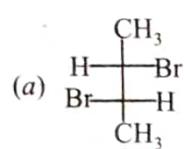
6. Which of the following pairs of molecules is/are structural isomers



Sol. (a,b,d)

Two or more different compounds having same molecular formula but different structures or connectivity of atoms are called as structural isomers.

7. Number of compound possess plane of symmetry?



(a) 6

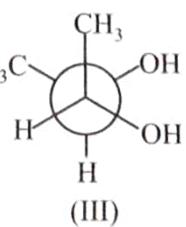
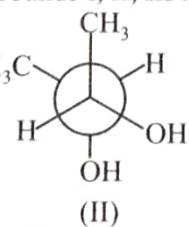
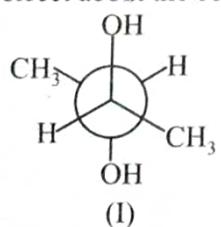
(b) 4

(c) 5

(d) 7

Sol. (c) b, c, d, f, g

8. Incorrect about the compounds I, II, III is:



(a) I & II are diastereomers

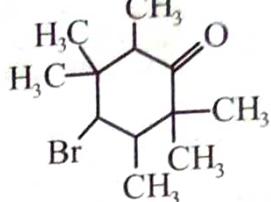
(b) I & III are identical

(c) II & III are diastereomers

(d) I & II are optically active

Sol. (d) I is optically inactive as it posses centre of symmetry
(i) and II compound is optically active.

9. Examine the compound below. How many stereoisomers having this constitution are possible?



We use the formula total stereoisomers = 2^n - meso structure
Where n = no. of stereo unit.

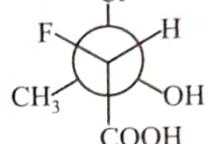
- (a) 2 (b) 4
(c) 6 (d) 8

Sol. (d) n = 3 (No. of stereo unit)

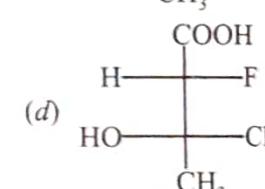
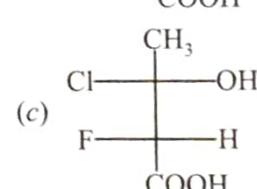
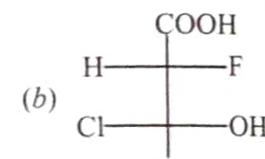
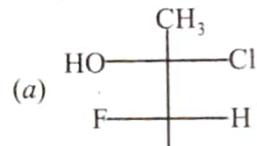
Meso structure = 0

Total stereoisomers = $2^3 - 0 = 8$

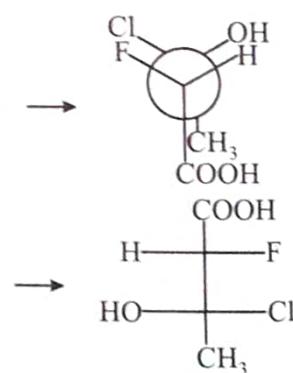
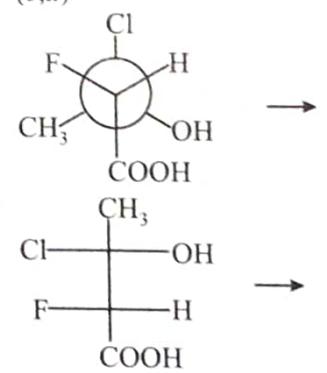
10.



Choose correct Fischer projection formula of above compound will be:



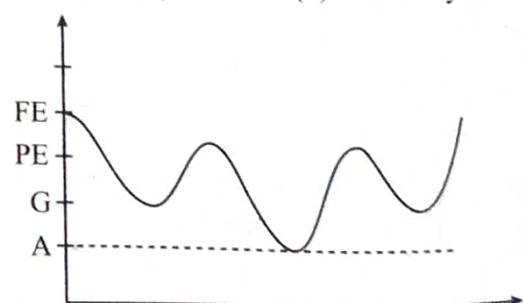
Sol. (c,d)



11. Among the butane conformers, which occur at energy minima on a graph of potential energy versus dihedral angle

- (a) Gauche only (b) Gauche and anti
(c) Eclipsed only (d) Anti only

Sol. (b)



12. Which one of the following structures would be named (2Z, 4E)-2,4-heptadiene?

- (a)
- (b)
- (c)
- (d)

Sol. (d) (2Z, 4E)-2,4-heptadiene

13. The Z-isomer among the following is:

- (a)
- (b)
- (c)
- (d)

Sol. (a)

- (a)
- (b)
- (c)
- (d)

14. The E-isomer among the following is:

- (a)
- (b)
- (c)
- (d)

Sol. (a)

- (a)
- (b)
- (c)
- (d)

15. The total number of geometrical isomers possible in following compound is:



- (a) 1
- (b) 2
- (c) 6
- (d) 8

Sol. (d) $2^n = 2^3 = 8$

16. Which of the following are correctly matched?

Compound

Number of
geometrical
isomers

- | | |
|---|----|
| (a) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{Ph}$ | 4 |
| (b) $\text{CH}_3 - (\text{CH} = \text{CH})_4 - \text{CH}_3$ | 2 |
| (c) $\text{H}_3\text{C} = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3$ | 10 |
| (d) $\text{H}_3\text{C} - (\text{CH} = \text{CH})_5 - \text{CH}_3$ | 20 |

Sol. (a,d) Number of geometrical isomers.

(a) $\Rightarrow 2^n = 4$ as both ends are different.

$$(b) 2^{n-1} + 2^{\frac{n-1}{2}} \Rightarrow 2^{4-1} + 2^{\frac{4-2}{2}} \Rightarrow 2^3 + 2^1 = 8 + 2 = 10$$

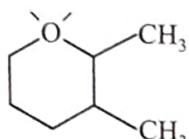
When both ends are same and even double bonds.

$$(c) 2^{2-1} + 2^{\frac{2-2}{2}} \Rightarrow 2 + 2^0 = 3$$

$$(d) 2^{n-1} + 2^{\frac{n-1}{2}} \text{ (when both ends are same and odd number of double bonds)}$$

$$\Rightarrow 2^{5-1} + 2^{\frac{5-1}{2}} \Rightarrow 2^4 + 2^2 \Rightarrow 16 + 4 = 20$$

17. Total number of geometrical isomers possible in given compound is:

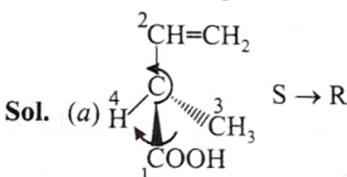
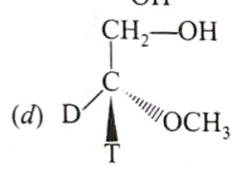
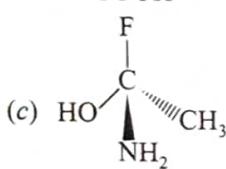
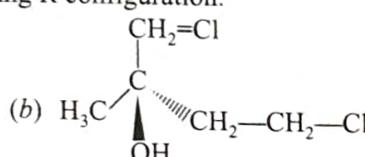
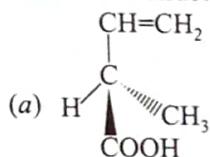


Sol. (2) Unsymmetrical compound

$$n = 1$$

$$\text{Total Geometrical Isomers} = 2^n \\ = 2^1 = 2$$

18. Indicate the structure/s having R configuration.



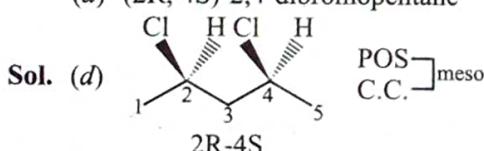
19. Which is a meso compound?

(a) (2R, 3R)-2,3-dibromobutane

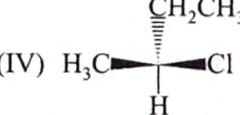
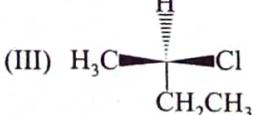
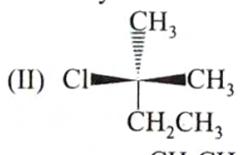
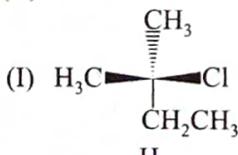
(b) (2R, 3S)-2,3-dibromopentane

(c) (2R, 4R)-2,4-dibromopentane

(d) (2R, 4S)-2,4-dibromopentane



20. (R)-2-chlorobutane is represented by:

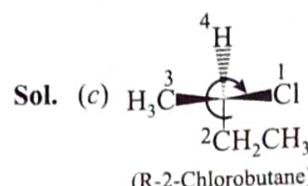


(a) I

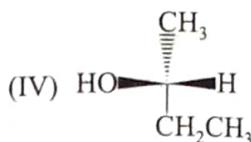
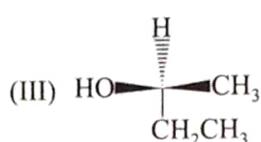
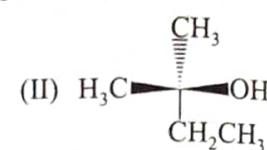
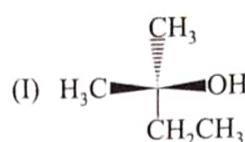
(c) III

(b) II

(d) IV



21. Which of the following represent (R)-2-butanol?

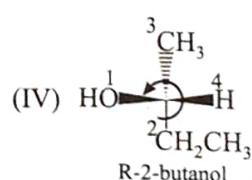
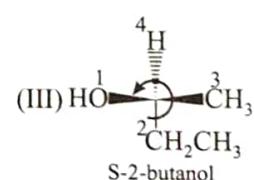
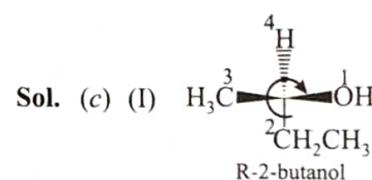


(a) III and IV

(b) I, III, and IV

(c) I and IV

(d) I and III

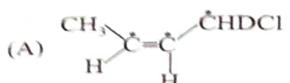


22. Match the Columns:

	Column-I	Column-II	Column-III
A.		p.	Optical active
B.		q.	Optically inactive
C.		r.	Plane of symmetry
D.		s.	Centre of symmetry
		w.	0
		x.	1
		y.	2
		z.	3.

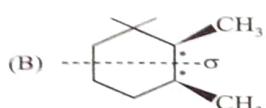
- (a) A → p,z; B → q,r,y; C → p,x; D → q,r,y
 (b) A → p,z; B → p,x; C → q,r,y; D → q,r,y
 (c) A → p,z; B → r,y; C → p,x; D → q,r,y
 (d) A → q,r,y; B → q,r,y; C → p,x; D → p,z

Sol. A \rightarrow p_z; B \rightarrow q_{ry}; C \rightarrow p_x; D \rightarrow q_{ry}



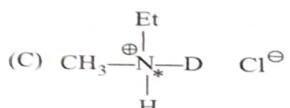
No POS & COS

S.C.=3



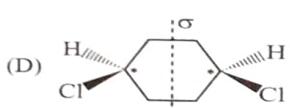
Optically inactive

S.C. = 2



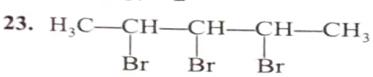
No POS & COS

$$S_i C_i = 1$$



Optically inactive

Optically

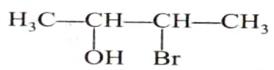


Total number of stereoisomers in the above compound is:

Sol. (b) $\text{H}_3\text{C}-\overset{\cdot}{\underset{\text{Br}}{\text{CH}}}-\overset{\cdot}{\underset{\text{Br}}{\text{CH}}}-\overset{\cdot}{\underset{\text{Br}}{\text{CH}}}-\text{CH}_3$

$$\left\{ \begin{array}{l} \text{R R S} \\ \text{S R R} \\ \text{S S R} \\ \text{R S S} \end{array} \right.$$

24. Total number of stereoisomers of the compound is given below:



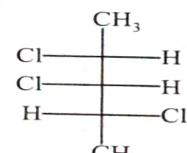
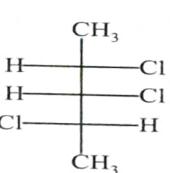
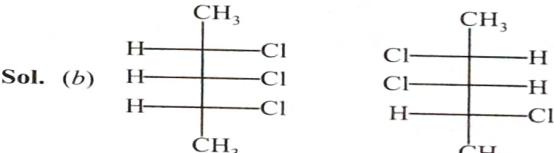
Sol. (b) $\text{H}_3\text{C}-\overset{*}{\underset{\text{OH}}{\text{CH}}}-\overset{*}{\underset{\text{Br}}{\text{CH}}}-\text{CH}_3$



Unsymmetrical n = 2

Total stereoisomer = $2^n = 2^2$

Total stereoisomer = 4

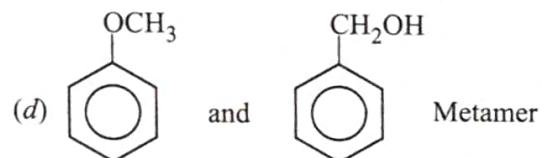
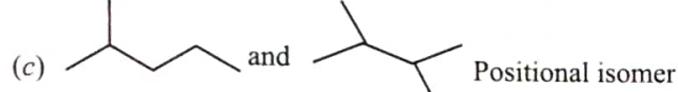
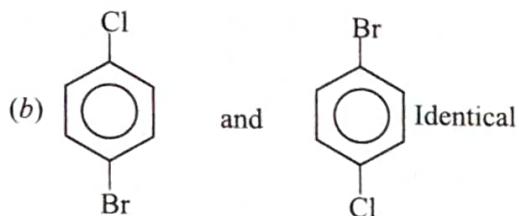
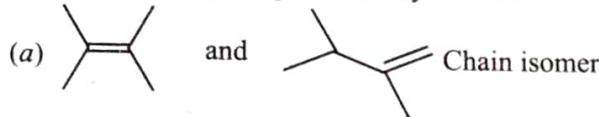


Total 3 diasteromers

Exercise-1 (Topicwise)

STRUCTURAL ISOMERISM

1. Which of the following is correctly matched?

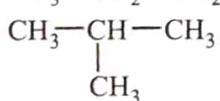


2. Name the compound, that is not isomer with diethyl ether:

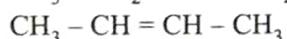
- (a) n-propyl methyl ether
- (b) butan-1-ol
- (c) 2-methylpropan-2-ol
- (d) Butanone

3. Which of the following parts is an example of position isomerism?

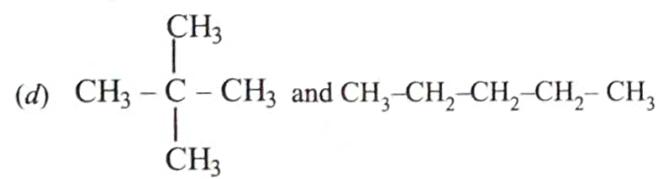
- (a) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ and



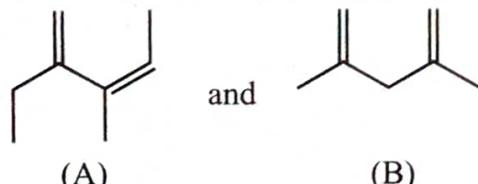
- (b) $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$ and



- (c) $\text{CH}_3 - \text{CH}_2\text{OH}$ and $\text{CH}_3 - \text{O} - \text{CH}_3$

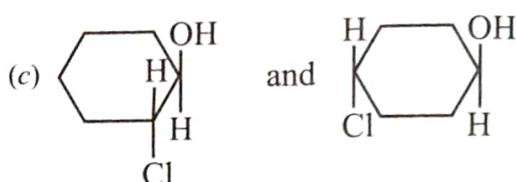
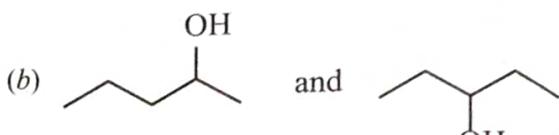
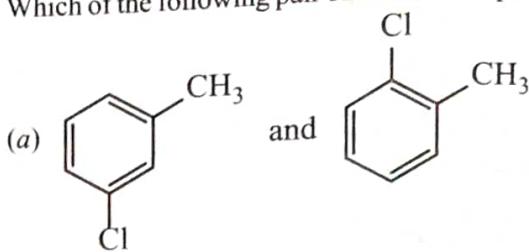


4. The relation between (A) and (B) is:

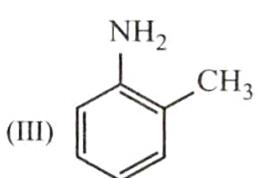
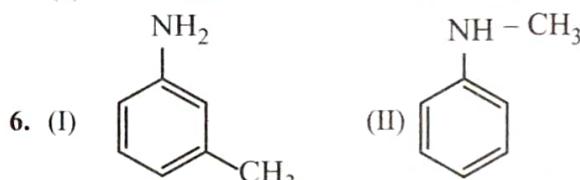


- (a) Chain Isomers
- (b) Homologues
- (c) Identical
- (d) Position Isomers

5. Which of the following pair of isomers are position isomers?



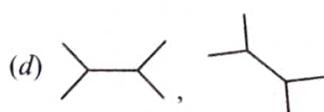
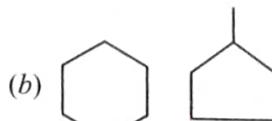
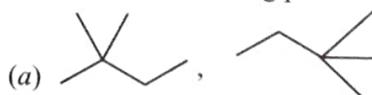
(d) All of these



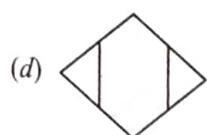
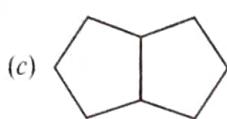
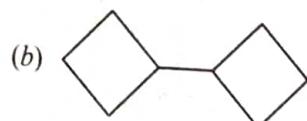
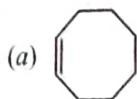
The correct relation statement between I, II and III are:

- (a) I and II are Positional Isomers.
- (b) II and III are Chain Isomers.
- (c) I and III are Metamers.
- (d) I and II are Functional Isomers.

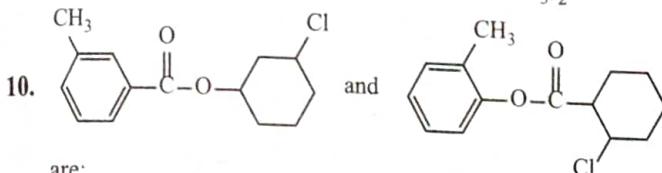
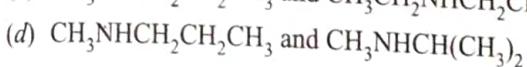
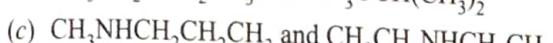
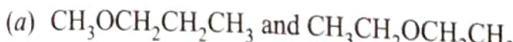
7. Which of the following pair is the chain isomer?



8. Which one of the compound is not isomer of others?



9. Which of the following pairs of compounds are not metamers?

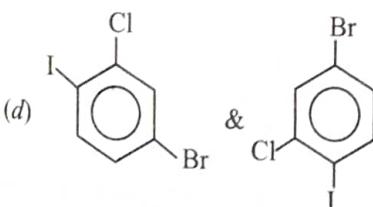
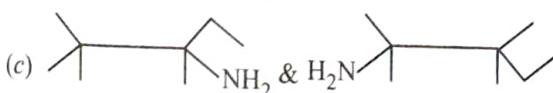
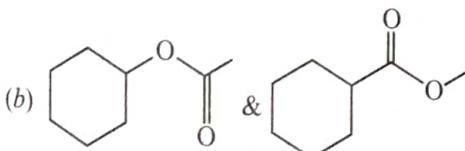
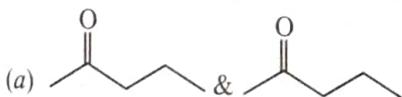


- (a) Position Isomer (b) Metamer
 (c) Homologous (d) Function Isomers

11. The following classes of organic compounds exhibit metamerism except:

- (a) Secondary amines (b) Esters
 (c) Ethers (d) Alkanols

12. Which of the following is a pair of metamers?



CALCULATION OF STRUCTURAL ISOMERS

13. Find out total number of structural isomers of $\text{C}_4\text{H}_9\text{Cl}$.

14. Which of the following is/are cyclic structural isomers of $\text{C}_4\text{H}_7\text{Cl}$?

- (a) Chloro cyclobutane
 (b) Chloro methyl cyclopropane
 (c) 1-chloro-1-methylcyclopropane
 (d) 1-chloro-3-methylcyclopropane

15. Number of derivative of phenol among given compounds will be:

16. Find out total number of cyclic structural isomers of C_6H_{12} (four & five member isomers only).

- (a) 2 (b) 3
 (c) 4 (d) 5

17. How many different terminal alkynes exist with a molecular formula of C_6H_{10} (structural isomers only)?

- (a) 1 (b) 2
 (c) 3 (d) 4

18. Minimum number of carbon atoms required for an alkane to show any kind of isomerism.

- (a) 3 (b) 4
 (c) 5 (d) 6

19. How many trimethyl substituted benzene are possible?

- (a) 2 (b) 6
 (c) 4 (d) 3

20. How many structural isomers are possible for $\text{C}_4\text{H}_9\text{Cl}$?

- (a) 2 (b) 3
 (c) 4 (d) 6

21. There are 8 isomers that have the molecular formula $\text{C}_5\text{H}_{11}\text{Br}$. How many of these are tertiary alkyl bromides?

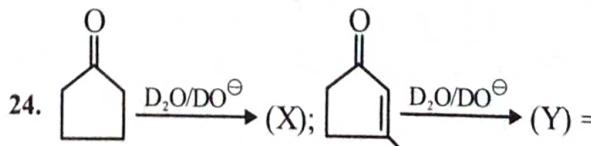
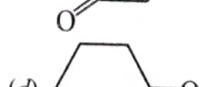
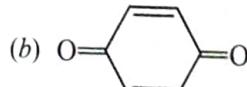
- (a) 0 (b) 1
 (c) 2 (d) 8

22. The number of ether isomers represented by formula $\text{C}_5\text{H}_{12}\text{O}$ is (only structural):

- (a) 4 (b) 6
 (c) 2 (d) 5

TAUTOMERISM

23. Tautomerism is not exhibited by:

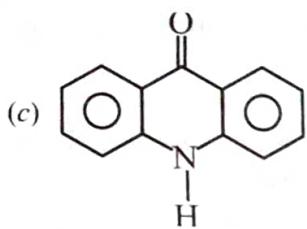
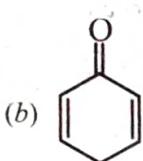
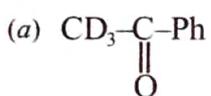


Number of hydrogen, replaced by deuterium.

Sum of X + Y =

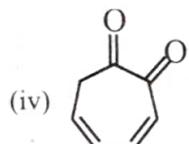
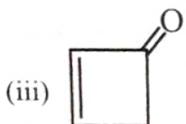
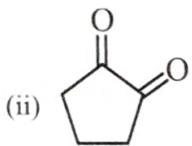
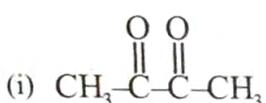
- (a) 9 (b) 10
 (c) 11 (d) 12

25. Which of the following can tautomerise?



(d) All

26. Which of the following compounds have higher enolic content than Keto content?



(a) ii & iv

(b) i, ii & iv

(c) ii, iii & iv

(d) Only

GEOMETRICAL ISOMERISM

27. 2-butene exhibits geometrical isomerism due to:

(a) Rotation about the double bond.

(b) Rotation about C_3-C_4 bond.

(c) Restricted rotation about the double bond.

(d) Rotation about C_1-C_2 bond.

28. Which can show the cis-trans isomerism?

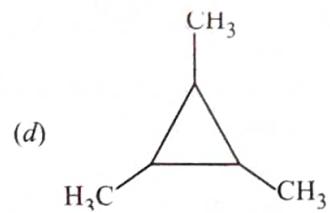
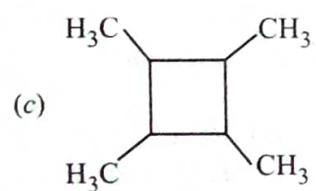
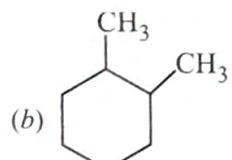
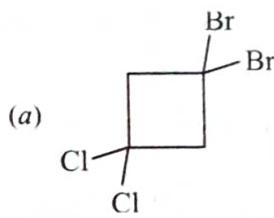
(a) $\text{ClCH}_2\text{CH}_2\text{Cl}$

(b) $\text{Cl}_2\text{C}=\text{CH}_2$

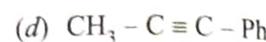
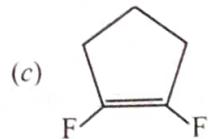
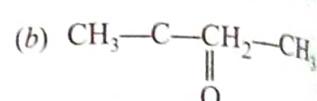
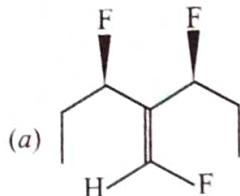
(c) $\text{Cl}_2\text{C}=\text{CCl}_2$

(d) $\text{ClCH}=\text{CHCl}$

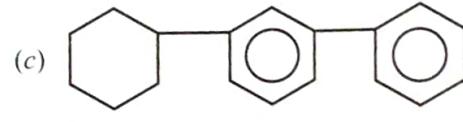
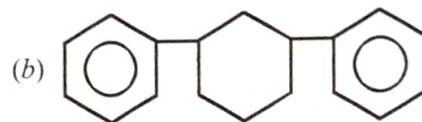
29. Which of the following compound can not show geometrical isomerism?



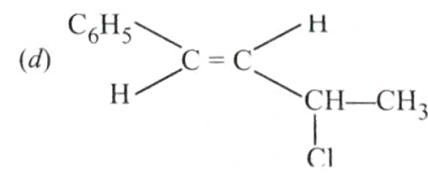
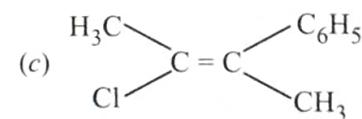
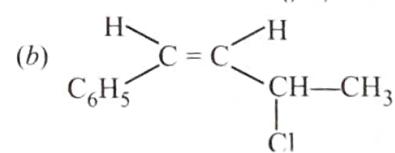
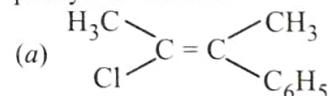
30. Which can show G.I.?



31. Which can show geometrical isomerism?



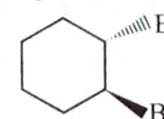
32. The correct stereochemical formula of trans-3-chloro-1-phenylbut-1-ene is:



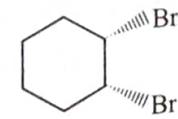
33. Following compounds are respectively Geometrical isomers. Choose the correct option.



(a) cis



(b) cis



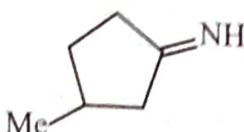
(c) cis

(d) cis

(e) trans

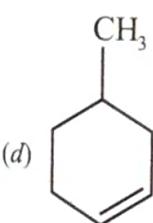
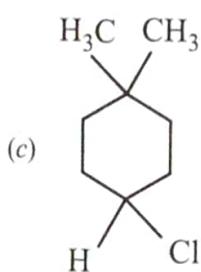
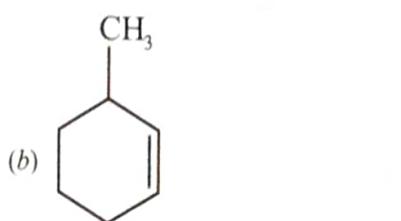
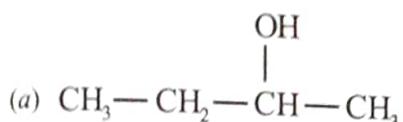
(f) trans

53. Given compound can show:

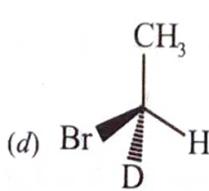
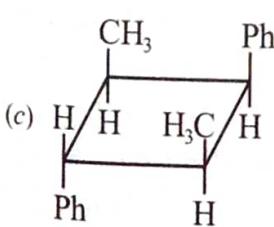
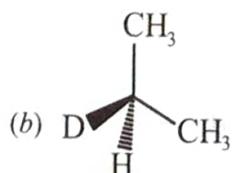
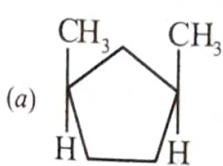


- (a) Geometrical isomerism
- (b) Optical isomerism
- (c) Geometrical and optical isomerism both
- (d) None of these

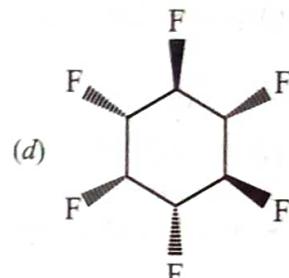
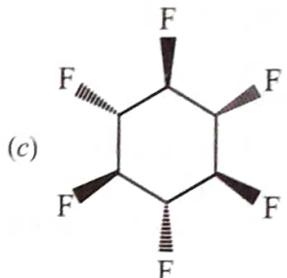
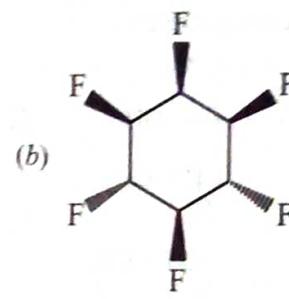
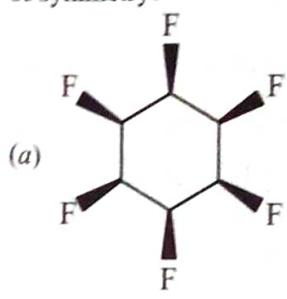
54. Which of the following compound is optically inactive?



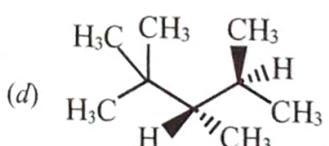
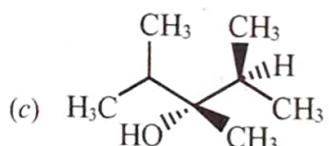
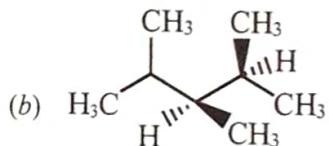
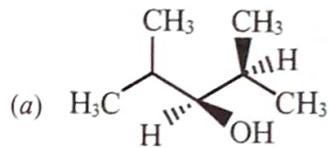
55. Which species do not have a plane of symmetry?



56. Which of the following has plane of symmetry and centre of symmetry?

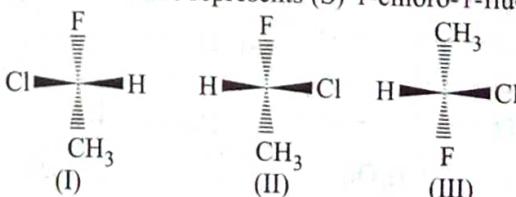


57. Which of the following structures represents a chiral compound?



OPTICAL ISOMERISM- R/S-CONFIGURATION & D/L-CONFIGURATION

58. Which structure represents (S)-1-chloro-1-fluoroethane?



- (a) I
- (b) II
- (c) III
- (d) More than one of the above

59. Which of the following molecules is achiral?

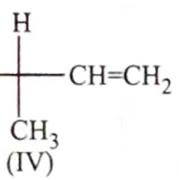
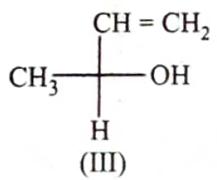
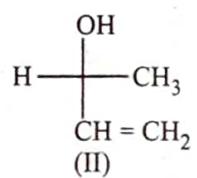
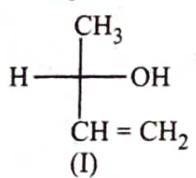
- (a) (2R, 3R)-2,3-dichloropentane.

- (b) (2R, 3S)-2,3-dichloropentane.

- (c) (2S, 4S)-2,4-dichloropentane.

- (d) (2S, 4R)-2,4-dichloropentane.

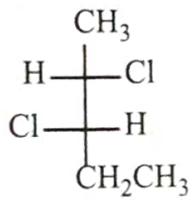
60. Which of the following combinations amongst the four Fischer projections represents the same absolute configurations?



- (a) (II) and (III)
(c) (II) and (IV)

- (b) (I) and (IV)
(d) (III) and (IV)

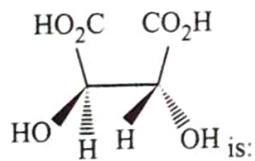
61. What is the configuration of the following molecule?



- (a) 2S, 3R
(c) 2S, 3S

- (b) 3R, 3S
(d) 2R, 3R

62. The absolute configuration of



- (a) R, R
(c) S, R

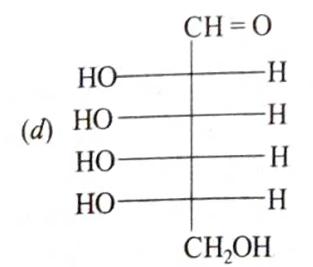
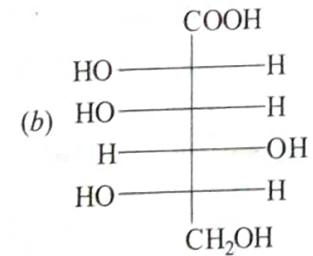
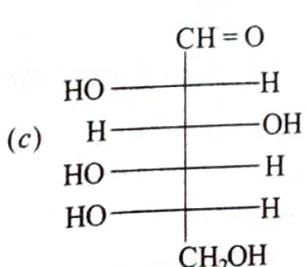
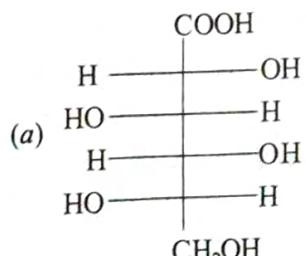
- (b) R, S
(d) S, S

63. HO——H represents the Fischer projection formula:
- $$\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CHO} \end{array}$$

- (a) D
(c) d

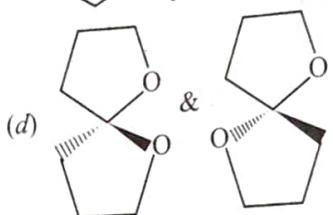
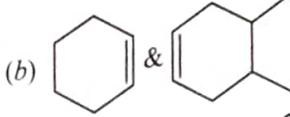
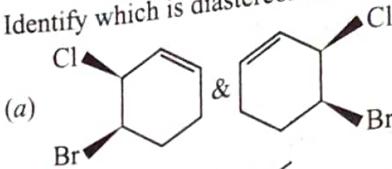
- (b) L
(d) l

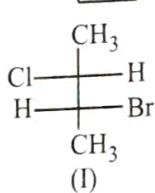
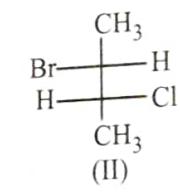
64. Which of the following is L-glucose?



OPTICAL ISOMERISM-ENANTIOMERS, DIASTEREOMERS, MESO

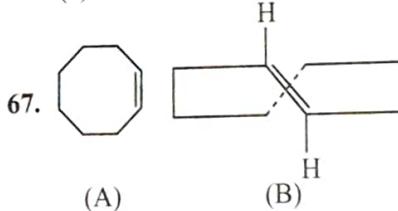
65. Identify which is diastereomer:



66.  (I)  (II)

Compound I and II are:

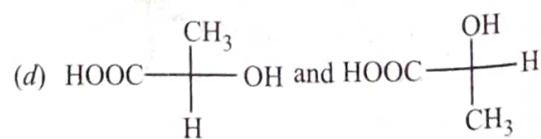
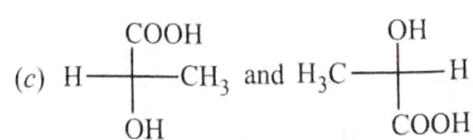
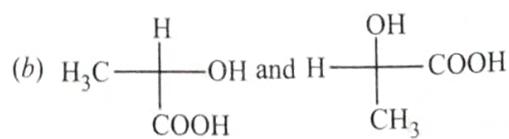
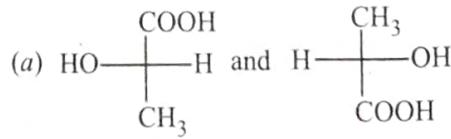
- (a) Identical
(c) Enantiomers
(b) Position Isomer
(d) Diastereomers



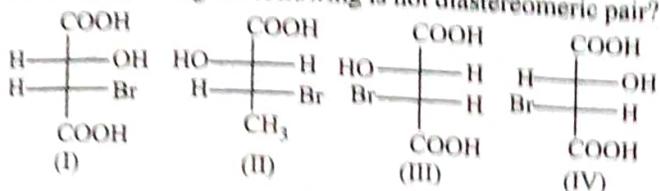
Correct relationship in between A and B is:

- (a) Diastereo isomer
(c) None of these
(b) Enantiomeric
(d) Geometrical isomers

68. Which of the following pairs of structures represent enantiomers?

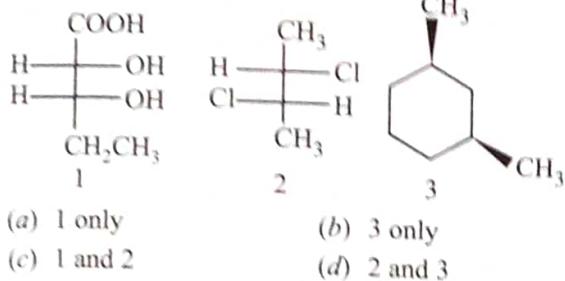


69. Which one among the following is not diastereomeric pair?



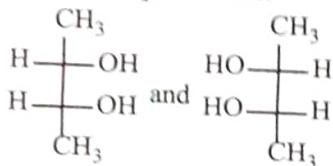
- (a) I and III (b) I and II
 (c) II and III (d) I and IV

70. Which of the following compounds are meso forms?



- (a) 1 only (b) 3 only
 (c) 1 and 2 (d) 2 and 3

71. The following two compounds are:



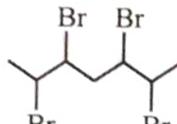
- (a) Enantiomers (b) Diastereomers
 (c) Identical (d) Geometrical Isomers

CALCULATION OF STEREO ISOMERS

72. How many stereoisomers are there for tartaric acid?

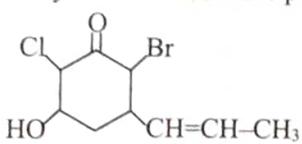
- (a) 2 (b) 3
 (c) 4 (d) 8

73. The maximum number of stereoisomers that could exist for the compound below?

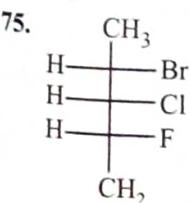


- (a) 6 (b) 8
 (c) 10 (d) 16

74. A naturally occurring substance has the constitution shown below. How many stereo isomers are possible for it?



- (a) 4 (b) 8
 (c) 16 (d) 32



Number of possible diastereomers for above compound are:

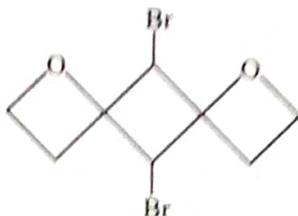
- (a) 2 (b) 6
 (c) 8 (d) 4



Total number of stereoisomers in above compound:

- (a) 6 (b) 4
 (c) 8 (d) 16

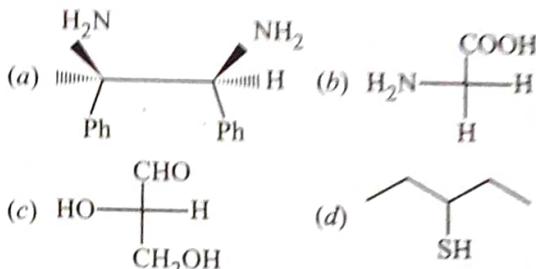
77.



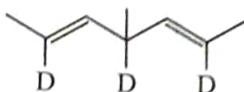
Number of optically active isomer is/are:

- (a) 0 (b) 1
 (c) 2 (d) 3

78. Which of the following molecules is expected to rotate the plane of polarised light?



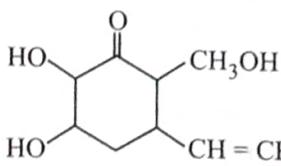
79. For the given compound which of the



following statement(s) are correct?

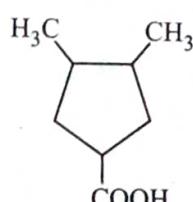
- (a) It has 4 stereoisomers.
 (b) It has 3 stereoisomers.
 (c) It has 2 chiral centres.
 (d) The compound does not show G.I.

80. A naturally occurring substance has the constitution shown below. How many may have this constitution?



- (a) 2 (b) 8
 (c) 15 (d) 64

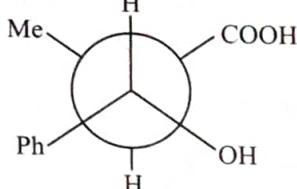
81. Number of stereoisomers of



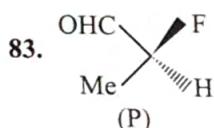
- (a) 2 (b) 3
 (c) 4 (d) 5

CONFORMATIONAL ISOMERISM

82. The correct Fischer projection formula of the Newman projection representation is:



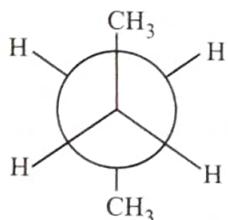
- (a) (b)
- (c) (d)



Correct fischer projection of above compound (P) will be:

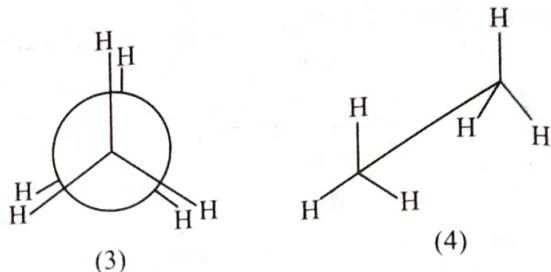
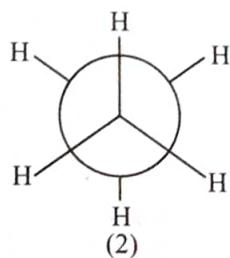
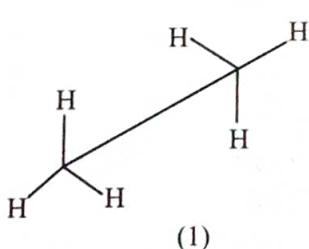
- (a) (b)
- (c) (d)

84. In the given conformation C₂ is rotated about C₂-C₃ bond anticlockwise by an angle of 120° then the conformation obtained is:



- (a) Fully eclipsed conformation.
 (b) Partially eclipsed conformation.
 (c) Gauche conformation.
 (d) Staggered conformation.

85. In the following structures, which two forms are staggered conformation of ethane?

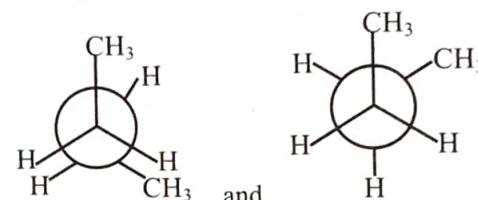


- (a) 1 and 4
 (c) 1 and 2
- (b) 2 and 3
 (d) 1 and 3

86. The most stable conformation of ethylene glycol is:

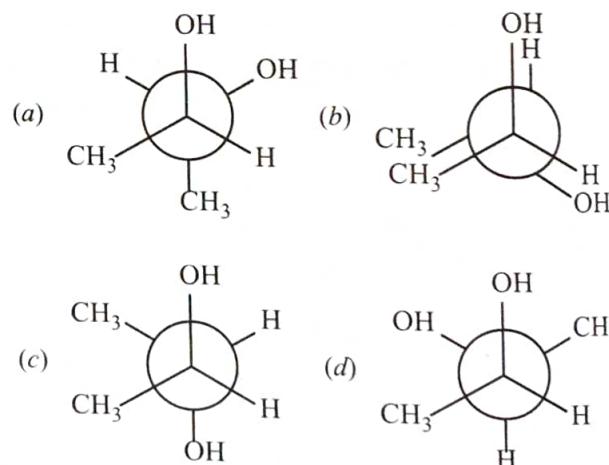
- (a) Anti
 (c) Partially eclipsed
- (b) Gauche
 (d) Fully eclipsed

87. What are the type of isomers in following pairs



- (a) Conformers
 (c) Optical
- (b) Position
 (d) Geometrical

88. Which conformer is most stable?



CYCLIC CONFORMER

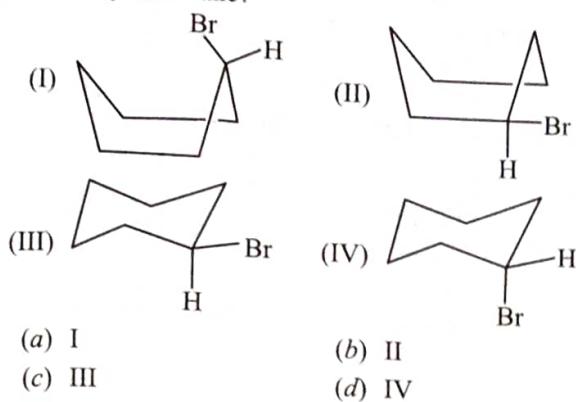
89. In the boat conformation of cyclohexane, the "flagpole" hydrogens are located:

- (a) on the same carbon
 (b) on adjacent carbons
 (c) on C-1 and C-3
 (d) on C-1 and C-4

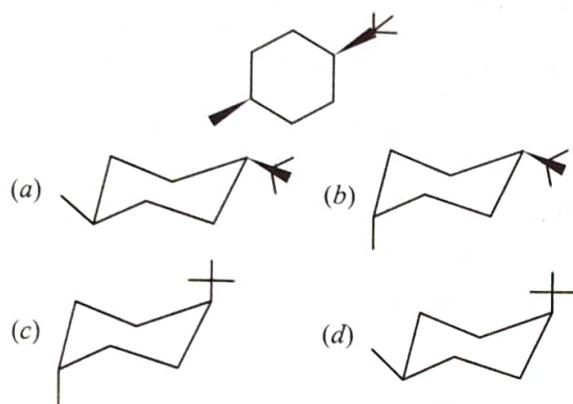
90. Which of the following correctly list the conformations of cyclohexane in order of increasing energy?

- (a) chair < boat < twist-boat < half-chair
 (b) half-chair < boat < twist-boat < chair
 (c) chair < twist-boat < half-chair < boat
 (d) chair < twist-boat < boat < half-chair

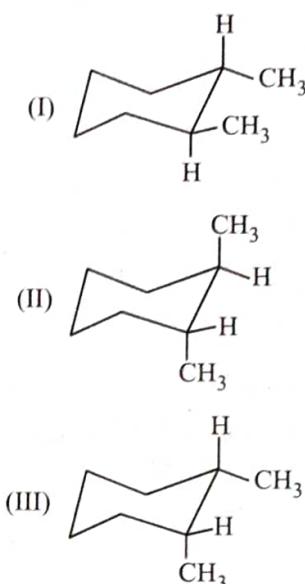
91. Which of the following is the most stable conformation of bromocyclohexane?



92. Most Stable conformer of:



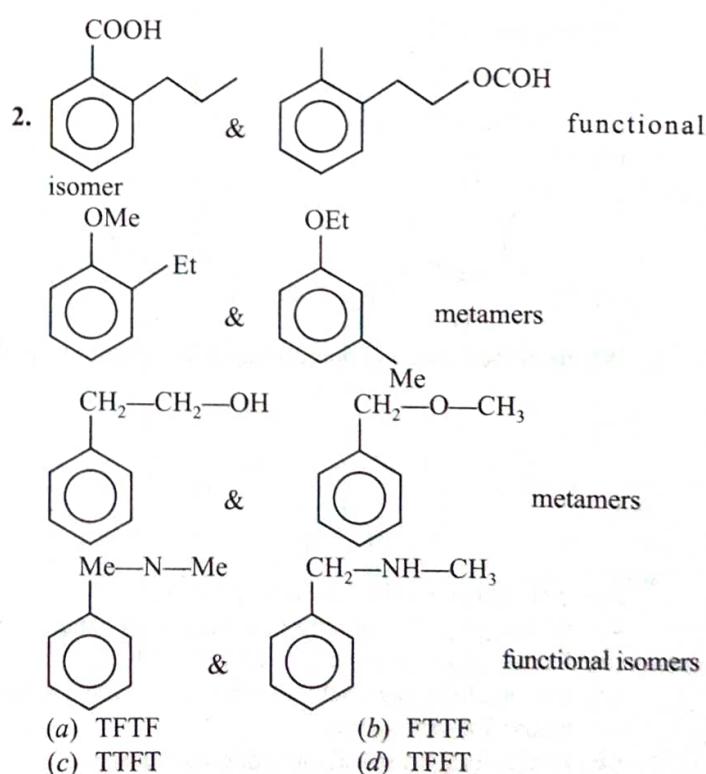
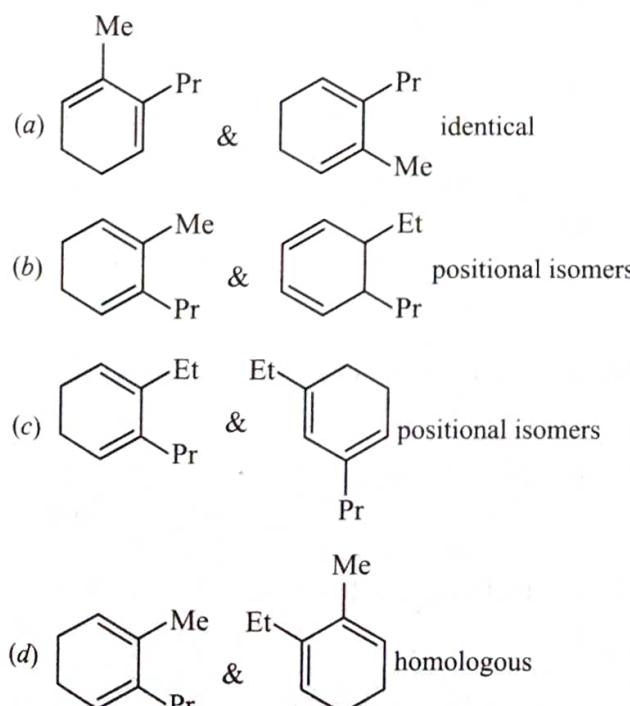
93. Choose the order that has the following structures correctly ranked with respect to increasing stability (the most stable structure is on the right):



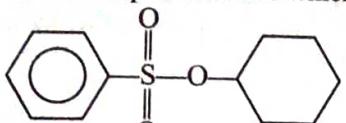
- (a) (I) < (II) < (III)
 (b) (II) < (I) < (III)
 (c) (III) < (II) < (I)
 (d) (II) < (III) < (I)

Exercise-2 (Learning Plus)

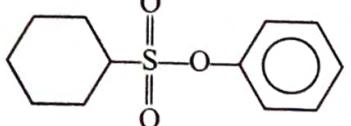
1. Which of the following has **incorrect** relation?



3. Given compound shows which type of isomerism?



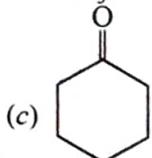
and



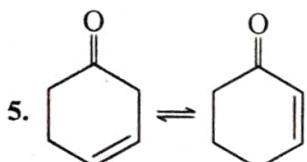
- (a) Chain isomerism
- (b) Positional isomerism
- (c) Metamerism
- (d) Functional group isomerism

4. Tautomer in which of the following is Diad system:

- (a) CH_3COCH_3
- (b) $\text{CH}_3\text{CH}_2\text{NO}_2$

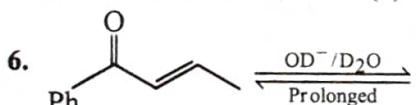


- (d) HCN



Above interconversion takes place in:

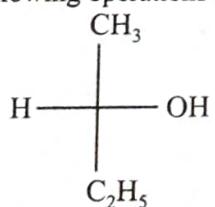
- (a) Acidic medium
- (b) Basic medium
- (c) Both medium
- (d) None of these



(P) final product is?

- (a)
- (b)
- (c)
- (d)

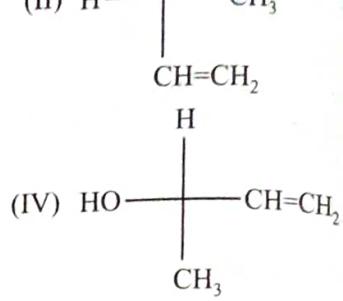
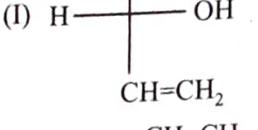
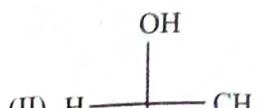
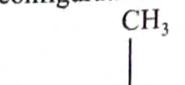
7. Which of the following operations on the Fischer formula



does not change its absolute configuration?

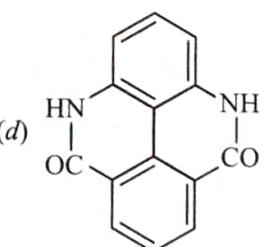
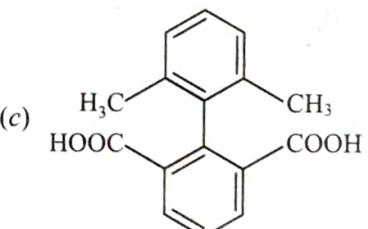
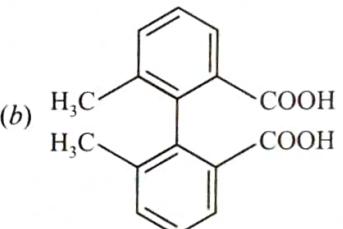
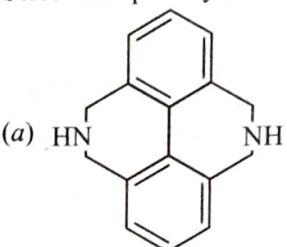
- (a) Exchanging groups across the horizontal bond.
- (b) Exchanging groups across the vertical bond.
- (c) Exchanging groups across the horizontal bond and also across the vertical bond.
- (d) Exchanging a vertical and horizontal group.

8. Which of the following combinations amongst the four Fischer projections represents the same absolute configurations?

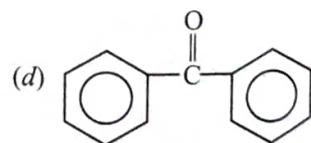
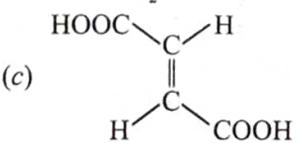
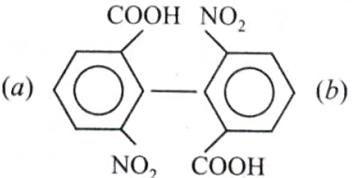
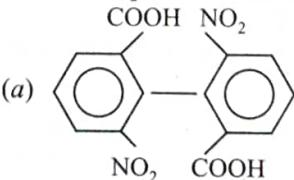


- (a) II and III
- (b) I and IV
- (c) II and IV
- (d) III and IV

9. Select the optically active compound among the following:



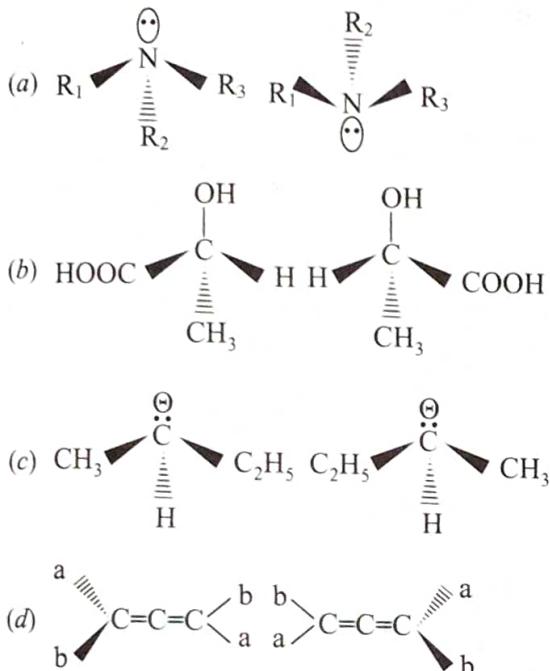
10. Which compound would exhibit optical isomers?



11. Which of the following starred C – atom is asymmetric:

- (a) $\text{CH}_3\text{CH}_2\overset{*}{\text{C}}\text{HCH}_3\text{CH}_2\text{OH}$
- (b) $\text{CH}_3\text{CH}_2\text{CH}\overset{*}{\text{C}}\text{H}_3\text{CH}_2\text{OH}$
- (c) $\text{CH}_3\overset{*}{\text{C}}\text{H}_2\text{CHCH}_3\text{CH}_2\text{OH}$
- (d) $\text{CH}_3\text{CH}_2\text{CHCH}_3\overset{*}{\text{C}}\text{H}_2\text{OH}$

12. Which of the following pairs can be resolved?



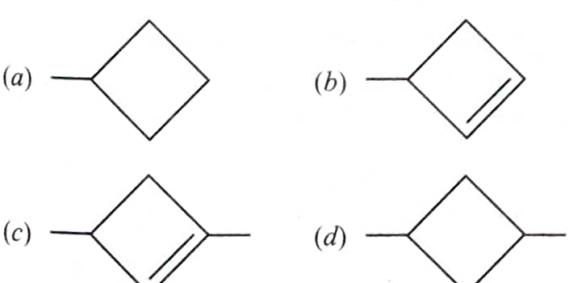
13. Which of the following statements is not correct?

- (a) Enantiomers are essentially chiral and optically active.
- (b) Diastereomers are not necessarily chiral and optically active.
- (c) All geometrical isomers are diastereomers.
- (d) All diastereomers are chiral and optically active.

14. Geometrical isomerism is possible in:

- (a) Isobutene
- (b) Acetone oxime
- (c) Acetophenone oxime
- (d) Benzophenone oxime

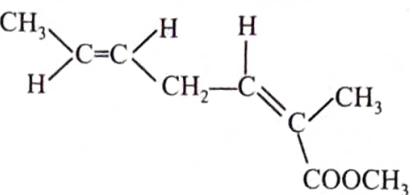
15. Which of the following will show geometrical isomerism?



16. Which of the following compounds has no geometrical isomer?

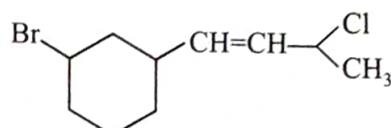
- (a) 1-Phenylpropene
- (b) 1, 2-Diphenylethene
- (c) 1, 2-Diphenylpropene
- (d) 1, 1-Diphenylpropene

17. The correct stereochemical name of



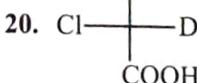
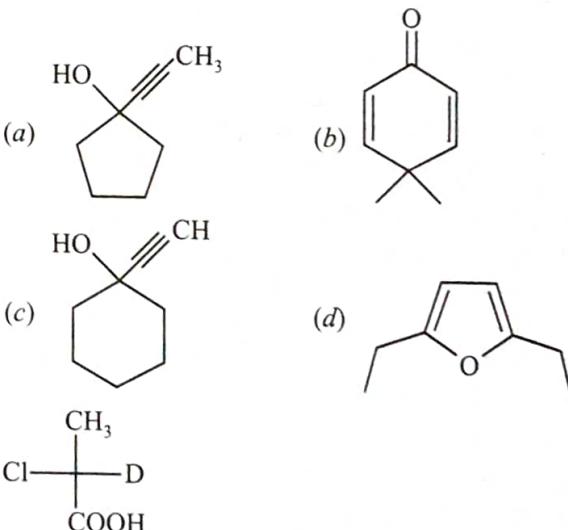
- (a) Methyl 2-methylhepta (2E, 5E) dienoate
- (b) Methyl 2-methylhepta (2Z, 5Z) dienoate
- (c) Methyl 2-methylhepta (2E, 5Z) dienoate
- (d) Methyl 2-methylhepta (2Z, 5E) dienoate

18. How many stereoisomer are possible for the following molecule?

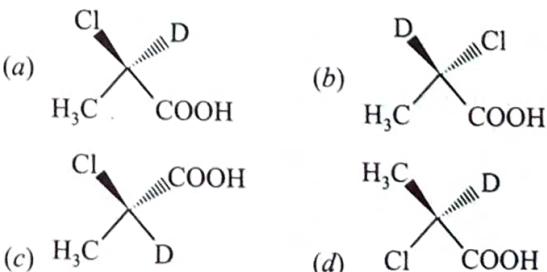


- (a) 4
- (b) 8
- (c) 16
- (d) 32

19. Among the following compounds, which compounds are structural isomers of each other.



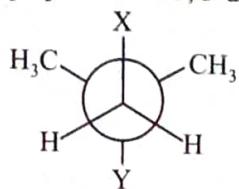
Correct wedge-dash representation of above compound will be:



21. Increasing order of stability among the three main conformation (i.e. Eclipse, Anti, Gauche) of 2-fluoroethanol is:

- (a) Eclipse, Gauche, Anti
- (b) Gauche, Eclipse, Anti
- (c) Eclipse, Anti, Gauche
- (d) Anti, Gauche, Eclipse

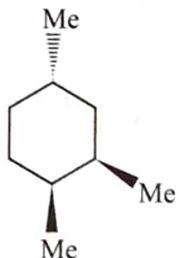
22. In the Newman projection for 3, 3-dimethylpentane



X and Y can respectively be:

- (a) H and H
- (b) CH₃ and C₂H₅
- (c) C₂H₅ and H
- (d) CH₃ and CH₃

23. Determine the position of substituents in the most stable conformation according to IUPAC nomenclature in given compound.



- (a) 1e, 2a, 4e
- (b) 1e, 3a, 4e
- (c) 1a, 2e, 4a
- (d) 1a, 3e, 4a

24. (I) and (II) , then

What will be the correct order of physical properties?

Dipole moment	B.P.	M.P.	Stability
(a) I > II	I > II	II > I	I > II
(b) II > I	II > I	II > I	II > I
(c) I > II	I > II	I > II	I > II
(d) II > I	II > I	I > II	I > II

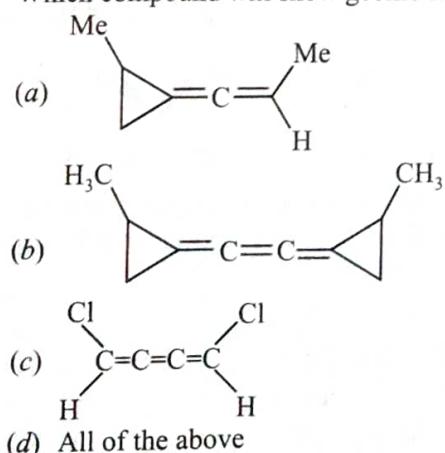
25. Which of the following does not show geometrical isomerism?

- (a) 1, 2-Dimethylcyclohexane
- (b) 1, 4-Dimethylcyclohexane
- (c) 1-Bromo-3-chlorocyclohexane
- (d) None of the three

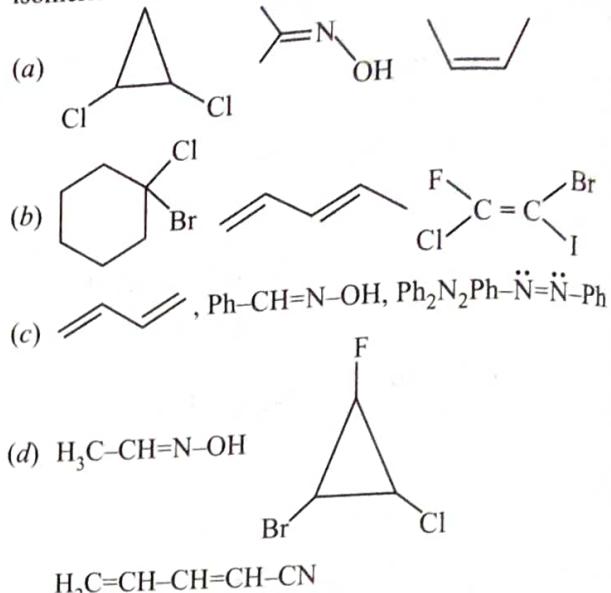
26. Lowest molecular mass of cyclic alcohol which can show geometrical isomerism, is x.

Then find the value of $\frac{x}{9}$.

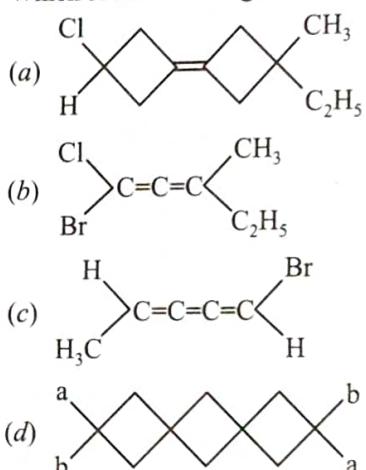
27. Which compound will show geometrical isomerism?



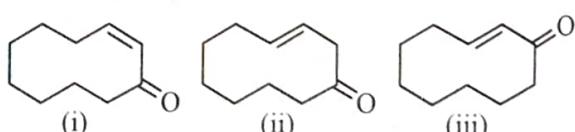
28. In which option all compounds can show geometrical isomerism?



29. Which of the following will not show geometrical isomerism?



30. Which of the following statement is not true about the following compounds?

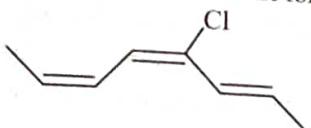


- (a) (i) and (iii) are identical
- (b) (i) and (iii) are geometrical isomers
- (c) (i) and (ii) are structural isomers
- (d) (ii) and (iii) are structural isomers

31. Geometrical isomers are possible for:

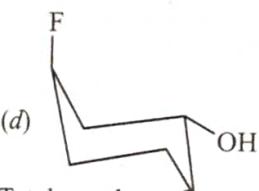
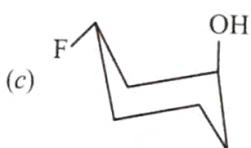
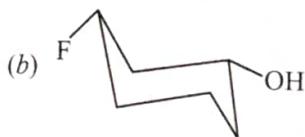
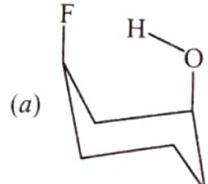
- (a) $\text{H}_3\text{C}-\text{CH}_2-\underset{\text{NOH}}{\overset{||}{\text{C}}}-\text{CH}_2\text{CH}_3$
- (b) $\text{H}_3\text{C}-\text{CH}_2-\underset{\text{O}}{\overset{||}{\text{C}}}-\text{CH}_3$
- (c) $\text{H}_3\text{C}-\text{CH}_2-\underset{\text{NOH}}{\overset{||}{\text{C}}}-\text{CH}_3$
- (d) $\text{H}_6\text{C}_5-\underset{\text{NOH}}{\overset{||}{\text{C}}}-\text{C}_6\text{H}_5$

32. What is the correct IUPAC name of the following compound?

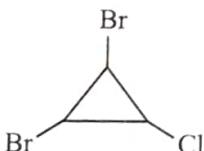


- (a) (2E, 4Z, 6Z)-4-chloro octa-2, 4, 6-triene
- (b) (2Z, 4E, 6E)-5-chloro octa-2, 4, 6-triene
- (c) (2E, 4E, 6Z)-4-chloro octa-2, 4, 6-triene
- (d) (2Z, 4Z, 6E)-5-chloro octa-2, 4, 6-triene

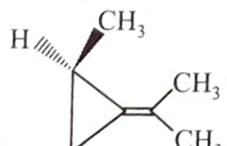
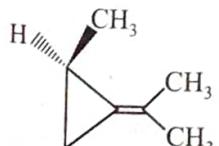
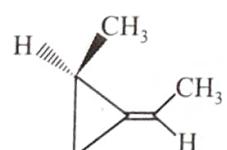
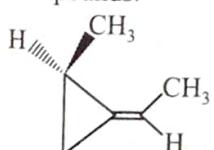
33. Find out most stable conformer of cis-3-fluorocyclohexanol.



34. Total number of geometrical isomers possible in given compound is:

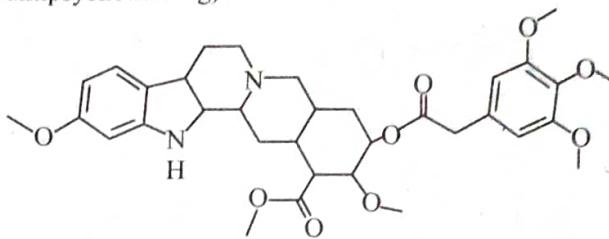


35. Find the sum of all the stereocenters that are present in below compounds:



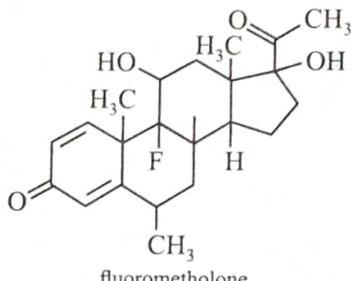
- (a) 8
- (c) 10
- (b) 9
- (d) 11

36. How many chiral carbons are there in reserpine (an antipsychotic drug)?



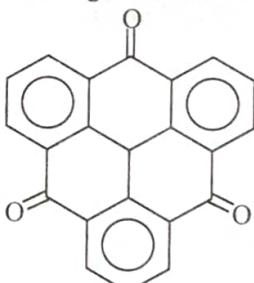
- (a) 9
- (b) 8
- (c) 7
- (d) 10

37. The following molecule is fluorometholone, a steroid anti-inflammatory agent. How many stereogenic centers does it contain?



- (a) 5
- (b) 6
- (c) 7
- (d) 8

38. Which of the following is correct for the given compound?

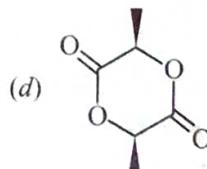
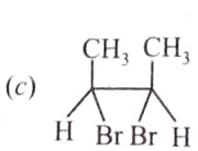
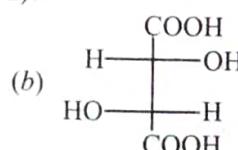
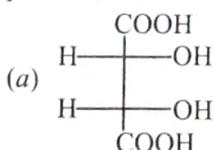


- (a) It posses center of symmetry.
- (b) It posses C₃ axis of symmetry.
- (c) It posses plane of symmetry.
- (d) (b) and (c) both are correct.

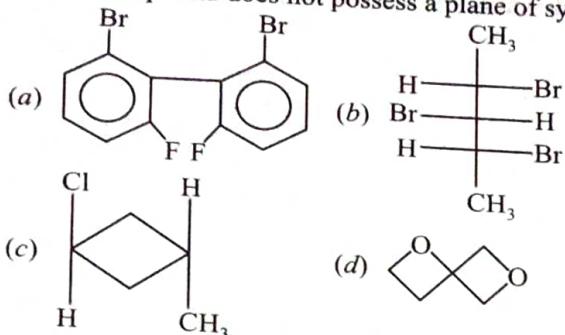
39. Number of isomers of C₇H₁₄ (having cyclopentane ring) which have plane of symmetry.

- (a) 3
- (b) 4
- (c) 5
- (d) 6

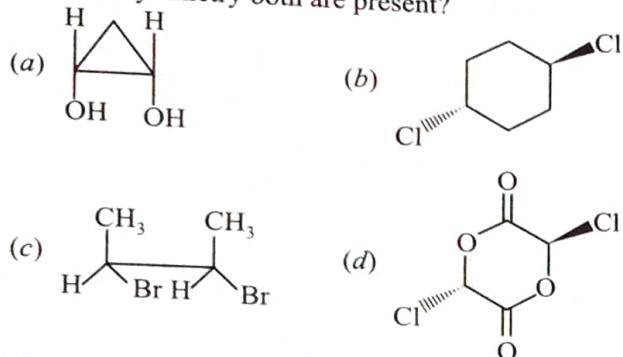
40. Which molecule has centre of symmetry present (in any possible stable conformation)?



41. Which compound does not possess a plane of symmetry?



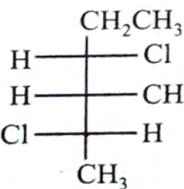
42. In which of the following compound plane of symmetry and centre of symmetry both are present?



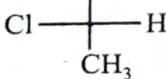
43. Match the following:

Column-I		Column-II	
A.		p.	Centre of symmetry
B.		q.	C_2 axis of symmetry
C.		r.	Plane of symmetry
D.		s.	Compound shows optical isomerism

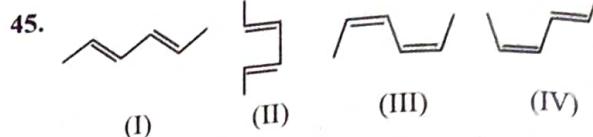
- (a) A \rightarrow r; B \rightarrow s; C \rightarrow p; D \rightarrow q
 (b) A \rightarrow r; B \rightarrow q; C \rightarrow p; D \rightarrow s
 (c) A \rightarrow s; B \rightarrow p; C \rightarrow q; D \rightarrow r
 (d) A \rightarrow s; B \rightarrow q; C \rightarrow p; D \rightarrow r



44. H-CH₂-CH₃ is properly named:



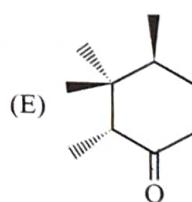
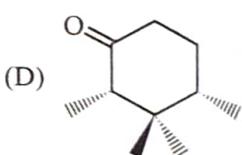
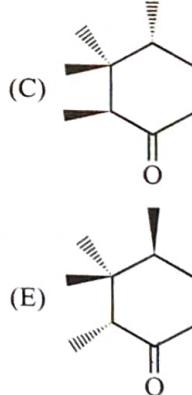
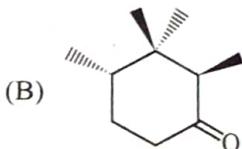
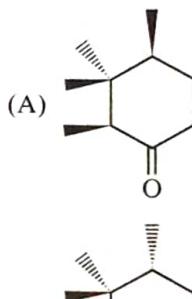
- (a) (3R, 4S, 5R)-3,5-dichloro-4-methylhexane
 (b) (2S, 3S, 4S)-2,4-dichloro-3-methylhexane
 (c) (2S, 3R, 4R)-2,4-dichloro-4-methylhexane
 (d) (2S, 3R, 4S)-2,4-dichloro-3-methylhexane



Correct statement regarding above given compounds

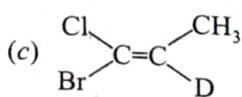
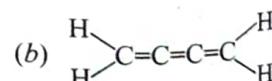
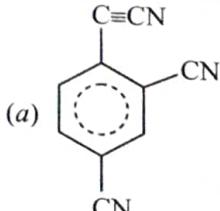
- (a) I and II are diastereomers
 (b) I and III are identical
 (c) III and IV are identical
 (d) I and II are conformers

46. Which of the structures is/are diastereomer of A?

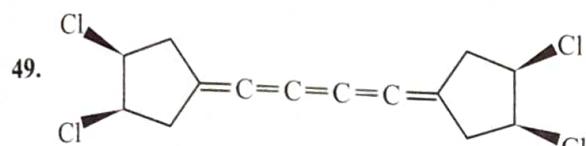
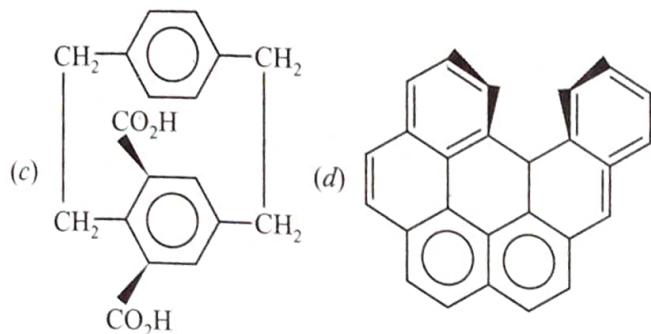
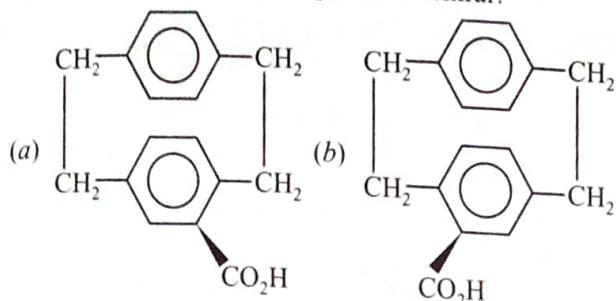


- (a) C
 (b) A and D
 (c) B and C
 (d) E

47. Find out the compound in which all the atoms lies in plane (in all conformations).

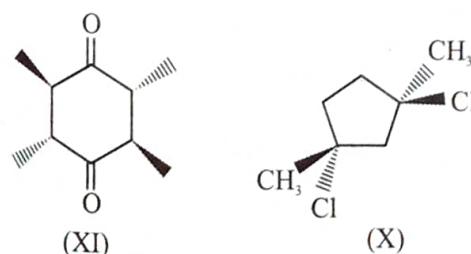
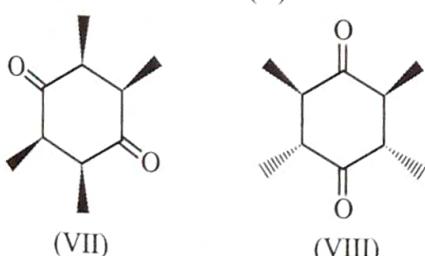
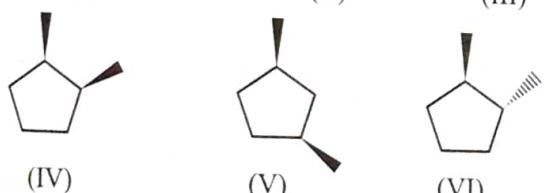
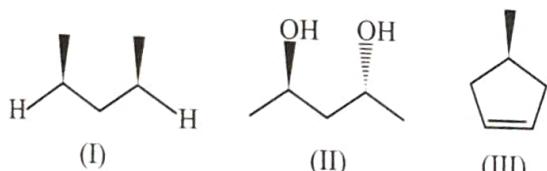


48. Which of the following compound is achiral?

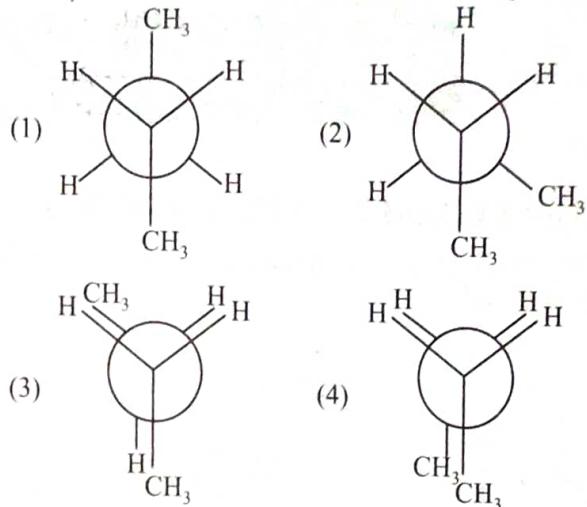


Number of meso-isomer are:

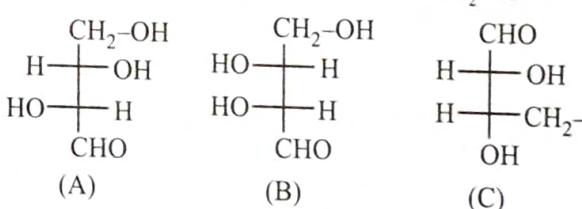
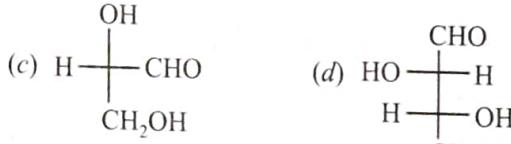
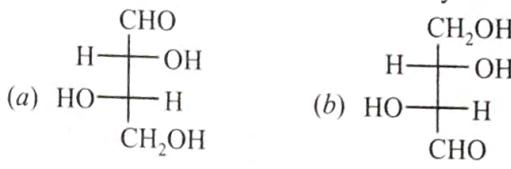
50. How many compounds shown below are chiral?



51. Which conformer of butane are chiral in the given form?

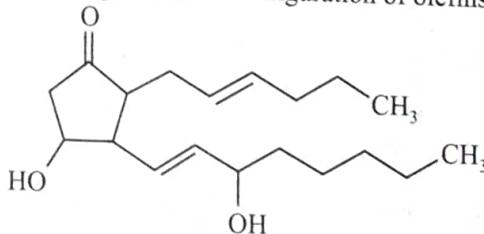


52. Which of the following is/are D-carbohydrate?

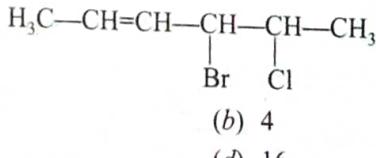


(D) & (L) configuration of above carbohydrate is:

54. The number of stereoisomers possible for the below compound (do not change cis/trans configuration of olefins) are:



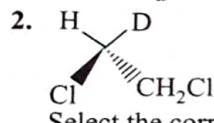
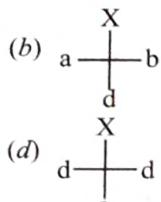
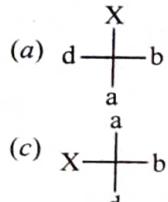
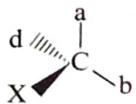
55. Total number of stereoisomers possible for the given compound is:



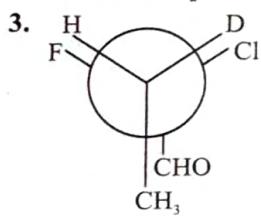
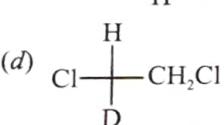
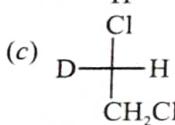
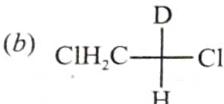
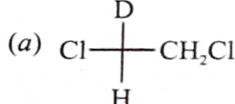
Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

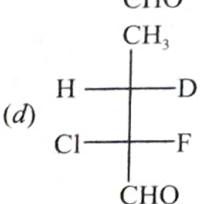
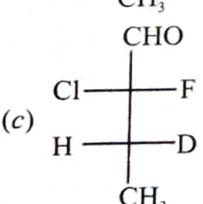
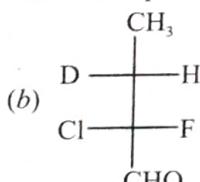
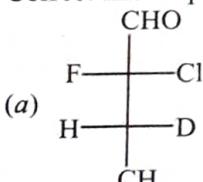
1. The Fischer projection of the molecule as represented in the wedge dash.



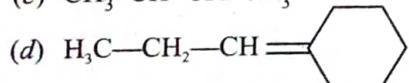
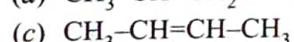
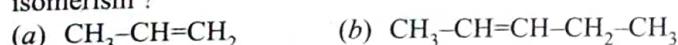
Select the correct fischer projection of above compound:



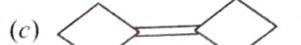
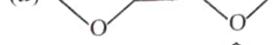
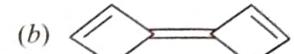
Correct fischer projection of above compound will be:



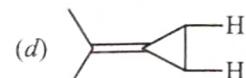
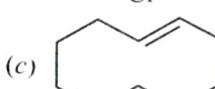
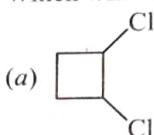
4. Which of the following compounds show are cis-trans isomerism?



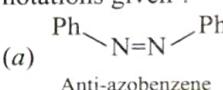
5. Which of following compound will not show geometrical isomerism?



6. Which will form geometrical isomers?

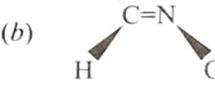


7. For which of the following pairs of compounds are the correct notations given?



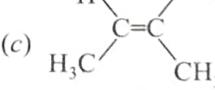
Anti-azobenzene

$\text{H}_3\text{C}/\text{H}_3\text{C}$



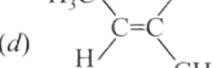
Syn-acetaldoxime

$\text{H}_3\text{C}/\text{H}_3\text{C}$

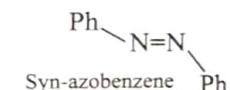


Z-isomer

$\text{H}_3\text{C}/\text{H}_3\text{C}$



Z-isomer



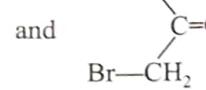
Syn-azobenzene

$\text{H}_3\text{C}/\text{H}_3\text{C}$



Anti-acetaldoxime

$\text{H}_3\text{C}/\text{H}_3\text{C}$



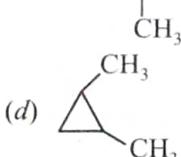
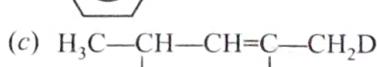
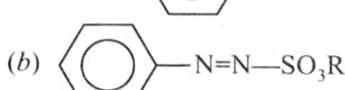
E-isomer

Cl/Br



E-isomer

8. Which will show geometrical isomerism?



9. Select the correct statements about the given compounds:

- (P) $\text{CH}_3 - \text{CH} = \text{CH} - \text{O} - \text{CH} = \text{CH}_2$
- (Q) $\text{CH}_3 - \text{O} - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2$
- (a) The compound Q($\text{CH}_3 - \text{O} - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2$) is a metamer of (P)
- (b) (P) has two geometrical isomers
- (c) (Q) has three stereoisomers
- (d) The IUPAC names of P and Q both have primary suffix diene.

10. Which of the following compounds can exhibit geometrical isomerism?

- (a)
- (b)
- (c)
- (d) $\text{C}_2\text{H}_5 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3$

11. Symmetries present in the given compound.



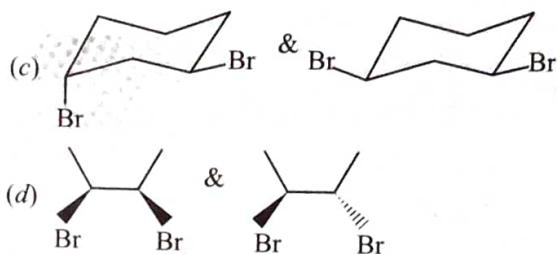
- (a) Plane of symmetry (POS)
- (b) Centre of symmetry (COS)
- (c) C_2 fold axis of symmetry
- (d) C_3 axis of symmetry

12. Indicate figure/s having S configuration.

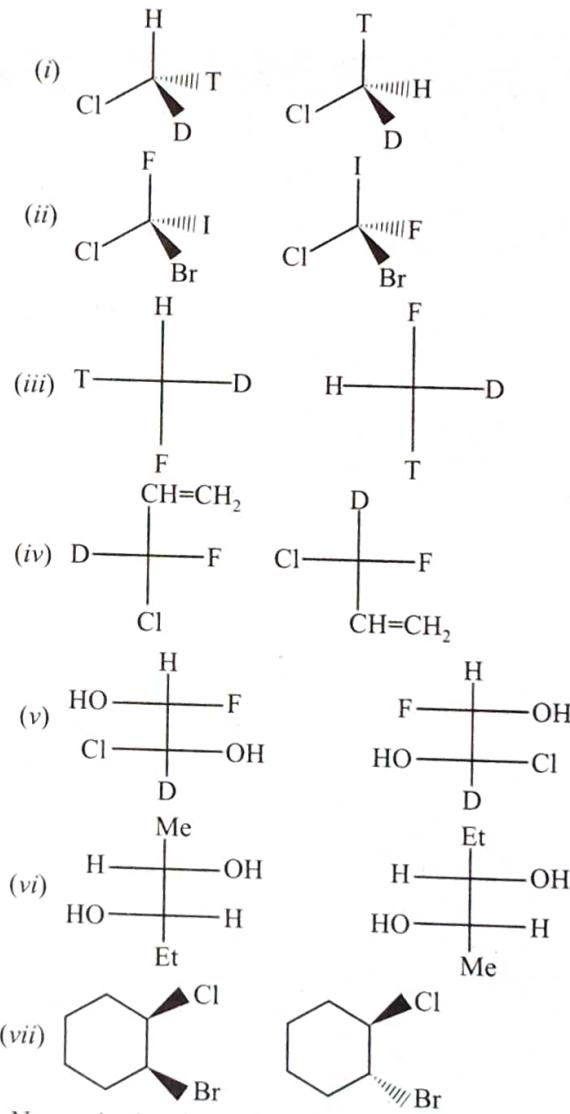
- (a)
- (b)
- (c)
- (d)

13. Identify which are configurational (optical or geometrical) isomer.

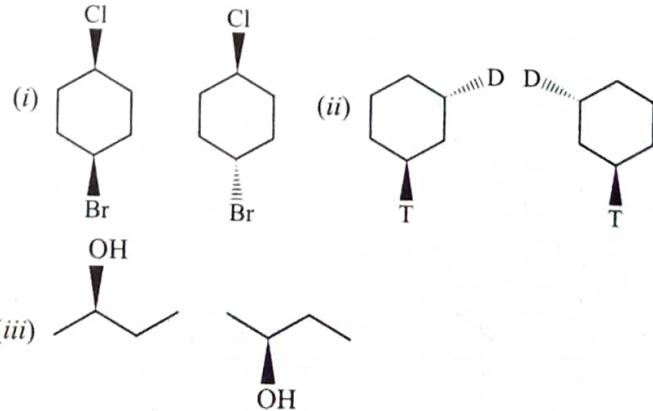
- (a)
- (b)

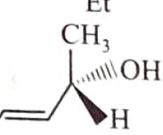
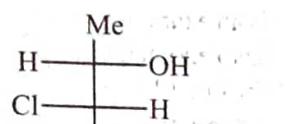
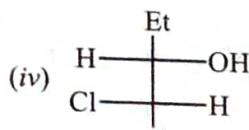


14. Calculate total number of enantiomeric pairs among given structures:



15. Numerical value of difference between number of enantiomeric pairs and diastereoisomers:



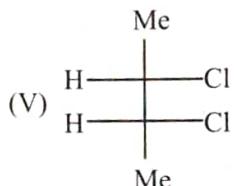
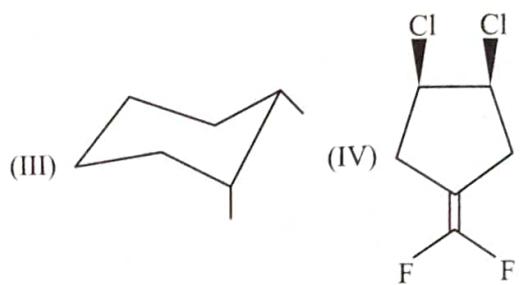
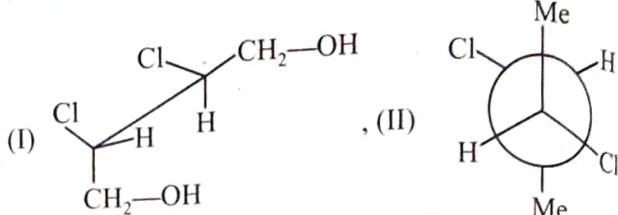


16. Match the following:

	Column-I	Column-II
A.	 	p. Identical
B.	 	q. Enantiomer
C.	 	r. Diastereomer
D.	 	s. Constitutional isomer
		t. Other

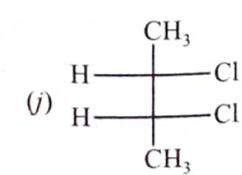
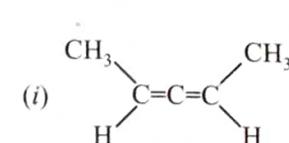
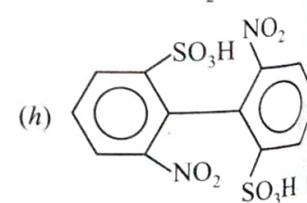
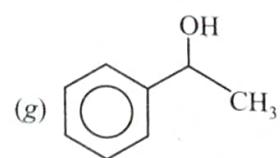
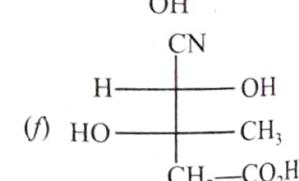
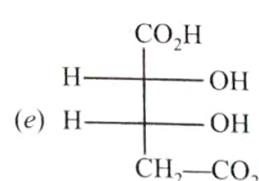
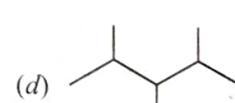
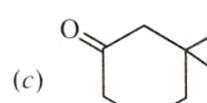
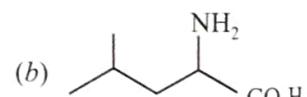
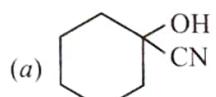
- (a) A → s; B → p; C → s; D → r
- (b) A → s; B → t; C → r; D → p
- (c) A → r; B → p; C → t; D → s
- (d) A → t; B → s; C → r; D → p

17. Correct statement/s regarding compounds.

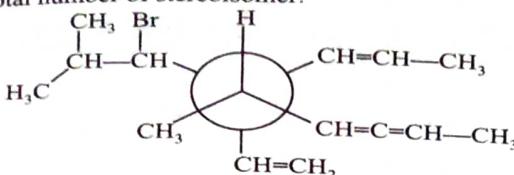


- (a) All are optically active and chiral molecule.
- (b) Number of chiral centre is exactly same in all molecules.
- (c) Only I is chiral and optically active.
- (d) All are optically inactive and achiral molecule.

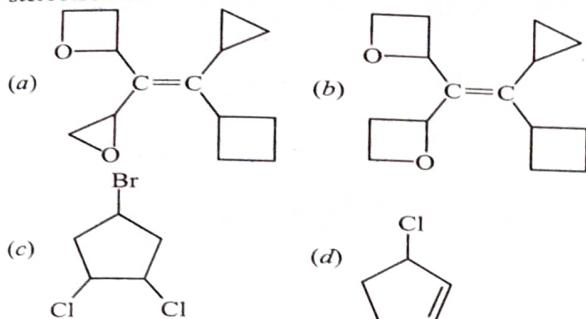
18. Calculate total number of chiral compounds?



19. Total number of stereoisomer:



20. Identify which compound is/are having even number of stereoisomer:



21. Which of the following statements is/are not correct?

- (a) Metamerism belongs to the category of structural isomerism.
- (b) Tautomeric structures are the resonating structures of a molecule.
- (c) Keto form is always more stable than the enol form.
- (d) Geometrical isomerism is shown only by alkenes.

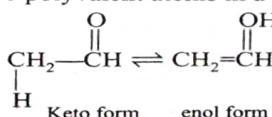
22. Which of the following is/are correct matchings?

- (a) $\text{CH}_3\text{C}(=\text{O})\text{OH}$ and $\text{H}-\text{C}(=\text{O})-\text{OCH}_3$ — Metamers
- (b) $\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{CH}$ and $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$ — Position isomers
- (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
 $\text{CH}_3-\text{CH}-\text{CH}_3$ — Tautomers
- (d) $\text{CH}_3\text{CH}_2\text{OH}$ and $(\text{CH}_3)_2\text{O}$ — Functional isomer

COMPREHENSION BASED QUESTIONS

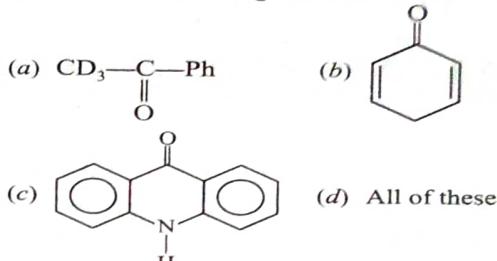
Comprehension (Q. 23 to 25): Tautomerism: Structural Isomers that undergo rapid interconversions and exist in dynamic equilibrium are known as Tautomers and relationship between them is known as Tautomerism. Tautomers generally have different functional groups.

At equilibrium more stable tautomer is present in higher amount but the ratio remains same until and unless change is made externally. Tautomerism actually arises due to rapid oscillation of an atom between two polyvalent atoms in a molecule.



Above is an example of Keto-enol tautomerism. Condition for this type of keto enol tautomerism is presence of α -H. Amount of enol at equilibrium is known as enolic content. It is more if enol is more stable and less if keto is more stable.

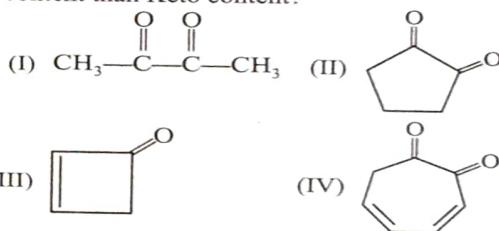
23. Which of the following can tautomerise?



24. Tautomer of which of the following can show geometrical isomerism:

- (a) CH_3-CHO
- (b) $\text{CH}_3\text{CH}_2-\text{CHO}$
- (c) $(\text{CH}_3)_2\text{CH}-\text{CH}=\text{O}$
- (d) Cyclohexene

25. Which of the following compounds have higher enolic content than Keto content?



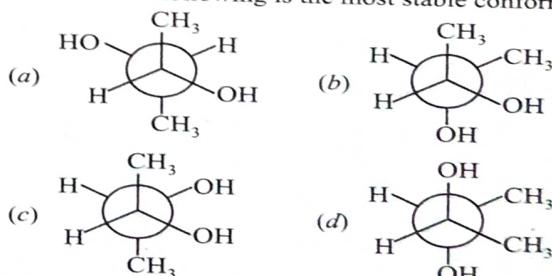
- (a) II & IV
- (b) I, II & IV
- (c) II, III & IV
- (d) II Only

Comprehension (Q. 26 to 27): Different spatial arrangements of the atoms that result from restricted rotation about a single bond are conformers. n-Butane has four conformers eclipsed, fully eclipsed, gauch and anti. The stability order of these conformers are as follows:

anti > gauch > eclipsed > fully eclipsed

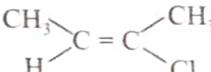
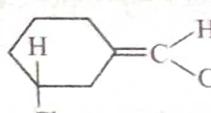
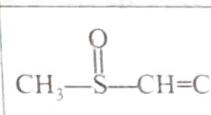
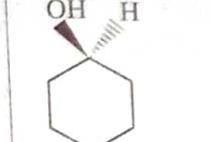
Although anti is more stable than gauch but in some cases gauch is more stable than anti.

26. Which of the following is the most stable conformer?



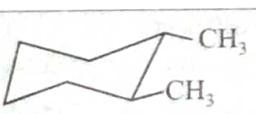
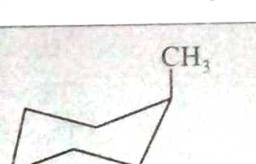
MATCH THE COLUMN TYPE QUESTIONS

- 28.** Match the column:

	Column-I		Column-II
A.		p.	Number of stereocenter is even number
B.		q.	Number of stereocenter is odd number
C.		r.	It will show geometrical isomerism
D.		s.	It will not show geometrical isomerism

- (a) A → p,r; B → q,r; C → q,r; D → p,r
 (b) A → q,r; B → p,r; C → q,r; D → p,r
 (c) A → p,s; B → q,s; C → q,r; D → q,r
 (d) A → p,s; B → q,s; C → p,r; D → q,r

- 29.** Match the column:

Column-I		Column-II	
A.		p.	cis-form
B.		q.	trans-form
C.		r.	Keq is greater than one or equal to one when compound undergo flip.
D.		s.	Keq is less than one when compound undergo flip.

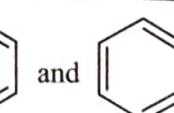
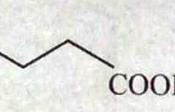
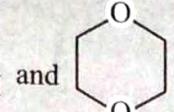
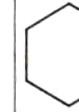
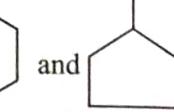
- (a) $A \rightarrow p,r; B \rightarrow q,s; C \rightarrow p,r; D \rightarrow q,r$
 (b) $A \rightarrow p,r; B \rightarrow q,r; C \rightarrow q,s; D \rightarrow q,r$
 (c) $A \rightarrow q,s; B \rightarrow p,r; C \rightarrow q,r; D \rightarrow p,r$
 (d) $A \rightarrow q,s; B \rightarrow q,r; C \rightarrow p,r; D \rightarrow p,r$

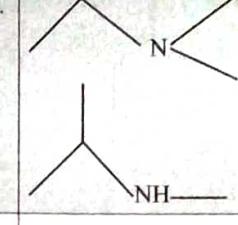
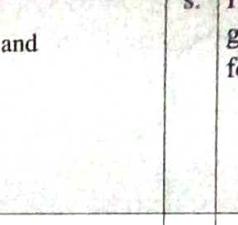
30. Match the column:

	Column-I		Column-II
A.	 and	p.	Structural isomer
B.	 and	q.	Identical
C.	 and	r.	Enantiomers
D.	 and	s.	Diastereomers

- (a) $A \rightarrow p; B \rightarrow s; C \rightarrow q; D \rightarrow r$
 - (b) $A \rightarrow r; B \rightarrow s; C \rightarrow p; D \rightarrow q$
 - (c) $A \rightarrow s; B \rightarrow r; C \rightarrow q; D \rightarrow p$
 - (d) $A \rightarrow p; B \rightarrow r; C \rightarrow q; D \rightarrow r$

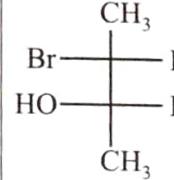
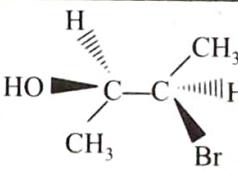
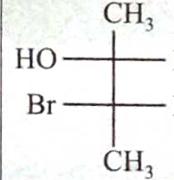
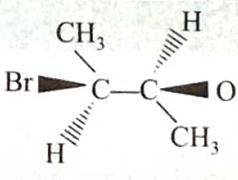
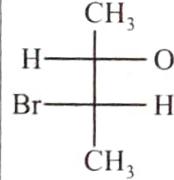
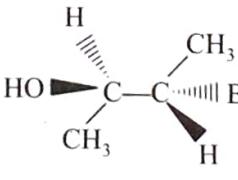
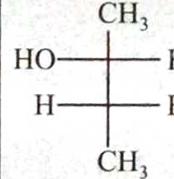
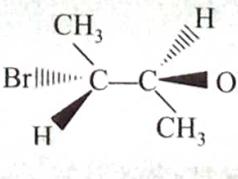
31. Match the following:

Column-I		Column-II	
A.	 and 	p.	Homologous
B.	 and 	q.	Functional isomers
C.	 and 	r.	Chain isomers

D.	 and 	s.	Have same general formula
		t.	Have same empirical formula

- (a) A → p,t; B → q,t; C → p,q; D → p,s
 (b) A → q,t; B → p,q; C → p,t; D → p,s
 (c) A → p,s; B → q,s; C → p,r; D → q,r
 (d) A → p,t; B → q,s; C → p,s; D → p,q

32. Match List-I, List-II & List-III:

List-I		List-II		List-III	
A.		1.		(i)	(2R, 3R)
B.		2.		(ii)	(2S,3S)
C.		3.		(iii)	(2S,3R)
D.		4.		(iv)	(2R, 3S)

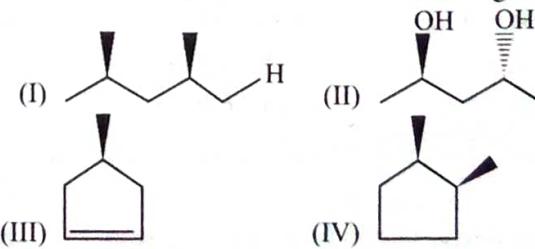
- (a) A → 4 → (iii); B → 3 → (iv); C → 2 → (ii); D → 1 → (i)
 (b) A → 3 → (iii); B → 2 → (iv); C → 4 → (ii); D → 1 → (i)
 (c) A → 2 → (ii); B → 3 → (iii); C → 1 → (iv); D → 4 → (i)
 (d) A → 1 → (i); B → 3 → (iv); C → 4 → (ii); D → 2 → (iii)

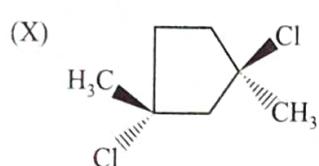
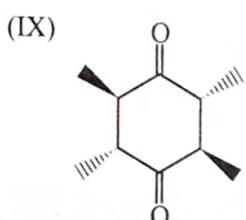
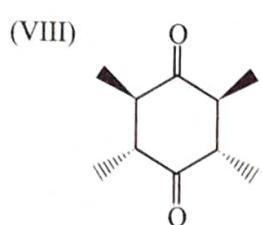
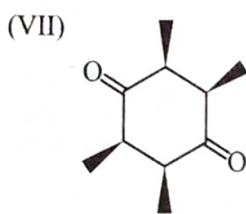
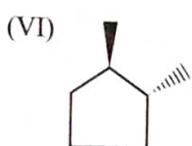
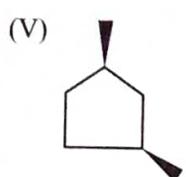
NUMERICAL TYPE QUESTIONS

33. In the following compound the total number of hydrogen atoms that occupy axial positions are:

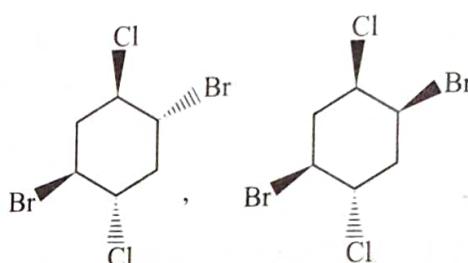
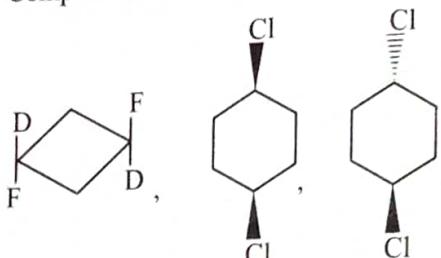


34. How many compounds shown below have single chiral center?





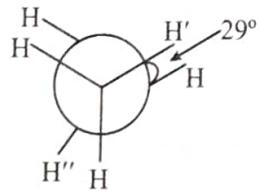
35. Number of compound having COS & POS both ?
Compound:



Exercise-4 (Past Year Questions)

JEE MAIN

1. In the following skew conformation of ethane
 $\text{H}'-\text{C}-\text{C}-\text{H}''$ dihedral angle is:



- (a) 120° (b) 58°
 (c) 149° (d) 151°

2. Which of these factors does not govern conformation in acyclic compounds?

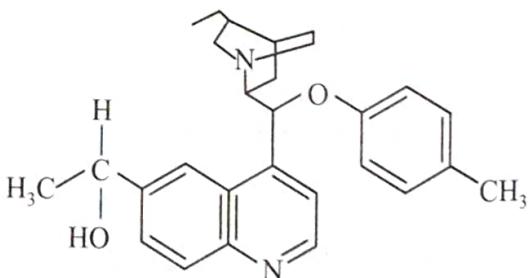
 - (a) Torsional strain
 - (b) Angle strain
 - (c) Steric interactions
 - (d) Electrostatic forces of interaction

3. Number of stereo centers present in linear and cyclic structures of glucose are respectively. (2010)

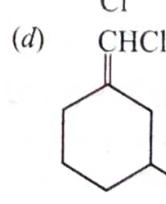
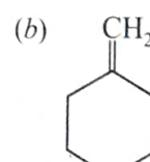
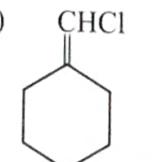
4. The number of chiral carbons in chloramphenicol is _____.
(2020)

5. The number of chiral centres in penicillin is _____. (2020)

6. The number of chiral carbons present in the molecule given below is _____. (2020)



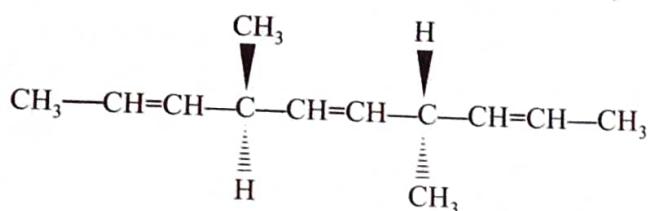
7. Among the following compounds geometrical isomerism is exhibited by: (2020)



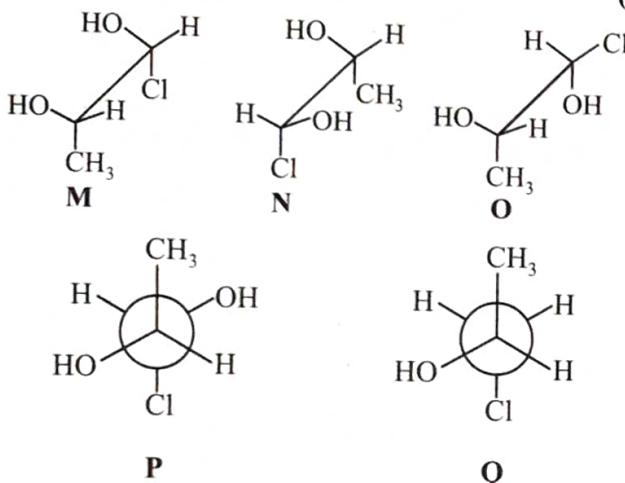
8. Which of the following compounds shows geometrical isomerism? (2020)

- (a) 2-methylpent-1-ene (b) 4-methylpent-1-ene
 (c) 2-methylpent-2-ene (d) 4-methylpent-2-ene

- 21.** The number of optically active product obtained from the complete ozonolysis of the given compound is: (2012)



22. Which of the given statement(s) about N, O, P and Q with respect to M is (are) correct? (2012)

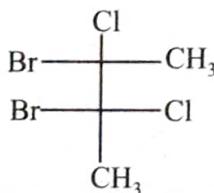


- (a) M and N are non-mirror image stereoisomers.
 - (b) M and O are identical.
 - (c) M and P are enantiomers.
 - (d) M and O are identical.

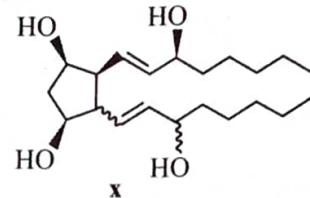
23. The correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are: (2014)

- (a) tert-butanol and 2-methylpropan-2-ol
 - (b) tert-butanol and 1, 1-dimethylethan-1-ol
 - (c) n-butanol and butan-1-ol
 - (d) iso-butyl alcohol and 2-methylpropan-1-ol

24. The total number(s) of stable conformers with non-zero dipole moment for the following compound is/are: (2014)



25. For the given compound X, the total number of optically active stereoisomers is _____. (2018)

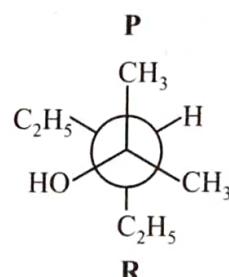
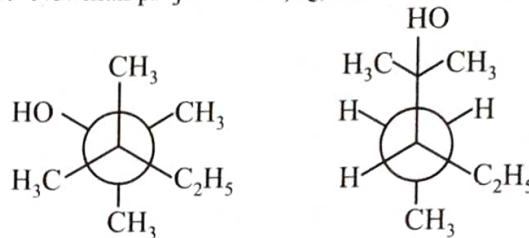


This type bond indicates that the configuration at the specific carbon and the geometry of the double bond is fixed

This type bond indicates that the configuration at the specific carbon and the geometry of the double bond is NOT fixed

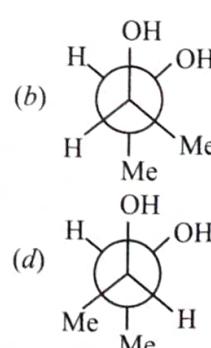
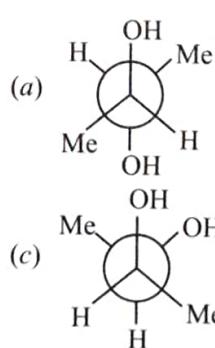
26. Total number of isomers, considering both structural and stereoisomers, of cyclic ethers with the molecular formula C_4H_8O is _____. (2019)

27. Newman projections P, Q, R and S are shown below:



Which one of the following options represents identical molecules? (2020)

28. Among the following, the conformation that corresponds to the most stable conformation of mesobutane- 2,3-diol is:



29. The total number of chiral molecules formed from one molecule of P on complete ozonolysis (O_3 , Zn/H_2O) is _____.

ANSWER KEY

CONCEPT APPLICATION

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (c) | 3. (a) | 4. (b) | 5. (c) | 6. (d) | 7. (c) | 8. (a) | 9. (b) | 10. (c) |
| 11. (d) | 12. (c) | 13. (d) | 14. (c) | 15. (d) | 16. (d) | 17. (b) | 18. (c) | 19. (b) | 20. (a) |
| 21. (c) | 22. (d) | 23. (a) | 24. (c) | 25. (c) | 26. (d) | 27. (d) | 28. (a) | 29. (d) | 30. (d) |
| 31. (c) | 32. (a) | 33. (a) | 34. (c) | 35. (a) | 36. (d) | 37. (c) | | | |

EXERCISE-1 (TOPICWISE)

- | | | | | | | | | | |
|---------|---------|---------|-------------|---------|---------|-----------|---------|---------|---------|
| 1. (b) | 2. (d) | 3. (b) | 4. (b) | 5. (d) | 6. (d) | 7. (b) | 8. (d) | 9. (d) | 10. (b) |
| 11. (d) | 12. (b) | 13. [4] | 14. (a,b,c) | 15. [3] | 16. (d) | 17. (c) | 18. (b) | 19. (d) | 20. (c) |
| 21. (b) | 22. (b) | 23. (b) | 24. (d) | 25. (d) | 26. (a) | 27. (c) | 28. (d) | 29. (a) | 30. (a) |
| 31. (b) | 32. (d) | 33. (d) | 34. (d) | 35. [2] | 36. (d) | 37. (c) | 38. (c) | 39. (a) | 40. (b) |
| 41. (b) | 42. (b) | 43. (d) | 44. (d) | 45. (a) | 46. (4) | 47. (b) | 48. (d) | 49. (c) | 50. (a) |
| 51. (a) | 52. (a) | 53. (c) | 54. (c) | 55. (d) | 56. (c) | 57. (d) | 58. (d) | 59. (d) | 60. (c) |
| 61. (c) | 62. (a) | 63. (a) | 64. (c) | 65. (c) | 66. (a) | 67. (a,d) | 68. (b) | 69. (a) | 70. (b) |
| 71. (c) | 72. (b) | 73. (c) | 74. (d) | 75. (d) | 76. (c) | 77. (a) | 78. (c) | 79. (a) | 80. (d) |
| 81. (c) | 82. (c) | 83. (a) | 84. (c) | 85. (c) | 86. (b) | 87. (a) | 88. (d) | 89. (d) | 90. (d) |
| 91. (c) | 92. (b) | 93. (d) | | | | | | | |

EXERCISE-2 (LEARNING PLUS)

- | | | | | | | | | | |
|---------|---------|---------|----------|---------|---------|-----------|---------|-------------|---------|
| 1. (b) | 2. (c) | 3. (c) | 4. (d) | 5. (c) | 6. (c) | 7. (c) | 8. (c) | 9. (b) | 10. (a) |
| 11. (a) | 12. (b) | 13. (d) | 14. (c) | 15. (d) | 16. (d) | 17. (d) | 18. (b) | 19. (a,c,d) | 20. (a) |
| 21. (c) | 22. (b) | 23. (a) | 24. (d) | 25. (d) | 26. (8) | 27. (d) | 28. (d) | 29. (b) | 30. (a) |
| 31. (c) | 32. (c) | 33. (a) | 34. [3] | 35. (c) | 36. (b) | 37. (d) | 38. (d) | 39. (b) | 40. (a) |
| 41. (a) | 42. (b) | 43. (a) | 44. (d) | 45. (d) | 46. (b) | 47. (a,b) | 48. (c) | 49. (c) | 50. (a) |
| 51. (b) | 52. (d) | 53. (b) | 54. [16] | 55. (c) | | | | | |

EXERCISE-3 (JEE ADVANCED LEVEL)

- | | | | | | | | | | |
|---------------|-------------|-------------|----------|---------|----------|-----------|------------|----------|-------------|
| 1. (a,c) | 2. (a,c) | 3. (a,b) | 4. (b,c) | 5. (c) | 6. (a,b) | 7. (b,d) | 8. (a,b,d) | 9. (a,b) | 10. (a,c,d) |
| 11. (a,b,c,d) | 12. (b,c,d) | 13. (b,c,d) | 14. [3] | 15. [2] | 16. (a) | 17. (b,c) | 18. [6] | 19. [32] | 20. (a,c,d) |
| 21. (b,c,d) | 22. (b,d) | 23. (d) | 24. (b) | 25. (a) | 26. (c) | 27. (d) | 28. (b) | 29. (a) | 30. (d) |
| 31. (c) | 32. (a) | 33. [8] | 34. [0] | 35. [2] | | | | | |

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|----------|---------|----------|---------|
| 1. (c) | 2. (b) | 3. (a) | 4. [2] | 5. [3] | 6. [5] | 7. (c,d) | 8. (d) | 9. (d) | 10. (c) |
| 11. (d) | 12. (d) | 13. (c) | 14. (b) | 15. (b) | 16. (c) | 17. [3] | 18. [7] | 19. [60] | |

JEE Advanced

- | | | | | | | | | | |
|---------|---------|-------------|-------------|---------|---------|----------|---------|---------|---------|
| 20. (b) | 21. (a) | 22. (a,b,c) | 23. (a,c,d) | 24. [3] | 25. [7] | 26. [10] | 27. (c) | 28. (b) | 29. [2] |
|---------|---------|-------------|-------------|---------|---------|----------|---------|---------|---------|

CHAPTER

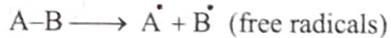
14

General Organic Chemistry

BOND FISSION

Breaking of covalent bond of the compound is known as bond fission. A bond can be broken by two ways

- Homolytic Fission:** Occurs in gas phase or in non-polar solvents and is catalysed by reagents. In such fission, free radicals are formed. Here the bond pair is equally shared after the fission.

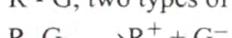


Condition for Homolytic Bond Fission

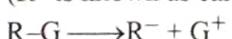
Homolysis takes place in the presence of peroxide, UV light, heat ($\geq 500^{\circ}\text{C}$), presence of electricity and free radical. The process is known as initiation of free radical reaction.



- (i) Homolytic bond fission gives free radical as the reaction intermediate.
- (ii) Reaction mechanism of the reaction is known as **free radical or homolytic mechanism**.
- 2. Heterolytic Fission:** Occurs in polar solvents, catalysed by acids or bases, greatly influenced by polarity of solvents. Here, the ions are formed. In an organic compound such as R - G, two types of ions are formed.



(R^+ is known as carbocation ion)



(R^- is known as carbanion ion)

The factor which favours heterolysis is a greater difference of electronegativity between A and B.

Thus,

- (i) Heterolytic bond fission gives carbocation or carbanion as reaction intermediate.
- (ii) Mechanism of the reaction in which heterolytic bond fission takes place is known as heterolytic mechanism or ionic mechanism.
- (iii) The energy required for heterolytic bond fission is always greater than that for homolytic bond fission due to electrostatic force of attraction between ions.

REACTION INTERMEDIATES

In the study of organic chemistry, following intermediates are important:

- (i) Carbocation
- (ii) Carbanion
- (iii) Carbon free radical
- (iv) Carbene
- (v) Nitrene

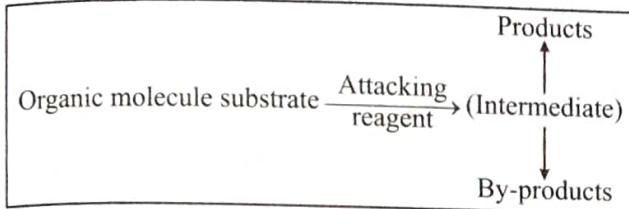
Property	Carbocation	Carbanion	Carbon Free Radical
Representation	$\begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}^{\oplus}$	$\begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}^{\ominus}$	$\begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}$
Bond fission	Heterolysis	Heterolysis	Homolysis
Electrical nature	Positive	Negative	Neutral
No. of electrons in valence shell	6	8	7
Hybridisation	sp^2	sp^3	sp^2
Shape	Planar	Pyramidal	Planar

Carbene and Nitrene are of following Two Types

Property	Singlet Carbene	Triplet Carbene	Singlet Nitrene	Triplet Nitrene
Representation	$\begin{array}{c} \boxed{1} \\ \\ -\text{C}- \end{array}$	$\begin{array}{c} \boxed{1} \\ \\ -\text{C}- \\ \\ \boxed{1} \end{array}$	$\begin{array}{c} \boxed{1} \\ \\ -\text{N} \leftarrow : \end{array}$	$\begin{array}{c} \boxed{1} \\ \\ -\text{N} \leftarrow : \\ \\ \boxed{1} \end{array}$
Electrically nature	Neutral	Neutral	Neutral	Neutral
No. of electrons in valence shell	6	6	6	6
Hybridisation	sp^2	sp	sp^2	sp
Shape	V-shape	Linear	Linear	Linear
Stability	Less	More	Less	More

FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

In an organic reaction, the reactant organic molecule known as substrate which reacts with an attacking reagent and leads to the formation of one or more intermediates and finally forms the products. The general reaction may be represented as follows:



The substrate is that reactant which provides carbon to form the new bond and the other reactant is called reagent. However, if both the reactants supply carbon to the new bond then choice of substrate is arbitrary and in that case, the molecule which we are interested to study is the substrate.

During organic reactions, a covalent bond between two carbon atoms or a carbon atom and some other atom is broken and a new bond is formed. The detailed study of stepwise description of a reaction, electron movement, energetics during bond breaking and bond formation and the details of time required for the steps, when a reactant is transformed into the product is called Reaction Mechanism. The knowledge of reaction mechanism is very important because it helps to understand the reactivity of organic compounds.

Reaction Reagents

Organic reagents can be classified in two categories:

(A) **Electrophile:** Electron deficient species or electron acceptor is electrophile.

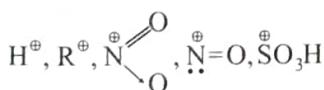
(B) **Nucleophile:** Electron rich species or electron donor is nucleophile.

(A) **Electrophiles:** It can be classified into two categories:

(I) Charged electrophiles

(II) Neutral electrophiles

(I) **Charged electrophiles:** Positively charged species in which central atom has incomplete octet is charged electrophile.



Note: All cations are charged electrophiles except cations of a group elements, Al^{3+} and NH_4^+ .

(II) **Neutral electrophiles:** They can be classified into three categories:

(i) Neutral covalent compounds in which central atom has incomplete octet are neutral electrophiles.

E.g.: BeCl_2 , BH_3 , ZnCl_2 , AlX_3 , FeX_3 , $\ddot{\text{C}}\text{H}_2$, $\ddot{\text{C}}\text{X}_2$

(ii) Neutral covalent compounds in which central atom has complete or expanded octet and central atom has unfilled d-subshell are neutral electrophiles.

E.g.: SnCl_4 , SiCl_4 , PCl_5 , SF_6 , IF_7

(iii) Neutral covalent compounds in which central atom is bonded only with two or more than two electronegative atoms are neutral electrophiles.
E.g.: BeCl_2 , BX_3 , AlX_3 , FeX_3 , SnCl_4 , PCl_3 , PCl_5 , NF_3 , $\ddot{\text{C}}\text{X}_2$, CO_2 , SO_3 , CS_2 , CX_4

Note:

- Cl_2 , Br_2 and I_2 also behave as neutral electrophiles.
- Electrophiles are Lewis acids.

(B) **Nucleophiles:** Nucleophiles can be classified into three categories:

(I) **Charged nucleophiles:** Negatively charged species are charged nucleophiles.



(II) **Neutral nucleophiles:** They can be classified into two categories:

(i) Neutral covalent compounds, in which central atom has complete octet, has at least one lone pair of electrons and none of the atoms present on central atom are electronegative, are called neutral nucleophiles.

E.g.: $\ddot{\text{N}}\text{H}_3$, $\text{R}\ddot{\text{N}}\text{H}_2$, $\text{R}_2\ddot{\text{N}}$, $\text{R}_3\ddot{\text{N}}$, $\ddot{\text{N}}\text{H}_2-\text{NH}_2$ (Nitrogen nucleophile)

$\text{H}-\ddot{\text{O}}-\text{H}$, $\text{R}-\ddot{\text{O}}-\text{H}$, $\text{R}-\ddot{\text{O}}-\text{R}$ (Oxygen nucleophiles)

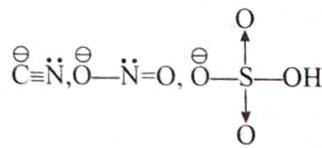
$\text{H}-\ddot{\text{S}}-\text{H}$, $\text{R}-\ddot{\text{S}}-\text{H}$, $\text{R}-\ddot{\text{S}}-\text{R}$ (Sulphur nucleophiles)

$\ddot{\text{P}}\text{H}_3$, $\text{R}-\ddot{\text{P}}\text{H}_2$, $\text{R}_2-\ddot{\text{P}}\text{H}$, $\text{R}_3-\ddot{\text{P}}$ (Phosphorus nucleophiles)

(ii) Organic compounds containing carbon–carbon multiple bonds behave as nucleophiles.

E.g.: Alkenes, Alkynes, Benzene,
 $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$

(III) **Ambident nucleophiles:** Species having two nucleophilic centres, one is neutral (complete octet and has at least one lone pair of electrons) and other is charged (negative charge) behave as ambident nucleophiles.



Note:

- Organometallic compounds are nucleophiles.
- Nucleophiles are Lewis bases.

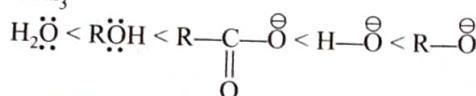
Organic compounds which behave as electrophile as well as nucleophile: Organic compound in which carbon is bonded with electronegative atom (O, N, S) by multiple bond behaves as electrophile as well as nucleophile.

E.g.: $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{H}$, $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{R}$, $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$, $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{Cl}$, $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{OR}$,
 $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}_2$, $\text{R}-\text{CN}$, $\text{R}-\overset{\oplus}{\text{N}}\equiv\overset{\ominus}{\text{C}}$

Note: During the course of chemical reaction electrophile reacts with nucleophile.

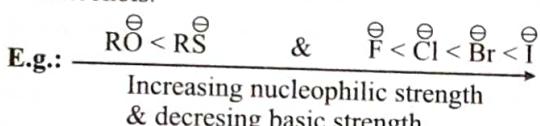
NUCLEOPHILICITY AND BASICITY

If the nucleophilic atoms are from the same period of the periodic table, strength as a nucleophile parallels strength as a base.
E.g.: $\text{H}_2\text{O} < \text{NH}_3$

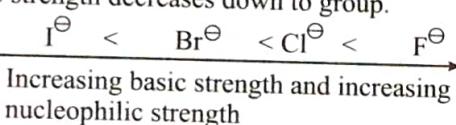


→
Increasing basic strength increasing
nucleophilic strength

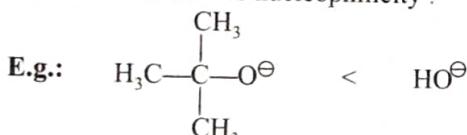
Nucleophilic strength increases down a column of the periodic table in protic solvents that can have hydrogen bond, such as water and alcohols.



In aprotic solvents such as DMF, DMA, DMSO, HMPA, nucleophilic strength decreases down to group.

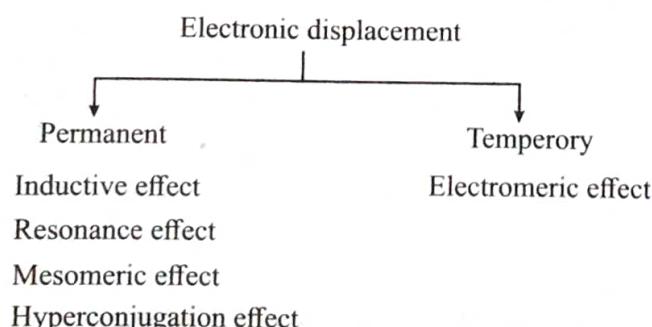


Steric bulk decreases nucleophilicity.



Weaker nucleophile Stronger nucleophile
Stronger base Weaker base

ELECTRONIC DISPLACEMENT IN ORGANIC COMPOUNDS



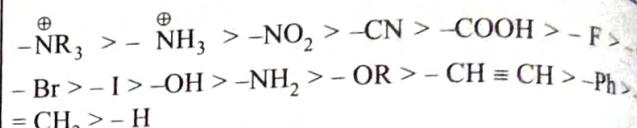
INDUCTIVE EFFECT

- It involves partial displacement of σ electrons towards more electronegative atom or group. It is permanent effect.

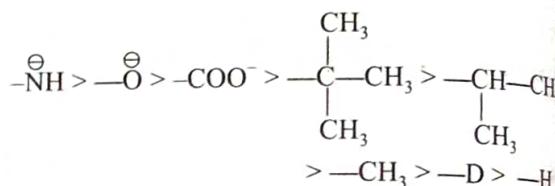
$$\text{I-effect} \propto \frac{1}{\text{distance}}$$

- I-effect is of two types: + I effect and - I effect

- I effect: The element or group which attracts σ electrons as compared to hydrogen shows this effect. Order of - I effect of some standard species is:



- +I effect: The element or groups which repels σ electrons as compare to the hydrogen shows this effect. Order of effect of some standard species is:



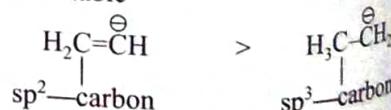
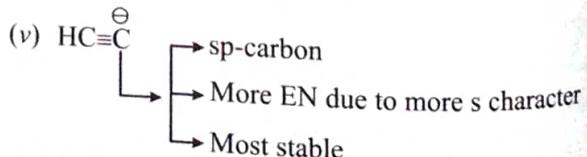
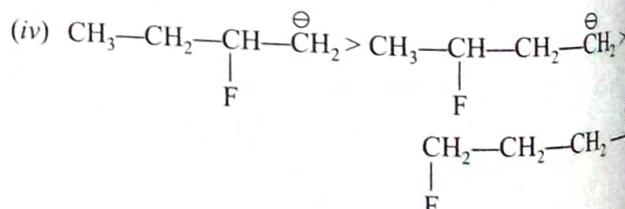
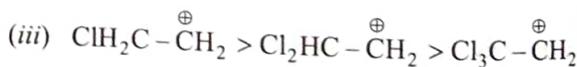
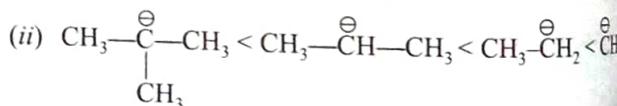
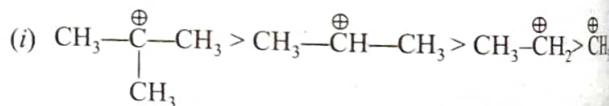
APPLICATIONS OF INDUCTIVE EFFECT

1. Stability of intermediates:

$$\text{Stability of carbocation} \propto +\text{I} \propto \frac{1}{-\text{I}}$$

$$\text{Stability of carbanion} \propto -\text{I} \propto \frac{1}{+\text{I}}$$

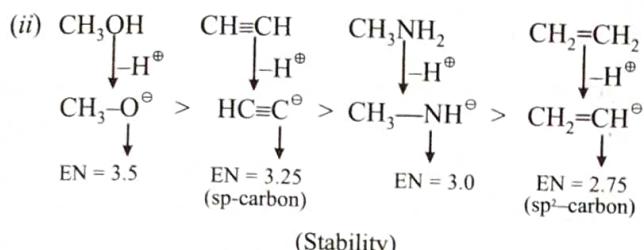
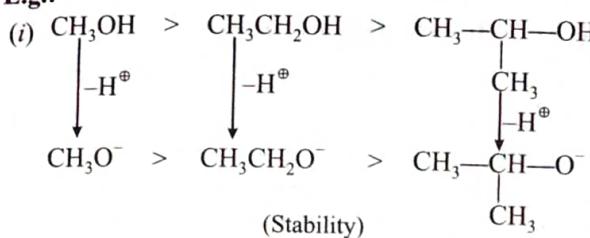
E.g.:



- Acidic strength: The proton donating tendency of compound is called its acidic strength.

Generally, $\text{Acidic strength} \propto \text{Stability of anion}$
(Conjugate Base)

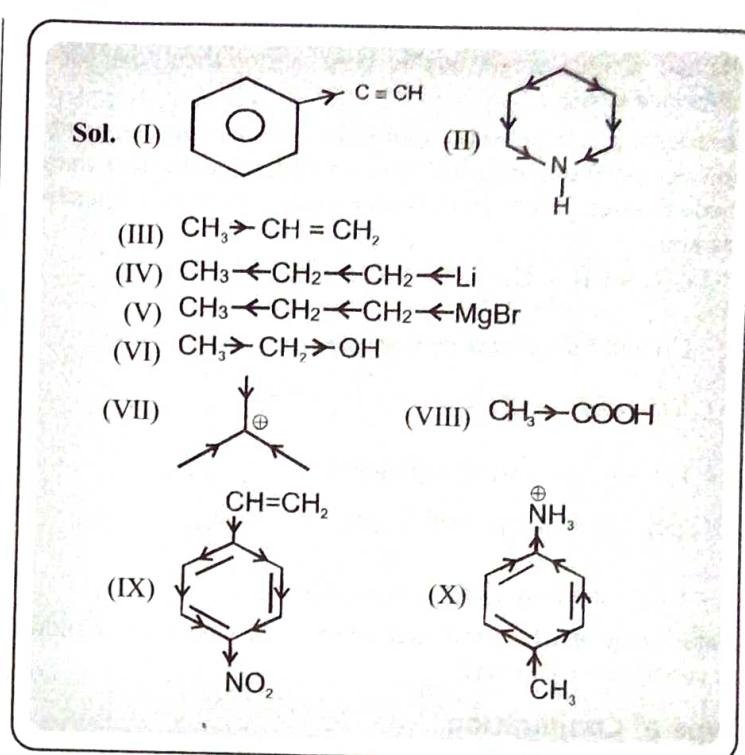
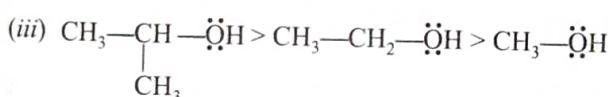
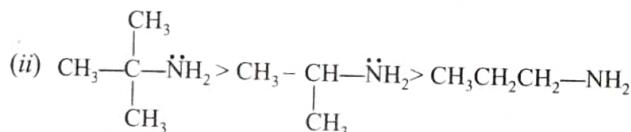
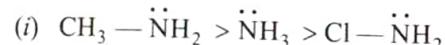
E.g.:



3. Basic Strength: The lone-pair donating tendency of the atom in any compound is called as basic strength.

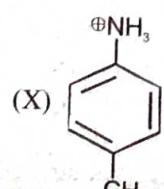
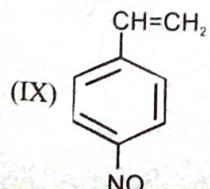
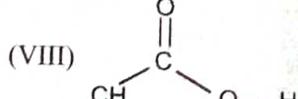
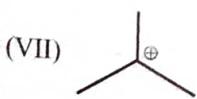
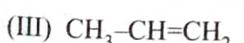
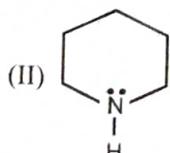
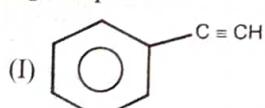
Generally, $\boxed{\text{Basic strength} \propto +I \propto \frac{1}{-I}}$

E.g.:



Train Your Brain

Example 1: Show the direction of inductive effect in following compounds:



Concept Application

- Which of the following group shows +I-effect?
 (a) $-\text{Br}$ (b) $-\text{COOH}$
 (c) $-\text{OR}$ (d) $-\text{COO}^-$
- Which of the following alkyl group has the maximum +I effect?
 (a) $(\text{CH}_3)_2\text{CH}-$ (b) $(\text{CH}_3)_3\text{C}-$
 (c) CH_3CH_2- (d) CH_3-
- Decreasing -I effect of given groups is:
 (i) $-\text{CN}$ (ii) $-\text{NO}_2$
 (iii) $-\text{NH}_2$ (iv) $-\text{F}$
 (a) iii > ii > i > iv (b) ii > iii > iv > i
 (c) iii > ii > iv > i (d) ii > i > iv > iii
- Which of the following is the strongest -I group?
 (a) $-\overset{+}{\text{N}}(\text{CH}_3)_3$ (b) $-\overset{+}{\text{NH}}_3$
 (c) $-\overset{+}{\text{S}}(\text{CH}_3)_2$ (d) $-\text{F}$

RESONANCE EFFECT

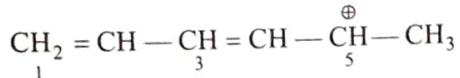
When a molecule or ion can be represented by two or more structures which have the same arrangement of atomic nuclei but differ in distribution of electrons, the phenomenon is called as Resonance. The various structures are called contributing or resonating structures. None of these structures truly represents all the properties of that molecule or ion. The actual structure is a resonance hybrid of several contributing structures. Resonance

generally occurs when there is a conjugation of π -electrons (alternate double-single-double bond arrangement) known as conjugated system.

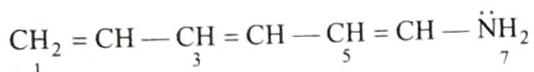
Conjugate positions of the molecule: Alternate positions of the molecule having π bond with positive charge or negative charge or odd electron or lone pair of electrons are known as conjugative positions.



1, 3 and 5 are conjugate positions.



1, 3 and 5 are conjugate positions.



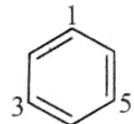
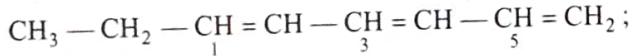
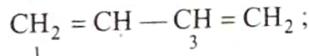
1, 3, 5 and 7 are Conjugate positions

Note: Compound having at least two conjugate positions is known as conjugated compound.

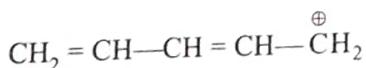
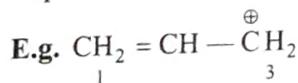
Type of Conjugation

1. **π, π conjugation:** If all conjugate positions have π bonds, then conjugation is known as π, π conjugation.

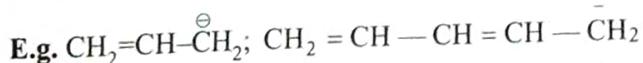
E.g.



2. **Positive charge, π conjugation:** In this case, all conjugate positions have π bonds and only one conjugate position has positive charge. If this is the case, then conjugation is known as positive charge, π conjugation.



3. **Negative charge, π conjugation:** If all conjugate positions have π bonds and only one conjugate position has negative charge, then conjugation is known as negative charge, π conjugation.



4. **Odd electron, π conjugation:** If all conjugate positions have π bonds and one conjugate position has odd electron, then conjugation is known as odd electron, π conjugation.



5. **Lone pair, π conjugation:** If all conjugate positions have π bonds and only one conjugate position has lp then conjugation is known as lp, π conjugation.

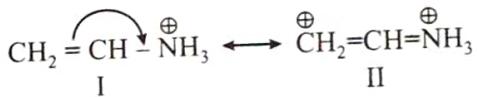


Resonance Stabilisation Energy or Resonance Energy or Delocalization Energy

The resonance hybrid is always more stable than any one of its canonical form. The stability of resonance hybrid is attributed to resonance energy which is equal to difference in energy of resonance hybrid and its most stable canonical form. The stability of resonance hybrid increases with increasing number of equivalent contributing resources. For benzene, the resonance energy is 150.62 kJ or 36 kCal.

Important Characteristic Features of Resonance

- (i) The resonance structure should differ only in position of electrons and not in the relative position of atom.
- (ii) The number of unpaired electrons should be same in all canonical forms. The various forms in which octet rule is violated for elements of second period are not considered as resonating structure. For example

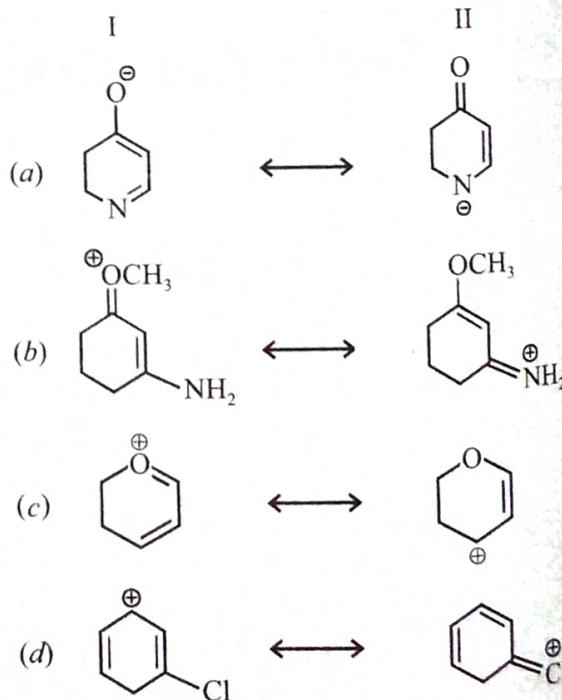


Since in structure-II, N violates octet rule, therefore structure will not be formed.



Train Your Brain

Example 2: Write the stability order of following resonating structures:



Sol. (a) I > II

(b) II > I

(c) I > II

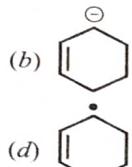
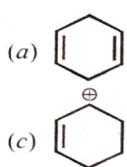
(d) II > IV



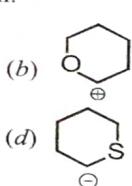
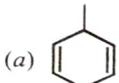
Concept Application

5. Resonance structure of the molecule does not have
(a) Higher energy than their hybrid structure.
(b) Identical arrangement of atoms.
(c) The same number of paired electrons.
(d) Always equal contribution to the resonance hybrid.

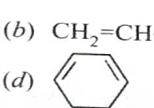
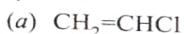
6. Which of the following species can not show resonance?



7. Resonance is not possible in:



8. Which of the following does not have conjugated system?



MESOMERIC EFFECT

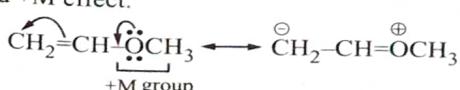
Groups or atoms which release or withdraw π -electron density from the conjugated system are called mesomeric group and this effect is called mesomeric effect.



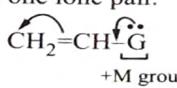
Note: (i) It is distance independent effect.
(ii) It is permanent and strong effect.
(iii) It operates in π -bonds.

It is of two types:

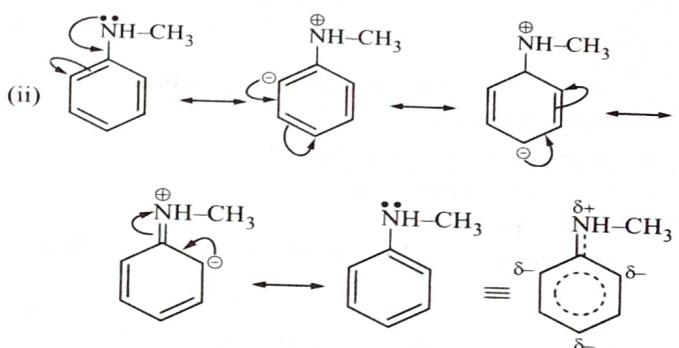
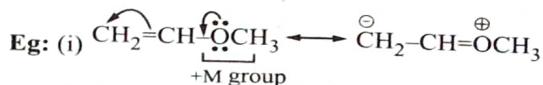
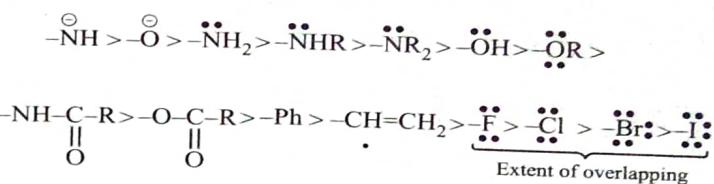
(i) **+M effect:** Groups or atoms which release π -electrons to the conjugated system are known as +M group and the effect is called +M effect.



- ❖ **Conditions:** To show $+M$ effect, the first atom of the group should have at least one lone pair.

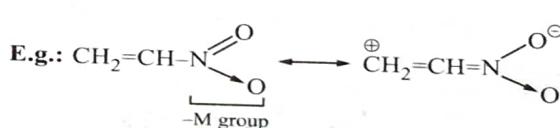


❖ Order of +M effect:



- +M group increases electron density in benzene ring, so they activate the benzene ring towards electrophilic substitution reaction and are known as activating groups.
 - +M groups increase rate of ESR.

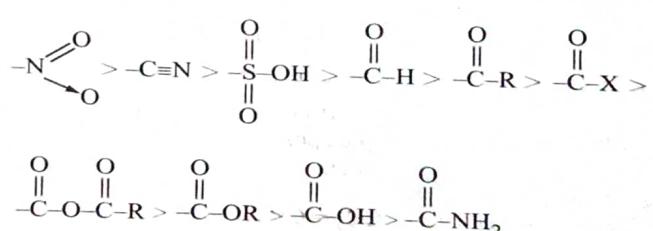
- $+M$ groups are ortho, para directing.
- (ii) **$-M$ effect:** Groups or atoms which withdraw π -electrons from the conjugated system are known as $-M$ groups and this effect is called $-M$ effect.

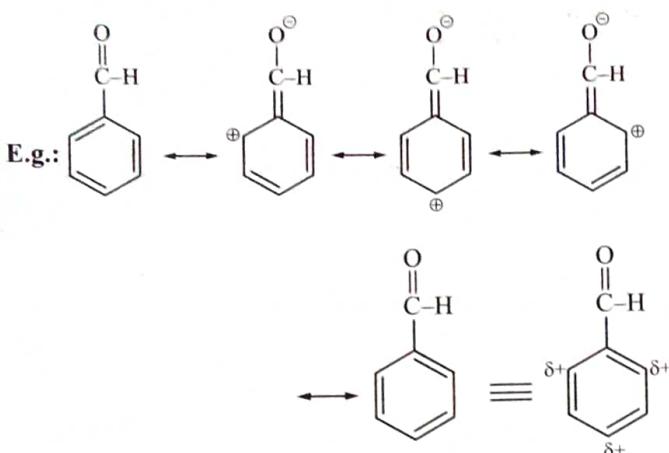


❖ **Condition:** $\text{CH}_2=\text{CH}-\underset{\substack{| \\ -\text{M group}}}{\text{X}}=\text{Y}$ as $\text{CH}_2=\text{CH}-\overset{\substack{| \\ \text{O} \\ \text{O}}}{\text{C}}$ Vacant orbital

π -bonds on heteratoms or vacant orbitals above M_{∞}

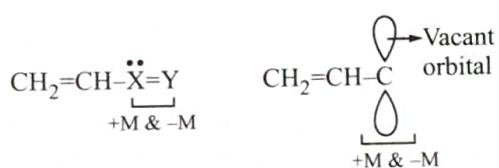
❖ Order of -M effect:





- ❖ –M group decreases electron density in benzene ring, so rate of ESR decreases.
 - ❖ –M groups are deactivating groups
 - ❖ –M groups are meta directing.
 - ❖ **Some important points:**

❖ Some important points:



E.g.: $\text{--}\ddot{\text{C}}\text{l}\text{:}$, $\text{--}\ddot{\text{S}}\text{H}$, $\text{--}\ddot{\text{N}}=\text{O}$, --NC etc.

- Generally, mesomeric effect dominates over inductive effect but in case of halogen, NO and NC, inductive effect dominates over mesomeric effect.
 - Priority:** Mesomeric > Resonance > Inductive
 - Mesomeric effect does not operate at meta position.

Train Your Brain

Example 3: Arrange the following groups in the increasing order of $+M$.

(i) $-I$, $-Cl$, $-F$, $-Br$ (ii) $-NH_2$, $-OH$, $-O^\ominus$

Sol. (i) +M:- I < - Br < - Cl < - F

(ii) +M: -OH < -NH₂ < -O[⊖]

Example 4: Arrange the following groups in the increasing order of $-M$

(i) --NO_2 , --COOR , --CHO , --CN , --COR

(ii) NO_2 , CO_2 , O
 C=O , C=O , C=O^-

Sel (i) $-M \cdot -COOR < -COR < CHO < CN < NO_2$

$$(ii) -M: \text{---C=O} < \text{---C=NH}_2 < \text{---C=F}$$



Concept Application

9. Which of the following group shows +M effect?

 - --CN
 - --O--NO
 - --CCl_3
 - --CHO

10. Which of the following group show -M effect?

 - --CMe_3
 - --O--S(=O)--O--R
 - $\text{--NH--C}(=\text{O})\text{--CH}_3$
 - --S(=O)--O--R

11. Which of the following group shows both +M and -I effect?

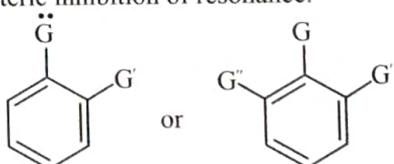
 - $\text{--C}(=\text{O})\text{--F}$
 - $\text{--C}(=\text{O})\text{--OR}$
 - --O^\ominus
 - --OH

12. Which of the following group shows +M > -I effect?

 - --F
 - $\text{--O--C}(=\text{O})\text{--R}$
 - $\text{--C}(=\text{O})\text{--R}$
 - --COOH

Steric Inhibition of Resonance

- ❖ In case of 1,2 - disubstituted benzene, if the substituents are bulky then due to steric repulsion (vanderwall repulsion) the groups go out of plane with respect to benzene ring.
 - ❖ Due to this change in planarity, the conjugation between the substituent on benzene ring is slightly diminished, this effect is called steric inhibition of resonance.

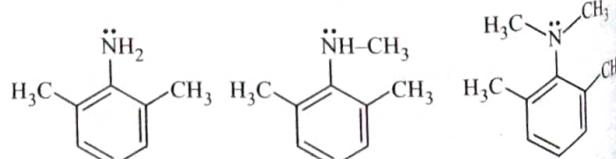


If $G \equiv OH_-, -NH_2, -CN$, SIR does not operate.

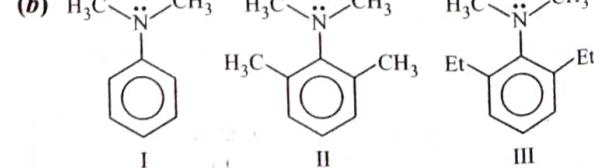
SIR effect \propto size of group

E.g.: Give order of SIR in the following:

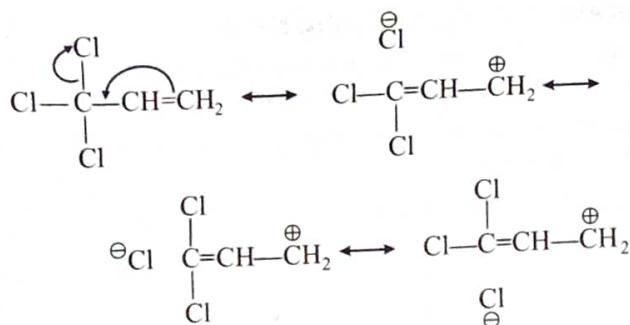
(a)



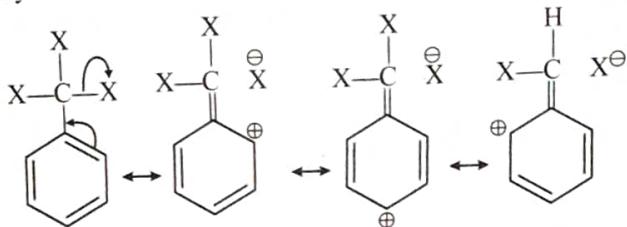
$$I < II < III$$



SIR: I < II < III

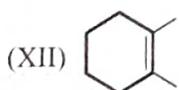
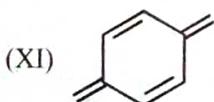
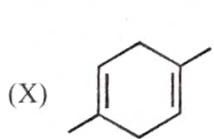
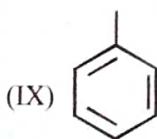
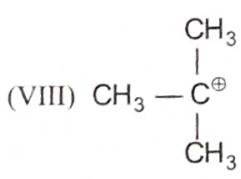
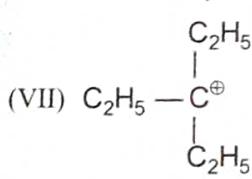
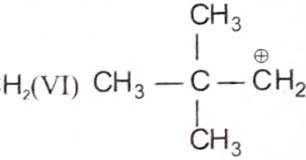
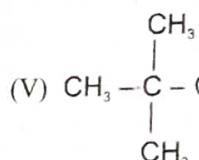
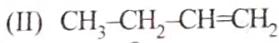
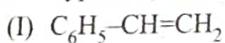


The meta directing and deactivating effect of —CX_3 group for electrophilic aromatic substitution reaction can be explained by this effect.



Train Your Brain

Example 5: In the following molecules or ions, write the number of hyperconjugable hydrogen atoms.



Sol. (I) 0

(II) 2

(III) 0

(IV) No hyperconjugation

(V) 0

(VI) 0

(VII) 6

(VIII) 9

(IX) 3

(X) 10

(XI) 0

(XII) 10

Concept Application

13. In hyperconjugation, there is overlap between:

- (a) p- and π -orbitals
- (b) 2π -orbitals
- (c) d- and π -orbitals
- (d) σ - and p-orbitals

14. Which of the following cannot exhibit hyperconjugation?

- (a) $\text{CH}_3\overset{\bullet}{\text{CH}}_2$
- (b) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\overset{+}{\text{C}} \end{array}$
- (c) $\text{CH}_3\text{CH}=\text{CH}_2$
- (d) $(\text{CH}_3)_3\text{C}-\overset{+}{\text{CH}}_2$

15. Which of the following alkenes will show maximum number of hyperconjugation forms?

- (a) $\text{CH}_2=\text{CH}_2$
- (b) $\text{CH}_3-\text{CH}=\text{CH}_2$
- (c) $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$
- (d) $\text{CH}_3-\overset{\text{CH}_3}{\text{CH}}-\text{CH}=\text{CH}_2$

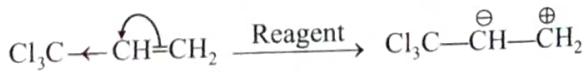
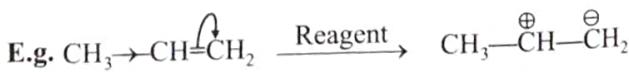
16. Which one of the following has inductive, mesomeric and hyperconjugation effect?

- (a) CH_3Cl
- (b) $\text{CH}_3-\text{CH}=\text{CH}_2$
- (c) $\text{CH}_3\text{CH}=\text{CH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$
- (d) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$

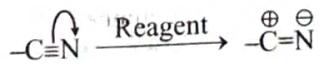
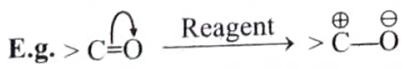
ELECTROMERIC EFFECT

- ❖ Electromeric effect is a temporary effect in which a shared pair of electrons (π -electron pair) is completely transferred from a double or a triple bond to one of the atoms joined by the bond at the requirement of attacking reagent.
- ❖ If the attacking reagent is removed, charge disappears and substrate attains its original form. Thus, this effect is reversible and temporary.
- ❖ The electromeric effect can be decided by other permanent effects in various conditions as follows:

Case-I: Electromeric effect may be decided by I-effect as –



Case-II: If the multiple bond is present between two different atoms, the electromeric shift will take place in the direction of the more electronegative atom.



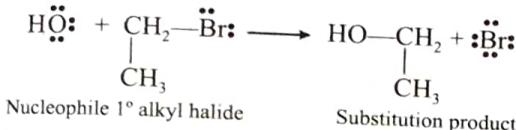
TYPES OF ORGANIC REACTIONS

Organic reactions can be classified into the following categories:

- (i) Substitution reactions
 - (ii) Addition reactions
 - (iii) Elimination reactions
 - (iv) Rearrangement reactions

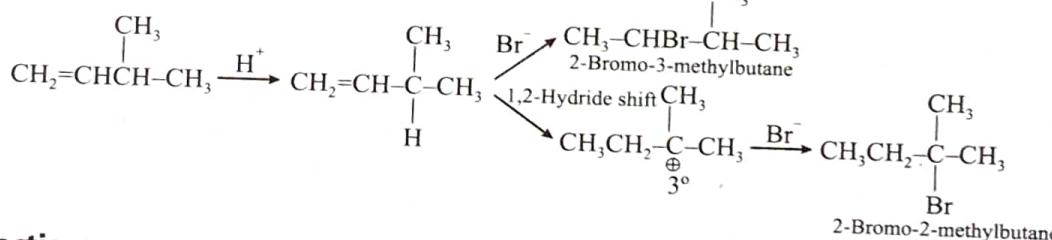
Substitution Reactions

- ❖ A reaction in which one group or atom is replaced by another is called a substitution reaction.
 - ❖ The incoming group is bonded to the same carbon to which the leaving group was bonded.
 - ❖ The substituting species may be either a nucleophile, an electrophile or a free radical.



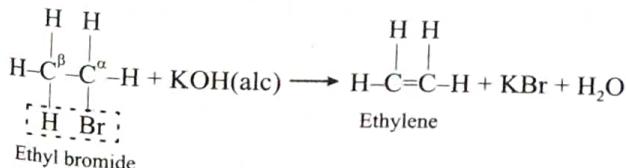
Addition Reactions

- ❖ A reaction in which the reagent is added to the substrate to form a product is called addition reaction.
 - ❖ It is characteristic to compounds containing multiple bond ($>C=C<$, $-C\equiv C-$, $>C=O$, $-C\equiv N$ etc.).



Elimination Reactions

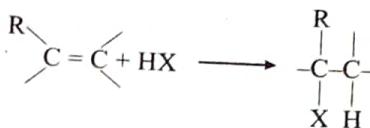
- ❖ When two atoms or groups from adjacent carbons are eliminated with the formation of unsaturated compounds (alkene or alkyne), the reaction is called elimination reaction.
 - ❖ Most commonly a leaving group (from the α - carbon) and a proton from the β - carbon are eliminated. Hence, the reaction is known as 1,2- or α,β - elimination or simply β - elimination.
 - ❖ As for example, dehydrohalogenation of alkyl halides with alcoholic solution of KOH.



Rearrangement Reactions

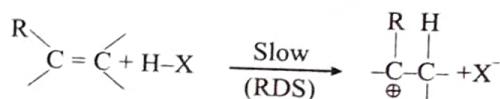
- ❖ It involves the migration of an atom or a group from one atom to another within the molecule.
 - ❖ The type of migration depends on the number of electrons the migrating atom or group carries with it.

- The reactivity of these compounds is due to the loosely held π electrons which are particularly available to a reagent that is seeking electrons like an electrophile or a free radical.
 - As for example, hydrogen halides (HCl , HBr and HI) add to the double bond of alkenes.

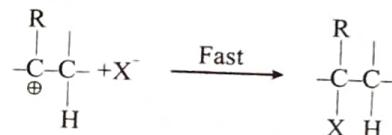


- Mechanisms for addition of hydrogen halide to an alkene involves the following two steps:

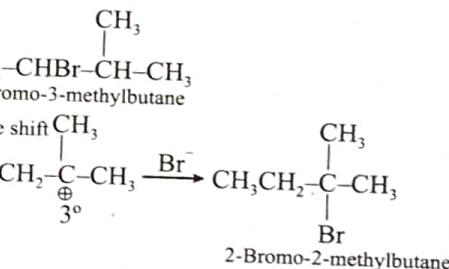
Step 1:



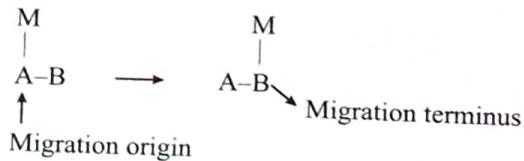
Step 2:



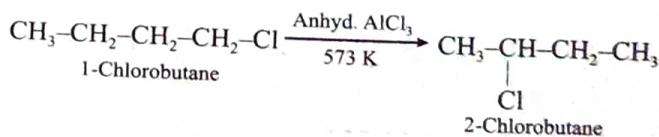
- The addition of HBr to some alkenes give a mixture of the expected alkyl bromide and an isomer formed by rearrangement.



- The most common type are 1, 2– rearrangements in which the migrating group moves to the adjacent atom with its bonding pair of electron (nucleophilic rearrangement or anionotropic rearrangement).



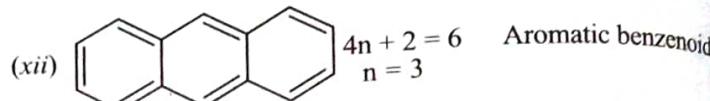
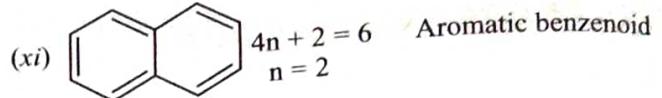
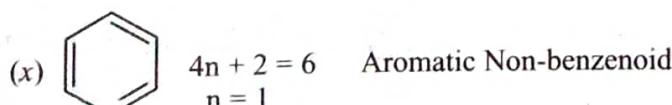
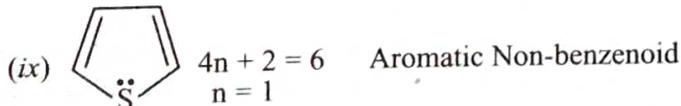
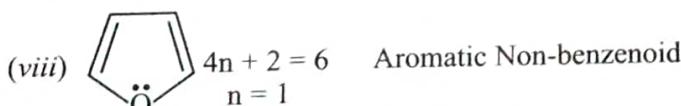
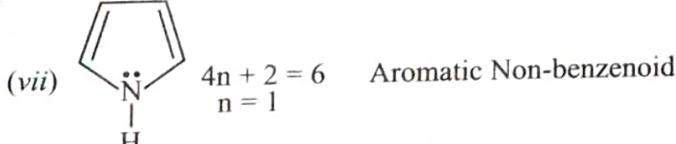
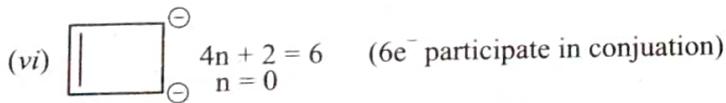
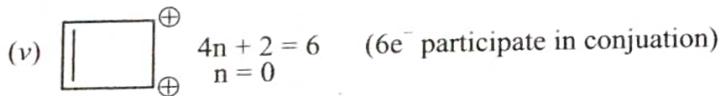
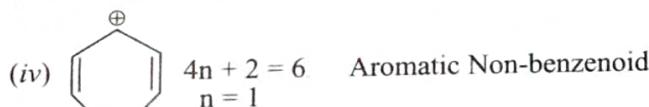
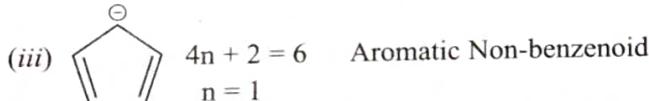
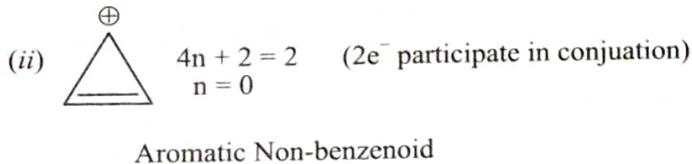
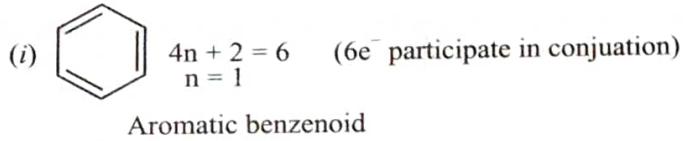
- The group may move without the bonding pair (cationotropic rearrangement) or with a single electron (free radical rearrangement) and may not be 1, 2 but longer rearrangements.
 - As for example, 1-chlorobutane rearranges to form 2-chlorobutane when heated in the presence of anhydrous AlCl_3 at 573K.



AROMATICITY

Aromatic Compounds:

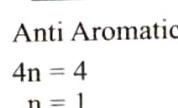
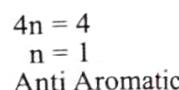
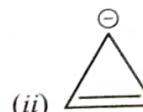
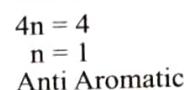
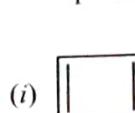
- Molecule should be cyclic and planar (i.e. all atoms of the molecule should be sp or sp^2 hybridised).
- Complete cyclic conjugation should be present in molecule.
- The number of π -electrons which take part in conjugation should be equal to $4n + 2$, where $n = 0, 1, 2, 3, \dots$



Aromatic compounds burn with sooty flame due to high percentage of carbon.

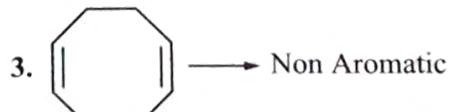
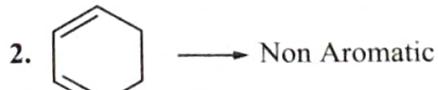
Anti-aromatic compounds:

- Molecule should be cyclic and planar.
- Complete cyclic conjugation should be present in a molecule.
- No. of π -electron which take part in conjugation should be equal to $4n$, where $n = 1, 2, 3, \dots$

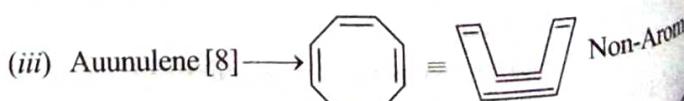
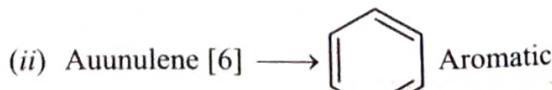


Note: Anti Aromatic compounds do not exist at room temp i.e. they are not stable at room temp.

Non-Aromatic compounds:



Annulenes: Monocyclic conjugated polyenes are called annulenes.

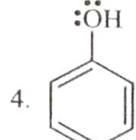
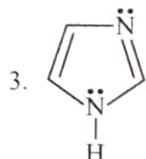
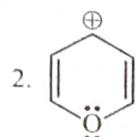
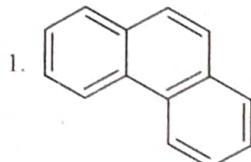


Derivatives of Annulene [8] are aromatic.

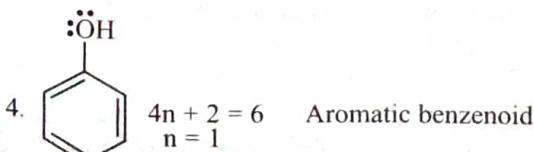
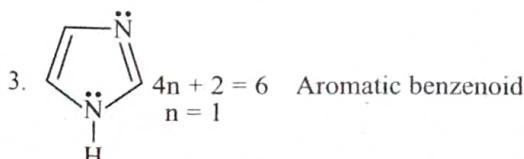
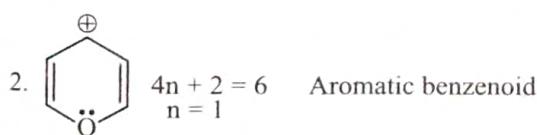
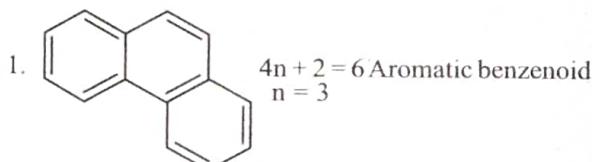


Train Your Brain

Example 6: Identify the nature of following compounds

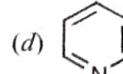
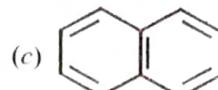
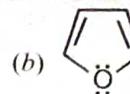
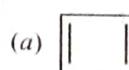


Sol.

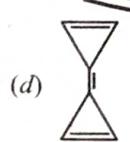
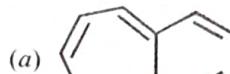


Concept Application

17. Which out of the following is aromatic hydrocarbon?



18. Identify the aromatic compound amongst the following:



19. Aromatic compounds burn with sooty flame because:

- (a) They have a ring structure of carbon atoms.
- (b) They have relatively high percentage of hydrogen.
- (c) They resist reaction with oxygen or air.
- (d) They have relatively high percentage of carbon.

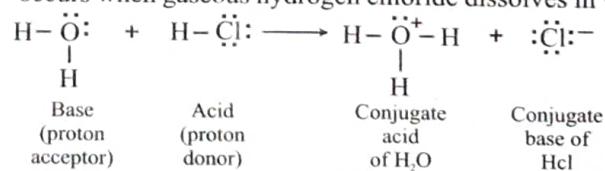
ACIDIC AND BASIC STRENGTH

Basic Strength

(a) **Arrhenius base:** Base is a substance that can donate (or lose) OH^- ions in H_2O .

(b) **The Bronsted Lowry definition of bases:** A base is a substance that can accept a proton.

Let us consider an example of this concept, the reaction that occurs when gaseous hydrogen chloride dissolves in water:



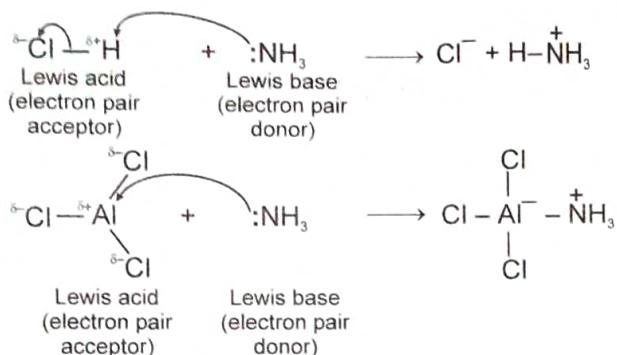
Hydrogen chloride a very strong acid, transfers its proton to water. Water acts as a base and accepts the proton. The products that result from this reaction are hydronium ion (H_3O^+) and chloride ion (Cl^-).

The molecule or ion that forms when an acid loses its proton is called the conjugate base of that acid.

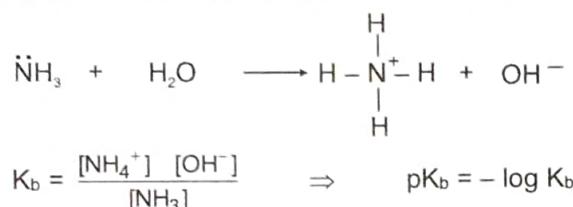
The chloride ion is the conjugate base of HCl. The molecule or ion that is formed when a base accepts a proton is called the conjugate acid of that base.

(c) **The Lewis definition of acids and bases:** Lewis proposed that acids are electron pair acceptors and bases are electron pair donors.

For example; aluminium chloride reacts with ammonia in the same way that a proton donor does.



Base dissociation constant:



Basicity order in periodic table:

- (1) As we move down the group electron density decreases, so basic strength decreases.
- (2) As electronegativity increases along the period, electron donor tendency decreases by which basic strength decreases.

BASIC STRENGTH OF ORGANIC BASES

- ❖ Strength of bases is related to the ease of accepting a proton, which in turn depends on the availability of electron pair on the nitrogen atom (or some other basic atom).
- ❖ More is the availability of electron pair, more easily the proton will be accepted and more will be the basic strength.

Aliphatic Amines

- ❖ If we compare the basicities of NH_3 , MeNH_2 , Me_2NH and Me_3N , then at a glance it would seem like $\text{NH}_3 < \text{MeNH}_2 < \text{Me}_2\text{NH} < \text{Me}_3\text{N}$ is the basicity order but the result is quite different in aqueous media.
 - ❖ The correct order is $\text{Me}_2\text{NH} > \text{MeNH}_2 > \text{Me}_3\text{N} > \text{NH}_3$. This order can be explained considering the solvation effect of the protonated amines.
 - ❖ But in absence of a polar protic solvent i.e. in the presence of non-polar solvent or gaseous phase, the order of basicity is $\text{Me}_3\text{N} > \text{Me}_2\text{NH} > \text{MeNH}_2 > \text{NH}_3$.
- ❖ Tetraalkylammonium salts, e.g. $\text{R}_4\text{N}^+\text{I}^-$ on treatment with moist silver oxide (AgOH) yield basic solutions comparable in strength with the mineral alkalies. This is readily understandable as $\text{R}_4\text{N}^+\text{OH}^-$ formed is completely ionized to give R_4N^- and free OH^- .
- ❖ The effect of introducing electron-withdrawing groups, e.g. Cl , NO_2 , close to a basic centre decreases the basicity, due to their electron-withdrawing inductive effect. Thus, the amine Tris (trifluoro methyl) amine is found to be virtually non-basic due to the presence of three powerful electron-withdrawing CF_3 groups.

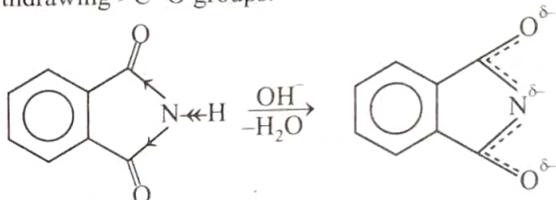


Amides

- ❖ The amides are found to be only very weakly basic in water because of the $-I$ and $-R$ effect of RCO group which makes the electron pair very slightly available on nitrogen atom.

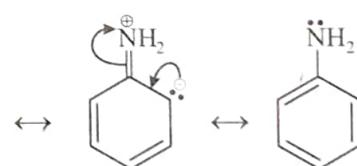
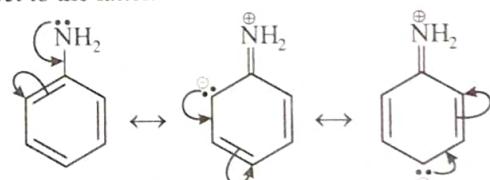


- ❖ If two C=O groups are present, the resultant imides often become sufficiently acidic to form alkali metal salts. For example, benzene-1,2-dicarboximide is not basic but is acidic in nature because of the presence of two electron-withdrawing $>\text{C=O}$ groups.

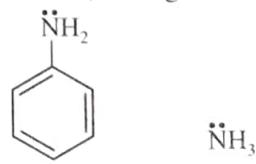


Aromatic Amines

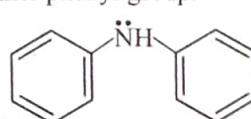
- ❖ In aniline, owing to resonance, the lone pair of electrons on the nitrogen atom is less available for co-ordinating with a proton and at the same time, small positive charge on the nitrogen atom would tend to repel a proton. Alternatively, since there are more resonating structures possible for aniline itself than for the cation $\text{C}_6\text{H}_5\text{NH}_3^+$ the former will be stabilized with respect to the latter.



- ❖ Aniline is a weaker base than ammonia or cyclohexylamine. It is because of the fact that the electron pair on nitrogen is involved in delocalization, making it less available for donation.



- ❖ Diphenylamine is even a weaker base than aniline due to the presence of another phenyl group.



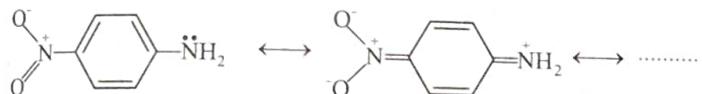
and triphenylamine (Ph_3N) is not basic at all by any means

❖ Introduction of alkyl group (like Me) on the nitrogen atom of aniline results in small increase in the basic strength.
 $C_6H_5NH_2 < C_6H_5NHMe < C_6H_5NMe_2$

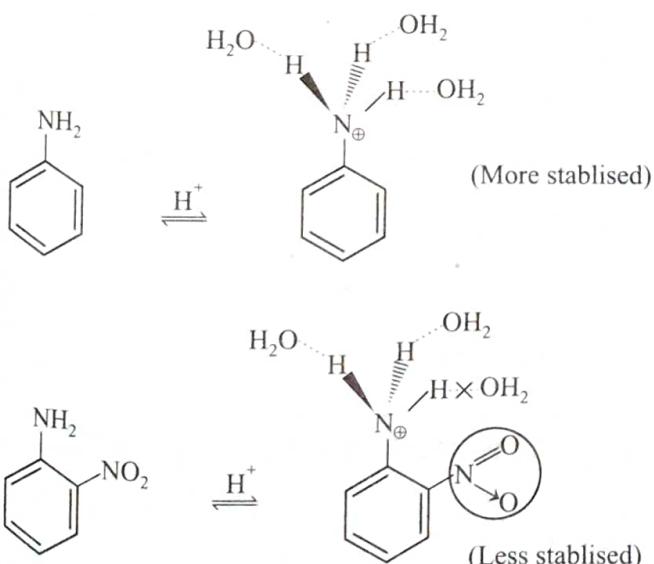
❖ Unlike such introduction in aliphatic amines, this small increase in basic strength is progressive, indicating that cation stabilization through hydrogen-bonded solvation, here has less influence on the overall effect.

Substituted Aromatic Amines

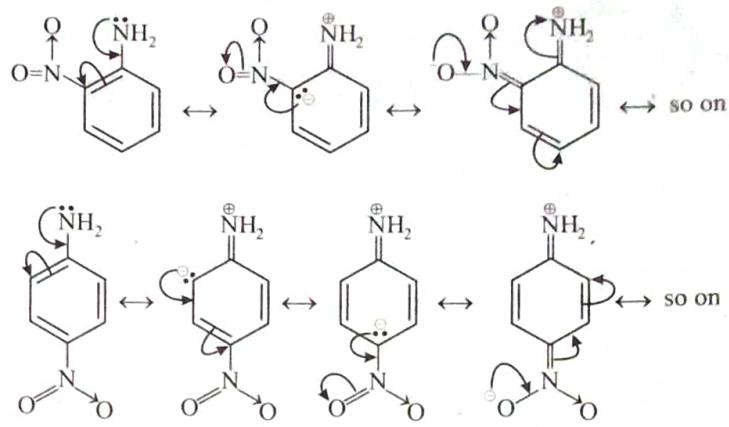
- ❖ The effect of a ring substituent on basicity depends on whether the substituent is electron attracting or releasing, its ability to enter into resonance with the amino-group and its position.
- ❖ All the nitroanilines are weaker bases than aniline. The nitro-group has a strong $-R$ effect and o- and p- nitroaniline are therefore, more resonance stabilised than aniline itself.



- ❖ A m-nitro group cannot enter into resonance with the amino-group, but nevertheless m-nitroaniline is a much weaker base than aniline. In this case, nitro-group has a strong $-I$ effect. This $-I$ effect tends to draw into the ring the lone pair of N, thus decreasing its basicity.
- ❖ In ortho nitro substituted aniline, the ortho effect is observed in the conjugate acid, which leads to decrease in basic strength of o-nitro aniline with respect to aniline and m- and p- nitro aniline.

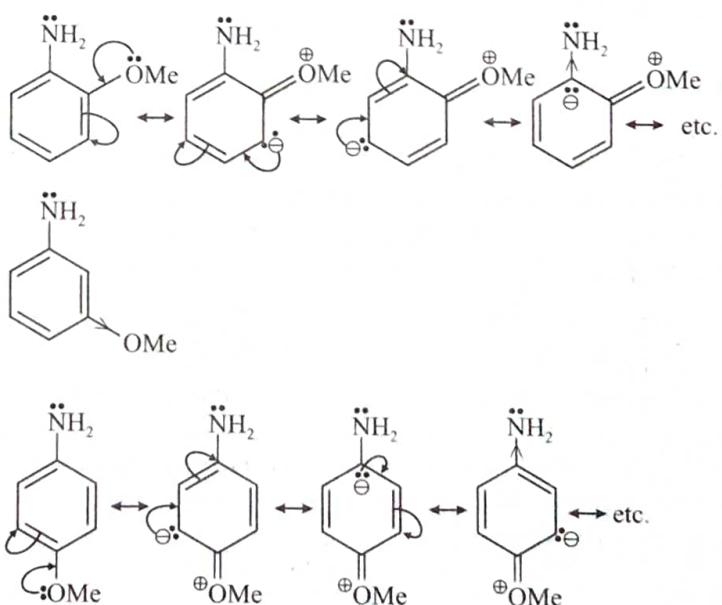


Thus, the order of basicity of nitroanilines is $C_6H_5NH_2 > m-NO_2C_6H_4NH_2 > p-NO_2C_6H_4NH_2 > o-NO_2C_6H_4NH_2$.



❖ When the ring contains an electron-releasing group, this reduces resonance of the NH_2 group with the ring and consequently should increase basicity. The methyl group raises the electron density more at the o- and p-positions than at the m-position. Thus, the carbon atom para to the methyl group has a high electron density and the lone pair on the nitrogen atom is therefore prevented to some extent from entering into resonance with the ring. A methyl group raises the electron density at the m-position only to a very small extent. Hence, resonance with the ring of NH_2 group at this position is prevented less than for the p-position. Consequently, a methyl group in the ring increases the basicity of the aniline, more so from the p-position than from the m-position. Thus, order of basicity of methyl anilines is $p-CH_3C_6H_4NH_2 > m-CH_3C_6H_4NH_2 > o-CH_3C_6H_4NH_2$. (Similar ortho effect is observed in the conjugate acid of o-methyl aniline, which decreases the basic strength.)

❖ The p-OMe group has a $+R$ effect and its presence increases basicity. In the m-position, it can exert only a $-I$ effect and this decreases the basicity. The order of basicity of methoxy anilines is $p-CH_3OC_6H_4NH_2 > C_6H_5NH_2 > o-CH_3OC_6H_4NH_2 > m-CH_3OC_6H_4NH_2$. (Similar ortho effect is observed in the conjugate acid of o-methoxy aniline, which decreases the basic strength but not lower than m-methoxy aniline.)





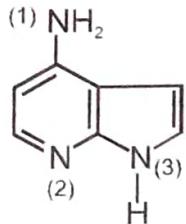
Train Your Brain

Example 7: Compare the basic strength of the following compounds:

- (i) $\text{C}_2\text{H}_5\text{O}^-$
- (ii) C_2H_5^-
- (iii) $\text{C}_2\text{H}_5\text{NH}^-$
- (iv) NH_2^-
- (v) F^-

Sol. II > III > IV > I > V

Example 8: Which of the following group is most basic in the given compounds:

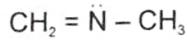


Sol. (2) As the nitrogen is sp^2 hybridized, the lone pair is localised by which it is most basic.

Example 9: Which of the following is a stronger base? Give reason to justify your answer.



(I)



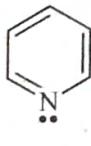
(II)

Sol. I is less basic than II because in compound (I) the lone pair of electrons are involved in resonance but not in II.

Example 10: Compare the basicities of following compounds:



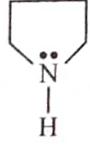
(I)



(II)



(III)



(IV)

Sol. In pyrrole(I), the lone pair on nitrogen is involved in resonance, while in other three, it is not involved. So, (I) is least basic. Among (II), (III) and (IV), the lone pair on nitrogen in (II) lies in sp^2 hybrid orbital (which is smaller than sp^3 hybrid orbital and is held more strongly by the nucleus, so the electron pair is less available for donation), while in (III) and (IV) it lies in sp^3 hybrid orbital. Among (III) and (IV), (III) has greater electron releasing groups by induction (+I) than (IV). So, the correct order of basicity is (III) > (IV) > (II) > (I).



Concept Application

20. The correct basic strength order of following anions is:

- (a) $\text{CH}_3\text{CH}_2^- > \text{NH}_2^- > \text{CH}_2=\text{CH}^- > \text{CH}\equiv\text{C}^- > \text{HO}^- > \text{F}^-$
- (b) $\text{NH}_2^- > \text{CH}_3\text{CH}_2^- > \text{CH}_2=\text{CH}^- > \text{CH}\equiv\text{C}^- > \text{F}^- > \text{HO}^-$
- (c) $\text{CH}_3\text{CH}_2^- > \text{CH}_2=\text{CH}^- > \text{NH}_2^- > \text{CH}\equiv\text{C}^- > \text{HO}^- > \text{F}^-$
- (d) $\text{F}^- > \text{HO}^- > \text{CH}\equiv\text{C}^- > \text{CH}_2=\text{CH}^- > \text{NH}_2^- > \text{CH}_3\text{CH}_2^-$

21. Which of the following shows the correct order of decreasing basicity in gas phase?

- (a) $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3$
- (b) $(\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > \text{NH}_3$
- (c) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$
- (d) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3 > (\text{CH}_3)_3\text{N}$

22. Find the order of basic strength if ($\text{R} = \text{Me}$)

- | | |
|---------------------------------------|---------------------------|
| (I) $\text{R}_4\text{N}^+\text{OH}^-$ | (II) R_3N |
| (III) R_2NH | (IV) RNH_2 |
| (a) I > III > IV > II | (b) IV > III > I > II |
| (c) II > IV > III > I | (d) II > IV > I > III |

Acidic Strength

(a) **Arhenius acid:** An acid is a substance that can donate (or lose) a proton in H_2O .

(b) **The Bronsted Lowry definition of acids:** An acid is a substance that can donate (or lose) a proton.

(c) **The Lewis definition of acids and bases:** Lewis proposed that acids are electron pair acceptors and bases are electron pair donors.

Acid dissociation constant (K_a):



$$K_{\text{eq}} = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}][\text{H}_2\text{O}]}$$

$$K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

$$\text{p}K_a = -\log K_a$$

ACIDIC STRENGTH OF ORGANIC ACIDS

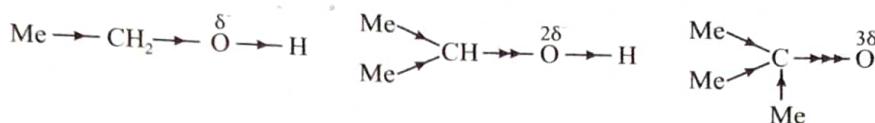
The factors responsible for influencing the acidity of an organic compound, $\text{H}-\text{X}$ are

- ❖ The strength of the $\text{H}-\text{X}$ bond
- ❖ The electronegativity of X
- ❖ Factors stabilizing X^- as compared to HX and the nature of the solvent.

- The most important factors among all is (c). More stable (less basic) the conjugate base is, more acidic the compound will be.
- On comparing the acidic strength of two compounds, the compound having greater acidity will have higher value of K_a and lower pK_a value.
- Now let us see using any of these factors, how we can predict the order of acidic strength for organic acids.

Alcohols

If we were to predict the order of acidic strength of ethanol, iso-propanol and tertiary butanol, we can proceed

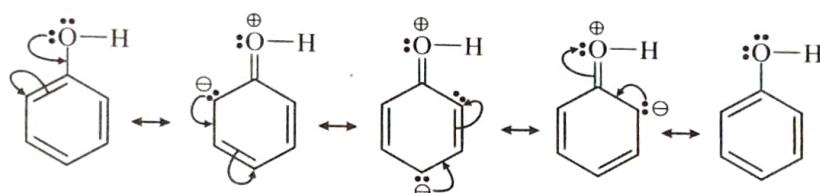


- As alkyl groups (methyl group) have a +I effect, the electron density at the oxygen atom will increase. More the number of alkyl groups, more will be the intensity of negative charge on oxygen.
- Greater the negative charge on the oxygen atom, the closer is the electron pair in the O-H bond driven to the hydrogen atom and consequently separation of a proton becomes increasingly difficult.
- Thus, the acidic strength of given alcohols will be in the order Ethanol > iso - propanol > t - butanol
- In general, electron releasing groups decreases the acidity while electron withdrawing group increases the acidity of a compound.

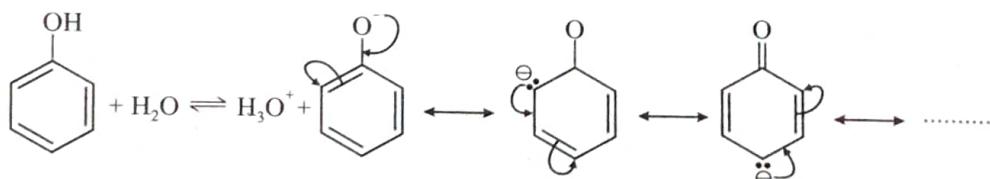
Phenols and Substituted Phenols

Phenol

- Because of resonance in phenol, the oxygen atom of the OH group acquires a positive charge and so proton release is facilitated,



- It might be noted that since the carbon atom of C-OH group is sp^2 hybridised, it is more electron attracting than an sp^3 carbon atom (as in alcohols) and therefore there is an increased -I effect which facilitates proton release. But this inductive effect alone is not large enough to explain the increased acid strength of phenols as compared with alcohols.
- When phenol ionizes, the phenoxide ion is also a resonance hybrid, but it is more stabilised by resonance than is the unionized phenol molecule because of spreading of negative charge only.
- In the unionized molecule, unlike charges are spread and so is less stable.



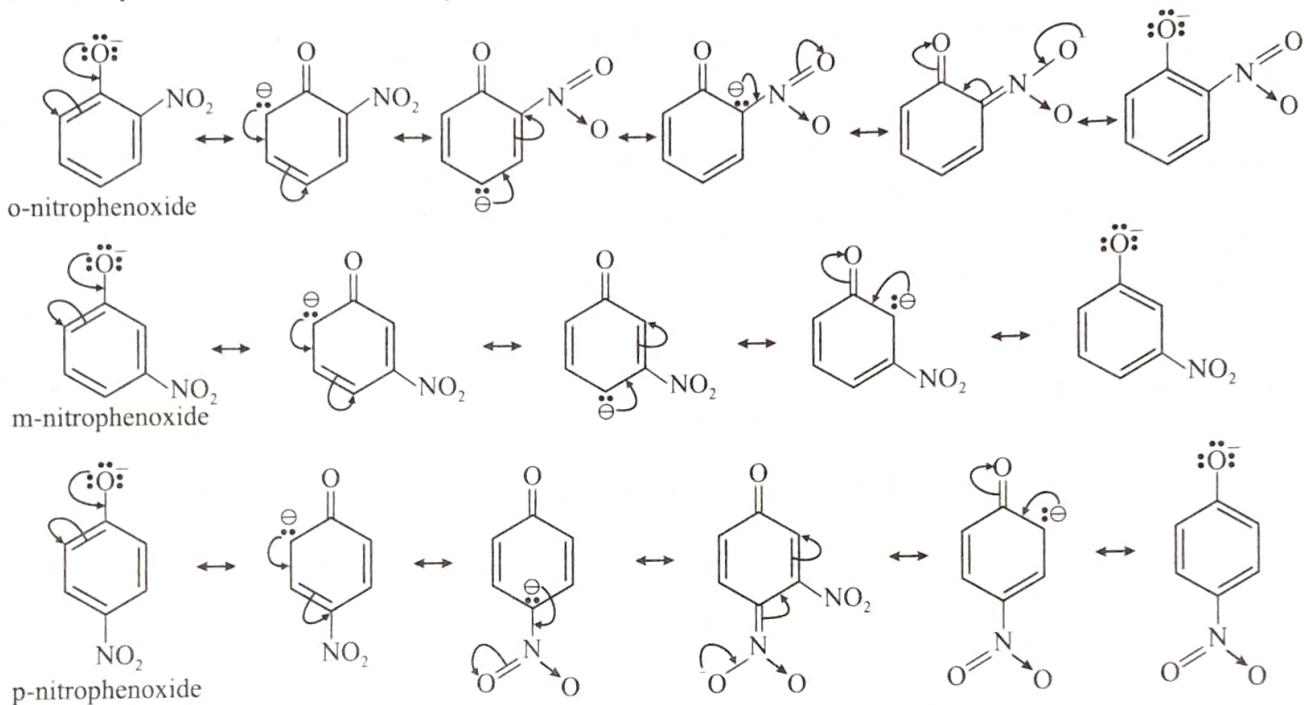
Phenols are stronger acids than alcohols. This is attributed to the fact that in phenoxide anion (obtained by the loss of proton from phenol), there is possibility of the delocalization of its negative charge through interaction with the p-orbitals of the aromatic nucleus while alkoxide cannot be stabilized by such effect. Thus phenoxide is a weaker base than alkoxide. Consequently, the phenol would be stronger acid than alcohol.

Substituted phenols

The effect of a ring substituent on the acid strength of phenol depends on whether the group is electron attracting or releasing, its ability to enter into resonance with the hydroxyl group and its position.

- Effects in the o-position are similar to those in the p-position, but there are added complications due to the steric effect and hydrogen bonding (when this is possible). Effects from meta position are altogether different from ortho and para position.
- In general, the presence of electron withdrawing groups in phenol increases its acidity while the presence of electron releasing groups decreases the acidity of phenol.
- Let us compare the acidic strength of o-, m- and p- methylphenols.

- The methyl group decreases the acid strength of phenol from all ring positions. The methyl group is electron releasing and so release of a lone pair from oxygen of the OH group in the unionized phenol or from the O⁻ in the phenoxide ion into the ring is opposed. This results in diminished resonance in the contributing structures and consequently the phenoxide ion is more resonance stabilised with respect to phenol than is the methylphenoxide ion with respect to methylphenol.
- Hence, phenol is a stronger acid than all methylphenols. The order of acidity of methyl phenols is phenol > m-methyl phenol > p-methylphenol > o-methyl phenol.
 - Now, let us compare the acidic strength of o-, m- and p- nitrophenols. The corresponding phenoxide ions obtained from the three nitrophenols would be stabilized by delocalization as

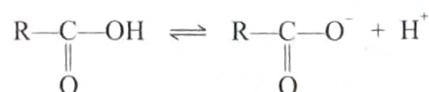


- From the structures of phenoxide ions, it is evident that o- and p-nitrophenoxides are more extensively stabilized with respect to m-nitro phenoxide (as additional contributing structure is obtained by the dispersal of negative charge over oxygen atom of NO₂ group in o- and p-nitrophenoxide but not in m-nitrophenoxide).
- Thus, corresponding o- and p-nitrophenols are much stronger acids than m-nitrophenol.
- A meta-nitro group cannot enter into resonance with the hydroxyl group but can exert -I effect for this position. Hence, meta-nitrophenol is also stronger acid than phenol.
- Out of o- and p-nitrophenols, p-nitrophenol is slightly stronger than o- isomer as o- isomer involves intramolecular hydrogen bonding, thus having a reduced tendency to release proton.
- The order of acidic strength of the nitrophenols is p-nitrophenol > o-nitrophenol > m-nitrophenol > phenol
 - The cumulative effect of three nitro groups in the 2, 4, 6 positions is shown by the fact that 2, 4, 6-trinitrophenol (picric acid) is a very strong acid.
 - All the halophenols are stronger acids than phenol and it follows that the -I effect of halogen atom is greater than its +R effect.
- Thus, the order of acidity of halophenols is o-halophenol > m-halophenol > p-halophenol > phenol.

- Among methoxy phenols, the order of acidity is: m-methoxyphenol > phenol > o-methoxy phenol > p-methoxy phenol.

Aliphatic Carboxylic Acids

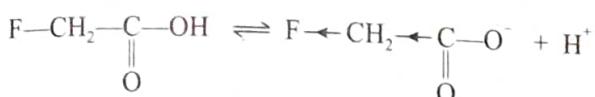
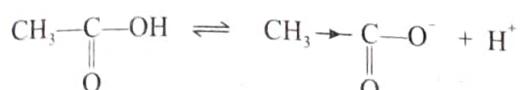
- The aliphatic carboxylic acids are much stronger acids than phenols and alcohols.
- This is attributed to the fact that the carboxylate ion (obtained by the loss of proton from carboxylic acid) is relatively more stabilized by delocalization than the phenoxide and alkoxide ions with respect to their undissociated molecules.



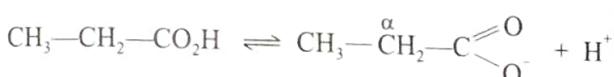
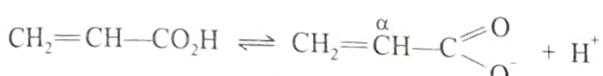
- The delocalization of the negative charge in the carboxylate anion involves structures of identical energy content (as the negative charge resides on more electronegative atom, oxygen) while in phenoxide anion, the negative charge also resides on the less electronegative atom (carbon) making these structures of high energy content with respect to those structures in which the negative charge is on oxygen.

- The presence of electron-withdrawing substituents in simple aliphatic acids increases their acidity while the electron-releasing substituents have reverse effect.

- For instance, let us compare the acidic strength of fluoroacetic acid and acetic acid.



- The fluoro acetate ion is stabilized more due to strong $-I$ effect of fluorine, with respect to acetate ion. Hence, fluoro acetate ion is less basic than acetate ion, thereby making fluoroacetic acid stronger than acetic acid.
- If there is a doubly bonded carbon atom adjacent to the carboxyl group, the acidic strength is increased. This will be evident if we compare the acidic strength of propanoic acid and propenoic (acrylic) acid.



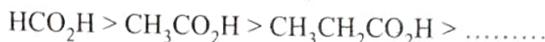
As we know that unsaturated α -carbon atom in propenoate ion is sp^2 hybridised, which means that electrons are drawn closer to the carbon nucleus than in a saturated, sp^3 hybridised α -carbon atom, due to greater s-contribution in the sp^2 hybrid orbital.

The result is that sp^2 hybridised carbon atoms are less electron-donating than saturated hybridised ones, thus, propanoate ion will be comparatively less stabilized than propenoate ion, thereby making propenoic acid stronger than propanoic acid (but propanoic will still be weaker than methanoic acid).

If there is a triple bonded carbon atom adjacent to carboxyl group, the acid strength is more with respect to the presence of a doubly bonded carbon atom adjacent to $-\text{CO}_2\text{H}$ group.

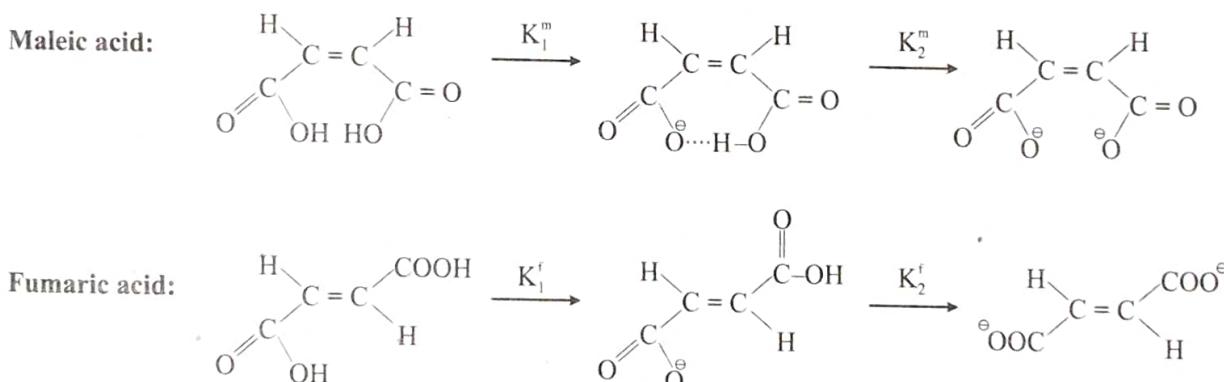
This is attributed to the fact that sp hybridized carbon atoms are less electron-releasing than sp^2 hybridized carbon atoms.

Some other trends of acidity are:



These trends reflect that in any homologous series, when we move from lower members to higher members, the acidity decreases.

Comparison between two Geometrical Isomers



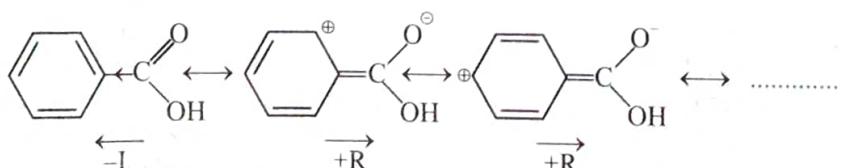
- $K_1^m > K_1^f$, since the conjugate base of maleic acid is stabilised by intramolecular H bonding but not that of fumaric acid.
- But $K_2^f > K_2^m$ since in maleate ion, after donation of H^+ two $-\text{COO}^-$ groups face each other and would be destabilised due to repulsion making the system unstable. In fumarate ion, this repulsion is minimised because two CO_2^- groups are on opposite side.

Aromatic Carboxylic Acids

- It has been pointed out that replacement of the hydrogen atom in formic acid by an alkyl group weakens the strength of the acid and the greater the $+I$ effect of the R group, the weaker is the acid.
- Phenylacetic acid, $\text{PhCH}_2\text{CO}_2\text{H}$ is stronger than acetic acid and therefore the phenyl group has an overall $-I$ effect.

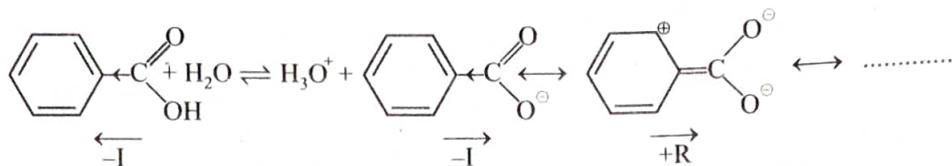
Benzoic acid

On the other hand, benzoic acid is weaker than formic acid. In this case, the phenyl group has an overall releasing effect (which is smaller than that of methyl group). These apparently contradictory results may be explained as follows. When the carboxyl group is directly attached to the nucleus, the resonance effect ($+R$) overcomes the $-I$ effect (in phenylacetic acid, the phenyl group is insulated from the carboxyl group by a CH_2 group and so the $+R$ effect is not possible):



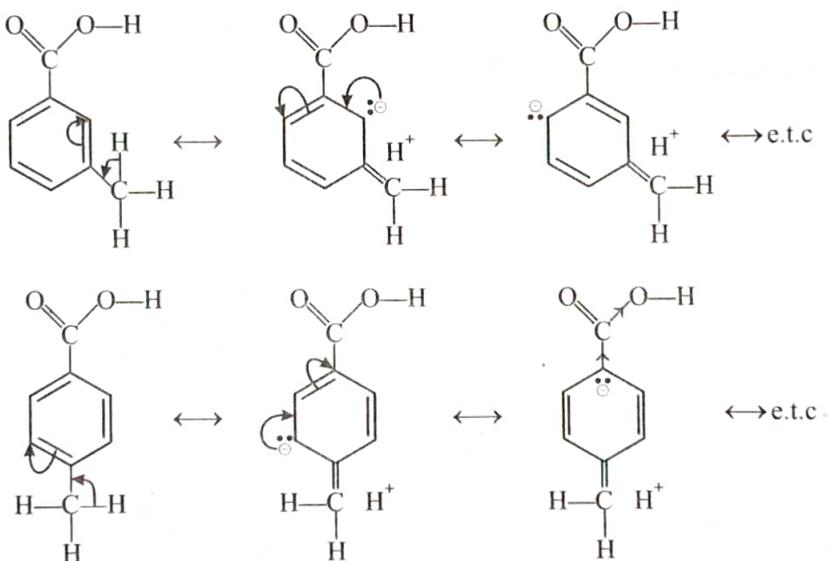
- This prevents to a large extent, the lone-pair on the O atom of the OH group from entering into resonance with the CO group.

- The result is a smaller positive charge on the O atom of the OH group and so proton release is more difficult than in formic acid.
 - The fact that benzoic acid is stronger than acetic acid means that $[-I+(+R)]$ of phenyl group < $[+I+(+H)]$ of the methyl group.
 - The same arguments may be applied to ionised benzoic acid.

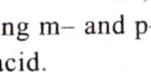
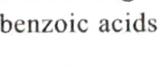


Substituted Benzoic acids

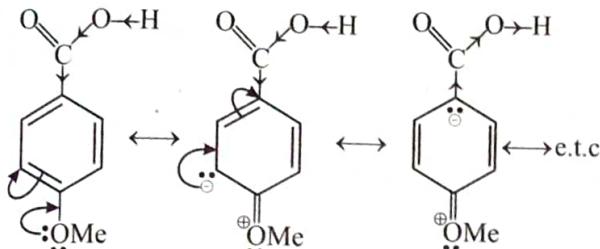
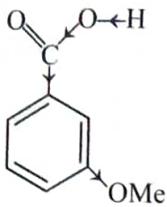
- Now let us consider substituted benzoic acids. At this point, we will consider the effect of substituents from m- and p-positions only.
 - First let us take methyl substituted benzoic acids. As the methyl group has +I effect, so the net result will be to increase the +R effect in the m- or p-tolyl group.
 - Since, the inductive effect decreases with distance, so the +I effect of CH_3 from para position would be less than the +I effect of CH_3 group from meta position. Thus, the electron-density in the O-H bond of m-methyl benzoic acid would be greater than that in p-methyl benzoic acid. Accordingly, the p-isomer should be more acidic than the m-isomer. But in real practice, the order is reverse.
 - Actually, we have ignored the hyperconjugation effect of CH_3 group. Due to hyperconjugation effect of CH_3 in p-isomer, the electron density in the O-H bond would be increased greatly with respect to that in m-isomer.



- Thus, the release of proton is facilitated easily in m-isomer than in p-isomer.
 - Secondly, let us take nitro substituted benzoic acids. As the --NO_2 group exerts $-I$ and $-R$ effect (both reinforcing each other), the electron-density from the O-H bond would be withdrawn, thus destabilizing the O-H bond and making m- and p- nitro benzoic acids stronger than benzoic acid.

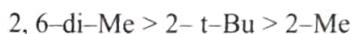



 - As it is clear that --NO_2 group exerts its electron withdrawing resonance effect from the p-position and not from m-position, thus withdrawal of electron density from the O-H bond is greater in p-nitro benzoic acid than m-nitro benzoic acid. Thus, p-nitro benzoic acid is stronger acid than m-nitro benzoic acid.
 - Thirdly, we compare the acid strength of m- and p- methoxy benzoic acid. OMe group exerts $-I$ and $+R$ effects. The electron-releasing resonance effect ($+R$) is operative in p-methoxy benzoic acid and not in m-methoxy benzoic acid while $-I$ effect is operative in both the isomers. Thus, the electron density is greatly increased in the O-H bond in p-isomer than in m-isomer, thereby making m-isomer stronger acid than p-isomer.



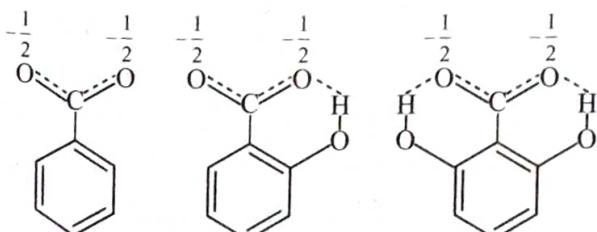
Ortho-effect

- This is a steric effect that is shown by *o*-substituted benzoic acids. Nearly all *o*-substituted benzoic acids are stronger than benzoic acid due to this ortho effect irrespective of the polar nature of the *o*-substituent.
- As we have seen that benzoic acid is a resonance hybrid and so the carboxyl group is coplanar with the ring. An *o*-substituent tends to prevent this coplanarity. Thus, resonance is diminished (or prevented) and so the O atom of the OH group has a greater positive charge, resulting in increased acid strength. It follows from this that greater the steric inhibition of resonance, the stronger is the acid. Support for this is the following order of strengths of substituted benzoic acids.



- Here again, if we consider the stability of the anion, steric inhibition of resonance prevents the $+R$ effect of the ring coming into operation and since this weakens acid strength, its absence results in increased acid strength.
- o*-Hydroxybenzoic acid (salicylic acid) is far stronger than the corresponding *m*- and *p*- isomers. Steric inhibition of resonance cannot explain this very large increase, since the corresponding methoxybenzoic acids all have almost similar strengths. The carboxylate ions of *o*-hydroxybenzoic acid is stabilised by intramolecular hydrogen bonding while such hydrogen bonding is not feasible in *o*-methoxybenzoic acid and support for this is given by the following order of acid strength, $2,6\text{-di-OH} > 2\text{-OH} > \text{benzoic acid}$

It can be seen that two hydrogen bonds would be expected to bring about more stabilization than one hydrogen bonds.

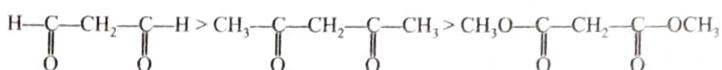


- Including ortho effect, the order of acidity of some substituted benzoic acids is given as:
- $\text{o-nitro benzoic acid} > \text{p-nitrobenzoic acid} > \text{m-nitro benzoic acid} > \text{benzoic acid}$.

- $\text{o-methyl benzoic acid} > \text{benzoic acid} > \text{m-methyl benzoic acid} > \text{p-methyl benzoic acid}$
- $\text{o-methoxy benzoic acid} > \text{m-methoxy benzoic acid} > \text{benzoic acid} > \text{p-methoxy benzoic acid}$.

Carbon Acids

- Carbon acids are those compounds in which H^+ is lost from a carbon. Generally, C-acids are weaker than most O-acids.
- A CH_2 group flanked between two electron withdrawing groups has acidic hydrogen. Aldehydic group is more electron withdrawing than ketonic group, which is more electron attracting than ester groups. Thus, order of acidity of carbon acids is



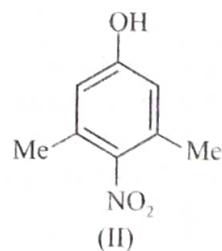
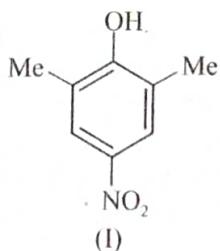
- CHCl_3 is more acidic than CHF_3 because the conjugate base of CHCl_3 i.e. $\begin{array}{c} \text{Cl} \\ | \\ :\text{C}-\text{Cl} \\ | \\ \text{Cl} \end{array}$ is stabilised by $-I$ effect of Cl as well as by $\pi - d\pi$ delocalization (which is absent in CF_3 : due to the absence of d-orbital in F).

- For the same reason, is more acidic than .



Train Your Brain

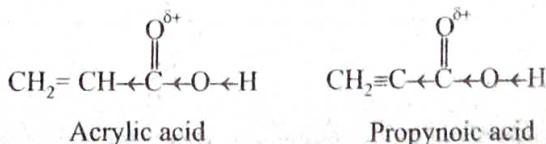
Example 11: Which of the following phenol is more acidic?



Sol. Compound (I) is more acidic than compound (II) because NO_2 group can show $-I$ and $-R$ effects in compound (I) while NO_2 group will show only $-I$ effect in compound (II). NO_2 group in compound (II) is unable to show resonance effect because of the steric crowding by adjacent methyl groups.

Example 12: Explain why acrylic (propenoic) acid is weaker acid than propynoic acid?

Sol.



If we look at these two acids, electron withdrawing effect of sp^2 carbon adjacent to carbonyl group in acrylic acid is less than the electron withdrawing effect of sp hybridized carbon. Thus, OH bond of propynoic acid has greater polarization than the OH group of propenoic acid. Hence, propynoic acid is a stronger acid than propenoic acid.

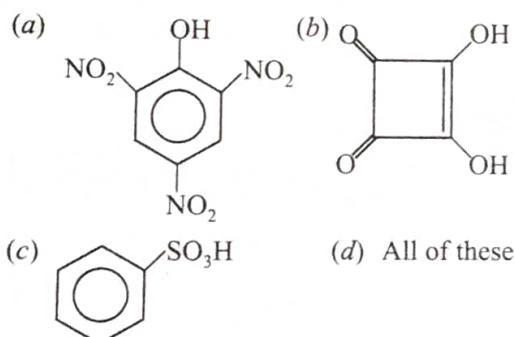
Example 13: Account for the fact that salicylic acid, $\text{o-HOC}_6\text{H}_4\text{CO}_2\text{H}$ is a stronger acid than $\text{o-CH}_3\text{OC}_6\text{H}_4\text{CO}_2\text{H}$.

Sol. CH_3O group is bigger in size than OH group. Therefore, CH_3O group can cause greater ortho effect than OH group. Based on this, $\text{o-CH}_3\text{OC}_6\text{H}_4\text{CO}_2\text{H}$ should have been a stronger acid than $\text{o-HOC}_6\text{H}_4\text{CO}_2\text{H}$ but in reality, it is opposite. This is attributed to stability of conjugate base formed by the loss of proton from $\text{o-HOC}_6\text{H}_4\text{CO}_2\text{H}$, which will be stabilised by intramolecular hydrogen bonding. This is not possible with the conjugate base formed by the loss of proton from $\text{o-CH}_3\text{OC}_6\text{H}_4\text{CO}_2\text{H}$.

Example 14:

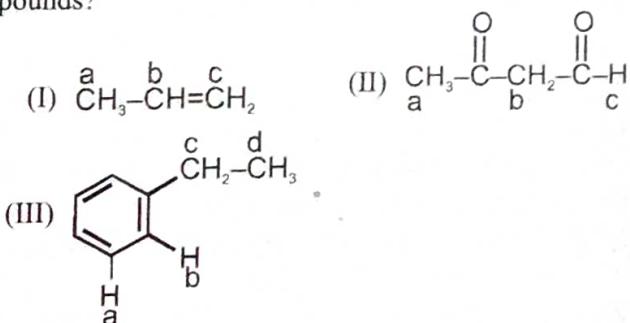
Which of the following would produce effervescence with sodium bicarbonate?

(pK_{a1} of $H_2CO_3 = 6.3$)



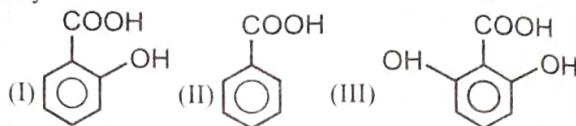
Sol. (d) All the given acids are stronger than carbonic acid and will thus produce effervescence on reacting with sodium bicarbonate as HCO_3^- will pull out H^+ from them to form H_2CO_3 or CO_2 gas as effervescences.

Example 15: Which 'H' atom is most acidic in the following compounds?



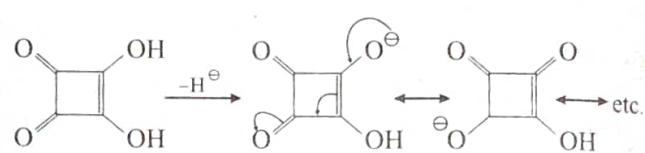
Sol. I - a, II - b, III - c; (acidic strength \propto stability of conjugate base)

Example 16: Arrange the following in decreasing order of acidity.



Sol. III > I > II (acidic strength \propto stability of conjugate base). In III, conjugate base is highly stabilised by intra molecular H-bonding.

Example 17: The given compound; X =  is a strong acid. Justify this statement.



Its conjugate base (anion) is resonance stabilised like RCOO^- anion of carboxylic acid.



Concept Application

23. Among the following compounds, the strongest acid is:

 - (a) $\text{HC} \equiv \text{CH}$
 - (b) C_6H_6
 - (c) C_2H_6
 - (d) CH_3OH

24. Which of the following is not correct decreasing order of K_a ?

 - (a) $\text{CH}_4 > \text{NH}_3 > \text{H}_2\text{O} > \text{HF}$
 - (b) $\text{CH}_3\text{--OH} > \text{CH}_3\text{--NH}_2 > \text{CH}_3\text{--F} > \text{CH}_3\text{--CH}_3$
 - (c) $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
 - (d) $\text{PhOH} > \text{H}_2\text{O} > \text{C}_2\text{H}_5\text{OH} > \text{CH}_3\text{--C} \equiv \text{CH}$

25. Which of the following acid has the smallest dissociation constant?

 - (a) $\text{CH}_3\text{--CH}(\text{NO}_2)\text{--COOH}$
 - (b) $\text{O}_2\text{N--CH}_2\text{--CH}_2\text{--COOH}$
 - (c) $\text{Cl--CH}_2\text{--CH}_2\text{--COOH}$
 - (d) $\text{NC--CH}_2\text{--CH}_2\text{--COOH}$

Short Notes

Electrophiles are electron deficient species.

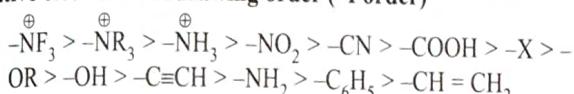
E.g. H^{\oplus} , R^{\oplus} , NO_2^{\oplus} , X^{\oplus} , PCl_3 , PCl_5

(NH_4^+ and H_3O^+ are not electrophile)

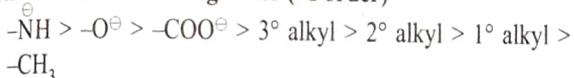
Nucleophiles are electron rich species.

E.g. Cl^{\ominus} , CH_3^{\ominus} , OH^{\ominus} , RO^{\ominus} , CN^{\ominus} , NH_3^{\ddagger} , $\text{R}^{\ddagger}\text{OH}$, $\text{CH}_2 = \text{CH}_2$, $\text{CH} \equiv \text{CH}$

Relative electron withdrawing order (-I order)

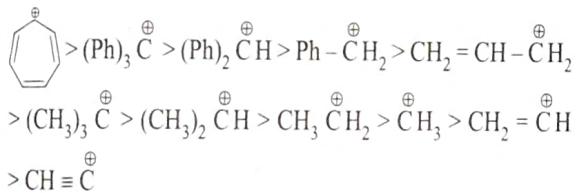


Relative electron releasing order (+I order)

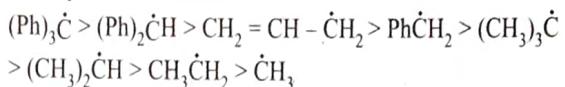


Relative Stability Order

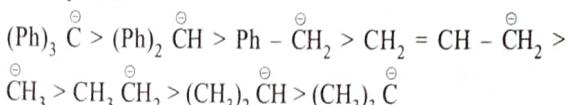
(A) Stability of carbocation



(B) Stability of free radical



(C) Stability of carbanion



Reactivity towards nucleophile (NAR)

- (1) $\text{HCHO} > \text{CH}_3\text{CHO} > (\text{CH}_3)_2\text{CO}$
- (2) $\text{CCl}_3\text{CHO} > \text{CHCl}_2\text{CHO} > \text{CH}_2\text{ClCHO}$

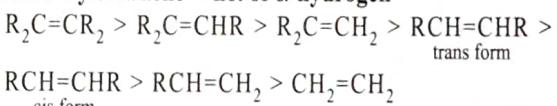
❖ **Reactivity order towards acyl nucleophilic substitution reaction**

Acid chloride > anhydride > ester > amide

❖ **Order of electronic effect**

Mesomeric > Hyperconjugation > Inductive effect

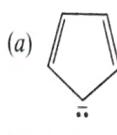
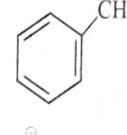
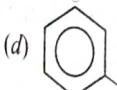
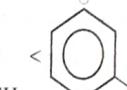
❖ **Stability of alkene \propto no. of α -hydrogen**



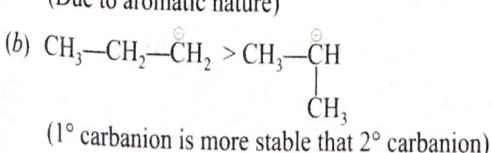
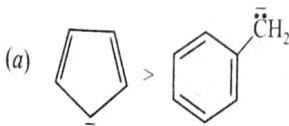
❖ **Heat of hydrogenation $\propto \frac{1}{\text{Stability of alkene}}$**

Solved Examples

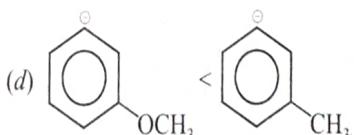
1. Which of the following is/are correct order of stability of carbanion?

- (a)  > 
- (b) $\text{CH}_3-\text{CH}_2-\overset{\ominus}{\text{CH}_2} > \text{CH}_3-\overset{\ominus}{\text{CH}}-\text{CH}_3$
- (c) $\overset{\ominus}{\text{CF}_3} > \overset{\ominus}{\text{CCl}_3}$
- (d)  < 

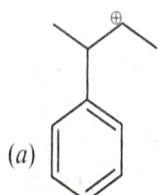
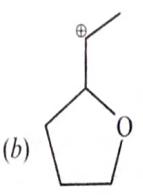
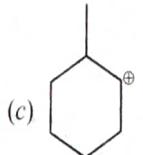
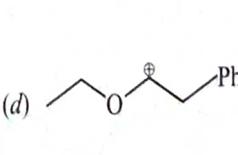
Sol. (a,b)

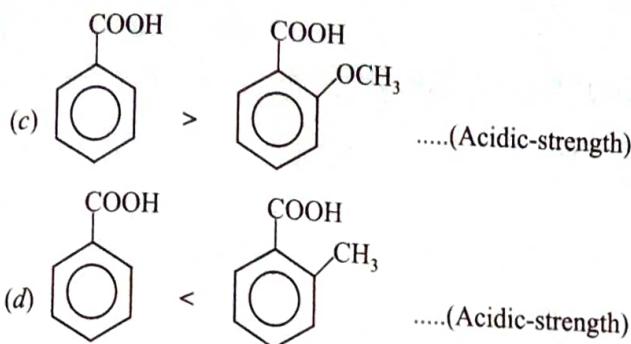


(Due to delocalization of e^- in vacant d-orbital of -Cl atom)



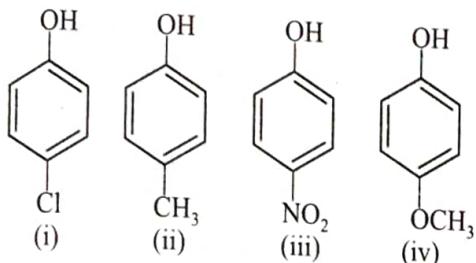
2. In which of the following carbocation/s rearrangement takes place?

- (a) 
- (b) 
- (c) 
- (d) 



Sol. (c) (a) → Intramolecular H-bonding
 (b) → Due to ortho effect.
 (c) → Due to ortho effect.
 (d) → Due to ortho effect.

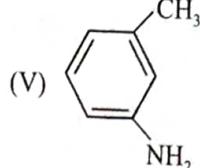
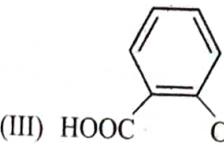
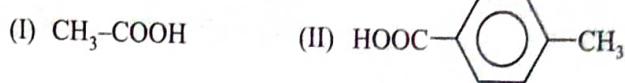
11. Arrange the following compounds in order of decreasing acidity.



- (a) (i) > (ii) > (iii) > (iv) (b) (iii) > (i) > (ii) > (iv)
 (c) (iv) > (iii) > (i) > (ii) (d) (ii) > (iv) > (i) > (iii)

Sol. (b) Electron withdrawing group increases acidic strength and electron releasing group decreases acidic strength

12. The compound in which the CH_3 -group causes increase in acidic strength and decrease in basic strength are, respectively:



Sol. (c) Due to ortho effect, $-\text{CH}_3$ group in III increases acidic strength & in IV, it decreases basic strength.

13. The correct order of decreasing acidic strength of trichloroacetic acid (A), trifluoroacetic acid (B), acetic acid (C) and formic acid (D) is:

- (a) B > A > D > C (b) B > D > C > A
 (c) A > B > C > D (d) A > C > B > D

Sol. (a) $\text{CF}_3\text{-COOH} > \text{CCl}_3\text{-COOH} > \text{HCOOH} > \text{CH}_3\text{COOH}$
in accordance of decreasing acidity order.

Exercise-1 (Topicwise)

INTRODUCTION

10. Carbon atoms in the compound, $(\text{CN})_4\text{C}_2$ are
 (a) sp hybridized
 (b) sp^2 hybridized
 (c) sp and sp^2 hybridized
 (d) sp , sp^2 and sp^3 hybridized

11. Which of the following is an acidic hydrocarbon?
 (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ (b) $\text{CH}_3\text{C} \equiv \text{CCH}_3$
 (c) $\text{CH}_3\text{C} \equiv \text{CH}$ (d) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$

12. Toluene has
 (a) 6σ and 3π -bond (b) 9σ and 3π -bond
 (c) 9σ and 6π -bond (d) 15σ and 3π -bond

13. Conjugated double bond is present in
 (a) 1, 2-butadiene (b) 1, 3-butadiene
 (c) 1, 4-pentadiene (d) β -butylene

14. Hydrogen bonding is maximum in
 (a) $\text{C}_2\text{H}_5\text{OH}$ (b) $\text{CH}_3 - \text{O} - \text{CH}_3$
 (c) $(\text{CH}_3)_2\text{C} = \text{O}$ (d) CH_3CHO

15. The enolic form of acetone contains
 (a) 8σ -bonds, 2π -bonds and 1 lone pair
 (b) 9σ -bonds, 1π -bond and 2 lone pairs
 (c) 9σ -bonds, 2π -bonds and 1 lone pair
 (d) 10σ -bonds, 1π -bond and 1 lone pair

16. Which of the following compound contains the functional group —OH?
 (a) 1, 2-ethandiol (b) 2-butanone
 (c) Nitrobenzene (d) Ethanal

17. General formula of alkyne is
 (a) $\text{C}_n\text{H}_{2n+2}$ (b) C_nH_{2n}
 (c) $\text{C}_n\text{H}_{2n-2}$ (d) C_nH_n

18. General formula of alkene and alkane are
 (a) C_nH_{2n} and $\text{C}_n\text{H}_{2n+1}$
 (b) C_nH_{2n} and $\text{C}_n\text{H}_{2n+2}$
 (c) $\text{C}_n\text{H}_{2n-1}$ and C_nH_{2n}
 (d) $\text{C}_n\text{H}_{2n-1}$ and $\text{C}_n\text{H}_{2n+2}$

19. Which one of the following order is correct regarding the inductive effect of the substituents?
 (a) $-\text{NR}_2 < -\text{OR} > -\text{F}$ (b) $-\text{NR}_2 > -\text{OR} > -\text{F}$
 (c) $-\text{NR}_2 < -\text{OR} < -\text{F}$ (d) $-\text{NR}_2 > -\text{OR} < -\text{F}$

20. The order of decreasing stability of the carbanions is
 (I) $(\text{CH}_3)_3\bar{\text{C}}$ (II) $(\text{CH}_3)_2\bar{\text{C}}\text{H}$
 (III) $\text{CH}_3\bar{\text{C}}\text{H}_2$ (IV) $\text{C}_6\text{H}_5\bar{\text{C}}\text{H}_2$
 (a) I > II > III > IV (b) IV > III > II > I
 (c) IV > I > II > III (d) I > II > IV > III

21. Decreasing order of $-I$ effect of the triad $[-\text{NO}_2, -\overset{\oplus}{\text{NH}_3}, -\text{CN}]$ is:

- (a) $-\overset{\oplus}{\text{NH}_3} > -\text{NO}_2 > -\text{CN}$
- (b) $-\overset{\oplus}{\text{NH}_3} > -\text{CN} > \text{NO}_2$
- (c) $-\text{CN} > -\text{NO}_2 > -\overset{\oplus}{\text{NH}_3}$
- (d) $-\text{NO}_2 > -\text{CN} > -\overset{\oplus}{\text{NH}_3}$

22. Which of the following carbocation is least stable?

- (a) $\text{CH}_3 - \overset{\oplus}{\text{C}} - \text{CH}_3$
- (b) $\text{CH}_3 - \text{CH}_2 - \overset{\oplus}{\text{CH}_2}$
- (c) $\text{CH}_3 - \overset{\oplus}{\text{C}}(\text{CH}_3)_2$
- (d) $\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}} - \overset{\oplus}{\text{CH}} - \text{C}_6\text{H}_5$

23. Which of the following group/atom shows $+I$ -effect?

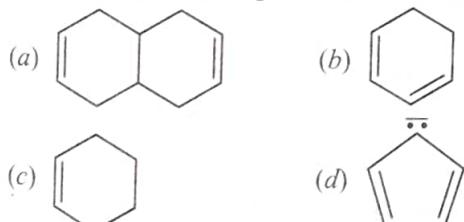
- (a) $-\text{OH}$
- (b) $-\text{OCH}_3$
- (c) $-\text{CH}_3$
- (d) $-\text{Cl}$

RESONANCE AND IT'S APPLICATION

24. Resonance structure of molecule does not have

- (a) Identical arrangement of atoms.
- (b) Nearly the same energy content.
- (c) The same number of paired electrons.
- (d) Identical bonding

25. Which of the following will show aromatic behaviour?



26. Which of the following is the most stable compound?

- (a) $\text{Ph}_3\overset{+}{\text{C}}$
- (b) $\text{Ph}_2\overset{+}{\text{CH}}$
- (c) $\text{Ph}_3\overset{+}{\text{C}}\text{CH}_2$
- (d) $\text{Ph}\overset{+}{\text{CH}}_2$

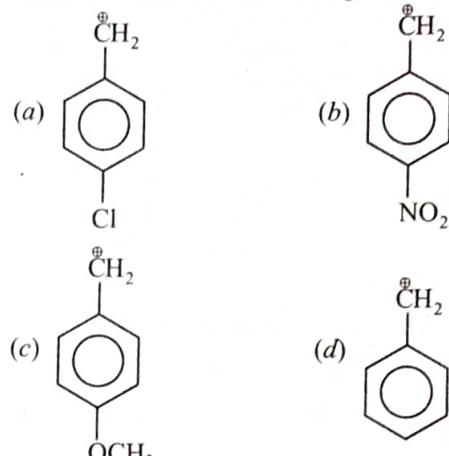
27. Which of the following resonating structures of 1-methoxy-1,3-butadiene is least stable?

- (a) $\text{CH}_2 - \overset{\oplus}{\text{CH}} = \text{CH} - \text{CH} = \overset{\oplus}{\text{O}} - \text{CH}_3$
- (b) $\text{CH}_2 = \text{CH} - \overset{\ominus}{\text{CH}} - \text{CH} = \overset{\oplus}{\text{O}} - \text{CH}_3$
- (c) $\overset{\ominus}{\text{CH}_2} - \overset{\oplus}{\text{CH}} - \text{CH} = \text{CH} - \text{O} - \text{CH}_3$
- (d) $\text{CH}_2 = \text{CH} - \overset{\ominus}{\text{CH}} - \overset{\oplus}{\text{CH}} - \text{O} - \text{CH}_3$

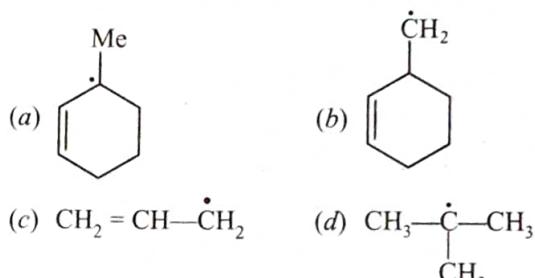
28. Which of the following is the decreasing order of stability?

- (i) $\text{CH}_3 - \overset{\oplus}{\text{CH}} - \text{CH}_3$
- (ii) $\text{CH}_3 - \overset{\oplus}{\text{CH}} - \text{O} - \text{CH}_3$
- (iii) $\text{CH}_3 - \overset{\oplus}{\text{CH}} - \text{CO} - \text{CH}_3$
- (a) (ii) $>$ (i) $>$ (iii)
- (b) (i) $>$ (ii) $>$ (iii)
- (c) (iii) $>$ (ii) $>$ (i)
- (d) (ii) \geq (iii) $>$ (i)

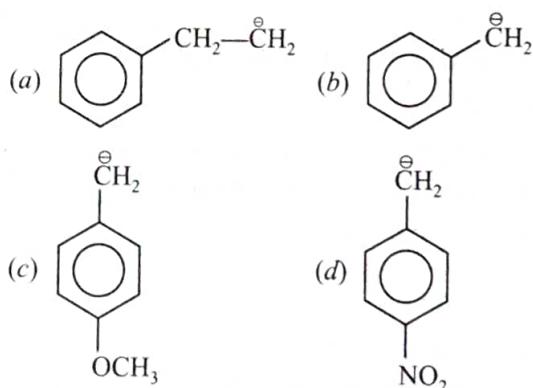
29. Most stable carbocation amongst the following is:



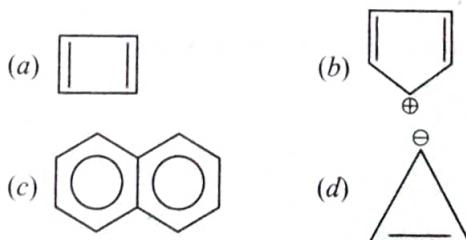
30. Which one is the most stable free radical?



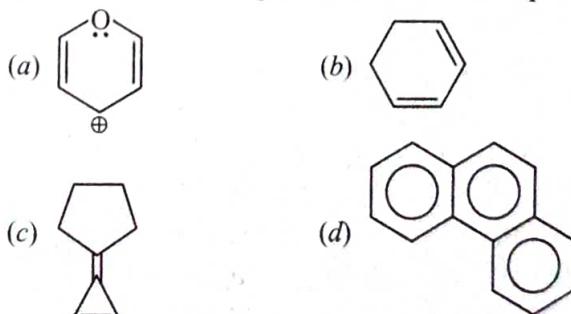
31. The most stable carbanion among the following is



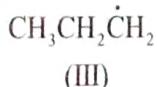
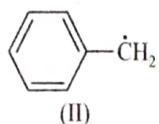
32. Among the following, the aromatic compound/species is



33. Which of the following is not an aromatic compound?

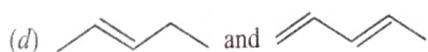
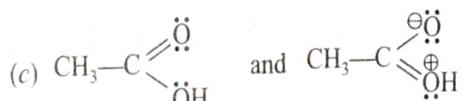
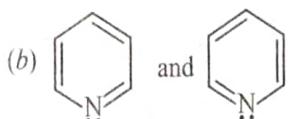
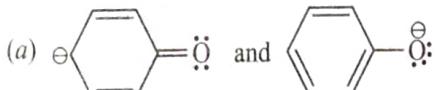


34. The correct order of stability of following carbon free radicals is:



- (a) I > II > III > IV (b) IV > III > II > I
 (c) II > III > I > IV (d) II > I > III > IV

35. Which of the following is not a pair of resonating structures?

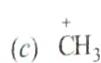
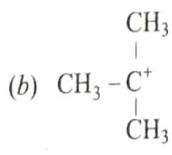
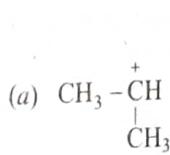


HYPERCONJUGATION AND IT'S APPLICATION

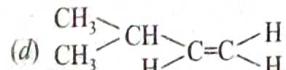
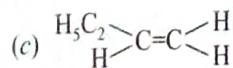
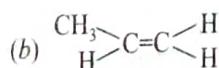
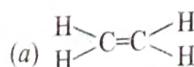
36. Orbital interaction between the sigma bonds of a substituent group and a neighbouring π -orbital is known as

- (a) Hyperconjugation
 (b) Inductive effect
 (c) Steric effect
 (d) Dipole-dipole interactions

37. Which amongst the following is the most stable carbocation?

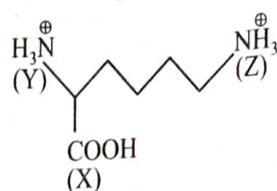


38. Which of the following is most stable alkene?



ACIDIC STRENGTH AND BASIC STRENGTH

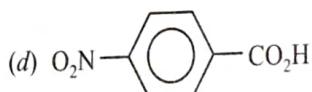
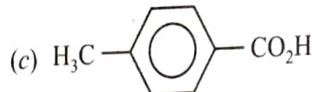
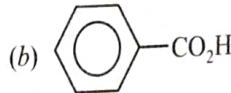
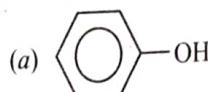
39. In the compound given below



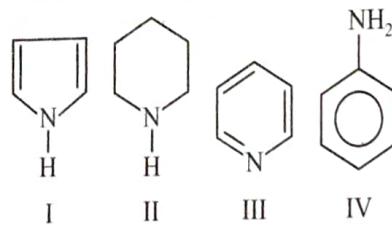
The correct order of the acidity of the positions (X), (Y) and (Z) is

- (a) (Z) > (X) > (Y) (b) (X) > (Y) > (Z)
 (c) (X) > (Z) > (Y) (d) (Y) > (X) > (Z)

40. Most acidic compound among the following is:

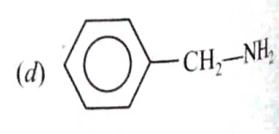
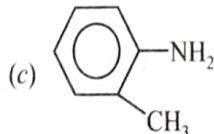
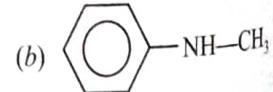
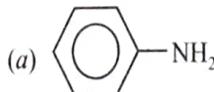


41. The correct order of decreasing basic strength is

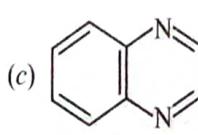
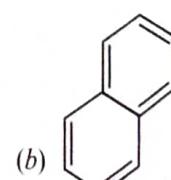
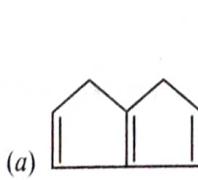


- (a) I > II > III > IV (b) II > III > I > IV
 (c) II > IV > I > III (d) II > III > IV > I

42. Which of the following is the strongest base?

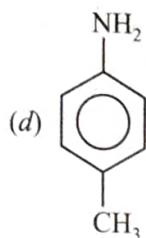
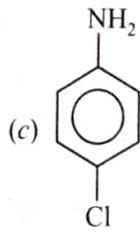
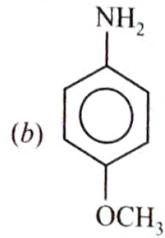
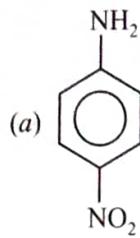


43. Which of the following is an aromatic compound?



- (d) Both (b) and (c)

44. Which of the following compound is least basic?



45. Which of the following orders of acidic strength is correct?

- (a) RCOOH > ROH > HOH > HC ≡ CH
- (b) RCOOH > HOH > ROH > HC ≡ CH
- (c) RCOOH > HOH > HC ≡ CH > ROH
- (d) RCOOH > HC ≡ CH > HOH > ROH

REACTION MECHANISM INTRODUCTION

46. Which of the following can act as an electrophile?

- (a) H₂O
- (b) SO₃
- (c) NH₃
- (d) ROR

47. The presence of Chlorine atom on benzene ring makes the second substituent enter at _____ position.

- (a) Ortho
- (b) meta
- (c) Para
- (d) Ortho & para

48. Conversion of alkane into alkyl halide is an example of which of the following reaction?

- (a) Electrophilic substitution
- (b) Free radical addition
- (c) Nucleophilic substitution
- (d) Free radical substitution

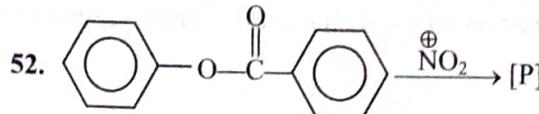
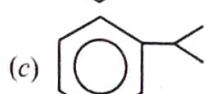
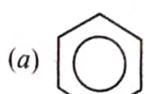
49. Which of the following can act as an electrophile?

- (a) AlCl₃
- (b) CN⁻
- (c) NH₃
- (d) CH₃OH

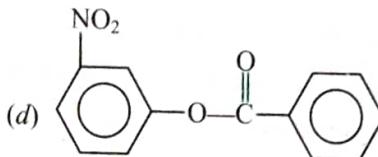
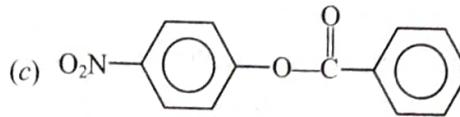
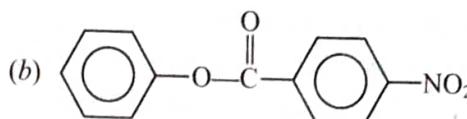
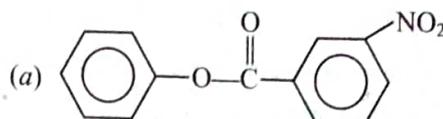
50. Strongest nucleophile among the following is

- (a) RNH₂
- (b) ROH
- (c) C₆H₅O⁻
- (d) CH₃O⁻

51. Which of the following is most reactive towards E.S.R.?



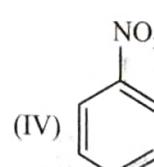
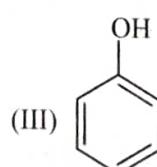
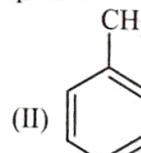
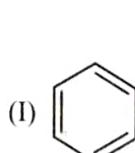
The product [P] is:



53. Nitration of benzene is

- (a) Nucleophilic substitution
- (b) Nucleophilic addition
- (c) Electrophilic substitution
- (d) Electrophilic addition

54. Consider the following compounds:

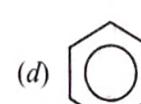
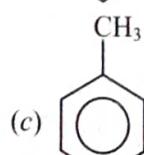
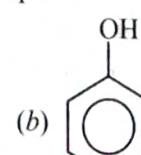
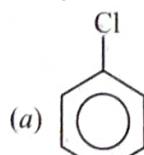


Correct order of their reactivity in electrophilic substitution reaction would be:

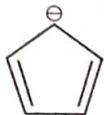
- (a) I > II > III > IV
- (b) IV > III > II > I
- (c) III > II > I > IV
- (d) III > IV > I > II

MISCELLANEOUS

55. Which of the following aromatic compound will be most easily attacked by an electrophile?



56. How many π -electrons are there in the following species?



- (a) 2 (b) 4 (c) 6 (d) 8

57. Which of the following is the correct statement about benzene?

- (a) All the C–C bond lengths are not equal.
 (b) All the bond angles are not equal.
 (c) All the C-atoms are not in sp^2 hybridisation state.
 (d) Three C–C bond lengths are not different than other three C–C bond lengths.

58. The number of benzylic hydrogen atoms in ethylbenzene are:

- (a) 3 (b) 5 (c) 2 (d) 7

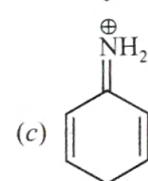
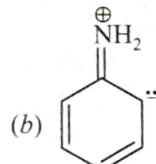
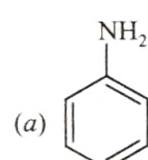
59. In amines, hybridisation state of N is:

- (a) sp (b) sp^2 (c) sp^3 (d) sp^3d

60. Which of the following is most basic?

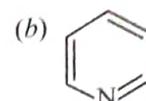
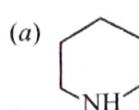
- (a) Aniline (b) o-Nitroaniline
 (c) m-Nitroaniline (d) p-Nitroaniline

61. The most stable resonating structure of aniline is



- (d) All are equally stable

62. Which of the following is most basic?



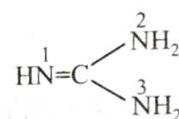
- (c) RCN

- (d) $C_6H_5NH_2$

63. The correct order of basic strength of substituted aniline is:

- (a) p-methylaniline > p-chloroaniline > p-aminoacetophenone > aniline
 (b) p-methylaniline > p-aminoacetophenone > o-chloroaniline > aniline
 (c) p-aminoacetophenone > p-methylaniline > p-chloroaniline
 (d) p-aminoacetophenone > p-chloroaniline > p-methylaniline

64. Which of the nitrogen is protonated readily in guanidine?



- (a) 1 (b) 2
 (c) 3 (d) All are equally protonated

65. Which of the following compound is most acidic?

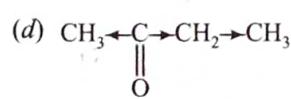
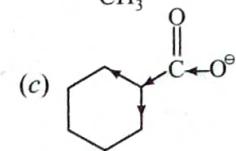
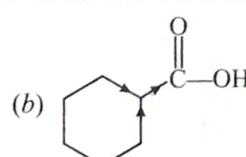
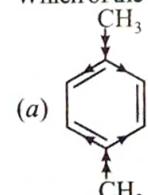
- (a) Picric acid (b) p-nitrophenol
 (c) m-nitrophenol (d) o,p-dinitrophenol

Exercise-2 (Learning Plus)

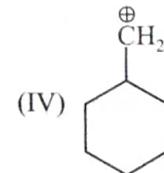
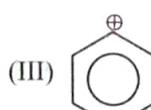
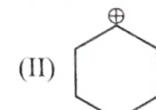
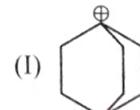
1. Inductive effect involves:

- (a) Delocalisation of σ - electrons
 (b) Partial displacement of σ - electrons
 (c) Delocalisation of π - electron
 (d) Displacement of lone pair electrons

2. Which of the following has incorrect direction of Inductive effect?

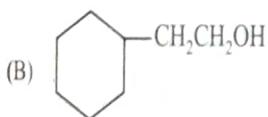
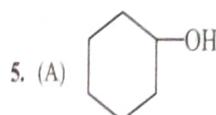
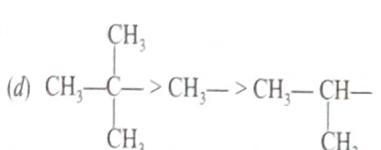
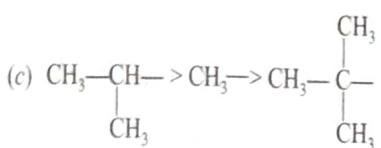
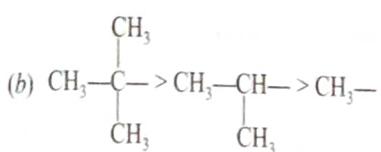
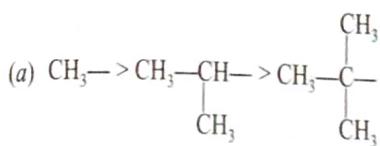


3. The stability order of following carbocation is:



- (a) I > II > IV > III
 (b) III > I > II > IV
 (c) IV > II > III > I
 (d) II > IV > III > I

4. When $-\text{CH}_3$, $\text{CH}_3-\text{CH}-$ and $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-$ groups are introduced on benzene ring, then correct order of their inductive effect is



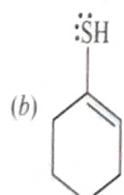
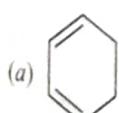
True statement for the above compounds is

- (a) (A) is phenol while (B) is alcohol
- (b) Both (A) and (B) are primary alcohol
- (c) (A) is primary and (B) is secondary alcohol
- (d) (A) is secondary and (B) is primary alcohol

6. In which of the following, delocalisation of π -electron is possible?

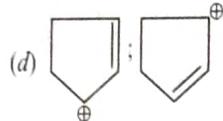
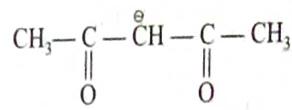
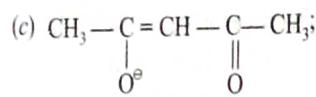
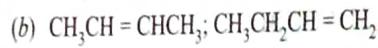
- (a) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CHO}$
- (b) $\text{CH}_2 = \text{CH} - \text{CH} = \text{O}$
- (c) $\text{CH}_3-\overset{\text{OH}}{\underset{\text{CH}_3}{\text{CH}}}-\text{CH}_3$
- (d) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH}_2$

7. Which of the following species has conjugation?

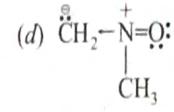
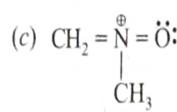
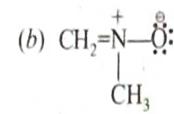
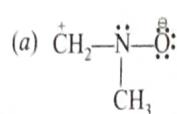


- (c) $\text{CH}_2 = \text{C} = \text{CH} - \text{NH}_2$
- (d) All of these

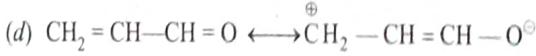
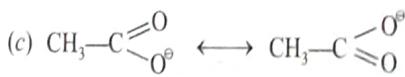
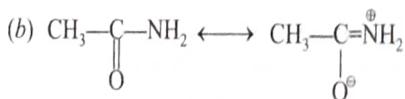
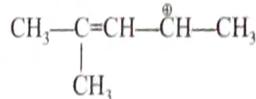
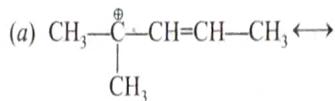
8. Which of the following is not a pair of resonating structures?



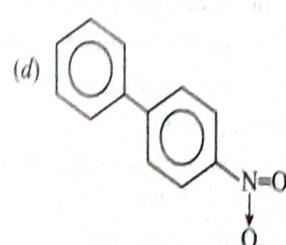
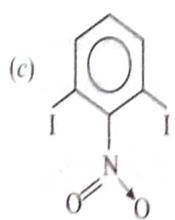
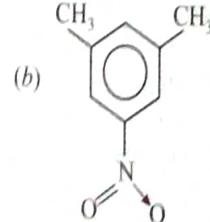
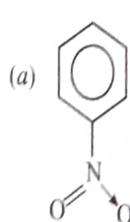
9. Which of the following is not a permissible resonating structure?



10. Which of the following resonating structure contributes equally to the resonance hybrid?



11. In which of the following molecules, $-\text{NO}_2$ group is not coplanar with phenyl ring?



33. Correct arrangement of the following nucleophiles in the order of their nucleophilic strength is

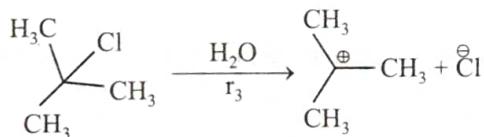
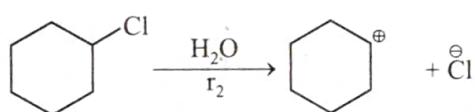
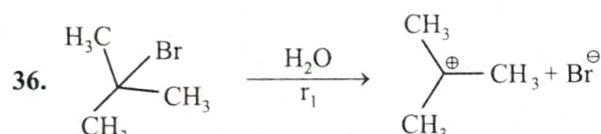
- (a) $\text{C}_6\text{H}_5\text{O}^- < \text{CH}_3\text{O}^- < \text{CH}_3\text{COO}^- < \text{OH}^-$
- (b) $\text{CH}_3\text{COO}^- < \text{C}_6\text{H}_5\text{O}^- < \text{CH}_3\text{O}^- < \text{OH}^-$
- (c) $\text{C}_6\text{H}_5\text{O}^- < \text{CH}_3\text{COO}^- < \text{CH}_3\text{O}^- < \text{OH}^-$
- (d) $\text{CH}_3\text{COO}^- < \text{C}_6\text{H}_5\text{O}^- < \text{OH}^- < \text{CH}_3\text{O}^-$

34. Decreasing order of relative nucleophilicity of the following nucleophiles in protic solvent is

- $\text{SH}, \text{AcO}^\ominus, \text{PhO}^\ominus, \text{OH}, \text{H}_2\text{O}$
- (a) $\text{SH}^\ominus > \text{OH}^\ominus > \text{H}_2\text{O} > \text{AcO}^\ominus > \text{PhO}^\ominus$
 - (b) $\text{SH}^\ominus > \text{OH}^\ominus > \text{PhO}^\ominus > \text{AcO}^\ominus > \text{H}_2\text{O}^\ominus$
 - (c) $\text{SH}^\ominus > \text{PhO}^\ominus > \text{OH}^\ominus > \text{H}_2\text{O} > \text{AcO}^\ominus$
 - (d) $\text{OH}^\ominus > \text{SH}^\ominus > \text{PhO}^\ominus > \text{AcO}^\ominus > \text{H}_2\text{O}^\ominus$

35. The correct order of leaving ability is:

- (a) $\text{OH}^\ominus > \text{H}_2\text{O}$
- (b) $\text{OH}^\ominus > \text{SH}^\ominus$
- (c) $\text{O}^\ominus > \text{C}_2\text{H}_5\text{O}^\ominus$
- (d) $\text{Cl}^\ominus > \text{I}^\ominus$

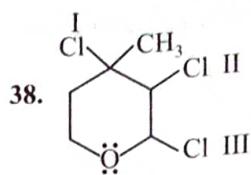


The rates r_1, r_2 and r_3 are in the order:

- (a) $r_1 = r_3 > r_2$
- (b) $r_3 > r_1 > r_2$
- (c) $r_1 > r_3 > r_2$
- (d) $r_2 > r_1 > r_3$

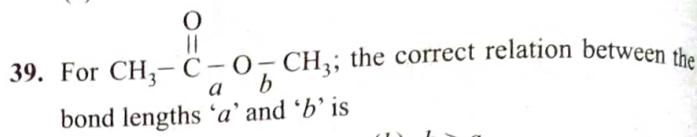
37. The increasing order of reactivity of the following isomeric halides with AgNO_3 ($\text{H}_2\text{O} + \text{alcohol}$) is:

- (I) $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{Cl}$
 - (II) $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CH}(\text{Cl})-\text{CH}_3$
 - (III) $\text{C}_6\text{H}_5-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}}=\text{CH}-\text{CH}_2-\text{CH}_3$
 - (IV) $\text{C}_6\text{H}_5-\overset{\text{C}_6\text{H}_5}{\underset{\text{Cl}}{\text{C}}}=\text{CH}-\text{CH}_2$
- (a) III < IV < II < I
 - (b) I < III < IV < II
 - (c) III < I < II < IV
 - (d) I < II < IV < III



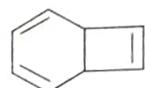
The rate of reaction with AgNO_3 will be:

- (a) I > II > III
- (b) III > I > II
- (c) III > II > I
- (d) I > III > II



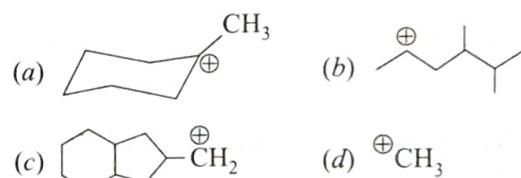
- (a) $a = b$
- (b) $b > a$
- (c) $b < a$
- (d) Impossible to predict

39. The number of $\text{sp}^2 - \text{sp}^2$ sigma bonds in the compound given below is

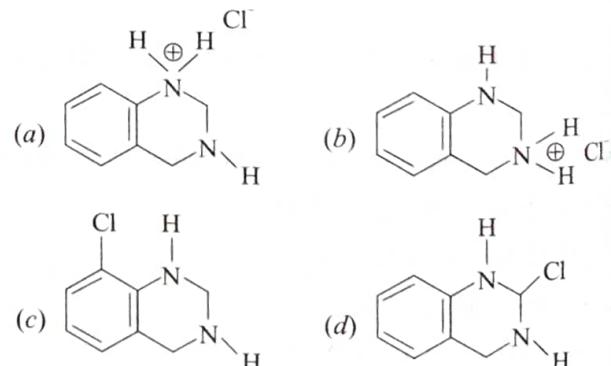
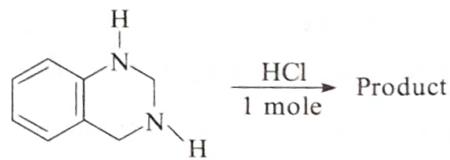


- (a) 1
- (b) 3
- (c) 4
- (d) 5

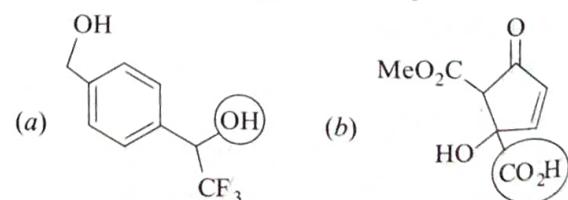
40. Most stable carbocation among the following is

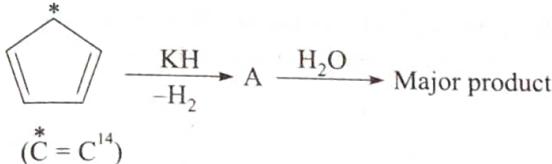
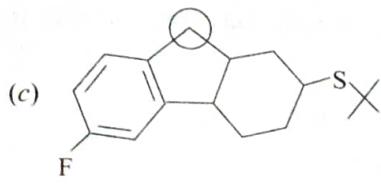


41. Which is the major product of the following reaction?



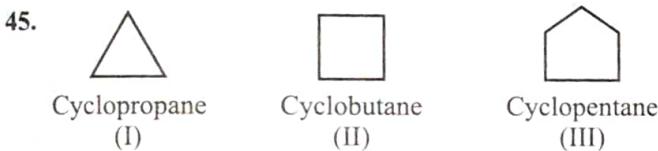
43. Circle represent most acidic hydrogens in these molecules. Which of the following is correct representation?





Major products of the reaction is/are

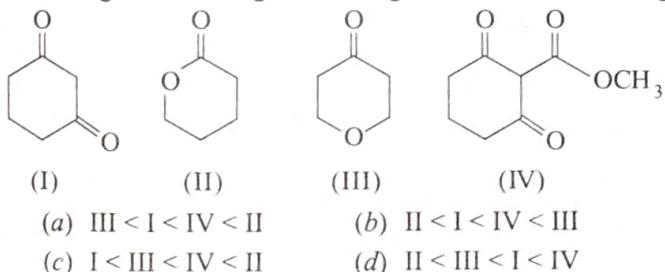
- (a)
(b)
(c)
(d) Both (b) and (c)



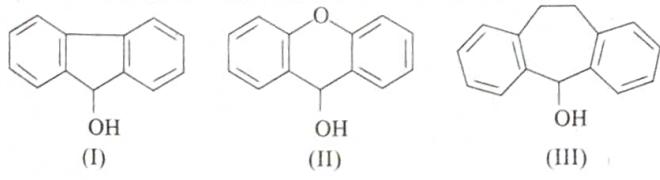
The correct order of heats of combustion of above compounds is

- (a) I > II > III (b) II > I > III
(c) III > II > I (d) III > I > II

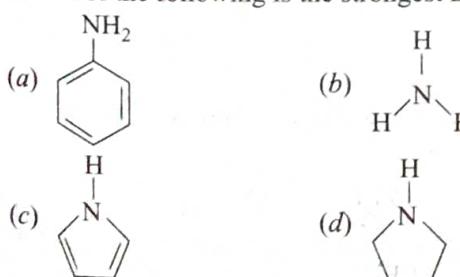
46. Arrange the following in increasing order of their acidic strength.



47. Arrange the following alcohols in decreasing order of the ease of the ionization under acidic conditions.



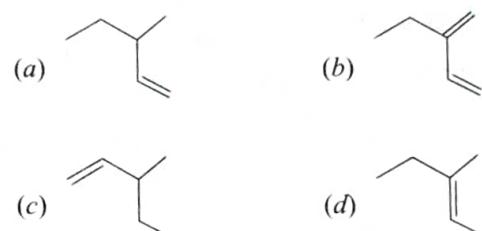
48. Which of the following is the strongest Bronsted base?



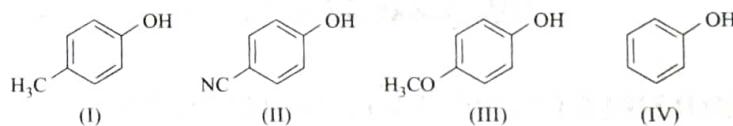
49. Some pairs of ions are given below. In which pair, first ion is more stable than second?

- (a) $\text{CH}_3-\overset{\oplus}{\text{CH}}-\text{CH}_3$ and $\text{CH}_3-\overset{\oplus}{\text{CH}}-\text{OCH}_3$
(b) $\text{CH}_3-\overset{\oplus}{\text{CH}_2}-\text{CH}-\text{CH}_3$ and $\text{CH}_2=\overset{\oplus}{\text{CH}}-\text{CH}_2-\overset{\oplus}{\text{CH}_2}$
(c)
and
(d) $\overset{\oplus}{\text{CH}_3}-\text{CH}-\text{CH}_3$ and $\overset{\oplus}{\text{CH}_3}-\text{N}-\text{CH}_3$
 $\text{CH}_3-\overset{\oplus}{\text{C}}-\text{CH}_3$ and $\text{CH}_3-\overset{\oplus}{\text{C}}-\text{CH}_3$

50. Which of the following alkenes is the most stable?

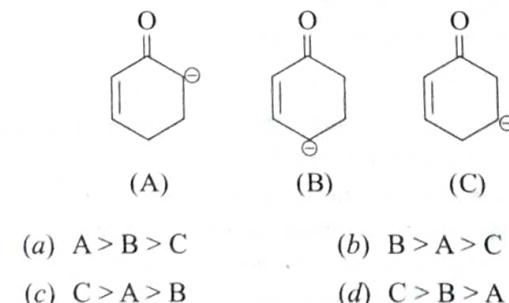


51. Increasing order of acidic strength of given compounds is

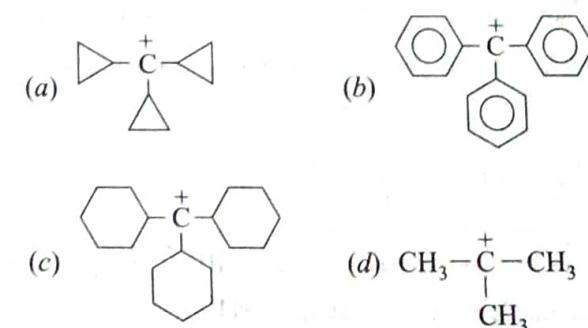


- (a) III < I < IV < II (b) II < I < IV < III
(c) I < III < IV < II (d) I < III < II < IV

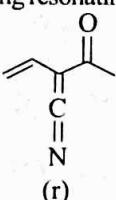
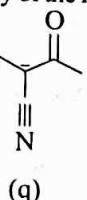
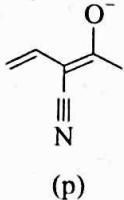
52. Compare basic strengths of the below compounds:



53. Which one among the following carbocations has the longest half-life?



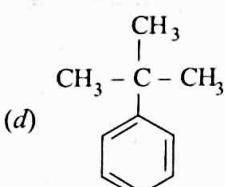
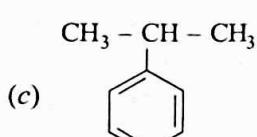
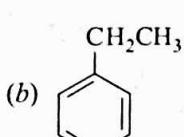
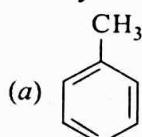
54. Compare relative stability of the following resonating structures.



- (a) $p > q > r$
(c) $q > r > p$

- (b) $q > p > r$
(d) $p > r > q$

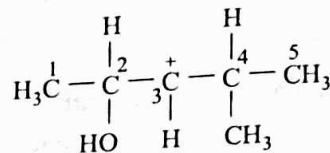
55. Which of the following alkyl benzene has maximum electron density?



56. Among the following compounds, the most acidic is

- (a) p-nitrophenol
(b) p-hydroxybenzoic acid
(c) o-hydroxybenzoic acid
(d) p-tolueic acid

57. In the following carbocation, H/CH₃ that is most likely to migrate to the positively charged carbon is



- (a) CH₃ at C - 4
(b) H at C - 4
(c) CH₃ at C - 2
(d) H at C - 2

Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

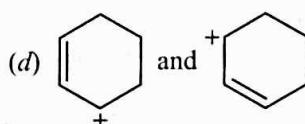
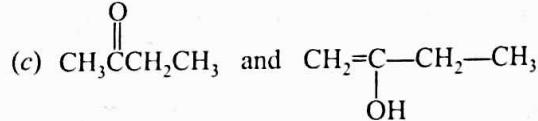
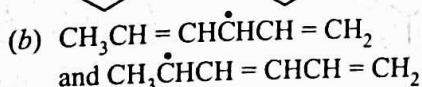
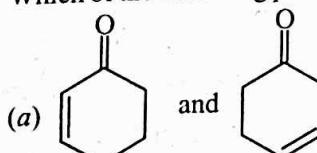
1. Which of the following statement/s is/are correct for the inductive effect?

- (a) It is a permanent effect.
(b) It transmits through sigma electrons.
(c) It is represented by \longleftrightarrow .
(d) It is represented by \longrightarrow or \longleftarrow .

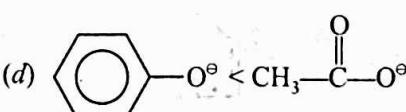
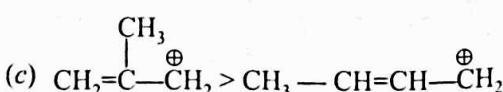
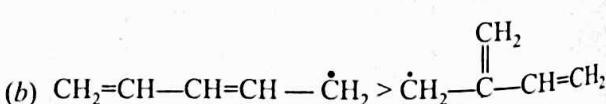
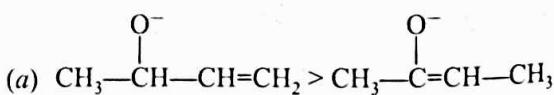
2. Which of the following statements is/are correct?

- (a) The energy of resonance hybrid is always less than that of any resonating structure.
(b) The resonance energy is the difference between the enthalpies of formation of the molecule and the resonating structure having maximum energy.
(c) The resonance structures are hypothetical structure and they do not represent any real molecule.
(d) In delocalized structure of benzene, the π -charge cloud is spread equally above and below the plane of molecule.

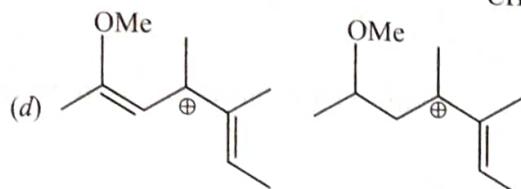
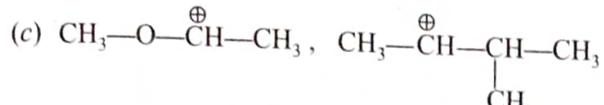
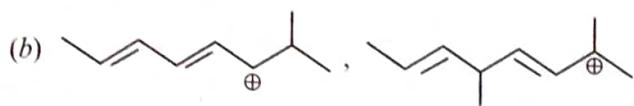
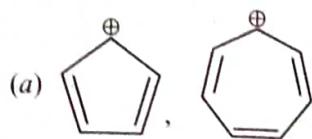
3. Which of the following pair represent resonating structures?



4. Which of the following is/are correct for the stability of structures?



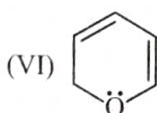
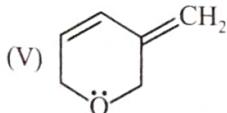
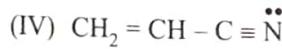
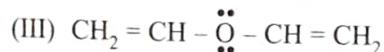
5. In which of the following, first carbocation is more stable than second one?



6. Identify electron - donating groups in resonance among the following:

- | | |
|-------------------------|-------------------------|
| (I) $-\text{CONH}_2$ | (II) $-\text{NO}_2$ |
| (III) $-\text{OCOCH}_3$ | (IV) $-\text{COOCH}_3$ |
| (V) $-\text{CHO}$ | (VI) $-\text{NHCOCH}_3$ |
| (a) (III), (VI) | (b) (II), (III), (V) |
| (c) (III), (IV), (V) | (d) (I), (II), (III) |

7. In which of the following, lone-pair indicated is not involved in resonance?



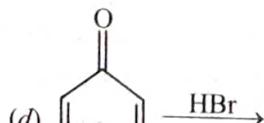
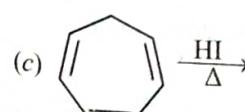
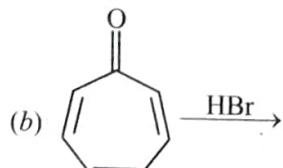
- (a) (III), (VI)

- (b) (II), (IV), (V)

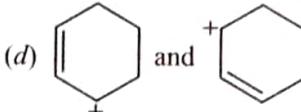
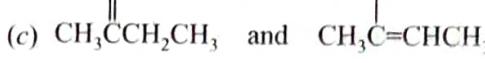
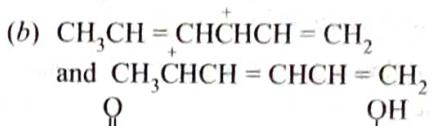
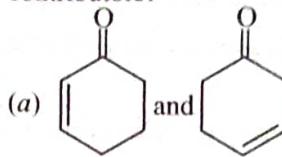
- (c) (III), (IV), (V)

- (d) (I), (II), (III)

8. Which of the following reactions give aromatic compound?



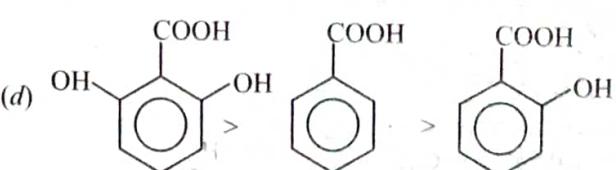
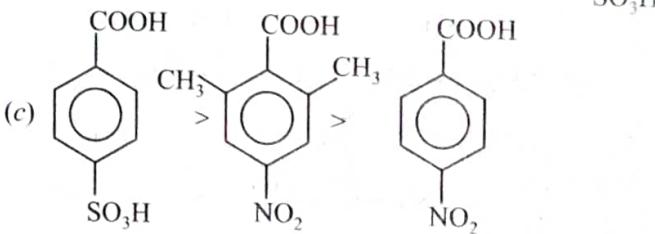
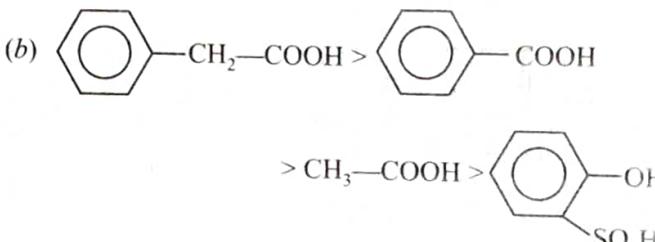
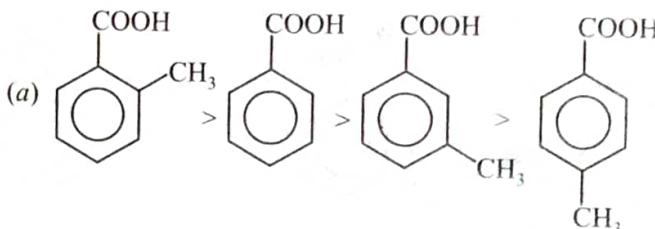
9. Which of the following pairs of structures are resonance contributors?



10. Select the correct statement/s among the following:

- (a) All canonical forms do not always contribute equally to the resonance hybrid.
 (b) In ethanamine and ethenamine, nitrogen is sp^3 hybridised
 (c) All 'C—O' bond length in carbonate dianion are equal.
 (d) $\text{CH}_2 = \text{C} = \text{O}$ does not exhibit resonance because it is not a conjugated system.

11. Which of the following is/are correct order of K_a of the given compounds?



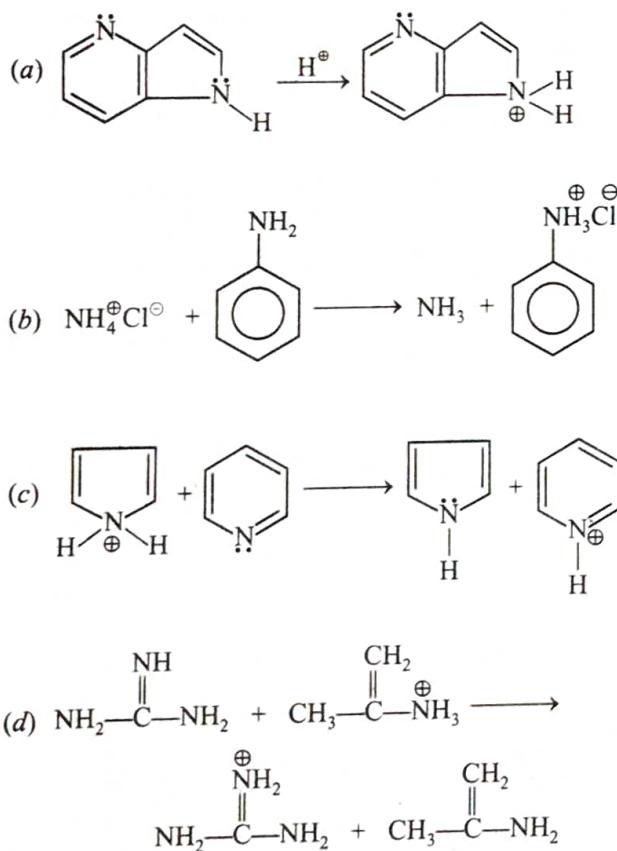
12. Select the correct statement/s among the following:

- (a) Carbonic acid is weaker acid than acetic acid.
- (b) The boiling points of acids are higher than corresponding alcohols.
- (c) Chloroacetic acid is stronger acid than acetic acid.
- (d) Phenol is more acidic than ethanol.

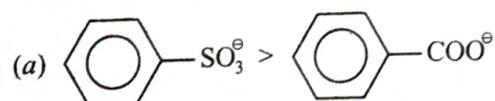
13. In which of the following pairs, the first one is the stronger base than second?

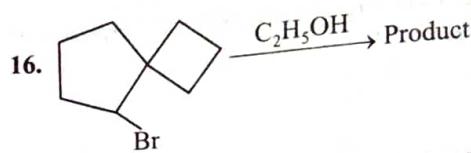
- (a) $\text{CH}_3\text{COO}^\ominus, \text{HCOO}^\ominus$
- (b) $\text{HO}^\ominus, \text{NH}_2^\ominus$
- (c) $\text{CH}_2=\overset{\ominus}{\text{C}}\text{H}, \text{H}-\text{C}\equiv\overset{\ominus}{\text{C}}$
- (d) $\text{CH}_3\text{NH}_2, \text{CH}_3\text{OH}$

14. Which of the following reactions are feasible?

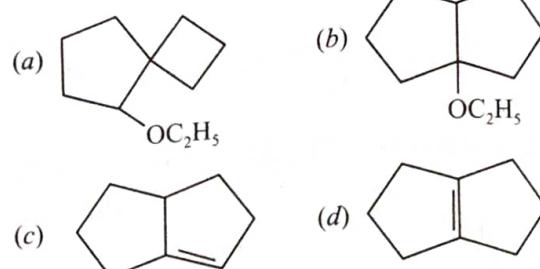


15. The correct order of leaving group ability is/are:

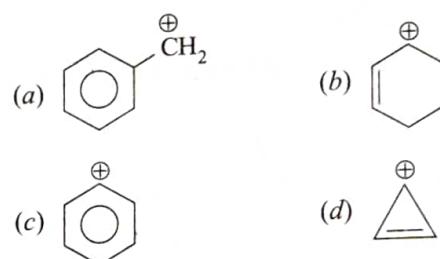
- (a) 
- (b) $\text{CF}_3\text{SO}_3^\ominus > \text{CCl}_3\text{SO}_3^\ominus$
- (c) $\text{CN}^\ominus > \text{I}^\ominus$
- (d) $\text{NH}_2^\ominus > \text{OH}^\ominus$



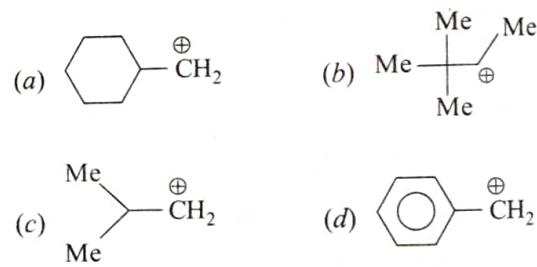
Which of the following products are possible?



17. Which of the following carbocations is/are resonance stabilized?



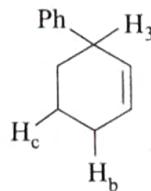
18. In which of the following carbocation, ΔG decreases if there is some intramolecular rearrangement?



19. Select the correct statements among the following:

- (a) Singlet: CCl_2 is more stable than singlet: CF_2 .
- (b) Triplet: CH_2 is more stable than singlet: CH_2 .
- (c) Singlet: CH_2 has planar geometry.
- (d) The electron affinity of CH_3 free radical is less than its ionization energy.

20. Select the correct statements about the given compound:



- (a) H_a is abstracted by bromine radical rapidly.
- (b) H_b is abstracted by bromine radical rapidly.
- (c) H_b is more acidic than H_c .
- (d) H_b is less acidic than H_c .

36. Match the column:

Column-I		Column-II	
A.		p.	Non aromatic
B.		q.	Anti aromatic
C.		r.	Resonance
D.		s.	Aromatic

- (a) A → p; B → p,r; C → r,s; D → r
- (b) A → p,r; B → r; C → r,s; D → p,r
- (c) A → p,r; B → p,r; C → r,s; D → p,r
- (d) A → p,r; B → p,r; C → s; D → p

37. Match the column:

Column-I		Column-II	
A.	$\text{CH}_3\text{OCH}_2^+$ or $\text{CH}_2\text{NHCH}_2^+$	p.	First is more stable than second
B.	$\text{CH}_3\text{OCH}_2^+\text{CH}_2$ or $\text{CH}_3\text{OCH}_2^+$	q.	Second is more stable than first
C.		r.	Not resonating structure of each other
D.		s.	Resonance is present in both carbocations

- (a) A → q,r,s; B → q,r; C → p,r; D → p,r
- (b) A → q,s; B → q,r; C → p,r; D → p
- (c) A → q,r,s; B → q; C → p,r; D → p,r
- (d) A → q,r,s; B → q,r; C → r; D → r

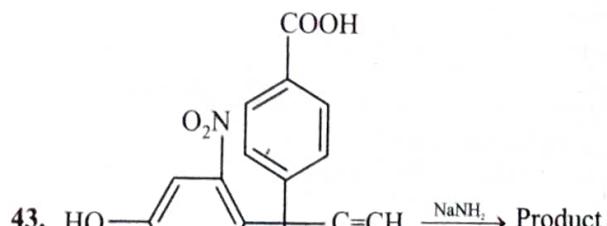
38. Match the pKa values with members of List I

Column-I (Compounds)		Column-II (pKa)	
A.		p.	-6.4
B.		q.	-12
C.		r.	4.60
D.		s.	-7

- (a) A → p; B → s; C → q; D → r
- (b) A → r; B → s; C → p; D → q
- (c) A → r; B → s; C → q; D → p
- (d) A → s; B → q; C → r; D → p

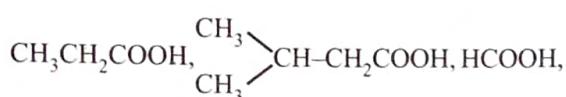
NUMERICAL TYPE QUESTIONS

39. How many of the given compounds are electrophiles?
 CO_2 , SnCl_2 , FeCl_3 , NH_4^+ , BF_3
40. Out of following, how many of these species are electrophiles?
 NO_2^+ , NH_4^+ , : CCl_2 , AlCl_3 , CCl_3^- , SO_3^-
41. How many hyperconjugative structures are possible in $(\text{CH}_3)_2\overset{+}{\text{CH}}$?
42. How many conjugated electrons are there in cyclopentadienyl anion?

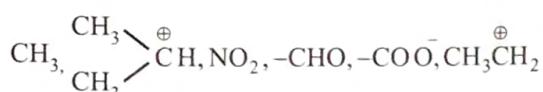


How many mole of NaNH_2 react in above reaction?

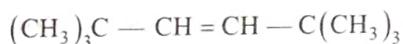
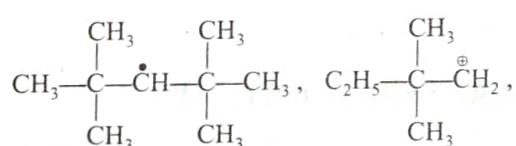
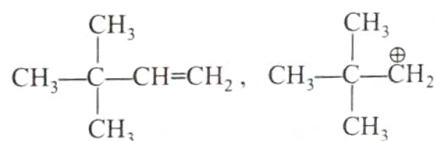
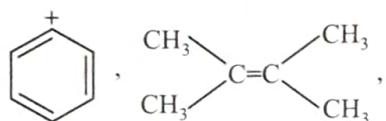
44. How many among the following are stronger acid than CH_3COOH ?



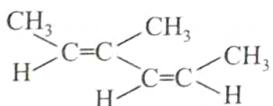
45. How many groups among the following show -I effect?



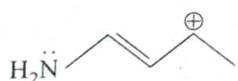
46. How many of the following compounds do not show hyperconjugation?



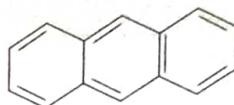
47. The number of hyperconjugating structure for the given compound are:



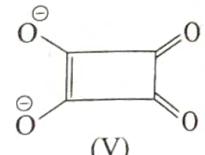
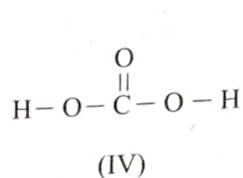
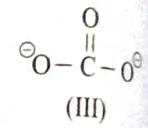
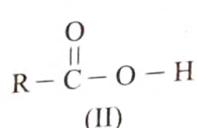
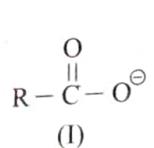
48. How many resonance structures can be drawn for the following molecule?



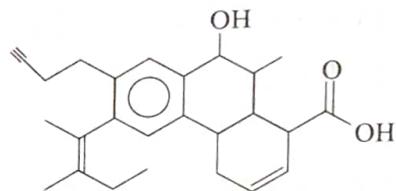
49. How many uncharged resonance structures are there in anthracene?



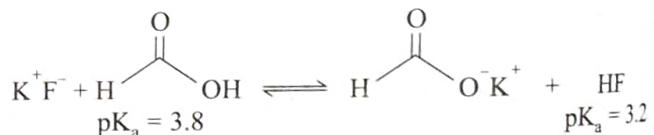
50. The total number of compounds which contain equal (C-O) bound length are



51. How many degree of unsaturation are there in the following compounds?



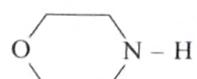
52. Consider the following reaction involving two acids shown below: Formic acid and HF.



How many of the following statements about this reaction are true?

- (a) Formic acid is the strongest Bronsted acid in the reaction.
- (b) HF is the strongest Bronsted acid in the reaction.
- (c) KF is the strongest Bronsted base in the reaction.
- (d) KO_2CH is the strongest Bronsted base in the reaction.
- (e) The equilibrium favours the reactants.
- (f) The equilibrium favours the products.
- (g) Formic acid has a weaker conjugate base.
- (h) HF has a weaker conjugate base.

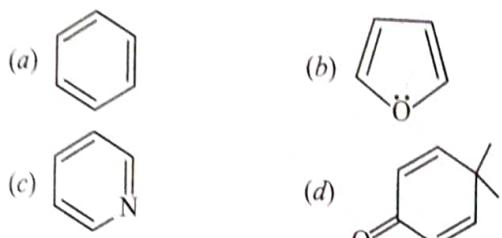
53. The total number of lone pair of electrons in the given molecule is



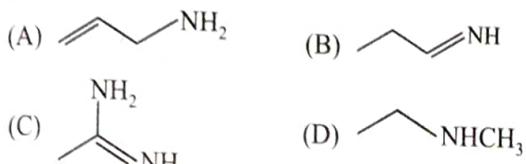
Exercise-4 (Past Year Questions)

JEE MAIN

1. Which of the following molecule is least resonance stabilized? (2017)



2. The increasing order of basicity of the following compounds is: (2018)

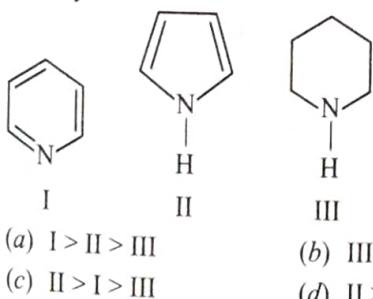


- (a) (B) < (A) < (C) < (D) (b) (B) < (A) < (D) < (C)
(c) (D) < (B) < (A) < (C) (d) (A) < (B) < (C) < (D)

3. The correct order for acid strength of compounds: CH ≡ CH, CH₃ – C ≡ CH, CH₂ = CH₂ is as follows: (2019)

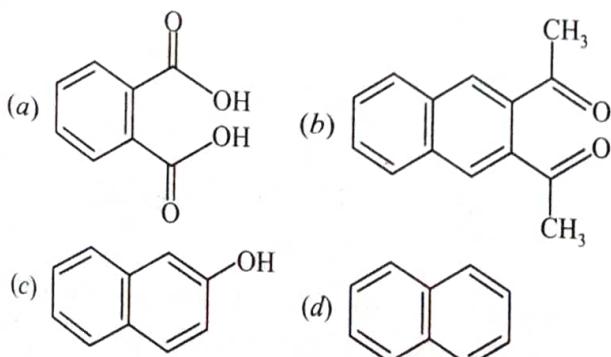
- (a) CH ≡ CH > CH₂ = CH₂ > CH₃ – C ≡ CH
(b) CH₃ – C ≡ CH > CH ≡ CH > CH₂ = CH₂
(c) CH₃ – C ≡ CH > CH₂ = CH₂ > HC ≡ CH
(d) HC ≡ CH > CH₃ – C ≡ CH > CH₂ = CH₂

4. Arrange the following amine in the decreasing order of basicity: (2019)

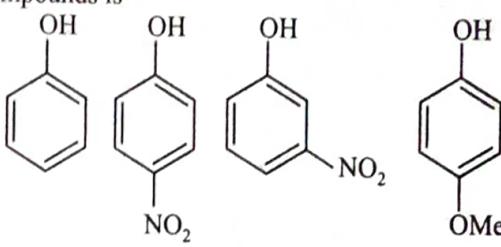


- (a) I > II > III (b) III > I > II
(c) II > I > III (d) II > III > I

5. Which of the following has lowest freezing point? (2019)



6. The increasing order of pKa values of the following compounds is (2019)

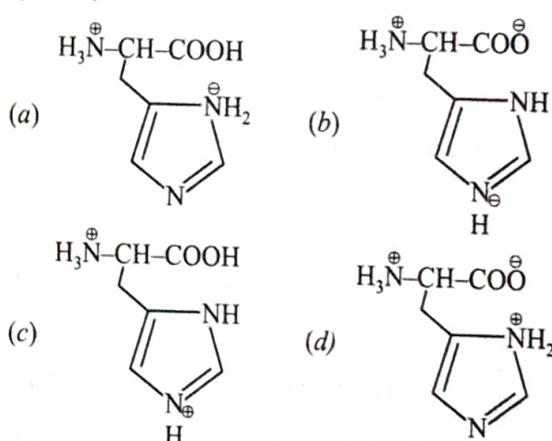


- (a) C < B < A < D (b) B < C < D < A
(c) D < A < C < B (d) B < C < A < D

7. Which amongst the following is the strongest acid? (2019)



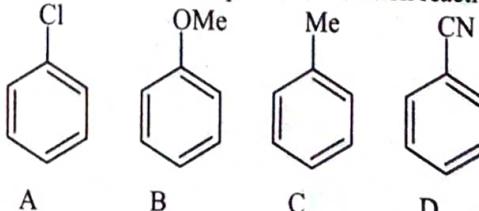
8. The correct structure of histidine in a strongly acidic solution (pH = 2) is: (2019)



9. The correct decreasing order for acidic strength is (2019)

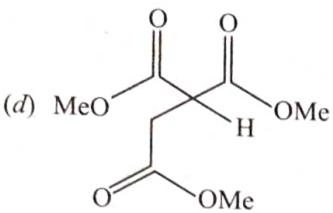
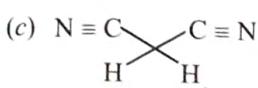
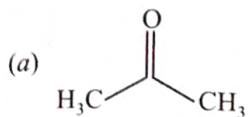
- (a) NO₂CH₂COOH > FCH₂COOH > CNCH₂COOH > ClCH₂COOH
(b) FCH₂COOH > NCCH₂COOH > NO₂CH₂COOH > ClCH₂COOH
(c) CNCH₂COOH > O₂NCH₂COOH > FCH₂COOH > ClCH₂COOH
(d) NO₂CH₂COOH > NCCH₂COOH > FCH₂COOH > ClCH₂COOH

10. The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is: (2019)

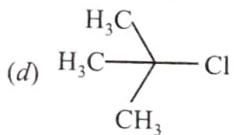
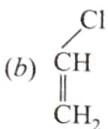
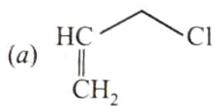


- (a) D < B < A < C (b) A < B < C < D
(c) D < A < C < B (d) B < C < A < D

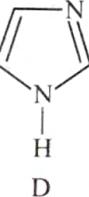
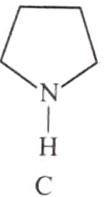
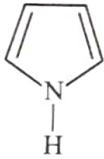
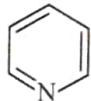
21. Which one of the following compounds possesses the most acidic hydrogen? (2020)



22. Among the following compounds, which one has the shortest C—Cl bond? (2020)

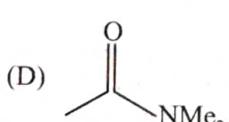
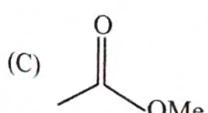
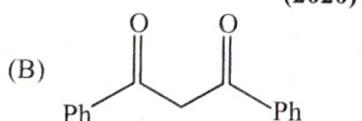
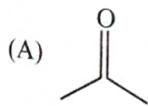


23. The increasing order of basicity of the following compounds is (2020)



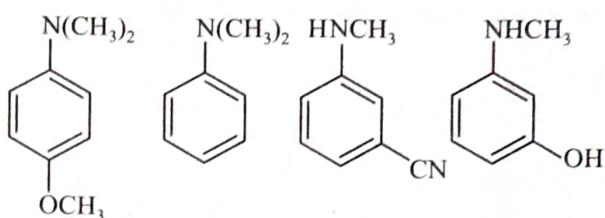
- (a) (B) < (A) < (D) < (C)
 (b) (D) < (A) < (B) < (C)
 (c) (B) < (A) < (C) < (D)
 (d) (A) < (B) < (C) < (D)

24. The increasing order of the acidity of the α -hydrogen of the following compounds is (2020)



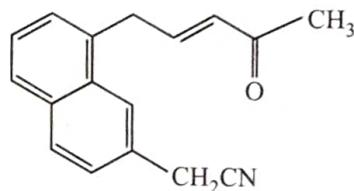
- (a) (C) < (A) < (B) < (D) (b) (B) < (C) < (A) < (D)
 (c) (A) < (C) < (D) < (B) (d) (D) < (C) < (A) < (B)

25. The increasing order of pK_b values of the following compounds is (2020)



- (a) I < II < IV < III (b) I < II < III < IV
 (c) II < I < III < IV (d) II < IV < III < I

26. Number of electrophilic centres in the given compound is _____ (2022)



27. The correct order of nucleophilicity is

- (a) $\text{F}^- > \text{OH}^-$ (b) $\text{H}_2\ddot{\text{O}} > \text{OH}^-$
 (c) $\text{R}\ddot{\text{O}}\text{H} > \text{RO}^-$ (d) $\text{NH}_2^- > \text{NH}_3$

28. Match Column-I with Column-II (2022)

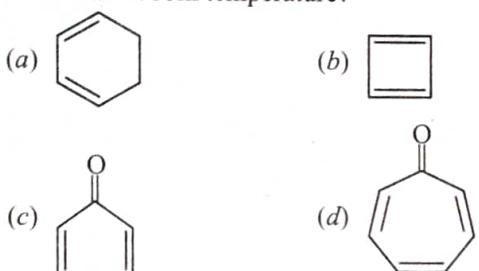
	Column-I		Column-II
A.		p.	Spiro compound
B.		q.	Aromatic compound
C.		r.	Non-planar heterocyclic compound
D.		s.	Bicyclo compound

Choose the correct answer from the options given below:

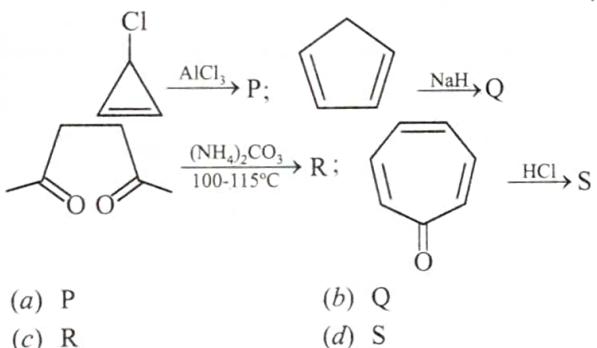
- (a) A \rightarrow q; B \rightarrow p; C \rightarrow s; D \rightarrow r
 (b) A \rightarrow s; B \rightarrow r; C \rightarrow p; D \rightarrow q
 (c) A \rightarrow r; B \rightarrow s; C \rightarrow p; D \rightarrow q
 (d) A \rightarrow s; B \rightarrow r; C \rightarrow q; D \rightarrow p

JEE ADVANCED

29. Which of the following molecules in pure form, is (are) **unstable** at room temperature? (2012)



30. Among P, Q, R and S, the aromatic compound(s) is/are (2013)



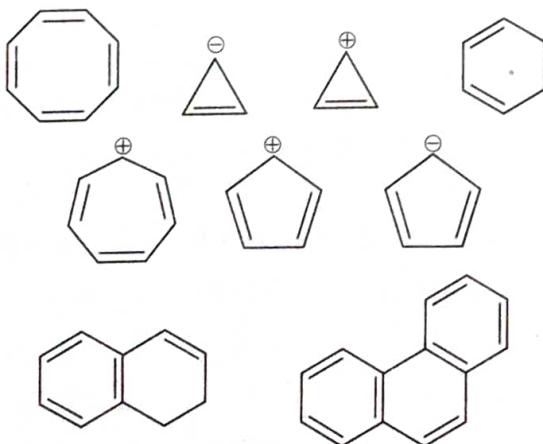
31. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to

- (a) $\sigma \rightarrow p$ (empty) and $\sigma \rightarrow \pi^*$ electron delocalisations
 - (b) $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ electron delocalisations
 - (c) $\sigma \rightarrow p$ (filled) and $\sigma \rightarrow \pi$ electron delocalisations
 - (d) p (filled) σ^* and $\sigma \rightarrow \pi^*$ electron delocalisations

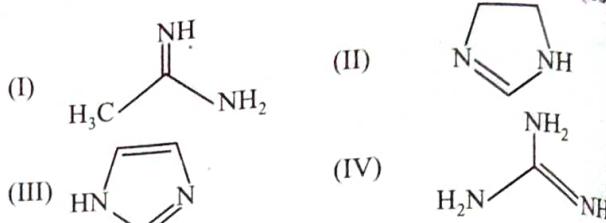
32. The correct combination of names for isomeric alcohols with molecular formula $C_4H_{10}O$ is/are (2014)

- (a) tert-butanol and 2-methylpropan-2-ol
 - (b) tert-butanol and 1, 1-dimethylethan-1-ol
 - (c) n-butanol and butan-1-ol
 - (d) iso-butyl alcohol and 2-methylpropan-1-ol

33. Among the following, the number of aromatic compound(s) is/are: (2017)

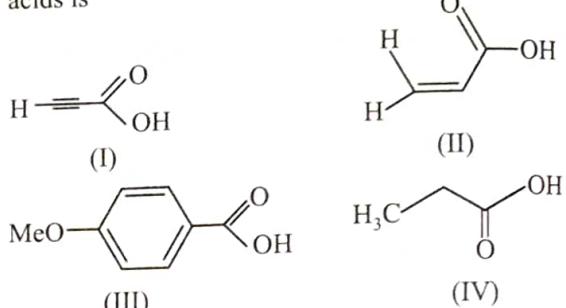


34. The order of basicity among the following compounds (2012)



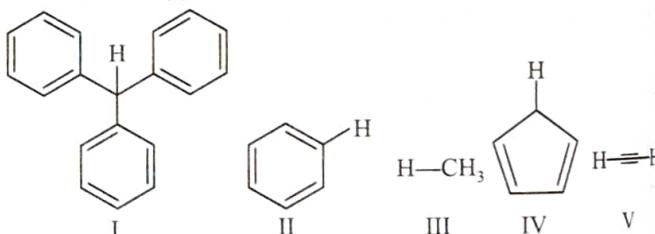
- (a) II > I > IV > III (b) I > IV > III > II
 (c) IV > II > III > I (d) IV > I > II > III

35. The correct order of acid strength of the following carboxylic acids is $\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H}$ (2019)



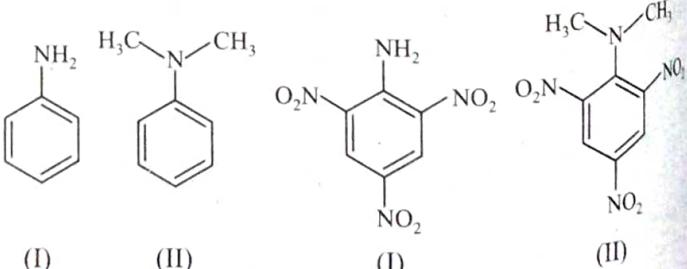
- (a) I > III > II > IV (b) III > II > I > IV
 (c) II > I > IV > III (d) I > II > III > IV

36. With respect to the compounds I-V, choose the correct statement(s). (2020)



- (a) The acidity of compound I is due to delocalization in the conjugate base.
 - (b) The conjugate base of compound IV is aromatic.
 - (c) Compound II becomes more acidic, when it has a -NO_2 substituent.
 - (d) The acidity of compounds follows the order:
 $I > IV > V > II > III$

37. Consider the following four compounds I, II, III, and IV
(2020)



Choose the correct statement(s).

- (a) The order of basicity is II > I > III > IV.
 (b) The magnitude of pK_b difference between I and II is more than that between III and IV.
 (c) Resonance effect is more in III than in IV.
 (d) Steric effect makes compound IV more basic than III.

ANSWER KEY

CONCEPT APPLICATION

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (d) | 2. (b) | 3. (d) | 4. (a) | 5. (d) | 6. (a) | 7. (a) | 8. (c) | 9. (b) | 10. (d) |
| 11. (d) | 12. (b) | 13. (d) | 14. (d) | 15. (b) | 16. (c) | 17. (c) | 18. (b) | 19. (d) | 20. (c) |
| 21. (a) | 22. (a) | 23. (d) | 24. (a) | 25. (c) | | | | | |

EXERCISE-1 (TOPICWISE)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (c) | 3. (d) | 4. (c) | 5. (c) | 6. (c) | 7. (a) | 8. (d) | 9. (c) | 10. (c) |
| 11. (c) | 12. (d) | 13. (b) | 14. (a) | 15. (b) | 16. (a) | 17. (c) | 18. (b) | 19. (c) | 20. (b) |
| 21. (a) | 22. (b) | 23. (c) | 24. (d) | 25. (d) | 26. (a) | 27. (c) | 28. (a) | 29. (c) | 30. (a) |
| 31. (d) | 32. (c) | 33. (b) | 34. (d) | 35. (d) | 36. (a) | 37. (b) | 38. (b) | 39. (b) | 40. (d) |
| 41. (d) | 42. (d) | 43. (d) | 44. (a) | 45. (b) | 46. (b) | 47. (d) | 48. (d) | 49. (a) | 50. (d) |
| 51. (b) | 52. (c) | 53. (c) | 54. (c) | 55. (b) | 56. (c) | 57. (d) | 58. (c) | 59. (c) | 60. (a) |
| 61. (a) | 62. (a) | 63. (a) | 64. (a) | 65. (a) | | | | | |

EXERCISE-2 (LEARNING PLUS)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (d) | 3. (d) | 4. (b) | 5. (d) | 6. (b) | 7. (d) | 8. (b) | 9. (c) | 10. (c) |
| 11. (c) | 12. (d) | 13. (c) | 14. (a) | 15. (d) | 16. (a) | 17. (d) | 18. (d) | 19. (b) | 20. (b) |
| 21. (c) | 22. (b) | 23. (d) | 24. (a) | 25. (a) | 26. (b) | 27. (a) | 28. (c) | 29. (b) | 30. (a) |
| 31. (a) | 32. (a) | 33. (d) | 34. (b) | 35. (c) | 36. (c) | 37. (c) | 38. (b) | 39. (b) | 40. (c) |
| 41. (a) | 42. (b) | 43. (d) | 44. (d) | 45. (c) | 46. (d) | 47. (c) | 48. (d) | 49. (b) | 50. (d) |

EXERCISE-3 (JEE ADVANCED LEVEL)

- | | | | | | | | | | |
|------------|---------------|-----------|-------------|-------------|-------------|---------------|-------------|-------------|-------------|
| 1. (a,b,d) | 2. (a,c,d) | 3. (b,d) | 4. (b,d) | 5. (b,c,d) | 6. (a) | 7. (b) | 8. (a,b,c) | 9. (b,d) | 10. (a,c) |
| 11. (a,c) | 12. (a,b,c,d) | | 13. (a,c,d) | 14. (c,d) | 15. (a,b) | 16. (a,b,c,d) | 17. (a,b,d) | 18. (a,b,c) | 19. (b,c,d) |
| 20. (a,c) | 21. (b,c,d) | 22. (a,b) | 23. (a,b,c) | 24. (a,b,d) | 25. (a,c,d) | 26. (d) | 27. (c) | 28. (d) | 29. (a) |
| 30. (c) | 31. (d) | 32. (d) | 33. (d) | 34. (a) | 35. (b) | 36. (c) | 37. (a) | 38. (d) | 39. [4] |
| 40. [4] | 41. [6] | 42. [6] | 43. [4] | 44. [2] | 45. [3] | 46. [6] | 47. [9] | 48. [3] | 49. [4] |
| 50. [3] | 51. [13] | 52. [4] | 53. [3] | | | | | | |

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (d) | 2. (b) | 3. (d) | 4. (b) | 5. (d) | 6. (d) | 7. (c) | 8. (c) | 9. (d) | 10. (c) |
| 11. (b) | 12. (a) | 13. (c) | 14. (a) | 15. (c) | 16. (c) | 17. (a) | 18. (c) | 19. (b) | 20. (a) |
| 21. (d) | 22. (b) | 23. (a) | 24. (d) | 25. (a) | 26. [3] | 27. (d) | 28. (c) | | |

JEE Advanced

- | | | | | | | | | | |
|-----------|---------------|--|---------|-------------|---------|---------|---------|-------------|-----------|
| 29. (b,c) | 30. (a,b,c,d) | | 31. (a) | 32. (a,c,d) | 33. [5] | 34. (d) | 35. (d) | 36. (a,b,c) | 37. (c,d) |
|-----------|---------------|--|---------|-------------|---------|---------|---------|-------------|-----------|

CHAPTER

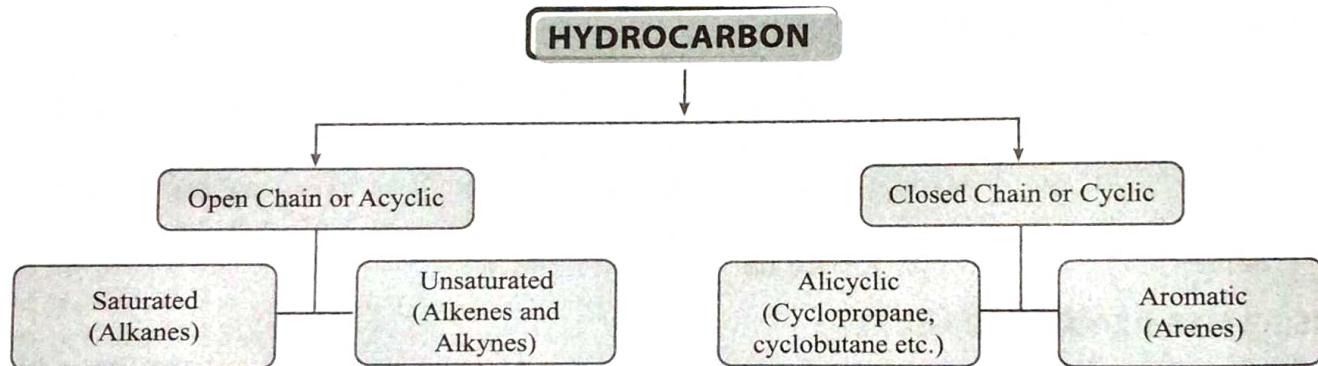
15

Hydrocarbon

ALKANES

HYDROCARBON

- (i) Organic compounds of carbon and hydrogen only are called **hydrocarbon**.
- (ii) Petroleum and coal are main source of hydrocarbon.
- (iii) Hydrocarbons are broadly classified as :



Alkanes and Arenes are quite stable compound and gives substitution reaction while alkenes and alkynes are more reactive and give addition reactions.

Hydrocarbon	Functional group	Example
Alkanes	none	$\text{CH}_3-\text{CH}_2-\text{CH}_3$, propane
Alkenes	$>\text{C}=\text{C}<$	$\text{CH}_2 = \text{CH}-\text{CH}_3$, propene
Alkynes	$-\text{C} \equiv \text{C}-$	$\text{H}-\text{C} \equiv \text{C}-\text{CH}_3$, propyne
Aromatics	benzene ring 	CH_2CH_3 ethylbenzene

ALKANES

Introduction

- (i) The alkanes or the paraffins are the saturated hydrocarbons. Many occur naturally, and the chief source of the alkanes is mineral oil or petroleum, which occurs in many parts of the world.
- (ii) These are also called as 'Paraffins' (Parum + Affinis i.e. less reactive).
- (iii) General formula is $\text{C}_n\text{H}_{2n+2}$.
- (iv) Hybridisation state of carbon is sp^3 .
- (v) Geometry of carbon is tetrahedral.
- (vi) Bond angle is $109^\circ 28'$.
- (vii) Number of bond angle ($109^\circ 28'$) in methane are six, while in ethane are twelve.
- (viii) C – C bond length is 1.54 \AA while C – H bond length is 1.11 \AA .

(ix) Isomerism : Alkanes show chain and position isomerism.

Examples:

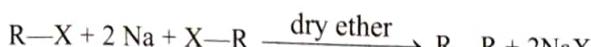
Methane, Ethane and Propane – No isomers.

Alkanes with at least 4 carbon atoms show isomerism.

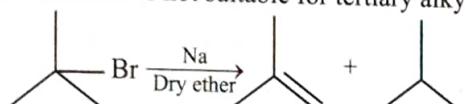
Butane	-	2 isomers
Pentane	-	3 isomers
Hexane	-	5 isomers
Heptane	-	9 isomers

PREPARATION OF ALKANES

Wurtz's reaction: When alkyl halide reacts with Sodium in presence of dry ether then we get higher alkane. Mechanism of the reaction is based on ionic and free radical both.

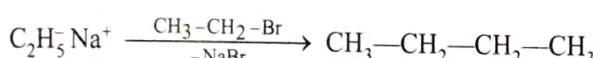
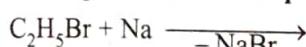


Note: Current reaction is not suitable for tertiary alkyl halides

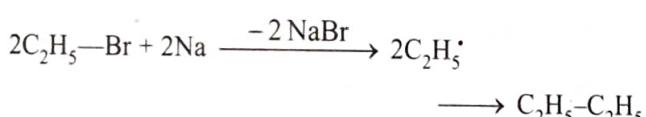


Mechanism: Two mechanisms has been suggested for Wurtz's reaction.

(i) Via organometallic compound

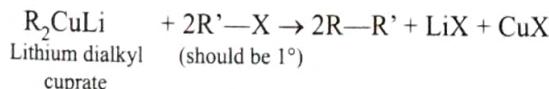


(ii) Via free radical



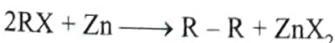
Reactivity of the compound \propto Stability of the free radical
 $3^\circ > 2^\circ > 1^\circ$

(iii) Corey-House Synthesis



This method is better than Wurtz and can be used for preparing symmetrical as well as unsymmetrical alkanes (having an odd number of carbon atoms).

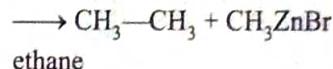
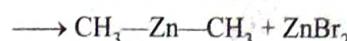
Frankland's reaction/Method: If alkyl halide is treated with Zn dust in closed tube then higher symmetrical alkanes will be formed.



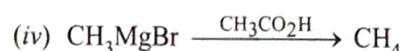
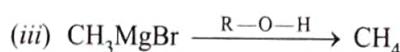
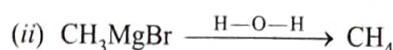
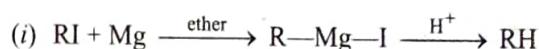
This is known as Frankland's reaction, in this reaction first Frankland's reagent ($R-Zn-R$, dialkyl Zinc) is formed. Which then react with alkyl halide to give higher alkanes.

[Where $R = CH_3$]

For Example:



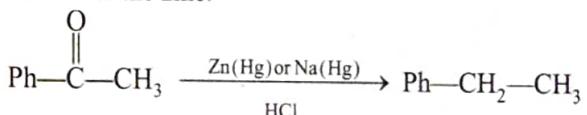
Grignard reagents: Alkyl halides in ether reacts with magnesium to form alkyl magnesium halides or Grignard reagents which on treatment with water or dilute acid are decomposed to alkanes.



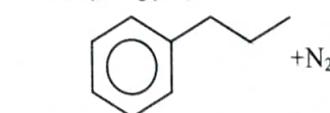
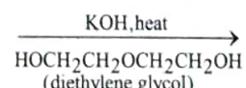
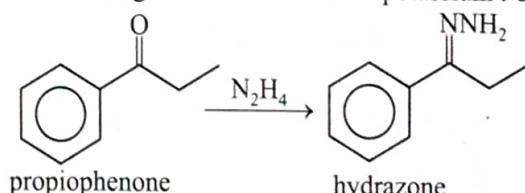
By Reduction

From aldehydes and Ketones

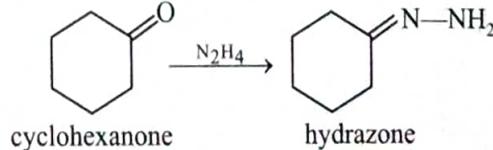
Clemmensen Reduction: The Clemmensen reduction is most commonly used to convert acylbenzenes to alkylbenzenes, but it also works with other ketones and aldehydes that are not sensitive to acid. The carbonyl compound is heated with an excess of amalgamated zinc (zinc treated with mercury) and hydrochloric acid. The actual reduction occurs by a complex mechanism on the surface of the zinc.

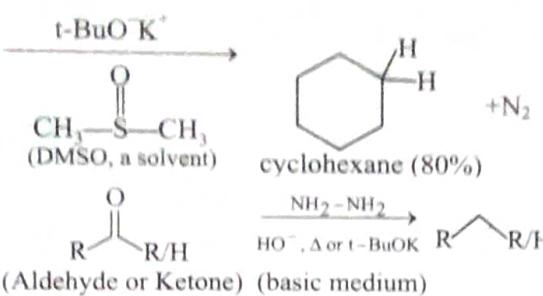


Wolff-Kishner Reduction: Compounds that cannot survive treatment with hot acid can be deoxygenated using the Wolff-Kishner reduction. The ketone or aldehyde is converted to its hydrazone, which is heated with a strong base such as KOH or potassium t-butoxide.



n-propylbenzene (82%)





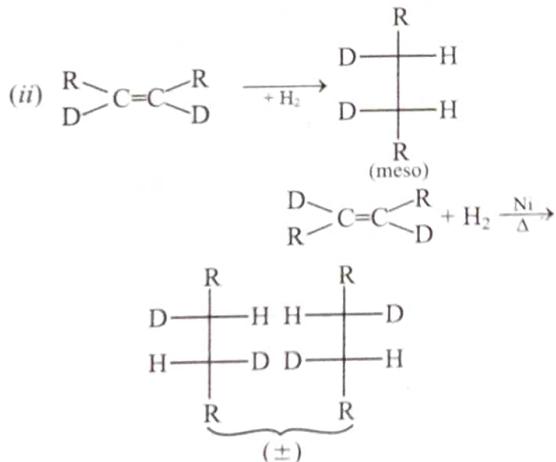
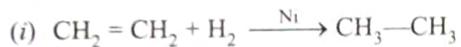
From Red P + HI: It is a powerful reducing agent which will convert, aldehyde, ketone, alcohol, carboxylic acid to alkanes with same number of carbon.



From Alkenes:

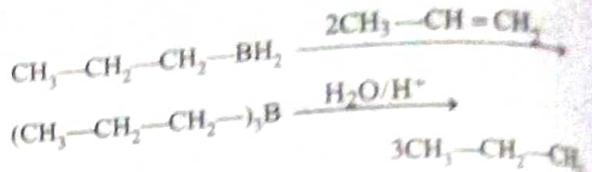
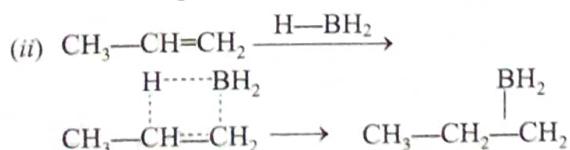
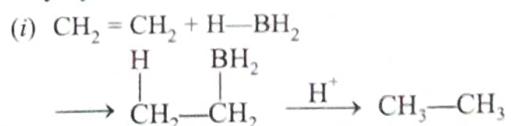
By catalytic hydrogenation: Addition of H_2 on alkene takes place in *cis* manner in the presence of Pt or Ni or Pd to give alkane.

eg.



Note: This reaction is exothermic and heat of hydrogenation depend upon no. of 'α' hydrogen.

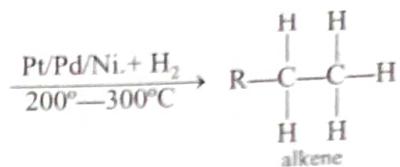
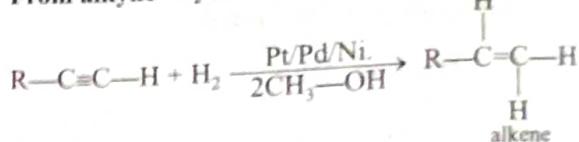
By hydroboration followed protolysis



Note: Long-chain alkane may be possible by the coupling of alkyl boranes.

If $(\text{AgNO}_3 + \text{NaOH})$ is used instead of $\text{H}_2\text{O}/\text{H}^+$
 $(\text{R}-)_3\text{B} \xrightarrow[\text{NaOH}]{\text{AgNO}_3} \text{R}-\text{R}$

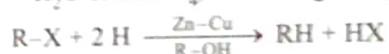
From alkyne - by reduction:



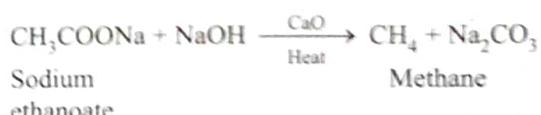
In the above reaction if catalyst palladium or platinum is used, it is called simple reduction and if Ni is used, it is called *Sabatier-Senderen's* reaction (catalytic hydrogenation).

From Alkyl halides:

By reduction: When alkyl halide is reduced with Zn-Cu couple + ROH or Na + EtOH/ Na-Hg + H_2O or LiAlH_4 , then we get respective alkane.

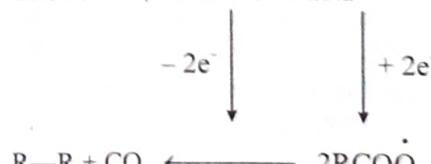
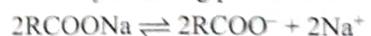


By decarboxylation with soda lime



The alkane formed has one carbon less than the starting material.

By Kolbe's electrolysis: In this method concentrated aqueous solution of sodium or potassium salt of a carboxylic acid is electrolyzed using platinum electrodes.

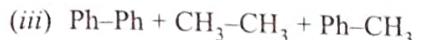
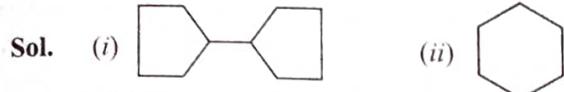
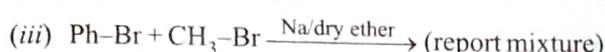
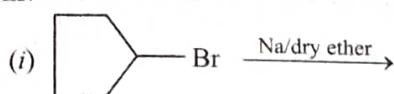


If n is the number of carbon atoms in the acid, the alkane formed has $2(n-1)$ carbon atoms.

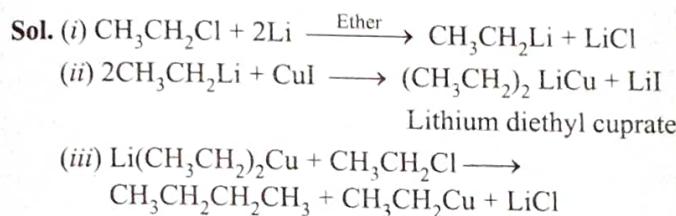


Train Your Brain

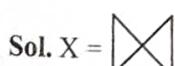
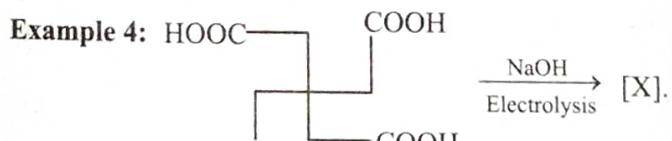
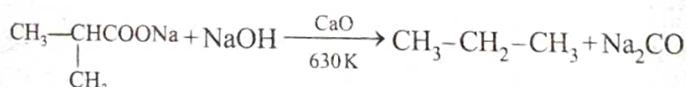
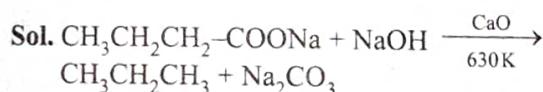
Example 1: Write the major product of following reactions.



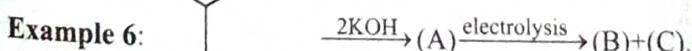
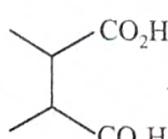
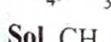
Example 2: Prepare butane from chloroethane using the Corey-House synthesis.



Example 3: Sodium salt of which acid will be needed for preparation of propane? Write chemical equation for the reaction.

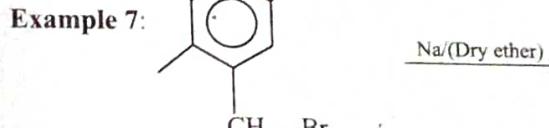
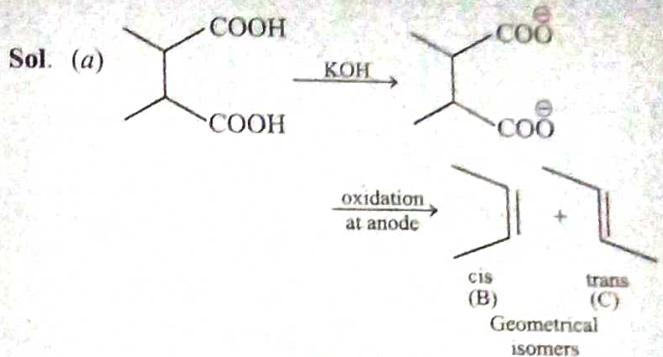


Example 5: Which of the following can't be produced by Wurtz reaction.

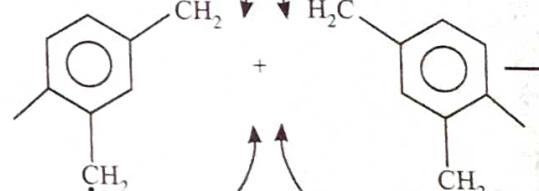
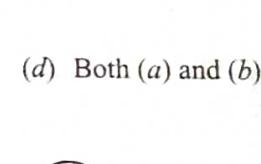
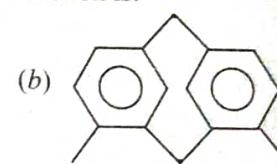
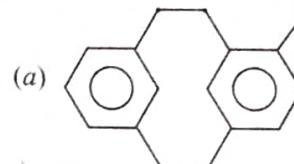


Products (b) and (c) are:

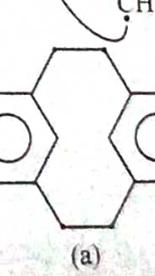
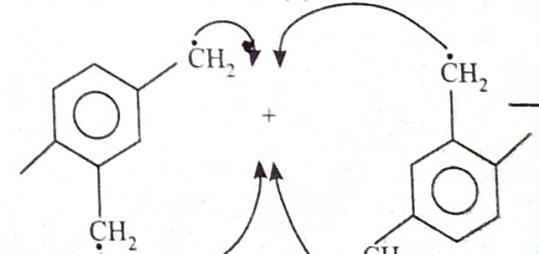
- (a) Geometrical isomers (b) Enantiomer
- (c) Positional isomer (d) Structural isomer

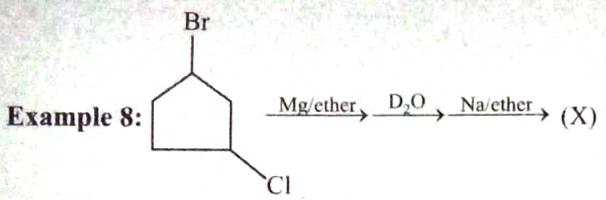


Products obtained in above Wurtz reaction is:



Sol. (d)





The compound (X) is:

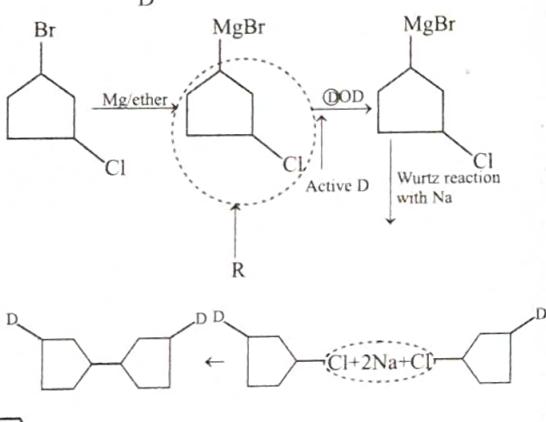
- (a)

- (b)

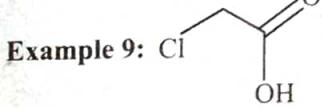
- (c)

- (d)

Sol. (b)

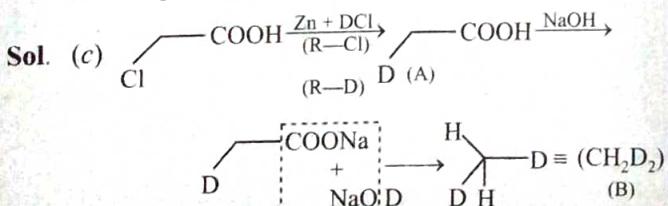


(Cyclohexane contains only 2° H atoms.)



The compounds (A) and (B) in the equation given above are:

- | (A) | (B) |
|--------------------------------|--------------------------|
| (a) CH_3COOH | CH_3CH_3 |
| (b) CH_3CH_3 | CH_4 |
| (c) DCH_2-COOH | CH_2D_2 |
| (d) CH_3-COOD | CH_3D |

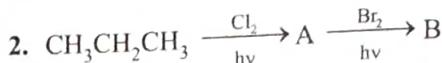


Concept Application

1. Which of the following is/are the chain termination step during photochlorination of ethane?

- (1) $\text{CH}_3\text{CH}_2^{\cdot} + \text{Cl}^{\cdot} \rightarrow \text{CH}_3\text{CH}_2\text{Cl}$
- (2) $\text{CH}_3\text{CH}_2^{\cdot} + \text{CH}_3\text{CH}_2^{\cdot} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- (3) $\text{Cl}^{\cdot} + \text{Cl}^{\cdot} \rightarrow \text{Cl}_2$
- (4) $\text{Cl}^{\cdot} + \text{H}^{\cdot} \rightarrow \text{HCl}$

- (a) 1 and 2 (b) 1 and 3
(c) 1, 2 and 3 (d) 1, 2, 3 and 4



A and B are:



(a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ and $\text{CH}_3\text{CH}-\text{CH}_2-\text{Cl}$



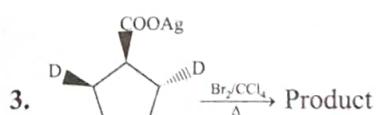
(b) CH_3CHCH_3 and $\text{CH}_3\text{CHCH}_2\text{Cl}$



(c) CH_3CHCH_3 and $\text{CH}_3\text{CH}-\text{CH}_2-\text{Br}$



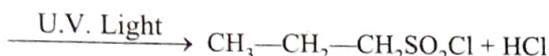
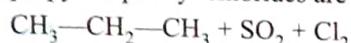
(d) CH_3CHCH_3 and $\text{CH}_3-\text{C}-\text{CH}_3$



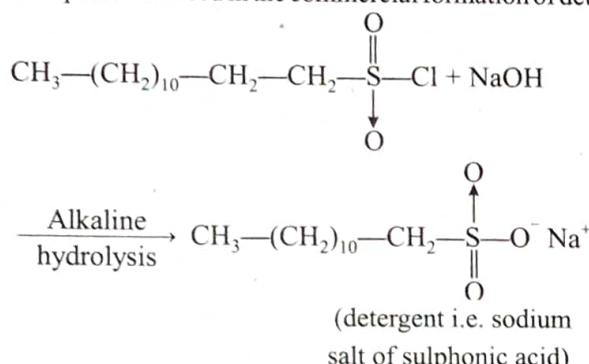
Formed product and relationship between them is:

- (a)
- (b)
- (c)
- (d)

- 4. Chlorosulphonation/Reaction with SO_2 and Cl_2 :** The reaction is also called as **Reed's reaction**. When propane reacts with SO_2 and Cl_2 in presence of ultraviolet light then propyl sulphonyl chlorides are formed.

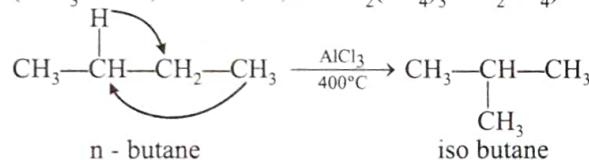


This process is used in the commercial formation of detergents.

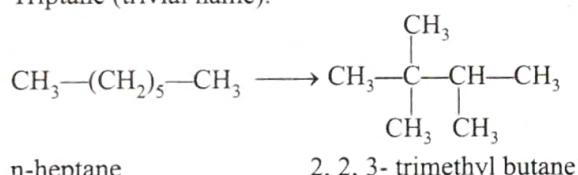


- 5. Isomerisation:** Lower alkanes are not isomerised but butane or higher number of alkanes if heated with aluminium chloride at high temperature then they convert into stable isomers by the rearrangement reaction. Isomerisation is also held by heating alkane with-

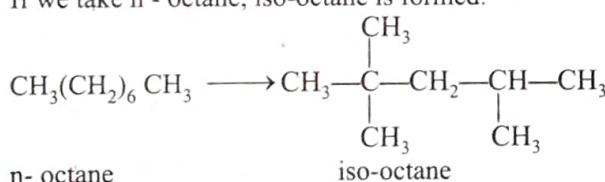
$(\text{AlX}_3 + \text{HX}; \text{X} = \text{Cl}, \text{Br}, \text{I} \text{ or } \text{Al}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4)$ at 200°C .



If we take n-heptane then it converts into most stable form Triptane (trivial name).

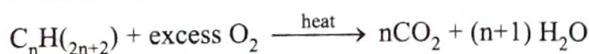


If we take n - octane, iso-octane is formed.

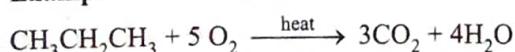


Reaction is used in Petroleum industries, with the help of this reaction, we can convert unbranched alkane to branched alkane.

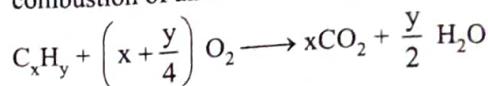
- 6. Combustion:** Combustion is a rapid oxidation that takes place at high temperatures, converting alkanes to carbon dioxide and water. Little control over the reaction is possible, except for moderating the temperature and controlling the fuel / air ratio to achieve efficient burning.



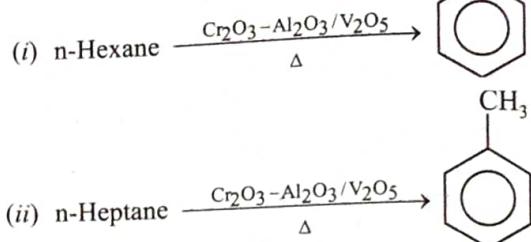
Example:



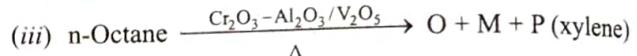
Facilities that use these more environment-friendly sources are more expensive than those that rely on the combustion of alkanes, however.



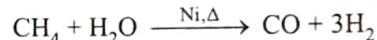
7. Aromatization:



For converting aliphatic to aromatic.

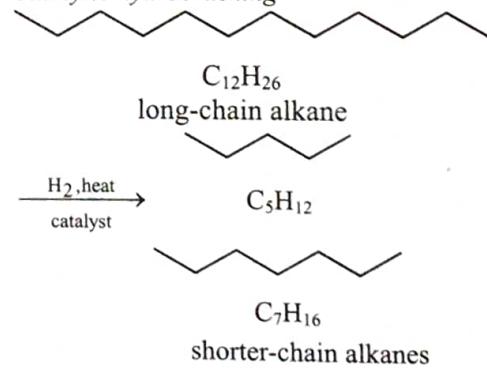


- 8. Reaction with Steam:** Methane reacts with steam at 1273K in the presence of nickel catalyst to form carbon monoxide and dihydrogen. This method is used for industrial preparation of dihydrogen gas.

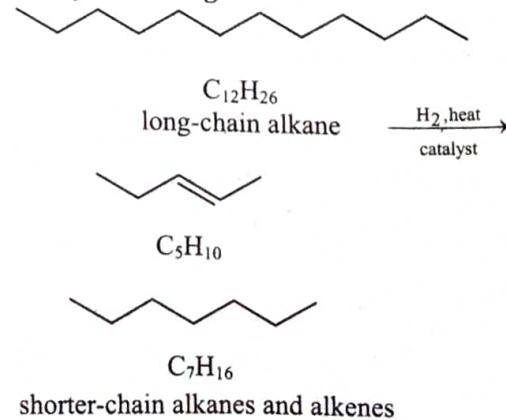


- 9. Cracking and Hydrocracking:** Cracking of large hydrocarbons at high temperatures produces smaller hydrocarbons. The cracking process usually operates under conditions that gives the maximum yields of gasoline. In hydrocracking, hydrogen is added to give saturated hydrocarbons; cracking without hydrogen gives mixture of alkanes and alkenes.

Catalytic hydrocracking



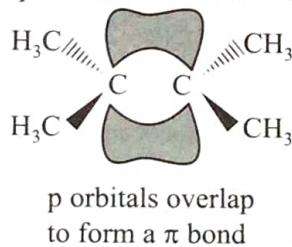
Catalytic cracking



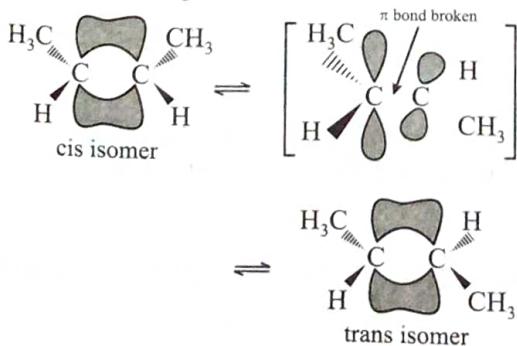
ALKENES

1. General Introduction

- Hydrocarbons that contain a carbon–carbon double bond are called alkenes.
- Early chemists noted that an oily substance was formed when ethene ($\text{H}_2\text{C} = \text{CH}_2$), the smallest alkene, reacted with chlorine. Based on this observation, early organic chemists called alkenes as olefins (oil forming substance).
- Insects communicate by releasing pheromones, chemical substances that other insects of the same species detect with their antennae. There are sex, alarm, and trail pheromones, and many of these are alkenes.
- Many of the flavors and fragrances produced by certain plants also belong to the alkene family.
- Each double-bonded carbon of an alkene has three sp^2 orbital of another atom to form a σ bond.
- Thus, one of the carbon–carbon bonds in a double bond is a σ bond, formed by the overlap of an sp^2 orbital of one carbon with an sp^2 orbital of the other carbon.
- The second carbon–carbon bond in the double bond (the π bonds) is formed from side-to-side overlap of the remaining p-orbitals on the sp^2 carbons. Because three points determine a plane, each sp^2 hybridized carbon and two of the three atoms bonded to it are in a plane.
- In order to achieve maximum orbital-orbital overlap, the two p-orbitals must be parallel to each other. Therefore, all six atoms of the double bond system are in the same plane. A molecular orbital description of a carbon-carbon double bond.
- It is important to remember that the π bond represents the cloud of electrons that is above and below the plane defined by the two sp^2 carbons and the four atoms bonded to them.



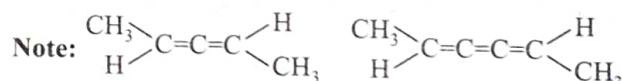
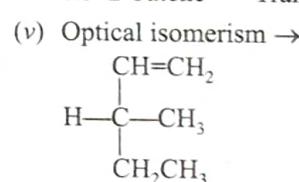
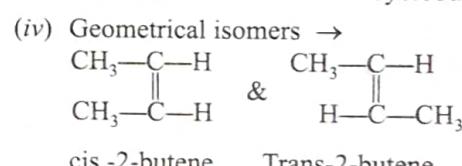
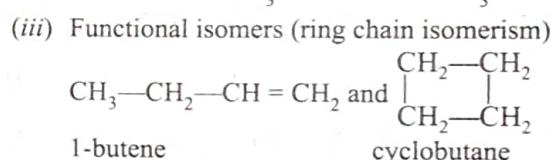
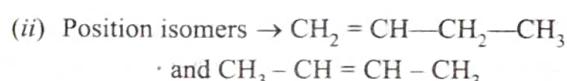
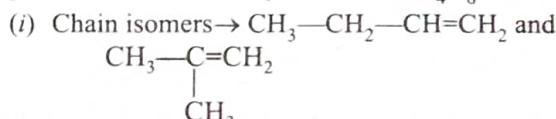
- Because the two p orbitals that form the π bond must be parallel to one another to achieve maximum overlap, rotation about a double bond does not occur. If rotation about a double bond did occur, the two p-orbitals would cease to overlap and the π bond would be destroyed.



2. Characteristics of Alkene:

- General formula: C_nH_{2n} .
- Functional group: in alkenes is $>\text{C}=\text{C}<$
- The double bond is made up of one sigma and one pi bond.
- The double bonded carbon atoms are sp^2 hybridized.
- Geometry of unsaturated 'C' carbon is trigonal planar.
- $\text{C}=\text{C}$ bond length is 1.34 \AA .
- $\text{C}-\text{H}$ bond length is 1.10 \AA .
- $\text{C}=\text{C}$ bond energy is $143.1 \text{ k cal mol}^{-1}$.
- $\text{C}-\text{H}$ bond energy is $98.69 \text{ k cal mol}^{-1}$.
- Alkene shows chain, position, functional (ring chain), optical and geometrical isomerism.

Note: Cumulated polyene can exhibit geometrical as well as optical isomerism. for eg. Isomers of C_4H_8 :



Ist is simplest example of cumulated poly-ene which can exhibit optical isomerism. Because this is a chiral molecule. Similarly suitably substituted polyene containing odd no. of double bond can exhibit geometrical isomerism as because this is a planer molecule.

- Cumulated polyene having even no. of double bonds (eg. I) which has $=\text{C} \begin{smallmatrix} \diagup \\ \text{a} \\ \diagdown \\ \text{b} \end{smallmatrix}$ system at the both end can exhibit optical isomerism but cannot exhibit geometrical isomerism.
- Cumulated polyene having odd no. double bonds (eg. II) which have $=\text{C} \begin{smallmatrix} \diagup \\ \text{a} \\ \diagdown \\ \text{b} \end{smallmatrix}$ system at both end can exhibit geometrical isomerism but cannot exhibit optical isomerism.

3. Methods of Preparation of Alkenes

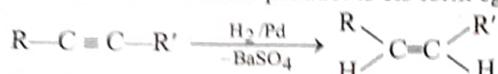
3.1 From Alkynes



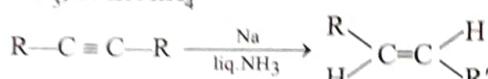
poison of catalyst such as BaSO_4 , CaCO_3 are used to stop the reaction after the formation of alkene, otherwise alkanes are formed.

Mechanism

- (i) The reaction takes place at the surface of Pd, that is why it is **cis addition** and the product is cis form eg.

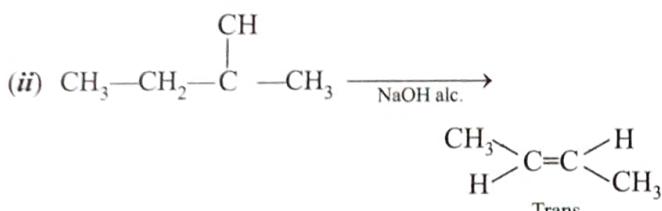
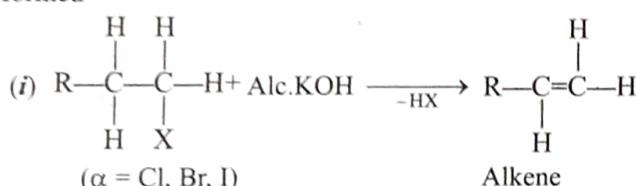


- (ii) Alkynes can be reduced to trans alkenes by using Na + liq. NH_3 , or LiAlH_4



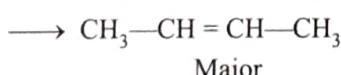
Terminal alkynes are not reduced by the Na - liq. NH_3 until presence of $(\text{NH}_4)_2\text{SO}_4$.

- 3.2 From mono halides:** When mono halide react with alcoholic KOH or NaOH then respective alkenes are formed



Note: $\text{CH}_3-\text{CH}_2\text{CHX}-\text{CH}_3 \longrightarrow \text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$

Minor

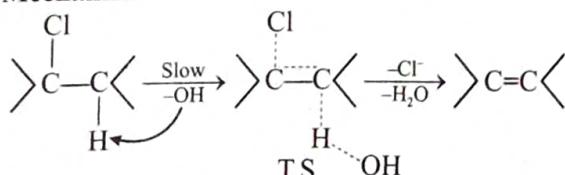


$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$ (Trans) is the major product because it is more stable as having six 'α' Hydrogen in the comparison to $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$ having only two 'α' hydrogen.

This is in accordance with the **Saytzeff rule**.

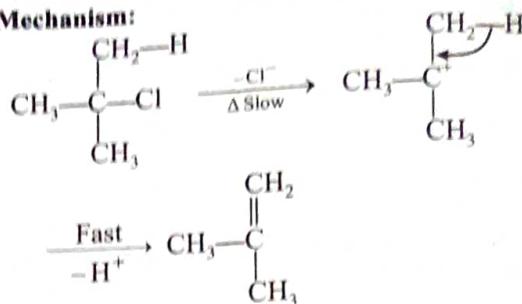
Mechanism: E2 and E1 are possible.

E2 Mechanism:



As molecularity of slowest step is two i.e. E2 mechanism.

E1 Mechanism:



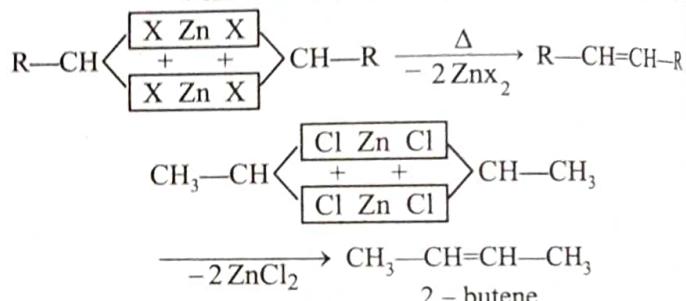
As molecularity of slowest step is one. That is why it is termed as E1. **Remember:** Possibility of E1 increases with increasing stability of carbocation. Similarly possibility of E2 increases with decreasing stability of expected carbocation.

Iodine > Bromine > Chlorine for different halogens and for alkyl groups it is:

Tertiary > Secondary > Primary

3.3 From Dihalides

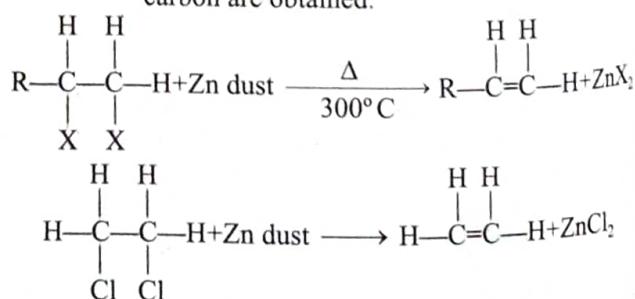
- 3.3.1 From gem dihalides :** When gem dihalide is heated with Na in ether then higher alkenes are formed.



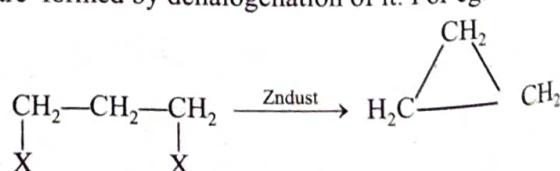
Conclusion: If we take two different types of gemdihalides then we obtain three different types of alkenes.

Note: The above reaction is used in the formation of symmetrical alkenes only, because if we take two different type of halides then mixture of alkenes is obtained so the yield of an individual alkene is reduced and it is improper to separate each alkene from the mixture because the difference of boiling points in alkenes is very less.

- 3.3.2 From vicinal dihalides:** When vicinal dihalides are heated with Zn dust, alkenes of same no. of carbon are obtained.

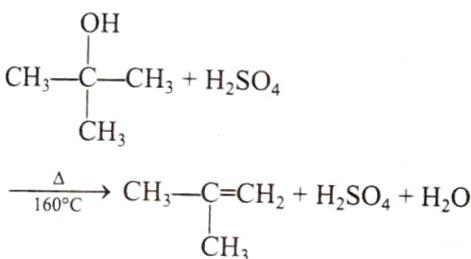
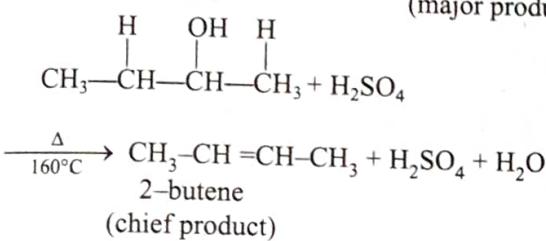
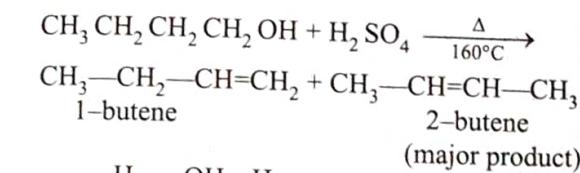
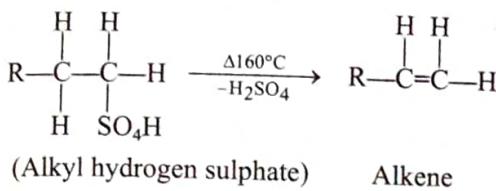
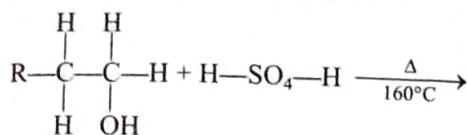


Note: Alkenes are not formed from 1,3 dihalides. Cyclo alkanes are formed by dehalogenation of it. For eg.

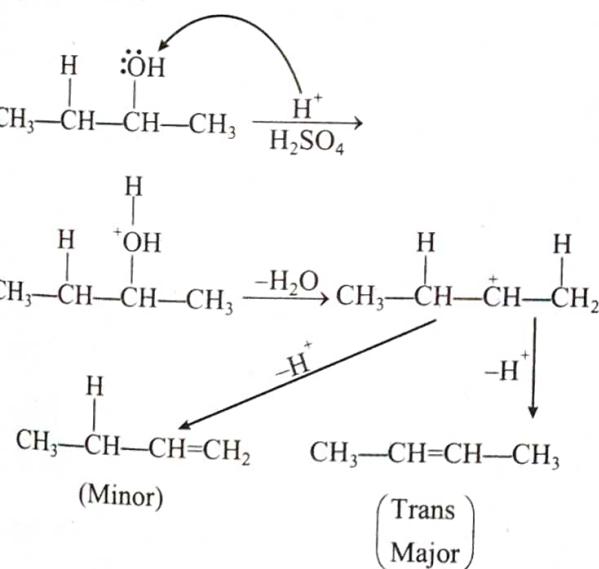


3.4 From Alcohols

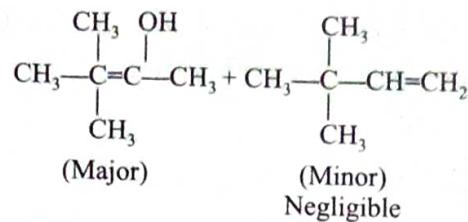
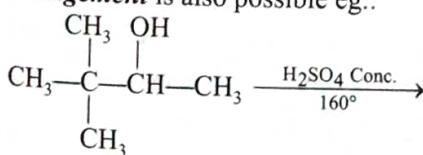
When alcohol is heated with conc. H_2SO_4 at about $160^{\circ}C$, alkenes are formed after dehydration.



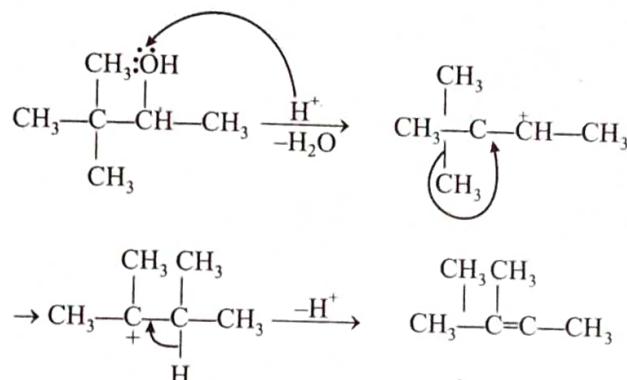
Mechanism



Note: Since the mechanism proceeds via- C^+ ion therefore **rearrangement** is also possible e.g.:



Mechanism

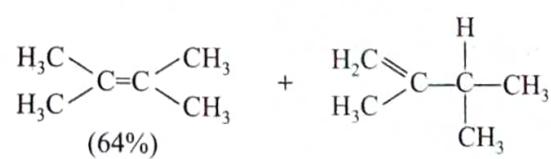
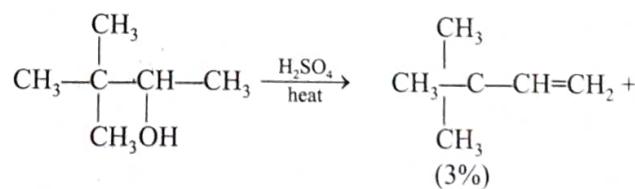


Characteristics of Dehydration of Alcohol

1. Since the carbocation is formed as an intermediate in the R.D.S. of dehydration of alcohol. The relative reactivity of alcohols decreases in the order.
Tertiary > Secondary > Primary
 2. Since the R.D.S. is reversible it is necessary to remove the H_2O molecule produced in the reaction. Therefore in experimental condition conc. H_2SO_4 is added in a regular interval.
 3. For dehydration, different dehydrating agent like Al_2O_3 , ThO_2 can also be employed.
 4. Rearrangement of carbocation can take place.
 5. $-\text{OH}$ is not a good leaving group, in alcohols so turn it into a good leaving group, it is converted into $-\text{H}_2\text{O}$ by protonation
 6. H_2O is a good leaving group.

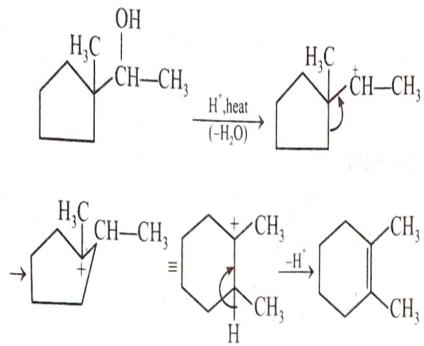
Rearrangement in Alcohol Dehydration

1. Some alcohols undergo dehydration to form alkene having carbon skeleton different from those of the starting alcohol.
 2. This is due to rearrangement of carbocation formed in the reaction to more stable carbocation.
 3. An example of alcohol dehydration that is accompanied by rearrangement is:



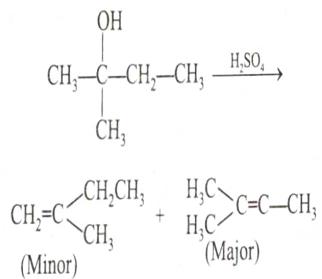
4. Percent yield of alkenes formed from rearranged carbocation is greater than the percent yield of alkene obtained from unarranged carbocation.

5. Rearrangement of carbocations can also lead to a change in ring size, as the following example shows



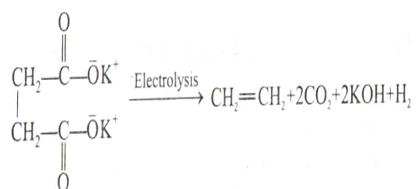
Regioselectivity in Alcohol Dehydration

- In alcohols such as 2-methyl-2-butanol, dehydration can occur in two different directions to give alkenes that are constitutional isomers.
- More substituted alkene forms the major product and is called Saytzeff alkene or Zaitsev alkene.
- Less substituted forms the minor product and is called Hofmann's alkene.

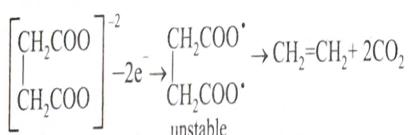


3.5 Kolbe's Synthesis

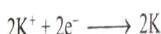
When aqueous solution of K or Na succinate is electrolysed, ethylene is released at anode.



At Anode



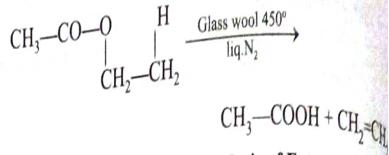
At Cathode



Note: If we use methyl succinic acid as reactant then propylene is formed.

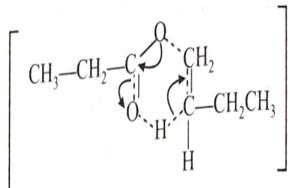
3.6 From Esters

When esters are heated in presence of liq. N₂ and glass wool, then alkyl part of ester converts into respective alkene while alkanoate part of ester is converted into respective acid.

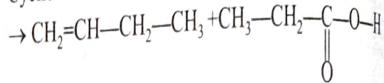


The reaction is called as 'Pyrolysis of Ester'.

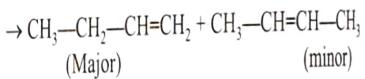
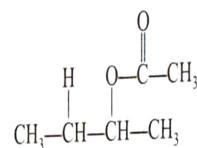
Mechanism: Pyrolysis of Ester is a type of E1 elimination which proceed via cyclic T.S. that is why the product becomes 'cis'



Cyclic Transition state

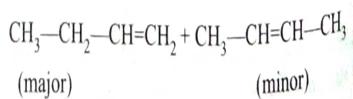
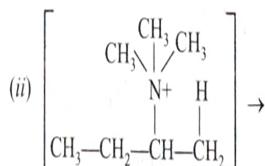
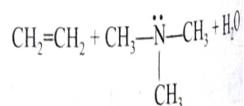
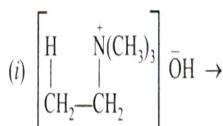


It is interesting to note that, in this case major product is 1-alkene in the comparison to 2-alkene.



3.7 From Quaternary Ammonium Hydroxide

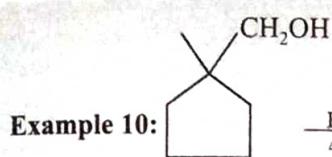
When quaternary ammonium hydroxide is heated strongly it decomposes to give alkene. e.g.



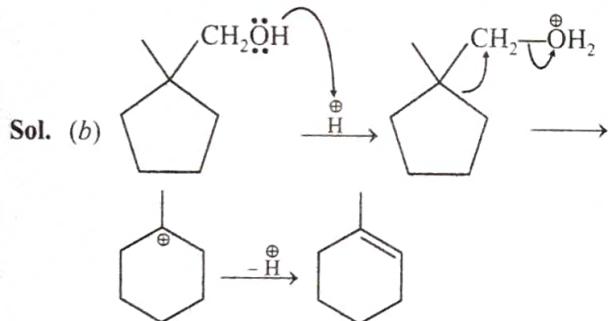
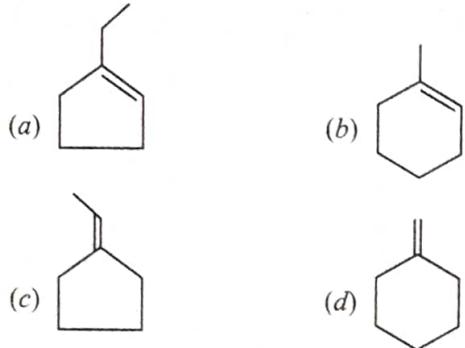
This elimination is called **Hofmann's elimination**. It is markable that in this reaction more acidic H is preferably eliminated.



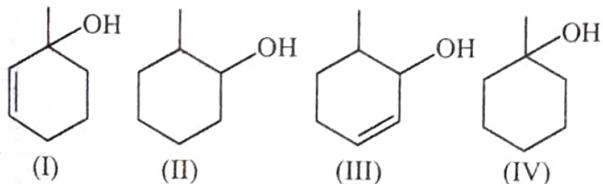
Train Your Brain



Major-product 'A' is

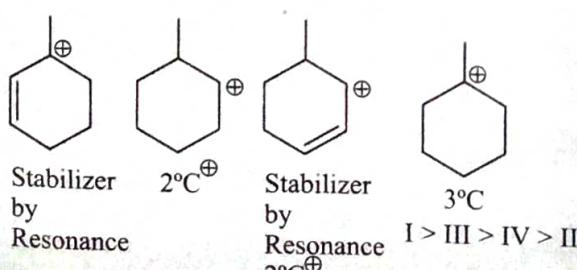


Example 11: Find out the correct order of rate of dehydration for given compounds with conc. H_2SO_4 .

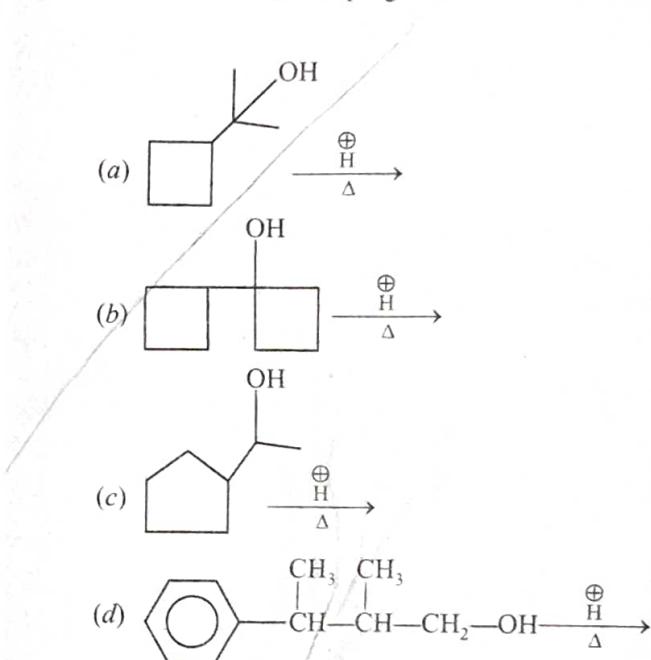
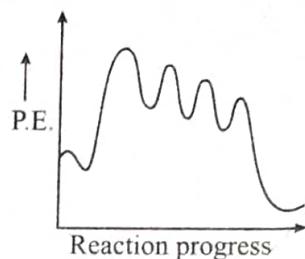


- (a) I > II > III > IV
- (b) I > III > II > IV
- (c) I > III > IV > II
- (d) III > I > II > IV

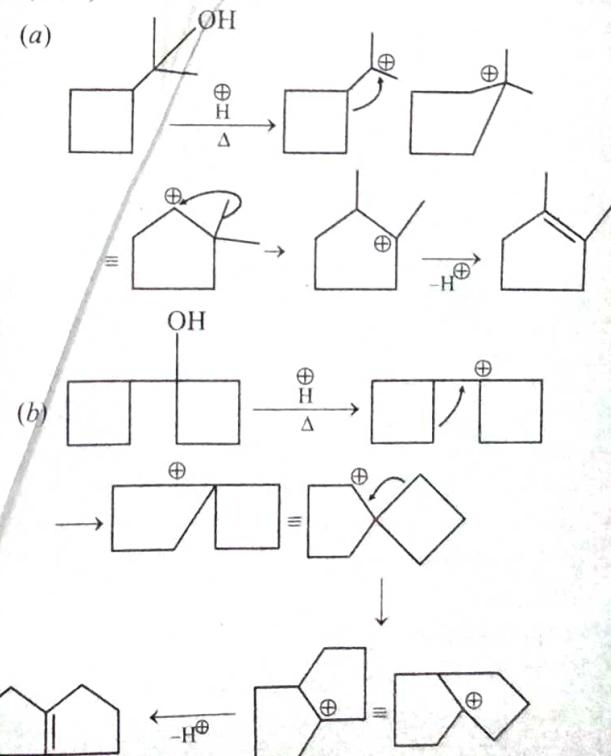
Sol. (c)



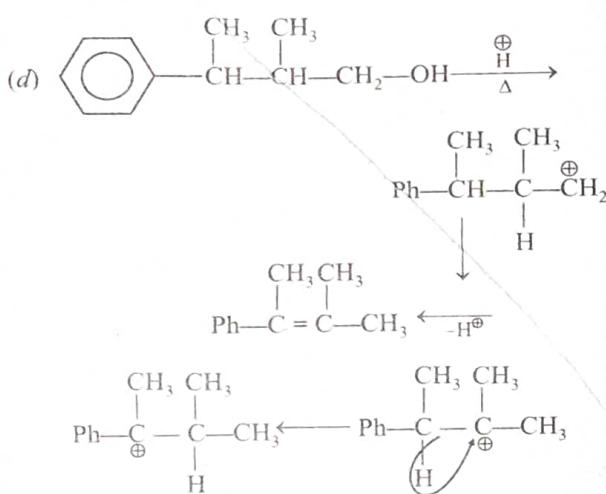
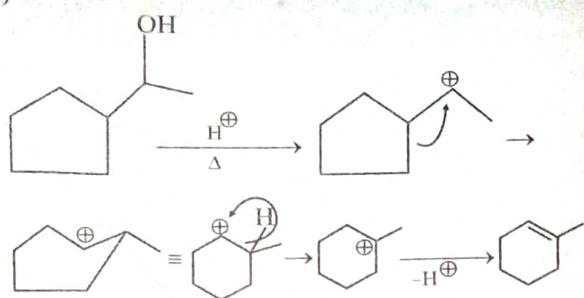
Example 12: Which of the following reaction(s) follow the same pattern of energy graph for the formation of major product only?



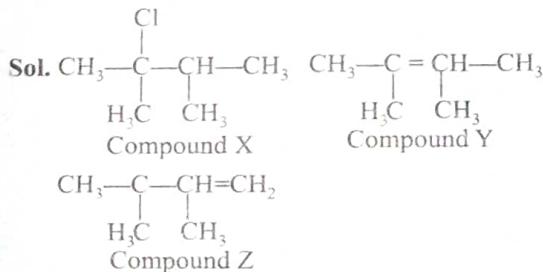
Sol. (b,c,d)



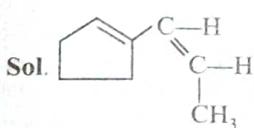
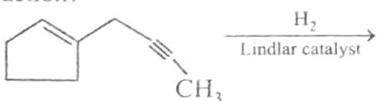
(c)



Example 13: An alkyl halide, X, of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation gives 2, 3-dimethyl butane. Predict the structures of X, Y and Z.



Example 14: What would be the major product in the following reaction?



Example 15: Give reasons for the following in one or two sentences :

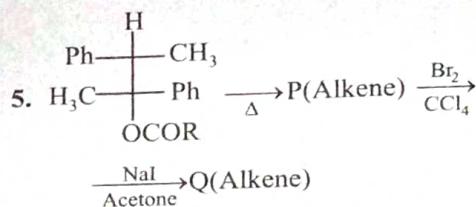
"The central carbon-carbon bond in 1, 3-butadiene is shorter than that of n-butane".

Sol. 1, 3 butadiene shows the property of resonance.

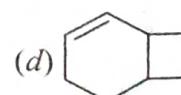
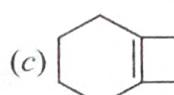
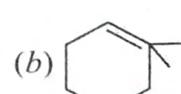
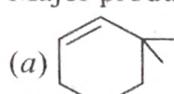
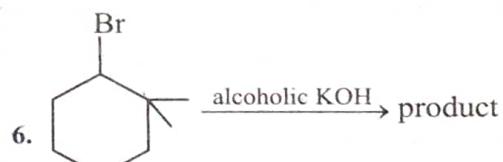
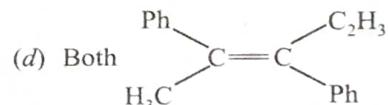
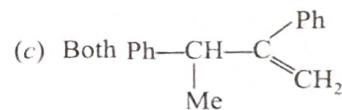
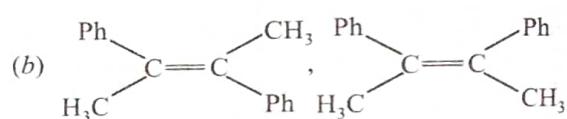
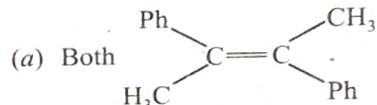
$CH_2 = CH - CH = CH_2 \longleftrightarrow CH_2^+ - CH = CH_2 - \bar{CH}_2^-$
So bond between second and third C-atoms show partial double character. Hence, bond length is shorter than C-C bond in n-butane (due to presence of resonance).



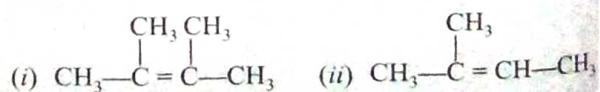
Concept Application

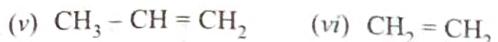
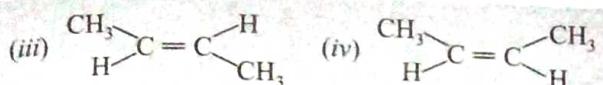


Alkene (P) and (Q) respectively are:



7. The relative stability of the compounds.





is in the order:

- (a) $i > ii > iii > iv > v > vi$
- (b) $vi > v > iv > iii > ii > i$
- (c) $i > iii > v > ii > iv > vi$
- (d) $ii > i > iv > iii > v > vi$

8. How many propenyl radical is possible from propene?

- (a) 1 (b) 2
- (c) 3 (d) 4

9. Action of RMgX with vinyl chloride gives:

- (a) Alkane (b) Alkyne
- (c) Alkene (d) All of these

10. Ethene can be formed by:

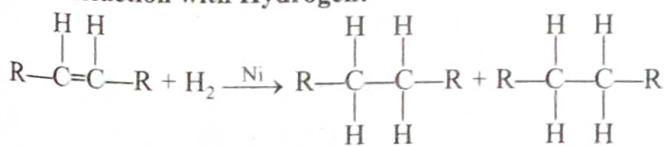
- (a) Fumaric acid (b) Malic acid
- (c) Succinic acid (d) Oxalic acid

4. Physical Properties:

- (i) From $\text{C}_2 - \text{C}_4$ they are colourless, odourless gases, from $\text{C}_5 - \text{C}_{17}$ they are colourless liquids, C_{18} onwards alkenes are solids.
- (ii) Alkenes are practically insoluble in water because they cannot form hydrogen bonds with H_2O molecule. They dissolve freely in organic solvents like benzene, chloroform, CCl_4 petroleum ether, etc. (Like dissolves like).
- (iii) B.P. and M.P. decreases with increasing branches in alkene.
- (iv) The melting points of cis isomers are lower than trans isomers because cis isomer is less symmetrical than trans. Thus trans packs more tightly in the crystal lattice and hence has a higher melting point.
- (v) The boiling points of cis isomers are higher than trans isomers because cis-alkenes have greater polarity (Dipole moment) than trans one.
- (vi) These are lighter than water.
- (vii) The increase in branching in carbon chain decreases the boiling point among isomeric alkenes.

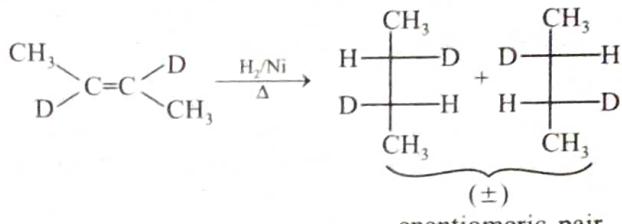
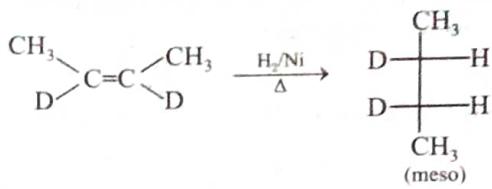
5. Chemical Reactions

5.1 Reaction with Hydrogen:



Mechanism : The reaction takes place at the surface of Ni, therefore the addition is cis addition.

eg :

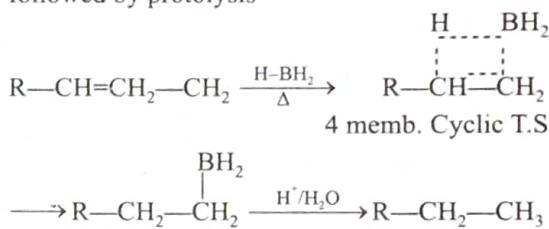


Note: Hydrogenation (catalytic hydrogenation) of alkene is a cis addition and is an exothermic reaction. Thus the heat evolved decreases with increasing stability of alkene.

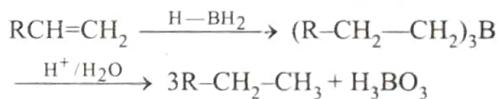
Remember: Stability of alkene depends upon hyperconjugation and type of geometrical isomerism

5.2 Reduction of alkene via hydroboration

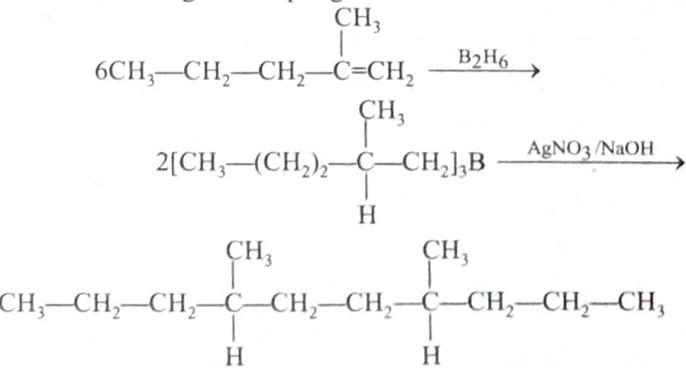
- (i) Alkene can be converted into alkane by hydroboration followed by protolysis



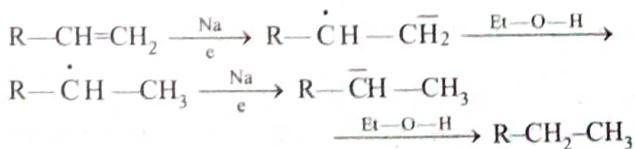
This reaction is also represented as



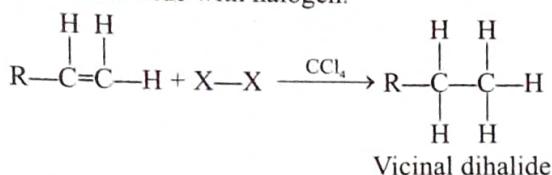
- (ii) Alkenes can be converted into alkanes by hydroboration followed by treatment with $\text{AgNO}_3 + \text{NaOH}$. This method gives coupling.



5.3 Birch Reduction: A terminal double bond may be reduced by sodium in liq. NH_3 in the presence of alcohol. This method is known as the **Birch Reduction** and is believed to proceed via an anionic free radical

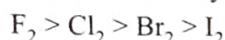


5.4 Halogenation: In presence of polar medium alkene form vicinal dihalide with halogen.

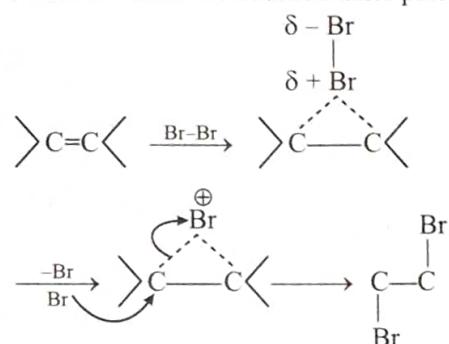


Order of reactivity of halogens is :

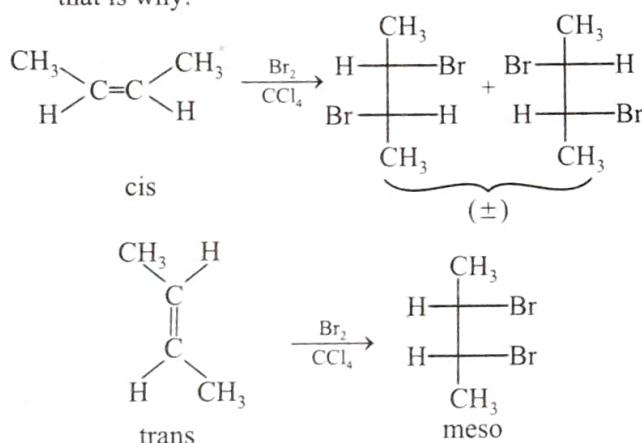
\text{F} > \text{Cl} > \text{Br} > \text{I}



Mechanism: It is an electrophilic addition by molecular attack in which the addition takes place in trans manner.



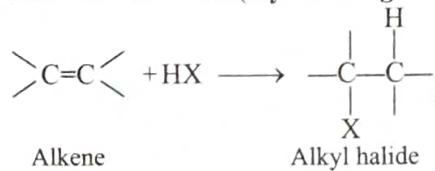
that is why;



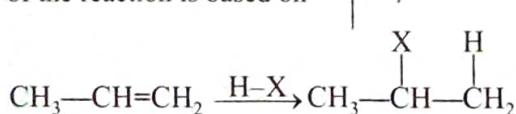
Note: For suitable condition

- (i) Cis addition on cis form results meso.
 - (ii) Cis addition on trans form results (\pm) .
 - (iii) Trans addition on cis form results (\pm) .
 - (iv) Trans addition on trans form results meso.

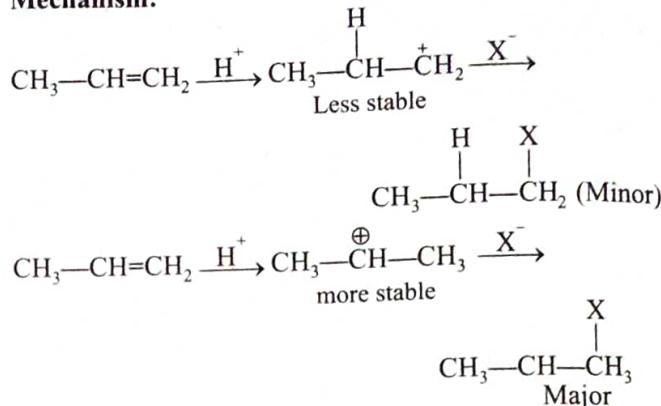
5.5 Reaction with HX (Hydrohalogenation) –



5.5.1 Markovnikov's Rule: When an unsaturated unsymmetrical hydrocarbon reacts with HX then halogen goes on that unsaturated carbon which has minimum number of hydrogen atom. Mechanism of the reaction is based on— C^+ —



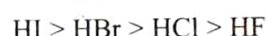
Mechanism:



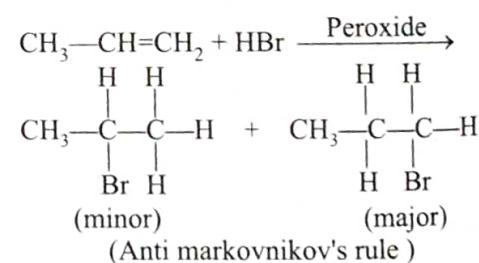
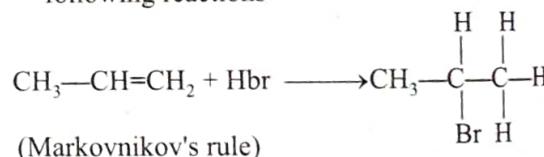
- (i) Formation of Carbocation is Rate determining step.
 - (ii) Rearrangement of carbocation to more stable carbocation can occur to form a more stable product.
 - (iii) Regiochemistry - Markovnikov's Addition of HX.

Addition of HX on unsymmetrical alkenes ($R-CH=CH_2$) takes place according to Markovnikov's rule which states that, "the negative part of addendum is added on the carbon atom carrying lesser number of hydrogen atoms".

- (iv) Reactivity order of different hydrogen halide towards addition

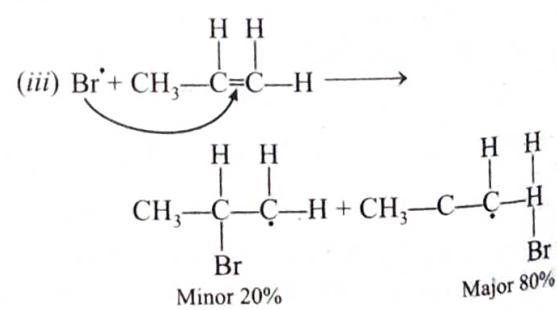
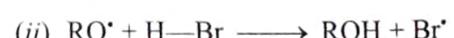
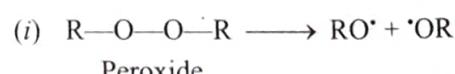


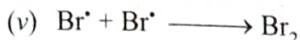
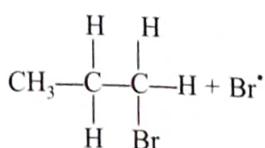
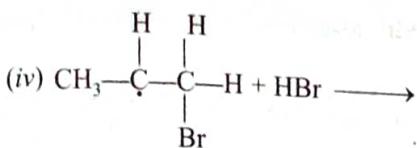
5.5.2 Anti Markovnikov's Principle/Kharasch Effect/Peroxide Effect: To understand Antimarkovnikov's principle let us consider the following reactions



It is based on free radical mechanism.

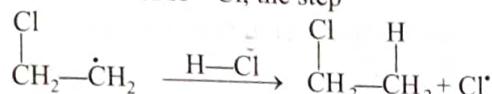
(a) Mechanism Concept





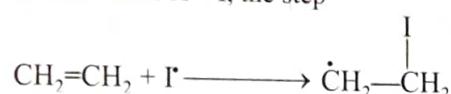
Note: It is interesting to note that anti markovnikov addition in the presence of peroxide is not applicable for HCl and HI.

(i) In the case of H – Cl, the step



is endothermic (as $\Delta H^\circ = +12.6 \text{ kJ mol}^{-1}$)

(ii) In the case of H – I, the step

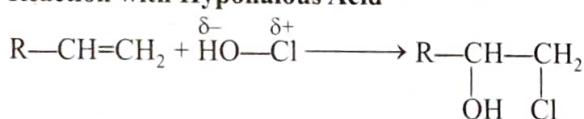


endothermic (as $\Delta H = + 46 \text{ kJ mol}^{-1}$)

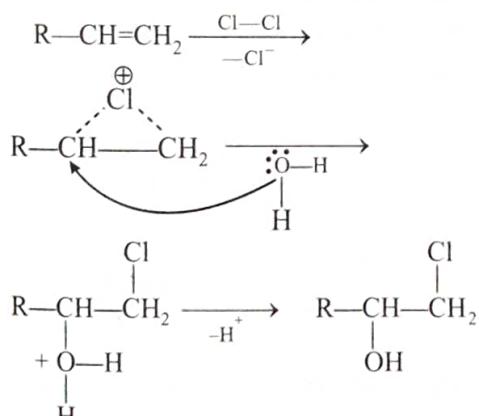
But in the case of HBr both of the steps are exothermic, which results spontaneous reaction.

CCl_4 , CBrCl_3 etc. can also be added to alkene in anti markovnikov manner.

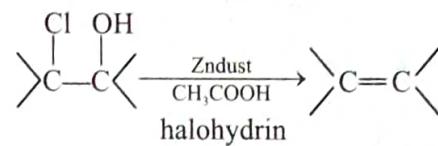
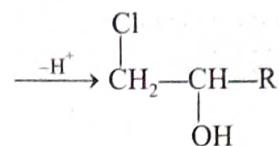
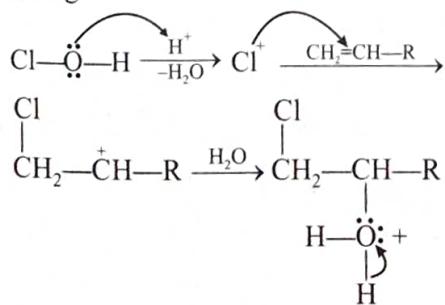
5.6 Reaction with Hypohalous Acid



(i) When chlorine water or bromine water is used.

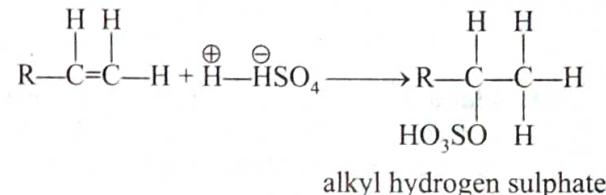


(ii) When aq. solution of HOCl is added in the presence of strong acid.

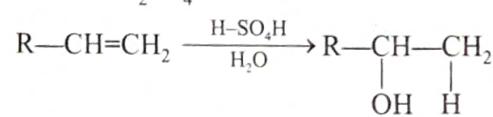


5.7 Reaction with H_2SO_4^-

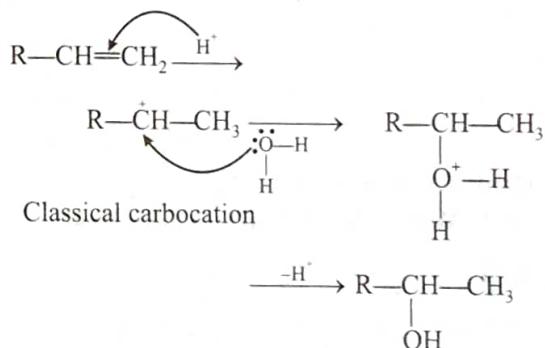
(a) With conc. H_2SO_4



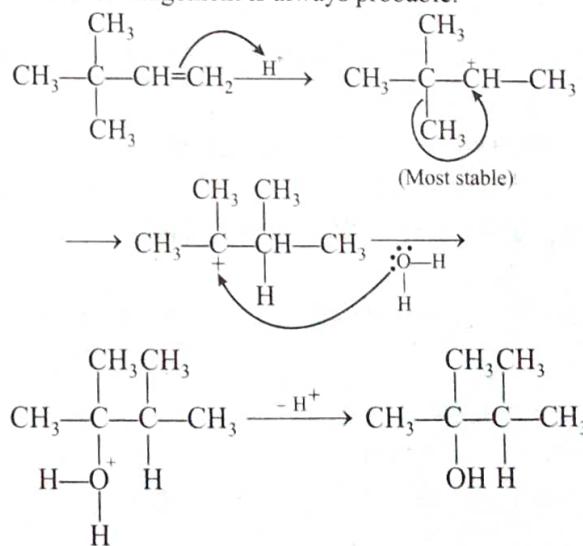
(b) With dil. H_2SO_4



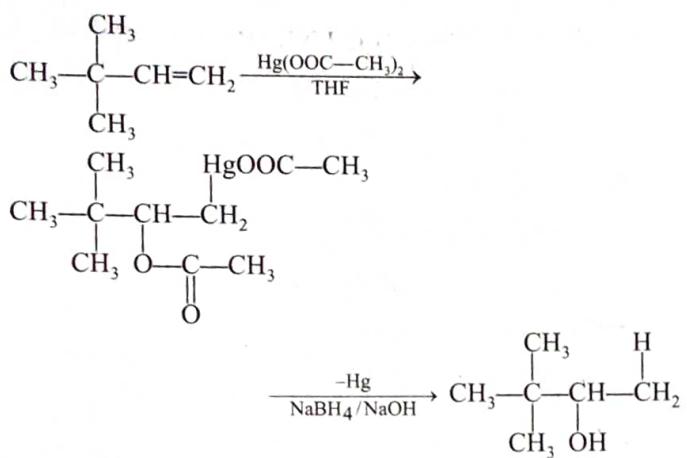
Mechanism:



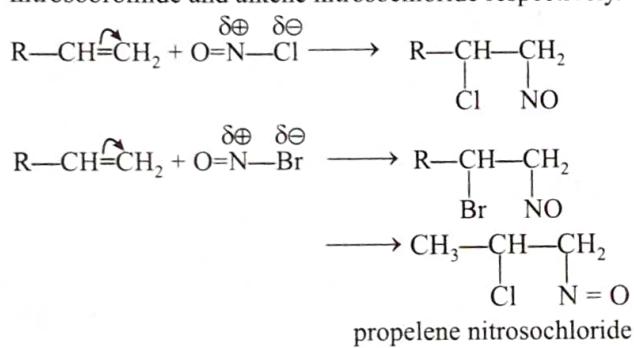
- ❖ The hydration of alkene is not stereoselective, as in the case of HCl addition. This fact can be explained on the basis of classical carbon cation formation.
 - ❖ Since hydration proceeds via carbocation intermediate therefore rearrangement is always probable.



- ❖ Rearrangement, however, may be avoided by treatment of alkene by *oxymercuration-demercuration method*

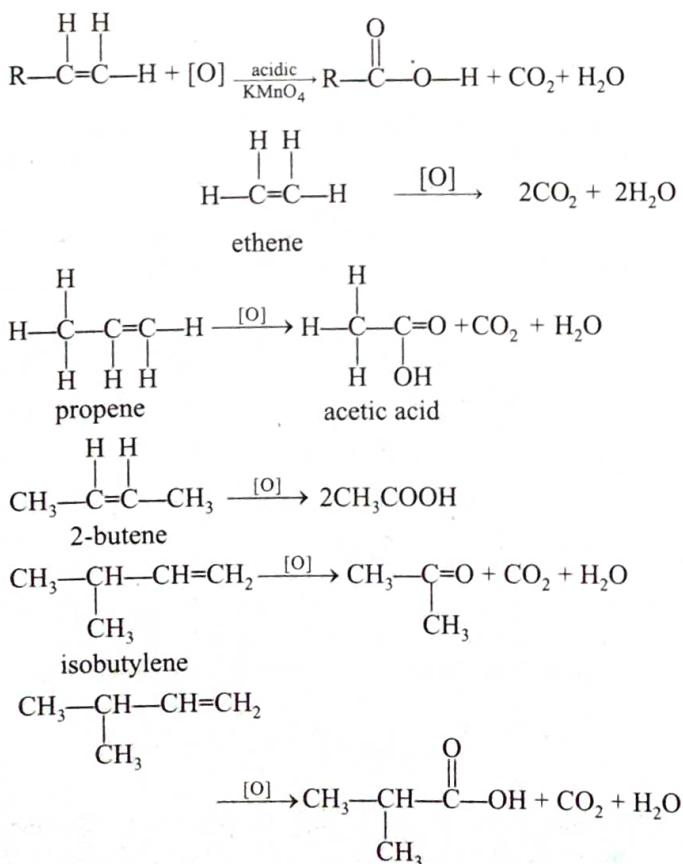


5.8 Addition of Nitrosyl halide: Alkene with nitrosyl bromide or nitrosyl chloride (**Tilden's reagent**) react according to Markovnikov's rule to give alkene nitrosobromide and alkene nitrosochloride respectively.

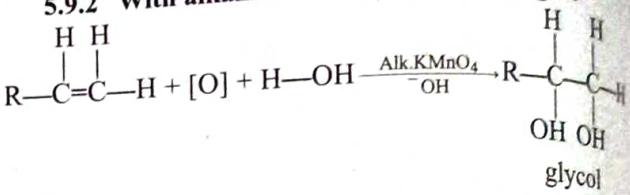


5.9 Oxidation: Oxidation is completed by the following ways.

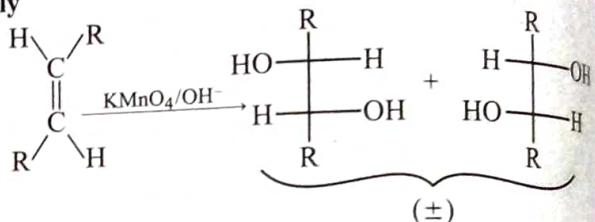
5.9.1 With Acidic KMnO₄ / Hot KMnO₄



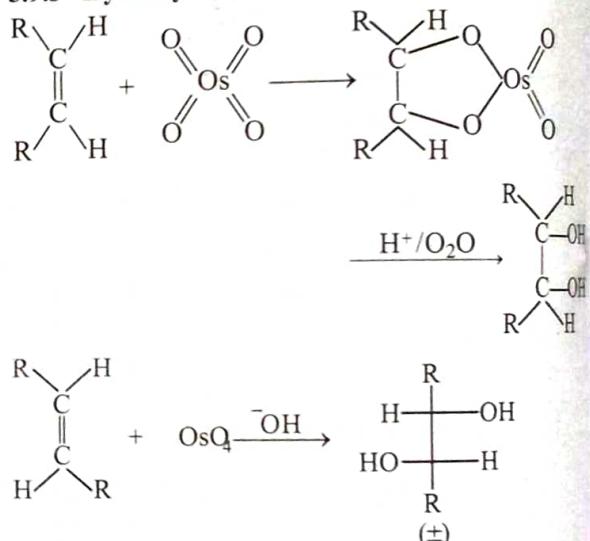
5.9.2 With alkaline KMnO_4 / Bayer's reagent



Similarly



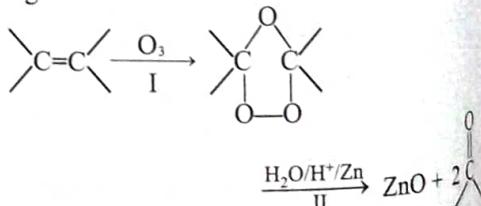
5.9.3 Hydroxylation by OsO₄:



5.9.4 Ozonolysis: This is the two step reaction

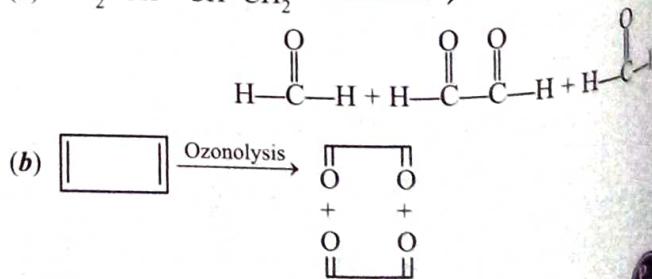
(i) Ozonide formation.

(ii) Decomposition of ozonide (reductive hydrolysis)
e.g.:

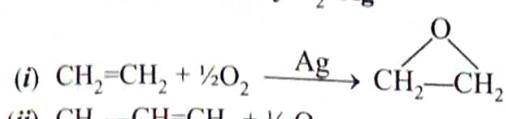


Remember : Ozonolysis gives oxidative cleavage of alkene to form two carbonyl group for each >C=C< . Whether it is in acyclic or cyclic or in aromatic compound. e.g.:

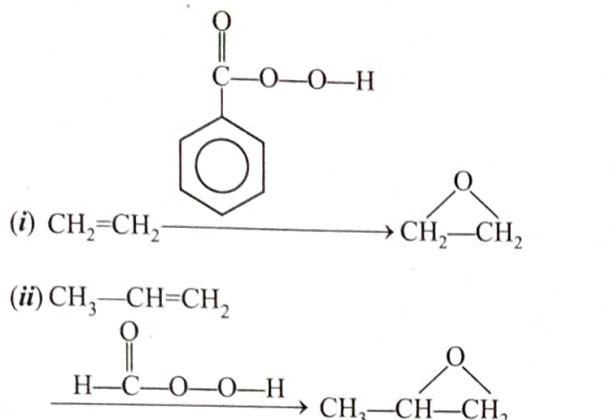
(a) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \xrightarrow{\text{Ozonolysis}}$



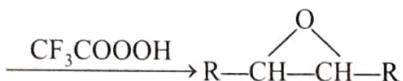
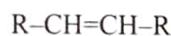
5.9.5 Epoxidation by O_2/Ag



5.9.6 Epoxidation by performic acid or perbenzoic acid



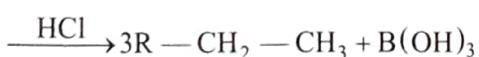
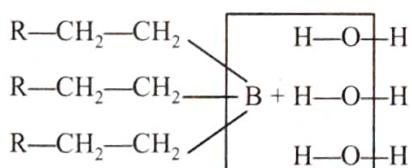
It is observed that CF_3COOOH is an excellent reagent for epoxidation.



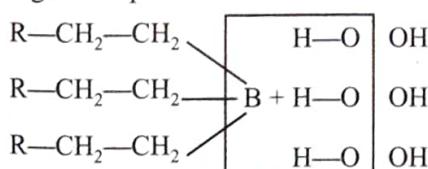
5.10 Hydroboration: Alkene with borane hydride form an important compound called trialkyl borane.



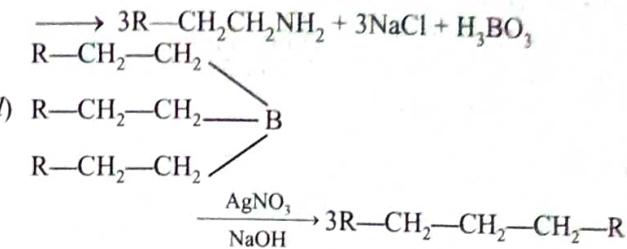
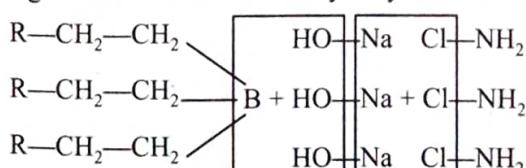
(a) Trialkyl borane is an important compound because it gives respective alkane on acidic hydrolysis.



(b) It gives respective alcohol on alkaline hydrolysis

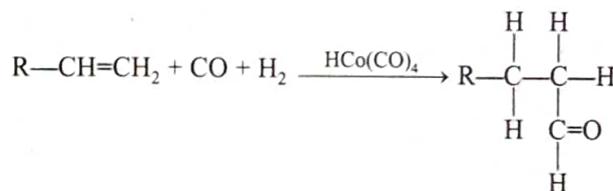


(c) It gives 1° amine on alkaline hydrolysis with chloramine

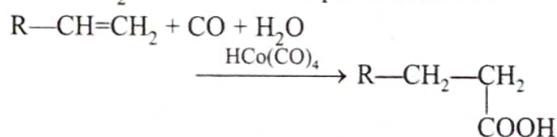


- (e) In the overall hydroboration-oxidation reaction, three moles of alkene reacts with one mole of BH_3 to form three moles of alcohol.
- (f) Because carbocation intermediates are not formed in the reaction carbocation rearrangement do not occur.
- (g) Regiochemistry Anti-Markovnikov's Addition of water.
- (h) Alkyl boranes undergo coupling by means of silver nitrate in the presence of NaOH at $25^\circ C$. Higher alkanes are the products of this reaction.

5.11 Hydroformylation Reaction with CO and H_2



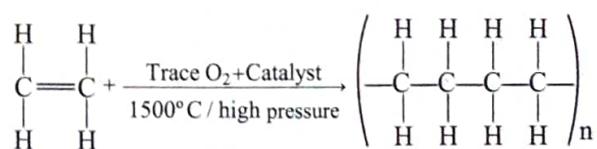
Note: If $CO + H_2O$ is taken then respective acid is formed



The above reaction is also called as 'Oxo reaction' or 'Carbonylation'.

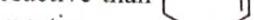
5.12 Polymerisation of Alkene

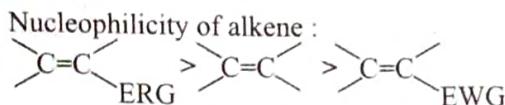
- (a) Mechanism is based on ionic or free radical both.
- (b) In alkene polymer name of polymer is given on the basis of name of monomer, only 'Poly' prefix is used.
- (c) If in polymerisation Zeigler-Natta catalyst (trialkyl aluminium + Titanium tetrachloride- $(C_2H_5)_3Al + TiCl_4$) is used than polymerisation is named as Ziegler-Natta Polymerisation. e.g.



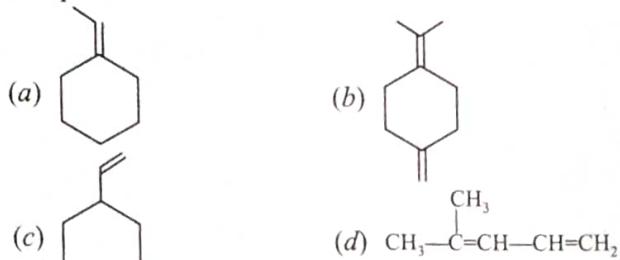
Polymer or $(-\text{CH}_2-)_n$ polythene

- Note:
- (i) If propylene is reacted then polypropylene is formed its commercial name is 'Koylene'.
 - (ii) By the use of vinyl chloride polyvinyl chloride is formed.
 - (iii) By the use of Vinyl cyanide (Acrylonitrile), polyacrylonitrile or orlon is formed.
 - (iv) Zeigler-Natta catalyst is used in addition polymerisation.

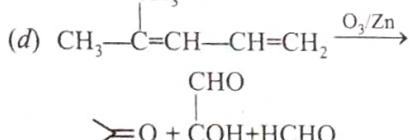
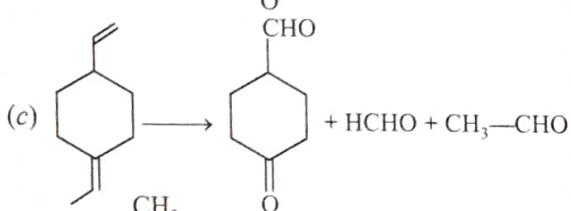
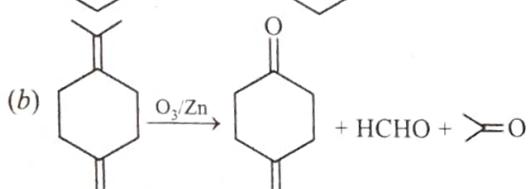
Sol.  are more reactive than  toward electrophilic addition reaction.



Example 20: Which of following on ozonolysis give 2-different product?



Sol. (a)  + CH₃-CHO



Example 21: $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SH} \xrightarrow[\text{CCl}_4]{\text{Br}_2} ?$

Major product of this reaction is:

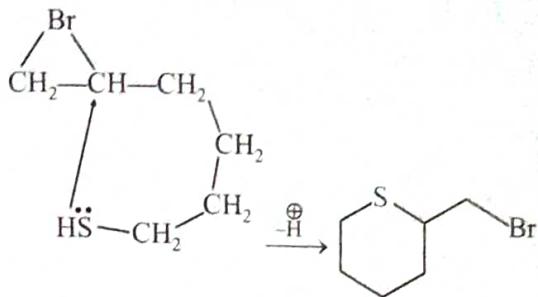
- (a) $\text{Br}_2\text{---CH}_2\text{---}\underset{\text{Br}}{\overset{|}{\text{CH}}}\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}$

(b) $\text{Br}_2\text{---CH}_2\text{---}\underset{\text{CCl}_3}{\overset{|}{\text{CH}}}\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}$

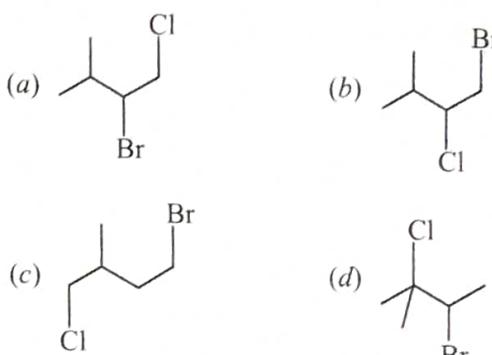
(c) $\text{Br}_2\text{---CH}_2\text{---}\underset{\text{Cl}}{\overset{|}{\text{CH}}}\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}$

(d) 

Sol. (d) $\text{CH}_2 = \text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SH} \xrightarrow[\text{CCl}_4]{\text{Br}}$



Example 22: 



Sol. (b) $X = \begin{array}{c} | \\ \text{C=C} \\ | \\ \text{CH}_2\text{CH}_2\text{Cl} \end{array}$; $Y = \begin{array}{c} \text{CH}_3\text{CH}_2 \\ | \\ \text{CH}_2\text{CH}_2\text{Br} \end{array}$

1,4 addition Peroxide effect

Example 23: 

(i) (ii) (iii) (iv)
Arrange the given alkenes in decreasing order of their reactivity towards bromination-

- (a) i > ii > iii > iv (b) iv > iii > ii > i
 (c) i > ii > iv > iii (d) iii > iv > ii > i

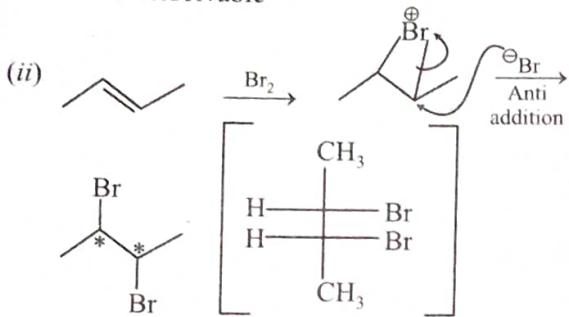
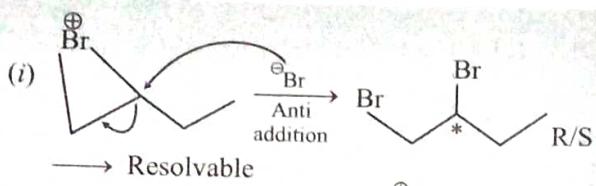
Sol. (a) More the e^- density on alkene, more is its nucleophilic nature.

Example 24:  

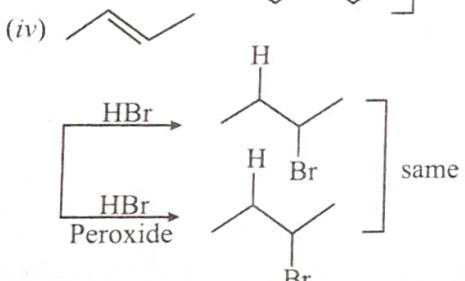
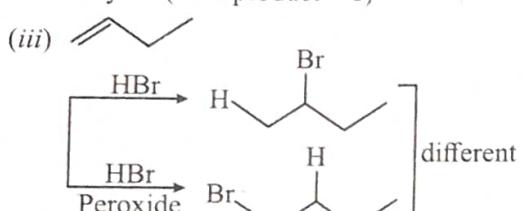
Compound I Compound II
Select the correct statement about compound I and compound II from the following.

- (a) I gives resolvable product with $\text{Br}_2 / \text{CCl}_4$
 - (b) II gives non resolvable product with $\text{Br}_2 / \text{CCl}_4$
 - (c) I gives different product with HBr in presence or absence of peroxide.
 - (d) II gives same product with HBr in presence or absence of peroxide.

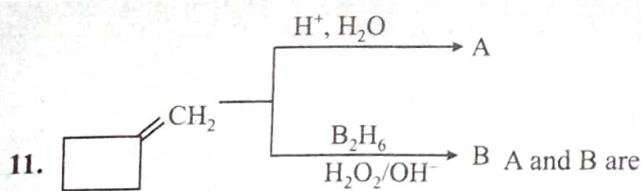
Sol.(a, b, c, d)

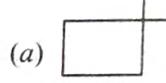
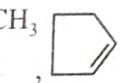
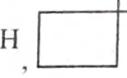
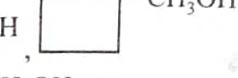
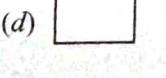
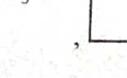


Non resolvable (meso) → contain POS
Erythro (total product = 1)

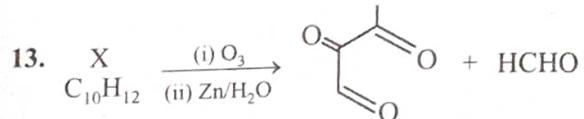
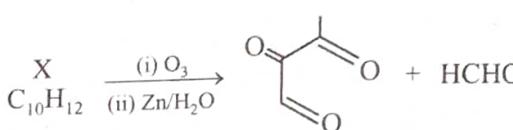
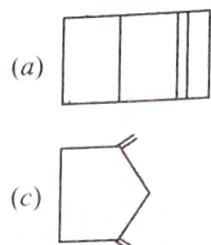
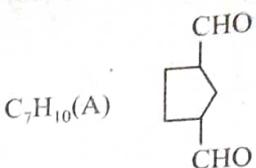


Concept Application

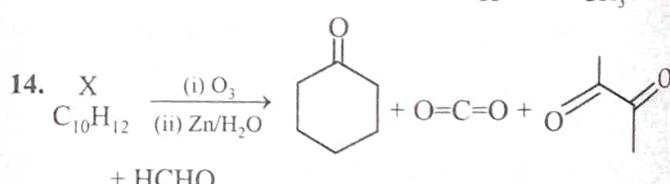
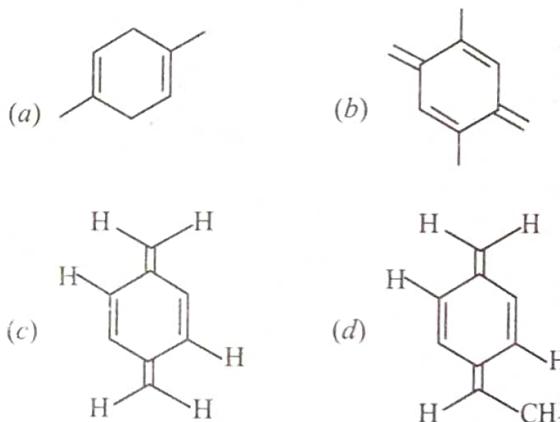


- (a)  , 
- (b)  , 
- (c)  , 
- (d)  , 

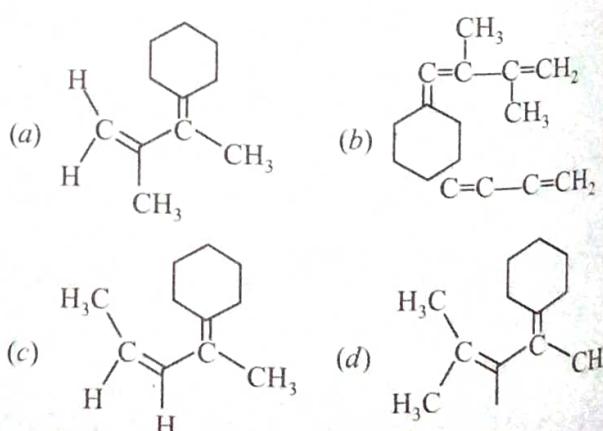
12. Identify the starting compound 'A':

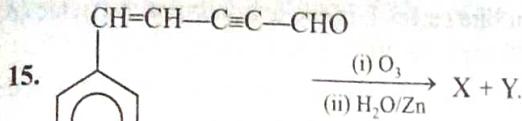


Which of the following options on ozonolysis gives the following products?

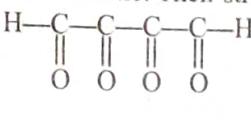
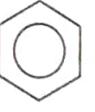
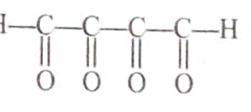
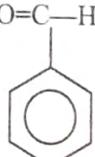
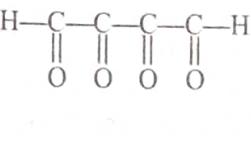


Which of the following options on ozonolysis gives the following products?





One of the product is aromatic. Their structures are

- (a)  , 
- (b)  , 
- (c)  , 
- (d) All of these

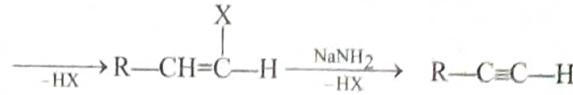
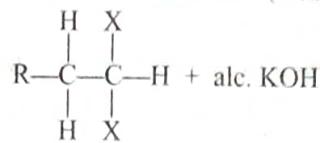
ALKYNES

1. General Introduction

- (1) The chemistry of the carbon-carbon triple bond is similar to that of the double bond. In this chapter, we see that alkynes undergo most of the reactions of alkenes, especially the addition and the oxidation. We also consider reactions that are specific to alkynes. Some that depends on the unique characteristics of the ($-C \equiv C-$) triple bond, and others that depend on the unusual acidity of the acetylenic ($-C \equiv C-$) bond.
- (2) Alkynes are hydrocarbons that contains carbon–carbon triple bond. Alkynes are also called acetylenes because they are derivatives of acetylene, the simplest alkyne.
- (3) Alkynes are not as common in nature as alkenes, but some plants do use alkynes to protect themselves against disease or predators. Cicutoxin is a toxic compound found in water hemlock, and capillin protects a plant against fungal diseases. The alkyne functional group is not common in drugs, but parsaltamide is used as an analgesic, and ethynodiol (a synthetic female hormone) is a common ingredient in birth control pills.
- (4) Acetylene is by far the most important commercial alkyne. Acetylene is an important industrial feedstock, but its largest use is as the fuel for the oxyacetylene welding torch. Acetylene is a colourless, foul-smelling gas that burns in air with a yellow, sooty flame. When the flame is supplied with pure oxygen, however, the color turns to light blue, and flame temperature increases dramatically.
- (5) Bond angle in alkyne is 180° .
- (6) Their general formula is C_nH_{2n-2}
- (7) C–C triple bond length is 1.20 \AA .
- (8) C–H bond length is 1.08 \AA .

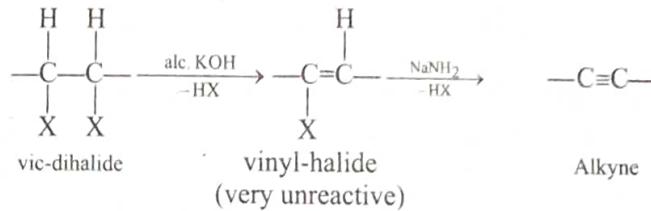
2. Methods of Preparation

2.1 From Gem Dihalides (Dehydrohalogenation):



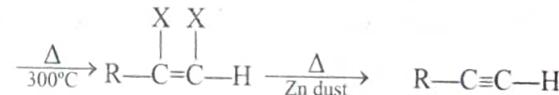
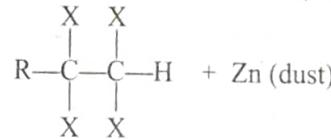
Note: Alc.KOH is not used for elimination in second step because in this case elimination takes place from doubly bonded carbon atom which is stable due to resonance so strong base NaNH_2 is used for elimination of HX .

2.2 From vicinal dihalides:



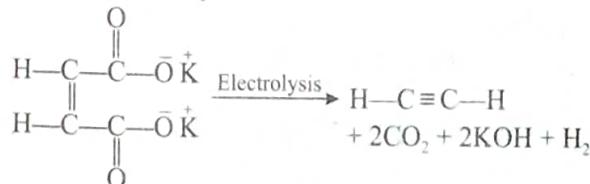
The elimination of one molecule of hydrogen halide yields vinyl halide which is very unreactive. Under mild conditions, the dehydrohalogenation stops at vinylic halide stage but more vigorous conditions like the use of a stronger base like amide ion ($-\text{NH}_2^-$) are required for alkyne formation.

2.3 From Tetrahaloalkanes (Dehalogenation):



In the above reaction it is necessary that the four halogen atoms must be attached at vicinal carbons. If they are attached at the two ends then the product cyclo alkene is obtained.

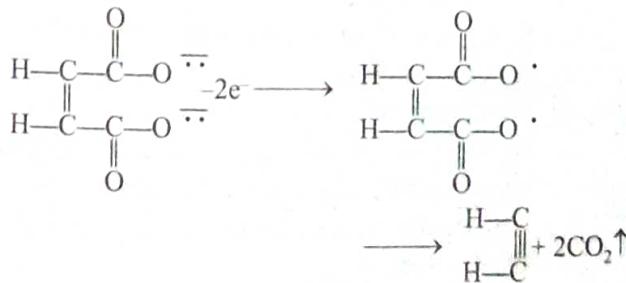
2.4 From Kolbe's Synthesis:



Potassium Malate

Mechanism

At Anode :



At Cathode :

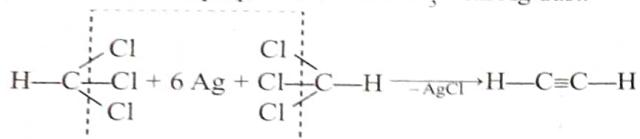


2.5 Laboratory method of preparation of Acetylene :

- (a) In laboratory acetylene is prepared by hydrolysis of calcium carbide.

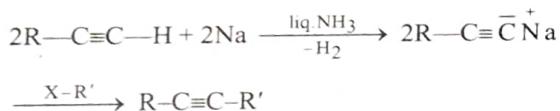
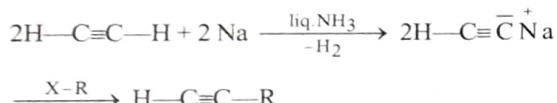


- (b) It can also be prepared from $CHCl_3$ with Ag dust.

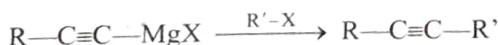
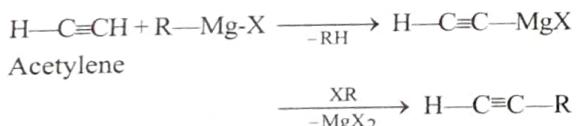


2.6 From Alkynes : (To form higher Alkynes)

- 2.6.1 With Na:** When acetylene or 1- alkyne react with Na in presence of liq. NH_3 then an intermediate compound sodium acetylide or sodium alkynide is formed which gives higher alkyne with alkyl halide.



- 2.6.2 With Grignard reagent (GR):** When acetylene or 1- alkyne react with GR then alkane and unsaturated GR is formed which further react with alkyl halide and form higher alkyne.



3. Physical Properties:

- (a) Alkynes are colourless, odourless and tasteless.
- (b) Lower alkynes are partially soluble in H_2O . (It is due to its polarisability).
- (c) Higher alkynes are insoluble in water due to more % of covalent character.
- (d) Completely soluble in organic solvents.
- (e) Melting point and boiling point increases with molecular mass and decreases with number of branches.
- (f) Upto C_4 alkynes are gaseous, C_5-C_{11} are liquid, C_{12} and above are solids.

(g) Pure acetylene is odourless and impure acetylene has odour like garlic. It is due to impurities of arsenic (AsH_3) and Phosphine (PH_3).

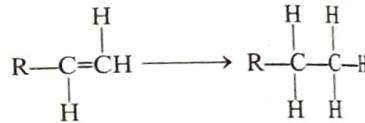
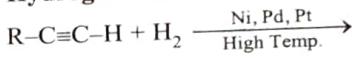
(h) Acetylene and 1- alkyne are acidic in nature. It is due to greater electronegativity of sp hybridised 'C'.

(i) Acetylene has two acidic hydrogen atoms. It can neutralise two equivalents of base at the same time. So it is also called as dibasic acid. But the base should be very strong as $(-NH_2)$ or $(-CH_3)$ etc.

4. Chemical Properties:

The chemical behaviour of alkynes is similar to that of alkenes. Alkynes form addition products with two or four univalent atoms or groups. They are generally less reactive than alkenes towards electrophilic addition reactions even though π electron density is higher in alkynes. This is because on moving from alkene to alkyne, the C—H bond has more of s character (33% in alkenes as compared to 50% in alkynes). Therefore, the π -electrons are more firmly held by carbon nuclei in alkynes and are thus less reactive to an electrophile.

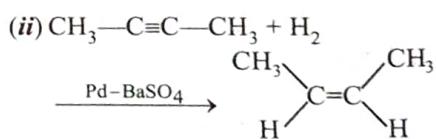
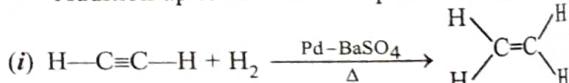
4.1 Hydrogenation



The above reaction is called as **Sabatier Sendorson's reaction**.

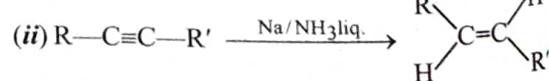
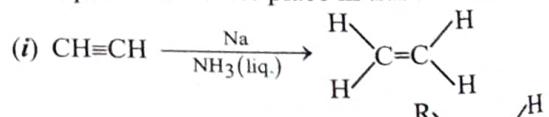
4.1.1 Hydrogenation in the presence of Lindlar's Catalyst:

Addition up to alkene takes place in cis manner

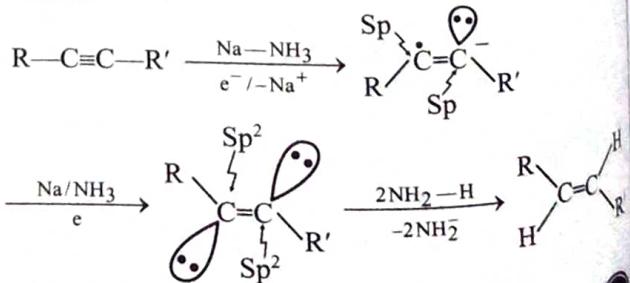


4.1.2 Hydrogenation by Na + NH₃ (liq.):

Addition upto alkene takes place in trans manner

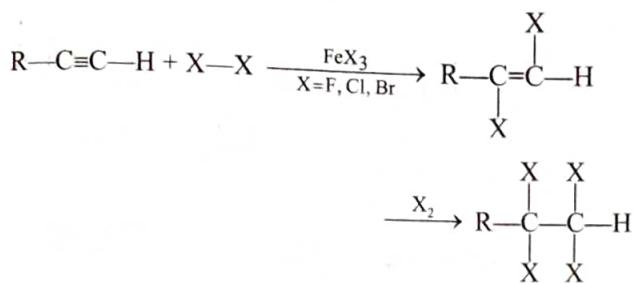


Mechanism :

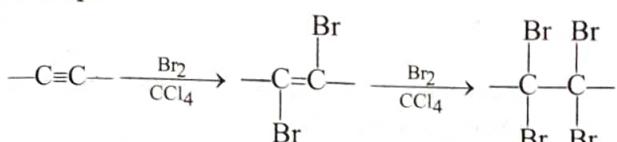


4.2 Halogenation

In presence of Lewis acid as a catalyst alkyne form tetrahaloderivative with halogen.



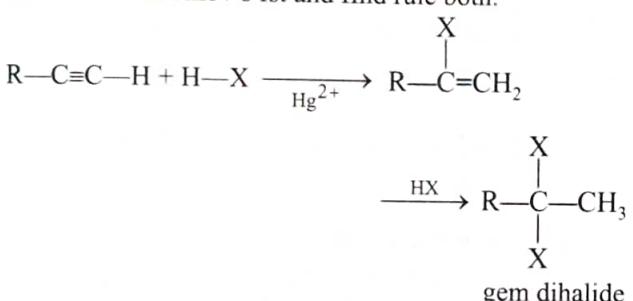
Example:



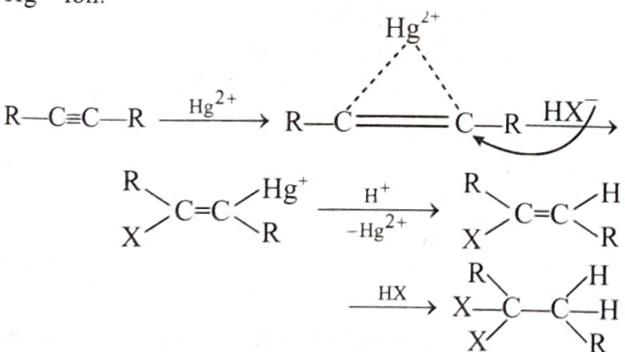
Alkynes add two molecules of Br_2 in CCl_4 and decoloration of bromine water is used to detect the presence of a double or triple bond.

4.3 Reaction with HX (Hydrohalogenation)

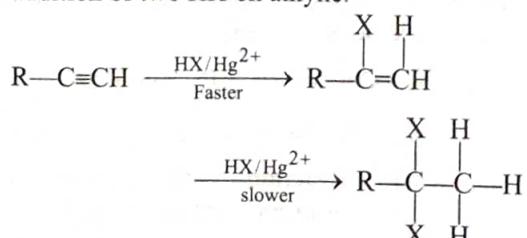
Alkyne form gem dihalide with HX because reaction follows Markovinov's Ist and IInd rule both.



Mechanism: The reaction takes place in the presence of Hg^{2+} ion.

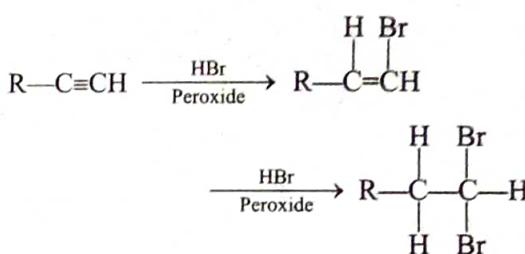


Note: (i) First step is faster than the second step among addition of two HX on alkyne.



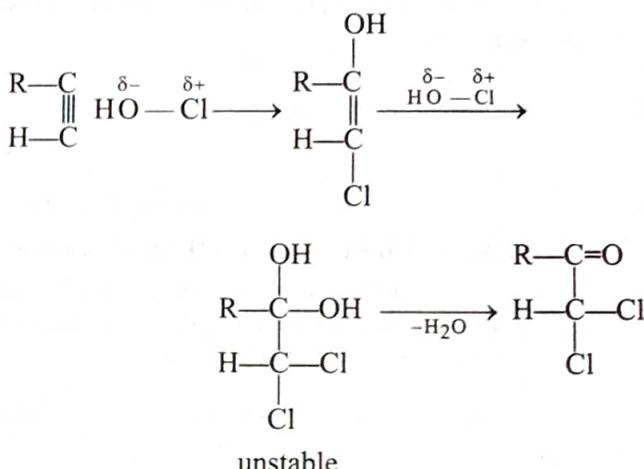
Slower rate of addition of 2nd molecule is caused by lower electron cloud density on $C \equiv C$, due to ... effect of 'Cl'.

(ii) Peroxide give same effect as in alkene.



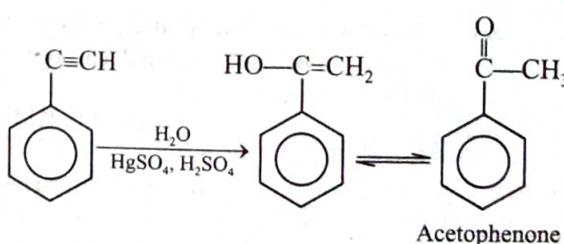
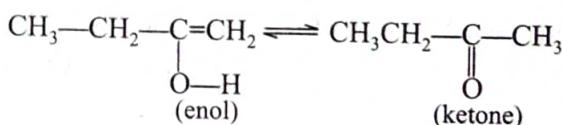
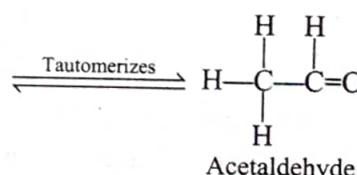
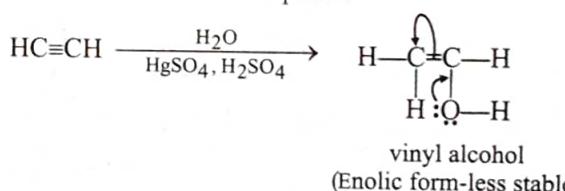
4.4 Reaction with Hypochlorous acid or Chlorine water

Hypochlorous acid is broken into OH^- and Cl^+ ions and gives addition. According to Markovnikov's rule.

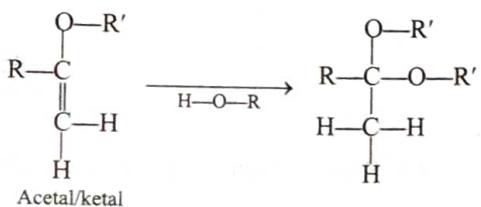
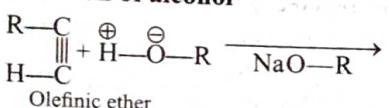


4.5 Hydration

Addition of water to alkynes is carried out in the presence of acid and mercuric sulphate.

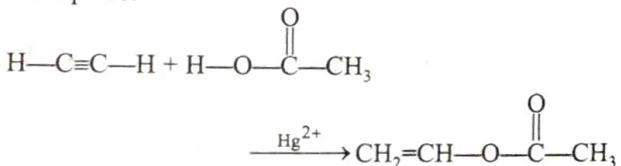


4.6 Addition of alcohol



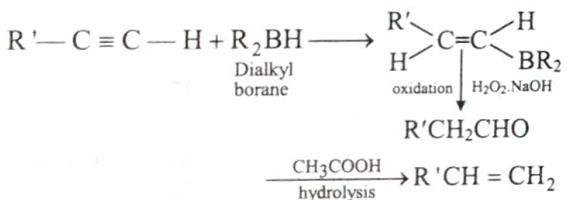
4.7 Addition of Carboxylic Acid

In the presence of Hg^{2+} unioxylation of carboxylic acid takes place.

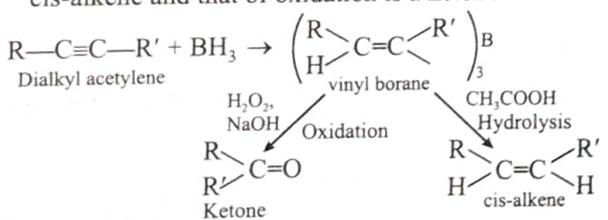


4.8 Addition of Boron Hydride (Hydroboration)

- (i) With mono-alkyl acetylene, R_2BH gives an intermediate which on hydrolysis gives alkene but on alkaline oxidation yields aldehyde.



- (ii) With dialkyl acetylenes, the product of hydrolysis is cis-alkene and that of oxidation is a ketone.



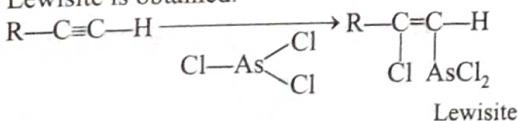
4.9 Addition of HCN

Addition takes place in the presence of CuCl .



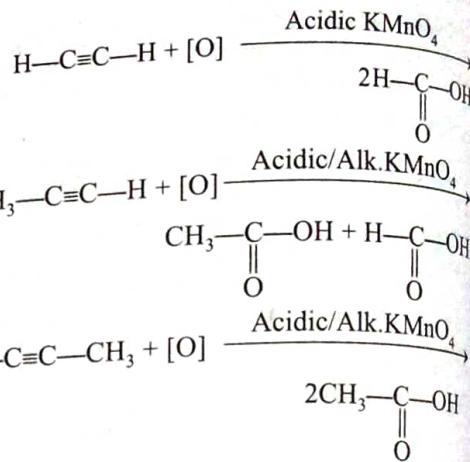
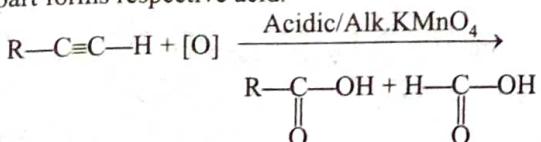
4.10 Addition of AsCl_3

Lewisite is obtained.

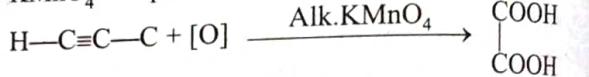


4.11 Oxidation

- 4.11.1** With acidic or alkaline KMnO_4 alkynes break into two parts from triply bonded carbon and every part forms respective acid.

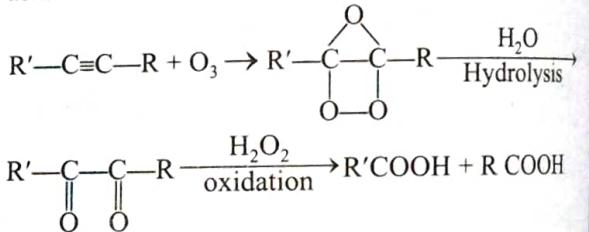


Exception: Acetylene forms oxalic acid with alkaline KMnO_4 exceptionally.



4.12 Ozonolysis

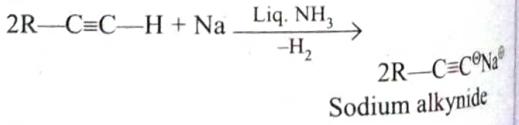
The ozonolysis of alkynes yields a mixture of carboxylic acids.



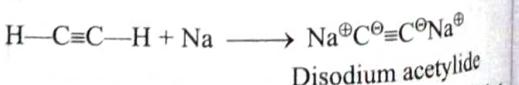
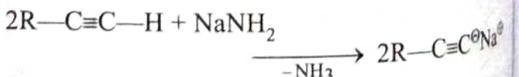
4.13 Acidic Nature of 1-Alkyne or Acetylene

In 1- alkyne or acetylene, the H which is linked with sp hybridised carbon is called as acidic or active H. It can easily be substituted by metal or alkaline species. Hence 1- alkyne or acetylene are acidic in nature.

4.13.1 Reaction with Na



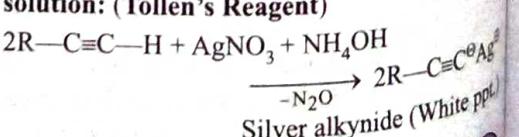
or



Note: Where this alkynide is treated with alkyl halide higher alkyne is obtained.

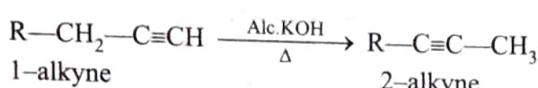


4.13.2 Reaction with Ammonical Silver Nitrate solution: (Tollen's Reagent)

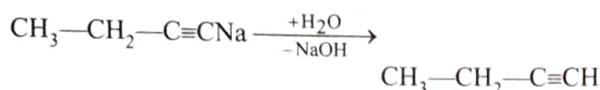
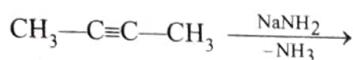


4.17 Isomerisation

- (a) When 1-alkyne is treated with alcoholic KOH, 2-alkyne is formed.



- (b) When 2-alkyne is treated with sodamide then it is converted into 1-alkyne.



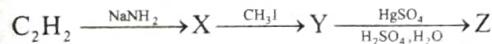
Train Your Brain

Example 25: Which compound does not give precipitate with ammoniacal silver nitrate solution?

- (a) $\text{C}_2\text{H}_5-\text{C}\equiv\text{CH}$
- (b) $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$
- (c) $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{C}\equiv\text{CH}$
- (d) $\text{Ph}-\text{CH}_2-\text{C}\equiv\text{CH}$

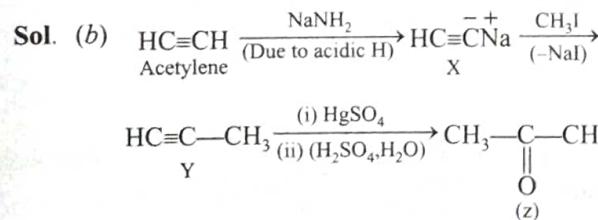
Sol. (b) Only terminal alkynes give precipitate with ammoniacal silver nitrate solution. Among the given, $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$ is not a terminal alkyne. Thus, it does not give precipitate with ammoniacal AgNO_3 .

Example 26: In the series,

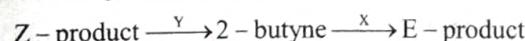


The compound Z is

- (a) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$
- (b) CH_3COCH_3
- (c) CH_3CHO
- (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$

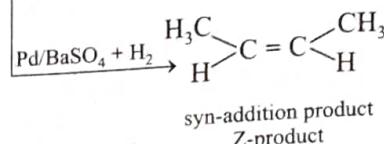
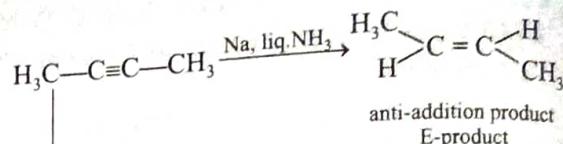


Example 27: What are X and Y respectively in the following reaction?



- (a) $\text{Na}/\text{NH}_3(\text{liq.})$ and $\text{Pd}/\text{BaSO}_4 + \text{H}_2$
- (b) $\text{Ni}/140^\circ\text{C}$ and $\text{pd}/\text{BaSO}_4 + \text{H}_2$
- (c) $\text{Ni}/140^\circ\text{C}$ and $\text{Na}/\text{NH}_3(\text{liq.})$
- (d) $\text{Pd}/\text{BaSO}_4 + \text{H}_2$ and $\text{Na}/\text{NH}_3(\text{liq.})$

Sol. (a)



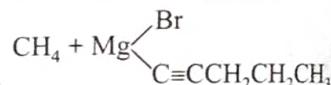
Z-product

Example 28: Which one of the following compounds will react with methyl magnesium bromide?

- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{CH}_3$
- (b) $\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$
- (c) $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_2\text{CH}_3$
- (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$

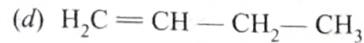
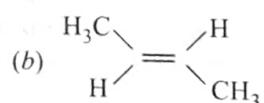
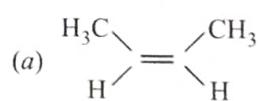
Sol. (d) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CH} + \text{CH}_3\text{MgBr}$

Methyl magnesium
bromide

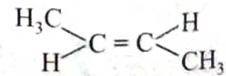
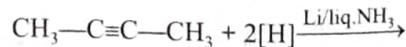


Due to the presence of acidic hydrogen (hydrogen attached to triply bonded carbon atom), terminal alkyne (d) will react with methyl magnesium bromide.

Example 29: The major product in the reaction of 2-butyne with $\text{Li}/\text{liq NH}_3$ is



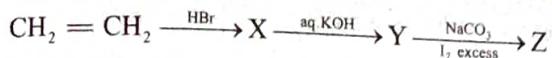
Sol. (b) Reaction of a non-terminal alkyne with a solution of an alkali metal (usually Na or Li or K) in liquid ammonia give a *trans*-alkene.



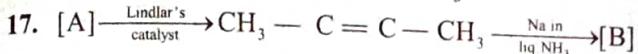


Concept Application

16. Identify Z in the series,



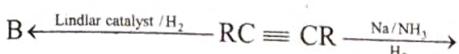
- (a) $\text{C}_2\text{H}_5\text{I}$ (b) $\text{C}_2\text{H}_5\text{OH}$
 (c) CHI_3 (d) CH_3CHO



[A] and [B] are respectively

- (a) cis, trans-2-butene (b) Both trans-2-butene
 (c) trans, cis-2-butene (d) Both cis-2-butene

18. In the reactions,



A and B are geometrical isomers. Then,

- (a) A is cis and B is trans.
 (b) A is trans and B is cis.
 (c) A and B are cis.
 (d) A and B is trans.

AROMATIC COMPOUNDS

Benzene

- (i) Aromatic compounds contains high percentage of carbon. They burn with smoky flame.
 (ii) Aromatic compounds have the cyclic system and contains $(4n + 2)\pi$ electrons [Huckel rule].

Where $n = 0, 1, 2, 3, \dots$

Dipropylcyclopropenium $n = 0$ 2π -electron

Perchlorate

Benzene, Pyridine, Pyrrole, $n = 1$ 6π -electron

Furan, Thiophene etc.

Naphthalene $n = 2$ 10π -electron

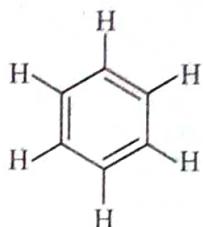
Anthracene $n = 3$ 14π -electron

Aromatic Compounds (Main Source): Bituminous coal when subjected to destructive distillation in the absence of air [1000 °C–1200 °C], the chief constituent obtained is coal tar.

Fractional distillation of coal tar : Different fractions are :

Fraction	Temperature	Main constituents
(a)	Light oil	80 °C – 170 °C
		Benzene, Toluene, Xylene etc.
(b)	Middle oil (carbolic oil)	170 °C – 230 °C
		Naphthalene, Phenol etc.
(c)	Heavy oil	230 °C – 270 °C
		Cresols, Naphthalene
(d)	Green oil	270 °C – 360 °C
		Anthracene

Structure of Benzene



(i) **Discoverer :** Michael Faraday.

(ii) C-hybridisation : sp^2

(iii) Geometry – Hexagonal

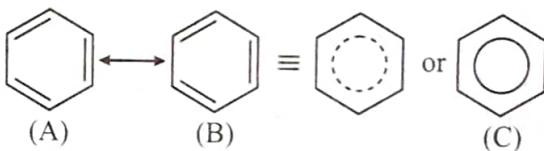
(iv) Bond angle : 120°

(v) C-C Bond length : 1.39\AA

(vi) C-H Bond length : 1.09\AA

Resonance and Stability of Benzene: Two modern hypothesis had been given to explain the stability and structure of benzene. These two theories are :

(i) **Resonance or valence-bond theory:** According to valence-bond theory, the oscillating nature of double bonds in benzene (as proposed by Kekule) is now proposed by resonance. Even though the double bonds keep on changing their positions. The structures produced is such that the position of nucleus remains the same in each of the structure. The structural formula of such a compound is somewhat intermediate (hybrid) between the various proposed formulas. This state is known as Resonance.



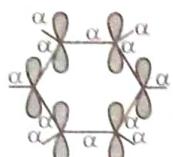
The structures proposed by Kekule are the two main contributing structures of benzene. The hybrid structure is represented by inserting a circle or a dotted line in the hexagon as shown in figure (C). The circle represents the six electrons which are delocalized between the six carbon atoms of the benzene ring.

X-ray diffraction data reveals that benzene is a planar molecule. Had any one of the above structures of benzene (A and B) been correct. Two types of C-C bond lengths were expected. However, X-ray data indicates that all the six C-C bond lengths are of the same order (139 pm) which is intermediate between C-C single bond (154 pm) and C-C double bond (133 pm). The C-C bond length in benzene (139 pm) indicates that each bond in benzene had acquired the characteristics differently due to resonance. The single bond acquires the characteristic of double bond and the double bond acquires the characteristic of single bond, thus changing the bond lengths. This is why the absence of pure double bond in benzene accounts for the reluctance of benzene to show addition reactions under normal conditions, thus explaining the unusual behaviour of benzene.

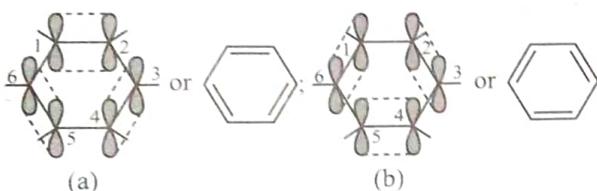
(ii) **Molecular orbital theory to explain benzene structure:**



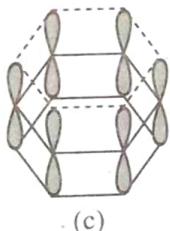
The orbital overlapping gives us better picture about the structure of benzene. All the six carbon atoms in benzene are sp^2 hybridized. Two sp^2 hybrid orbitals of adjacent carbon atoms overlap with sp^2 hybrid orbitals of each carbon atom which also overlaps with s-orbital of a hydrogen atom to form six C–H sigma bonds. Each carbon atom is now left with one unhybridised p-orbital perpendicular to the plane of the ring as shown below.



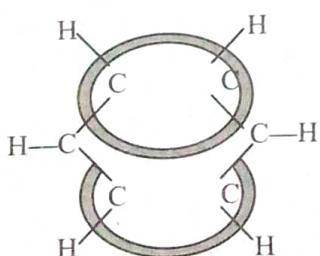
The unhybridised p-orbital of carbon atoms are close enough to form a π -bond by lateral overlap. There are two equal possibilities of forming three π -bonds by overlap of p-orbitals of $C_1-C_2, C_3-C_4, C_5-C_6$ or $C_2-C_3, C_4-C_5, C_6-C_1$ respectively as shown in following figures.



Structures shown in the above figures correspond to two Kekulé's structures with localised Pi-bonds. The internuclear distance determined between all the carbon atoms in the ring by the X-ray diffraction is found to be the same showing, there is equal probability for the p-orbital of each carbon atom to overlap with the p-orbitals of adjacent carbon atoms (c). This can be represented in the form of two doughnuts (rings) of electron clouds (d), one above the plane and one below the plane of the hexagonal ring as shown below:



The six π -electrons are thus delocalised and are free to move about the six carbon nuclei, instead of any two as shown in (a) and (b). This spreading of π -electrons in the form of ring of π -electrons above and below the plane of carbon atoms is called delocalisation of π -electrons.



The delocalized π -electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localised between two carbon atoms. Therefore, presence of delocalised π -electrons in benzene makes it more stable than the hypothetical cyclohexatriene.

Methods of Preparation of Benzene

(i) **Isolation From 'Light Oil Fraction: Industrial method:**
Light oil $\xrightarrow[\text{NaOH}]{\text{H}_2\text{SO}_4}$ Basic impurities removed (like pyridine) $\xrightarrow{\text{Distillation}}$ Phenol removed (acidic impurities) $\xrightarrow{\text{Benzene (255 K-257 K)}}$

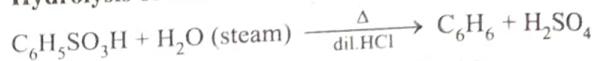
(ii) **Decarboxylation of Sodium Benzoate: Laboratory Method:**
Benzene is formed by dry distillation of sodium benzoate with soda lime.



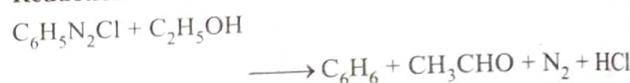
(iii) **Reduction of Phenol:**



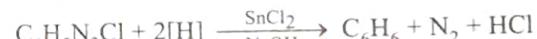
(iv) **Hydrolysis of Benzene sulphonic Acid:**



(v) **Reduction of Benzenediazonium Chloride:**



Hypophosphorous acid (H_3PO_2) or sodium stannite ($\text{SnCl}_2 + \text{NaOH}$) or formic acid can also be used for reduction in place of ethanol.



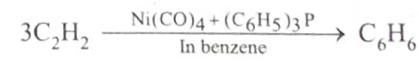
(vi) **Hydrolysis of Phenylmagnesium bromide:**



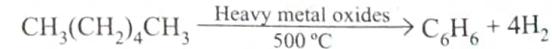
(vii) **Reduction of Chlorobenzene:**



(viii) **Trimerisation of Acetylene:**



(ix) **Hydroforming of n-Hexane:**



Physical Properties: Benzene is a colourless liquid (boiling point, 80°C), having a characteristic smell. It forms a colourless crystalline solid (melting point, 5.4°C) on cooling. It burns with smoky or sooty flame. It is lighter than water (relative density, 0.8790 g/m) and is immiscible with water. Being nonpolar in nature, it is miscible with many organic solvents, like alcohol, ether, acetone, acetic acid, carbon tetrachloride, carbon disulphide, etc.

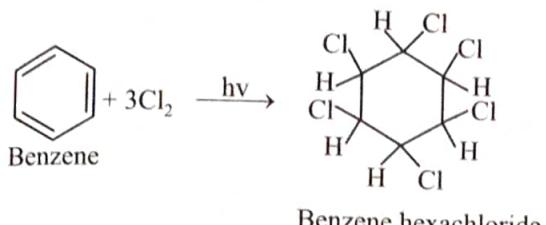
Reaction: Benzene is a compound having very low reactivity, because it remains unaffected by many common reagents, like HCl, KOH, NaOH, KMnO₄, K₂Cr₂O₇, etc.

Benzene shows the following types of reactions :

- (a) Addition
- (b) Electrophilic substitution
- (c) Oxidation

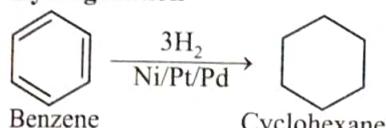
Addition Reaction

1. Halogenation

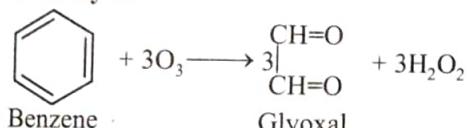


Benzene hexachloride is also known by many other names e.g., **B.H.C.**, **gammoxene**, **gammone**, **lindane 666** (triple six) and **1,2,3,4,5,6-hexachlorocyclohexane**. It was found that the γ isomer is a very strong **insecticide** and **pesticide**, hence the names gammoxene and gammone.

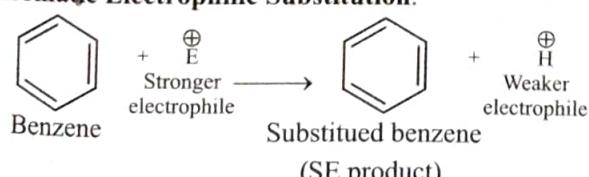
2. Hydrogenation



3. Ozonolysis

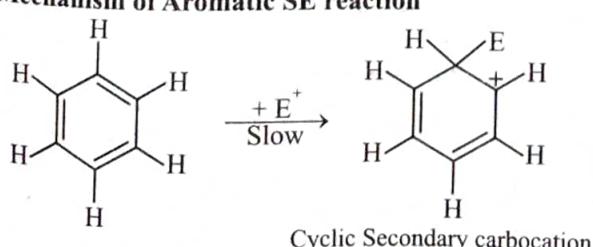


Electrophilic Substitution: A continuous π cloud is spread above and below the benzene ring. Due to this, an electrophile is attracted towards the benzene ring. This electrophile removes proton (the weaker electrophile) and take its place in order to gain greater stability and forms an **Electrophilic Substitution Product or SE product**. This process is called **Aromatic Electrophilic Substitution**.

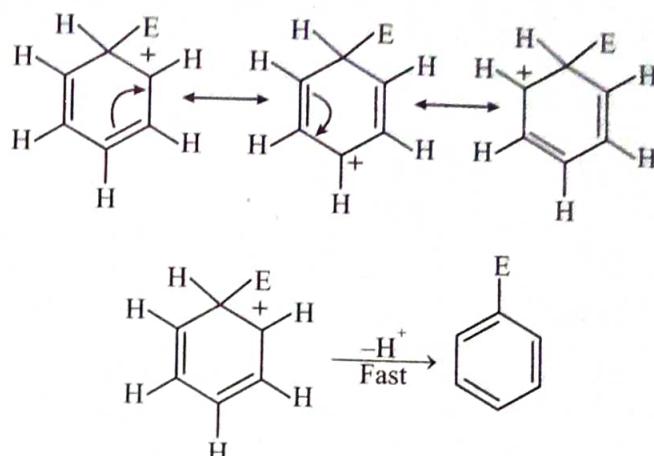


Nonaromatic intermediate formed in an aromatic electrophilic substitution reaction is known as **Wheland intermediate**.

Mechanism of Aromatic SE reaction

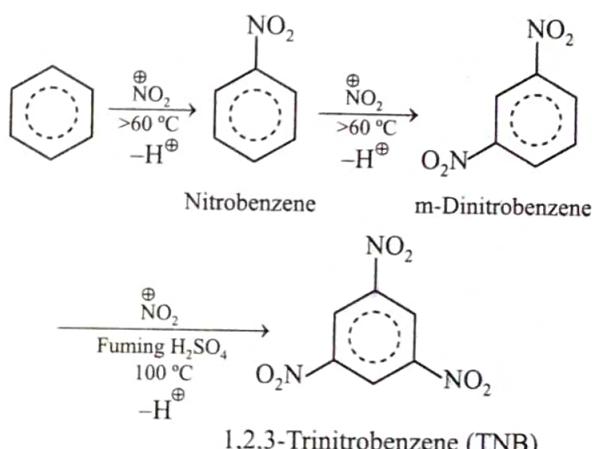


Cyclic secondary carbocation formed is stabilised by resonance.

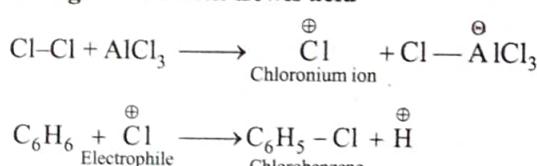


This is called as **SE²** mechanism i.e.; substitution electrophilic bimolecular reaction.

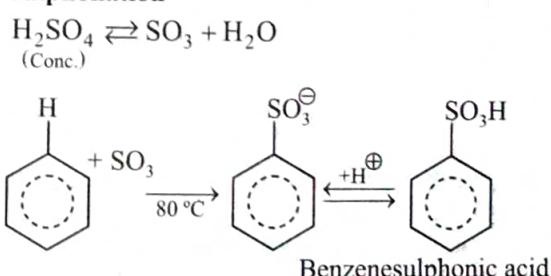
4. Nitration



5. Halogenation with Lewis acid



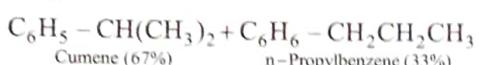
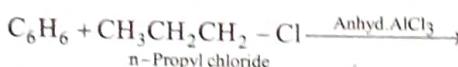
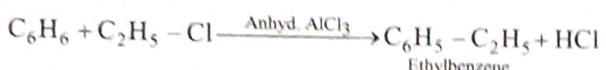
6. Sulphonation



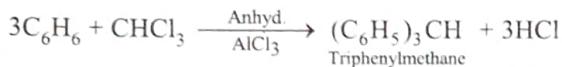
7. Friedel-Crafts Reaction

Friedel-Crafts reaction involves replacement of hydrogen atom of an aromatic ring by a carbocation species obtained from a compound in the presence of anhydrous aluminium chloride. Friedel-Crafts reaction is always carried out in nitrobenzene (boiling point 211 °C) medium and in the presence of anhydrous AlCl₃.

(i) Friedel-Crafts Alkylation :

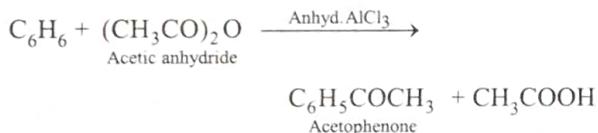
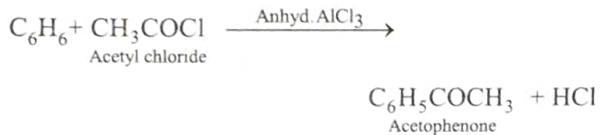


Note: A mixture of cumene and n-propylbenzene is also obtained on taking propylene in place of n-propyl chloride in the above reaction. Because intermediate 1° carbocation rearrange to give 2° carbocation.

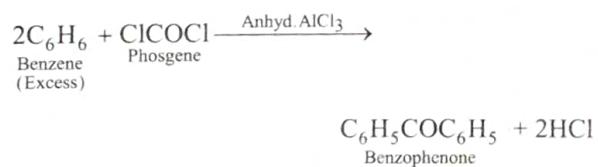
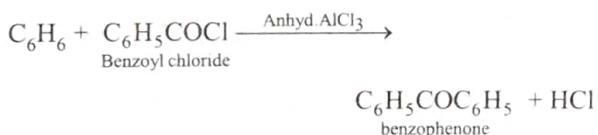


(ii) Friedel-Crafts Acylation: (Reaction with acyl chloride)

(a) Acetylation:



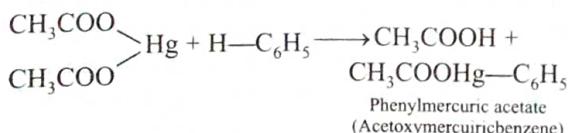
(b) Benzoylation:



The above conversions can be carried out by taking many other compounds in place of anhydrous AlCl_3 , FeCl_3 , FeBr_3 , SnCl_2 , ZnCl_2 , BF_3 , etc.

8. Mercuration

Benzene on heating with mercuric acetate forms **Acetoxymercuricbenzene**.

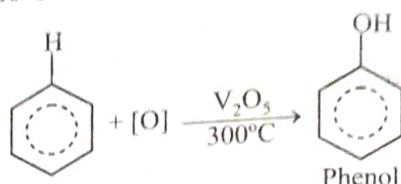


Oxidation

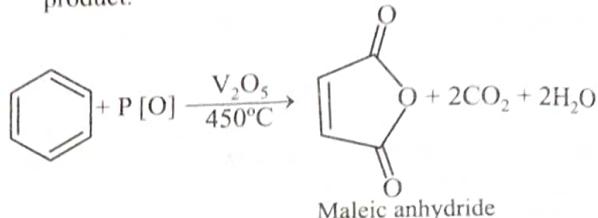
9. Catalytic Air Oxidation

Oxidation of benzene by air in the presence of vanadium pentaoxide (V_2O_5) can be carried out as follows :

(i) At 300°C – **Phenol** is obtained as the major product

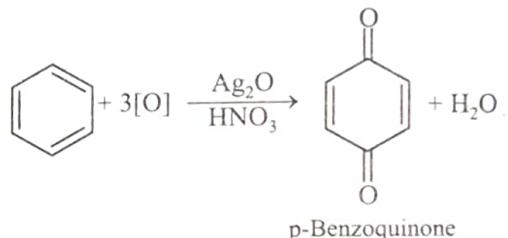


(ii) At 450°C – **Maleic anhydride** is obtained as the major product.



10. Silver Oxide Oxidation

Mainly **p-benzoquinone** is formed, when oxidation of benzene is carried out by silver oxide and HNO_3 .



11. Combustion

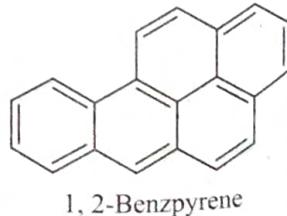
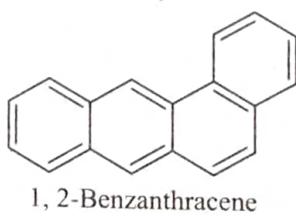


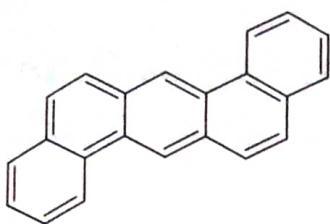
Catalytic Pyrolysis: When the vapours of benzene are passed through red-hot copper or iron tube at 600° , **biphenyl** is formed.



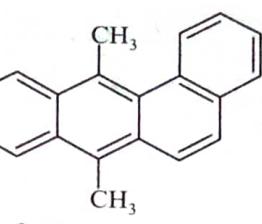
CARCINOGENICITY AND TOXICITY*

Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer-producing (carcinogenic) property. Such polynuclear hydrocarbons are formed on incomplete combustion of organic materials like tobacco, coal and petroleum. They enter into human body would undergo various biochemical reactions and finally damage DNA and cause cancer. Some of the carcinogenic hydrocarbons are given below.





1,2,5,6-Dienanthracene



9,10-Dimethyl-1,2-benzanthracene

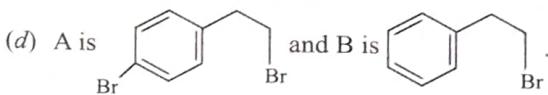
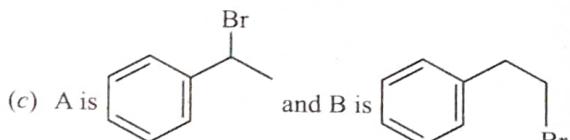
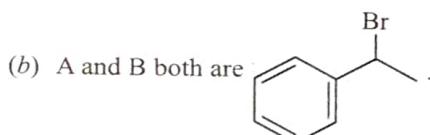
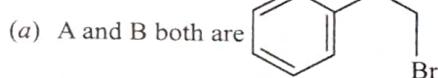
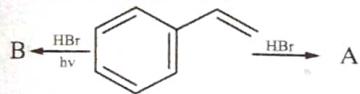
Uses of Benzene

- As an industrial solvent.
- In dry cleaning.
- As a constituent of power alcohol.
- In the manufacture of an insecticide and pesticide.
- In the manufacture of an explosive.
- In the manufacture of dyes.
- In the manufacture of medicines.
- In the manufacture of perfumes.
- In the synthesis of many aromatic compounds.
- As a fuel.

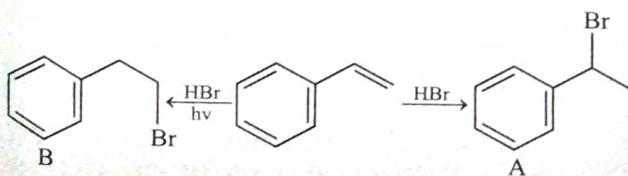


Train Your Brain

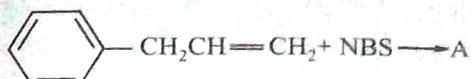
Example 30: Observe the following reactions and predict the nature of A and B



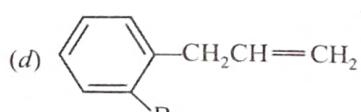
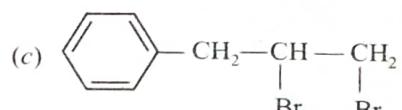
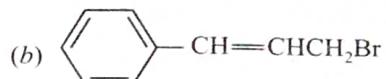
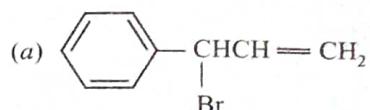
Sol. (c)



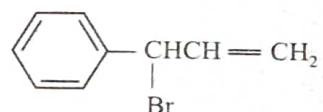
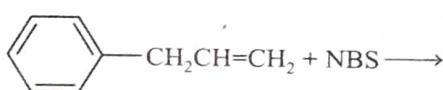
Example 31: Following compound is treated with NBS



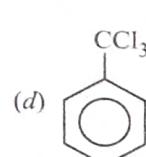
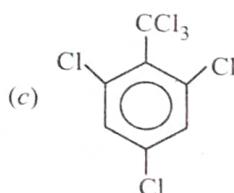
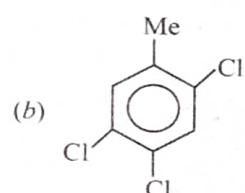
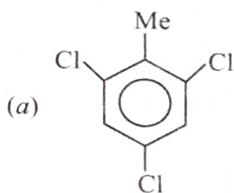
Compound formed A is



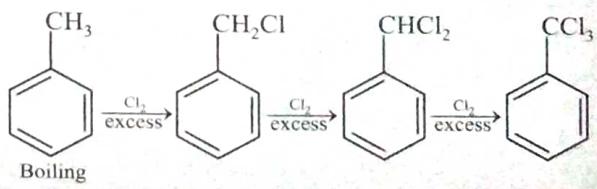
Sol. (a)



Example 32: By passing excess $\text{Cl}_2(g)$ boiling toluene, which one of the following compounds is exclusively formed



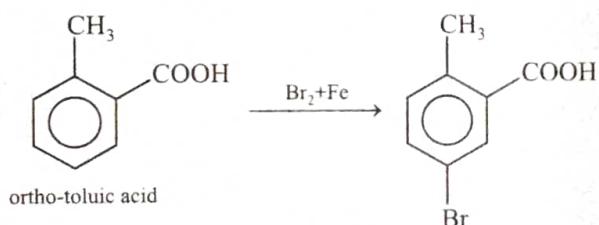
Sol. (d)



Example 33: O-toluic acid on reaction with $\text{Br}_2 + \text{Fe}$ gives

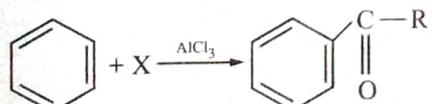
- (a)
- (b)
- (c)
- (d)

Sol. (c)



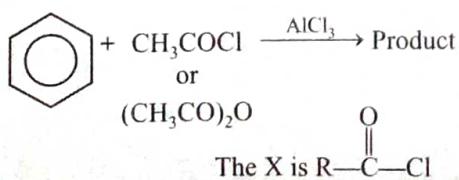
\therefore In the product, ($-\text{Br}$) is *para* to ($-\text{CH}_3$) and *meta* to ($-\text{COOH}$).

Example 34: Friedel - craft acylation can be given by X is



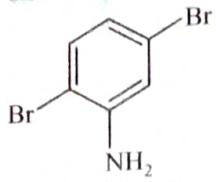
- (a) $\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{Cl}$
- (b) $\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{R}$
- (c) $\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}$
- (d) $\text{R}-\text{O}-\text{R}$

Sol. (a)



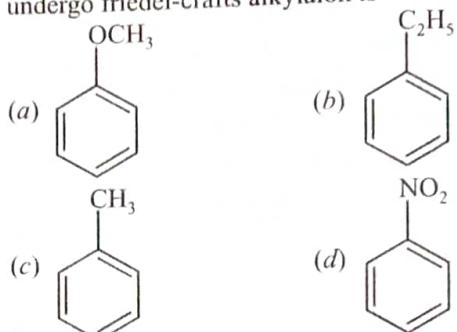
Concept Application

19. The correct name for the compound shown below is:

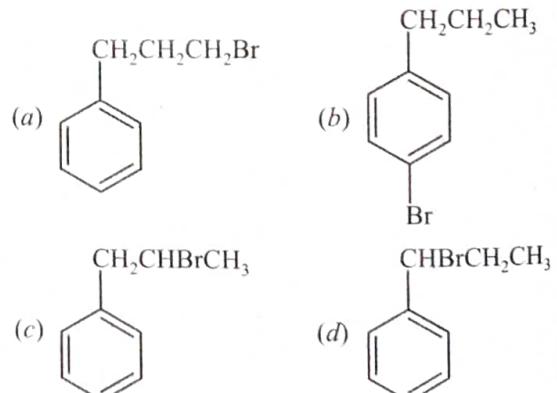
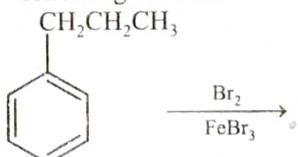


- (a) 3, 4-dibromoaniline
- (b) 2, 4-dibromoaniline
- (c) 2, 5-dibromoaniline
- (d) 3, 6-dibromoaniline

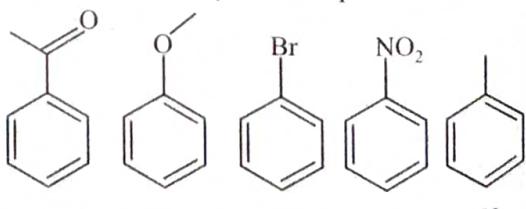
20. Among the following compounds the one that will not undergo Friedel-Crafts Alkylation is



21. Provide the structure of the major product(s) from the following reaction.



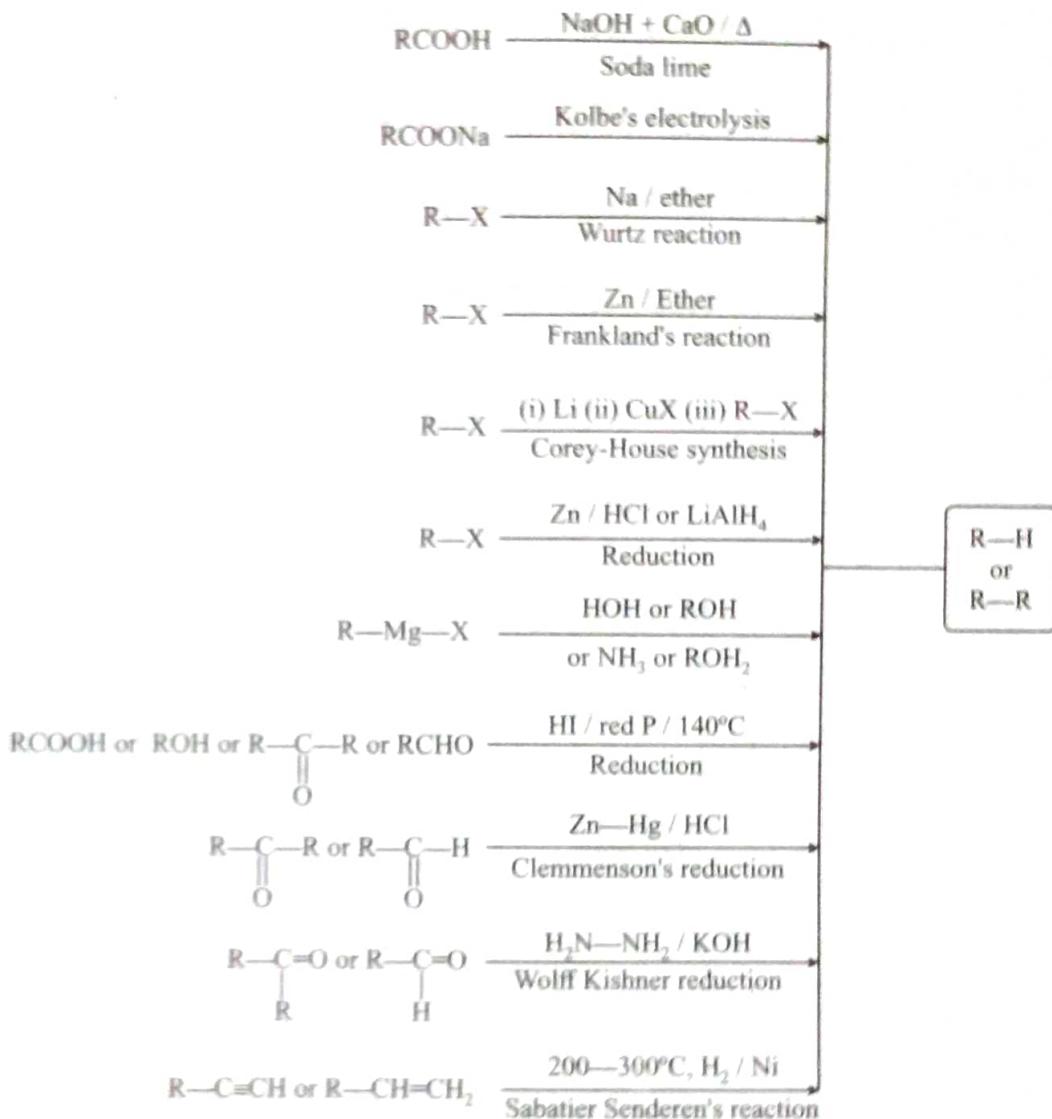
22. Arrange the following compounds in the order of decreasing reactivity in electrophilic substitution



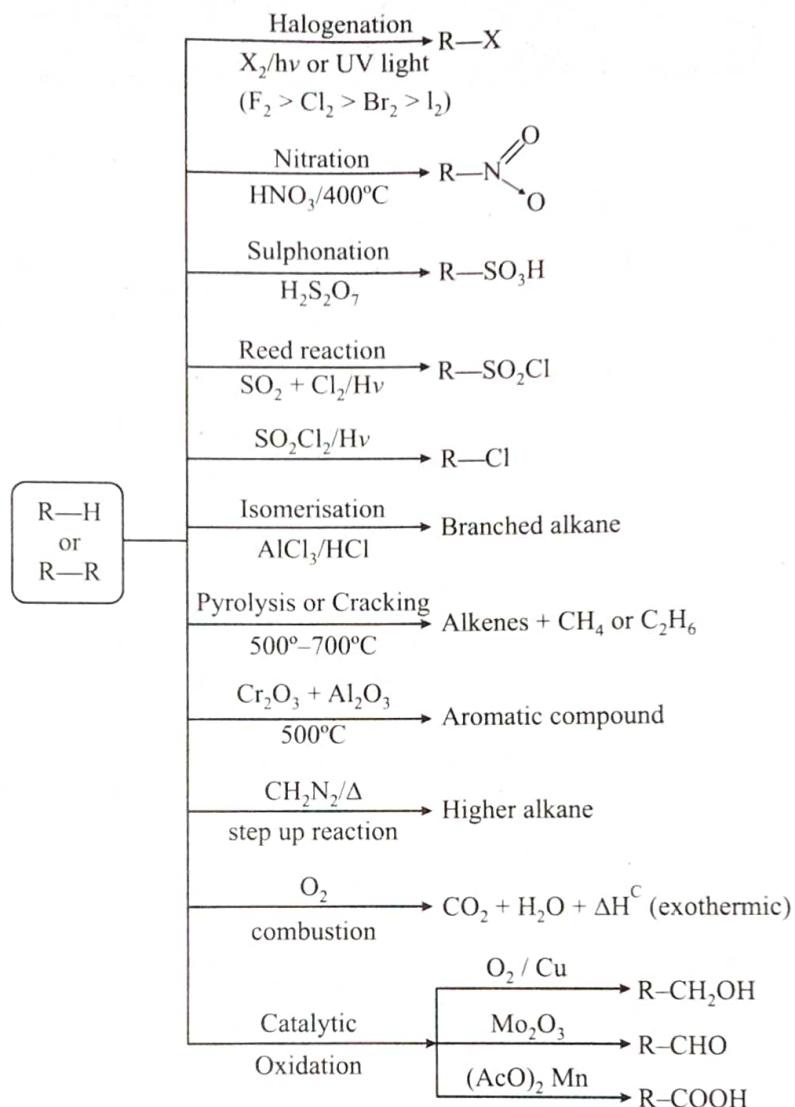
- (a) $\text{V} > \text{II} > \text{I} > \text{III} > \text{IV}$
- (b) $\text{II} > \text{V} > \text{III} > \text{I} > \text{IV}$
- (c) $\text{IV} > \text{I} > \text{III} > \text{V} > \text{II}$
- (d) $\text{III} > \text{II} > \text{I} > \text{IV} > \text{V}$

Short Notes

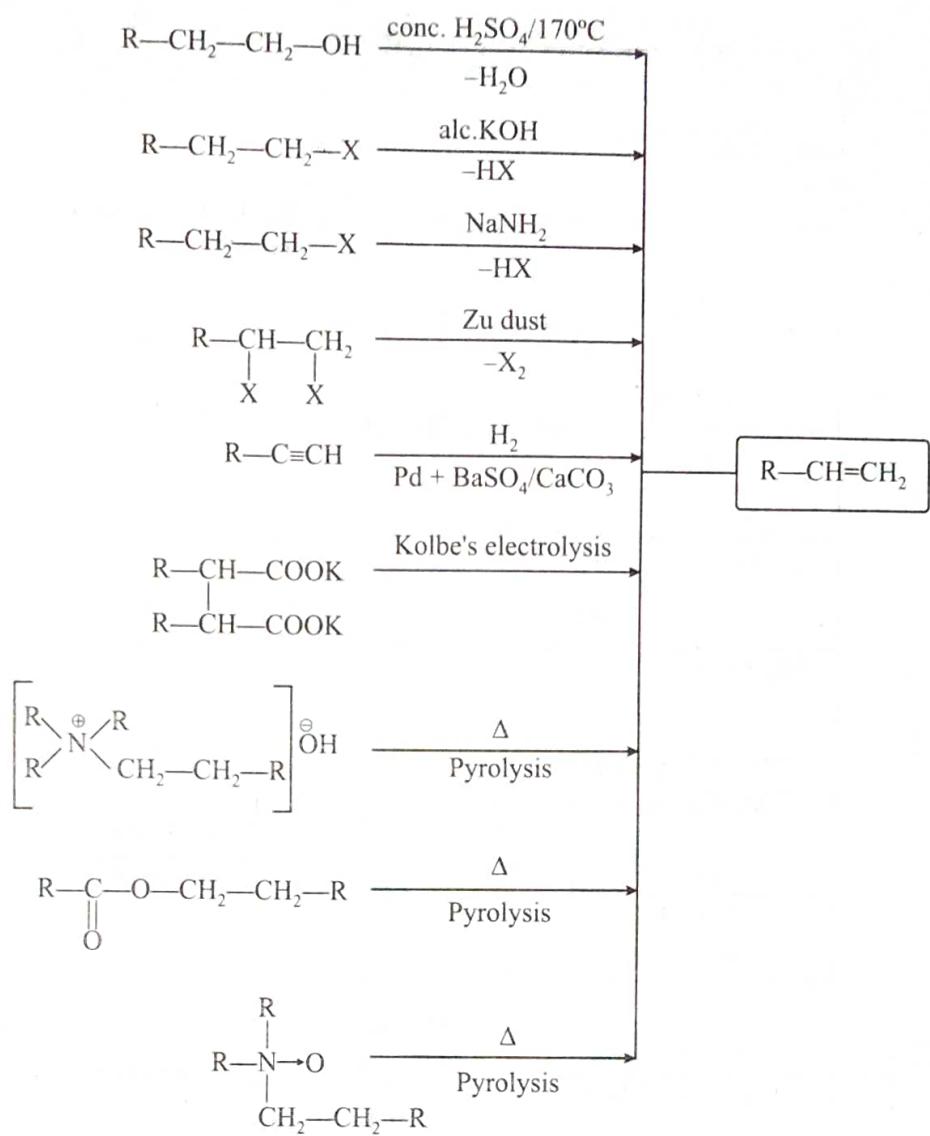
Preparation of Alkane



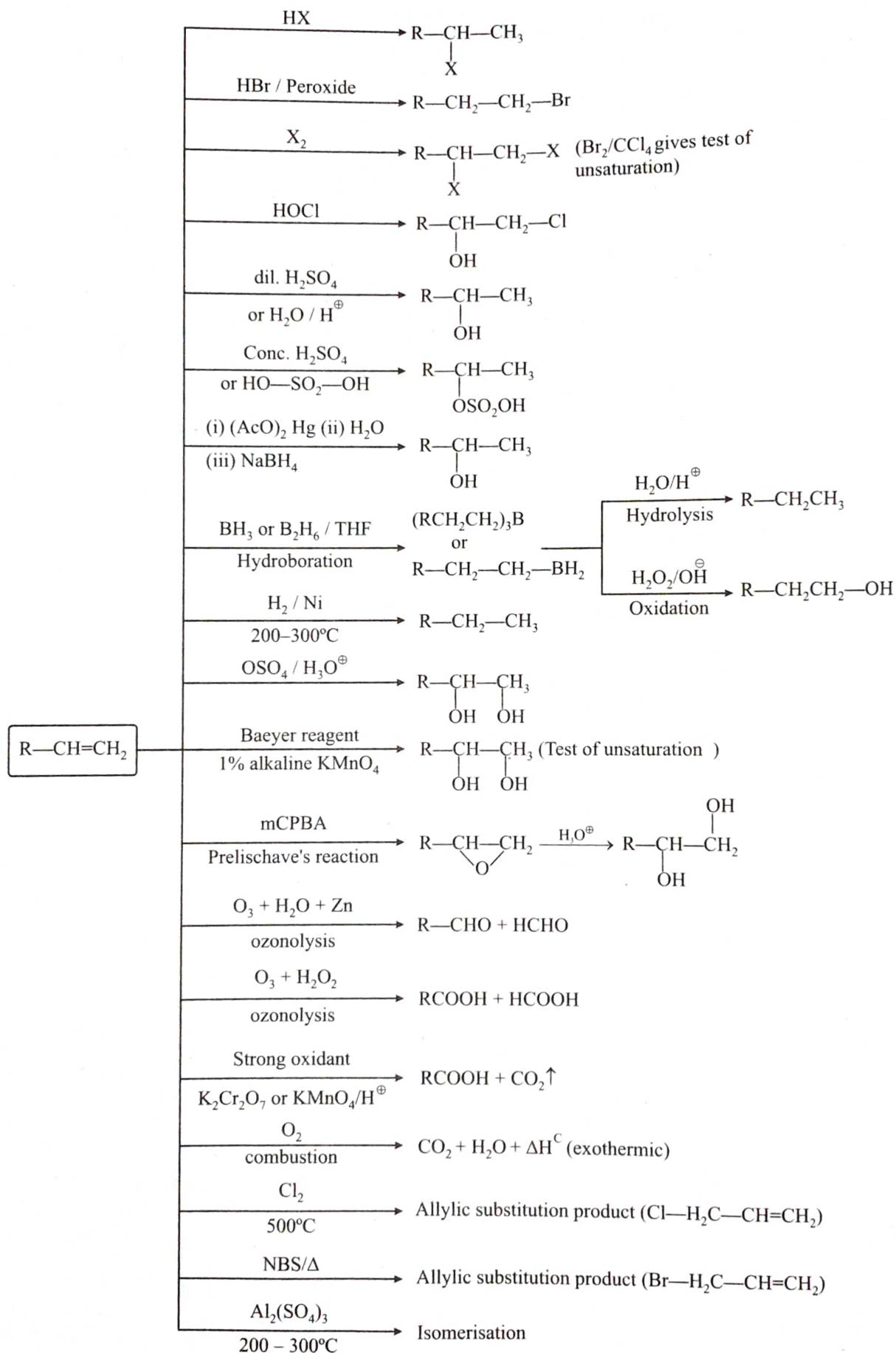
Chemical Reactions of Alkane



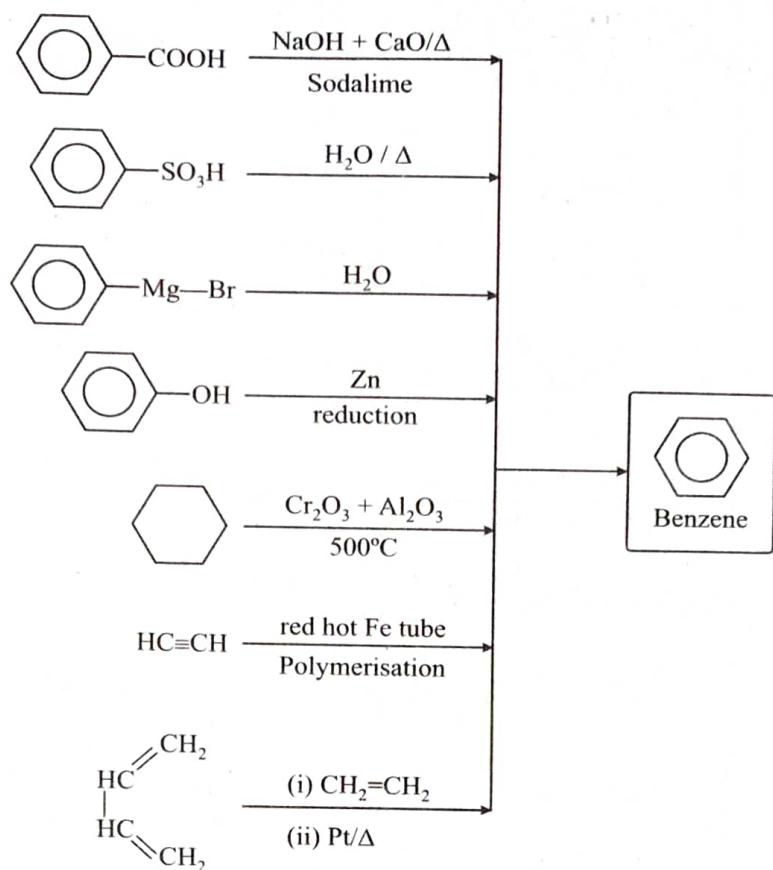
Preparation of Alkene



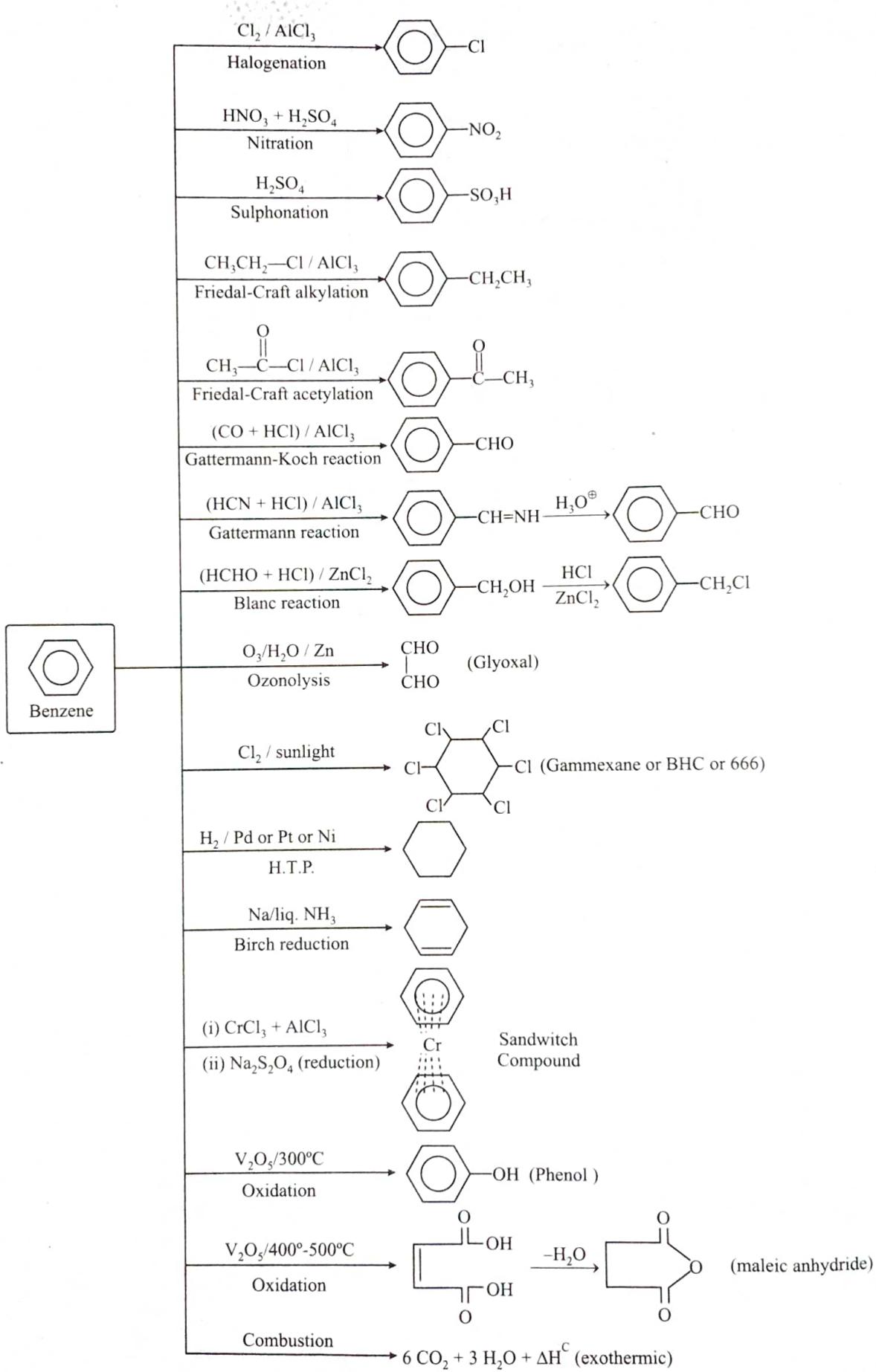
Chemical Reactions of Alkene



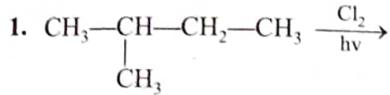
Preparation of Benzene



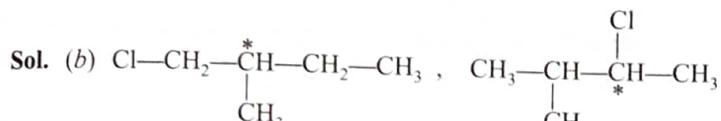
Chemical Reactions of Benzene



Solved Examples



Number of chiral centers generated during monochlorination in the above reaction :



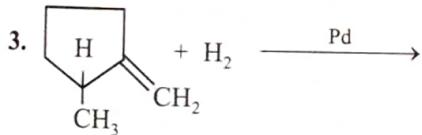
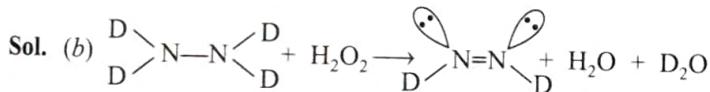
Product (P) is:

- (a) 

(b) 

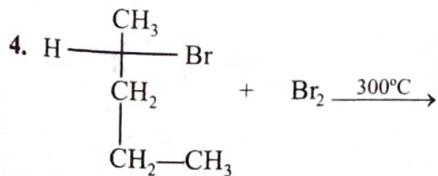
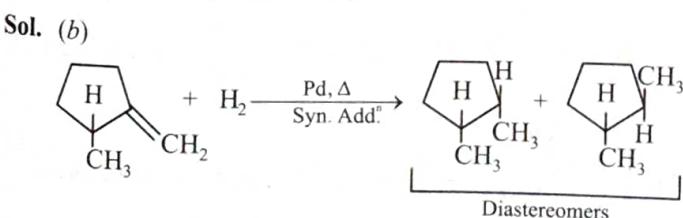
(c) 

(d) None of the above

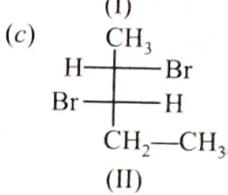
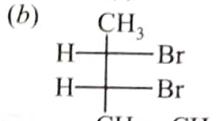
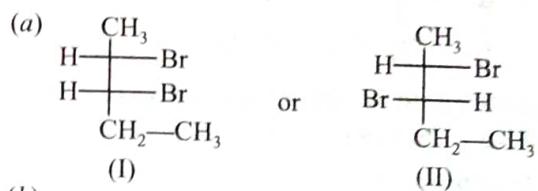


Product of the above reaction will be :

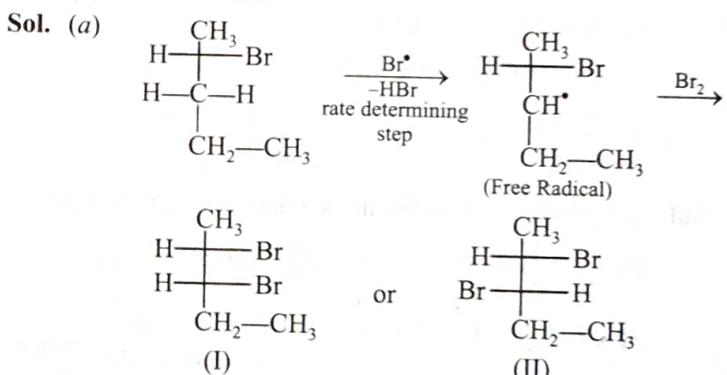
- (a) Racemic mixture
 - (b) Meso
 - (c) Diastereomers
 - (d) Constitutional isomers



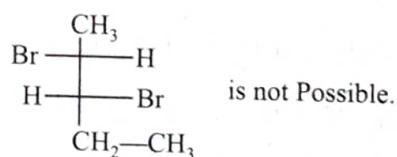
Which of the following compound will not be obtained as a product in the above reaction?



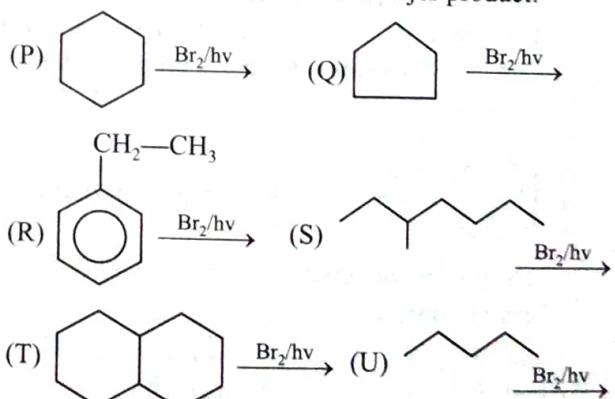
- (d) None of these



If Free radical (FR) is formed at 3rd carbon, product I and II are possible, configuration of 2nd carbon will not change, i.e.,



5. Among the following free radical bromination reactions, select those in which 2° halide is the major product:



Sol. (b) Bromine is more selective it will form 3° halide if there is presence of 3° hydrogen. Q, S, T, form 3° halide as major and P, R, U form 2° halide as major.

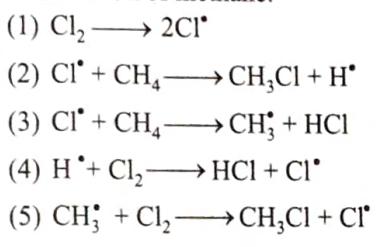


Major product in the above reaction is :

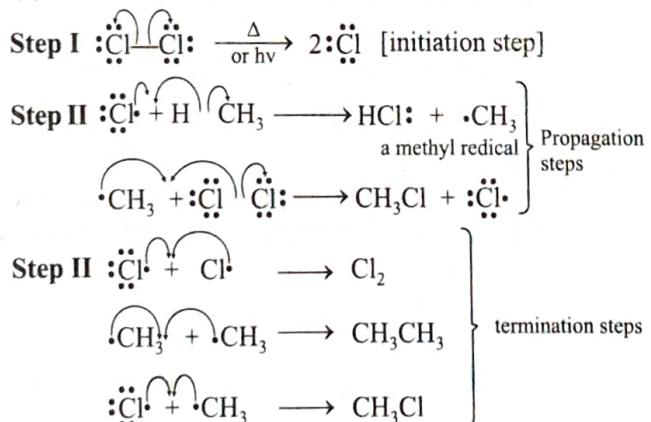
- (a) Racemic mixture
 - (c) Diastereomers
 - (b) Meso
 - (d) Constitutional isomers

Sol. (a) 2° halide is major, due to formation of sp^2 -hybridized free radical racemization take place.

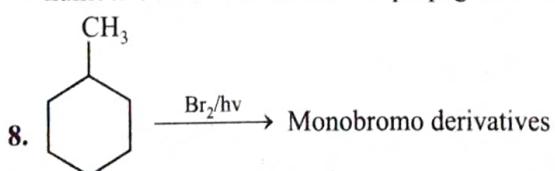
7. Select the chain propagation steps in the free-radical chlorination of methane.



Sol. (c) Mechanism for the monochlorination of methane.

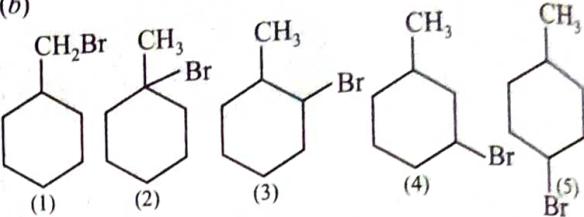


Any two radicals in the reaction mixture can combine to form a molecule in which all the electrons are paired. The combination of two radicals is called a termination step because it brings the reaction to an end by decreasing the number of radicals available to propagate the reaction.

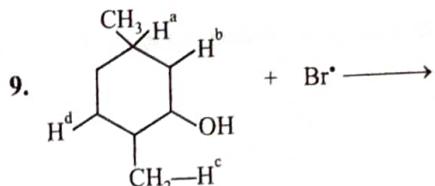


The number of possible monobromo products is (excluding stereoisomers):

Sol. (b)



Excluding stereoisomer = 5

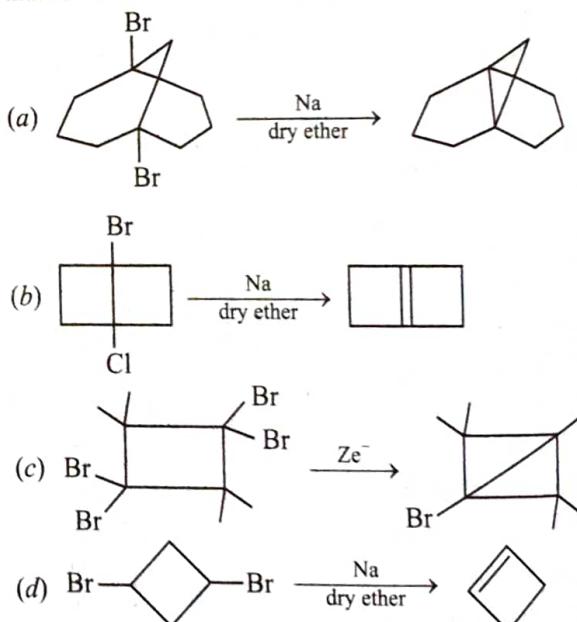


Br will abstract which of the hydrogen most readily?

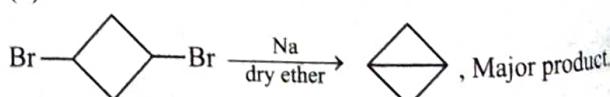
Sol. (a) As bromine is more selective

∴ abstract that hydrogen which forms stable free-radical

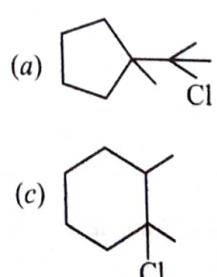
10. Which of the following does not represent major product of that reaction?



Sol. (d)

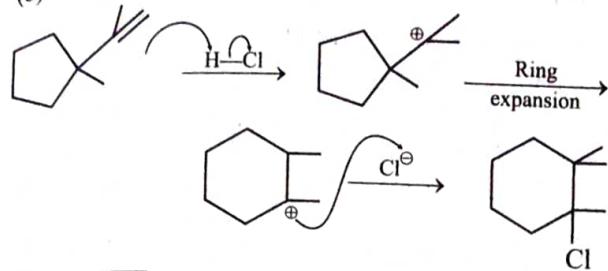


11.  $\xrightarrow{\text{HCl}}$; Major product of the reaction is:



JEE (XI) Module-4

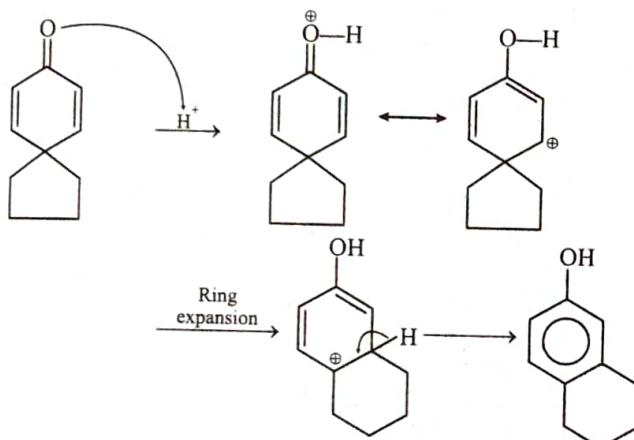
Sol. (c)



12. $\xrightarrow{H^+}$ Major product of the reaction is:

- (a)
 (b)
 (c)
 (d)

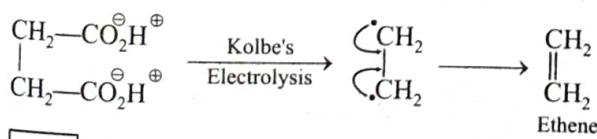
Sol. (b)



13. $\begin{array}{c} \text{CH}_2-\text{CO}_2\text{K} \\ | \\ \text{CH}_2-\text{CO}_2\text{K} \end{array} \xrightarrow{\text{Electrolysis}} \text{(A) (Kolbe's electrolysis)} \text{ (major)}$

- (a) CH_3-CH_3
 (b) $\text{CH}_2=\text{CH}_2$
 (c) $\text{CH}_3-\text{CH}=\text{CH}_2$
 (d) None of these

Sol. (b)

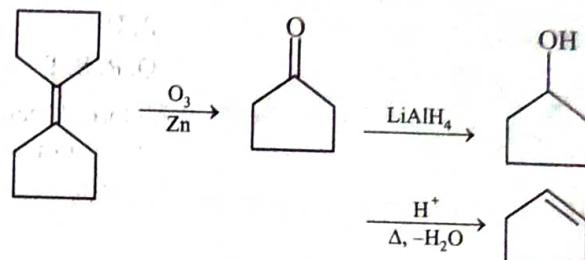


14. $\xrightarrow[\text{Zn}]{\text{O}_3} \text{A} \xrightarrow[\text{Or LiAlH}_4]{\text{H}_2/\text{Ni}} \text{B} \xrightarrow[\Delta]{\text{H}^+} \text{(C)}$

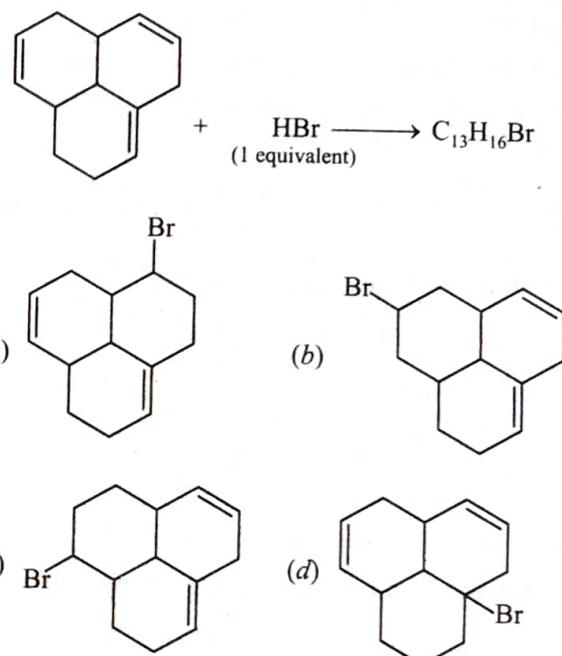
Product (C) of the reaction is :

- (a)
 (b)
 (c)
 (d)

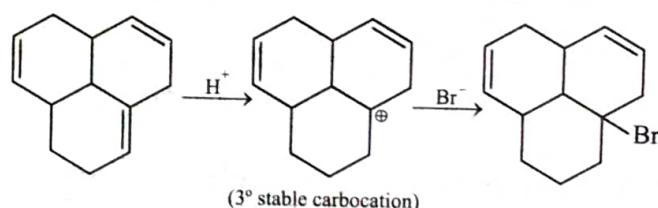
Sol. (c)



15. Which of the following bromides is the major product of the reaction shown below, assuming that there are no carbocation rearrangement?



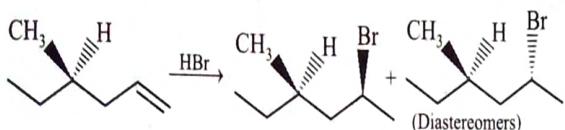
Sol. (d)



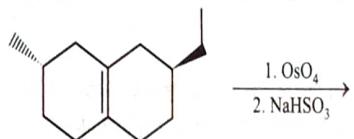
16. Which of the following reactions results in the formation of a pair of diastereomers?

- (a) $\xrightarrow{\text{HBr}}$
- (b) $\xrightarrow{\text{HBr}}$
- (c) $\xrightarrow[\text{ROOR, UV}]{\text{HBr}}$
- (d) $\xrightarrow[2. \text{H}_2\text{O}_2, \text{OH}^-]{1. \text{B}_2\text{H}_6, \text{THF}}$

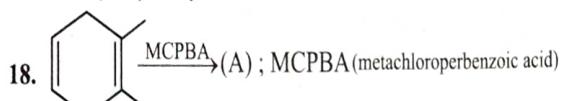
Sol. (b)



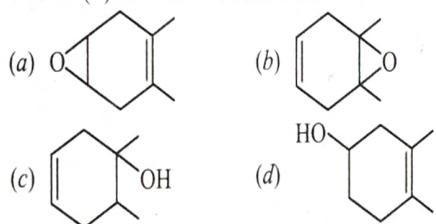
17. How many products will be formed in this reaction?



Sol. (b) Two products will be obtained by addition reaction above and below the plane of ring. It is the example of syn hydroxylation.

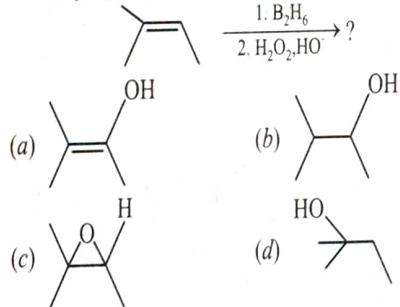


Product (I) of the above reaction is:



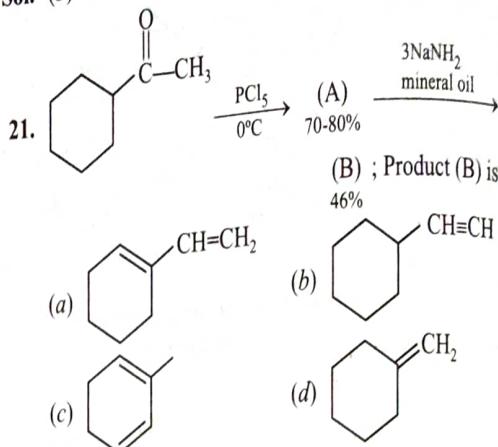
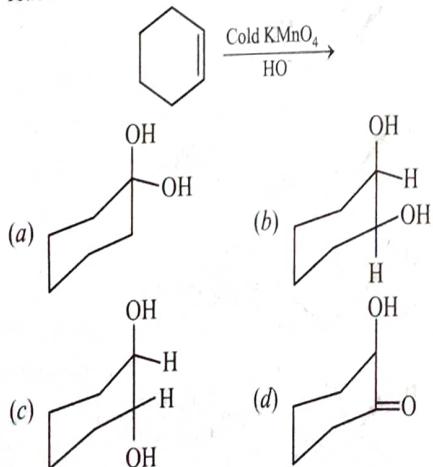
Sol. (b) More nucleophilic alkene will react.

19. The major product of the following reaction sequence is:

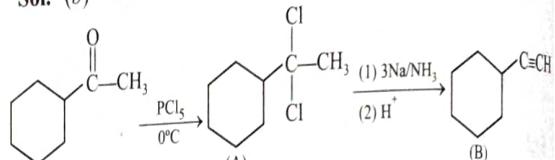


Sol. (b) Hydroboration oxidation reaction follows Anti-Markovnikov's rule where a hydroxy group attaches itself to the carbon which is less substituted.

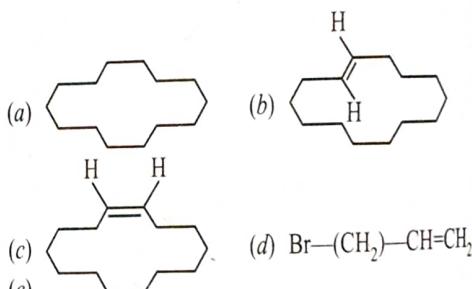
20. What is the major product expected from the following reaction?



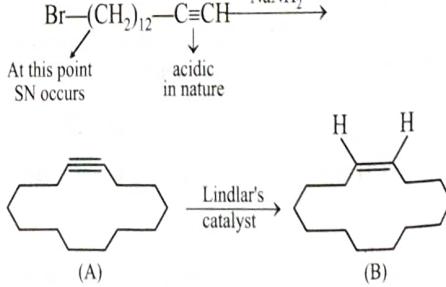
Sol. (b)



22. $\text{Br}-(\text{CH}_2)_{12}-\text{C}\equiv\text{CH} \xrightarrow{\text{NaNH}_2} (\text{A}) \xrightarrow[\text{Catalyst}]{\text{Lindlar}} (\text{B})$; Product (B) is



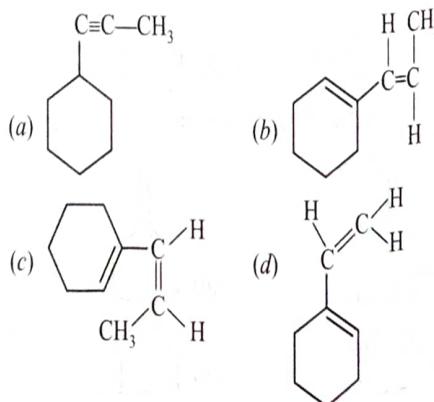
Sol. (c)  NaNH_2



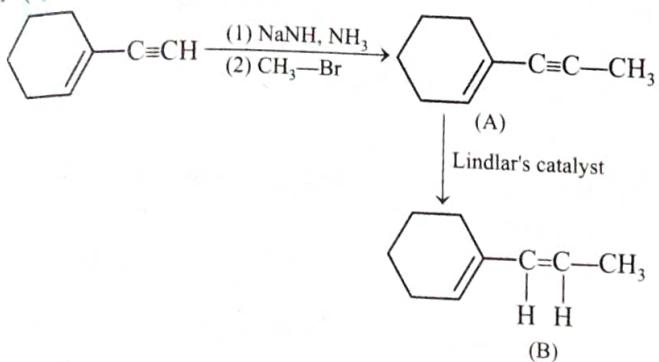
23. 

$$\text{Cyclohexene} \xrightarrow{\substack{(i) \text{NaNH}_2 \\ (ii) \text{CH}_3\text{Br}}} (\text{A}) \xrightarrow{\substack{\text{H}_2 \\ \text{Lindlar Catalyst}}} (\text{B})$$

(B); Product (B) is:



Sol. (c)



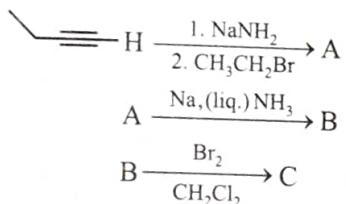
24. $\text{CaC}_2 \xrightarrow{\text{H}_2\text{O}} (\text{A}) \xrightarrow[\text{Red hot Cu tube}]{\text{Red hot Cu tube}} (\text{B})$, Product

(B) of the reaction is:

- | | |
|-------------|-------------------|
| (a) Toluene | (b) Ethyl benzene |
| (c) Benzene | (d) Butyne |

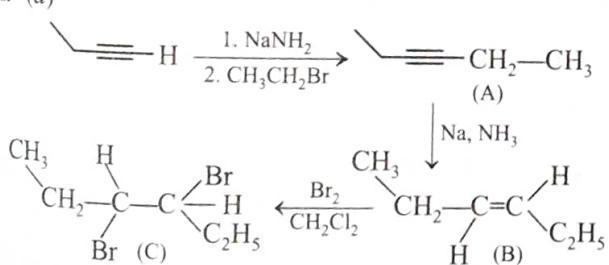
Sol. (c) $\text{CaC}_2 \xrightarrow{\text{H}_2\text{O}} (\text{A}) \xrightarrow[\text{Cu tube}]{\text{Red hot}} (\text{B})$ Benzene

25. What is the final product C, of the following reaction sequence?



- | | |
|-----|-----|
| (a) | (b) |
| (c) | (d) |

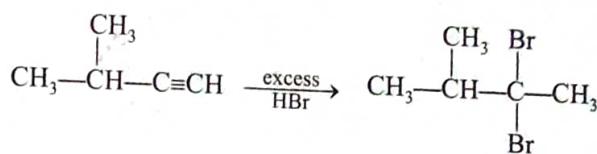
Sol. (a)



26. $\text{CH}_3---\text{CH}(\text{CH}_3)---\text{C}\equiv\text{CH} \xrightarrow{\text{excess HBr}}$

- | | |
|-----|-----|
| (a) | (b) |
| (c) | (d) |

Sol. (c)

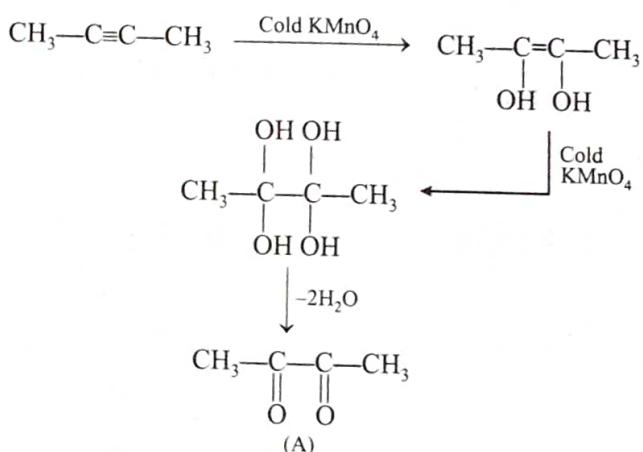


27. $\text{CH}_3---\text{C}\equiv\text{C}---\text{CH}_3 \xrightarrow{\text{Cold KMnO}_4} (\text{A})$

Product (A) is:

- (a) $\text{CH}_3---\text{CH}_2---\text{C}(=\text{O})---\text{C}(=\text{O})---\text{H}$
(b) $\text{CH}_3---\overset{\text{O}}{\underset{\text{OH}}{\text{C}}}---\overset{\text{O}}{\underset{\text{OH}}{\text{C}}}---\text{CH}_3$
(c) $\text{CH}_3---\overset{\text{OH}}{\underset{\text{OH}}{\text{CH}}}---\text{CH}---\text{CH}_3$
(d) $\text{O}=\text{CH}---\text{CH}_2---\text{CH}_2\text{CH}=\text{O}$

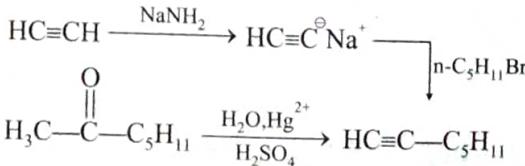
Sol. (b)



28. The best sequence of reactions to prepare 2-heptanone is:

- (a) Propyne $\xrightarrow{\text{NaNH}_2} \text{X} \xrightarrow{n-\text{C}_4\text{H}_9\text{Br}} \text{Y} \xrightarrow[\text{H}_2\text{SO}_4]{\text{Hg}^{2+}}$
(b) Ethyne $\xrightarrow{\text{NaNH}_2} \text{X} \xrightarrow{n-\text{C}_5\text{H}_{11}\text{Br}} \text{Y} \xrightarrow[\text{H}_2\text{SO}_4]{\text{Hg}^{2+}}$
(c) 1-hexyne $\xrightarrow{\text{NaNH}_2} \text{X} \xrightarrow{\text{CH}_2\text{Br}} \text{Y} \xrightarrow[\text{H}_2\text{SO}_4]{\text{Hg}^{2+}}$
(d) 1-pentyne $\xrightarrow{\text{NaNH}_2} \text{X} \xrightarrow{\text{C}_2\text{H}_5\text{Br}} \text{Y} \xrightarrow[\text{H}_2\text{SO}_4]{\text{Hg}^{2+}}$

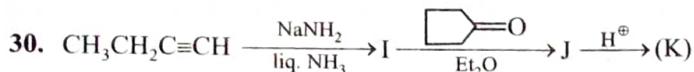
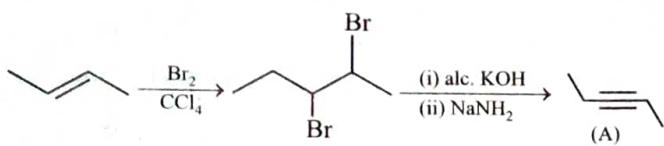
Sol. (b)



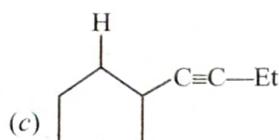
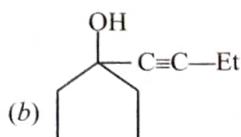
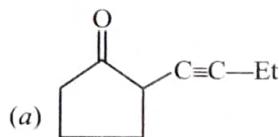
29. $\begin{array}{c} \text{---CH}_2 \\ | \\ \text{---CH}=\text{CH}_2 \end{array} \xrightarrow[\text{CCl}_4]{\text{Br}_2} \frac{\text{(i) alc. KOH}}{\text{(ii) NaNH}_2} \text{ (A)}$; Product (A) is:

- (a) $\text{H}_2\text{C}=\text{CH---CH=CH}_2$
(b) $\text{CH}_3---\text{CH}_2---\text{C}\equiv\text{CH}$
(c) $\text{CH}_3---\text{C}\equiv\text{C---CH}_3$
(d) $\text{CH}_3---\text{CH}=\text{C=CH}_2$

Sol. (c)

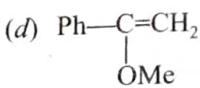
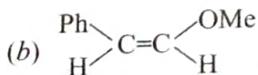
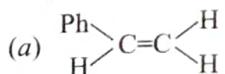
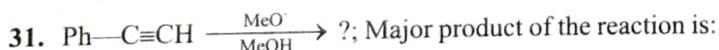
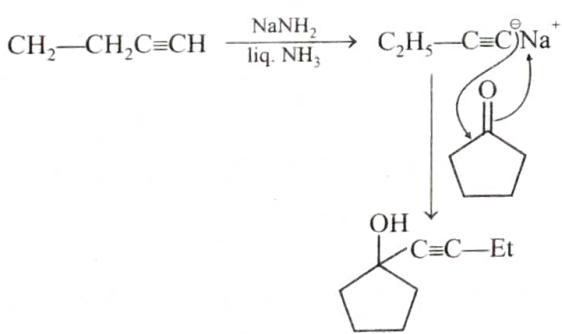


Product (K) of the above reaction is:

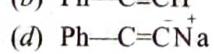
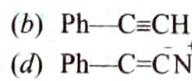
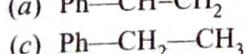
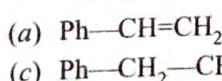
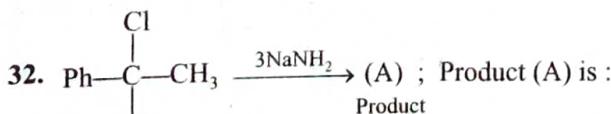
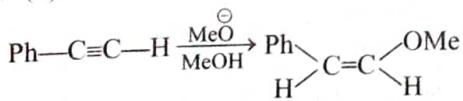


(d) None of these

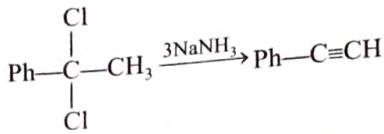
Sol. (b)



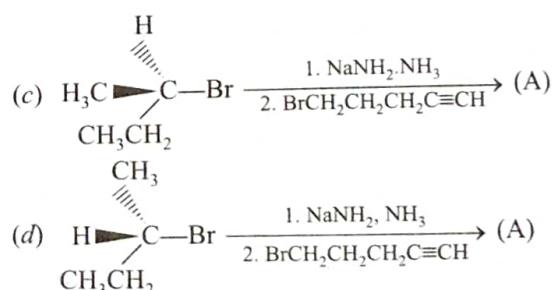
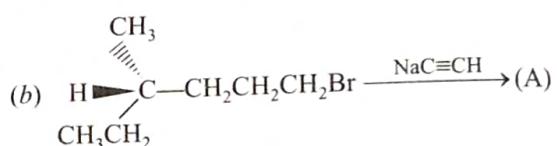
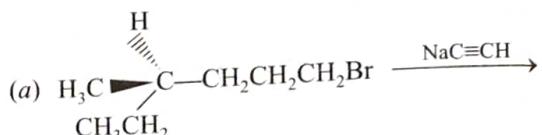
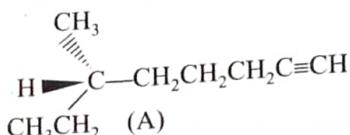
Sol. (b)



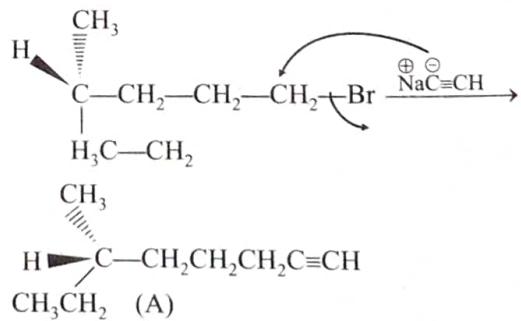
Sol. (b)



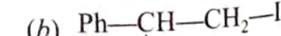
33. Which combination is best for preparation of the compound
(A) shown below?



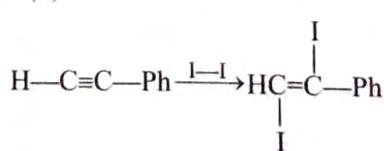
Sol. (b)



34. $\text{H---C}\equiv\text{C---Ph} \xrightarrow{\text{I}_2}$ Product; Product obtained in this reaction is:



Sol. (a)



36. An unknown compound (A) has a molecular formula C_4H_6 . When (A) is treated with excess of Br_2 a new substance (B) with formula $C_4H_6Br_4$ is formed. (A) forms a white ppt. with ammonical silver nitrate solution. (A) may be :

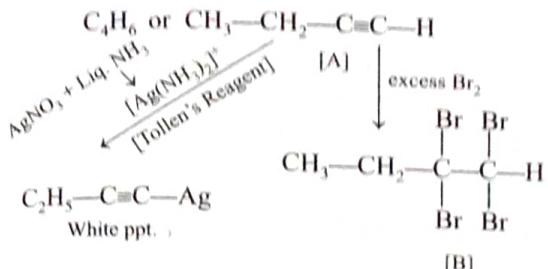
(a) But-1-yne

(b) But-2-yne

(c) But-1-ene

(d) But-2-ene

Sol. (a)



36. In which reaction last product is $\text{Ph}-\text{C}\equiv\text{CH}_2$?

$$(a) \text{C}_6\text{H}_5-\begin{array}{c} \text{Br} \\ | \\ -\text{C}- \\ | \\ \text{Br} \end{array}-\text{CH}_3 \xrightarrow[\text{Mineral oil, heat}]{3\text{NaNH}_2} \xrightarrow{\text{NH}_4\text{Cl}} \dots$$

$$(b) \text{C}_6\text{H}_5\text{CH}=\text{CH}_2 \xrightarrow[\text{CCl}_4]{\text{Br}_2} \xrightarrow[\text{Mineral oil, heat}]{3\text{NaNH}_2} \xrightarrow{\text{NH}_4\text{Cl}} \dots$$

$$(c) \text{C}_6\text{H}_5-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_3 \xrightarrow{\text{PCl}_5} \text{C}_6\text{H}_5-\text{NH}-\text{CH}_3 \xrightarrow[\text{Mineral oil, heat}]{3\text{NaNH}_2} \text{C}_6\text{H}_5-\text{NH}_2 + \text{NH}_4\text{Cl}$$

(d) All of these

Sol. (d)

$$(a) \text{Ph}-\overset{\text{Br}}{\underset{\text{Br}}{\underset{|}{\underset{|}{\text{C}}}}}-\text{CH}_3 \xrightarrow[\text{(ii) NH}_4\text{Cl}]{\text{(i) } 3\text{NaNH}_2} \text{Ph}-\text{C}\equiv\text{CH}$$

$$(b) \text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 \xrightarrow[\text{CCl}_4]{\text{Br}_2} \begin{array}{c} \text{Br} \\ | \\ \text{C}_6\text{H}_5-\text{C}-\text{CH}_2 \\ | \\ \text{H} \quad \text{Br} \\ \downarrow \\ \text{(i) } 3\text{NaNH}_2 \\ \text{(ii) } \text{NH}_4\text{Cl} \\ \downarrow \\ \text{Ph}-\text{C}\equiv\text{CH} \end{array}$$

$$(c) \text{C}_6\text{H}_5-\text{C}-\text{CH}_3 \xrightarrow{\text{PCl}_5} \begin{array}{c} \text{Cl} \\ | \\ \text{C}_6\text{H}_5-\text{C}-\text{CH}_3 \\ | \\ \text{Cl} \end{array}$$

$$\text{C}_6\text{H}_5-\text{C}\equiv\text{CH} \xleftarrow[\text{NH}_3\text{Cl}]{3\text{NaNH}_2}$$

Exercise-1 (Topicwise)

ALKANE

1. Propane can be best prepared by the reaction:

- (a) $\text{CH}_3\text{CH}_2\text{I} + \text{CH}_3\text{I} + \text{Na} \xrightarrow{\text{Et}_2\text{O}}$
- (b) $\text{CH}_3\text{CH}_2\text{COONa} + \text{CH}_3\text{COONa} \xrightarrow[\text{electrolysis}]{\text{H}_2\text{O}}$
- (c) $\text{CH}_3\text{CH}_2\text{Br} + (\text{CH}_3)_2\text{CuLi} \xrightarrow{\text{Et}_2\text{O}}$
- (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COONa} \xrightarrow[\text{CaO, heat}]{\text{NaOH}}$

2. Which represents an alkane?

- (a) C_5H_8
- (b) C_8H_6
- (c) C_9H_{10}
- (d) C_7H_{16}

3. The decreasing order of boiling points is:

- (a) n-Pentane > iso-Pentane > neo-Pentane
- (b) iso-Pentane > n-Pentane > neo-Pentane
- (c) neo-Pentane > iso-Pentane > n-Pentane
- (d) n-Pentane > neo-Pentane > iso-Pentane

4. Which of the following reaction would not produce saturated hydrocarbon as a major product?

- (a) $\text{CH}_3\text{CH}_2\text{Br} + \text{Na} \xrightarrow{\text{ether}} \text{(b)} \text{CH}_3\text{COCH}_3 \xrightarrow{\text{Zn(Hg)/HCl, } \Delta} \text{(c)} \text{CH}_3\text{CHO} \xrightarrow{\text{N}_2\text{H}_4/\text{KOH}} \text{(d)} \text{CH}_3\text{COOCH}_3 \xrightarrow[2\text{-H}^+]{1\text{-LiAlH}_4}$

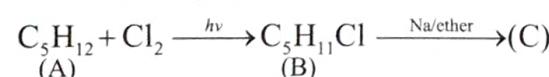
5. Which branched chain isomer of the hydrocarbon with molecular mass 72 u gives only one isomer of monosubstituted alkyl halide?

- (a) Tertiary butyl chloride
- (b) Neopentane
- (c) Isohexane
- (d) Neohexane

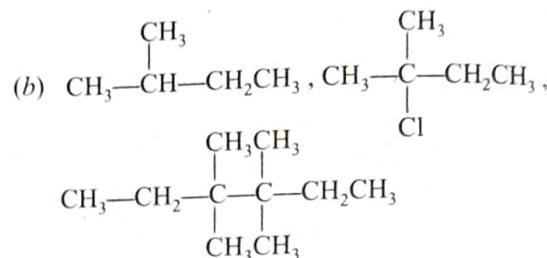
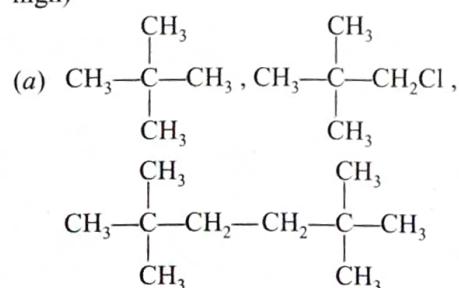
6. The major product obtained in the photocatalyzed bromination of 2-methylbutane is:

- (a) 1-bromo-2-methylbutane
- (b) 1-bromo-3-ethylbutane
- (c) 2-bromo-3-methylbutane
- (d) 2-bromo-2-methylbutane

7. For the following reaction



The products (A), (B) and (C) are (yield of (C) is sufficiently high)



- (c) Both (a) and (b)
- (d) None of these

ALKENE

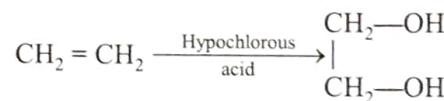
8. The addition of Br_2 to trans-2-butene produces:

- (a) (+) 2,3-dibromobutane
- (b) (-) 2,3-dibromobutane
- (c) rac-2,3-dibromobutane
- (d) meso-2,3-dibromobutane

9. Addition of bromine to 1, 3-butadiene gives:

- (a) 1,2 addition product only
- (b) 1,4 addition product only
- (c) Both 1, 2 and 1, 4 addition products
- (d) No reaction

10. In a reaction



Where M = molecule; R = reagent M and R are:

- (a) $\text{CH}_3\text{CH}_2\text{Cl}$ and NaOH
- (b) $\text{CH}_2\text{Cl}-\text{CH}_2\text{OH}$ and aq. NaHCO_3
- (c) $\text{CH}_3\text{CH}_2\text{OH}$ and HCl
- (d) $\text{CH}_2 = \text{CH}_2$ and heat

11. A gas formed by the action of alcoholic KOH on ethyl iodide, decolourises alkaline KMnO_4 . The gas is:

- (a) C_2H_6
- (b) CH_4
- (c) C_2H_2
- (d) C_2H_4

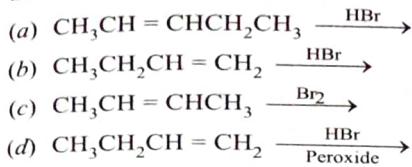
12. $\text{CH}_2 = \text{CH}_2 \xrightarrow[\text{KOH/H}_2\text{O}]{\text{KMnO}_4}$. Product 'X' in above reaction is:

- (a) Ethylene glycol
- (b) Glucose
- (c) Ethanol
- (d) All of these

13. Ozonolysis of which one of the following will give two molecules of acetaldehyde:

- (a) 1-butene
- (b) 2-butene
- (c) 1-pentene
- (d) 2-pentene

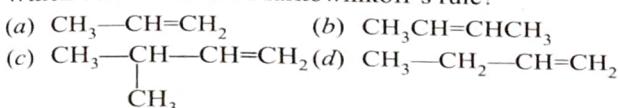
14. Which one of the following reactions would be the best for the formation of 2-bromobutane?



15. Ethylene reacts with ozone to give:

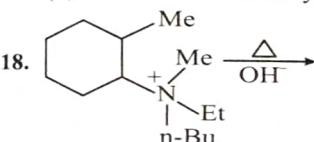
- (a) Formaldehyde (b) Ethyl alcohol
 (c) Ozonide (d) Acetaldehyde

16. Which doesn't follow Markownikoff's rule?

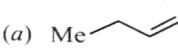
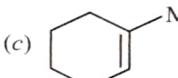
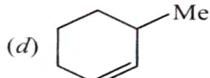


17. When ethyl alcohol is heated with conc. H_2SO_4 at 433 K, ethylene is formed by :

- (a) Intramolecular hydration.
 (b) Intermolecular hydration.
 (c) Intermolecular dehydration.
 (d) Intramolecular dehydration.



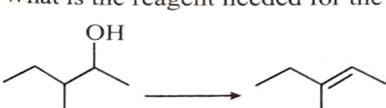
The alkene formed as a major product in the above elimination reaction is:

- (a)  (b) $\text{CH}_2=\text{CH}_2$
 (c)  (d) 

19. The gas liberated by the electrolysis of dipotassium succinate solution is:

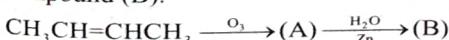
- (a) Ethane (b) Ethyne
 (c) Ethene (d) Propene

20. What is the reagent needed for the following reaction?



- (a) Concentrated sulphuric acid and high heat.
 (b) 85% phosphoric acid and high heat.
 (c) Dilute sulphuric acid and heat.
 (d) Both (a) and (b).

21. In the following sequence of reactions, the alkene forms the compound (B).



The compound (B) is:

- (a) $\text{CH}_3\text{CH}_2\text{CHO}$ (b) CH_3COCH_3
 (c) $\text{CH}_3\text{CH}_2\text{COCH}_3$ (d) CH_3CHO

22. One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is:

- (a) Ethane (b) Propene
 (c) 1-Butene (d) 2-Butene

ALKYNE

23. Acetylene on passing into excess of HOCl solution forms:

- (a) Ethylene chlorohydrin (b) Acetaldehyde
 (c) Dichloroacetaldehyde (d) Methyl Chloride

24. Which of the following gases is used for welding?

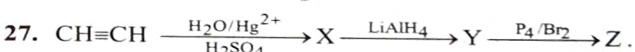
- (a) Methane (b) Ethane
 (c) Acetylene (d) Ethene

25. The product formed when acetylene is passed through red hot tube is:

- (a) Benzene (b) Cyclohexane
 (c) Neoprene (d) Ethane

26. Products of the following reaction $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_3 \xrightarrow[(2)\text{Hydrolysis}]{(1)\text{O}_3}$ are:

- (a) $\text{CH}_3\text{CHO} + \text{CH}_3\text{CH}_2\text{CHO}$
 (b) $\text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{CHO}$
 (c) $\text{CH}_3\text{COOH} + \text{HOOCCH}_2\text{CH}_3$
 (d) $\text{CH}_3\text{COOH} + \text{CO}_2$



Here Z is:

- (a) Ethylene bromide (b) Ethanol
 (c) Ethyl bromide (d) Ethylidene bromide

28. The product(s) obtained via oxymercuration

$(\text{HgSO}_4 + \text{H}_2\text{SO}_4)$ of 1-butyne would be:

- (a) $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{CH}_3$
 (b) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CHO}$
 (c) $\text{CH}_3-\text{CH}_2-\text{CHO} + \text{HCHO}$
 (d) $\text{CH}_3\text{CH}_2\text{COOH} + \text{HCOOH}$

29. Among the following compounds which have more than one type of hybridisation for carbon atom?

- (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ (ii) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$
 (iii) $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$ (iv) $\text{H}-\text{C}\equiv\text{C}-\text{H}$
 (a) (ii) and (iii) (b) (ii)
 (c) (iii) and (iv) (d) (iv)

30. Which of the following catalyst is used in the polymerisation of $\text{CH}\equiv\text{CH}$ to C_6H_6 ?

- (a) AlCl_3 (b) HgSO_4
 (c) NbCl_3 (d) HCl

The hydrocarbon is:

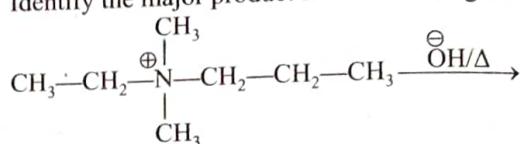
CH_3

37. The compound $\text{CH}_3-\overset{|}{\text{C}}=\text{CH}-\text{CH}_3$ on reaction with NaIO_4 in the presence of KMnO_4 gives:

- $$(a) \text{CH}_3\text{CHO} + \text{CH}_3 \quad (b) \text{CH}_3\text{COCH}_3$$

$$(c) \text{CH}_3\text{COCH}_3 + \text{CH}_3\text{COOH} \quad (d) \text{CH}_3\text{COCH}_3 + \text{CH}_3\text{CH}_2\text{CHO}$$

38. Identify the major product in the following reaction?



- (a) $\text{CH}_3-\text{CH}=\text{CH}_2$ (b) $\text{CH}_2=\text{CH}_2$
 |
 CH_3
 (c) $\text{CH}_3\text{CH}_2-\overset{\oplus}{\underset{\text{CH}_3}{\text{N}}}-\text{OH}$ (d) CH_3OH

39. Ozonolysis of toluene gives:

 - (a) Two molecule of glyoxal.
 - (b) Three molecule of glyoxal.
 - (c) Two molecule of glyoxal and one molecule of methyl glyoxal.
 - (d) Two molecule of methyl glyoxal and one molecule of glyoxal.

40. Benzene in presence of u.v. light reacts with chlorine to form:
(a) Benzenehexachloride (b) Benzyl chloride
(c) 1,3,5-Trichlorobenzene (d) Chlorobenzene

MISCELLANEOUS

33. Action of hydrogen chloride on $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}_2$ and
 on $\text{CH}\equiv\text{CH}$ will predominantly give the compounds, respectively:

 - $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2\text{Cl}$ and $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$
 - $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{CCl}}}-\text{CH}_3$ and $\text{CH}_3-\text{CHCl}_2$
 - $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_2\text{Cl}$ and $\text{CH}_3-\text{CHCl}_2$
 - $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_3$ and $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$

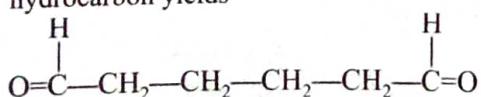
34. The relative acidity of ethyne, ethene and ethane follows the order:

 - (a) Ethane > Ethyne < Ethene
 - (b) Ethyne > Ethene > Ethane
 - (c) Ethyne < Ethene < Ethane
 - (d) Ethene < Ethane < Ethyne

35. Chlorination can be done on:

 - $\text{CH}_3-\text{CH}=\text{CH}_2$
 - $\text{CH}_2=\text{CH}_2$
 - $\text{CH} \equiv \text{CH}$
 - All of the above

36. A hydrocarbon of formula C_6H_{10} absorbs only one molecule of H_2 upon catalytic hydrogenation. Upon ozonolysis, the hydrocarbon yields



42. The reaction of $\text{CH}_3\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$ with HBr gives:

- (a) $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_4-\text{OH}$

- (b) $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_4-\text{OH}$

- (c) $\text{CH}_3\text{CHBrCH}_2-\text{C}_6\text{H}_4-\text{Br}$

- (d) $\text{CH}_3\text{CH}_2\text{CHBr}-\text{C}_6\text{H}_4-\text{Br}$

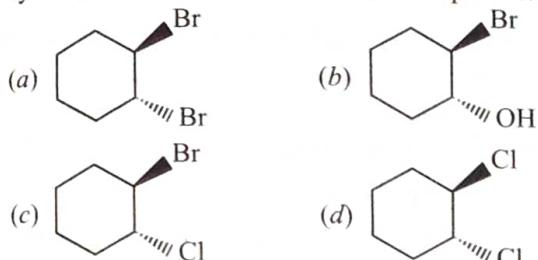
43. In the hydroboration – oxidation reaction of propene with diborane, H_2O_2 and NaOH, the organic compound formed is:

- (a) $\text{CH}_3\text{CH}_2\text{OH}$ (b) $\text{CH}_3\text{CHOHCH}_3$
 (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (d) $(\text{CH}_3)_3\text{COH}$

44. In the presence of peroxide, HCl and HI do not follow anti Markovnikov's addition. Addition of HCl or HI to alkenes in the given way occurs because:

- (a) One of the steps is endothermic in HCl and HI.
- (b) Both HCl and HI are strong acids.
- (c) HCl is oxidizing and the HI is reducing agent.
- (d) All the steps are exothermic in HCl and HI.

45. Which of the following product is not possible when cyclohexene reacts with bromine in the presence of brine?



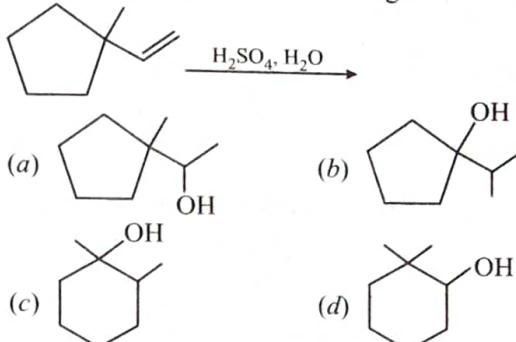
46. 1-Butene reacts with the following reagents given in the options. Out of these, which will react through free radical mechanism?

- (a) HCl + peroxide
- (b) (i) BH_3 , (ii) H_2O_2 , OH^-
- (c) HBr
- (d) HBr + peroxide

47. The correct order of reactivity of the following alkenes to acid-catalyzed hydration is:

- (a) $(\text{CH}_3)_2\text{CH}=\text{CH}_2 > \text{H}_3\text{C}-\text{CH}=\text{CH}_2 > \text{H}_2\text{C}=\text{CH}_2$
- (b) $\text{H}_3\text{C}-\text{CH}=\text{CH}_2 > (\text{CH}_3)_2\text{C}=\text{CH}_2 > \text{H}_2\text{C}=\text{CH}_2$
- (c) $\text{H}_2\text{C}=\text{CH}_2 > (\text{CH}_3)_2\text{C}=\text{CH}_2 > \text{H}_3\text{C}-\text{CH}=\text{CH}_2$
- (d) $\text{H}_2\text{C}=\text{CH}_2 > \text{H}_3\text{C}-\text{CH}=\text{CH}_2 > (\text{CH}_3)_2\text{C}=\text{CH}_2$

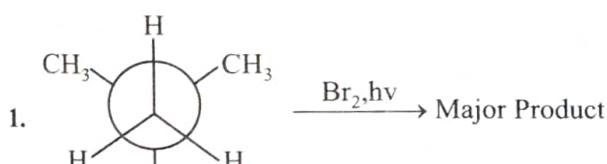
48. The major product of the reaction given below is:



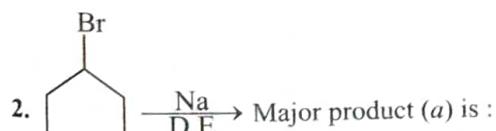
49. 3-Phenylpropene on reaction with HBr gives major product as:

- (a) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$
- (b) $\text{C}_6\text{H}_5\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$
- (c) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
- (d) $\text{C}_6\text{H}_5\text{CH}(\text{Br})\text{CH}=\text{CH}_2$

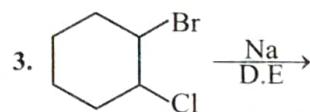
Exercise-2 (Learning Plus)



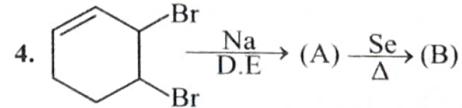
- (a) $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{H}}{\text{CH}}}-\text{CH}_2\text{Br}$
- (b) $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{Br}}{\text{C}}}-\text{CH}_2\text{CH}_3$
- (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$
- (d) $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}}}-\text{CH}_2\text{CH}_3$



- (a)
- (b)
- (c)
- (d)



- (a)
- (b)
- (c)
- (d)



Product (B) will be:

- (a)
- (b)
- (c)
- (d)

18. In which reaction the product following antimarkovnikoff rule is observed:

- (a) $\text{CF}_3\text{CH} = \text{CH}_2 \xrightarrow{\text{HCl}} \text{X}$ (b) $\text{ClCH} = \text{CH}_2 \xrightarrow{\text{HCl}} \text{Y}$
 (c) $\text{CH}_3\text{OCH} = \text{CH}_2 \xrightarrow{\text{HCl}} \text{Z}$ (d) None of these

19. $\text{CCl}_3\text{CH} = \text{CH}_2 \xrightarrow{\text{Cl}_2 + \text{H}_2\text{O}} \text{P}$,

Identify major product 'P':

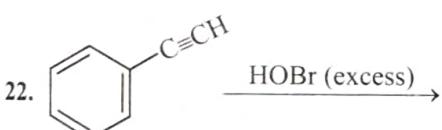
- (a) $\text{CCl}_3\text{CH}(\text{Cl})\text{CH}_2\text{OH}$ (b) $\text{CCl}_3\text{CH}(\text{OH})\text{CH}_2\text{Cl}$
 (c) $\text{CCl}_3\text{CH}(\text{Cl})\text{CH}_2\text{Cl}$ (d) $\text{CCl}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$

20. $\text{CH}_2 = \text{CHCH}_2\text{CH} = \text{CH}_2 \xrightarrow{\text{NBS}} \text{X}$ (Major), (X) is

- (a) $\text{CH}_2 = \text{CH} - \text{CH}(\text{Br})\text{CH} = \text{CH}_2$
 (b) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH}_2 - \text{Br}$
 (c) $\text{CH}_2 = \text{CHCH}_2\text{CH} = \text{CHBr}$
 (d) $\text{CH}_2 = \text{CHCH}_2\text{C}(\text{Br}) = \text{CH}_2$

21. Which will form 2, 2-Dibromopropane with HBr?

- (a) $\text{CH}_2 = \text{CH} - \text{CH}_3$ (b) $\text{CH}_3 - \text{C} \equiv \text{CH}$
 (c) $\text{CH}_3 - \text{C}(\text{Br}) = \text{CH}_2$ (d) Both (b) and (c)



- (a) (b)
 (c) (d)

23. The reaction of one equivalent of HBr with

$\text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH}$ gives:

- (a) $\text{CH}_2 = \text{CH} - \text{C}(\text{Br}) = \text{CBr}$ (b) $\text{CH}_2 = \text{CH} - \text{C}(\text{Br}) = \text{CH}_2$
 (c) $\text{CH}_3 - \text{CH} - \text{C} \equiv \text{CH}$ (d) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CHBr}$
 Br

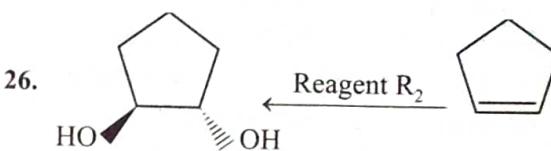
24.

- (a) CH_3COOH (b) $\text{CH}_2(\text{COOH})_2$
 (c) Both (a) and (b) (d) None of these

25. 1-Butyne $\xrightarrow{\text{KMnO}_4/\Delta} \text{X} + \text{Y}$

Identify X and Y ?

- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{O}_2$
 (b) $\text{CH}_3\text{CH}_2\text{COOH}$
 (c) $\text{CH}_3\text{CH}_2\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}$
 (d) $\text{CH}_3\text{CH}_2\text{COCH}_3 + \text{HCOOH}$



R_1 and R_2 are:

- (a) Cold alkaline KMnO_4 , $\text{OsO}_4/\text{H}_2\text{O}_2$
 (b) Cold alkaline KMnO_4 , HCO_3H and H_3O^+
 (c) Cold alkaline KMnO_4 , $\text{C}_6\text{H}_5\text{CO}_3\text{H}$
 (d) $\text{C}_6\text{H}_5\text{CO}_3\text{H}$, HCO_3H

27. To prepare But-2-yne from 2, 2, 3, 3-Tetrachlorobutane, reagent used is:

- (a) Zinc dust/ Δ (b) Soda lime
 (c) Alc. KOH (d) aq. KOH

28. Acetylene may be prepared by electrolysis of:

- (a) Potassium oxalate (b) Potassium acetate
 (c) Potassium maleate (d) Potassium succinate

29. Which gas is obtained when iodoform is heated with Ag powder?

- (a) CH_4 (b) C_2H_4
 (c) C_2H_6 (d) C_2H_2

30. Which of the following shows least reactivity towards bromination?

- (a) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$ (b) $\text{CH}_2 = \text{CH}_2$
 (c) $\text{CH} \equiv \text{CH}$ (d) $\text{CH}_3 - \text{CH} = \text{CH}_2$

31. Which of the following compounds on hydrolysis gives acetylene?

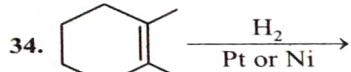
- (a) CaC_2 (b) Mg_2C_3
 (c) Al_4C_3 (d) Cu_2Cl_2

32. Which of the following statements is correct?

- (a) Alkynes are more reactive than alkenes towards halogen addition.
 (b) Alkenes are more reactive than alkynes towards halogen addition.
 (c) Both alkynes and alkenes are equally reactive towards halogen addition.
 (d) Primary vinylic cation $\text{RCH} = \overset{\oplus}{\text{C}}\text{H}$ is less reactive than secondary vinylic cation $\text{RC} = \overset{\oplus}{\text{C}}\text{H}_2$.

33. Methyl group attached to benzene can be oxidised to carboxyl group by reacting with:

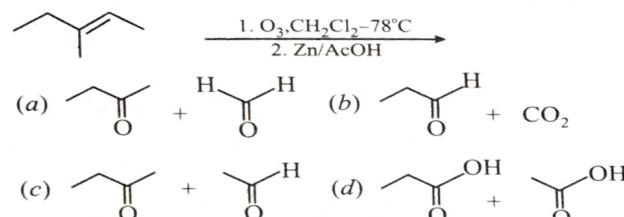
- (a) Fe_2O_3 (b) AgNO_3
 (c) KMnO_4 (d) CrO_3



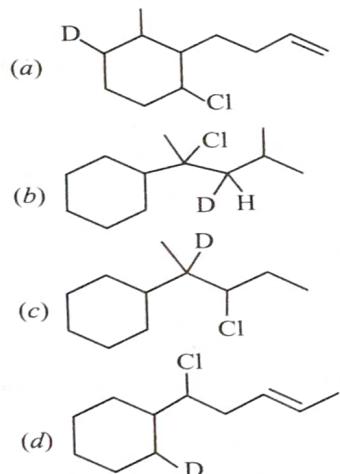
Product of above reaction is obtained by:

- (a) racemic mixture (b) Diastereomers
 (c) Meso (d) Optically-active product

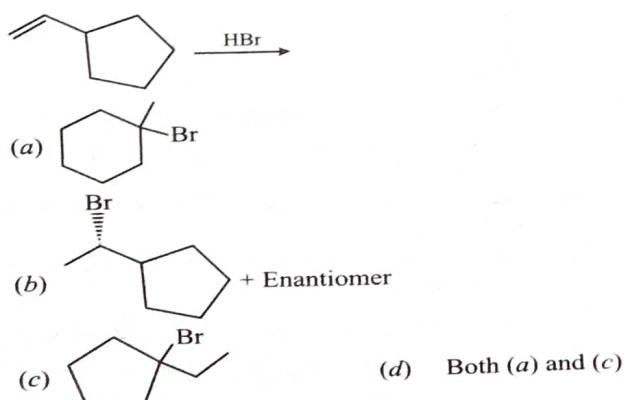
35. What is the product of the following reaction?



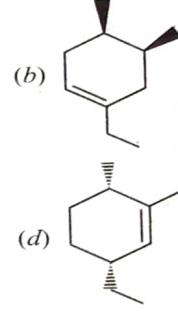
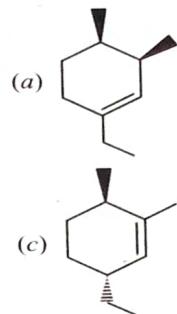
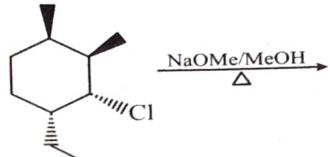
36. What product would you expect from the addition of deuterium chloride to 2-cyclohexyl-4-methyl-2-pentene?



37. What are possible major products for the following reaction?



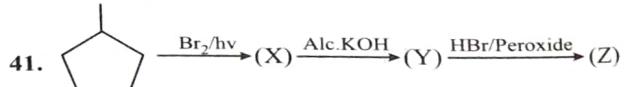
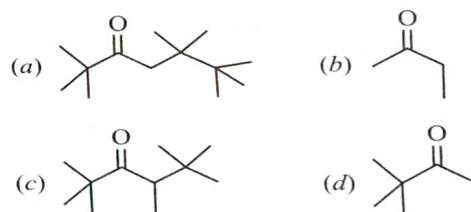
38. What is the major product of the following reaction?



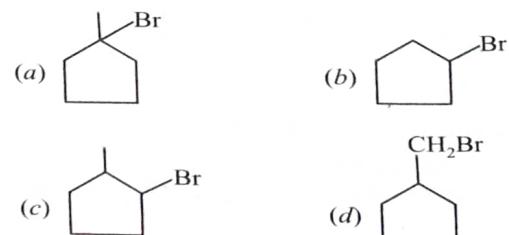
39. The treatment of CH_3MgX with $\text{CH}_3 - \text{C} \equiv \text{C} - \text{H}$ produces:

- (a) $\text{CH}_3 - \text{CH} = \text{CH}_2$ (b) $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$
 (c) $\text{CH}_3\text{CH} = \text{CHCH}_3$ (d) CH_4

40. Which of the following ketones could not be prepared by an acid catalyzed hydration of an alkyne?



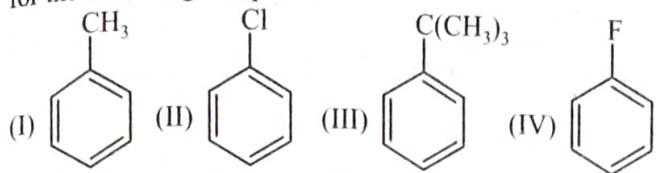
The compound (Z) is:



42. Which of the following reactions will give an alkyne?

- (a) $\text{CH}_3\text{CBr}_2\text{CHBr}_2 \xrightarrow{\text{Zn}/\text{CH}_3\text{CO}_2\text{H}}$
 (b) $\text{CH}_3\text{CH}_2\text{CHBr}_2 \xrightarrow{\text{alc.KOH, high T}}$
 (c) $\text{CH}_3\text{CHBrCH}_2\text{Br} \xrightarrow{\text{NaOH, high T}}$
 (d) All of the above

43. What is the order of rate of electrophilic substitution reaction for the following compounds?



- (a) I > III > II > IV
(b) III > I > II > IV
(c) I > III > IV > II
(d) IV > II > III > I

44. Of the five isomeric hexanes, the isomer which can give two monochlorinated compounds is:

- (a) 2-methylpentane
(b) 2,2-dimethylbutane
(c) 2,3-dimethylbutane
(d) n-hexane

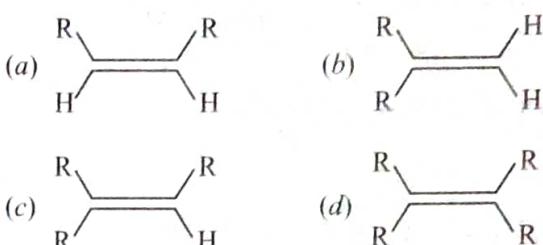
45. Acid catalyzed hydration of alkenes except ethene leads to the formation of:

- (a) Mixture of secondary and tertiary alcohols.
(b) Mixture of primary and secondary alcohols.
(c) Secondary or tertiary alcohol.
(d) Primary alcohol.

46. The reaction of propene with HOCl ($\text{Cl}_2 + \text{H}_2\text{O}$) proceeds through the intermediate:

- (a) $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2^+$ (b) $\text{CH}_3-\text{CHCl}-\text{CH}_2^+$
(c) $\text{CH}_3-\text{CH}^+-\text{CH}_2-\text{OH}$ (d) $\text{CH}_3-\text{CH}^+-\text{CH}_2-\text{Cl}$

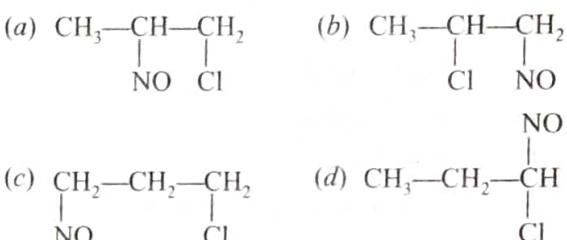
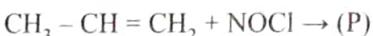
47. Which one of the following alkene will react fastest with H_2 under catalytic hydrogenation condition?



48. The nodal plane in the π -bond of ethene is located in:

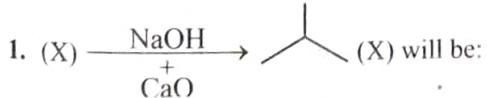
- (a) The molecular plane.
(b) A plane parallel to the molecular plane.
(c) A plane perpendicular to the molecular plane which bisects the carbon - carbon σ -bond at right angle.
(d) A plane perpendicular to the molecular plane which contains the carbon - carbon σ -bond.

49. Identify the product, (P) in the following reaction.



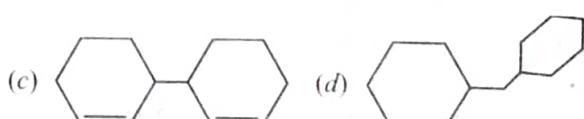
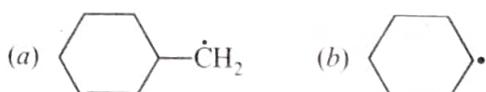
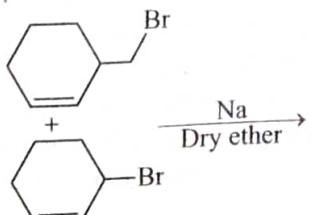
Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

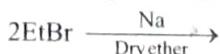


- (a) (b) (c) (d)

2. Which of the following is not produced as a product during the reaction?



3. Possible product during the reaction will be:

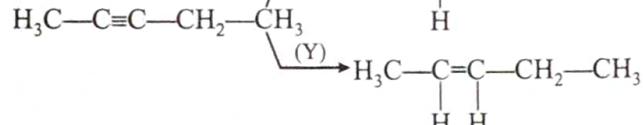
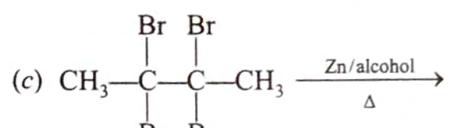
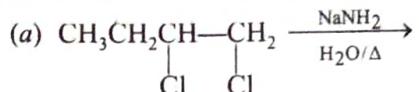


- (a) (b)
(c) CH_3-CH_3 (d)

4. Which of the following acid salt does not give alkene as a major product when it is electrolysed?

- (a) Maleic acid (b) Oxalic acid
(c) Succinic acid (d) Adipic acid

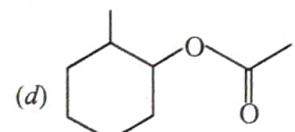
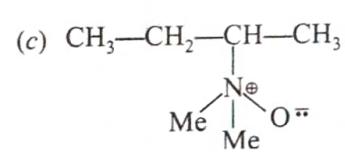
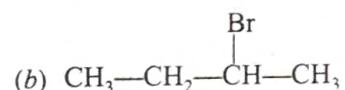
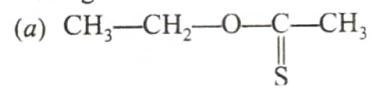
5. Which of the following reactions will give alkyne?



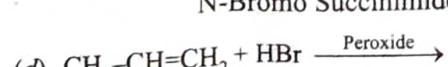
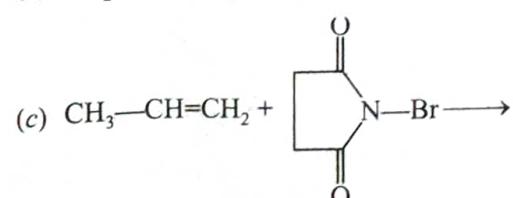
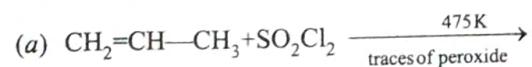
In the above reaction the using reagents X and Y are:

- (a) Na/ liq. NH₃ for X
- (b) H₂, Pd/ BaSO₄ for Y
- (c) BH₃-THF + CH₃COOH for Y
- (d) H₂+Ni/Pt/Pd for X

7. Which of the following substrate give alkene only by heating?

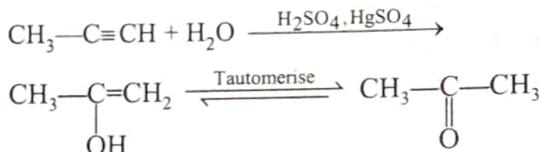
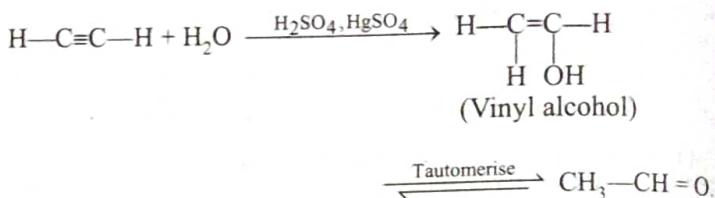


8. Which of the following will produce Allyl halide?



COMPREHENSION BASED QUESTIONS

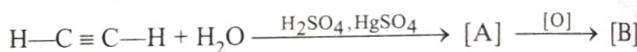
Comprehension (Q. 9 to 11): When alkyne passed into dilute sulphuric acid at 330 K in the presence of HgSO₄ (catalyst), alkynes add one molecule of H₂O to form carbonyl compound.



In fact, enols are formed in the hydration of alkynes. An alcohol contain OH group on a double bonded carbon is called an enol. Enols can not be isolated because they are unstable and are rapidly converted into corresponding aldehydes or ketones.

Based on above passage answers the given questions.

9. In the sequence of reactions:



The compounds A and B are :

- (a) Acetone and acetic acid respectively.
- (b) Acetaldehyde and acetic acid respectively.
- (c) Acetaldehyde and ethyl alcohol respectively.
- (d) Ethyl alcohol and acetaldehyde respectively.

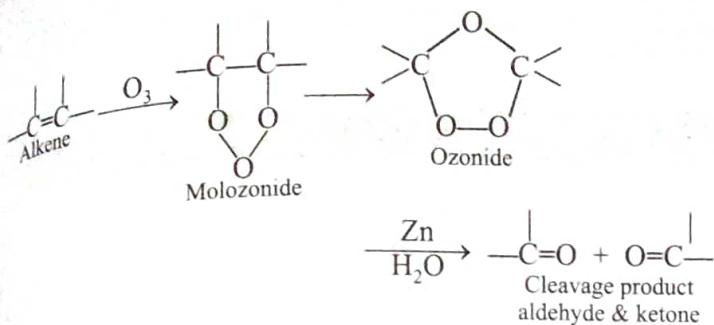
10. The reagent required to convert But-1-yne to Butanone and Butanal respectively are:

- (a) dilute H₂SO₄ and BH₃ – THF + H₂O₂.
- (b) ZnCl₂ + conc. HCl and BH₃ – THF + H₂O₂.
- (c) Hg²⁺ + H₂SO₄ (dilute) and BH₃–THF + H₂O₂
- (d) BH₃ – THF + H₂O₂ and Hg²⁺ + H₂SO₄ (dilute).

11. 3-Methylbut-1-yne reacts with mercuric acetate in presence of water to form a product, which on reduction with NaBH₄ yield?

- (a) 2-Methylbuten-2-ol
- (b) 3-Methylbutanone
- (c) 3-Methylbutan-2-ol
- (d) 2-Methylbutan-2-ol

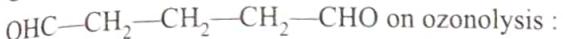
Comprehension (Q. 12 to 14): The classical reagent for cleaving the carbon-carbon double bond is ozone. Ozonolysis (cleavage by ozone) is carried out in two stage : first addition of ozone to the double bond to form an ozonide; and second, hydrolysis of the ozonide to yield the cleavage product. Ozone gas is passed evaporation of the solvent leaves the ozonide as a viscous oil. This unstable, explosive compound is not purified, but is treated directly with water generally in the presence of a reducing agent.



The compounds containing the C=O group are aldehydes and ketones.

Based on above passage answers given questions.

12. Give the structure of alkenes that yields



- (a) 1, 4-pentadiene
- (b) 2, 4-pentadiene
- (c) 1, 3-pentadiene
- (d) Cyclopentene

13. Which alkene on ozonolysis will give only acetone?

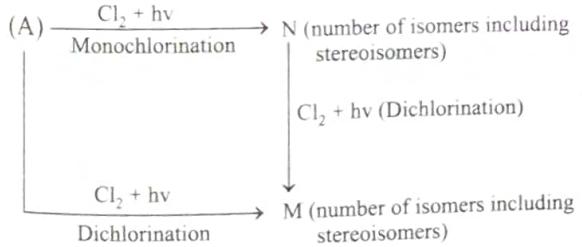
- (a) 2, 3-Dimethylbut-2-ene
- (b) 2-Methylpent-2-ene
- (c) 3-Methylpent-2-ene
- (d) 2, 3-Dimethylbut-1-ene

14. Which alkene would give CH_3CHO and



- (a) 4-methylpent-2-ene
- (b) 2-methylbut-1-ene
- (c) 2-methylbut-2-ene
- (d) 4-methylpent-3-ene

Comprehension (Q. 15 to 19): 15 mL of gaseous hydrocarbon (A) required for complete combustion 357 mL of air (21% oxygen by volume) and gaseous products occupied 327 mL (all volumes being measured at STP).



15. The molecular formula of the hydrocarbon (A) is

- (a) C_2H_6
- (b) C_2H_4
- (c) C_3H_6
- (d) C_3H_8

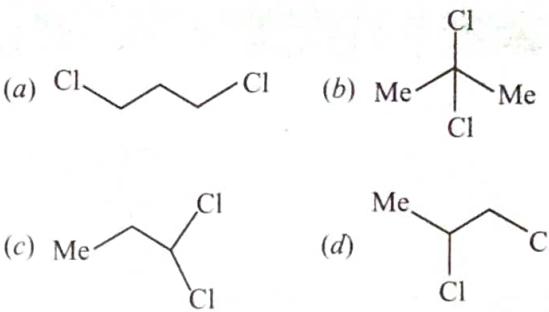
16. The value of N is

- (a) 2
- (b) 3
- (c) 4
- (d) 5

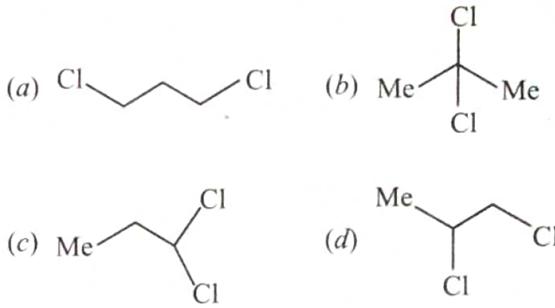
17. The value of M is

- (a) 2
- (b) 3
- (c) 4
- (d) 5

18. Which isomers of M on reaction with diethylmalonate (DEM) in presence of sodium ethoxide will give cyclobutane derivative?



19. Which isomers of M on reaction with Mg or Na will give cyclopropane?



Comprehension (Q. 20 to 22): The structures of two compounds (I) and (II) are given below. Which of the given statement is correct?



20. Which of the statement is correct about compound (I) and compound (II)?

- (a) Compound (I) shows dipole moment but compound (II) does not.
- (b) Compound (II) shows dipole moment but compound (I) does not.
- (c) Both compounds show dipole moment.
- (d) Neither of them shows dipole moment.

21. Which of the statement is correct about compound (I) and compound (II)?

- (a) Compound (I) is resolvable but compound (II) is non-resolvable.
- (b) Compound (II) is resolvable but compound (I) is non-resolvable.
- (c) Both compounds are resolvable.
- (d) Neither of them is resolvable.

22. Which of the statement is correct about compound (I) and compound (II)?

- (a) Reductive ozonolysis of both gave the same product.
- (b) Reductive ozonolysis of both gave different products.
- (c) Reductive and oxidative ozonolysis of both gave different products.
- (d) Reductive and oxidative ozonolysis of (I) gave the same product but of (II) gave different products.

MATCH THE COLUMN TYPE QUESTIONS

23. Match the following

	List-I	List-II
A.		p. Regioselectivity
B.		q. Stereoselectivity
C.		r. Chemoselectivity
D.		s. Rearrangement

- (a) A → r; B → q, r; C → p, r; D → r, s
 (c) A → s; B → q, r; C → p, r; D → r, s

- (b) A → q; B → s; C → q, r; D → r, s
 (d) A → p; B → s; C → r, s; D → p, r

24. Match the following

	List-I	List-II
A.	$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3 \rightarrow \text{cis-2-butene}$	p. $\text{Na}/\text{NH}_3(\ell)$
B.	$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3 \rightarrow \text{trans-2-butene}$	q. $\text{H}_2/\text{Pd}/\text{BaSO}_4$
C.	$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3 \rightarrow 1\text{-Butyne}$	r. alc. KOH, Δ
D.	$\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{CH} \rightarrow 2\text{-Butyne}$	s. NaNH_2, Δ

- (a) A → q; B → p; C → r; D → s
 (c) A → p; B → q; C → r; D → s

- (b) A → p; B → q; C → s; D → r
 (d) A → q; B → p; C → s; D → r

25. Match the column.

	Column-I	Column-II
A.	$\text{Pent-2-yne} \xrightarrow[\text{+Hg}^{2+}]{\text{Dil. H}_2\text{SO}_4} \text{rac-2,3-Dibromo butane}$	p. rac-2,3-Dibromo butane
B.	$\text{Pent-2-yne} \xrightarrow[\text{(2)H}_2\text{O}_2 + \text{OH}^-]{\text{(1)BH}_3 + \text{THF}} \text{meso-2,3-Dibromo butane}$	q. meso-2,3-Dibromo butane
C.	$\text{Pent-2-yne} \xrightarrow[\text{(2)H}_2\text{O}_2 + \text{OH}^-]{\text{(1)Sia}_2\text{BH}} \text{Pentan-2-one}$	r. Pentan-2-one
D.	$\text{But-2-yne} \xrightarrow[\text{(2)Br}_2]{\text{(1)H}_2 + \text{Ni}_2\text{B}} \text{Pentan-3-one}$	s. Pentan-3-one
E.	$\text{But-2-yne} \xrightarrow[\text{(2)Br}_2]{\text{(1)Na} + \text{EtOH}} \text{Pentan-3-one}$	

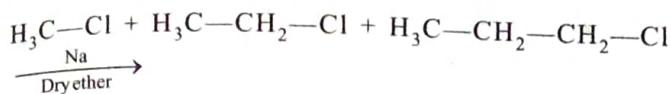
The correct match is:

- (a) A → r, s; B → s; C → r; D → q; E → p
 (c) A → r, s; B → r, s; C → r; D → p; E → q

- (b) A → r, s; B → r; C → q; D → p; E → q
 (d) A → r, s; B → r, s; C → p; D → q; E → q

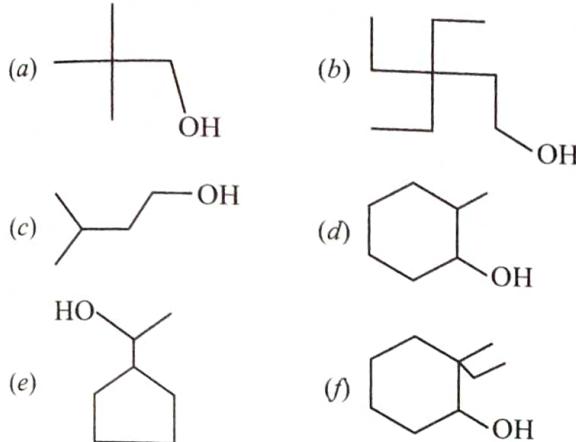
NUMERICAL BASED QUESTIONS

26. Find out the number of dimerized products obtained by following reaction.

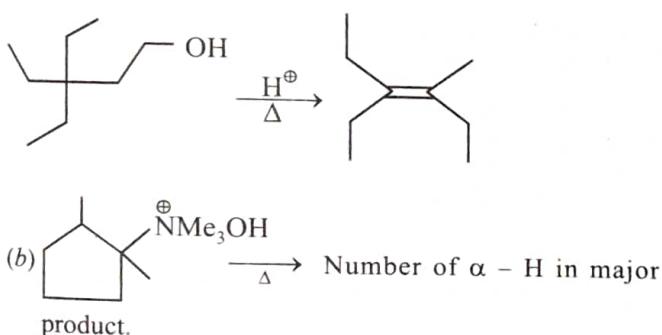


27. If 2-chloro-3-methyl pentane is treated with ethanolic KOH solution, how many different alkenes would be formed via E₂ elimination reaction?

28. How many alcohols out of following on dehydration with hot conc. H₂SO₄ will give alkene having 9 α H as major product.

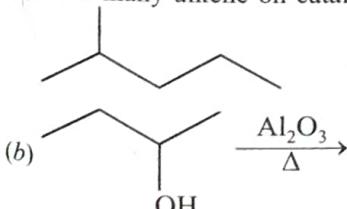


29. (a) How many 1,2-shifts are involved.



Write answer of part (a) and (b) in the same order and present the two digit number as answer in OMR sheet. For example : If all these answers (a) is 9 and (b) is 5 then fill as 0905 in OMR sheet

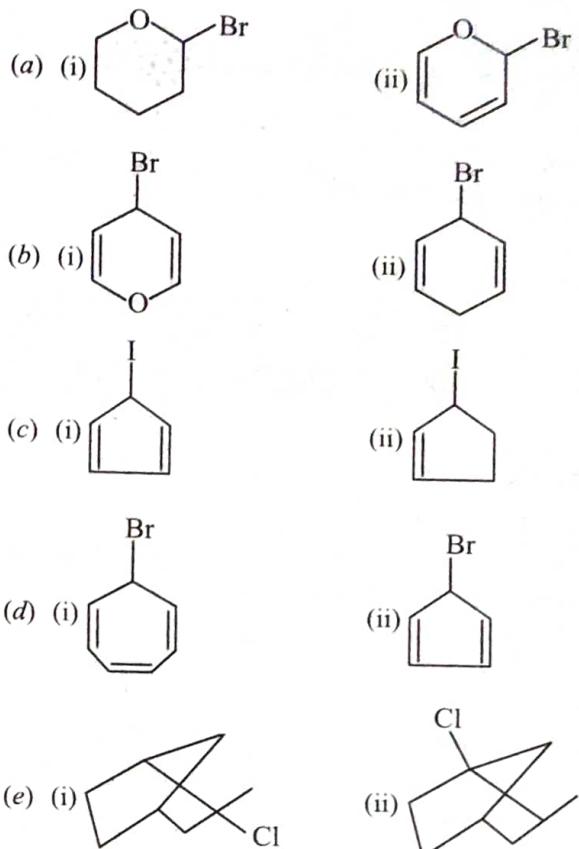
30. (a) How many alkene on catalytic reduction will produce



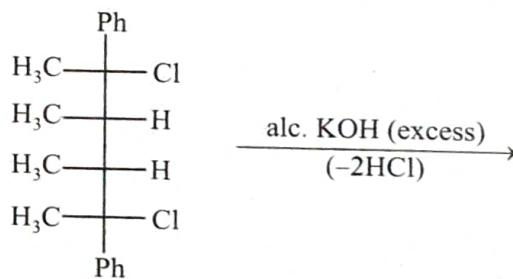
Total number of alkene produced

Write answer of part (a) and (b) in the same order and present the two digit number as answer in OMR sheet. For example : If all these answers (a) is 9 and (b) is 5 then fill as 0905 in OMR sheet.

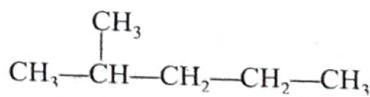
31. Among given pairs, how many pairs in which (i) is more reactive than (ii) towards AgNO₃:



32. What is the number of stereoisomer/s of major product formed in the following reaction?



33. How many monochlorinated products are possible for the following organic compound including stereoisomers?

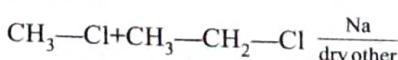


34. Number of mono chloro products of 2-methyl butane are:

35. n-Pentane $\xrightarrow[\text{hv}]{\text{Cl}_2}$ (A) number of monochloro product:

36. Number of required O₂ mole for complete combustion of one mole of propane.

37. How many product (s) will be formed in the following reaction?



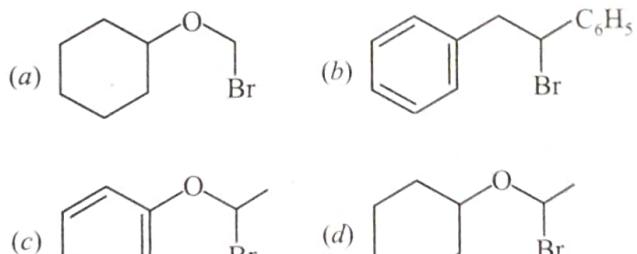
38. How many carbon-hydrogen bond orbitals are available for overlap with the vacant p-orbital in ethyl carbocation?
39. How many isomers of C_8H_{10} when reacts with hot alkaline $KMnO_4$ to give di-carboxylic acid as a product?
40. One mole of 1, 2-dibromopropane on treatment with X moles of $NaNH_2$ followed by treatment with ethyl bromide gave a pentyne. The value of X is

41. How many reagents from the list given below give effervescence when reacted with 1-pentyne?
- (a) C_6H_5Li (b) CH_3CH_2Li
 (c) $NaOH$ (d) CH_3CH_2
 (e) CH_3CH_2MgBr (f) $NaHCO_3$
 (g) $[(CH_3)_2CH]_2NLi$ (h) Na
 (i) $NaNH_2$ (j) NaH

Exercise-4 (Past Year Questions)

JEE MAIN

1. 3-Methylpent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is: (2017)
- (a) Six (b) Zero
 (c) Two (d) Four
2. Which of the following, upon treatment with tert-BuONa followed by addition of bromine water, fails to decolorize the colour of bromine? (2017)

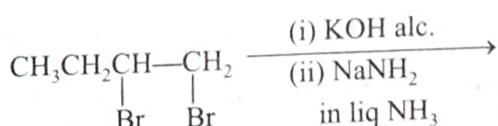


3. Which hydrogen in compound (E) is easily replaceable during bromination reaction in presence of light?



- (a) α -hydrogen (b) γ -hydrogen
 (c) δ -hydrogen (d) β -hydrogen

4. The major product of the following reaction is: (2019)

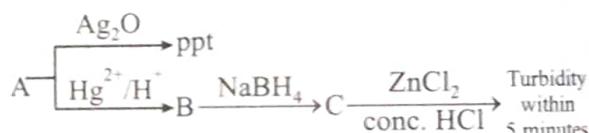


- (a) $CH_3CH=C=CH_2$ (b) $CH_3CH_2CH(NH_2)-CH_2$
 (c) $CH_3CH=CHCH_2NH_2$ (d) $CH_3CH_2C\equiv CH$

5. Which one of the following alkenes when treated with H_2 yields majorly an anti Markovnikov product? (2019)

- (a) $F_3C-CH=CH_2$ (b) $Cl-CH=CH_2$
 (c) $CH_3O-CH=CH_2$ (d) $H_2N-CH=CH_2$

6. Consider the following reactions: (2019)



'A' is:

- (a) $CH\equiv CH$ (b) $CH_3-C\equiv CH$
 (c) $CH_2=CH_2$ (d) $CH_3-C\equiv C-CH_3$

7. The major product of the following addition reaction is: (2019)



- (a) $CH_3-\underset{Cl}{CH}-CH_2$ (b) $H_3C-\underset{OH}{CH}-CH_2$



8. But-2-ene on reaction with alkaline $KMnO_4$ at elevated temperature followed by acidification will give: (2019)

- (a) one molecule of CH_3CHO and one molecule CH_3COOH
 (b) $CH_3-\underset{OH}{CH}-CH(OH)-CH_3$
 (c) 2 molecules of CH_3COOH
 (d) 2 molecules of CH_3CHO

9. In the following reaction ; $x A \rightarrow y B$

$$\log_{10} \left[-\frac{d[A]}{dt} \right] = \log_{10} \left[\frac{d[B]}{dt} \right] + 0.3010$$

'A' and 'B' respectively can be :

- (a) n-Butane and Iso-butane
- (b) C_2H_4 and C_4H_8
- (c) N_2O_4 and NO_2
- (d) C_2H_2 and C_6H_6

10. Consider the following reactions:

(2020)

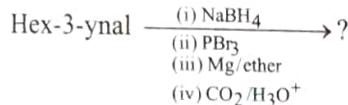
- (A) $(CH_3)_3CCH(OH)CH_3 \xrightarrow{\text{Conc. } H_2SO_4}$
- (B) $(CH_3)_2CHCH(Br)CH_3 \xrightarrow{\text{Alc. KOH}}$
- (C) $(CH_3)_2CHCH(Br)CH_3 \xrightarrow{(CH_3)_3O^+ K^\oplus}$
- (D) $(CH_3)_2C(OH)-CH_2-CHO \xrightarrow{\Delta}$

Which of these reaction(s) will not produce Saytzeff product?

- (a) (B) and (D) (b) (A), (C) and (D)
- (c) (D) only (d) (C) only

11. What is the product of following reaction?

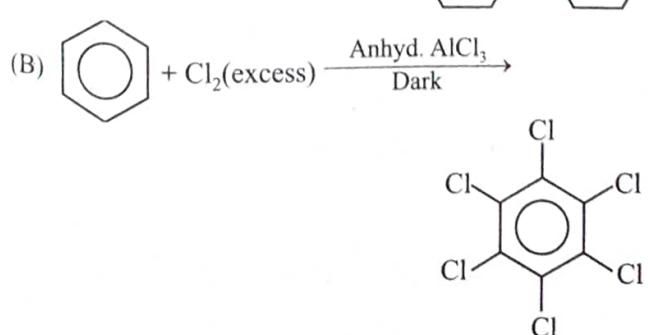
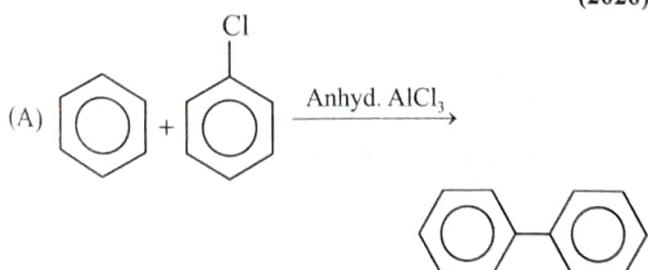
(2020)



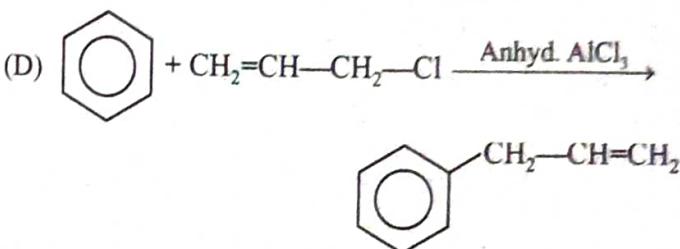
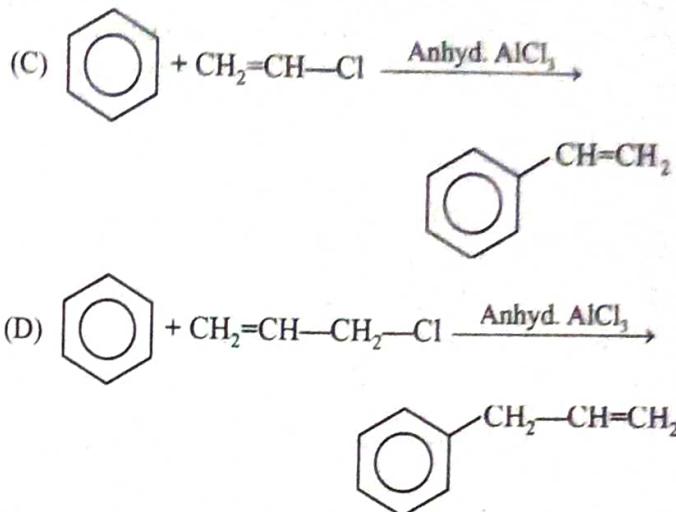
- (a)
- (b)
- (c)
- (d)

12. Consider the following reactions:

(2020)



(2019)

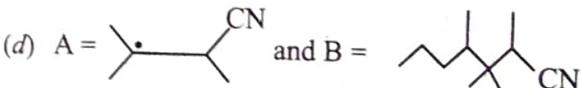
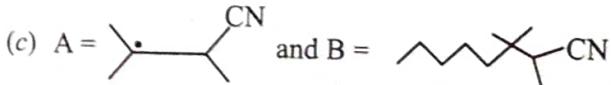
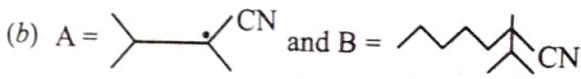
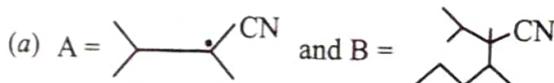
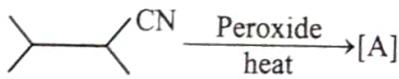


Which of these reactions are possible?

- (a) (A) and (D) (b) (A) and (B)
- (c) (B) and (D) (d) (B), (C) and (D)

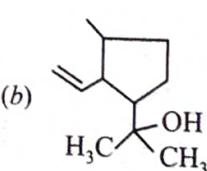
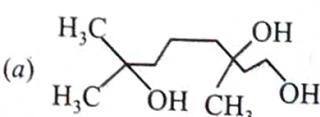
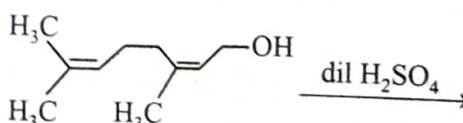
13. The major products A and B in the following reactions are:

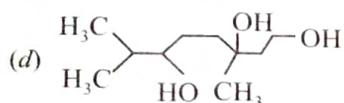
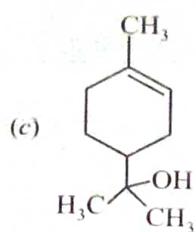
(2020)



14. The major product of the following reaction is:

(2020)

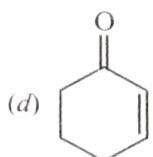
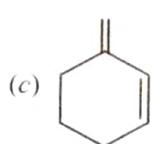
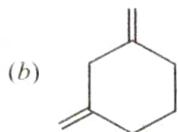
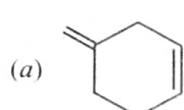




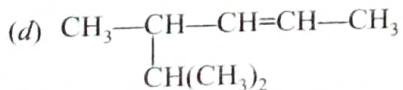
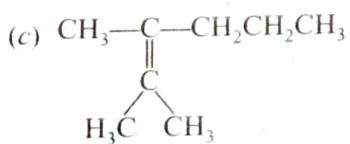
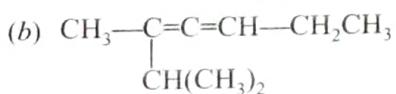
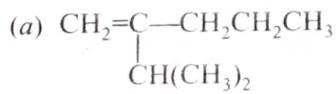
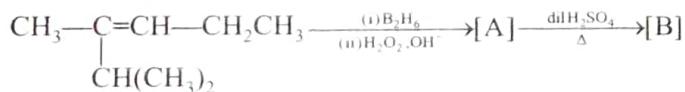
15. An unsaturated hydrocarbon X absorbs two hydrogen molecules on catalytic hydrogenation, and also gives following reaction: (2020)



X will be:



16. The major product [B] in the following sequence of reactions is: (2020)

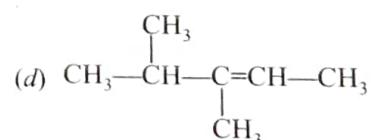
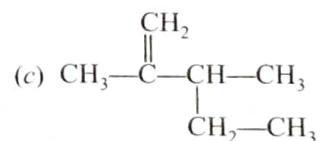
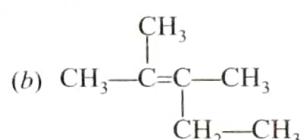
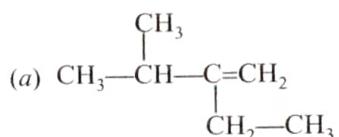
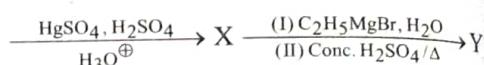
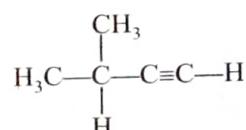


17. In the following sequence of reactions the maximum number of atoms present in molecule 'C' in one plane is (2020)

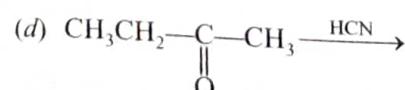
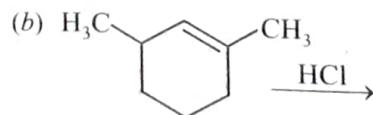


(A is a lowest molecular weight alkyne)

18. The major product (Y) in the following reactions is: (2020)

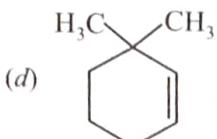
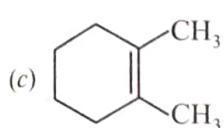
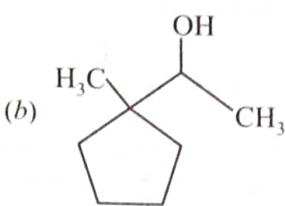
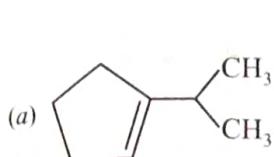
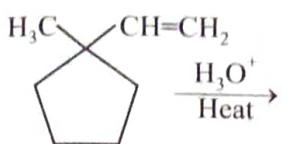


19. Which of the following reactions will not produce a racemic product? (2020)



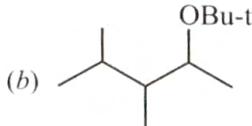
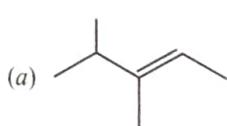
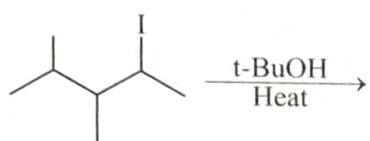
20. The major product in the following reaction is:

(2020)



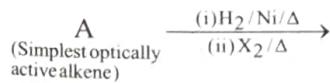
21. The major product in the following reaction is:

(2020)



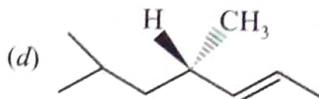
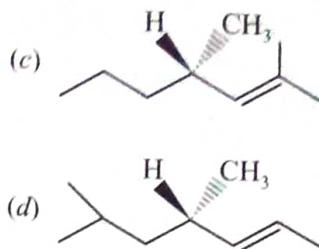
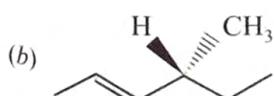
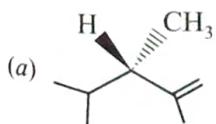
22. The total number of monohalogenated organic products in the following (including stereoisomers) reaction is _____.

(2020)



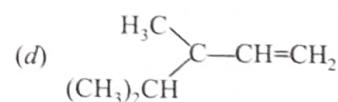
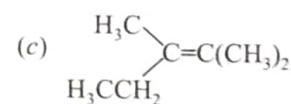
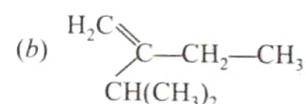
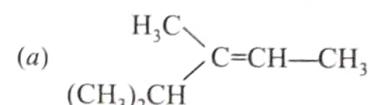
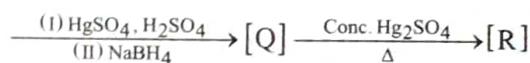
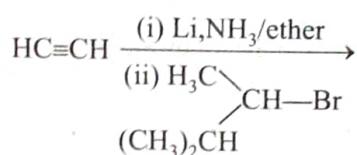
23. Which of the following compounds produces an optically inactive compound on hydrogenation?

(2020)



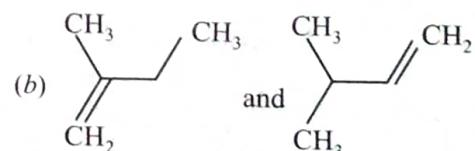
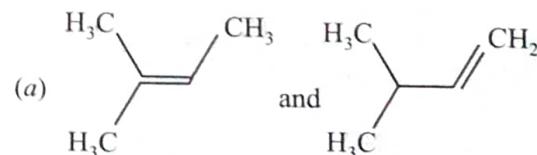
24. The major product [R] in the following sequence of reactions is:

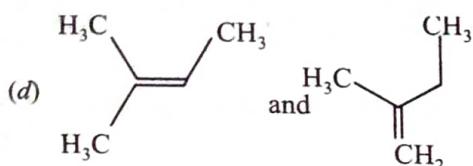
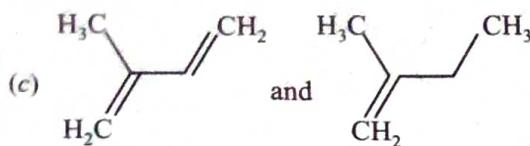
(2020)



25. When neopentyl alcohol is heated with an acid, it slowly converted into an 85 : 15 mixture of alkenes A and B, respectively. What are these alkenes?

(2020)



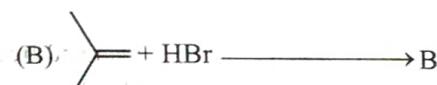
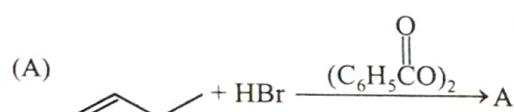


26. The major product formed in the following reaction is:
(2020)



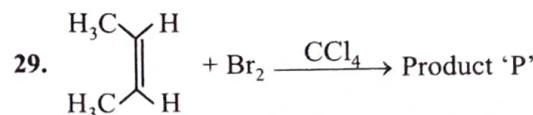
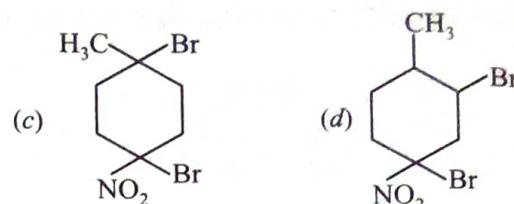
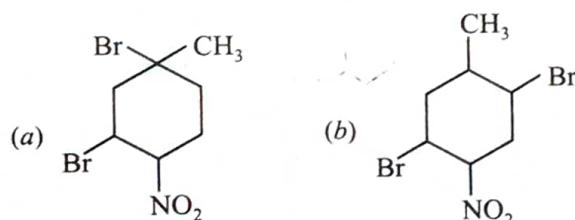
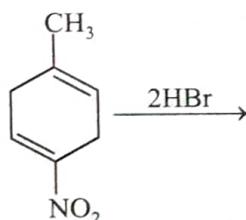
- (a) $\text{Br}(\text{CH}_2)_3\text{CH}(\text{CH}_3)_2$
 (b) $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}(\text{CH}_3)_2$
 (c) $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}(\text{CH}_3)_2$
 (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{Br})(\text{CH}_3)_2$

27. The increasing order of the boiling points of the major products A, B and C of the following reactions will be:
(2020)



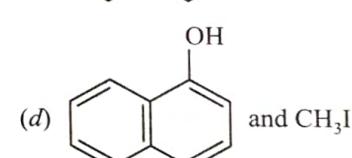
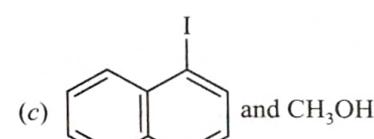
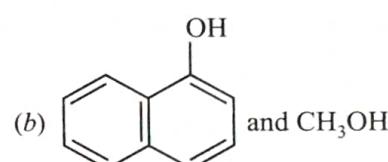
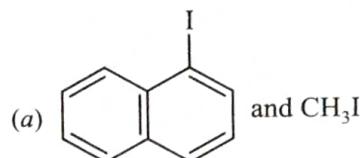
- (a) A < C < B
 (b) C < A < B
 (c) B < C < A
 (d) A < B < C

28. The major product of the following reaction is:
(2020)



Consider the above chemical reaction. The total number of stereoisomers possible for Product 'P' is.
(2021)

30. Main products formed during a reaction of 1-methoxy naphthalene with hydroiodic acid are:
(2021)



31. Match List-I with List-II :
(2021)

List - I (Chemicals)

(A) Alcoholic potassium hydroxide

(B) Pd/BaSO₄

(C) BHC (Benzene hexachloride)

(D) Polyacetylene

List-II (Use/Preparation/Constituent)

(i) Electrodes in batteries

(ii) Obtained by addition reaction

(iii) Used for β - elimination reaction

(iv) Lindlar's catalyst

Choose the most appropriate match:

(a) (A) - (ii), (B) - (i), (C) - (iv), (D) - (iii)

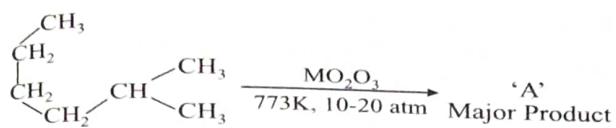
(b) (A) - (iii), (B) - (iv), (C) - (ii), (D) - (i)

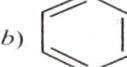
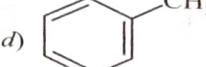
(c) (A) - (iii), (B) - (i), (C) - (iv), (D) - (ii)

(d) (A) - (ii), (B) - (iv), (C) - (i), (D) - (iii)

32. Identify A in the given chemical reaction.

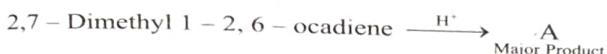
(2021)



- (a)  (b) 
- (c)  (d) 

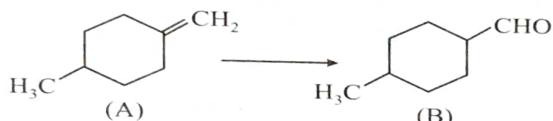
33. The major product 'A' of the following given reaction has _____ sp^2 hybridized carbon atoms.

(2022)



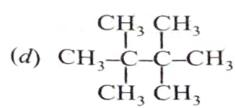
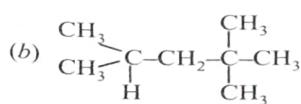
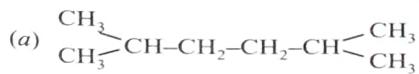
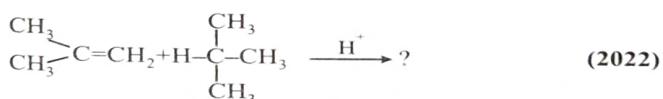
34. Which of the following reagents/reactions will convert 'A' to 'B'?

(2022)



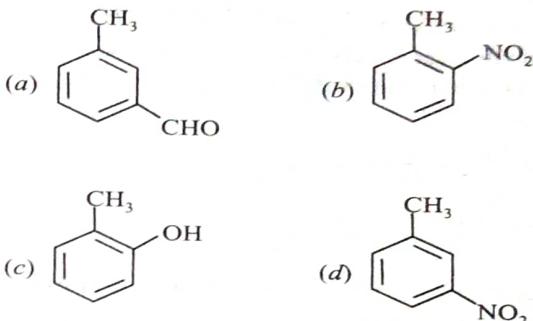
- (a) PCC oxidation
 (b) Ozonolysis
 (c) $\text{BH}_3, \text{H}_2\text{O}_2/\text{OH}$ followed by PCC oxidation
 (d) HBr , hydrolysis followed by oxidation by $\text{K}_2\text{Cr}_2\text{O}_7$

35. The products formed in the following reaction.



36. Halogenation of which of the following will yield m-substituted product with respect to methyl group as a major product?

(2022)



37. Two isomers 'A' and 'B' with molecular formula C_4H_8 give different products on oxidation with KMnO_4 in acidic medium. Isomer 'A' on reaction with KMnO_4/H^+ results in effervescence of a gas and gives ketone. The compound 'A' is:

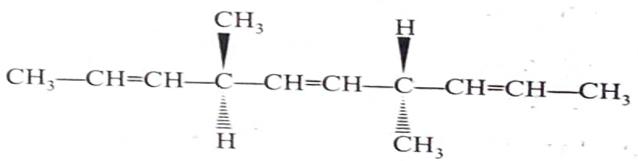
(2022)

- (a) But-1-ene
 (b) Cis-But-2-ene
 (c) Trans-But-2-ene
 (d) 2-methyl propene

JEE ADVANCED

38. The number of optically active products obtained from the complete ozonolysis of the given compound is:

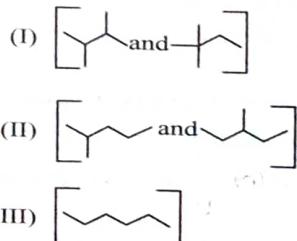
(2012)



- (a) 0 (b) 1
 (c) 2 (d) 4

39. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure

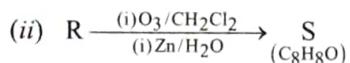
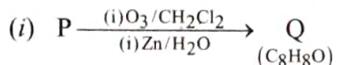
(2014)



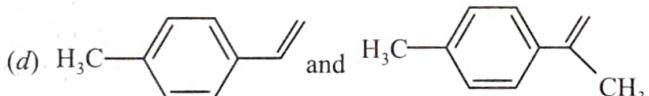
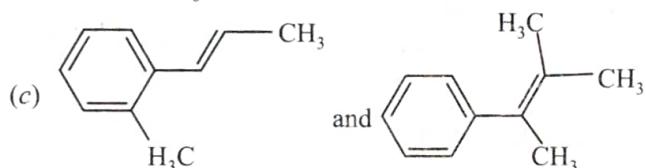
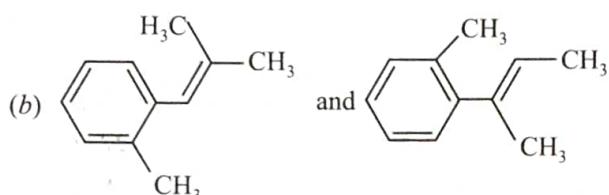
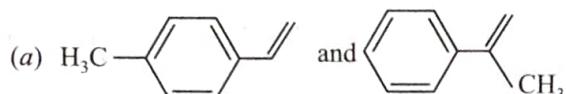
The correct order of their boiling point is:

- (a) (I) > (II) > (III) (b) (III) > (II) > (I)
 (c) (II) > (III) > (I) (d) (III) > (I) > (II)

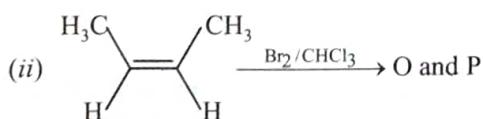
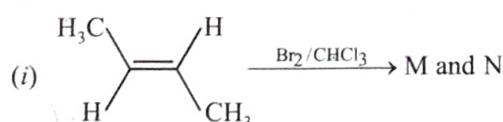
40. Compounds P and R upon ozonolysis produce Q and S, respectively. The molecular formula of Q and S is C_8H_8O . Q undergoes Cannizzaro reaction but not haloform reaction, whereas S undergoes haloform reaction but not Cannizzaro reaction. (2017)



The option(s) with suitable combination of P and R, respectively, is (are):

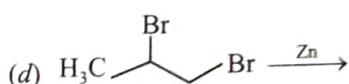


41. The correct statement(s) for the following addition reactions is(are): (2017)

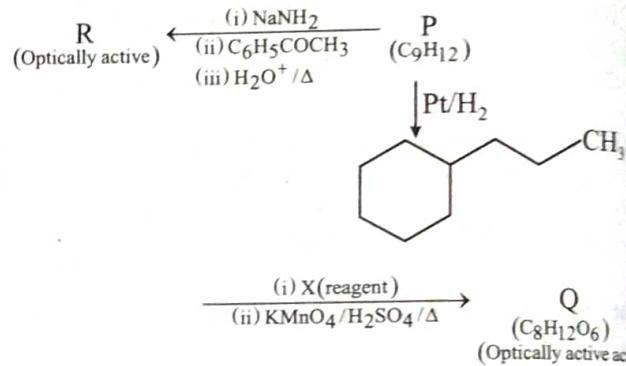


- (a) (M and O) and (N and P) are two pairs of enantiomers.
 (b) Bromination proceeds through trans-addition in both the reactions.
 (c) (M and O) and (N and P) are two pairs of diastereomers.
 (d) O and P are identical molecules.

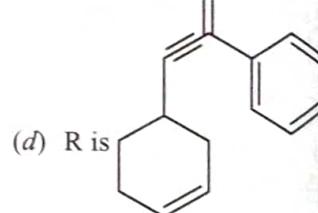
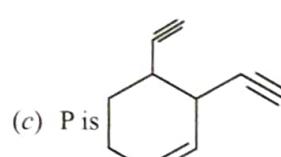
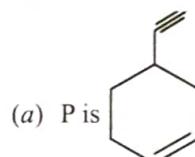
42. Which of the following reactions produce(s) propane as a major product? (2019)



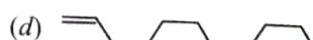
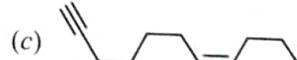
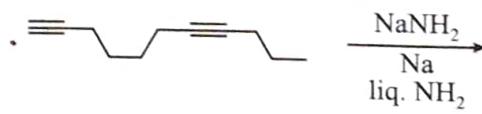
43. Consider the following transformations of a compound P (2020)



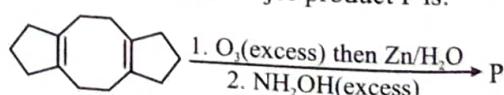
Choose the correct option(s):



44. The major product formed in the following reaction is: (2021)



45. In the reaction given below, the total number of atoms having sp^2 hybridization in the major product P is: (2021)



ANSWER KEY

CONCEPT APPLICATION

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (b) | 3. (c) | 4. (c) | 5. (c) | 6. (a) | 7. (a) | 8. (c) | 9. (c) | 10. (c) |
| 11. (c) | 12. (b) | 13. (b) | 14. (b) | 15. (a) | 16. (c) | 17. (a) | 18. (b) | 19. (c) | 20. (d) |
| 21. (d) | 22. (b) | | | | | | | | |

EXERCISE-1 (TOPICWISE)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (c) | 2. (d) | 3. (a) | 4. (d) | 5. (b) | 6. (d) | 7. (a) | 8. (d) | 9. (c) | 10. (b) |
| 11. (d) | 12. (a) | 13. (b) | 14. (b) | 15. (c) | 16. (b) | 17. (d) | 18. (b) | 19. (c) | 20. (d) |
| 21. (d) | 22. (d) | 23. (c) | 24. (c) | 25. (a) | 26. (c) | 27. (c) | 28. (a) | 29. (a) | 30. (a) |
| 31. (b) | 32. (c) | 33. (b) | 34. (b) | 35. (d) | 36. (c) | 37. (c) | 38. (b) | 39. (c) | 40. (a) |
| 41. (d) | 42. (b) | 43. (c) | 44. (a) | 45. (d) | 46. (d) | 47. (a) | 48. (c) | 49. (b) | |

EXERCISE-2 (LEARNING PLUS)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (a) | 3. (c) | 4. (b) | 5. (a) | 6. (c) | 7. (c) | 8. (d) | 9. (d) | 10. (c) |
| 11. (a) | 12. (c) | 13. (d) | 14. (c) | 15. (c) | 16. (a) | 17. (d) | 18. (a) | 19. (b) | 20. (b) |
| 21. (d) | 22. (a) | 23. (b) | 24. (a) | 25. (c) | 26. (b) | 27. (a) | 28. (c) | 29. (d) | 30. (c) |
| 31. (a) | 32. (b) | 33. (c) | 34. (c) | 35. (c) | 36. (b) | 37. (d) | 38. (a) | 39. (d) | 40. (c) |
| 41. (c) | 42. (d) | 43. (c) | 44. (c) | 45. (a) | 46. (d) | 47. (a) | 48. (a) | 49. (b) | |

EXERCISE-3 (JEE ADVANCED LEVEL)

- | | | | | | | | | | |
|----------|----------|------------|------------|--------------|------------|------------|------------|------------|------------|
| 1. (c,d) | 2. (a,b) | 3. (a,c,d) | 4. (a,b,c) | 5. (a,b,c,d) | 6. (a,b,c) | 7. (a,c,d) | 8. (a,b,c) | 9. (b) | 10. (c) |
| 11. (c) | 12. (d) | 13. (a) | 14. (a) | 15. (d) | 16. (a) | 17. (d) | 18. (a) | 19. (a) | 20. (d) |
| 21. (d) | 22. (a) | 23. (a) | 24. (a) | 25. (c) | 26. (6) | 27. [4] | 28. [4] | 29. [0303] | 30. [0503] |
| 31. [3] | 32. [1] | 33. [8] | 34. [4] | 35. [4] | 36. [5] | 37. [4] | 38. [3] | 39. [3] | 40. [3] |
| 41. [5] | | | | | | | | | |

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|----------------------|---------|---------|---------|
| 1. (d) | 2. (a) | 3. (d) | 4. (d) | 5. (a) | 6. (b) | 7. (b) | 8. (c) | 9. (b) | 10. (d) |
| 11. (a) | 12. (c) | 13. (b) | 14. (c) | 15. (a) | 16. (c) | 17. [13.00 to 13.00] | | 18. (b) | 19. (a) |
| 20. (c) | 21. (c) | 22. (8) | 23. (a) | 24. (c) | 25. (d) | 26. (d) | 27. (c) | 28. (a) | 29. (2) |
| 30. (d) | 31. (b) | 32. (d) | 33. [2] | 34. (c) | 35. (b) | 36. (c) | 37. (d) | | |
| 41. [5] | | | | | | | | | |

JEE Advanced

- | | | | | | | | |
|---------|---------|-----------|-----------|-----------|-----------|---------|----------|
| 38. (a) | 39. (b) | 40. (a,c) | 41. (b,c) | 42. (b,c) | 43. (b,c) | 44. (b) | 45. [12] |
|---------|---------|-----------|-----------|-----------|-----------|---------|----------|

CHAPTER

16

Environmental Chemistry

INTRODUCTION

Pollution may be defined as any undesirable change in the physical, chemical or biological characteristics of air, water and soil which may cause any harm to man and other living organisms of the environment.

TYPES OF POLLUTANTS

The agents causing pollution are termed as **pollutants**.

- ❖ On the basis of form of their occurrence, pollutants are divided into two categories.

- (i) **Primary pollutants:** These are present in the same form in which they are produced. eg. carbon monoxide, DDT
- (ii) **Secondary pollutants:** These are formed by reaction between the primary pollutants in the presence of sunlight eg. PAN, Ozone, HNO_3 , H_2SO_4 etc. Nitrogen oxides and hydrocarbons react photochemically to produce peroxyacetyl nitrates (PAN) and ozone.

The secondary pollutants may be more toxic than the primary ones. The phenomenon is called **synergism**.

- ❖ On the basis of their degradation, pollutants are divided into two categories:

- (i) **Biodegradable Pollutants:** Pollutants which are decomposed or degraded by biological or microbial action are called biodegradable pollutants eg. domestic sewage.
- (ii) **Non-biodegradable Pollutants:** Pollutants which are not decomposed or degraded by living organisms or microorganisms are called non-biodegradable pollutants eg. DDT, glass, plastics, aluminium cans, phenolic compounds, pesticides, radioactive substances, heavy metals like mercury, lead, cadmium etc.

- ❖ On the basis of their existence in nature, pollutants are divided into two categories:

- (i) **Quantitative Pollutants:** These are naturally present in nature and are also added by man. These become pollutants only when their concentration reaches beyond a threshold value in the environment. eg. CO_2

- (ii) **Qualitative Pollutants:** These are not present in the nature but are added in nature only due to human activities eg. insecticides, fungicides, herbicides etc.

ENVIRONMENTAL POLLUTION

Environmental pollution is the effect of undesirable changes in our surroundings that have harmful effects on plants, animals and human beings. A substance, which causes pollution, is known as pollutant. Pollutants can be solid, liquid or gaseous substances present in greater concentration than in natural abundance and are produced due to human activities or due to natural happenings. Do you know, an average human being requires nearly 12-15 times more air than the food. So, even small amounts of pollutants in the air become significant compared to similar levels present in the food. Pollutants can be degradable, like discarded vegetables which rapidly break down by natural processes. On the other hand, pollutants which are slowly degradable, remain in the environment in an unchanged form for many decades. For example, substances such as dichlorodiphenyltrichloroethane (DDT), plastic materials, heavy metals, many chemicals, nuclear wastes etc., once released into the environment are difficult to remove. These pollutants cannot be degraded by natural processes and are harmful to living organisms. In the process of environmental pollution, pollutants originate from a source and get transported by air or water and dumped into the soil by human beings.

ATMOSPHERIC POLLUTION

The atmosphere that surrounds the earth is not of the same thickness at all heights. There are concentric layers of air or regions and each layer has different density. The lowest region of atmosphere in which the human beings along with other organisms live is called troposphere. It extends up to the height of ~ 10 km from sea level. Above the troposphere, between 10 and 50 km above sea level lies stratosphere. Troposphere is a turbulent, dusty zone containing air, much water vapour and clouds. This is the region of strong air movement and cloud formation. The stratosphere, on the other hand, contains dinitrogen, dioxygen, ozone and little water vapour.

Atmospheric pollution is generally studied as tropospheric and stratospheric pollution. The presence of ozone in the stratosphere prevents about 99.5 per cent of the sun's harmful ultraviolet (UV) radiations from reaching the earth's surface and thereby protecting humans and other animals from its effect.

KINDS OF POLLUTION

On the basis of environmental study pollution is of following types.

- (a) Air pollution
 - (b) Water pollution
 - (c) Soil pollution
 - (d) Noise pollution
 - (e) Radioactive pollution

TROPOSPHERIC POLLUTION

Tropospheric pollution occurs due to the presence of undesirable solid or gaseous particles in the air. The following are the major gaseous and particulate pollutants present in the troposphere:

- (i) **Gaseous Air Pollutants:** These are oxides of sulphur, nitrogen and carbon, hydrogen sulphide, hydrocarbons, ozone and other oxidants.
 - (ii) **Particulate Pollutants:** These are dust, mist, fumes, smoke, smog etc.

AIR POLLUTION

- (i) It is mainly caused by industries and automobiles. Automobiles are the greatest pollutor of the atmosphere and are responsible for 75% of noise pollution and about 60-80% of air pollution of big cities.
 - (ii) The combustion of fossil fuels (coal, oil, gas etc.) releases CO, CO₂, nitrogen oxides, fluorides, hydrocarbons etc. into atmosphere usually in the form of smoke causing air pollution.
 - (iii) Particulate matters released by mills, factories and mines also cause air pollution.
 - (iv) Some of the natural air pollutants are pollen grains, spores, volcanoes etc.

Major Air Pollutants

Carbon Monoxide

- (i) It is formed by incomplete combustion of fuels in various industries, automobiles etc.
 - (ii) CO accounts for about 50% of total air pollution. It is largest pollutant in Delhi's air.
 - (iii) CO combines with haemoglobin, produces **carboxyhaemoglobin** and therefore decreases oxygen carrying capacity leading to hypoxia, headache, decreased vision, muscular weakness, nausea, exhaustion etc.
 - (iv) When 50% of haemoglobin has been transformed into carboxyhaemoglobin, then death occurs due to CO-poisoning leading to anoxia (oxygen starvation)

Carbon Dioxide

- (i) It is a **green house gas**. It is produced due to combustion of fuels, volcanic eruptions and during the process of respiration.

- (ii) Its average concentration in the atmosphere is 300 ppm (0.03%).
 - (iii) It is normally not an atmospheric pollutant, but under very high concentration it may act as a pollutant.
 - (iv) It causes **Global warming**.

Sulphur Dioxide (SO_2)

- (i) It is produced during combustion of fossil fuels (mainly coal) and smelting of sulphur containing ores.
 - (ii) It causes acid rain (gaseous SO_2 oxidises to SO_3 , which on combination with water forms H_2SO_4).
 - (iii) Acid rain is 60-70% due to SO_2 and SO_3 , and 30-40% due to NO_2 and NO_3 .
 - (iv) Due to acid rain the leaves develop chlorotic and necrotic spots.
 - (v) SO_2 corrodes stones, metals, leather, paper and fabrics. There is deterioration of colour and lusture of fabrics, stones and painted surfaces.
 - (vi) **Tajmahal of Agra** is affected by gases (SO_2 , H_2S etc.) discharged from oil refinery of Mathura.
 - (vii) **Lichens** (e.g. *Usnea*) are extremely sensitive to SO_2 and could be regarded as indicators of SO_2 pollution. (indicators of air pollution).
 - viii) Garden pea is another SO_2 pollution indicator.
 - (ix) Lichen vegetation (*parmelia*, *usnea*, *cladonia*) Garden pea and mosses are completely destroyed due to SO_2 .
 - (x) SO_2 causes chlorosis (destruction of chlorophyll) and necrosis of vegetation, membrane damage and yield reduction.
 - (xi) In plants and animals, SO_2 destroys all membrane systems.
 - xii) In human beings SO_2 increases the chances of occurrence of asthma, bronchitis and emphysema.
 - xiii) It produces eye irritation, damage respiratory tract.

Hydrocarbons

- (i) They are produced naturally (e.g. marsh gas CH_4) and by burning of petroleum.
 - (ii) Benzene (C_6H_6) is a major constituent of petrol and automobile exhaust.
 - (iii) Hydrocarbons are carcinogenic, cause irritation of eyes and mucous membrane.
 - (iv) Benzene is a known carcinogen causing **leukemia**.
 - (v) Ethylene (C_2H_4) causes premature senescence and abscission in many plants especially in orchids and cotton.
 - (vi) Methane (marsh gas) has the potential to destroy ozone.

Nitrogen Oxides

- (i) There are three oxides of nitrogen which acts as air pollutants: Nitric oxide (NO), nitrogen dioxide (NO_2) and nitrogen trioxide.
 - (ii) Nitrogen and oxygen combine together at high temperature in any combustion process to produce nitrogen oxides.

- (iii) These are also released by furnaces, forest fires, industries and denitrifying bacteria.
- (iv) NO is less toxic but NO₂ is a poisonous gas.
- (v) Nitrogen oxides are responsible for forming photochemical smog.
- (vi) They also cause acid rain due to formation of HNO₃.
- (vii) They produce lesions, necrosis, defoliation, dieback and death of many plants.
- (viii) Like SO₂, they corrode metals and deteriorate paints, textiles as well as various articles.
- (ix) They cause eye irritation, dilation of arteries, injury of lungs, liver and kidneys.

Fluorides

- (i) Fluorides are emitted during refinement of aluminium and rock phosphates.
- (ii) Fluorides cause necrosis and chlorosis of leaf tips and leaf margins.
- (iii) In human fluorides cause mottling of teeth, weak bones, boat-shaped posture, knocking knees etc.
- (iv) Disease caused by fluoride is known as **fluorosis**.

Particulate Matter

- (i) It is the non-gaseous matter in the atmosphere.
- (ii) It consists of soot, dust, mist, fibres, fly ash, fur, spores, pollen grains etc.
- (iii) It is of two types: Settleable (larger than 10 μm) and suspended (less than 10μm)
- (iv) SPM (suspended particulate matter) is classified into 3 categories:
 - (a) Aerosols (less than 1 μm)
 - (b) Dust (solid particles with more than 1 μm diameter)
 - (c) Mist (liquid particles with more than 1 μm diameter)
- (v) It is added in the atmosphere by burning of fuels.
- (vi) Particulate matter causes about 10-15% of air pollution.
- (vii) Under condition of high humidity, the particulate matter causes corrosion and erosion of surfaces.
- (viii) In human beings, it may cause respiratory problems.
- (ix) Particulate matter from processing industries (eg. cotton dust, iron mill dust, flour mill dust, mine dust) causes **pneumoconiosis**, byssinosis, siderosis, emphysema and other pulmonary problems.
- (x) The asbestos fibers cause asbestosis which is a type of cancer.
- (xi) Dust and smoke produce smog.
- (xii) The ill effects of different kinds of dusts are listed below:
 - (a) Coal dust – **Anthracosis**
 - (b) Silica – **Silicosis**
 - (c) Asbestos – **Asbestosis**, Lung cancer

- (d) Iron – **Siderosis**
- (e) Cotton dust – **Byssinosis**
- (f) Hay or grain dust – **Farmer's lung**

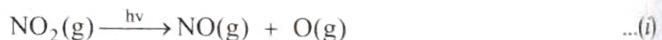
Smog

The word smog is derived from smoke and fog. This is the most common example of air pollution that occurs in many cities throughout the world. There are two types of smog:

- (a) Classical smog occurs in cool humid climate. It is a mixture of smoke, fog and sulphur dioxide. Chemically it is a reducing mixture and so it is also called as reducing smog.
- (b) Photochemical smog occurs in warm, dry and sunny climate. The main components of the photochemical smog result from the action of sunlight on unsaturated hydrocarbons and nitrogen oxides produced by automobiles and factories. Photochemical smog has high concentration of oxidising agents and is, therefore, called as oxidising smog.

Formation of Photochemical Smog

When fossil fuels are burnt, a variety of pollutants are emitted into the earth's troposphere. Two of the pollutants that are emitted are hydrocarbons (unburnt fuels) and nitric oxide (NO). When these pollutants build up to sufficiently high levels, a chain reaction occurs from their interaction with sunlight in which NO is converted into nitrogen dioxide (NO₂). This NO₂ in turn absorbs energy from sunlight and breaks up into nitric oxide and free oxygen atom.



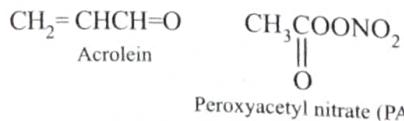
Oxygen atoms are very reactive and combine with the O₂ in air to produce ozone.



The ozone formed in the above reaction (ii) reacts rapidly with the NO(g) formed in the reaction (i) to regenerate NO₂. NO₂ is a brown gas and at sufficiently high levels can contribute to haze.



Ozone is a toxic gas and both NO₂ and O₃ are strong oxidising agents and can react with the unburnt hydrocarbons in the polluted air to produce chemicals such as formaldehyde, acrolein and peroxyacetyl nitrate (PAN).



Effects of Photochemical Smog

The common components of photochemical smog are ozone, nitric oxide, acrolein, formaldehyde and peroxyacetyl nitrate (PAN). Photochemical smog causes serious health problems. Both ozone and PAN acts as powerful eye irritants. Ozone and nitric oxide irritate the nose and throat and their high concentration causes

headache, chest pain, dryness of the throat, cough and difficulty in breathing. Photochemical smog leads to cracking of rubber and extensive damage to plant life. It also causes corrosion of metals, stones, building materials, rubber and painted surfaces.

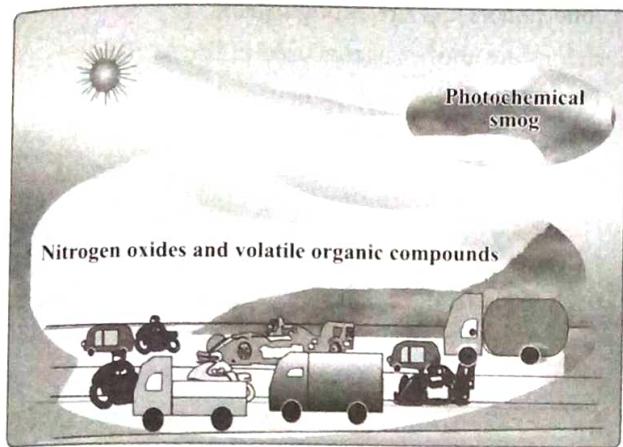


Fig. Photochemical smog occurs where sunlight acts on vehicle pollutants

How can Photochemical Smog be Controlled?

Many techniques are used to control or reduce the formation of photochemical smog. If we control the primary precursors of photochemical smog, such as NO_2 and hydrocarbons, the secondary precursors such as ozone and PAN, the photochemical smog will automatically be reduced. Usually catalytic converters are used in the automobiles, which prevent the release of nitrogen oxide and hydrocarbons to the atmosphere. Certain plants e.g., Pinus, Juniperus, Quercus, Pyrus and Vitis can metabolise nitrogen oxide and therefore, their plantation could help in this matter.

Aerosols

- These are chemicals released in the air with force in the form of mist or vapour by jet planes.
- Aerosols contain **CFC (chlorofluorocarbons)** which destroy ozone layer in the stratosphere.
- This permitting some more harmful U.V. radiations to reach the earth surface, U.V. radiations cause skin cancer and increases mutation rates.
- Ozone acts as preventive shield against the U.V. rays.
- Freons are several CFMS (chlorofluoromethanes) released into troposphere where they dissociates and release free chlorine that causes depletion of ozone.
- Freon or CFC also used in refrigerator, air conditioners and in making plastic foams.

Green House Effect and Global Warming

- The sunlight that reaches to the earth, warms both atmosphere and the earth surface. The earth's atmospheric system then reradiates the heat as infrared radiations.
- Gases like CO_2 , CH_4 , CFCs, NO_2 are strong absorbers of long-wave or infra-red radiations emitted by the surface of the earth, and warm the earth's atmosphere. This is called the **green house effect** because it is like the glass panel of a green house that allows sunlight to pass through and then traps the resulting heat inside the structure.

- CO_2 is the principal green house gas responsible for warming of the earth.

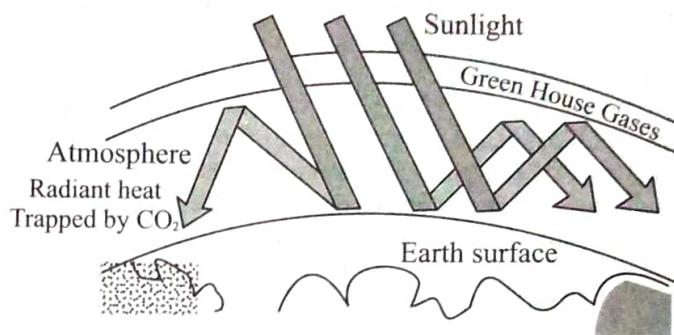


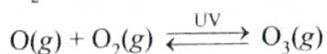
Fig. The green house effect of CO_2

- CO_2 is rising into the atmosphere slowly as a result of large scale burning of fossil fuels (coal, oil etc), volcanic activities and respiration.
- 50% of the increase in earth's temperature is due to CO_2 , 20% is due to CFCs and remaining 30% is due to other gases.
- Some ecologists visualise that the green house effect shall lead to global warming. In the next fifty years time the temperature of earth shall rise by $2^\circ - 5^\circ\text{C}$.
- A rise of global temperature by 2 to 5°C may lead to
 - Melting of glaciers and polar ice caps.
 - Flooding of low lying coastal plains.
 - Increase in the flow of rivers and change in rainfall pattern.
 - Possible submersion of islands.
- The UNEP (United Nations Environment Programme) has appropriately chosen the slogan "Global Warming: Global Warning" and since 1989, 5th june is celebrated as World Environment Day.

STRATOSPHERIC POLLUTION

Formation and Breakdown of Ozone: The upper stratosphere consists of considerable amount of ozone (O_3), which protects us from the harmful ultraviolet (UV) radiations ($\lambda = 255 \text{ nm}$) coming from the sun. These radiations causes skin cancer (melanoma) in humans. Therefore, it is important to maintain the ozone shield.

Ozone in the stratosphere is a product of UV radiations acting on dioxygen (O_2) molecules. The UV radiations split apart molecular oxygen into free oxygen (O) atoms. These oxygen atoms combine with the molecular oxygen to form ozone.

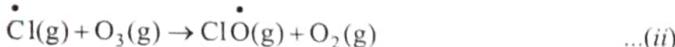


Ozone is thermodynamically unstable and decomposes to molecular oxygen. Thus, a dynamic equilibrium exists between the production and decomposition of ozone molecules. In recent years, there have been reports of the depletion of this protective ozone layer because of the presence of certain chemicals in the

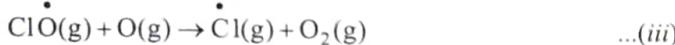
stratosphere. The main reason of ozone layer depletion is believed to be the release of chlorofluorocarbon compounds (CFCs), also known as freons. These compounds are nonreactive, non flammable, non toxic organic molecules and therefore used in refrigerators, air conditioners, in the production of plastic foam and by the electronic industry for cleaning computer parts etc. Once CFCs are released in the atmosphere, they mix with the normal atmospheric gases and eventually reach the stratosphere. In stratosphere, they get broken down by powerful UV radiations, releasing chlorine free radical.



The chlorine radical then react with stratospheric ozone to form chlorine monoxide radicals and molecular oxygen.

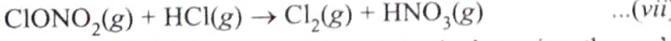
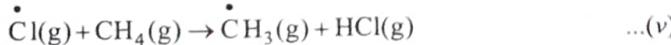
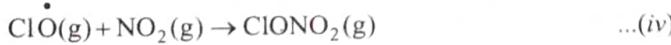


Reaction of chlorine monoxide radical with atomic oxygen produces more chlorine radicals.

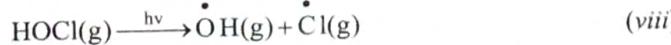


The chlorine radicals are continuously regenerated and cause the breakdown of ozone. Thus, CFCs are transporting agents for continuously generating chlorine radicals into the stratosphere and damaging the ozone layer.

The Ozone Hole: In 1980s atmospheric scientists working in Antarctica reported about depletion of ozone layer commonly known as ozone hole over the South Pole. It was found that a unique set of conditions was responsible for the ozone hole. In summer season, nitrogen dioxide and methane react with chlorine monoxide (reaction iv) and chlorine atoms (reaction v) forming chlorine sinks, preventing much ozone depletion, whereas in winter, special type of clouds called polar stratospheric clouds are formed over Antarctica. These polar stratospheric clouds provide surface on which chlorine nitrate formed (reaction iv) gets hydrolysed to form hypochlorous acid (reaction vi). It also reacts with hydrogen chloride produced as per reaction (v) to give molecular chlorine.



When sunlight returns to the Antarctica in the spring, the sun's warmth breaks up the clouds and HOCl and Cl₂ are photolysed by sunlight, as given in reactions (viii) and (ix).



The chlorine radicals thus formed, initiate the chain reaction for ozone depletion as described earlier.

Ozone Layer Depletion

- (i) The ozone layer present in the stratosphere acts as an ultraviolet absorbant thus protecting the earth from its harmful effect.

- (ii) Depletion/destruction of ozone layer is primarily caused by CFCs (Chlorofluoro carbons) and halons (halocarbons C_xF_xBr_x).
- (iii) CFCs are heat transfer agents used in refrigerators, air conditioners and fire extinguishers.
- (iv) Halons are antifire agents used in fire extinguishers.
- (v) The CFCs react with ozone and thus cause thinning of ozone layer which permits more UV radiations to reach the surface of earth.

Important Points

- (i) Benzpyrene/polycyclic hydrocarbon is a powerful carcinogen (cancer causing agent). It is emitted by cigarette smoking, combustion of petrol, diesel etc.
- (ii) Carbon monoxide (CO) accounts for about 50% of total air pollution.
- (iii) Sulphur dioxide (SO₂) accounts for 6% of total air pollution.
- (iv) Particulate matter accounts for 10-15% of total air pollution.
- (v) First Earth Summit of United Nations Conference on Environment and Development (UNCED) was held at Rio-de-Janerio (Brazil) in 1992.
- (vi) First International Conference on "Environment and Development" was held at Stockholm in 1972.
- (vii) Second International Conference on "Environment and Development" was held at New Delhi in 1985.
- (viii) Cyclon collector is used for minimising air pollution.
- (ix) Most polluted city of the world – Tokyo (Japan)
- (x) Most polluted city of India – Kolkata.
- (xi) In Delhi and Kolkata pollution is mainly due to automobiles and fire.
- (xii) In Mumbai pollution is mainly due to industries.
- (xiii) Cotton dust is main source of air pollution in Surat and Ahmedabad.
- (xiv) Level of suspended particulate matter (SPM) concentration is highest in the atmosphere of Kolkata.
- (xv) In Bihar and Andhra Pradesh major source of air pollution is thermal power plants.
- (xvi) Pittsburgh city (USA) was once named as "Smoke city".
- (xvii) The automobile emission can be reduced by adding barium salts in the petrol.
- (xviii) CFCs have maximum Ozone Depleting Potential (ODP).
- (xix) Ozone, PAN, HNO₃ and H₂SO₄ are secondary pollutants.
- (xx) **Green Charter:** Drawn by the World Wildlife Fund for Nature for India in December, 1997. It states that "Protection of environment is crucial for human survival and well being now and in future".
- (xxi) Excessive inhalation of manganese causes pneumonia.
- (xxii) Methane is released by cud-chewing domestic animals.
- (xxiii) Excess of pollen causes allergic reactions in several human beings. The common reactions are collectively called hay fever.

- (xxiv) The smoke reduces visibility. To visualise the extent of darkness caused due to smoke Ringelmann charts are used.
 - (xxv) Tocopherol produces resistance against carcinogen.
 - (xxvi) Formation of ozone hole is maximum over Antarctica.



Train Your Brain

Example 1: The basic component of smog is:

Sol. (c) Smog is made up of many chemicals including nitrogen oxides (NO_x), sulphur dioxide (SO_x), carbon monoxide (CO), and volatile organic compounds (VOCs), but the two main components of smog are particulate matter (PM) and groundlevel ozone O_3 .

Example 2: The ozon layer forms Naturally by.

- (a) The interaction of CFC with oxygen
 - (b) The interaction of UV radiation with oxygen
 - (c) The interaction of IR radiation with oxygen.
 - (d) The interaction of oxygen & water vapour

Sol. (b) Ozone is a gas found in the atmosphere made up of 3 atoms of oxygen. Ozone is formed in the atmosphere when energetic UV radiation dissociates molecules of oxygen into separate oxygen atoms. Free oxygen atoms can recombine to form the oxygen molecules. It joins up forming ozone.

Ozone molecules can also be decomposed by UV radiation into a free atom and an oxygen molecule. Ozone is thus continuously created and destroyed in the atmosphere by UV radiation coming from the sun.



Concept Application

1. Which of the following is responsible for depletion of ozone layer in upper strata of the atmosphere?
(a) Polyhalogen (b) Ferrocene
(c) Fullerenes (d) Freons
 2. The pKa values of -COOH , -SH and -NH_3^+ groups present in the amino acid, cysteine are 1.8, 8.2 and 10.8, respectively. The structure of cysteine at a pH = 5 will be:
(a) Green-house gas
(b) A fertilizer
(c) Biodegradable pollutants
(d) Non-biodegradable pollutant

WATER POLLUTION

Water pollution is defined as the addition of some substances (organic, inorganic, biological, radio logical) or factor (eg. heat) which degrades the quality of water so that, it either becomes health hazard or unfit for use.

Kinds of water pollution: The water pollution may be physical, chemical or biological.

- (a) **Physical pollution:** It involves the changes in the physical properties of water eg. colour, taste, odour, temperature, turbidity etc.

- (b) **Chemical pollution:** It is caused due to change in the chemical properties of water. They mainly include the pH, dissolved O₂, inorganic or organic chemicals, heavy metals etc.

Inorganic chemicals include fluorides, chlorides, phosphates and nitrates. Organic chemicals include phenols, dyes, pesticides and chlorocompounds.

- (c) **Biological pollution:** It is caused due to the presence of living organisms in water such as algae, fungi, bacteria, viruses, protozoans, insects etc.

Sources of water pollution and effects of water pollutants:
Water pollution is a serious health hazard in India, especially in villages. It is estimated that 50-60% of Indian population suffers from diseases caused by it. 30-40% of all deaths are believed to be due to it. The principal sources of water pollution and effects of water pollutants are as follows.

Domestic Wastes and Sewage

- (i) Sewage containing human faeces, urine, kitchen and cloth washings, organic waste, industrial waste etc. is usually poured into water bodies which cause water pollution.
 - (ii) The villagers often wash their animals, cloths and take bath in the same pond. Such water get contaminated with infectious agents for cholera, typhoid, dysentery, Jaundice and skin diseases.
 - (iii) Sewage provide food for decomposers, so the population of decomposers increases.
 - (iv) Decomposers/microorganisms causing decomposition of sewage take up most of the oxygen present dissolved in water. So in this water BOD (Biological oxygen demand or Biochemical oxygen demand) increased very much.
 - (v) BOD is the amount of oxygen in milligrams required by microorganisms for five days to metabolise waste present in one litre of water at 20°C.
 - (vi) A weak organic waste will have BOD below 1500 mg/litre, medium organic waste between 1500 – 4000 mg/litre while in strong waste above 4000 mg/litre.
 - (vii) The degree of pollution is directly proportional to BOD.
 - (viii) In sewage phosphorous and nitrogen compounds are present which are necessary for the growth of algae. In polluted water these are accumulated which result into excessive growth of algae on water surface. Excessive growth of algae is called **water bloom**.

- (ix) The phosphates present in detergents stimulate algae growth in the water bodies and cause eutrophication.
- (x) Presence of extra nutrients brings about dense growth of plants and animals life. The phenomenon is called **eutrophication**.
- (xi) Eutrophication leads to organic loading, depletion of oxygen, death of animals and fouling of water.
- (xii) Sewage produces foul odour and makes the water brownish and oily.

Industrial effluents (or industrial discharges): Industries usually discharge waste water into ponds, lakes and rivers. Industrial waste water contains heavy metals (mercury, lead, copper, arsenic and cadmium), inorganic pollutants (acids, alkalies and bleaching liquors), organic pollutants (phenol, naphtha, proteins, aromatic compounds, cellulose fibres etc.) Industrial effluents are the most hazardous pollutants on land and water.

(a) Fluoride: Soluble fluoride is often added to drinking water to bring its concentration upto 1 ppm or 1 mg dm^{-3} .

However, F^- ion concentration above 2 ppm causes brown mottling of teeth. At the same time, excess fluoride (over 10 ppm) causes harmful effect to bones and teeth.

(b) Sulphate: Excessive sulphate ($>500 \text{ ppm}$) in drinking water causes laxative effect, otherwise at moderate levels it is harmless.

(c) Nitrate: The maximum limit of nitrate in drinking water is 50 ppm. Excess nitrate in drinking water can cause disease such as methemoglobinemia ('blue baby' syndrome).

(d) Mercury (Hg)

(i) It is released during combustion of coal, smelting of metallic ores, paper and paint industries.

(ii) Mercury is highly persistent. In water it gets changed into water soluble dimethyl form $[(\text{CH}_3)_2\text{Hg}]$ and enters the food chain (undergoes biomagnification).

(iii) It kills fish and poisons the remaining fauna. Human beings feeding on such poisoned animals develop a crippling deformity called **minamata disease** which is characterised by impairment of various senses, diarrhoea, haemolysis, meningitis and death.

(iv) The minamata disease was first detected in Japan.

(v) Mercury inhibits chromosomal disjunction during gamete formation. So it brings about genetic changes also.

(e) Lead (Pb)

(i) The sources of lead pollution are smelters, battery industry, paint, chemical and pesticide industry, automobiles exhausts etc.

(ii) Lead is pollutant of air, soil and water.

(iii) It is used as anti-knock reagent in petrol and released by automobile exhausts.

(iv) Lead is a persistent pollutant and may show biological amplification or biomagnification.

(v) It is a mutagenic and causes anemia, headache, vomiting, colic, loss of muscle power, bluish lines around the gums, loss of appetite and damage of liver, kidney and brain.

(f) Cadmium (Cd)

- (i) It is added to the environment by metal industries, welding and electroplating, pesticides and phosphate industries.
- (ii) Cd shows biological amplification and accumulates inside kidneys, liver, pancreas and spleen.
- (iii) It causes hypertension, anemia, diarrhoea and damage liver and kidneys.

Table: Maximum prescribed concentration of some metals in Drinking Water

Metal	Maximum concentration (ppm or mg dm^{-3})
Fe	0.2
Mn	0.05
Al	0.2
Cu	3.0
Zn	5.0
Cd	0.005

(g) Oil

- (i) During extraction and transportation of oil from the sea to different parts, some of the oil spreads over the surface of water. Refineries also discharge a lot of oil present in their effluents into rivers.
- (ii) Oil spreading on the surface of water prevents its oxygenation and inhibits photosynthetic activity of aquatic plants. Animal life is destroyed due to reduced availability of oxygen, food and toxic effects of oil.
- (iii) Oil spilled over the surface of water may catch fire and hence kill all organic life.

Thermal Pollution

- (i) Hot water is produced by many industries, power generation plants and thermal power plants.
- (ii) Thermal pollution is caused by addition of hot water effluents in water bodies, it bring about rise in water temperature.
- (iii) Warmer water contains less oxygen. Therefore, there is decrease in the rate of decomposition of organic matter.
- (iv) In hot water green algae are replaced by less desirable blue green algae.
- (v) Many organisms fail to reproduce in hot water e.g. Salmon Trout.

Radioactive Wastes

- (i) The nuclear tests performed into sea pollute the water.
- (ii) The animals and plants are affected by the remaining radioactivity of the wastes. Radioactive elements (e.g. cesium-137, strontium-90, Iodine-131) enter the human system.
- (iii) Cesium-137 accumulates inside body muscles, strontium-90 in bones while Iodine-131 in thyroid.

- (iv) Cesium-137 brings about functional and genetic changes.
 - (v) Strontium-90 causes blood and bone cancer.
 - (vi) Iodine-131 affects normal functioning of thyroid.

Important Points Related to Water Pollution

- (i) Some organism like Daphnia, Trout and fishes are sensitive to water pollution, they are indicator of water pollution.
 - (ii) **I.W.P.: Indices of Water Pollution.**
 - (iii) Drinking water rich in nitrates cause methaemoglobinemia.
 - (iv) Faecal pollution is indicated by *Escherichia coli*. MPN is Most Probable Number of *E-coli*. It is indicator of water pollution.
 - (v) **Algal Genus Index:** High organic pollution is indicated by presence of 20 or more genera of algae in a water body. Growth of less than 5 genera of algae is indication of clear water. It is called as **Algal Genus Index (AGI)**
 - (vi) Water (Prevention and control of pollution) Act, 1974. It has been amended in 1988.
 - (vii) **Putrescibility:** Decay and decomposition of organic matter present in water by bacteria and micro-organisms.
 - (viii) **Silent spring:** Novel written by Rachel Carson (1962) mentioning the effect of DDT on birds. DDT use has been banned in USA since then.
 - (ix) In India, DDT banned for agricultural use in 1985. It is a chlorinated hydrocarbon and show biomagnification.
 - (x) **Fluorosis:** 13 states of India possess high fluoride content in drinking water (more than 1.5 mg/l) which causes fluorosis in human.
 - (xi) **ABS (Alkyl Benzene Sulphonate):** It is most harmful component of detergents causing water pollution.
 - (xii) Maize (*Zea mays*) is sensitive indicator of fluoride pollution.
 - (xiii) Ganga Action Plan started in 1985 for controlling pollution in Ganga.
 - (xiv) Reed plants yellow iris are used to purify water. This method of purifying water is called "Green method of water cleaning". Yellow iris plant is less affected by herbicides, so reed beds are highly effective in those areas where pesticides are in use and provides microbiological methods of pesticide detoxification. These plants filter out the particulate matter, while the microbes living in association with the plants, decompose the organic wastes.
 - (xv) **Endrin** is most toxic amongst chlorinated hydrocarbons.
 - (xvi) **Aldrin** in most persistent insecticide in the water and soil.
 - (xvii) Water hyacinth (*Eichornia*) popularly known as Jalkumbhi or Kaloi, can purify water polluted by biological or chemical wastes. It can also filter out heavy metals like cadmium, mercury, lead and nickel as well as other toxic substances found in industrial waste waters.
 - (xviii) **Biotic index:** It gives an idea of pollution of a particular water body. Any water body with a biotic index of more than 15 is clean, while index lower than 10 is polluted.
 - (xix) **C.O.D. (Chemical Oxygen Demand):** It is amount of oxygen required to oxidise all pollutant materials in one litre of water at 20°C in five days. The value of COD is much higher than BOD. (xx) B.O.D. of pure drinking water - Less than 1 ppm or mg/l
 - (xx) Soil salinity can be measured by conductivity meter.

Major Water Pollutants

Pollutant	Source
Micro-organisms	Domestic sewage
Organic wastes	Domestic sewage, animal excreta and waste, decaying animals and plants, discharge from food processing factories.
Plant nutrients	Chemical fertilizers
Toxic heavy metals	Industries and chemical factories
Sediments	Erosion of soil by agriculture and strip mining
Pesticides	Chemicals used for killing insects, fungi and weeds
Radioactive substances	Mining of uranium containing minerals
Heat	Water used for cooling in industries



Train Your Brain

Example 3: Which of the following will increase the BOD of water supply?

Sol. (a) CO_2 the BOD water

Example 4: Sewage water is purified by:

- (a) Microorganism (b) Light
 (c) Fishes (d) Aquatic plants

Sol. (a) Sewage is composed of organic matter and domestic waste. The pollutants are removed by the sewage treatment process of mitigate its' adverse impact on the environment when it is released. The sewage pass through primary, secondary and tertiary treatment.



Concept Application

3. Which causes water pollution?

 - (a) Pathogens
 - (b) Automobile exhausts
 - (c) PCBs
 - (d) Both (a) and (c)

4. Most abundant water pollutant is:

 - (a) Detergents
 - (b) Pesticides
 - (c) Industrial wastes
 - (d) Ammonia

5. Drained sewage has biological oxygen demand (BOD):

 - (a) More than that of water
 - (b) Less than that of water
 - (c) Equal to that of water
 - (d) None of the above

SOIL POLLUTION

India being an agriculture based economy gives high priority to agriculture, fisheries and livestock development. The surplus production is stored by governmental and non-governmental organisations for the lean season. The food loss during the storage also needs special attention. Have you ever seen the damages caused to the crops, food items by insects, rodents, weeds and crop diseases etc? How can we protect them? You are acquainted with some insecticides and pesticides for protection of our crops. However, these insecticides, pesticides and herbicides cause soil pollution. Hence, there is a need for their judicious use.

Soil Pollution

- (i) Unfavourable alteration of soil by addition or removal of substances and factors which decrease soil productivity, quality of plant products and ground water is called soil pollution.
- (ii) The soil pollutants include pesticides, fertilizers, industrial wastes, salts, radio-nuclids, tin, iron, lead, copper, mercury, aluminium, plastics, paper, glass, broken bottles, discarded food etc.

Types of Soil Pollution

Soil pollution is of two main types:

Negative soil pollution

Positive soil pollution

❖ Negative Soil Pollution

- (i) It includes over use of soil and erosion.
- (ii) Soil erosion is caused by water and wind.
- (iii) Water erosion of soil is found near the hills where high speed flooding removes top soil.
- (iv) Soil erosion also occurs by high speed winds which bring sand particles from dry desert.

❖ Positive Soil Pollution: It is caused by addition of undesirable substances (eg. pesticides, fertilizers, industrial waste, air pollutant washed down from atmosphere through rain)

(A) Pesticides:

- (i) These include insecticides (kill insects), fungicides (kill fungi), algicides (kill algal blooms), weedicides or herbicides (kill weeds), rodenticides (kill rodents).
- (ii) Pesticides are generally broad-spectrum and affect other animals, man and even plants. They are hence, also called **biocides**.
- (iii) DDT (dichloro diphenyl trichloroethane), BHC (benzene hexachloride or gamaxine), aldrin, dieldrin, endrin, heptachlor etc. are chlorinated hydrocarbons used as pesticides.
- (iv) Dieldrin is five times more toxic than DDT when ingested and 40 times more poisonous when absorbed.
- (v) Endrin is the most toxic amongst chlorinated hydrocarbons.
- (vi) Chlorinated hydrocarbons are persistent, fat soluble and show **biomagnification**.

- (vii) DDT and other chlorinated hydrocarbons affect CNS, cause softening of brain, cirrhosis of liver (liver cancer), cerebral haemorrhage, cancer, hypertension, thinning of egg shells in birds, malformation of sex hormones, failure of gonad development.
- (viii) The population of certain birds (e.g. Bald eagle) has declined due to these biocides.
- (ix) DDT also affects the photosynthetic activity of plants, especially phytoplankton.
- (x) DDT was banned in 1985 for agricultural purpose in India.
- (xi) In India concentration of DDT in fat tissue of people is 18-31 ppm.
- (xii) The weedicides (or herbicides) are usually metabolic inhibitors which stop photosynthesis and other metabolic activities and hence kill the plants.
- (xiii) 2,4-D, 2,4,5-T, DCMU and CMU are weedicides.

(B) Fertilizers:

- (i) The fertilizers contain plant nutrients particularly N, P and K, but the soil also gets polluted mainly due to organic pollutants present as impurities.
- (ii) Excessive use of fertilizers cause soil deterioration through decrease of natural microflora (nitrogen fixing, nitrifying bacteria)
- (iii) Fertilizers added to soil enter the crop plants. Nitrogen fertilizers produce toxic concentration of nitrate in the leaves and fruits. When these leaves and fruits are eaten, nitrates changed into nitrites by the activity of bacteria in the alimentary canal. The nitrites enter the blood and combine with haemoglobin to form methaemoglobin. As a result oxygen transport is reduced. It gives rise to disease known as **methaemoglobinaemia**. In infants it produces **cyanosis (blue baby syndrome)**

(C) Industrial Wastes:

- (i) Wastes of the industries are dumped over the soil. They contain a number of toxic substances including cyanides, acids, chromates, alkalies and metals like mercury, copper, zinc, lead, cadmium etc.
- (ii) The industrial pollutants increase the toxicity level of the soil.
- (iii) Heavy metals destroy useful micro organisms of the soil.
- (iv) In 1970 some 200 people died in Japan by Cd pollution of soil due to itai-itai disease.

NOISE POLLUTION

- (i) Various kinds of undesirable loud sounds, which disturb our environment are called noise pollutants.
- (ii) Noise pollution is produced by loud sounds of various machines, loudly played radio, automobiles, thundering of jet planes, loud speakers etc.
- (iii) The intensity of noise is measured in decibels (or dB).
- (iv) The sound above 80 dB causes noise pollution.
- (v) Moderate conversation produces 60 dB sound, loud conversation 70dB.

- (vi) Scooter, buses, trucks etc. create noise of about 90 dB, Jet aeroplanes 150 dB, rocket 180 dB.
- (vii) Noise pollution may cause hypertension (high B.P), respiratory and cardiac problems.
- (viii) Noise stimulates the secretion of adrenaline which increases irritability, nervousness, neuromuscular tension and feeling of fatigue, so decreasing the working efficiency.
- (ix) Noise has an adverse effect on mind health and behaviour of man.
- (x) Noise may damage ear drum and eye sight.
- (xi) Noise brings about interference in conversation and hearing.
- (xii) The first effects of noise are anxiety and stress.
- (xiii) Noise can impair the development of nervous system of unborn babies which leads to abnormal behaviour in later life.
- (xiv) Plantation of trees is very essential for reducing the noise pollution.
- (xv) Green plants are being planted along the road sides to check the noise pollution. This is called as **Green muffler**.

RADIOACTIVE POLLUTION

- (i) It is a special type of physical pollution of air, water and soil with radioactive materials.
- (ii) Nuclear explosion results into production of radioactive substances as Sr^{90} , U^{235} , I^{131} and cause pollution of air, water and soil.

♦ Sources of Radioactive Pollution

Natural (Background) Radiations:

- (i) These include cosmic rays that reach the earth surface from outer space and terrestrial radiations from radioactive elements (radium-224, thorium-232, uranium-235, uranium-238, radon-222, carbon-14, potassium-40 etc.) present in the earth's crust. These radioactive elements are present in rocks, soil and water.
- (ii) Maximum background radiation is found in Kerala beach where 75% of thorium deposits of the world are found.
- (iii) Monazite is the source of thorium.

♦ Man-made Radiations:

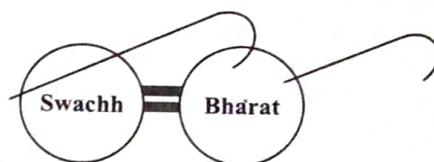
Man made sources of radiations include mining and refining of plutonium, uranium and thorium, production and explosion of nuclear weapons, nuclear power plants, nuclear fuels and preparation of radioactive isotopes.

Strategies to Control Environmental Pollution

After studying air, water, soil and industrial waste pollution in this unit, by now you must have started feeling the need of controlling environmental pollution: How can you save your immediate environment? Think of the steps/activities, which you would like to undertake for controlling air, water, soil and industrial waste pollution in your neighbourhood. Here, an idea about the strategies for the management of waste is given.

Waste Management: Solid waste is not the only waste, which you see in your household garbage box. Besides household discards, there are medical, agricultural, industrial and mining wastes. The improper disposal of wastes is one of the major causes of environmental degradation. Therefore, the management of wastes is of utmost importance.

You must be aware of the 'Swachh Bharat Abhiyan' or 'Clean India Mission' launched by the Government of India.



Ek Kadam Swachhta ki or

Two programmes are being implemented under the broad umbrella of the Swachh Bharat Abhiyan. These are Swachh Bharat Mission-Urban (SBM-U) and Swachh Bharat Mission Gramin (SBM-G). The SBM-U primarily aims at making Urban India free from open defecation and achieving 100% scientific management of solid waste in the country. The SBM-G targets to bring about an improvement in the general quality of life in rural areas by promoting cleanliness and hygiene, and eliminating open defecation. It is accelerating its efforts to achieve the goal of universal sanitation coverage by 2 October, 2019, which is the birth anniversary of Mahatma Gandhi.

Collection and Disposal: Domestic wastes are collected in small bins, which are then transferred to community bins by private or municipal workers. From these community bins, these are collected and carried to the disposable site. At the site, garbage is sorted out and separated into biodegradable and non-biodegradable materials. Non-biodegradable materials such as plastic, glass, metal scraps etc. are sent for recycling. Biodegradable wastes are deposited in land fills and are converted into compost. The waste if not collected in garbage bins, finds its way into the sewers. Some of it is eaten by cattle. Non-biodegradable wastes like polythene bag, metal scraps, etc. choke the sewers and cause inconvenience. Polythene bags, if swallowed by animals can cost their lives also.

As a normal practice, therefore, all domestic wastes should be properly collected and disposed. The poor management causes health problems leading to epidemics due to contamination of ground water. It is specially hazardous for those who are in direct contact with the waste such as rag pickers and workers involved in waste disposal, as they are the ones who handle waste materials mostly without protective device such as gloves or water proof boots and gas masks. What can you do for them?

GREEN CHEMISTRY IN DAY TO DAY LIFE

- (i) **Dry Cleaning of Clothes:** Tetra chloroethene ($\text{Cl}_2\text{C=CCl}_2$) was earlier used as solvent for dry cleaning. The compound contaminates the ground water and is also a suspected carcinogen. The process using this compound is now being replaced by a process, where liquefied carbondioxide, with a suitable detergent is used. Replacement of halogenated solvent by liquid CO_2 will result in less harm to ground water.

These days hydrogen peroxide (H_2O_2) is used for the purpose of bleaching clothes in the process of laundry, which gives better results and makes use of lesser amount of water.

- (ii) **Bleaching of Paper:** Chlorine gas was used earlier for bleaching paper. These days, hydrogen peroxide (H_2O_2) with suitable catalyst, which promotes the bleaching action of hydrogen peroxide, is used.
- (iii) **Synthesis of Chemicals:** Ethanal (CH_3CHO) is now commercially prepared by one step oxidation of ethene in the presence of ionic catalyst in aqueous medium with an yield of 90%.
- (iv) 'Green Solution' to Clean Turbid Water Powder of kernel of tamarind seeds has been found to be an effective material to make municipal and industrial waste water clean. It is non-toxic, biodegradable and cost effective material. This powder is usually discarded as agricultural waste. The present practice is to use alum to treat such water. It has been found that alum increases toxic ions in treated water and can cause diseases. Green chemistry, in a nutshell, is a cost effective approach which involves reduction in material, energy consumption and waste generation.



Train Your Brain

Example 5: Which of the following is not used in nail polish

- (a) Acetone
- (b) Cellulose nitrate
- (c) Red dye
- (d) Benzene

Sol. (d) Benzene (a Carcinogenic) is not used as a solvent in nail polish.

Example 6: Detergents are prepared by the action of H_2SO_4 followed by neutralization by starting with

- | | |
|------------------|---------------------------|
| (a) Cholesterol | (b) Lauryl alcohol |
| (c) Cyclohexanol | (d) <i>p</i> -Nitrophenol |

Sol. (b) Detergents can be obtained by the sulphonation of Lauryl alcohol followed by neutralisation.

Example 7: Sodium alkyl benzene sulphonate is used as

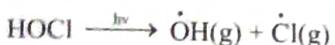
- | | |
|----------------|-----------------|
| (a) Soap | (b) Fertilizers |
| (c) Pesticides | (d) Detergents |

Sol. (d) It is used as detergents.



Concept Application

6. The major source (s) of soil pollution is/are
 - (a) Industrial waste
 - (b) Fertilizers and pesticides.
 - (c) Organic compost.
 - (d) Both (a) and (b)
7. Domestic waste will lead to
 - (a) Biodegradable pollution
 - (b) Nondegradable pollution
 - (c) Thermal pollution of soil
 - (d) Air pollution
8. The example (s) of pesticide is/are
 - (a) aldrin
 - (b) sodium chlorate
 - (c) dieldrin
 - (d) Both (a) and (c)



Water pollution

Cause of Water Pollution

- (i) Pathogen
- (ii) Organic waste
- (iii) Organic waster

BOD: The amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water, is called Biochemical Oxygen Demand (**BOD**). Clean water would have BOD value of less than 5 ppm where as highly polluted water could have a BOD value of 17 ppm or more.

Fluoride: Soluble fluoride is often added to drinking water to bring its concentration upto 1 ppm or 1 mg dm^{-3} .

However, F^- ion concentration above 2 ppm causes brown mottling of teeth. At the same time, excess fluoride (over 10 ppm) causes harmful effect to bones and teeth.

Lead: The prescribed upper limit concentration of lead in drinking water is about 50 ppm. Lead can damage kidney, liver, reproductive system etc.

Sulphate: Excessive sulphate (>500 ppm) in drinking water causes laxative effect, otherwise at moderate levels it is harmless.

Nitrate: The maximum limit of nitrate in drinking water is 50 ppm. Excess nitrate in drinking water can cause disease such as methemoglobinemia ('blue baby' syndrome).

Table: Maximum Prescribed Concentration of Some Metals in Drinking Water

Metal	Maximum concentration (ppm or mg dm^{-3})
Fe	0.2
Mn	0.05
Al	0.2
Cu	3.0
Zn	5.0
Cd	0.005



Solved Examples

1. What would have happened if the greenhouse gases were totally missing in the earth's atmosphere? Discuss.

Sol. The solar energy radiated back from the earth surface is absorbed by the greenhouse gases (i.e. CO_2 , CH_4 , O_3 , CFC's and water vapour) present near the earth's surface. They heat up the atmosphere near the earth's surface and keep it warm. As a result, they keep the temperature of the earth constant and help in the growth of plants and existence of life on the earth. If there were no greenhouse gases, there would have been no vegetation and life on the earth.

2. A large number of fish are suddenly found floating dead on a lake. There is no evidence of toxic dumping but you find an abundance of phytoplankton. Suggest a reason for the fish kill.

Sol. Excessive phytoplankton (organic pollutants such as leaves, grass, trash, etc.) present in water is biodegradable. A large population of bacteria decomposes this organic matter in water. During this process they consume the oxygen dissolved in water. Water has already limited dissolved oxygen ($= 10$ ppm) which is further depleted. When the level of dissolved oxygen falls below 6 ppm, the fish cannot survive. Hence, they die and float dead in water.

3. How can domestic waste be used as manure?

Sol. Domestic waste comprises of two types of materials, biodegradable such as leaves, rotten food, etc., and non-biodegradable such as plastics, glass metal, scrap, etc. The non-biodegradable waste is sent to industry for recycling and the biodegradable waste should be deposited in the land fills. With the passage of time, it is converted into compost manure.

4. For your agricultural field or garden, you have developed a compost producing pit. Discuss the process in the light of bad odour, flies and recycling of wastes for a good produce.

Sol. The compost producing pit should be set up at a suitable place or in a tin to protect ourselves from bad odour and flies. It should be kept covered so that flies cannot make entry into it and the bad odour is minimized. The recyclable material like plastics, glass, newspapers, etc. should be sold to the vendor who further sells it to the dealer. The dealer further supplies it to the industry involved in recycling process.

5. Answer the following subparts

- (i) What is loam soil?
- (ii) What are asbestosis and silicosis?
- (iii) What are particulates and what is their approximate size?

- (iv) Name three natural sources of air pollution
 (v) How are flue gases from industries feed from oxides of nitrogen and sulphur?

- Sol.** (i) Soil containing 34% air, 66% water along with humus is called loam soil. It is best for crops.
 (ii) Asbestosis and silicosis are lung diseases caused by particulates.
 (iii) Particulates are finely divided solid or liquid particles suspended in air. Their size varies from $2 \times 10^{-4} \mu$ to 500μ .
 (iv) Volcanic eruptions, forest fires and pollen grains of flowers.
 (v) The flue gases are subjected to scrubbing with conc. H_2SO_4 or with alkaline solutions such as Ca(OH)_2 or Mg(OH)_2 etc.
6. (i) Name two important sinks of CO_2 .
 (ii) What is marine pollution
 (iii) What is humification?
 (iv) What are viable and non-viable particulates?

- Sol.** (i) Oceans (which dissolve it) and plants (which use it for photosynthesis)
 (ii) Pollution of sea water due to discharge of wastes into it is called marine pollution.
 (iii) The decomposition of organic material (leaves, root etc.) in the soil by microorganism to produce humus is called humification.
 (iv) Viable particulates are small size living organisms such as bacteria, fungi, moulds, algae, etc. Nonviable particulates are formed by disintegration of large size materials or condensation of small size particles or droplets e.g. mist, smoke, fume and dust.

7. (i) What is the composition of photochemical smog and classical smog? How do the two differ in their behaviour?
 (ii) What should be the tolerable limit of fluoride ions in drinking water? What happens if it is higher than 10 ppm?

- Sol.** (i) Photochemical smog is mixture of a number of irritation causing compounds like NO_2 , O_3 aldehydes, peroxyacetyl nitrates, ketones, hydrocarbons and CO. It is formed in summer months after sunrise. Classical smog is a mixture of oxides of sulphur and carbons (soot). It is formed in early hours of winter months. Photochemical

smog is oxidising in nature whereas classical smog is reducing in nature.

- (ii) 1 ppm or 1 mg dm^{-3} . Higher concentration is harmful to bones and teeth.

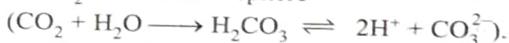
8. What do you understand by greenhouse effect? What are the major gases?

- Sol.** The warming of the earth or global warming due to re-emission of sun's energy absorbed by the earth followed by its absorption by CO_2 molecules and H_2O vapour present near the earth's surface and then its radiation back to the earth is called greenhouse effect.

Though CO_2 is the main gas in the greenhouse effect, there are some other greenhouse gases like methane, chlorofluorocarbons, ozone, nitrous oxide and water vapours.

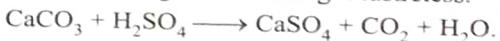
9. (i) Why does rain water normally have a pH of about 5.6? When does it become acid rain?
 (ii) Why is acid rain considered as a threat to Taj mahal?
 (iii) Explain by giving reason "The presence of CO reduces the amount of haemoglobin available in the blood for carrying oxygen to the body cells."
 (iv) State briefly the reactions causing ozone layer depletion in the stratosphere.

- Sol.** (i) Normally rain has a pH of about 5.6 due to dissolution of CO_2 into the atmosphere



When the pH of rain falls below 5.6, it becomes acid rain.

- (ii) Taj mahal is made of marble. The acid rain contains H_2SO_4 which attacks the marble (CaCO_3) thereby pitting it, discolouring it and making it lustreless.



- (iii) CO combines with haemoglobin of the red blood cells (RBCs) about 300 times more easily than oxygen to form carboxyhaemoglobin reversibly as follows.



Thus it is not able to combine with oxygen to form oxyhaemoglobin and transport of oxygen to different body cells cannot take place.

- (iv) The decomposition products of CFCs destroy ozone as shown in the following reaction:



Exercise-1 (Topicwise)

1. Domestic waste contains
 - Hydrocarbons
 - Non-biodegradable pollutants
 - Biodegradable pollutants
 - None of the above
2. The substance which produces resistance against carcinogen is
 - Tocoferol
 - Afflatoxin
 - Streptomycin
 - Penicillic acid
3. Drawback of DDT as pesticide is
 - It is less effective than others
 - It is not easily/rapidly degraded in nature
 - Its high cost
 - It becomes ineffective after some time
4. World environment day is celebrated on
 - 4th May
 - 15th April
 - 5th June
 - 15th March
5. Air pollutants that produce photochemical smog
 - Ozone, chlorine and sulphur dioxide
 - Oxygen, chlorine and nitric acid
 - Nitrous oxide, PAN and acrolein
 - CO₂, CO and SO₂
6. Freon is
 - Metal fluoride
 - Iron containing polycyclic
 - Chlorofluorocarbon
 - Ferrous sulphide pollutant
7. Burning of fossil fuels is the main source of pollution
 - Nitric oxide
 - Sulphur dioxide
 - Nitrogen oxide
 - Nitrous oxide
8. Which of the following is not a general pollutant of atmosphere
 - Hydrocarbons
 - SO₃
 - CO₂
 - SO₂
9. PAN (Peroxy Acetyl Nitrate) is an important constituent of photochemical smog, is a
 - Quantitative pollutant
 - Primary pollutant
 - Natural pollutant
 - Secondary pollutant
10. Which is the not a green house gas
 - CFC's
 - Methane
 - H₂
 - CO₂
11. Taj Mahal is threatened by pollution from
 - Carbon dioxide
 - Oxygen
 - Sulphur dioxide
 - Chlorine
12. Acid rain occurs in areas where
 - There are big industries and the atmosphere is polluted with SO₂
 - There are large plantation of pine plants
 - Citrus plants are grown
 - There are large plantation of eucalyptus
13. Protection from ultraviolet rays coming from sun is provided by
 - SO₂
 - CO₂
 - Ozone
 - Oxygen
14. Trapping of reflected heat radiation by atmospheric dust, water vapour, ozone, CO₂ etc. is known as
 - Radioactive effect
 - Ozone layer effect
 - Solar effect
 - Green house effect
15. UV radiations cause
 - Liver cancer
 - Skin cancer
 - Mouth cancer
 - Blood cancer
16. Green house effect is related to
 - Cultivation of green plants
 - Cultivation of vegetables in houses
 - Global warming
 - Global green algae
17. Ozone layer of upper atmosphere is being destroyed by
 - Photochemical oxidants/O₂ and CO₂
 - Chlorofluorocarbon
 - Smog
 - SO₂
18. Ultraviolet radiations from sunlight causes a reaction that produces
 - Ozone
 - Fluorides
 - Carbon monoxide
 - Sulphur dioxide
19. Which of the following does not cause air pollution
 - Pollen grains
 - Hydroelectric power
 - Diesel engine
 - Thermoelectric power
20. Carbon monoxide (CO) is harmful to man because
 - It competes with O₂ for haemoglobin
 - It forms carbolic acid
 - It generates excess CO₂
 - It is carcinogenic

- 21.** When PO_4 and NO_3 is more in the water of a lake it causes
 (a) Growth of bacteria (b) Growth of fishes
 (c) Death of algae (d) Algal bloom
- 22.** The 'blue baby syndrome' is caused due to pollution by
 (a) Nitrates (b) Chlorides
 (c) Cyanides (d) Fluorides
- 23.** Minimata disease was caused due to water pollution by
 (a) Cyanides (b) Mercury
 (c) Lead (d) Methyl isocyanate
- 24.** Which disease in children is caused by the intensive use of nitrate fertilizers
 (a) Jaundice (b) Septicaemia
 (c) Mumps (d) Methaemoglobinemia
- 25.** BOD is
 (a) Biochemical oxygen demand
 (b) Biological oxygen deficit
 (c) Biosphere oxygen demand
 (d) None of the above
- 26.** Indiscriminate use of DDT is undesirable because
 (a) It is harmful
 (b) It is degradable
 (c) It causes mutation
 (d) It is accumulated in food chain
- 27.** A persistent insecticide is
 (a) Chlorinated hydrocarbons
 (b) Organophosphates
 (c) Carbamates
 (d) Thiocarbamates
- 28.** Noise pollution is measured in
 (a) Nanometres (b) Decibels
 (c) Fathoms (d) Hertz
- 29.** Biodegradable pollutant is
 (a) Sewage (b) Mercury
 (c) Plastic (d) Asbestos
- 30.** Which of the following is present in highest concentration in exhaust emission
 (a) CO_2 (b) Hydrocarbons
 (c) CO (d) Oxides of nitrogen
- 31.** By what method the quantity of organic pollutants in water can be determined
 (a) By measuring BOD
 (b) By pH Measurement
 (c) By transparency measurements
 (d) By measuring the change of colour/CFC
- 32.** A dental disease characterised by mottling of teeth is due to presence of a certain chemical element in drinking water. Which is the element
 (a) Fluorine (b) Mercury
 (c) Boron (d) Chlorine
- 33.** Chlorine treatment of water
 (a) Disinfect by killing germs
 (b) Remove hardness of water
 (c) Remove all the air pollutants
 (d) All of the above
- 34.** Pollution is rising due to
 (a) Automobiles and industries
 (b) Population explosion
 (c) Rains
 (d) Research institute
- 35.** Sudden mass death of fishes from oxygen depletion is more likely in case of
 (a) Oligotrophic lake
 (b) Oxalotrophic lake
 (c) Eutrophic lake
 (d) Mesotrophic lake
- 36.** Continuous sewage flow into a stream would lead to
 (a) Increase in temperature
 (b) Algal bloom
 (c) Eutrophication
 (d) Depletion of oxygen
- 37.** Which of the following types of pollution causes the outbreak of jaundice
 (a) Water (b) Land
 (c) Thermal (d) Air
- 38.** The pollutants chlorofluorocarbons are major source of air pollution contributed by
 (a) Sewage pollutants (b) Aerosols
 (c) Industrial effluents (d) All of the above
- 39.** Acid rains are produced by
 (a) Excess production of NH_3 by industry and coal gas
 (b) Excess release of carbon monoxide by incomplete combustion
 (c) Excess formation of CO_2 by combustion and animal respiration
 (d) Excess NO_2 and SO_2 from burning of fossil fuels
- 40.** The basic component of the smog may be
 (a) O_3 and PAN (b) O_3
 (c) PAN (d) PVC
- 41.** Water pollution causes
 (a) Increased deoxygenation and turbidity
 (b) Decreased turbidity
 (c) Increased oxygenation
 (d) Increased photosynthesis
- 42.** Most harmful types of environment pollutants are
 (a) Human organic wastes
 (b) Non biodegradable chemicals
 (c) Natural nutrients present in excess
 (d) Wastes from feed lots

Exercise-2 (Learning Plus)

1. If there was no CO₂ in the earth's atmosphere, the temperature of earth's surface would be
(a) Less than the present
(b) The same
(c) Dependent on the amount of oxygen in the atmosphere
(d) Higher than the present

2. Gas responsible for Bhopal tragedy of 1984 was
(a) Carbon monoxide (b) Methyl Isocyanate
(c) SO₂ & NO₂ (d) Ethyl isocyanate

3. Green house effect refers to
(a) Warming of earth (b) Production of cereals
(c) Trapping of UV rays (d) Cooling of earth

4. Aerosol of a jet air liner which destroys the Ozone-layer of atmosphere is
(a) CF₂Cl₂ (b) CO₂ and SO₂
(c) SO₂ (d) NH₃ and CCl₄

5. The minamata disease in Japan was caused through the pollution of water by
(a) Methyl isocyanate (b) Lead
(c) Mercury (d) Cyanide

6. Which of the following is water pollution related disorder
(a) Leprosis (b) Fluorosis
(c) Pneumonicosis (d) Silicosis

7. Which of the following organism is likely to have more concentration of DDT in its body
(a) Carnivores (b) Top carnivores
(c) Primary producers (d) Herbivores

8. The maximum biomagnification would be in which of the following in case of aquatic ecosystem
(a) Phytoplankton (b) zooplankton
(c) Birds (d) Fishes

9. Lichens are best indicators of
(a) Water pollution
(b) Soil pollution
(c) Air pollution/SO₂ Pollution
(d) All types of pollution

10. Eutrophication is caused by
(a) Increase nutrient concentration
(b) Petrochemical and fertilizer plant effluents
(c) NO₃⁻ and SO₄⁻² present in acid rains
(d) Mine effluents

11. Increase asthmatic attacks in certain seasons are related to
(a) Inhalation of seasonal pollen
(b) Eating of seasonal vegetables
(c) Low temperature
(d) Wet and dry environment

- 12.** SO₂ pollution is indicated by
 (a) *Sphagnum* (mosses)
 (b) *Cucurbita* (climbers)
 (c) *Deschampsia* (grasses)
 (d) *Usnea* (lichens)
- 13.** Highest DDT deposition shall occur in
 (a) Crab (b) Eel
 (c) Sea Gull (d) Phytoplankton
- 14.** Often in water bodies subjected to sewage pollution, fishes die because of the
 (a) Foul smell
 (b) Reduction in dissolved oxygen caused by microbial activity
 (c) Clogging of their gills by solid substances
 (d) Pathogens released by the sewage
- 15.** When huge amount of sewage is dumped into a river the BOD will
 (a) Remain unchanged (b) Slightly decrease
 (c) Increase (d) Decrease
- 16.**water pollutant causes brittleness of teeth
 (a) Hg (b) Fluorine
 (c) Cd (d) All of the above
- 17.** Measurement of the rate of O₂ consumption in unit volume of water over a period of time is done to find out
 (a) Biosynthetic oxygen demand
 (b) Biogas generation
 (c) Biochemical oxygen demand
 (d) Fermentation
- 18.** Sewage drained into water bodies kill fishes because
 (a) It increases competition with fishes to dissolved oxygen
 (b) It removes the competition with fishes to dissolve CO₂
 (c) Excessive CO₂ is added in water
 (d) It gives off a bad smell
- 19.** Eutrophication causes reduction in:
 (a) dissolved hydrogen (b) dissolved oxygen
 (c) dissolved salts (d) All the above
- 20.** Pick up the correct statement
 (a) CO which is major pollutant resulting from the combustion of fuels in automobiles plays a major role in photochemical smog
 (b) Classical smog has an oxidizing character while the photochemical smog is reducing in character
 (c) Photochemical smog occurs in day time whereas the classical smog occurs in early morning hours
 (d) During formation of smog the level of ozone in the atmosphere goes down
- 21.** In Antarctica ozone depletion is due to the formation of following compound:
 (a) Acrolein (b) Peroxy acetyl nitrate
 (c) Chlorine nitrate (d) SO₂ and SO₃
- 22.** Main cause of Ozone decay is
 (a) CFC (b) BFC
 (c) LMC (d) DKP
- 23.** Which of the following statement is true about ozone layer
 (a) It is harmful because ozone is dangerous to living organism
 (b) It is beneficial because oxidation reaction can proceed faster in the presence of ozone
 (c) It is beneficial because ozone cuts out the ultraviolet radiation of the sun
 (d) It is harmful because ozone cuts out the important radiation of the sun which are vital for photosynthesis
- 24.** Ozone depict due to the formation of following compound in Antarctica
 (a) Acrolein (b) Peroxy acetyl nitrate
 (c) SO₂ and SO₃ (d) Chlorine nitrate
- 25.** Which of the following statement is correct?
 (a) Lower stratosphere consists of considerable amount of ozone.
 (b) Ozone layer protects humans living on earth from the harmful effect of ultraviolet radiations coming from sun.
 (c) Ozone is thermodynamically stable.
 (d) Smoke clouds play significant role in creating ozone over antarctica.
- 26.** Which of the following compound belong to the class of freons?
 (a) CCl₄ (b) COCl₂
 (c) C₂O₂ (d) CF₂Cl₂
- 27.** The extensive use of CFC'S as refrigerant fluids and in aerosol is because of:
 (a) Its high chemical stability
 (b) Good absorber of UV radiation
 (c) Its polar nature
 (d) High toxicity
- 28.** In stratosphere, which of the following radical retards the formation of O₃?
 (a) $\dot{\text{C}}\text{H}_3$ (b) $\dot{\text{C}}\text{l}$
 (c) $\dot{\text{F}}$ (d) $\dot{\text{C}}\text{l}_2$
- 29.** Which of the following helps in creating ozone over antarctica?
 (a) Radioactive clouds
 (b) Polar stratospheric clouds
 (c) Spring clouds
 (d) Smoke clouds
- 30.** Eutrophication is a source of water pollution. It occurs when water :
 (a) Is low in nutrients
 (b) Is high in nutrients
 (c) Has high temperature
 (d) Has excess amount of organic matter

- 31.** Which of the following statements is false?
- Absorption of the terrestrially radiated heat by the carbondioxide is the main cause of global warming.
 - The global warming will increases the rate of melting of polar ice caps increasing the sea level.
 - The global warming of the earth surface is mainly due to reforestation.
 - CO_2 , NO , CH_4 , O_3 , CCl_4 and water vapour are green house gases.
- 32.** Which of the following is the primary precursor of photochemical smog?
- Hydrocarbon
 - Ozone
 - PAN
 - Water vapour
- 33.** Photochemical smog can be reduced by:
- Using catalytic converter in the automobiles
 - Plantation of certain plants like pinus, juniperus, vitis etc.
 - Both (a) and (b)
 - None of the above
- 34.** In stratosphere CFCs gets broken down by the action of powerful UV radiation releasing :
- $\bullet \text{CH}_3$
 - $\bullet \text{ClO}$
 - $\bullet \text{Cl}$
 - $\bullet \text{CFCl}_2$
- 35.** Which of the following is false.
- Photochemical smog has high concentration of reducing agents and is, therefore, called as reducing smog.
 - Non-viable particulates consist of smoke, dust, mist, fumes etc.
 - Classical smog occurs in cool humid climate and it is mixture of smoke, fog and sulphurdioxide.
 - Ozone reacts with unburnt hydrocarbons in polluted air to produce peroxyacetyl nitrate (PAN).
- 36.** Which of the following is incorrect about the size of particulates?
- Soot particles have diameter of about 5 nm.
 - H_2SO_4 fog particles have size of 500–1000 nm.
 - Fly ash particles have diameter of 5×10^5 nm.
 - All particulates have same size.



Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

- Photochemical smog causes:
 - Headache
 - Cracking of rubber
 - Corrosion of painted surface
 - Extensive damage to plant life
- Choose the wrong statements:
 - CO_2 is responsible for greenhouse effect.
 - CO_2 can absorb infrared radiation but does not allow them to pass through.
 - NO is more harmful than NO_2 .
 - Acid rain contains mainly HNO_3 .
- Which of the following is/are correct about the size of particulates?
 - Soot particles have diameter of about 5 nm.
 - H_2SO_4 fog particles have size of 500–1000 nm.
 - Fly ash particles have diameter of 5×10^5 nm.
 - All particulates have same size.
- Which of the following is/are weedicides?
 - Sodium chlorate
 - DDT
 - Sodium arsenate
 - BHC
- The depletion of ozone layer is caused by:
 - NO
 - SO_2
 - C_xH_y
 - CFCs

- Which of the following is/are proper method(s) to dispose sludge?
 - Incineration
 - Dumping
 - Anaerobic digestion by microbes
 - Filtration
- Which of the following metal(s) is/are toxic and pollutants?
 - Cadmium
 - Lead
 - Mercury
 - Zinc
- Which of the following is/are greenhouse gases?
 - Ozone
 - Methane
 - carbon dioxide
 - Water vapours

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 9 to 11): Ozone is an unstable, dark blue diamagnetic gas. It absorbs strongly the UV radiation, thus protecting the people on the earth from the harmful UV radiation from the sun. The use of chlorofluorocarbon (CFC) in aerosols and refrigerators, and their subsequent escape into the atmosphere, is blamed for making holes in the ozone layer over the Antarctic, and Arctic.

Ozone acts as a strong oxidising agent in acidic and alkaline medium. For this property ozone is used as a germicide and disinfectant for sterilising water and improving the atmosphere of crowded places.

9. CFCs damage ozone layer by reactions:

- $O_3 + h\nu \rightarrow O + O_2$
- $Cl + O_3 \rightarrow ClO + O_2$
- $ClO + O \rightarrow Cl + O_2$
- All of the above

10. Identify the incorrect statement with respect to ozone?

- Ozone is formed in the upper atmosphere by a photochemical reaction involving dixygen.
- Ozone protects the earth's inhabitants by absorbing UV radiations.
- Ozone can also be made by heating O_2 over 250°C and quenching.
- Chlorine gas is preferred over ozone for the purification of drinking water and for water treatment in swimming pools.

11. Which of the following statement is correct?

- The dark blue colour of ozone is due to intense absorption of green light.
- Oxides of nitrogen and the halogen cannot damage the O_3 layer.
- Ozone oxidises dry sodium to Na_2O_3 .
- Ozone forms orange coloured compound KO_3 with potassium hydroxide.

Comprehension (Q. 12 to 14): Pesticides are synthetic toxic chemicals which are used in agriculture to control the damages caused by insects, rodents, weeds and various crop diseases. Their repeated use give rise to pests that are resistant to that group of pesticides. As a result these pesticides become ineffective for those pests. Examples are DDT, aldrin, dieldrin etc.

Herbicides are the chemicals used to control weeds, earlier inorganic compounds such as sodium chlorate and sodium arsenite were used but arsenic compounds being toxic to mammals, are no longer preferred instead organic compounds such as triazines, are now considered as better herbicides, especially for the corn-fields.

12. Which of the following is a biodegradable pesticide?

- DDT
- Aldrin
- Dieldrin
- None of these

13. Which of the following compounds belongs to herbicides?

- Sodium arsenite
- Sodium chlorate
- Triazines
- All of these

14. Which of the following statements is false?

- The fly ash and slag of steel industry is being used by the cement industries.
- Industrial wastes, agricultural pollutants and radioactive pollutants are the sources of soil pollutants.
- The recycling of material such as paper, glass and some kinds of plastics would help in the conservation of natural sources.
- Barium malathion and chlorinated hydrocarbons are herbicides.

MATCH THE COLUMN TYPE QUESTIONS

15. Match the entries of column-I with appropriate entries of column-II. Each entry in column-I may have one or more than one correct option(s) from column-II.

Column-I	Column-II
A. Acid rain	p. Oxides of nitrogen
B. Green house effect	q. Oxides of sulphur
C. Ozone hole	r. Carbon dioxide
D. Eutrophication	s. Phosphate fertilizer i.e. plant nutrient (excess).
	t. Chlorofluorocarbons (CFCs)

- $A \rightarrow p, q; B \rightarrow r; C \rightarrow p, t; D \rightarrow s$
- $A \rightarrow q, r; B \rightarrow q, s; C \rightarrow p; D \rightarrow t$
- $A \rightarrow q, r; B \rightarrow p, t; C \rightarrow q; D \rightarrow s$
- $A \rightarrow q, r; B \rightarrow s, t; C \rightarrow p; D \rightarrow p$

16. Match the entries of column-I with appropriate entries of column-II. Each entry in column-I may have one or more than one correct option(s) from column-II.

Column-I	Column-II
A. Classical smog	p. SO_2
B. Photochemical smog	q. NO_x
C. Particulate Pollutants	r. Bacteria
D. Gaseous pollutants	s. Smoke
	t. Fe_2O_3

- $A \rightarrow s; B \rightarrow q; C \rightarrow p, q, t; D \rightarrow s, t$
- $A \rightarrow t; B \rightarrow r; C \rightarrow p, q, t; D \rightarrow s, q$
- $A \rightarrow p; B \rightarrow q; C \rightarrow r, q, t; D \rightarrow p, q$
- $A \rightarrow q; B \rightarrow p; C \rightarrow p, s, t; D \rightarrow p, q$

17. Match the column-I and column-II pick the correct matching from the codes given below.

Column-I	Column-II
A. Polyy aromatic	p. Monovalent chlorine nitrate
B. Polyacrylic	q. Chloral - swelling agent Hydrochloric acid
C. Irg compounds	r. Photochemical smog
D. IRH action	s. Amine-gum Medicament

- $A \rightarrow p; B \rightarrow q; C \rightarrow r; D \rightarrow s$
- $A \rightarrow r; B \rightarrow s; C \rightarrow p; D \rightarrow q$
- $A \rightarrow q; B \rightarrow r; C \rightarrow s; D \rightarrow p$
- $A \rightarrow r; B \rightarrow q; C \rightarrow p; D \rightarrow q$

Exercise-4 (Past Year Questions)

JEE MAIN

16. Which of the following conditions in drinking water causes methemoglobinemia? (2019)
- (a) > 50 ppm of lead (b) > 50 ppm of chloride
 - (c) > 50 ppm of nitrate (d) > 100 ppm of sulphate
17. A water sample has ppm level concentration of the following metals: (2019)
- $\text{Fe} = 0.2, \text{Mn} = 5.0, \text{Cu} = 3.0, \text{Zn} = 5.0$. The metal that makes the sample unsuitable for drinking is
- (a) Cu (b) Mn
 - (c) Fe (d) Zn
18. The concentration of dissolved oxygen (DO) is cold water can go upto: (2019)
- (a) 14 ppm (b) 8 ppm
 - (c) 10 ppm (d) 16 ppm
19. Water filled in two glasses A and B have BOD values of 10 and 20 respectively. The correct statement regarding them is (2019)
- (a) B is more polluted than A
 - (b) A is suitable for drinking, whereas B is not
 - (c) Both A and B are suitable for drinking
 - (d) A is more polluted than B
20. Among the gases (a) – (e), the gases that cause greenhouse effect are: (2020)
- (A) CO_2 (B) H_2O
 - (C) CFC's (D) O_2
 - (E) O_3
 - (a) (A), (C), (D) and (E) (b) (A), (B), (C) and (E)
 - (c) (A), (B), (C) and (D) (d) (A) and (D)
21. Biochemical Oxygen Demand (BOD) is the amount of oxygen required (in ppm): (2020)
- (a) For the photochemical breakdown of waste present in 1m^3 volume of a water body.
 - (b) For sustaining life in a water body.
 - (c) By bacteria to break-down organic waste in a certain volume of a water sample
 - (d) By anaerobic bacteria to breakdown inorganic waste present in a water body
22. If you spill a chemical toilet cleaning liquid on your hand, your first aid would be (2020)
- (a) Aqueous NaOH (b) Aqueous NaHCO_3
 - (c) Aqueous NH_3 (d) Vinegar
23. The statement that is not true about ozone is (2020)
- (a) In the stratosphere, CFCs release chlorine free radicals (Cl) which reacts with O_3 to give chlorine dioxide radicals
 - (b) It is a toxic gas and its reaction with NO gives NO_2
 - (c) In the atmosphere, it is depleted by CFCs
 - (d) In the stratosphere, it forms a protective shield against UV radiation
24. The incorrect statement(s) among (a) – (d) regarding acid rain is (are) (2020)
- (A) It can corrode water pipes.
 - (B) It can damage structures made up of stone.
 - (C) It cannot cause respiratory ailments in animals.
 - (D) It is not harmful for trees.
 - (a) (A), (C) and (D) (b) (A), (B) and (D)
 - (c) (C) and (D) (d) (C) only
25. Thermal power plants can lead to (2020)
- (a) Eutrophication (b) Ozone layer depletion
 - (c) Blue baby syndrome (d) Acid rain
26. Glycerol is separated in soap industries by (2020)
- (a) Fractional distillation
 - (b) Differential extraction
 - (c) Distillation under reduced pressure
 - (d) Steam distillation
27. The mechanism of action of "Terfenadine" (Seldane) is: (2020)
- (a) Activates the histamine receptor
 - (b) Helps in the secretion of histamine
 - (c) Inhibits the secretion of histamine
 - (d) Inhibits the action of histamine receptor
28. The processes of calcination and roasting in metallurgical industries, respectively, can lead to (2020)
- (a) Global warming and photochemical smog
 - (b) Photochemical smog and ozone layer depletion
 - (c) Photochemical smog and global warming
 - (d) Global warming and acid rain
29. The condition that indicates a polluted environment is (2020)
- (a) 0.03% of CO_2 in the atmosphere
 - (b) pH of rain water to be 5.6
 - (c) Eutrophication
 - (d) BOD value of 5 ppm
30. The presence of soluble fluoride ion upto 1 ppm concentration in drinking water, is (2020)
- (a) Safe for teeth (b) Harmful to skin
 - (c) Harmful for teeth (d) Harmful to bones
31. Water sample is called cleanest on the basis of which one of the BOD values given below (2021)
- (a) 11 ppm (b) 15 ppm
 - (c) 3 ppm (d) 21 ppm
32. BOD values (in ppm) for clean water (A) and polluted water (B) are expected respectively: (2021)
- (a) $A > 50, B < 27$ (b) $A > 25, B < 17$
 - (c) $A < 5, B > 17$ (d) $A > 15, B > 47$

37. Given below are two statements: One is labelled as Assertion (A) and the other is labelled as Reason (R)
Assertion (A): Polluted water may have a value of BOD of the order of 17 ppm.
Reason (R): BOD is a measure of oxygen required to oxidise both the biodegradable and non-biodegradable organic material in water.

In the light of the above statements, choose the most appropriate answer from the options given below. (2022)

(a) Both (A) and (R) are correct and (R) is the correct explanation of (A)
(b) Both (A) and (R) are correct but (R) is not the correct explanation of (A)
(c) (A) is correct but (R) is not correct
(d) (A) is not correct but (R) is correct

38. Which amongst the following is not a pesticide? (2022)

(a) DDT (b) Organophosphates
(c) Dieldrin (d) Sodium arsenite

39. The mixture of chloroxylenol the terpineol is an example of (2022)

(a) Antiseptic (b) Pesticide
(c) Disinfectant (d) Narcotic analgesic

ANSWER KEY

CONCEPT APPLICATION

1. (d) 2. (d) 3. (d) 4. (a) 5. (a) 6. (d) 7. (a) 8. (d)

EXERCISE-1 (TOPICWISE)

1. (c)	2. (a)	3. (b)	4. (c)	5. (c)	6. (c)	7. (b)	8. (c)	9. (d)	10. (c)
11. (c)	12. (a)	13. (c)	14. (d)	15. (b)	16. (c)	17. (b)	18. (a)	19. (b)	20. (a)
21. (d)	22. (a)	23. (b)	24. (d)	25. (a)	26. (d)	27. (a)	28. (b)	29. (a)	30. (c)
31. (a)	32. (a)	33. (a)	34. (a)	35. (a)	36. (d)	37. (a)	38. (b)	39. (d)	40. (a)
41. (a)	42. (b)	43. (d)	44. (c)	45. (c)	46. (c)	47. (a)	48. (d)	49. (c)	50. (a)

EXERCISE-2 (LEARNING PLUS)

1. (a)	2. (b)	3. (a)	4. (a)	5. (c)	6. (b)	7. (b)	8. (c)	9. (c)	10. (a)
11. (a)	12. (d)	13. (c)	14. (b)	15. (c)	16. (b)	17. (c)	18. (a)	19. (b)	20. (c)
21. (c)	22. (a)	23. (c)	24. (d)	25. (b)	26. (d)	27. (a)	28. (b)	29. (b)	30. (b)
31. (c)	32. (a)	33. (c)	34. (c)	35. (a)	36. (d)				

EXERCISE-3 (JEE ADVANCED LEVEL)

1. (a,c,d)	2. (c,d)	3. (a,b,c)	4. (a,c)	5. (a,d)	6. (a,b,c)	7. (a,b,c)	8. (a,b,c,d)	9. (d)	10. (d)
11. (d)	12. (d)	13. (d)	14. (d)	15. (a)	16. (c)	17. (d)			

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

1. (c)	2. (b)	3. (c)	4. (a)	5. (c)	6. (a)	7. (d)	8. (b)	9. (a)	10. (c)
11. (d)	12. (d)	13. (c)	14. (c)	15. (a)	16. (c)	17. (b)	18. (c)	19. (a)	20. (b)
21. (c)	22. (b)	23. (a)	24. (c)	25. (d)	26. (c)	27. (d)	28. (d)	29. (c)	30. (a)
31. (c)	32. (c)	33. (c)	34. (d)	35. (d)	36. (a)	37. (c)	38. (d)	39. (a)	

CHAPTER

17

Purification, Quantitative and Qualitative Analysis of Organic Compounds

METHODS OF PURIFICATION AND SEPARATION OF ORGANIC COMPOUNDS

Organic compounds obtained either from natural sources or synthesized in lab are contaminated with impurities.

Various methods are used for removal of impurities from an organic compound, depends on the nature of compound and type of impurities present in it. The following methods are commonly used for purification.

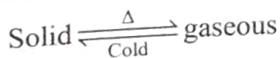
1. Filtration
2. Sublimation
3. Crystallization
4. Distillation
5. Solvent extraction (differential extraction)
6. Chromatography
7. Chemical methods

Filtration

- Only one of the compounds is soluble in the given solvent e.g.
 - (i) Urea and Naphthalene
 - (ii) Benzoic acid and anthracene

Sublimation

- In sublimation, a solid is converted directly into gaseous state on heating and vice versa in case of cooling.



For example, camphor, naphthalene, benzoic acid, iodine, ammonium chloride, anthracene, anthroquinone and phthalic anhydride are purified by sublimation.

- It is suitable for the solids which have non-volatile impurities and undergo sublimation on heating.

Crystallization

- Crystallization is based on the fact that during the crystal formation, impurities are left out as they are insoluble or feebly soluble in the used solvent. For crystallization, a suitable solvent like H_2O , $\text{R}-\text{OH}$, $\text{R}-\text{O}-\text{R}$, CCl_4 , C_6H_6 , acetone or petroleum are used. For example,

- (a) A mixture of benzoic acid and naphthalene is separated by hot water in which only benzoic acid dissolves.
- (b) The impurities of common salt in sugar can be removed by hot ethanol as only sugar dissolves in it.

Fractional Crystallization

- Fractional crystallization involves repeated crystallization.
- It is used when the substances differ slightly in the solubilities. For example, in a mixture of KClO_3 and KCl , KCl is more soluble than KClO_3 in cold water.

Distillation

The vapourisation of a liquid by heating and subsequent condensation of vapours by cooling is known as distillation.

Distillation is an important method used to separate

- (a) Volatile liquids from non-volatile impurities.
- (b) Liquids having sufficient difference in boiling points.

Distillation can be further divided into

(i) Simple Distillation

The substances which do not decompose on heating at their boiling point and have non-volatile impurities are purified by this method. It is used when liquids differ in their boiling point by 30 – 50 K. For example

- (i) Chloroform (B.P. 334 K) & Aniline (B.P. 457 K)
- (ii) Ether (B.P. 308 K) & Toluene (B.P. 384 K)
- (iii) Benzene (B.P. 353 K) & Aniline (B.P. 475 K)

(ii) Fractional Distillation

- Fractional distillation is used when the substances have nearly same boiling points (5°C to 10°C difference only). It involves repeated distillations and condensations.

This process is carried out by using fractionating columns. Fractionating column is a special type of long glass tube provided with obstructions to the passage of the vapour upwards and that of liquid downwards.

- The more volatile liquid (with a lower boiling point) distils off before the less volatile liquid (with higher boiling point).

This method may be used to separate a mixture of acetone (b.p. 330 K) and methyl alcohol (b.p. 338 K) or a mixture of benzene and toluene. One of the technological applications of fractional distillation is to separate different fractions of crude oil in petroleum industry into various useful fractions such as gasoline, kerosene oil, diesel oil and lubricating oil etc.

(iii) Distillation Under Reduced Pressure (Vacuum Distillation)

- This method is used to purify liquids having very high boiling points, which decompose at or below their boiling points.

It is based on the assumption that a liquid boils at a temperature when its V.P. becomes equal to that of the atmospheric pressure. It means if pressure is reduced distillation can occur below the Boiling Point of the substance.

- Here the pressure is reduced during distillation to avoid decomposition, so it is also called distillation at reduced pressure.
- Glycerine is purified by vacuum distillation.
- H_2O_2 , formaldehyde are purified by vacuum distillation.
- Glycerol can be separated from spent-lye in soap industry by using vacuum distillation.
- Sugarcane juice is concentrated in sugar industry by evaporation under reduced pressure which saves lot of fuel.

(iv) Steam Distillation

- This method is used for separation and purification of organic compounds (solids or liquids) which
 - are steam volatile
 - are insoluble in water
 - Possess high vapour pressure (10 – 15 mm of Hg at 373 K)
 - Contains non volatile impurities.
- Compounds which can be purified by steam distillation are aniline, nitrobenzene, bromobenzene, o-nitrophenol, o-hydroxy benzaldehyde (salicylaldehyde), o-hydroxy acetophenone, turpentine oil and essential oils.

Solvent Extraction (Differential Extraction)

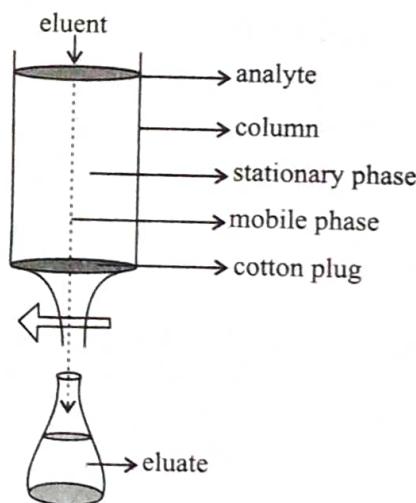
- The process of isolating an organic compound from its aqueous solution by shaking with a suitable solvent is called differential extraction. It is also called solvent extraction.
- When an organic compound is present in an aqueous medium, then it is separated by shaking it with an organic solvent in which it is more soluble than in water.
- Solvent should be immiscible with water and organic compound to be separated should be highly soluble in it.
- Organic solvent and aqueous solution are immiscible with each other, so they can form two distinct layers which can be separated by separatory funnel.
- Organic solvent is distilled or evaporated to get organic compound.

- Organic compound is less soluble in organic solvent so large quantity of solvent is required to extract small quantity of compound, which is said to be continuous extraction.
- Benzoic acid can be extracted from its aqueous solution using benzene as solvent.
- Ether is a better solvent in differential extraction due to:
 - Its less polarity
 - Least reactivity
 - Higher solubility of organic compounds

Chromatography

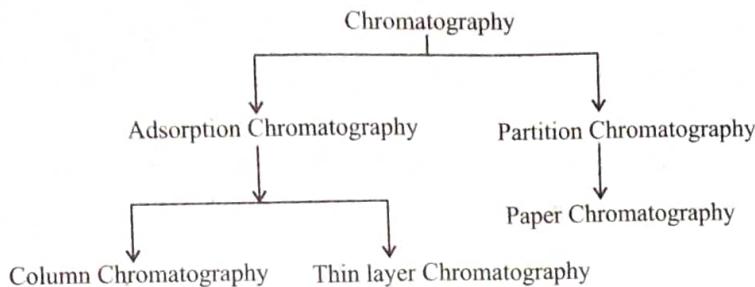
- Chromatography was introduced by Tswett in 1906.
- Here the separation and purification is carried out based on the difference in movement of components of a mixture through a stationary phase under the influence of a mobile phase.
- It is used for the separation of any substance which is present in a very small amount or which cannot be purified by other methods like distillation or crystallization.

some commonly used terms



Term	Definition
Mobile phase or carrier	solvent moving through the column
Stationary phase or adsorbent	substance that stays fixed inside the column
Eluant	fluid entering the column
Eluate	fluid exiting the column (that is collected in flask)
Elution	the process of washing out a compound through a column using a suitable solvent
Analyte	mixture whose individual components have to be separated and analyzed

Classification of Chromatography

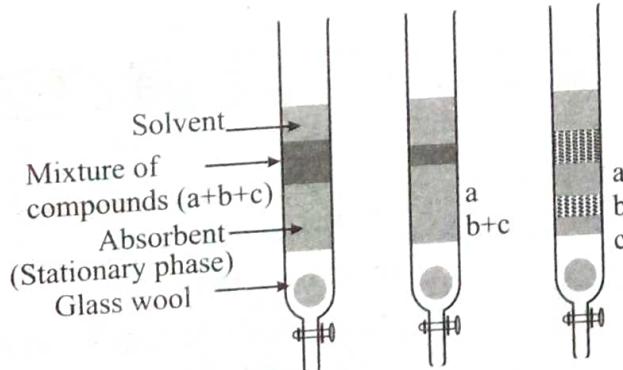


Adsorption Chromatography: Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina. When a mobile phase is allowed to move over a stationary phase (adsorbent), the components of the mixture move by varying distances over the stationary phase. Following are two main types of chromatographic techniques based on the principle of differential adsorption.

- (a) Column chromatography
- (b) Thin layer chromatography.

Column Chromatography

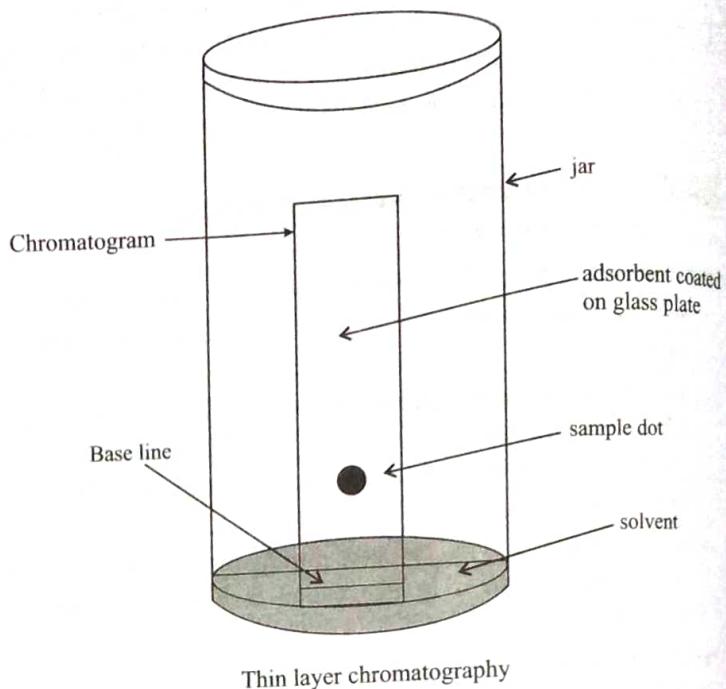
- Column chromatography involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube.
- The column is fitted with a stopcock at its lower end.
- The mixture adsorbed on adsorbent is placed on the top of the adsorbent column packed in a glass tube.
- An appropriate eluant which is a liquid or a mixture of liquids is allowed to flow down the column slowly.
- Depending upon the degree to which the compounds are adsorbed, complete separation takes place.
- The most readily adsorbed substances are retained near the top and others come down to various distances in the column.



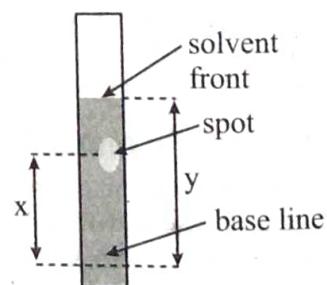
Thin Layer Chromatography

- Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate.

- A thin layer (about 0.2mm thick) of an adsorbent (silica gel or alumina) is spread over a glass plate of suitable size.



- The plate is known as thin layer chromatography plate or chromaplate.
- The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of the TLC plate.
- The glass plate is then placed in a closed jar containing the eluant.
- As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place.
- The relative adsorption of each component of the mixture is expressed in terms of its retardation factor i.e. R_f value



Developed chromatogram

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

- The spots of coloured compounds are visible on TLC plate due to their original colour.
- The spots of colourless compounds, can be detected by putting the plate under ultraviolet light.

- Another detection technique is to place the plate in a covered jar containing a few crystals of iodine. Spots of compounds, which adsorb iodine, will show up as brown spots.
- Sometimes an appropriate reagent may also be sprayed on the plate for example: Amino acids may be detected by spraying the plate with ninhydrin solution.

Partition Chromatography

- Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases.
- Paper chromatography is a type of partition chromatography.
- In paper chromatography, a special quality paper known as chromatography paper (made of cellulose and water is absorbed in it) is used.
- Chromatography paper contains water trapped in it, which acts as the stationary phase.
- A strip of chromatography paper spotted at the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents.
- This solvent acts as the mobile phase.
- The solvent rises up the paper by capillary action and flows over the spot.

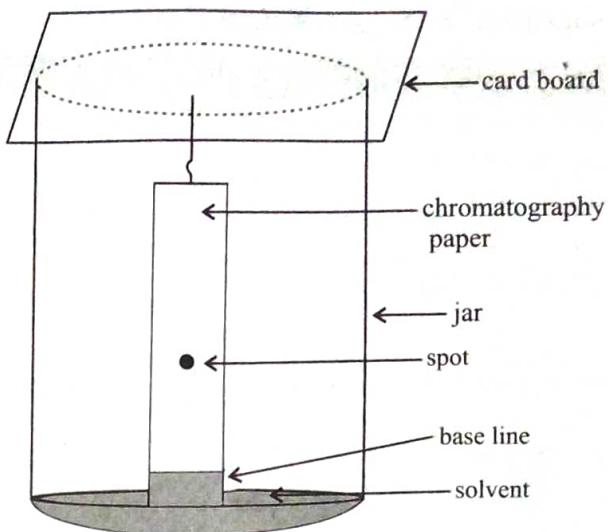
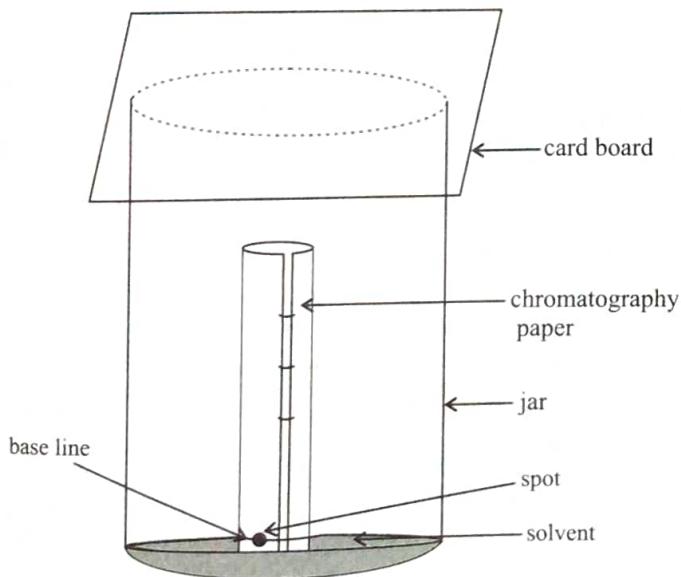


Fig. Paper chromatography (chromatography paper in two different shapes)

- The paper strip so developed is known as a chromatogram.
- The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram.
- The spots of the separated colourless compounds may be observed either under ultraviolet light or by the use of an appropriate spray reagent as discussed under thin layer chromatography.

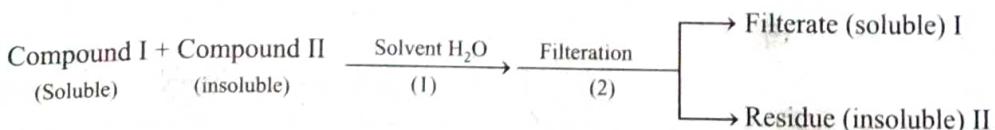
Note:

- Main difference between TLC and Paper Chromatography are-

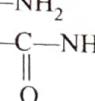
Thin Layer Chromatography	Paper Chromatography
It is based on Adsorption.	It is based on Partition
Stationary Phase → Glass Plate Coated with Silica gel	Stationary Phase → Water Trapped in the cellulose filter paper.
Corrosive reagent can be used.	Corrosive reagent can destroy the paper.

Chemical Methods

- ❖ Chemical methods of separation depend upon the nature of the functional group present in the component. Hence these can be applied to solid as well as liquid compounds.
- ❖ A chemical method can be applied only when one of the components of the mixture is soluble in a particular solvent while the other is insoluble in the same solvent.



The Solubility of Organic Compounds

Compound	H ₂ O(cold)	aq.NaHCO ₃	aq. NaOH	aq. HCl
(I) Small aliphatic compound with F.G. (Hydrogen bonding C ₁ to C ₂) (a) R—COOH (b) R—OH (c) R—NH ₂ (d) R—C—NH ₂ 	Soluble	Soluble	Soluble	Soluble
(II) Small aliphatic compound containing two F.G. (Hydrogen bonding) C ₁ to C ₅ (a) 2(COOH) – diacids (b) 2(—OH) – diols/glycol/sugar (c) 2(NH ₂) (d) —CONH ₂	Soluble	Soluble	Soluble	Soluble
Some common compounds are urea, glucose, oxalic acid, succinic acid				
(III) Aromatic acids (H ₂ O insoluble) benzoic acid and derivative (a) Ar—COOH (b) Ar—SO ₃ H (c) picric acid (d) Ar—C—Cl 	Insoluble	Soluble ArCOONa	Soluble ArCOONa	Insoluble
(IV) Phenols Ar—OH	Insoluble	Insoluble	Soluble Ph—ONa	Insoluble
(V) Anilines Ar—NH ₂	Insoluble	Insoluble	Insoluble	Soluble ArNH ₃ ⁺ Cl ⁻



Train Your Brain

Example 1. Liquid which decompose below their normal boiling points can be distilled at lower temperature by-

- (a) Increasing the pressure
- (b) Decreasing the pressure
- (c) Heating in water bath
- (d) Heating in sand bath

Sol. (b) B.pt. gets lowered at low pressure.

Example 2. A bottle containing two immiscible liquids is given to you. They may be separated by using

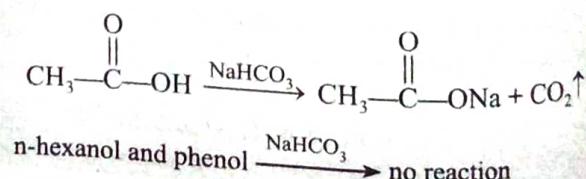
- (a) Fractionating column
- (b) Separating funnel
- (c) Vacuum distillation
- (d) Steam distillation

Sol. (b) Being immiscible liquids, they form different layers.

Example 3. Which one of the following compounds will react with NaHCO₃ solution to give sodium salt and carbon dioxide?

- (a) Acetic acid
- (b) n-hexanol
- (c) Phenol
- (d) Both (b) and (c)

Sol. (a)





Concept Application

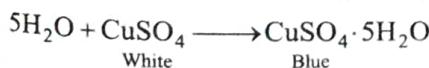
- A mixture contains four solid organic compounds, A, B, C and D. On heating only C changes from solid to vapour state. C can be separated from the rest in the mixture by-
 - Distillation
 - Sublimation
 - Fractional distillation
 - Crystallisation
- The best method to separate the mixture of ortho and para nitrophenol (1:1) is-
 - Steam distillation
 - Crystallization
 - Vapourisation
 - Colour spectrum
- The separation of mixture of two compounds by chromatographic technique is based upon-
 - Differential solubilities
 - Different densities
 - Different absorption
 - Differential adsorption

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS (DETECTION OF ELEMENTS)

The qualitative analysis of an organic compound involves detection of all elements present in it.

Detection of Carbon and Hydrogen

Carbon and hydrogen are detected by heating the compound with copper(II) oxide. Carbon present in the compound is oxidised to carbon dioxide (tested with lime-water, which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue).



Anhydrous copper sulphate

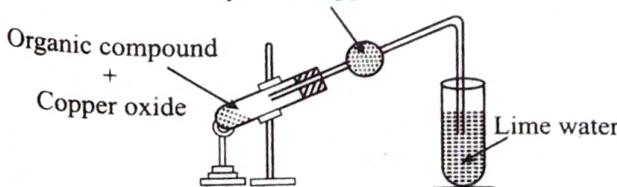


Fig. Detection of carbon and hydrogen in an organic compound



Detection of Other Elements

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by "Lassaigne's test". The elements present in the compound are converted from covalent form into the ionic form by fusing the compound with sodium metal. Following reactions take place:

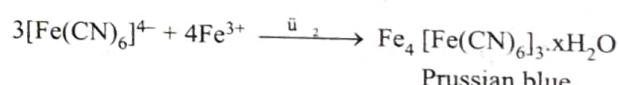


C, N, S and X come from organic compound.

Cyanide, sulphide and halide of sodium so formed on sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as **sodium fusion extract**.

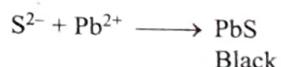
Test for Nitrogen

The sodium fusion extract is boiled with iron (II) sulphate and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen. Sodium cyanide first reacts with iron (II) sulphate and forms sodium hexacyanoferrate(II). On heating with concentrated sulphuric acid some iron (II) ions are oxidised to iron (III) ions which react with sodium hexacyanoferrate(II) to produce iron(III) hexacyanoferrate(II) (ferriferrocyanide) which is Prussian blue in colour.

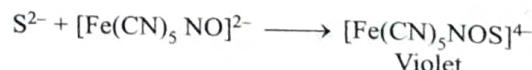


Test for Sulphur

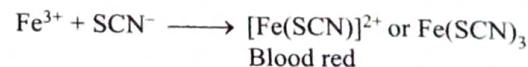
(i) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.



(ii) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour further indicates the presence of sulphur.

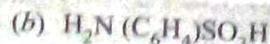
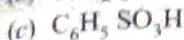


In case, nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. It gives blood red colour and no Prussian blue since there are no free cyanide ions.

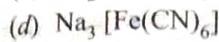
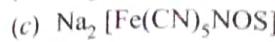
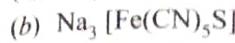
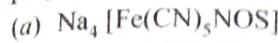


If sodium fusion is carried out with excess of sodium, then thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests.





7. In a Lassaignes's test for sulphur in the organic compound with sodium nitroprusside solution the purple colour formed is due to-

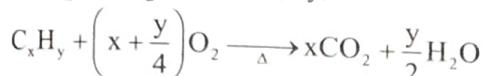


QUANTITATIVE ANALYSIS

It involves the estimation of percentage composition of various elements by suitable methods.

Estimation of Carbon and Hydrogen

- Carbon and hydrogen are estimated by Liebig's combustion method.
- A known mass of an organic compound is burnt in the presence of excess of oxygen (free from CO_2) and Cupric oxide (CuO).
- Carbon and hydrogen present in the compound are oxidised to CO_2 and H_2O respectively.



- CO_2 and H_2O produced are weighed by absorbing in concentrated solution of potassium hydroxide and anhydrous calcium chloride (or) magnesium perchlorate respectively.

$$\% \text{C} = \frac{12}{44} \times \frac{\text{wight of CO}_2 \text{ formed}}{\text{weight of organic Compound}} \times 100$$

$$\% \text{H} = \frac{2}{18} \times \frac{\text{wight of H}_2\text{O formed}}{\text{weight of organic Compound}} \times 100$$

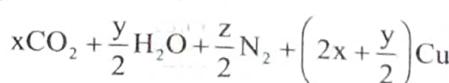
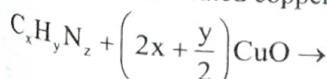
Estimation of Nitrogen

Nitrogen present in organic compound is estimated by

- Dumas method
- Kjeldahl's method

Dumas Method

- In this method nitrogen present in the organic compound is converted into N_2 .
- A weighed amount of organic compound is heated with cupric oxide in an atmosphere of carbondioxide.
- Carbon and hydrogen present in the compound are oxidised to CO_2 and H_2O , while N_2 is set free.
- Some oxides of nitrogen formed are reduced to free nitrogen by passing over heated copper gauze.

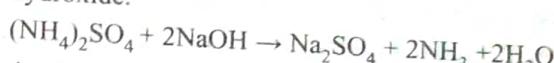


- Oxides of nitrogen + $\text{Cu} \rightarrow \text{N}_2 + \text{CuO}$
- The mixture of gases produced is collected over caustic potash solution (KOH solution) which absorbs CO_2 .

$$\% \text{N} = \frac{28}{22400} \times \frac{\text{Volume of nitrogen in ml at STP}}{\text{Weight of organic compound}} \times 100$$

Kjeldahl's Method

- In this method nitrogen present in the organic compound is converted into ammonia (NH_3).
- A known mass of organic compound containing nitrogen is heated with concentrated sulphuric acid in presence of K_2SO_4 and CuSO_4 then nitrogen present in the compound is converted into ammonium sulphate.
- Organic compound + $\text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4$
- The resulting solution is distilled with excess of sodium hydroxide.



- Ammonia evolved is absorbed in a known but excess volume of standard HCl (or) H_2SO_4 solution.

- The acid left unreacted is estimated by titration against standard solution of sodium hydroxide.

Percentage of Nitrogen =

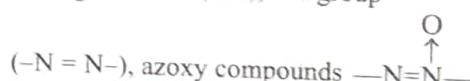
$$\frac{14}{1000} \times \frac{V \times N}{\text{wt.of organic compound}} \times 100$$

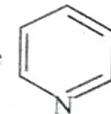
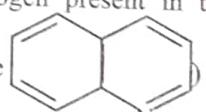
$$\% \text{N} = \frac{1.4 \times V \times N}{\text{Weight of organic compound}}$$

Where V = Volume of acid in mL neutralised by ammonia

N = Normality of acid.

- This method is simpler and more convenient.
- It is mainly used to find percentage of nitrogen present in food stuffs, soils, fertilizers and various agricultural products.
- This method is not applicable to compounds containing nitro ($-\text{NO}_2$), Nitroso (NO), azo group



and nitrogen present in the ring (pyridine  and quinoline ) because nitrogen present in these compounds is not quantitatively converted into ammonium sulphate.

- K_2SO_4 increases boiling point of H_2SO_4 and CuSO_4 acts as catalyst.

Estimation of Halogens (Carius Method)

- A weighed amount of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as carius tube.
- Carbon and hydrogen present in the compound is converted into CO_2 and H_2O .

- ❖ Halogen present in the organic compound is converted into silver halide.
- ❖ The precipitate is washed, dried and weighed.

Percentage of halogen =

$$\frac{\text{Atomic weight of halogen}}{\text{M.wt of silver halide}} \times \frac{\text{Weight of silver halide formed}}{\text{Weight of organic compound}} \times 100$$

$$\% \text{Cl} = \frac{35.5}{143.5} \times \frac{\text{w.t. of AgCl formed}}{\text{Wt.of organic compound}} \times 100$$

$$\% \text{Br} = \frac{80}{188} \times \frac{\text{wt.of AgBr formed}}{\text{Wt.of organic compound}} \times 100$$

$$\% \text{I} = \frac{127}{235} \times \frac{\text{wt.of AgI formed}}{\text{Wt.of organic compound}} \times 100$$

Estimation of Sulphur (Carius Method)

- ❖ A weighed amount of organic compound is heated in a carius tube with sodium peroxide or fuming nitric acid.
- ❖ Sulphur present in the compound is oxidised into sulphuric acid, which is treated with BaCl_2 solution gives precipitate of BaSO_4 .
- ❖ It is filtered, the precipitate is washed, dried and weighed.

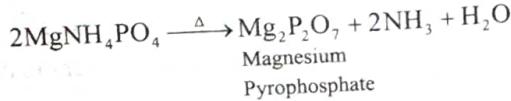
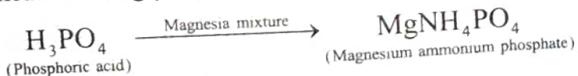
$$\% \text{S} = \frac{\text{Atomic wt.of sulphur}}{\text{Mol.wt. of BaSO}_4} \times \frac{\text{wt.of BaSO}_4 \text{ formed}}{\text{wt.of organic compound}} \times 100$$

$$\% \text{S} = \frac{32}{233} \times \frac{\text{wt. of BaSO}_4 \text{ formed}}{\text{wt.of organic compoud}} \times 100$$

Estimation of Phosphorus (Carius Method)

A weighed amount of organic compound is heated with fuming nitric acid, then phosphorus present in the compound is oxidised to phosphoric acid.

- ❖ Phosphoric acid is precipitated as magnesium ammonium phosphate (MgNH_4PO_4), by addition of magnesia mixture ($\text{MgCl}_2 + \text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$)
- ❖ Magnesium ammonium phosphate is washed, dried and it is heated strongly to get magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$).



$$\% \text{P} = \frac{62}{222} \times \frac{\text{wt. of Mg}_2\text{P}_2\text{O}_7 \text{ formed}}{\text{wt.of organic compound}} \times 100$$

- ❖ Phosphoric acid is precipitated as ammonium phosphomolybdate ($(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$) by adding ammonia and ammonium molybdate.

(Molecular mass of $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 = 1877$)

$$\% \text{P} = \frac{31}{1877} \times \frac{\text{wt. of } (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \text{ formed}}{\text{wt.of organic compound}} \times 100$$

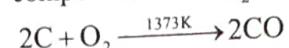
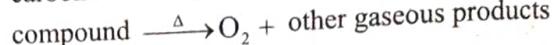
Estimation of Oxygen

- ❖ Usually percentage of oxygen in organic compound is determined by method of difference.
 $\% \text{ of oxygen} = 100 - (\text{sum of the percentages of all other elements})$

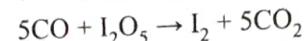
- ❖ Oxygen present in the organic compound is estimated by **Aluise's method**.

- ❖ A known amount of organic compound is subjected to pyrolysis in a stream of nitrogen.

- ❖ The mixture of gaseous products containing oxygen is passed over red-hot coke, then all the oxygen is converted into carbon monoxide.



- ❖ CO formed is quantitatively converted into CO_2 by passing over warm Iodine pentoxide (I_2O_5).



The resulting gaseous mixture (CO_2 and I_2) is passed through potassium iodide solution, which absorbs iodine, and then passed over KOH to absorb CO_2 .

$$\% \text{ of oxygen} = \frac{16}{44} \times \frac{\text{wt.of CO}_2 \text{ formed}}{\text{wt.of organic compound}} \times 100$$



Train Your Brain

Example 7. Liebig method is used for the estimation of

(a) Nitrogen

(b) Sulphur

(c) Carbon and Hydrogen

(d) Halogens

Sol. (c) Liebig method is used for the estimation of carbon and hydrogen.

Example 8. The quantitative determination of halogen in an organic compound is known as-

(a) Dumas method

(b) Carius method

(c) Kjeldahl method

(d) Leibig method

Sol. (b) The quantitative determination of halogen in an organic compound is called as carius method.

Example 9. 0.2475 g of an organic compound gave on combustion 0.4950 g of carbon dioxide and 0.2025 g of water. The percentage of carbon and hydrogen are-

(a) 54.54, 9.09

(b) 52.54, 8.09

(c) 120, 5.8

(d) None of these

Sol. (a) Wt. of organic compound = 0.2475 g

Wt. of CO_2 produced = 0.4950 g

Wt. of H_2O produced = 0.2025 g

Percentage of carbon

$$= \frac{12}{44} \times \frac{\text{Wt. of } \text{CO}_2}{\text{Wt. of compound}} \times 100$$

$$= \frac{12}{44} \times \frac{0.4950}{0.2475} \times 100 = 54.54$$

Percentage of hydrogen

$$= \frac{2}{18} \times \frac{\text{Wt. of } \text{H}_2\text{O}}{\text{Wt. of compound}} \times 100$$

$$= \frac{2}{18} \times \frac{0.2025}{0.2475} \times 100 = 9.09$$

Concept Application

8. Duma's method involves the determination of content of nitrogen in the organic compound in the form of-

- (a) Gaseous NH_3
- (b) Gaseous N_2
- (c) NaCN
- (d) $(\text{NH}_4)_2\text{SO}_4$

9. 0.59 g of an organic substance when treated with caustic soda evolved ammonia, which required 20 c.c. of $\text{N}/2$ sulphuric acid for neutralization. The percentage of nitrogen is-

- (a) 40%
- (b) 53.6%
- (c) 63.6%
- (d) 23.73%

10. If 0.2 gram of an organic compound containing carbon, Hydrogen and oxygen on combustion, yielded 0.147 gram carbon dioxide and 0.12 gram water. What will be the content of oxygen in the substance?

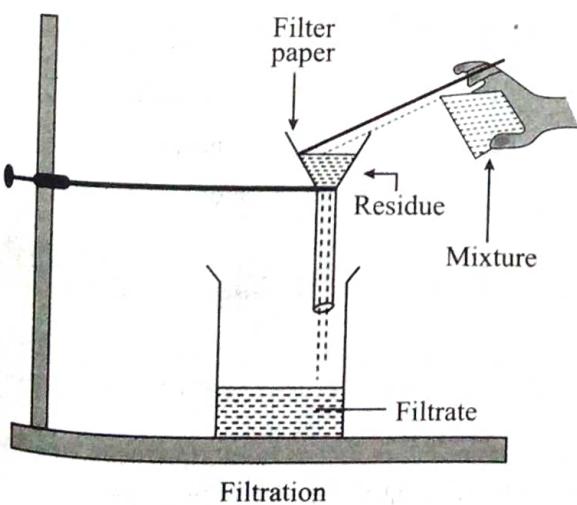
- (a) 73.29 %
- (b) 78.45 %
- (c) 83.23 %
- (d) 89.50 %



Short Notes

Filtration: Only one of the compounds is soluble in the given solvent e.g.

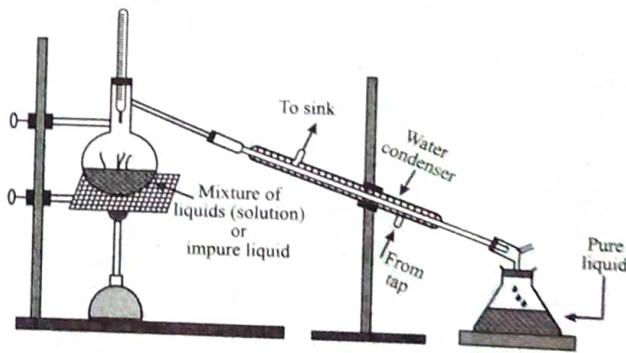
- (i) Urea and Naphthalene
- (ii) Benzoic acid and anthracene



Fractional Crystallization: Difference in solubilities of organic compounds and impurities are very less. e.g. urea and copper sulphate.

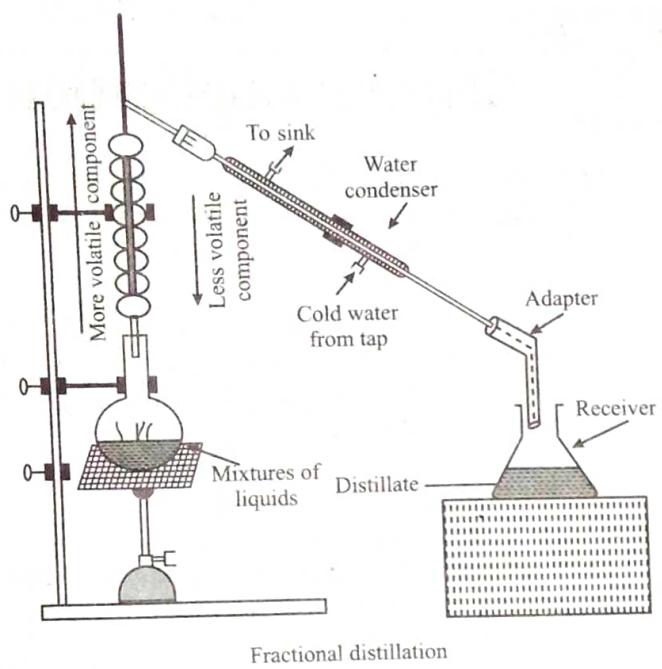
Distillation

(i) **Simple distillation:** Difference in boiling points of compounds is more than 40°C . e.g. chloroform (b. p. 334K) and aniline.

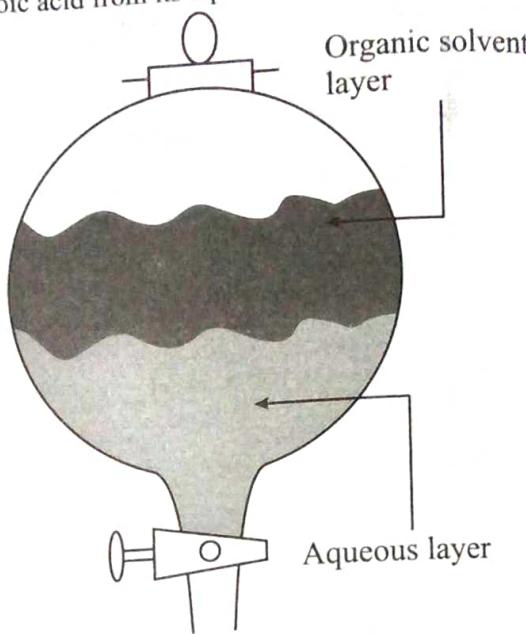


(ii) **Fractional distillation:** Difference in boiling points of compounds is very less (5°C to 10°C). e.g. - acetone (b. p. 329K) and methyl alcohol (b. p. 338K).

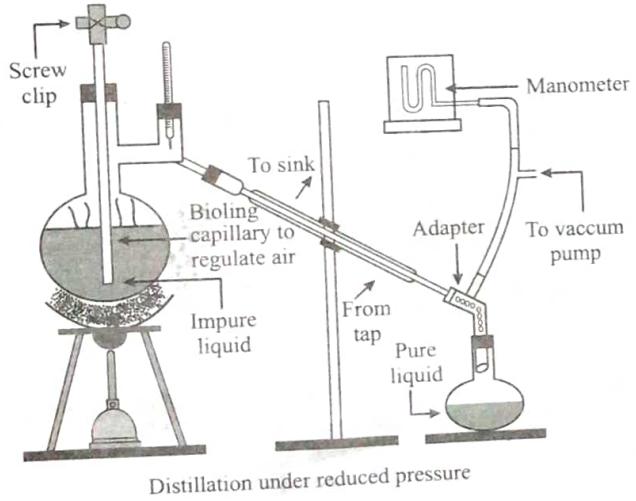
Crystallisation: It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent.



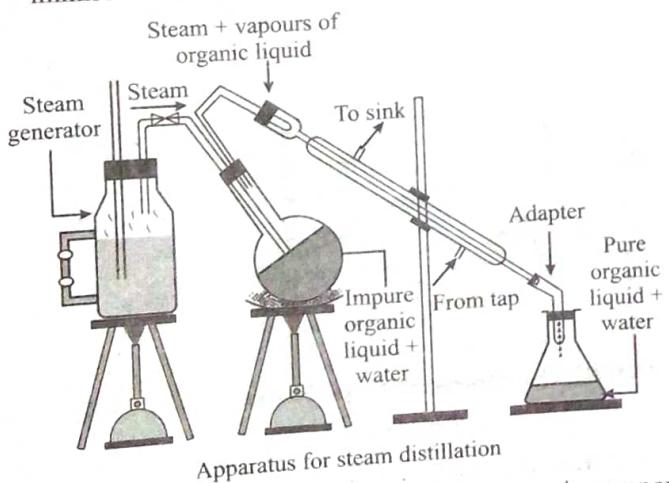
e.g. Benzoic acid from its aqueous solution using benzene.



(iii) **Vacuum distillation:** Used for organic compounds which decompose at or below their boiling points. e.g. Glycerol.



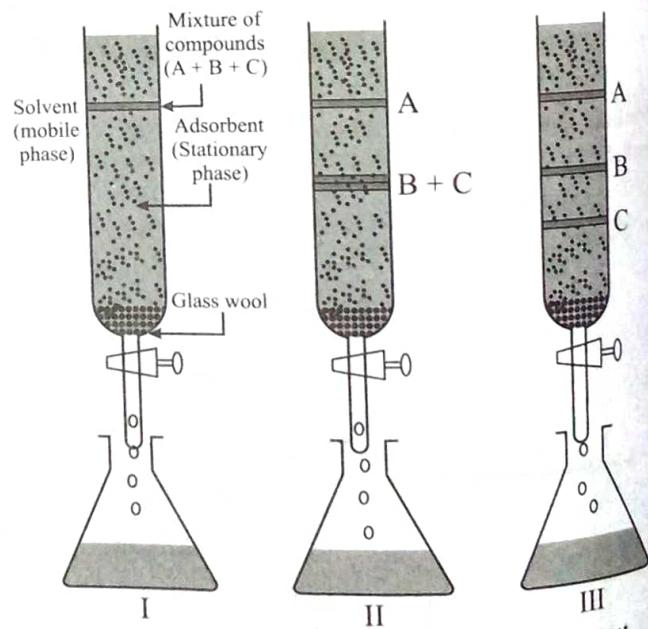
(iv) **Steam distillation:** Used for organic compounds which are immiscible with water and are steam volatile. e.g. Aniline.



Differential extraction: Used to extract pure organic compounds from their aqueous solution by shaking with organic solvent in which they are highly soluble.

Chromatography

- ❖ Used to purify small samples.
- ❖ Based on selective adsorption or partition between stationary and mobile phase.
- ❖ Column Chromatography based on adsorption, used for bulk quantities.
- ❖ Thin layer Chromatography based on adsorption, used for quantitative analysis.



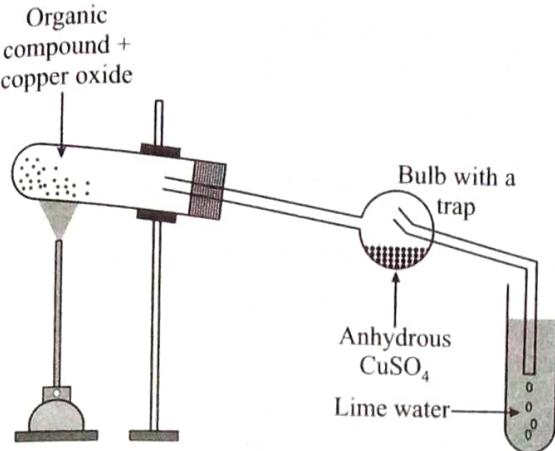
Column chromatography-stage I, II and III represent the progressive separation of the mixture into three bands

- ❖ Paper Chromatography - based on partition and used for quantitative and qualitative analysis.

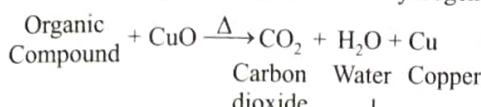
QUALITATIVE ANALYSIS

Detection of C, H, N, halogens P, S, and oxygen.

Detection of Carbon and Hydrogen



Detection of carbon and hydrogen



Passed into
lime water

$\text{Ca}(\text{OH})_2$

Lime water turns milky

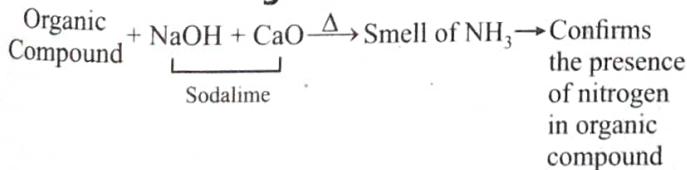
Carbon (C) present
In organic compound

Passed into
anhydrous
 CuSO_4

Copper Sulphate turns blue

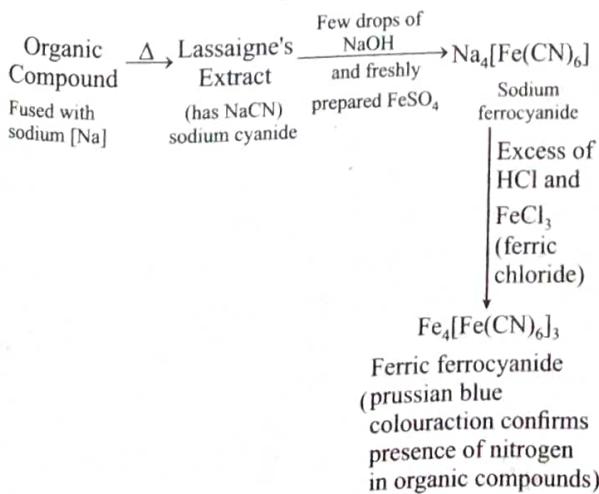
Hydrogen (H)
present in
Organic
Compound

Detection of Nitrogen



Lassaigne's Extract

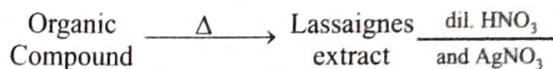
Lassaigne's extract is prepared to convert covalency of organic compound into electrovalency by fusing with Na.



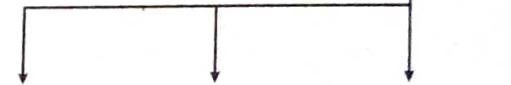
Detection of Halogen

Beilstein's test

Organic compound $\xrightarrow{\text{Heated over Copper wire}}$ Green flame confirms the presence of halogen's in the organic compound



Fuse with sodium
(has covalent bonds with carbon and halogens)

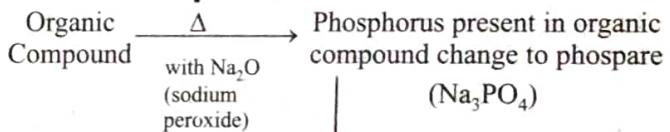


White ppt of silver chloride (AgCl) soluble in ammonia confirms the presence of chlorine in organic compound

Pale yellow ppt. of silver bromide (AgBr) sparingly soluble in ammonia confirms the presence of bromine in organic compound

Yellow ppt. of silver iodide (AgI) insoluble in ammonia confirms the presence of iodine in organic compound

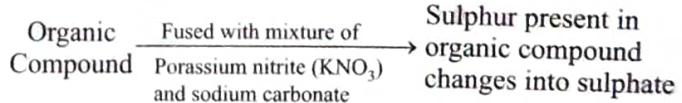
Detection of Phosphorus



boiled with nitric acid (HNO_3) and added ammonium molybdate $[(\text{NH}_4)_2\text{MoO}_4]$

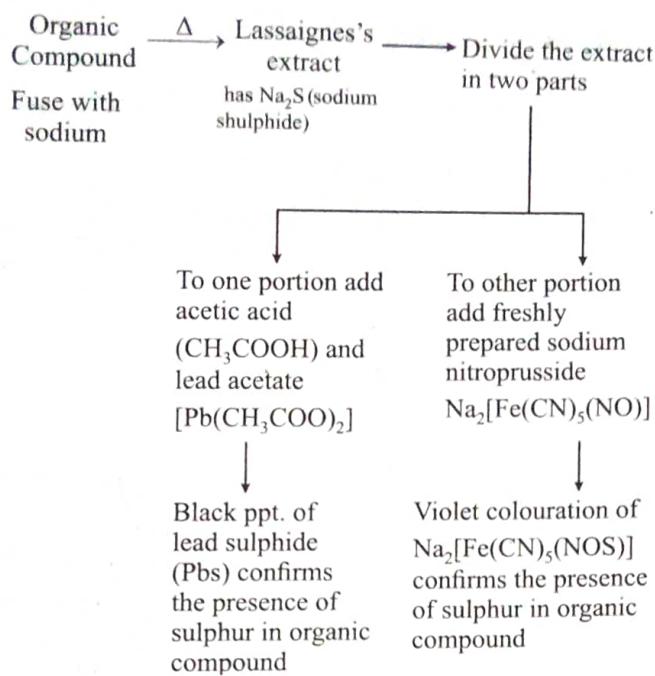
Yellow ppt. of ammonium phosphomolybdate $[(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3]$ confirms the presence of phosphorus in organic compound

Detection of Sulphur



Extracted with water, filtered and added dil. HCl BaCl_2

White ppt. of barium sulphate (BaSO_4) confirms the presence of sulphur inorganic compound



Detection of Oxygen

Presence of oxygen in organic compound is detected by testing for functional group containing oxygen e.g. alcohol ($-\text{OH}$), aldehyde ($-\text{CHO}$), ketone (RCOR), carboxylic acid ($-\text{COOH}$), ester ($-\text{COOR}$) and nitro ($-\text{NO}_2$).

Quantitative Analysis

$$\% \text{C} = \frac{12}{44} \times \frac{\text{wt. of } \text{CO}_2}{\text{Wt. of org. compound}} \times 100$$

$$\% \text{H} = \frac{2}{18} \times \frac{\text{wt. of } \text{H}_2\text{O}}{\text{Wt. of org. compound}} \times 100$$

$$\% \text{N} = \frac{28}{22400} \times \frac{\text{Vol. of } \text{N}_2 \text{ at STP}}{\text{Wt. of org. comp.}} \times 100$$

or

$$\% \text{N} = \frac{\text{Volume of } \text{N}_2 \text{ at STP}}{8 \times \text{Wt. of org. compound}} \quad (\text{Duma's method})$$

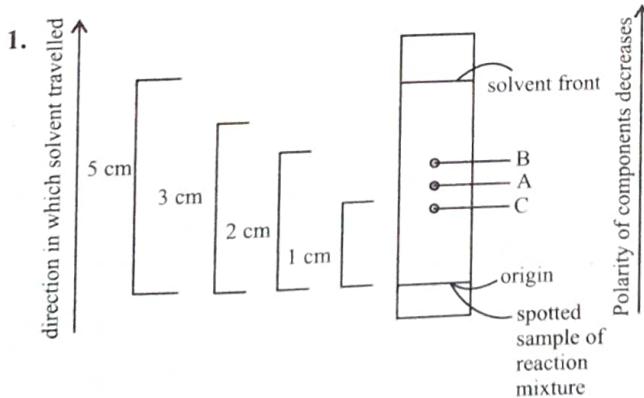
$$(\% \text{N}) = \frac{1.4 \times \text{N} \times V}{\text{wt. of org. compound}} \quad (\text{Kjeldhal's method})$$

$$\% \text{X} = \frac{\text{At. wt. of X}}{\text{Mol. wt. AgX}} \times \frac{\text{Wt. of AgX}}{\text{wt. of org. compound}}$$

$$\% \text{S} = \frac{32}{233} \times \frac{\text{Wt. BaSO}_4}{\text{wt. of org. compound}} \times 100$$

$$\% \text{P} = \frac{62}{222} \times \frac{\text{Mass of Mg}_2\text{P}_2\text{O}_7}{\text{Wt. of org. compound}} \times 100$$

Solved Examples



So just by looking at a TLC plate, can you tell which component is more polar and which component is less polar.

Sol. The relative adsorption of each component of the mixture is expressed in terms of its retardation factor i.e. R_f value.

$$R_f = \frac{\text{Distance moved by the substance from base line}}{\text{Distance moved by the solvent from base line}}$$

'Lower the R_f value, more polar the component.'

Component	Distance travelled by the component (cm)	Distance travelled by the solvent (cm)	retention factor (R_f)
C	1	5	$R_f = 1/5 = 0.2$
A	2	5	$R_f = 2/5 = 0.4$
B	3	5	$R_f = 3/5 = 0.6$

Based on the R_f values (as calculated above), component C is the most polar and component B is the least polar.

2. 0.25g of an organic compound gave 30 cm³ of moist dinitrogen at 288 K and 745 mm pressure. Calculate the percentage of nitrogen. (Aqueous tension at 288 K = 12.7 mm)

Sol. Mass of the substance = 0.25 g

Volume of moist dinitrogen = 30 cm³

Temperature = 288 K, Pressure $745 - 12.7 = 732.3$ mm

Volume of dinitrogen at STP:

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{732.3 \times 30 \times 273}{288 \times 760} = 27.4 \text{ cm}^3$$

Percentage of nitrogen

$$= \frac{14 \times 26.8 \times 100}{10 \times 1000 \times 0.257} = 14.6\%$$

10. Hydrazine and diazonium salts do not give Lassaigne's test. Why?

Sol. In the Lassaigne's test, nitrogen is converted to cyanide by combining with carbon of the compound. Hydrazine does not contain carbon and hence, cyanide cannot be formed. Diazonium salts are unstable and lose nitrogen as N_2 gas on heating. Hence during fusion, no sodium cyanide is formed in Lassaigne's extract due to the loss of nitrogen.

11. A certain organic compound was found to contain 33.8% C, 5.6% H and 49.6% chlorine. Find the empirical formula of the organic compound.

Sol.

Element	%	Atomic ratio	Simplest ratio
C	33.8	$33.8/12 = 2.8$	$2.8/0.7 = 4$
H	5.6	$5.6/1 = 5.6$	$5.6/0.7 = 8$
Cl	49.6	$49.6/35.5 = 1.4$	$1.4/0.7 = 2$
O	11.0	$11/16 = 0.7$	$0.7/0.7 = 1$

Thus, $C_4H_8Cl_2O$ is the empirical formula of the compound.

12. A well known antibiotic penicillin, contains, 57.49 % C, 5.39% H, 8.39% N, 9.58% S and the remainder being oxygen. Given that penicillin contains one atom of sulphur per molecule, calculate the molecular formula of the antibiotic.

% C = 57.49

% H = 5.39

% N = 8.39

% S = 9.58

% O = 100 - (57.49 + 5.39 + 8.39 + 9.58)

= 19.15

Element	%	Atomic ratio	Simplest ratio
C	57.49	$57.49/12 = 4.79$	16
H	5.39	$5.39/1 = 5.39$	18
N	8.39	$8.39/14 = 0.599$	2
S	9.58	$9.58/32 = 0.299$	1
O	19.15	$19.15/16 = 1.196$	4

Empirical formula is $C_{16}H_{18}N_2SO_4$

As the given antibiotic contains only one atom of sulphur per molecule. The calculated empirical formula $C_{16}H_{18}N_2SO_4$ contains only one atom of sulphur. Hence, the same is the molecular formula of the antibiotic.

Exercise-1 (Topicwise)

PURIFICATION AND SEPARATION OF ORGANIC COMPOUNDS

1. Sublimation is process where a solid-
 - Melts
 - Changes into liquid form.
 - Boils
 - Changes into vapour form directly.
2. A mixture of acetone and methanol can be separated by-
 - Vaccum distillation
 - Steam distillation
 - Fractional distillation
 - None of these
3. Turpentine oil can be purified by-
 - Vaccum distillation
 - Fractional distillation
 - Steam distillation
 - Simple distillation
4. Chromatography is used for the purification of-
 - Solids
 - Gases
 - Liquids
 - All of these
5. Steam distillation is applied to those organic compounds which are steam volatile and:
 - Soluble in water.
 - Insoluble in water.
 - Sparingly soluble in water.
 - Insoluble in all solvents.
6. Distillation involves all the following processes except:
 - Change of state
 - Boiling
 - Condensation
 - Evaporation
7. Turpentine oil and essential oil can be purified by:
 - Fractional distillation
 - Steam distillation
 - Vacuum distillation
 - Simple distillation
8. Chromatography technique is used for the separation of:
 - Small samples of mixtures
 - Plant pigments
 - Dye stuffs
 - All of the above
9. Two volatile and miscible liquids can be separated by fractional distillation into pure components under the conditions when :
 - They have low boiling points.
 - The difference in their boiling points is large.
 - The boiling points of the liquids are close to each other.
 - They do not form azeotropic mixture.

10. A fractional column is used in:
 - Sublimation
 - Distillation
 - Fractional distillation
 - Chromatography
 11. Glycerol is purified by:
 - Steam distillation
 - Vacuum distillation
 - Fractional distillation
 - Simple distillation
 12. Anthracene is purified by
 - Filtration
 - Distillation
 - Crystallisation
 - Sublimation
- ### QUALITATIVE ANALYSIS
13. The compound that does not give a blue colour in Lassaigne's test is-
 - Aniline
 - Glycine
 - Hydrazine
 - Urea
 14. In Lassaigne test thiourea is converted into-
 - NaCNS
 - Na_2S
 - NaCN
 - Na_2SO_4
 15. In the Lassaigne's test, one of the organic compounds give red colour with FeCl_3 . Compound can be:
 - Na_2S
 - NH_2CSNH_2
 - $\text{C}_6\text{H}_5\text{Cl}$
 - NaCN
 16. Lassaigne's test is used in qualitative analysis to detect
 - Nitrogen
 - Sulphur
 - Chlorine
 - All of these
 17. The compound that does not give a blue colour in Lassaigne's test is
 - $\text{C}_6\text{H}_5-\text{NH}_2$
 - CH_3CONH_2
 - NH_2-NH_2
 - $\text{C}_6\text{H}_5-\text{NO}_2$
 18. Nitrogen containing organic compound when fused with sodium metal forms:
 - NaNO_2
 - NaCN
 - NaNH_2
 - NaNC
 19. The sodium extract of an organic compound on acidification with acetic acid and addition of lead acetate solution gives a black precipitate. The organic compound contains
 - Nitrogen
 - Halogen
 - Sulphur
 - Phosphorus
 20. The prussian blue colour obtained during the test of nitrogen by Lassaigne's test is due to the formation of:
 - $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
 - $\text{Na}_3[\text{Fe}(\text{CN})_6]$
 - $\text{Fe}(\text{CN})_3$
 - $\text{Na}_4(\text{Fe}(\text{CN})_5\text{NOS})$
 21. Copper wire test of halogens is known as:
 - Liebig's test
 - Lassaigne's test
 - Fusion test
 - Beilstein's test

QUANTITATIVE ANALYSIS

22. If 0.32 gm of an organic compound containing sulphur produces 0.233g of BaSO_4 Then the percentage of sulphur in it is-

 - (a) 10
 - (b) 15
 - (c) 20
 - (d) 25

23. In Duma's method, the gas which is collected in Nitrometer is-

 - (a) N_2
 - (b) NO
 - (c) NH_3
 - (d) H_2

24. In Kjeldahl's method, CuSO_4 acts as-

 - (a) Oxidising agent
 - (b) Catalytic agent
 - (c) Reducing agent
 - (d) Hydrolysing agent

25. Nitrogen in an organic compound can be estimated by-

 - (a) Kjeldahl's method only
 - (b) Duma's method only
 - (c) Both method
 - (d) None of these

Exercise-2 (Learning Plus)

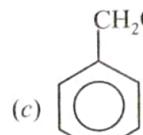
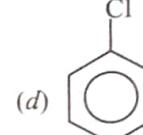
11. Boiling point of a liquid can be increased by-
- Increasing the pressure.
 - Decreasing the pressure.
 - Purifying the liquid.
 - Adding water to it.
12. In organic compounds P is estimated as-
- H_3PO_4
 - P_2O_5
 - $Mg_3(PO_4)_2$
 - $(NH_4)_3 PO_4 \cdot 12MoO_3$
13. Which statement apply best to vacuum distillation-
- Distil liquids quickly with decomposition.
 - It is very easy to distill.
 - Distil liquid to avoid decomposition.
 - None of these
14. A mixture of naphthalene and benzoic acid can be separated by-
- Extraction with solvent
 - Sublimation
 - Fractional crystallisation
 - Distillation
15. If on adding $FeCl_3$ solution to acidified Lassaigne's solution, a blood red colouration is produced, it indicates the presence of -
- S
 - N
 - N and S
 - S and Cl
16. In carius tube the compound $ClCH_2-COOH$ was heated with fuming HNO_3 and $AgNO_3$. After filtration and washing, a white ppt. was formed. The ppt is-
- $AgCl$
 - $AgNO_3$
 - Ag_2SO_4
 - $CH_2(ClCOOAg)_2$
17. During Lassaigne's test, N and S present in an organic compound changes into-
- Na_2S and $NaCN$
 - $NaSCN$
 - Na_2SO_4 and $NaCN$
 - Na_2S and $NaCNO$
18. Two solids A and B have appreciable different solubilities in water but their melting points are very close. The mixture of A and B can be separated by-
- Sublimation
 - Fractional crystallisation
 - Distillation
 - Specific method
19. The sodium extract prepared from sulphanilic acid, contains SCN^- . It gives blood red colouration with:
- a mixture of Na_2S and CS_2
 - $FeCl_3$
 - $FeSO_4$
 - Na_2SO_3
20. Kjeldahl's method cannot be used for the estimation of nitrogen in:
- Pyridine
 - Nitrocompounds
 - Azo compounds
 - All of these
21. The latest technique used for purification of organic compounds is:
- Chromatography
 - Vacuum distillation
 - Fractional distillation
 - Crystallization
22. 0.765 g of an acid gives 0.535 g of CO_2 and 0.138 g of H_2O . Then the ratio of the percentage of carbon and hydrogen is:
- 19 : 2
 - 18 : 11
 - 20 : 17
 - 1 : 7
23. 2.79 g of an organic compound when heated in Carius tube with conc. HNO_3 and H_3PO_4 formed converted into $MgNH_4PO_4$ ppt. The ppt. on heating gave 1.332 g of $Mg_2P_2O_7$. The percentage of P in the compound is
- 23.33
 - 13.33
 - 33.33
 - 26.66
24. In Lassaigne's solution, pink/violet colour is produced when sodium nitroprusside solution is added. It indicates the presence of :
- sulphur
 - nitrogen
 - chlorine
 - none of these
25. The sodium extract of an organic compound on boiling with HNO_3 and addition of ammonium molybdate solution gives a yellow precipitate. The compound contains:
- Nitrogen
 - P
 - S
 - Cl
26. The sodium extract of an organic compound on treatment with $FeSO_4$ solution, $FeCl_3$ and HCl gives a red solution. The organic compound contains:
- Both nitrogen and sulphur
 - Nitrogen only
 - Sulphur only
 - Halogen
27. In Carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 g of $AgBr$. What is the percentage of bromine in the compound.
- 18%
 - 94%
 - 63%
 - 34%
28. A miscible mixture of $C_6H_6 + CHCl_3$ can be separated by
- Sublimation
 - Distillation
 - Filtration
 - Crystallization
29. Which of the following will not be soluble in sodium hydrogen carbonate ?
- 2, 4, 6-trinitrophenol
 - Benzoic acid
 - o-Nitrophenol
 - Benzenesulphonic acid

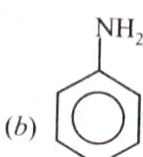
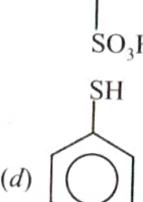
- 30.** Paper chromatography is an example of:
- Column chromatography
 - Adsorption chromatography
 - Partition chromatography
 - Thin layer chromatography
- 31.** Which is incorrect for paper chromatography
- It is a part of partition chromatography.
 - It is a stationary phase.
 - Rf value decrease when rate of adsorption increase.
 - None of these
- 32.** In Kjeldahls method of estimation of nitrogen, K_2SO_4 acts as
- catalytic agent
 - boiling point elevator
 - hydrolysis agent
 - oxidizing agent
- 33.** During formation of sodium extract, generally the substance that ignites is
- Na
 - O_2
 - CO_2
 - H_2
- 34.** Sorbic acid consists of C = 64.3%, H = 7.2% and 28.5% oxygen. Find the empirical formula.
- $C_2H_4O_3$
 - $C_3H_4O_2$
 - C_3H_4O
 - CH_2O
- 35.** A mixture of benzene and aniline can be separated by
- alcohol
 - NaOH
 - HCl
 - Hot water

Exercise-3 (JEE Advanced Level)

MULTIPLE CORRECT TYPE QUESTIONS

- When pieces of human hair are heated strongly with soda-lime, smell of ammonia can be detected. Which one of the following conclusion can be drawn from this observation?
 - Hair contains amino acids.
 - Ammonium salt is present in hair.
 - Ammonia is present in the human hair.
 - None of the above
- Which of the following is the best scientific method to test presence of water in a liquid?
 - Taste
 - Smell
 - Use of litmus paper
 - Use of anhydrous copper sulphate.
- When petroleum is heated gradually, first batch of vapours evolved will be rich in
 - Kerosene
 - Petroleum ether
 - Diesel
 - Lubricating oil
- In paper chromatography,
 - mobile phase is liquid and stationary Phase is solid.
 - mobile phase is solid and stationary phase in solid.
 - mobile phase is liquid and stationary phase is liquid.
 - mobile phase is solid and stationary phase is liquid.
- Which of the following compound will not produce a white precipitate of $AgCl$ on warming with ethanolic silver nitrate solution?

- CH_3-CH_2-Cl
 - $CH_2=CH-CH_2-Cl$
 - 
 - 
- Two organic compounds (X) and (Y), both containing only C and H yields on analysis, the same percentage composition by mass C = 92.3% and H = 7.7%. (X) decolourizes bromine water and (Y) does not. Identify (X) and (Y).
 - $X = C_2H_2$, $Y = C_3H_8$
 - $X = C_2H_4$, $Y = C_2H_6$
 - $X = C_6H_6$, $Y = C_2H_2$
 - $X = C_2H_2$, $Y = C_6H_6$
 - An organic compound on heating with CuO produces CO but not water. It may be
 - CH_4
 - CCl_4
 - $CHCl_3$
 - C_2H_5I
 - 60 g of a compound on analysis produced 24 g carbon, 4 g hydrogen and 32 g oxygen. The empirical formula of the compound is
 - CH_4O
 - CH_2O_2
 - $C_2H_4O_2$
 - CH_2O
 - Mark the incorrect statement in Kjeldahls method of estimation of nitrogen
 - copper sulphate or mercury acts as a catalyst.
 - nitrogen is quantitatively decomposed to give ammonium sulphate.
 - nitrogen gas is collected over caustic potash solution.
 - potassium sulphate is used as boiling point elevator. H_2SO_4 .

- 10.** Which of the following statements is wrong?
- in the estimation of carbon, an organic compound is heated with CaO in a combustion tube.
 - using Lassaigne's test nitrogen and sulphur present in an organic compound can be tested.
 - using Beilstein's test the presence of halogen in a compound can be tested.
 - Lassaigne's test fails to identify nitrogen in diazo compound.
- 11.** When thiourea is heated with metallic sodium, the compound formed is/are
- Na_2SO_4
 - Na_2S
 - NaCN
 - NaCNS
- 12.** In Lassaigne's test which of the following organic compound will produce a blood red colour when its sodium extract is treated with FeCl_3 solution?
- (a) 
- (b) 
- (c) 
- (d) 
- 13.** On combustion, 0.2 g of an organic compound containing carbon, hydrogen and oxygen yields 0.147 g carbon dioxide and 0.12 g water. The percentage of carbon, hydrogen and oxygen respectively in the compound is
- 22.5, 8.7 and 68.8
 - 20, 6.7 and 73.3
 - 18.2, 9.5 and 72.3
 - 28.9, 12.8 and 58.8
- 14.** Which of the following pair of compounds can be separated by using fractional distillation?
- Acetone and methyl alcohol
 - Benzene and toluene
 - Ethyl alcohol (95.5%) and water (4.5%)
 - Crude petroleum (gasoline and kerosene)
- 15.** Which of the following compounds can be distilled by using steam Distillation?
- Aniline
 - O-hydroxy phenol
 - O-hydroxy bezaldehyde
 - Glycerol
- 16.** Select the correct statements regarding Lassaigne's test?
- Li and K are not used in this test.
 - NH_4Cl , NH_2-NH_2 Can't be detected by this test.
 - Urea, Acetamide can not give this test.
 - Benzamide, Azobenzene can give this test.
- 17.** In the detection of N by Lassaigne's test which of the following compounds are formed during this test?
- $\text{Fe}(\text{OH})_2$
 - $\text{Na}_4[\text{Fe}(\text{CN})_6]$
 - FeCl_3
 - $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
- 18.** Beilslein Test is given by which of these compounds
- CuF_2
 - CuCl_2
 - $\text{C}_6\text{H}_5\text{N}$
 - Thiourea
- 19.** Kjeldahl's method can not be used to detect 96% of N in which of these compounds?
- Pyridine
 - Pyrole
 - Aniline
 - Diazo compounds
- 20.** For the crystallisation technique, which of the following statement is correct regarding choice of solvent.
- The solvent should dissolve the impurities.
 - The solvent should not react chemically with the substance.
 - The organic substance should dissolve in solvent upon heating and get separated on heating.
 - None of these
- 21.** Distillation technique is used for purification of which liquids:
- Which boil without decomposition.
 - Which boil with decomposition.
 - Which contains volatile impurities.
 - Which contains non-volatile impurities.
- 22.** Correct statement regarding differential extraction:
- Organic compound should be in aqueous medium.
 - Organic solvent is used which is immisible in water.
 - Organic compound is more soluble in organic solvent than water.
 - Very large quantity of solvent is required to extract small quantity of compound.
- 23.** Correct statement about chromatography:
- It can be used to separate ortho and para nitro-anilines.
 - It is used to separate blue and red dyes.
 - It is used to purify plant pigments.
 - It is used to separate compounds having dissimilar boiling points.
- 24.** Which of the following element is confirmed when soda-extract is treated with FeCl_3 and blood red colour appears in the Lassaigne test.
- Nitrogen
 - Sulphur
 - Iodine
 - Bromine
- 25.** Which of the following element is identified when red brown fumes are produced by sodium extract and conc. H_2SO_4
- Iodine
 - Nitrogen
 - Bromine
 - Chlorine

26. The incorrect statement for Lassaigne's test regarding sodium extract:
- It is used to form sodium derivative which are non-soluble.
 - It is used to convert elements into soluble ionic compound.
 - It is used to make element flammable.
 - It is used as an oxidising agent.

COMPREHENSION BASED QUESTIONS

Comprehension (Q. 27-29): Carius method can be used to find of halogen sulphur in organic compounds. Here the compound is heated with fuming HNO_3 to get HX or H_2SO_4 followed by addition of AgNO_3 or BaCl_2 to get ppt. of AgX or BaSO_4 .

27. 0.189 gm of an organic compound gives 0.287 g of AgCl . The % of Cl in it is?

- 18.75%
- 37.56%
- 55.25
- 74%

28. A compound having 'S' having a weight of 0.243 g on heating give 0.934g BaSO_4 in Carrus Test the % of sulphur is?

- 25.52%
- 48.46%
- 52.78%
- 72.36%

29. In Carius method sodium extract is boiled with HNO_3 , it is for

- To decompose NaCN into HCN(g) .
- To decompose Na_2S into $\text{H}_2\text{S(g)}$.
- To neutralise free alkali.
- All of the above

MATCH THE COLUMN TYPE QUESTIONS

30. Match the following

Method used for detections		Element detections	
Column-I		Column-II	
A.	Liebig's method	p.	Carbon
B.	Duma's method	q.	Nitrogen
C.	Carius method	r.	Sulphur
D.	Kjeldahl's method	s.	Hydrogen
		t.	Halogen

- $\text{A} \rightarrow \text{p}, \text{s}; \text{B} \rightarrow \text{q}; \text{C} \rightarrow \text{r}, \text{t}; \text{D} \rightarrow \text{q}$
- $\text{A} \rightarrow \text{p}, \text{q}; \text{B} \rightarrow \text{s}; \text{C} \rightarrow \text{r}, \text{s}; \text{D} \rightarrow \text{q}$
- $\text{A} \rightarrow \text{p}, \text{r}; \text{B} \rightarrow \text{r}; \text{C} \rightarrow \text{q}, \text{t}; \text{D} \rightarrow \text{p}$
- $\text{A} \rightarrow \text{q}, \text{s}; \text{B} \rightarrow \text{p}; \text{C} \rightarrow \text{s}, \text{t}; \text{D} \rightarrow \text{s}$

31. Match the following

Column-I		Column-II	
Element		Coloured ppt formed	
A.	Nitrogen	p.	Black sulphide
B.	Sulphur	q.	Violet Complex

C.	Chloride	r.	Prussian Blue
D.	Bromide	s.	Light yellow
		t.	White

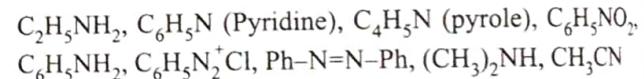
- $\text{A} \rightarrow \text{r}; \text{B} \rightarrow \text{p}; \text{C} \rightarrow \text{t}; \text{D} \rightarrow \text{s}$
 - $\text{A} \rightarrow \text{p}; \text{B} \rightarrow \text{s}; \text{C} \rightarrow \text{p}; \text{D} \rightarrow \text{q}$
 - $\text{A} \rightarrow \text{p}; \text{B} \rightarrow \text{r}; \text{C} \rightarrow \text{q}; \text{D} \rightarrow \text{p}$
 - $\text{A} \rightarrow \text{q}; \text{B} \rightarrow \text{p}; \text{C} \rightarrow \text{r}; \text{D} \rightarrow \text{s}$
32. Match the compound in Column-I to the best technique of separation listed in Column-II.

	Column-I	Column-II
A.	Camphour containing non-volatile impurities	p. Differential extraction
B.	Impure sample of aniline	q. Sublimation
C.	Ortho and para nitro-anilines	r. Distillation
D.	Ether from ethyl alcohol	s. Chromatography

- $\text{A} \rightarrow \text{q}; \text{B} \rightarrow \text{r}; \text{C} \rightarrow \text{r}, \text{s}; \text{D} \rightarrow \text{r}$
- $\text{A} \rightarrow \text{r}; \text{B} \rightarrow \text{r}; \text{C} \rightarrow \text{r}, \text{p}; \text{D} \rightarrow \text{q}$
- $\text{A} \rightarrow \text{p}; \text{B} \rightarrow \text{q}; \text{C} \rightarrow \text{r}, \text{s}; \text{D} \rightarrow \text{s}$
- $\text{A} \rightarrow \text{r}; \text{B} \rightarrow \text{q}; \text{C} \rightarrow \text{s}, \text{p}; \text{D} \rightarrow \text{s}$

NUMERICAL TYPE QUESTIONS

33. Kjeldahl method can not be used to detect %N in which of the following compounds.



34. How many of the following elements can be tested by using Lassaigne's Test.



35. 0.1 g of an organic monobasic acid on complete combustion gave 0.254 g CO_2 and 0.0443g H_2O . For complete neutralisation 0.122 g of the acid required 10 ml of 0.1 M KOH. The molecular formula of the acid is $\text{C}_x\text{H}_6\text{O}_2$ the value of 'X' is?

36. An organic compound contain 58.52% C, 4.08% H, and 11.38% N by mass. The empirical formula of the compound is $\text{C}_6\text{H}_y\text{N}_2\text{O}$. The value Y is:

37. Among the compounds, benzene, Carbon tetrachloride, Naphthalene, Benzoic acid, Isooctane and Anthracene, how many can be purified by sublimation.

38. A compound has molar mass of 147 g. It contains 49% C and 2.72% H. On Carius estimation 2.561 mg of the compound gave 5 mg of AgCl . Calculate number of carbon atoms present in the molecular formula of compound.

Exercise-4 (Past Year Questions)

JEE MAIN

1. Which of the following reagents may be used to distinguish between phenol and benzoic acid?

(2011)

- (a) Aqueous NaOH (b) Tollen's reagent
- (c) Molish reagent (d) Aqueous NaHCO_3

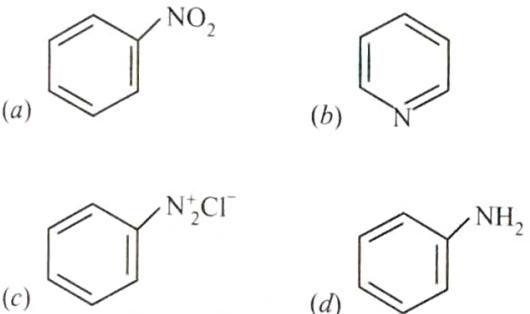
2. The distillation technique most suited for separating glycerol from spent-lye in the soap industry is:

(2016)

- (a) Distillation under reduced pressure
- (b) Simple distillation
- (c) Fractional distillation
- (d) Steam distillation

3. Which of the following compounds will be suitable for Kjeldahl's method for nitrogen estimation?

(2018)



4. The correct match between Item-I and Item-II is:

(2019)

Item-I	Item-II
(A) Benzaldehyde	(p) Mobile phase
(B) Alumina	(q) Adsorbent
(C) Acetonitrile	(r) Adsorbate
(a) (A) → (q); (B) → (p); (C) → (r)	
(b) (A) → (r); (B) → (q); (C) → (p)	
(c) (A) → (q); (B) → (r); (C) → (p)	
(d) (A) → (p); (B) → (r); (C) → (q)	

5. If dichloromethane (DCM) and water (H_2O) are used for differential extraction, which one of the following statements is correct? (2019)

- (a) DCM and H_2O would stay as lower and upper layer respectively in the S.F.
- (b) DCM and H_2O will make turbid/colloidal mixture
- (c) DCM and H_2O would stay as upper and lower layer respectively in the separating funnel (S.F.)
- (d) DCM and H_2O will be miscible clearly

6. The correct match between items I and II is: (2019)

Item – I

(Mixture)

- (A) H_2O : Sugar
- (B) H_2O : Aniline
- (C) H_2O : Toluene

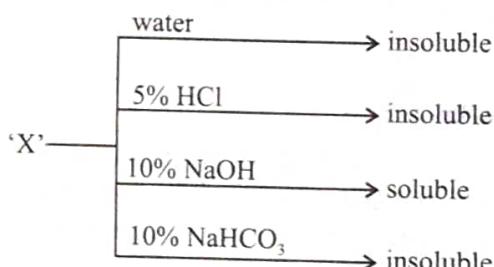
(p) Sublimation
(q) Recrystallization
(r) Steam distillation
(s) Differential extraction

- (a) (A) → (s); (B) → (r); (C) → (p)
- (b) (A) → (q); (B) → (r); (C) → (s)
- (c) (A) → (r); (B) → (p); (C) → (s)
- (d) (A) → (q); (B) → (r); (C) → (p)

7. An organic compound is estimated through Dumas method and was found to evolve 6 moles of CO_2 , 4 moles of H_2O and 1 mole of nitrogen gas. The formula of the compound is: (2019)

- (a) $\text{C}_{12}\text{H}_8\text{N}$
- (b) $\text{C}_{12}\text{H}_8\text{N}_2$
- (c) $\text{C}_6\text{H}_8\text{N}_2$
- (d) $\text{C}_6\text{H}_8\text{N}$

8. An organic compound 'X' showing the following solubility profile is: (2019)



- (a) o-Toluidine
- (b) Oleic acid
- (c) m-Cresol
- (d) Benzamide

9. The principle of column chromatography is:

(2019)

- (a) Gravitational force.
- (b) Capillary action.
- (c) Differential absorption of the substances on the solid phase.
- (d) Differential adsorption of the substances on the solid phase.

10. In chromatography, which of the following statement is INCORRECT for R_f ? (2019)

- (a) R_f value depends on the type of chromatography.
- (b) The value of R_f can not be more than one.
- (c) Higher R_f value means higher adsorption.
- (d) R_f value is dependent on the mobile phase.

11. An organic compound 'A' is oxidized with Na_2O_2 followed by boiling with HNO_3 . The resultant solution is then treated with ammonium molybdate to yield a yellow precipitate. Based on above observation, the element present in the given compound is:

- (2019)
- (a) Nitrogen
 - (b) Phosphorus
 - (c) Fluorine
 - (d) Sulphur

12. Two liquids isohexane and 3-methylpentane has boiling point 60°C and 63°C . They can be separated by

- (2020)
- (a) Simple distillation and isohexane comes out first.
 - (b) Fractional distillation and isohexane comes out first.
 - (c) Simple distillation and 3-Methylpentane comes out first.
 - (d) Fractional distillation and 3-Methylpentane comes out first.

13. Kjeldahl's method cannot be used to estimate nitrogen for which of the following compounds?

(2020)

- (a)
- (b)
- (c) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{N}$
- (d)

14. In Carius method of estimation of halogen, 0.172 g of an organic compound showed presence of 0.08 g of bromine. Which of these is the correct structure of the compound?

(2020)

- (a)
- (b)
- (c) $\text{H}_3\text{C}-\text{Br}$
- (d) $\text{H}_3\text{C}-\text{CH}_2-\text{Br}$

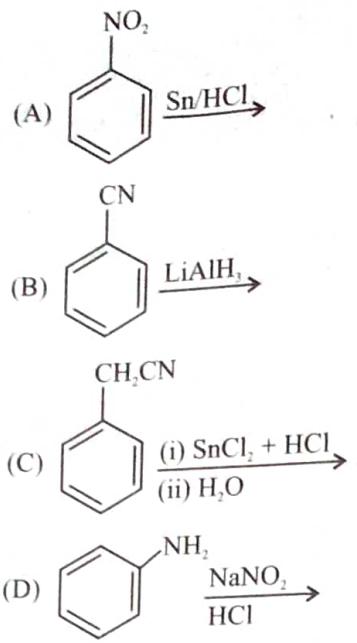
15. Glycerol is separated in soap industries by

(2020)

- (a) Fractional distillation
- (b) Differential extraction
- (c) Distillation under reduced pressure
- (d) Steam distillation

16. The Kjeldahl method of Nitrogen estimation fails for which of the following reaction products?

(2020)



- (a) (A), (C) and (D)
- (b) (A) and (D)
- (c) (C) and (D)
- (d) (B) and (C)

17. In an estimation of bromine by Carius method, 1.6 g of an organic compound gave 1.88 g of AgBr . Mass percentage of bromine in the compound is (Atomic Ag = 108, Br = 80 g mol⁻¹)

(2020)

18. Match the following:

(2020)

Test/Method	Reagent
(i) Lucas Test	(a) $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}/\text{aq. KOH}$
(ii) Dumas method	(b) $\text{HNO}_3/\text{AgNO}_3$
(iii) Kjeldahl's method	(c) CuO/CO_2
(iv) Hinsberg test	(d) Conc. HCl and ZnCl_2
	(e) H_2SO_4
(a) (i) - (b), (ii) - (d), (iii) - (e), (iv) - (a)	
(b) (i) - (d), (ii) - (c), (iii) - (e), (iv) - (a)	
(c) (i) - (b), (ii) - (a), (iii) - (c), (iv) - (d)	
(d) (i) - (d), (ii) - (c), (iii) - (b), (iv) - (e)	

19. A chromatography column, packed with silica gel as stationary phase, was used to separate a mixture of compounds consisting of (A) benzanilide (B) aniline and (C) acetophenone. When the column is eluted with a mixture of solvents, hexane : ethyl acetate (20 : 80), the sequence of obtained compounds is:

(2020)

- (a) (B), (C) and (A)
- (b) (A), (B) and (C)
- (c) (B), (A) and (C)
- (d) (C), (A) and (B)

20. Using the provided information in the following paper chromatogram: (2021)

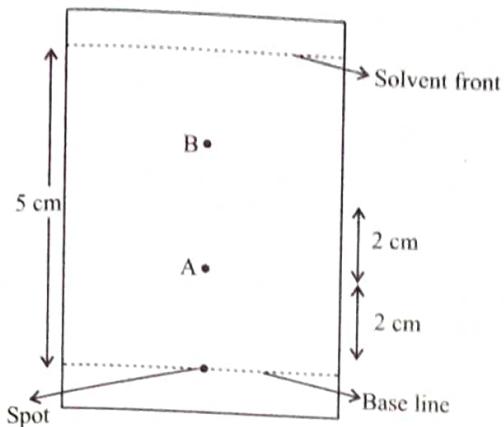


Fig: Paper chromatography for compounds A and B
The calculate R_f value of A $\times 10^{-1}$

21. Which of the following is 'a' FALSE statement? (2021)

- (a) Carius tube used in the estimation of sulphur in an organic compound.
- (b) Kjeldahl's method is used for the estimation of nitrogen in an organic compound.
- (c) Phosphoric acid produced on oxidation of phosphorus present in an organic compound is precipitated as $Mg_2P_2O_7$ by adding magnesia mixture.
- (d) Carius method is used for the estimation of nitrogen in an organic compound.

22. Given below are two statements: (2021)

Statement-I: A mixture of chloroform and aniline can be separated by simple distillation.

Statement-II: When separating aniline from a mixture of aniline and water by steam distillation aniline boils below its boiling point.

In the light of the above statements, choose the most appropriate answer from the options given below

- (a) Statement-I is true, Statement-II is false.
- (b) Both Statement-I and Statement-II are true.
- (c) Both Statement-I and Statement-II are false.
- (d) Statement-I is false, Statement-II is true.

23. Match List-I with List-II (2021)

List-I Test/Reagent/Observation		List-II Species detected	
A.	Lassaigne's Test	p.	Carbon
B.	Cu (II) oxide	q.	Sulphur
C.	Silver nitrate	r.	N, S, P, and halogen
D.	The sodium fusion extract gives black precipitate with acetic acid and lead acetate	s.	Halogen Specifically

The correct match is:

- (a) A \rightarrow p; B \rightarrow q; C \rightarrow r; D \rightarrow s
- (b) A \rightarrow p; B \rightarrow r; C \rightarrow s; D \rightarrow q
- (c) A \rightarrow r; B \rightarrow p; C \rightarrow s; D \rightarrow q
- (d) A \rightarrow s; B \rightarrow r; C \rightarrow q; D \rightarrow p

24. In Duma's method of estimation of nitrogen, 0.1840 g of an organic compound gave 30 mL of nitrogen collected at 287 K and 758 mm of Hg pressure. The percentage composition of nitrogen in the compound is (Round off to the Nearest Integer). (2021)

[Given : Aqueous tension at 287 K = 14 mm of Hg]

25. Given below are two statements:

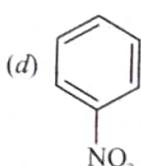
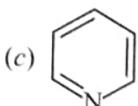
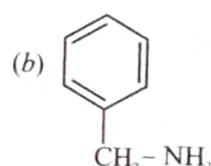
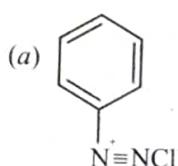
Statement-I: Retardation factor (R_f) can be measured in meter/centimeter.

Statement-II: R_f value of a compound remains constant in all solvents.

Choose the most appropriate answer from the options given below: (2021)

- (1) Statement-I is true but Statement-II is false
- (2) Both statement-I and Statement-II are true
- (3) Both statement-I and Statement-II are false
- (4) Statement-I is false but Statement-II is true

26. Nitrogen can be estimated by Kjeldah's method for which of the following compound? (2021)



27. In chromatography technique, the purification of compound is independent of: (2021)

- (a) Mobility or flow of solvent system.
- (b) Solubility of the compound.
- (c) Length of the column or TLC Plate.
- (d) Physical state of the pure compound.

28. 0.2 g of an organic compound was subjected to estimation of nitrogen by Dumas method in which volume of N_2 evolved (at STP) was found to be 22.400 mL The percentage of nitrogen in the compound is _____. [nearest integer]

(Given: Molar mass of N_2 is 28 mol^{-1} . Molar volume of at STP : 22.4 L) (2021)

29. Phenol on reaction with dilute nitric acid, gives two products. Which method will be most effective for large scale separation? (2022)

- (a) Chromatographic separation
- (b) Fractional Crystallisation
- (c) Steam distillation
- (d) Sublimation

30. Given below are two statements: one is labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A): A mixture contains benzoic acid and naphthalene. The pure benzoic acid can be separated out by the use of benzene. (2022)

Reason (R): Benzoic acid is soluble in hot water.

In the light of the above statements, choose the most appropriate answer from the options given below.

- (a) Both A and R are true and R is the correct explanation of A.
- (b) Both A and R are true but R is NOT the correct explanation of A.
- (c) A is true but R is false.
- (d) A is false but R is true.

31. Given below are two statements: (2022)

Statement-I: In 'Lassaigne's Test, when both nitrogen and sulphur are present in an organic compound, sodium thiocyanate is formed.

Statement-II: If both nitrogen and sulphur are present in an organic compound, then the excess of sodium used in sodium fusion will decompose the sodium thiocyanate formed to give NaCN and Na₂S.

In the light of the above statements, choose the most appropriate answer from the options given below:

- (a) Both Statement-I and Statement-II are correct.
- (b) Both Statement-I and Statement-II are incorrect.
- (c) Statement-I is correct but Statement-II is incorrect.
- (d) Statement-I is incorrect but Statement-II is correct.

32. Compound 'P' on nitration with dil. HNO₃ yields two isomers (A) and (B). These isomers can be separated by steam distillation. Isomers (A) and (B) show the intramolecular and intermolecular hydrogen bonding respectively. Compound (P) on reaction with conc. HNO₃ yields a yellow compound 'C', a strong acid. The number of oxygen atoms is present in compound 'C'. (2022)

33. 0.25 g of an organic compound containing chlorine gave 0.40 g of silver chloride in Carius estimation. The percentage of chlorine present in the compound is . [in nearest integer] (Given: Molar mass of Ag is 108 g mol⁻¹ and that of Cl is 35.5 g mol⁻¹) (2022)

34. Which one of the following techniques is not used to spot components of a mixture separated on thin layer chromatographic plate? (2022)

- (a) I₂ (Solid)
- (b) U.V. Light
- (c) Visualisation agent as a component of mobile phase
- (d) Spraying of an appropriate reagent.

35. The formula of the purple colour formed in Lassaigne's test for sulphur using sodium nitroprusside is (2022)

- (a) NaFe[Fe(CN)₆]²⁻
- (b) Na[Cr(NH₃)₂(NCS)₄]⁺
- (c) Na₂[Fe(CN)₅(NO)]³⁻
- (d) Na₄[Fe(CN)₅(NOS)]⁴⁻

36. In the estimation of bromine, 0.5 g of an organic compound gave 0.40 g of silver bromide. The percentage of bromine in the given compound is (nearest integer) (Relative atomic masses of Ag and Br are 108 u and 80 u, respectively). (2022)

37. Kjeldahl's method was used for the estimation of nitrogen in an organic compound. The ammonia evolved from 0.55 g of the compound neutralised 12.5 mL of 1 M H₂SO₄ solution. The percentage of nitrogen in the compound is . (Nearest integer) (2022)

38. While estimating the nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.25 g of the compound neutralized 2.5 mL of 2 M H₂SO₄. The percentage of nitrogen present in organic compound is. (2022)

39. The separation of two coloured substances was done by paper chromatography. The distances travelled by solvent, substance A and substance B from the base line are 3.25 cm, 2.08 cm and 1.05 cm, respectively. The ratio of R_f values of A to B is (2022)

40. Which technique among the following, is most appropriate in separation of a mixture of 100 mg of p-nitrophenol and picric acid? (2022)

- (a) Steam distillation
- (b) 2-5 ft long column of silica gel
- (c) Sublimation
- (d) Preparative TLC (Thin Layer Chromatography)

41. In Carius method of estimation of halogen, 0.45g of an organic compound gave 0.36 g of AgBr. Find out the percentage of bromine in the compound. (2022)

(Molar masses : AgBr = 188 g mol⁻¹ : Br = 80 g mol⁻¹)

- (a) 34.04%
- (b) 40.04%
- (c) 36.03%
- (d) 38.04%

42. Match List-I with List-II

List-I (Mixture)

- (A) Chloroform and Aniline
- (B) Benzoic acid and Naphthalene
- (C) Water and Aniline
- (D) Naphthalene & Sodium chloride

List-II (Purification Process)

- (I) Steam distillation
 - (II) Sublimation
 - (III) Distillation
 - (IV) Crystallisation
- (a) (A)-(IV), (B)-(III), (C)-(I), (D)-(II)
 - (b) (A)-(III), (B)-(I), (C)-(IV), (D)-(II)
 - (c) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)
 - (d) (A)-(III), (B)-(IV), (C)-(I), (D)-(II)

43. Given below are two statements: One is labelled as Assertion (A) and the other is labelled as Reason (R)

Assertion (A) : Thin layer chromatography is an adsorption chromatography.

(2022)

Reason (R) : A thin layer of silica gel is spread over a glass plate of suitable size in thin layer chromatography which acts as an adsorbent.

In the light of the above statements, choose the correct answer from the options given below

(2022)

- (a) Both A and R are true and R is the correct explanation of A.
- (b) Both A and R are true but R is NOT the correct explanation of A.
- (c) A is true but R is false.
- (d) A is false but R is true.

44. A sample of 0.125 g of an organic compound when analysed by Duma's method yields 22.78 mL of nitrogen gas collected over KOH solution at 280 K and 759 mmHg. The percentage of nitrogen in the given organic compound is (Nearest integer).

(2022)

Given,

- (a) The vapour pressure of water at 280 K is 14.2 mmHg
- (b) $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$

ANSWER KEY

CONCEPT APPLICATION

1. (b) 2. (a) 3. (d) 4. (d) 5. (c) 6. (b) 7. (a) 8. (b) 9. (d) 10. (a)

EXERCISE-1 (TOPICWISE)

1. (d) 2. (c) 3. (c) 4. (d) 5. (b) 6. (d) 7. (b) 8. (d) 9. (d) 10. (c)
11. (b) 12. (d) 13. (c) 14. (a) 15. (b) 16. (d) 17. (c) 18. (b) 19. (c) 20. (a)
21. (d) 22. (a) 23. (a) 24. (b) 25. (c) 26. (b) 27. (c) 28. (a) 29. (c)

EXERCISE-2 (LEARNING PLUS)

1. (b) 2. (a) 3. (a) 4. (b) 5. (d) 6. (b) 7. (b) 8. (b) 9. (b) 10. (b)
11. (a) 12. (d) 13. (c) 14. (b) 15. (c) 16. (a) 17. (a) 18. (b) 19. (b) 20. (d)
21. (a) 22. (a) 23. (b) 24. (a) 25. (b) 26. (a) 27. (d) 28. (b) 29. (c) 30. (c)
31. (b) 32. (b) 33. (d) 34. (c) 35. (c)

EXERCISE-3 (JEE ADVANCED LEVEL)

1. (a) 2. (d) 3. (b) 4. (c) 5. (d) 6. (d) 7. (c) 8. (d) 9. (c) 10. (a)
11. (b,c,d) 12. (b) 13. (b) 14. (a,b,d) 15. (a,b,c) 16. (a,b,d) 17. (a,b,d) 18. (b,c,d) 19. (a,b,d) 20. (b,c)
21. (a,d) 22. (a,b,c,d) 23. (a,b,c) 24. (a,b) 25. (c) 26. (a,c,d) 27. (b) 28. (c) 29. (d) 30. (a)
31. (a) 32. (a) 33. [4] 34. [5] 35. [7] 36. [5] 37. [3] 38. [6]

EXERCISE-4 (PAST YEAR QUESTIONS)

JEE Main

1. (d) 2. (a) 3. (d) 4. (b) 5. (a) 6. (b) 7. (c) 8. (c) 9. (d) 10. (c)
11. (b) 12. (b) 13. (a) 14. (a) 15. (c) 16. (c) 17. [50] 18. (b) 19. (d) 20. [0.4]
21. (d) 22. (b) 23. (c) 24. [19] 25. [3] 26. (b) 27. (d) 28. [14] 29. (c) 30. (d)
31. (a) 32. [7] 33. [40] 34. (c) 35. (d) 36. [34] 37. [64] 38. [56] 39. [2] 40. (d)
41. (a) 42. (d) 43. (a) 44. [22]