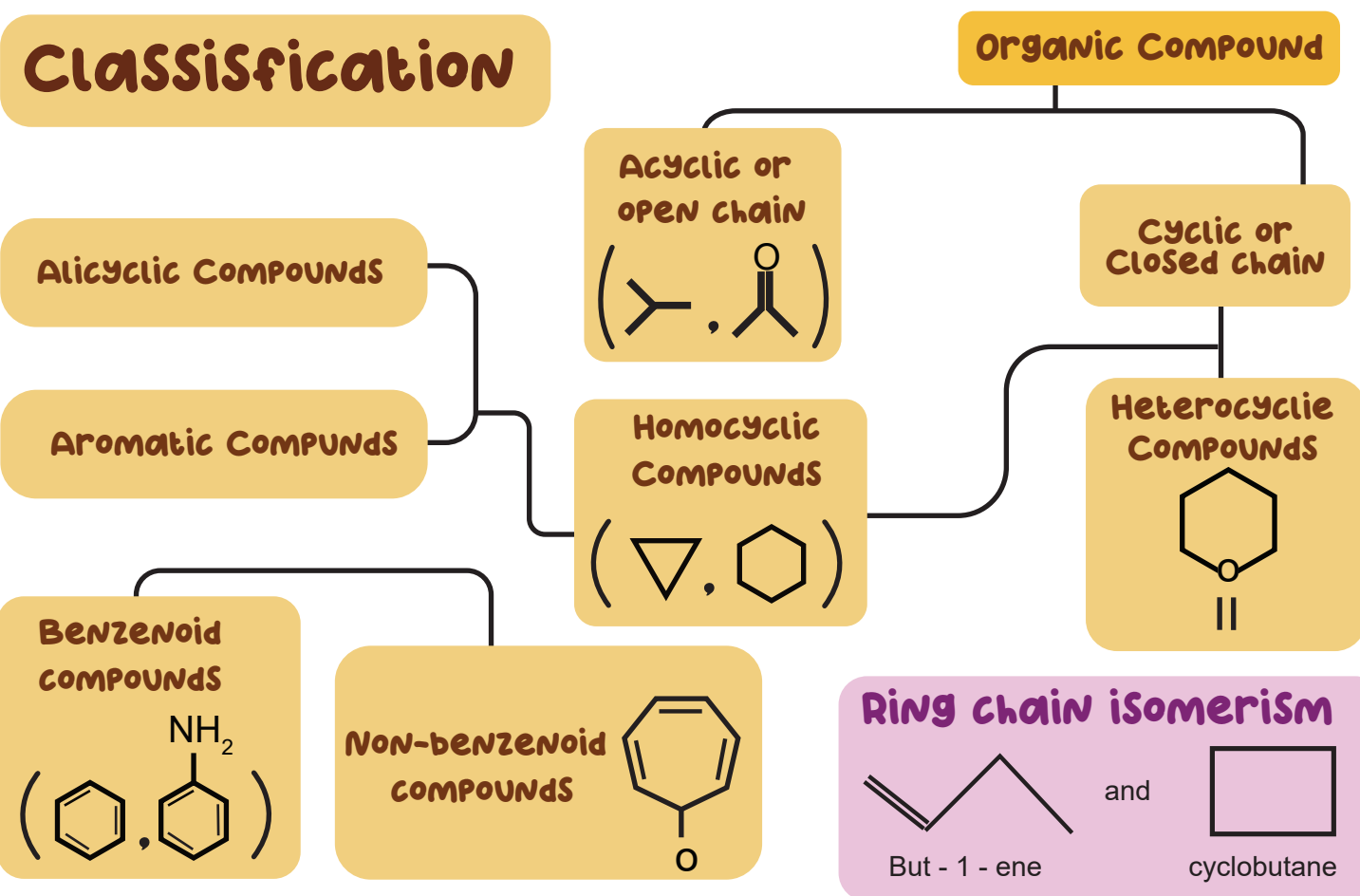
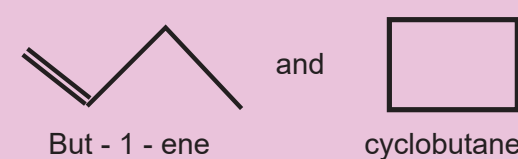


Classification



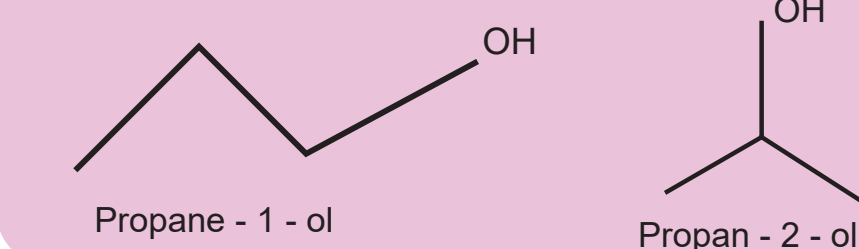
Ring chain isomerism



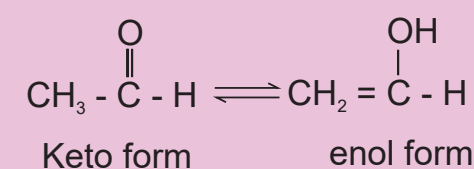
Structural Isomerism

Compounds that have same chemical formula but different chemical bond arrangement are called structural isomers.

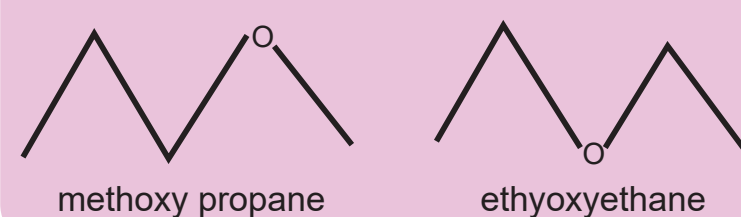
Position Isomerism



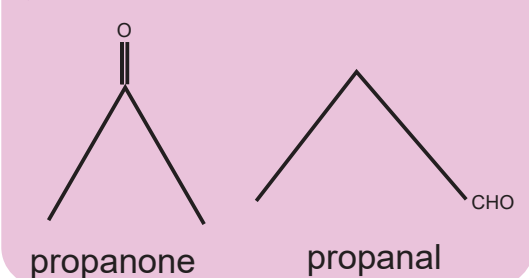
Tautomerism



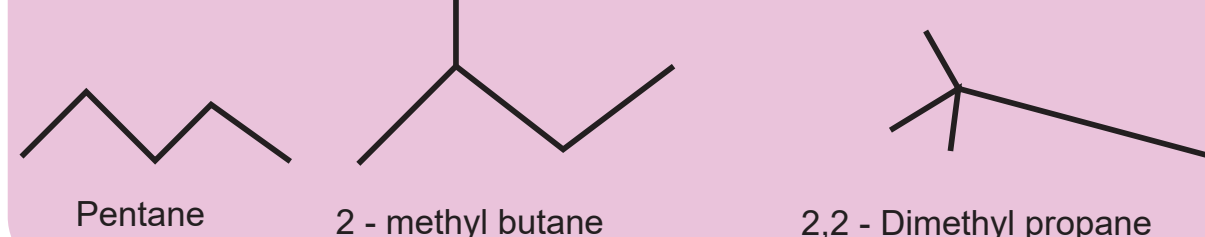
Metamerism



Functional Isomerism



Chain Isomerism



Parts of IUPAC Name

- Prefix
- Root word
- Primary Suffix
- Secondary Suffix

Rules for IUPAC Naming

- Rule 1:** Select the longest possible carbon chain.
- Rule 2:** Numbering of parent chain is done from that side where functional group, multiple bond and substituent get the lowest number.
- Rule 3:** Lowest sum rule — If first substituent gets same number from all side then chain selected should have lowest sum of all substituent numbering.
- Rule 4:** Alphabet rule — Naming should be done in alphabetical order if the numbering of all substituent is same.
- Rule 5:** If the molecule has more than one functional group, the functional group with highest priority receives the lowest number.

ISOMERISM

Stereo Isomerism
Compounds that have same chemical formula and sequence of covalent bonds but differ in spatial arrangement are called stereo isomers

Geometrical Isomerism

Optical Isomerism

Hyperconjugation Effect

delocalisation of σ electrons of C-H bond of an alkyl group directly attached to an atom with unshared p-orbital.

Electromeric Effect

In the presence of reagent, the double or triple bonds get broken double or it is a temporary effect.

Electronic displacement Effect

Inductive Effect

Partial displacement of sigma electrons towards more electronegative atom/group. It is a permanent effect

+I Effect
 CH_3 , C_2H_5 , etc.

-I Effect
 $-\text{CN}$, $-\text{COOH}$, etc.

Resonance Effect

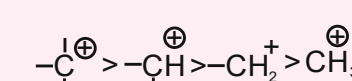
When a molecule can be represented by two or more structures which have same arrangement of atoms but differ in distribution of electrons is called resonance.

+R Effect
halogen, $-\text{OH}$, OR

-R effect
 $-\text{COOH}$, $-\text{CHO}$, $-\text{CN}$

Carbocation

- Carbon atom having a positive charge with only six electrons in its valence shell.
- Carbocation carbon is sp^2 hybridised.



Quantitative Analysis

Carbon and Hydrogen

$$\%C = \frac{12 \times m_2 \times 100}{44 \times m} \quad \%H = \frac{2 \times m_1 \times 100}{18 \times m}$$

m-Mass of org. Compound
 M_2 -mass of CO_2 produced
 M_1 -mass of H_2O produced

Nitrogen

Dumas method
 $\%N = \frac{28 \times V \times 100}{22400 \times m}$

Kjeldahl's method
 $\%N = \frac{1.4 \times N \times V}{m}$

m-Mass of org. Compound
N-Normality of acid
V-Volume of acid

Halogen

Carius method
 $\% \text{halogen} = \frac{\text{at.mass of } \times M_1 \times 100}{\text{molar mass of Ag} \times m}$

m-Mass of org. Compound
 M_1 -mass of AgX formed

Sulphur

Carius method
 $\%S = \frac{32 \times m_1 \times 100}{233 \times m}$

m-Mass of org. Compound
 M_1 -mass of BaSO_4 formed

Phosphorus

$$\%P = \frac{62 \times m_1 \times 100}{222 \times m}$$

m-Mass of org. Compound
 M_1 -mass of $\text{Mg}_2\text{P}_2\text{O}_7$ formed

Organic Reaction

Types

- Addition reaction
- Substitution reaction
- Elimination reaction

Bond Fission

- Homolytic**
free radicals are formed.
- Heterolytic**
Carbocation and carbanion is formed.

Electrophile

Electron deficient species.
Lewis's acid.
Example- Cl^+ , Br^+ , NO_2^+ , CH_3^+ , AlCl_3 , etc.

Nucleophile

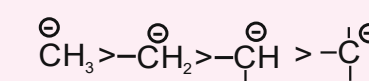
Electron rich species
Lewis's base.
Example- H_2O , NH_3 , OH^- , Cl^- , F^- , CH_3^-

Attaching Reagent

Organic molecule \rightarrow Intermediate \rightarrow Product(s)

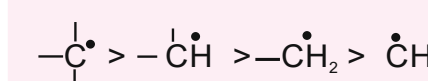
Carbanion

- Carbon atom having a negative charge on it.
- Carbanion carbon is sp^3 hybridised.



Free Radical

- Carbon atom having 7 electrons in the valence shell is called carbon free radical.
- Carbon of free radical is sp^2 hybridised.



Organic Chemistry : Some Basic Principles and Techniques



BASIC PRINCIPLES & TECHNIQUES IN ORGANIC CHEMISTRY (GOC)

Introduction

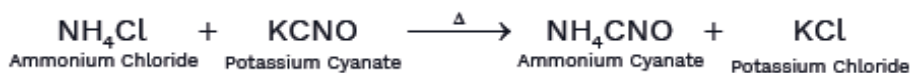
'The branch of chemistry dealing with these compounds, which are widely distributed in nature and play an important role in our daily lives', is called organic chemistry.



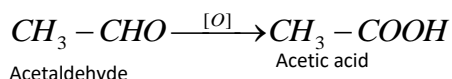
In earlier period of development of chemistry, compounds were classified as follows

1. **Organic compounds** derived from 'living matter' (plants and animals).
2. **Inorganic compounds** prepared from 'non-living matter' (mineral sources).

Berzelius, a Swedish chemist proposed the mistaken notion that a '**vital force**' present in living matter was essential for the synthesis of organic compounds. However, the synthesis of urea an organic compound present in urine, from **ammonium cyanate**, an inorganic compound by **Frederic Wohler** in 1828 effectively destroyed the myth of organic compounds being associated with a 'vital force'.



Soon afterwards the pioneering work of Herman Kolbe who synthesized acetic acid and of Berthelot who synthesized methane showed conclusively that organic compounds are essentially the compounds formed by carbon with itself and other elements and that they can be synthesized in a laboratory as easily as inorganic compounds.



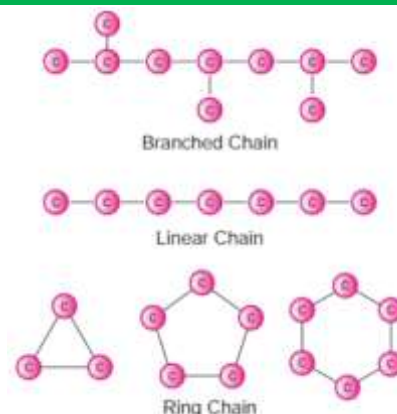
(First organic compound synthesized from its elements)

The chemistry of hydrocarbons and their derivatives constitutes organic chemistry.

The number of organic compounds available today is more compare to total inorganic compounds of all elements except carbon. This is due to unique **catenation** property of Carbon.

Some properties of Carbon

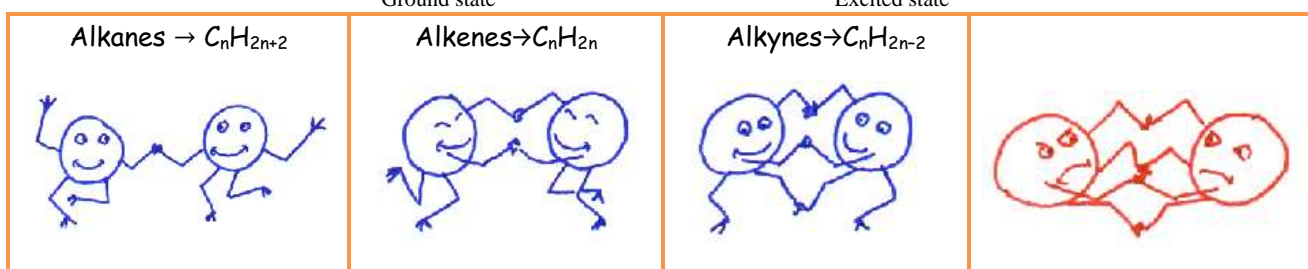
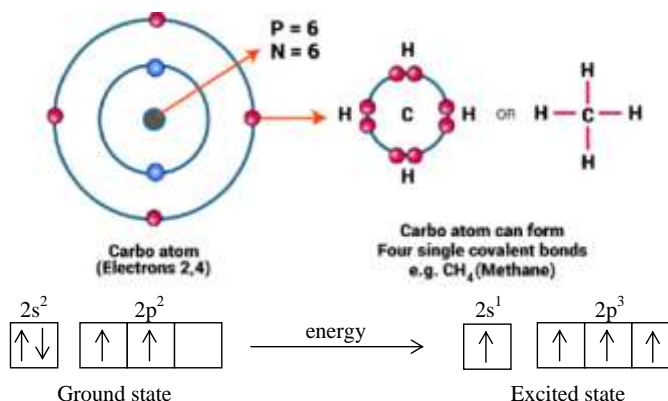
- Catenation:** is the property of an element where a large number of its own atoms join together through covalent bonds. Due to which it forms single as well as multiple covalent bonds with other carbon atoms. It is further supplemented by the fact that it also forms covalent bonds with atoms of other elements like hydrogen, oxygen, nitrogen, Sulphur, phosphorus and halogens in a variety of ways (i.e., single and multiple bonds).



This property gives a scope for the Chemists to synthesize new compounds.

- Tetravalency of carbon atom**

The atomic number of carbon is 6 and it has four electrons in its valence shell. In order to acquire a stable noble gas configuration, it can share its 4 electrons with the electrons of its atom or electrons of other atoms to form **four covalent bonds**. The bonds can be sigma(σ) or pi(π).



As per Lewis theory, Carbon can easily form tetra-bonds with other carbon atoms & other atoms. $C-C$, $C=C$, $C\equiv C$ exists in nature but not Carbon-Carbon tetrabonds.

Carbon can form single, double or triple bond (covalent). When a single bond is formed between carbon atoms (or any atoms), energy is released. Changing the molecule's electron arrangement to make a double bond releases more energy, but not as much as when the first bond was made. Making a triple bond again releases energy, but again to a lesser degree. However, when a fourth bond is attempted, the overcrowded electrons between the atoms resist the change so strongly that it releases little, if any, energy. This arrangement is therefore unstable, so a quadruple bond will be essentially impossible.

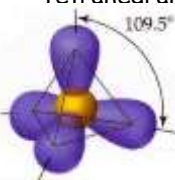
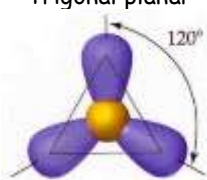
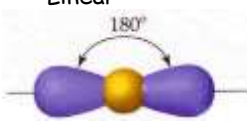
- Hybridization in carbon compounds**

Hybridization is defined as intermixing of degenerate orbitals (orbitals at nearly same energy) to produce entirely equivalent number of new orbitals of same energy, identical shapes and symmetrically disposed in planes. The orbitals formed are called hybrid orbitals.

- The orbitals of an isolated atom can undergo hybridization.
- Numbers of hybrid orbitals generated are equal to number of contributing atomic orbitals.
- The hybrid orbitals orient in the space providing definite geometry to molecule or ion.
- Like atomic orbital, a hybrid orbital cannot have more than two electrons of opposite spins. In diamond carbon is sp^3 hybridized and in graphite carbon is sp^2 hybridized.

There are three types of hybridization,

- (i) **sp^3 hybridization** (contain saturated organic compounds with only single covalent bonds)
- (ii) **sp^2 hybridization** (here organic compounds having carbon atoms linked by double bonds)
- (iii) **sp hybridization** (here organic compounds having carbon atoms linked by a triple bonds).

Type of hybridization	sp^3	sp^2	sp
Number of orbitals used	1s and 3p	1s and 2p	1s and 1p
Number of unused p-orbitals	Nil	One	Two
Bond	Four σ	Three σ , One π	Two σ , Two π
Bond angle	109.5°	120°	180°
Geometry	Tetrahedral 	Trigonal planar 	Linear 
% s-character	25 or $1/4$	33.33 or $1/3$	50 or $1/2$

Prediction of hybridization- It can be done by two methods,

(i) **First Method:** In this method hybridization can be known by the number of π - bonds present on that particular atom.

Number of π - bond/s	0	1	2
Type of hybridization	sp^3	sp^2	sp
<p>(i)</p> $ \begin{array}{ccccccc} & & & \text{O} & & & \\ & & & & & & \\ \text{CH}_3 & - & \text{CH} & = & \text{CH} & - & \text{C} & - & \text{CH}_3 \\ \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow \\ sp^3 & & sp^2 & & sp^2 & & sp^2 & & sp^3 \end{array} $	<p>(ii)</p> $ \begin{array}{ccccc} \text{CH}_2 & = & \text{C} & = & \text{CH}_2 \\ \downarrow & & \downarrow & & \downarrow \\ sp^2 & & sp & & sp^2 \end{array} $		
<p>(iii)</p> $ \begin{array}{ccccccc} \text{CH}_3 & - & \text{CH} & = & \text{CH} & - & \text{CH}_2 & - & \text{C} & \equiv & \text{N} \\ \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow \\ sp^3 & & sp^2 & & sp^2 & & sp^3 & & sp & & sp \end{array} $	<p>(iv)</p> $ \begin{array}{ccccccc} \text{HC} & \equiv & \text{C} & - & \text{CH} & = & \text{CH}_2 \\ \downarrow & & \downarrow & & \downarrow & & \downarrow \\ sp & & sp & & sp^2 & & sp^2 \end{array} $		

(ii) **Second Method** (Electron pair method): The hybridized state of an atom of a molecule or an ion or radical can be predicted by calculating number of orbitals or electron pairs involved in hybridization (H) which is evaluated as follows.

$H = (\text{number of } \sigma \text{ bonds formed with adjoined atom/s} + \text{number of lone pairs of electrons})$

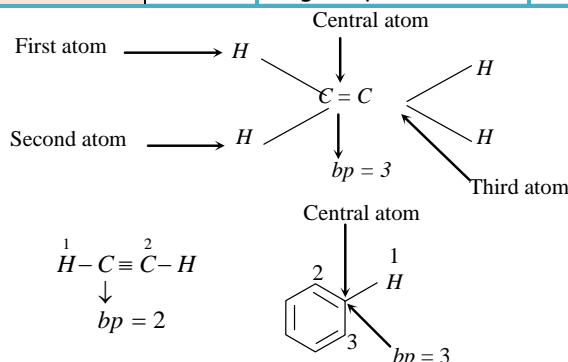
$$ep = bp + lp;$$

where, ep = electron pair present in hybrid orbitals,

bp = bond pair present in hybrid orbitals

Number of bp = Number of atoms attached to the central atom of the species (do not include π electron pairs).

Value of H	2	3	4
Hybridization	sp	sp ²	sp ³
Structure	linear	trigonal planar	tetrahedral

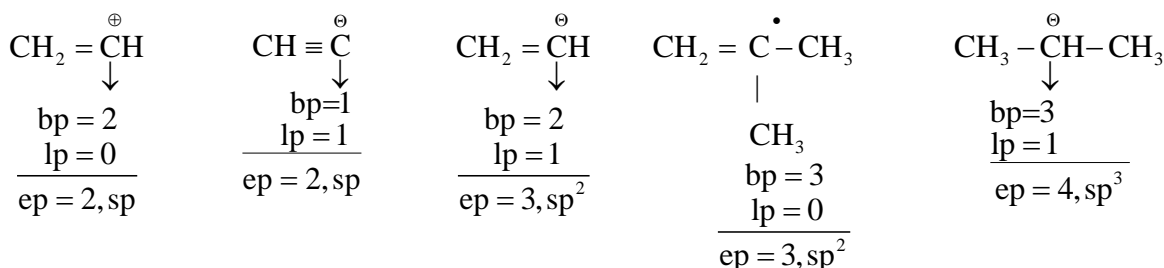


Number of lp's can be determined as follows,

(a) If C has π -bonds or positive charge or odd electron, then lp on C will be zero.

(b) If carbon has negative charge, then lp will be equal to one.

Example:



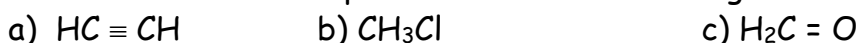
Pitfall - It may be noted that, the hybridized state of a heteroatom containing lone pair electrons or carbanion or free radical bonded in conjugation with multiple bond/s is sp². For example, hybridized state of allylic or benzylic carbanions or free radicals or atoms of aromatic ring is sp².

Problem 1: How many sigma (σ) and pi (π) bonds are present in each of the following molecules? a) $\text{CH}_2 = \text{C} = \text{CH}_2$ b) $\text{CH}_3 - \text{CH} = \text{CH} - \text{C} \equiv \text{C} - \text{CH}_3$

Solution: Every single bond is a σ bond; every double bond contains one σ -bond and one π -bond while every triple bond consists of one σ - and two π -bonds. Thus



Problem 2: Predict the shape of each of the following molecules.



Solution: sp³ hybridization can always be correlated to tetrahedral shape, sp² to trigonal planar and sp to linear. Thus,

- sp hybridized carbon atoms, linear
- sp³ hybridized carbon, tetrahedral
- sp² hybridized carbon, trigonal planar

Applications of hybridization

(i) **Size of the hybrid orbitals:** Since s- orbitals are closer to the nucleus than p-orbitals, it is reasonable to expect that greater the s-character of an orbital the smaller it is. Thus, the decreasing order of the size of the three hybrid orbitals is opposite to that of the decreasing order of s orbital character in the three hybrid orbitals. $sp^3 > sp^2 > sp$

(ii) Electro negativity of different orbitals

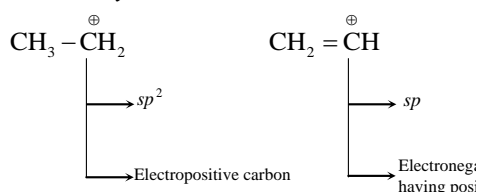
(a) Electro negativity of s-orbital is maximum.

(b) Electro negativity of hybrid orbital \propto % s-character in hybrid orbitals

Orbital	sp	sp ²	sp ³
% s -character	50	33.33	25

s-character in decreasing order and electronegativity in decreasing order

Thus sp-hybrid carbon is always electronegative in character and sp³-hybrid carbon is electropositive in character. sp²-hybrid carbon can behave as electropositive (in carbocation) as well as electronegative (in carbanion) in character.



(c) Electro negativities of hybrid & unhybrid orbitals in decreasing order is as follows

$$s > sp > sp^2 > sp^3 > p$$

% s-character and electronegativity in decreasing order.

(iii) **Bond length in hydrocarbons,** % of s orbital character $\propto \frac{1}{\text{C}-\text{C bond length}} \propto \frac{1}{\text{C}-\text{H bond length}}$

Bond type (C - H)	Bond length	Bond type (C - C)	Bond length
sp ³ - s (alkanes)	1.112 Å	sp ³ - sp ³ (alkanes)	1.54 Å
sp ² - s (alkenes)	1.103 Å	sp ² - sp ² (alkenes)	1.34 Å
sp - s (alkynes)	1.08 Å	sp - sp (alkynes)	1.20 Å

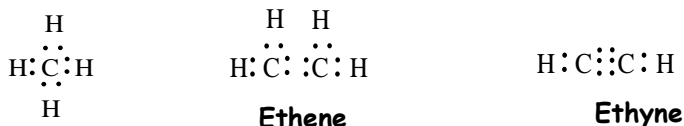
(iv) **Bond strength in hydrocarbons:** The shorter is the bond length, the greater is the compression between atomic nuclei and hence greater is the strength of that bond.

Bond type (C - H)	Bond energy (kcal/mole)	Bond type (C - C)	Bond energy (kcal/mole)
sp ³ -s (in alkanes)	104	sp ³ -sp ³ (in alkanes)	80 - 90
sp ² -s (in alkene)	106	sp ² -sp ² (in alkenes)	122 - 164
sp-sp (in alkynes)	121	sp-sp (in alkynes)	123 - 199

Structural representation of Organic Compounds

Structural formula (structure) is the sequence in which different atoms constituting the molecule are bonded to one another. Structures of molecules of organic compounds can be described in various ways. The most common types of representations are:

1) Lewis structure (or electron dot structure) Here dots are used to represent all of the valence electrons of all the bonded atoms in the molecule:

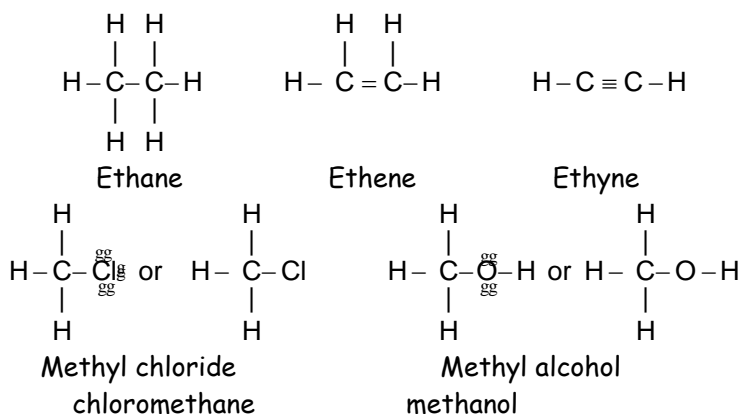


Writing dot structure is **tedious and time-consuming**. The other representations are more convenient and are, therefore, more often used.

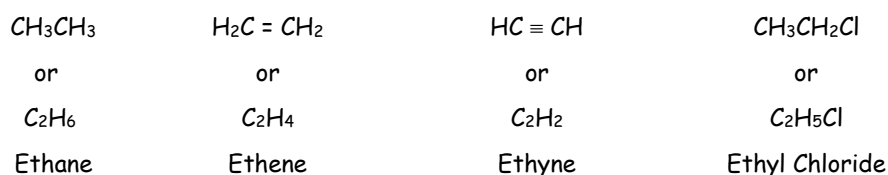
2) Dash structural formula The Lewis structure can be simplified by representing a shared electron pair by a 'stick' (dash, -) between the bonded atoms. When there is one dash between two atoms, the atoms are said to be bonded by a single covalent bond. A double covalent bond, in which two pairs of electrons are shared, is shown by two dashes between the atoms. A triple bond is represented by three dashes between the atoms.

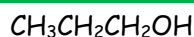
The valence electrons that are not included in covalent bonds are called **nonbonding electrons (lone pairs)**. These are assigned to specific atoms and are represented by dots drawn next to the symbols for these atoms.

Lone pair of electrons on hetero atoms (e.g. oxygen, nitrogen, sulphur, phosphorus, halogens) may or may not be shown. Such structural formulae which focus only on the valence electrons involved in bond formation are called **complete structural formulae**.



3) Condensed structural formula Complete structural formulae can be shortened by leaving out some or all of the covalent bonds and by denoting the number of identical groups attached to an atom by a subscript. The resulting description of the molecule is called a condensed structural formula. Thus,

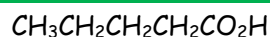




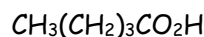
or



Methanol

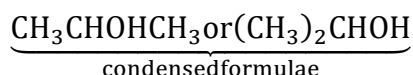
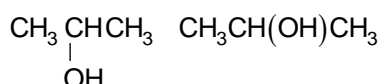


or

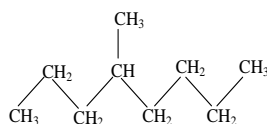
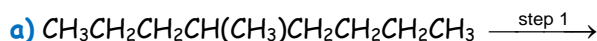


Pentanoic acid

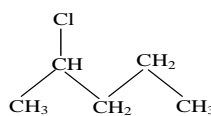
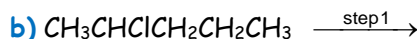
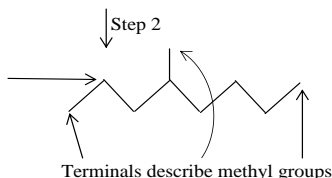
Condensed structural formulae are easier to write than dash formulae. In condensed formulae all of the hydrogen atoms that are attached to a particular carbon are usually written immediately after the carbon. In fully condensed formulae, all of the atoms that are attached to the carbon are usually written immediately after that carbon, listing hydrogens first. For example, the condensed formula for isopropyl alcohol can be written in four different ways:



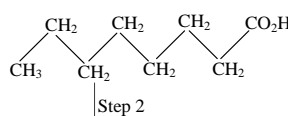
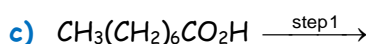
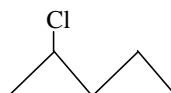
4) Bond-line structural formula: For further simplification only lines are used to represent the structures of organic molecules. Here carbon and hydrogen atoms are not shown. The lines denoting the carbon - carbon bonds are drawn in a zig - zag fashion. The only atoms especially written are the hetero atoms (oxygen, nitrogen etc). They are neither carbon nor hydrogen bonded to carbon. The termini describe methyl ($\text{CH}_3 -$) groups (unless denoted otherwise by a functional group). The line junctions indicate carbon atoms bonded to suitable number of hydrogens needed to satisfy the covalency of the carbon atoms: Thus The bond-line representation is the quickest of all to write because it shows only the carbon skeleton.



Line junctions denote carbon atoms



step 2

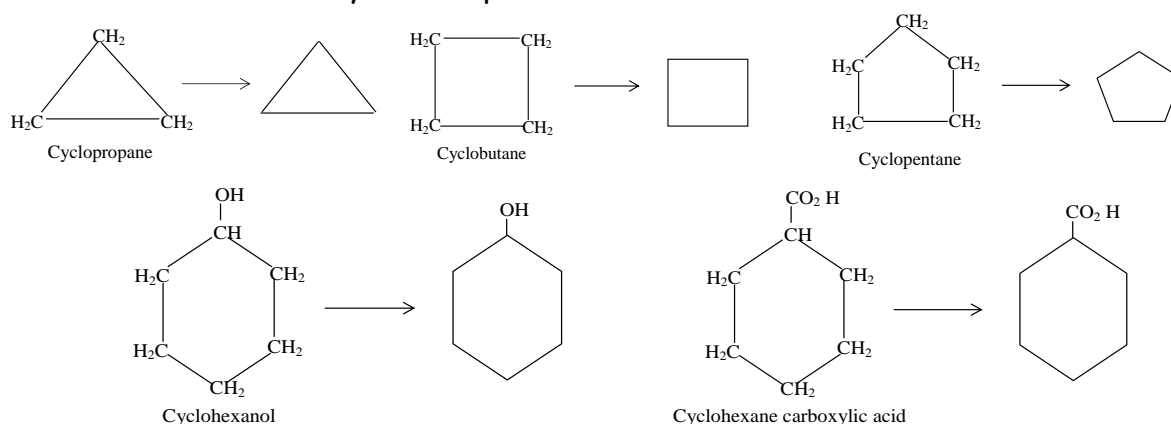


Step 2



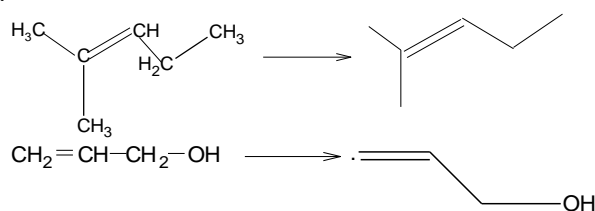
Ring or cyclic compounds - An organic compound in which carbon atoms are not bonded in chain but are bonded in closed structures called rings are known as **cyclic compounds**. Such a compound containing one or more rings is represented by drawing the suitable ring (polygon) without indicating the carbon and hydrogen atoms. The corner of the polygon denotes a carbon atom and its sides represent a carbon - carbon bond. An atom or a group of atoms (other than hydrogen) bonded to the carbon is however shown in the structure.

Bond-line formulae of some cyclic compounds are:

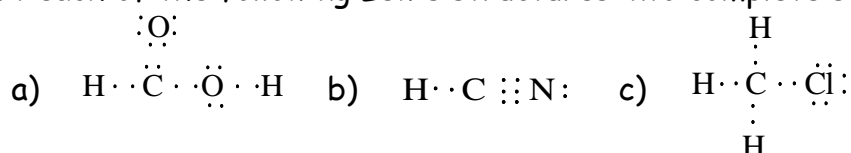


Multiple bonds are also indicated in bond-line formulae.

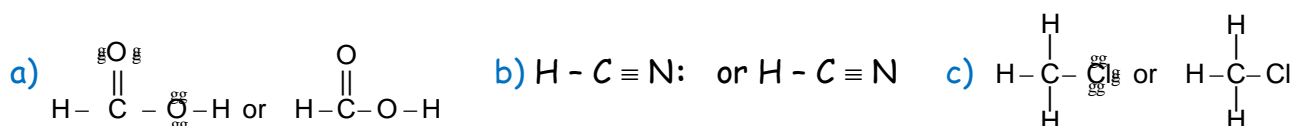
For example:



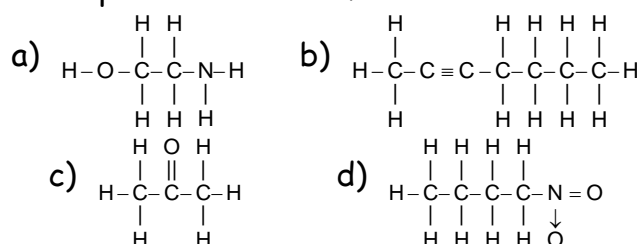
Exp 1: Convert each of the following Lewis structures into complete structural formulae:



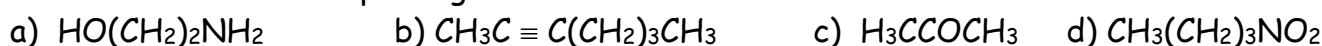
Solution: Use the dash to represent the shared electron pair.



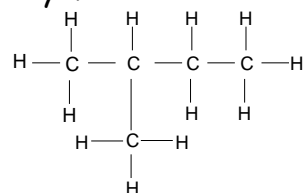
Exp2: Convert each of the complete structural formulae into condensed formulae.



Solution: Omitting some or all of the dashes and indicating the number of identical groups by a subscript we get



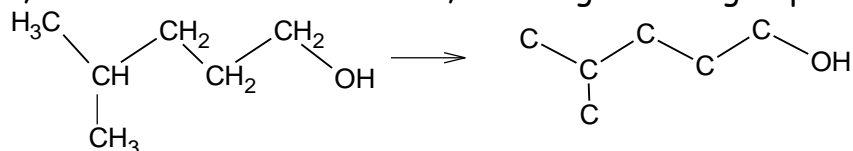
Exp 3: Write the condensed structural formulae for the compound that follows in different ways.



Solution: $\text{CH}_3\text{-CH(CH}_3\text{)CH}_2\text{CH}_3$ or $\text{CH}_3\text{CH(CH}_3\text{)CH}_2\text{CH}_3$ or $\text{CH}_3\text{CH}_2\text{CH(CH}_3\text{)CH}_3$
 or $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$ or $\text{CH}_3\text{CH}_2\text{CH(CH}_3\text{)}_2$

Exp 4: Write the bond-line formula for $\text{H}_3\text{C-CH(CH}_3\text{)-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$

Solution: First, outline the carbon skeleton, including the OH group as follows:

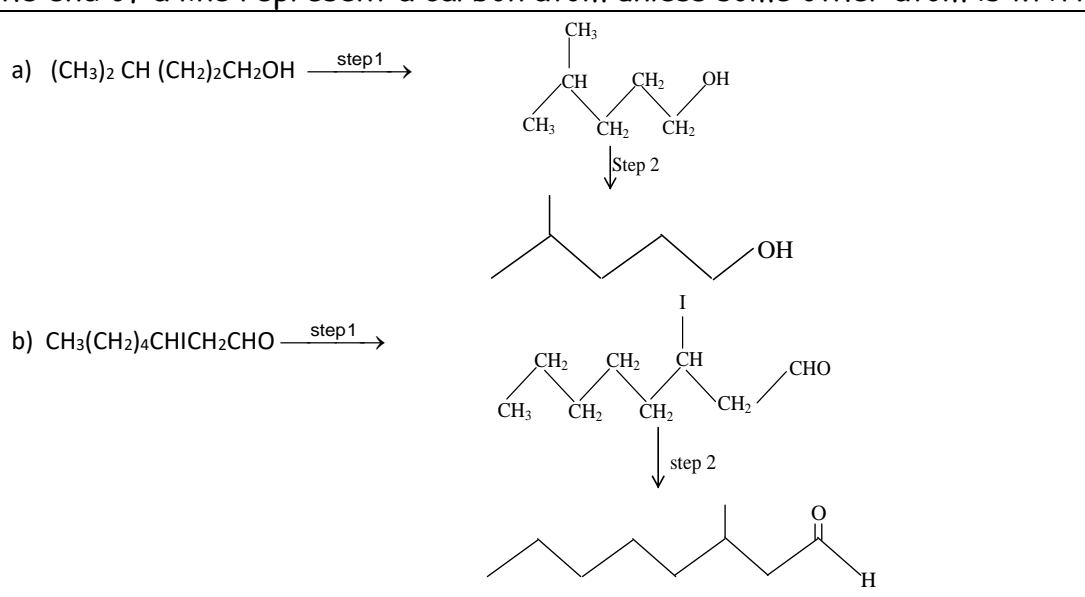


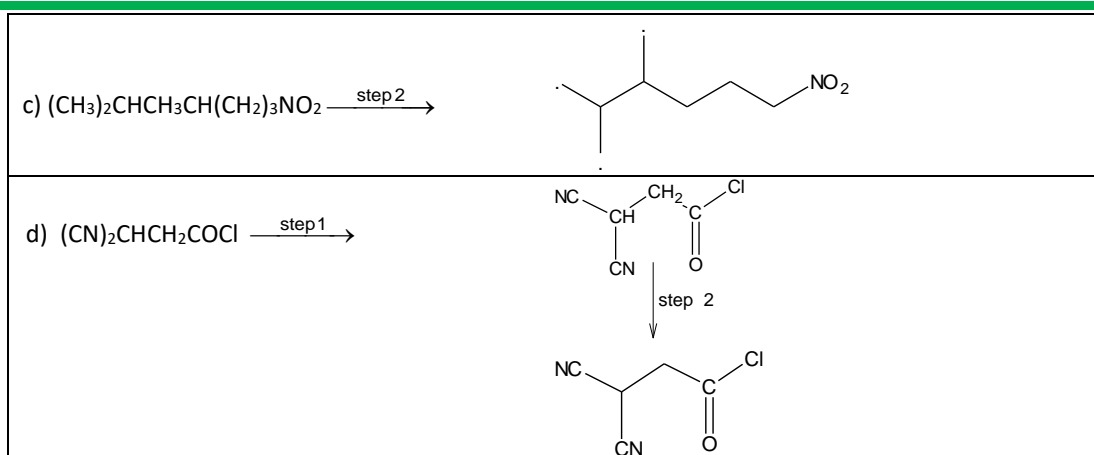
Thus, the bond-line formula is

Exp 5: For following condensed formulae write the corresponding bond-line formula.

- a) $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{CH}_2\text{OH}$ b) $\text{CH}_3(\text{CH}_2)_4\text{CHICH}_2\text{CHO}$
 c) $(\text{CH}_3)_2\text{CHCH}_3\text{CH}(\text{CH}_2)_3\text{NO}_2$ d) $(\text{CN})_2\text{CHCH}_2\text{COCl}$

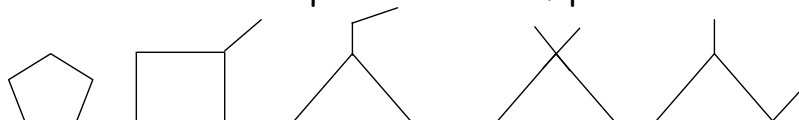
Solution: In bond-line formula carbon and hydrogen atoms except those that are part of the functional groups are not shown. We show only the carbon skeleton. The number of hydrogen atoms necessary to fulfill the carbon atoms' valences is assumed to be present, but we do not write them in. Other atoms (e.g., Cl, O, N) are written in. Each intersection of two or more lines and the end of a line represent a carbon atom unless some other atom is written in.





Exp 6: Draw all possible bond-line formulae for a cyclic compound, C_5H_{10} .

Solution: Start with the maximum number of carbon atoms in the ring and move towards the ring of 3 carbon atoms. Explore all sorts of possibilities on this route:

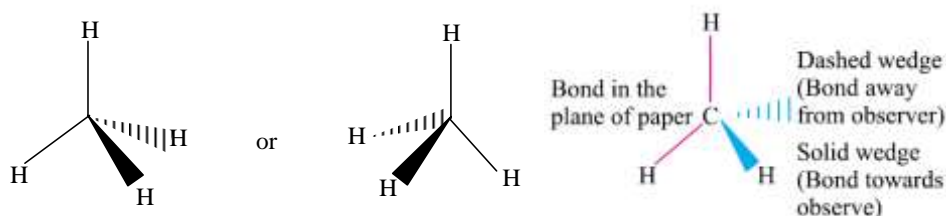


Three-dimensional representation of organic molecules

None of the formulae that we have described so far conveys any information about how the atoms of a molecule are arranged in space. Shape or the three-dimensional (3-D) structure of organic molecules can be described on a paper (two-dimensional) by exploring certain conventions. For instance, by using solid and dashed wedge formula the 3-D image of an organic molecule can be perceived on a two-dimensional paper.

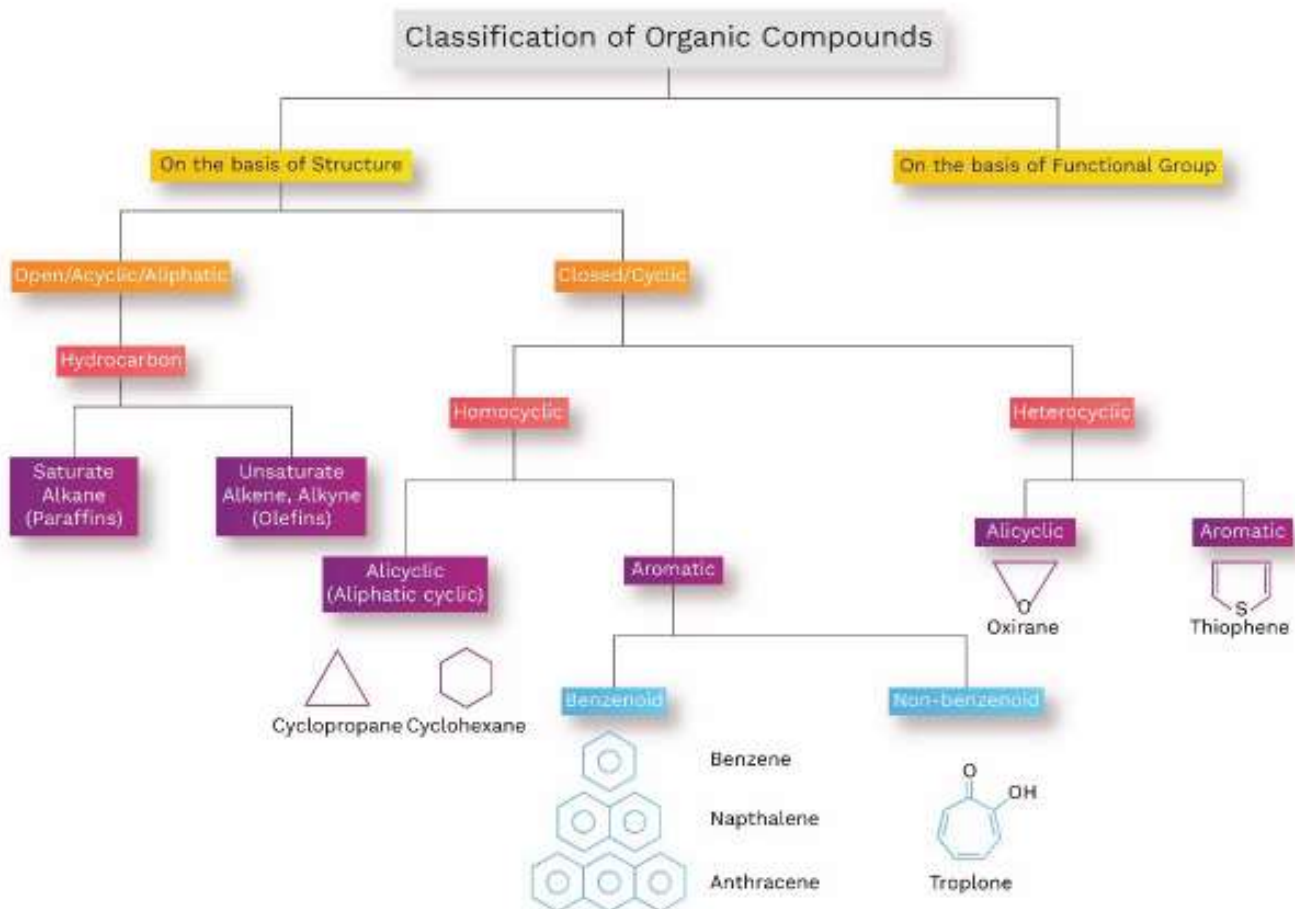
In solid-wedge and dashed-wedge description the **solid-wedge denotes a bond projecting out of the plane of the paper towards the viewer**. The dashed-wedge depicts the bond projecting behind the plane of the paper and going away from the viewer. Both the wedges are drawn in such a way that the broad end of the wedge is near the viewer. The other two bonds lying in the plane of the paper are shown by using a normal line (—).

Let's consider the wedge- and dashed-wedge representation of methane (CH_4) molecule:



The two carbon-hydrogen bonds represented by normal lines are in the plane of paper, whereas the carbon-hydrogen bond represented with a solid wedge is aimed to be in front of the plane of paper. The hydrogen bonded to carbon by dashed wedge is intended to be behind the plane of paper. Note that the carbon atom is lying in the plane of paper. Wedge and dashed-wedge formulae are an important tool for clearly showing three dimensions.

Classification of organic compounds



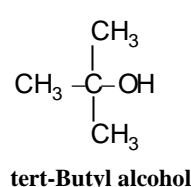
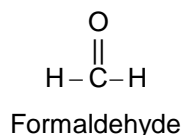
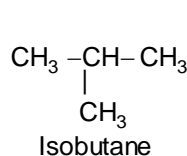
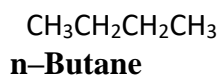
The compounds with C and H are called **hydrocarbons**. Organic compounds are considered as the derivatives of hydrocarbons obtained by replacing H-atoms by other atoms or groups. Based on C - skeleton, organic compounds divided as below,

1. **Acyclic compounds** - The open chain organic compounds are called acyclic compounds. The carbon chains may be linear or branched.

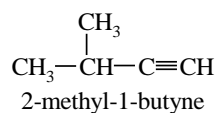
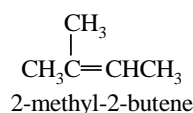
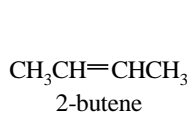
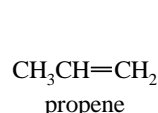
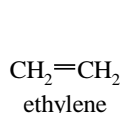
The open chain compounds are classified into **two groups**.

- a. **Saturated compounds**: Open chain compounds in which carbon atoms of parent chain are bonded with single bonds are called saturated acyclic compounds.

Example:



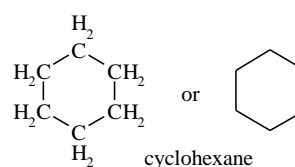
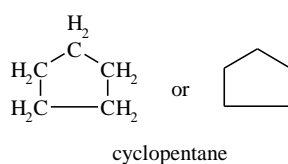
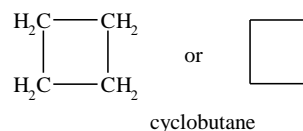
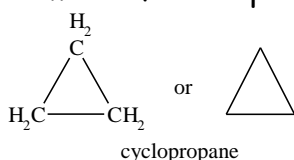
- b. **Unsaturated compounds**: The open chain organic compounds in which parent chain contains one or more carbon-carbon double bonds or triple bonds are called unsaturated acyclic compounds.



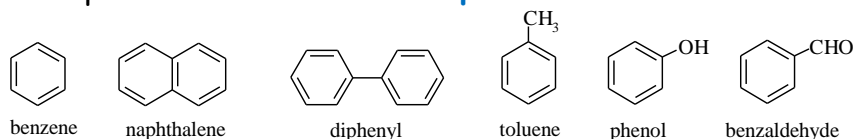
2. Cyclic Compounds - Here carbon atoms are linked by covalent bonds to form ring structures are called cyclic compounds. Depending upon the constituents of ring, these compounds are further classified into two groups.

A. Carbocyclic compounds (Homocyclic compounds): The cyclic compounds containing only carbon atoms in their ring are called carbocyclic compounds. They are further divided into two groups.

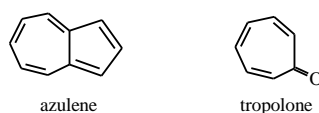
➤ **Alicyclic compounds:** The carbocyclic compounds which resemble with aliphatic compounds in most of their properties are called alicyclic compounds.



Aromatic compounds: Benzene is the parent aromatic hydrocarbon. The organic compounds containing one or more isolated or fused benzene rings and their functionalized derivatives are called aromatic compounds or **benzenoid compound**.

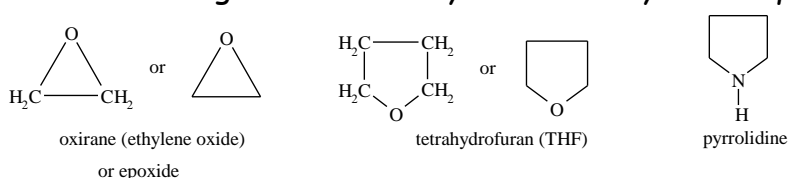


The aromatic compounds which resemble benzene in most of their properties are called **non-benzenoid aromatic compounds**.

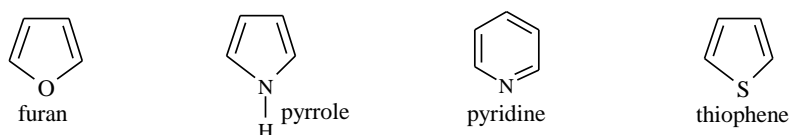


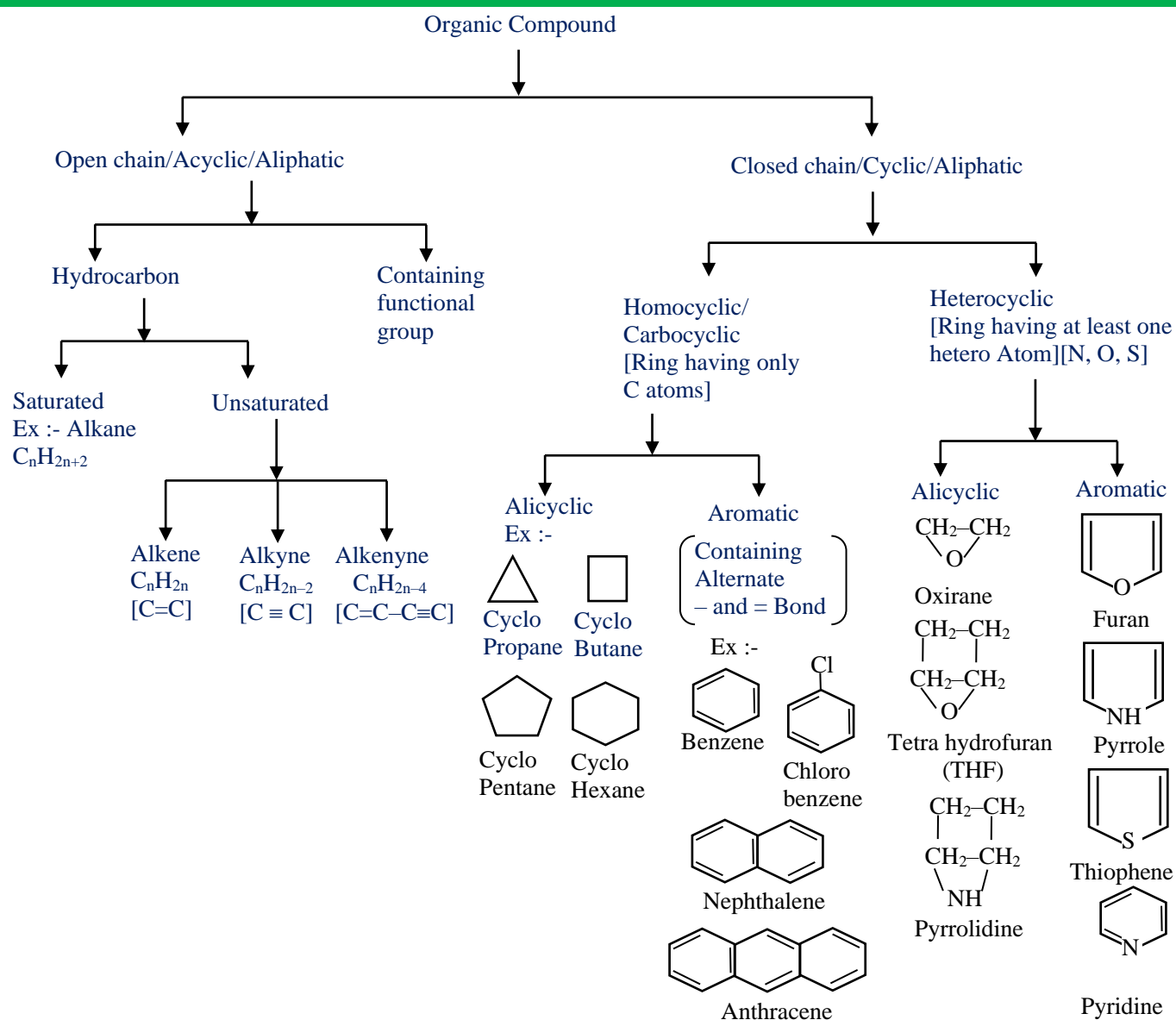
➤ **Heterocyclic compounds:** The cyclic compounds containing one or more heteroatoms (atom other than C it may be O, N, S, etc.) in their ring are called *heterocyclic compounds*. Depending upon their chemical behaviors, they are further classified into two groups.

i. Alicyclic heterocyclic compounds: The aliphatic cyclic compounds containing one or more hetero atoms in their ring are called *alicyclic heterocyclic compounds*.



ii. Aromatic heterocyclic compounds: The aromatic cyclic compounds containing one or more hetero atoms in their molecules are called aromatic heterocyclic compounds.





Functional groups: is defined as "an atom or group of atoms present in a molecule which decides the chemical properties of the organic compounds".

Double and triple bonds are also considered as functional groups.

The organic compounds are further classified into different classes depending upon the nature of functional group. Classification of organic compounds based on functional group is summarized in the table.

Functional Group	Compound Type	Prefix or Suffix of Name	Example		Systematic Name (Common Name)
			Lewis Structure	Ball-and-Stick Model	
	alkene	-ene			ethene (ethylene)
	alkyne	-yne			ethyne (acetylene)
	alcohol	-ol			methanol (methyl alcohol)
	haloalkane (X = halogen)	halo-			chloromethane (methyl chloride)
	amine	-amine			ethanamine (ethylamine)
	aldehyde	-al			ethanal (acetaldehyde)
	ketone	-one			2-propanone (acetone)
	carboxylic acid	-oic acid			ethanoic acid (acetic acid)
	ester	-oate			methyl ethanoate (methyl acetate)
	amide	-amide			ethanamide (acetamide)
	nitrile	-nitrile			ethanenitrile (acetonitrile, methyl cyanide)

Homologous Series

A series of structurally related organic compounds with same functional group can be represented by a general formula and differ by $-\text{CH}_2$ group is called homologous series. The individual members of such series are called homologue and this phenomenon is known as homology.

S. NO.	NAME OF SERIES	I-HOMOLOGUE	II-HOMOLOGUE
(i)	Alkane ($\text{C}_n\text{H}_{2n+2}$)	CH_4	CH_3-CH_3
(ii)	Alkene (C_nH_{2n})	$\text{CH}_2=\text{CH}_2$	$\text{CH}_2=\text{CH}-\text{CH}_3$
(iii)	Alkyne ($\text{C}_n\text{H}_{2n-2}$)	$\text{HC}\equiv\text{CH}$	$\text{HC}\equiv\text{C}-\text{CH}_3$
(iv)	Halo alkane ($\text{C}_n\text{H}_{2n+1}\text{X}$)	CH_3-X	$\text{CH}_3-\text{CH}_2-\text{X}$
(v)	Alcohol ($\text{C}_n\text{H}_{2n+2}\text{O}$)	CH_3-OH	$\text{CH}_3-\text{CH}_2-\text{OH}$
(vi)	Ether ($\text{C}_n\text{H}_{2n+2}\text{O}$)	$\text{CH}_3-\text{O}-\text{CH}_3$	$\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_3$
(vii)	Aldehyde ($\text{C}_n\text{H}_{2n}\text{O}$)	$\text{H}-\text{CHO}$	CH_3-CHO
(viii)	Ketone ($\text{C}_n\text{H}_{2n}\text{O}$)	$\text{CH}_3-\text{CO}-\text{CH}_3$	$\text{CH}_3-\text{CO}-\text{CH}_2-\text{CH}_3$
(ix)	Carboxylic acid ($\text{C}_n\text{H}_{2n}\text{O}_2$)	$\text{H}-\text{COOH}$	CH_3-COOH
(x)	Ester ($\text{C}_n\text{H}_{2n}\text{O}_2$)	HCOOCH_3	$\text{HCOOCH}_2\text{CH}_3$
(xi)	Amide ($\text{C}_n\text{H}_{2n+1}\text{NO}$)	$\text{H}-\text{CONH}_2$	$\text{CH}_3-\text{CONH}_2$
(xii)	Nitro alkane ($\text{C}_n\text{H}_{2n+1}\text{NO}_2$)	CH_3NO_2	$\text{CH}_3\text{CH}_2\text{NO}_2$
(xiii)	Amine ($\text{C}_n\text{H}_{2n+3}\text{N}$)	CH_3-NH_2	$\text{CH}_3-\text{CH}_2-\text{NH}_2$

Characteristics of a homologous series are as follows.

- Each homologues series can be represented by general molecular formula.
Exp - General molecular formula of alkane is $\text{C}_n\text{H}_{2n+2}$. Molecular formula $\text{C}_n\text{H}_{2n}\text{O}_2$ represents alkanoic acids (carboxylic acids) and alkyl-alkanoates (esters).
- All members of a given homologous series (homologues) possess the same functional group.
- The successive members of a homologous series differ by a $-\text{CH}_2-$ group or by mass units.
- Homologues of a homologous series can be prepared by general methods.
- The physical properties such as boiling point, melting point, density, etc., of the members of a homologues series show a regular gradation with increase in molecular mass.

The First Ten Straight-Chain Alkanes			
Name	Molecular formula	Structural formula	Boiling point (°C)
Methane	CH ₄	CH ₄	−161.0
Ethane	C ₂ H ₆	CH ₃ CH ₃	−88.5
Propane	C ₃ H ₈	CH ₃ CH ₂ CH ₃	−42.0
Butane	C ₄ H ₁₀	CH ₃ CH ₂ CH ₂ CH ₃	0.5
Pentane	C ₅ H ₁₂	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃	36.0
Hexane	C ₆ H ₁₄	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	68.7
Heptane	C ₇ H ₁₆	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	98.5
Octane	C ₈ H ₁₈	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	125.6
Nonane	C ₉ H ₂₀	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	150.7
Decane	C ₁₀ H ₂₂	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	174.1

- Chemical properties of the members of a homologous series are similar though the first homologue may vary considerably from the rest of the homologues.

Nomenclature of Organic Compounds

The nomenclature deals with the naming of millions of organic compounds. The following systems are employed.

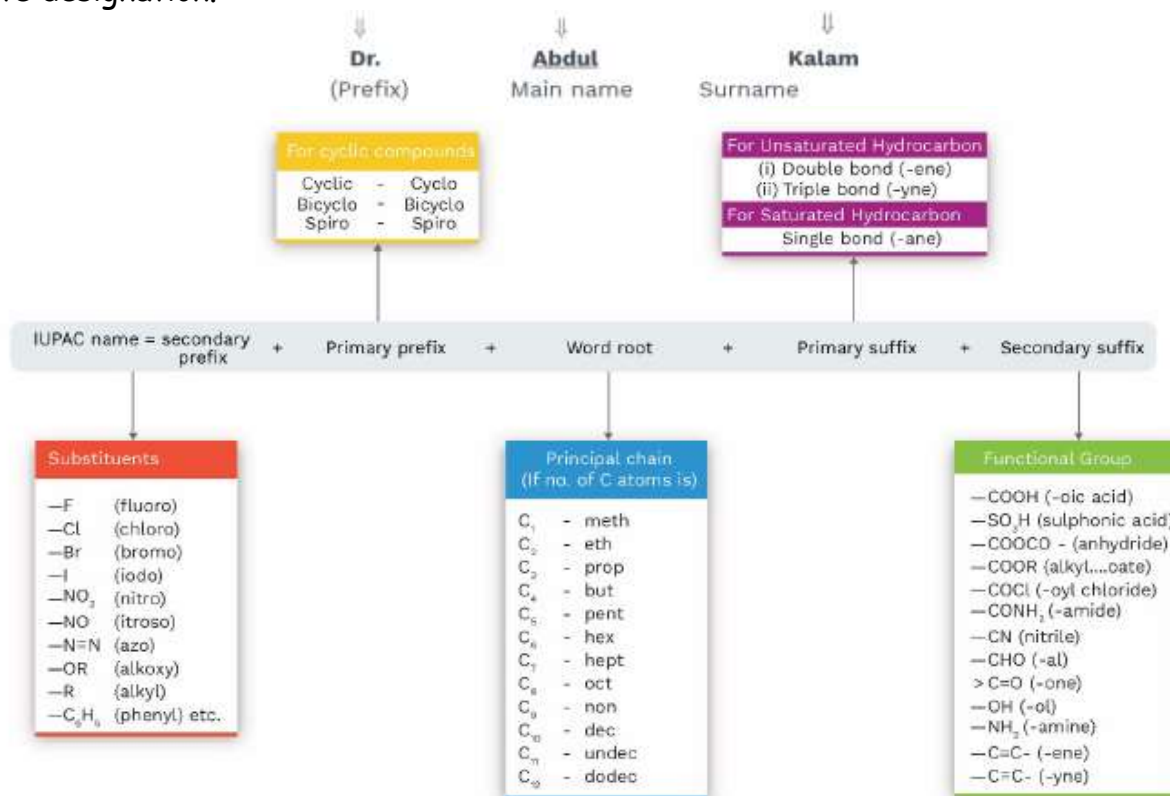
1. Trivial system (common system)

It is the oldest system of naming organic compounds. In the early stages of the development of organic chemistry, organic compounds were named after the source from which they were first isolated. Generally, the names chosen had Latin or Greek roots. The following illustrations justify the statement.

S. NO.	ORGANIC COMPOUND	TRIVIAL NAME	SOURCE
1	CH ₃ OH	Wood spirit or Methyl spirit	Obtained by destructive distillation of wood
2	NH ₂ CONH ₂	Urea	Obtained from urine
3	CH ₄	Marsh gas (fire damp)	It was produced in marshy places
4	CH ₃ COOH	Vinegar	Obtained from Acetum –i.e. Vinegar
5	$\begin{array}{c} \text{COOH} \\ \\ \text{COOH} \end{array}$	Oxalic acid	Obtained from oxalis plant
6	HCOOH	Formic acid	Obtained from formicus [Red ant]
7	$\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{COOH} \\ \\ \text{OH} \end{array}$	Lactic acid	Obtained from sour milk
8	$\begin{array}{c} \text{H}_2\text{C}-\text{COOH} \\ \\ \text{CH}(\text{OH})\text{COOH} \end{array}$	Malic acid	Obtained from apples
9	CH ₃ CH ₂ CH ₂ COOH	Butyric acid	Obtained from butter
10	CH ₃ (CH ₂) ₆ COOH	Caproic acid	Obtained from goats

2. IUPAC System - Saturated hydrocarbons are the parent compounds and other organic compounds as their derivatives obtained by substituting one or more hydrogen atoms with functional groups. IUPAC name of any organic compound may consist of three parts. **"prefix-root word-suffix"**.

IUPAC system for naming is something that is very similar to addressing a person with his complete designation.



a. Root word - is assigned to organic molecule based on the number of carbon atoms present in the main parent chain

No. of C atoms	Root word	Molecular formula	Molecular structure	IUPAC name
1	Meth	CH ₄	CH ₄	Methane
2	Eth	C ₂ H ₆	CH ₃ CH ₃	Ethane
3	Prop	C ₃ H ₈	CH ₃ CH ₂ CH ₃	Propane
4	But	C ₄ H ₁₀	CH ₃ (CH ₂) ₂ CH ₃	Butane
5	Pent	C ₅ H ₁₂	CH ₃ (CH ₂) ₃ CH ₃	Pentane
6	Hex	C ₆ H ₁₄	CH ₃ (CH ₂) ₄ CH ₃	Hexane
7	Hept	C ₇ H ₁₆	CH ₃ (CH ₂) ₅ CH ₃	Heptane
8	Oct	C ₈ H ₁₈	CH ₃ (CH ₂) ₆ CH ₃	Octane
9	Non	C ₉ H ₂₀	CH ₃ (CH ₂) ₇ CH ₃	Nonane
10	dec	C ₁₀ H ₂₂	CH ₃ (CH ₂) ₈ CH ₃	Decane
11	Undec			
12	dodec			

b. Suffix - is based on the nature of bonds and functional group present in the molecules. It is of 2 types,

- Primary suffix:** A primary suffix is added next to the root word to indicate whether the parent chain is saturated or unsaturated.

Type of carbon chain	root word	primary suffix	generic name
Saturated (C-C single bonds)	alk	ane	alkane
Unsaturated [C=C bond]	alk	ene	alkene
Unsaturated [C≡C-]	alk	yne	alkyne

Note: A carbon-carbon double bond or triple bond must be included in parent chain even if it contains less number of carbon atoms.

- Secondary suffix** added next to the primary suffix to indicate the presence of a functional group in organic compounds which determines the class of organic compounds.

Secondary suffix of a few **functional groups** are given.

Functional group	Structure	Secondary suffix	Class of organic compounds
Hydroxyl	-OH	- ol	Alcohols
Aldehydic	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \end{array}$	- al	Aldehydes
Ketonic	$\begin{array}{c} >\text{C}=\text{O} \end{array}$	- one	Ketones
Carboxy	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$	-oic acid	Carboxylic acids
Ester	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OR} \end{array}$	alkylalkanote	Esters
Amino	-NH ₂	- amine	Amines

Note - While adding the secondary suffix, the letter 'e' of the primary suffix (i.e., ane, ene and yne) is dropped if the secondary suffix begins with a vowel (a, e, i, o or u). It is retained if secondary suffix begins with a consonant.

C. Prefix (substituent)

All the groups which are not names in parent chain and functional groups are called as substituents. Its name placed before the root word.

Exp - Alkyl group, halo atoms, nitro group

Substituents group	Prefix
-CH ₃	Methyl
-C ₂ H ₅	Ethyl
-NO ₂	Nitro
-Cl	Chloro
-OR	Alkoxy
$\begin{array}{c} \text{C}-\text{C} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$	Epoxy
-NO	Nitroso

Alkyl groups - derived from an alkane, by removing a hydrogen atom bonded to carbon.

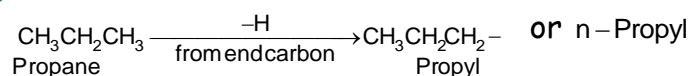
These groups are named simply by dropping -ane from the name of the corresponding alkane and replacing it by -yl. R is a general symbol, general formula for an alkyl group is C_nH_{2n+1}, because it contains one less hydrogen atom than the parent alkane, C_nH_{2n+2}.

Alkane	Alkyl group	Abbreviation
Methane, CH ₄	Methyl, CH ₃ -	Me-
Ethane, CH ₃ CH ₃	Ethyl, CH ₃ CH ₂ - or C ₂ H ₅ -	Et -
Propane, CH ₃ CH ₂ CH ₃	n-propyl, CH ₃ CH ₂ CH ₂ - Isopropyl, CH ₃ CH(CH ₃)CH ₂ -	n-Pr - or Pr - i-Pr-
n-Butane, CH ₃ CH ₂ CH ₂ CH ₃	n-Butyl, CH ₃ CH ₂ CH ₂ CH ₂ - sec-Butyl, CH ₃ CH ₂ CH(CH ₃)CH ₂ -	n-Bu- or Bu-s-Bu-
Isobutane, CH ₃ CH(CH ₃)CH ₃	Isobutyl, CH ₃ CH(CH ₃)CH ₂ - tert-Butyl, CH ₃ C(CH ₃) ₂ -	i-Bu- t-Bu-

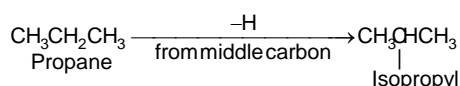
Among the alkyl groups we encounter the problem of isomerism.

- While only one alkyl group can be derived from methane (the methyl, CH_3-)
- Ethane (the ethyl, CH_3CH_2-)
- Two or more alkyl groups can be derived from higher alkanes.

Exp - (1) From **propane (C_3H_8)**, two alkyl groups can be derived. **Removal of one of the hydrogens from one of the end carbon atoms** gives an alkyl group that is called the propyl group or **n-propyl group**.

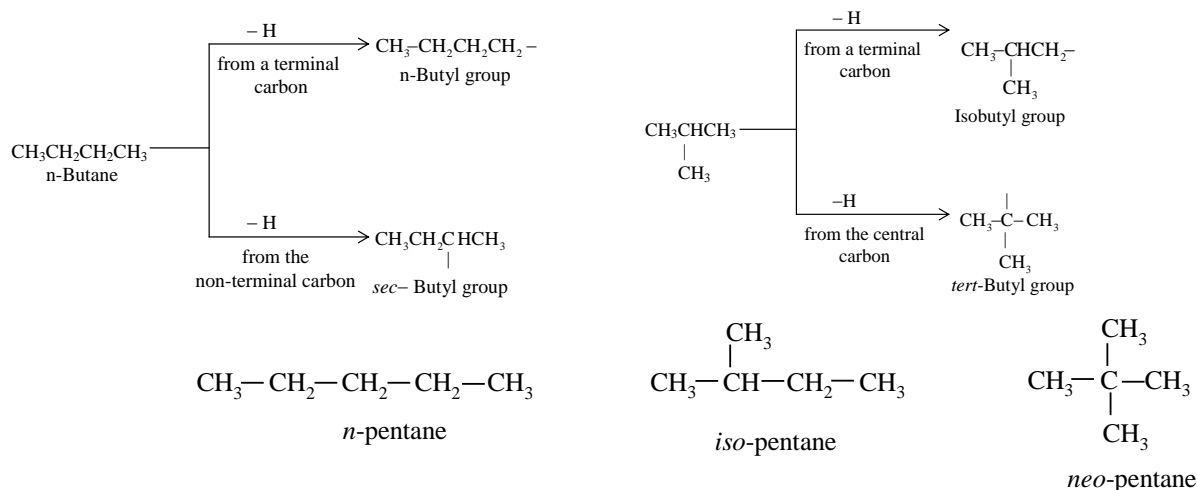


Removal of one of the hydrogens from the middle carbon atom gives an alkyl group that is called the **isopropyl group**.



Both these alkyl groups contain the propane chain, but differ in the point of attachment of the group to the rest of the molecule.

(2) There are four butyl groups, two derived from the straight-chain **n-butane**, and two derived from the branched-chain isobutane. These are given the designations: **n-** (normal), **sec-** (secondary), **iso-** and **tert-** (tertiary) as shown below:



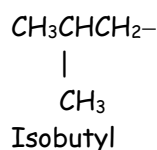
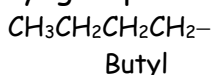
An alkyl group is described as,

- ❖ **primary** if the carbon at the point of attachment is bonded to only one other carbon,
- ❖ as **secondary** if bonded to two other carbons,
- ❖ **tertiary** if bonded to three other carbons. Thus, if R is any hydrocarbon radical, the different kinds of alkyl groups are

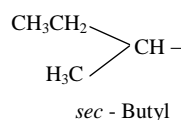
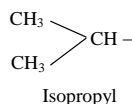
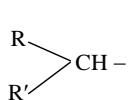
RCH_2-	R_2CH-	R_3C-
Primary	Secondary	Tertiary

Problem 1: Classify each of the following alkyl groups as primary, secondary or tertiary: Butyl, Isopropyl, Isobutyl, sec-Butyl and tert-Butyl.

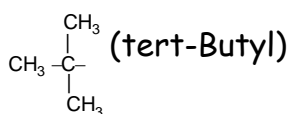
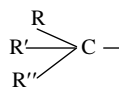
Solution: Primary alkyl group is RCH_2-



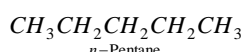
Secondary alkyl group is



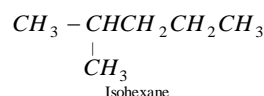
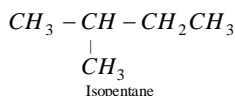
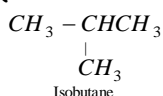
Tertiary alkyl group is



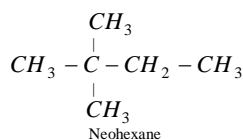
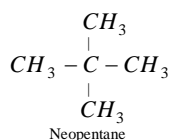
• **Prefix n-(normal)** is used for those alkanes in which all the carbon atoms form a continuous chain with no branching.






• **Prefix iso** is used for those alkanes in which one methyl group is attached to the next-to-end carbon atom (second last) of the continuous chain.



• **Prefix neo** is used for those alkanes which have two methyl groups attached to the second last carbon atom of the continuous chain.



Compound	2° prefix	1° prefix	Word root	1° suffix	2° suffix	IUPAC name
$\text{CH}_3\text{CH}_2\text{CH}_3$	—	—	prop	ane	—	Propane
$\text{CH}_3-\text{CH}=\text{CH}_2$	—	—	prop	ene	—	Propene
$\text{CH}_3-\text{C}\equiv\text{CH}$	—	—	prop	yne	—	Propyne
$\text{HC}\equiv\text{CH}$	—	—	eth	yne	—	Ethyne
	—	cyclo	but	ane	—	Cyclobutane
	—	cyclo	but	ene	—	Cyclobutene
	—	cyclo	oct	yne	—	Cyclooctyne

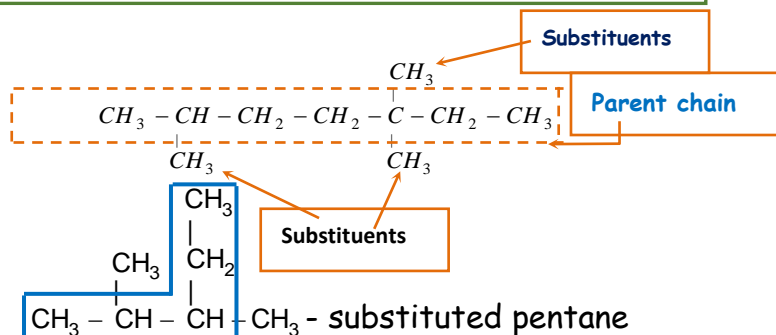
Rules for naming of open chain Organic compound.

Rule 1 - Longest chain rule (root word rule)

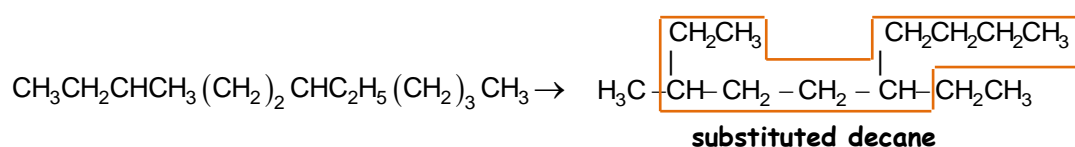
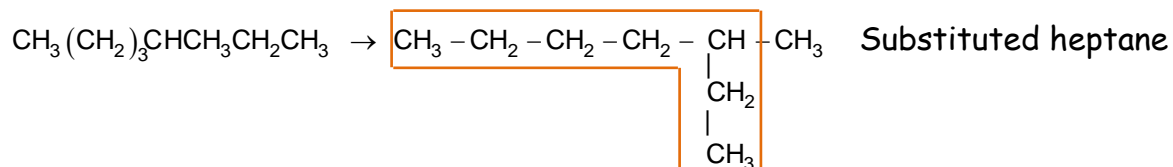
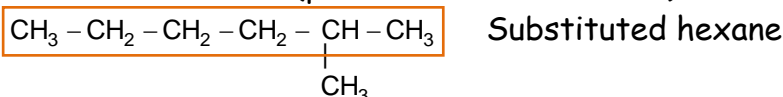
The **continuous carbon chain containing maximum carbon atoms including the function group is selected**. It is called the **parent chain**. For one to four carbon atoms of the parent chain, special root words are used but for chains of five or more carbon atoms *Greek number roots* are employed.

The generic root word for any parent chain is 'alk'.

Priority order: Functional group > Multiple bond (= or \equiv) > Substituent

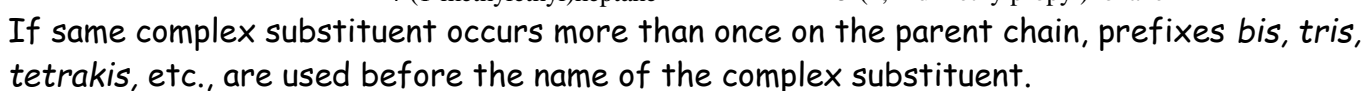
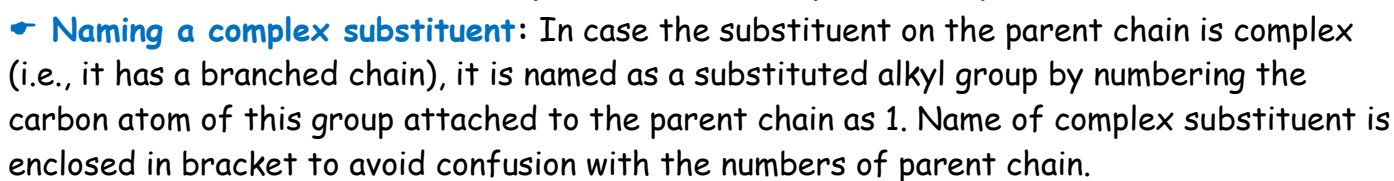


Similarly, the following hydrocarbon will be regarded as a substituted hexane because the longest continuous carbon chain (parent chain/ root chain) contains six carbon atoms.



$\begin{array}{ccccccc} & & \text{Br} & & \\ & & | & & \\ {}^1\text{CH}_3 - & {}^2\text{CH} - & {}^3\text{CH} - & {}^4\text{CH}_3 & \leftarrow \dots\dots \text{correct} \\ & | & & & \\ & \text{Cl} & & & \\ & & {}^2 & & {}^1 \\ & & | & & \\ & & \text{Cl} & & \\ & & & & \leftarrow \dots\dots \text{incorrect} \end{array}$

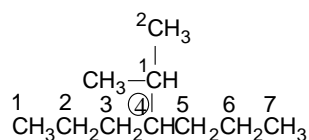
- **Presence of the same substituent more than once:** If the same substituent occurs more than once, the prefixes *di*, *tri*, *tetra* are prefixed to the name of the substituent. It may be noted that the position and name of the substituent are separated by a *hyphen* (-) whereas the numerals representing the positions of the substituents are separated by *commas*.


$$\begin{array}{ccccccc} & & \text{CH}_2-\text{CH}_3 & & & & \\ & & | & & & & \\ \text{CH}_3-\text{CH}-\text{CH}-\text{CH}-\text{CH}_3 & & & & & & \\ 5 & 4 & 3 & 2 & 1 & & \\ & | & & | & & & \\ & \text{CH}_3 & & \text{Br} & & & \end{array}$$

- Parent chain has 5 carbon atoms, and it has more number of substituents. The root word is 'pent'.
- Primary suffix is 'ane'
- Sum of locants is 9, the substituent which comes first in alphabetical order gets the lower number.
- Prefixes to the rootword are bromo, ethyl and methyl. Hence, IUPAC name is
- "2-bromo-3-ethyl-4-methylpentane"
-

A few examples are given below:

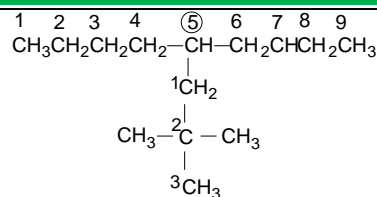
<div><div><div><div><div></div><div>CH₃</div><div></div></div><div><div><div>CH₃</div><div>CH₃-C-CH₂-CH-CH₃</div><div></div></div><div><div><div></div><div>CH₃</div><div></div></div><div><div></div><div>CH₃</div><div></div></div></div><div>2,2,4-trimethylpentane</div></div></div></div></div>	<div><div><div><div><div></div><div>Br</div><div></div></div><div><div><div>CH₃</div><div>CH₃-CH-CH-CH-CH₂-CH₃</div><div></div></div><div><div><div></div><div>CH₂-CH₃</div><div></div></div></div><div>2-bromo-3-ethyl-4-methylhexane</div></div></div></div></div>	
<div><div><div><div><div>1</div><div>2</div><div>3</div><div>4</div><div>5</div><div>6</div></div><div><div>CH₃</div><div>CH</div><div>CH₂</div><div>CH₂</div><div>CH₂</div><div>CH₃</div></div><div><div><div></div><div>CH₃</div><div></div></div></div></div><div>2-Methylhexane</div></div></div>	<div><div><div><div><div>1</div><div>2</div><div>3</div><div>4</div><div>5</div><div>6</div><div>7</div><div>8</div><div>9</div></div><div><div>CH₃</div><div>CH</div><div>CH₂</div><div>CH₂</div><div>CH₂</div><div>CH</div><div>CH₂</div><div>CH₂</div><div>CH₃</div></div><div><div><div></div><div>CH₃</div><div></div></div><div><div><div></div><div>CH₂CH₃</div><div></div></div></div></div><div>6-Ethyl-2-methylnonane</div></div></div></div>	
<div><div><div><div><div>1</div><div>2</div><div>3</div><div>4</div><div>5</div><div>6</div><div>7</div></div><div><div>CH₃</div><div>CH₂</div><div>CH</div><div>CH₂</div><div>CH₂</div><div>CH₂</div><div>CH₃</div></div><div><div><div></div><div>CH₃</div><div></div></div></div></div><div>3-Methylheptane</div></div></div>	<div><div><div><div><div></div><div>CH₃</div><div></div></div><div><div><div>1</div><div>2</div><div>3</div><div>4</div><div>5</div><div>6</div><div>7</div></div><div><div>CH₃</div><div>CH₂</div><div>C</div><div>CH₂</div><div>CH₂</div><div>CH₂</div><div>CH₃</div></div><div><div><div></div><div>CH₂</div><div></div></div><div><div><div></div><div>CH₃</div><div></div></div></div></div><div>3-Ethyl-3-methylheptane</div></div></div></div></div>	
<div><div><div><div><div>1</div><div>2</div><div>3</div><div>4</div><div>5</div><div>6</div></div><div><div>CH₃</div><div>CH</div><div>CH₂</div><div>CH</div><div>CH₂</div><div>CH₃</div></div><div><div><div></div><div>CH₃</div><div></div></div><div><div><div></div><div>CH₂</div><div></div></div><div><div><div></div><div>CH₃</div><div></div></div></div></div><div>4-Ethyl-2-methylhexane</div><div>not</div><div>2-Methyl-4-ethylhexane because ethyl comes before methyl alphabetically</div></div></div></div></div>		
<div><div><div><div><div>1</div><div>2</div><div>3</div></div><div><div>CH₃</div><div>CH</div><div>CH</div><div>CH₃</div></div><div><div><div></div><div>CH₃</div><div></div></div><div><div><div></div><div>CH₂</div><div></div></div><div><div><div></div><div>CH₃</div><div></div></div></div></div><div>2,3-Dimethylpentane</div></div></div></div></div>	<div><div><div><div><div></div><div>CH₃</div><div></div></div><div><div><div>1</div><div>2</div><div>3</div><div>4</div><div>5</div></div><div><div>CH₃</div><div>CH</div><div>CH</div><div>CH</div><div>CH₃</div></div><div><div><div></div><div>CH₃</div><div></div></div><div><div><div></div><div>CH₃</div><div></div></div></div></div><div>2,3,4-Trimethylpentane</div></div></div></div></div>	<div><div><div><div><div></div><div>CH₃</div><div></div></div><div><div><div></div><div>CH₃</div><div></div></div></div><div><div><div>1</div><div>2</div><div>3</div><div>4</div><div>5</div></div><div><div>CH₃</div><div>C</div><div>CH₂</div><div>C</div><div>CH₃</div></div><div><div><div></div><div>CH₃</div><div></div></div><div><div><div></div><div>CH₃</div><div></div></div></div></div><div>2,2,4,4-Tetramethylpentane</div></div></div></div></div>
<div><div><div><div><div>1</div><div>2</div><div>3</div><div>4</div><div>5</div><div>6</div><div>7</div></div><div><div>CH₃CH₂CH₃</div><div>CH₃</div><div>CH₃CH₂CH₂CH₃</div><div>CH₃</div></div><div>3-Ethyl-4,4-dimethylheptane</div></div></div></div>	<div><div><div><div><div>8</div><div>7</div><div>6</div><div>5</div><div>4</div><div>3</div><div>2</div><div>1</div></div><div><div>CH₃</div><div>CH₃</div><div>CH₃</div><div>CH₃</div><div>CH₃</div><div>CH₃</div><div>CH₃</div><div>CH₃</div></div><div>4-Ethyl-2,2,7-trimethyloctane</div></div></div></div>	
<div><div><div><div><div>1</div><div>2</div><div>3</div><div>4</div><div>5</div><div>6</div><div>7</div><div>8</div><div>9</div><div>10</div></div><div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div><div></div></div></div><div>4,5-Diethyl-3,6-dimethyldecane</div></div></div>	<div><div><div><div><div>7</div><div>6</div><div>5</div><div>4</div><div>3</div><div>2</div><div>1</div></div><div><div></div><div></div><div></div><div></div><div></div><div></div><div></div></div></div><div>5-Ethyl-2,2-dimethyloctane ("di" not considered in alphabetical ordering)</div></div></div>	
<div><div><div><div><div>8</div><div>7</div><div>6</div><div>5</div><div>4</div><div>3</div><div>2</div><div>1</div></div><div><div></div><div></div><div></div><div></div><div></div><div></div><div></div></div></div><div>5-(1,1-Dimethylethyl)-3-ethyl-6-methyloctane ("di" is being part of substituent name)</div></div></div>	<div><div><div><div><div></div><div>CH₃</div><div></div></div><div><div><div>1</div><div>2</div><div>3</div><div>4</div><div>5</div><div>6</div><div>7</div><div>8</div><div>9</div><div>10</div></div><div><div>CH₃</div><div>CH₃</div><div>CH₃</div><div>CH₃</div><div>CH₃</div><div>CH₃</div><div>CH₃</div><div>CH₃</div></div><div><div><div></div><div>CH₃</div><div></div></div><div><div><div></div><div>CH₃</div><div></div></div></div></div><div>5-sec-Butyl-4-isopropyldecane</div></div></div></div></div>	



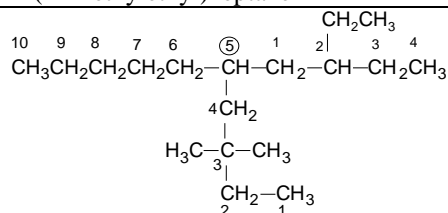
4 - Isopropylheptane

or

4-(1-Methylethyl)heptane



5-(2, 2-Dimethylpropyl)nonane



5-(2-Ethylbutyl)-3, 3-dimethyldecane

N.B. Longest chain selected has maximum number of side chains.

Naming of organic compounds containing a functional group

Prefix and suffix names of a few common functional groups and their **decreasing order of priority** are given in the table.

Group	Prefix name	Suffix name	Class of organic compounds
-COOH	-	-oic acid	Carboxylic acids
-COOR	-	alkyl....oate	Esters
-COX	-	-oyl halide	Acid halides
-CONH ₂	carbamoyl	-amide	Amides
-CHO	formyl	-al	Aldehydes
-CO	oxo	-one	Ketones
-OH	hydroxyl	-ol	Alcohols
-NH ₂	amino	-amine	Amines
>C=C<	-	-ene	Alkenes
$\text{-C}\equiv\text{C-}$	-	-yne	Alkynes
-X (halogen)	halo	-	Alkyl halides
-NO ₂	nitro	-	Nitroalkanes
-OR	alkoxy	-	Ethers

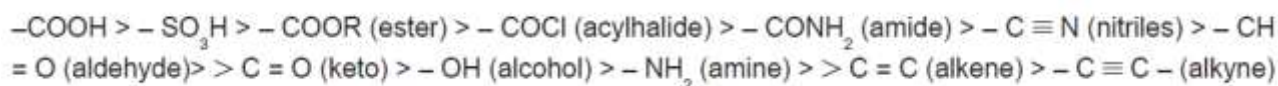
It may be noted that the groups $-R$, $-OR$, $-NO_2$, $-X$, etc. are considered as substituents and are indicated as prefixes.

- Longest chain-** The parent chain is the one which has functional group directly attached to it, even if it violates the longest chain rule.
- Numbering of parent chain-** The numbering should be done in such a way that the carbon linking to the functional group gets the lowest number even if it violates the lowest sum rule or locant rule.

When the functional group itself contains carbon atom, then that carbon atom is assigned as number 1.

- Naming of compounds with polyfunctional group-** If there is more than one functional group present in a compound, then one of the functional group is chosen as the principal functional group (secondary suffix) and the remaining functional groups are treated as (substituents) subordinate functional groups.

The functional group with higher priority in the sequence given below is termed as principal functional group.



KNOWLEDGE BUILDER

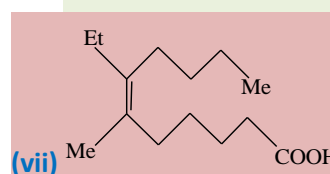
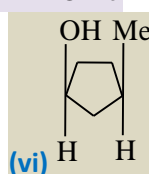
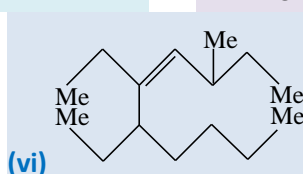
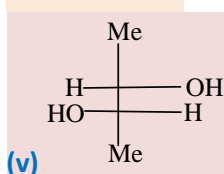
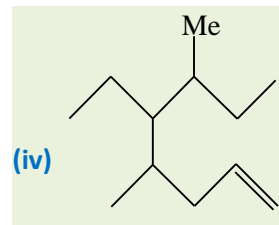
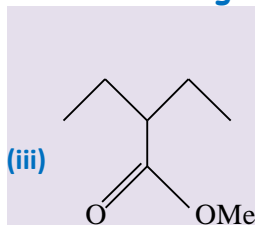
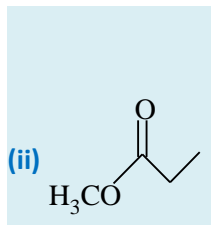
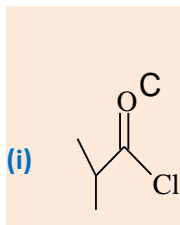
- When the names of two or more substituents are composed of identical words

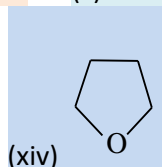
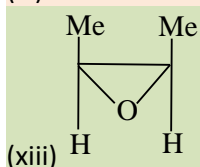
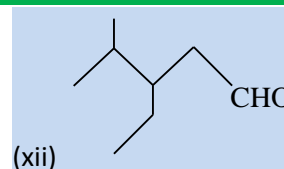
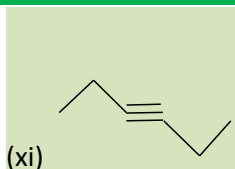
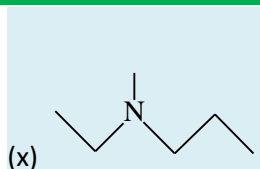
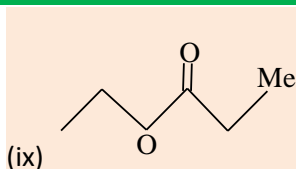
The priority of citation is given to the substituent which has the first cited point of difference with in the complex substituent.

- Poly-functional compounds containing more than two like-functional groups

According to the latest convention (1993 recommendation for IUPAC nomenclature), if an unbranched carbon chain is directly linked to more than two like-functional groups, then the organic compound is named as a derivative of the parent alkane which does not include the carbon atoms of the functional groups.

- Write the correct IUPAC names of the following bond line formula:

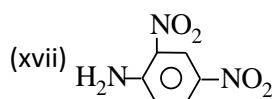
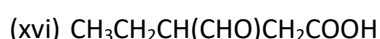
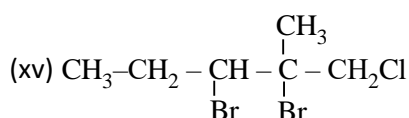
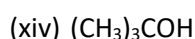
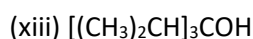
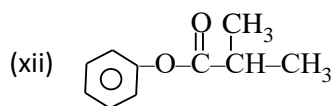
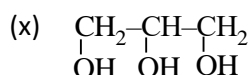
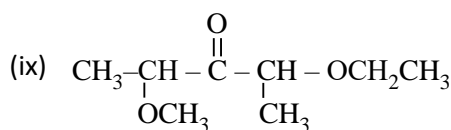
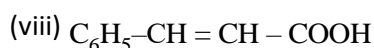
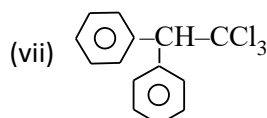
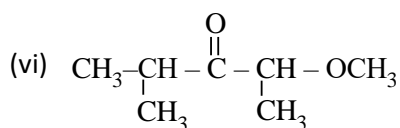
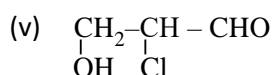
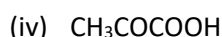
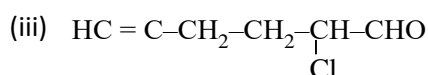
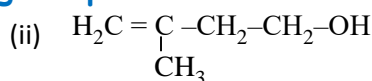
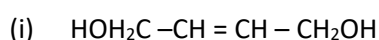




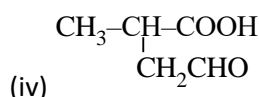
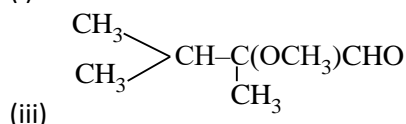
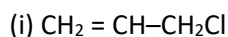
Answers

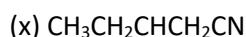
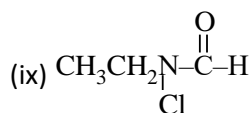
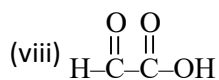
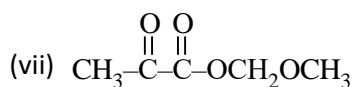
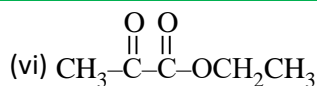
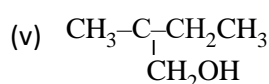
- | | |
|---------------------------------|---|
| (i) 2-Methylpropanoyl chloride | (ii) Methyl propanoate |
| (iii) Methyl 2-ethylbutanoate | (iv) 5-Ethyl-4, 6-dimethyloct-1-ene |
| (v) Butane-2,3-diol | (vi) 5,6-Diethyl-3-methylundec-4-ene |
| (vii) 3-Methyl cyclopentam-1-ol | (viii) 7-Ethyl-6-methylundec-6-cnoic acid |
| (ix) Ethyl propanoate | (x) N-Ethyl-N-methyl propan-1-amine |
| (xi) Hex-3-yne | (xii) 3-Ethyl-4-methylpentanal |
| (xiii) 2,3-Dimethyloxirane | (xiv) Tetrahydrofuran |

2. Write the IUPAC names of the following compounds:

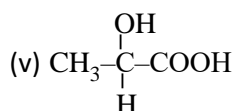
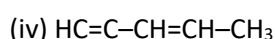
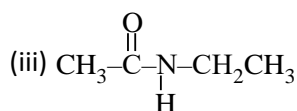
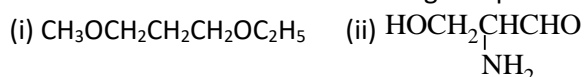


3. Write correct IUPAC names of the following polyfunctional compounds:





4. Write IUPAC names of the following compounds:



Answers

- (i) $-\text{C}=\text{N} > -\text{C}- > -\text{OH}$ (ii) $-\text{SO}_3\text{H} > -\text{COCl} > -\text{CHO}$

(i) $-\text{COOR} > -\text{CONH}_2 > -\text{CHO}$
- (i) But-2-ene-1, 4-diol (ii) 3-Methyl-but-3-en-1-ol

(iii) 2-Chlorohex-5-yn-1-ol (iv) 2-Ketopropanoic acid

(v) 2-Chloro-3-hydroxypropanal (vi) 2-Methoxy-4-methylpentan-3-one

(vii) 1,1,1-Trichloro-2,2-diphenylethane (viii) 3-Phenylprop-2-en-1-oic acid

(ix) 2-Ethoxy-4-methoxypentan-3-one (x) Propane 1,2,3-triol

(xi) 2-Methoxybenzoic acid (xii) Phenyl 2-methylpropanoate

(xiii) 2,4-Dimethyl-3-(1-nethylethyl) pentan-3-ol (xiv) 2-Methylpropan-2-ol

(xv) 2,3-Dibromo-1-chloro-2-methylpentane (xvi) 3-Formylpentanoic acid

(xvii) 2,4-Dinitro benezamine
- (i) 3-chloroprop-1-ene (ii) butane-1,2,3-triol

(iii) 2-Methoxy-2,3-dimethylbutanal (iv) 3-Formyl-2-methylproanoic acid

(v) 2-Ethyl-3-hydroxy-2-methyl propanal (vi) Ethyl-(2-oxo) propanoate

(vii) 1-Methoxy-2,3,-butanedione (viii) Formylmethanoic acid

(ix) N-Chloro-N-ethyl methanamide (x) 2-Ethyl-butane-1,4-dinitrile
- (i) 1-Ethoxy-3-methoxypropane (ii) 2-Amino-3-hydroxypropanal

(iii) N-Ethyl ethanamide (iv) Pent-3-en-1-yne

(v) 2-Hydroxypropanoic acid

Nomenclature of substituted benzene compounds

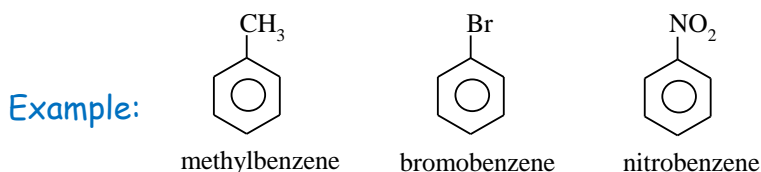
Benzene is a six membered cyclic compound with alternate single and double bonds. It is represented in any one of the following ways:



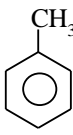
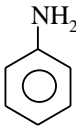
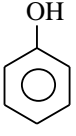
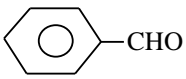
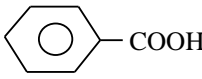
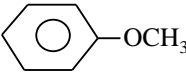
(i) Naming of monosubstituted benzene

It is derived by adding the name of the substituent with the word benzene.

Substituent + benzene → substituted benzene

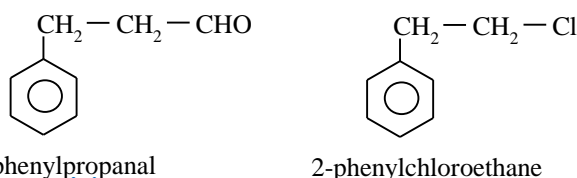


Special names of some monosubstituted benzene compounds

Molecular formula	Structural formula	IUPAC name	Special name
$C_6H_5CH_3$		methylbenzene	Toluene
$C_6H_5NH_2$		benzenamine	Aniline
C_6H_5OH		phenol	Phenol
C_6H_5CHO		Benzene Carbaldehyde	Benzaldehyde
C_6H_5COOH		Benzene Carboxylic acid	Benzoic acid
$C_6H_5OCH_3$		methoxybenzene	Anisole

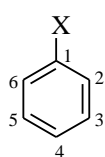
If the functional group is attached to the carbon chain connected to benzene ring, then benzene ring is considered as substituent and is prefixed before the root word as phenyl.

Example:



(ii) Naming of disubstituted benzene

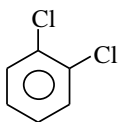
(a) If the substituents are same: In such case, the relative position of the substituents must be indicated by adding the symbols o – (1, 2) ; m – (1, 3) ; p – (1, 4).



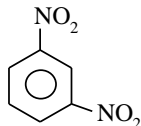
o-ortho : positions 2, 6
 m-meta : positions 3, 5
 p-para : positions 1, 4

In the trivial system of nomenclature, the terms ortho(o), meta(m) and para(p) are used as prefixes to indicate the relative positions 1, 2-; 1, 3 and 1, 4-respectively.

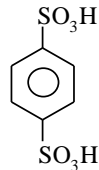
Example:



1,2-dichlorobenzene
(or) o-dichlorobenzene

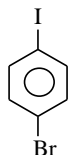


1,3-dinitrobenzene
(or) m-dinitrobenzene

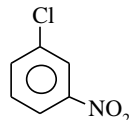


1,4-benzenedisulphonic acid
(p-benzenedisulphonic acid)

(b) If the two substituents are different, they are named in the alphabetical order.

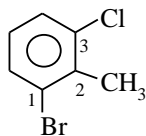


1-bromo-4-iodobenzene
(or) p-bromiodobenzene

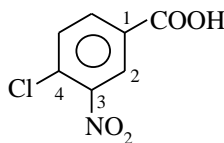


1-chloro-3-nitrobenzene
(or) m-chloronitrobenzene

(c) If there are more than two substituents: The numbering is done in such a way that it satisfies the lowest sum rule.



1-bromo-3-chloro-2-methylbenzene

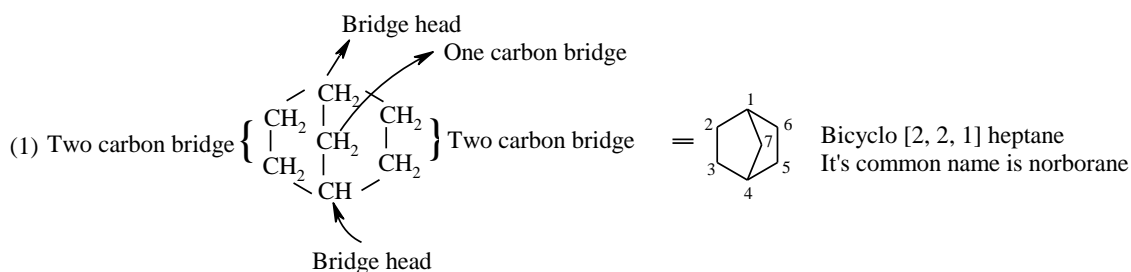


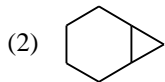
4-chloro-3-nitrobenzoic acid

Nomenclature of Bicyclo compounds

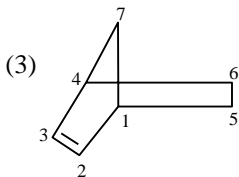
- (i) Bicyclo compounds contain two fused rings with the help of a bridge. We use the name of the alkane corresponding to the total number of carbon atoms as the base name. The carbon atoms common to both the rings are called bridge heads, and each bond or chain of atoms connecting the bridgehead atoms called a bridge.
- (ii) While naming the bi-cycloalkane we write an expression between the word bicyclo and alkane (in square bracket), that denotes the number of carbon atoms in each bridge. The numerals are written in descending order and the numbers are separated by a point.
- (iii) If substituents are present, we number the bridged ring system beginning at one bridge head, proceeding first along the longest bridge to the other bridge head, then along the second next longest bridge back to first bridge head. The shortest bridge is numbered in the last.

Example:

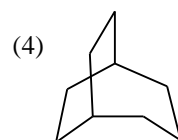




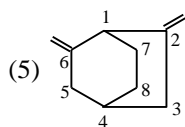
Bicyclo [4.1.0] heptane



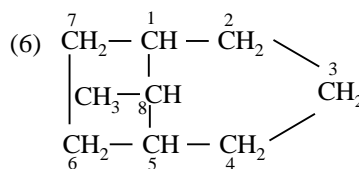
Bicyclo [2.2.1] hept-2-ene



Bicyclo [3.2.2] nonane



Bicyclo [2.2.2] octa-2,6-dione



8-Methylbicyclo [3.2.1] octane

Chapter Summary

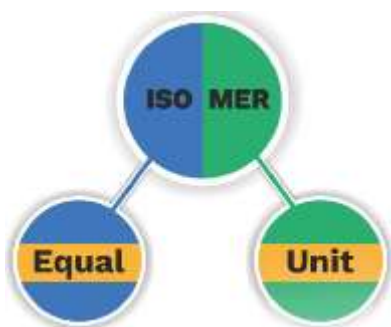


- ♦ A carbon atom can share 4 electrons with other carbons & can form multiple bond. The bonds formed are single, double and triple by sharing of 2, 4 & 6 electrons respectively.
- ♦ Priority order of functional group :
- ♦ $-\text{COOH} > -\text{SO}_3\text{H} > -\text{COOR} > -\text{COX} > -\text{CONH}_2 > -\text{CN} > -\text{NC} > -\text{CHO} > >\text{C}=\text{O} > -\text{OH}$
 $> -\text{SH} > -\text{NH}_2 > -\text{OR} > -\text{C}-\text{C}- > \text{C}=\text{C} > -\text{C}\equiv\text{C}- > -\text{N}=\text{N}- > -\text{NO}_2 > -\text{NO} > -\text{X}$
- ♦ IUPAC name = sec. prefix + primary prefix + word root + primary suffix + sec. suffix.
- ♦ IUPAC system of nomenclature is valid for various types of organic compounds such as : Complex branched chain, cyclic compound, polyfunctional groups compounds, bicyclo and spiro compounds.
- ♦ If a hydrocarbon has both double and triple bond, it is named as alkyne. While numbering of double bond is preferred over triple bond.
- ♦ If more than two carbon containing functional groups are directly attached to unbranched alkane then that carbon chain is considered as principle carbon chain and we use special 2° suffix.
- ♦ When two similar functional groups are present at the ends of chain, then carbon of both functional groups is counted in chain.
- ♦ When two different carbon containing functional groups are present at the ends of carbon chain, only one carbon atom of principal functional groups is considered in parent chain.
- ♦ If two atoms or group of atoms of same priority occupy identical positions from either end of the parent chain, the lower number must be given to atom/group which comes first in alphabetic order.
- ♦ Bicyclo compounds contain two fused or infused rings.
- ♦ Spiro compounds contain one common carbon.

Isomerism

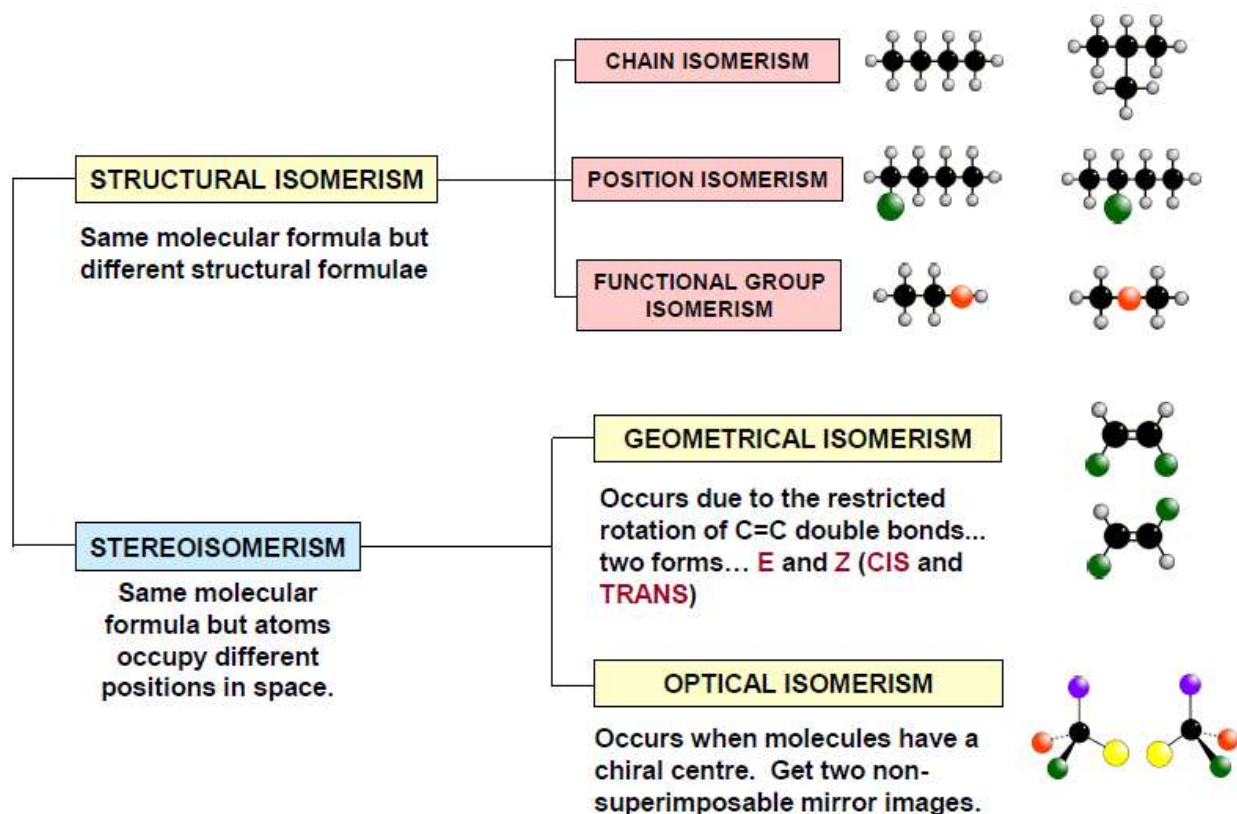
The existence of two or more compounds with the same molecular formula but different physical and chemical properties is known as **isomerism** and the molecules themselves called as isomers.

The term was given by Berzelius. The difference in properties of the two isomers is due to difference in the arrangement of atoms within their molecules.



Concept Ladder

Isomerism is resultant factor of thermodynamic system "entropy".



Isomerism is mainly classified into structural isomerism and stereoisomerism.

1. Structural isomerism

It is due to the differences in structures of the isomers. Structural isomerism is further classified into 5 types.

(i) Chain isomerism (nuclear isomerism)

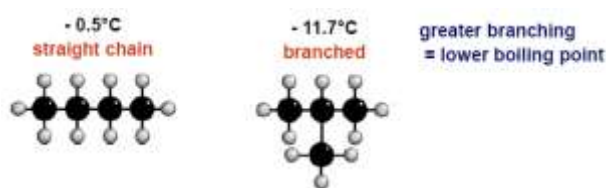
Compounds with **same molecular formula** but **differ in the arrangement and number of carbon atoms** within the molecule are called *chain isomers* and the phenomenon as chain isomerism.

DIFFERENCES BETWEEN CHAIN ISOMERS

Chemical properties- Isomers show similar chemical properties because the same functional group is present.

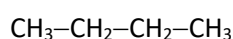
Physical Properties- such as density and boiling point show trends according to the degree of branching

Boiling Point of straight chain isomers have higher values than branched ones the greater the degree of branching the lower the boiling point branching decreases the effectiveness of intermolecular forces less energy has to be put in to separate the molecules

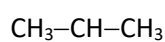


For example,

(i) Butane (C_4H_{10}) has two isomers - normal butane and isobutane. One isomer has a straight chain and the other has a branched chain.

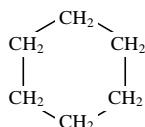


n-butane

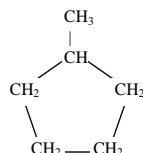


isobutane

(ii) cyclohexane and methylcyclopentane are nuclear isomers.



cyclohexane

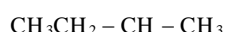


methylcyclopentane

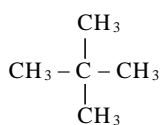
(iii) C_5H_{12} has three chain isomers.



n-pentane



Isopentane

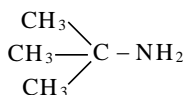


neopentane

(iv) $C_4H_9NH_2$ also shows two chain isomers.

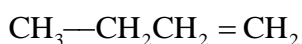


n-butylamine

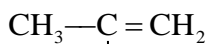


tert.butylamine

Solve 1 - How many chain isomers does butane have?

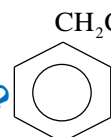


n-Butylene (1-Butene)

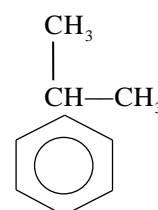


Isobutylene (2-Methylpropene)

Solve 2 - How many chain isomers does propyl benzene have?



n-Propylbenzene



Isopropylbenzene

S.NO.	HYDROCARBON	NO. OF CARBON ATOMS	ISOMER 1	ISOMER 2
1.	Alkane	4	$\boxed{\text{C}-\text{C}-\text{C}-\text{C}}$	$\begin{array}{c} \boxed{\text{C}-\text{C}-\text{C}} \\ \\ \text{C} \end{array}$
2.	Alkene	4	$\boxed{\text{C}-\text{C}-\text{C}=\text{C}}$	$\begin{array}{c} \boxed{\text{C}-\text{C}=\text{C}} \\ \\ \text{C} \end{array}$
3.	Alkyne	5	$\boxed{\text{C}-\text{C}-\text{C}-\text{C}\equiv\text{C}}$	$\begin{array}{c} \boxed{\text{C}-\text{C}-\text{C}\equiv\text{C}} \\ \\ \text{C} \end{array}$
4.	Alkadiene	5	$\boxed{\text{C}-\text{C}=\text{C}-\text{C}=\text{C}}$	$\begin{array}{c} \boxed{\text{C}=\text{C}-\text{C}=\text{C}} \\ \\ \text{C} \end{array}$
5.	Alkenyne	5	$\boxed{\text{C}-\text{C}=\text{C}-\text{C}\equiv\text{C}}$	$\begin{array}{c} \boxed{\text{C}=\text{C}-\text{C}\equiv\text{C}} \\ \\ \text{C} \end{array}$
6.	Alcohol	4	$\begin{array}{c} \boxed{\text{C}-\text{C}-\text{C}-\text{C}} \\ \\ \text{OH} \end{array}$	$\begin{array}{c} \boxed{\text{C}-\text{C}-\text{C}-\text{OH}} \\ \\ \text{C} \end{array}$

(ii) Functional isomerism

Compounds with same molecular formula but differ in functional groups are called functional isomers and the phenomenon is known as functional isomerism.

For example

ALCOHOLS and ETHERS



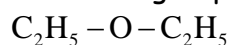
ALDEHYDES and KETONES



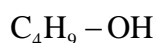
ACIDS and ESTERS



- Diethyl ether butyl alcohol both has the molecular formation $\text{C}_4\text{H}_{10}\text{O}$, but contains different functional groups.



diethyl ether



butyl alcohol

Thus, functional group in diethyl ether is $(-\text{O}-)$, while is butyl alcohol it is $(-\text{OH})$.

- Acetone and propionaldehyde both with the molecular formula $\text{C}_3\text{H}_6\text{O}$ are functional isomers.



acetone



acetaldehyde

In acetone the functional group is $(-\text{CO}-)$, while in acetaldehyde it is $(-\text{CHO})$

- Cyanides are isomeric with isocyanides;

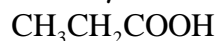


Alkyl cyanide



Alkyl isocyanide

- Carboxylic acids are isomeric with esters.

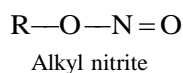
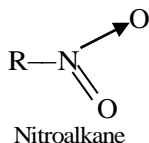


Propanoic acid



Methyl ethanoate

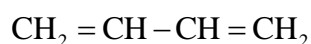
- Nitroalkanes are isomeric with alkyl nitrites:



- Sometimes a double bond containing compound may be isomeric with a triple bond containing compound. This also is called as functional isomerism. Thus, butyne is isomeric with butadiene (molecular formula C_4H_6).

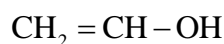


1 - Butyne



1, 3 - Butadiene

- Unsaturated alcohols are isomeric with aldehydes. Thus,

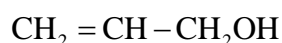


Vinyl alcohol



Acetaldehyde

- Unsaturated alcohols containing three or more carbon atoms are isomeric to aldehydes as well as ketones:



Allyl alcohol

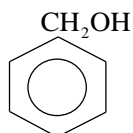


Propionaldehyde

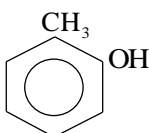


Acetone

- Aromatic alcohols may be isomeric with phenols

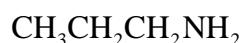


Benzyl alcohol



o-Cresol

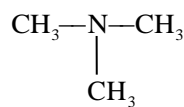
- Primary, secondary and tertiary amines of same molecular formula are also the functional isomers.



n-propylamine (1°)

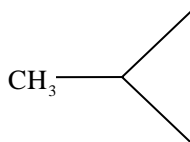
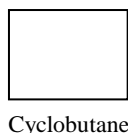


Ethylmethyle amine (2°)



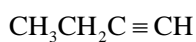
Trimethylamine (3°)

- Alkenes are isomeric with cycloalkanes:

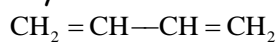


Methylcyclopropane

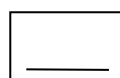
- Such isomers in which one is cyclic and other is open chain are called ring-chain isomers. Alkynes and alkenes are isomeric with cycloalkanes.



1 - Butyne



1,3 - Butadiene



Cyclobutene

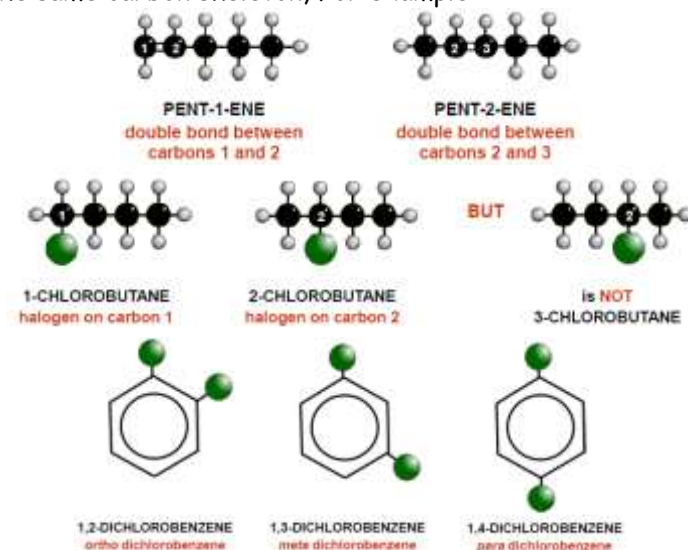
(iii) Position isomerism

Compounds which have the same structure (arrangement) of carbon chain (carbon skeleton) but differ in the position of the multiple bond or the functional group are called position isomers and the phenomenon is known as position isomerism.

Thus the following compounds can exhibit position isomerism:

- (a) Alkenes (b) Alkynes (c) Arenes d) Alkyl halides
(e) Aryl halides (f) Alcohols (g) Amines and h) Nitro compounds

a) Alkenes containing four or more carbon atoms can exhibit position isomerism due to the difference in the position of double bond on the same carbon skeleton, For example:

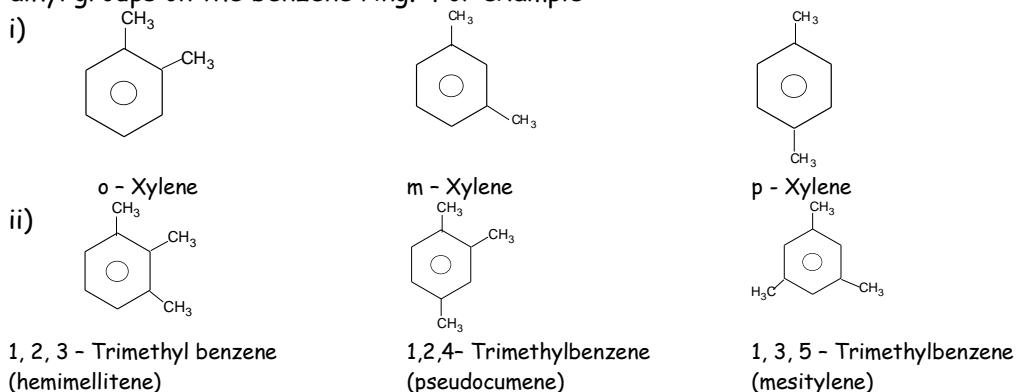


- | | |
|--|---|
| i) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$
But-1-ene | $\text{CH}_3\text{CH}=\text{CHCH}_3$
But-2-ene |
| ii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$
Pent-1-ene | $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$
Pent-2-ene |
| iii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$
Hex-1-ene | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$
Hex-2-ene |
| $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$
Hex-3-ene | |

b) Alkynes containing four or more carbon atoms can exhibit position isomerism due to the difference in the position of triple bond on the same carbon skeleton. For example:

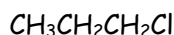
- | | |
|--|--|
| i) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$
But-1-yne | $\text{CH}_3\text{C}\equiv\text{CCH}_3$
But-2-yne |
| ii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$
Pent-1-yne | $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_3$
Pent-2-yne |

c) Arenes containing eight or more carbon atoms exhibit position isomerism due to the difference in the position of alkyl groups on the benzene ring. For example:

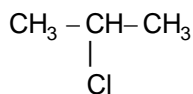


d) Alkyl halides containing three or more carbon atoms can exhibit position isomerism due to the difference in the position of halogen atom on the same carbon skeleton. For example

i) C_3H_7Cl has two position isomers:

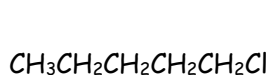


1 - Chloropropane

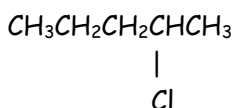


2 - Chloropropane

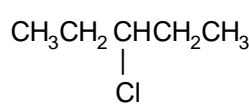
ii) n - Pentane on monochlorination gives three isomeric chloropentanes:



1 - Chloropentane

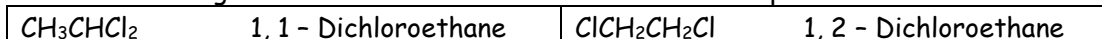


2 - Chloropentane

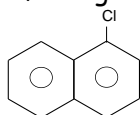


3 - Chloropentane

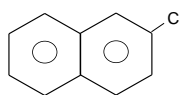
Polyhalogen derivatives containing two or more carbon atoms can also exhibit position isomerism. For example:



e) Aryl halides containing two or more benzene rings can exhibit position isomerism due to the difference in the position of halogen atom. For example:

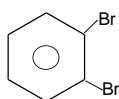


1 - Chloronaphthalene

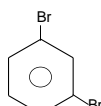


2 - Chloronaphthalene

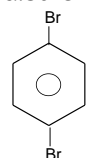
Polyhalogen compounds containing just one benzene ring can also exhibit position isomerism. For example:



1, 2 - Dibromobenzene



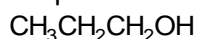
1, 3 - Dibromobenzene



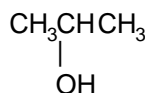
1, 4 - Dibromobenzene

f) Alcohols containing three or more carbon atoms exhibit position isomerism due to the difference in the position of functional group ($-OH$). For example :

i) The molecular formula C_3H_8O represents two isomeric alcohols:

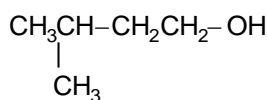


Propan-1-ol

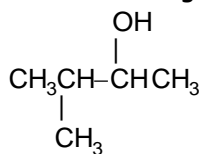


Propan-2-ol

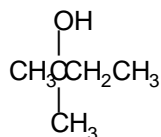
ii) Four monohydric alcohols differing in the position of $-OH$ group can be derived from isopentane:



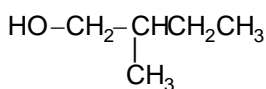
3 - Methylbutan-1-ol



3 - Methylbutan-2-ol

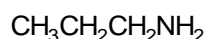


2 - Methylbutan-2-ol

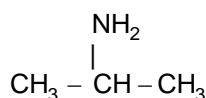


2 - Methylbutan-1-ol

g) Primary amines (RNH_2) containing three or more carbon atoms can exhibit position isomerism due to the difference in the position of amino group on the same carbon skeleton. For example:

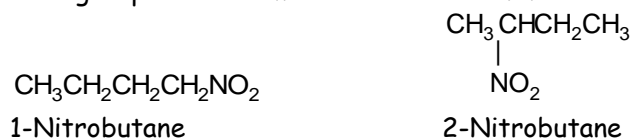


1 - Aminopropane



2 - Aminopropane

h) Nitro compounds (RNO_2) containing three or more carbon atoms can exhibit position isomerism due to the difference in the position of nitro group on the same carbon skeleton. For example:

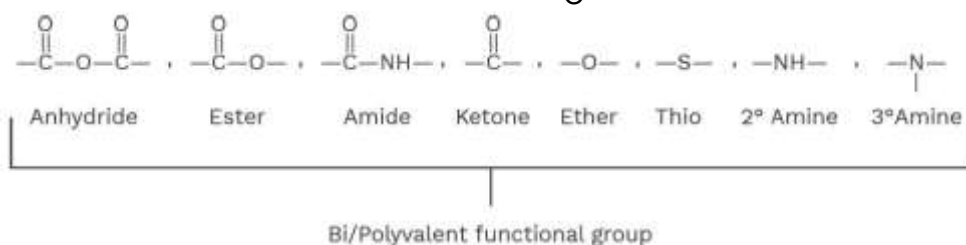


(iv) Metamerism

Here two or more different compounds having the same molecular formula but **different number and arrangement of carbon atoms on either side of the functional group** is called metamerism. Such compounds are known as metamers.

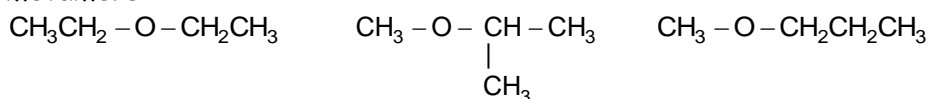
Metamerism is never possible in compounds possessing the univalent functional group.

Metamerism is due to the difference in the nature of alkyl groups attached to the same polyvalent functional group such as $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$, $-\ddot{\text{O}}-$, $-\ddot{\text{S}}-$, $-\dot{\text{N}}\text{H}-$, $-\dot{\text{N}}-$ and $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$.

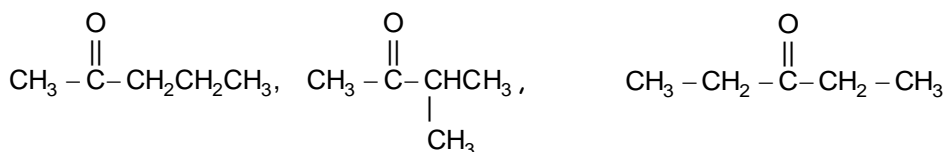


Metamerism is exhibited by compounds of the same homologous series.

a) Ethers, $R-O-R'$, exhibit metamerism due to difference in the nature of the alkyl groups attached to the oxygen atom. Thus, the molecular formula, $C_4H_{10}O$, represents the following metamers:



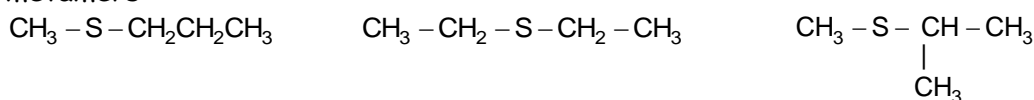
b) Ketones, $R-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-R'$, exhibit metamerism due to the difference in the nature of the alkyl groups attached to the carbonyl group. Thus, the molecular formula, $C_5H_{10}O$, represents the following metamers:



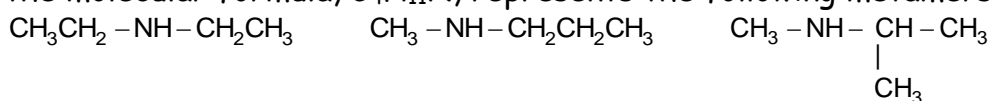
DID YOU KNOW

Ketones shows position isomerism as well as metamerism but preferentially it is considered position isomerism.

c) Thioethers, $R-S-R'$, exhibit metamerism due to the difference in the nature of the alkyl groups attached to the sulphur atom. Thus, the molecular formula, $C_4H_{10}S$, represents the following metamers:



d) Secondary and tertiary amines exhibit metamerism due to the difference in the nature of the alkyl groups attached to the -NH- group and the -N- atom respectively. Thus the molecular formula, $\text{C}_4\text{H}_{11}\text{N}$, represents the following metamers:



e) Esters, $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}'$, exhibit metamerism due to the difference in the nature of the alkyl groups attached to the $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$ group. Thus, the following esters are metamers:



Note- If same polyvalent functional group is present in two or more organic compounds, then instead of chain or position isomerism, treat the phenomenon as metamerism.

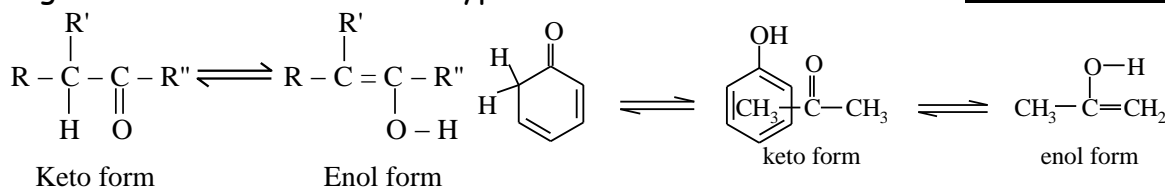
(i) Pentan - 2- one and pentan - 3- one are metamers and not position isomers. They can be included in position isomerism, if metamerism is not mentioned.

(ii) Similarly, pentan - 2- one and 3 - methylbutan-2-one are metamers and not chain isomers. Metamers may be considered as position isomers. For instance, pentan - 2- one and penta-3-one may be regarded as position isomers as well as metamers.

(v) Tautomerism

Here a single compound exists in two readily interconvertible structures that differ in position of hydrogen atom. Tautomer exhibits dynamic equilibrium with each other.

A very common form of tautomerism is that between a carbonyl compound containing an α - hydrogen and its enol form. This type of isomerism is also known as **keto-enol isomerism**.



The percentage of enol form increases in the order simple aldehydes and ketones < β -keto esters < β -diketones < β -diketones having phenyl group < phenols. This increase in the enol content is due to the fact that the enol form of the above type of compounds is increasingly stabilized by resonance and hydrogen bonding than the corresponding keto form.

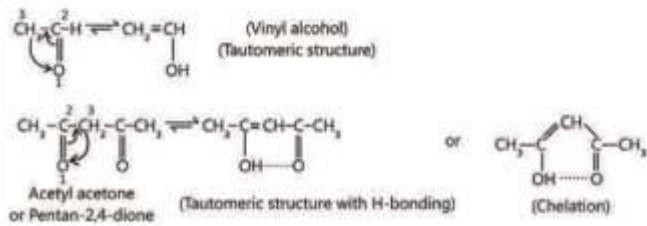
DID YOU KNOW

In general, enol forms are less stable and present in negligible amount but in ethyl acetoacetate and pentane-2,4-dione, enol form has intramolecular H bond. Thus, stability increases.

In ethyl acetoacetate, enol form is upto 7% and in pentane-2,4-dione, enol form is upto 76%.

Difference between resonance and tautomerism:

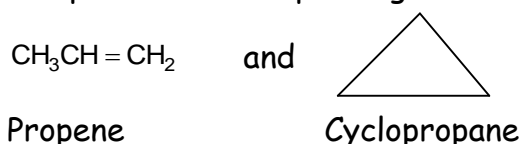
Table 14.1: Difference between Tautomerism and Resonance

Tautomerism	Resonance
1. Being a real concept, tautomers are definite compounds, which can be separated and characterized by suitable methods.	1. Being a hypothetical concept, the resonating structures are the imaginary structures of the same compound which cannot be isolated.
2. There is a simultaneous shift of an H atom and π -bond, taking place at 1, 3-positions (1, 3-shift). For example: 	2. In resonance, position of atoms or nuclei are fixed.
3. Tautomeric forms have different functional groups	3. Resonating structures have the same functional group.
4. Tautomeric forms have no effect on bond lengths.	4. Resonance affects the bond length.
5. These structures are obtained by delocalisation of σ - and π -bond.	5. These structures are obtained by the delocalisation of π or non-bonding e ^s or both,
6. Tautomers are interconvertible, indicating the dynamic nature. Thus, it is represented by \rightleftharpoons .	6. These structures are not interconvertible, i.e. not dynamic in equilibrium with each other. Thus, it is represented by \longleftrightarrow .
7. Tautomerism does not contribute for the structure stabilization.	7. Resonance causes a low energy which in turn gives stability to the molecule.

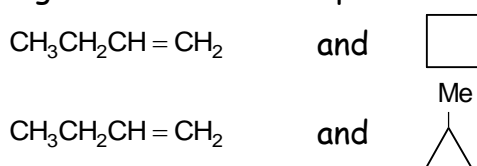
(vi) Ring - chain isomerism

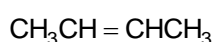
The phenomenon of existence of two or more compounds having the same molecular formula but possessing open chain and closed chain (cyclic structure) is called ring - chain isomerism. This type of isomerism arises due to different modes of linking of carbon atoms. Thus ring-chain isomers possess open chain or closed chain structures as illustrated by the following examples:

i) Two ring-chain isomers are possible corresponding to the molecular formula C_3H_6 :

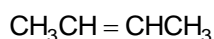


ii) Six pairs of ring-chain isomers are possible for the molecular formula C_4H_8 :

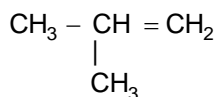
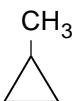




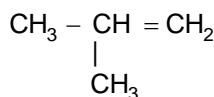
and



and



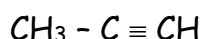
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iii) The molecular formula C_3H_4 represents the two ring-chain isomers:



and

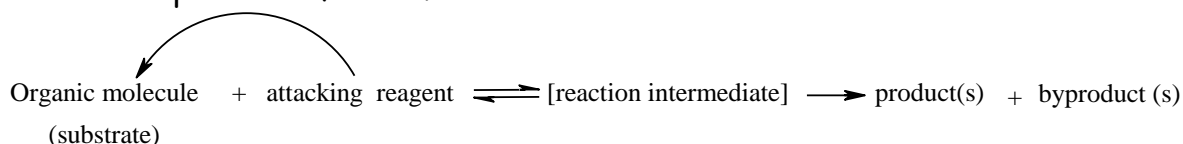


Ring chain isomerism, can be included in functional isomerism, if not considered separately.

Concepts in organic reaction mechanism

The organic reactions involve the breaking of covalent bonds in the reacting molecules and formation of new bonds to give product molecules

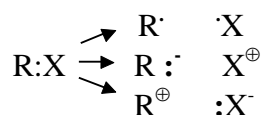
The organic molecule which reacts with attacking reagent is called **substrate**. In multistep organic reactions, substrate react with reagent and leads to the formation of one or more **reaction intermediates**. The general reaction path involving the formation of one reaction intermediate is depicted as follows.



Fission or Cleavage of covalent bond

The fission of covalent bond can take place in two ways depending on the **nature of covalent bond**, **nature of attacking reagent** and **conditions of the reaction**.

Like other chemical reactions, organic reactions are also a process of bond breaking and bond making. A covalent bond between two atoms can be broken in essentially the following ways:



1) Homolytic cleavage (Homolytic fission)

"In this type of fission bond breaks symmetrically and each fragment formed gets an odd electron from the shared bond pair electrons".

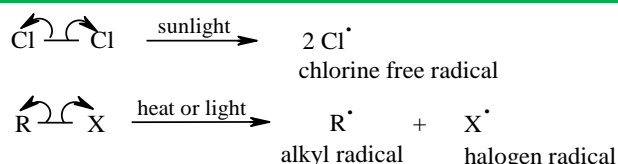
This cleavage results in the formation of specie(s) with unshared electron called **free radicals**. It is also known as **free radical cleavage** or **non-polar bond fission**. The homolytic fission of a sigma (σ) bond is shown as follows.



HOMOLYTIC
FISSION



BOTH X AND Y HAVE TAKEN AN
ELECTRON FROM THE COVALENT BOND



The free radicals contain unpaired electron (with odd number of electrons), **electrically neutral and paramagnetic**.

The conditions favorable for homolytic cleavage are

- The difference in **electro negativity between A and B is less or zero**.
- Homolysis takes place in **gaseous phase** or in the presence of **non polar solvents**(CCl_4 , CS_4), **peroxide**, **UV light**, **high temperature** ($\geq 500^\circ\text{C}$), **electricity** and free radical.

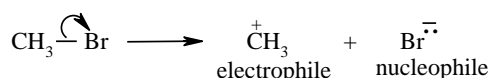
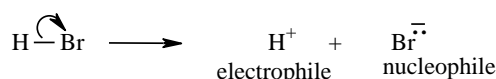
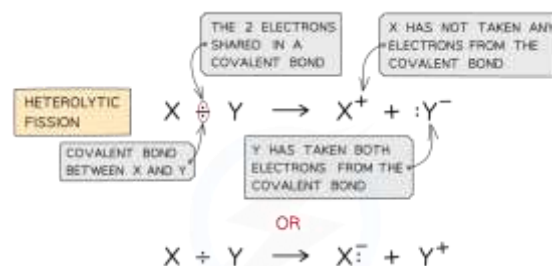
2) Heterolytic cleavage (Heterolytic fission)

In this type of cleavage, covalent bond breaks asymmetrically & one of the two species gets both the electrons and other loses resulting in the formation of ions. Heterolytic cleavage results in formation of electron deficient and electron rich fragments.

It is also known as ionic cleavage or polar bond or ionic fission.

The electron deficient fragment is called **electrophile** while electron rich fragment is known as **nucleophile**.

In case of organic compounds, if positive charge is present on the carbon then cation is termed as **carbocation**. If negative charge is present on the carbon then anion is termed as **carbanion**. The heterolytic fission is shown below



Both electrophile and nucleophile contain even number of electrons, influenced by strong electrical field as they possess positive or negative charge and they are **diamagnetic**.

- The factor which favors heterolysis is **greater difference of electro negativities** between A and B.
- The energy required for heterolysis is always greater than that for homolysis due to electrostatic forces of attraction between ions.
- Low temperature
- Polar nature of substrate and attacking reagent
- Presence of acid or base catalyst

Reaction intermediates

Highly reactive, short lived and energetic intermediate formed in multistep organic reactions by the action of reagent on substrate and readily transformed into product(s) is called reaction intermediate.

The important reaction intermediates are free radicals, carbocations, carbanions, carbenes, benzyne and nitrenes.

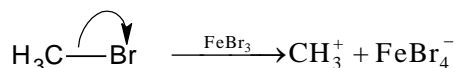
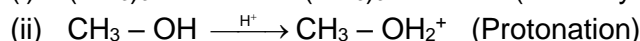
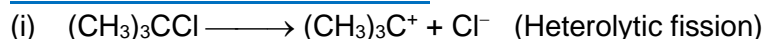
(i) Carbocations or Carbonium ions

A reaction intermediate formed by heterolytic fission of a covalent bond which contains one positively charged carbon with three bond pair electrons (sextext of electrons) is called carbocation.

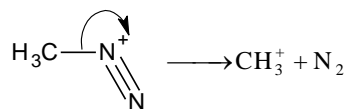
For example,



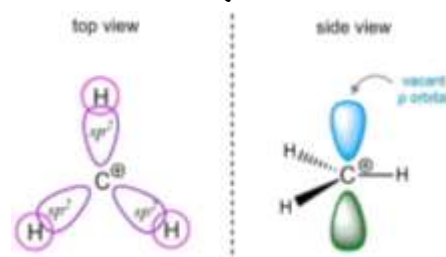
Formation of carbocations:



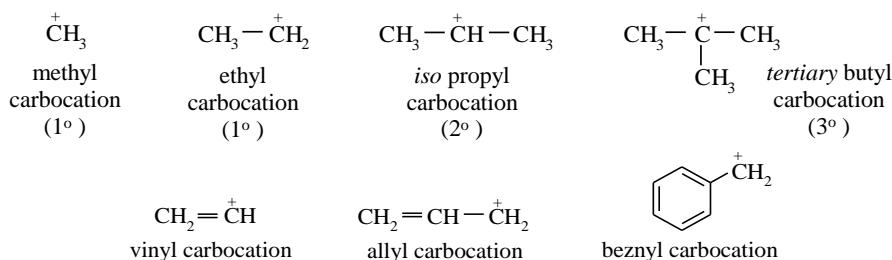
(Abstraction of halide ion by Lewis acid)



(Removal of N_2 from diazonium cation)



The carbocations are classified into different groups depending upon the nature of carbon bearing the positive charge. Alkyl carbocations may be **primary (1°)**, **secondary (2°)** or **tertiary (3°) carbocations**.

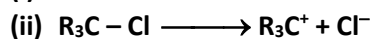
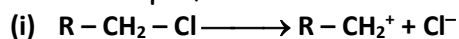


Structure of carbocation: The carbocations are electron deficient and contain six electrons (three bond pair electrons). In strong electrical field, carbocations move towards cathode. The carbocations have trigonal planar structure and the positively charged carbon in sp^2 hybridized.

Rate of formation of carbocations:

More stable carbocation forms at faster rate as compared to less stable carbocation.

For example,



A tertiary carbocation is more stable, the transition state of tertiary carbocation is lower in energy than transition state of primary carbocation. As a result, a tertiary carbocation will form more rapidly than primary carbocation.

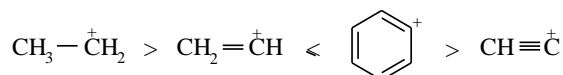
Stability of carbocations:

- Electron deficient carbocations are stabilized by **electron releasing group**. Participation of empty p-orbital in lateral overlap with completely filled orbital is the major contributing factor for stability to stability in which positive charge is delocalized. Alkyl group directly bonded to the positively charged carbon stabilize the carbocations due to inductive and hyperconjugation effects. The dispersal of the positive charge due to hyperconjugation stabilize the carbocation. The observed order of carbocation stability is

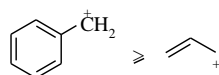
$$(C_6H_5)_3C^+ > (C_6H_5)_2CH^+ > C_6H_5CH_2^+ > CH_2=CH-CH_2^+ > 3^\circ > 2^\circ > 1^\circ > CH_3^+$$

$$CH_3-\overset{+}{C}(CH_3)_2 > CH_3-\overset{+}{CH}(CH_3) > CH_3-\overset{+}{CH}_2 > \overset{+}{CH}_3$$

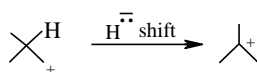
$$\text{2}^\circ \qquad \qquad \qquad \text{1}^\circ$$
- The reaction intermediates are highly reactive, usually **order of reactivity of such intermediates is reverse that of its stability**. Therefore, order of reactivity of carbocations follows the sequence: $\overset{+}{CH}_3 > 1^\circ > 2^\circ > 3^\circ$
- **Electron attractors** (–I effect) increases the positive charge on carbon atom and thus reduces the stability of carbocation, e.g. $O_2N-CH_2-CH_2^+$, $Cl-CH_2-CH_2^+$.]
- Carbocation are **sp² hybridized and have trigonal planar structure**, so the attacking species can approach both from top and bottom.
- **Hybridized state of carbon:**
 Higher the s-character, lesser the stability. The order of stability is



- **Resonance:** The greater the delocalization of positive charge of carbocations, higher is the stability. The stability of benzyl carbocation is comparable with allyl carbocation as resonance energies is nearly the same

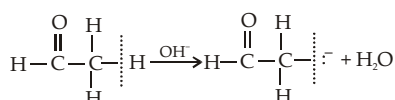
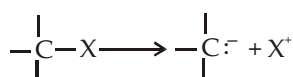


- Carbocations, undergo rearrangement forming more stable carbocations.



(ii) Carbanions

A reaction intermediate formed by heterolytic fission of a covalent bond which results negatively charged carbon with eight electrons in its valence shell is called carbanion. The heterolytic cleavage of a covalent bond as indicated in the following reactions gives carbanions.

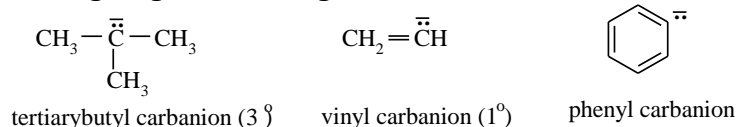


For example, CH_3^- , $CH_3CH_2^-$, $(CH_3)_2CH^-$, CH_2^-CHO etc.

Formation of carbanion:

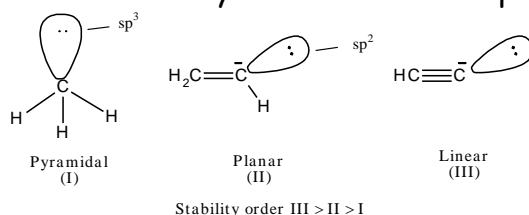
- $CH_3-CHO + OH^- \xrightarrow{\text{base}} CH_2^-CHO + H_2O$
- $C_2H_5O^- + CH_3-COOC_2H_5 \longrightarrow CH_2^-COOC_2H_5 + C_2H_5OH$

The carbanions are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the nature of carbon bearing negative charge.



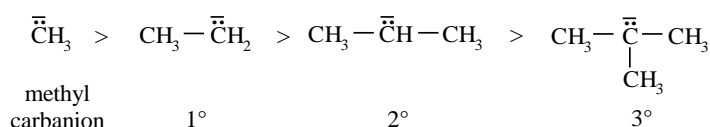
Structure of carbanion: The carbanions are electron rich with complete octate configuration. Shape of alkyl carbanion is usually **pyramidal** like ammonia when carbon atom carrying the negative charge is sp^3 hybridised.

In contrast, carbnions which are stabilised by resonance are **planar** and carbon atom carrying negative charge is **sp^2 hybridised**. The vinyl carbanion, phenyl carbanion and cyclopentadiene carbanion are sp^2 hybridised where as acetylide carbanion is sp hybridised.

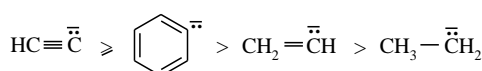


Stability of carbanions:

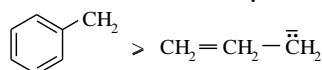
- Alkyl group bonded to negatively charged carbon increases the intensity of negative charge due to +I effect and destabilize the carbanion. The order of stability of alkyl carbanions is:



- The order of **reactivity of carbanions is reverse that of its stability**. Therefore, order of reactivity of carbanions follows the sequence: $3^\circ > 2^\circ > 1^\circ > \overset{\cdot\cdot}{\text{C}}\text{H}_3$
- **Higher the s character greater the stability** of carbanion. Order of stability is



- **Resonance:** Greater the delocalisation of negative charge by resonance, higher the stability. The stability of benzyl carbanion is comparable with allyl carbanions.

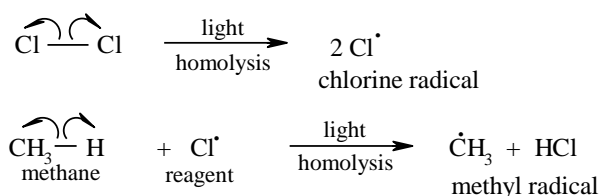


(iii) Free radicals

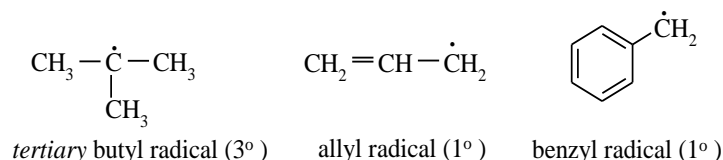
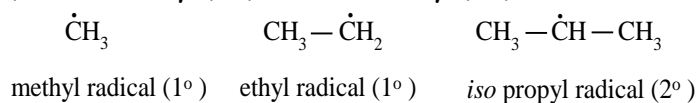
A reaction intermediate formed by the homolytic cleavage of a covalent bond which contains an unpaired electron is called free radical.

The homolytic cleavage is favored for nonpolar covalent bond. Such cleavage for bond is initiated by the action of heat, light or a reagent.

For example, $\text{CH}_3\cdot, \text{CH}_3\text{CH}_2\cdot, (\text{CH}_3)_2\text{CH}\cdot, \text{CH}_2=\text{CH}\cdot\text{CH}_2\cdot, \text{C}_6\text{H}_5\text{CH}_2\cdot$ etc.

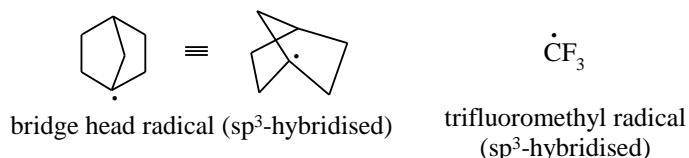


Depending upon nature of carbon atom carrying the unpaired electron, free radicals are also classified as primary (1°), secondary (2°) and tertiary (3°) free radicals.

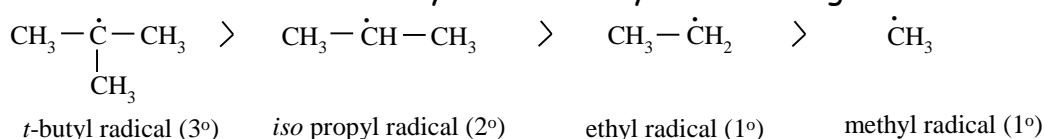


Structure of free radical: The free radicals are electron deficient since they contain seven electrons on carbon atom. They are electrically neutral and paramagnetic. The structure of alkyl radical is not known with certainty. For alkyl radicals two possible structures have been proposed. The first is a planar sp^2 hybridised radical similar to a carbocation. The second one is a pyramidal sp^3 hybridised radical similar to a carbanion.

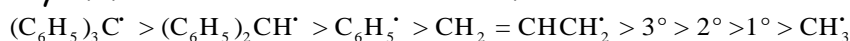
- Resonance stabilised free radicals such as allyl radicals and benzyl radicals are planar sp^2 hybridised.
- The bridge head free radicals are pyramidal (sp^3 -hybridised) because they cannot assume planar geometry due to angle strain. Further, the free radicals in which carbon is bonded to highly electronegative atoms are pyramidal.



Stability of free radicals: The relative stability of alkyl free radicals is explained on the basis of hyperconjugation and inductive effects. Greater the number of alkyl groups attached to the carbon atom carrying unpaired electron, higher the delocalisation and hence more stable is the alkyl radical. The order of stability of a few alkyl radicals is given below

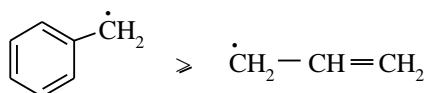


The order of stability of free radicals on the basis of resonance inductive effect is as follows:



Like carbocations and carbanions, free radicals are highly reactive and short-lived intermediates because of the strong tendency of the carbon atom carrying the unpaired electron to acquire one more electron from an atom or a group to complete its octate. The reactivity of alkyl radical is reverse the order of stability $\dot{\text{C}}\text{H}_3 > 1^\circ > 2^\circ > 3^\circ$

The allyl and benzyl radicals are stabilised by resonance. The stability of allyl and benzyl radicals is comparable.



The allyl or benzyl radicals are more stable than alkyl radicals.

The reactions involving free radicals are

- catalysed by light, heat etc.
- proceed in vapour phase or in non-polar solvents.
- autocatalytic.

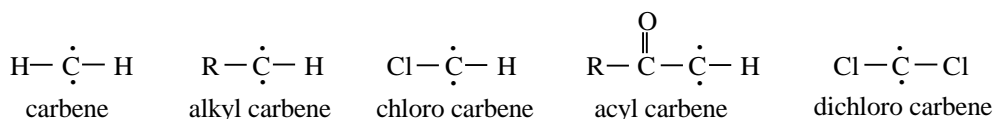
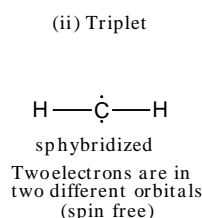
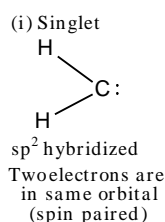
(iv) Carbenes

They are neutral and highly reactive species generally obtained by successive elimination of an electrophile and a nucleophile from the same carbon atom (α -elimination). The carbon atom of carbene has six electrons in valence shell, out of which two constitute unshared electrons and two bond pair electrons. So they are divalent carbon species containing two unshared electrons and electrically neutral.

Carbenes exist in two possible forms

(i) Singlet

(ii) Triplet



	Free Radical	Carbocation	Carbanion
(1) Lone pair	0	0	1
(2) Bond pair	3	3	3
(3) Unpaired e^-	1	\times	\times
(4) Bond Angle	120°	120°	107°
(5) Hybridisation	sp^2	sp^2	sp^3
(6) Shape	Trigonal planar	Trigonal planar	Pyramidal
(7) Magnetic property	Paramagnetic	Diamagnetic	Diamagnetic
(8) Stability order (As per inductive effect)	$3^\circ > 2^\circ > 1^\circ$	$3^\circ > 2^\circ > 1^\circ$	$1^\circ > 2^\circ > 3^\circ$
(9) e^- rich/deficient/poor	ED(Deficient)	ED	ER(Rich)
(10) Reactivity order	$1^\circ > 2^\circ > 3^\circ$	$1^\circ > 2^\circ > 3^\circ$	$3^\circ > 2^\circ > 1^\circ$
(11) +I/-I (stabilized)	+I	+I	

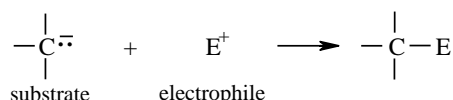
Attacking Reagents

The organic reactions proceed by the attack of highly reactive reagents on the substrate molecule. These reagents are called attacking reagents which may be electron deficient or electron rich. They are classified into two groups.

Electrophiles

The electron deficient molecules or positively charged ions which are capable of accepting an electron pair from substrate molecule are called electrophiles.

These species act as Lewis acids and attack the electron rich centre of the organic molecules.



They are of following types,

(i) **Positively charged:** The species having a positive charge, e.g.



(ii) **Neutral:** The molecules containing electron deficient atom (i.e. Lewis acids) e.g. :CH_2 , AlCl_3 , BF_3 , ZnCl_2 , FeCl_3 , SO_3 , etc.

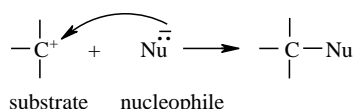
(iii) **Ambident:** Molecules with 2 electrons deficient centers, e.g. α, β -unsaturated carbonyl compounds.

It may be noted that **all the positively charged species do not act as electrophiles**. The positively charged species which can accept an electron pair can act as electrophiles. The positively charged ions such as H_3O^+ , NH_4^+ , Na^+ , Ca^{2+} , etc. do not act as electrophile as they cannot accept electron pair, since all the ions have an octet configuration.

Nucleophiles

The molecules or negatively charge ions which are capable of donating an electron pair to electron deficient centre of the substrate are called nucleophiles.

These species act as Lewis bases & attack on electron deficient centre of organic molecule.



The common examples of nucleophiles are given below:

(i) **Negatively charged:** The species having a negative charge, e.g. Cl^- , Br^- , OH^- , CN^- , NO_2^- etc.

(ii) **Neutral:** The molecules having an unshared pair of electrons (i.e. Lewis base), e.g. NH_3 , $\text{R}-\text{NH}_2$, R_2-NH , H_2O , $\text{R}-\ddot{\text{O}}-\text{H}$ etc.

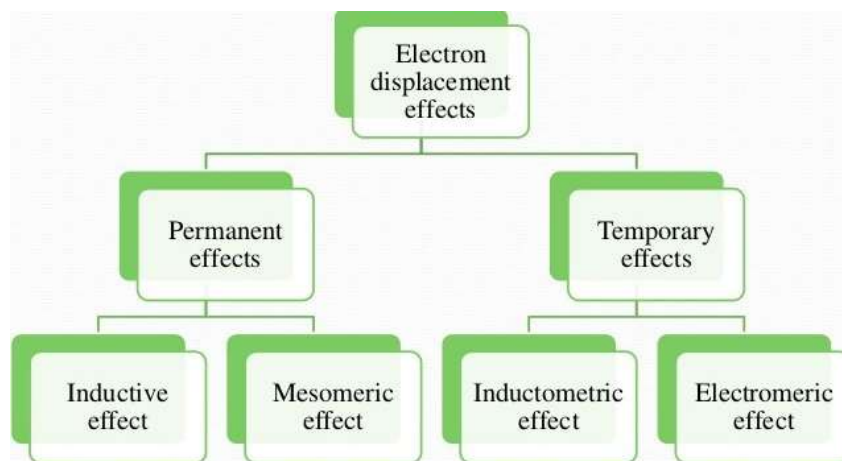
(iii) **Ambident:** The molecule with two electron rich centres, e.g. $^-\text{C} \equiv \text{N}$, $\text{N}=\ddot{\text{O}}$, $\ddot{\text{O}} \leftarrow \text{N}-\ddot{\text{O}}$ etc.

Comparison between Nucleophiles and electrophiles

Nucleophiles	Electrophiles
<ul style="list-style-type: none"> Electron rich, donate electron pair, generally anions. Act as Lewis bases Attack an region of low electron density of substrate They are represented by a general symbol (Nu^-) 	<ul style="list-style-type: none"> Electron deficient, accept electron pair, generally cations Act as Lewis acids Attack on region of high electron density of substrate They can be represented by a general symbol (E^+)

Electron Displacement Effects in Covalent Bonds

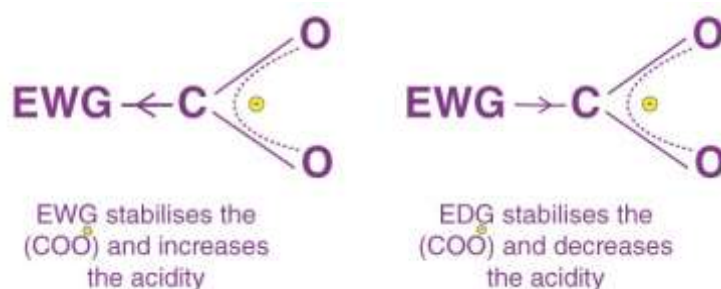
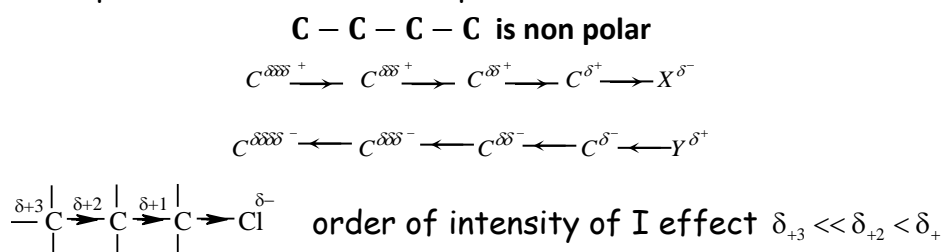
The electron pair displacement in organic molecules takes place under the influence of a hetero atom/group or by the attacking reagent. The displacement or shift of electron pair in the organic molecule under the influence of substituent makes the molecule permanently polar.



(i) Inductive effect (I effect)

The inductive effect is defined as "the permanent displacement of sigma (σ) bond pair of electrons towards more electronegative atom or group and as a result molecule becomes permanently polar".

Larger the displacement of σ bond pair electrons greater the polarity. Consider the carbon chain in which terminal carbon is bonded to a chlorine atom. Since chlorine is more electronegative bond pair of electrons are displaced towards chlorine.

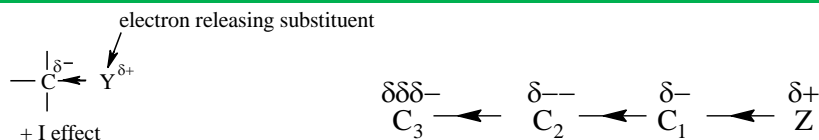


There are two types of Inductive effect,

a. Positive inductive effect (+I effect)

Here substituent (Y) releases electron pair away from itself. In other words, σ bond pair of electrons are displaced away from the substituent towards the C-chain.

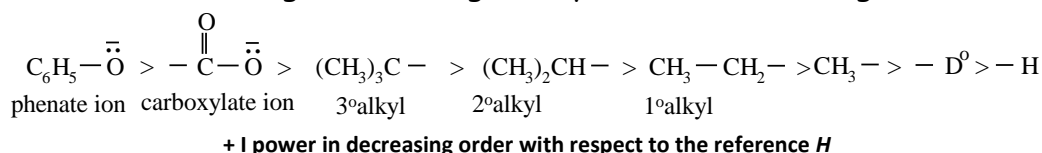
When less electronegative atom is attached to carbon atom (i.e. electron donating group), the inductive effect is called + I effect.



Electronegativity of Y or Z is less than carbon atom, so the Y or Z group releases electron and gets a partial positive charge (i.e. δ^+) and induces a partial negative charge (i.e. δ^-) on C_1 . As we move along the chain from C_1 to C_3 , the partial negative charge decreases.

The examples of electron donating group are $(\text{CH}_3)_3\text{C}$, $(\text{CH}_3)_2\text{CH}$, CH_3CH_2 , CH_3 etc.

The order of electron releasing or releasing ability of substituent is given below.

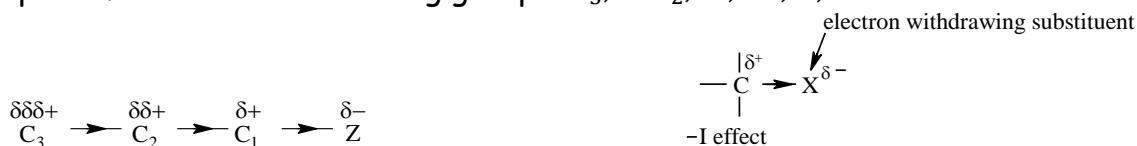


b. Negative inductive effect (-I effect)

Here, the sigma bond pair of electrons are displaced towards electron withdrawing substituent (X) or away from the carbon chain.

More electronegative atom is attached to carbon atom (i.e. electron withdrawing group), the inductive effect is called - I effect.

The examples of electron withdrawing group $^+\text{NR}_3$, NO_2 , F , Cl , I , OH etc.



Order of electron withdrawing ability (-I effect) of a few substituents is given below.

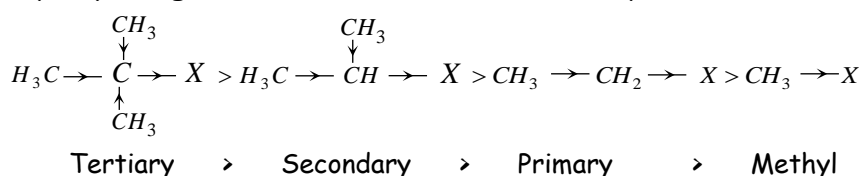


Applications of inductive effect:

(i) **Magnitude of +ve and -ve charges:** can be compared by + I or - I groups present in it.

- Magnitude of +ve charge $\propto \frac{1}{+I \text{ power of the group}} \propto -I \text{ power of the group}$.
- Magnitude of -ve charge $\propto \frac{1}{-I \text{ power of the group}} \propto +I \text{ power of the group}$.

(ii) **Reactivity of alkyl halide:** + I effect of methyl group enhances - I effect of the halogen atom by repelling the electron towards tertiary carbon atom.



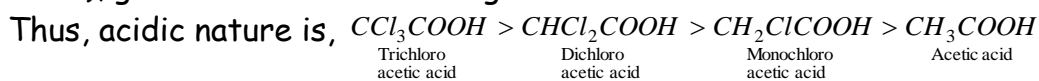
(iii) **Relative strength of the acids:**

(a) Any group or atom showing +I effect decreases the acid strength as it increases the negative charge on the carboxylate ion which holds the hydrogen firmly. Alkyl groups have + I effect. Thus, acidic nature is, $\text{HCOOH} > \text{CH}_3\text{COOH} > \text{C}_2\text{H}_5\text{COOH} > \text{C}_3\text{H}_7\text{COOH} > \text{C}_4\text{H}_9\text{COOH}$

+I effect increases, so acid strength decreases

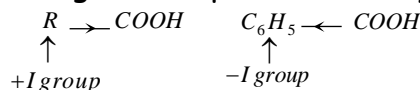
Formic acid, having no alkyl group, is the most acidic among these acids.

(b) The group or atom having - I effect increases the acid strength as it decreases the negative charge on the carboxylate ion. Greater is the number of such atoms or groups (having - I effect), greater is the acid strength.



(- Inductive effect increases, so acid strength increases)

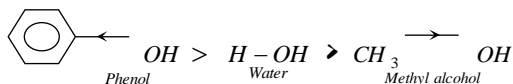
(c) Strength of aliphatic carboxylic acids and benzoic acid



Hence benzoic acid is stronger acid than aliphatic carboxylic acids but exception is formic acid. Thus, $\text{HCOOH} > \text{C}_6\text{H}_5\text{COOH} > \text{RCOOH}$

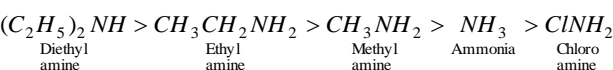
Acid strength in decreasing order

As compared to water, phenol is more acidic (-I effect) but methyl alcohol is less acidic (+I effect).



(vi) Relative strength of the bases (Basic nature of $-\text{NH}_2$)

The difference in base strength in various amines can be explained on the basis of inductive effect. The +I effect increases the electron density while -I effect decreases it. The amines are stronger bases than NH_3 as the alkyl groups increase electron density on nitrogen due to + I effect while ClNH_2 is less basic due to -I effect. "So more is the tendency to donate electron pair for coordination with proton, the more is basic nature, i.e., more is the negative charge on nitrogen atom (due to +I effect of alkyl group), the more is basic nature". Thus, the basic nature decreases in the order;



The order of basicity is as given below:

Alkyl groups (R-)	Relative base strength
CH_3	$\text{R}_2\text{NH} > \text{RNH}_2 > \text{R}_3\text{N} > \text{NH}_3$
C_2H_5	$\text{R}_2\text{NH} > \text{RNH}_2 > \text{NH}_3 > \text{R}_3\text{N}$
$(\text{CH}_3)_2\text{CH}$	$\text{RNH}_2 > \text{NH}_3 > \text{R}_2\text{NH} > \text{R}_3\text{N}$
$(\text{CH}_3)_3\text{C}$	$\text{NH}_3 > \text{RNH}_2 > \text{R}_2\text{NH} > \text{R}_3\text{N}$

(vii) **Basicity of alcohols:** The decreasing order of base strength in alcohols is due to +I effect of alkyl groups. $(\text{CH}_3)_3\text{COH} > (\text{CH}_3)_2\text{CHOH} > \text{CH}_3\text{CH}_2\text{OH} > \text{CH}_3\text{OH}$

(3°)
(2°)
(1°)

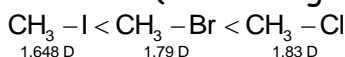
(viii) **Stability of carbonium ion:** +I effect tends to decrease the (+ve) charge and -I effect tends to increase the +ve charge on carbocation.



(ix) **Stability of carbanion:** Stability of carbanion increases with increasing - I effect.



(x). **Dipole moment:** Inductive effect produces dipole moment in a molecule. As this effect increases (electronegativity difference increases) the dipole moment also increases.



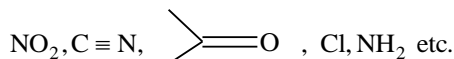
(ii) Resonance effect (R-effect) or Mesomeric effect

"The permanent polarity produced in the molecule by the shift of $\pi(\pi)$ or lone pair electrons in the conjugate system creating electron deficient and electron rich centres called resonance effect (R-effect).

The conditions required for M or R effect:

1. Molecule should be unsaturated with conjugated system (presence of alternate single and double bond or heteroatom containing one or more lone pair electrons linked to multiple bonded atom) of double bond.
1,3-butadiene, aniline, phenol, nitrobenzene, etc. In such systems, π or lone pair electrons are delocalised and the molecule develops polarity.
2. Negative charge is in conjugation with double (or multiple) bond.
3. Lone pair of electrons in conjugation with double bond.

The reactivity of compounds is affected by the presence of groups like

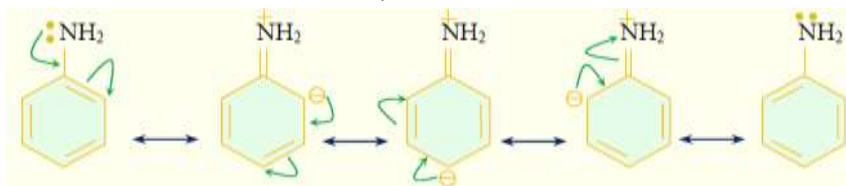


The movement of π electrons from one end to the other end of the chain through a conjugated system of double bond is observed in resonance effect. It is a permanent effect.

Depending upon the direction of shift of electron pair in conjugate system, R-effect is classified into two types.

a. Positive resonance effect (+R effect / +M effect): In this effect, of electron pair (π or lone pair) moves away from the substituent or towards the conjugate system.

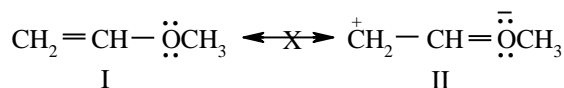
The **+R effect** in aniline as shown below.



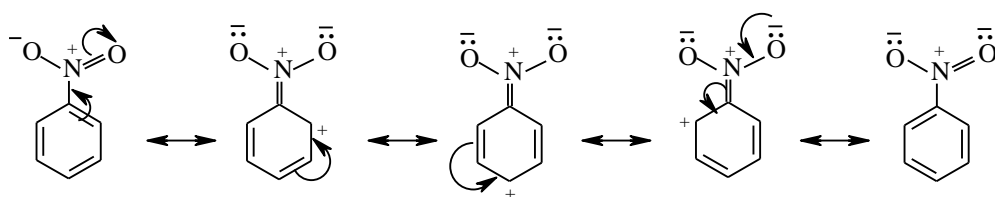
Substituents exert only +R effect as follows, $-\text{Cl}, -\text{Br}, -\text{I}, -\ddot{\text{N}}\text{H}_2, -\text{NR}_2, -\text{OH}, -\text{OR}, -\text{SH}, -\text{OCH}_3, -\ddot{\text{S}}\text{R}$

The substituent which exerts +R effect are called **electron releasing groups**.

The resonance effect in which resonance structure violates the octate rule should not be considered. For example, structure (II) cannot be considered as resonance structure since it violates the octate rule because oxygen has 10 electrons in the valence shell.



b. Negative resonance effect (-R effect / -M effect): is the shift of π or lone pair electrons is towards the substituent attached to the conjugate system. The electron displacement depicted in nitrobenzene represents -R effect.



Substituents, which exert $-R$ effect are given below. $-NO_2$, $-C \equiv N$, $-\overset{\overset{O}{||}}{C}-$, $-CHO$, $-COOH$, $-SO_3H$, $-COOR$
 The substituent which exerts $-R$ effect is called **electron withdrawn group**. Resonance effect provides explanation to least reactivity of haloalkenes and aryl halides towards nucleophilic substitution reactions, acidic nature of phenols and carboxylic acids, mechanism of electrophilic substitution reactions of benzene.

Substituents like $-\ddot{N} \equiv O$, $-\text{C}_6\text{H}_5$ (phenyl) etc. exert both $+R$ and $-R$ effects.

> Resonance

- Delocalization of p-electrons in conjugation is known as resonance.
- When one structure is not sufficient to explain each and every property (chemical & physical) then, a different structure has been drawn which is known as **Resonating Structure** (canonical structure).
- All these structures contribute to the formation of a Real structure, known as Resonating Hybrid.

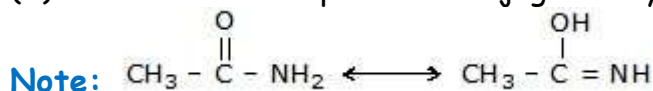


(Actual Structure)

(resonating structures) (Resonance hybrid)

Condition for showing resonance:

- Molecule should be planar, nearly planar or a part of it is planar
- Molecule should possess conjugated system.

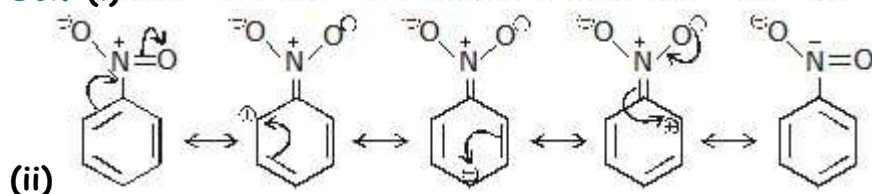
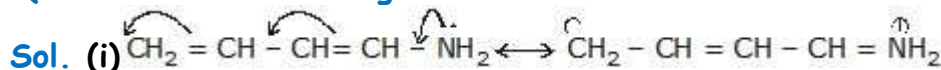


They are not resonating structures rather they are **tautomers**.

> Resonating Structure

- Hypothetical structure existing on paper.
- The energy difference b/w different resonating structure is very small.
- All R.S. contribute towards the formation of resonance hybrid (Their contribution may be different).
- A single R.S. can't explain each & every property of that particular compound.

Q. Draw the resonating structures:



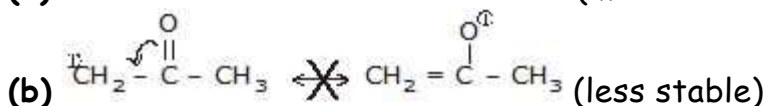
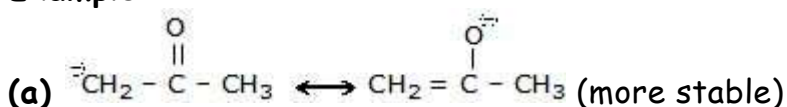
- **Resonance hybrid:** It is a real structure that explains all the properties of a compound formed by the contribution of different R.S. It has got maximum stability as compared to any R.S.
- **Resonance Energy:** It is the difference b/w theoretical value of H.O.H & experimental value. Or it can be defined as the difference b/w more stable R.S. & R. H.
The more resonance energy, the more stable will be the molecule.
Resonance energy is an absolute term.

Note: Cyclohexane is thermodynamically more stable than benzene, even though the resonance energy of benzene is more.

Contribution of different R. S. towards resonance hybrid:

- Non-polar R.S. contributes more than polar R.S.
Example: (a) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ (b) $\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2$ (c) $\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2$
Order of stability of given R.S. $\Rightarrow a > b = c$
- Polar R. S. with complete octet will contribute more as compared with the one with an incomplete octet
 $\text{CH}_3 - \text{CH} - \text{OCH}_3$ (Incomplete octet) \longleftrightarrow $\text{CH}_3 - \text{CH} = \text{:O} - \text{CH}_3$ (Complete octet)
- In polar R. S. the -ve charge should be on more electro - ve atom & +ve charge should be on more electro +ve atom.

Example:

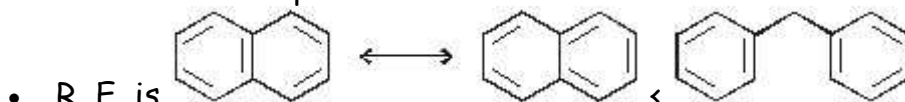


- Compound with more covalent bonds will contribute more.
- Unlike charges should be closer to each other whereas like charges should be isolated.
- Extended conjugation contributes more than cross conjugation.



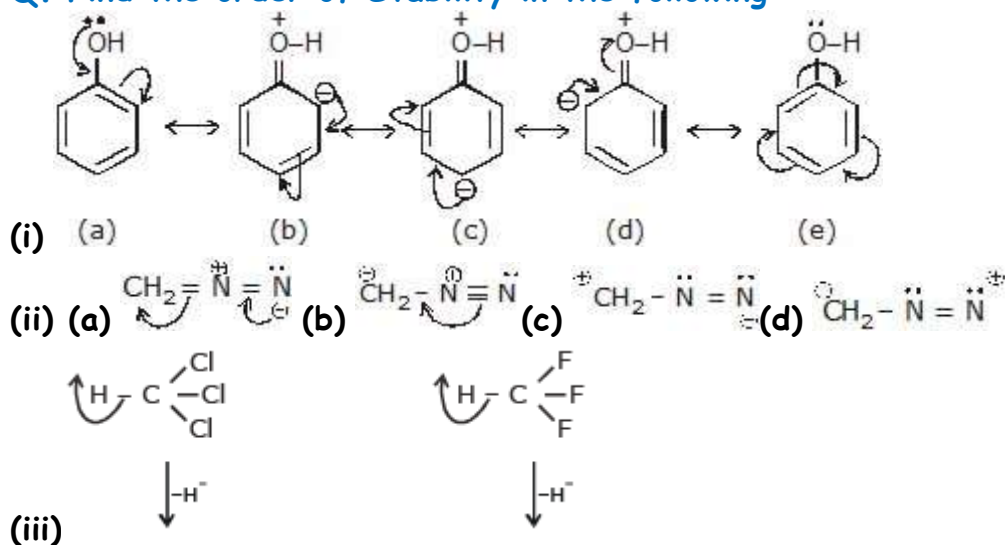
➤ **Fries Rule:**

- Compounds with **more benzenoid structures are more stable.**
- As the Resonance energy is greater than those in which lesser no. of benzenoid structures are present.



- If a double bond is participating in resonance then it will acquire a partial single bond character as a result of which bond length increases & bond strength decreases.
- If a single bond is involved in resonance then it will acquire partial double bond character. As a result of which bond length decreases & bond strength increase.

Q. Find the order of Stability in the following:

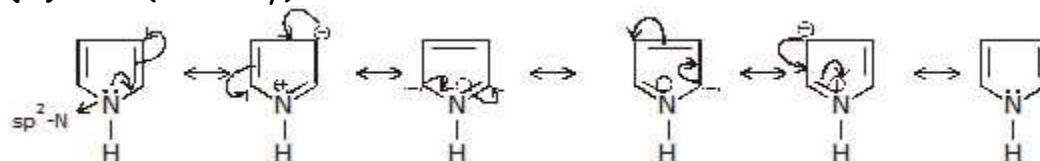


Sol. (i) $a = e > b = d > c$

(ii) $a > b > c > d$, c and d are in complete

(iii) $+CCl_3 < +CF_3$, due to back bonding in $+CF_3$

(iv) $a > b$ (stability)



Note:

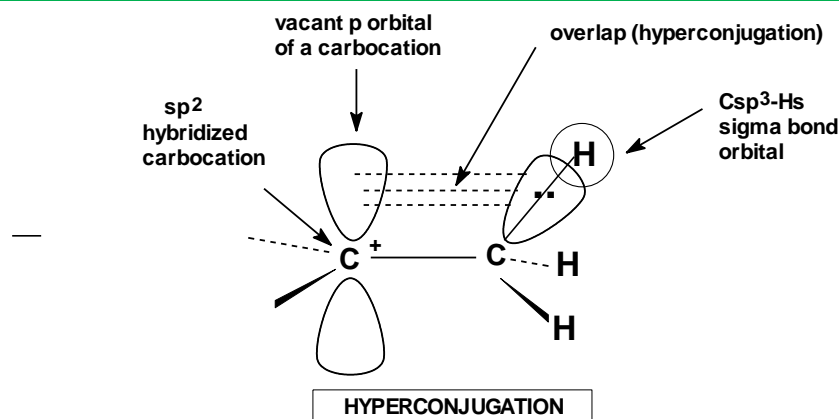
When lone pair, as well as a double bond, is present in some atom then only p bond will be participating in resonance. Whereas lone pair remains sp^2 hybridized orbital. When an atom has two or more than two lone pairs then only one lone pair will participate in resonance and the other one remains in sp^2 hybridized orbital.

(iii) Hyperconjugation (No bond resonance)

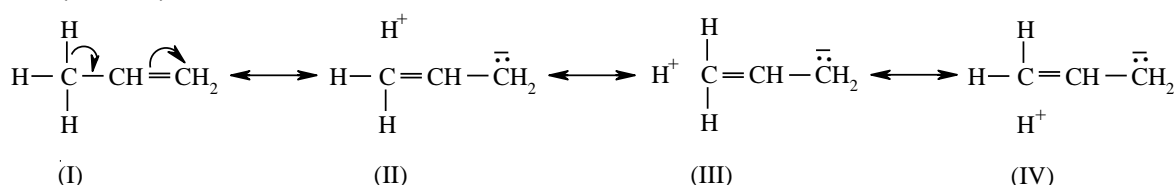
The phenomenon of hyperconjugation is also known as **Baker-Nathan effect** as it was proposed by Baker and Nathan. The hyperconjugation effect is much **weaker compared to resonance effect**, yet it is quite useful in explaining **relative stability, physical and chemical properties** of organic molecules.

This effect is extension of resonance in which C-H sigma (σ) bond pair electrons are involved in delocalization. It is a **permanent effect** in which **electron releasing alkyl group bonded to unsaturated system** in which delocalization of electrons takes place through overlap between C-H sigma (σ) orbital and $Pi(\pi)$ bond orbital or vacant p-orbital is known as hyperconjugation.

The hyperconjugation is a stabilizing interaction. The delocalization of electrons by hyperconjugation in propene molecule is depicted as in figure

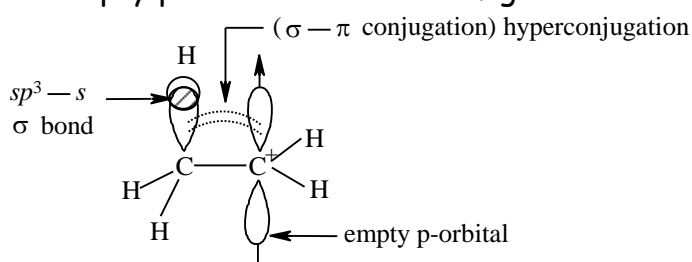


Propene molecule may be regarded as the resonance hybrid of the following hyperconjugative structures (I - IV).



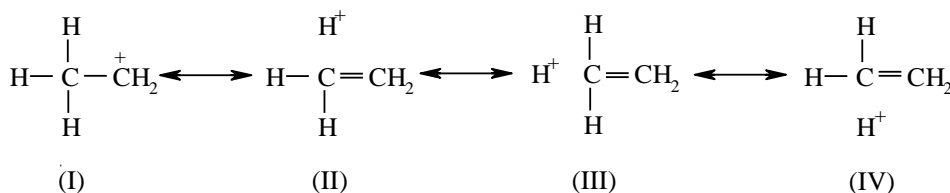
Since there is no bond between carbon and hydrogen atoms in these structures (II -IV), hyperconjugation is also called **no bond resonance**. It may be noted that although a free proton (H⁺) has been shown in the above structures, it is still bound firmly to the π- cloud and hence is not free to move.

Hyperconjugation effect in carbocations, let us take an example of ethyl carbocation (CH₃-CH₂⁺), in which the positively charged carbon atom has an empty p orbital. One of the C-H_α σ bond orbital of methyl group align in the plane of empty p orbital and this bond pair electrons delocalise into the empty p-orbital as shown in figure.



Orbital diagram showing hyperconjugation in ethylcarbocation

The overlap of completely filled C-H σ bond orbital with empty p-orbital of carbocation causes dispersion of positive charge and stabilize the carbocation. The ethyl carbocation is resonance hybrid of following contributing structures.

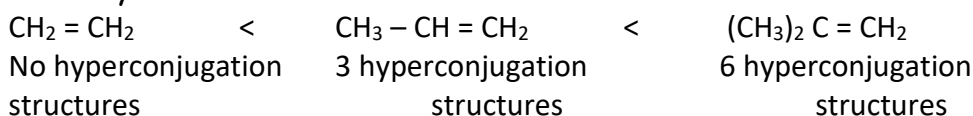


In general, larger the number of α-hydrogen atoms of alkyl groups attached to a positively charged carbon atom greater the stability of carbocations.

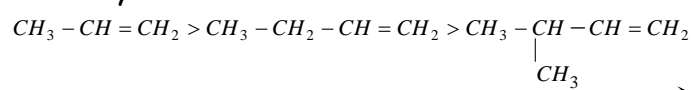
Applications of hyperconjugation effect:

1. **Stability of alkenes:** Larger the number of hyperconjugative structures higher the delocalization of electron pairs and greater the stability of alkene. Number of hyperconjugative structures is equal to number of α -hydrogen atoms plus one.

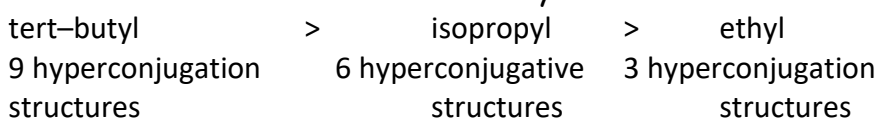
More number of methyl groups attached to double bonded carbon atom more would be the stability of alkene.



This order of stability is because of greater number of hyperconjugative contributing structures causing larger delocalisation of π -electrons solve and hence accounts for higher stability of alkene.

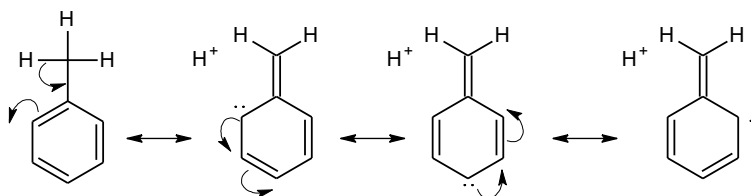


2. **Stability of carbonium ions:** More, number of hyperconjugation structures of the carbocation more will be its stability.



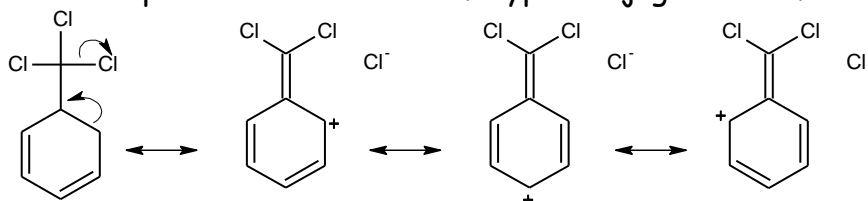
3. **Bond lengths:** The bond length in a molecule change if there is hyperconjugation. In $\text{C}^3\text{H}_3 - \text{C}^2\text{H} = \text{C}^1\text{H}_2$, the $\text{C}^1 - \text{C}^2$ bond length is found to be more than 1.34 \AA (normal $\text{C} = \text{C}$ bond length) while the $\text{C}^2 - \text{C}^3$ bond distance is less than 1.54 \AA (normal $\text{C} - \text{C}$ bond length).

4. **Directive influence of the group:** +M effect of methyl group in toluene is due to hyperconjugation.



Due to hyperconjugation, there are nine different structures having negative charge at ortho and para positions. Hence, + M effect of alkyl group attached to benzene ring follows the order: **methyl > ethyl > isopropyl > tert - butyl**.

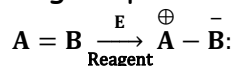
In the same way, the meta directing influence and deactivating effect of $-\text{CCl}_3$ group in benzotrichloride can be explained on the basis of hyperconjugation as follows,



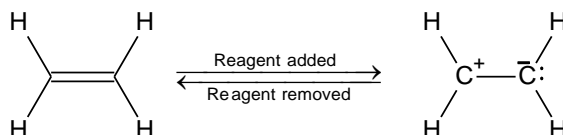
Due to low electron density at ortho and para positions, the meta position becomes point of high electron density, hence electrophilic substitution takes place in meta position.

(iv) Electromeric effect (E effect)

The complete transfer or shift of π electron pair of a multiple bond to one of the bonded atoms during the attack of positively or negatively attacking agents. As soon as the reagent is removed, the molecule reverts back to original position.

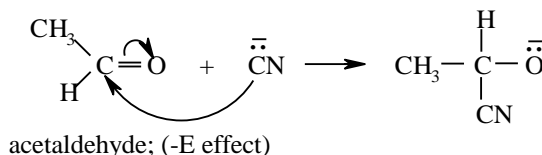


Temporary polarization of the substrate molecule at the site of multiple bonds, by complete shift of an π electron pair from one atom to the other under the influence of attacking reagents.



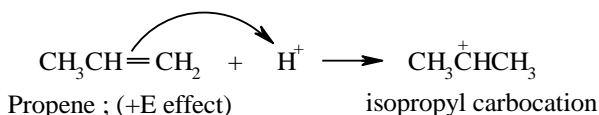
Depending upon the direction of displacement, E effect is also of two types.

- **-E effect:** An attacking reagent is said to have -E effect when the direction of π electron pair transfer of multiple bond is away from the attacking reagent.

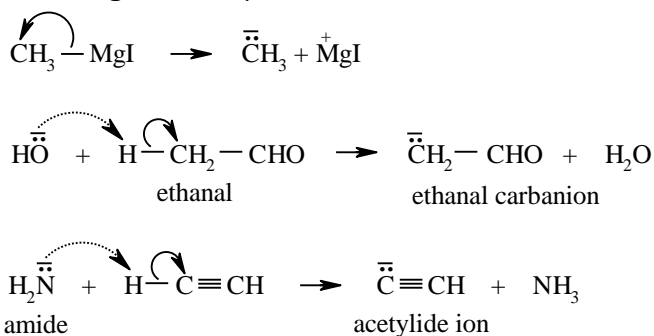


The -E effect operates during nucleophilic addition reaction of aldehydes and ketones.

- **+E effect:** An attacking reagent is said to have +E effect when the direction of π electron pair transfer of a multiple bond is towards the attacking reagent.



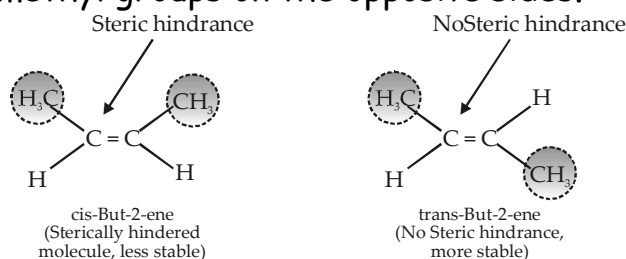
The +E effect is observed during electrophilic addition reaction of alkenes and alkynes



Steric Hindrance or Steric Strain

When two atoms are closer to each other than the sum of their van der Waal's radii they repel each other due to spatial crowding. Steric hindrance or steric strain refers to non-bonded repulsive interactions between atoms which arise when the atoms come too close due to the shape of the molecule. The repulsion arises due to nuclear-nuclear and electron-electron repulsive forces which start dominating the attractive forces. Molecules with steric strain are relatively less stable than those having no strain or less strain.

For example, in cis-but-2-ene steric hindrance is present because the two methyl groups are quite close to each other whereas in trans-but-2-ene no steric hindrance is there because the two methyl groups are on the opposite sides.



Steric factors have great influence on orientation and reactivity of organic molecules in various reactions.

Types of Organic Reactions

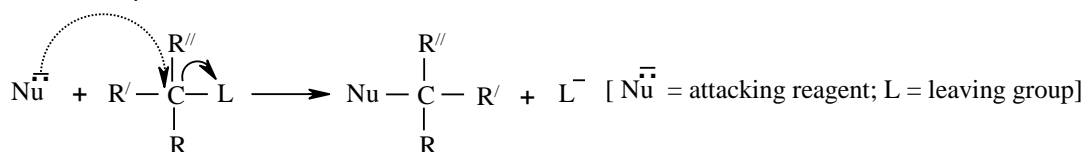
I. Substitution reaction

The reactions in which an atom or a group in a molecule is replaced by another are called substitution reactions. The incoming group gets attached to the same carbon atom to which leaving group was attached. The substituting species may be a nucleophile, an electrophile or a free radical.

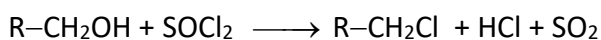
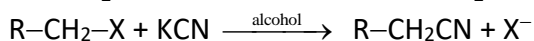
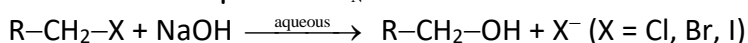


(i) Nucleophilic substitution (S_N) reactions

The substitution reactions which are brought about by the attack of nucleophile (Nu^-) are called nucleophilic substitution reactions.

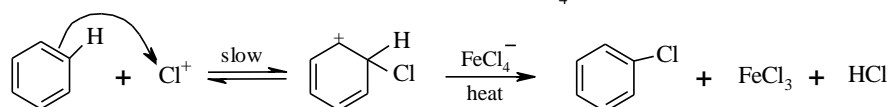
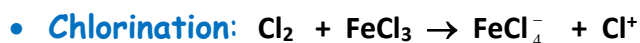


The common examples of S_N reactions are as follows.



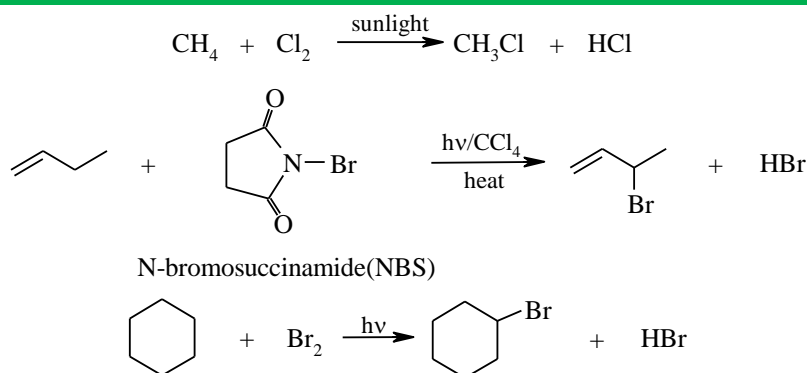
(ii) Electrophilic substitution (S_E) reactions

The substitution reactions which are brought about by the attack of an electrophile are called electrophilic substitution reactions. The substitution reactions of aromatic compound such as chlorination, nitration of benzene are representatives of S_E reactions.



(iii) Free radical substitution

The substitution reactions which are brought about by the attack of free radical are called free radical substitution reactions. The chlorination of aliphatic hydrocarbons in presence of diffused sunlight is common example of free radical substitution.



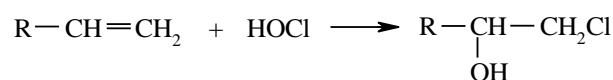
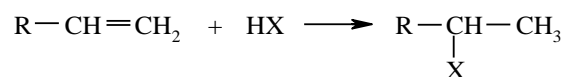
II. Addition reaction

"An addition reaction is defined as one in which an unsaturated molecule combines with reagent (addendum) to give a single saturated or nearly saturated compound". If one π bond is broken then two σ bonds are formed. A few examples for different types of addition reactions are given below



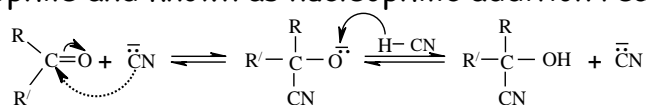
(i) Electrophilic addition reactions

The addition of common reagents like X_2 ($X = \text{Cl}, \text{Br}$ or I), HX , H_2O , HOCl , etc to alkenes and alkynes are common examples of electrophilic addition reaction. The addition of unsymmetrical molecules like HX , H_2O , HOCl , etc. to unsymmetrical alkenes or alkynes takes place according to Markownikoffs' rule.



(ii) Nucleophilic Addition Reactions

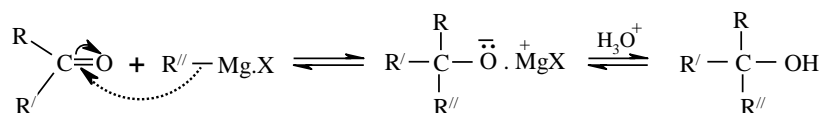
The electron deficient carbonyl group of aldehydes or ketones is easily attacked by nucleophile which can supply an electron pair. Thus the addition reactions of carbonyl compounds initiated by nucleophile and known as nucleophilic addition reactions.



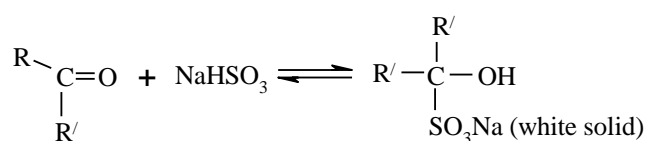
Addition of hydrogen cyanide

$\text{R}' = \text{H}$ or alkyl ($-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, etc.) or aryl (C_6H_5-) or aralkyl ($\text{C}_6\text{H}_5\text{CH}_2-$)

Addition to Grignard reagent

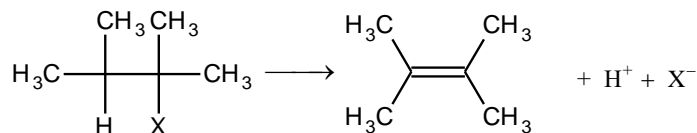


Addition of sodium bisulphite



III. Elimination reactions

The loss of atoms or group from adjacent carbon atoms (one in the form of a nucleophile and other in the form of an electrophile) resulting in the formation of an unsaturated compound is known as elimination reaction.



[Note: If these two groups or atoms are removed from adjacent carbon atoms, then it is known as β elimination reaction.]



The elimination reactions are two types, β -elimination reactions and α -elimination reactions

(i) β -elimination reactions

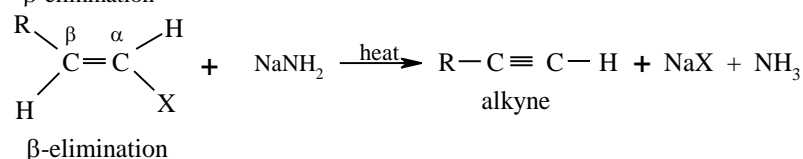
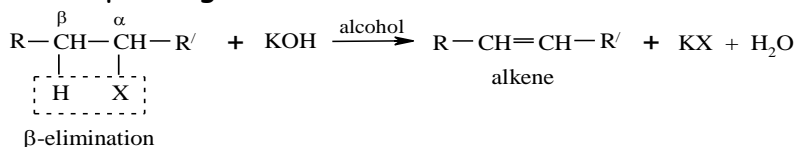
This type of reaction involves loss of two atoms or groups from vicinal (adjacent) carbon atoms resulting in the formation of a π bond. Thus, it is the reverse of addition reactions.

The most familiar example of

β -elimination reactions are dehydrohalogenation reactions of alkylhalides, dehalogenation of dihaloalkanes, dehydration of alcohols, pyrolysis of esters, Hofmann elimination of quaternary ammonium hydroxide.

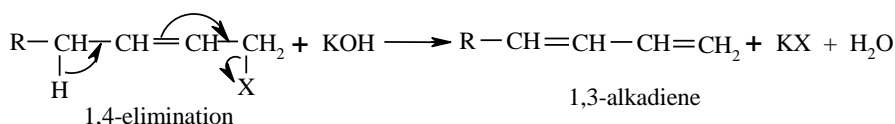
Dehydrohalogenation

When alkylhalides are treated with alcoholic potassium hydroxide solution or sodamide the corresponding alkenes are formed with the elimination of hydrogen halide.



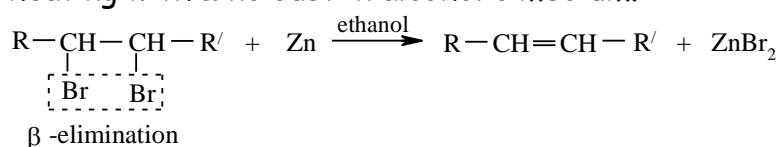
(i) Sodamide (NaNH_2) is stronger dehydrohalogenating agent.

(ii) An example of 1,4-elimination (δ -elimination) is



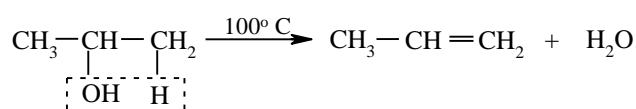
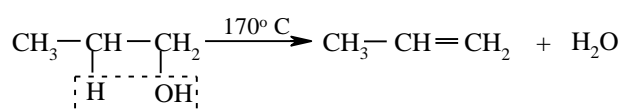
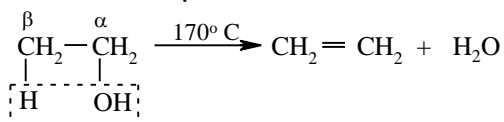
Dehalogenation

The dehalogenation involves the removal of halogen molecule (X_2) from vicinal dihalide by heating with zinc dust in alcoholic medium.

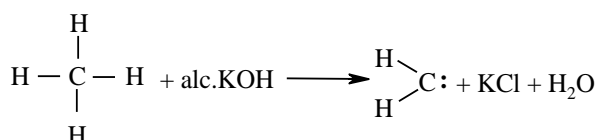


Dehydration of alcohols

When alcohols are heated with dehydrating agent like concentrated sulphuric acid, the corresponding alkenes are formed with the elimination of water (β -elimination). The reaction is called dehydration of alcohols.

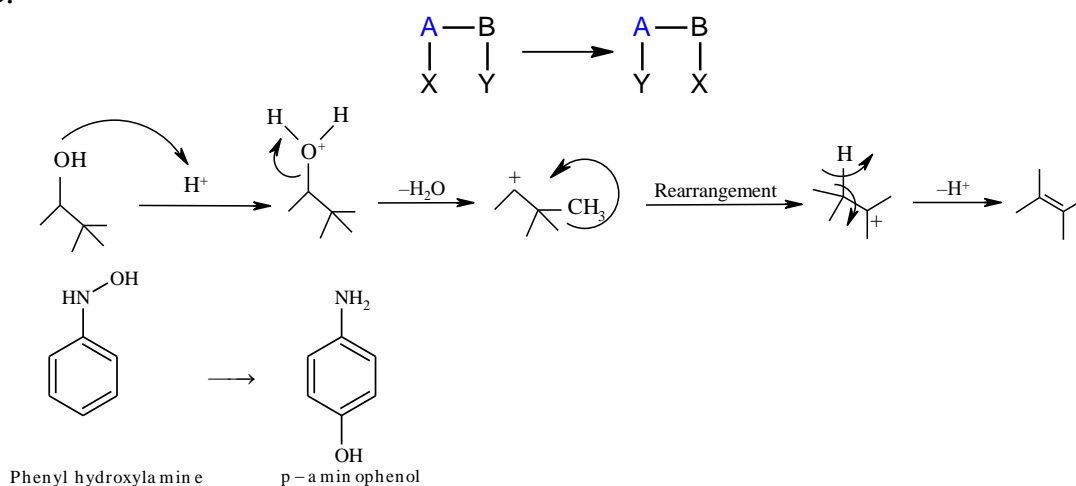


(ii) **α -elimination:** It involves loss of two atoms from same atom resulting in the formation of reaction intermediates like carbene



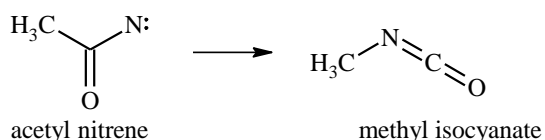
IV. Rearrangement reactions

The reactions which proceed by a rearrangement or reshuffling of atoms or groups in the molecule to produce a structural isomer of the original substance are called rearrangement reactions.

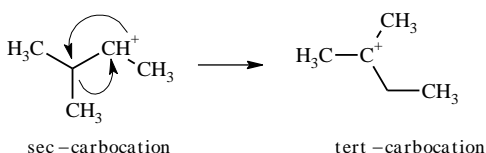


(i)

(ii)



(iii)



Purification and Characteristics of Organic Compounds

The study of organic compounds starts with the characterization of the compound and the determination of its molecular structure. The procedure generally employed for this purpose consists of the following steps:

- (1) Purification of organic compounds
- (2) Qualitative analysis of organic compounds
- (3) Quantitative analysis of organic compounds
- (4) Determination of molecular mass of organic compounds
- (5) Calculation of Empirical formula and Molecular formula of organic compounds

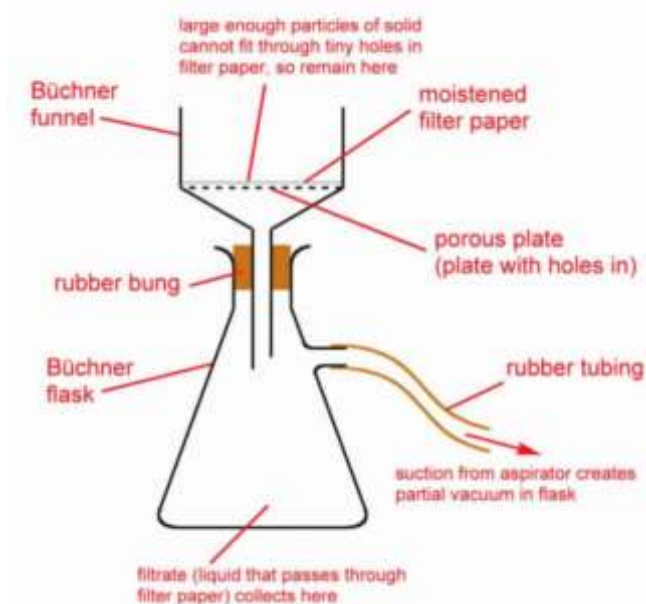
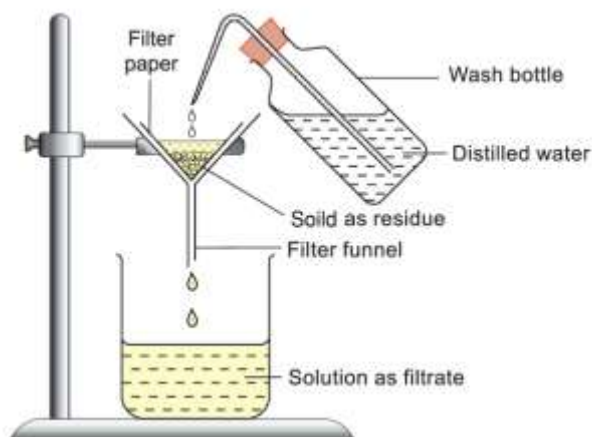
(1) Purification of organic compounds: A large number of methods are available for the purification of substances. The choice of method, however, depends upon the nature of substance (whether solid or liquid) and the type of impurities present in it. Following methods are commonly used for this purpose,

(i) Filtration

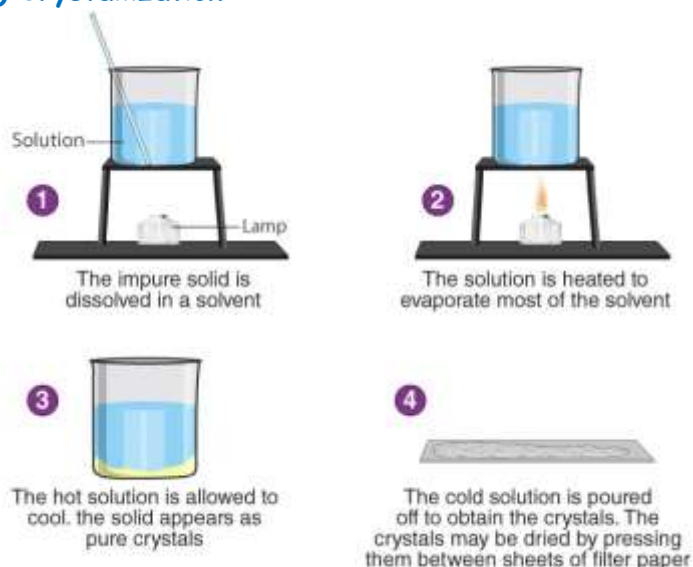
The process of filtration is used to separate insoluble solid component of a mixture from the soluble components in a given solvent.

Exp- It is used to separate a mixture of Naphthalene and Urea using a water as solvent. Urea dissolves in water while Naphthalene remains insoluble. Upon filtration, naphthalene remains on the filter paper while urea is recovered from the filtrate by evaporating water.

Filtration is very slow and takes along time. In such cases, filtration is carried out under reduced pressure using a Buchner funnel and water suction pump.



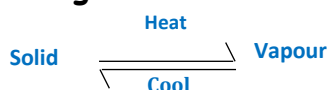
(ii) Crystallization



The method is based on the difference in the solubilities of the compound and the impurities in a suitable solvent. Pure compound crystallises out from the solution and highly soluble impurities remain in the solution. Impure organic compounds like glucose, urea, cinnamic acid, etc are purified. Fractional crystallisation is used for the separation of a mixture of two compounds which are soluble in the same solvent but to a different extent.

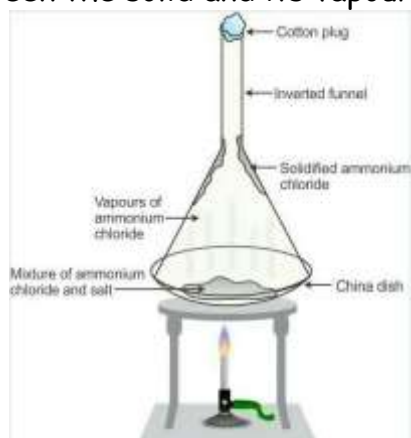
Ex: Separation of sugar and salt.

(ii) Sublimation is the process of direct conversion of a solid into the gaseous state on heating without passing through the intervening liquid state and vice versa on cooling.



Only those substances whose vapour pressure becomes equal to the atmospheric pressure much before their respective melting points are capable of undergoing sublimation.

There exists an equilibrium between the solid and its vapours.



Camphor, naphthalene, anthracene, iodine, benzoic acid, salicylic acid, NH_4Cl , HgCl_2 , etc are purified by sublimation.

(iii) Distillation– Distillation is a method used to separate constituents of a liquid mixture which differ in their boiling points.

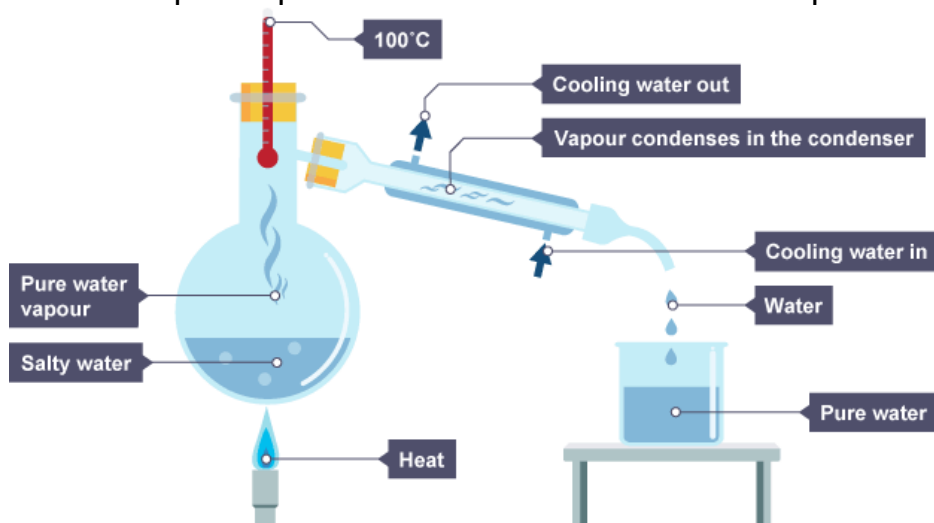
Distillation is a process which involves two steps:

Vapourisation: Liquid is converted into vapours.

Condensation: Vapours are condensed again into liquid.

Depending upon the difference in the boiling points of the constituent liquids, different types of distillation methods are employed.

- **Simple distillation:** Simple distillation is applied only for volatile liquids which boil without decomposition at atmospheric pressure and contain non-volatile impurities.

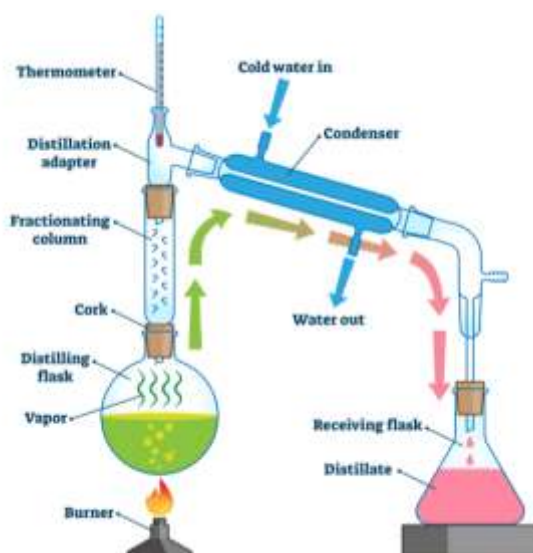


This method can also be used for separating liquids having sufficient difference in their boiling points. For example,

- benzene (boiling point 353 K) and aniline (boiling point 475 K)
- chloroform (boiling point 334 K) and aniline (boiling point 457 K)
- ether (boiling point 308 K) and toluene (boiling point 383 K)

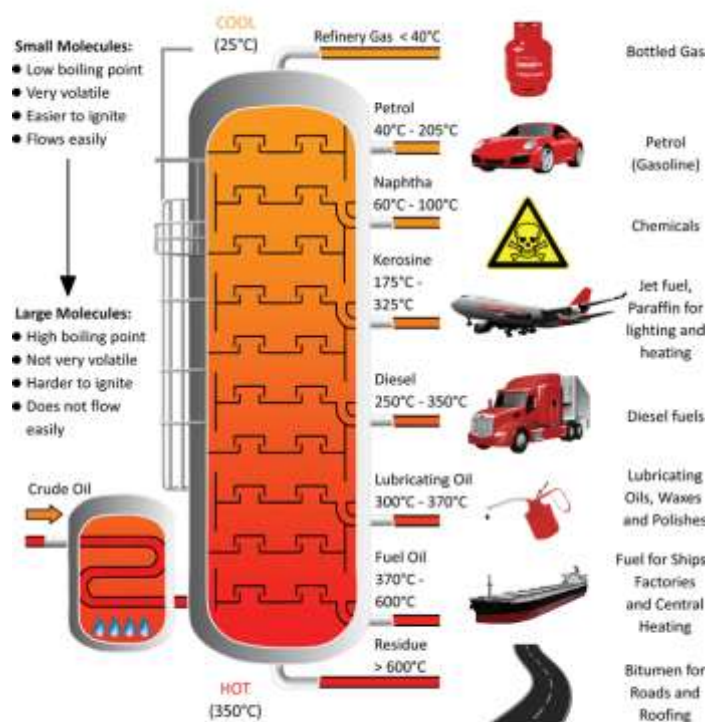
Nitrobenzene prepared in the laboratory can also be purified by distillation.

- **Fractional distillation:** This method is used for the separation of two or more volatile liquids from a liquid mixture which has boiling points close to each other. Liquids forming a constant boiling mixture (azeotropic mixture) such as rectified spirit cannot be separated by this method.



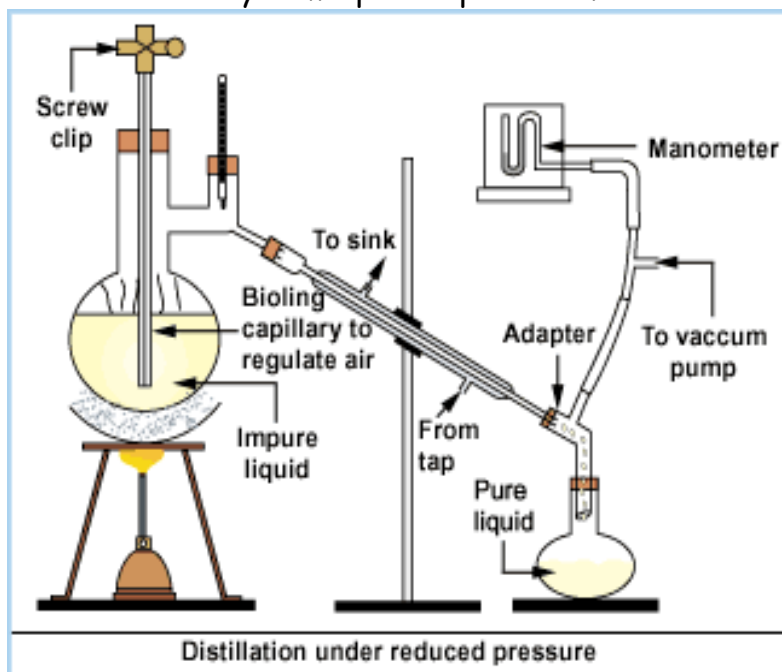
Fractional distillation is used these days in industries, especially, in the **distillation of petroleum, coal tar and crude alcohol**. A mixture of methanol (boiling point 338 K) and propanone (boiling point 330 K) or a mixture of benzene and toluene may be separated by fractional distillation.

Fractional Distillation of Crude Oil



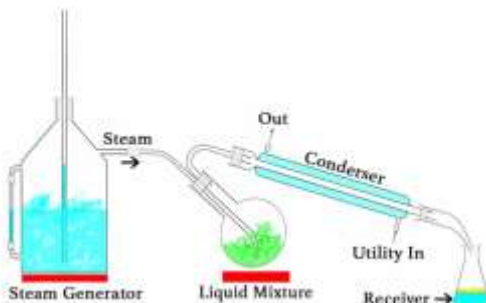
Fractionating column

- **Distillation under reduced pressure (Vacuum distillation):** The compounds, which decompose at a temperature below their normal boiling points, cannot be purified by distillation under ordinary atmospheric pressure.



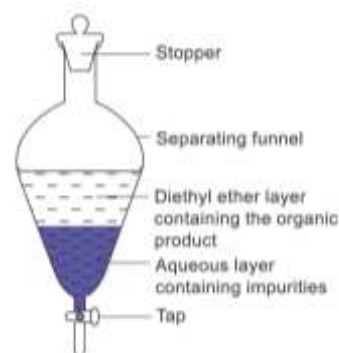
Glycerin is one such compound which decomposes at its boiling point. The pressure is reduced by suction pump and the distillation is carried out at lower temperature as glycerine can be distilled at 453 K (normal boiling point 563 K) under a pressure of 10-12 mm. Cane juice can also be concentrated by this method. This technique can be used to separate glycerol from spent lye in soap industry.

- **Steam distillation:** This method is used to purify the organic compounds which
 - ❖ Are volatile in steam but are immiscible with water.
 - ❖ Possess high vapour pressure at the boiling point of water.
 - ❖ Contain nonvolatile impurities.



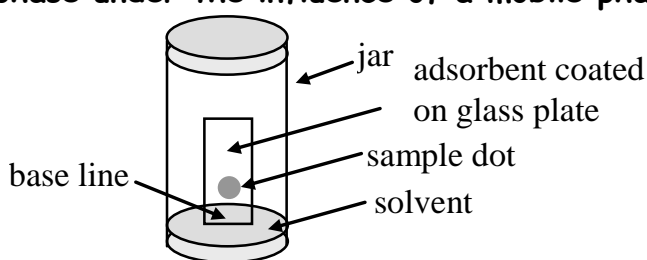
The compound to be purified is distilled with steam and impurities being nonvolatile remain in mother liquor. For example, o-nitrophenol (volatile) and p-nitrophenol (non volatile) are separated by this method.

(iv) Differential extraction (or solvent extraction): The process of separation of an organic compound (solid or liquid) from its aqueous solution by shaking with a suitable organic solvent is termed as **solvent extraction**. This method is employed for non-volatile compounds. For example, benzoic acid is extracted from its aqueous solution using benzene as solvent.

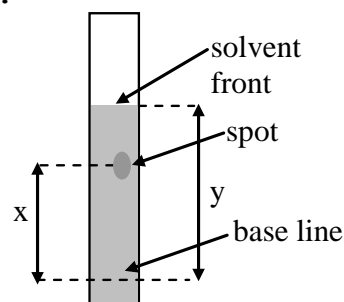


(v) Chromatography

Chromatography is the technique of separating the components of mixture in which the separation is achieved by the differential movement of individual components through a stationary phase under the influence of a mobile phase.



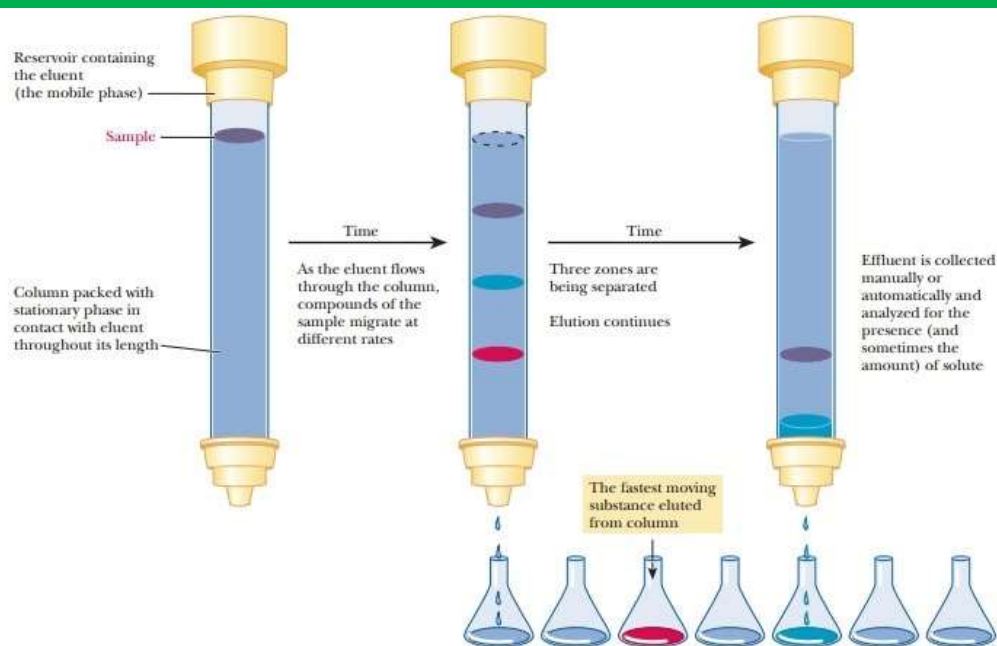
Thin layer chromatography chromatogram being developed



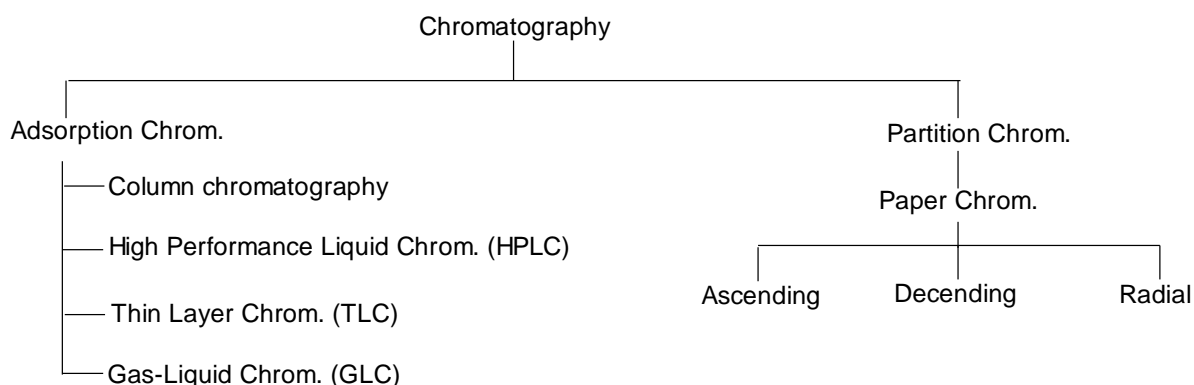
Developed chromatogram

$$R_f = \frac{\text{Distance moved by the substance from baseline (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

Depending upon the nature of the stationary phase (either a solid or a liquid tightly bound on a solid support) and the nature of the mobile phase (either a liquid or a gas), different types of chromatographic techniques are followed.



■ **FIGURE 5.2** Column chromatography. A sample containing several components is applied to the column. The various components travel at different rates and can be collected individually.



Type of chromatography	Stationary phase	Mobile phase	Application
Column/adsorption	Solid	Liquid	Large scale separation
Thin layer chromatography (TLC)	Solid	Liquid	Qualitative analysis
High performance liquid chromatography (HPLC)	Solid	Liquid	Qualitative analysis and also for separation
Gas liquid chromatography (GLC)	Liquid	Gas	Qualitative analysis and also for separation
Proper chromatography	Liquid	Liquid	Qualitative analysis and also for separation

The various components on the developed TLC plate are identified through their retardation factor, i.e., **R_f values**.

$$R_f = \frac{\text{distance moved by the substance from base line}}{\text{distance moved by the solvent from base line}}$$

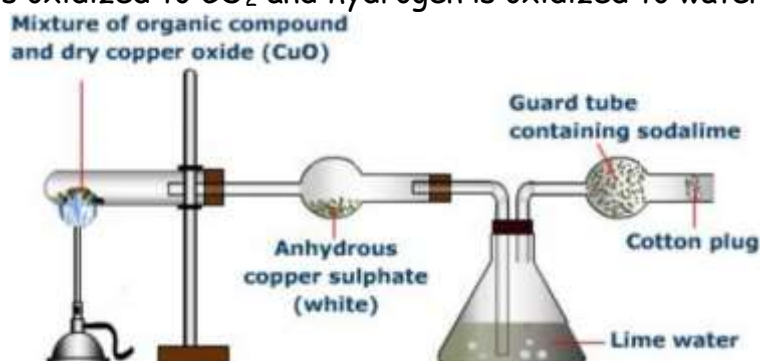
A component with highest value of R_f elute first. A component with greater tendency to adsorb on solid has lesser the R_f value.

2. Qualitative Analysis (Detection of Elements)

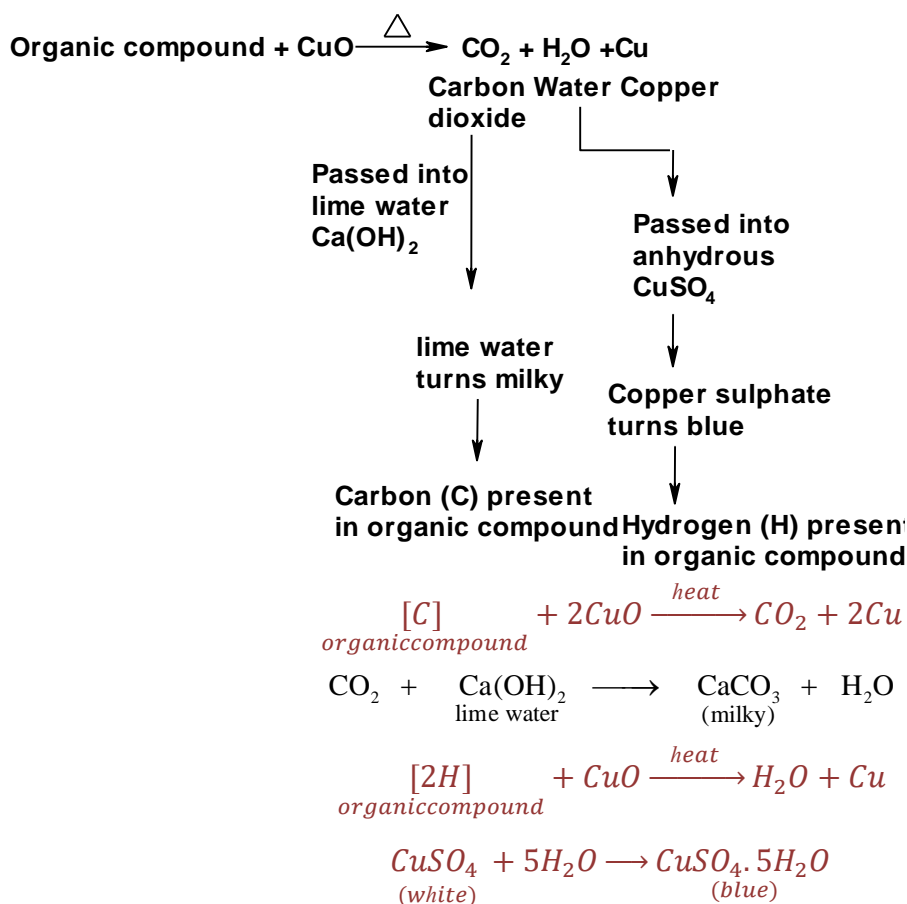
The qualitative analysis of an organic compound involves the detection of all the elements present in it. Carbon and hydrogen are generally present in all organic compounds. Other elements which may be present in organic compounds are oxygen, nitrogen, sulphur, halogens, phosphorus, etc. These elements are detected by the following tests.

Detection of Carbon and Hydrogen by Copper oxide test

Principle Organic compounds undergo oxidation in the presence of a suitable oxidizing agent. In this process, carbon is oxidized to CO_2 and hydrogen is oxidized to water.



Procedure The compound is intimately mixed with dry cupric oxide. The mixture is strongly heated in a hard glass test tube fitted with a cork and a delivery tube. The liberated gases are passed into lime water.



Detection of Nitrogen, Halogen and Sulphur by Lassaigne's test

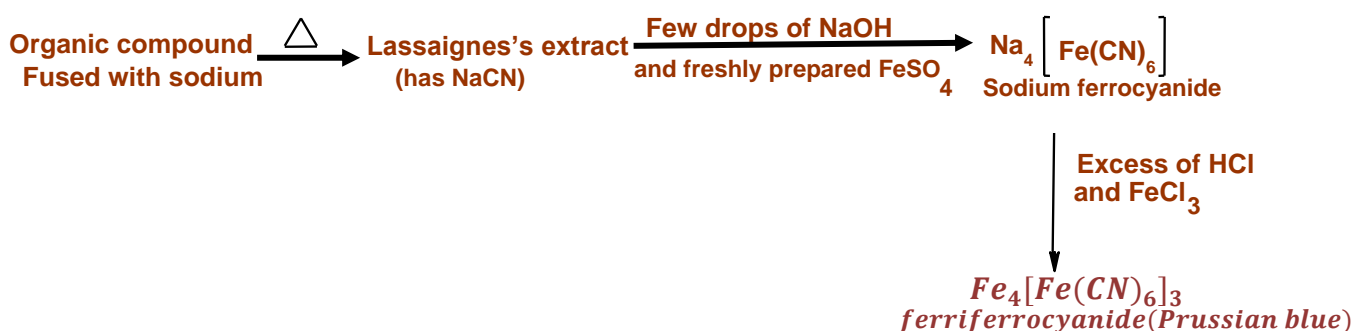
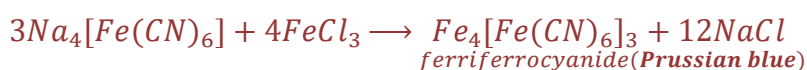
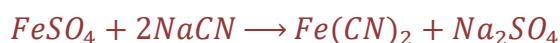
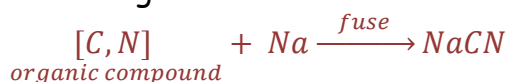
Principle This is the most reliable test for the detection of nitrogen, sulphur, halogens etc. In this method sodium fusion extract of organic compound is prepared. In this fusion process, carbon and nitrogen present in the organic compounds get converted into cyanide ion (CN^-), sulphur (S) into sulphide ion S^{2-} and halogens (X) into halide ion (X^-). By testing for radicles, presence of these elements can be find.

Preparation of Sodium fusion extract

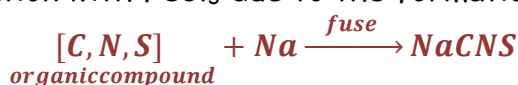
A piece of Na metal taken in a fusion tube and heated. Na melts to form shining globule. Organic compound added to it and heated to red hot. Red hot tube is now dropped into water taken in a porcelain dish. The contents are heated to concentrate the solution. Solution is then filtered. The filtrate is called sodium fusion extract.

Test for nitrogen

Ferrous sulphate are added to the sodium fusion extract. The mixture is boiled and cooled. It is acidified with hydrochloric acid and a few drops of ferric chloride solution are added. Sodium cyanide in the filtrate reacts with ferrous sulphate to give sodium ferrocyanide. It further reacts with ferric chloride to give a blue coloured solution of ferric ferrocyanide.

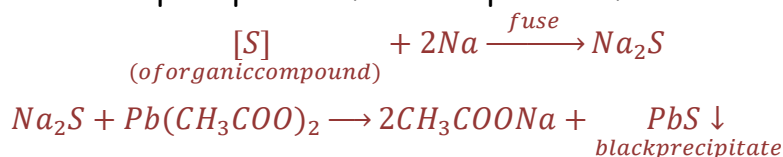


Note- If organic compound contains N and S, sodium thiocyanate is formed in sodium extract which gives blood red colouration with $FeCl_3$ due to the formation of ferric thiocyanate.

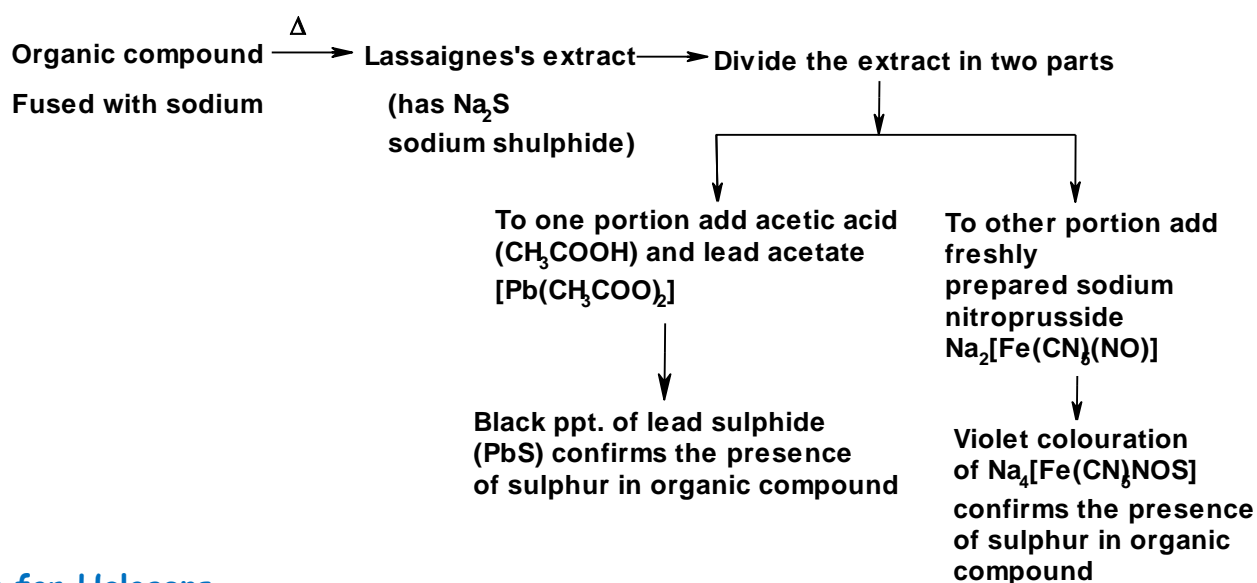
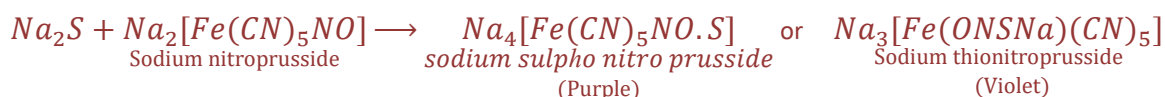


Test for Sulphur

Lead acetate test: Second part of the filtrate is treated with excess of acetic acid and lead acetate solution. A black precipitate of lead sulphide is formed.



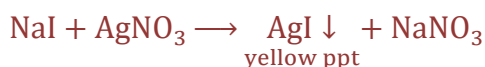
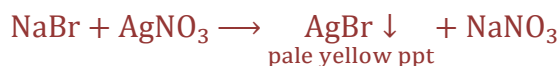
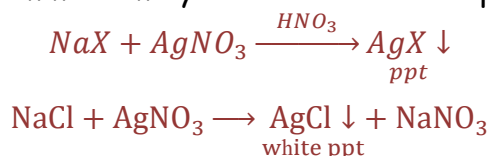
Sodium nitroprusside test: To the sodium fusion extract, a few drops of sodium nitroprusside are added. The appearance of **violet or purple colour** indicates the presence of sulphur.



Test for Halogens

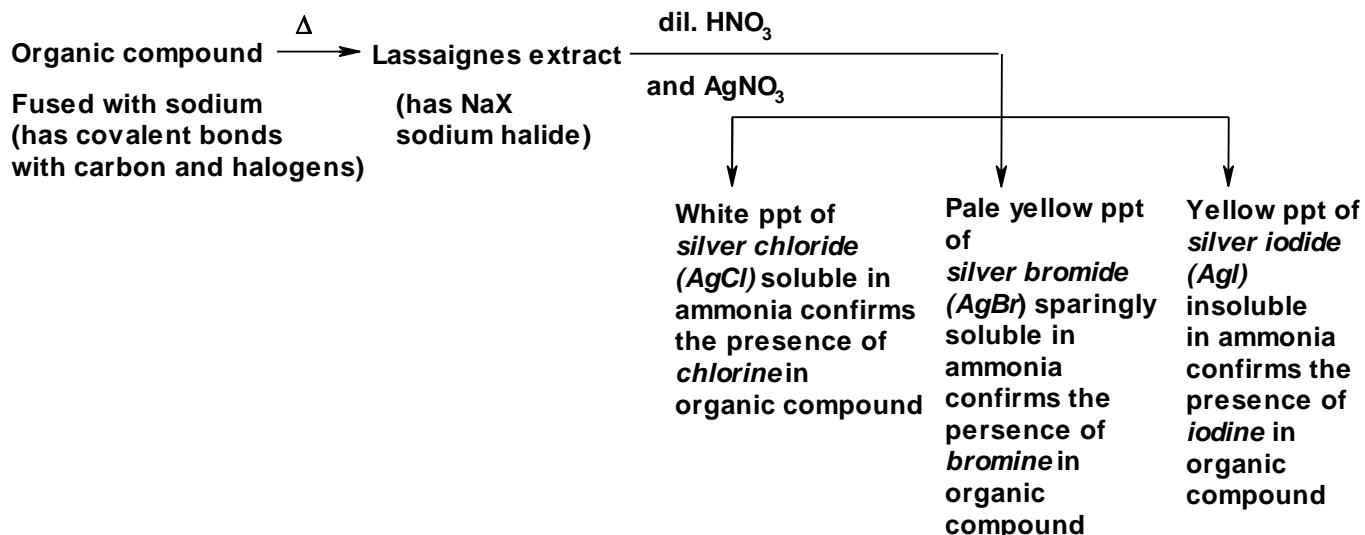
Silver nitrate test A portion of the stock solution is boiled with dil. HNO_3 , cooled and silver nitrate is added.

A white precipitate soluble in ammonium hydroxide shows the presence of *chlorine*. A pale yellow precipitate slightly soluble in ammonium hydroxide shows the presence of *bromine*. A yellow precipitate insoluble in ammonium hydroxide shows the presence of *iodine*.



Note: During the detection of halogens, the sodium fusion extract is boiled with nitric acid in order to expel the N and S as HCN and H_2S .

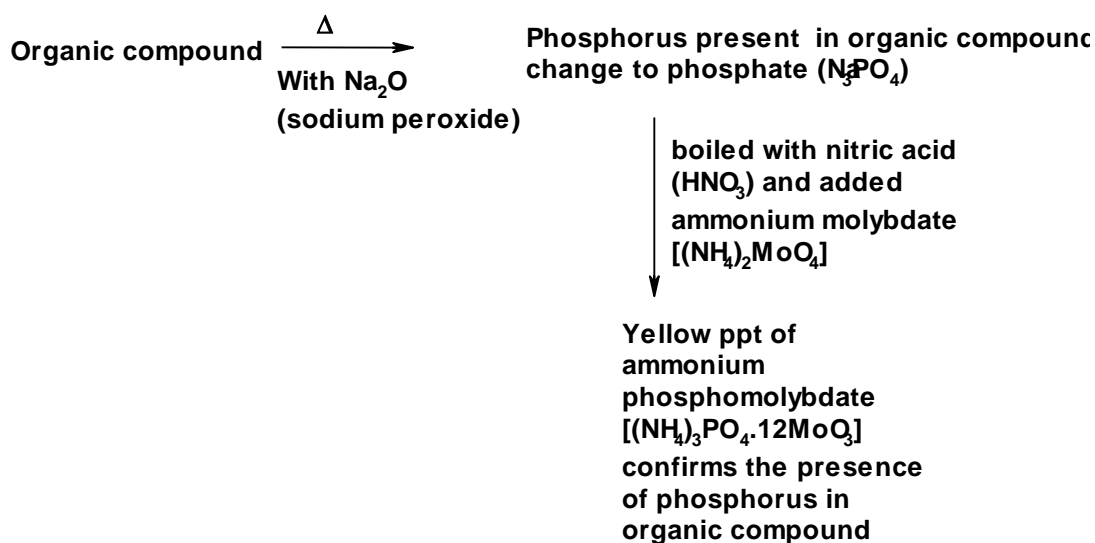
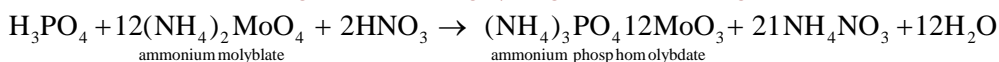
When $AgNO_3$ added cyanide gives white ppt, sulphide gives black ppt and interfere with observation.



Note: Beilstein's test: Beilstein's test is used to detect the halogen in an organic compound. A copper wire is heated in a Bunsen flame till no colour is imparted to the flame. The copper wire is dipped in the given organic compound and exposed to the non-luminous zone of the Bunsen flame. A *bluish green coloured* flame indicates the presence of halogen.

Test for Phosphorus

Organic compound containing phosphorus is fused with sodium peroxide. The phosphorus of the compound is oxidised to phosphate. The fused mass is extracted with water and filtered. The filtrate containing sodium phosphate is boiled with nitric acid and then treated with ammonium molybdate. A yellow solution or precipitate indicates the presence of phosphorus.

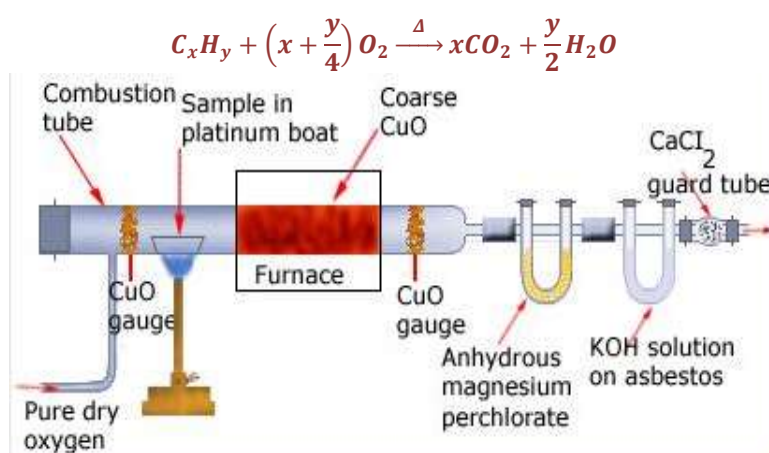


(3) Quantitative analysis The quantitative analysis deals with the determination of percentage of various elements. The following methods are employed for the determination of percentage composition of elements present in the organic compounds.

Estimation of carbon and hydrogen by Liebig's combustion method

Principle: A known mass of organic compound is oxidized with cupric oxide in CO_2 free atmosphere. C gets oxidized to CO_2 , H to H_2O . Water formed is absorbed in weighed anhydrous CaCl_2 U bulbs and carbon dioxide absorbed in weighed KOH bulbs. Increase in mass of CaCl_2 and KOH bulbs are determined. Difference in mass corresponds to the mass of H_2O and CO_2 respectively.

Knowing the increase in mass, the percentage of C and H in the organic compound can be calculated.



Calculations

- Let the mass of organic compound taken = m g
- Mass of water formed = m_1 g
(increase in CaCl_2 U-tube)
- Mass of carbon dioxide formed = m_2 g
(increase in potash tubes)

(a) Percentage of Carbon

We know that 1 mole of carbondioxide (44 g) contains 1 gram atom of carbon (12g).

44 g of CO_2 contain C = 12g

m_2 g of CO_2 contains C = $\frac{12}{44} \times m_2$ g

Hence Percentage of carbon = $\frac{12m_2}{44 \times m} \times 100$

(b) Percentage of Hydrogen

We know that one mole of water (18g) contains 2gram atom of hydrogen (2g)

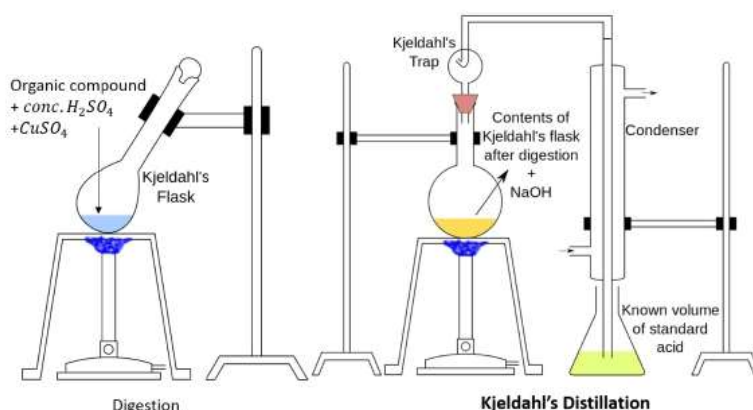
$\text{H}_2\text{O} = 2\text{H}$

18g of H_2O contain H = 2g

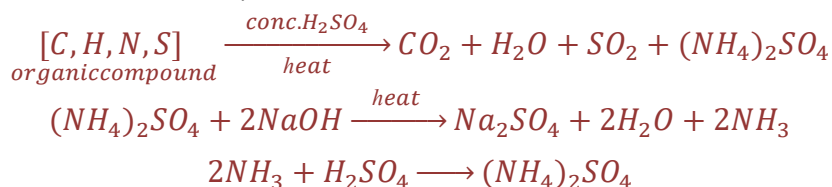
m_1 g of H_2O contains H = $\frac{2}{18} \times m_1$ g

Percentage of hydrogen = $\frac{2m_1}{18 \times m} \times 100$

Estimation of nitrogen by Kjeldahl's method



Principle: Kjeldahl's method is based on the quantitative conversion of nitrogen of the organic compound to ammonium sulphate by sulphuric acid. The reaction product is treated with an alkali and the ammonia released is determined. From this the amount of nitrogen in the organic compound is calculated.



This method is simple, convenient and largely used for the estimation of nitrogen in food stuffs, drugs, fertilizers and many other organic compounds. However, this method cannot be employed for the estimation of nitrogen in following types of organic compounds.

- Organic compound containing nitrogen in aromatic ring such as pyridine, quinoline, etc.,
- Organic compounds containing nitro ($-NO_2$) and diazo ($-N=N-$) groups.

Calculations

Let the mass of organic compound = w g

Volume of standard acid taken = V cm³

Normality of acid = N_1

Let vol. of standard alkali used for neutralisation of unused acid = V_2 cm³

Normality of standard alkali = N_2

$$\underbrace{N_1 V_1}_{\text{alkali}} = \underbrace{N_2 V_2}_{\text{acid}}$$

Let this volume of v cm³

Vol. of acid used for neutralisation of ammonia = $(V - v)$ cm³ of N_1 normality

Ammonia liberated = $(V - v)$ cm³ of N_1 solution

Now, 1000 cm³ of 1N NH_3 solution contains nitrogen = 14 g

$(V - v)$ cm³ of N_1 NH_3 solution contains

$$\text{nitrogen} = \frac{14(V - v) \times N_1}{1000} \text{ g}$$

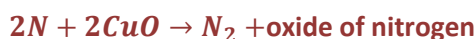
$$\text{Percentage of nitrogen} = \frac{\text{Mass of nitrogen}}{\text{Mass of organic compound}} \times 100$$

$$= \frac{14(V-v) \times N_1}{1000} \times \frac{100}{w} = \frac{14(V-v) \times N_1}{w}$$

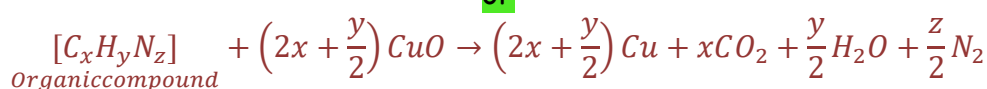
$$\text{Percentage of nitrogen in the compound} = \frac{\text{volume of the acid (cm}^3\text{)} \times \text{normality of the acid} \times 1.4}{\text{mass of organic compound in g}}$$

Estimation of Nitrogen by Duma's method

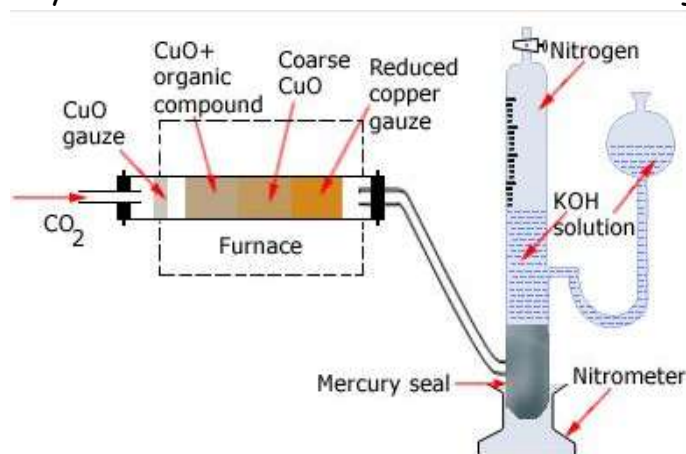
Principle: The organic compound containing nitrogen when heated with excess of copper oxide in the atmosphere of carbon dioxide, yields nitrogen in addition to carbon dioxide and water.



or



Traces of nitrogen oxides formed during combustion of organic compound are reduced to nitrogen by passing the gaseous mixture over a heated copper gauze. The percentage of nitrogen present in a given organic compound is calculated from the volume of nitrogen collected over potassium hydroxide solution from a known mass of organic compound.



Calculations

Let the mass of organic compound = w g

The volume of nitrogen collected = V cm³

Atmospheric pressure from barometer = P mm of Hg

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

Aqueous tension at $t^\circ\text{C}$ = a mm of Hg

Pressure of dry nitrogen = $(P - a)$ mm of Hg

Let us first convert the volume of nitrogen to volume at S.T.P.

Experimental conditions

$$P_1 = (P - a) \text{ mmHg}$$

$$T_1 = (273 + t) \text{ K}$$

$$V_1 = V \text{ cm}^3$$

S.T.P. conditions

$$P_2 = 760 \text{ mm}$$

$$T_2 = 273$$

$$V_2 = ?$$

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

$$V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{(P-a)xVx273}{760(273+t)} = x \text{ cm}^3 \text{ (say)}$$

Now 22400 cm³ of N₂ at S.T.P. weight = 28 g

$$x \text{ cm}^3 \text{ of N}_2 \text{ at S.T.P. will weigh} = x \times \frac{28}{22400} \text{ g}$$

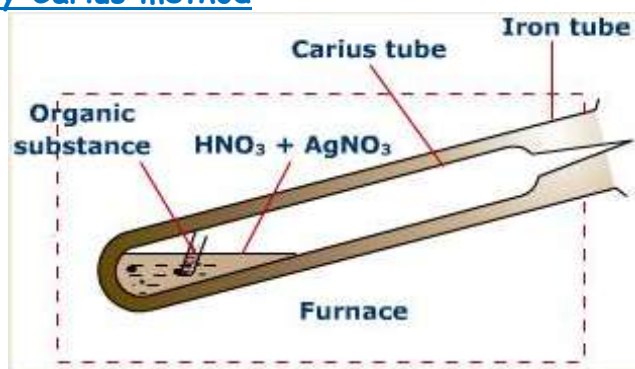
$$\text{Percentage of nitrogen} = \frac{\text{Mass of nitrogen}}{\text{Mass of organic compound}} \times 100 = \frac{28xx100}{22400xw}$$

$$\% \text{ of N} = \frac{28}{22400} \times \frac{V}{W} \times 100$$

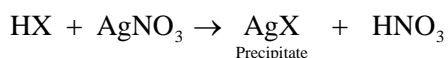
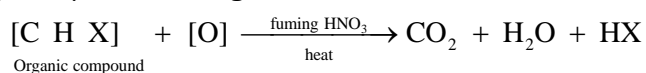
Where, V = volume of N₂ in nitrometer (in ml) at NTP,

$$W = \text{Weight of substance taken; } \% \text{ of N} = \frac{1.4 \times N \times V}{W}$$

Estimation of Halogen by Carius method



Principle: A known mass of an organic compound is heated with fuming nitric acid and a few crystals of silver nitrate in a sealed tube called Carius tube. The Carbon, hydrogen or sulphur present in the compound will be oxidised to CO₂, H₂O and H₂SO₄ respectively. Halogen is precipitated to give silver halide.



- This method does not give satisfactory results in the estimation of iodine as AgI is slightly soluble in nitric acid and iodide may oxidise to iodine to some extent.
- The results of this method is not very accurate in case of polyhalogenated aromatic compounds
- Estimation of fluorine can not be carried out as AgF is soluble in water.

Calculations:

Let the mass of organic compound be w g

Mass of silver halide formed = a g

Now, AgX = X

108 + X parts by weight of silver halide contains X parts by weight of halogen (X is its atomic mass)

(108 + X) g of silver halide give halogen = X

$$a \text{ g of silver halide will give halogen} = \frac{X}{(108+X)} \times a \text{ g}$$

$$\text{Percentage of halogen} = \frac{\text{atomic mass of X}}{\text{molecular mass of AgX}} \times \frac{\text{mass of silver halide in grams}}{\text{mass of organic compound in grams}} \times 100 = \frac{X \times a}{(108 + X)} \times \frac{100}{w}$$

Here X is the atomic mass of halogen, e.g. Cl = 35.5, Br = 80 (79.9 exact), I = 127 (126.9 exact)

$$\text{Percentage of chlorine} = \frac{35.5}{(108 + 35.5)} \times \frac{\text{mass of silver chloride in grams}}{\text{mass of organic compound in grams}} \times 100$$

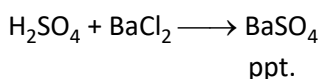
$$\text{Percentage of bromine} = \frac{80.0}{(108 + 80)} \times \frac{\text{mass of silver bromide in grams}}{\text{mass of organic compound in grams}} \times 100$$

$$\text{Percentage of iodine} = \frac{127}{(108 + 127)} \times \frac{\text{mass of silver iodide in grams}}{\text{mass of organic compound in grams}} \times 100$$

Estimation of sulphur by Carius method

Principle: An organic compound is digested with fuming nitric acid in a sealed tube. The sulphur present in the compound is quantitatively oxidised into sulphuric acid. Sulphuric acid so formed is precipitated as barium sulphate by adding excess of barium chloride.

The main reactions are : $\text{S} + \text{H}_2\text{O} + 3\text{O} \xrightarrow{\text{HNO}_3} \text{H}_2\text{SO}_4$



Calculations :

Let the mass of organic compound = w g

Mass of BaSO₄ formed = a g

BaSO₄ [137 + 32 + 64 = 233]

233 g of BaSO₄ contain sulphur = 32 g

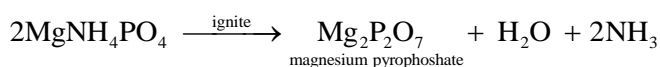
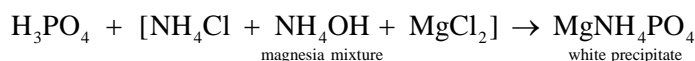
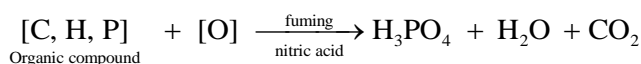
a g of BaSO₄ will contain sulphur = $\frac{32 \times a}{233}$ g

$$\text{Percentage of sulphur} = \frac{\text{Mass of sulphur}}{\text{Mass of organic compound}} \times 100 = \frac{32a}{233} \times \frac{100}{w}$$

$$\text{Percentage of sulphur} = \frac{32}{233} \times \frac{\text{mass of barium sulphate in grams}}{\text{mass of organic compounds in grams}} \times 100$$

Estimation of phosphorus by Carius method

Principle: The phosphorus present in the organic compound is oxidised to orthophosphoric acid by heating with fuming nitric acid. The phosphoric acid so obtained is precipitated as MgNH₄PO₄ which on ignition is converted into Mg₂P₂O₇.



$$\text{Percentage of phosphorus} = \frac{62}{222} \times \frac{\text{mass of Mg}_2\text{P}_2\text{O}_7 \text{ in grams}}{\text{mass of organic compound in grams}} \times 100$$

Estimation of oxygen

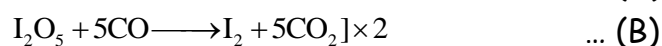
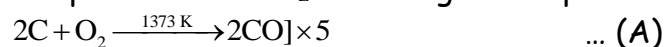
There is no direct method for the estimation of oxygen present in the organic compound. The percentage of oxygen in the compound is generally estimated by difference.

Percentage of oxygen = $100 - [\text{sum of percentage of all other elements present in it}]$

The percentage of oxygen in an organic compound is usually found by difference between the total percentage composition (100) and the sum of the percentages of all other elements. However, oxygen can also be estimated directly as follows:

A definite mass of an organic compound is decomposed by heating in a stream of nitrogen gas. The mixture of gaseous products containing oxygen is passed over red-hot coke when all the oxygen is converted to carbon monoxide. This mixture is passed through warm Iodine pentoxide (I_2O_5) when carbon monoxide is oxidised to carbon dioxide producing iodine.

Compound $\xrightarrow{\text{heat}}$ $\text{O}_2 + \text{other gaseous products}$



On making the amount of CO produced in equation (A) equal to the amount of CO used in equation (B) by multiplying the equations (A) and (B) by 5 and 2 respectively; we find that each mole of oxygen liberated from the compound will produce two moles of carbon dioxide.

Thus 88 g carbon dioxide is obtained if 32 g oxygen is liberated.

Let the mass of organic compound taken be m g

Mass of carbon dioxide produced be m_1 g

$\therefore m_1$ g carbon dioxide is obtained from $\frac{32 \times m_1}{88}$ g O_2

$\therefore \text{Percentage of oxygen} = \frac{32 \times m_1 \times 100}{88 \times m} \%$

The percentage of oxygen can be derived from the amount of iodine produced also.

Presently, the estimation of elements in an organic compound is carried out by using microquantities of substances and automatic experimental techniques. The elements, carbon, hydrogen and nitrogen present in a compound are determined by an apparatus known as CHN elemental analyser. The analyser requires only a very small amount of the substance (1-3 mg) and displays the values on a screen within a short time. A detailed discussion of such methods is beyond the scope of this book.

TRY IT YOURSELF

1. Leibig combustion method: (Estimation of C and H)

$$\text{Percentage of C} = \frac{12}{44} \times \frac{\text{Mass of CO}_2}{\text{Mass of compound}} \times 100$$

$$\text{Percentage of H} = \frac{2}{18} \times \frac{\text{Mass of H}_2\text{O}}{\text{Mass of compound}} \times 100$$

2. Carius's method (Estimation of halogens):

$$(A) \text{ Percentage of X} = \frac{\text{Atomic mass of X}}{\text{Molecular mass of AgX}} \times \frac{\text{Mass of AgX} \times 100}{\text{Mass of compound}}$$

$$(B) \text{ Percentage of Cl} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl} \times 100}{\text{Mass of compound}}$$

$$(C) \text{ Percentage of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr} \times 100}{\text{Mass of compound}}$$

$$(D) \text{ Percentage of I} = \frac{127}{235} \times \frac{\text{Mass of AgI} \times 100}{\text{Mass of compound}}$$

3. Estimation of sulphur:

$$\begin{aligned} \text{Percentage of S} &= \frac{\text{Atomic mass of S}}{\text{Molecular mass of BaSO}_4} \times \frac{\text{Mass of BaSO}_4 \times 100}{\text{Mass of compound}} \\ &= \frac{32}{233} \times \frac{\text{Mass of BaSO}_4 \times 100}{\text{Mass of compound}} \end{aligned}$$

4. Carius method (Estimation of phosphorous):

$$\text{Percentage of P} = \frac{\text{Atomic mass of P}}{\text{Molecular mass of Mg}_2\text{P}_2\text{O}_7} \times \frac{\text{Mass of Mg}_2\text{P}_2\text{O}_7 \times 100}{\text{Mass of compound}}$$



$$= \frac{62}{222} \times \frac{\text{Mass of Mg}_2\text{P}_2\text{O}_7 \times 100}{\text{Mass of compound}}$$

5. Dumas's method (Estimation of nitrogen):

$$\text{Percentage of nitrogen in the compound} = \frac{28V}{22400} \times \frac{100}{W}$$

6. Kjeldahl's method (Estimation of nitrogen):

Percentage of nitrogen in the sample

$$= \frac{1.4 \times \text{Normality of HCl} \times \text{Volume of HCl used for complete neutralization of NH}_3}{\text{Mass of the compound taken}}$$

7. Estimation of oxygen in general:

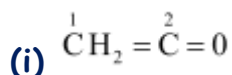
Percentage of O = 100 – (Percentage of C + Percentage of H + Percentage of N +)

Molecular Formula = n × (Empirical formula)

Ques 12.1: What are hybridisation states of each carbon atom in the following compounds?

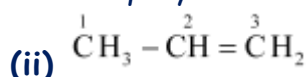
$\text{CH}_2=\text{C}=\text{O}$, $\text{CH}_3\text{CH}=\text{CH}_2$, $(\text{CH}_3)_2\text{CO}$, $\text{CH}_2=\text{CHCN}$, C_6H_6

Ans:



C-1 is sp^2 hybridised.

C-2 is sp hybridised.

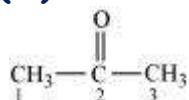


C-1 is sp^3 hybridised.

C-2 is sp^2 hybridised.

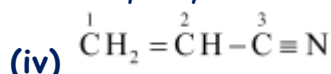
C-3 is sp^2 hybridised.

(iii)



C-1 and C-3 are sp^3 hybridised.

C-2 is sp^2 hybridised.



C-1 is sp^2 hybridised.

C-2 is sp^2 hybridised.

C-3 is sp hybridised.

(v) C_6H_6

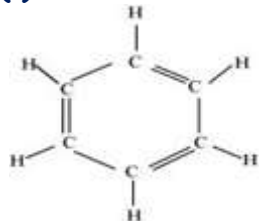
All the 6 carbon atoms in benzene are sp^2 hybridised.

Ques 12.2: Indicate the σ and π bonds in the following molecules:

C_6H_6 , C_6H_{12} , CH_2Cl_2 , $\text{CH}_2=\text{C}=\text{CH}_2$, CH_3NO_2 , HCONHCH_3

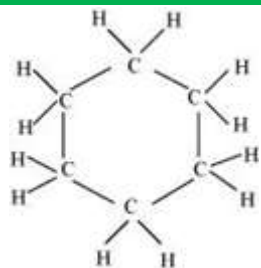
Ans:

(i) C_6H_6



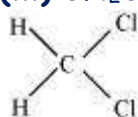
There are six C-C sigma ($\sigma_{\text{C-C}}$) bonds, six C-H sigma ($\sigma_{\text{C-H}}$) bonds, and three C=C pi ($\pi_{\text{C-C}}$) resonating bonds in the given compound.

(ii) C_6H_{12}



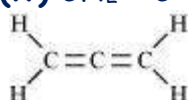
There are six C-C sigma (σ_{C-C}) bonds and twelve C-H sigma (σ_{C-H}) bonds in the given compound.

(iii) CH_2Cl_2



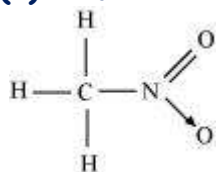
There two C-H sigma (σ_{C-H}) bonds and two C-Cl sigma (σ_{C-Cl}) bonds in the given compound.

(iv) $\text{CH}_2 = \text{C} = \text{CH}_2$



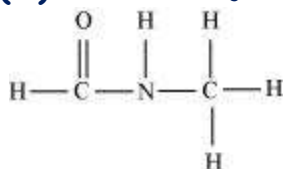
There are two C-C sigma (σ_{C-C}) bonds, four C-H sigma (σ_{C-H}) bonds, and two C=C pi (π_{C-C}) bonds in the given compound.

(v) CH_3NO_2



There are three C-H sigma (σ_{C-H}) bonds, one C-N sigma (σ_{C-N}) bond, one N-O sigma (σ_{N-O}) bond, and one N=O pi (π_{N-O}) bond in the given compound.

(vi) HCONHCH_3

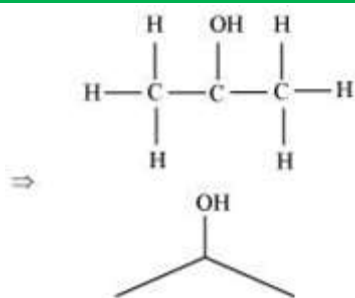


There are two C-N sigma (σ_{C-N}) bonds, four C-H sigma (σ_{C-H}) bonds, one N-H sigma bond, and one C=O pi (π_{C-C}) bond in the given compound.

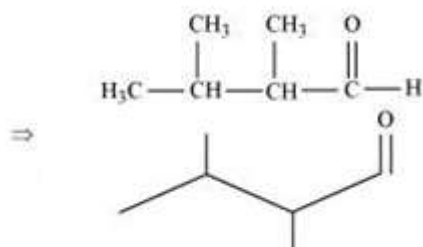
Ques 12.3: Write bond line formulas for: Isopropyl alcohol, 2,3-Dimethyl butanal, Heptan-4-one.

Ans: The bond line formulae of the given compounds are:

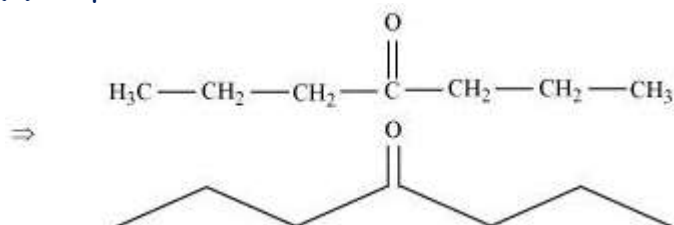
(a) Isopropyl alcohol



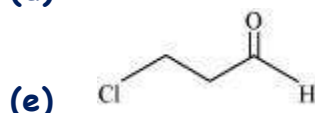
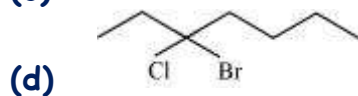
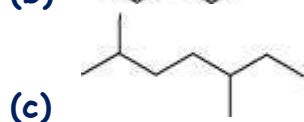
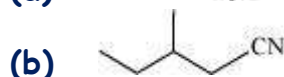
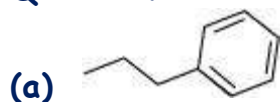
(b) 2, 3-dimethyl butanal



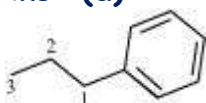
(c) Heptan-4-one



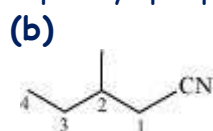
Ques 12.4: Give the IUPAC names of the following compounds:



Ans: (a)

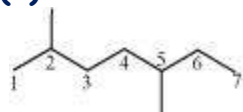


1-phenyl propane



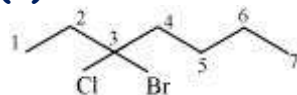
3-methylpentanenitrile

(c)



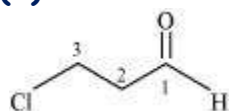
2, 5-dimethyl heptane

(d)



3-bromo-3-chloroheptane

(e)



3-chloropropanal

(f) $\text{Cl}_2\text{CHCH}_2\text{OH}$

2, 2-dichloroethanol

Ques 12.5: Which of the following represents the correct IUPAC name for the compounds concerned?

(a) 2,2-Dimethylpentane or 2-Dimethylpentane

(b) 2,4,7-Trimethyloctane or 2,5,7-Trimethyloctane

(c) 2-Chloro-4-methylpentane or 4-Chloro-2-methylpentane

(d) But-3-yn-1-ol or But-4-ol-1-yne

Ans: (a) The prefix *di* in the IUPAC name indicates that two identical substituent groups are present in the parent chain. Since two methyl groups are present in the C-2 of the parent chain of the given compound, the correct IUPAC name of the given compound is 2, 2-dimethylpentane.

(b) Locant number 2, 4, 7 is lower than 2, 5, 7. Hence, the IUPAC name of the given compound is 2, 4, 7-trimethyloctane.

(c) If the substituents are present in the equivalent position of the parent chain, then the lower number is given to the one that comes first in the name according to the alphabetical order. Hence, the correct IUPAC name of the given compound is 2-chloro-4-methylpentane.

(d) Two functional groups - alcoholic and alkyne - are present in the given compound. The principal functional group is the alcoholic group. Hence, the parent chain will be suffixed with *ol*. The alkyne group is present in the C-3 of the parent chain. Hence, the correct IUPAC name of the given compound is But-3-yn-1-ol.

Ques 12.6: Draw formulas for the first five members of each homologous series beginning with the following compounds.

(a) H-COOH

(b) CH_3COCH_3

(c) H-CH=CH_2

Ans: The first five members of each homologous series beginning with the given compounds are shown as follows:

(a)

H-COOH : Methanoic acid

$\text{CH}_3\text{-COOH}$: Ethanoic acid

$\text{CH}_3\text{-CH}_2\text{-COOH}$: Propanoic acid

$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-COOH}$: Butanoic acid

$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-COOH}$: Pentanoic acid

(b)

CH_3COCH_3 : Propanone

$\text{CH}_3\text{COCH}_2\text{CH}_3$: Butanone

$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$: Pentan-2-one

$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$: Hexan-2-one

$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$: Heptan-2-one

(c)

H-CH=CH_2 : Ethene

$\text{CH}_3\text{-CH=CH}_2$: Propene

$\text{CH}_3\text{-CH}_2\text{-CH=CH}_2$: 1-Butene

$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH=CH}_2$: 1-Pentene

$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH=CH}_2$: 1-Hexene

Ques 12.7: Give condensed and bond line structural formulas and identify the functional group(s) present, if any, for :

(a) 2,2,4-Trimethylpentane

(b) 2-Hydroxy-1,2,3-propanetricarboxylic acid

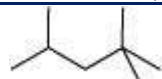
(c) Hexanedial

Ans: (a) 2, 2, 4-trimethylpentane

Condensed formula:

$(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{CH}_3)_3$

Bond line formula:

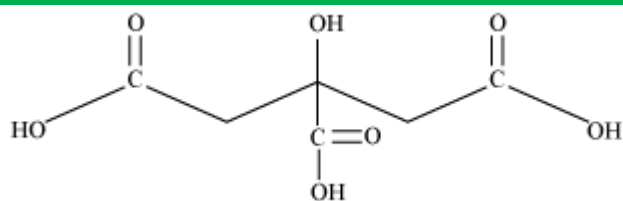


(b) 2-hydroxy-1, 2, 3-propanetricarboxylic acid

Condensed Formula:

$(\text{COOH})\text{CH}_2\text{C}(\text{OH})(\text{COOH})\text{CH}_2(\text{COOH})$

Bond line formula:



The functional groups present in the given compound are carboxylic acid ($-\text{COOH}$) and alcoholic ($-\text{OH}$) groups.

(c) Hexanedial

Condensed Formula:

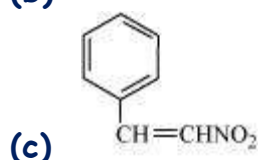
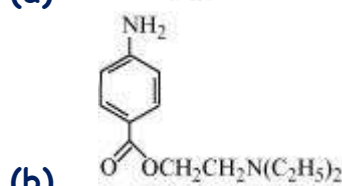
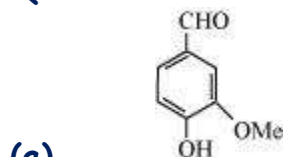
$(\text{CHO})(\text{CH}_2)_4(\text{CHO})$

Bond line Formula:



The functional group present in the given compound is aldehyde ($-\text{CHO}$).

Ques 12.8: Identify the functional groups in the following compounds



Ans: The functional groups present in the given compounds are:

(a) Aldehyde ($-\text{CHO}$),

Hydroxyl ($-\text{OH}$),

Methoxy ($-\text{OMe}$),

$\text{C}=\text{C}$ double bond $\left(\begin{array}{c} \text{ } \\ \text{ } \end{array} \begin{array}{c} \text{ } \\ \text{ } \end{array} \right)$

(b) Amino ($-\text{NH}_2$); primary amine,

Ester ($-\text{O}-\text{CO}-$),

Triethylamine ($\text{N}(\text{C}_2\text{H}_5)_2$); tertiary amine

(c) Nitro ($-\text{NO}_2$),

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

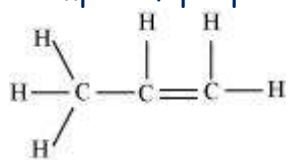
$\left(\begin{array}{c} \text{ } \\ \text{ } \end{array} \begin{array}{c} \text{ } \\ \text{ } \end{array} \right)$

Ques 12.9: Which of the two: $\text{O}_2\text{NCH}_2\text{CH}_2\text{O}^-$ or $\text{CH}_3\text{CH}_2\text{O}^-$ is expected to be more stable and why?

Ans: NO_2 group is an electron-withdrawing group. Hence, it shows $-I$ effect. By withdrawing the electrons toward it, the NO_2 group decreases the negative charge on the compound, thereby stabilising it. On the other hand, ethyl group is an electron-releasing group. Hence, the ethyl group shows $+I$ effect. This increases the negative charge on the compound, thereby destabilising it. Hence, $\text{O}_2\text{NCH}_2\text{CH}_2\text{O}^-$ is expected to be more stable than $\text{CH}_3\text{CH}_2\text{O}^-$.

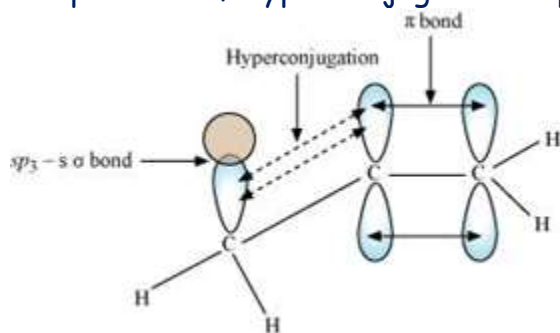
Ques 12.10: Explain why alkyl groups act as electron donors when attached to a π system.

Ans: When an alkyl group is attached to a π system, it acts as an electron-donor group by the process of hyperconjugation. To understand this concept better, let us take the example of propene.

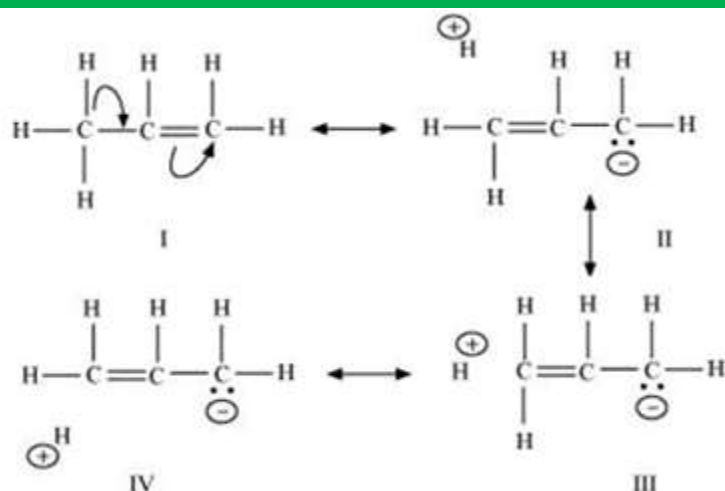


In hyperconjugation, the sigma electrons of the C-H bond of an alkyl group are delocalised. This group is directly attached to an atom of an unsaturated system. The delocalisation occurs because of a partial overlap of a sp^3 -s sigma bond orbital with an empty p orbital of the π bond of an adjacent carbon atom.

The process of hyperconjugation in propene is shown as follows:



This type of overlap leads to a delocalisation (also known as no-bond resonance) of the π electrons, making the molecule more stable.



Ques 12.11: Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.

(a) $\text{C}_6\text{H}_5\text{OH}$

(b) $\text{C}_6\text{H}_5\text{NO}_2$

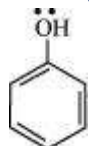
(c) $\text{CH}_3\text{CH}=\text{CH}-\text{CHO}$

(d) $\text{C}_6\text{H}_5\text{CHO}$

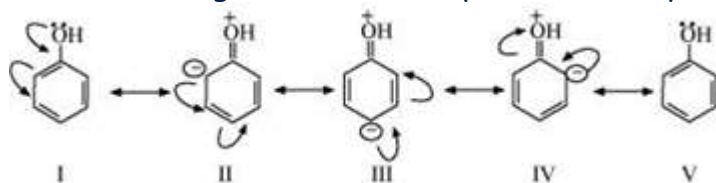
(e) $\text{C}_6\text{H}_5-\overset{+}{\text{C}}\text{H}_2$

(f) $\text{CH}_3\text{CH}=\text{CH}\overset{+}{\text{C}}\text{H}_2$

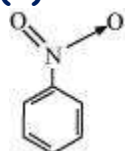
Ans: (a) The structure of $\text{C}_6\text{H}_5\text{OH}$ is:



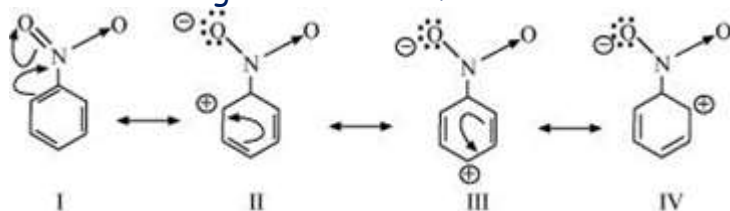
The resonating structures of phenol are represented as:



(b) The structure of $\text{C}_6\text{H}_5\text{NO}_2$ is:

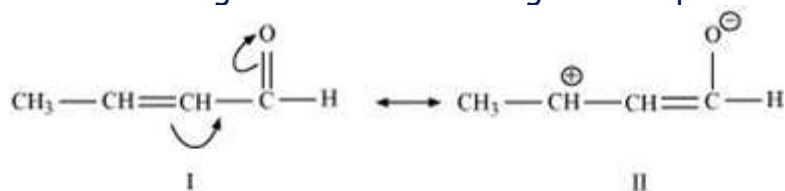


The resonating structures of nitro benzene are represented as:

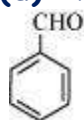


(c) $\text{CH}_3\text{CH}=\text{CH}-\text{CHO}$

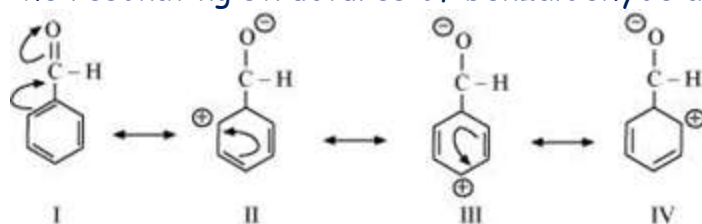
The resonating structures of the given compound are represented as:



(d) The structure of $\text{C}_6\text{H}_5\text{CHO}$ is:

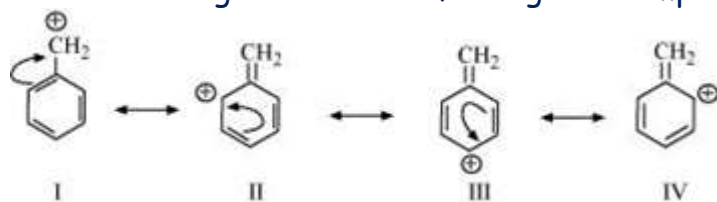


The resonating structures of benzaldehyde are represented as:



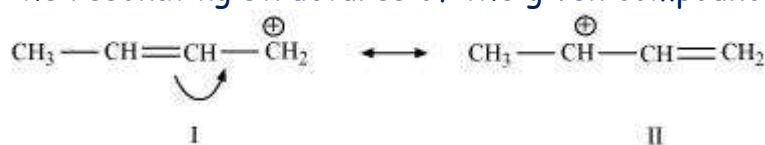
(e) $\text{C}_6\text{H}_5\text{CH}_2^+$

The resonating structures of the given compound are:



(f) $\text{CH}_3\text{CH}=\text{CHCH}_2^+$

The resonating structures of the given compound are:



Ques 12.12: What are electrophiles and nucleophiles? Explain with examples.

Ans: An electrophile is a reagent that takes away an electron pair. In other words, an electron-seeking reagent is called an electrophile (E^+). Electrophiles are electron-deficient and can receive an electron pair.

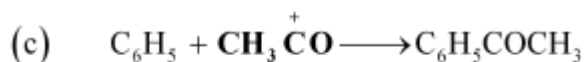
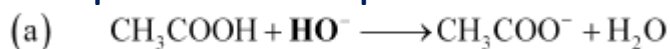
Carbocations (CH_3CH_2^+) and neutral molecules having functional groups such as carbonyl group (>C=O) are examples of electrophiles.

A nucleophile is a reagent that brings an electron pair. In other words, a nucleus-seeking reagent is called a nucleophile (Nu^-).

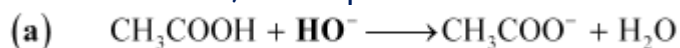
Example: OH^- , NC^- , carbanions (R_3C^-), etc.

Neutral molecules such as H_2O and ammonia also act as nucleophiles because of the presence of a lone pair.

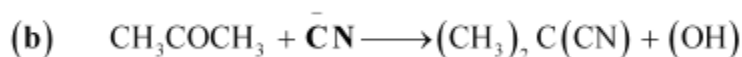
Ques 12.13: Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles:



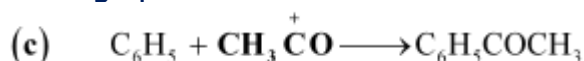
Ans: Electrophiles are electron-deficient species and can receive an electron pair. On the other hand, nucleophiles are electron-rich species and can donate their electrons.



Here, HO^- acts as a nucleophile as it is an electron-rich species, i.e., it is a nucleus-seeking species.



Here, CN^- acts as a nucleophile as it is an electron-rich species, i.e., it is a nucleus-seeking species.



Here, CH_3CO^+ acts as an electrophile as it is an electron-deficient species.

Ques 12.14: Classify the following reactions in one of the reaction type studied in this unit.



Ans:

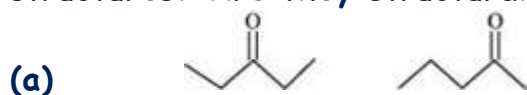
(a) It is an example of substitution reaction as in this reaction the bromine group in bromoethane is substituted by the $-\text{SH}$ group.

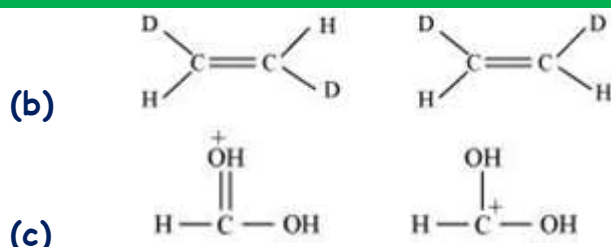
(b) It is an example of addition reaction as in this reaction two reactant molecules combine to form a single product.

(c) It is an example of elimination reaction as in this reaction hydrogen and bromine are removed from bromoethane to give ethene.

(d) In this reaction, substitution takes place, followed by a rearrangement of atoms and groups of atoms.

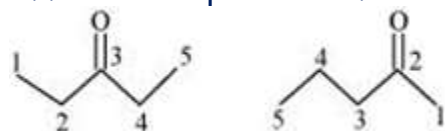
Ques 12.15: What is the relationship between the members of following pairs of structures? Are they structural or geometrical isomers or resonance contributors?





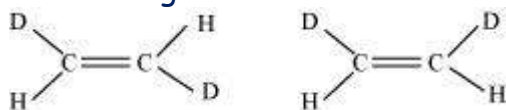
Ans:

(a) Compounds having the same molecular formula but with different structures are called structural isomers. The given compounds have the same molecular formula but they differ in the position of the functional group (ketone group).



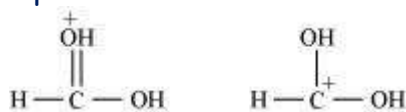
In structure I, ketone group is at the C-3 of the parent chain (hexane chain) and in structure II, ketone group is at the C-2 of the parent chain (hexane chain). Hence, the given pair represents structural isomers.

(b) Compounds having the same molecular formula, the same constitution, and the sequence of covalent bonds, but with different relative position of their atoms in space are called geometrical isomers.

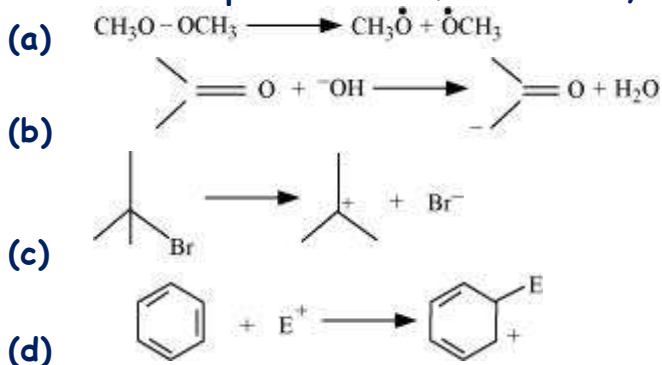


In structures I and II, the relative position of Deuterium (D) and hydrogen (H) in space are different. Hence, the given pairs represent geometrical isomers.

(c) The given structures are canonical structures or contributing structures. They are hypothetical and individually do not represent any real molecule. Hence, the given pair represents resonance structures, called resonance isomers.



Ques 12.16: For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion.

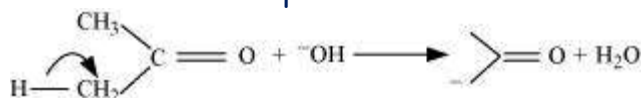


Ans: (a) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



It is an example of homolytic cleavage as one of the shared pair in a covalent bond goes with the bonded atom. The reaction intermediate formed is a free radical.

(b) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



It is an example of heterolytic cleavage as the bond breaks in such a manner that the shared pair of electrons remains with the carbon of propanone. The reaction intermediate formed is carbanion.

(c) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



It is an example of heterolytic cleavage as the bond breaks in such a manner that the shared pair of electrons remains with the bromine ion. The reaction intermediate formed is a carbocation.

(d) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



It is a heterolytic cleavage as the bond breaks in such a manner that the shared pair of electrons remains with one of the fragments. The intermediate formed is a carbocation.

Ques 12.17: Explain the terms Inductive and Electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?

(a) $\text{Cl}_3\text{CCOOH} > \text{Cl}_2\text{CHCOOH} > \text{ClCH}_2\text{COOH}$

(b) $\text{CH}_3\text{CH}_2\text{COOH} > (\text{CH}_3)_2\text{CHCOOH} > (\text{CH}_3)_3\text{C.COOH}$

**Ans: **

• **Inductive effect:** The permanent displacement of sigma (σ) electrons along a saturated chain, whenever an electron withdrawing or electron donating group is present, is called inductive effect.

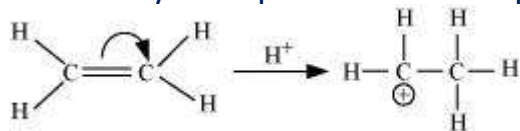
Inductive effect could be +I effect or - I effect. When an atom or group attracts electrons towards itself more strongly than hydrogen, it is said to possess - I effect. **Example:** $\text{F} \longleftarrow \text{CH}_2 \longleftarrow \text{CH}_2 \longleftarrow \text{CH}_2 \longleftarrow \text{CH}_3$

When an atom or group attracts electrons towards itself less strongly than hydrogen, it is said to possess I effect.

Example: $\text{CH}_3 \longrightarrow \text{CH}_2 \longrightarrow \text{Cl}$

• Electrometric effect

It involves the complete transfer of the shared pair of π electrons to either of the two atoms linked by multiple bonds in the presence of an attacking agent.



For example,

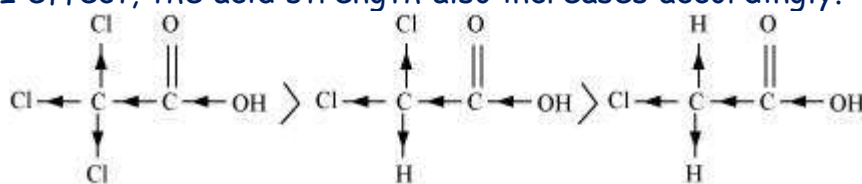
Electrometric effect could be +E effect or - E effect.

+E effect: When the electrons are transferred towards the attacking reagent.

- E effect: When the electrons are transferred away from the attacking reagent

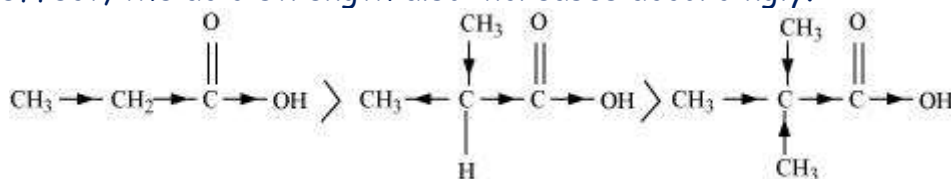
(a) $\text{Cl}_3\text{CCOOH} > \text{Cl}_2\text{CHCOOH} > \text{ClCH}_2\text{COOH}$

The order of acidity can be explained on the basis of Inductive effect (- I effect). As the number of chlorine atoms increases, the - I effect increases. With the increase in - I effect, the acid strength also increases accordingly.



(b) $\text{CH}_3\text{CH}_2\text{COOH} > (\text{CH}_3)_2\text{CHCOOH} > (\text{CH}_3)_3\text{C.COOH}$

The order of acidity can be explained on the basis of inductive effect (I effect). As the number of alkyl groups increases, the +I effect also increases. With the increase in +I effect, the acid strength also increases accordingly.



Ques 12.18: Give a brief description of the principles of the following techniques taking an example in each case.

(a) Crystallisation

(b) Distillation

(c) Chromatography

Ans: (a) Crystallisation

Crystallisation is one of the most commonly used techniques for the purification of solid organic compounds.

Principle: It is based on the difference in the solubilities of the compound and the impurities in a given solvent. The impure compound gets dissolved in the solvent in which it is sparingly soluble at room temperature, but appreciably soluble at higher

temperature. The solution is concentrated to obtain a nearly saturated solution. On cooling the solution, the pure compound crystallises out and is removed by filtration. For example, pure aspirin is obtained by recrystallising crude aspirin. Approximately 2 - 4 g of crude aspirin is dissolved in about 20 mL of ethyl alcohol. The solution is heated (if necessary) to ensure complete dissolution. The solution is then left undisturbed until some crystals start to separate out. The crystals are then filtered and dried.

(b) Distillation

This method is used to separate volatile liquids from non-volatile impurities or a mixture of those liquids that have a sufficient difference in their boiling points.

Principle: It is based on the fact that liquids having different boiling points vapourise at different temperatures. The vapours are then cooled and the liquids so formed are collected separately.

For example, a mixture of chloroform (b.p = 334 K) and aniline (b.p = 457 K) can be separated by the method of distillation. The mixture is taken in a round bottom flask fitted with a condenser. It is then heated. Chloroform, being more volatile, vaporizes first and passes into the condenser. In the condenser, the vapours condense and chloroform trickles down. In the round bottom flask, aniline is left behind.

(c) Chromatography

It is one of the most useful methods for the separation and purification of organic compounds.

Principle: It is based on the difference in movement of individual components of a mixture through the stationary phase under the influence of mobile phase.

For example, a mixture of red and blue ink can be separated by chromatography. A drop of the mixture is placed on the chromatogram. The component of the ink, which is less adsorbed on the chromatogram, moves with the mobile phase while the less adsorbed component remains almost stationary.

Ques 12.19: Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.

Ans: Fractional crystallisation is the method used for separating two compounds with different solubilities in a solvent S. The process of fractional crystallisation is carried out in four steps.

(a) Preparation of the solution: The powdered mixture is taken in a flask and the solvent is added to it slowly and stirred simultaneously. The solvent is added till the solute is just dissolved in the solvent. This saturated solution is then heated.

(b) Filtration of the solution: The hot saturated solution is then filtered through a filter paper in a China dish.

(c) Fractional crystallisation: The solution in the China dish is now allowed to cool. The less soluble compound crystallises first, while the more soluble compound remains in the solution. After separating these crystals from the mother liquor, the latter is concentrated once again. The hot solution is allowed to cool and consequently, the crystals of the more soluble compound are obtained.

(d) Isolation and drying: These crystals are separated from the mother liquor by filtration. Finally, the crystals are dried.

Ques 12.20: What is the difference between distillation, distillation under reduced pressure and steam distillation ?

Ans: The differences among distillation, distillation under reduced pressure, and steam distillation are given in the following table.

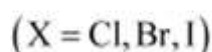
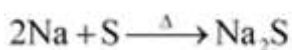
	Distillation	Distillation under reduced pressure	Steam distillation
1.	It is used for the purification of compounds that are associated with non-volatile impurities or those liquids, which do not decompose on boiling. In other words, distillation is used to separate volatile liquids from non-volatile impurities or a mixture of those liquids that have sufficient difference in boiling points.	This method is used to purify a liquid that tends to decompose on boiling. Under the conditions of reduced pressure, the liquid will boil at a low temperature than its boiling point and will, therefore, not decompose.	It is used to purify compound, which is immiscible in water. In steam, the compound and the steam gets separated from water. After some time, the mixture of water and liquid passes through the condenser. The condensed mixture of liquid is then separated in a separating funnel.
2.	Mixture of petrol and kerosene is separated by this method.	Glycerol is purified by this method. It boils with decomposition at a temperature of 593 K. At a reduced pressure, it boils at 453 K without decomposition.	A mixture of water and oil is separated by steam distillation.

Ques 12.21: Discuss the chemistry of Lassaigne's test.

Ans:

Lassaigne's test

This test is employed to detect the presence of nitrogen, sulphur, halogens, and phosphorous in an organic compound. These elements are present in the covalent form in an organic compound. These are converted into the ionic form by fusing the compound with sodium metal.



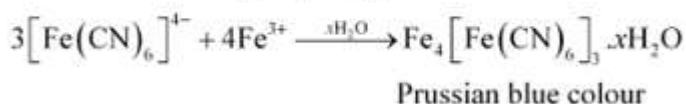
The cyanide, sulphide, and halide of sodium formed are extracted from the fused mass by boiling it in distilled water. The extract so obtained is called Lassaigne's extract. This Lassaigne's extract is then tested for the presence of nitrogen, sulphur, halogens, and phosphorous.

(a) Test for nitrogen



Chemistry of the test

In the Lassaigne's test for nitrogen in an organic compound, the sodium fusion extract is boiled with iron (II) sulphate and then acidified with sulphuric acid. In the process, sodium cyanide first reacts with iron (II) sulphate and forms sodium hexacyanoferrate (II). Then, on heating with sulphuric acid, some iron (II) gets oxidised to form iron (III) hexacyanoferrate (II), which is Prussian blue in colour. The chemical equations involved in the reaction can be represented as

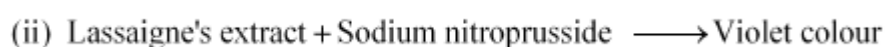
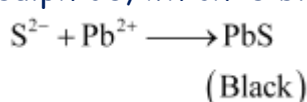


(b) Test for sulphur



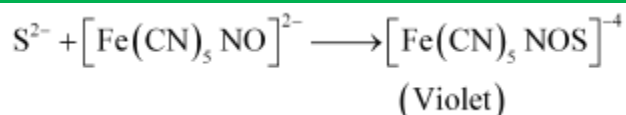
Chemistry of the test

In the Lassaigne's test for sulphur in an organic compound, the sodium fusion extract is acidified with acetic acid and then lead acetate is added to it. The precipitation of lead sulphide, which is black in colour, indicates the presence of sulphur in the compound.



Chemistry of the test

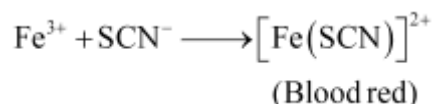
The sodium fusion extract is treated with sodium nitroprusside. Appearance of violet colour also indicates the presence of sulphur in the compound.



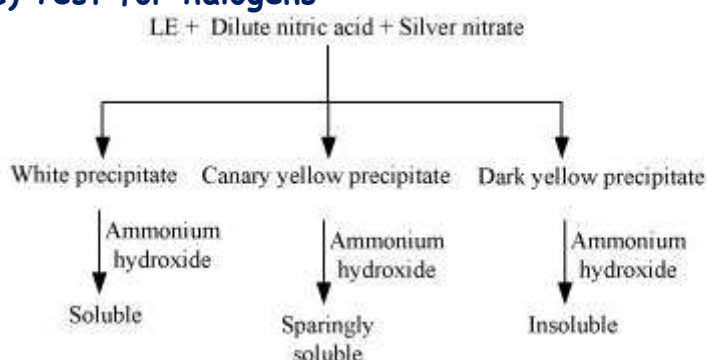
If in an organic compound, both nitrogen and sulphur are present, then instead of NaCN, formation of NaSCN takes place.



This NaSCN (sodium thiocyanate) gives a blood red colour. Prussian colour is not formed due to the absence of free cyanide ions.

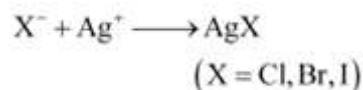


(c) Test for halogens



Chemistry of the test

In the Lassaigne's test for halogens in an organic compound, the sodium fusion extract is acidified with nitric acid and then treated with silver nitrate.

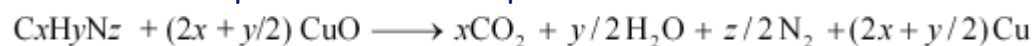


If nitrogen and sulphur both are present in the organic compound, then the Lassaigne's extract is boiled to expel nitrogen and sulphur, which would otherwise interfere in the test for halogens.

Ques 12.22: Differentiate between the principle of estimation of nitrogen in an organic compound by

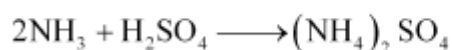
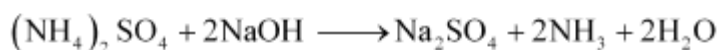
(i) Dumas method and (ii) Kjeldahl's method.

Ans: In Dumas method, a known quantity of nitrogen containing organic compound is heated strongly with excess of copper oxide in an atmosphere of carbon dioxide to produce free nitrogen in addition to carbon dioxide and water. The chemical equation involved in the process can be represented as



The traces of nitrogen oxides can also be produced in the reaction, which can be reduced to dinitrogen by passing the gaseous mixture over a heated copper gauge. The dinitrogen produced is collected over an aqueous solution of potassium hydroxide. The volume of nitrogen produced is then measured at room temperature and atmospheric pressure.

On the other hand, in Kjeldahl's method, a known quantity of nitrogen containing organic compound is heated with concentrated sulphuric acid. The nitrogen present in the compound is quantitatively converted into ammonium sulphate. It is then distilled with excess of sodium hydroxide. The ammonia evolved during this process is passed into a known volume of H_2SO_4 . The chemical equations involved in the process are



The acid that is left unused is estimated by volumetric analysis (titrating it against a standard alkali) and the amount of ammonia produced can be determined. Thus, the percentage of nitrogen in the compound can be estimated. This method cannot be applied to the compounds, in which nitrogen is present in a ring structure, and also not applicable to compounds containing nitro and azo groups.

Ques 12.23: Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound.

Ans: Estimation of halogens

Halogens are estimated by the Carius method. In this method, a known quantity of organic compound is heated with fuming nitric acid in the presence of silver nitrate, contained in a hard glass tube called the Carius tube, taken in a furnace. Carbon and hydrogen that are present in the compound are oxidized to form CO_2 and H_2O respectively and the halogen present in the compound is converted to the form of AgX . This AgX is then filtered, washed, dried, and weighed.

Let the mass of organic compound be m g.

Mass of AgX formed = m_1 g

1 mol of AgX contains 1 mol of X.

Therefore,

$$\text{Mass of halogen in } m_1 \text{ g of AgX} = \frac{\text{Atomic mass of X} \times m_1 \text{ g}}{\text{Molecular mass of AgX}}$$

$$\text{Thus, \% of halogen will be} = \frac{\text{Atomic mass of X} \times m_1 \times 100}{\text{Molecular mass of AgX} \times m}$$

Estimation of Sulphur

In this method, a known quantity of organic compound is heated with either fuming nitric acid or sodium peroxide in a hard glass tube called the Carius tube. Sulphur, present in the compound, is oxidized to form sulphuric acid. On addition of excess of barium chloride to it, the precipitation of barium sulphate takes place. This precipitate is then filtered, washed, dried, and weighed.

Let the mass of organic compound be m g.

Mass of BaSO_4 formed = m_1 g

1 mol of BaSO_4 = 233 g BaSO_4 = 32 g of Sulphur

$$\text{Therefore, } m_1 \text{ g of BaSO}_4 \text{ contains } \frac{32 \times m_1}{233} \text{ g of sulphur.}$$

$$\text{Thus, percentage of sulphur} = \frac{32 \times m_1 \times 100}{233 \times m}$$

Estimation of phosphorus

In this method, a known quantity of organic compound is heated with fuming nitric acid. Phosphorus, present in the compound, is oxidized to form phosphoric acid. By adding ammonia and ammonium molybdate to the solution, phosphorus can be precipitated as ammonium phosphomolybdate.

Phosphorus can also be estimated by precipitating it as MgNH_4PO_4 by adding magnesia mixture, which on ignition yields $\text{Mg}_2\text{P}_2\text{O}_7$.

Let the mass of organic compound be m g.

Mass of ammonium phosphomolybdate formed = m_1 g

Molar mass of ammonium phosphomolybdate = 1877 g

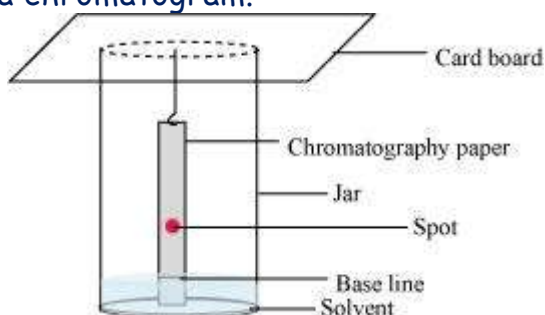
$$\text{Thus, percentage of phosphorus} = \frac{31 \times m_1 \times 100}{1877 \times m} \%$$

If P is estimated as $\text{Mg}_2\text{P}_2\text{O}_7$,

$$\text{Then, percentage of phosphorus} = \frac{62 \times m_1 \times 100}{222 \times m} \%$$

Ques 12.24: Explain the principle of paper chromatography.

Ans: In paper chromatography, chromatography paper is used. This paper contains water trapped in it, which acts as the stationary phase. On the base of this chromatography paper, the solution of the mixture is spotted. The paper strip is then suspended in a suitable solvent, which acts as the mobile phase. This solvent rises up the chromatography paper by capillary action and in the procedure, it flows over the spot. The components are selectively retained on the paper (according to their differing partition in these two phases). The spots of different components travel with the mobile phase to different heights. The paper so obtained (shown in the given figure) is known as a chromatogram.



Ques 12.25: Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?

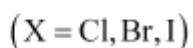
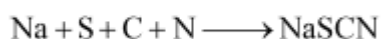
Ans: While testing the Lassaigne's extract for the presence of halogens, it is first boiled with dilute nitric acid. This is done to decompose NaCN to HCN and Na_2S to H_2S and to expel these gases. That is, if any nitrogen and sulphur are present in the form of

NaCN and Na₂S, then they are removed. The chemical equations involved in the reaction are represented as



Ques 12.26: Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens.

Ans: Nitrogen, sulphur, and halogens are covalently bonded in organic compounds. For their detection, they have to be first converted to ionic form. This is done by fusing the organic compound with sodium metal. This is called "Lassaigne's test". The chemical equations involved in the test are



Carbon, nitrogen, sulphur, and halogen come from organic compounds.

Ques 12.27: Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

Ans: The process of sublimation is used to separate a mixture of camphor and calcium sulphate. In this process, the sublimable compound changes from solid to vapour state without passing through the liquid state. Camphor is a sublimable compound and calcium sulphate is a non-sublimable solid. Hence, on heating, camphor will sublime while calcium sulphate will be left behind.

Ques 12.28: Explain, why an organic liquid vaporises at a temperature below its boiling point in its steam distillation?

Ans: In steam distillation, the organic liquid starts to boil when the sum of vapour pressure due to the organic liquid (p_1) and the vapour pressure due to water (p_2) becomes equal to atmospheric pressure (p), that is, $p = p_1 + p_2$

Since $p_1 < p_2$, organic liquid will vapourise at a lower temperature than its boiling point.

Ques 12.29: Will CCl₄ give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer.

Ans: CCl₄ will not give the white precipitate of AgCl on heating it with silver nitrate. This is because the chlorine atoms are covalently bonded to carbon in CCl₄. To obtain the precipitate, it should be present in ionic form and for this, it is necessary to prepare the Lassaigne's extract of CCl₄.

Ques 12.30: Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?

Ans: Carbon dioxide is acidic in nature and potassium hydroxide is a strong base. Hence, carbon dioxide reacts with potassium hydroxide to form potassium carbonate and water as



Thus, the mass of the U-tube containing KOH increases. This increase in the mass of U-tube gives the mass of CO_2 produced. From its mass, the percentage of carbon in the organic compound can be estimated.

Ques 12.31: Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

Ans: Although the addition of sulphuric acid will precipitate lead sulphate, the addition of acetic acid will ensure a complete precipitation of sulphur in the form of lead sulphate due to common ion effect. Hence, it is necessary to use acetic acid for acidification of sodium extract for testing sulphur by lead acetate test.

Ques 12.32: An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.

Ans: Percentage of carbon in organic compound = 69 %
That is, 100 g of organic compound contains 69 g of carbon.

$\therefore 0.2 \text{ g of organic compound will contain } = \frac{69 \times 0.2}{100} = 0.138 \text{ g of C}$

Molecular mass of carbon dioxide, $\text{CO}_2 = 44 \text{ g}$

That is, 12 g of carbon is contained in 44 g of CO_2 .

Therefore, 0.138 g of carbon will be contained in $\frac{44 \times 0.138}{12} = 0.506 \text{ g of CO}_2$

Thus, 0.506 g of CO_2 will be produced on complete combustion of 0.2 g of organic compound.

Percentage of hydrogen in organic compound is 4.8.

i.e., 100 g of organic compound contains 4.8 g of hydrogen.

Therefore, 0.2 g of organic compound will contain $\frac{4.8 \times 0.2}{100} = 0.0096 \text{ g of H}$

It is known that molecular mass of water (H_2O) is 18 g.

Thus, 2 g of hydrogen is contained in 18 g of water.

$\therefore 0.0096 \text{ g of hydrogen will be contained in } \frac{18 \times 0.0096}{2} = 0.0864 \text{ g of water}$

Thus, 0.0864 g of water will be produced on complete combustion of 0.2 g of the organic compound.

Ques 12.33: A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.5 M H_2SO_4 . The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.

Ans: Given that, total mass of organic compound = 0.50 g
60 mL of 0.5 M solution of NaOH was required by residual acid for neutralisation.

60 mL of 0.5 M NaOH solution $= \frac{60}{2}$ mL of 0.5 M $H_2SO_4 = 30$ mL of 0.5 M H_2SO_4

\therefore Acid consumed in absorption of evolved ammonia is (50-30) mL = 20 mL

Again, 20 mL of 0.5 M $H_2SO_4 = 40$ mL of 0.5 M NH_3

Also, since 1000 mL of 1 M NH_3 contains 14 g of nitrogen,

\therefore 40 mL of 0.5 M NH_3 will contain $\frac{14 \times 40}{1000} \times 0.5 = 0.28$ g of N

Therefore, percentage of nitrogen in 0.50 g of organic compound $= \frac{0.28}{0.50} \times 100 = 56\%$

Ques 12.34: 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound.

Ans: Given that,

Mass of organic compound is 0.3780 g.

Mass of AgCl formed = 0.5740 g

1 mol of AgCl contains 1 mol of Cl.

Thus, mass of chlorine in 0.5740 g of AgCl

$$= \frac{35.5 \times 0.5740}{143.32} = 0.1421 \text{ g}$$

\therefore Percentage of chlorine $= \frac{0.1421}{0.3780} \times 100 = 37.59\%$

Hence, the percentage of chlorine present in the given organic chloro compound is 37.59%.

Ques 12.35: In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find out the percentage of sulphur in the given compound.

Ans: Total mass of organic compound = 0.468 g [Given]

Mass of barium sulphate formed = 0.668 g [Given]

1 mol of $BaSO_4 = 233$ g of $BaSO_4 = 32$ g of sulphur

Thus, 0.668 g of $BaSO_4$ contains $\frac{32 \times 0.668}{233}$ g of sulphur = 0.0917 g of sulphur
 $= \frac{0.0917}{0.468} \times 100 = 19.59\%$

Therefore, percentage of sulphur = 19.59 %

Hence, the percentage of sulphur in the given compound is 19.59 %.

Ques 12.36: In the organic compound $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CH}$, the pair of hybridised orbitals involved in the formation of: $\text{C}_2 - \text{C}_3$ bond is:

- (a) $sp - sp^2$
- (b) $sp - sp^3$
- (c) $sp^2 - sp^3$
- (d) $sp^3 - sp^3$

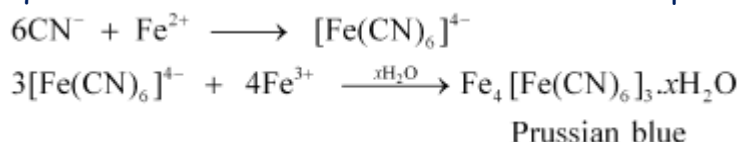
Ans: $\overset{6}{\text{CH}_2}=\overset{5}{\text{CH}}-\overset{4}{\text{CH}_2}-\overset{3}{\text{CH}_2}-\overset{2}{\text{C}}\equiv\overset{1}{\text{CH}}$

In the given organic compound, the carbon atoms numbered as 1, 2, 3, 4, 5, and 6 are sp , sp , sp^3 , sp^3 , sp^2 , and sp^2 hybridized respectively. Thus, the pair of hybridized orbitals involved in the formation of C_2-C_3 bond is $sp - sp^3$.

Ques 12.37: In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue colour is obtained due to the formation of:

- (a) $\text{Na}_4[\text{Fe}(\text{CN})_6]$
- (b) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
- (c) $\text{Fe}_2[\text{Fe}(\text{CN})_6]$
- (d) $\text{Fe}_3[\text{Fe}(\text{CN})_6]_4$

Ans: In the Lassaigne's test for nitrogen in an organic compound, the sodium fusion extract is boiled with iron (II) sulphate and then acidified with sulphuric acid. In the process, sodium cyanide first reacts with iron (II) sulphate and forms sodium hexacyanoferrate (II). Then, on heating with sulphuric acid, some iron (II) gets oxidised to form iron (III) hexacyanoferrate (II), which is Prussian blue in colour. The chemical equations involved in the reaction can be represented as



Hence, the Prussian blue colour is due to the formation of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

Ques 12.38: Which of the following carbocation is most stable?

- (a) $(\text{CH}_3)_3\text{C} \cdot \overset{+}{\text{C}}\text{H}_2$
- (b) $(\text{CH}_3)_3\overset{+}{\text{C}}$
- (c) $\text{CH}_3\text{CH}_2\overset{+}{\text{C}}\text{H}_2$
- (d) $\text{CH}_3\overset{+}{\text{C}}\text{HCH}_2\text{CH}_3$

Ans: $(\text{CH}_3)_3\overset{+}{\text{C}}$ is a tertiary carbocation. A tertiary carbocation is the most stable carbocation due to the electron releasing effect of three methyl groups. An increased +I effect by three methyl groups stabilizes the positive charge on the carbocation.

Ques 12.39: The best and latest technique for isolation, purification and separation of organic compounds is:

- (a) Crystallisation
- (b) Distillation
- (c) Sublimation
- (d) Chromatography

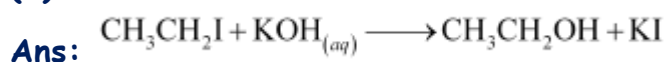
Ans: Chromatography is the most useful and the latest technique of separation and purification of organic compounds. It was first used to separate a mixture of coloured substances.

Ques 12.40: The reaction:



is classified as :

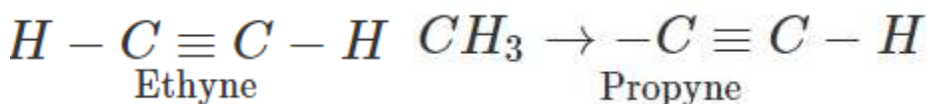
- (a) electrophilic substitution
- (b) nucleophilic substitution
- (c) elimination
- (d) addition



It is an example of nucleophilic substitution reaction. The hydroxyl group of KOH (OH^-) with a lone pair of itself acts as a nucleophile and substitutes iodide ion in $\text{CH}_3\text{CH}_2\text{I}$ to form ethanol.

Q.1 Ethyne is a stronger acid than propyne. Explain.

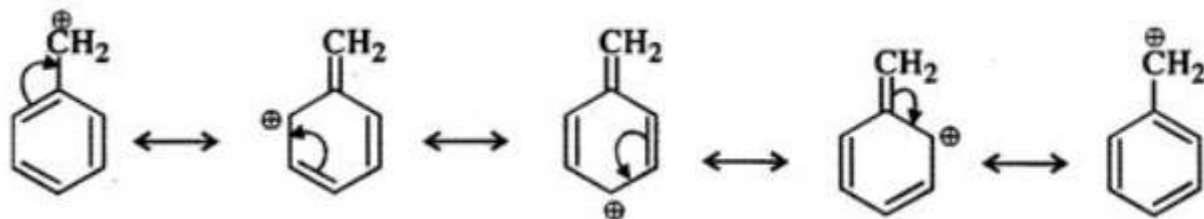
Answer: Terminal alkynes ($\text{R}-\text{C}\equiv\text{C}-\text{H}$) are weakly acidic in nature because of sp -hybridised state of the triple bonded carbon atom. Due to substantial s -character (50%), the triple bonded carbon is electronegative in nature and this enables the release of H^+ ion from $\equiv\text{C}-\text{H}$ bond. However, ethyne is a stronger acid than propyne. This is attributed to the electron releasing +I effect of the methyl group which tends to increase the electron density on the triple bonded carbon atom in propyne. The release of H^+ ion from propyne is more difficult than from ethyne or it is a weaker acid than ethyne.



Q.2 Electromeric effect is a temporary effect. Assign reason.

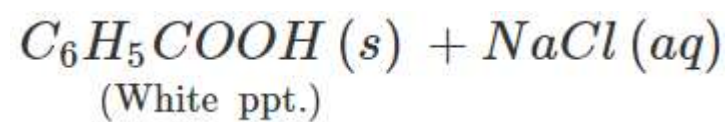
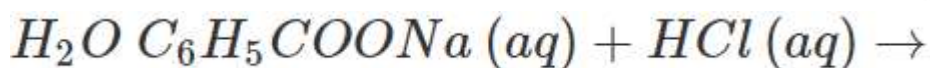
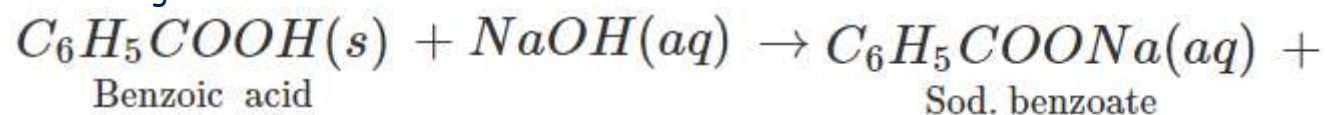
Answer: The electromeric effect is noticed in the organic compounds containing multiple bond i. e., double bond ($>\text{C}=\text{C}<$ or $>\text{C}=\text{O}<$) or triple bond ($-\text{C}\equiv\text{N}$) under the influence of the attacking reagent. The moment the attacking reagent is removed, π (π) electron pair comes back to its original position forming multiple bond again. Therefore, electromeric effect is a temporary effect.

Q.3 Alcohols are weaker acids than water. Why?

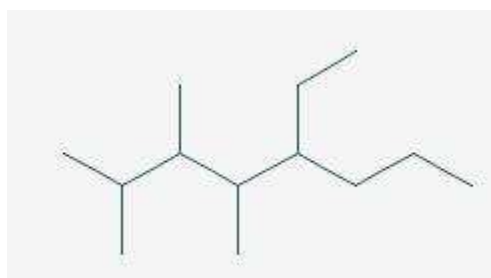


Q.7 How will you separate a mixture of benzoic acid and naphthalene?

Answer: Both these solids sublime on heating. Therefore, these cannot be separated by sublimation. The mixture is heated with water when only benzoic acid will dissolve. Upon filtration, naphthalene is separated and the solution upon cooling gives crystals of benzoic acid. Alternatively the mixture is reacted with strong aqueous sodium hydroxide when benzoic acid is converted to soluble sodium benzoate while naphthalene is unaffected. It can be separated by filtration. The filtrate is then treated with dilute HCl to regenerate benzoic acid.

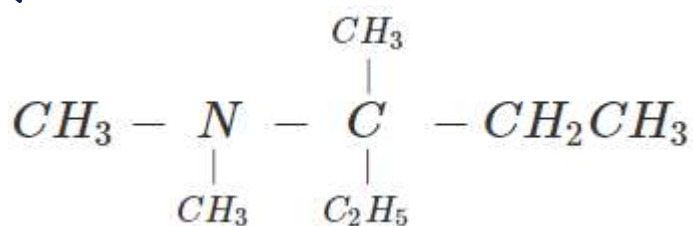


Q.8 Give the IUPAC name of the saturated hydrocarbon having the following carbon skeleton.



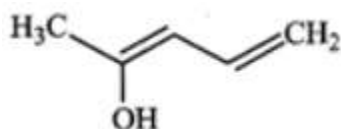
Answer: 5-Ethyl-2, 3, 4-trimethyloctane

Q.9 Give the IUPAC name for the amine.

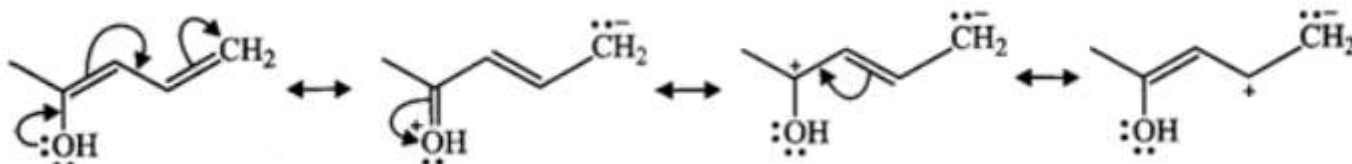


Answer: N, N, 3-Trimethylpentan-3-amine (Alphabets are given preference over numerals).

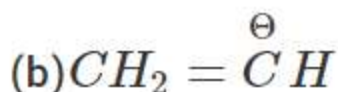
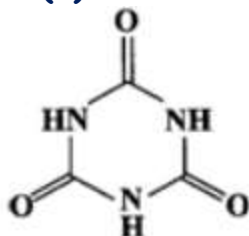
Q.10 Write resonance structures of the given compound.



Answer: The following four resonance structures can be written for the given compound.

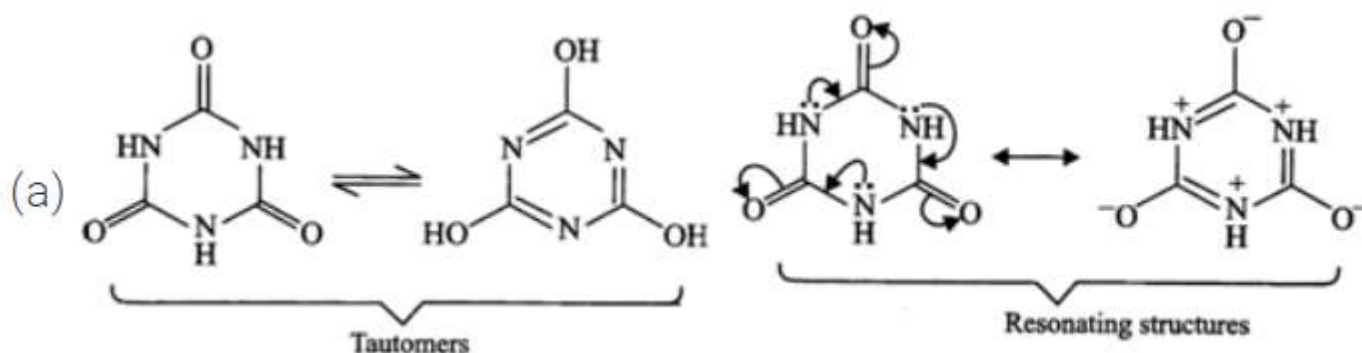


Q.11 (a) Write down resonating structure and tautomer



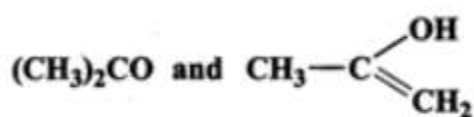
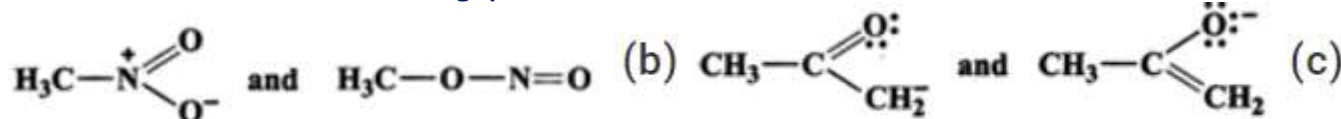
of $CH_2 = \overset{\ominus}{C}H$ is more basic than $HC \equiv C^-$. Explain why.

Answer:



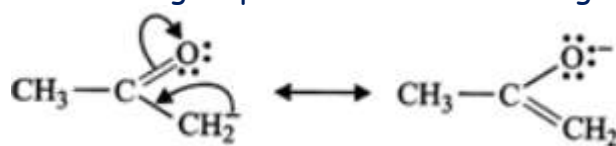
(b) $CH_2 = \overset{sp^2}{CH}^-$ $HC \equiv \overset{sp}{C}^-$ Since, sp -carbon is more electronegative than sp^2 -carbon, therefore, $CH \equiv C^-$ is less willing to donate a pair of electrons than $H_2C=CH^-$. In other words, $H_2C=CH^-$ is more basic than $HC \equiv C^-$.

Q.12 Which of the following pairs do not constitute resonance structures? (a)

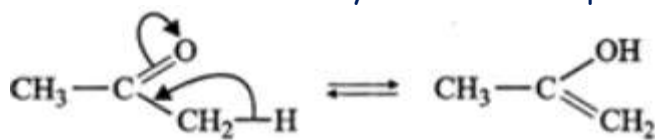


(d) $CH_3CH=CHCH_3$ and $CH_3CH_2CH=CH_2$

Answer: (a) The two structures differ in the position of atoms and hence they are not resonance structures. In fact, these are functional isomers, i.e., $\text{CH}_3\text{-NO}_2$ having nitro ($-\text{NO}_2$) group as the functional group and $\text{CH}_3\text{-ONO}$ having nitrite ($\text{O}=\text{N}-\text{O}^-$) as the



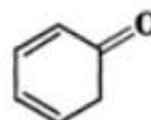
functional group. (b) These two are resonance structures because they differ in the position of electrons only and not atoms. (c) These are not resonance structures since they differ in the position of atoms. They are, in



fact, tautomers. (d) These are not resonance structures since these differ in the position of double bond. In fact, these are position isomers.



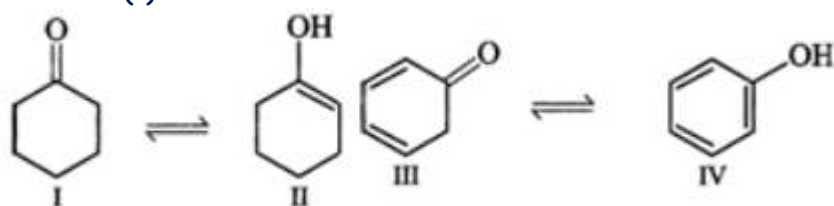
Q.13 Explain the following: (i) exists in keto form but



exists in

enol form. (ii) $\text{CH}_2=\text{CH}^-$ is a better nucleophile than $\text{HC}\equiv\text{C}^-$.

Answer: (i)



Enol form (II) is not stabilized and hence it exists in the keto form (I). Enol form (IV) is stabilized by resonance energy (150.6kJmol^{-1}) of the benzene ring and hence (III) exists in the enol form (IV). (ii) In $\text{H}_2\text{C}=\text{CH}^-$, the carbon atom carrying the $-ve$ charge is sp^2 -hybridized while in $\text{HC}\equiv\text{C}^-$, the carbon atom carrying the $-ve$ charge is sp -hybridized. Since a sp^2 -hybridized carbon is less electronegative than a sp -hybridized carbon, therefore, $\text{H}_2\text{C}=\text{CH}^-$ is a better nucleophile than $\text{HC}\equiv\text{C}^-$.

Q.14 When do we use a fluted filter paper or hot water funnel for filtration?

Answer: To avoid crystallization during filtration, fluted filter paper is used when the volume of the solution to be filtered is small and hot water funnel when the volume is large.

Q.15 How will you purify a liquid having non-volatile impurities?

Answer: Simple distillation will give us the pure liquid while the non-volatile impurities will remain in the flask as residue.

Q.16 Suggest a method to purify: (i) Camphor containing traces of common salt. (ii) Kerosene oil containing water. (iii) A liquid which decomposes at its boiling point.

Answer: (i) Sublimation. Camphor sublimes while common salt remains as residue in the china dish. (ii) Since the two liquids are immiscible, the technique of solvent extraction

with a separating funnel is used. The mixture is thoroughly shaken and the separating funnel is allowed to stand. Kerosene being lighter than water forms the upper layer while water forms the lower layer. The lower water layer is run off when kerosene oil is obtained. It is dried over anhydrous CaCl_2 or MgSO_4 and then distilled to give pure kerosene oil. (iii) Distillation under reduced pressure.

Q.17 A mixture contains two components A and B. The solubilities of A and B in water near their boiling point are 10 grams per 100 mL and 2 g per 100 mL respectively. How will you separate A and B from this mixture?

Answer: Fractional crystallization. When the saturated hot solution of this mixture is allowed to cool, the less soluble component B crystallizes out first leaving the more soluble component A in the mother liquor.

Q.18 Suggest methods for the separation of the following mixtures. (i) A mixture of liquid A (b.p. 365 K) and liquid B (b.p. 356 K). (ii) A mixture of liquid C (b.p. 353 K) and liquid D (b.p. 413 K).

Answer: (i) Fractional distillation because the boiling points of the two liquids differ by just 9° . (ii) Simple distillation since the boiling points of the two liquids are widely apart.

Q.19 How will you purify essential oils?

Answer: Essential oils are volatile and are insoluble in water. Therefore, they are purified by steam distillation.

Q.20 How will you separate a mixture of o-nitrophenol and p-nitrophenol?

Answer: Steam distillation. o-Nitrophenol being steam volatile distils over along with water while p-nitrophenol being non-volatile remains in the flask.

Q.21 (a) Write the IUPAC name of



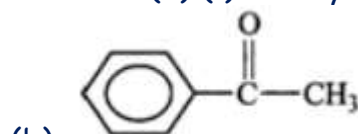
(i)


(b) Out



of which will be eluted first in moderately polar solvent and why?

Answer: (a) (i) Methyl 3-chlorobut-2-en-1-oate (ii) 3-Methylcyclohexyne



(b) has significant dipole moment while  being symmetrical has zero dipole moment. Therefore, di-tert-butyl benzene is non-polar and hence will not be adsorbed strongly on the adsorbent and hence it will be eluted first in moderately polar solvent.

Q.22 A liquid (1.0 g) has three components. Which technique will you employ to separate them?

Answer: Column chromatography.

Q.23 The R_f value of A and B in a mixture determined by TLC in a solvent mixture are 0.65 and 0.42 respectively. If the mixture is separated by column chromatography using the same solvent mixture as a mobile phase, which of the two components, A or B, will elute first? Explain.

Answer: Since the R_f value of A is 0.65, therefore, it is less strongly adsorbed as compared to component B with R_f value of 0.42. Therefore, on extraction of the column, A will elute first.

Q.24 A mixture contains benzoic acid and nitrobenzene. How can this mixture be separated into its constituents by the technique of extraction using an appropriate chemical reagent?

Answer: The mixture is shaken with a dilute solution of NaHCO_3 and extracted with ether or chloroform when nitrobenzene goes into the organic layer. Distillation of the solvent gives nitrobenzene. The filtrate is acidified with dil. HCl when benzoic acid gets precipitated. The solution is cooled and benzoic acid is obtained by filtration.

Q.25 Without using column chromatography, how will you separate a mixture of camphor and benzoic acid?

Answer: Sublimation cannot be used since both camphor and benzoic acid sublime on heating. Therefore, a chemical method using NaHCO_3 solution is used when benzoic acid dissolves leaving camphor behind. The filtrate is cooled and then acidified with dil. HCl to get benzoic acid.

Q.26 Name two compounds which do not contain halogen but give positive Beilstein test.

Answer: Urea and thiourea give positive Beilstein test due to the formation of volatile cupric cyanide.

Q.27 Will sodium cyanide give a positive Lassaigne's test for nitrogen?

Answer: Yes. During fusion with Na metal, the N of the organic compound is actually converted into NaCN which is the primary requirement for Lassaigne's test for nitrogen.

Q.28 How will you test the presence of nitrogen in hydrazine?

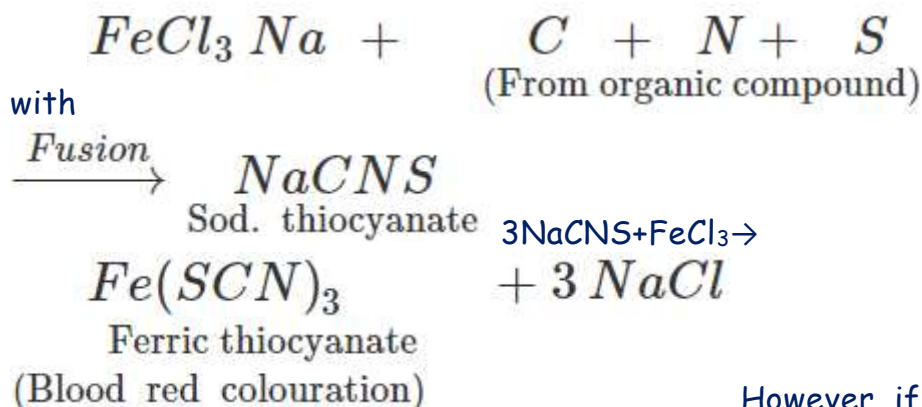
Answer: If hydrazine (NH_2NH_2) is fused with Na metal, it does not form NaCN since it does not contain carbon and hence will not give +ve test for nitrogen. In order to test the presence of N in such compounds, during fusion with Na, some charcoal or preferably starch (which contains C but not N, S, halogens, etc.) is added. Under these conditions, C of starch or charcoal combines with N of the compound to form NaCN which will now give a +ve test for nitrogen.

Q.29 Lassaigne's test is not shown by diazonium salts. Why?

Answer: Diazonium salts usually lose N_2 on heating much before they have a chance to react with fused sodium metal. Therefore, diazonium salts do not show positive Lassaigne's test for nitrogen.

Q.30 Sometimes a red colour is not produced in the Lassaigne's test even if both nitrogen and sulphur are present in the organic compound. Explain.

Answer: In principle, if the organic compound contains both N and S, sodium thiocyanate should be formed in Lassaigne's test and this should give blood red colouration



However, if blood red colouration is not obtained, it does not necessarily mean that S is absent. This is because in presence of excess of sodium metal, sodium thiocyanate initially formed, decomposes to form sodium

cyanide and sodium sulphide. $2\text{Na} + 2\text{NaCNS} \xrightarrow{\Delta} \text{NaCN} + \text{Na}_2\text{S}$ As a result, blood red colouration is not obtained.

Q.31 Why is a freshly prepared saturated solution of ferrous sulphate used in the Lassaigne's test for nitrogen?

Answer: On keeping aq. FeSO_4 solution, it undergoes oxidative-hydrolysis to form basic ferric sulphate $4\text{FeSO}_4 + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{Fe(OH)SO}_4$ The pale yellow colour of Fe^{3+} ions interferes with the light green colour usually obtained in Lassaigne's test.

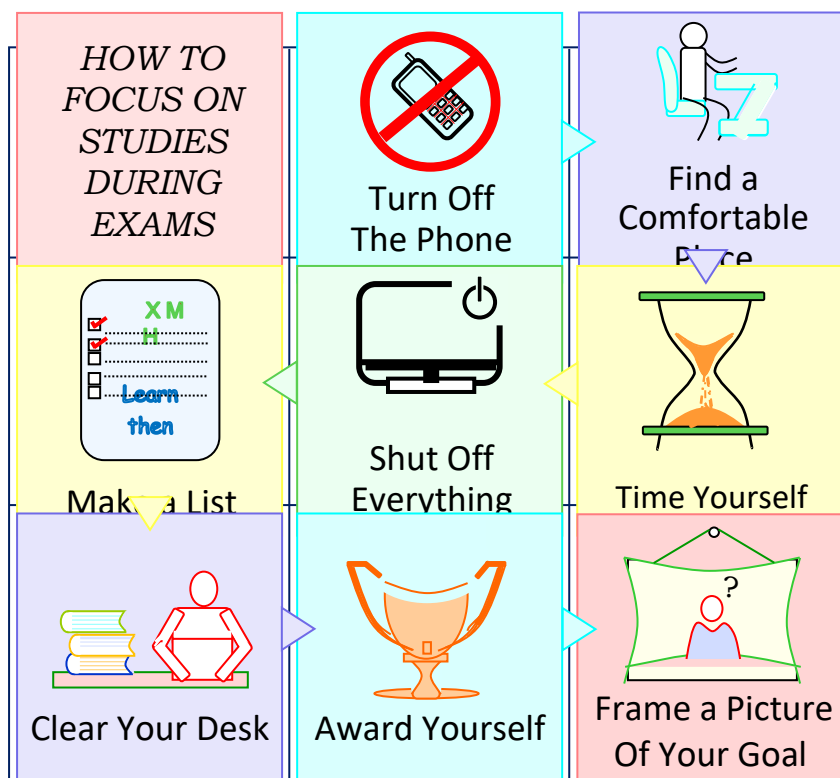
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Illustrations



Ortho-, Para- and Meta- Directors

When a functional group is already present on the aromatic ring, the substitutions occur at specific positions depending on whether the group is an *ortho*-, *meta*-, or a *para*- director.



All the activators are *ortho*-, *para*- director. All the deactivators are *meta*-directors, except the halogens which are deactivators and yet, *ortho*-, *para*-directors.