

I PUC

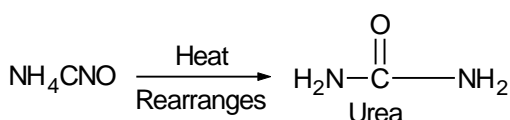
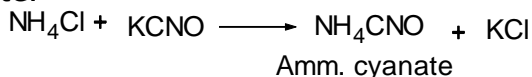
GENERAL ORGANIC CHEMISTRY

- **Vital Force Theory or Berzelius Hypothesis**

Berzelius proposed that organic compounds cannot be synthesized in the laboratory because they required the presence of a mysterious force (called vital force) which exists only in the living organisms.

- **Wohler's Synthesis**

The first organic compound synthesized in the laboratory was Urea. It was synthesized by Wohler, a German chemist by heating a mixture of ammonium chloride and potassium cyanate.



This reaction is called Wohler's synthesis.

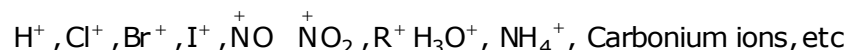
CONCEPTS IN ORGANIC CHEMISTRY

The electronic displacement in covalent bonds may occur either due to the presence of some atom or group in the molecule or under the influence of attacking reagent. As a result of these electron displacements, centres of different electron densities are created and these centres are susceptible to attack by the reagents.

Types of Reagent:

(A) **Electrophiles:** Electron deficient species are known as electrophiles. It may be positively charged or neutral also. Electrophile attack at electron rich centre of substrate. (These are also called electron loving group)

eg : **Positively charged electrophiles :**



Neutral electrophiles : $\overset{\bullet}{\text{R}}$ (free radicals) $\overset{\bullet}{\text{C}}\text{R}_2$ (carbene) , $\text{R}-\overset{\cdot\cdot}{\text{N}}$: (Nitrenes), BF_3 , AlCl_3 , FeCl_3 , ZnCl_2 , SnCl_4 etc.

(B) **Nucleophiles :** Electron rich species are called as nucleophiles. It may be negatively charged or neutral having at least one pair of electrons. Nucleophile attack at electron deficient centre of substrate (These are also called nucleus loving group).

e.g: **Negatively charged nucleophiles :**



Neutral Nucleophiles: $\text{H}_2\ddot{\text{O}}$: , $\ddot{\text{N}}\text{H}_3$, $\text{R}\ddot{\text{N}}\text{H}_2$, $\text{R}\ddot{\text{O}}\text{H}$, $\text{R}\ddot{\text{S}}\text{H}$, RMgX , RLi , NaBH_4 , LiAlH_4

Nucleophiles always attack the substrate molecule at the site of lowest electron density.

Types of organic reactions

Organic reactions are mainly classified into four types

- 1) Substitution or Displacement reactions
- 2) Addition reactions
- 3) Elimination reactions
- 4) Rearrangement reactions

Substitution reactions:

The replacement of atom or group of atoms by a different atom or group of atoms (substituent) is known as substitution reaction.

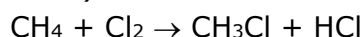
Depending upon the nature of substituent's substitution reactions are classified into three types.

1. Free radical substitution reactions
2. Electrophilic substitution reactions
3. Nucleophilic substitution reactions

Free radical substitution reaction

Substitution reactions which involve free radicals is called free radical substitution reaction.

For example: Reaction between methane and chlorine in the presence of uv light or sunlight, methyl chloride is formed. (hydrogen atom of methane is replaced by chlorine atom)

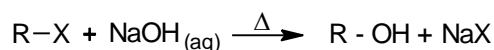


Nucleophilic substitution reaction

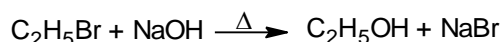
Substitution reaction in which an atom or group of atoms replaced by nucleophiles is called nucleophilic substitution reaction.

For example:

- 1) Haloalkanes when heated with aqueous NaOH or KOH corresponding alcohol is formed.



when bromo ethane is heated with aqueous KOH, ethanol is formed



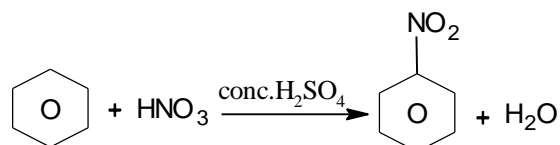
During the reaction halogen atom is replaced by -OH (nucleophiles)

Electrophilic substitution reaction

A reaction in which an atom is replaced by electrophile is called electrophilic substitution reaction.

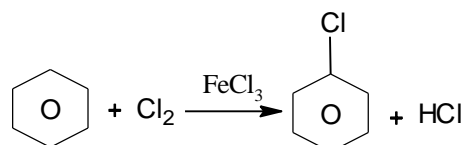
For example:

- 1) Benzene reacts with concentrated nitric acid and concentrated sulphuric acid to form nitrobenzene.



Hydrogen atom of benzene is replaced by NO_2^+ group (electrophile)

- 2) Benzene reacts with chlorine in the presence of halogene carrier like ferric chloride to form chlorobenzene.



(H-atom is replaced by Cl^+ (electrophile)).

Addition reactions:

Addition reactions are those in which the attacking reagent adds up to the substrate molecule without elimination to give a single molecule of the product. Such reactions are given by those compounds which possess double or triple bonds (π -bonded). In the process a triple bond may be converted into double bond or single bonds and a double bond is

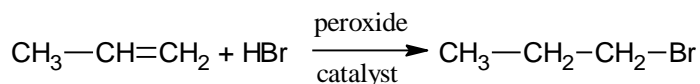
converted into single bonds. For each π - bond of the molecule two sigma bonds are formed and the hybridisation state of carbon atoms changes from sp to sp^2 and sp^2 to sp^3 .

There are three types of addition reactions

- 1) Free radical addition reactions
- 2) Nucleophilic addition reactions
- 3) Electrophilic addition reactions

For examples:

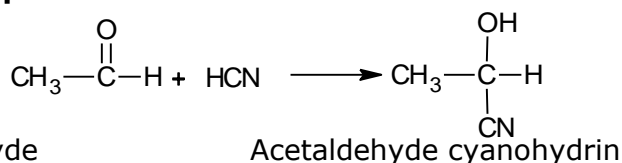
1) Free radical addition reaction



Propene

Bromopropane

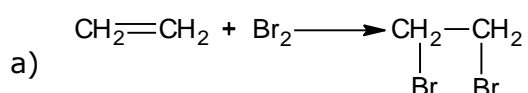
2) Nucleophilic addition reaction



Acetaldehyde

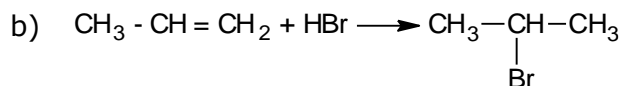
Acetaldehyde cyanohydrin

3) Electrophilic addition reaction



Ethylene

(Ethylene bromide or
1, 2 dibromoethane)



(Propene)

(2-Bromopropane)

Elimination reactions:

An elimination reaction is one in which two atoms or groups of atoms are removed from the same atom or adjacent carbon atoms resulting in the formation of multiple bonds (double or triple bonds). In this process two sigma bonds are lost and a new π bond is formed and the hybridization state changes from sp^3 to sp^2 and sp^2 to sp .

There are two types of elimination reactions

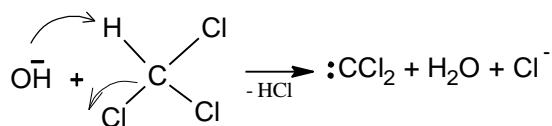
- 1) E_1 reactions (Unimolecular elimination)
- 2) E_2 reactions (Bimolecular elimination)

Depending upon the relative position of atoms or groups eliminated, these reactions further classified as α , β and γ eliminations.

α - Elimination:

It is the removal of two atoms or groups of atoms from the same carbon atom of the compound to form carbene.

For example: Base catalysed dehydrohalogenation of chloroform



(Dichlorocarbene)

Note:

- 1) Dichlorocarbene is the reactive intermediate involved in carbylamine reaction and Reimer Tiemann reaction

β - Elimination reactions:

In these reactions two atoms or groups of atoms are removed from the adjacent carbon atoms (α , β) in the substrate molecule to form multiple bond compound.

Example:

- (i) **Dehalogenation:** (Removal of halogens) when 1, 2 dibromoethane is heated with zinc dust, ethene is formed.
- (ii) **Dehydrohalogenation** (Removal of halogen and hydrogen) when bromoethane is heated with alcoholic potash, ethene is formed.
- (iii) **Dehydration (Removal of water molecule)**
When acetamide is heated with phosphorus pentoxide methyl cyanide is formed.
- (iv) **n-Propyl alcohol** when heated with conc. H_2SO_4 at 170°C propene is formed.

γ - Elimination reactions:

In this type of elimination two atoms or groups are removed from α - and γ - positions and produces a cyclic structure.

For example

When 1, 3 dibromopropane is heated with zinc dust cyclopropane is formed. (Freund reaction)

Rearrangement reactions:

The reactions which involve the migration of an atom or group from one site to another within the molecule resulting in a new molecular structure are known as rearrangement reactions. The new compound is actually the structural isomer of the original one.

For example:

1. When n-Butane is heated with anhydrous AlCl_3 to give isobutene.
2. When But-1-ene is heated with AlCl_3 or $\text{Al}_2(\text{SO}_4)_3$ forms But-2-ene and 2-methyl propene.
3. Ammonium cyanate on heating forms urea

Electronic displacement in covalent bonds

The electronic displacements in covalent bonds may occur either due to the presence of some atom or group in the molecule or under the influence of attacking reagent.

As a result of these electron displacements, centres are susceptible to attack by the reagents. The factors which create the centres of different electron densities in the substrate are mainly,

1. Inductive effect
2. Electrometric effect
3. Mesomeric effect
4. Hyperconjugation effect

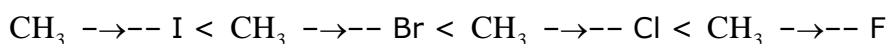
Inductive effect

- The permanent effect whereby the polarity is induced on the carbon atom and the substituent attached to it, due to the minor displacement of the bonding electron pair towards more electronegative atom is known as inductive effect.
- Inductive effect involves sigma electrons of a single bond.
- Inductive effect is of two types a) - I effect b) + I effect

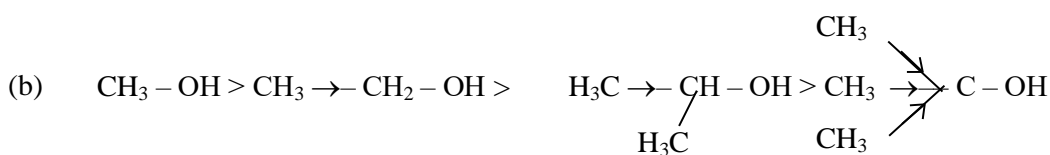
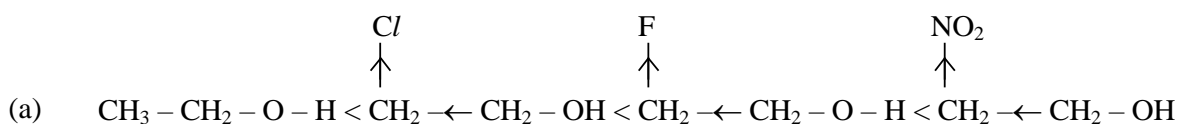
- The inductive effect where the electron displacement takes place towards the substituent group is called **-I effect**. Here the substituent group acquires a partial negative charge and the carbon atom to which the substituent group is attached gets partial positive charge.
- The groups that show -I effect (in the decreasing order) when joined to carbon atom are $-\text{NO}_2 > -\text{CN} > -\text{F} > -\text{COOH} > -\text{Cl} > -\text{Br} > -\text{I} > -\text{OCH}_3 > -\text{OH} > -\text{C}_6\text{H}_5$
- The inductive effect where the electron displacement takes place away from the substituent group is called **+I effect**. Here the substituent group acquires a partial positive charge and the carbon atom to which the substituent group is attached gets a partial negative charge.
Example: $(\text{CH}_3)_3\text{C}^- > (\text{CH}_3)_2\text{CH}^- > \text{CH}_3\text{CH}_2^- > \text{CH}_3^-$

PROPERTIES EFFECTED BY I - EFFECT :

(I) **Dipole moment :** Greater - I effect results greater dipole moment. e.g.,



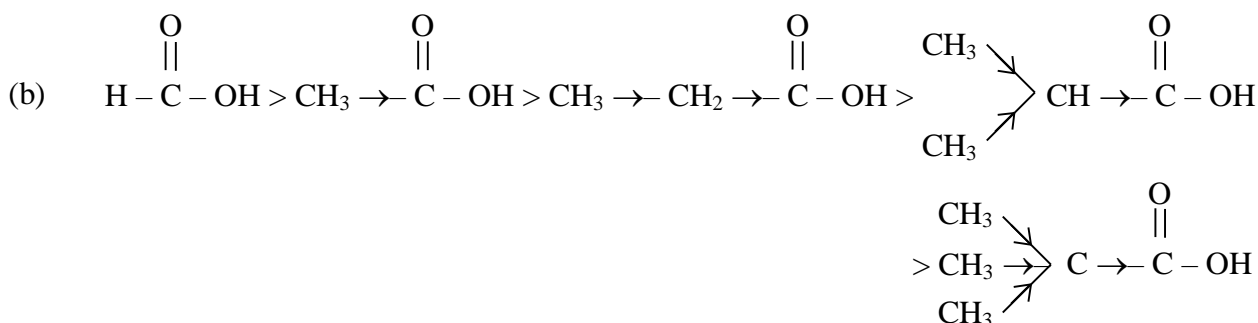
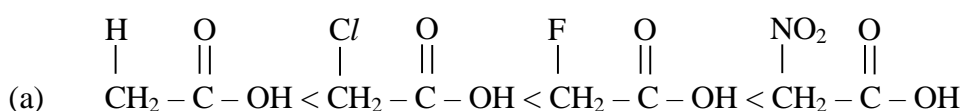
(II) **Acidic character of alcohol :** Acidic character of alcohol is supported by -I effect i.e. great -I effect results greater acidic character of alcohol. Similarly +I effect decreases the acidic character of alcohol. e.g.,



(III) **Acidic character of carboxylic acid:**

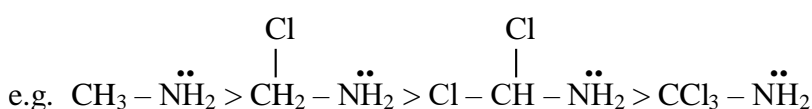
Acidic character of carboxylic acid increases with increasing - I effect and decreases with increasing + I effect.

e.g.

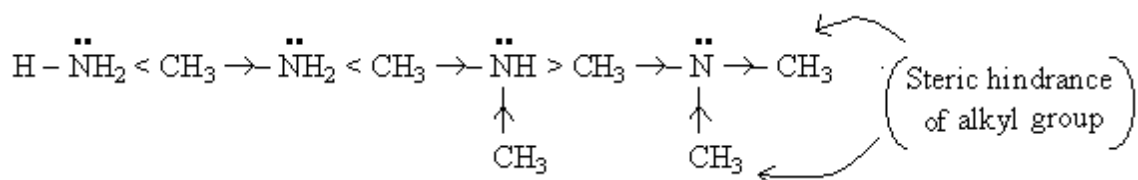


(IV) **Basic character of amine ($\text{C}-\ddot{\text{N}}<$):**

Amines are generally Lewis bases. Their basic character increases with increasing + I effect generally and decreases with increasing - I effect.

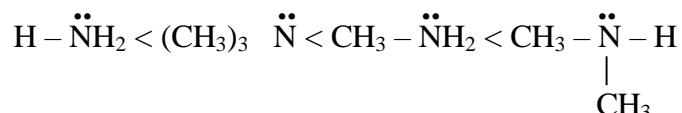


Similarly,



less than expected basic character of $\text{CH}_3 - \ddot{\text{N}}(\text{CH}_3)_2$ can be explained on the basis of

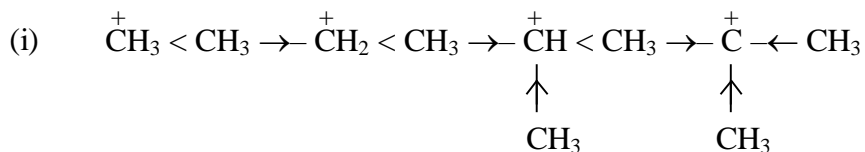
crowding of three bulkier- CH_3 group which make uneasy to attack the proton on lone pair the actual order of basic strength is



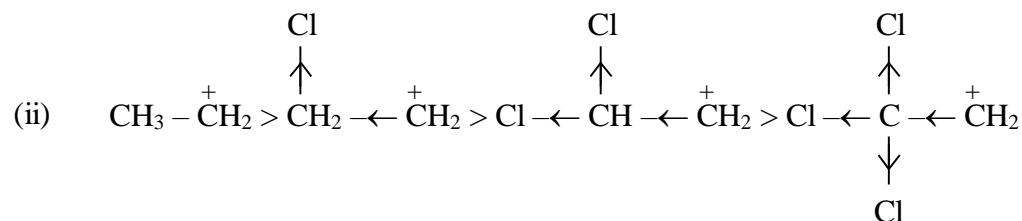
NOTE: Due to strong -I effect of CF_3 group $\text{CF}_3 - \ddot{\text{N}}(\text{CF}_3)_2$ does not exhibit any basic character.

(V) Stability of carbo-cation :

+I effect tends to decrease positive charge from +ve charge carbon and thus stability increases. But -I effect tends to increase the (+) ve charge at +ve charge carbon and results decreasing stability of carbocation.



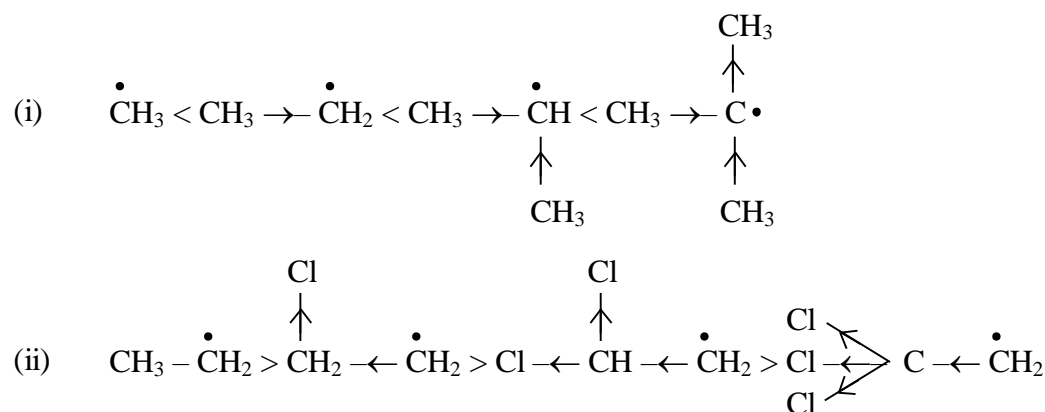
e.g. -



(VI) Stability of carbon free radical :

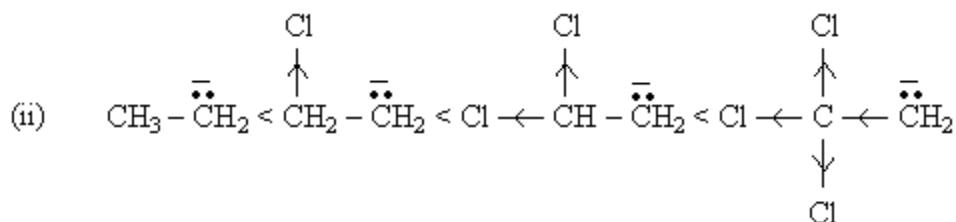
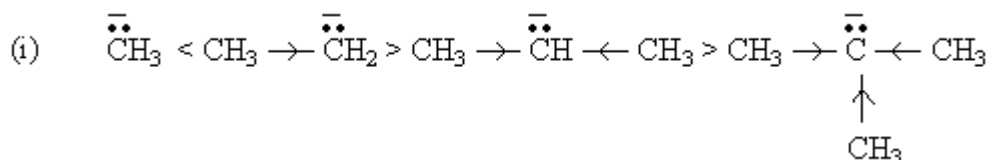
Stability of carbon free radical increases with +I group and decreases with -I group.

e.g. -



(VII) Stability of carbanion:

Stability of carbanion increases with increasing -I effect and decreases with increasing effect.

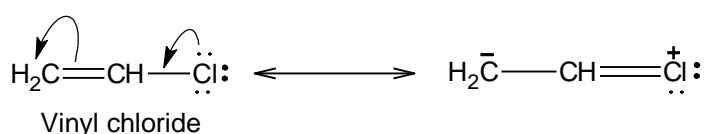


Significance of inductive effect

- Inductive effect weakens as the distance from the substituent group increases. In 1-chlorobutane, chlorine imparts maximum positive charge on C₁ and minimum on C₄ and becomes insignificant after C₄.
 - If the groups showing + I effect are present on amines their basic nature increases. Example: Basic strength of amines is NH₃ < CH₃ - NH₂ < (CH₃)₂ NH
 - Groups showing -I effect increases the strength of acids and vice versa. Hence acidic strength of following acid is CH₃COOH < ClCH₂COOH < Cl₂CH - COOH < Cl₃C-COOH
- Inductive effect brings changes in physical properties such as dipole moment, solubility etc. Carbon-hydrogen bond is taken as a standard of inductive effect. Zero effect is assumed for this bond.

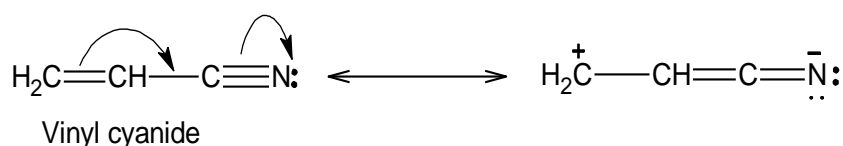
Mesomeric effect (Resonance effect)

- The permanent effect whereby the polarity is produced in a molecule as a result of interaction between two bonds or a bond and a lone pair of electrons is known as mesomeric effect. This effect is transmitted along the chain.
- Mesomeric effect is of two types: (i) +M effect (ii) - M effect.
- A group or atom said to show **+M effect** when the direction of electron displacement takes place away from it.

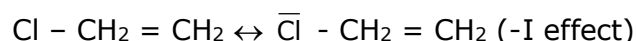


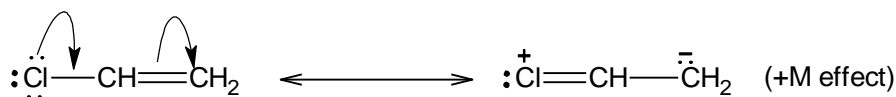
- Groups showing + M effect are - Cl, - Br, - I, - NH₂, - OCH₃.
- A group or atom said to show **- M effect** when the direction of electron displacement takes place towards it.

- Groups showing - M effect are - CHO, - COOH, - CN, - NO₂, - SO₃H.



The inductive and mesomeric effects, when present together, may act in the same direction or oppose each other. The mesomeric effect is more powerful than the former.





Electromeric effect

- The effect, which causes temporary polarization in the molecule having multiple bond by the shift of an electron pair of the multiple bond from one atom to the other, under the influence of an attacking reagent, is called electromeric effect.
- Electromeric effect is of two types +E effect and -E effect.
- An attacking reagent is said to have **+E effect** when the direction of electron displacement is towards it.
- Positive groups (electrophiles) when approach a multiple bond shows this effect. When H^+ approaches alkene, shows **+ E effect**.
- An attacking reagent is said to have **- E effect** when the direction of electron displacement is away from it. Negative groups (nucleophiles) when approach multiple bond show this effect.
- When CN^- approaches carbonyl group shows **-E effect**.

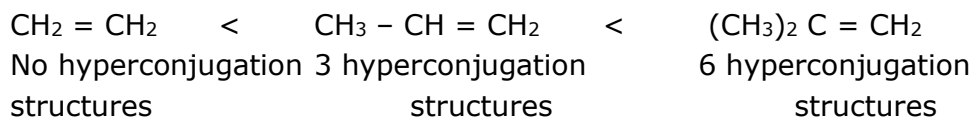
Inductive effect and electromeric effect simultaneously operate, usually electromeric effect predominates.

Hyperconjugative effect (Baker-Nathan effect or No bond resonance.)

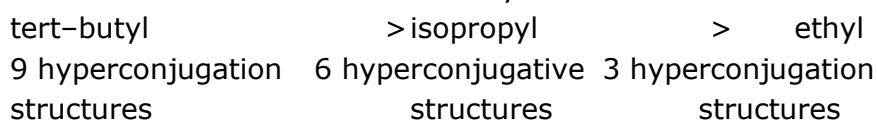
- It is the phenomenon in which electron displacement takes place resulting in the conjugation between electrons and electrons. This effect is also called Baker-Nathan effect or No bond resonance. Only the electrons of C-H bond give rise to this type of effect.
- The ortho-para directing nature of $-\text{CH}_3$ group can be explained by the hyperconjugative effect or no-bond resonance.

Applications of hyperconjugation effect.

- Stability of alkenes:** More number of methyl groups attached to double bonded carbon atom more would be the stability of alkene.



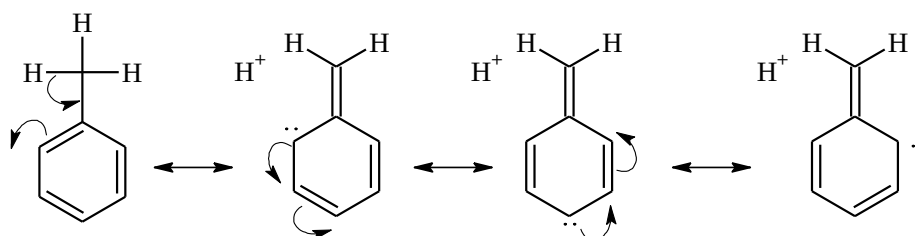
- Stability of carbonium ions:** More number of hyperconjugation structures of the carbocation more will be its stability.



- Bond lengths:** The bond length in a molecule changes if there is hyperconjugation. In

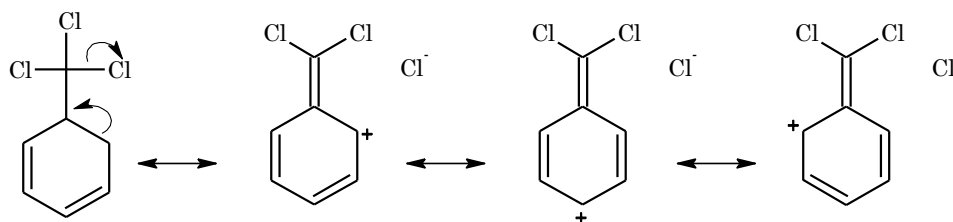
$\text{C}^3\text{H}_3 - \text{C}^2\text{H} = \text{C}^1\text{H}_2$, the $\text{C}^1 - \text{C}^2$ bond length is found to be more than 1.34 \AA (normal C = C bond length) while the $\text{C}^2 - \text{C}^3$ bond distance is less than 1.54 \AA (normal C - C bond length).

- 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 $-CCl_3$ 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.

Effect of substituents on further substitution in benzene-orientation effect

Depending on the directing nature, the groups are classified into 2 categories.

- **Ortho-para directors:** These groups contain key atom containing lone pair of electrons. These direct the incoming groups to ortho and para positions.

Examples: $-CH_3$, $-Cl$, $-NH_2$, $-OH$

- **Meta directors:** In meta directing groups the atoms of the substituent group which are attached to the key atom are more electronegative than the key atom. These electronegative atoms are connected to the key atom by multiple bonds. These direct the incoming groups to meta position.

Examples: $-NO_2$, $-CN$, $-COOH$, $-CHO$, $-SO_3H$

Activating and deactivating influence of substituents

- The electron donating groups increase the electron density on the benzene ring and hence increasing the activity of the benzene ring for electrophilic substitution. If these groups are present on the ring the reaction is faster than the reactions in the benzene ring. The groups are called activating groups or ring activators.
- On the other hand the electron-withdrawing groups decrease the electron density on the benzene ring and hence decreasing the activity of the benzene ring for electrophilic substitution. If these groups are present on the ring the reaction is slower than the reactions in the benzene ring. The groups are called deactivating groups or ring deactivators.

Examples :

Strongly activating: $-NH_2$, $-NHR$, $-NR_2$, $-OH$, $-O^-$

Moderately activating : $-NHCOCH_3$, $-NHCOR$, $-OCH_3$, $-OR$

Weakly activating : $-CH_3$, $-C_2H_5$, $-R$, $-C_6H_5$

Strongly deactivating : $-NO_2$, $-CF_3$, $-CCl_3$

Moderately deactivating : $-CN$, $-SO_3H$, $-COOH$, $-COOR$, $-CHO$, $-COR$

Weakly deactivating : $-F$, $-Cl$, $-Br$, $-I$

- **Cl is an ortho para directing group but deactivates the benzene ring**
- In chlorobenzene both +M and -I effects operate. Out of these two effects viz. electron donating nature (mesomeric effect, + M effect) and electron withdrawing nature (inductive effect, - I effect) the latter (inductive effect) predominates. Hence - Cl acts as a ring deactivator.

DETECTION AND ESTIMATION OF ELEMENTS

Detection of carbon and hydrogen by copper oxide test

The given organic compound is heated with cupric oxide in a hard glass tube . Cupric oxide oxidises carbon and hydrogen of the organic compound to carbon dioxide and water respectively.

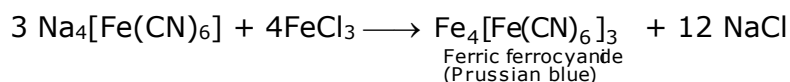
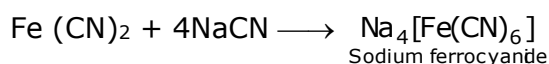
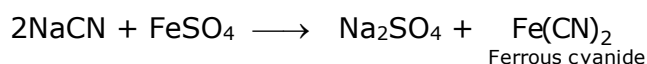
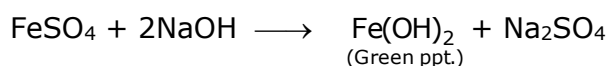
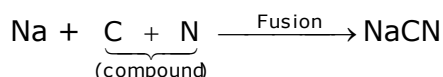
CO₂ formed is bubbled through lime water which turns milky. If hydrogen is present, water is formed and this is confirmed by anhydrous copper sulphate which turns blue by absorbing water.

Detection of nitrogen, sulphur and halogens by Lassaigne's test

Nitrogen sulphur and halogens in the organic compound can be detected by Lassaigne's test. In this method sodium fusion extract of the organic compound is prepared. During the fusion reaction nitrogen is converted to sodium cyanide, sulphur to sodium sulphide and halogen to sodium halides. By testing of these radicals, the element present in the given organic compound can be detected.

Detection of nitrogen

Sodium fusion extract + freshly prepared ferrous sulphate solution. Heated. Added a drop of ferric chloride. Acidified with hydrochloric acid	Blue precipitate or blue colour is obtained
---	---

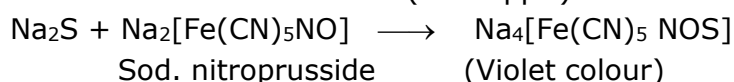
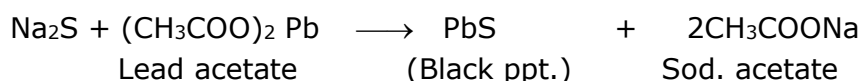
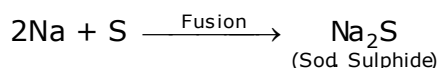


Note: The blue colour is formed due to the formation of ferric ferrocyanide

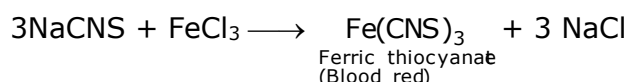
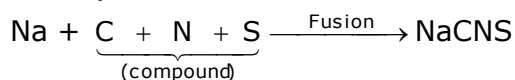
Fe₄ [Fe (CN)₆]₃(prussian blue)

Detection of sulphur

a	Lead acetate test: Sodium fusion extract is acidified with acetic acid and lead acetate	Black precipitate of lead Sulphide is formed
b	Sodium nitroprusside test: Sodium fusion extract + sodium nitroprusside	Purple colour is obtained

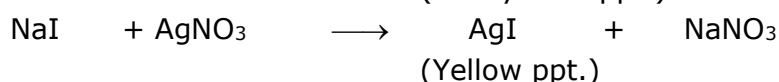
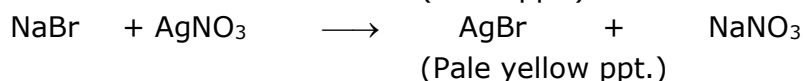
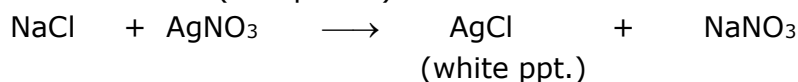
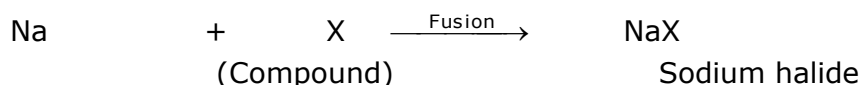


If organic compound contains both nitrogen and sulphur, they combine with sodium metal to form sodium thiocyanate. It reacts with ferric chloride to form ferric thiocyanate (blood red colour).

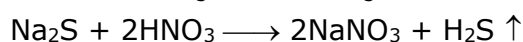
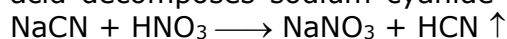


Detection of halogens

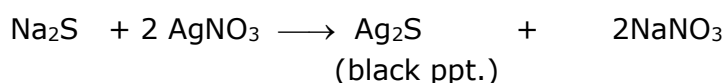
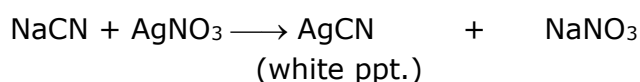
Sodium fusion extract + dilute nitric acid. Boiled, cooled. Added silver nitrate solution	Curdy white precipitate soluble in excess of ammonia.	Chlorine is present
	Pale yellow precipitate sparingly soluble in ammonia	Bromine is present
	Yellow precipitate insoluble in ammonia	Iodine is present



In case nitrogen and sulphur are also present along with the halogens in the organic compound, the Lassaigne's extract will contain sodium sulphide and sodium cyanide. Nitric acid decomposes sodium cyanide and sodium sulphide to form vapours of HCN and H₂S



In case, these are not decomposed, they will silver nitrate solution to form precipitates that will interfere with the colours of different silver halides.



Estimation of elements

Estimation of carbon and hydrogen: (Leibig's method)

Principle: A known mass of the organic compound is oxidised with cupric oxide in CO₂ free atmosphere. Carbon gets oxidised to carbon dioxide and hydrogen to water. The products obtained are passed through anhydrous calcium chloride where water gets absorbed and

then through potassium hydroxide solution where carbon dioxide is absorbed. The increase in the mass of calcium chloride and potassium hydroxide bulbs are determined. These correspond to the mass of water and carbon dioxide respectively. Knowing the increase in mass, the percentage of carbon and hydrogen in the given organic compound can be determined.

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

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

Example:

- 1) **0.2346 g an organic compound containing carbon, hydrogen and oxygen only was analysed by the combustion method. The increase in weight of the U-tube and the potash bulbs at the end of the operation was found to be 0.2754 g and 0.4488 g respectively. Determine the percentage composition of the compound.**

Solution: Mass of CO₂ (increase in mass of potash bulb) = 0.4488 g

Mass of H₂O (increase in mass of U-tube) = 0.2754 g

$$\therefore \text{Percentage of carbon} = \frac{12}{44} \times \frac{0.4488}{0.2346} \times 100 = 52.18\%$$

$$\text{Percentage of Hydrogen} = \frac{2}{18} \times \frac{0.2754}{0.2346} \times 100 = 13.04\%$$

$$\text{Percentage of Oxygen} = 100 - (52.18 + 13.04) = 34.78\%$$

- 2) **2.390 gram of an organic compound on combustion gave 0.88 gram of carbon dioxide and 0.18 gram of water. Calculate the percentage composition of carbon and hydrogen.**

[Atomic mass of C = 12, H = 1, O = 16]

Solution:

$$\begin{aligned} \text{Percentage of carbon} &= \frac{12}{44} \times \frac{\text{Weight of CO}_2}{\text{Weight of organic compound}} \times 100 \\ &= \frac{12}{44} \times \frac{0.88}{2.390} \times 100 = 10.04\% \end{aligned}$$

$$\begin{aligned} \text{Percentage of hydrogen} &= \frac{2}{18} \times \frac{\text{Weight of H}_2\text{O}}{\text{Weight of organic substance}} \times 100 \\ &= \frac{2}{18} \times \frac{0.18}{2.390} \times 100 = 0.836\% \end{aligned}$$

Estimation of nitrogen (Kjeldhal method)

Principle: A known mass of organic compound containing nitrogen is heated with concentrated sulphuric acid. Nitrogen gets converted into ammonium sulphate. It is then heated with sodium hydroxide. Ammonia gas is liberated. It is made to react with excess of standard hydrochloric acid. The amount of hydrochloric acid neutralized by ammonia is calculated by back titration. Knowing the amount of hydrochloric acid used up and hence the amount of ammonia is formed, the percentage of nitrogen can be calculated.

$$\% \text{ N}_2 = \frac{1.4 \times \text{normality of acid} \times \text{volume of acid used to neutralise NH}_3}{\text{mass of substance taken}}$$

In organic compounds Percentage of nitrogen can be calculated using

$$\therefore \text{Percentage of nitrogen} = \frac{\text{Mass of nitrogen}}{\text{Mass of organic substance taken}} \times 100$$

Estimation of Nitrogen:

Estimation of Nitrogen can be done by two methods

- 1) **Duma's method:** In Duma's method, organic compound is heated with dry cupric oxide in a combustion tube in atmosphere of CO₂ on heating, the carbon and hydrogen are oxidised to CO₂ and H₂O respectively, while nitrogen is set free. Any oxides of nitrogen produced during combustion are reduced back to nitrogen by passing the sample over a heated copper gauze. The gaseous mixture is collected in a Schiff's nitrometer which contains a solution of potassium hydroxide. The mercury at the bottom of nitrometer does not allow the potassium hydroxide solution to move from the nitrometer. All gases except nitrogen are absorbed in the KOH solution. The volume of nitrogen gas collected at the top of the tube is measured. This volume is then reduced to STP by applying gas equation.

$$\text{Percentage of nitrogen} = \frac{\text{mass of nitrogen}}{\text{mass of organic compound}} \times 100 = \frac{28 \times V_0}{22400} \times \frac{100}{m}$$

Estimation of Halogens- Carius method

In this method a known mass of the organic compound is taken in a hard glass sealed tube (Carius tube) with fuming nitric acid in the presence of silver nitrate. The Carius tube is then heated in a furnace on heating carbon and hydrogen are oxidised to CO₂ and H₂O respectively while halogens form a precipitate of silver halide (AgX). The silver halide precipitated is filtered and washed with water and alcohol. It is then dried and weighed.

Observations and calculations

Let the mass of the organic compound = 'a' g

Mass of silver halide (AgX) obtained = 'b' g

108 + x parts by mass of AgX contains X parts of halogen (x is the atomic mass of the halogen atom and 108 is the atomic mass of Ag)

(108 + x) g of AgX contains 'x' g of X

Therefore 'b' g of AgX contains $\frac{x}{108 + x} \times b$ g of X

Percentage of halogen X = $\frac{x}{(108 + x)} \times b \times \frac{100}{a}$

Percentage of halogen = $\frac{\text{Atomic mass of halogen} \times \text{mass of silver halide} \times 100}{\text{molecular mass of silver halide} \times \text{mass of organic compound}}$

$$\% \text{ of Chlorine} = \frac{35.5}{143.5} \times \frac{\text{weight of AgCl}}{\text{weight of compound}} \times 100$$

$$\% \text{ of bromine} = \frac{80}{188} \times \frac{\text{weight of AgBr}}{\text{weight of compound}} \times 100$$

$$\% \text{ of Iodine} = \frac{127}{235} \times \frac{\text{weight of AgI}}{\text{weight of compound}} \times 100$$

Estimation of Sulphur – Carius method

A known mass of the organic compound is heated with fuming nitric acid in the carius tube. Sulphur is converted to sulphuric acid, which is precipitated by barium chloride as barium sulphate. The precipitate of barium sulphate is filtered, washed, dried and weighed from the mass of barium sulphate obtained, the percentage of sulphur can be calculated.

Observations and calculations

Mass of organic compound = 'x' g

Mass of barium sulphate formed = 'y' g

Molecular mass of BaSO₄ = 233

$$\therefore \text{Percentage of Sulphur in organic compound} = \frac{y \times 32}{233} \times \frac{100}{x}$$

Estimation of Phosphorus – Carius method

A known mass of the organic compound is heated with fuming nitric acid. The phosphorus in the organic compound is oxidised to phosphoric acid. It is then heated with magnesia mixture. A precipitate of magnesium ammonium phosphate (MgNH_4PO_4) is obtained. It is filtered, washed, dried and then ignited to give magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$) which is weighed and the percentage of Phosphorus is calculated.

Observations and calculations

Mass of organic compound = 'x' g

Mass of $\text{Mg}_2\text{P}_2\text{O}_7$ obtained on ignition = 'y' g

Atomic mass of Phosphorus = 31

Molecular mass of $\text{Mg}_2\text{P}_2\text{O}_7$ = 222

$$\text{Percentage of phosphorus} = \frac{62 \times y}{222} \times \frac{100}{x}$$

Alternate method:

Phosphoric acid may be precipitated as ammonium phosphomolybdate ($(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{M}_0\text{O}_3$) by adding ammonia and ammonium molybdate

Atomic mass of Phosphorus = 31

Molecular mass of ammonium phosphomolybdate = 1877

$$\therefore \text{Percentage of phosphorus} = \frac{31}{1877} \times \frac{\text{mass of ammonium phosphomolybdate}}{\text{mass of organic compound}} \times 100$$

Estimation of oxygen

The percentage of oxygen in an organic compound is found indirectly by the difference between 100 and total percentage of other elements. However, it can be estimated directly by the following method.

A known amount of the organic compound is decomposed by heating in nitrogen gas. The mixture of the gaseous product formed is passed over red hot coke when all the oxygen is converted into carbon monoxide.

The mixture is then passed through warm iodine pentoxide (I_2O_5) when carbon monoxide is oxidised to carbon dioxide and iodine is reduced.

The percentage of oxygen can be calculated from the amount of carbon dioxide or iodine produced.

Mass of the organic compound = 'x' g

Mass of carbon dioxide produced = 'y' g

$$\text{Percentage of oxygen} = \frac{y \times 32}{44} \times \frac{100}{x}$$

PURIFICATION METHODS

The organic compounds obtained from natural sources or synthesized in the laboratories are contaminated with impurities. They are purified by different methods.

I) Methods of purification of solids

1) crystallization:

It is used to purify organic solids which dissolve in a suitable solvent while impurities do not dissolve.

The solubility of organic compound should increase with increase of temperature. A hot saturated solution of organic compound is prepared & the insoluble impurities are removed by filtration in the hot condition. On cooling the solution, as the solubility of organic compound decreases, the crystals of organic compound are formed in pure state. Water, acetone, alcohol, ether etc are used as solvents.

2) Fractional crystallization:

It is used to separate a mixture of organic solids which differ in their solubilities in a solvent. The compound having less solubility crystallizes out first on cooling & on further cooling the other substance with higher solubility crystallizes out.

3) Sublimation:

It is used to purify solids which on heating directly form their vapours. Vapours on cooling give back pure solid. Impurities should be non volatile.

Camphor, naphthalene, benzoic acid, anthracene, phthalic anhydride, iodine, anthraquinone etc are purified by sublimation.

4) Filtration:

It is used to separate an insoluble solid component of the mixture from the soluble component in a given solvent. Benzoic acid is soluble in hot water & can be separated from insoluble anthracene by filtration after dissolving in hot water & followed by crystallisation of benzoic acid by cooling. Urea is soluble in water & can be separated from insoluble naphthalene by filtration.

Filtration under reduced pressure is done using Buchner funnel.

II) Methods of purification of liquids

1) Simple distillation:

The vapourisation of a liquid by heating and subsequent condensation of vapour by cooling is known as distillation.

The liquids boiling under normal temperature & pressure without decomposition & containing non volatile impurities are purified by simple distillation.

Distillation is also used to separate a mixture of organic liquids which have considerable difference in boiling points.

2) Fractional distillation:

It is used to separate liquid mixtures which contain the components with close difference in boiling points. Eg water (b.pt. 100°C) & alcohol (b.pt. 78°C).

Acetone (b.pt. 60°C) & methanol (b.pt. 65°C) The vapours of the liquids pass through the fractionating column which provides more space for cooling. The vapours of high boiling fractions condense & fall back into distillation flask. The process is repeated till fractions of high volatility go up followed by lower volatility. They are collected separately. Fraction distillation is used in separating the components in petroleum refining.

3) Distillation under reduced pressure (or) Vacuum distillation :

This method is used to purify such liquids which decompose below their normal boiling points. At a reduced pressure the boiling point of a liquid is also reduced, hence its decomposition is avoided.

Eg. Glycerol, H₂O₂, Bromobenzene etc.

Glycerol which boils at 290°C with partial decomposition can be distilled without decomposition at 180°C under reduced pressure of 12 mm.

4) Steam distillation:

This method is used to such liquids which are insoluble in water, steam volatile, have high molecular weight & possess high vapour pressure at the boiling point of water. They should contain impurities which are non steam volatile.

The liquid boils when its vapour pressure becomes equal to the atmospheric pressure. For a mixture of liquid (P₁) and steam (P₂) at boiling point .

External pressure (P) = P₁ + P₂.

Hence liquid will boil at lower temperature than its normal boiling point.

The proportion of the organic substance that distils over with steam is related to the vapour pressure as well as molecular masses as

$$\frac{\omega_1}{\omega_2} = \frac{P_1 M_1}{P_2 M_2} . P_1 \text{ \& } P_2 \text{ represent vapour pressures of organic liquid \& steam respectively. } M_1$$

\& M₂ represent molar mass of organic compound \& water respectively if their corresponding weights are ω_1 \& ω_2 .

It is used in the extraction of oils from plants \& flowers and in the extraction of liquids like aniline, nitrobenzene, turpentine oil etc.

It is used separate ortho nitrophenol (steam volatile) from para nitro phenol (steam non volatile)

5) Differential extractions (solvent extraction)

Solvent extraction is used to extract traces of organic compounds from aqueous solutions. An organic solvent, immiscible with H₂O and having more solubility of the organic compound in it is used for the purpose. To the aqueous solution having the organic compound, an organic solvent is added in the separating funnel. The compound, which is more soluble in organic solvent, passes into it. The two layers (aqueous and organics) are separated. Organic solvent is distilled off to obtain the pure compound.

If the compound is less soluble in organic solvent, a large amount of solvent will be required; continuous extraction technique is used in such cases where, the same solvent is repeatedly used.

Multiple extractions are more efficient than single extraction.

e.g., if 200 ml organic solvent is to be used, it will give more amount of separated compound if used in aliquots of 20 ml each for 10 times in comparison to 200 mL × 1 time.

Aqueous solution of benzoic acid can be extracted with benzene.

I₂ can be extracted from dil. aq. solution (slightly soluble in water) using CCl₄.

6) Chromatography

(Greek, chroma = colour, graphein = to write)

Since, for the first time it was used for the separation of coloured compounds (chlorophylls) from plants by a Russian botanist Mikhail Tswett (1903), hence assigned the name.

The objectives of chromatography are:

- To separate mixtures into compounds (Separation)
- To purify them (Purification)
- To check their presence/identity (Identification)

It is efficient for even very small concentrations (upto $\mu\text{g L}^{-1}$).

The mixture is applied onto a stationary phase (adsorbent). Suitable solvents or a mixture of solvents (mobile phase) is passed over it slowly. The components of the mixture get separated gradually one after another in the order of their degree of interaction with adsorbent and mobile phase.

Broadly chromatography can be divided into:

Type of chromatography	Stationary phase	Mobile phase	Uses
Column Chrom.	Solid	Liquid	Large scale separation
HPLC	Solid	Liquid	Qualitative & quantitative analyses
TLC	Liquid	Gas	Quantitative analysis
GLC	Liquid	Gas	Qualitative & quantitative
Paper	Liquid	Liquid	Qualitative & quantitative analyses of polar organic & inorganic compounds

a) Column Chromatography

The mixture to be separated is made to adsorb over a column of adsorbent (stationary phase), packed in a glass tube. Some adsorbents are alumina, silica gel, calcium carbonate, magnesium oxide, cellulose paper etc.

Appropriate solvent or mixture of solvents (mobile phase called eluent) is allowed to flow down the adsorbed mixture slowly.

The combination of degree of adsorption of a compound onto adsorbent and its solubility in the eluent makes them separated and purified completely. The weakly adsorbed compound will move down the column (elute) more rapidly than those adsorbed strongly. More soluble compound in the eluent will move down faster than the others.

b) Thin Layer Chromatography

In TLC an adsorbent (Al_2O_3 or SiO_2) is spread in the form of very thin layer (~ 0.2 mm) supported by a glass plate or metal foil (generally aluminium) and is called TLC plate or chromatoplate.

The mixture to be analyzed is taken in solution form and applied as a dot at one end of the TLC plate. The plate is then put into a closed jar (chromatography chamber) having some eluent in it. As the eluent rises up, the more soluble and poorly adsorbed component moves up along with the solvent, followed by the others in the order of their interactions.

The relative adsorption of each component is given in the terms of retardation or retention factor or r_f value

$$r_f = \frac{\text{Distance travelled by the substance from base line (x)}}{\text{Distance travelled by the solvent front (y)}}$$

Coloured compounds give visible spots on the TLC plate. The spots of colourless compounds are identified by either of following methods:

Putting the plate under U.V. light where it may fluoresce

Placing it in I_2 jar, where some compounds give brown spots due to adsorption of I_2

By spraying the plate with suitable reagent to produce coloured spots (e.g., amino acid on spraying with ninhydrin solution)

Partition Chromatography

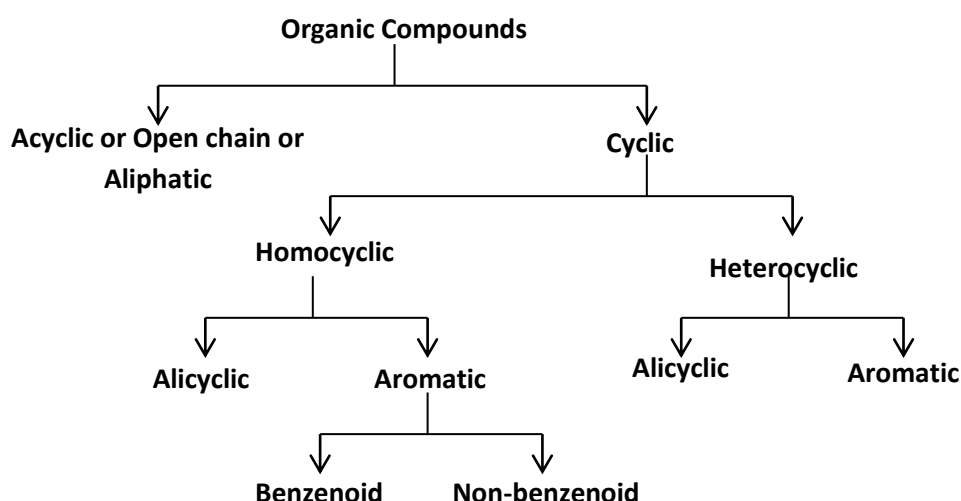
The principle of partition chromatography is the continuous differential partitioning of components of a mixture between stationary and mobile phases.

In Paper chromatography a special paper is used called chromatography paper, which contains water trapped in it. This water works as stationary phase and continuous partition between water and organic solvent used takes place during the chromatographic separation. The paper so obtained having coloured bands is called chromatogram.

Depending upon the method of development of chromatogram it can be ascending, descending or radial (circular) chromatography.

Classification

All the known organic compounds have been broadly divided into the following classes.



Classification of organic compounds:

Based on the structure, the organic compounds are classified as

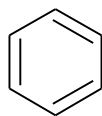
- i) Aliphatic compounds
- ii) Aromatic compounds
- iii) Alicyclic compounds
- iv) Heterocyclic compounds

i) **Aliphatic compounds:** Aliphatic compounds are those compounds which have open chain structure

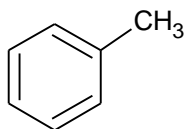
Example: Alkanes, alkenes and alkynes.

ii) **Aromatic compounds:** Aromatic compounds are those compounds which contain at least one benzene ring in them.

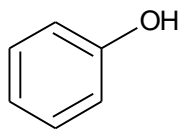
Example



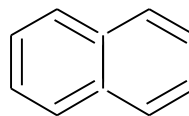
Benzene



Toluene



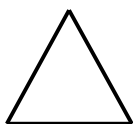
Phenol



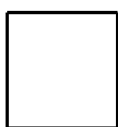
Naphthalene

iii) **Alicyclic compounds:** Alicyclic compounds are those compounds which are similar to aliphatic compounds but contain a ring structure

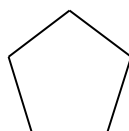
Example:



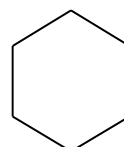
Cyclopropane



Cyclobutane

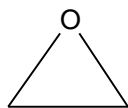


Cyclopentane



Cyclohexane

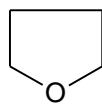
Alicyclic heterocyclic compounds. Heterocyclic compounds which resemble aliphatic compounds in their properties are called **alicyclic heterocyclic compounds**. For example,



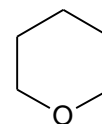
Oxirane or
Epoxyethane



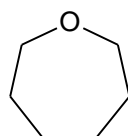
Oxetane



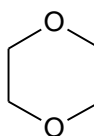
Tetrahydro-furan
(THF) or oxolane



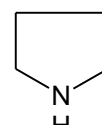
Tetra-hydropyran
or oxolane



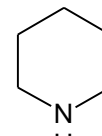
Oxepane



1, 4-Dioxane



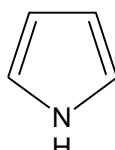
Pyrrolidine



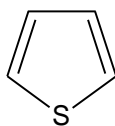
Piperidine

iv) **Heterocyclic compounds:** Heterocyclic compounds which have the ring structure where one or more carbon atoms of the ring are replaced by some other (hetero) atom.

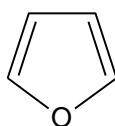
Example:



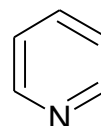
Pyrrole



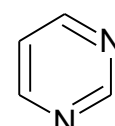
Thiophene



Furan



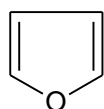
Pyridine



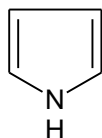
Pyrimidine

• **Aromatic heterocyclic compounds,**

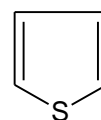
Heterocyclic compounds which resemble benzene and other aromatic compounds in most of their properties are called **aromatic heterocyclic compounds**. For example.



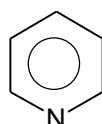
Furan



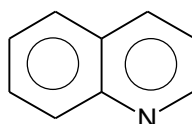
Pyrrole



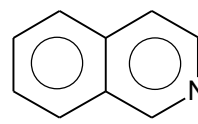
Thiophene



Pyridine



Quinoline



Isoquinoline

Functional group: Functional group is an atom or group of atoms, which determine the properties of the organic compound

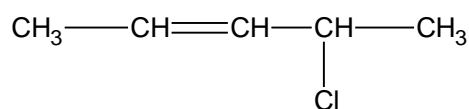
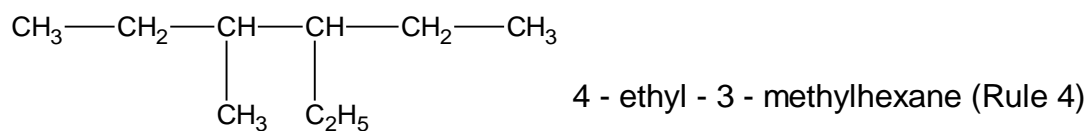
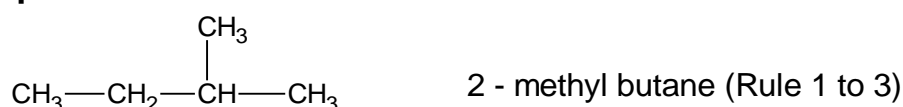
Example: - OH is the functional group of alcohols.

IUPAC method of naming compounds

1. Longest chain of carbon atoms is selected.
2. Carbon atoms are numbered from one end and the position of the side chains are indicated by the number of the carbon atom to which they are attached.
3. For numbering carbon atoms, that end is chosen which gives the lowest total for the locants of the side chains.
4. If different alkyl groups are present at equidistance with respect to the ends of the chain, then that end which contains the smaller group is chosen.
5. If a molecule contains a functional group, then, ignoring the lowest number rule, numbering is done from that end which gives lower number for the functional group.
6. Order of preference for numbering is in the following order : principal group, double bond, triple bond and other substituent's.

The order with respect to principal groups: acids, aldehydes, nitriles (cyanide), ketones, alcohols, amines, ethers C = C, C≡C, other substituent's.

Examples



Double bond is considered as a higher group. So numbering from the left hand side end, the IUPAC name becomes **4 - chloro - 2 - pentene**

NOMENCLATURE OF COMPOUNDS HAVING MORE THAN ONE FUNCTIONAL GROUP

If more than one functional group is present in the molecule the root word is given based on the principal function



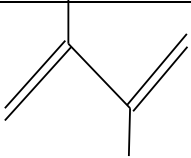
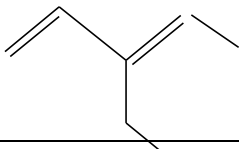

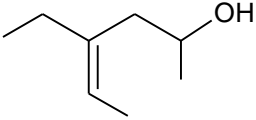
Selection of principal functional group is done based on the higherkary table

NOMENCLATURE OF COMPOUNDS HAVING MORE THAN ONE FUNCTIONAL GROUP

If more than one functional group is present in the molecule then the root word is given based on the principal functional group.

Selection of principal functional group is done based on the higherkary table

Sl. No	Order of Preference	Prefix	Suffix
1	- COOH	Carboxy	- oic acid
2	- SO ₃ H	Sulpho	sulphonic acid
3	- COOR	Alkoxy carbonyl	alkyl alkanoate
4	- COX	Haloformyl	oyl halide
5	- CONH ₂	Carbamoyl	- amide
6	- CN	Cyano	- nitrile
7	- CHO	Formyl	- al
8	- CO -	Oxo	- one
9	- OH	Hydroxy	- ol
10	- NH ₂	Amino	-
11	C = C	-	ene
12	C ≡ C	-	yne
13	- O -	Epoxy	-
14	- X	Halo	-
15	- NO ₂	Nitro	-

Bond line notation	Formula	IUPAC name of the compound
	$\begin{array}{cccc} 1 & 2 & 3 & 4 \\ \text{H}_3\text{C} & -\text{CH} & =\text{CH} & -\text{CH}_3 \end{array}$	But - 2 - ene
	$\begin{array}{cccccc} 1 & 2 & 3 & 4 & 5 & 6 \\ \text{H}_2\text{C} & =\text{CH} & -\text{CH} & =\text{CH} & -\text{CH} & -\text{CH}_2 \end{array}$	Hexa - 1, 3, 5 - triene
	$\begin{array}{cccc} 1 & 2 & 3 & 4 \\ \text{H}_2\text{C} & =\text{C} & -\text{C} & =\text{CH}_2 \\ & & & \\ & \text{CH}_3 & \text{CH}_3 & \end{array}$	2, 3-Dimethylbutta-1,3-diene
	$\begin{array}{ccccc} 1 & 2 & 3 & 4 & 5 \\ \text{H}_2\text{C} & =\text{CH} & -\text{C} & =\text{CH} & -\text{CH}_3 \\ & & & & \\ & & \text{C}_2\text{H}_5 & & \end{array}$	3-Ethylpenta-1,3-diene
	$\begin{array}{cccc} & \text{CH}_3 & & \\ & & & \\ 1 & 2 & 3 & 4 \\ \text{H}_3\text{C} & -\text{C} & -\text{CH}_2 & -\text{CH}_3 \\ & & & \\ & \text{CH}_3 & & \end{array}$	2,2-Dimethylbutane
	$\begin{array}{cccccc} 6 & 5 & 4 & 3 & 2 & 1 \\ \text{H}_3\text{C} & -\text{CH} & =\text{C} & -\text{CH}_2 & -\text{CH} & -\text{CH}_3 \\ & & & & & \\ & & \text{H}_5\text{C}_2 & & \text{OH} & \end{array}$	4-Ethylhex-4-en-2-ol

Homologous series

All the members of a homologous series can be represented by a general formula.

Each member of a homologous series differs from the preceding member by a $-CH_2-$ group.

Can be prepared by similar methods.

Show regular gradation in physical properties.

Have similar chemical properties.