# Chapter → 12

# Organic chemistry – Some Basic Principle

## → Organic chemistry :-

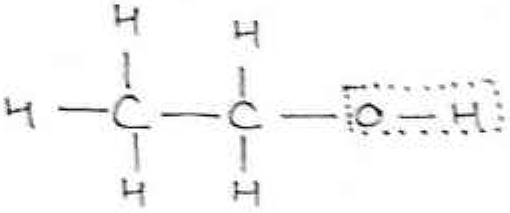
Organic chemistry is the branch of chemistry that deals with the study of hydrocarbons and their derivatives.

## The shape of compounds :-

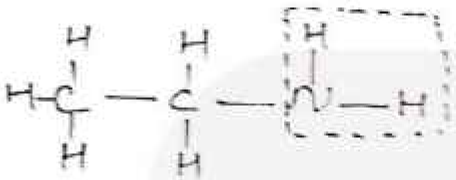
In organic carbon s and p orbitals are involved in hybridisation. This leads to y Three types of hybridisation which are $sp^3$ (in alkanes) – Tetrahedral in shape $sp^2$ (in allenes) – Planar structure $sp$ (in alkynes) – Linear molecule.

## functional Group :-

The functional Group are atom or group of atoms joined in a specific manner which determine the chemical properties of the organic compound. The examples are hydroxyl group ($-OH$), aldehyde group ($-CHO$) and carboxylic acid group ($-COOH$) etc.



functional group



functional group

## Homologous Series

A homologous series may be defined as a family of family organic compounds having the same functional group, similar chemical properties and the successive members differ from each other in molecular formula by $-CH_2$ units.
The members of a homologous series can be represented by same general molecular formula.

## Nomenclature of Organic Compounds

### Common name (common system) :-

Before the IUPAC system of nomenclature. organic compounds were named after the sources of origin, for example, urea was so name because it was obtained from the sources of origin, for example. mammals.

| Compound | Comman Name |
|---|---|
| $CH_4$ | $CH_4$ Methane |
| $H_3CCH_2CH_2CH_3$ | n-Butane |
| $(H_3C)_2CHCH_3$ | Isobutane |
| $(H_3C)_4C$ | Neopentane |
| $H_3CCH_2CH_2OH$ | n-Proply alcorol |
| $HCHO$ | formaldehyde |
| $(H_3C)_2CO$ | Acetone |
| $CHCl_3$ | cholouroform |
| $CH_3COOH$ | Acetic acid |
| $C_6H_5COCH$ | Anisole |
| $CH$ | |

## IUPAC (International Union of Pure and Applied chemistry)

According to IUPAC system, the name of an organic compound contains three parts:
(i) word root, (ii) suffix (iii) prefix.

### (i) word rood :-

word rood represents the number of carbon atom present in the principal chain, which is the longest possible chain of carbon atoms.

four special word root. four

meth —— $C_1$
eth —— $C_2$
Prop —— $C_3$
but —— $C_4$

## (ii) Suffix :

Suffix are of two types, primary suffix, Secondary suffix.

(a) primary suffix : It indication the types of bond in the carbon atoms.

for example: Primary suffix

ane for C–C bond
ene for C=C bond
yne for C≡C bond

b. Secondary Suffix :-

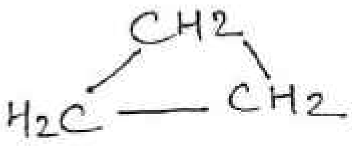
Secondary suffix is used to respresent the functional group.

## (iii) Prefix :-

Prefix is a part of IUPAC name which appears before the word root.

Prefix are of two type.

a. Primary prefix : for example, primary Prefix cyclo is used to differentiate cyclic compounds.



Cyclopropane.

## ⓑ. Secondary prefix :

Some functional group are considered as substituents and denoted by secondary prefix.

for example :

| Substituted Group | Secondary prefix. |
|---|---|
| — F | fluoro |
| — Cl | chloro |
| — Br | Bromo |
| — NO | Nitroso |
| — $NO_2$ | Nitro |
| — $CH_3$ | Methyl |
|  | Methoxy |

## → Naming of Compounds Containig Functional Groups :

The longest Chain of Carbon Atoms a Containing the functional group is numbered in Such a manner that number in the Chain. In Case of polyfunctional compound , one of the functional group is Selected as principle functional group is made on the basis of order of Perference.

The order of decresing priority for the functional group is

$-COOH$, $-SO_3H$ $-COOR$ ($R$ = alkyl group) $COCl$, $-CONH_2$, $COCl$, $-CONH_2$ $-CN$, $-C=O$, $>C=O$, $-OH$, $-NH_2$ $>C=<$, $-C\equiv C-$

## ⇛ Isomerism :-

When there are two or more compound Possessing the same molecular formula but different structural formula and different physical and Chemical properties, the phenomenon is called Isomerism. Such compounds are called isomers.

It is two types :

(1) Structural Isomerism

(2) Stereoisomerism

## (1) Structural Isomerism :

Structural isomerism is shown by compounds having the same molecular formula but a different physical Structural formula differing in the arrangement of atoms.

## ⇛ The Structural isomerism type :

- Chain
- Position
- functional
- meta - merism
- Tauto - meri

The different types of Stereoisomerism are :

- Geometrical
- Optical
- Conformational

Let us Study first Structural isomerism types :

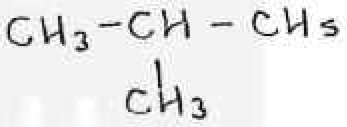
**1. Chain isomerism** – The Compound that have Same molecular formula, but different a arrangement of atoms within the Chain.

Example : $CH_3-CH_2-CH_3$

Propane will not Show Chain isomerism

$CH_3-CH_2-CH_2-CH_3$

Normal -Butane

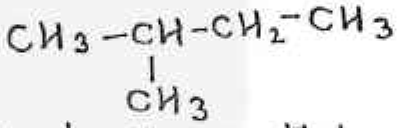


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

iso - butane

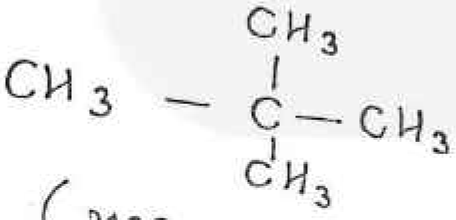
$CH_3-CH_2-CH_2-CH_2-CH_3$

Normal Pentane



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

iso-pentane(2 methyl butane)

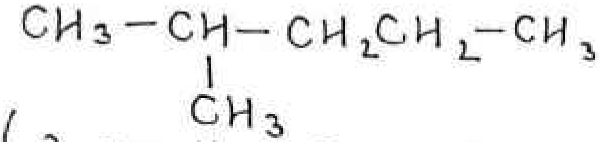


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$$

(neo - pentane)

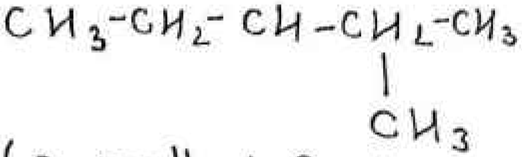
**2 – Position isomerism :**

The Compounds with same molecular formula, but differ in position of Substituent, side Chain or functional group.



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CH_2-CH_3$

(2-methyl Pentane)

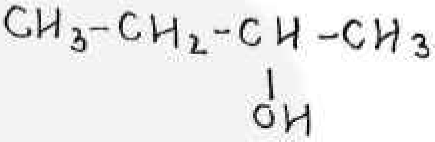


$CH_3-CH_2-CH-\underset{\displaystyle CH_3}{\underset{|}{CH_2}}-CH_3$

(3-methyl Pentene)

$CH_3-CH_2-CH_2-CH_2-OH$

(Butanol)



$CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

2-Butanol

## 3. functional isomerism :-

The compounds with same molecular formula, but differ type of functional group and also in physical and Chemical properties.

$CH_3CH_2OH$

Ethanol

(Alcohol)

$CH_3OCH_3$

Methyl methane

(ether)

$CH_3-CH_2-CH_2-CHO$

(Aldehyde)

$CH_3-CO-CH_2-CH_3$

(Ketone)

## 3. Metamerism :

The compounds that have same molecular formula, but differ in It is shown by functional groups like ether, esters, Ketones.

Example :-

$CH_3CH_2OCH_2CH_2$ Ethoxy-ethane

$CH_3OCH_2CH_2CH_3$ Methoxy-propane

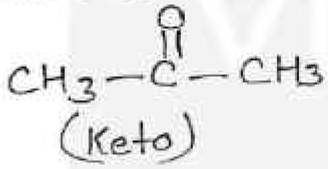
$CH_3CH_2COCH_4CH_3$ 3-pentanone

$CH_3OCH_3CH_2CH_3$ 2-pentanone

## 4. Tautomerism :

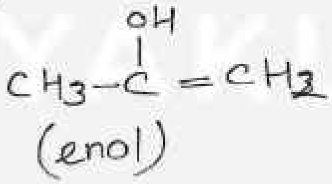
In this simultaneous movement of π electron cloud and Hydrogen takes place. Most common tautomerism is Keto-enol tautomerism.

Keto-en ol tautomerism
↓ ↓ ↓
Ketone = Alcohol



$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

(Keto)



$CH_3-\overset{OH}{\overset{|}{C}}=CH_2$

(enol)

## 2. Stereoisomerism :

When isomerism is caused by the different arrangements of atoms or groups in space, the phenomenon is called stereoisomerism. The stereoisomers have same structural formula but differ in arrangement of atoms in space. Stereoisomerism is of two types:

(i) Geometrical or Cis-Trans Isomerism

(ii) Optical Isomerism

- Fundamental Concepts in Organic Reaction Mechanism :-

Fission of a covalent bond : A covalent bond can undergo fission in two ways :

(i) By Homolytic fission or Homolysis

(ii) By Heterolytic fission or Heterolysis.

## Homolytic fission:

In this process each of the atoms acquires one of the bondings electrons :

$$A-B \text{ or } A:B \longrightarrow \dot{A} + \dot{B}$$

The products $\dot{A}$ and $\dot{B}$ are called free radicals. They are electrically neutral and have one unpaired electron associated with them. Homolytic fission is the most common mode of fission in vapour phase. Alkyl radicals are classified as Primary, secondary or tertiary. Alkyl radical stability increases as we proceed from primary to tertiary.

| Methyl free radical | Ethyl free radical | Isopropyl free radical |
|---|---|---|
| $\dot{C}H_3$ | $\dot{C}H_3CH_2$ | $\underline{CH}\ (\dot{C}H_3)_2$ |

Tert-butyl free radical

$\dot{C}\ (CH_3)_3$

## Heterolytic fission:

In this process one of atoms aquires both of the bonding electrons when the bond is broken. If B is more electronegative than A which thereby aquires both the bonding electrons and becomes negatively changed.

$$A \overset{\curvearrowright}{\longrightarrow} B \longrightarrow \overset{+}{A} + :\overset{-}{B}$$

The products of heterolytic fission are ions:

- **Reaction Intermediates:**

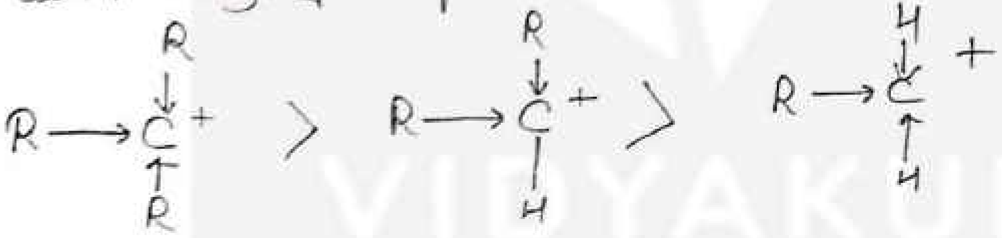
Heterolytic and homolytic both fission resul in the formation of short-lived fragments called reaction intermediates. Among the important reaction intermediates are carbonium ions, carbanions carbon free radicals and carbenes.

## • Carbonium Ions (carbocations):

Organic ions which contain a positively charged carbon atom are called carbonium ions or carbocations. They are formed by heterolytic bond fission.

$$-\overset{|}{\underset{|}{C}}:Z \longrightarrow -\overset{|}{\underset{|}{C}}{}^{+} + :Z$$

where Z is more electronegative than carbon. Tertiary carbonium ion is more stable than a secondary, which in turn is more stable than a primary because of +I effect associated with alkyl group.



$$R\rightarrow\overset{\overset{R}{\downarrow}}{\underset{\underset{R}{\uparrow}}{C}}{}^{+} > R\rightarrow\overset{\overset{R}{\downarrow}}{\underset{\underset{H}{|}}{C}}{}^{+} > R\rightarrow\overset{\overset{H}{\downarrow}}{\underset{\underset{H}{\uparrow}}{C}}{}^{+}$$

$3^{\circ}$ Tertiary  $2^{\circ}$ Secondary  $3^{\circ}$ Primary

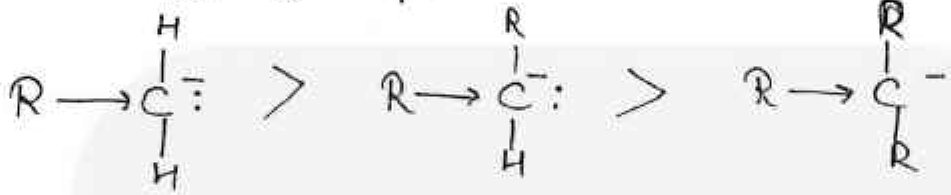
## Carbanion:

Organic ion which catains a negatively charged carbon atom are called carbanions. They are also formed by heterolytic bond fission.

$$-\overset{|}{\underset{|}{C}}:Z \longrightarrow -\overset{|}{\underset{|}{C}}\overset{-}{:} + Z^{+}$$

Carbanion

Where z is less electronegative than carbon. A primary carbanion is more stable than a secondary, which in turn is more stable than a tertiary, because of +1 effect associated with alkyl group.



$$R\rightarrow\overset{H}{\underset{H}{C}}{:}^{-} > R\rightarrow\overset{R}{\underset{H}{C}}{:}^{-} > R\rightarrow\overset{R}{\underset{R}{C}}^{-}$$

### • Electrophile :-

It is positively charged or neutral species which is electron deficient, eg.

$He^-$, $H_2O^+$, $CH_3$, $NH_4^+$, $AlCl_3$, $SO_3$, $CHCl_2$, $CCl_3$.

### • Nucleophile :-

It is negative charged or neutral species with lone pair of electrons

eg (HO⁻) Cyanide ($C=N$), $H_2O$: $R_3N$, $R_2NH$ etc.

### • Electron Displacement effect in Covalent Bond :-

Electronic displacement in cavelent bonds occurs due to the presence of an atom or group of different electrongativity or under the influence of some outside attaching group.

These lead to a number of effect which are as follows:

(i) Inductive effect (ii) Elecuromeric effect

(iii) Resonance or Mesomeric effct

(iv) Hyperconjugation effct.

- Inductive Effect :-

It involves c electron. the a electrons which form a covalent bond are seldom shared equally between the two atoms. Due to different. electronegatively electrons are displaced towards the more electronegative atom.

This introduces a certain degree of polarity in the bond.

The more electronegative atom acquires a small negative charge ($\delta-$). The less electronegative atom acquires a small positive charge ($\delta^-$).

Consider the carbon–chlorine bond.

As chlorine is more electronegative, it will become negatively charged with respect to the carbon atom.

I

II

Some common atoms or groups which cause +I or −I effects are shown below:

(i) −I Effect Groups (Electron-attracting)

$NO_2$ F, Cl, Br, I, OH, $C_6H_5-$

(ii) +I Effect Groups (Electron-releasing)

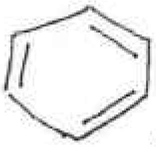
An inductive effect is not confined to the Polarization of one bond.

$$\underset{3}{-C}-\underset{2}{C}\rightarrow\underset{1}{C}\twoheadrightarrow\underset{-1}{Cl}$$

The inductive effect of $C_3$ upon $C_3$ is singnificantly less than the effect of the chlorine atom on C.

## • Resonance Structure :-

A number of organic compounds cannot be accurately represented by one structure. for example, benzene is ordinaarily represented as



Benzene

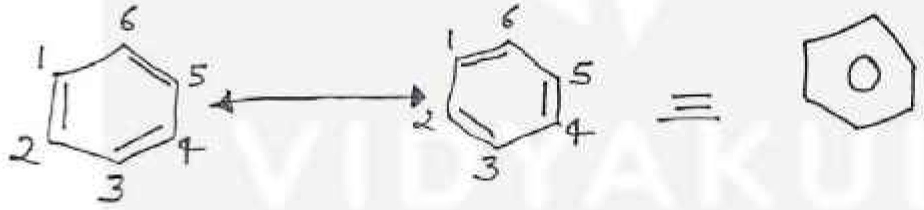
This structure has three C–C bond and three C = C bonds.

Carbon – Carbon single bond length = 1.54Å.

Carbon – Carbon double bond length = 1.34 Å

Experimentally that all carbon – carbon bond in benzene are identical and have same bond length (1.39 Å).

Thus the structure of benzene cannot be represented by single structure. It can be represented equally well by he energetically similar structures I and II.



Actual structure of benzene is resonance hybrid of structures I and II.

Another example of resonance is provided by nitromethane ($CH_3NO_2$) which can be represented by two Lewis structure.

the actual structure of nitromethane is a resonace hybrid of the two canoncial forms. I and II. Resonance energy: The difference in the energy between the most stable contributing structure for a compound and its resonance hybrid is called as resonance energy or resonance stablilisation energy.

## Resonance Effect :-

The polarity produced in the molecule by the interaction of two π-bonds or between a π-bond and a pair of electrons present on an adjecent atom. There are two types of resonance or mesomeric effects designated as R or M effect.

Positive Resonance Effect (+R effect):

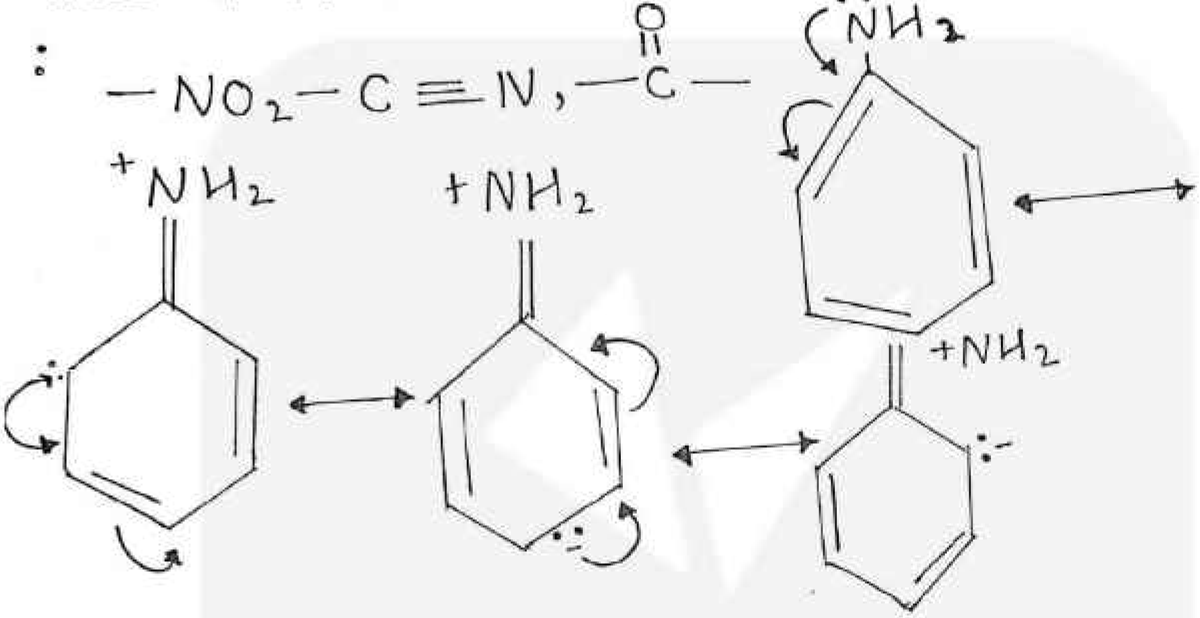
Those atoms which lose electrons towards a Carbon atom are said to have a +M effect or +R effect. for example:

$-Cl, -Br, -I - NH_2 -NR -OH, -OCH_3$

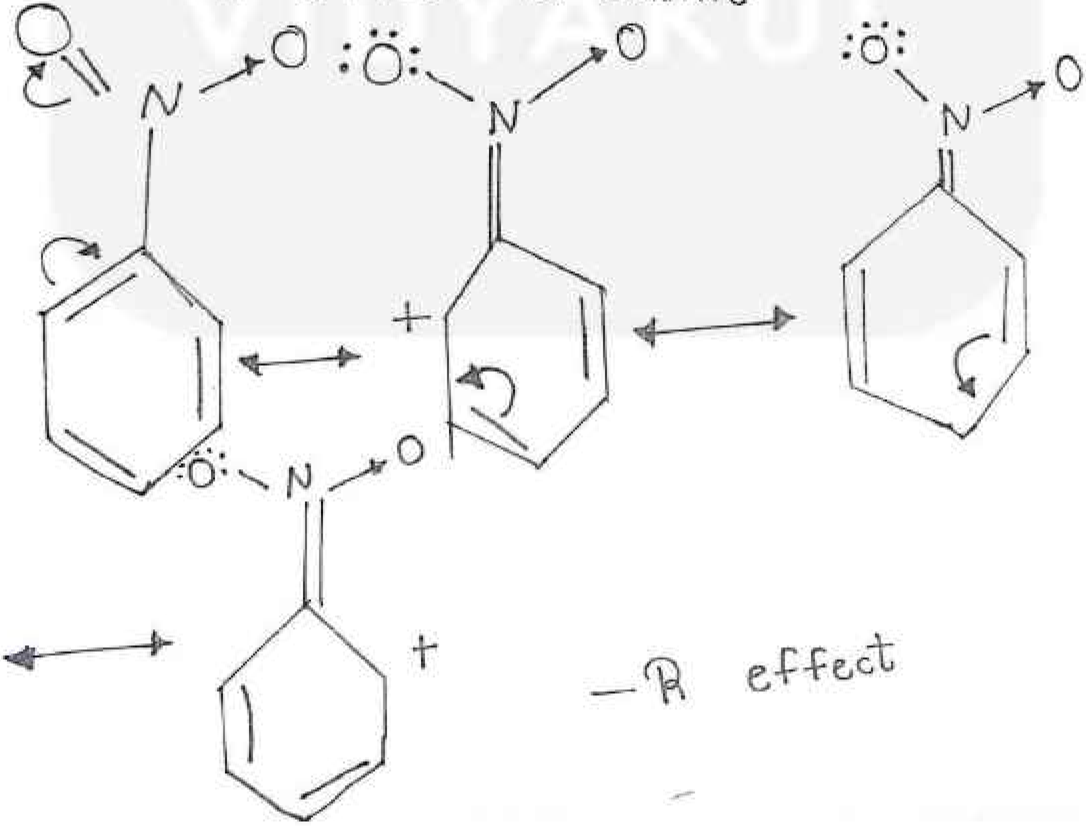
## Negative Resonance Effect (-R effect):

Those atom or grops with drow electrons away from a carbon atom are said to have a-M effect or -R effect. for example :

$-NO_2 - C\equiv N, -\overset{\overset{O}{\|}}{C}-$



+R effect in aniline



−R effect

## Electromeric Effect (E Effect):

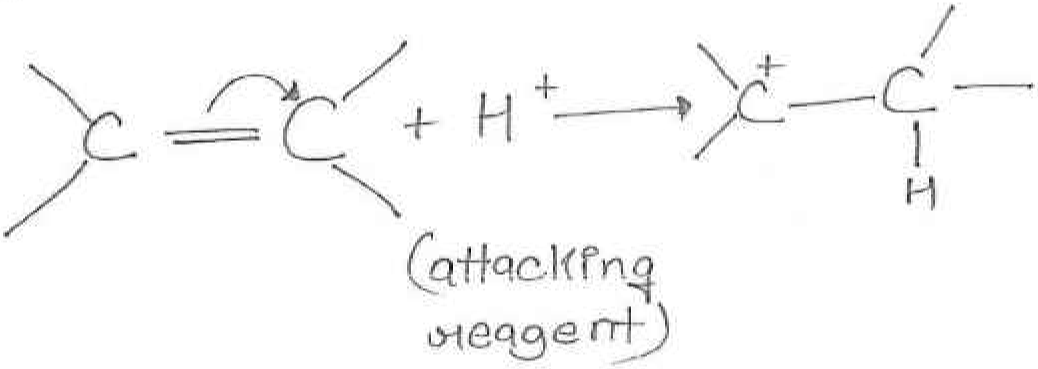
The electromeric effect refers to the polarity produced in a multiple bonded compound when it is attacked by a reagent when a bond is exposed to an attack by a reagent by electrophile $E^+$ (a reagent) the two n electrons which from the n bond are completely transferred to one atom or the other. The electromeric effect is represented as:

$$A \overset{\curvearrowright}{=} B \xrightarrow[\text{REAGENT}]{E^+} \overset{+}{A} — \overset{-}{\ddot{B}}$$

The curved arrow shows the displacement of the electron pair. This atom A has lost its share in the electron pair and B has gained this share.

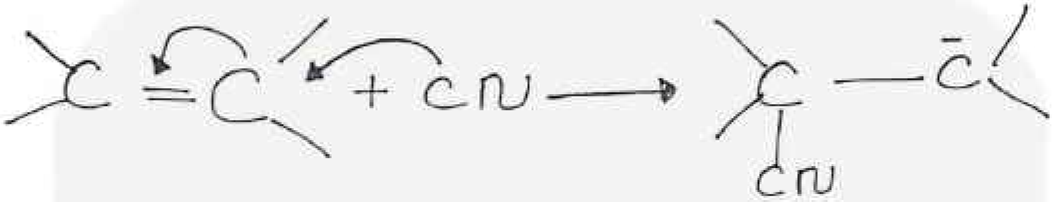
(i) Positive Electromeric effect (+E effect) :-

In this effect the π electrons of the multiple bond are shifted to that atom to which the reagent gets attached.



(ii) Negative electromeric effect :

In this effect the $\pi$ electrons of the multiple bond are transferred to the atom to which the reagent gets attached.



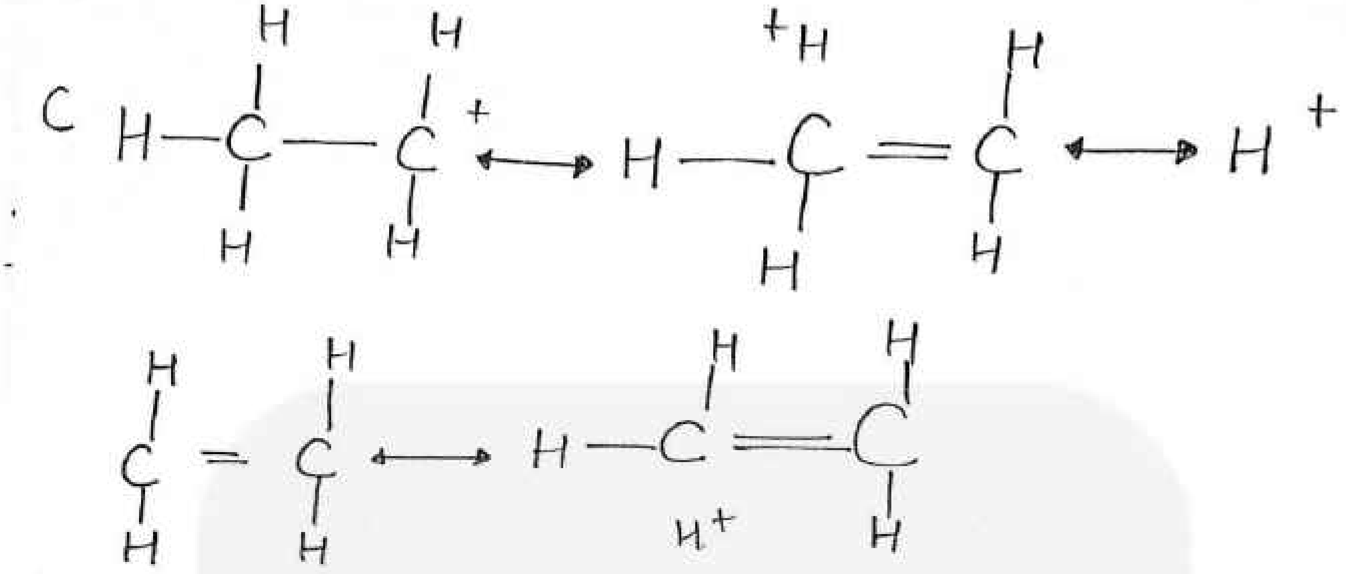
(attacking reagent)

- Hyperconjugation or No Bond Resonance :-

when the alkyl group is attached to an unsaturated system such as $-CH=CH_2$ group the order of inductive effect gets reversed. the behaviour can be explained by hyperconjugation effect.

Such structure are arrived at by shifting the bonding electrons from an adjacent C – H bond to the electron deficient carbon.

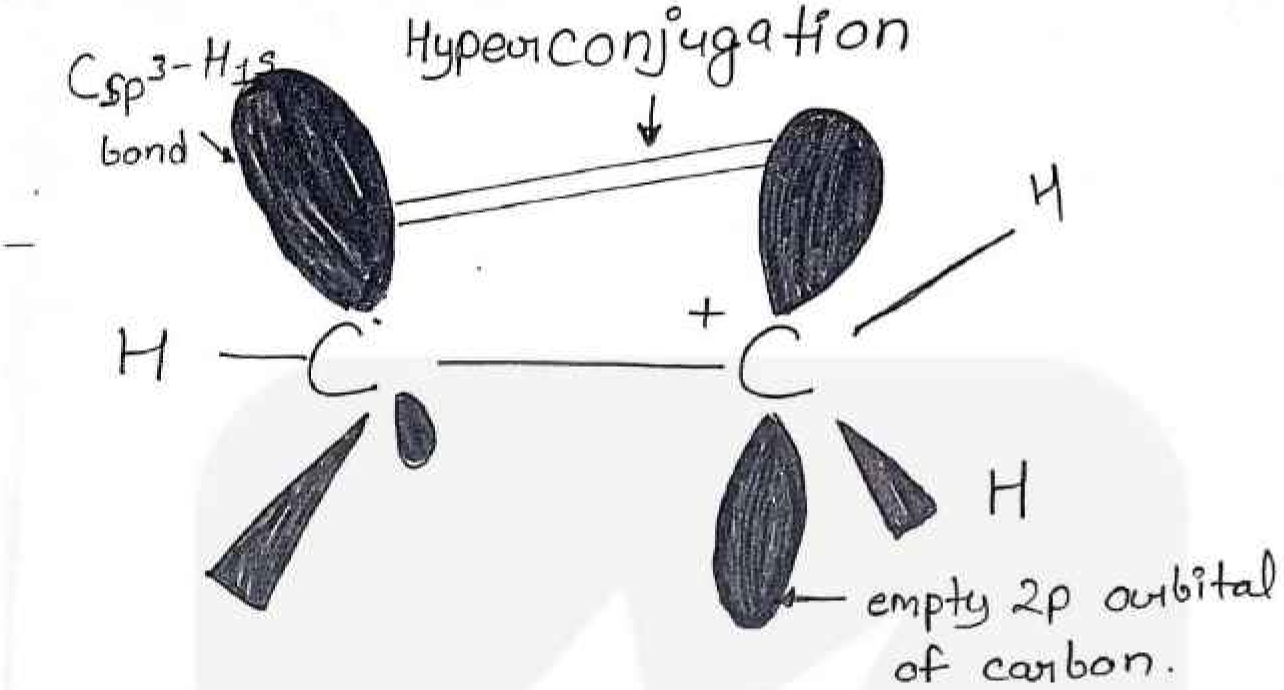
This way of electron release by assuming no bond character in the adjacent C – H bond is called No - Band Resonance or Hypeconjugation.



## • Orbital Concept of Hyperconjugation

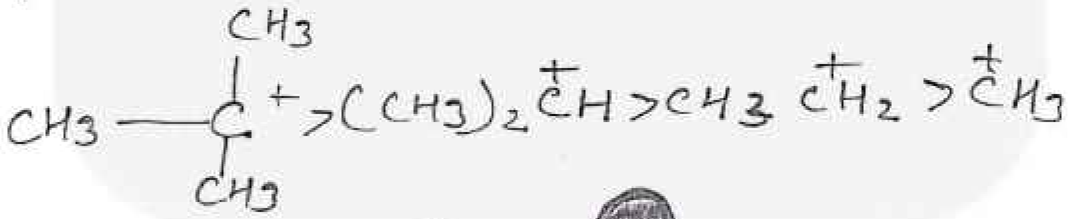
In involves delocalisation of a electrons of C–H bond of an alkyl group which is attached directly to an atom of the C–H bonds of the unsaturated system or to an atom with an unshared p-orbital.

Let us consider $CH_3CH_2$ (ethyl cation) in which the positively charged carbon atom has an empty p-orbital. One of the C–H bond of the methyl group can align in the plane of this empty p-orbitals and electron constituting the C–H bond in plane wrt this p-orbital can then be delocalised into the empty p-orbital as.

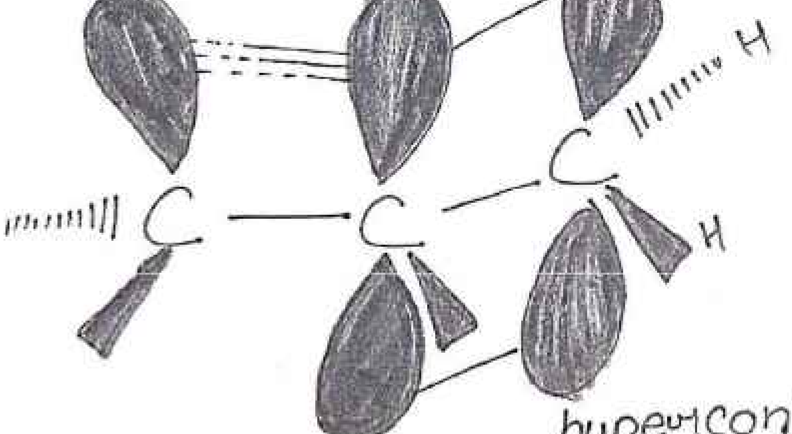


Orbital diagram showing hyperconjugation in ethyl cation.

In general, greater the number of alkly group attached to a positively charged carbon atom, the gretaer is the hyperconjugation.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{+}{C}}} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$



hyperconjugation propene

# METHOD of Purification of Organic compound

### • Sublimation :-

this method is used to separate the sublimable Compounds from non sublimable compounds.

### • Crystallisation :-

This method is based on the different in the Solubilities of compound and impurities in a suitable solvent. the impure compounds is dissolved in solvent at heated at higher temp.

### • Distillation :

This method is used to separate volatile liquids from non volalatile liquids and liquids havings sufficient diffenent in their boiling points.

### • fractional distillation :

If the boilings points of two liquids is used to purify liquids having high boiling paints.

### • Different Extraction :-

when an organic compound is present in an aqueous medium it is separated by shaking it with organic solvent in which it is more soluble than in water. the aqueous solution is mixed with organic solvent in a separating funnel and shaken four sometimes and then allowed to stand four some time.

## • Chuomatoguaphy :-

This technique is used to sepauate mixtuue in to theiu components. puuify the compounds and test the puuity of compaunds.

- Adsouption Chuomatoguaphy :-

  It is based on the fact that diffeuent Compounds aue adsouubed on an adsoubent to diffeuent deguee.

- Pautition Chuomatoguaphy :

  It based on the fact that diffeuent Poutioning of components of a mixtuue between stationauy and mobile phase.

## • Quality Analysis of Ouganic Compounds :-

### • Detection of Caubon and Hyduogen :-

The caubon and hyduoge pueesent in the Ouganic Compound is dected by heating the compaund with Coppeu II oxide in a haud glass tube when caubon Puesent in the compaund is oxidized to $CO_2$ which can be tested with lime wateu and hydrogenis converted to water can be tested with anhydrous copper sulphate which turns blue.

$C + CuO \longrightarrow 2Cu + CO_2$

$2H + CuO \quad CH + H_2O$

$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$

$5H_2O + CuSO_4 \longrightarrow CuSO_4 + 5H_2O$

## • DETECTION OF OTHER ELEMENTS :-

### • Sodium fusion Extract :-

A small piece of dry Sodium metals is heated with a organic compound in a fusion tube for 2-3 minutes and the red hot tube a plunged in to distilled water contained in a china dish. The contained of the china dish is boiled cooled and filtered.

### • Test for Nitrogen :-

The sodium fusion extract is boiled with iron II sulphate and then acidified with Conc sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen.

$$6CN^- + Fe^{2+} \longrightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{3H_2O} Fe_4[Fe(CN)_6]_3 \cdot xH_2O$$

- Test for Sulphur :-

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

$$S^{2-} + Pb^{2+} \longrightarrow PbS.$$

- QUANTITIVE ANALYSIS (carbon and hydrogen)

Let the mass of organic o Compound be m.g
Mass of water and carbon dioxide produced be $m_1$ and $m_2$ g respectively :

$$\% \text{ of Carbon} = \frac{12 \times m_2 \times 100}{44 \times m}$$

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

- Nitrogen

- Dumas method :-

A Known mass of organic compound is heated with excess of CuO in an atmosphere of $CO_2$. when nitrogen of the organic compound is converted into $N_2$ gas. The volume of $N_2$ thus obtanined is converted into STP and the precentage of nitrogen determined by applying the equation :

$$\text{valume of Nitrogen at STP} = \frac{P_1 V_1 \times 273}{760 \times T_1}$$

$$\% N = \frac{28 \times \text{vol of } N_2 \text{ at STP} \times 100}{22400 \times \text{mass of the substance taken}}$$

## • KJELDAHL'S METHOD :–

A Known mass of organic compound is heated with Conc. $H_2SO_4$ in presence of $K_2SO_4$ and litle $CuSO_4$ or Hg in a long necked flask called Kjeldahl's flask when nitrogen present in the organic compound is quantitiant converted into $(NH_4)SO_4$. $(NH_4)SO_4$, thus obtained is boiled with excess of NaOH solutions. to liberate $NH_3$ gas which is absorbed in a Known excess of a standand acid such as $H_2SO_4$ or HCl.

$$\% N = \frac{1.4 \times \text{molarity of the acid} \times \text{Basicity of the acid} \times \text{vol of}}{\text{Mass of the substance taken.}}$$

- **Halogens:**

- **Carius method:-**

A Known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass test tube known as carius tube in a furnace. Carbon and hydrogens present in the compound are oxidized to carbon dioxide and water.

Let the mass of the organic compound take = m g.

mass of AgX formed = $m_1$ g

1 mol of AgX Contains 1 mol of X

Mass of halogen in $m_1$ g of AgX

$$= \frac{\text{at mass of X} \times m_1 \text{ g}}{\text{molecular mass of AgX}}$$

% of halogen

$$= \frac{\text{at mass of X} \times m_1 \text{g} \times 100}{\text{molecular mass of AgX} \times m} \%$$

## • Sulphur :-

Let the mass of the organic compound taken = Mg

mass of BaSO4 formed = $m_1$ g

$$\% \text{ of sulphur} = \frac{32 \times m_1 \times 100}{233 \times m}$$

## • Phosphorous :-

Let the mass of the organic compound taken = Mg

mass of ammonium phosphorous = $m_1$ g

$$\% \text{ of phosphorous} = \frac{31 \times m_1 \times 100}{1877 \times m} \%$$