

# Introduction to Organic Chemistry

## STRUCTURAL FORMULAE

## Section - 1

We have already discussed that carbon has tetravalency and the formation of covalent bonds by it is explained in terms of its electronic configuration and the hybridization of  $s$  and  $p$  orbitals. It may be recalled that formation and shapes of molecules like Methane ( $\text{CH}_4$ ), Ethene ( $\text{C}_2\text{H}_4$ ), and Ethyne ( $\text{C}_2\text{H}_2$ ) were explained in the terms of  $sp^3$ ,  $sp^2$ , and  $sp$  hybridization of the respective carbon atoms.

Organic chemists use a variety of ways to represent structural formulae for an organic compound. The most common types of representations are shown below.

### Dot Structure (Lewis Structure)

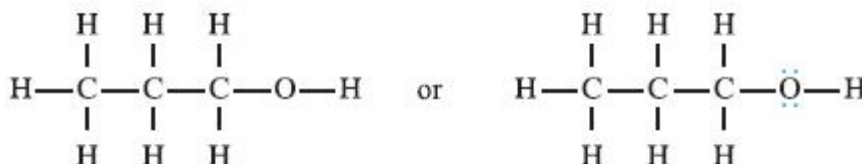
This shows all of the valence electrons, For example, given below is the dot structure of n-propyl alcohol.



Writing dot structure is tedious and time consuming. The other representations are more convenient and are, therefore, most often used.

### Dash Structural Formula

Here, the pair of two electrons forming the covalent bond is represented by a dash. A single dash represents a single bond, double dash is used for double bond and a triple dash represents a triple bond. The lone pair of electrons on hetero-atoms like oxygen, nitrogen, sulphur, halogens, etc. may or may not be shown. Given below is the dash structure of n-propyl alcohol.



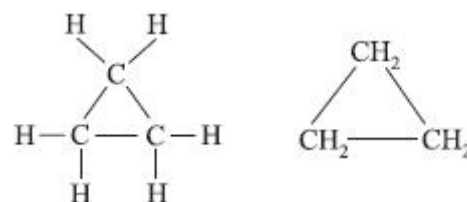
### Condensed Structural Formula

Condensed structural formulae are easier to write than dash formulae and, when we become familiar with them, they will impart all the information that is contained in the dash structure. In the condensed formula, all the atoms bonded to a carbon atom are written after 'C' in the same line but their bonds are shown. Identical group are omitted by indicating their number as a subscript. The atoms or groups other than hydrogen are written after the hydrogen atom. (in brackets)

Given below is the condensed formulae for n-propyl alcohol and isopropyl alcohol.

$\text{CH}_3(\text{CH}_2)_2\text{OH}$	<i>n</i> -Propyl alcohol
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	Isopropyl alcohol
$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	<i>n</i> -Hexane

**Note:** The carbon atoms in organic compounds may also be arranged in rings (Cyclic compounds). For example : cyclopropane, whose structural formula is given alongside.



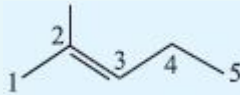
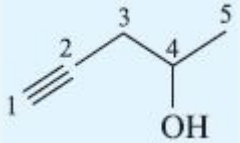
### Bond-Line Formula

A very simplified formula called Bond-line formula can also be used to represent structures of organic compounds. In this representation, the C and H atoms are not shown; the chain of carbon atoms is represented by a zig-zag line. Each intersection of 2 or more lines (junction) and the end of a line represent a carbon atom. Hetero-atoms (other than carbon and hydrogen) or functional groups are specifically written. Hydrogen atoms necessary to fulfil the valence of carbon atoms is assumed to be present.

Bond line formulas are very frequently used for cyclic compounds.

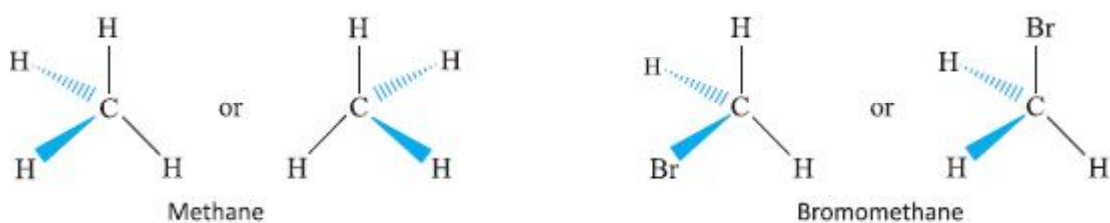
Condensed formula	Bond line formula
$\text{CH}_3\text{CH}_2\text{CH}_3$	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	

Multiple bonds are also included in bond-line formula. For example :

Condensed formula	Bond line formula
$  \begin{array}{c}  \text{1} \quad \text{2} \quad \text{3} \quad \text{4} \quad \text{5} \\  \text{CH}_3 - \text{C} = \text{CH} - \text{CH}_2 - \text{CH}_3 \\    \\  \text{CH}_3  \end{array}  $	
$  \begin{array}{c}  \text{1} \quad \text{2} \quad \text{3} \quad \text{4} \quad \text{5} \\  \text{HC} \equiv \text{C} - \text{CH}_2\text{CH}(\text{OH})\text{CH}_3  \end{array}  $	

### Three-Dimensional Representation

None of the formulae that we have described so far conveys any information about how the atoms of a molecule are arranged in space. There are several ways to represent the three dimensional structure of the organic molecule on paper. For example: by using a solid and dashed wedge formula, the three dimensional image of a molecule from a two dimensional picture can be perceived. In this representation, bonds that project upwards out of the plane of the paper are indicated by a solid wedge (▶), those that lie behind the plane are indicated with a dashed wedge (◄), and those bonds that lie in the plane of the paper are indicated by a line (—). Wedges are shown in such a way that the broad end of the wedge is towards the observer. Generally, we only use three-dimensional formulae when it is necessary to convey information about the shape of the molecule.

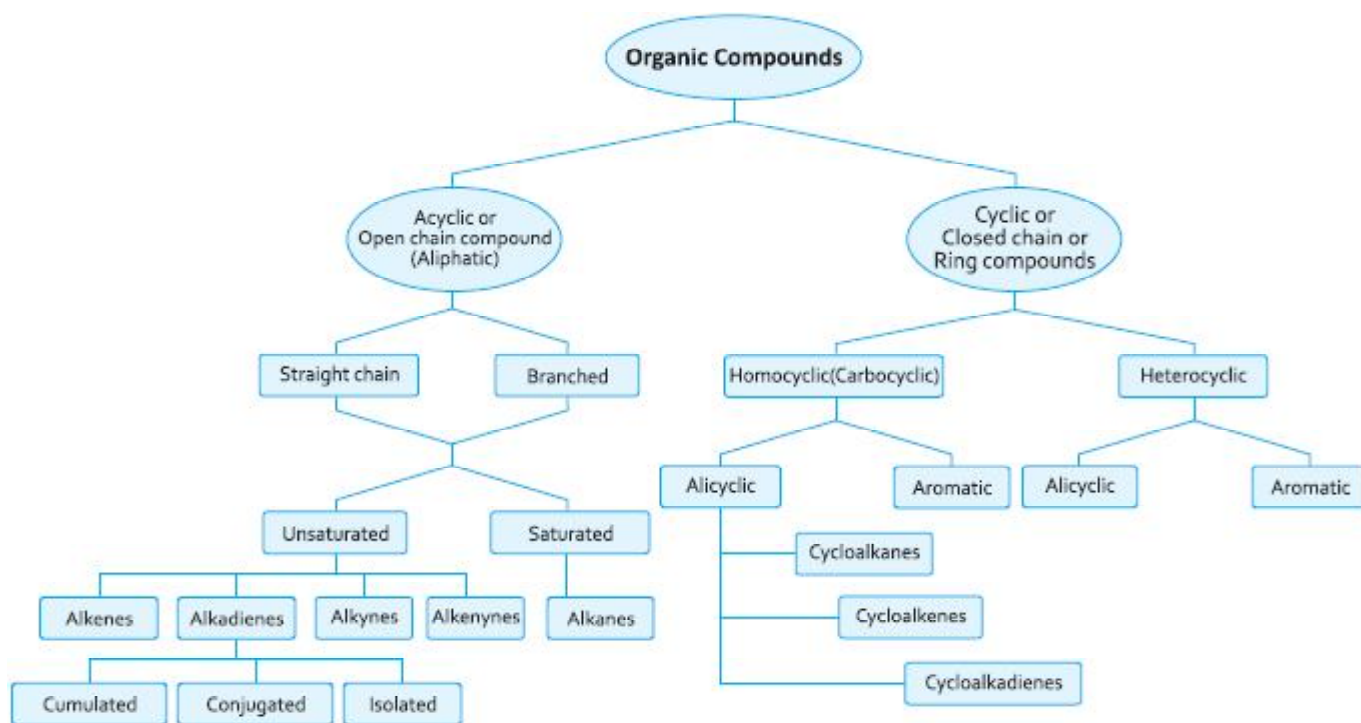


Wedge and Dash Representation

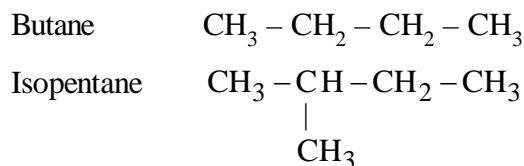
## CLASSIFICATION OF ORGANIC COMPOUNDS

## Section - 2

Based upon the nature of carbon atom skeleton, the organic compounds have been classified into two categories : **Acyclic or Open Chain** and **Cyclic or Closed chain**.



- I. **Open Chain or Acyclic Compounds :** Compounds of carbon having open chain of carbon atoms, branched or unbranched are called acyclic compounds.



Open chain compounds are also known as **aliphatic compounds** since the earlier compounds of this class were obtained either from animals or vegetable fats. (Greek, aliphatos  $\equiv$  fats).

- II. **Cyclic or Closed Chain or Ring Compounds :** Compounds of carbon having closed chain of carbon as well as of other atoms are called cyclic compounds. Depending upon the constitution of the ring, these are further divided into the following categories.

1. Homocyclic or carbocyclic compounds      2. Heterocyclic compounds

1. **Carbocyclic or Homocyclic Compounds :** Compounds of carbon having closed chain entirely made up of carbon atoms are called carbocyclic or homocyclic compounds. These are further divided into two groups.

- (i) **Alicyclic Compounds :** Closed carbon chains except characteristic benzene ring, resembling in properties with acyclic compounds. These include cycloalkanes, cycloalkenes and cycloalkadienes.

For e.g.,



- (ii) **Aromatic Compounds :** Closed chain of only carbon atoms with alternate single and double bonds. Benzene and its derivatives belong to this category. Some important examples of monocyclic, bicyclic and tricyclic aromatic compounds are as follows.

- (a) Monocyclic aromatic compounds :



- (b) Bicyclic and Tricyclic aromatic compounds :

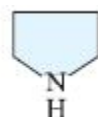


2. **Heterocyclic compounds** : Compounds of carbon having closed chain made up of carbon and other atoms. The hetero atoms commonly found in these compounds are oxygen, nitrogen and sulphur and occasionally, phosphorus, boron, silicon and some metal atoms like tin, selenium etc, may also be present. Depending upon the chemical behaviour, these are further classified into the following two categories.

- (i) **Alicyclic heterocyclic compounds** : Alicyclic compounds containing one or more heteroatoms in their rings are called alicyclic heterocyclic compounds. For example:



Tetrahydro Furan  
(THF)



Pyrrolidine



Pyran

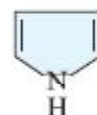
- (ii) **Aromatic heterocyclic compounds** : Aromatic cyclic compounds containing one or more heteroatoms in their molecules are called aromatic heterocyclic compounds. For example :



Pyridine



Furan



Pyrrole

**Note:** An aliphatic compound burns with non-smoky flame (except  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ). All aromatic compounds burn with a smoky flame.

## NOMENCLATURE OF ORGANIC COMPOUNDS

### Section - 3

The IUPAC (International Union of Pure and Applied Chemistry) has developed a systematic method of naming organic compounds. This system gives a unique IUPAC name to every organic compound. However before the IUPAC system came into existence, the trivial or common names for organic compounds were used. These were based on their origin or certain properties. Some examples are as follows : (Please note that the contents of following table are NOT to be memorised).

Compound	Trivial Name	Source of Compound
$\text{CH}_3\text{OH}$	Wood spirit	Obtained by destructive distillation of wood
$\text{CH}_3\text{OH}$	Methyl alcohol	Methu-spirit and hule-wood
$\text{NH}_2\text{CONH}_2$	Urea	Obtained from urine
$\text{CH}_3\text{COOH}$	Acetic acid	Obtained from Acetum-vinegar
$(\text{COOH})_2$	Oxalic acid	Obtained from oxalis plant
$\text{HCOOH}$	Formic acid	Obtained from ants, in Latin Ants $\equiv$ Formicae.
$\text{C}_2\text{H}_5\text{OH}$	Grain alcohol (Ethanol)	Obtained by fermentation of grains.

These older names for organic compounds are still widely used by chemists and bio-chemists, and in commerce. For this reason it is necessary to learn the common names (Trivial Names) for some of the organic compounds.

## Trivial System Of Nomenclature

### Classification of carbon atoms :

In trivial system of naming an organic compound, the carbon atoms of an alkane were classified on the basis of the number of other carbon atoms attached to them, into four categories, viz., Primary carbon atoms, Secondary carbon atoms, Tertiary carbon atoms and Quarternary carbon atoms.

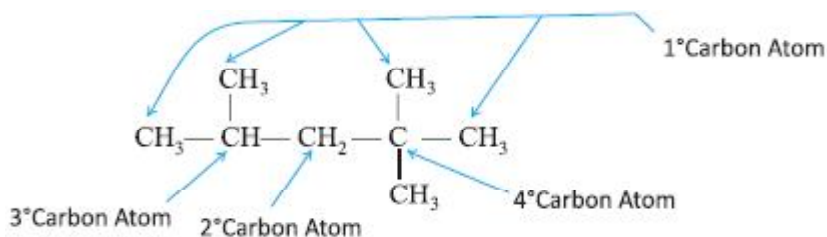
**Primary carbon atom :** When a carbon atom is attached to one carbon atom, then it is primary carbon atom or  $1^\circ$  carbon atom.

**Secondary carbon atom :** When a carbon atom is attached to two carbon atoms, then it is secondary carbon atom or  $2^\circ$  carbon atom.

**Tertiary carbon atom :** When a carbon atom is attached to three carbon atoms, then it is tertiary carbon atom or  $3^\circ$  carbon atom.

**Quaternary carbon atom :** When a carbon atom is attached to four carbon atoms, then it is quaternary carbon atom or  $4^\circ$  carbon atom.

Consider following structure showing all four types of carbons.



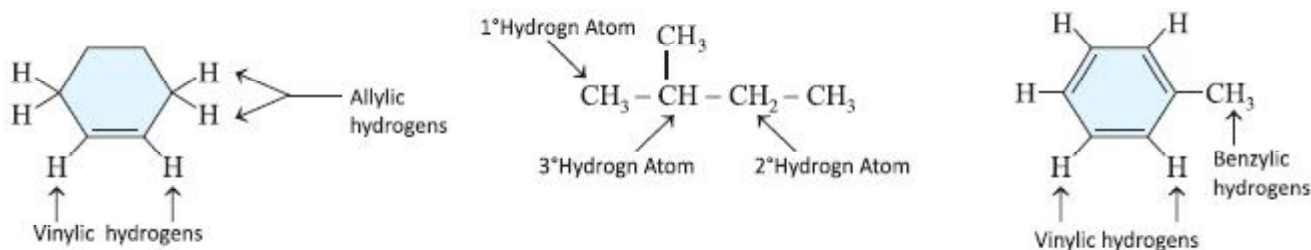
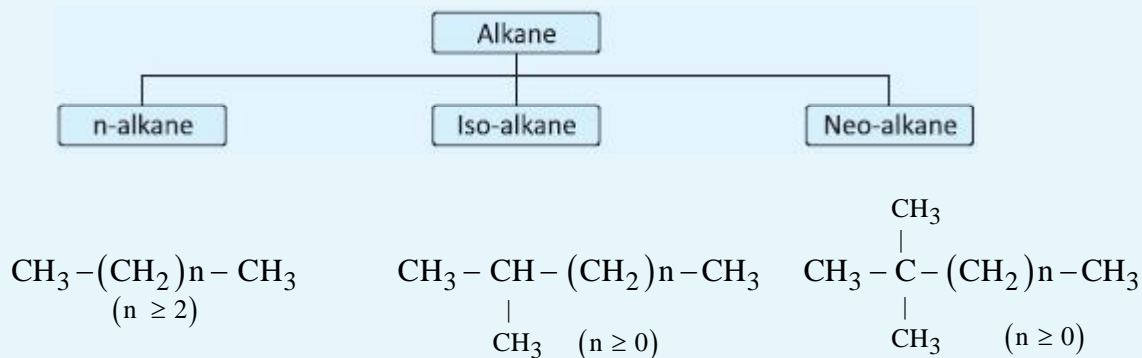
**Vinylic Carbon atom :** Carbon atom of  $\text{C}=\text{C}$  is called as vinylic carbon atom.

**Allylic Carbon atom :**  $\text{sp}^3$  hybridized Carbon atom next to  $\text{C}=\text{C}$  is called as allylic carbon atom.

**Benzylic Carbon atom :** Carbon atom directly bonded to benzene ring is called as benzylic carbon atom.

### Classification of Hydrogen atoms :

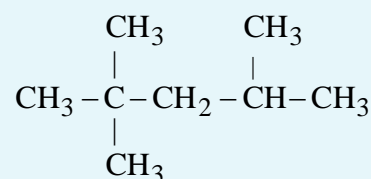
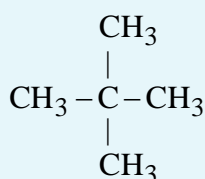
The hydrogen atoms of a  $\text{sp}^3$  carbon are classified on the basis of the carbon atoms to which they are attached. A hydrogen atom attached to a primary carbon atom is a primary hydrogen atom, hydrogen atom attached to a secondary carbon atom is secondary hydrogen atom and so forth. But there are no quaternary hydrogen atoms as no hydrogen atom is attached to a quaternary carbon atom.

**Note :**

**Normal ( $n$ )** stand for unbranched chain of carbon atoms. **Iso** indicate one  $\text{CH}_3$ -side chain on second carbon atom of the chain. **Neo** indicate two  $\text{CH}_3$ -side chains on second carbon atom of the chain.

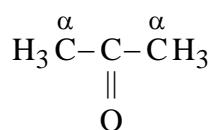
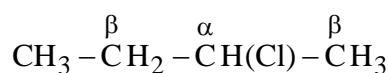
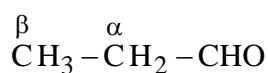
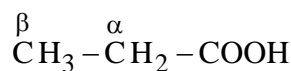
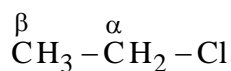
**Note:** Neopentane has only primary hydrogen atoms.

**Note:** Isooctane has different structure.



### $\alpha$ - Carbon and $\beta$ - Carbon atoms :

Carbon atom in the structure of compound to which a functional group ( $-\text{OH}$ ,  $-\text{CHO}$ ,  $\text{Cl}$ , . . . . . etc.) is attached is known as  $\alpha$  - carbon and the corresponding hydrogen is referred to as  $\alpha$  - hydrogen. The carbon atom(s) adjacent to  $\alpha$  - carbon is known as  $\beta$  - carbon(s).



$\text{HCHO}$       No  $\alpha$  - Carbon and no  $\alpha$  - Hydrogen



## IUPAC System of Nomenclature

The formal system of nomenclature used today is one proposed by the International Union of Pure and Applied Chemistry (IUPAC). This system was first developed in 1892 and has been revised at regular intervals to keep it up to date. The principle of IUPAC system is: *Each different compound should have a different name.*

The IUPAC nomenclature involves the use of following terms :

1. Word root      2. Primary suffix      3. Secondary suffix      4. Prefix

1. **Word Root :** The word root represents the *number of carbon atoms in the parent chain*. For the chains up to four carbon atoms special word roots are used whereas words (pent, hex, hept...etc.) indicating the number of carbons in the chain are used for the compounds containing more than four carbon atoms.

Some (straight) unbranched chains and their names :

Name	Number of C -Atoms	Structure	Name	Number of C -Atoms	Structure
Methane	1	CH <sub>4</sub>	Octane	8	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>
Ethane	2	CH <sub>3</sub> CH <sub>3</sub>	Nonane	9	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>
Propane	3	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	Decane	10	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>
Butane	4	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	Undecane	11	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> CH <sub>3</sub>
Pentane	5	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	Dodecane	12	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub>
Hexane	6	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	Tridecane	13	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> CH <sub>3</sub>
Heptane	7	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	Tetradecane	14	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> CH <sub>3</sub>

The word root of different carbon chains are obtained by leaving 'ane' from the name of the carbon chain of the respective molecule. Some word roots are given below :

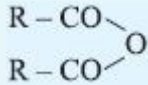
Chain Length	Word Root	Chain Length	Word Root
C <sub>1</sub>	Meth –	C <sub>7</sub>	Hept (a) –
C <sub>2</sub>	Eth –	C <sub>8</sub>	Oct (a)–
C <sub>3</sub>	Prop (a) –	C <sub>9</sub>	Non (a) –
C <sub>4</sub>	But (a) –	C <sub>10</sub>	Dec (a)–
C <sub>5</sub>	Pent (a) –	C <sub>11</sub>	Undec (a) –
C <sub>6</sub>	Hex (a) –	C <sub>12</sub>	Dodec (a) –

**Note:** Extra 'a' given in parenthesis is used only if the primary suffix (explained later) to be added to the word root begins with a consonant (except y). In general, the word root for any carbon chain is alk.

2. **Primary Suffix :** Primary suffix is used to indicate *saturation or unsaturation in the carbon chain*. While writing the name, primary suffix is added to the word root. Some of the primary suffixes are given below in the following table.

Nature of Carbon Chain	Primary Suffix
Saturated Carbon Chain	ane
Unsaturated Carbon Chains	
One C=C bond	ene
Two C=C bonds	diene
Three C=C bonds	triene
One C≡C bond	yne
Two C≡C bonds	diyne

3. **Secondary Suffix :** Secondary suffix is used to indicate the *functional group in the organic compound*. It is added to the primary suffix by dropping its terminal 'e'. Secondary suffixes for various functional groups are given in the following table.

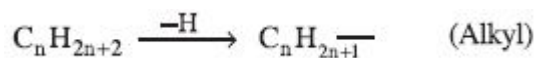
Family of Compound	General Formula	Functional Group	Secondary Suffix	IUPAC name of the family (Saturated)
Alcohols	R-OH	-OH	-ol	alkanol
Thioalcohols	R-SH	-SH	-thiol	alkanethiol
Amines	R-NH <sub>2</sub>	-NH <sub>2</sub>	-amine	alkanamine
Aldehydes	R-CHO	-CHO	-al	alkanal
Ketones	R-COR	>C=O	-one	alkanone
Sulphonic Acids	R-SO <sub>3</sub> H	-SO <sub>3</sub> H	-sulphonic	alkane sulphonic acid
Anhydrides		-(CO) <sub>2</sub> O	-oic anhydride	alkanoic anhydride
Carboxylic acids	R-COOH	-COOH	-oic	alkanoic acid
Amides	R-CONH <sub>2</sub>	-CONH <sub>2</sub>	-amide	alkanamide
Acid chlorides	R-COCl	-COCl	-oyl	alkanoyl chloride
Esters	R-COOR	-COOR	-oate	alkyl alkanoate
Nitriles	R-C≡N	-C≡N	-nitrile	alkane nitrile

In addition to these some functional groups are represented as prefixes. They are discussed later

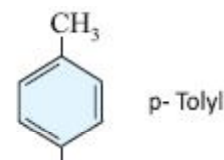
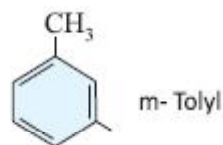
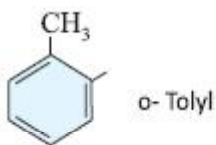
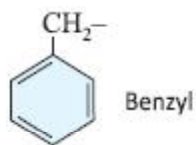
- Note:** (i) If the name of the secondary suffix begins with a consonant (except y), the terminal 'e' of the primary suffix is retained while adding secondary suffix to it. For example : Thioalcohols have secondary suffix thiol and thus 'e' of ane should not be dropped, i.e., IUPAC name is Alkane -thiol.
- (ii) The terminal 'e' of primary suffix is also retained if some numerical prefixes like di, tri etc. are used before the secondary suffix.

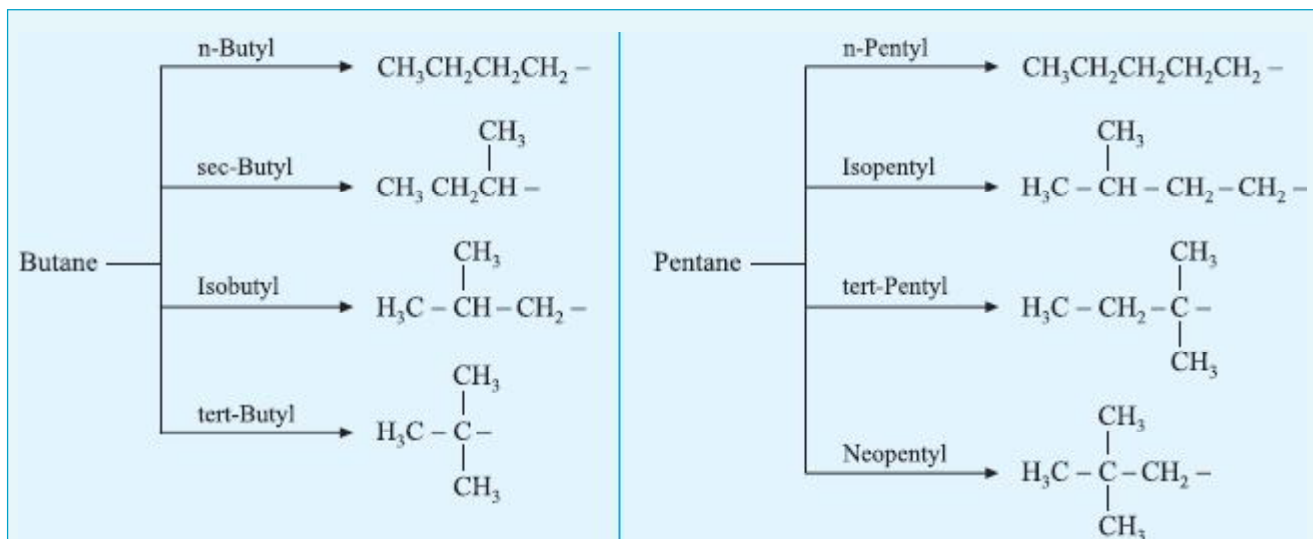
4. **Prefix :** The part of the name which appears before the word root is called prefix. Different prefixes are used for different categories of groups present in molecule.

(i) **Alkyl Groups :** The univalent groups or radicals obtained by the removal of one H atom from a molecule of paraffin are called alkyl groups. These alkyl groups have names that end in -yl. The symbol 'R' is often used to represent an alkyl group. Some alkyl groups with their prefixes are given in the following table.




Alkane	Alkyl Group	Abbreviation	Prefix
CH <sub>4</sub> (Methyl)	CH <sub>3</sub> –	Me–	Methyl
C <sub>2</sub> H <sub>6</sub> (Ethyl)	CH <sub>3</sub> CH <sub>2</sub> –	Et–	Ethyl
C <sub>3</sub> H <sub>8</sub> (n – Propyl)	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> –	n–Pr–	n–Propyl
C <sub>3</sub> H <sub>8</sub> (Isopropyl)	$\begin{array}{c} \text{CH}_3 - \text{CH} - \\   \\ \text{CH}_3 \end{array}$	iso–Pr–	Isopropyl or (1 – Methylethyl)
C <sub>2</sub> H <sub>4</sub> (Ethene)	CH <sub>2</sub> = CH–	-	Vinyl (Ethenyl)
C <sub>3</sub> H <sub>6</sub> (Propene)	CH <sub>2</sub> = CH-CH <sub>2</sub> -	-	Allyl
C <sub>6</sub> H <sub>6</sub> (Benzene)	C <sub>6</sub> H <sub>5</sub> -	Ph-	Phenyl





- (ii) Some functional Groups are always indicated by prefixes instead of secondary suffixes. These with their prefixes are given in the following table.

Functional Group	Prefix	Family	IUPAC Name
$-\text{NO}_2$	Nitro	$\text{R}-\text{NO}_2$	Nitroalkane
$-\text{OR}'$	Alkoxy	$\text{R}-\text{OR}'$	Alkoxyalkane
$-\text{Cl}$	Chloro	$\text{R}-\text{Cl}$	Chloroalkane
$-\text{Br}$	Bromo	$\text{R}-\text{Br}$	Bromoalkane
$-\text{I}$	Iodo	$\text{R}-\text{I}$	Iodoalkane
$-\text{F}$	Fluoro	$\text{R}-\text{F}$	Fluoroalkane
$-\text{N} = \text{O}$	Nitroso	$\text{R}-\text{NO}$	Nitrosoalkane
	epoxy		epoxyalkane

- (iii) In polyfunctional compounds (compounds with more than one functional groups), one of the functional groups is treated as principal functional group and is indicated by the secondary suffix whereas other functional groups, treated as substituents, are indicated by the prefixes. The order of priority among various functional groups to be treated as principal functional group has been discussed later in this chapter. The prefixes for various functional groups are given in the following table.

Prefixes for functional groups in polyfunctional compounds

Functional Group	Prefix	Functional Group	Prefix
–OH	Hydroxy	–COOH	Carboxy
–CN	Cyano	–COOR	Carbalkoxy
–NC	Isocyano	–COX	Haloformyl
–CHO	Formyl	–CONH <sub>2</sub>	Carbamyl
–SH	Mercapto	–NH <sub>2</sub>	Amino
–SR	Alkylthio	=NH	Imino
–NHR	alkylamino	–NR <sub>2</sub>	dialkylamino
–SO <sub>3</sub> H	sulpho	>C = O	keto / oxo

### Writing the IUPAC name of Organic Compounds :

While writing the IUPAC name of a compound word root, prefix, primary suffix, secondary suffix, follow the order:

Prefix(es) + Word root + Primary suffix + Secondary suffix

The above arrangement is illustrated by the following examples :

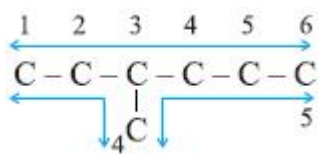
Compound	Prefix	Word root	P. suffix	Sec. suffix	IUPAC Name
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2\text{OH} \\   \\ \text{CH}_3 \end{array}$	Methyl	but	an	ol	3-Methylbutane-1-ol
$\begin{array}{c} \text{CH}_3-\text{C}=\text{CHOH} \\   \\ \text{Br} \end{array}$	Bromo	prop	en	ol	2-Bromoprop-1-en-1-ol

## The Rules for naming Organic Compounds :

### I. For Saturated Compounds

#### 1. Selection of longest chain :

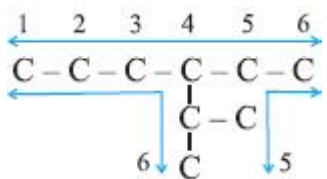
- The longest possible carbon chain is selected and the compound is named as derivative of hydrocarbon using word root.



The chain of 6 carbon atoms is *selected*.

- If more than one sets of longest possible chains are there, the selected longest chain should have :

- Maximum number of side chains or
- Minimum number of branched side chains



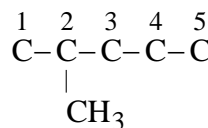
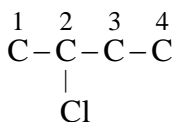
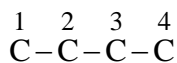
6 atoms chain with one side chain or one branched side chain is *rejected*.

6 atoms chain with two side chains or two unbranched side chains is *selected*.

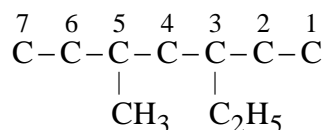
#### 2. Numbering of selected chain :

The selected chain is numbered from one end to other. The numbers are called *locants*.

- Lowest number is assigned to first side chain (alkyl groups) or substituent group.

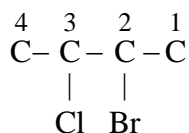
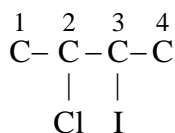


- If two different alkyl groups are at same position from opposite ends, lowest number is given to the one coming first in alphabetical listing.

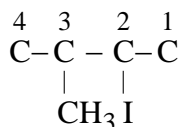


Note that ethyl gets '3' as the locant, not methyl.

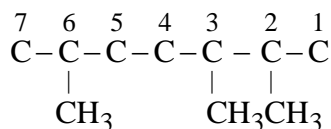
- If two different substituents are at same position from opposite ends, lowest number is assigned in order of their alphabets.



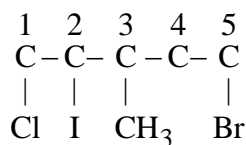
- If a substituent (such as halogen, or nitro group) and a side chain are at same position from opposite ends, lowest number is assigned to substituents.



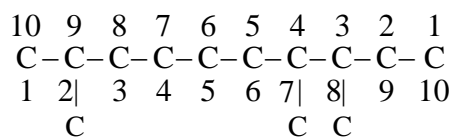
- If more than two substituents and side chains are present, then the set of locants are compared term by term, and that set is preferred which gets the least term at the first point of difference. This is the lowest set of locants rule.



2, 3, 6 is *accepted*.  
2, 5, 6 is *rejected*.



1, 2, 3, 5 is *accepted*.  
1, 3, 4, 5 is *rejected*.

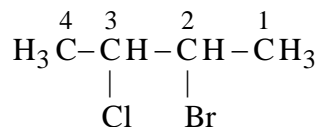


2, 7, 8 is *accepted*.  
3, 4, 9 is *rejected*.

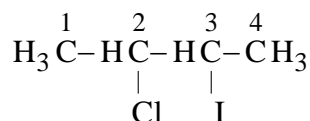


### 3. Arrangement of prefixes :

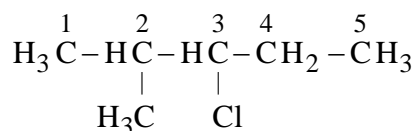
- Alkyl nature of side chain or substituent group is identified and reported as prefix with its number (locant) in hydrocarbon name in alphabetic order.



2-Bromo-3-chlorobutane

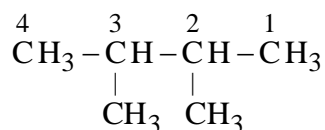


2-Chloro-3-iodobutane



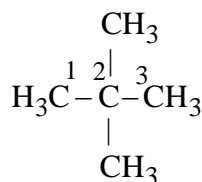
3-Chloro-2-methylpentane

- If more than one similar alkyl chains or substituents are present, prefix names are modified by putting di, tri....terms.



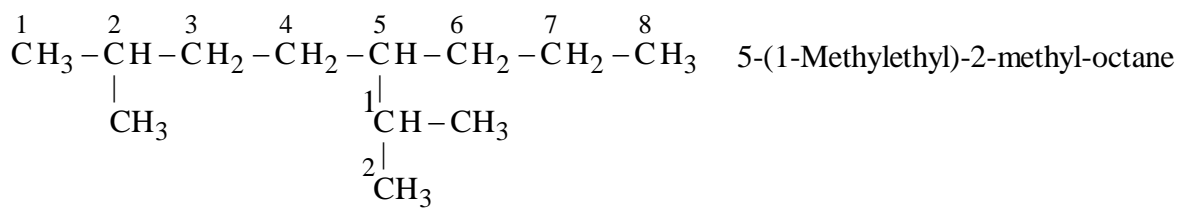
2, 3-Dimethylbutane

- If more than one similar alkyl groups or substituents are present at same position, their locant is also repeated.

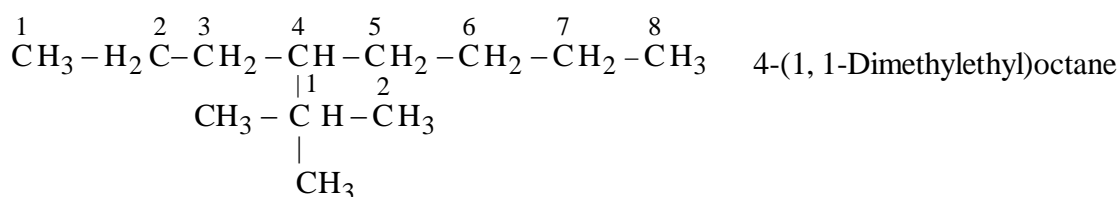


2, 2-Dimethylpropane

- In case side chain is also branched, it is numbered from the carbon atom attached to main chain and is generally written in brackets.

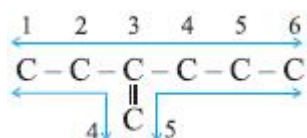


5-(1-Methylethyl)-2-methyl-octane



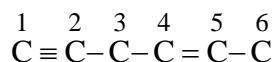
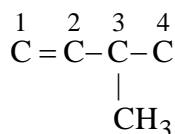
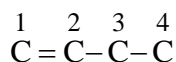
## II. For Unsaturated Hydrocarbons

1. Select the longest possible carbon chain having maximum number of unsaturated carbon atoms or maximum number of double or triple bonds, even if prior rule is violated.



5 carbon atoms chain with two unsaturated carbons or one double bond is *selected*.

2. Lowest number (locant) is assigned to first unsaturated carbon even if prior rule is violated.



3. In case of unsaturation suffix, name of unsaturation is used with hydrocarbon name, i.e.

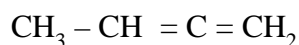
$\text{C} = \text{C}$  bond

ane of hydrocarbon is replaced by ene.

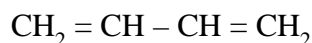
$\text{C} \equiv \text{C}$  bond

ane of hydrocarbon is replaced by yne.

4. In case of more than one double bonds we use di, tri etc. For example: diene or triene.

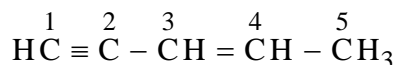


Buta-1, 2-diene



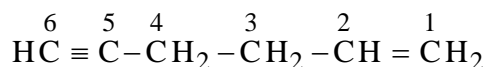
Buta-1, 3-diene

5. If a compound contains both the unsaturations then compound is named as *Alkenyne* with numbering as low as possible given to multiple bonds, following the lowest set of locant rule.



Pent-3-en-1-yne

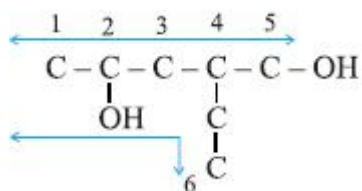
If there is a choice i.e. when the double bond and the triple bond are at the same distance from the two ends then the double bond gets the preference over the triple bond in the numbering.



Hex-1-en-5-yne

### III. For Functional Groups

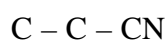
1. Select the longest possible carbon chain having maximum number of functional groups even if prior rules are violated, For example :



5 carbon chain inclusive of two functional groups is selected

2-ethylpentane-1, 4-diol

2. When the functional group itself contains a C atom, then the carbon atom of functional group is to be included in deciding the longest carbon chain.

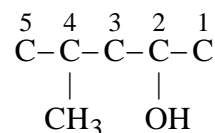
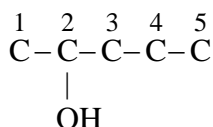
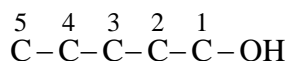


3 carbon chain, i.e., C atom of cyanide is also included.



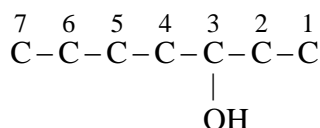
4 carbon chain, i.e., C atom of aldehyde is also included.

3. The lowest number (locant) is assigned to the functional group even if prior rules are violated.

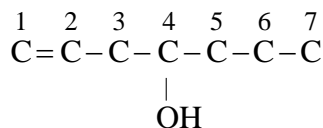


4. The order for numbering a carbon chain, thus follows the order :

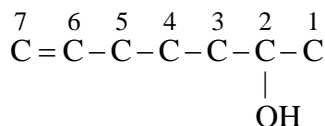
Functional Group then Unsaturation then Substituents and Side chains (or alkyl groups)



Lowest number to OH group.



OH is at equidistant from two ends and thus next lowest number to unsaturations.



Lowest locant to OH group (not to double bond).

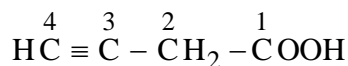
### IUPAC names of some families of Organic Compounds :

1. **Carboxylic Acids** : The IUPAC name of acids is derived from the name of the corresponding alkane by dropping the ending –e and putting the suffix –oic acid.

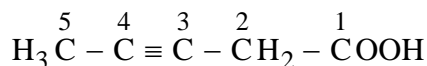
HCOOH  
Methanoic acid

CH<sub>3</sub>COOH  
Ethanoic acid

The position of the substituent is indicated by the usual numerals

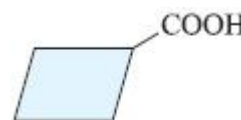


But-3-yn-1-oic acid



Pent-3-ynoic acid

The cyclic acids cannot be named in this manner. To name them, the name of the corresponding cycloalkane precedes the word carboxylic acid.

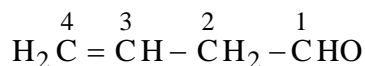


Cyclobutanecarboxylic acid

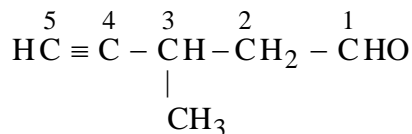
- 2. Aldehydes :** Aldehydes have a hydrogen atom attached to the carbonyl group. The common name of an aldehyde is derived from the corresponding carboxylic acid by dropping the suffix –oic acid and adding the suffix –al. For example :

HCOOH  
Methanoic acid

HCHO  
Methanal

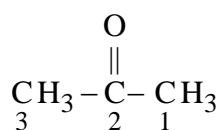


But-3-en-1-al

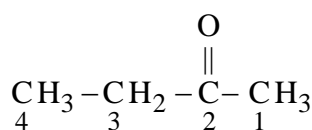


3-Methylpent-4-yn-1-al

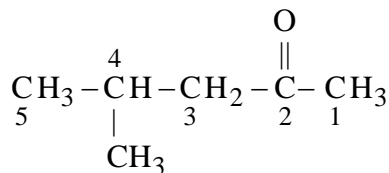
- 3. Ketones :** The suffix ane is changed to –one i.e. alkanone. The numbering commences from that end of the chain which gives the lowest number to the carbonyl group. It is always necessary to prefix the name by a number to specify the position of the carbonyl group.



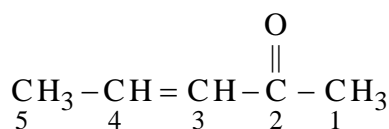
Acetone (Propan-2-one)



Butan-2-one

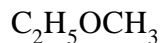


4-Methylpentan-2-one



Pent-3-en-2-one

4. **Ethers** : The common name of ethers is derived by naming the alkyl groups and adding the word ether. The smaller group is written first.



Methyl ethyl ether

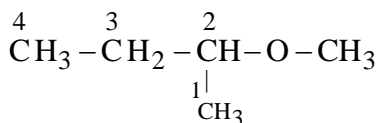


t-Butyl phenyl ether

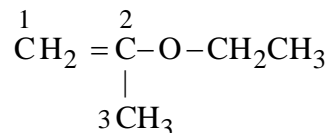
The IUPAC nomenclature is rarely used. Ethers are named as Alkoxy Alkanes. The larger alkyl group is chosen as the parent.



Methoxy ethane

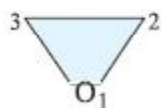
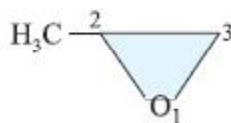
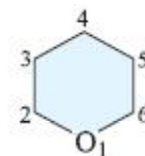


2 - Methoxybutane

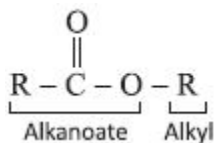


2 - Ethoxy propene

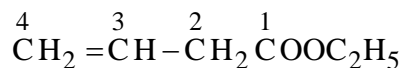
In cyclic ethers, the oxygen atom is contained in a ring of carbon atoms. While numbering the cyclic group, oxygen atom is always given number – 1. While naming a prefix Epoxy is added to the name of carbon atoms in the cyclic chain.

Epoxy ethane  
(Oxirane)2 - Methyl epoxy ethane  
(2-Methyl oxirane)Epoxy pentane  
(Oxane)

5. **Esters** : In the IUPAC system the acid chain is used as the stem in naming the ester. The suffix –oate replaces the –oic acid of carboxylic acids. It is necessary to number the substituent on the chain. The first part of the name is derived from the alkyl group of the corresponding alcohol.



Ethylpropanoate



Ethylbut-3-en-1-oate

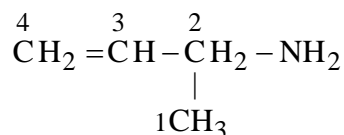
6. **Amines** : In the IUPAC system of nomenclature, amines are named similar to alcohols. The longest continuous carbon chain having max. no of amines determines the root name. The –e ending in the alkane named is replaced by suffix - amine. A number is needed to specify the position of the substituents.



Ethanol



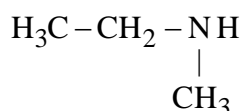
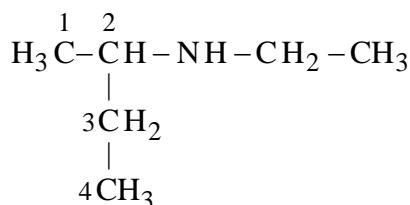
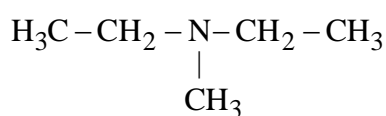
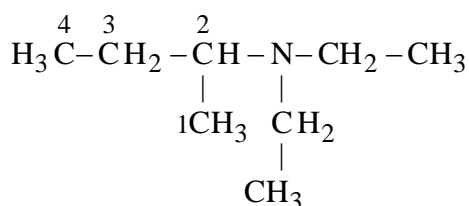
Ethanamine



But-3-en-2-amine

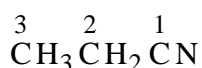
### Secondary amines and Tertiary amines :

The name of any alkyl group bonded to nitrogen is preceded by an “*N*” (in Italic) to indicate that the group is bonded to a nitrogen rather than to carbon.

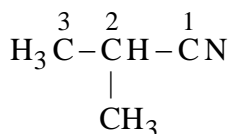
*N*-Methylethanamine*N*-Ethylbutan-2-amine*N*-Ethyl-*N*-methylethanamine*N,N*-Diethylbutan-2-amine

All the substituents (regardless of whether they are attached to the nitrogen or to the parent hydrocarbon) are listed in alphabetical order. The chain is numbered such that the functional group suffix gets the lowest possible number.

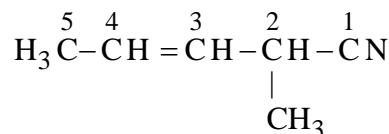
- 7. Nitriles :** While writing the IUPAC name, the cyano group takes the preference and its carbon atom is numbered as 1, only suffix -nitrile is added to the name of parent hydrocarbon (including the carbon of group).



Propanenitrile



2-Methylpropanenitrile

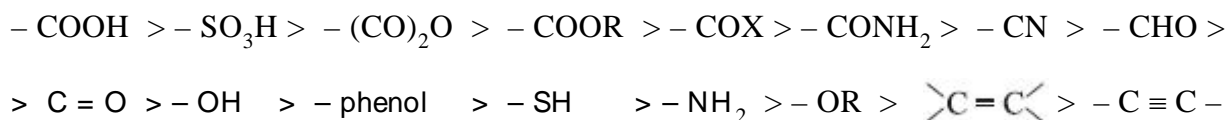


2-Methylpent-3-enitrile

## Rules for IUPAC Nomenclature of Polyfunctional Compounds :

Organic compounds having polyfunctional groups are named as follows :

- 1. Principal functional group :** When an organic compound contains two or more different functional groups, one of the functional groups is selected as the principal functional group while all other groups (also called the secondary functional groups) are treated as substituents. The choice of the principal functional group is made on the basis of the following order of preference.



The secondary suffixes for these functional groups have already been listed before.

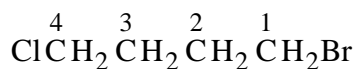
All the remaining functional groups such as halo (fluoro, chloro, bromo, iodo), nitroso ( $-\text{NO}$ ), nitro ( $-\text{NO}_2$ ), and R (alkyl),  $\text{C}_6\text{H}_5$  etc. are always treated as substituent group.

It may be noted that while writing the names of the polyfunctional compounds, the principal functional group is indicated by adding the secondary suffix to the word root while the secondary functional groups are indicated by adding suitable prefixes to the word root. The prefixes for secondary functional groups are listed before.

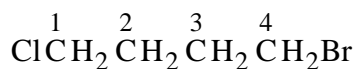
- 2. Selecting the principal chain :** While selecting the principal chain present in a polyfunctional compound care should be taken that it must contain the principal functional group and the maximum number of secondary functional groups and multiple bonds, if any.
- 3. Numbering the principal chain :** The principal chain present in a polyfunctional compound must be numbered in such a way that the principal functional group gets the lowest possible number followed by double bond, triple bond and the substituents, i.e.

Principal functional group > Double bond > Triple bond > Substituents.

- 4. Alphabetical order :** The prefixes for the secondary functional groups and other substituents should be placed in alphabetical order before the word root as explained earlier. If, however, two groups of the same family (eg. halogens) occupy identical positions from either end of the parent chain, the lower number must be given to the group whose prefix comes first in the alphabetical order. For example :



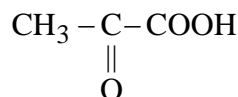
1-Bromo-4-chlorobutane (Correct)



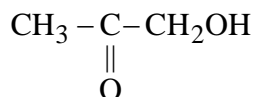
4-Bromo-1-chlorobutane (Wrong)

The rest of the rules for numerical prefixes are the same as explained earlier.

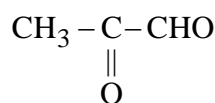
If more than one kind of functional groups are present, the functional group placed above (in the order of preference) decides suffix name.



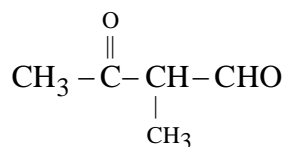
2-Ketopropanoic acid



1-Hydroxypropan-2-one



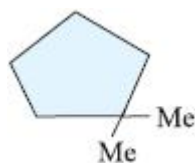
2-Ketopropanal



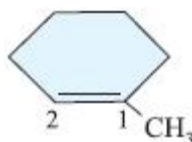
2-methyl-3-oxobutan-1-al

### Naming of Alicyclic Compounds :

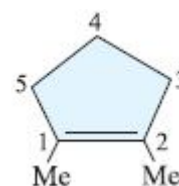
The nomenclature for alicyclic compounds is derived by putting another prefix 'cyclo' before the word root of carbon atoms in ring. The suffixes ane, ene are written depending upon the nature of molecule, i.e., saturated (–ane) or unsaturated (–ene) for double bond.



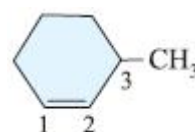
1,1-Dimethylcyclopentane



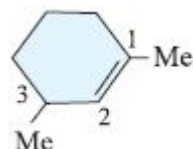
1-Methylcyclohex-1-ene



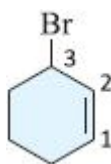
1,2-Dimethylcyclopent-1-ene



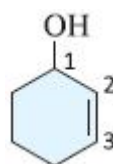
3-Methylcyclohex-1-ene



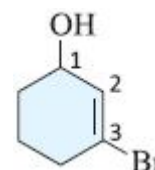
1,3-Dimethylcyclohex-1-ene



3-Bromocyclohex-1-ene



Cyclohex-2-en-1-ol



3-Bromocyclohex-2-en-1-ol

**Note :** From above examples, we can see that substituted cycloalkanes are named as derivatives of parent cycloalkanes. The substituted alkyl groups or functional groups around the ring from the point of greatest substitution providing the lowest series of numbers.



**Bicyclic Compounds :** (*This topic is for reference only, not in JEE syllabus*).

Bicyclic compounds are compounds that contain two rings.

1. If the two rings share one carbon, the compound is a spirocyclic compound or simply spiro compound.

For example :



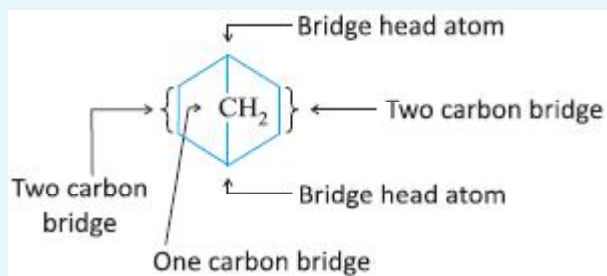
2. If the two rings share two adjacent carbons, the compound is a fused bicyclic compound.



3. If the two rings share more than two carbons, the compound is a bridged bicyclic compound.

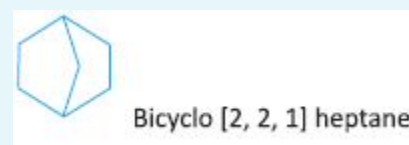
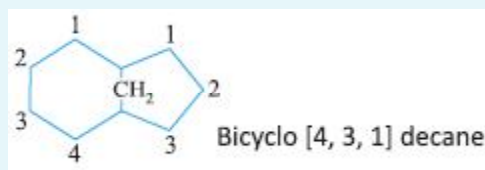
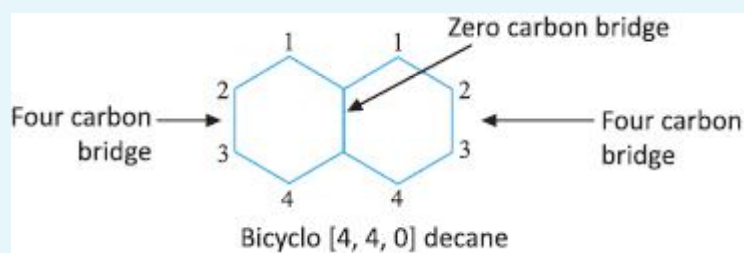
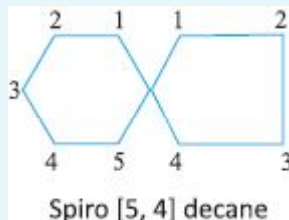
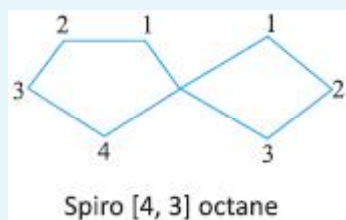
**Nomenclature of Bicyclic Compounds :**

1. Bicyclic compounds are named by using the alkane name to designate the total number of carbons and the prefix bicyclo or spiro to indicate the number of shared carbons.
2. Prefix spiro indicates one shared carbon and bicyclo indicates two or more shared carbons. The following compound, for example, contains seven carbon atoms and is therefore, a bicycloheptane.

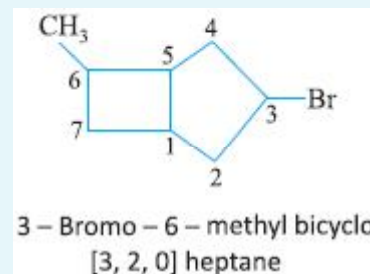
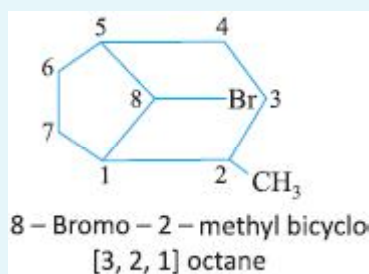
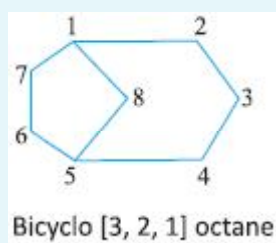


The carbon atoms common to both rings (Number of such carbons is either one in spiro or two in bicyclic) are called bridgeheads and each carbon chain of atoms, connecting the bridgehead atoms is called a bridge.

3. After the prefix spiro or bicyclic comes brackets that contain numbers indicating the number of carbons in each bridge. These are listed in order of decreasing bridge length. For example :



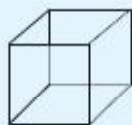
4. Numbering in bicyclic compounds starts at any one bridge head carbon and moves along the longest carbon bridge to the next bridge head carbon. Continue along the next longest carbon bridge to return to the first bridge head carbon so that the shortest bridge is numbered last.



**Note:** Number of rings in polycyclic compounds = (S - A + 1) where 'S' is the number of single bonds in the ring and A is the number of carbon atoms in the ring.



Bicyclo [2.2.1] heptane  
Bicyclo (two rings)



Cubane  
Pentacyclo (five rings)

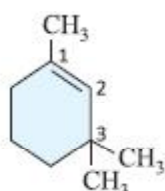
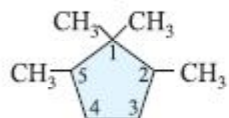


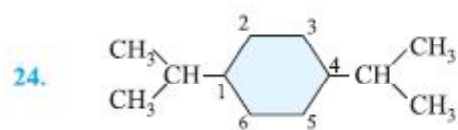
Prismane  
Tetracyclo (four rings)

## Some Prominent IUPAC Examples

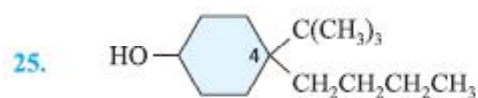
\* PIN : Preferred IUPAC Name

- 2-Cyclopentyl butanoic acid (PIN)
- 2-hydroxy propane - 1, 2, 3,-tricarboxylic acid.
- Ethane-1,1,2,2-tetracarboxylic acid (PIN)
- 3-(carboxymethyl) heptanedioic acid (PIN)
- Ethyl methyl benzene-1, 3-dicarboxylate
- Pentane dinitrile (PIN)
- Butan-1, 1, 1-tricarbonitrile (PIN)
- Pentanedial (PIN)
- Butan-1, 2, 4-tricarbaldehyde
- N, N-diethyl ethan-1-amine (PIN)

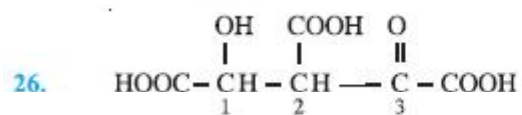
11.  $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \overset{\text{CH}_2\text{CH}_2\text{CH}_3}{\underset{|}{\text{N}}} - \text{CH}_2\text{CH}_3$  N-ethyl-N-propyl butan-1-amine
12.  $\text{CH}_2 = \overset{\text{CH}_3}{\underset{5}{\text{C}}} - \overset{4}{\text{C}} \equiv \overset{3}{\text{C}} - \overset{2}{\text{CH}_2} - \overset{1}{\text{N}} - (\text{CH}_2\text{CH}_2\text{CH}_3)_2$  4-Methyl-N, N-dipropylpent-4-en-2-yn-1-amine (PIN)
13.  $\text{CH}_3 - \text{CH}_2 - \overset{\text{N}(\text{CH}_3)_2}{\underset{|}{\text{CH}}} - \overset{2}{\text{C}} \equiv \overset{1}{\text{CH}}$  N, N-dimethyl pent-1-yn-3-amine (PIN)
14.  $\text{H}_2\text{N} - \overset{3}{\text{CH}_2} - \overset{2}{\text{CH}_2} - \overset{1}{\text{COOH}}$  3-Amino propanoic acid (PIN)
15.  $\text{H}_2\text{N} - \overset{2}{\text{CH}_2} - \overset{1}{\text{CH}_2} - \text{NH}_2$  Ethane-1, 2-diamine (PIN)
16.  $\text{CH}_2 = \overset{2}{\text{CH}_2} - \overset{1}{\text{CH}_2} - \text{NH}_2$  Prop-2-en-1-amine
17.  $\text{CH}_3 - \overset{\text{OH}}{\underset{|}{\text{CH}}} - \text{COOH}$  2-hydroxy propanoic acid (PIN) (*Lactic acid*)
18.  $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{COOH}$  2-oxopropanoic acid (PIN) (*Pyruvic acid*)
19.  $\begin{array}{c} \text{COOH} \\ | \\ \text{CH} - \text{OH} \\ | \\ \text{CH} - \text{OH} \\ | \\ \text{COOH} \end{array}$  2, 3-dihydroxy butanedioic acid (PIN) (*Tartaric acid*)
20.  $\begin{array}{c} \text{CH}_2 - \text{OH} \\ | \\ \text{COOH} \end{array}$  2-Hydroxy ethanoic acid (*Glycolic acid*)
21.  $\begin{array}{c} \text{CHO} \\ | \\ \text{COOH} \end{array}$  Formylmethanoic acid (*Glyxolic acid*)
22.  1, 3, 3-trimethylcyclohex-1-ene
23.  1, 1, 2, 5-tetramethyl cyclopentane  
and not (1, 2, 2, 3-tetramethyl cyclopentane)



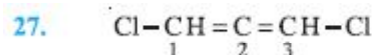
1, 4-di(isopropyl) cyclohexane



4-Butyl-4-tert-butylcyclohexan-1-ol (PIN)



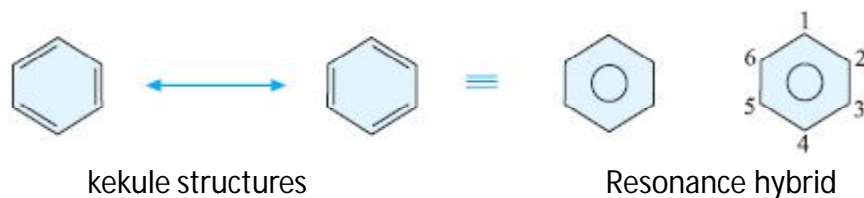
1-hydroxy-3-oxopropane-1,2,3-tricarboxylic acid (PIN)



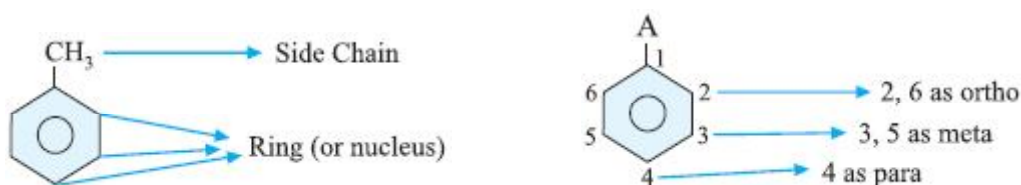
1,3-dichloropropa-1,2-diene (PIN)

## Nomenclature of Aromatic Compounds :

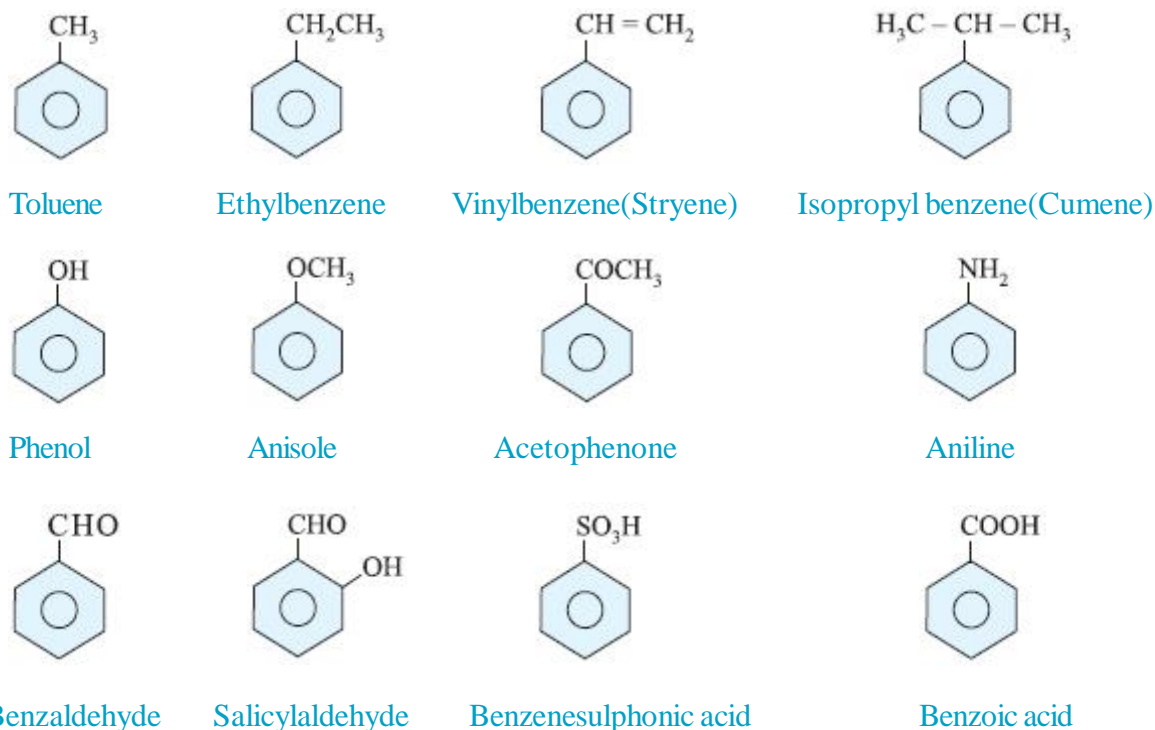
Aromatic compounds are cyclic compounds which contain one or more benzene type rings. Benzene is the simplest hydrocarbon of aromatic series which has a planar cyclic ring of six carbon atoms having three double bonds in alternate positions as shown below :

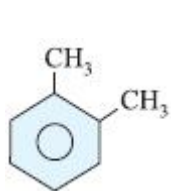


The carbon atoms of benzene are numbered from 1 to 6 as shown above. The benzene ring is called the nucleus and groups containing at least one carbon atom that too directly attached to benzene nucleus are called side chains. Benzene forms only one mono substituted derivative. However, it can form three disubstituted derivatives; namely 1, 2 ; 1, 3 and 1, 4 derivatives or ortho (*o*-), meta (*m*-) and para (*p*-) derivatives respectively.

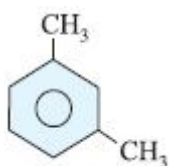


## Some Important Aromatic Hydrocarbons :





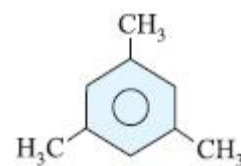
o-Xylene



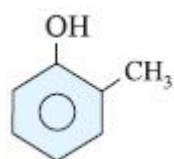
m-Xylene



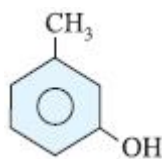
p-Xylene



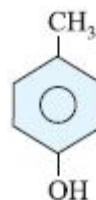
Mesitylene



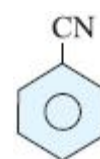
o-Cresol



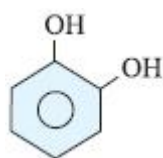
m-Cresol



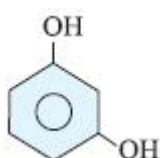
p-Cresol



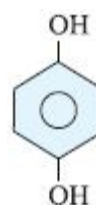
Cyano benzene



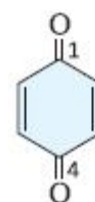
Catechol



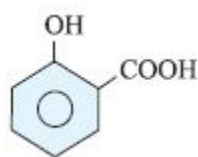
Resorcinol



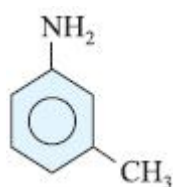
Hydroquinol



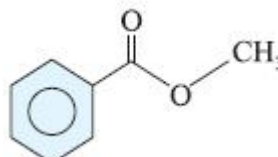
1, 4-Benzouilone



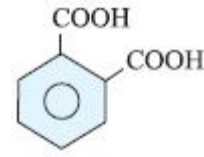
Salicylic acid



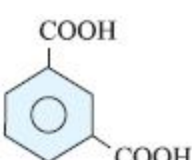
m-Toluidine



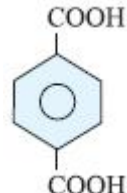
Methyl benzoate



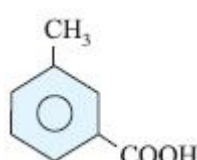
Phthalic acid



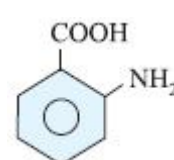
Isophthalic acid



Terephthalic acid

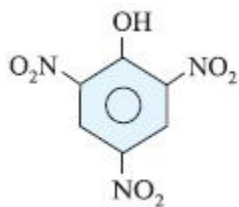


m-Toluic acid

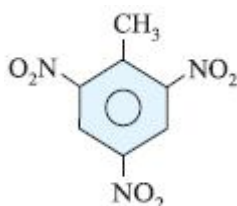


Anthranilic acid

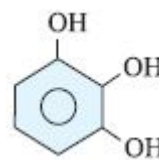




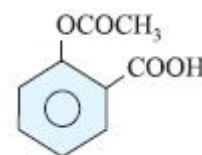
Picric acid



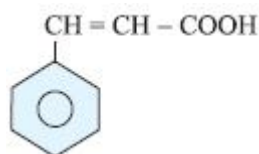
2, 4, 6-Trinitrotoluene (TNT)



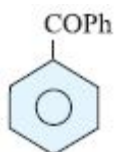
Pyrogallol



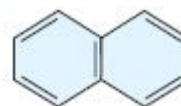
Aspirin



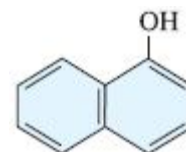
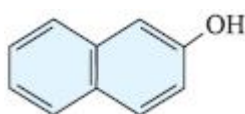
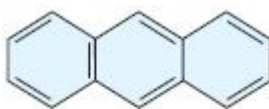
Cinnamic acid



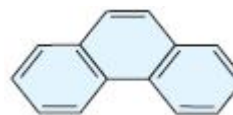
Benzophenone



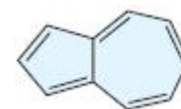
Naphthalene

 $\alpha$ -Naphthol $\beta$ -Naphthol

Anthracene



Phenanthrene



Azzulene

**Homologous Series :** A homologous series is defined as a family or group of structurally similar organic compounds all the members of which contain the same functional group, show a gradation in physical and similarity in chemical properties and any two adjacent (or consecutive) members of which differ by a  $-\text{CH}_2$  group. For example: alkanes constitute a homologous series.

The first six members of this series are :

$\text{CH}_4$	$\text{C}_2\text{H}_6$	$\text{C}_3\text{H}_8$	$\text{C}_4\text{H}_{10}$	$\text{C}_5\text{H}_{12}$	$\text{C}_6\text{H}_{14}$
Methane	Ethane	Propane	Butane	Pentane	Hexane

These hydrocarbons can be represented by the same general formula,  $\text{C}_n\text{H}_{2n+2}$  where  $n$  is the number of carbon atoms. Further, any two adjacent members of this class differ by a  $\text{CH}_2$  group.

If a hydrogen atom from the above hydrocarbons is replaced by a hydroxyl group i.e.,  $-\text{OH}$ , we get a new homologous series. This homologous series is called alcohols. The different members of this series can be represented by the general formula  $\text{C}_n\text{H}_{2n+1}\text{OH}$ . The first four members of this series are :

$\text{CH}_3\text{OH}$	$\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
Methanol	Ethanol	Propan-1-ol	Butan-1-ol

Some other homologous series are alkenes, alkynes, alkyl halides, ethers, aldehydes, ketones, amines, esters and carboxylic acids etc.



### Characteristics of a Homologous Series :

1. Each homologous series can be represented by a general formula. For example,  $C_nH_{2n+1}COOH$  is the general formula of carboxylic acids.
2. All the members of a given homologous series possess the same functional group. For example, the functional group of alcohols is the hydroxyl group i.e.,  $-OH$  group. Similarly, the functional group of aldehydes is the aldehydic group i.e.,  $-CHO$  and that of the ketones is the ketonic group, i.e.,  $>C=O$ .
3. The successive members of a homologous series differ by a  $CH_2$  group or by  $12 + 2 \times 1 = 14$  mass units.
4. The individual members of a homologous series can be prepared by the general methods of preparation developed for that series.
5. The physical properties such as density, melting point, boiling point of the members of a homologous series show a regular gradation with rise in molecular mass.
6. The chemical properties of the members of a homologous series are similar though the first member may vary considerably from rest of the members.

### Degree of Unsaturation (DU)

Degree of Unsaturation also known as “index of Hydrogen deficiency (IHD)” or “rings plus double bonds” is helpful in Organic Chemistry while drawing Chemical structures.

For a compound with formula :  $C_aH_bN_cO_dX_e$  where X is F, Cl, Br or I,

$$DU = \frac{1}{2}(2 + 2a - b + c - e) \quad \text{or} \quad DU = \frac{1}{2}[2 + 2 \times \text{No. of C atoms} - \text{No. of H atoms} + \text{No. of N atoms} - \text{No. of Halide atoms}]$$

#### Rules :

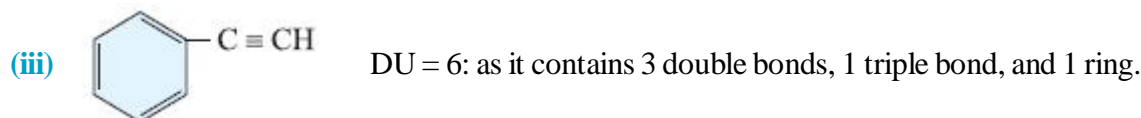
- (i) Do not count group 16 elements e.g. O, S etc. Remove them from the formula but count H-atoms attached to them.
- (ii) Each double bond, adds ‘one’ to DU.
- (iii) Each triple bond, adds ‘two’ to DU.
- (iv) Each ring adds ‘one’ to DU.

#### Illustrating the Concept:

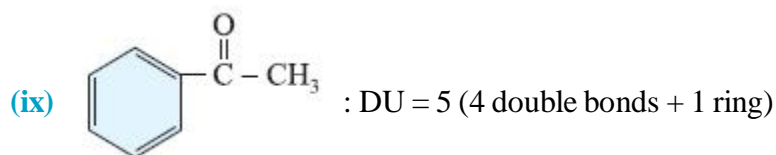
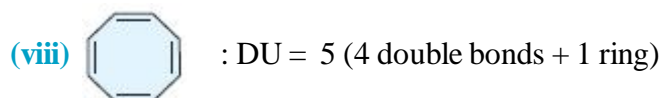
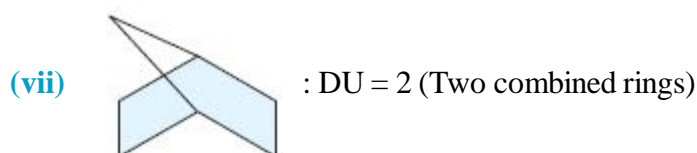
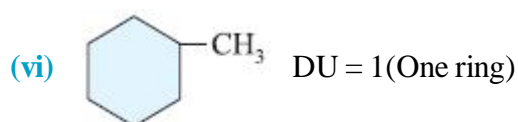
$$(i) \quad C_3H_6 : DU = \frac{1}{2}[2 + 2 \times 3 - 6] = 1 \quad \Rightarrow \quad \text{It contains a double bond OR a ring.}$$

(ii)  $C_5H_8 : DU = \frac{1}{2}[2 + 2 \times 5 - 8] = 2$

$\Rightarrow$  Two double bonds OR 1 triple bond OR 2 rings OR 1 double bond and 1 ring.



(iv)  $C_6H_{12}O_6 : DU = \frac{1}{2}[2 + 2 \times 6 - 12] = 1$       (v)  $C_6H_{12}N_2Br_2 : DU = \frac{1}{2}[2 + 2 \times 6 - 12 + 2 - 2] = 1$



**Note:**  $DU \geq 4$  doesn't demand but suggest the possibility of an aromatic (benzene) ring.

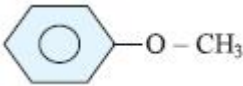
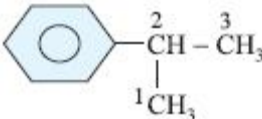
### Illustration - 1

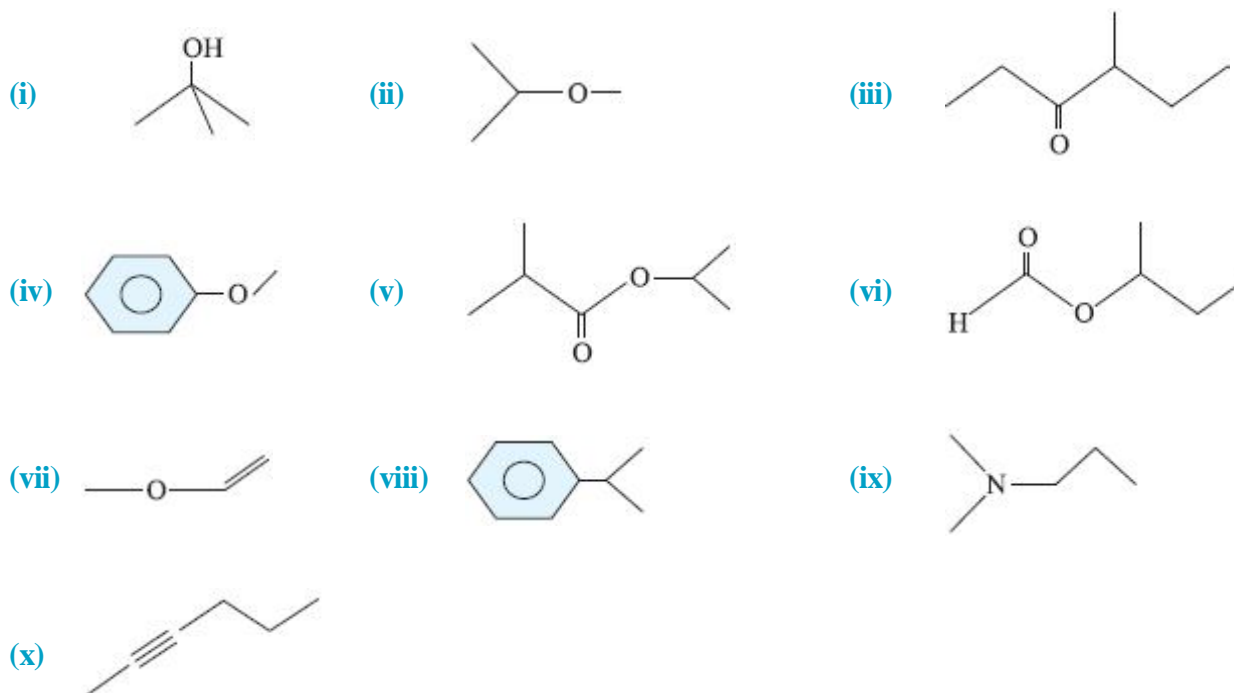
Draw the condensed structures of following compounds. Also write their IUPAC name.

- |                                       |                             |                                      |
|---------------------------------------|-----------------------------|--------------------------------------|
| (i) <i>tert</i> -Butyl alcohol        | (ii) Isopropyl methyl ether | (iii) <i>sec</i> -Butyl ethyl ketone |
| (iv) Phenyl methyl ether              | (v) Isopropyl isobutyrate   | (vi) <i>sec</i> -Butyl formate       |
| (vii) Methyl vinyl ether              | (viii) Isopropyl benzene    | (ix) Dimethyl <i>n</i> -propyl amine |
| (x) Methyl <i>n</i> -propyl acetylene |                             |                                      |

### SOLUTION :



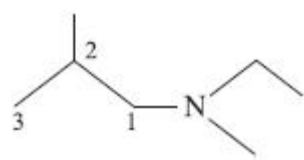
- (ii)  $\begin{array}{c} 1 \quad 2 \\ \text{CH}_3 - \text{C} - \text{O} - \text{CH}_3 \\ | \\ \text{CH}_3 \\ 3 \end{array}$  : 2-Methoxypropane
- (iii)  $\begin{array}{c} 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ || \quad | \\ \text{O} \quad \text{CH}_3 \end{array}$  : 4-Methylhexan-3-one
- (iv)  : Methoxybenzene ; (called as **anisole** : trade name as IUPAC name)
- (v)  $\begin{array}{c} \text{O} \\ || \\ 3 \quad 2 \quad 1 \quad 1 \quad 2 \\ \text{CH}_3 - \text{C} - \text{O} - \text{C} - \text{CH}_2 - \text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$  : (1-Methylethyl) 2-methyl propanoate
- (vi)  $\begin{array}{c} \text{O} \\ || \\ \text{H} - \text{C} - \text{O} - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$  : (1-Methylpropyl) methanoate
- (vii)  $\text{CH}_3 - \text{O} - \text{CH} = \text{CH}_2$  : Methoxyethene
- (viii)  : (2-propyl) benzene (or cumene)  
or (1-Methylethyl) benzene.
- (ix)  $\begin{array}{c} \text{CH}_3 - \text{N} - \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CH}_2 - \text{CH}_3 \\ 1 \quad 2 \quad 3 \end{array}$  : N, N-Dimethyl-1-propan - 1 - amine
- (x)  $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$  : Hex - 2 - yne

**Illustration - 2***Draw the bond line structures for each of above compounds in Illustration - 1***SOLUTION :****Illustration - 3***Give the IUPAC names of the following structures.***SOLUTION :**

- $$\begin{array}{ccccccc} & & \text{OH} & & & & \\ & & | & & & & \\ 4 & 3 & 2 & 1 & & & \\ \text{CH}_3 - & \text{CH} - & \text{CH}_2 - & \text{COOC}_2\text{H}_5 \end{array}$$

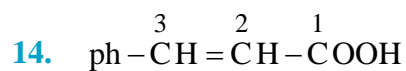
Ethyl 3-hydroxybutanoate
- $$\begin{array}{ccccccc} 4 & 3 & 2 & 1 & & & \\ \text{CH}_3 - & \text{CH}_2 - & \text{CH}_2 - & \text{COCl} \\ & & | & & & & \\ & & \text{Br} & & & & \end{array}$$

2-Bromobutanoyl chloride
- $$\begin{array}{ccccccc} 6 & 5 & 4 & 3 & 2 & 1 & \\ \text{H}_2\text{C} = & \text{C} - & \text{CH}_2 - & \text{CH}_2 - & \text{CH}_2 & \text{COOH} \\ & | & & & | & & \\ & \text{CH}_3 & & & \text{OH} & & \end{array}$$

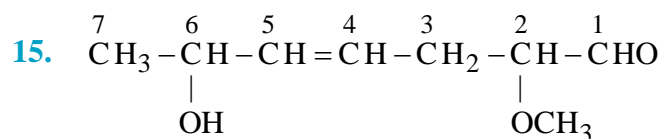
2-Hydroxy-5-methylhex-5-enoic acid
- 

N-Ethyl-N-methyl-2-methylpropan-1-amine

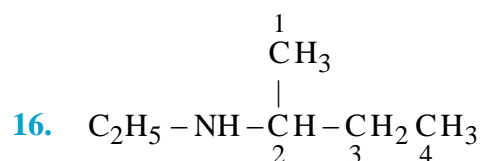




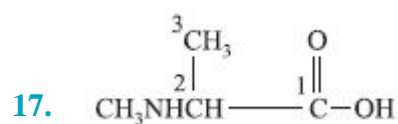
3-Phenylprop-2-enoic acid



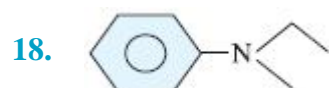
6-Hydroxy-2-methoxyhept-4-en-1-al



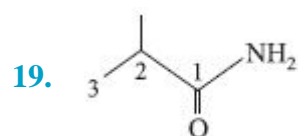
N-Ethylbutan-2-amine



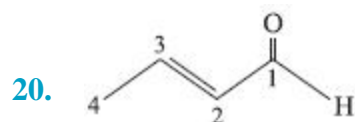
2(N-Methylamino)propanoic acid



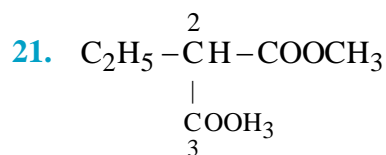
N-Ethyl-N-methylaniline



2-Methylpropanamide



But-2-en-1-al



Trivial Name : (Dimethyl)- $\alpha$ -ethylmalonate  
 IUPAC Name: (Dimethyl)-2-ethylpropan-1, 3-dioate



Methylenecyclopentane

## IN-CHAPTER EXERCISE-A

1. Give the dash structures of the following :

- |                                   |                                |
|-----------------------------------|--------------------------------|
| (i) Isobutyl radical              | (ii) Neopentyl radical         |
| (iii) <i>tert</i> -Pentyl radical | (iv) <i>sec</i> -Butyl radical |
| (v) <i>tert</i> -butyl radical    | (vi) Benzyl radical            |

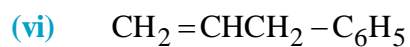
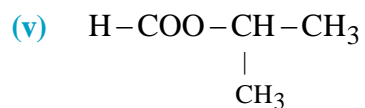
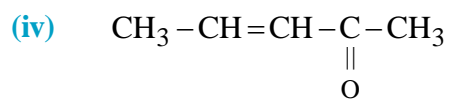
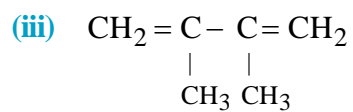
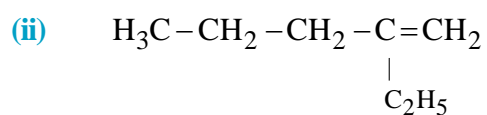
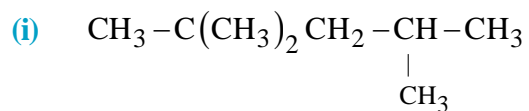
2. Give IUPAC name of following :

- |   |   |
|---|---|
| (i) $(\text{CH}_3)_3\text{C}-\text{COOCH}_3$  | (ii) $(\text{CH}_3)_2\text{CH}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{CH}}}-\text{CH}=\text{CH}_2$  |
| (iii) $\text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\text{CH}_2\text{COOH}$  | (iv) $(\text{CH}_3)_2\text{CH}-\underset{\text{OH}}{\text{C}}(\text{CH}_3)_2$   |
| (v) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\underset{\text{COOH}}{\text{CH}}-\text{C}_2\text{H}_5$  | (vi) $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_2}{\text{C}}-\text{CH}_2\text{CH}_3$  |
| (vii) $(\text{CH}_3)_2\text{CH}-\underset{\text{CH}(\text{CH}_3)_2}{\text{CH}}-\overset{\text{CH}_3}{\text{C}}=\text{CH}_2$                           | (viii) $(\text{CH}_3)_2\text{CH}-\underset{\text{N}-\text{CH}_3}{\overset{\text{CH}_3}{\text{CH}}}-\text{CH}(\text{CH}_3)_2$  |
| (ix) $\text{CH}_3-\underset{\text{CH}_3}{\overset{\text{C}_2\text{H}_5}{\text{C}}}-\underset{\text{C}_2\text{H}_5}{\text{C}}=\text{C}(\text{CH}_3)_2$ | (x) $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-\text{O}-\text{CH} < \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$ |

3. Give the structure of following aromatic compounds :

- |                         |                          |                             |
|-------------------------|--------------------------|-----------------------------|
| (i) <i>o</i> -Cresol    | (ii) <i>p</i> -Toluidine | (iii) <i>m</i> -Toluic acid |
| (iv) Benzoyl chloride   | (v) Benzo phenome        | (vi) Aniline                |
| (vii) Benzoic anhydride | (viii) Acetophenone      | (ix) Phenol                 |
| (x) Terephthalic acid   |                          |                             |

4. Give IUPAC name of following :



NOW ATTEMPT IN-CHAPTER EXERCISE-A FOR REMAINING QUESTIONS



## ISOMERISM IN ORGANIC COMPOUNDS

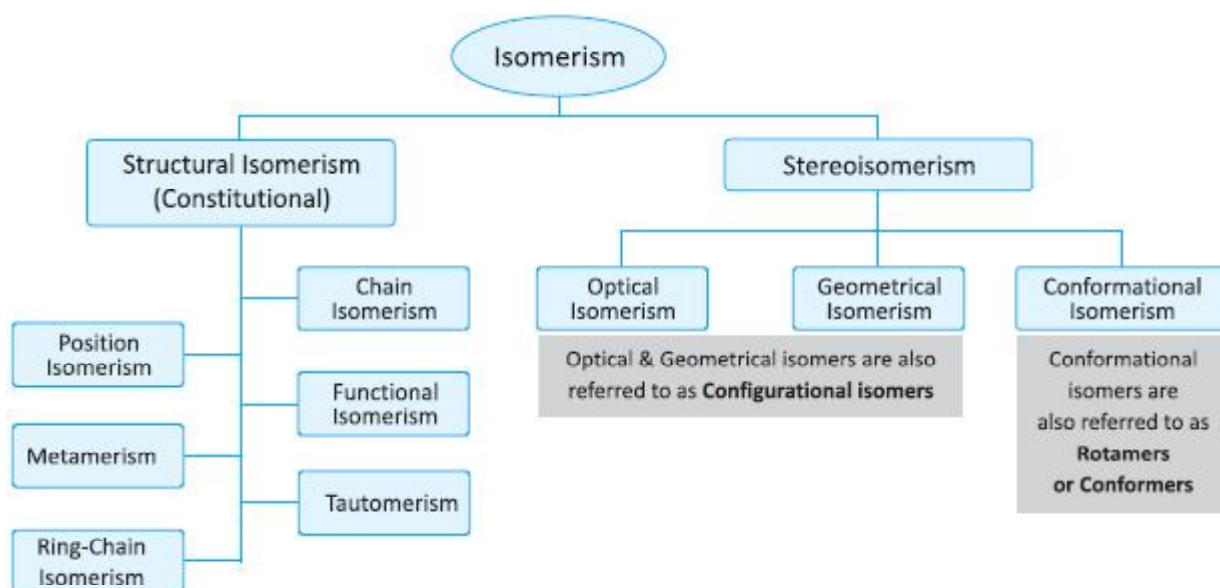
## Section - 4

**Isomerism :** The phenomenon of existence of two or more compounds possessing the same molecular formula but different chemical and physical properties is known as isomerism. Such compounds are individually referred to as isomers. For example :  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{OCH}_3$  are isomers of each other.

We have two types of isomerisms:

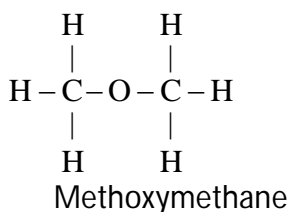
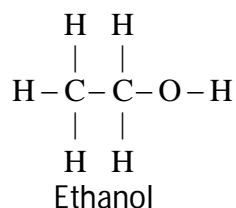
1. **Structural Isomerism :** There are also called as Constitutional Isomers.
2. **Stereo Isomerism :**

**Types of isomerism :**



### Structural Isomerism :

In this type of isomerism, the compounds possessing same molecular formula differ in their properties due to the difference in the linkages of atoms inside the molecule, i.e., due to the difference in their structure. For example:  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{OCH}_3$ . Both have the molecular formula  $\text{C}_2\text{H}_6\text{O}$  but they differ in their structures (Ethanol has C–C–O linkage while Methoxymethane has C–O–C linkage).

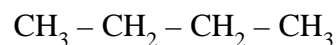


Structural isomers differ both in their physical as well as chemical properties.

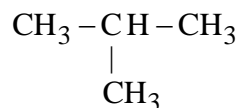
Structural isomerism is classified into following six types.

- Chain Isomerism :** In this type of isomerism, the compounds possessing same molecular formula differ in their properties due to the difference in the arrangement of carbon chain present in them. In one of them the chain may be straight while in other the chain may be branched.

- Butane ( $C_4H_{10}$ ) has two chain isomers :



n-Butane

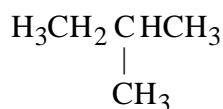


Isobutane

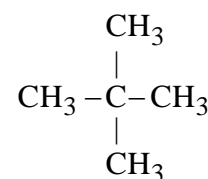
- Pentane ( $C_5H_{12}$ ) has three chain isomers :



n-Pentane

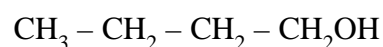


Isopentane

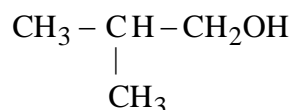


Neopentane

- Butyl alcohol (Butanol) has a chain isomer :

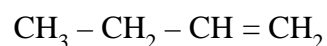


n-Butyl alcohol

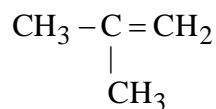


Isobutyl alcohol

- 1-Butene has a chain isomer :

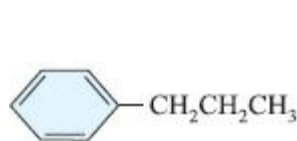


But-1-ene

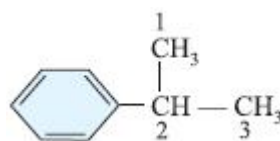


Isobutene

- Aromatic Compounds may also have chain isomers :



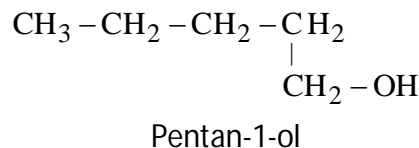
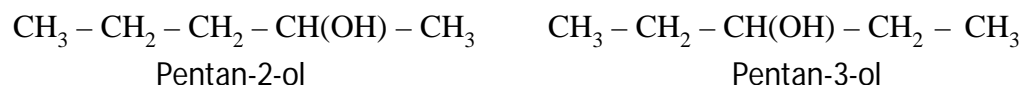
n-Propylbenzene



Isopropylbenzene

2. **Positional Isomerism** : In this type of isomerism, the compounds possessing same molecular formula differ in their properties due to the difference in the position of either the functional group or the multiple bond or the branched chain attached to the main carbon chain. For example :

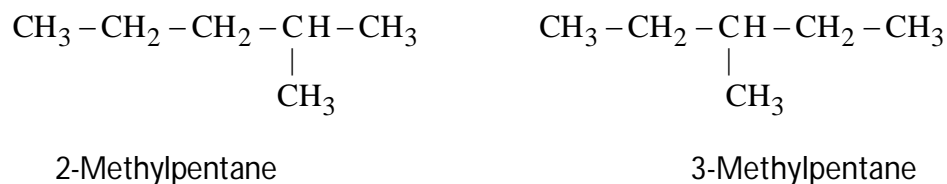
- Pentan-2-ol and Pentan-3-ol are the positional isomers :



- Butene has two position isomers :

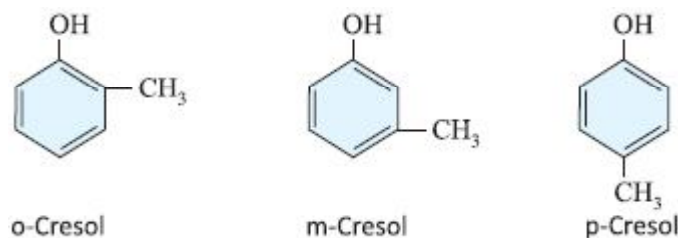


- Methylpentane has position isomers :



*Note that the position isomers have same parent chain.*

- In aromatic compounds, for example, in benzene ring three different positions are possible for a disubstituted product. They are 1-2 (called as ortho), 1-3 (called as meta), and 1-4 (called as para). Disubstituted benzene has three positional isomers. For example :
- Cresol has three positional isomers.



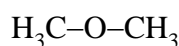
3. **Functional Isomerism** : In this type of isomerism the compounds possessing same molecular formula differ in their properties due to the difference in their functional group, i.e., the functional isomers differ in the functional group present in them. For example :

- Alcohols (except methanol) have their isomeric ethers.

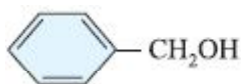
eg. Ethyl alcohol and Dimethyl ether having molecular formula of  $C_2H_6O$  are functional isomers :



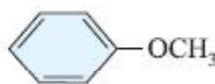
Ethanol



Methoxymethane



Benzyl alcohol



Anisole (Methylphenyl ether)

- Aldehydes have isomeric ketones.

Propionaldehyde (Propanal) and Acetone (Propanone) are functional isomers:



Propanal



Propanone

Methanal, Ethanal, and Benzaldehyde have no isomeric ketones.

- An acid may be isomeric to an ester.

Propionic acid and Methyl acetate (Methyl ethanoate) are functional isomers:



Propanoic acid

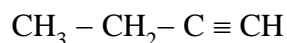


Methyl ethanoate

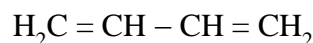
Only Methanoic acid cannot have its isomeric ester.

Note that sometimes an alkadiene may be isomeric with an alkyne. This is also called as functional isomerism.

- Butyne is isomeric to Butadiene :

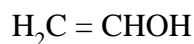


But-1-yne

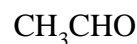


Buta-1, 3-diene

- Unsaturated alcohols are isomeric to Aldehydes :

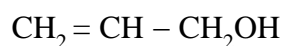


Vinyl Alcohol

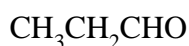


Acetaldehyde

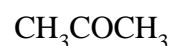
- Unsaturated alcohols containing three or more carbon atoms are isomeric to Aldehydes as well as Ketones :



Allyl alcohol

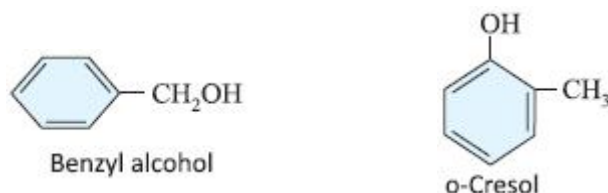


Propionaldehyde

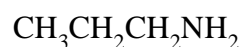


Acetone

- Aromatic alcohols may be isomeric to Phenols :



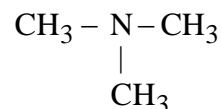
- Primary, Secondary, and Tertiary amines of same molecular formula are functional isomers :



n-Propyl amine ( $1^\circ$ )



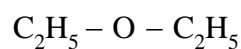
Ethyl methyl amine ( $2^\circ$ )



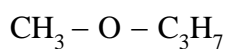
Trimethyl amine ( $3^\circ$ )

4. **Metamerism** : In this type of isomerism the compounds possessing same molecular formula differ in their properties due to the difference in alkyl groups present in them. Thus, the metamers differ only in the alkyl groups present and they have same functional group, i.e., they belong to same homologous series. For example :

- Diethyl ether (Ethoxyethane) and Methyl propyl ether (Methoxy propane) are the metamers :



Ethoxy ethane



Methoxy propane

- Diethylamine and Methylpropylamine are also the metamers :

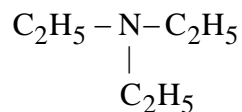


Diethyl amine

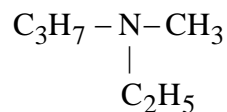


Methyl propyl amine

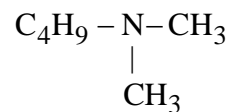
- Metamers of  $3^\circ$  amines ( $\text{C}_6\text{H}_{15}\text{N}$ ) :



Triethyl amine



Ethyl methyl propyl amine



Dimethyl butyl amine

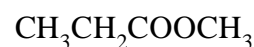
- Esters also show metamerism, n-Propyl formate has Ethyl acetate and Methyl propionate as its metamers.



n-Propyl formate



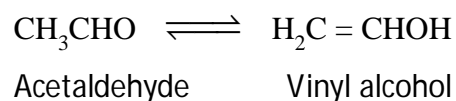
Ethyl acetate



Methyl propionate

5. **Tautomerism** : This is a special case of functional isomerism. In this type of isomerism two functional isomers exist together in equilibrium. The two forms existing in equilibrium are called as tautomers. For example :

- Consider tautomerism in Acetaldehyde (keto group) and Vinyl alcohol (enol group).

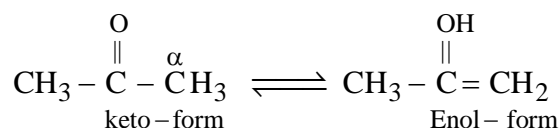


Out of the two tautomeric forms, generally the keto form is more stable and exists in larger proportion. The equilibrium between the two forms is dynamic, i.e., if one form is somehow removed by a reaction, some of the amount of the other form changes into the first form so that similar equilibrium exists again.

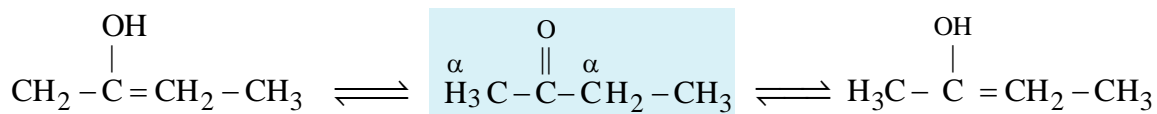
Due to the presence of keto and enol form this type of tautomerism is known as keto–enol tautomerism. It is the most commonly observed type of tautomerism.

The keto-enol tautomerism is possible only in those Ketones and Aldehydes in which at least one  $\alpha$ -hydrogen atom is present so that it may convert the carbonyl group to enol group.

- Consider the compound Acetone, it has two tautomers, one has a keto group and other has an enol group.



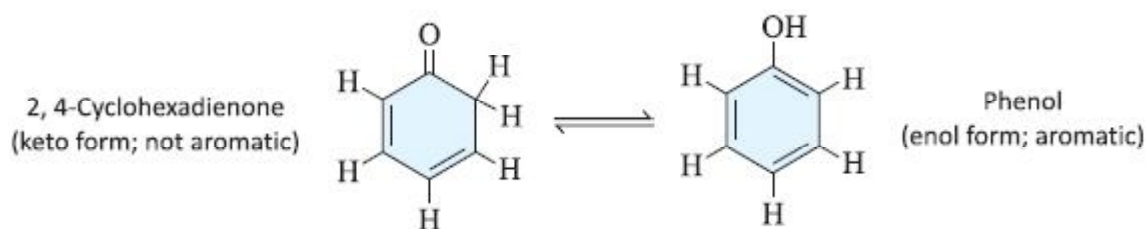
- Another example of keto–enol tautomerism is observed in 2-Butanone. It has two enol forms :



Hence It is observed that (as above), if the  $\alpha$ -hydrogen atoms are present on both the carbons attached to carbonyl group, it can have more than one enol. Thus, larger the number of different  $\alpha$ -hydrogens in a ketone, more is the number of enols. In most of the cases, the keto form is more stable than the enol by some 45-60 kJ/mol (11-14 kcal/mol). The main reason for this difference is that a carbon-oxygen double bond is stronger than a carbon-carbon double bond.

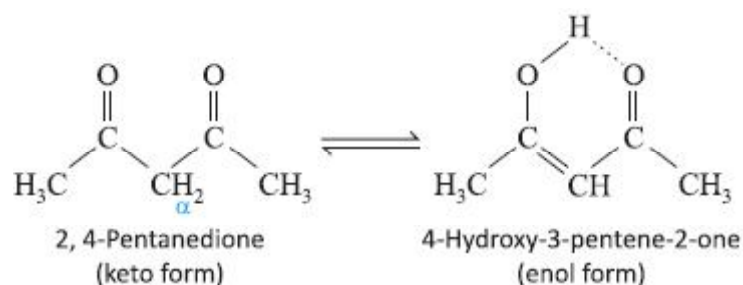
### Stabilized Enols :

Certain structural features can make the keto-enol equilibrium more favourable by stabilizing the enol form such as **extended conjugation**, **intramolecular H-bonding** and **aromatic characters** etc.



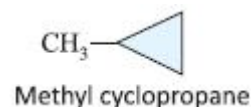
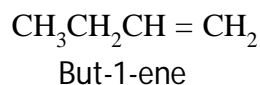
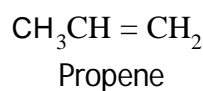
The enol form is phenol, and the stabilization gained by forming an aromatic ring is more than enough to overcome the normal preference for the keto form.

The 1, 3- arrangement of two carbonyl groups in  $\beta$ -diketones leads to a situation in which the keto and the enol forms are of comparable stability.

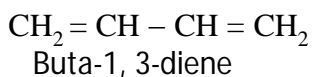
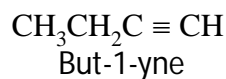


**6. Ring chain isomerism :** Compounds having the same molecular formula but possessing open chain and cyclic structures are called ring chain isomers and the phenomenon is called ring chain isomerism. For example:

➤ Alkenes are isomeric with Cycloalkanes :

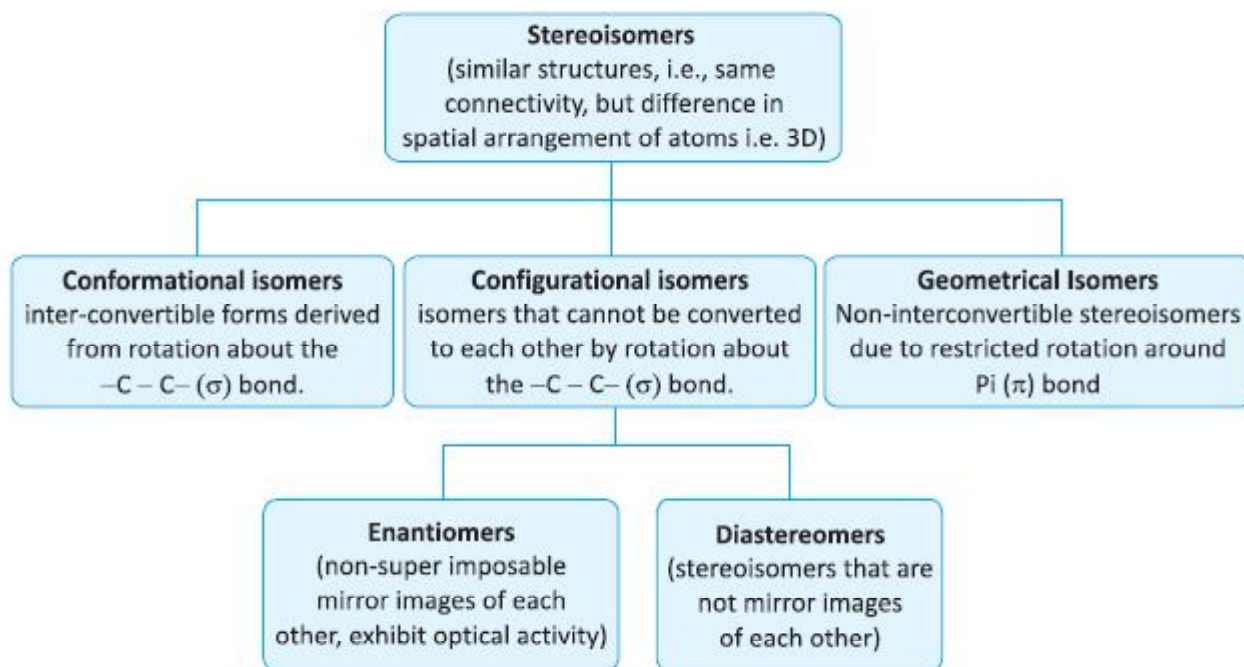


➤ Alkynes and Alkadienes are isomeric with Cycloalkenes :



## Stereo-isomerism :

The stereoisomerism is defined as the type of isomerism in which compounds possessing same molecular formula and same structural formula, differ in their properties due to the difference in the arrangement in space of their atoms in the molecule. Stereoisomers usually differ in some of their physical properties but they may not differ much in their chemical properties.



In order to understand stereoisomerism, we need to familiarize ourselves with the following concepts.

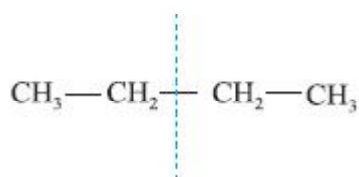
## Chirality

A molecule or any other object that cannot be superimposed onto its mirror image is said to be chiral, and the phenomenon is known as chirality. Chirality arises from asymmetry in a molecule.

Objects and molecules that are super-imposable on their mirror images are achiral.

A test for chirality is to look for a plane of symmetry in the molecule. If there exists such a plane of symmetry that divides the molecule into two identical halves, then such a molecule is achiral.

for e.g. n-butane is achiral while 2-chlorobutane is chiral.



Plane of symmetry  
n-Butane - ACHIRAL

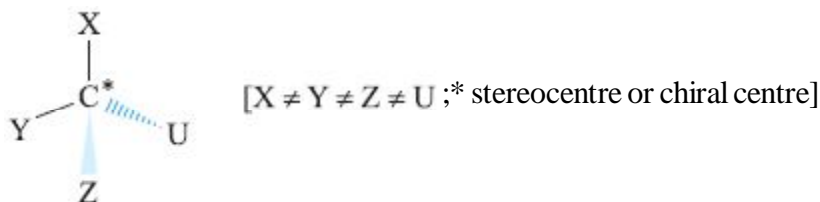


No plane of symmetry  
2-Chlorobutane - CHIRAL

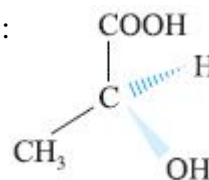


## Stereocentre-An-Asymmetric Carbon

A  $sp^3$  hybridised carbon atom that is bonded to four different substituents or groups (including hydrogen) is a stereocentre.



For example, consider Lactic acid (2-Hydroxy propanoic acid):



A molecule with only one stereocentre will be chiral, because such a molecule does not possess a plane of symmetry and hence is non-superimposable on its mirror image.

**Note:** Molecules containing more than one stereocentre may or may not exhibit chirality depending on whether they have a plane of symmetry and are superimposable on their mirror images or not.

## Plane Polarized Light

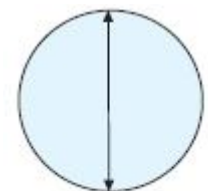
Light is an electromagnetic wave, with oscillating electric and magnetic fields.

If we were to view a beam of ordinary light from one end, and if we could actually see the planes in which the electrical oscillations were occurring, we would find that oscillations of the electric field were occurring in all possible-planes, perpendicular to the direction of propagation. (The same would be true for magnetic field)



Un-polarised light

Oscillations of the electric field of ordinary light occur in all possible planes, perpendicular to the direction of propagation [Note that the direction of propagation is perpendicular to the plane of paper].



Plane-polarised light

When ordinary light is passed through a polarizer like Nicol prism, the light that emerges from the polarizer is oscillating only in one plane. Such light is called plane-polarized light. In the given figure, the plane of oscillation of the electric field of plane-polarized light is vertical.

## Optical Activity

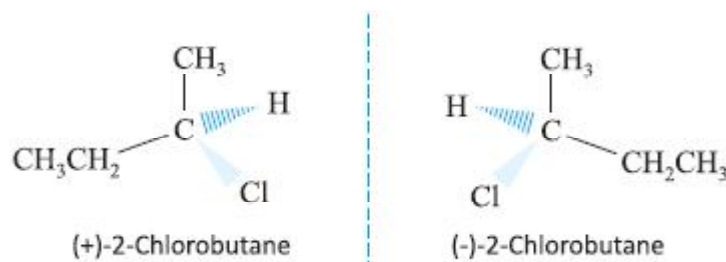
It is found that some compounds have a tendency to rotate the plane of plane-polarised light i.e., when any such compound is placed in the path of plane - polarised light, the compound rotates the plane of this light by a certain angle. Such a rotation is known as optical rotation and the phenomenon is called as **Optical activity**.

This optical rotation may be clockwise (+) or anti-clockwise (-). The molecules rotating the plane in clockwise direction are termed as dextro-rotatory (d) or (+), while the molecules rotating the plane in anti-clockwise direction are termed as laevo-rotatory (l) or (-). The instrument used to measure optical rotation is called as Polarimeter.

Optical activity is a characteristic of chiral molecules only. We know that a chiral molecule is one that cannot be superimposed on its mirror image. Such a molecule and its non-super imposable mirror image form a pair of enantiomers.

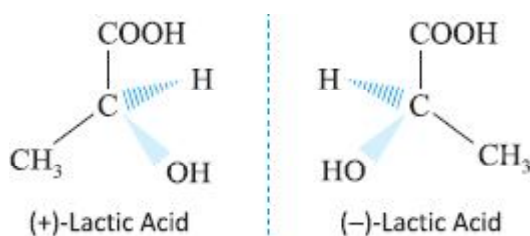
Enantiomers rotate the plane of plane polarized light to the same extent but in opposite direction. i.e., one of them is dextro-rotatory and the other is laevo-rotatory.

Consider 2-Chlorobutane,  $\text{CH}_3\text{-CH}(\text{Cl})\text{-CH}_2\text{CH}_3$ .



Whether a compound is dextro-rotatory or laevo-rotatory can only be determined experimentally, and not by merely looking at the 3-D structure of compound.

Another very common example is of Lactic Acid,  $\text{CH}_3\text{-CH}(\text{OH})\text{-COOH}$ .

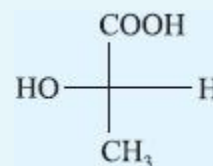


**Note:** Any dissymmetric compound having non-superimposable mirror image is optically active compound.

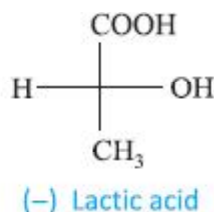
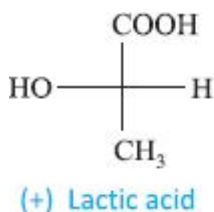
### Racemic mixture

An equimolecular mixture of (+) and (–) (i.e., d– and l–) forms of an optically active compound is not able to rotate the plane of plane - polarised light because of the mutual cancellation. Such a mixture is known as a racemic mixture or dl– mixture or ( $\pm$ ) mixture and is optically inactive. The phenomenon is called as racemisation. Thus, lactic acid can be said to be of three types, i.e. (+) lactic acid, (–) lactic acid, and ( $\pm$ ) lactic acid.

- Note:** ➤ Representation of a molecule in tetrahedral three dimensional shapes is a little bit difficult. A simplified way to represent such molecules on plane of paper is by using the Fischer projection formula. In a Fischer projection formula, (+) lactic acid is represented as:
- Fischer projection formula can't be rotated by  $90^\circ$  and can't be lifted from the plane of the paper.



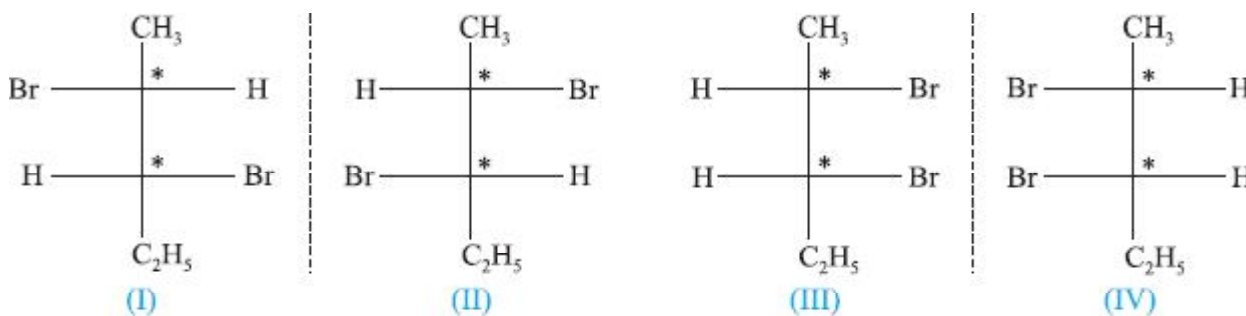
The chiral carbon atom is represented by a point of intersection of a horizontal and a vertical line. Atoms or groups attached with horizontal line are supposed to be coming forward above the plane of paper (i.e., towards the viewer) while the groups attached with vertical line are going back behind the plane of paper (away from the viewer). Thus, the two enantiomers of lactic acid are represented as follows :



### Compounds Containing Two Stereocentres

A useful rule gives the maximum number of stereoisomers of a compound. Total number of stereoisomers =  $2^n$  (only configurational), where  $n$  = number of stereocentres in the molecule. So, a molecule with 2 stereocentres can have a maximum of  $2^2 = 4$  stereoisomeric forms.

Consider 2, 3-Dibromopentane,  $\text{CH}_3-\overset{*}{\underset{\text{Br}}{\text{CH}}}-\overset{*}{\underset{\text{Br}}{\text{CH}}}-\text{CH}_2\text{CH}_3$  has 4 stereoisomers as shown below.



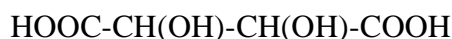
- Enantiomers are non-super imposable mirror images.
- Diastereomers are non-super imposable non-mirror images.

Note that the pairs **I** & **II** and **III** & **IV** form pairs of Enantiomers (Optical Isomers).

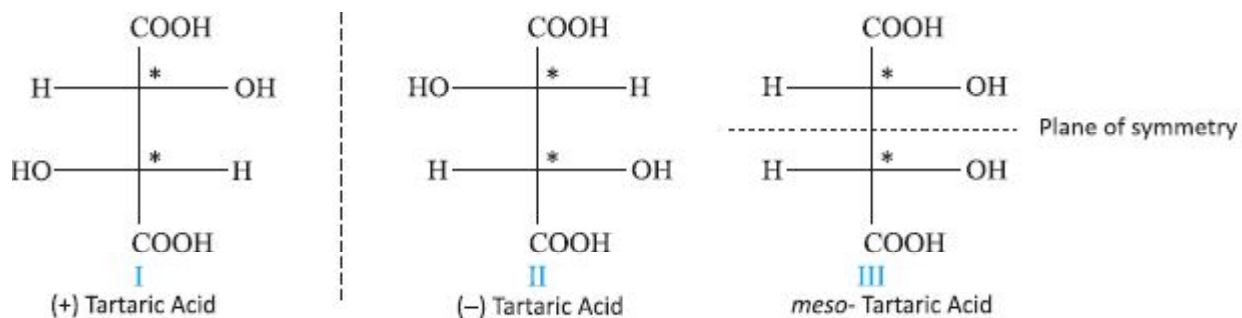
And pairs **I** and **III** and **I** and **IV** and **II** and **III** etc. form pairs of diastereomers.

## Meso Compounds and Diastereomers

A structure with two stereocentres does not always have four possible stereoisomers. Sometimes, there are only three. This happens because some molecules are achiral even though they contain stereocentres. To understand this, let us consider the example of tartaric acid:



Tartaric Acid has only three stereoisomers.



I and II are non-superimposable mirror images of each other (ENANTIOMERS).

If we look at structure III, it also has 2 stereocentres. But we can also note the presence of a plane of symmetry in it. As described earlier, such a molecule is achiral, despite the presence of 2 stereocentres, and it shall be impossible on its mirror image. Such an isomer, which has stereocentres, but the molecule is overall Achiral is called a meso-isomer.

**Note:** Observe that in the case of 2, 3-Dibromopentane (above), there is no plane of symmetry in either of stereoisomers.

- Note:**
- (i) The meso compound and its mirror image both represent a single configuration (i.e., one isomer)
  - (ii) The meso-isomer is optically inactive (achiral). In the meso-isomer, half part of the molecule gives clockwise while the other half gives anti-clockwise rotation (due to a plane of symmetry), and thus, because of internal compensation, the molecule is optically inactive. While the racemic mixture is not able to show optical rotation because of external compensation, the meso form is not able to show any rotation because of internal compensation.
  - (iii) The meso-tartaric acid is not the enantiomer of either I or II forms. The molecules (configurations) which are not mirror images of one another are called **diastereomers**. The meso-tartaric acid is a diastereomer of I and II forms of tartaric acid.

**Geometrical Isomerism :**

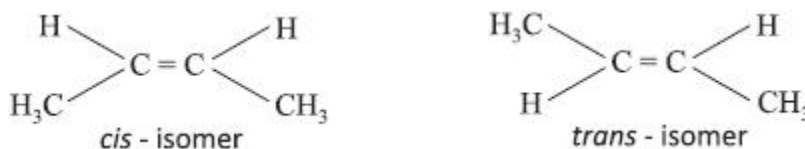
Consider the compound, 2-Butene-1, 4-dioic acid,  $\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$ . This compound can be expressed in two different forms as follows:



Since free rotation about  $\text{C}=\text{C}$   $\text{Pi} (\pi)$  bond is not allowed, these two geometries are non-inter convertible and different. These are geometrical isomers of each other.

In Maleic acid, both  $-\text{COOH}$  groups are attached in the same direction, while in Fumaric acid, the two  $-\text{COOH}$  groups are attached in opposite direction. The geometrical isomer in which the similar groups are present in same direction (on the same side of double bond) is called as the *cis isomer*, while the one in which similar groups are in opposite direction is called as the *trans isomer*. Geometrical isomerism is also known as *cis-trans* isomerism. Maleic acid is a *cis* isomer while Fumaric acid is the *trans* isomer.

- 2-Butene also exhibits geometrical isomerism :



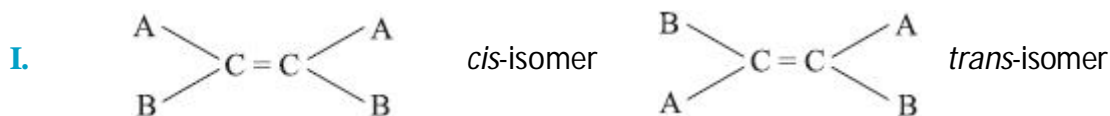
- 1, 2-Dichloroethene is another example of geometrical isomerism :

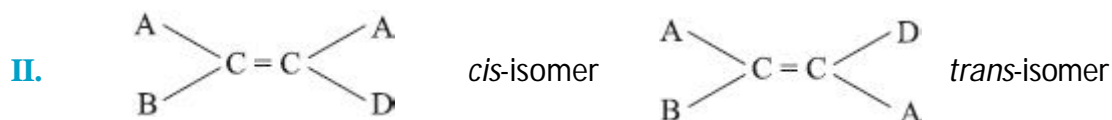


- Note that an organic compound having a  $\text{>C}=\text{C}<$  bond may or may not show geometrical isomerism.

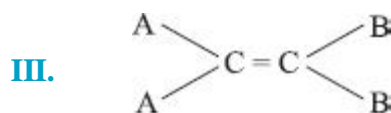
If two similar groups (or atoms) are attached to same carbon atom (forming a double bond) in a compound, then it does not show geometrical isomerism.

An organic compound having  $\text{>C}=\text{C}<$  can have the following different forms :



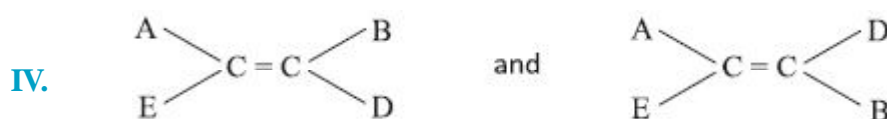


Such compounds show geometrical isomerism and we can classify them as having *cis* and *trans* forms.



Such compounds where 2 similar groups are attached to one carbon atom, do not show geometrical isomerism.

Important Alkenes which do not show geometrical isomerism include Ethene ( $\text{CH}_2=\text{CH}_2$ ), Propene ( $\text{CH}_3\text{CH}=\text{CH}_2$ ), 1-Butene ( $\text{C}_2\text{H}_5\text{CH}=\text{CH}_2$ ), Isobutene ( $\text{Me}_2\text{C}=\text{CH}_2$ ) and Styrene ( $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ ).



Such a pair of compound are geometrical isomers, but cannot be classified as *cis-trans*.

**Note:** *cis* form is comparatively less stable because of the mutual repulsion between the groups. Thus, Maleic acid is less stable than Fumaric acid. Geometrical isomers differ in their physical properties and also in some of their chemical properties. The *trans* form, being symmetrical has a zero dipole moment. Even in the cases when the *trans* form is not symmetrical, it has a low dipole moment in comparison to the *cis* form. Since the *trans* form is less polar, it is less soluble in water.

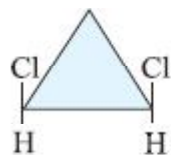
Also, being polar the *cis* isomer has comparatively higher boiling point. However, melting point of *trans* isomer is higher because of better packing in crystal due to symmetry in molecule. Besides, the *cis* isomer has higher [heat of hydrogenation](#), [heat of combustion](#), [density](#), and [refractive index](#). Accordingly, Fumaric acid has higher melting point and is very sparingly soluble in water in comparison to Maleic acid.

### Geometrical Isomerism in Cyclic Compounds :

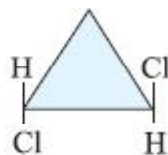
In cyclic compounds the rotation about a C–C single bond is not free because of the rigidity caused by the presence of other carbons of the ring which keep them tightly held. Thus, a disubstituted cyclic compound (having the two substitutions at separate carbons) will exist as geometrical isomers. For example, consider 1, 2-Dimethylcyclopentane:



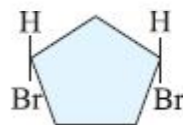
Other examples of Cycloalkanes and their derivatives showing Geometric Isomerism are illustrated below :



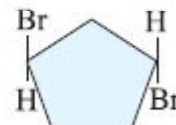
*cis*-1, 2-Dichlorocyclopropane



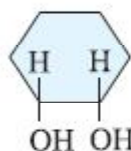
*trans*-1, 2-Dichlorocyclopropane



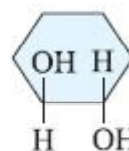
*cis* - 1, 3-Dibromocyclopentane



*trans* - 1, 3-Dibromocyclopentane



*cis*-Cyclohexane-1, 2-diol



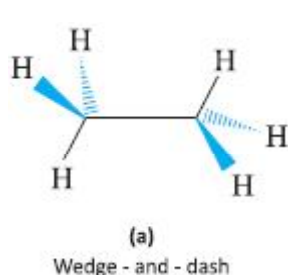
*trans*-Cyclohexane-1, 2-diol

## Conformational Isomerism :

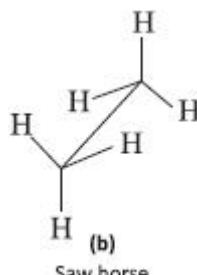
Conformations are different spatial arrangements of a molecule that are generated by rotation about single bonds. Conformational analysis is the study of how conformational factors affect the structure of a molecule and its physical and chemical properties.

- I. **Conformational analysis of Ethane:** Ethane is the simplest hydrocarbon that can have distinct conformations. These two conformations are the staggered conformation and the eclipsed conformation. In the staggered conformation, each C–H bond of one carbon bisects an H–C–H angle of the other carbon.

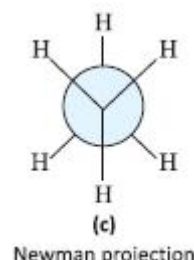
Some commonly used drawing of the staggered conformation of ethane.



(a)  
Wedge - and - dash



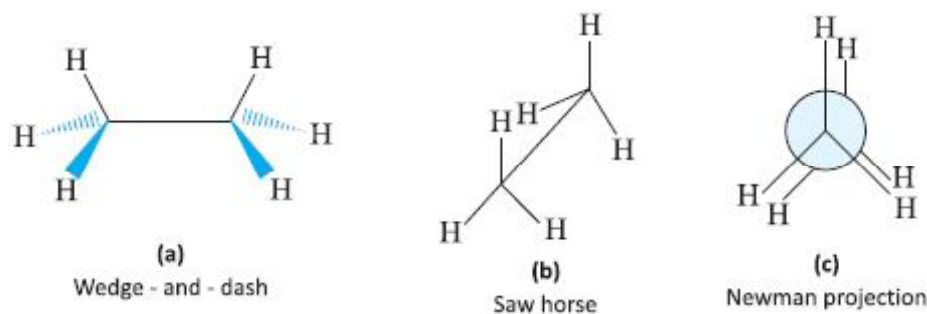
(b)  
Saw horse



(c)  
Newman projection

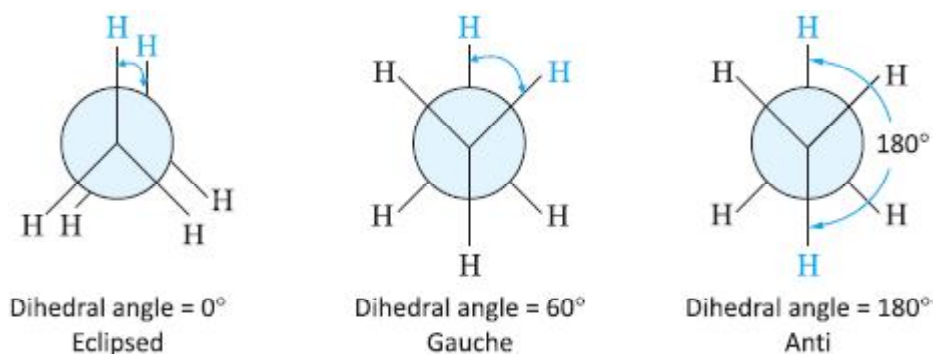
In the eclipsed conformation, each C–H bond of one carbon is aligned with a C–H bond of the other carbon. Some commonly used drawings of the eclipsed conformation of ethane.





**Note:** In a Newman projection (figure C), we sight down the C–C bond, and represent the front carbon by a point and the back carbon by a circle. Each carbon has three other bonds that are placed symmetrically around it.

The structural feature that above mentioned figure illustrate is the **spatial relationship** between atoms on adjacent carbons. Each H-C-C-H unit in ethane is characterized by a **torsion angle** or **dihedral angle**, which is the angle between the H-C-C plane and the C-C-H plane. The **dihedral angle** is easily seen in a Newman projection of ethane as the angle between C-H bonds of adjacent carbons.



**Note:** The staggered conformations have only gauche or anti-relationship between bonds on adjacent atoms. The staggered and eclipsed conformation inter convert by rotation around the C-C bond, and do so very rapidly.

**Note:** Different conformations of the same compound are sometimes called conformers or rotamers. Of the two conformations of ethane, the staggered is 12kJ/mol more stable than the eclipsed. The staggered conformation is most stable conformations; the eclipsed is the least stable conformation.

Conformations in which the dihedral angle between adjacent bonds are other than  $60^\circ$  are said to have torsional strain. Eclipsed bonds produce the most torsional strain; staggered bonds none.

**Note:** In principle ethane has an infinite number of conformations that differ by only tiny increments in their dihedral angle. Not only is the staggered conformation more stable than the eclipsed, it is the most stable of all of the conformations; the eclipsed is the least stable.



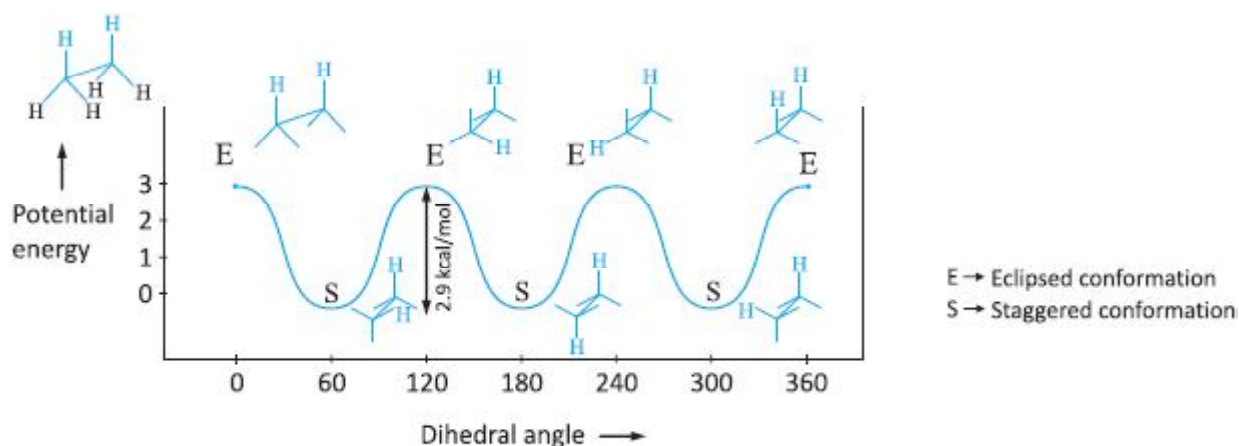
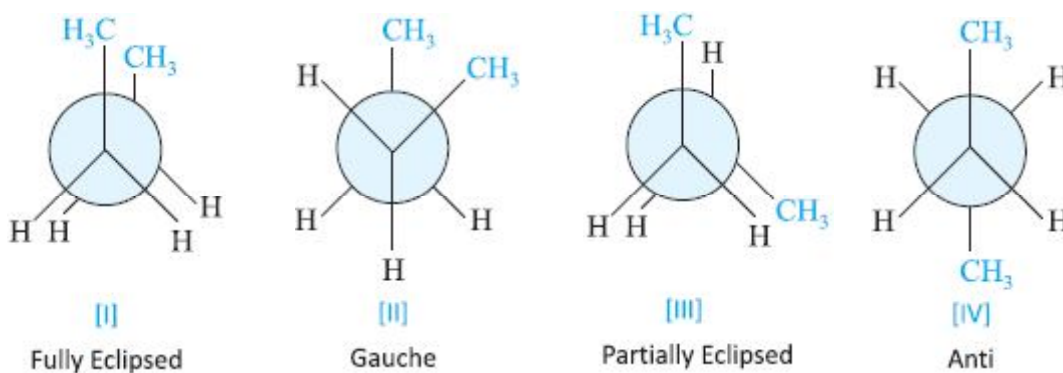


Figure: Potential energy diagram for rotation about the carbon-carbon bond in ethane

## II. Conformational Analysis of Butane :

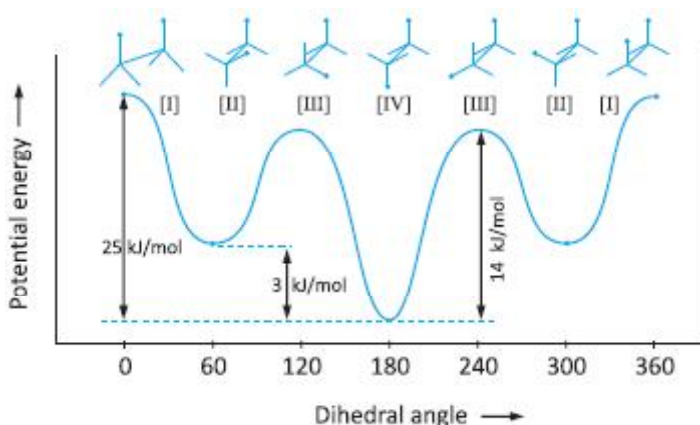
We consider conformations related by rotation about the bond between the middle two carbon ( $\text{CH}_3\text{CH}_2\text{-CH}_2\text{CH}_3$ ). Butane has four main conformations [two eclipsed type and two staggered type].

Unlike ethane, in which the staggered conformations are equivalent, two different staggered conformations occur in butane.

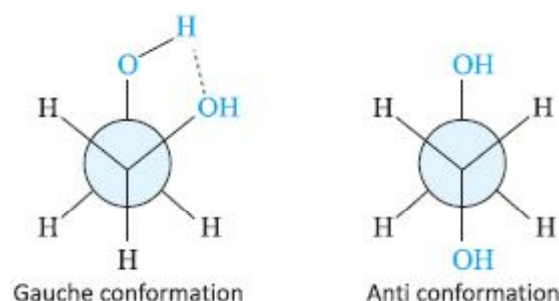


The gauche conformation and anti-conformation both are staggered, so are free of torsional strain, but two of the methyl hydrogens of the gauche conformations lie within 210 pm of each other. This distance is less than the sum of their van der Waals radii (240 pm), and there is a repulsive force between them. The destabilization of a molecule that results when two of its atoms are too close to each other is called van der Waals strain, or steric hindrance and contributes to the total steric strain.

In the case of butane, **van der Waals strain** makes the gauche conformation approximately 0.8 kcal/mol less stable than the anti.

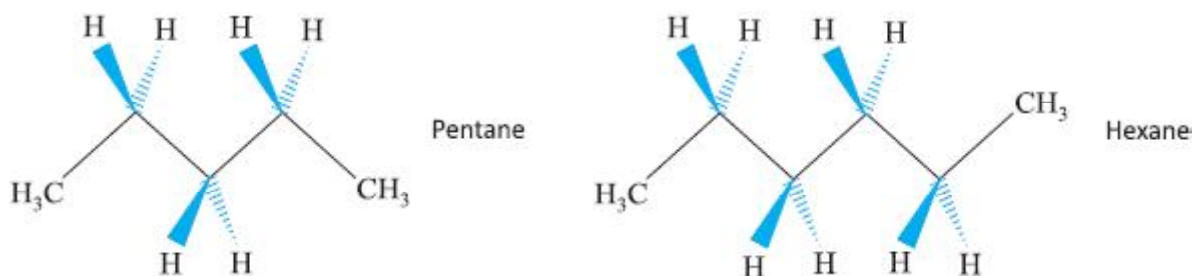


**Note:** For ethane-1, 2-diol(ethylene glycol HO-CH<sub>2</sub>-CH<sub>2</sub>-OH) gauche conformation is more stable than the anti-conformation because of H-bonding in gauche conformation.

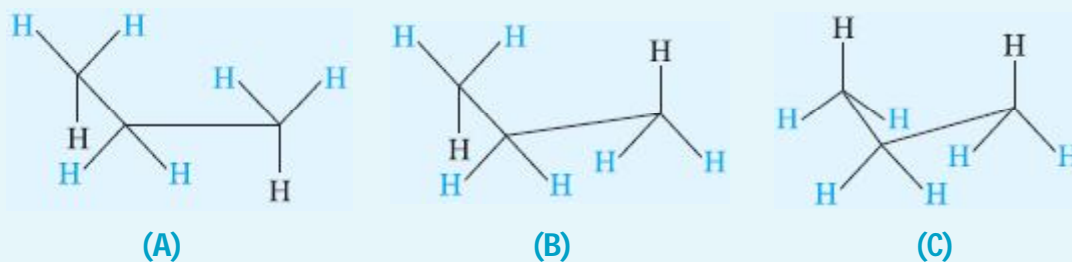


### III. Conformations of Higher alkanes:

Higher alkanes having unbranched carbon chain are, like butane, most stable in their all-anti conformations. In depicting the conformations of higher alkanes it is often more helpful to look at them from the side rather than end-on as in Newman projection. Viewed from this perspective, the most stable conformations of pentane and hexane have their carbon “backbones” arranged in a zig-zag fashion as shown in the figure. All the bonds are staggered, and the chain are characterized by anti-arrangement of C-C-C-C units.



**Illustration - 4** Of the three conformations of propane shown, which one is the most stable? Which one is the least stable? Why?



**SOLUTION :**

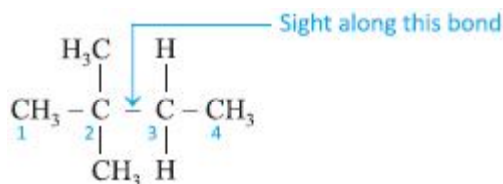
Conformation (A) is the most stable ; all its bonds are staggered. Conformation (C) is the least stable ; all its bonds are eclipsed.

**Illustration - 5** Sight down the C-2-C-3 bond, and draw Newman projection formulas for the :

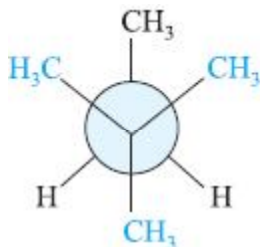
- Most stable conformation of 2, 2-dimethyl butane.
- Two most stable conformations of 2-methyl butane.
- Two most stable conformations of 2, 3-dimethyl butane.
- One of the two staggered conformations of 2-methyl butane is more stable than the other. Which one is more stable? Why?

**SOLUTION :**

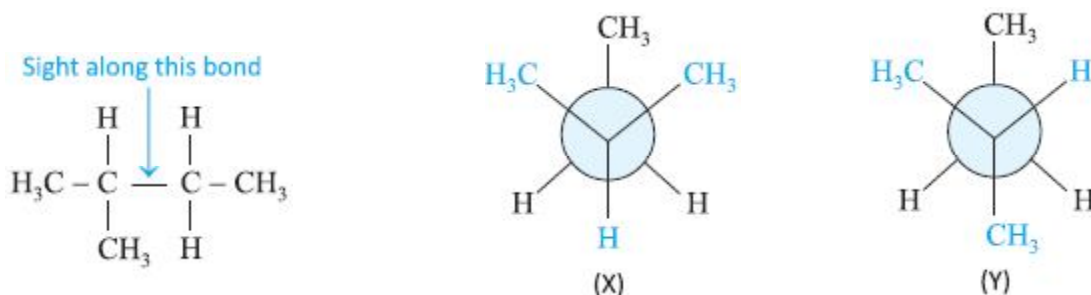
- First write out the structural formula of 2, 2-dimethyl butane in order to identify the substituent groups attached to C-2 and C-3.



As shown in above structure C-2 bears three methyl groups, and C-3 bears two hydrogens and a methyl group. The most stable conformation is the staggered one as shown below. All other staggered conformations are equivalent to this one.

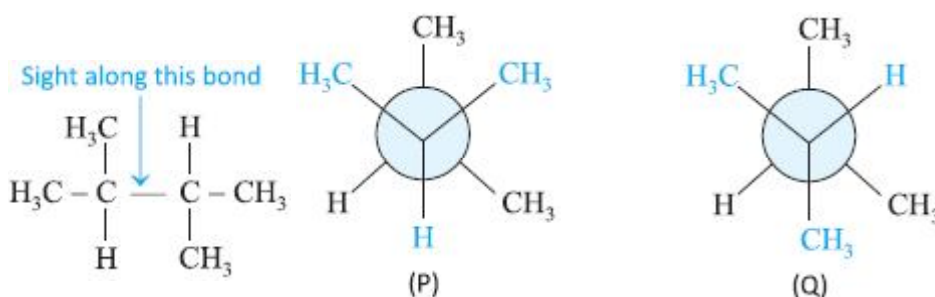


- (b) The constitution of 2-methylbutane and its two most stable conformations are shown.



Both conformations are staggered. In one Newman projection (X), the methyl group at the back is gauche to the two methyl groups in the front. In the other (Y), it is gauche to one and anti to the other.

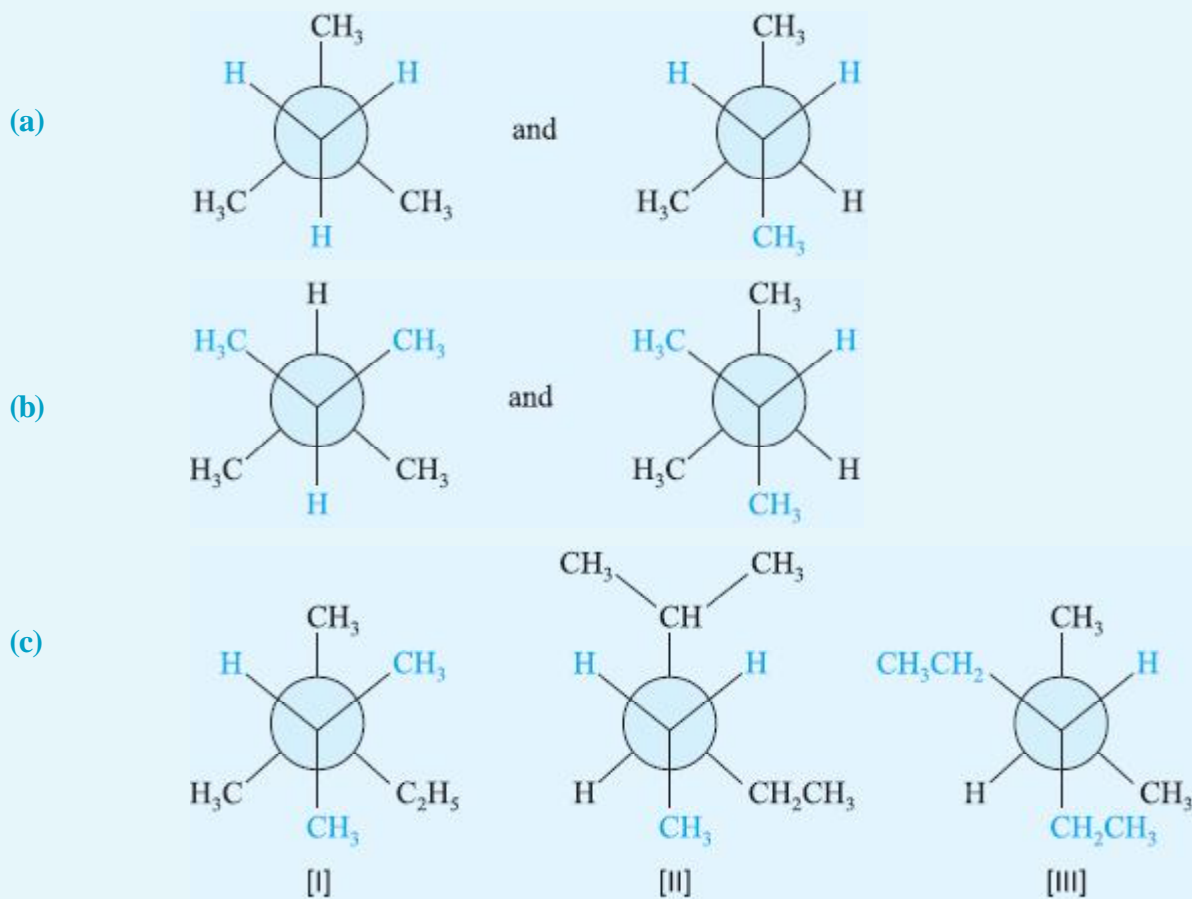
- (c) The hydrogen at C-2 and C-3 may be gauche to one another (P), or they may be anti (Q).



- (d) The 2-methylbutane conformation with one gauche  $\text{CH}_3 \cdots \text{CH}_3$  and one anti  $\text{CH}_3 \cdots \text{CH}_3$  relationship is more stable than the one with two gauche  $\text{CH}_3 \cdots \text{CH}_3$  relationships. The more stable conformation has less van der Waals strain.

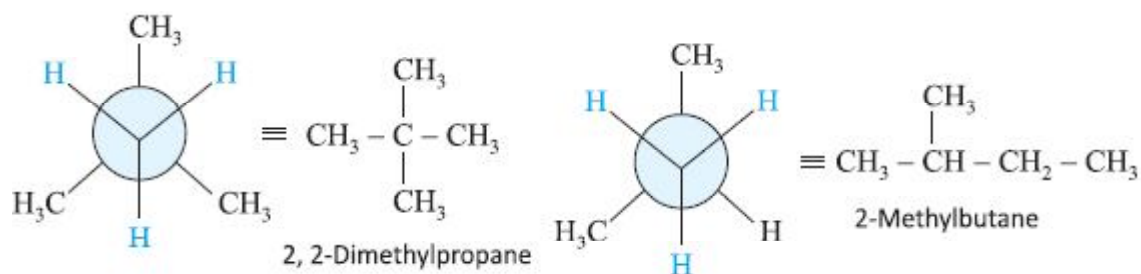


**Illustration - 6** Determine whether the two/three structures in each of the following pairs represent constitutional (structural) isomers or different conformations of the same compound.



### SOLUTION:

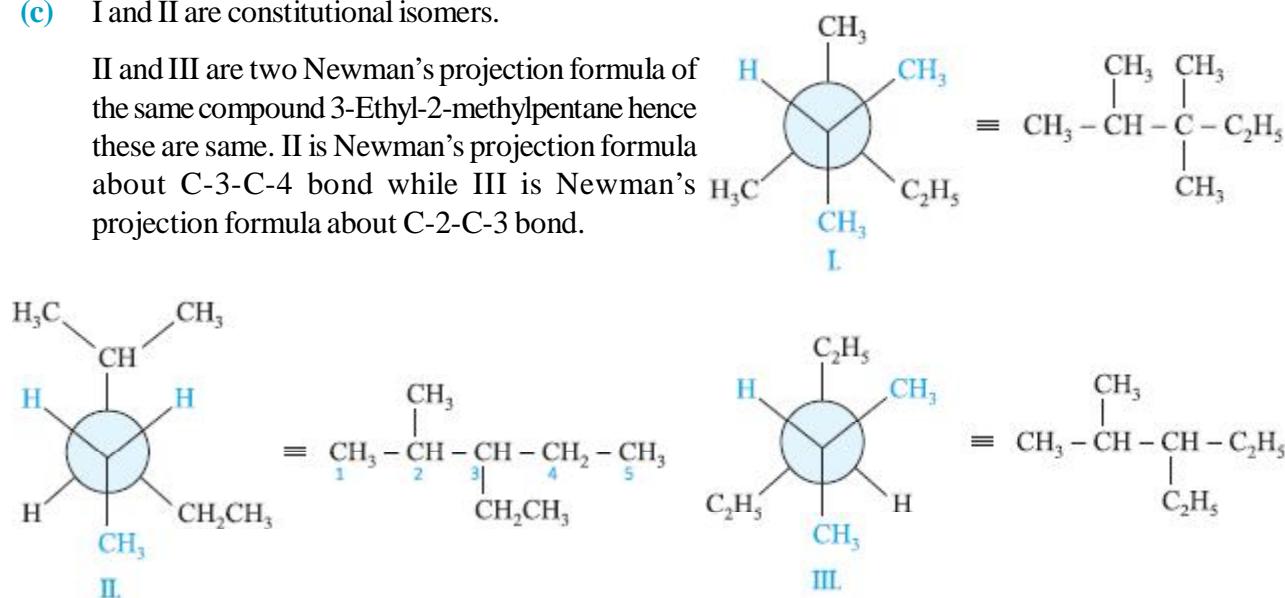
- (a) By rewriting the structures in a form that shows the order of their atomic connections, it is apparent that the two structures are constitutional (structural) isomers.



- (b) Two compounds have the same constitution (structure); both are  $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$ . The Newman projections represent different staggered conformations of the same molecule; in one the hydrogens are anti to each other whereas in the other they are gauche. Both are different conformations of 2, 3-dimethylbutane.

(c) I and II are constitutional isomers.

II and III are two Newman's projection formula of the same compound 3-Ethyl-2-methylpentane hence these are same. II is Newman's projection formula about C-3-C-4 bond while III is Newman's projection formula about C-2-C-3 bond.

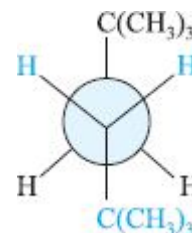


### Illustration - 7

Write a structural formula for the most stable conformation of 2, 2, 5, 5-tetramethyl hexane using Newman's projection of conformation about C-3- C-4 bond.

### SOLUTION :

The structural formula of compound is  $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$ . Both C-3 and C-4 have two hydrogens and a tert-butyl groups attached. The most stable conformation has the large tert-butyl groups anti to each other.



### Illustration - 8

(a) Write Newman projections for the gauche and anti conformations of 1, 2-dichloroethane ( $\text{Cl}-\text{CH}_2\text{CH}_2-\text{Cl}$ ).

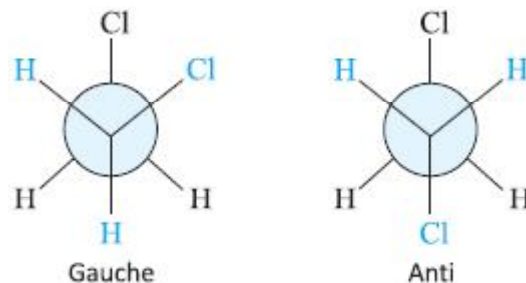
(b) The measured dipole moment of  $\text{ClCH}_2\text{CH}_2\text{Cl}$  is 1.12 D. Which one of the following statements about 1, 2-dichloroethane is false?

- (i) It may exist entirely in the anti-conformation
- (ii) It may exist entirely in the gauche conformation.
- (ii) It may exist as a mixture of anti and gauche conformations.



**SOLUTION:**

- (a) The dihedral angle between chlorine substituents is  $60^\circ$  in the gauche conformation and  $180^\circ$  in the anti conformation of  $\text{Cl-CH}_2\text{-CH}_2\text{-Cl}$ .



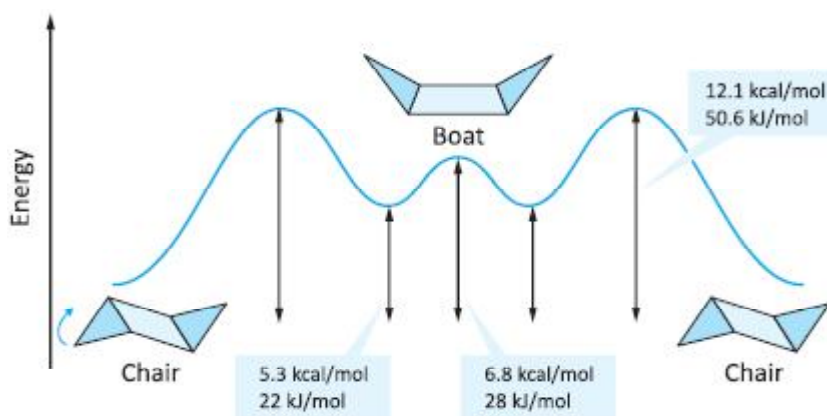
- (b) All the individual bond dipole moments cancel in the anti conformation of  $\text{Cl-CH}_2\text{-CH}_2\text{-Cl}$ , and this conformation has no dipole moment. Because  $\text{ClCH}_2\text{CH}_2\text{Cl}$  has a dipole moment of 1.12 D, it can exist entirely in the gauche conformation or it can be a mixture of anti and gauche conformations, but it cannot exist entirely in the anti conformation. Statement I is false.

**Conformers of Cyclohexane:**

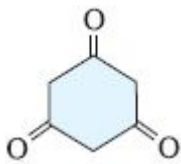
The cyclic compounds most commonly found in nature contain six-membered rings because carbon rings of that size can exist in a conformation-called a chair conformer-that is almost completely free of strain.

Cyclohexane can also exist as a boat conformer, shown in figure like the chair conformer, the boat conformer is free of strain. However, the boat conformer is not as stable because some of the bonds are eclipsed.

**Order of Stability :** Chair form > Twisted boat > Boat > Half chair.



## IN-CHAPTER EXERCISE-B

1. Write structural formulae for each of the following :
- (i) Three primary alcohols and one tertiary alcohol with the formula  $C_4H_8O$
  - (ii) A secondary alcohol with the formula  $C_3H_6O$
  - (iii) A cyclic ester with the formula  $C_4H_4O_4$
  - (iv) Two unsaturated dibasic acids with formula  $C_4H_4O_4$
2. Write all the isomers of the formula  $C_5H_{10}O_2$  and select pair of one type of isomers.
3. Make tautomer of : 
4. Write structure that correspond to the following description :
- (i) four esters with the formula  $C_4H_8O_2$
  - (ii) Two aldehydes with the formula  $C_4H_8O$
  - (iii) three ketones with the formula  $C_5H_{10}O$
  - (iv) a tertiary amine with the formula  $C_4H_{11}N$

NOW ATTEMPT IN-CHAPTER EXERCISE-B FOR REMAINING QUESTIONS



## RESONANCE &amp; AROMATICITY

## Section - 5

## Resonance

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.

It generally occurs when there is a conjugation of  $\pi$ -bonds (alternate double-single-double bond arrangement) known as *conjugated system*. It also takes place when there is double bond ( $C=C$  or  $C=O$ ) along with a group (G) present in the carbon chain having a lone pair.

*Consider resonance in 1,3-Butadiene (having a conjugated system):*

- $\pi$ -electrons move from first carbon atom to last carbon atom resulting in different structure.

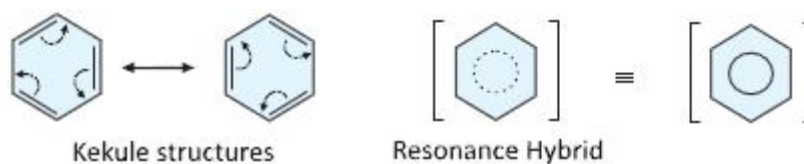


Note that the relative atomic arrangement of four carbon atoms is same in both the structures (I) and (II).

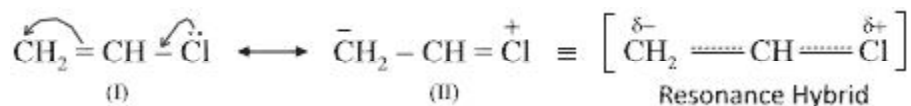
Resonance hybrid (actual structure) of butadiene is represented as follows (in square brackets) :



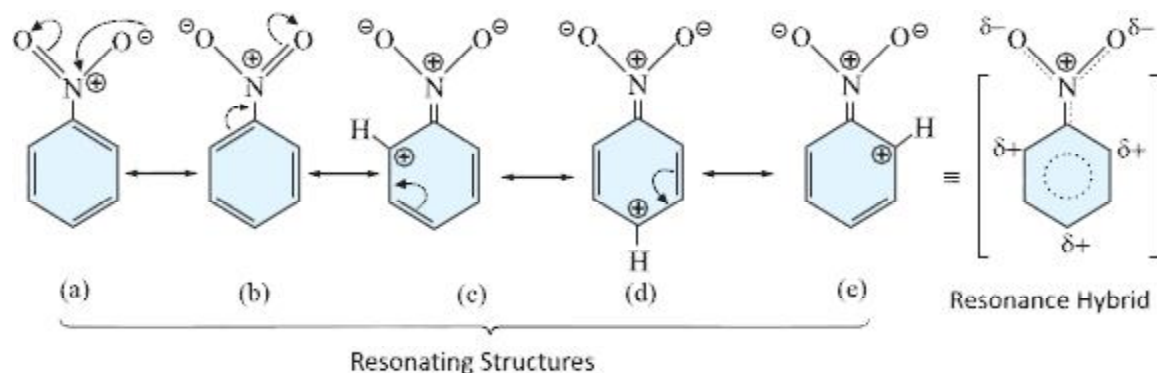
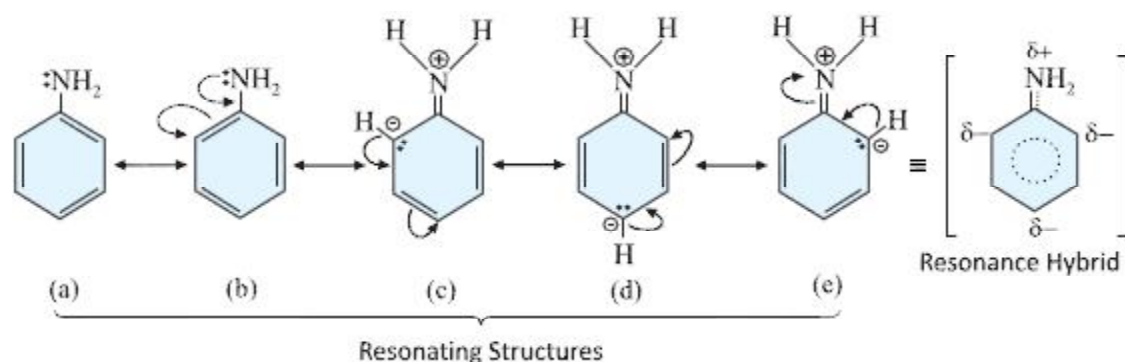
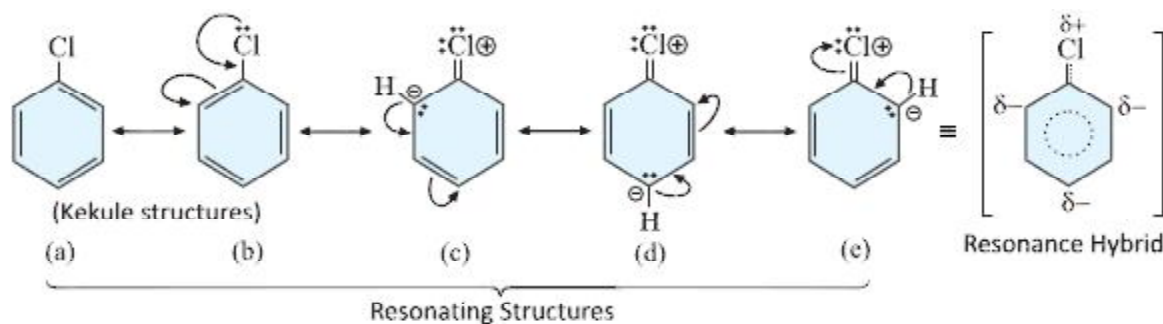
- *Consider resonance in Benzene ( $\text{C}_6\text{H}_6$ ) :*



- *Consider resonance in Vinyl Chloride :* Observe that group having a lone pair i.e., Cl is in conjugation with double ( $C=C$ ).

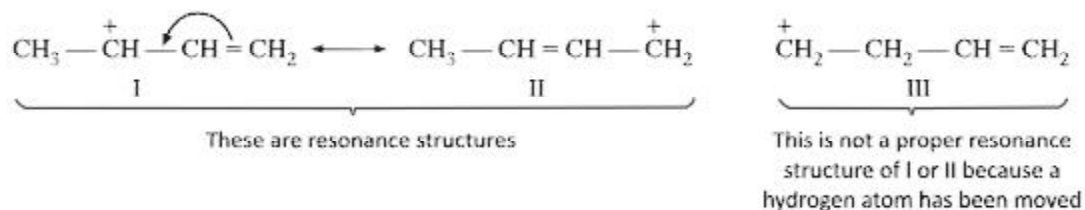


The various resonating structures of chlorobenzene, aniline and nitrobenzene are illustrated in following diagrams.



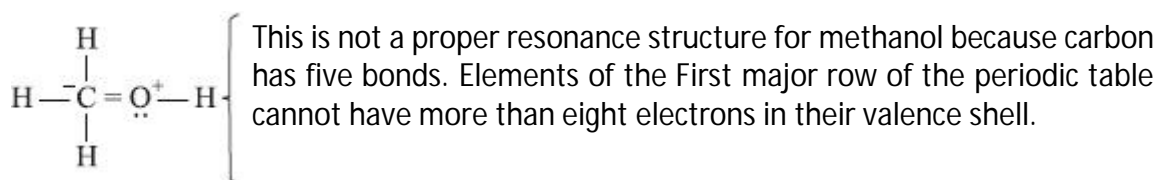
## Rules for Resonance

- No real existence of Resonance structures:** Although the resonating structures have no real existence of their own, these structures are useful because they allow us to describe molecules and ions for which a single Lewis structure is inadequate. We write two or more Lewis structures, calling them resonating structures or contributing structures. We connect these structures by double-headed arrows ( $\leftrightarrow$ ), and we say that the real molecule or ion is a hybrid of all of them.
- While writing Resonance structures we are only allowed to move electrons:** The relative positions of the nuclei of the atoms must remain the same in all of the structures. Structure III is not a resonance structure of I or II, in the given example, because in order to form it, we would have to move a hydrogen atom and this is not permitted :



Actually speaking, when we move electrons, we move only those of  $\pi$  bonds (as in the example above) and those of non-bonding pairs (such as lone pairs).

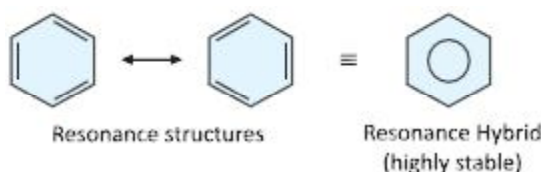
3. **All of the structures must be proper Lewis structures :** We should not write structure in which carbon has five bonds, for example:



4. **Resonance Stabilisation:** The energy of the actual molecule (Resonance hybrid) is lower than the energy of any one of all the contributing structures. Hence the resonance hybrid is more stable form.

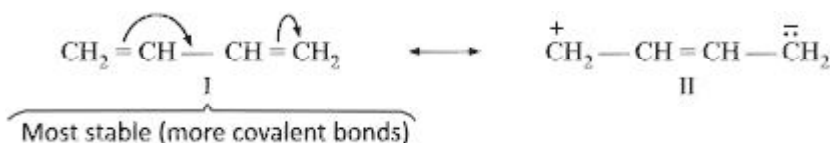
- 5. The more stable a structure is, the greater is its contribution to the hybrid.**

For example, benzene is highly resonance stabilized because it is hybrid of the two equivalent forms that are highly stable.



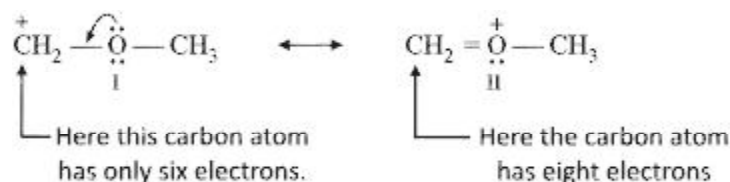
- 6.** The following rules will help us in making decisions about the relative stabilities of resonance structures.

- (a) **The more covalent bonds a structure has, the more stable it is :** This is because a covalent bond lowers the energy of atoms. This means that out of the following two structures for 1, 3-Butadiene, I is the most stable and hence imparts greater contribution to the stability of resonance hybrid.

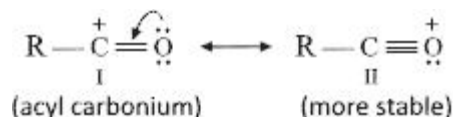


- (b) **Structure in which all of the atoms have a complete valence shell of electrons are especially stable and make large contributions to the hybrid :** In the following example, the structure II makes a larger stabilizing contribution to the cation than the structure I because all of the atoms of structure II have a complete valence shell.

Also note that structure II has more covalent bonds than structure I.



On the same pattern the structure II of the acyl carbonium ion is more stable than I

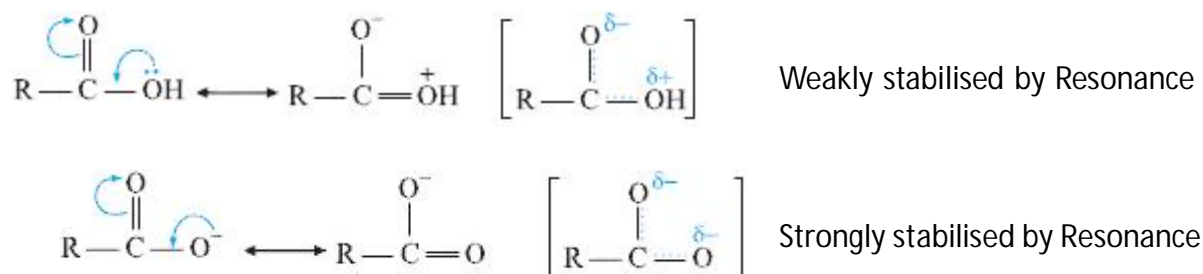


- (c) **Charge separation decreases stability** : Separating opposite charges requires energy, hence the structures in which opposite charges are separated have greater energy (lower stability) than those that have no charge separation. This means that of the following two structures for vinyl chloride, structure I makes a larger contribution because it does not have charge separation (This does not mean that structure II does not contribute to the hybrid ; it just means that the contribution made by II is smaller).



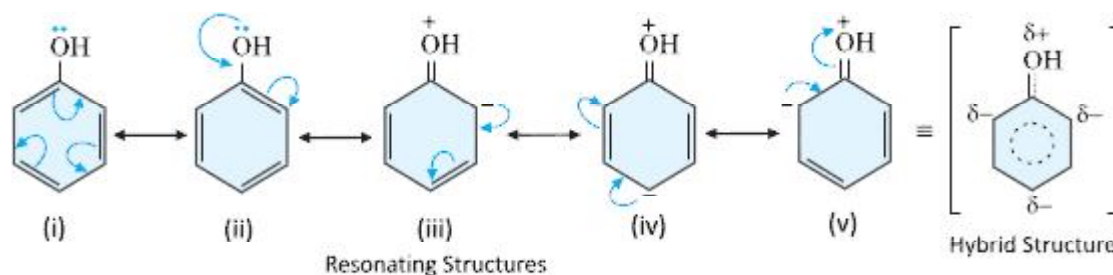
- (d) **Resonance contributors with negative charge on highly electronegative atoms are more stable than ones with negative charge on less or nonelectronegative atoms** : Conversely, resonance contributors with positive charge on highly electronegative atoms are less stable than ones with positive charge on nonelectronegative atoms.

► Observe the rules (c) and (d) above are illustrated beautifully in the following illustration:



Carboxylic acids ( $\text{RCOOH}$ ) are less stable than carboxylate ions ( $\text{RCOO}^-$ ) because in carboxylic acids, there is charge separation in one of the resonating structure.

Structures where *formal charges* don't suit the electronegativity of the atom on which they rest, are less stable e.g., consider the resonating structure of phenol.



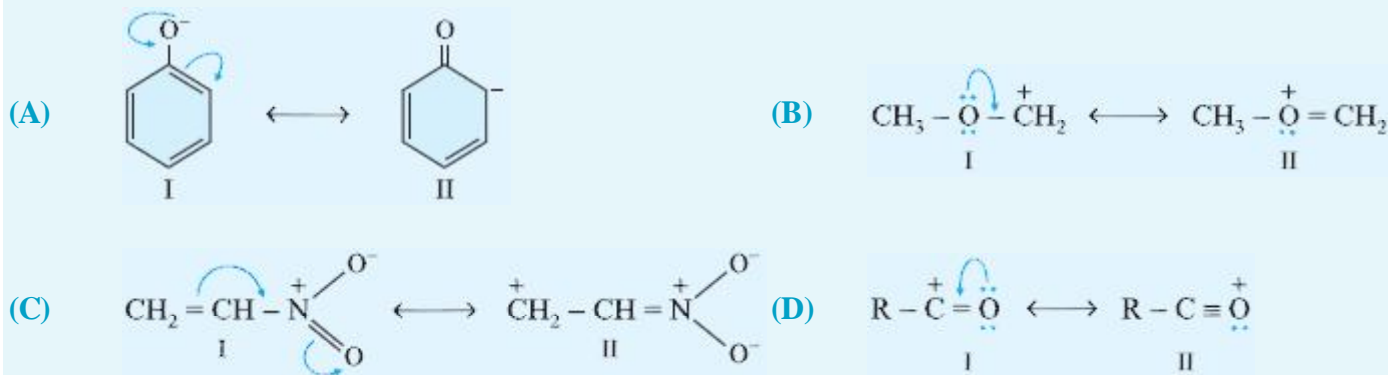
Structure (i) and (ii) are more stable than the others. These are also known as Kekulé Structures.

Structures (iii), (iv) and (v) are less stable due to:

- (a) charge separation      (b) +ve charge over Oxygen atom

### Illustration - 9

In each of the following pairs showing resonating structures, identify which is more stable and why?



### SOLUTION :

- (A) I is more stable than II, because in II, the formal charge (-) is on carbon atom which does not suit its electronegativity.
- (B) II is more stable than I. In II, all atoms (except H-atom) have an octet, whereas in I, carbon has sixet (incomplete octet).
- (C) I is more stable than II, since in I all have complete octets.
- (D) II is more stable than I because in the former, all the atoms have complete octet.

### Aromatic (Hückel Rule), Anti-aromatic and Not Aromatic

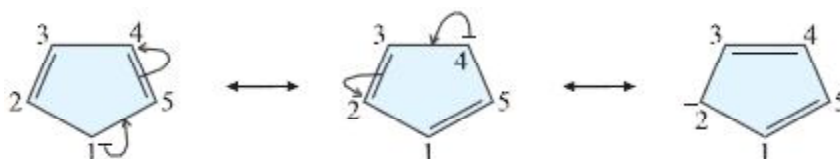
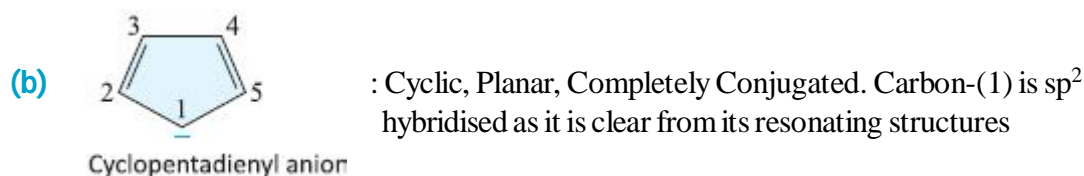
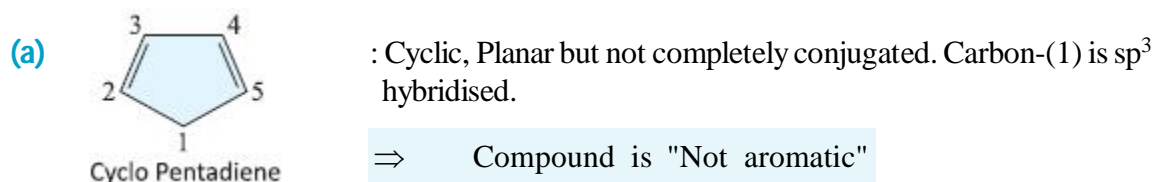
Among planar, monocyclic, fully conjugated polyenes, only those possessing  $(4n + 2) \pi$  electrons, where  $n$  is a whole number, will have special stability ; that is, be aromatic.

Condition for a compound to be :

- (i) **Aromatic :** Cyclic, Planar, Complete Conjugation,  $(4n + 2)\pi e^-$ s ( $n = 0, 1, 2, \dots$ )
- (ii) **Anti-aromatic :** Cyclic, Planar, Complete Conjugation,  $4n \pi e^-$ s ( $n = 1, 2, \dots$ )
- (iii) **Not-aromatic :** Not cyclic OR Not Planar OR Not Completely Conjugated.

What is Complete Conjugation? Alternate single and double bonds. In other words, every Carbon has to be  $sp^2$  hybridised.

### Examples :



Now count the number of  $\pi e^-$ s in the compound as per the following rules:

- (i) Each '=' bond is counted as  $2\pi e^-$ s
- (ii) Count the number of lone pairs.

If the number of lone pairs is: Singly Bonded: Count as  $2\pi e^-$ s

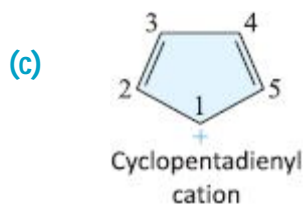
=1 : Check bonding of atom with lone pair Doubly Bonded: Do not count

>1 : Count them as exactly one lone pair and go back to the above condition corresponding to 1 lone pair.

Number of  $\pi e^-$ s =  $4$  (From 2 double bonds) +  $2$  (one lone pair at C-1 and is single bonded)

$$= 6e^- \Rightarrow \text{Compound is "Aromatic"}$$





: Cyclic, Planar, Completely Conjugated (See Resonating Structure)

However, in anti-aromatic species delocalization of  $\pi$ -electron does not take place. i.e., they have conjugation but no delocalisation.

Now, count the number of p e-s : 4 (From 2 double bonds)

$\Rightarrow$  Compound is "Anti-aromatic"



: Cyclic, Planar, Completely Conjugated.

Now, count number of  $\pi$ e's : 2 (From 1 double bond)

$\Rightarrow$  Compound is "Aromatic"

**Note :** Cyclopropenyl cation is smallest aromatic species.

(e) **Pyridine : ( $C_5H_5N$ ) :**

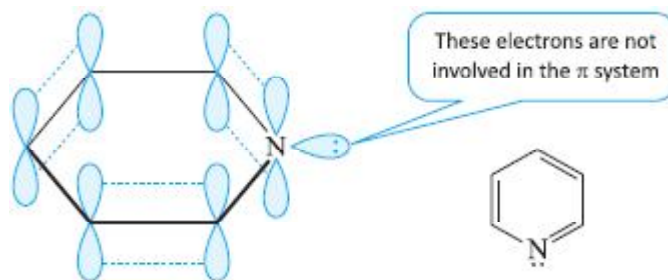
Cyclic, Planar, Completely Conjugated.

$6\pi$ e's (From 3 double bonds)

**Note :** 'N' has 1 lone pair and is doubly bonded.

So, this will not be counted.

$\Rightarrow$  Compound is "Aromatic"



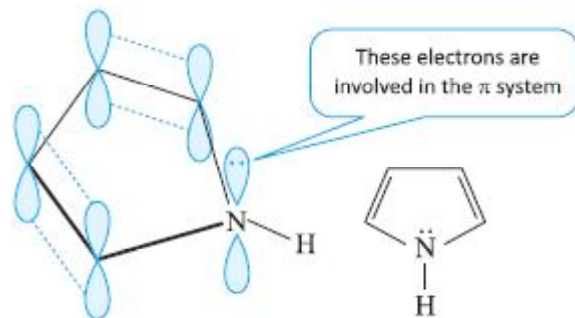
(f) **Pyrrole :  $C_4H_4NH$**

Cyclic, Planar, Completely Conjugated.

$4\pi$ e's (From 2 double bonds) +  $2\pi$ e's (From 1 lone pair)

$\Rightarrow$  Compound is "Aromatic"

**Note :** 'N' has 1 lone pair and is singly bonded.

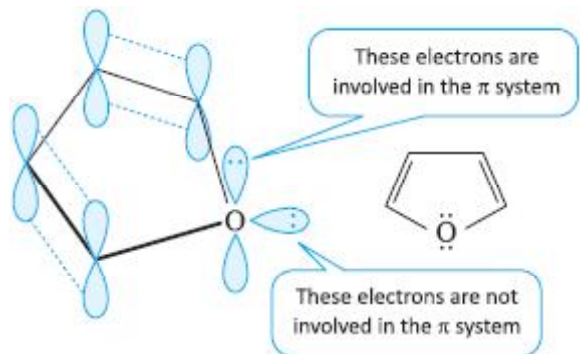


(g) **Furan :**

Cyclic, Planar, Completely Conjugated.

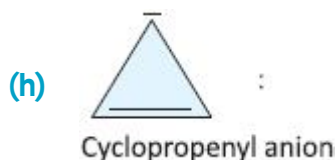
Number of  $\pi$ e's

= 4 (From 2 double bonds) + 2 (From 1 lone pair)



**Note :** 'O' has 2 lone pairs. Count only one lone pair.

⇒ Compound is "Aromatic"



Cyclic, Planar, Completely Conjugated

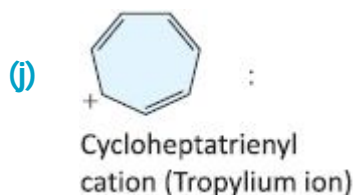
Number of  $\pi e^-$ s = 2(From 1 double bond) + 2(From 1 lone pair) = 4

⇒ Compound is "Anti-aromatic"



Cyclic, Planar, Not Completely Conjugated.

⇒ Compound is "Not Aromatic"

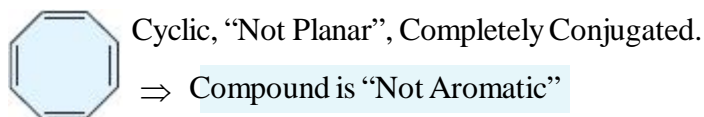


Cyclic, Completely Conjugated.

Number of  $\pi e^-$ s = 6 (From 3 double bonds)

⇒ Compound is "Aromatic"

(k) **Cyclo-Octatetraene :**



**Note:** It has a tub shape structure



Number of  $\pi e^-$ s = 4(From 2 double bonds) ⇒ Compound is "Anti-Aromatic"

- If a compound is Anti-aromatic, it is less stable than its open chain counter part i.e.,  $\pi$  electrons conjugation adds de-stability to the compound, if it is anti-aromatic.
- If a compound is aromatic, it adds stability to the compound through  $\pi$  electrons delocalisation.

**Note :** There are thousands of aromatic compounds that are not monocyclic such as naphthalene, azzulene, anthracene etc. are polycyclic aromatic hydrocarbons.

**NOW ATTEMPT IN-CHAPTER EXERCISE-C BEFORE PROCEEDING AHEAD IN THIS EBOOK**



## ORGANIC REACTIONS [BASICS]

## Section - 6

Organic compounds are covalent bonded. The carbon atom in these may be  $sp^3$ ,  $sp^2$  or  $sp$  hybridised. Hydrocarbons are almost non-polar, but their derivatives containing functional group are polar covalent compounds. To understand and visualise the mechanisms of organic reactions, first we must go into details of various types of electrical effects that monitor the properties of various organic compounds. Then we have to understand various types of **Substrates** (main organic compound) ; **Intermediates** formed from these substrates ; the various types of **Reagents** and the **Medium(solvent) in which** organic reactions occur.

All organic reactions can be classified into one of the following three categories for the purpose of understanding reaction mechanisms :

(i) Substitution Reactions    (ii) Addition Reactions    (iii) Elimination Reactions

Above three categories of reactions may involve : Rearrangement, Cyclisation (Ring opening & Ring closing) and stereo specific changes (involving optical and geometrical isomers), oxidation and reduction.

- 1. Substrate :** It is the main organic compound acting as reactant and reacts with a reagent to give an new organic compound as main product. Substrates in general are of two types :

**Nucleophilic:** The organic compounds which have “electron rich centre or area” are referred to as nucleophilic in nature. They are acted upon by electron seeking reagents.

Alkenes, alkynes and benzene and its derivatives are some of such important substrates.

**Electrophilic :** The organic compounds which have “electron deficient centre or area” are referred to as Electrophilic in nature. They are acted upon by electron rich reagents usually most of organic derivatives containing functional groups act as electrophilic substrates. Organic Halides, Alcohols, Ethers, Aldehydes & Ketones and Carboxylic Acids & Derivatives are some of the important electrophilic substrates.



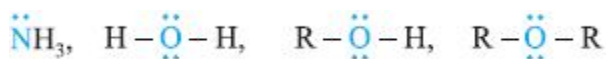
- 2. Reagents :** Based on the attack by the type of attacking reagent, these are further categorised.

The main type of attacking reagents are:

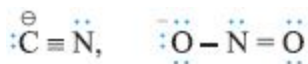
- (a) Nucleophile:** Electron rich species, looking to attack a +vely charged centre (Electrophilic substrate). These are classified as follows:

**Charged :**  $\text{H}^-$ ,  $\text{OH}^-$ ,  $\text{RO}^-$ ,  $\text{CH}_3^-$ ,  $\text{X}^-$ ,  $\text{HS}^-$  .....etc.

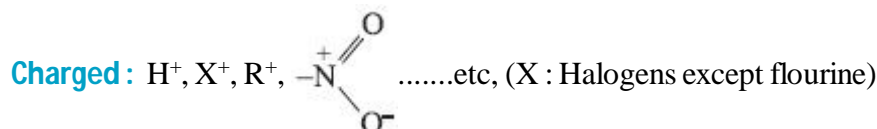
**Neutral :** Covalent compounds in which central atom has complete octet, has atleast one lone pair.



**Ambident** : Species having two nucleophilic centres, one is neutral (complete octet and has atleast one lone pair of electrons) and other is charged (negative charge). They basically have two nucleophilic sites / atoms.



(b) **Electrophiles** : Electron deficient species, looking to attack an electron rich site (Nucleophilic substrate). These are classified as follows:



**Neutral** :  $\text{CO}_2$ ,  $\text{AlCl}_3$ ,  $\text{CS}_2$  . . . . .etc.

(c) **Free radicals** : Atom or group of atoms with their valencies unsatisfied, looking to attack a place so that they can satisfy their valencies. e.g.,  $\text{Cl}^\bullet$ ,  $\text{Br}^\bullet$ ,  $\text{R}^\bullet$  (alkyl)

### 3. Reaction Mechanism :

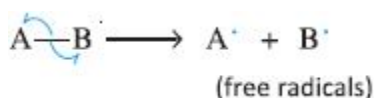
It gives detailed aspect of as to “How actually an organic reaction proceeds”. It depicts step-by-step visualisation of an organic reaction.

Organic reactions always involve breaking and reforming of covalent bonds. A covalent bond can break into two ways; In one of the ways, one of the fragments takes away the bonded electron pair (*Heterolytic cleavage*) and in other, each fragment takes away one of the electrons of bond (*Homolytic cleavage*).

Such fragments are known as **Reaction intermediates** such as;  $\text{C}^+$  (carbocations),  $\text{C}^-$  (carbanions) and  $\text{C}^\bullet$  (free radicals).

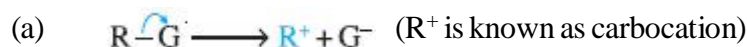
#### I. Homolytic Fission:

Such type of fission occurs in gas phase or in non-polar solvents (i.e., absence of polarising solvents) and is catalysed by free radical initiators. In such fission, free radicals are formed. Here the bond pair is equally shared after the fission.



#### II. Heterolytic fission :

Such type of fission occurs in polarising solvents (such as  $\text{H}_2\text{O}$ , alcohols and acids), catalysed by acids or bases, greatly influenced by polarity of solvents. Here, the ions are formed. In an organic compound such as  $\text{R}-\text{G}$ , two types of ions are formed.



#### 4. Electrical Effects:

For the detailed analysis of Reaction Mechanism, we have to first understand “Electrical Effects” existing in the Organic Substrate and induced by External Reagents.

There are four kinds of Electrical Effects to be studied for the understanding of Reaction Mechanism.

- |                                 |   |
|---------------------------------|---|
| <b>I.</b> Inductive Effect      | <b>II.</b> Resonance (Mesomeric) Effect |
| <b>III.</b> Electromeric Effect | <b>IV.</b> Hyperconjugation Effect      |

##### I. Inductive Effect (Polar nature of covalent bonds):

The displacement of an electron (shared) cloud along the carbon atom chain due to the presence of an electron withdrawing (*electron attracting*) or electron releasing (*electron repelling*) groups in the carbon chain is known as Inductive Effect (**I-effect**).

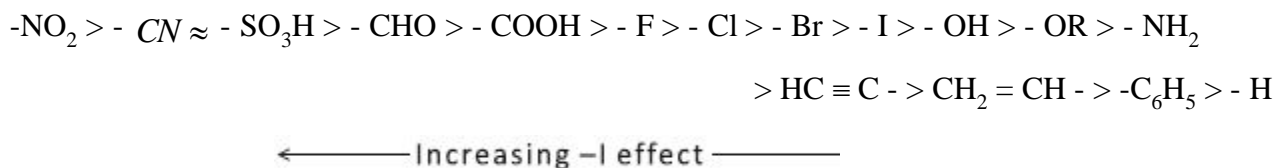
- It is a permanent effect which is transmitted along the carbon-carbon chain.



But the effect is insignificant beyond the third carbon atom.

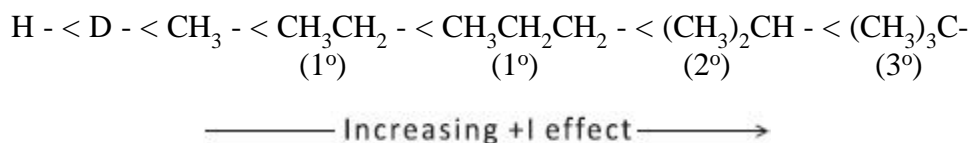
- Any atom or group which attracts electrons more strongly than hydrogen is said to exert a negative effect (**-I effect**); an atom or group which attracts electrons less strongly than hydrogen is said to exert a positive inductive effect (**+I effect**).

##### Group producing -I effect : (All functional groups)

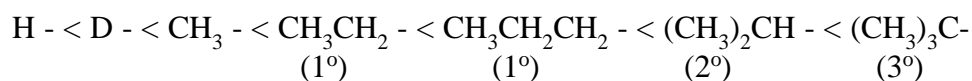


- Note:** (i) Alkynyl, vinyl and phenyl groups, because of  $sp$  and  $sp^2$  hybrid carbon atom exert weak -I effect. Carbon atoms which are  $sp$  and  $sp^2$  hybridised are electronegative in character due to dominance of 's' character over 'p' character. [50% 's' character in  $sp$  and 33% 's' character in  $sp^2$  hybrid carbon]
- (ii) All such groups are called as **Electron Withdrawing Groups (EWG)**.

##### Groups producing +I effect : (Only alkyl groups)



### Groups producing +I effect : (Only alkyl groups)



————— Increasing +I effect —————>

- Note:** (i) All alkyl and cycloalkyl groups because of  $sp^3$  hybrid carbon atom exert +I effect. An  $sp^3$  hybrid carbon atom is an electron releasing (donating) due to dominance of 'p' character over 's' character. [75% p character]
- (ii) All these alkyl groups are called as: **Electron Releasing Groups (ERG)** or **Electron Donating Group (EDG)**.

## II. Resonance (or Mesomeric) 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.

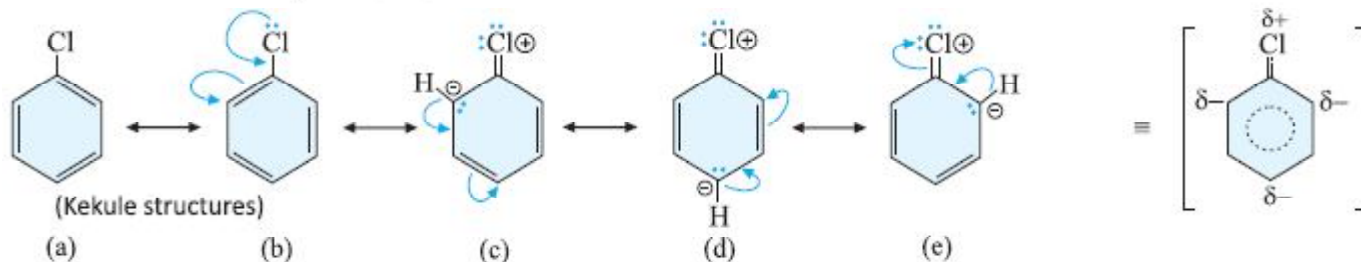
When multiple bonding is in conjugation with a functional group (G), then as per the electronic movement, we can visualise resonance in two ways illustrated below.

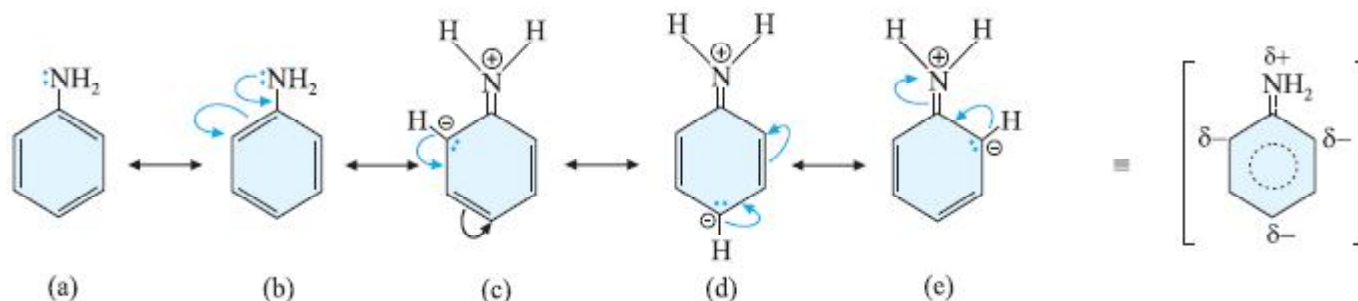
**+M effect (+R -effect) :** When the movement of electrons starts from a particular group (G) towards the carbon chain ( $\text{C} = \text{C}$ ).

It takes place when group (G) has a lone pair or an extra electron (in an anion).

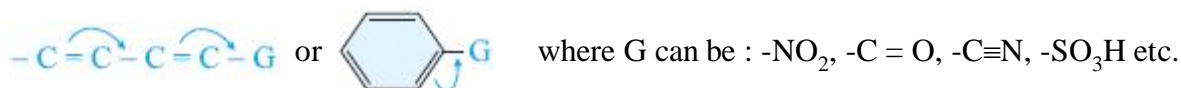


where G can be :  $-\text{NH}_2, -\text{OH}, -\text{Cl}, -\text{OR}$  etc.

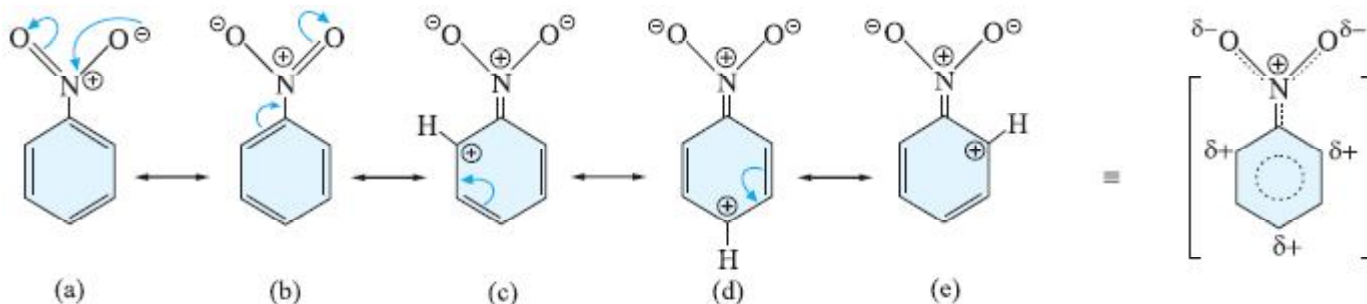
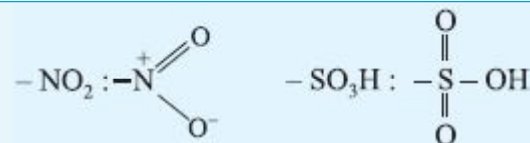




**-M effect (-R-effect) :** When the movement of electrons takes place towards a particular group (G) from carbon chain (C = C).



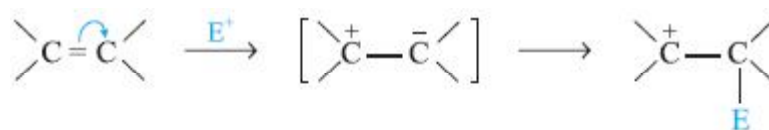
**Note:** In general, in the groups showing (-R/-M) effect, the “attached atom” of the group is unsaturated with a more electronegative atom e.g.



### III. Electromeric Effect:

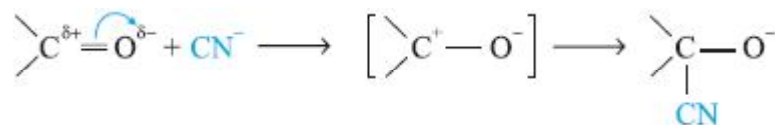
It is a temporary polarising effect and operates only in molecules having  $\pi$ -electrons (i.e., multiple bonded compounds) induced by the attacking reagents (nucleophiles & electrophiles) in a chemical reaction.

- In presence of electrophiles ( $\text{E}^+$ ),  $\pi$ -electrons shift to other carbon to make adjustment for the incoming electrophile to be added.



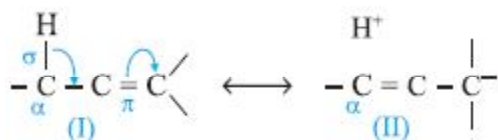
Observe that  $\text{E}^+$  (electrophile) adds to the atom(group) where electrons are transferred. Such effect is known as **+E effect**, when the transfer of electrons takes place towards the attacking reagent.

- In polar bonds, in presence of attacking reagents, a complete transfer of electron (one of  $\pi e^-$  pair) to more electronegative atom takes place, e.g., in  $\text{>C}^{\delta+}=\text{O}^{\delta-}$  in presence of nucleophiles like  $\text{R}^-$ ,  $\text{CN}^-$ ,  $\text{HSO}_3^-$ ,  $\pi$  electrons shifts over to O.



Observe that  $\text{CN}^-$  (nucleophile) adds to the atom (group) from where electrons are transferred. Such effect is known as **-E effect** i.e., when the transfer of electrons takes place away from the attacking reagent.

#### IV. Hyperconjugation Effect:

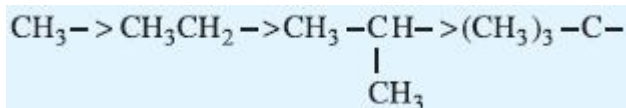


'Baker and Nathan' observed that alkyl groups (R) with at least one hydrogen (H) atom on the  $\alpha$ -carbon, attached to an unsaturated carbon atom (i.e., having a  $\text{---C=C---}$  bond), or positive charge (as in carbocation,  $\text{C}^+$ ) or odd electrons (as in free radicals,  $\text{C}^\bullet$ ) are able to release electrons by a mechanism quite similar to that of 'electrometric effect' (*but it is a permanent effect*).

This type of electron released by alkyl group is called as **hyperconjugation**. It involves delocalisation of  $\sigma$  and  $\pi$  bond orbitals ( $\sigma-\pi$  conjugation). In structure (II), note that there is no definite bond between carbon and one hydrogen atom, hence it is also known as **No bond resonance**,

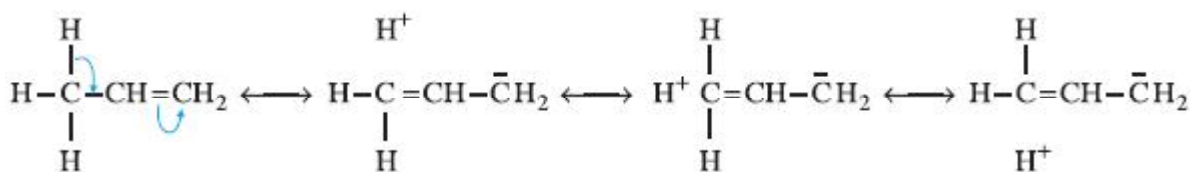
- Greater the number of C-H bond at  $\alpha$ -carbon to the unsaturated system, greater will be the electron release and greater the hyperconjugation effect.

Hence electron release due to presence of three alpha ( $3\alpha$ ) - C-H bonds in methyl groups is greater than that by an ethyl group, in which there are only two alpha ( $2\alpha$ ) - C-H bonds. Similarly, the effect decrease in isopropyl group and further in tert-butyl group (no  $\alpha$ -C-H bond).

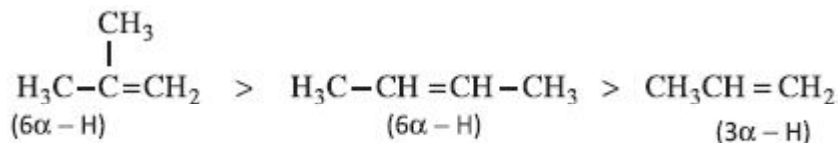


← increasing hyperconjugation effect ——— and ——— increasing +I effect →

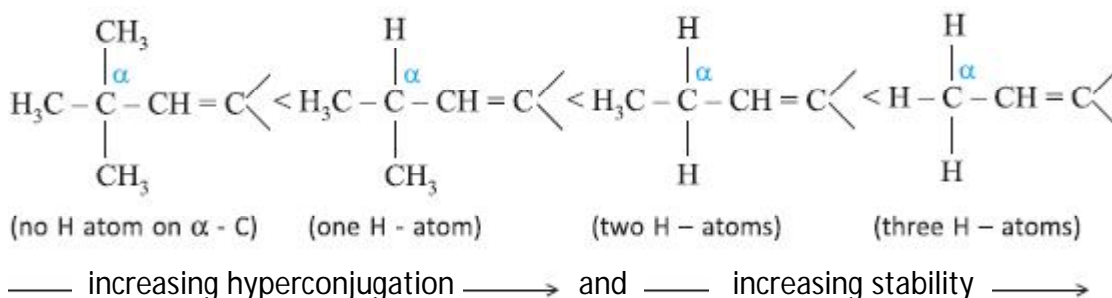
- **Stability of Alkenes**: Hyperconjugation explains the order of stability of alkenes. Propene is more stable than ethene because in propene, there are three H-C hyperconjugated bonds and hence  $\sigma$ -electrons of C-H bonds can delocalise over three different structures.



Hence greater the number of Methyl (each methyl group has  $3\alpha - \text{H}$ ) groups, attached to doubly bonded carbons, the more stable the alkene is



[more H-C bond on same carbon give greater effect]



### ➤ Illustrating the Concept of Hyperconjugation :

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)  $\rightarrow \sigma^*$  and  $\sigma \rightarrow \pi^*$  electron delocalisations

**Note :**  $\pi^*$  refers to  $\pi$  anti-bonding molecular orbitals.

**Correct answer is (A)**

Hyperconjugation in tert-butyl carbocation refers to delocalisation of s-electrons over the empty p-orbitals of carbocation. In 2-butene, it refers to delocalisation of  $\sigma$  – electrons over the  $\pi^*$  orbitals of  $\text{C}=\text{C}$ .

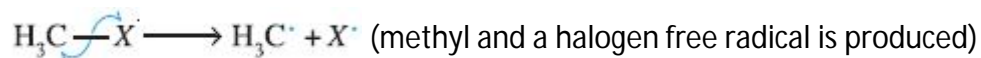


## 5. Reaction Intermediates:

While understanding a reaction in detail (Reaction Mechanism), we have to visualise the overall reaction in small steps. These steps involve various type of reaction intermediates, whose stability is the key to the acceptance of a particular reaction mechanism (path). Most typically there are three kinds of intermediate: **Free Radicals Carbocations and Carbanions.**

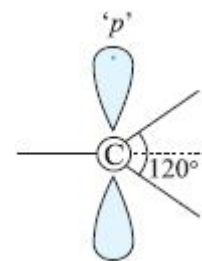
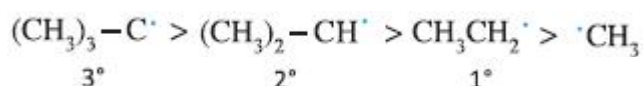
### (a) Free Radicals :

An atom (or group of atoms) having an unpaired electron is called as Free Radical. These are formed via homolytic fission.



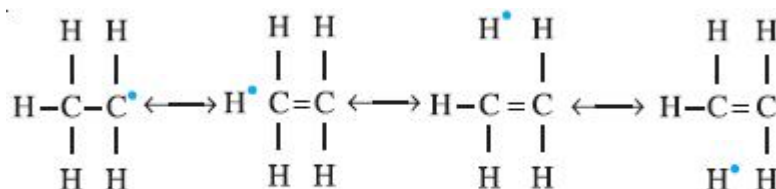
'C' of free radical (alkyl) is  $\text{sp}^2$  hybridised and hence the shape is planar, having an unhybridised  $p$ -orbital containing an odd electron (Paramagnetic in nature).

Tertiary alkyl free radicals are more stable than others. The stability of free radicals follows the order:



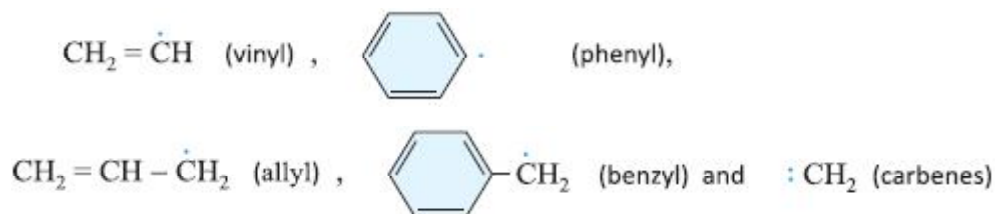
The stability of free radicals is explained via *hyperconjugation effect*. In methyl free radical, there is no hyperconjugation, as there is no  $\alpha$ -C-H bond.

Let us draw various hyperconjugation structure of ethyl radical.



Similarly a  $2^\circ$  radical is more stable than a  $1^\circ$  alkyl radical (as number of  $\alpha$  H-atoms are increasing, the hyperconjugation effect is increasing and hence stability increases).

Apart from alkyl free radicals, other important free radicals are :



Allyl and benzyl free radicals are highly stable due to resonance.






**Note :** Another kind of free radicals, **Carbenes** are also formed. Carbenes are neutral, divalent and highly reactive intermediates.

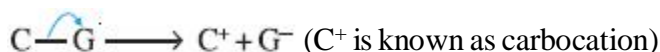


Free radicals are formed with the help of free radicals generators such as : benzoyl peroxide, tert butyl peroxide.

There are also some special type of intermediates such as Nitrene;  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\dot{\text{N}}$  and Benzyne; 

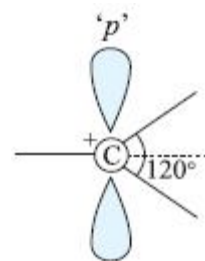
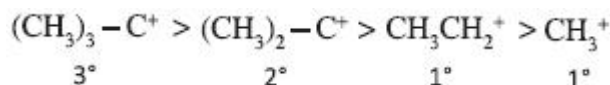
### (b) Carbocations:

The organic compounds which  $\alpha$ -carbon is electrophilic due to function attached to it, generally undergo heterolytic cleavage to form carbocations as follows :



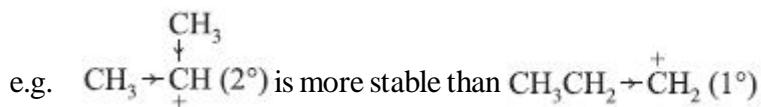
'C' of carbocation (alkyl) is  $\text{sp}^2$  hybridised with one vacant unhybridised  $p$ -orbital. Hence the structure is planar. Important carbocations include : Alkyl, allyl ( $\text{CH}_2 = \text{CHCH}_2^+$ ) and benzyl ( $\text{C}_6\text{H}_5\text{CH}_2^+$ ).

The order of stability of carbocations is:



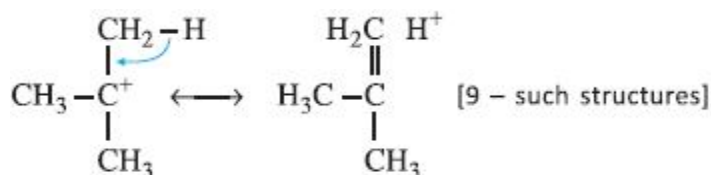
*Stabilisations of carbocation* is through +I effect and hyperconjugation effect.

- Electron releasing alkyl groups ( $\text{R} \rightarrow \text{---}$ ) disperse +ve charge over carbon.



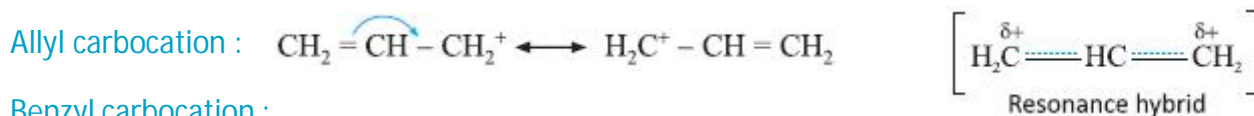
More is the number of  $\alpha$ -H attached to carbon atom having +ve charge, more is the number of hyperconjugative structures. Hence more stable is carbocation.

Observe that  $3^\circ$  butyl carbocation has 9  $\alpha$ -H and hence more stable than  $2^\circ$  and  $1^\circ$  alkyl carbocations.

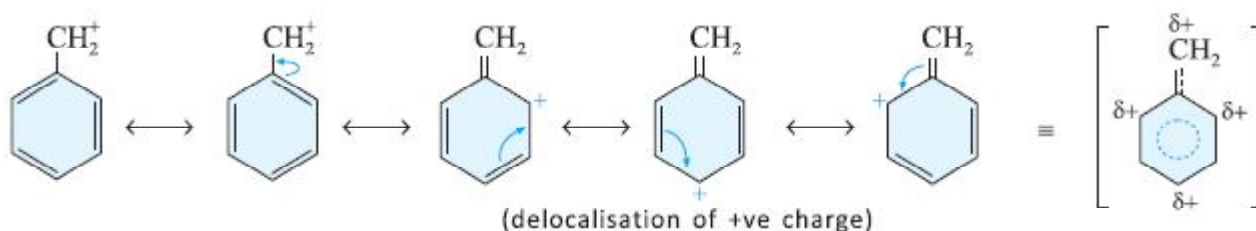


- Electron withdrawing ( $G \leftarrow \leftarrow \leftarrow C^+$ ) pulls electron density away from  $C^+$  carbon and hence stability of carbocation decrease.  $G : CN^-, CL, CHO, NO_2$  etc. e.g.  $\overset{+}{CH_2} - CH_2CHO$  is more stable than  $CH_3\overset{+}{CH} - CHO$

*Stabilisation of carbocation* is also takes place through resonance.

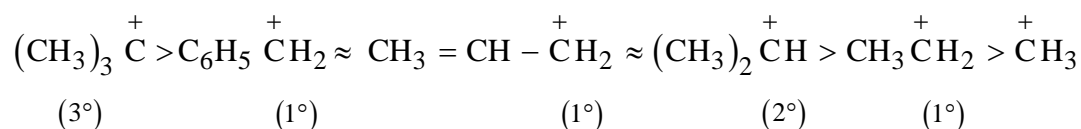


Benzyl carbocation :

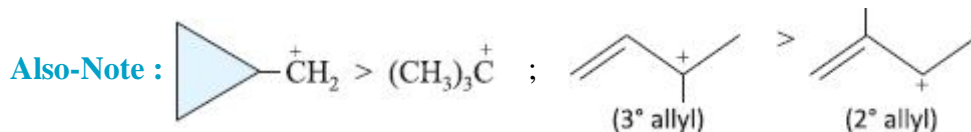


**Note:** More is the number of resonating structures dispersing the +ive charge over carbon, more is the carbocation stability e.g. Stability order follows :  $C_6H_5 - \underset{\substack{| \\ C_6H_5}}{\overset{+}{C}} - C_6H_5 > C_6H_5 - \overset{+}{CH} - C_6H_5 > C_6H_5 - \overset{+}{CH_2}$

**Order of stability of carbocation follows:**



[tert-butyl  $>$   $1^\circ$  Benzyl  $\approx$   $1^\circ$  allyl  $>$   $3^\circ$  alkyl  $>$   $2^\circ$  alkyl  $>$   $1^\circ$  alkyl  $>$  methyl]

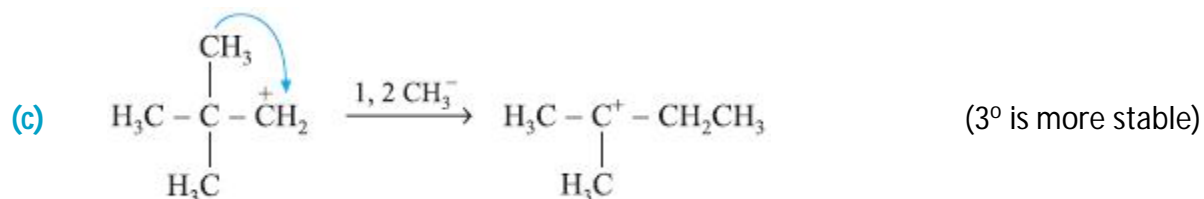
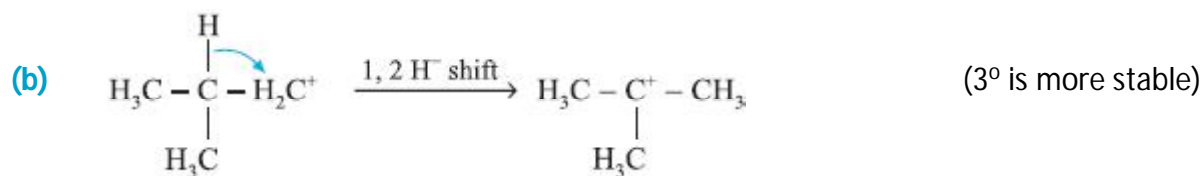
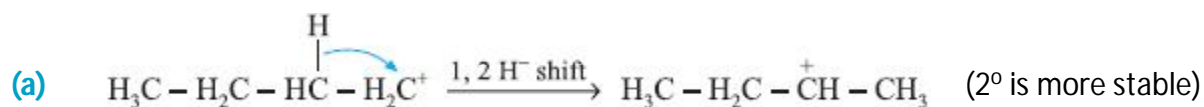


[A carbocation attached to a cyclopropyl group is exceptionally stable]

**Properties of carbocations :**

- (i)  $\text{H}_3\text{C}-\text{H}_2\text{C}^+ + \text{Nu}^- \longrightarrow \text{CH}_3\text{CH}_2\text{Nu}$  (combination with a nucleophile)
- (ii)  $\text{H}_3\text{C}-\text{H}_2\text{C}^+ \xrightarrow{\Delta} \text{CH}_2 = \text{CH}_2 + \text{H}^+$  (elimination of proton at high temperature or in presence of strong bases)

➤ In order to achieve stability (before above two properties), carbocations go through rearrangement through shift of hydride ion ( $\text{H}^-$ ) or methide ion ( $\text{CH}_3^-$ ) from adjacent carbon atom. Hence these shifts are known as 1, 2-shifts.

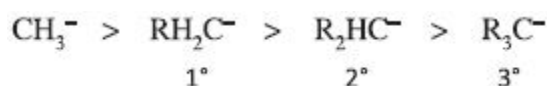


'C' of carbanions (alkyl) is  $\text{sp}^3$  hybridised, hence structure is pyramidal with one of  $\text{sp}^3$  hybrid-orbital containing a pair of electrons.

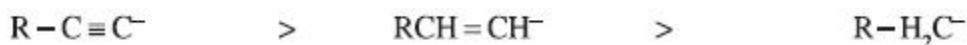


**Stabilisation of carbanion** (through -I effect)

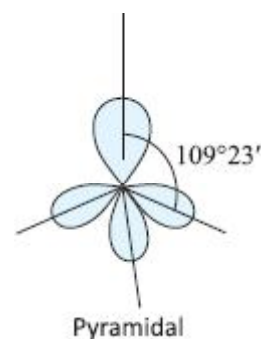
➤ Electron-withdrawing group enhances stability whereas electron-releasing (R) group decreases stability.



➤ The stability of carbanions increases with increase in 's' character (electron withdrawing).

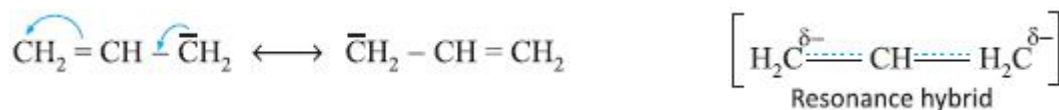


An alkynide ion 50% 's' ( $\text{sp}$ )    A vinylic ion 33% 's' ( $\text{sp}^2$ )    An alkyl ion 25% 's' Character ( $\text{sp}^3$ )

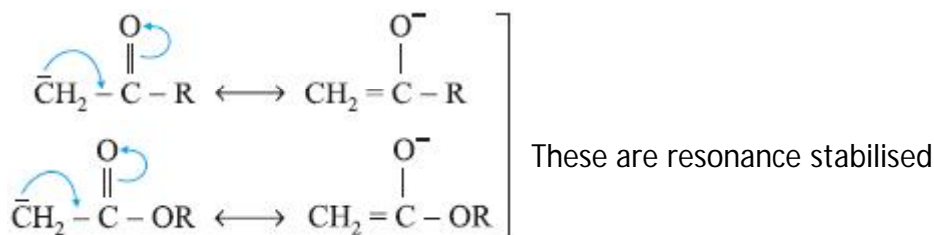


*Stabilisation of carbanion* (through resonance).

- Allyl carbanions is resonance stabilised.



- Carbanions are negatively charged particles acting as nucleophiles. Other important carbanions are from carbonyl compounds, esters, nitro compounds.



- Anions in which negative charge is present on the carbon of aromatic system is known as aromatic carbanions.

These are most stable carbanions.

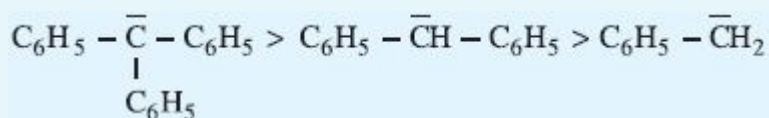


cyclopentadienyl carbanion

It obeys Hückel rule and is aromatic.

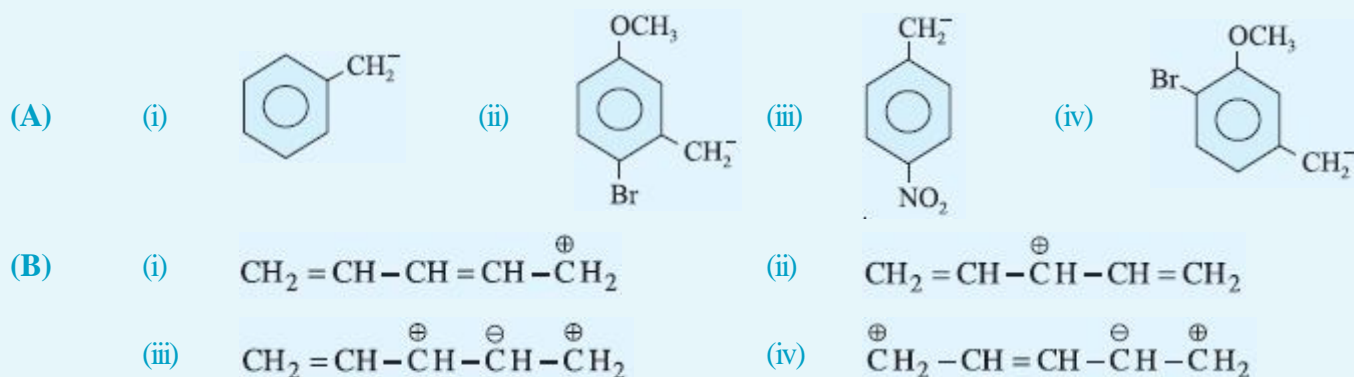
- Carbanions participate mainly in condensation reactions (to be studied later).

**Note:** (i) More is the number of resonating structure for a carbanion, more is its stability. e.g. consider the stability order:



- (ii)  $\cdot\text{CCl}_3$  is more stable than  $\cdot\text{CF}_3$  even though -I effect is more pronounced in the later and this is due to the formation of  $p\pi-d\pi$  back bonding between the unhybridised p-orbital of carbanion and empty d-orbitals of Cl atom.

**Illustration - 10** Arrange the following in increasing order of stability on the basis of resonance:



### SOLUTIONS :

(A) (i) < (iv) < (ii) < (iii)

In (iii) there is strong -M effect of  $-\text{NO}_2$ .

In (ii) and (iv) -I effect of Br and  $-\text{OCH}_3$  are prominent.

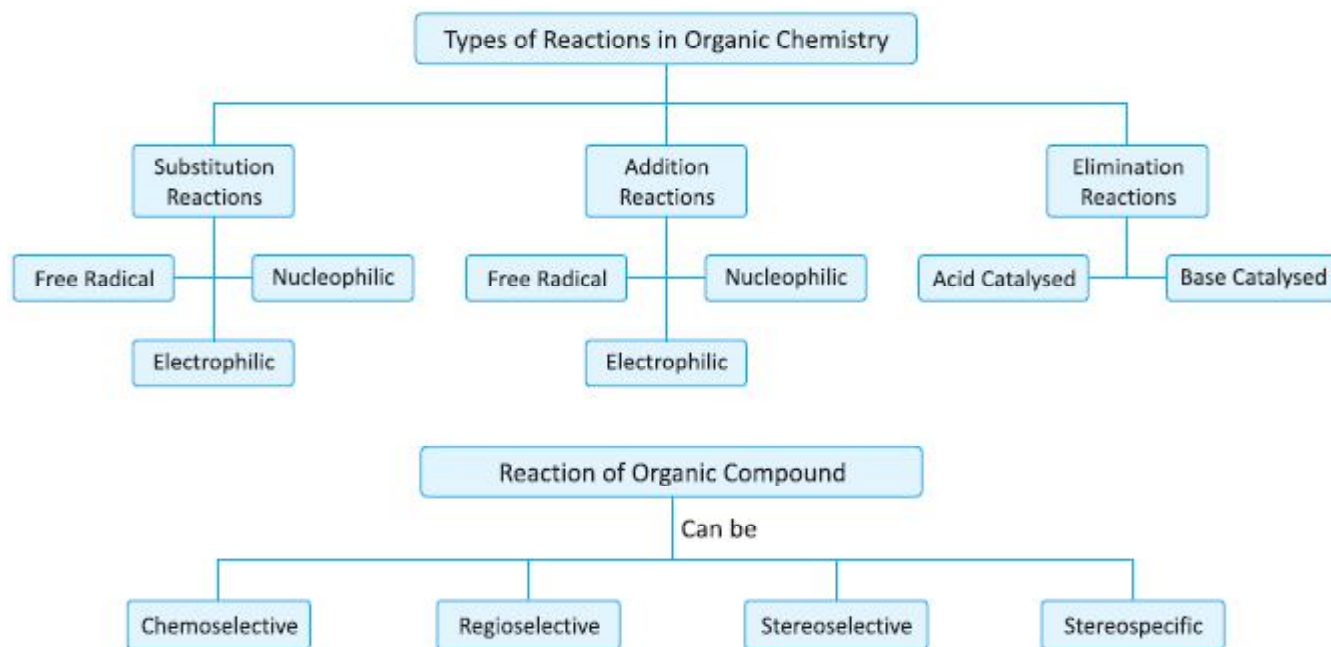
In (i) delocalisation due to only phenyl ring is there.

(B) (ii) < (i) < (iii) < (iv)

(i) and (ii) should have greater stability as compared to (iii) and (iv) because of greater number of covalent bonds. Also (ii) has got  $2^\circ$  carbocation whereas (i) has  $1^\circ$  carbocation.

(iii) has unlike charges close (less charge separation) to each other but (iv) has no such factor.

### Types of Reactions in Organic Chemistry :



**Note :** The detailed discussion of each of above reactions will be done later in Class XIIth in the chapter of "Theoretical Organic Concepts"

### Qualitative Analysis:

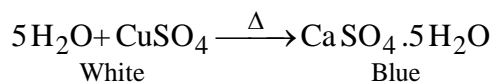
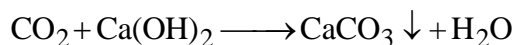
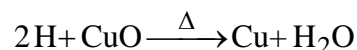
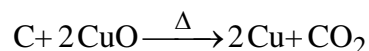
Detection of functional groups is an important step in the analysis of organic compounds. It entirely depends on the correct determination of the constituent elements.

### Elemental Detection :

The elements present in organic compounds are carbon and hydrogen. In addition to these, they may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

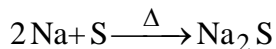
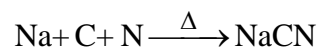
### Detection of Carbon and Hydrogen:

Carbon and Hydrogen are detected by heating the compound with copper (II) oxide. Carbon present in 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).



### 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 reaction take place :

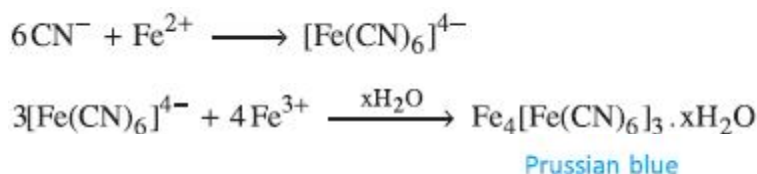


C, N, S and X come from organic compound.

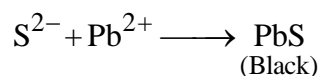
Cyanide, sulphide and halide of sodium so formed on sodium fusion are extracted from the fused masses by boiling it with distilled water. This extract is known as **sodium fusion extract**.

**(A) Test for Nitrogen :**

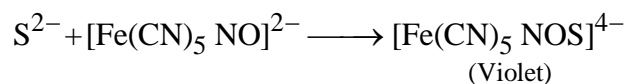
The sodium fusion extract is boiled with iron (II) sulphate and then acidified with concentrated sulphuric acid. The formation of **Prussian blue** color confirms the presence of nitrogen. Sodium cyanide first reacts with iron(II) sulphate and forms sodium hexacyanoferrate (II). On heating with concentrated 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.

**(B) Test for Sulphur :**

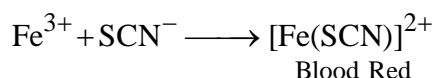
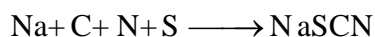
- (a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.



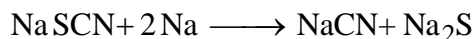
- (b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour further indicates the presence of sulphur.



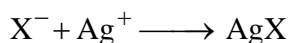
In case, nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. It gives blood red colour and no Prussian blue since there are no free cyanide ions.



If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests.

**(C) Test for Halogens :**

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.



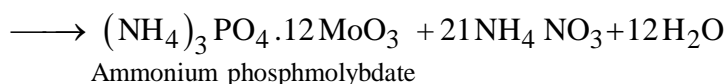
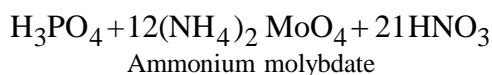
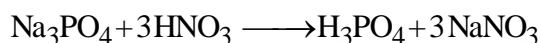


X represents a halogen -Cl, Br or I.

If nitrogen or sulphur is also present in the compound, the sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium formed during Lassaigne's test. These ions would otherwise interfere with silver nitrate test for halogens.

#### (D) Test for phosphorus :

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

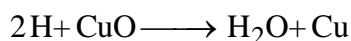
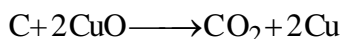


#### Quantitative Elemental Analysis :

After determining the constituent elements of an organic compound, the next step is to determine their amounts by quantitative methods. The methods usually involve combustions, oxidation etc. of an organic compound so that they may change into such inorganic compounds as can be estimated either by volumetric or gravimetric method.

#### Estimation of Carbon and Hydrogen :

**Liebig's Combustion Method :** A weighed amount of the compound is heated in a current of dry air free from carbon dioxide or pure oxygen till the carbon of the compound changes to  $\text{CO}_2$  and hydrogen into water. Carbon dioxide and water thus formed are trapped in a suitable apparatus and weighed.



The percentage composition is then calculated.

**Calculation:**

Let the weight of the sample = Wg

Let the weight of water formed = x g (Increase in weight of  $\text{CaCl}_2$  tube)

and let the weight of  $\text{CO}_2$  formed = y g (Increase in weight of potash bulb)



Since 44g of  $\text{CO}_2$  are formed from 12g of carbon.

$$\therefore y \text{ g of } \text{CO}_2 \text{ are formed from } \frac{12}{44} \times y \text{ g of carbon}$$

Since 18 g of water are formed from 2g of hydrogen.

$$\therefore x \text{ g of water are formed from } \frac{2}{18} \times x \text{ g of hydrogen} = \frac{1}{9} x \text{ g of hydrogen}$$

Now, Wg of the substance contains  $\frac{12}{44} \times y \text{ g of carbon}$

$$\therefore 100 \text{ g of the substance contains } \frac{12 \times 100y}{44 \times W} \text{ g carbon}$$

Again W g of the substance contain  $\frac{x}{9} \text{ g of hydrogen}$

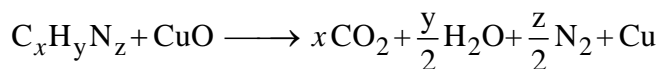
$$\therefore 100 \text{ g of the substance contain } \frac{100x}{9W} \text{ g of hydrogen}$$

$$\therefore \text{Percentage of carbon} = \frac{12 \times 100y}{44 \times W}$$

$$\text{and Percentage of hydrogen} = \frac{100x}{9W}$$

### Estimation of Nitrogen :

- (i) **Duma's Method :** In this method the organic compound is heated with copper oxide strongly. Carbon, hydrogen and sulphur are oxidized to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{SO}_2$  respectively, while nitrogen is set free. These gases are passed through a nitrometer containing 30% KOH solution. Carbon dioxide and sulphur dioxide are absorbed, steam condenses and nitrogen collects by the displacement of KOH solution. From the volume of the collected nitrogen, the percentage of nitrogen is calculated.



#### Calculation :

Let the weight of the sample = W g

Volume of moist  $\text{N}_2$  = Vcc

Room temperature =  $t^\circ\text{C}$

Barometric pressure =  $P$  mm

Aqueous tension at  $t^{\circ}\text{C}$  =  $f$  mm

We know,  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

Or  $\frac{(P-f) \times V}{(273+t)} = \frac{760 \times V_2}{273}$  ( $V_2$  = Volume of  $\text{N}_2$  at NTP)

$$V_2 = \frac{(P-f) \times 273 \times V}{760 \times (273+t)} \text{ cc}$$

Volume of  $\text{N}_2$  at NTP in cc =  $\frac{(P-f) \times 273 \times V}{760 \times (273+t)}$

Now, 22400 cc of  $\text{N}_2$  at NTP weigh 28 g.

$$\therefore \frac{(P-f) \times 273 \times V}{760 \times (273+t)} \text{ at NTP weigh } \left[ \frac{28(P-f) \times 273 \times V}{760 \times 22400(273+t)} \right] \text{ g}$$

W g of the substance contain  $\frac{28(P-f) \times 273 \times V}{760 \times 22400(273+t)} \text{ g } \text{N}_2$

$$\therefore 100 \text{ g of the substance contains } \frac{28(P-f) \times 273 \times V \times 100}{760 \times 22400 W(273+t)} \text{ g}$$

$$\text{Percentage of Nitrogen} = \frac{28}{22400} \times \frac{\text{Volume of } \text{N}_2 \text{ at NTP}}{\text{Weight of substance}} \times 100$$

- (ii) **Kjeldahl's Method :** The principle of this method is that when an organic compound containing nitrogen is heated with concentrated sulphuric acid, the nitrogen is converted into ammonium sulphate. The resulting solution on treatment with excess of sodium hydroxide solution gives off ammonia. Ammonia is then absorbed in excess of standard sulphuric acid. The amount of ammonia and hence the amount of nitrogen is determined by finding the amount of acid neutralized by back titration of the residual acid with a standard alkali solution. From this the percentage of nitrogen is calculated. **This method is not good for those nitrogen compounds which produce nitrogen gas  $\text{N}_2$  on heating such as compound containing N in ring, nitro compounds, axo compounds etc.**

**Calculation :**

Let the weight of the substance =  $W$  g and let  $V$  cc of  $\text{N}$  acid is required to neutralize the ammonia evolved.

$$\therefore V \text{ cc of N acid} = V \text{ cc of N NH}_3$$

$$1000 \text{ cc of N NH}_3 = 17 \text{ g of NH}_3 = 14 \text{ g of nitrogen}$$

$$V \text{ cc of N NH}_3 = \frac{14}{1000} \times V \times N = 0.014 N V \text{ g}$$

$$\therefore \text{Percentage of nitrogen} = \text{Weight of nitrogen} \times \frac{100}{\text{Weight of substance}} = \frac{0.014 \times N \times V \times 100}{W}$$

### Estimation of Halogen :

- (i) **Carius Method :** The compound containing halogen is heated with fuming nitric acid in a sealed tube (Carius tube) in presence of silver nitrate. Carbon and hydrogen present are oxidized to carbon dioxide and water. The halogens react with silver nitrate to give the precipitate of silver halide. The precipitate is collected, washed, dried and weighed.

#### Calculation :

Let the weight of the substance be  $W$  g.

Weight of the silver halide be  $y$  g.

$$\text{Weight of halogen} = \frac{\text{Atomic weight of halogen}}{\text{Molecular weight of silver halide}} \times y \text{ g}$$

$$\therefore \text{Percentage of halogen} = \frac{\text{Atomic weight of halogen}}{\text{Molecular weight of silver halide}} \times y \times \frac{100}{W}$$

### Estimation of Sulphur :

The compound is heated with fuming nitric acid. Sulphur present is oxidized to sulphuric acid. Barium chloride solution is added. The precipitate of barium sulphate is obtained. It is collected, washed, dried and weighed.

$$\% \text{ of Sulphur} = \frac{\text{Weight of BaSO}_4}{\text{Molecular weight of BaSO}_4} \times \frac{\text{Atomic weight of Sulphur}}{\text{Weight of Organic compound}} \times 100$$

### Silver Salt method for determining molecular weight of Organic acids :

This method on the fact that organic acids form insoluble silver salts which on ignition leave a residue to metallic silver.

A small quantity of organic acid is treated with water or a suitable solvent and then a slight excess of ammonia solution added. The solution is boiled to expel excess of ammonia. Excess of silver nitrate solution is added to this solution when a white precipitate of insoluble silver salt is obtained. The precipitate is filtered and washed successively with water, alcohol and ether and then dried in an air oven.

A known weight of the silver salt is taken in a weighed crucible and ignited till decomposition is complete. The crucible is cooled and then weighed. Heating, cooling and weighing is continued till the final weight is constant.

#### Calculation :

Weight of crucible + lid =  $W$  g

Weight of crucible + lid + silver salt =  $W_1$  g

Weight of crucible + lid + residual silver =  $W_2$  g

Weight of silver salt =  $(W_1 - W)$  g

And Weight of silver =  $(W_2 - W)$  g

$(W_2 - W)$  g of silver is obtained from  $(W_1 - W)$  g of silver salt.

108 g of silver is obtained from  $\frac{(W_1 - W) \times 108}{(W_2 - W)}$  g of silver salt.

Equivalent weight of silver salt =  $\frac{(W_1 - W) \times 108}{(W_2 - W)}$

But equivalent weight of acid = Equivalent weight of Ag salt - 108 + 1 = Equivalent weight of Ag salt - 107

$\therefore$  Molecular weight of the acid =  $\left\{ \frac{(W_1 - W) \times 108}{(W_2 - W)} - 107 \right\} \times n$  (where  $n$  = basicity of the acid)

#### Platinichloride method for determining molecular weight of Organic Bases :

Organic bases (e.g. amines) form insoluble salts known as platinichlorides when treated with hydrochloroplatinic acid  $[H_2PtCl_6]$ . These salts are represented by the general formula  $B_2H_2PtCl_6$ , where  $B$  is one equivalent of the base. These salts on ignition leave a residue of metallic platinum.

The base is dissolved in HCl and a solution of platinum chloride  $PtCl_4$  is added. The yellow crystalline salt that separates out is filtered, washed and dried. A known weight of the dried salt is ignited in a crucible.

#### Calculation :

Let  $X_1$  g of the platinichloride leave on ignition  $X_2$  g of platinum

$X_2$  g of Pt is left by  $X_1$  g of the salt on ignition.

195 g (At. weight of Pt) is left by  $\left( \frac{X_1 \times 195}{X_2} \right)$  g of the salt on ignition.

Molecular weight of the salt =  $\frac{X_1}{X_2} \times 195$

Molecular weight of  $\text{H}_2\text{PtCl}_6 = 410$

$$\text{Equivalent weight of base B} = \frac{M_{\text{B}_2\text{H}_2\text{PtCl}_6} - M_{\text{H}_2\text{PtCl}_6}}{2} = \frac{\left(\frac{X_1}{X_2} \times 195\right) - 410}{2}$$

If the acidity of the base is  $n$ , then

$$\text{Molecular weight of base} = \left[ \left( \frac{X_1}{X_2} \times 195 \right) - 410 \right] \times \frac{n}{2}$$

**Illustration - 11** 0.25 g of an organic compound on combustion gave 0.495 g of  $\text{CO}_2$  and 0.2025 g of  $\text{H}_2\text{O}$ . Calculate the percentage of carbon and hydrogen in the compound.

**SOLUTION :**

Given weight of the substance = 0.25 g

Weight of  $\text{CO}_2$  formed = 0.495 g

Weight of  $\text{H}_2\text{O}$  formed = 0.2025 g

44 g of  $\text{CO}_2$  are formed from 12g of carbon.

$$\therefore 0.495 \text{ g are formed from } \frac{12}{44} \times 0.495 \text{ of carbon}$$

Now 0.25 g of the substance contains  $\frac{12 \times 0.495}{44}$  g carbon.

$$\therefore 100\text{g of the substance contains } \frac{12 \times 0.495 \times 100}{44 \times 0.25} = 54.55 \text{ g}$$

Since 18 g of  $\text{H}_2\text{O}$  are formed from 2g of hydrogen.

$$\therefore 0.2025 \text{ g } \text{H}_2\text{O} \text{ are formed from } \frac{2}{18} \times 0.2025 \text{ g hydrogen}$$

Now, 0.25 g of the substance contains  $\frac{2 \times 0.2025}{18}$  g hydrogen

$$\therefore 100 \text{ g of the substance contains } \frac{2 \times 0.2025 \times 100}{0.25 \times 18} = 9.09 \text{ g hydrogen}$$

% of carbon = **54.55**

% of hydrogen = **9.09**

**Illustration - 12** 0.159 g of an organic compound gave 14.01 cc of nitrogen at 19°C and 719.5 mm pressure by Duma's method. Calculate % of nitrogen in the organic compound. Given: Aqueous tension of water = 11.5 mm of Hg at 19°C.

**SOLUTION :**

Aqueous tension at 19°C = 11.5 mm

We know,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{or } \frac{(719.5 - 11.5) \times 14.01}{(273 + 19)} = \frac{760 \times V_{N_2} \text{ at NTP}}{273}$$

$$V_{N_2} \text{ at NTP} = \frac{708 \times 14.01 \times 273}{760 \times 292} \text{ cc}$$

Now, 22400 cc of  $N_2$  at NTP weight 28g

$$\therefore 1 \text{ cc of } N_2 \text{ at NTP weigh } \frac{28}{22400} \text{ g}$$

$$\therefore \frac{708 \times 14.01 \times 273}{760 \times 292} \text{ cc} = \frac{28 \times 708 \times 14.01 \times 273}{22400 \times 760 \times 292} \text{ g}$$

$$0.159 \text{ g of the compound contains } \frac{28 \times 708 \times 14.01 \times 273}{22400 \times 760 \times 292} \text{ g } N_2$$

$$\therefore 100 \text{ g of the compound contains } \frac{28 \times 708 \times 14.01 \times 273 \times 100}{22400 \times 760 \times 292 \times 0.159} = 9.60\%$$

Percentage of nitrogen = 9.60%

**Illustration - 13** 0.69 g of an organic compound after heating with concentrated sulphuric acid was distilled with excess of NaOH. Ammonia liberated was passed into 100 cc of N HCl solution. The excess of the acid neutralized 80 cc of N NaOH. Calculate the percentage of nitrogen in the compound.

**SOLUTION :**

80 cc of N NaOH = 80 cc of N HCl = Volume of residual acid

Volume of acid neutralised = (100-80) cc of N HCl = 20 cc of N HCl = 20 cc of N  $NH_3$

Now, 1000 cc N  $\text{NH}_3$  = 14 g of nitrogen

$$20 \text{ cc N } \text{NH}_3 = \frac{14 \times 20}{1000} \text{ g of nitrogen}$$

$$0.69 \text{ g of the substance contains } \frac{14 \times 20}{1000} \text{ g of nitrogen}$$

$$\therefore 100 \text{ g of the substance contains } \frac{14 \times 20 \times 100}{0.69 \times 1000} = 40$$

$$\therefore \text{Percentage of nitrogen} = \mathbf{40\%}$$

**Illustration - 14** 0.26 g of an organic compound on heating with fuming nitric acid and silver nitrate give 0.31 g of silver bromide. Calculate the percentage of bromine in the compound.

**SOLUTION :**

Now,  $\text{AgBr} \longrightarrow \text{Br}$

or  $(108 + 80)\text{g} \equiv 80\text{g}$

$\therefore$  188 g of AgBr give 80 g of bromine.

$$\therefore 0.31 \text{ g of AgBr give } \frac{80}{188} \times 0.31 = 0.1319 \text{ g bromine}$$

Now, 0.26 g of the substance give 0.1319 g bromine.

$\therefore$  100 g of the substance gave

$$\frac{0.1319 \times 100}{0.26} = 50.7$$

$\therefore$  Percentage of bromine = **50.7**

**Illustration - 15** 0.40 g of an organic compound gave 0.60 g of barium sulphate after Carius method. Find out the percentage of sulphur in the compound.

**SOLUTION :**

Since,  $\text{BaSO}_4 \equiv \text{S}$   
233 g    32 g

233 g of  $\text{BaSO}_4$  gives 32 g of sulphur.

0.60 g of  $\text{BaSO}_4$  gives  $\frac{32}{233} \times 0.60$  g of sulphur = 0.082 g sulphur

$$\therefore \text{Percentage of sulphur} = \frac{0.082}{40} \times 100 = 0.205\%$$

**Illustration - 16** 0.167 g of the silver salt of a monobasic organic acid left on ignition 0.108 g of silver. Calculate the molecular weight of the acid.

**SOLUTION :**

Weight of Ag salt = 0.167 g and weight of Ag left = 0.108 g.

The weight of Ag salt that would leave 108 g of silver =  $\frac{0.167}{0.108} \times 108 = 167$  g

Equivalent weight of the acid =  $167 - 108 + 1 = 167 - 107 = 60$

Molecular weight of the acid =  $60 \times 1$  (acidity) = **60**

**Illustration - 17** Calculate the molecular weight of a monobasic base, 0.298 g of whose platinumchloride left 0.0975 g of platinum on ignition.

**SOLUTION :**

Weight of the platinumchloride = 0.298 g ( $X_1$ ) and weight of platinum = 0.0975 g ( $X_2$ )

Equivalent weight of the base =  $\frac{\frac{0.298}{0.0975} \times 195 - 410}{2} = \frac{596 - 410}{2} = \frac{186}{2} = 93$

Molecular weight of the base =  $93 \times 1$  (acidity) = **93**



**Illustration - 18** A mono acid organic base on analysis gave the following results: 0.10 g of the base gave 0.28 g of  $\text{CO}_2$  and 0.075 g of water and 0.30 g of the base gave 31.32 ml  $\text{N}_2$  measured at  $15^\circ\text{C}$  and 760 mm, 0.30 g of the platinumchloride left on ignition 0.093 g of platinum. What is the molecular formula of the base?

**SOLUTION :**

The molecular formula is derived as follows

(a) Calculation of % of elements

$$\% \text{ of carbon} = \frac{12}{44} \times \frac{0.28}{0.10} \times 100 = 76.36\%$$

$$\% \text{ of hydrogen} = \frac{2}{18} \times \frac{0.075}{0.10} \times 100 = 8.33\%$$

$$\% \text{ of nitrogen} = \frac{28}{22400} \times \frac{\text{Volume of } \text{N}_2 \text{ at NTP} \times 100}{\text{Weight of organic compound}}$$

$$\% \text{ of nitrogen} = \frac{28 \times 31.32 \times 100}{22400 \times 0.3} = 13.05\%$$

(b) Calculation of relative number of each atom :

$$\text{C} = \frac{76.36}{12} = 6.36; \text{H} = \frac{8.33}{1} = 8.33 \text{ and } \text{N} = \frac{13.05}{14} = 0.90$$

(c) Calculation of simplest ratio:

$$\text{C} = \frac{6.36}{0.90} = 7; \text{H} = \frac{8.33}{0.90} = 9 \text{ and } \text{N} = \frac{0.90}{0.90} = 1$$

(d) Determination of empirical formula :

It comes to be  $\text{C}_7\text{H}_9\text{N}$ , its empirical formula weight =  $84 + 9 + 14 = 107$

(e) Determination of molecules weight :

The molecular weight of the base is given by,

$$B = \frac{1}{2} \left[ 195 \times \frac{\text{Weight \% hexachloroplatinate salt}}{\text{Weight \% platinum}} - 410 \right]$$

$$B = \frac{1}{2} \left[ \frac{195 \times 0.3}{0.093} - 410 \right] = \frac{1}{2} [629 - 410] = 109.5$$

$$B = 109.5$$

$$n = \frac{\text{Molecular weight}}{\text{Empirical weight}} = \frac{109.5}{107} \approx 1$$

Hence, molecular formula = empirical formula =  $\text{C}_7\text{H}_9\text{N}$

**Illustration - 19** A sample of a gaseous hydrocarbon occupying 1.12 litre at NTP was completely burnt in air and gave 2.2g of  $\text{CO}_2$  and 1.8 g of  $\text{H}_2\text{O}$ . Calculate the weight of compound taken and volume of  $\text{O}_2$  at NTP required for its burning. Also calculate the molecular formula of the hydrocarbon.

**SOLUTION :**

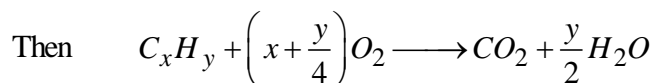
$$\text{Mole of compound} = \frac{\text{Volume evolved at NTP}}{22400 \text{ ml or } 22.4 \text{ litres}}$$

$$= \frac{1.12}{22.4} = 0.05 \text{ mol}$$

$$\text{Moles of } \text{CO}_2 \text{ produced} = \frac{2.2}{44} = 0.05 \text{ mol}$$

$$\text{Moles of } \text{H}_2\text{O} \text{ produced} = \frac{1.8}{18} = 0.10 \text{ mol}$$

Suppose the hydrocarbon is  $\text{C}_x\text{H}_y$



$$\therefore 1 \text{ mole of } \text{C}_x\text{H}_y \text{ gives } = 0.05 x \text{ mol of } \text{CO}_2$$

$$\therefore 0.05 x = 0.05$$

$$\therefore x = \frac{0.05}{0.05} = 1$$

$$\text{Now, 1 mole of } \text{C}_x\text{H}_y \text{ gives } = \frac{y}{2} \text{ mol of } \text{H}_2\text{O}$$

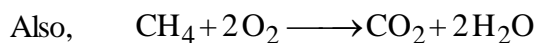
$$\therefore 0.05 \text{ mol of } \text{C}_x\text{H}_y \text{ will give } = 0.05 \frac{y}{2} \text{ mol of } \text{H}_2\text{O}$$

$$0.05 \frac{y}{2} = 0.10$$

$$\therefore y = 4$$

Hence, the hydrocarbon is  $\text{CH}_4$

$$\text{Weight of 1.12 litre } \text{CH}_4 \text{ at STP} = \frac{16 \times 1.12}{22.4} = 0.8 \text{ g}$$



1 mol of  $\text{CH}_4$  requires  $2 \times 32 \text{ g}$  oxygen

$$\therefore 0.05 \text{ mol of } \text{CH}_4 \text{ requires } 2 \times 32 \times 0.05 = 3.2 \text{ g } \text{CO}_2$$

**$\text{CH}_4$  requires  $\text{O}_2 = 3.2 \text{ g}$**

**Illustration - 20** An organic compound, A containing C, H, N and O, on analysis gives 49.32 % carbon, 9.59% hydrogen and 19.18% nitrogen. A on boiling with NaOH gives off  $\text{NH}_3$  and a salt which on acidification gives a monobasic nitrogen free acid B. The silver salt of B contains 59.67% silver. Deduce the structures of A and B.

**SOLUTION:**

$$\text{Percentage of oxygen} = 100 - (49.32 + 9.59 + 19.18) = 21.91$$

Elements	Percentage composition	Atomic weight	Relative No. of atoms	Simplest ratio
C	49.32	12	$\frac{49.32}{12} = 4.11$	$\frac{4.11}{1.37} = 3$
H	9.59	1	$\frac{9.59}{1} = 9.59$	$\frac{9.59}{1.37} = 7$
N	19.18	14	$\frac{19.18}{14} = 1.37$	$\frac{1.37}{1.37} = 1$
O	21.91	16	$\frac{21.91}{16} = 1.37$	$\frac{1.37}{1.37} = 1$

Hence empirical formula of A =  $\text{C}_3\text{H}_7\text{NO}$

Because A, gives  $\text{NH}_3$  on boiling with NaOH, it can be an amide.

Now, silver salt of B, has 59.67 % silver.

$$\text{Hence equivalent weight of acid} = \left( \frac{100 \times 108}{59.67} \right) - 107 = 74$$

Molecular weight of monobasic acid =  $74 \times 1 = 74$

Molecular formula of acid =  $\text{C}_3\text{H}_6\text{O}_2$

$\therefore$  Structural formula of acid B is  $\text{C}_2\text{H}_5\text{COOH}$ .

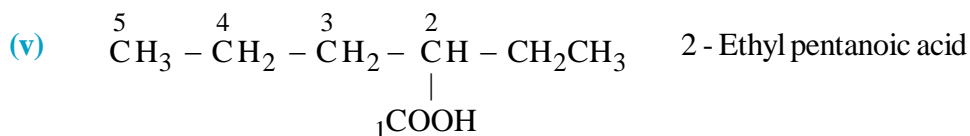
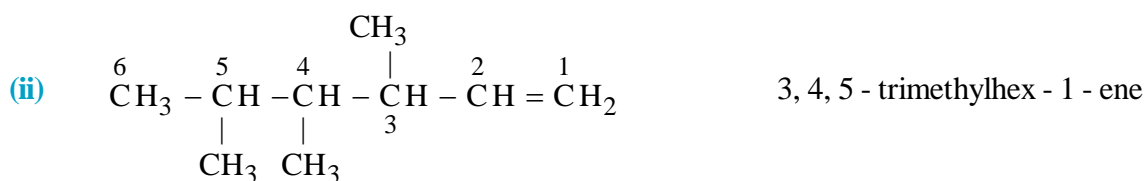
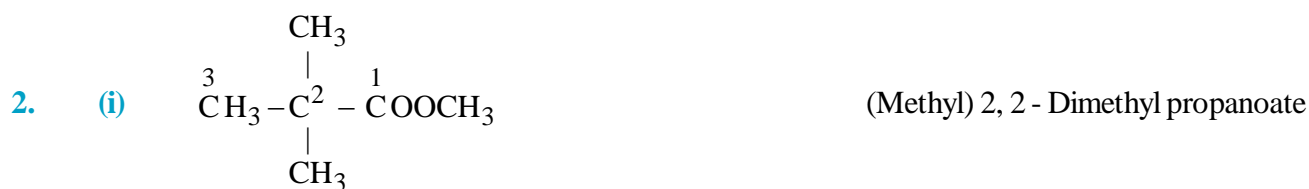
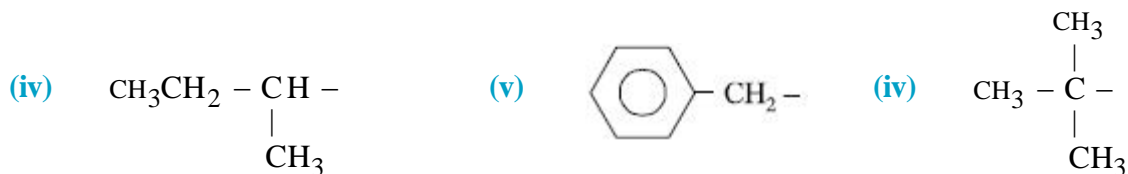
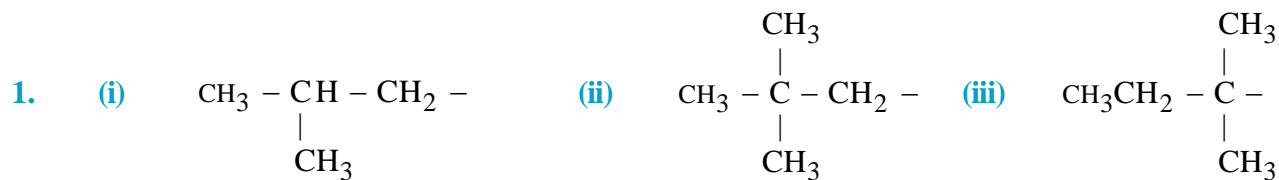
Molecular formula of amide =  $\text{C}_3\text{H}_7\text{NO}$ .

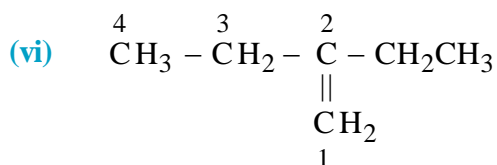
Hence structural formula of amide (A) is  $\text{C}_2\text{H}_5\text{CONH}_2$

**NOW ATTEMPT IN-CHAPTER EXERCISE-E BEFORE PROCEEDING AHEAD IN THIS EBOOK**

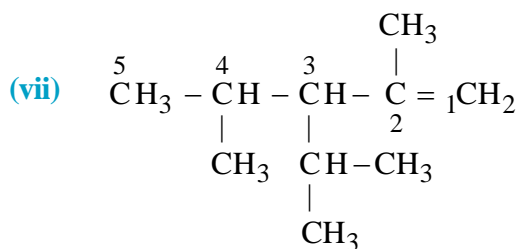
**NOW ATTEMPT OBJECTIVE WORKSHEET BEFORE PROCEEDING AHEAD IN THIS EBOOK**

## IN - CHAPTER EXERCISE - A

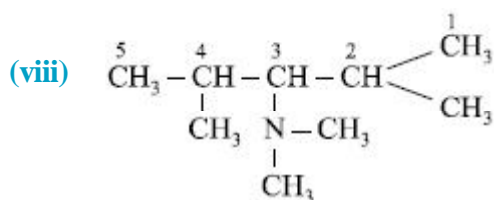




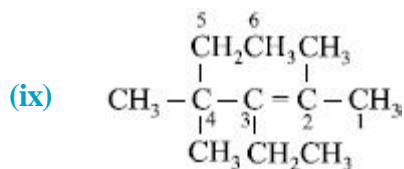
2 - Ethyl but - 1 - ene



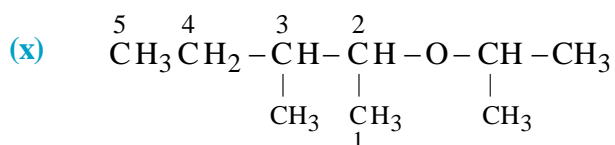
3 - (1 - Methylethyl) - 2, 4 - dimethyl pent - 1 - ene



3 - N, N - Dimethyl - 2, 4 - dimethyl pentan - 3 - amine

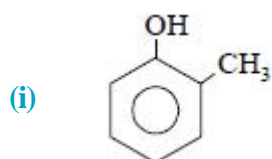


3 - Ethyl - 2, 4, 4 - trimethyl hex - 2 - ene

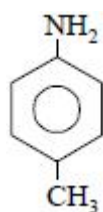


2 - (1 - Methyl ethoxy) - 3 - methyl pentane

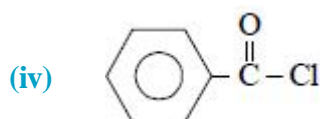
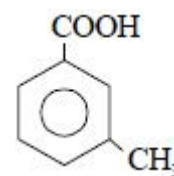
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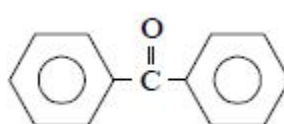
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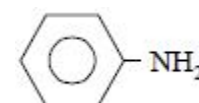
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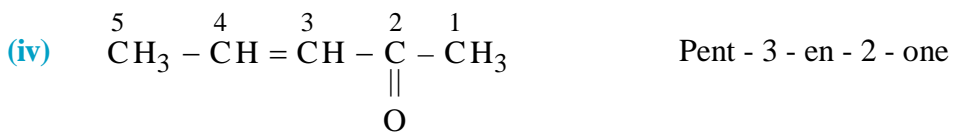
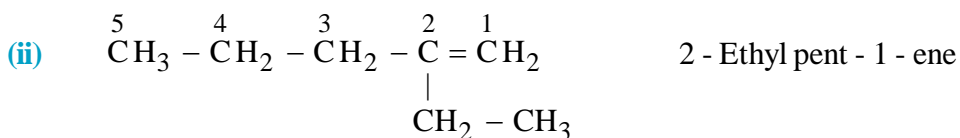
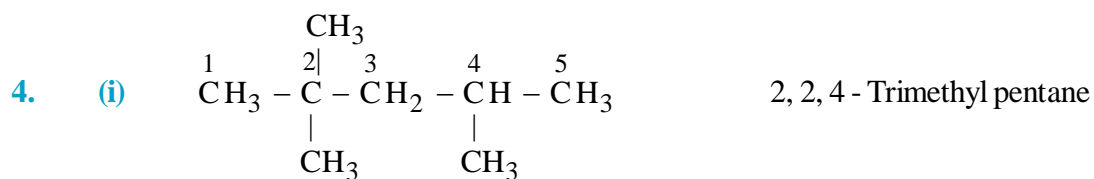
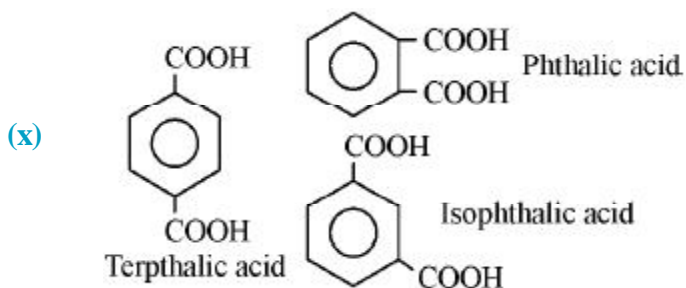
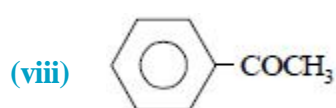
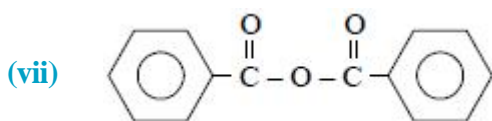


(v)

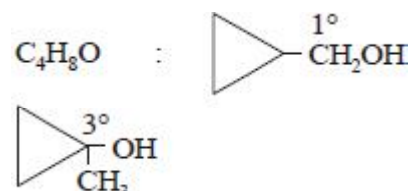
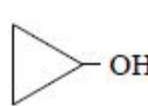
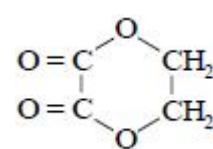
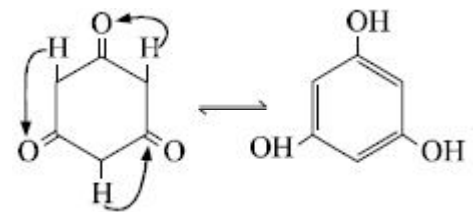


(vi)





## IN - CHAPTER EXERCISE - B

1. (A)  $C_4H_8O$  :   $CH_2 = CH - CH_2 - \overset{1^\circ}{CH_2OH}$   
 $CH_3 - CH = CH - \overset{1^\circ}{CH_2OH}$
- (B)  $C_3H_6O$  :  (C)  ;  $C_4H_4O_4$
- (D)  $\begin{array}{c} H - C - COOH \\ || \\ H - C - COOH \end{array}$  (cis -) maleic acid and  $\begin{array}{c} H - C - COOH \\ || \\ HOOC - C - H \end{array}$  (Trans -) fumaric acid;  $C_4H_4O_4$
2. You can draw \* Acids - Esters (functional isomers)  
 ↳ among esters : Metamers  
 ↳ among acids : chain and position (w.r.t  $CH_3$  groups)  
 \* hydroxy aldehydes and ketones
3. 
4. (A)  $CH_3CH_2COOCH_3$  ;  $CH_3COOC_2H_5$  ;  $H - COO - CH_2CH_2CH_3$  ;  $HCOOCH(CH_3) - CH_3$
- (B)  $CH_3CH_2CH_2CHO$  ;  $CH_3 - \underset{\substack{| \\ CH_3}}{CH} - CHO$
- (C)  $CH_3COCH_2CH_2CH_3$  ;  $CH_3 - CO - \underset{\substack{| \\ CH_3}}{CH} - CH_3$  ;  $CH_3CH_2 - \overset{\substack{O \\ ||}}{C} - CH_2 - CH_3$
- (D)  $CH_3 - \underset{\substack{| \\ CH_3}}{N} - CH_2CH_3$



## My Chapter Notes





