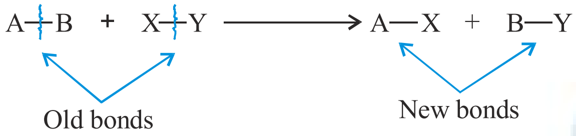
# GENERAL ORGANIC CHEMISTRY

**Reaction :** Breaking of old bond and formation of new bond is known as chemical reaction



A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism.

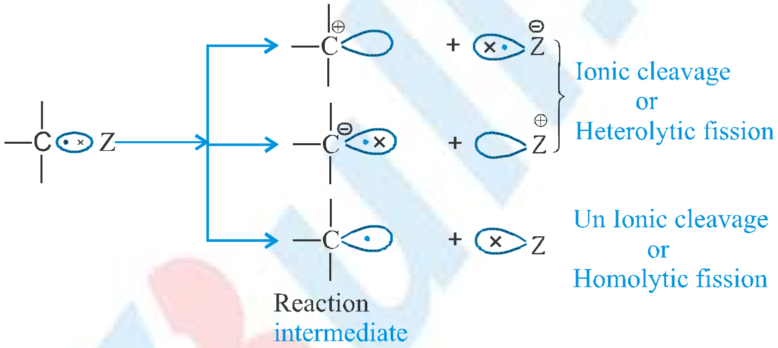
Species on which reagent is attacking is known as substrate or reactant.

Species which attack on substrate, is known as reagent.

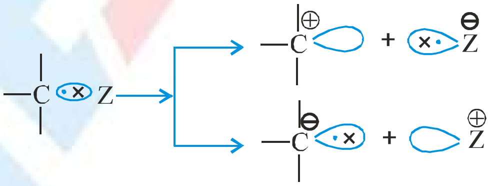
## Type of cleavage of bond

**(A)** **Heterolytical cleavage/fission**

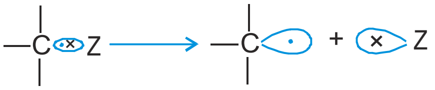
**(B)** **Homolytical cleavage/fission**



**(A)** Cleavage in which unequal distribution of electrons takes place during the bond cleavage is known as heterolytical cleavage. Due to unequal distribution of electrons, ions are formed. That’s why it is also known as ionic cleavage or heterolytical cleavage.



**(B)** Cleavage in which equal distribution of e$^-$s takes place during the chemical reaction is known as homolytical cleavage.



- Due to equally distribution of electrons, without charge unpaired electrons species is formed, which is known as free radical and cleavage is known as unionic cleavage/homolytical fission.
- By both cleavage [ionic/non ionic] three type of species are formed [One carrying positive charge, other carrying negative charge and third one is neutral with unpaired electrons] is known as reaction intermidiate.

## ATTACKING REAGENTS

The species which attack on a substrate molecule or intermediate and form a product is called as attacking reagent. These are of two types : **(A) Electrophiles (B) Nucleophiles**

### (A) ELECTROPHILIC REAGENT OR ELECTROPHILES

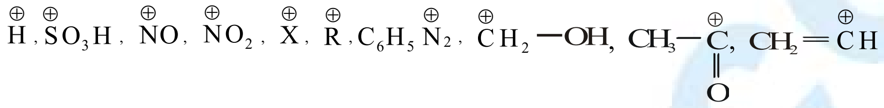
**Electrophilic (electro + philic)**

↓

**(electron + loving)**

The reagent which attacks on the **negative of the molecule** or loves electrons are called electrophiles. Electrophiles may be positively charged or electron deficient molecule (molecule with sextet or septet).

**(i) Positively charged electrophiles**



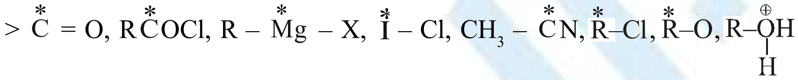
$\overset{\oplus}{H}, \overset{\oplus}{S}O_3H, \overset{\oplus}{N}O, \overset{\oplus}{N}O_2, \overset{\oplus}{X}, \overset{\oplus}{R}, C_6H_5\overset{\oplus}{N}_2, \overset{\oplus}{C}H_2-OH, CH_3-\underset{\underset{O}{\|}}{\overset{\oplus}{C}}, CH_2=\overset{\oplus}{C}H$

**(ii) Neutral electrophiles :-** Which possess a electron dificiency.

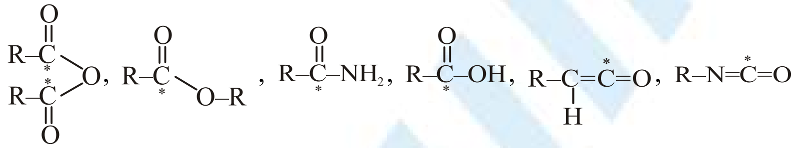
(a) All Lewis acids as :

$BF_3, AlCl_3, SO_3, ZnCl_2, BeCl_2, FeCl_3, SnCl_2, CO_2, SnCl_4$.

(b) The neutral atom that accept electrons from the substrates :



$>\overset{*}{C}=O, R\overset{*}{C}OCl, R-\overset{*}{Mg}-X, \overset{*}{I}-Cl, CH_3-\overset{*}{C}N, \overset{*}{R}-Cl, \overset{*}{R}-O, R-\underset{\underset{H}{|}}{\overset{\oplus}{O}}H$



$R-\underset{*}{\overset{\overset{O}{\|}}{C}}-NH_2, R-\underset{*}{\overset{\overset{O}{\|}}{C}}-OH, R-\underset{\underset{H}{|}}{C}=\overset{*}{C}=O, R-N=\overset{*}{C}=O$

The star (*) indicates the atom that accept electrons.

(c) Free radicals, carbenes & nitrene acts as electrophiles.

(d) Reasent with electrophilie centre :

$\dot{H}$, (H–F, H–Cl, H–Br, H–I), $H-O-\dot{C}l$, $H-O-\dot{B}r$, $O=\dot{N}-Cl$, $O=\dot{N}-Br$, $\dot{B}r-Cl$, $\dot{I}-Br$

### (B) NUCLEOPHILIC REAGENT OR NUCLEOPHILES

Which attack on the positive site of the substrate or loves nucleus.

**Nucleophilic (Nucleo + philes)**

↓

**(Nucleus + loving)**

Nucleophiles may be negatively charged ions or possess a lone pair of electron or donate an unshared electron pairs.

(i) Negatively charged nucleophiles.

$\overset{\ominus}{H}, \overset{\ominus}{O}H, \overset{\ominus}{O}R, \overset{\ominus}{C}N, \overset{\ominus}{X}(\overset{\ominus}{I}, \overset{\ominus}{Br}, \overset{\ominus}{Cl}, \overset{\ominus}{F}), \overset{\ominus}{R}, R-CO\overset{\ominus}{O}, \overset{\ominus}{N}H_2, \overset{\ominus}{C}H_2-COR, \overset{\ominus}{S}H, HS\overset{\ominus}{O}_4, N\overset{\ominus}{O}_3, R\overset{\ominus}{S}, C\overset{\ominus}{O}_3,$

$CH_2=\overset{\ominus}{C}H, \overset{\ominus}{N}=\overset{\oplus}{N}=\overset{\ominus}{N}$.

(ii) All Lewis base which contains lone pairs :

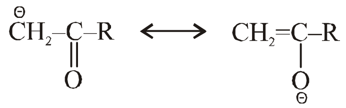
$H_2\ddot{\underset{..}{O}}, R-\ddot{\underset{..}{O}}H, R-\ddot{\underset{..}{O}}-R, \ddot{N}H_3, R-\ddot{N}H_2, R_3\ddot{N}, R\ddot{\underset{..}{S}}H, R-\ddot{\underset{..}{S}}-R, H_2\ddot{\underset{..}{S}}$

(iii) $\overset{*}{R}-Mg-X, \overset{*}{R}-Li, LiAl\overset{*}{H}_4, CH_3-C\overset{*}{N}, NaB\overset{*}{H}_4, \overset{*}{R}_2Zn, \overset{*}{R}_2CuLi, \overset{*}{R}_2Cd, \overset{*}{B}u_2Al\overset{*}{H}$

The star (*) indicates the atom which donates electrons to the substrate.

**Ambident nucleophile :** Nucleophiles which have two sites of electron rich centre or in which two or more atoms bear an unshared pair of electrons.

**Ex.** $K-O-N=O$, $NH_2-OH$, $\overset{\oplus}{K}\overset{\ominus}{C}\equiv\ddot{N}$

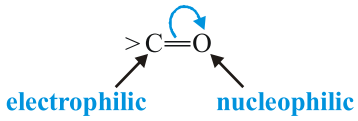


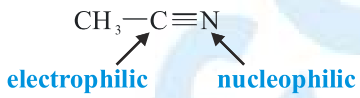
$$\overset{\ominus}{C}H_2-\underset{\underset{O}{\|}}{C}-R \longleftrightarrow CH_2=\underset{\underset{\overset{|}{O^{\ominus}}}{}}{C}-R$$

Resonating structures are also ambident nucleophile.

**Amphiphile :** Molecule containing a multiple bond between carbon and a more electronegative atom can act both as electrophiles or nucleophiles.

**Ex.**





| S.No. | Electrophile | Nucleophile |
|---|---|---|
| 1 | Accepts the electron pair | Supplies the electron pair |
| 2 | Electron deficient | Electron rich |
| 3 | Attacks the points of high electron density | Attacks the point of low electron density |
| 4 | Lewis acid | Lewis base |
| 5 | Possess an empty orbital to receive the electron pair | Possess an electron pair which is loosely held and can be supplied easily |
| 6 | Usually positively charged species | Usually negatively charged species |
| 7 | Forms an extra bond with the nucleophile | Increases its covalency by one unit |

## ELECTRONIC EFFECTS

There are four effect which affect the chemical reaction are –

**(1) Inductive effect** **(2) Mesomeric effect** **(3) Hyper conjugation** **(4) Electromeric effect**

## (1) INDUCTIVE EFFECT

- Polarity developed in Carbon–chain due to the **shifting of σ bond electron** by the group or atom present on carbon-chain is known as inductive effect,.
- Discovered by scientist **Ingold.**
- It is effective upto 3 or 4 carbons. After 3 or 4 carbons it becomes neutralized.

  So $\boxed{\textbf{Magnitude of I effect} \propto \frac{1}{\textbf{distance}}}$
- Inductive effect is measure with respect to hydrogen atom that means inductive effect of hydrogen is always zero.
- It is a permanent effect.
- Some atoms or groups have a greater tendency to attract the shared electron of the covalent bond. Such atoms or groups acquire partial negative charge by receiving electron density from the covalent bonds of the chain. Therefore, these are classified as the groups exerting **negative inductive (– I) effect.**

- If shifting of electron takes place from carbon chain to group or away from the carbon chain or towards the group , then it is known as **(–) I** effects.

$$\mathrm{C}-\underset{3}{\overset{\oplus\delta\delta\delta}{\mathrm{C}}}\ggg\underset{2}{\overset{\oplus\delta\delta}{\mathrm{C}}}\gg\underset{1}{\overset{\oplus\delta}{\mathrm{C}}}\rightarrow\overset{\ominus\delta}{\mathrm{Z}}$$

(I)

$C_1(\delta+) > C_2(\delta\delta+) > C_3(\delta\delta\delta+)$

- Due to –I effect positive charge develops over carbon chain or carbon chain becomes electron deficient such type of carbon chain will be **more reactive towards nucleophile** or less reactive will be towards electrophile.

  Group which shows (–) I are -

  The decreasing order of negative inductive effect of some important atoms and groups is given below :

**Order of – I effect** $\overset{\oplus}{\mathrm{O}}R_2 > -\overset{\oplus}{\mathrm{N}}R_3 > -\overset{\oplus}{\mathrm{N}}H_3 > -NO_2 > -SO_3H > -CN >$

$-COOH > -X > -OH > -OR > -NH_2 > -C_6H_5 > -H$

- Some groups are electron donor and therefore acquire partial positive charge by increasing electron ensity in the covalent bonds of a chain. Such groups exert **positive inductive (+ I) effect.**
- Or if shifting of electron takes place from group to carbon chain or away from the group or towards the carbon chain then it known as **(+) I effect**

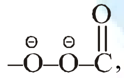
$$\mathrm{C}-\underset{3}{\overset{\ominus\delta\delta\delta}{\mathrm{C}}}\lll\underset{2}{\overset{\ominus\delta\delta}{\mathrm{C}}}\ll\underset{1}{\overset{\ominus\delta}{\mathrm{C}}}\leftarrow\overset{\oplus\delta}{\mathrm{Z}}$$

(II)

$C_1(\delta-) > C_2(\delta\delta-) > C_3(\delta\delta\delta-)$

- Due to +I effect electron density increase on carbon chain or negative charge comes on carbon chain such type of carbon chain will be **more reactive towards electrophile** or will be less reactive towards nucleophile.

  Group which shows +I effect are.

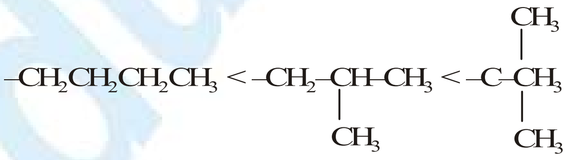


$-\overset{\ominus}{O}-\overset{\ominus}{O}-\overset{\overset{\displaystyle O}{\|}}{C}$, all alkyl groups

- In alkyl groups megnitude of **+I effect** $\propto$ **size of alkyl group**

  $-CH_3 < -CH_2CH_3 < -CH_2CH_2CH_3 < -CH_2CH_2CH_2CH_3$

  In isomeric alkyl group megnitude of **+I effect** $\propto$ **number of branches**.



$$-CH_2CH_2CH_2CH_3 < -CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3 < -\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

## APPLICATION OF I-EFFECT

### (i) Stability of carbocation

(a) If number of + I groups increases then stability of carbocation increases.

(b) If number of –I groups decreases then stability of carbocation increases.

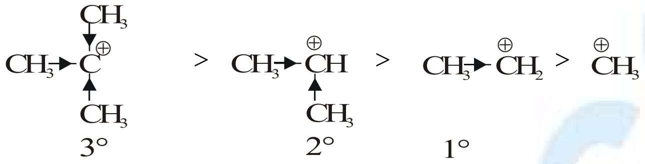
(c) Therefore

$$\boxed{\text{Energy µ charge} \propto \frac{1}{\text{stability}}}$$

$$\boxed{\text{Stability of Carbocation} \propto \text{No.of} + \text{I groups}}$$

$$\boxed{\text{Stability of carbocation} \propto \frac{1}{\text{No.of} - \text{I groups}}}$$

**Ex.** Stability order :



$CH_3\rightarrow\overset{\oplus}{C}(CH_3)_2$ (3°) $>$ $CH_3\rightarrow\overset{\oplus}{C}H\leftarrow CH_3$ (2°) $>$ $CH_3\rightarrow\overset{\oplus}{C}H_2$ (1°) $>$ $\overset{\oplus}{C}H_3$

**Sol.** Reason : More no. of +I group.
more stable carbocation.

**(ii) Stability of carbanion**

(a) If number of – I groups increases then stability of carbanion increases.

(b) If number of +I groups decreases then stability of carbanion increases.

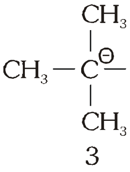
(c) Therefore

$$\boxed{\text{Stability of Carbanion} \propto \text{No.of - I groups}}$$

$$\boxed{\text{Stability of Carbanion} \propto \frac{1}{\text{No.of} + \text{I groups}}}$$

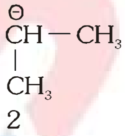
**Ex.**

(1)



$CH_3-\overset{\ominus}{C}(CH_3)_2-$ 3

(2)



$\overset{\ominus}{C}H(CH_3)-CH_3$ 2

(3) $CH_3-\overset{\ominus}{C}H_2$ (4) $\overset{\ominus}{C}H_3$

1°

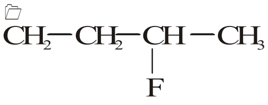
More No. of +I group.
Less stable carbanion.
So stability order 1 < 2 < 3 < 4

**Ex.**

(1)

$\overset{\ominus}{C}H_2-CH(F)-CH_2-CH_3$

(2)



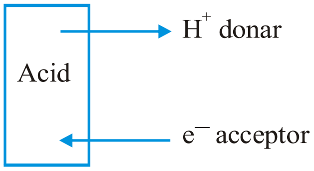
$\overset{\ominus}{C}H_2-CH_2-CH(F)-CH_3$

(3) $\overset{\ominus}{C}H_2-CH_2-CH_2-CH_2-F$

Minimum distance of –F.
Maximum –I of –F.
Minimum negative charge.
Maximum stable.
So stability order 1 > 2 > 3

## (iii) Acidic and Basic Strength

### ✎ Acidic strength

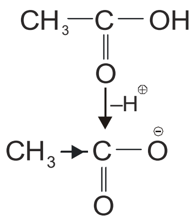


(i) If No. of – I groups increases then acidic strength increases.
(ii) If No. of + I groups increases then acidic strength decreases.

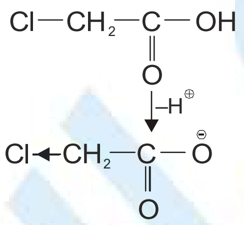
$$\boxed{\text{acidic strength} \propto \text{No. of - I groups} \propto \frac{1}{\text{No. of + I groups}} \propto K_a \propto \frac{1}{pK_a}}$$

**Ex.**

(i)

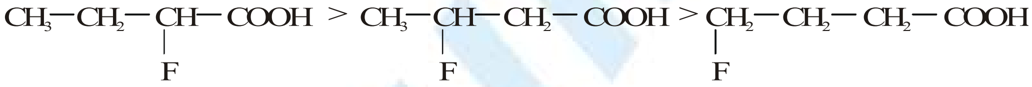


+I of $-CH_3$
so anion is less stable



–I of –Cl, so anion is more stable
and corresponding acid is more acidic.

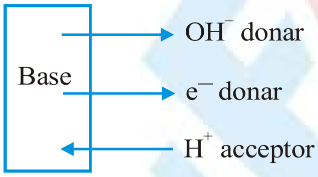
(ii)



$$CH_3-CH_2-\underset{\displaystyle F}{\underset{|}{CH}}-COOH > CH_3-\underset{\displaystyle F}{\underset{|}{CH}}-CH_2-COOH > \underset{\displaystyle F}{\underset{|}{CH_2}}-CH_2-CH_2-COOH$$

minimum distance of F
from –COOH maximum –I
of F. So maximum acidic.

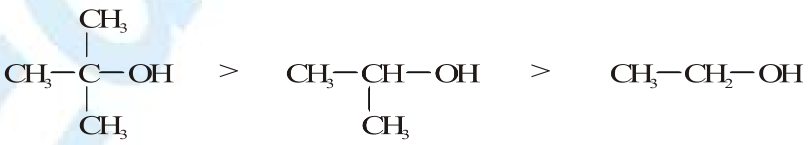
### ✎ Basic strength



(i) If No. of + I groups increases then basic strength increases.
(ii) If No. of – I groups increases then basic strength decreases.

$$\boxed{\text{Basic strength} \propto \text{No. of + I groups} \propto \frac{1}{\text{No. of – I groups}} \propto K_b \propto \frac{1}{pK_b}}$$

**Ex.**



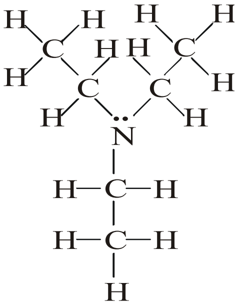
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH > CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH > CH_3-CH_2-OH$$

Maximum +I.
Maximum tendency to donate l.p.
Maximum basic.

**Ex.** Explain— Basicity order in aqeous solution and in liquid phase. $Et_2NH > Et_3N > EtNH_2$

**Sol.** Due to steric hindrance in 3° amine, it is less basic, than 2° amine.

Steric hindrance of three $-C_2H_5$ group protect the lone pair of nitrogen from the attack of $H^{\oplus}$.



**But in gaseous phase basic order is** $\boxed{R_3\ddot{N} > R_2\ddot{N}H > R\ddot{N}H_2 > \ddot{N}H_3}$

Some other basic order of different amine if alkyl group would be change (in aq. medium)

| | Alkyl groups (R–) | Relative base strength |
|---|---|---|
| (i) | $CH_3-$ | $R_2NH > RNH_2 > R_3N > NH_3$ |
| (ii) | $C_2H_5-$ | $R_2NH > R_3N > RNH_2 > NH_3$ |

**Ex.** Ethyl amine is more basic then aniline, why ?

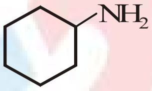
**Sol.** Due to the + I effect of ethyl group.

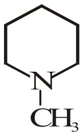
**Ex.** $Cl-NH_2$ is less basic then methyl amine, why ?

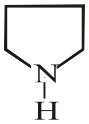
**Sol.** Due to – I effect of –Cl group and $p_\pi-d_\pi$ conjugation.

**Ex.** Correct basic order of the following different amine in chlorobenzene medium is -

(A) $CH_3-CH_2-NH_2$

(B) 

(C) 

(D) 

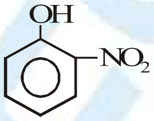
**Sol.** (C > D > B > A)

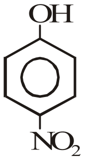
**Ex.** Which is most basic among the following :

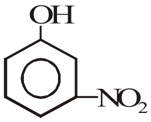
(A) $CH_3NH_2$ (B) $CH_3CH_2NH_2$ (C) $NH_3$ (D) $(CH_3)_2CHNH_2$

**Sol.** (D)

**Ex.** Which is most acidic compound –

(A) 

(B) 

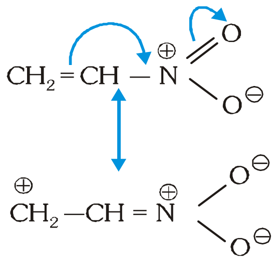
(C) 

(D) 

**Sol.** (B)

## (2) MESOMERIC EFFECT OR RESONANCE EFFECT

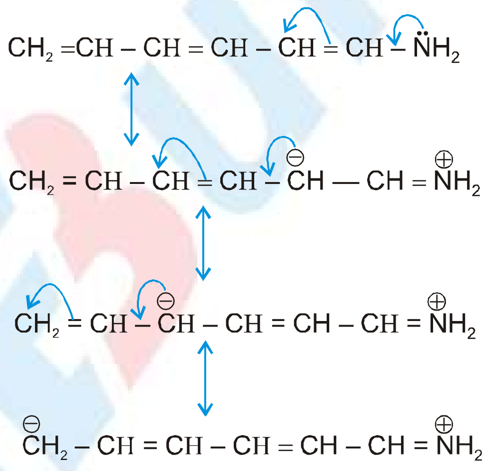
- Polarity developed in conjugate system by the complete transfer of non–bonding electron or π–bond electron due to the group or atom attach with conjugate system is known as mesomeric effect.
- If transfer of pi-bond electron takes place from conjugate system to group then it is known as **negative mesomeric (–M)** effect.



- For –M effect, group should have either be positive charge or should have vacant orbital.
- Due to –M effect positive charge comes over conjugate system or due to –M effect electron density decrease in conjugate system, such type of conjugate system will be more reactive towards nucleophile or will be less reactive towards electrophile.
- **Group which shows –M effect are -**

$-NO_2$, $-CN$, $-SO_3H$, $-CHO$, $-COR$, $-COOH$, $-COOR$, $-COX$, $-CONH_2$ etc.

- If transfer of non bonding electron takes place from group to conjugate system then it is known as **positive mesomeric (+M)** effect.



- For +M effect, group should have either be lone pair of electron or should have negative charge.
- Due to + M effect negative charge comes over conjugate system or electron density increase on conjugate system such type of conjugate system will be more reactive towards electrophile or will be less reactive towards nucleophile.
- **Group which shows + M effect are -**

$-\overset{\ominus}{O}$, $-\overset{\ominus}{N}H$, $-NR_2$, $-NHR$, $-NH_2$, $-OH$, $-OR$, $-SH$ $-SR$, $-F$, $-Cl$, $-NHCOR$, $-O-COR$ etc.

- In mesomeric effect polarity or charge migrate from one end to another end. During charge transfer, energy releases from the conjugate system which increase the stability of conjugate system also.
- Due to charge transfer compound form more then one structure without change in atomic orientation these structures are known as resonating structures.

- These structures are helpful in explanation of chemical reactivity or the chemical reaction of the compound thats why we can say resonance phenomenon is the result of mesomeric effect or delocalisation.

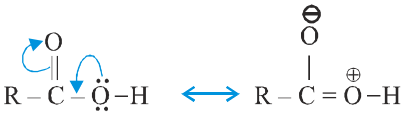
  (i) Resonating structure are not the real structures of conjugated compounds.

  (ii) The real structure of conjugated compound is a hybrid of all resonating structures. This phenomenon is known as resonance, mesomerism or delocalisation.

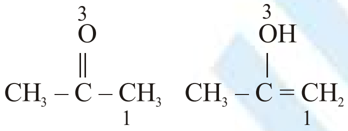
  (iii) Thus resonance is nothing but hybridisation of resonating structures and resonance phenomenon will take place in conjugated compounds.

  (iv) Conditions of Resonating Structures : Resonance structures should fulfil following conditions :

  **(a)** All resonating structures must have the same arrangement of atomic nuclei. Resonance differs from tautomerism in this very important aspect.



Positions of atomic nuclei in (I) and (II) are same.



$$\underset{\text{(I)}}{CH_3-\overset{\overset{3}{O}}{\overset{\|}{C}}-\underset{1}{CH_3}} \qquad \underset{\text{(II)}}{CH_3-\overset{\overset{3}{OH}}{\overset{|}{C}}=\underset{1}{CH_2}}$$

Position of hydrogen nuclei in (I) and (II) are different, hence (I) and (II) are not resonating structures, they are tautomer.

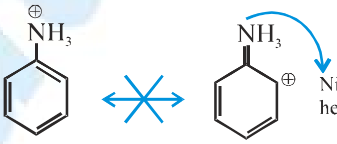
**(b)** The resonating structures must have the same numbers of paired and unpaired electrons. However, they differ in the way of distribution of electrons.

| Total number of paired electrons = 16<br>unparied electron =1 | Total number of paired electrons = 16<br>unparied electron =1 |
|---|---|

- The energy of the different resonating structures must be the same or nearly the same.
- All atoms that are part of the delocalisation system must be in a plane or be nearly planar.

  (v) All atoms of the resonating structure should follow the octet rule.

  For Example: All atoms follow octet rule.



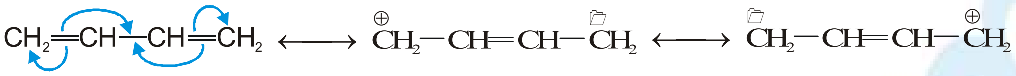
Nitrogen does not follow its octet rule hence (II) is not resonating structure (I)

## CONDITIONS FOR RESONANCE

**1.** If there are two π bonds at alternate position then $e^-$ of one π bond are transferred towards another π bond. (According to I–effect).

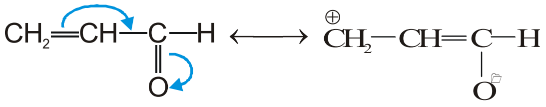
**Ex.**

(i)



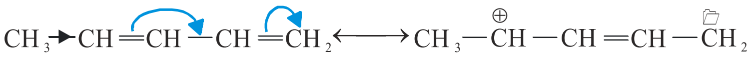
$CH_2=CH-CH=CH_2 \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH-\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2-CH=CH-\overset{\oplus}{C}H_2$

(ii)



$CH_2=CH-\underset{\underset{O}{\|}}{C}-H \longleftrightarrow \overset{\oplus}{C}H_2-CH=\underset{\underset{\overset{\ominus}{O}}{|}}{C}-H$

(iii)

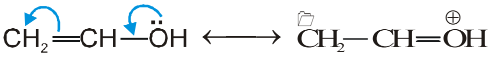


$CH_3\rightarrow CH=CH-CH=CH_2 \longleftrightarrow CH_3-\overset{\oplus}{C}H-CH=CH-\overset{\ominus}{C}H_2$

**2.** If there is one lone pair or a negative charge and one $\pi$ bond are at alternate position then $e^-$ of lone pair or negative charge are transferred towards $\pi$ bond.

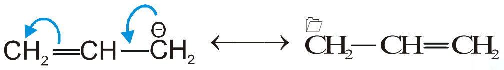
**Ex.**

(i)



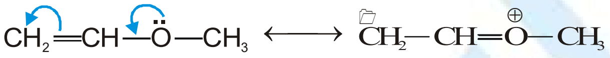
$CH_2=CH-\ddot{O}H \longleftrightarrow \overset{\ominus}{C}H_2-CH=\overset{\oplus}{O}H$

(ii)



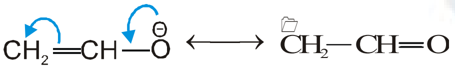
$CH_2=CH-\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2-CH=CH_2$

(iii)



$CH_2=CH-\ddot{O}-CH_3 \longleftrightarrow \overset{\ominus}{C}H_2-CH=\overset{\oplus}{O}-CH_3$

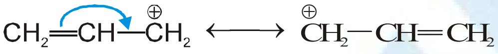
(iv)



$CH_2=CH-\overset{\ominus}{O} \longleftrightarrow \overset{\ominus}{C}H_2-CH=O$

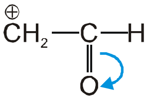
**3.** If there is one positive charge and one $\pi$ bond are at alternate position then $e^-$ of $\pi$ bond are transferred towards positive charge.

**Ex.**



$CH_2=CH-\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH_2$

**Note :**

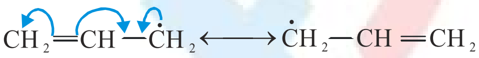


$\overset{\oplus}{C}H_2-\underset{\underset{O}{\|}}{C}-H$ does not show resonance because due to more EN of oxygen $\pi$ $e^-$ are always transferred towards oxygen.

**4.** If there is one free $e^-$ and one $\pi$ bond are at alternate position.

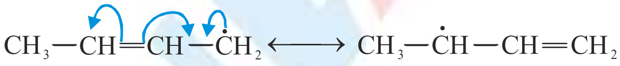
**Ex.**

(i)



$CH_2=CH-\dot{C}H_2 \longleftrightarrow \dot{C}H_2-CH=CH_2$

(ii)



$CH_3-CH=CH-\dot{C}H_2 \longleftrightarrow CH_3-\dot{C}H-CH=CH_2$

**5.** If there is one lone pair or negative charge and one positive charge are at adjacent atoms then $e^-$ of lone pair or negative charge are transferred towards positive charge.

**Ex.**

$\overset{\oplus}{C}H_2-\ddot{O}H \longleftrightarrow CH_2=\overset{\oplus}{O}H$

## ETOOS KEY POINTS

### Characteristics of Resonance

(i) In resonance only $e^-$ are transferred not atoms.

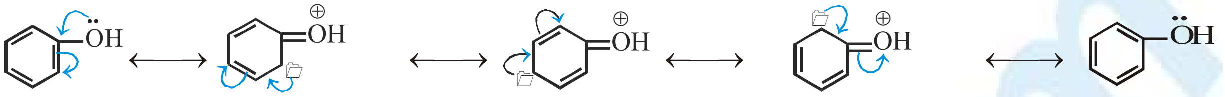
(ii) The number of $e^-$ or number of unpaired or paired $e^-$ in all resonating structures should be same.

(iii) The energy of resonating structures is almost same.

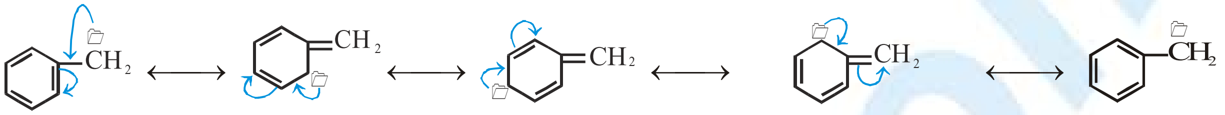
(iv) It is permanent effect.

(v) All the resonating or canonical structures must confirms to Lewis structures.

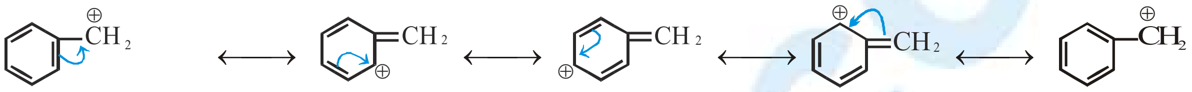
## Draw resonating structures of the following

1.


5-Resonating structure

2.


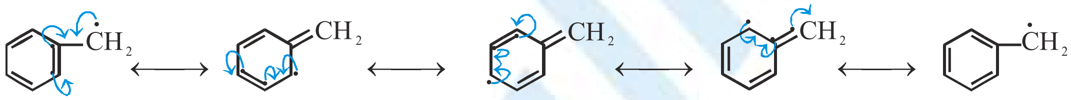
5-Resonating structure

3.


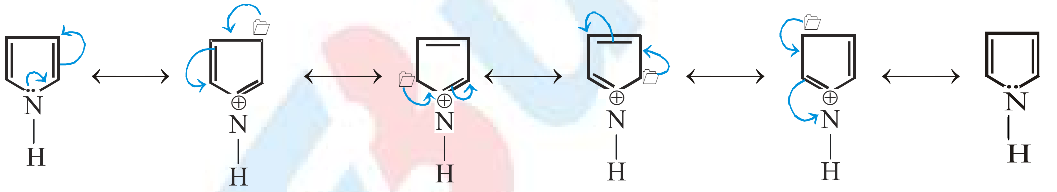
5-Resonating structure

4.

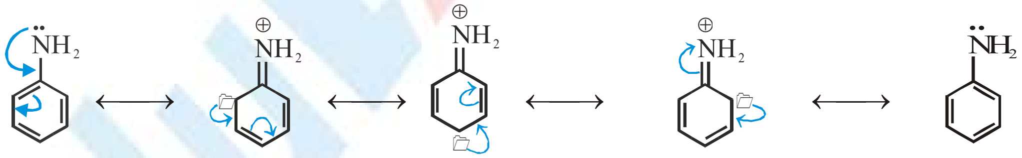

5-Resonating structure

5.


5-Resonating structure

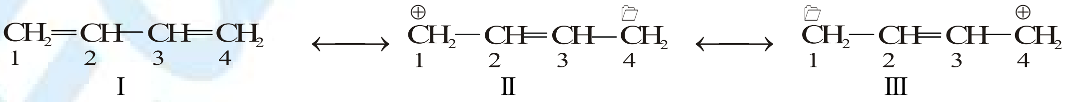
6.


6-Resonating structure

7.


5-Resonating structure

## Hybrid resonating structure



$$\underset{1}{CH_2}=\underset{2}{CH}-\underset{3}{CH}=\underset{4}{CH_2} \longleftrightarrow \underset{1}{\overset{\oplus}{C}H_2}-\underset{2}{CH}=\underset{3}{CH}-\underset{4}{\overset{\ominus}{C}H_2} \longleftrightarrow \underset{1}{\overset{\ominus}{C}H_2}-\underset{2}{CH}=\underset{3}{CH}-\underset{4}{\overset{\oplus}{C}H_2}$$

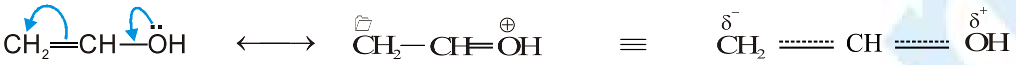
I II III

In the structure I $C_1—C_2$ has double bond while in II and III $C_1—C_2$ has single bond, so $C_1—C_2$ shows bond length in between single and double bond similarly in structure I $C_2—C_3$ has single bond. While in structure II and III $C_2—C_3$ has double bond, so $C_2—C_3$ shows bond length in between single and double bond.

So hybrid resonating structure from all its resonating structures is :

$$\equiv \quad CH_2 \cdots\cdots CH \cdots\cdots CH \cdots\cdots CH_2 \qquad \text{Hybrid structure}$$

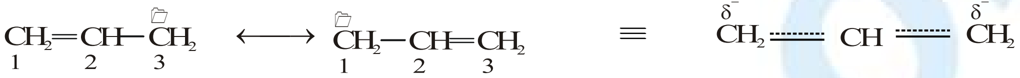
**Ex.**

(i) 

$$CH_2=CH-\ddot{O}H \longleftrightarrow \overset{\ominus}{C}H_2-CH=\overset{\oplus}{O}H \equiv \overset{\delta^-}{CH_2}\cdots\cdots CH \cdots\cdots \overset{\delta^+}{OH}$$

I II

(Resonating structure) (Hybrid structure)

(ii) 

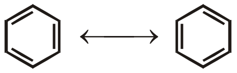
$$\underset{1}{CH_2}=\underset{2}{CH}-\underset{3}{\overset{\ominus}{CH_2}} \longleftrightarrow \underset{1}{\overset{\ominus}{CH_2}}-\underset{2}{CH}=\underset{3}{CH_2} \equiv \overset{\delta^-}{CH_2}\cdots\cdots CH \cdots\cdots \overset{\delta^-}{CH_2}$$

(Resonating structure) (Hybrid structure)

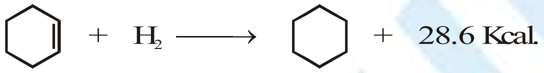
## Resonance energy

The difference in the experimental and calculated energies (heat of hydrogenation) by which the compound is stable, is known as the resonance or delocalization energy. Higher the value of resonance energy, greater is the resonance stabilization.

## Resonance energy (R.E.) of Benzene



The Resonance energy of benzene is calculated from the heat of hydrogenation as given below :



but experimental value is 49.8 Kcal. so,

Resonance energy = Calculated value – Experimental value

= 85.8 – 49.8 = 36 Kcal.

## APPLICATION OF M-EFFECT OR RESONANCE EFFECT

### (i) Stability of carbocation

**(a)** **Stability of carbocation is increased by resonance.**

**(b)** **Aromatic compound are more stable than non aromatic compound.**

**Ex.** Compare stability order of :-

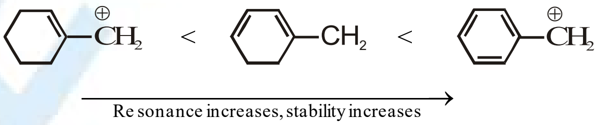
(i) 

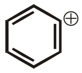
$$CH_2=CH-\overset{\oplus}{C}H_2 > CH_3\rightarrow CH_2-\overset{\oplus}{C}H_2 > CH_2=CH\leftarrow CH-\overset{\oplus}{C}H_2$$

stable by resonance +I of Alkyl group –I of Alkenyl group

(ii) 

1° 2° 3°

(iii) 

(iv)  ,  , 

(I) (II) (III)

stable by resonance more resonance localized ⊕ve charge

stability order II > I > III

**(ii) Stability of carbanion**

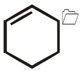
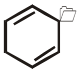
**(a) Stability of carbanion is increased by resonance.**

**Ex.** Compare stability order of :

(i) $CH_2{=}CH{-}\overset{\ominus}{C}H_2$ , $CH_2{=}\overset{\ominus}{C}H$ , $CH_3{-}\overset{\ominus}{C}H_2$

stable by resonance – ve charge on more EN atom

stability order I > II > III

(ii)  ,  ,

(I) (II)

stable by resonance more resonance

stability order II > I.

(iii) $\overset{\ominus}{C}H_2{-}NO_2$ $\overset{\ominus}{C}H_2{-}CH_2{-}NO_2$ $CH_3{-}\overset{\ominus}{C}H{-}NO_2$

stable by resonance no resonance stable by resoncance, but +I of $CH_3$

stability order I > III > II

**(iii) Stability of free radicals**

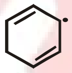
**(a) Stability of free radicals is increased by resonance.**

**Ex.** Compare stability order of :

(i) $CH_2{=}CH{-}\dot{C}H_2$ $CH_2{=}\dot{C}H$ $CH_2{=}CH{-}\dot{C}H{-}CH{=}CH_2$

less resonance no resonance more resonance

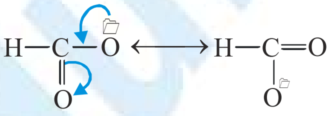
stability order III > I > II

(ii)  ,  , 

resonance more resonance localized

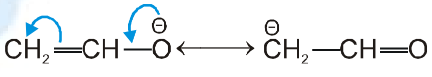
stability order II > I > III

**Equal resonating structures :** Resonating structures in which there is same charge on same atom.

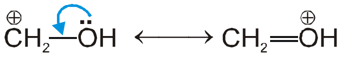
**Ex.** 

$H{-}C({=}O){-}\overset{\ominus}{O} \longleftrightarrow H{-}C({-}\overset{\ominus}{O}){=}O$ are equal R.S.

**Unequal resonating structures :** Resonating structures in which there is same charge on different atom or different charge on same atom or different charge on different atom.

**Ex.** 

$CH_2{=}CH{-}\overset{\ominus}{O} \longleftrightarrow \overset{\ominus}{C}H_2{-}CH{=}O$ are unequal R.S.



$\overset{\oplus}{C}H_2{-}\ddot{O}H \longleftrightarrow CH_2{=}\overset{\oplus}{O}H$

**Note :** Equal resonating structures are more stable than unequal resonating structures.

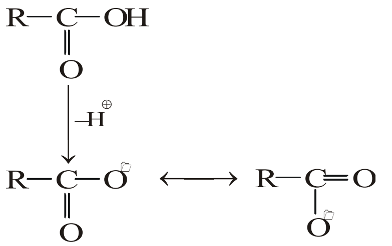
## (iv) Acidic and Basic strength

### (a) Acidic strength

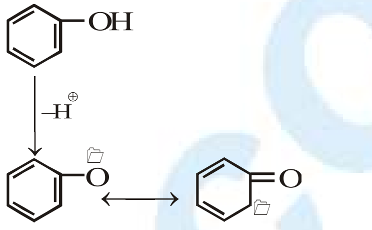
$$\boxed{\text{Acidic strength} \propto -M \propto -I \propto \frac{1}{+M} \propto \frac{1}{+I}}$$

**Ex.** Carboxylic acids are more acidic than phenols, why ?

**Sol.**



2, equal R.S. more stable anion
so corresponding acid is more acidic



5, unequal R.S. less stable anion

**Ex.** Phenol is more acidic than alcohols why ?

**Sol.**

$$Ph{-}OH \xrightarrow{-H^{\oplus}} Ph{-}O^{\ominus}$$

stable by resonance
So, it is more acidic.

$$R{-}OH \xrightarrow{-H^{\oplus}} R{-}O^{\ominus}$$

no resonance.

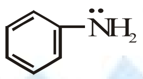
### (b) Basic strength

If there is more resonance of lone pair or negative charge then it will be more stable, means less basicity.

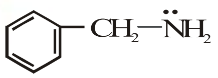
$$\boxed{\text{Basic strength} \propto +M \propto +I \propto \frac{1}{-M} \propto \frac{1}{-I}}$$

**Ex.** Give basic strength order :

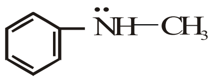
(i)



l.P. is stabilized by
resonance



no resonance of l.p.
so maximum basic



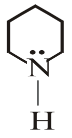
l.p. is stabilized by resonance
stabilized and +I of $CH_3$

basic order — II > III > I

(ii)

stable by
resonance

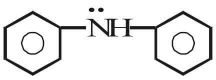
localized
l.p. on more EN



basic order — III > II > I

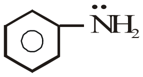
**Ex.** Give basic strength order for :

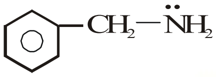
(i)



diphenyl amine

more resonance





benzyl amine

no resonance

**Sol.** 3 > 2 > 1

**Ex.** Aniline is less basic than alkyl amine, why ?

**Sol.** Due to delocalization of l.p. of nitrogen in aniline, aniline is less basic.

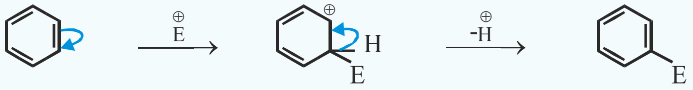
**Ex.** Which is weakest base :

(i) $C_6H_5—CH_2—NH_2$ (ii) $C_6H_5—CH_2—NH—CH_3$ (iii) $O_2N—CH_2—NH_2$ (iv) $CH_3—NH—CHO$

**Sol.** (iv) due to resonance of l.p.

**ETOOS KEY POINTS**

**Reactivity of benzene :** Characteristic reaction of benzene is electrophilic substitution (ESR)



(product)

In benzene ring due to more electron density first attack will be of electrophile.

### RULES FOR STABILITY OF RESONATING STRUCTURE (R.S) :

(i) Non-polar R.S. is more stable than polar resonating structures.

(ii) In polar R.S. complete octet is more stable than incomplete octet.

(iii) For incomplete R.S. positive charge on more EN is less stable.

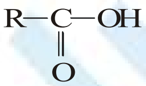
**Ex.** Arrange the following for stability order.

(i) $CH_2=CH-Cl$ $\overset{\ominus}{C}H_2-CH=\overset{\oplus}{Cl}$ $\overset{\ominus}{C}H_2-\overset{\oplus}{C}H-Cl$

non-polar complete octet incomplete octet

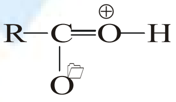
stability order : 1 > 2 > 3

(ii)



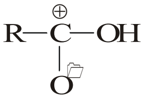
$R-\underset{\underset{O}{\|}}{C}-OH$

>



$R-\underset{\underset{O^{\ominus}}{|}}{C}=\overset{\oplus}{O}-H$

>



$R-\underset{\underset{O^{\ominus}}{|}}{\overset{\oplus}{C}}-OH$

non-polar complete octet incomplete octet

(iii) $R-\overset{\oplus}{C}=O$ < $R-C\equiv\overset{\oplus}{O}$

incomplete octet complete octet

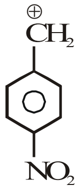
(Acylium ion)

(iv) $CH_2=CH-\overset{\ominus}{O}$ > $\overset{\ominus}{C}H_2-CH=O$

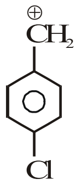
negative charge on more EN negative charge on less EN

**Ex.** Give stability order of :

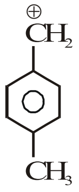
(i)



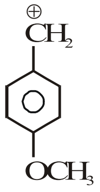
–M
charge↑↑



–I
charge↑



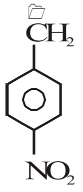
+I
charge↓



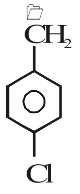
+M
charge↓↓

So stability order IV > III > II > I

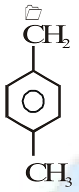
(ii)



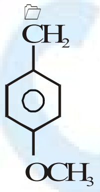
–M
charge↓↓



–I
charge↓



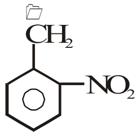
+I
charge↑

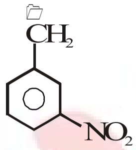


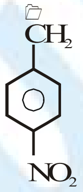
+M
charge↑↑

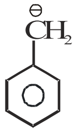
Stability order I > II > III > IV

(iii)









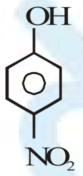
–M and
more –I
charge is minimum

M = 0
only –I

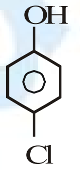
–M and
less –I

So stability order I > III > II > IV

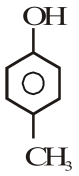
**Ex.** Give acidic strength order for :



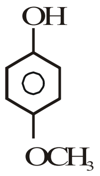
–M



–I



+I



+M

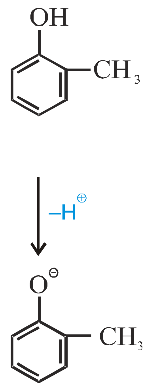
**Sol.** So acidic order is I > II > III > IV

**Ex.** The mixture of ortho-nitrophenol and para-nitrophenol can be separated by steam distillation why and which can be distilled out ?

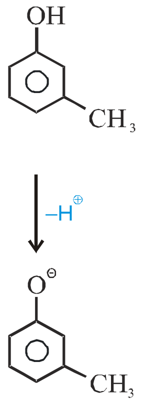
**Sol.** Ortho-nitrophenol is distilled out due to less B.P. of ortho-nitrophenol it is more volatile

**Ex.** Give acidic strength order for

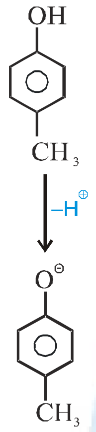
(i)



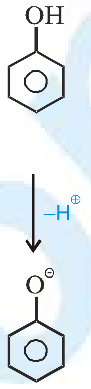
more +I and
H-effect of CH$_3$,So
anion is minimum stable



H = 0
only +I



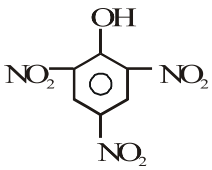
less +I and
H-effect

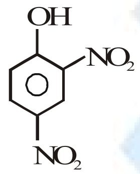


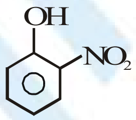
maximum stable anion
so corresponding acid is
maximum acidic

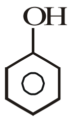
Acid ic order 4 > 2 > 3 > 1

(ii)









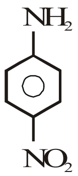
maximum –M and –I

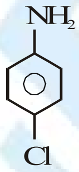
so maximum acidic

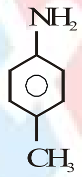
Acidic order 1 > 2 > 3 > 4

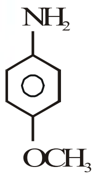
**Ex.** Give basic strength order for :

(i)







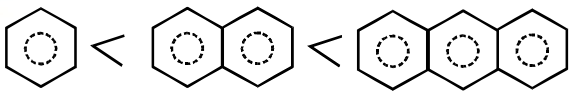


–M –I +I +M

So basic strength order IV > III > II > I

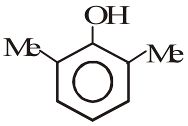
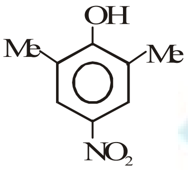
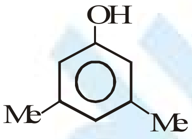
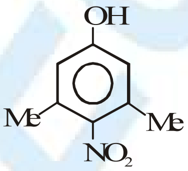
**Ex.** What is the increasing order of resonance stabilization of benzene, naphthalene and anthracene.

**Sol.** The values of resonance energy for benzene, naphthalene and anthracene are 36, 76 and 85 Kcal per mole respectively. It is clear from these values that the resonance stabilisation of naphthalene is more than that of benzene and less than that of anthracene. Thus, the increasing order of resonance stabilisation is as follows.



Benzene Naphthalene Anthracene

**Phenol : 9.98/1.10 × $10^{-10}$ pKa/Ka value**

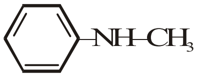
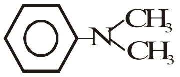
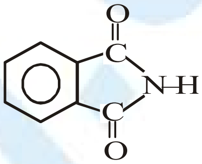
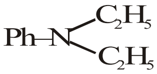
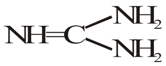
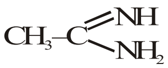
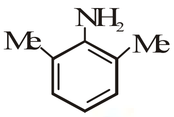
| Subtituent | O– | M– | P– |
|---|---|---|---|
| (i) Me | $10.28/0.63 \times 10^{-10}$ | $10.08/0.98 \times 10^{-10}$ | $10.14/0.67 \times 10^{-10}$ |
| (ii) $NO_2$ | $7.23/600 \times 10^{-10}$ | $8.40/50 \times 10^{-10}$ | $7.15/690 \times 10^{-10}$ |
| (iii) F | $8.81/15 \times 10^{-10}$ | $9.28/5.2 \times 10^{-10}$ | $9.98/1.1 \times 10^{-10}$ |
| (iv) Cl | $8.48/77 \times 10^{-10}$ | $9.02/16 \times 10^{-10}$ | $9.38/6.3 \times 10^{-10}$ |
| (v) $CH_3$–O | $9.98/1.05 \times 10^{-10}$ | $9.65/2.24 \times 10^{-10}$ | $9.38/0.62 \times 10^{-10}$ |
| (vi) OH | 9.48 | $9.44/3 \times 10^{-10}$ | 9.96 |
| (vii) $NH_2$ | $9.71/2.0 \times 10^{-10}$ | $8.16/68 \times 10^{-10}$ | 10.30 |
| (viii) Br | $41 \times 10^{-10}$ | $14 \times 10^{-10}$ | $5.6 \times 10^{-10}$ |
| (ix) I | $34 \times 10^{-10}$ | $13 \times 10^{-10}$ | $6.0 \times 10^{-10}$ |
| (x) 2.4- dinitrophenol | 4.00 | | |
| (xi) 2,4,6-trinitro phenol | pKa = 0.71 | $10.50 \times 10^{-2}$ | |
|  | 10.60 | | |
|  | 7.22 | | |
|  | 10.17 | | |
|  | 8.25 | | |

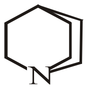
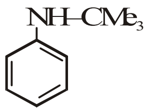
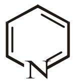
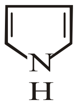
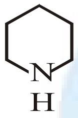
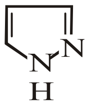
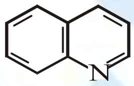
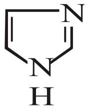
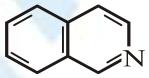
pKa/Benzoic acid → 4.20

| Substituent | pKa– | O– | M– | P– |
|---|---|---|---|---|
| H | **4.20** | 4.20 | 4.20 | 4.20 |
| Me | **–** | 3.91 | 4.27 | 4.37 |
| $NO_2$ | – | 2.17 | 3.48 | 3.43 |
| F | – | 3.27 | 3.87 | 4.14 |
| Cl | – | 2.94 | 3.83 | 3.98 |
| Br | – | 2.85 | 3.81 | 4.00 |
| OMe | – | 4.09 | 4.09 | 4.47 |
| OH | – | 2.98 | 4.08 | 4.58 |
| $NH_2$ | – | 4.92 | 4.72 | 4.98 |
| –COOH | – | 2.98 | 3.46 | 3.56 |
| H–COOH | 3.77 | | | |
| $CH_3$–COOH | 4.76 | | | |
| $CH_3$–$CH_2$–COOH | 4.88 | | | |
| HOOC–COOH | 1.23 | | | |
| HOOC–$CH_2$–COOH | 2.83 | | | |
| HOOC–$(CH_2)_2$–COOH | 4.19 | | | |
| Maleic acid | 1.92 ($pKa^1$) | 6.23 ($pKa^2$) | | |
| Fumaric acid | 3.02 ($pKa^1$) | 4.38 ($pKa^2$) | | |
| CH≡C–COOH | 1.84 | | | |
| $CH_2$=CH–COOH | 4.25 | | | |
| F–$CH_2$–COOH | 2.57 | | | |
| Cl–$CH_2$–COOH | 2.86 | | | |
| Br–$CH_2$–COOH | 2.90 | | | |
| I–$CH_2$–COOH | 3.16 | | | |
| $O_2N$–$CH_2$–COOH | 1.68 | | | |
| $Me_3N^+$–$CH_2$–COOH | 1.83 | | | |
| N≡C–$CH_2$–COOH | 2.47 | | | |
| $EtOCOCH_2COOH$ | 3.35 | | | |
| MeO–$CH_2$–COOH | 3.58 | | | |

pKa/Ka value-Aniline → 4.62

| Subtituent | O– | M– | P– |
|---|---|---|---|
| Me– | 4.39 | 4.69 | 5.12 |
| Me–O | 4.49 | 4.20 | 5.29 |
| $NH_2$ | 4.47 | 4.20 | 6.08 |
| $NO_2$ | –0.29 | 2.50 | 1.02 |
| Cl | 2.64 | 3.34 | 3.91 |
| Br | 2.60 | 3.51 | 3.91 |
| OH | 4.72 | 4.17 | 5.30 |

| | | | |
|---|---|---|---|
|  | 4.85 |  $CH-\overset{\overset{O}{\|}}{C}-\ddot{N}H_2$ | ~0.5 |
|  | 5.06 |  | shows some acidic nature |
|  | 5.11 | | |
|  $Ph-N\begin{matrix}C_2H_5\\C_2H_5\end{matrix}$ | 6.56 |  $NH=C\begin{matrix}NH_2\\NH_2\end{matrix}$ | 13.6 |
| $Ph_2NH$ | 0.9 | | |
| Ph–NH–AC | 0.4 |  $CH_3-C\begin{matrix}NH\\NH_2\end{matrix}$ | 12.4 |
|  | 5.69 | $(C_2H_5)_2NH$ | 10.93 |
| | | $Et_3N$ | 10.88 |
| | | $Et-NH_2$ | 10.67 |
|  | 4.60 | $NH_3$ | 9.25 |
| | | $Me_3N$ | 9.80 |
| | | $Me_2N$ | 10.77 |
| | | $Me-NH_2$ | 10.64 |

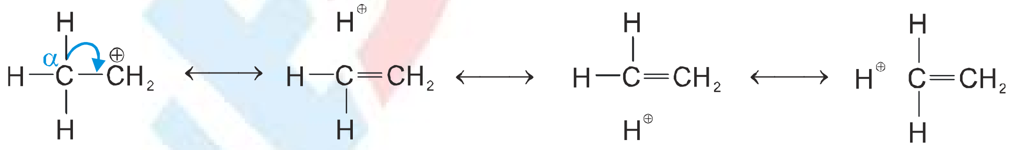
| | | | |
|---|---|---|---|
|  | 10.50 | $Bu_3N$<br>$Bu_2NH$<br>$BuNH_2$ | 9.87<br>11.28<br>10.61 |
|  | 7.1 |  | 5.23 |
|  | –0.27 |  | 11.22 |
|  | 2.53 |  | 4.94 |
|  | 7.03 |  | 5.2 |

## (3) HYPERCONJUGATION EFFECT OR H-EFFECT

**Complete** transfer of e$^-$ of –C–H σ bond towards π bond or positive charge or free electron is called as H-effect (permanent effect). It is also called as non-bonded resonance and given by Nathen and Baker.

**Conditions of H-effect**

**1.** If there is one C–H σ bond and one positive charge are at alternate position

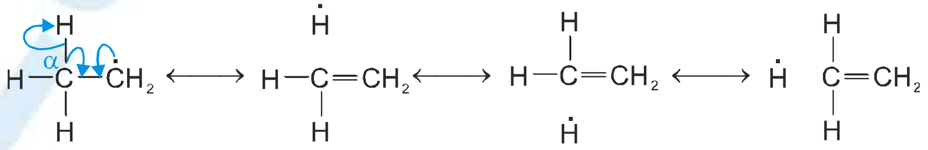


all are called as hyperconjugation structures or canonical structures.

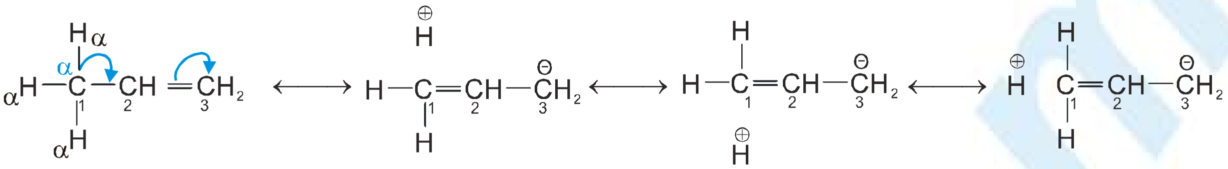
Carbon which is attached to positively charged carbon is called as α –C and H which is attached to α –C are called as α – H. So if number of α – H are more then there will be more number of hyperconjugation structures, so more stable carbocation.

**2.** Carbon which is attached to sp$^2$ C is called as α–C and H which are attached to α-C are called as α-H.

If there is one –C–H σ bond and one free e$^-$ are at alternate position then there will be H-effect.



**3.** If there is one –C–H σ bond and π bond are at alternate position then there will be H-effect.



## ETOOS KEY POINTS

**Special point**

(i) $\underset{1}{H_3C}-\underset{2}{CH}=\underset{3}{CH_2}$

$C_1$—$C_2$ bond length = 1.54 Å

$C_2$—$C_3$ = 1.34 Å.

but in propene the actual bond length is 1.54 > b.l. > 1.34 Å

It can be explained by H-effect. So C–C bond length order of

$CH_2=CH-CH=CH_2$ $CH_3-CH=CH_2$ $CH_3-CH_3$

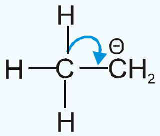
is III > II > I

Due to resonance bond length is shortest in I.

(ii) The effectivity order of M, H and I effect

M > H > I

**Note :** If there is one –C–H σ bond and one negative charge at alternate position then there will be no H-effect.



(No H - effect)

no shifting of —C—H σ bond, because anion have complete octet. ($8e^-$)

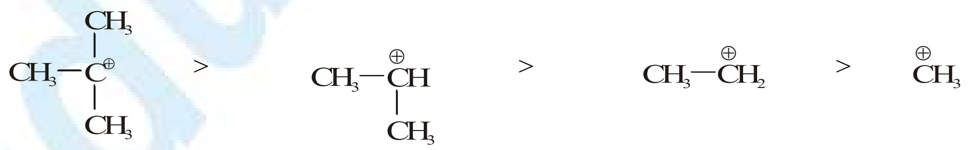
## APPLICATION OF H-EFFECT OR H-EFFECT

### (i) Stability of carbocation

- Stability of carbocation can be explained by M, I and H-effect.
- If more hyperconjugation structures (more α-H) then more stable cation.
- Stability of carbocation ∝ No. of canonical structures ∝ No. of α H.

**Ex.** Give stability order for :-

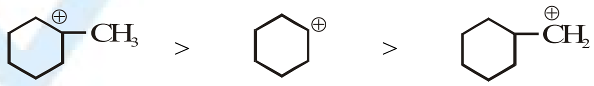
(i)



9 α-H 6 α-H 3 α-H Zero α-H

Maximum stable

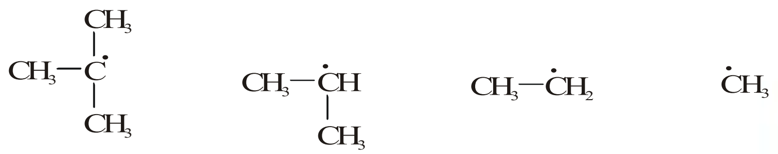
(ii)



**(ii) Stability of carbon free radicals**

- Stability of carbon free radical is explained by M and H-effect.
- More hyper conjugation structures (more $\alpha$-H) more stable free radical.

**Ex.** Give stability order for :-



| 3° | 2° | 1° | |
|---|---|---|---|
| 9 $\alpha$-H | 6 $\alpha$-H | 3 $\alpha$-H | Zero $\alpha$-H |

Maximum stable

Stability order I > II > III > IV

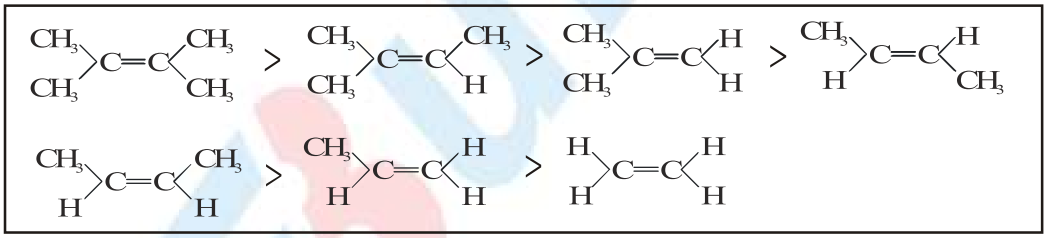
**(iii) Stability of alkenes :** More hyperconjugation structures (more $\alpha$-H) more stable alkene.

(i) $CH_3—CH{=}CH_2$ > $CH_2{=}CH_2$

3 $\alpha$-H Zero $\alpha$-H

more stable

(ii) Stability order of alkenes will be



**Ex.** Which of the following alkene is maximum stable.

(A) $R_2C{=}CR_2$ (B) $R—CH{=}CR_2$ (C) $R—CH{=}CH—R$ (D) $R—CH{=}CH_2$

**Sol.** (A) due to more substituted alkene.

**(iv) Heat of hydrogenation**

$R—CH{=}CH_2 + H_2 \longrightarrow R—CH_2—CH_3 + \Delta H$ (Heat of hydrogenation)

Heat evolved when any unsaturated hydrocarbon are hydrogenated is called heat of hydrogenation ($\Delta H$)

If alkene is more reactive towards hydrogen then it will evolve more $\Delta H$.

So, $$\boxed{\text{Heat of hydrogenation} \propto \frac{1}{\text{stability of alkene}} \propto \frac{1}{\text{number of } \alpha - H}}$$

**Ex.** Which of the following has minimum heat of hydrogenation.

(i) ethene (ii) Propene (iii) cis-2-butene (iv) trans-2-butene

**Sol.** (iv) maximum stable alkene means minimum reactive.

**Ex.** If Heat of hydrogenation of 1-butene is 30 Kcal then heat of hydrogenation of 1,3-butadiene is ?

(i) 30 (ii) 60 (iii) 57 (iv) 25

**Sol.** (iii) 1,3-butadiene requires two moles of hydrogen so heat of hydrogenation should be 60 Kcal but 1,3-butadiene is stabilized by resonance than propane so heat of hydrogenation of 1,3-butadiene will not be twice of 30.

Actual $\Delta H$ - $60 > \Delta H > 30$ Kcal.

**Ex.** Which of the following is maximum stable.

(i) Conjugated alkadiene ($CH_2{=}CH{-}CH{=}CH_2$)

(ii) Isolated alkadiene ($CH_2{=}CH{-}CH_2{-}CH{=}CH_2$)

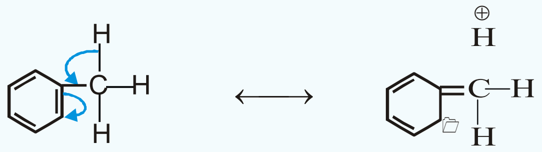
(iii) Cumulated alkadiene ($CH_2{=}C{=}CH_2$)

(iv) All are equal.

**Sol.** (i) Due to resonance conjugated alkadiene is maximum stable. Isolated is more stable than cumulated alkadiene due to H-effect.

**ETOOS KEY POINTS**

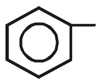
**Reactivity of Benzene :** H-effect of R groups increases electron density in benzene ring.

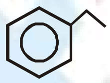


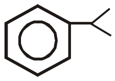
due to $CH_3$ group there is more $e^-$ density at ortho and para position so $CH_3$ is ortho/para directing and activating group.

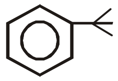
If H-effect is more than $e^-$ density will be more.

**Ex.** Give electrophilic sustitution reaction order :









Maximum α-H.

So maximum H-effect

So maximum $e^-$ density

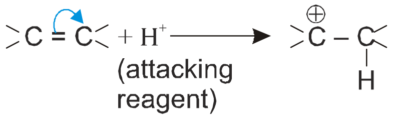
So maximum reactive

ESR order I > II > III > IV

## (4) ELECTROMERIC EFFECT : (E EFFECT)

It is a temporary effect. The organic compounds having a multiple bond (a double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of -electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. The effect is annulled as soon as the attacking reagent is removed from the domain of the reaction. It is represented by E and the shifting of the electrons is shown by a curved arrow (↷). There are two distinct types of electromeric effect.

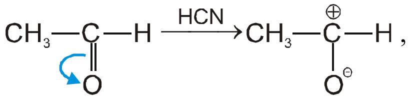
(i) **Positive Eelctromeric Effect (+ E effect) :** In this effect the $\pi$-electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :



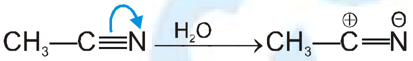
$$\gt C=C\lt + \underset{\text{(attacking reagent)}}{H^{+}} \longrightarrow \gt\overset{\oplus}{C}-\underset{\underset{H}{|}}{C}\lt$$

(ii) **Negative Electromeric Effect (-E effect) :** In this effect the $\pi$- electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example.

$$\gt C=O\lt + \underset{\text{(attacking reagent)}}{\overset{\ominus}{C}N} \longrightarrow \gt\underset{\underset{CN}{|}}{C}-\overset{\ominus}{O}\lt$$



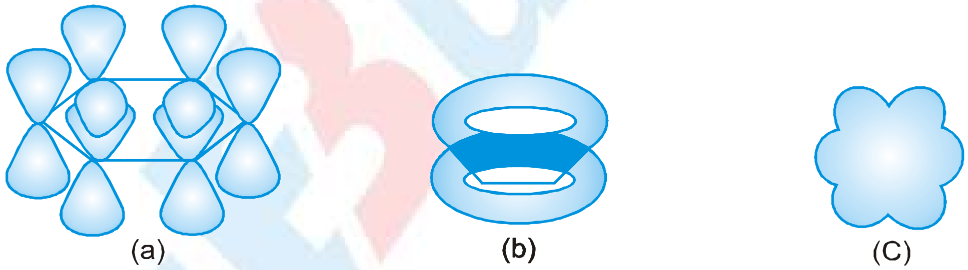
$$CH_3-\underset{\underset{O}{\|}}{C}-H \xrightarrow{HCN} CH_3-\overset{\oplus}{\underset{\underset{O^{\ominus}}{|}}{C}}-H\,,$$



$$CH_3-C\equiv N \xrightarrow{H_2O} CH_3-\overset{\oplus}{C}=\overset{\ominus}{N}$$

## AROMATICITY

Many cyclic, conjugated compounds possess markedly different physical and chemical properties from those expected by comparision of their structures with acyclic analogues. The simplest example is benzene, which may be regarded as the **parent** compound of the aromatic series. Benzene is a planar, cyclic compound with a cyclic cloud of delocalized $\pi$ electrons above and below the plane fo the ring, because its $\pi$-electrons are delocalized, all the carbon-carbon bonds have the same length-partway between the length of a typical single and a typical double bond. We also saw that benzene is a particularly stable compound because it has an un-usually large resonance energy (36 kcal/mol or 151 kJ/mol). Most compounds with delocalized electrons have much smaller resonance energies. Compounds such as benzene with unusually large resonance energies are called aromatic compounds.



(a) Each carbon of benzene has a p orbital.

(b) The overlap of the p orbitals forms a cloud of $\pi$ electrons above and below the plane of the benzene ring.

(c) the electrostatic potential map for benzene shows that all the carbon-carbon bonds have the same electron density.

For a compound to be classified as aromatic, it must fulfill both of the following criteria.

(i) It must have an uninterrupted cyclic cloud of $\pi$ electrons above and below the plane of the molecule (often called a $\pi$ cloud). This means that the compound / molecule should have continueous resonance (conjugation).

For the $\pi$ cloud to be cyclic, the molecule must be cyclic.

For the $\pi$ cloud to be uninterrupted, every atom in the ring must have a p orbital.

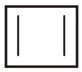
For the $\pi$ cloud to form, each p orbital must be able to overlap with the p orbitals on either side of it. Therefore, the molecule must be planar.

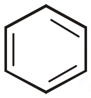
(ii) The $\pi$ cloud must contain an odd number of pairs of $\pi$ electrons. (i.e. 4n+2 $\pi$ electrons )

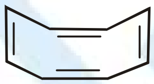
Benzene is an aromatic compound because it is cyclic and planar, every carbon in the ring has a p orbital and the $\pi$ cloud contains three pairs of $\pi$ electrons.

The german chemist Erich Huckel was the first to recognize that an aromatic compound must have an odd number of pairs of $\pi$ electrons. In 1931 he described this requirement by what has come to be known as Huckel's rule, or the 4n + 2 rule. The rule states that for a planar, cyclic compound to be aromatic, its uninterrupted $\pi$ cloud must contain (4n + 2) $\pi$ electrons, where n is any whole number. According to Huckel's rule, then an aromatic compound must have 2(n = 0), 6(n =1), 10 (n =2), 14 (n = 3), 18 (n = 4), etc., $\pi$ electrons. Because there are two electrons in a pair, Huckel's rule requires that an aromatic compound must have 1, 3, 5, 7, 9, etc. pairs of $\pi$ electron. Thus, Huckel's rule is just a mathematical way of saying that an aromatic compound must have an odd number of pairs of $\pi$ electrons.

Cyclobutadiene has two pairs of $\pi$ electrons and cyclooctatetraene has four pairs of $\pi$ electrons therefore, these compounds are not aromatic because they have an even number of pairs of $\pi$ electrons. There is an additional reason why cyclooctatetraene is not aromatic- it is not planar, it is tub-shaped. We saw that for an eight-membered ring to be planar, it must have bond angles of 135° and we know that $sp^2$ carbons have 120° bond angles. Therefore, If cyclooctatetraene were planar, it would have considerable angle strain. Because cyclobutadiene and cyclooctatetraene are not aromatic, they do not have the unusual stability of aromatic compounds.

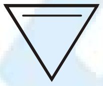

cyclobutadiene
[4]-annulene


benzene [6]
-annulene

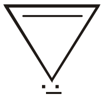

cyclooctatetraene
[8]-annulene

Monocyclic hydrocarbons with alternating single and double bonds are called an-nulenes. A prefix in brackets denotes the number of carbons in the ring.

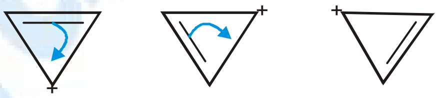
Which of the following three-membered ring structures is aromatic ? Cyclopropene is not aromatic because it does not have an uninterrupted ring of p orbital-bearing atoms. One of its ring atoms is $sp^3$ hybridized and only $sp^2$ and sp hybridized carbons have p orbitals. Therefore, cyclopropene does not fulfill the first criterion for aromaticity.

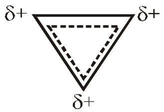

Cyclopropene


Cyclopropenyl cation


Cyclopropenyl anion

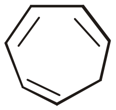
The cyclopropenyl cation is aromatic because it does have an uninterrupted ring of p orbital-bearing atoms and the $\pi$ cloud contains one pair of delocalized $\pi$ electrons. The cyclopropenyl anion is not aromatic because its $\pi$ cloud has two (an even number) pairs of $\pi$ electrons.

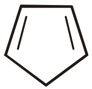

resonance contributors for the cyclopropenyl cation



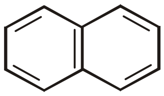
resonance hybrid

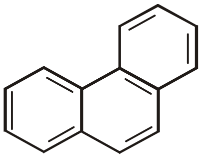
Cycloheptatriene is not aromatic. Although it has the correct number of pairs of π electrons to be aromatic (three pairs), it does not have an uninterrupted ring of p orbital-bearing atoms because one of the ring atoms is $sp^3$ hybridized. Cyclopentadiene is also not aromaitc. It has an even number of pairs of π electrons (two pairs) and it does not have an uninterrupted ring of p orbital bearing atoms.

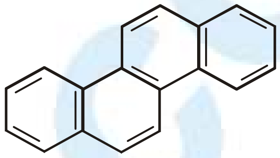

cycloheptatriene


cyclopentadiene

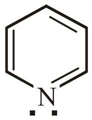
The criteria for determining whether a monocyclic hydrocarbon compound is aromatic can also be used to determine whether a polycyclic hydrocarbon compound is aromatic. Naphthalene (five pairs of π electrons), phenanthrene (seven paris of π-electrons)and chrysene (nine pairs of π electrons) are aromatic.


naphthalene

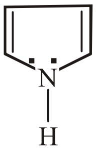

phenanthrene


chrysene

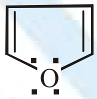
In cyclic compounds, when an element other than carbon is present in the ring, they are called heterocyclic compounds. They are aromatic in nature because of fulfilling both the conditions.



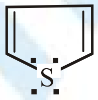
Pyridine



pyrrole



Furan



Thiophene

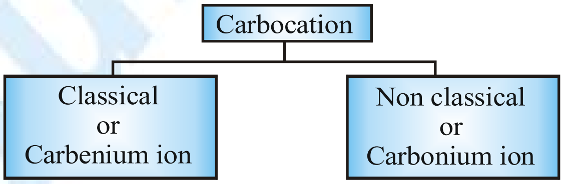
In pyrrole, furan and thiophene, the lone pairs are actually in $sp^3$ hybrid orbtials to form the aromatic sextet (4n + 2) π-electrons. In pyridine, the lone pair is in $sp^2$ hybrid orbital, which is not involved in delocalization. Thus, pyridine also has 6 π-electrons and is aromatic in nature.

## REACTION INTERMEDIATES

In the study of organic chemistry follwing intermediates are more important :

| | |
|---|---|
| (i) carbocation | (ii) carbanion |
| (iii) carbon free radical | (iv) carbene |
| (v) Benzyne | (v) nitrene |

**Carbocation :** Positively charged 'C' atom as reaction intermediate is called carbocation. Generally it contains only six electron in three bonds. It is electron deficent species act as electrophilic and lequid acid.



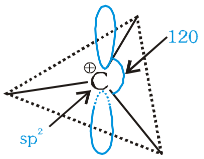
**ETOOS KEY POINTS**

According to modern nomenclature accepted by IUPAC $\overset{\oplus}{C}H_3$, $CH_3\overset{\oplus}{C}H_2$ etc. are termed as carbenium ion (but not carbonium ion). Althought some authors still refers to $\overset{\oplus}{C}H_3$, $CH_3\overset{\oplus}{C}H_2$ etc as carbonium ion but in modern nomenclature it is old pentavalent carbocation (i.e. carbonium ions) are much rare than carbenium ion.

## Classical Carbocation (carbenium ion)

### 1. Structure and Hybridisation

Classical carbocation (carbenium ion) are $sp^2$ hybridised and of planer structure. Unhybridised vaccant 'p'orbital lies below and above the plane.

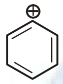


### 2. Stability : Carbocation are stabilised by :

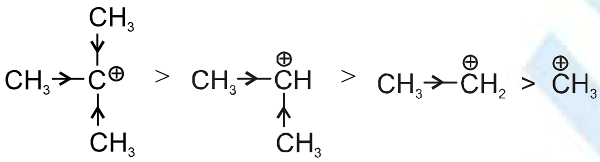
(i) + I effect (ii) + M effect (iii) Hyper-conjugation

**General stability order**

$$Ph_3\overset{\oplus}{C} > Ph_2\overset{\oplus}{C}H > Ph-\overset{\oplus}{C}H-R > CH_2=CH-\overset{\oplus}{C}H-R \gtrsim (CH_3)_3\overset{\oplus}{C} \gtrsim Ph\overset{\oplus}{C}H_2 > CH_2=CH-\overset{\oplus}{C}H_2 \gtrsim$$

$$(CH_3)_2\overset{\oplus}{C}H > CH_3-\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2=\overset{\oplus}{C}H \simeq$$ 

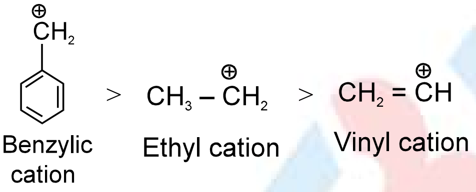
**Ex.**



$$(CH_3)_3\overset{\oplus}{C} > (CH_3)_2\overset{\oplus}{C}H > CH_3\rightarrow\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3$$

t-Butyl carbocation has +I effect of three Me–groups and also Hyperconjugation effect which makes it most stable.

**Ex.**



$$C_6H_5\overset{\oplus}{C}H_2 > CH_3-\overset{\oplus}{C}H_2 > CH_2=\overset{\oplus}{C}H$$

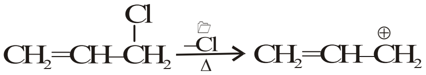
Benzylic cation  Ethyl cation  Vinyl cation

In Benzyl cation, Extensive Resonance is seen which stabilises $C^{\oplus}$.
In Ethyl carbocation + I and Hyperconjugation of Me – group stabilizes carbocation.
In vinyl carbocation stability decreases rapidly since carbon of $(CH_2)$ is $sp^2$ hybridized which is slightly more electronegative hence acts as – I group which increases (+) charge density.

### 3. The generation of $-\overset{|}{\underset{|}{C}}{}^{\oplus}$ (carbenium ion)

**(a) By the direct ionisation :** (In highly polar medium)

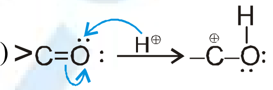
(i) $(CH_3)_3Cl \longrightarrow (CH_3)_3C^{\oplus} + Cl^{1}$

(ii) 

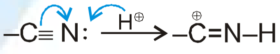
$$CH_2=CH-\overset{Cl}{\overset{|}{C}H_2} \xrightarrow[\Delta]{-Cl} CH_2=CH-\overset{\oplus}{C}H_2$$

**(b) By the protonation of unsaturated compound**

(i) $-CH=CH- \xrightarrow{H^{\oplus}} -\overset{H^{\oplus}}{CH\text{———}CH} \longrightarrow CH^{\oplus}-CH_2-$

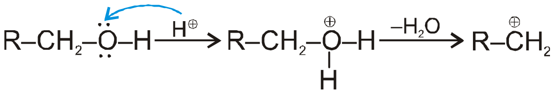
(ii) 

$$>C=\ddot{O}: \xrightarrow{H^{\oplus}} -\overset{\oplus}{C}-\overset{H}{\overset{|}{\underset{\cdot\cdot}{O}}}:$$

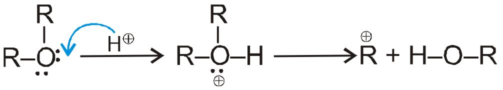
(iii) 

$$-C\equiv N: \xrightarrow{H^{\oplus}} -\overset{\oplus}{C}=N-H$$

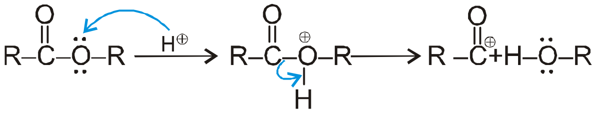
**(c) By the protonation of lone pair of electron**

(i) 

$$R{-}CH_2{-}\ddot{\underset{\cdot\cdot}{O}}{-}H \xrightarrow{H^{\oplus}} R{-}CH_2{-}\underset{H}{\overset{\oplus}{O}}{-}H \xrightarrow{-H_2O} R{-}\overset{\oplus}{C}H_2$$

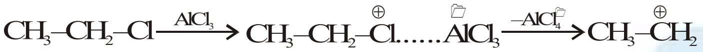
(ii) 

$$R{-}\overset{R}{\ddot{\underset{\cdot\cdot}{O}}}{:} \xrightarrow{H^{\oplus}} R{-}\underset{\oplus}{\overset{R}{O}}{-}H \longrightarrow \overset{\oplus}{R} + H{-}O{-}R$$

(iii) 

$$R{-}\overset{O}{\overset{\|}{C}}{-}\ddot{\underset{\cdot\cdot}{O}}{-}R \xrightarrow{H^{\oplus}} R{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{\overset{\oplus}{O}}{-}R \longrightarrow R{-}\overset{O}{\overset{\|}{\overset{\oplus}{C}}}+H{-}\ddot{\underset{\cdot\cdot}{O}}{-}R$$

**(d) By electrophilic attack on alkyl halide or acyl halide**

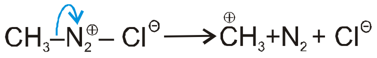
(i) 

$$CH_3{-}CH_2{-}Cl \xrightarrow{AlCl_3} CH_3{-}CH_2{-}\overset{\oplus}{Cl}\ldots\ldots\overset{\ominus}{Al}Cl_3 \xrightarrow{-AlCl_4^{\ominus}} CH_3{-}\overset{\oplus}{C}H_2$$

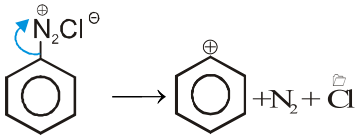
(ii) 

$$R{-}\overset{O}{\overset{\|}{C}}{-}\overset{\ominus}{Cl} \xrightarrow{AlCl_3} R{-}C{-}\overset{\oplus}{Cl}\ldots\ldots\overset{\ominus}{Al}Cl_3 \xrightarrow{-AlCl_4^{\ominus}} R{-}\overset{\oplus}{C}{=}\ddot{O}{:} \longleftrightarrow R{-}C{\equiv}\overset{\oplus}{O}{:}$$

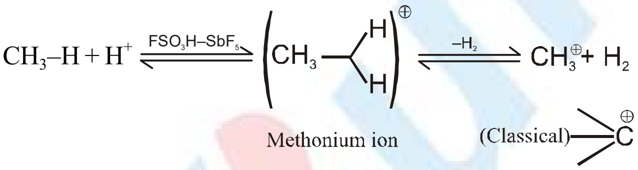
**(e) By the decomposition of diazonium salt**

(i) 

$$CH_3{-}\overset{\oplus}{N_2}{-}Cl^{\ominus} \longrightarrow \overset{\oplus}{C}H_3 + N_2 + Cl^{\ominus}$$

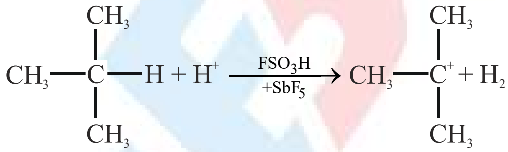
(ii) 

**(f) By attack of super acid on alkane**

(i) 

$$CH_3{-}H + H^{+} \xrightleftharpoons{FSO_3H{-}SbF_5} \left(CH_3{-}\langle^{H}_{H}\right)^{\oplus} \xrightleftharpoons{-H_2} CH_3^{\oplus} + H_2$$

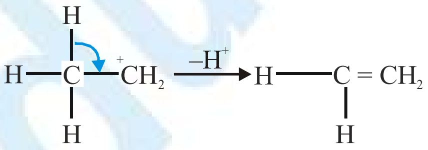
(ii) $CH_3{-}CH_3 + H^{+} \xrightarrow{FSO_3H+SbF_5} C_2H_5^{+} + H_2$

(iii) 

$$CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}H + H^{+} \xrightarrow[+SbF_5]{FSO_3H} CH_3{-}\underset{CH_3}{\overset{CH_3}{C^{+}}} + H_2$$

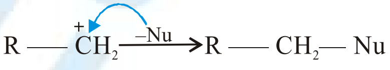
## 4. Reaction of Carbocation (carbenium ion)

**(a) Proton Loss :** To form a multiple bond.

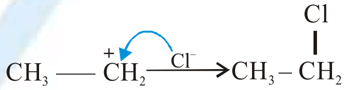
(i) 

$$H{-}\underset{H}{\overset{H}{C}}{-}\overset{+}{C}H_2 \xrightarrow{-H^{+}} H{-}\underset{H}{C}{=}CH_2$$

**(b) Combination with Nucleophiles**



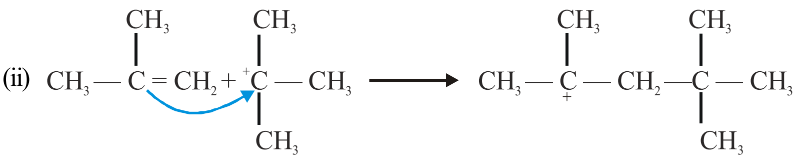
$$R{-}\overset{+}{C}H_2 \xrightarrow{-Nu} R{-}CH_2{-}Nu$$

(i) 

$$CH_3{-}\overset{+}{C}H_2 \xrightarrow{Cl^{-}} CH_3{-}\overset{Cl}{C}H_2$$

**(c) Addition to an alkene**

(i) $^{+}CH_3 + CH_2=CH_2 \rightarrow CH_3-CH_2-{}^{+}CH_2$



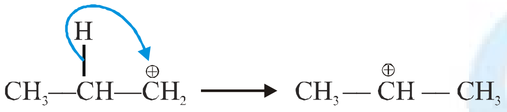
$$\text{(ii)}\; CH_3-\overset{CH_3}{C}=CH_2+\underset{CH_3}{\overset{CH_3}{\overset{+}{C}}}-CH_3 \longrightarrow CH_3-\underset{+}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

**(d) Molecular Rearrangement :**

A carbocation would undergo a molecular rearrangement when it could produce a more stable carbocation e.g.

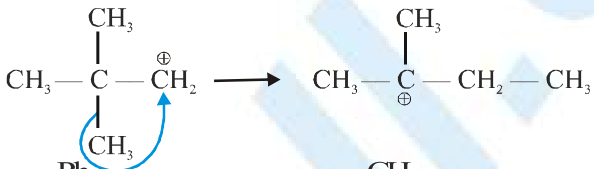
## Shifting of H, alkyl, aryl (1, 2, shift)

**(i) Hydride Shift :**



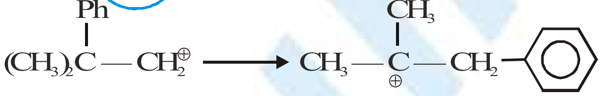
$$CH_3-\overset{H}{C}H-\overset{\oplus}{C}H_2 \longrightarrow CH_3-\overset{\oplus}{C}H-CH_3$$

**(ii) Methyl Shift :**



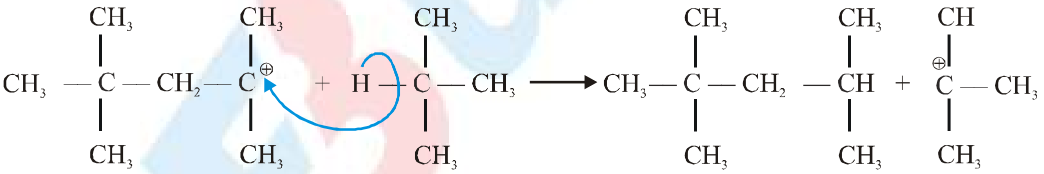
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{C}H_2 \longrightarrow CH_3-\underset{\oplus}{\overset{CH_3}{C}}-CH_2-CH_3$$

**(iii) Aryl Shift :**



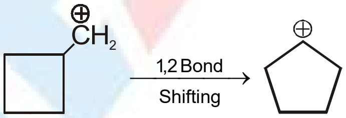
The case of the shift is as follows Ph-shift > Hydride shift > Me-shift.

**(e) Abstraction of hydride ion :**

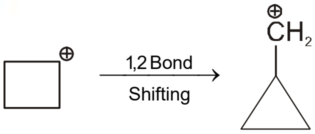


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{\overset{\oplus}{C}}}+H-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{CH}}+\underset{CH_3}{\overset{CH}{\overset{\oplus}{C}}}-CH_3$$

**(f) Ring expansion :**

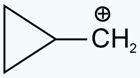


**(g) Ring contraction :**



**ETOOS KEY POINTS**

The unique stabilisation of cyclopropyl methyl carbocation due to σ electrons overlapping with vacant p-orbital of carbocation carbon is seen.

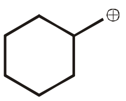


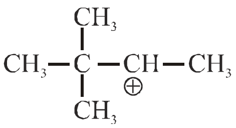
(more stable than Benzyl)

cyclopropyl methyl carbocation

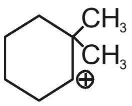
**Ex.** Rearrange (if applicable) the following carbocations into more stable form :-

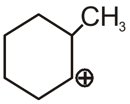
(a) $CH_3-CH_2-\overset{\oplus}{C}H_2$

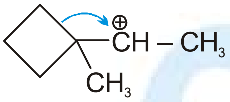
(b)


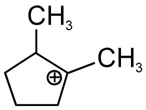
(c)


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\oplus}{C}H-CH_3$

(d)


(e)


(f)


**Ans.** For students only (f)


## Carbanion

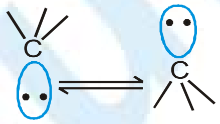
**(1)** A carbon intermediate which contain three bond pair and a negative charge on it, is called carbanion.

| Ex. | | |
|---|---|---|
| | $CH_3^{\ominus}$ , | Methyl carbanion |
| | $CH_3-CH_2^{\ominus}$ , | Ethyl carbanion |
| | $(CH_3)_2CH^{\ominus}$ | Isopropyl carbanion |

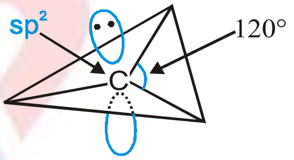
**(2)** **STRUCTURE AND HYBRIDISATION**

On the basis of the structure carbanion are of two types

(a) Carbanion ($sp^3$) hybridised (pyramidal)

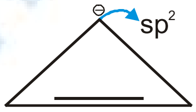


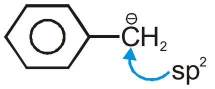
(b) Planer carbanion ($sp^2$) hybridised (–ve charge is attack to π bonded system)



Unhybridised pure 'p' orbital

**Ex.** (i) $CH_2=CH-\overset{\ominus}{C}H_2$ $sp^2$

(ii)


(iii)


(iv) $\overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-H$ $sp^2$

**(3)** **STABILITY OF CARBANION**

Carbanions are stabilised by electron withdrawing effects as

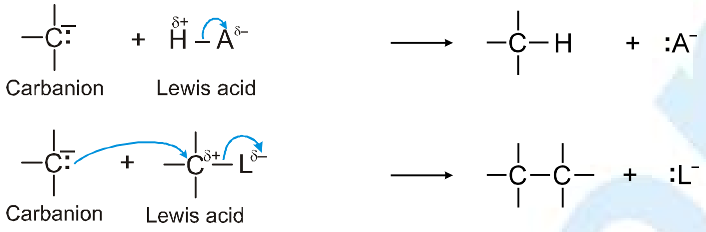
(a) –I effect

(b) –M effect

(c) Delocalisation of charge

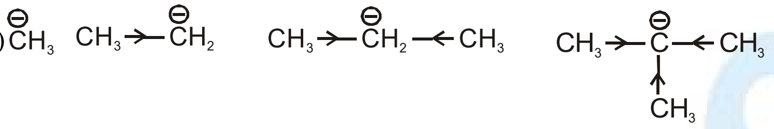
(d) Aromatization

Carbanions are Lewis bases. In their reactions they seek a proton or some other positive centre to which they can donate their electron pair and thereby neutralize their negative charge.



**Example of stability order**

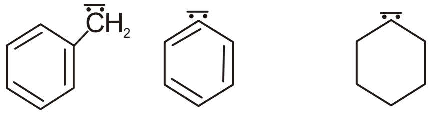
**Ex.** (a)



$\overset{\ominus}{C}H_3$ $\quad CH_3 \rightarrow \overset{\ominus}{C}H_2$ $\quad CH_3 \rightarrow \overset{\ominus}{C}H_2 \leftarrow CH_3$ $\quad CH_3 \rightarrow \underset{\underset{CH_3}{\uparrow}}{\overset{\ominus}{C}} \leftarrow CH_3$ (Stability order : 1 > 2 > 3 > 4)

(b) $\underset{1}{CH \equiv \bar{\ddot{C}}}$ $\quad \underset{2}{CH_2 = \bar{\ddot{C}}H}$ $\quad \underset{3}{CH_3 - \bar{\ddot{C}}H_2}$ (Stability order : 1 > 2 > 3)

(c)



1 2 3 (Stability order :1 > 2 > 3)

(d) $\underset{1}{CH_2 = CH - \overset{\ominus}{C}H_2}$ $\quad \underset{2}{C_6H_5 - \overset{\ominus}{C}H_2}$ $\quad \underset{3}{(C_6H_5)_3 \overset{\ominus}{\ddot{C}}}$ (Stability order : 1 < 2 < 3)

## (4) REARRANGEMENT

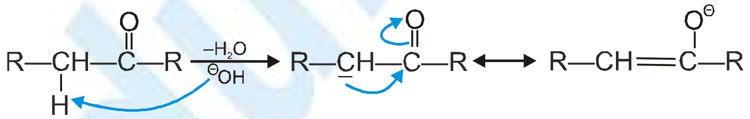
Generally carbanions do not undergo rearrangement.

## (5) GENERATION OF CARBANION

**By action of base on acidic hydrogen of C – H bond**

The acidic hydrogen of C – H may be of two types :

**(a)** By attack of base on 'H' of $\underset{\underset{H}{|}}{C}-x=y$ system (E.N. y > x)



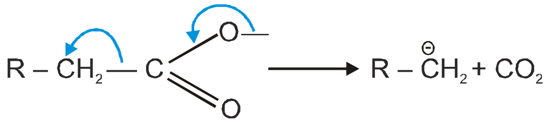
$R-\underset{\underset{H}{|}}{CH}-\overset{\overset{O}{||}}{C}-R \xrightarrow[\ominus OH]{-H_2O} R-\overset{\ominus}{C}H-\overset{\overset{O}{||}}{C}-R \longleftrightarrow R-CH=\overset{\overset{O^{\ominus}}{|}}{C}-R$

**(b)** By attack of base on ≡ C—H :

(i) $CH \equiv C—H \xrightarrow[-NH_3]{\ominus NH_2} CH \equiv \overset{\ominus}{C}$

(ii) $CH_3 - C \equiv C - H \xrightarrow[-NH_3]{\ominus NH_2} CH_3—C \equiv \overset{\ominus}{C}$

### (c) By decarboxylation of carboxylate ion



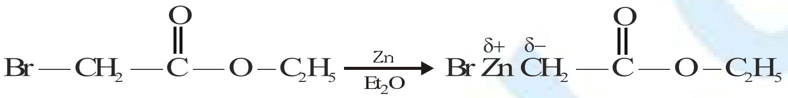
### (d) In the form of organometallic compound

(i) $CH_3-Cl \xrightarrow{Mg/\,ether} \overset{S-}{C}H_3\,\overset{S+}{M}gCl \longrightarrow \overset{\ominus}{C}H_3 + \overset{S+}{M}gCl$

(ii) $2CH_3-CH_2-Cl \xrightarrow{Cd} (CH_3-CH_2)_2Cd$

(iii) $2CH_3CH_2-Br \xrightarrow{Zn} (CH_3-CH_2)_2Zn + ZnBr_2$

(iv) $2CH_3-CH_2-I \xrightarrow[CuI]{Li} (CH_3-CH_2)_2CuLi$ (Gilmann Reagent)

(v)


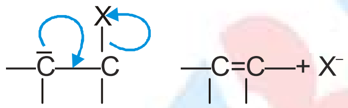
$$Br-CH_2-\overset{\overset{O}{\|}}{C}-O-C_2H_5 \xrightarrow[Et_2O]{Zn} Br\,\overset{\delta+}{Zn}\,\overset{\delta-}{C}H_2-\overset{\overset{O}{\|}}{C}-O-C_2H_5$$

### (6) REACTIONS OF CARBANION

**(a) Attachment of H+ : Ex.** $^1CH_3 + H^{\oplus} \rightarrow CH_4$ as

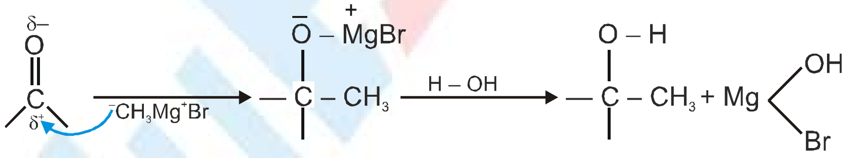
### (b) Loss of Leaving Group

In the system $\overset{\ominus}{C}-\overset{\overset{X}{|}}{C}$ carbanion losses leaving group to form a π bond.

i.e.


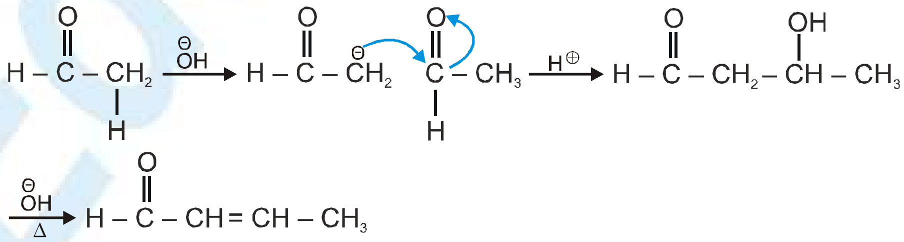
### (c) Addition Reaction

Carbanion gives Nucleophilic addition reaction :

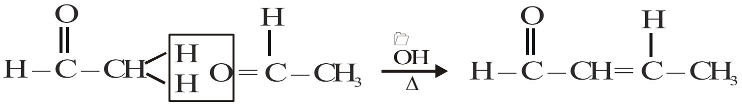
Ex.


### (d) Nucleophillic Addition plus condensation reaction

#### (i) Aldol condensation

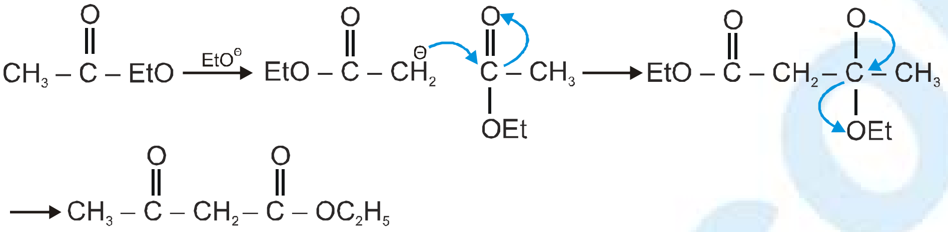


### Short cut



$$H-\overset{\overset{O}{\|}}{C}-CH\boxed{\begin{matrix}H\\H\end{matrix}\ O}=\overset{\overset{H}{|}}{C}-CH_3 \xrightarrow[\Delta]{\overset{\ominus}{O}H} H-\overset{\overset{O}{\|}}{C}-CH=\overset{\overset{H}{|}}{C}-CH_3$$

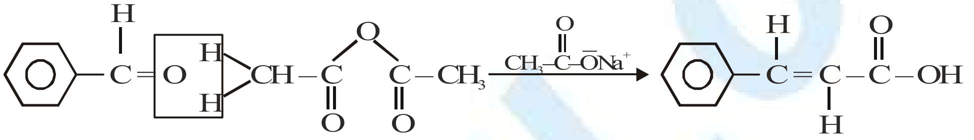
### (ii) Claisen condensation



$$CH_3-\overset{\overset{O}{\|}}{C}-EtO \xrightarrow{EtO^{\ominus}} EtO-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{C}H_2 \quad \underset{\underset{OEt}{|}}{\overset{\overset{O}{\|}}{C}}-CH_3 \longrightarrow EtO-\overset{\overset{O}{\|}}{C}-CH_2-\underset{\underset{OEt}{|}}{\overset{\overset{O}{|}}{C}}-CH_3$$

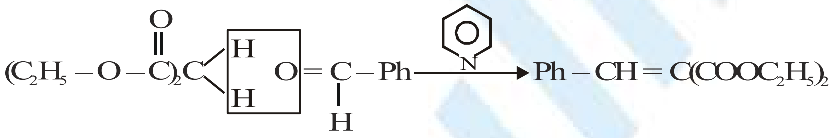
$$\longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5$$

### (iii) Perkin reaction



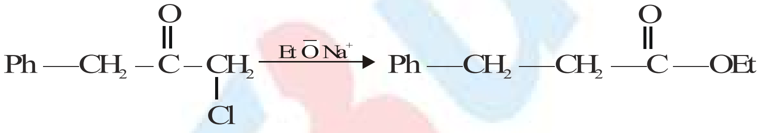
Cinnamic acid

### (iv) Knoevengel reaction



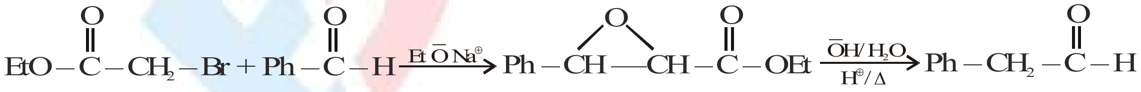
$$(C_2H_5-O-\overset{\overset{O}{\|}}{C})_2C\boxed{\begin{matrix}H\\H\end{matrix}\ O}=\underset{\underset{H}{|}}{C}-Ph \longrightarrow Ph-CH=C(COOC_2H_5)_2$$

### (v) Favorskii reaction



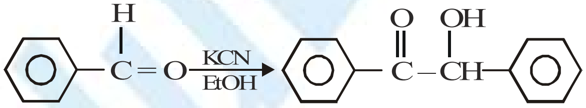
$$Ph-CH_2-\overset{\overset{O}{\|}}{C}-\underset{\underset{Cl}{|}}{CH_2}\xrightarrow{Et\bar{O}Na^{+}} Ph-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OEt$$

### (vi) Darzen reaction



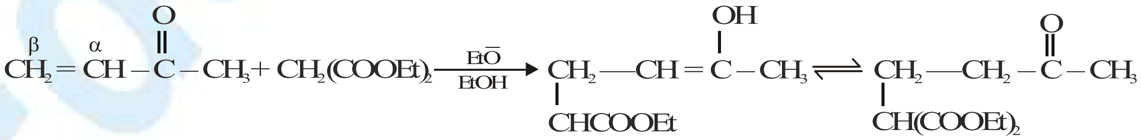
$$EtO-\overset{\overset{O}{\|}}{C}-CH_2-Br+Ph-\overset{\overset{O}{\|}}{C}-H\xrightarrow{Et\bar{O}Na^{\oplus}} Ph-CH\overset{O}{\frown}CH-\overset{\overset{O}{\|}}{C}-OEt\xrightarrow[H^{\oplus}/\Delta]{\bar{O}H/H_2O} Ph-CH_2-\overset{\overset{O}{\|}}{C}-H$$

### (vii) Benzoin condensation



Benzoin

### (viii) Micheal addition

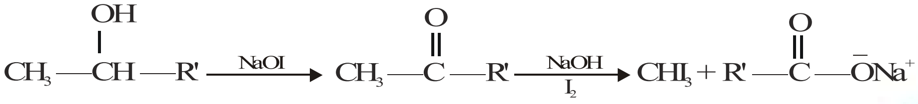


$$\overset{\beta}{C}H_2=\overset{\alpha}{C}H-\overset{\overset{O}{\|}}{C}-CH_3+CH_2(COOEt)_2\xrightarrow[EtOH]{Et\bar{O}}\underset{\underset{CHCOOEt}{|}}{CH_2}-CH=\overset{\overset{OH}{|}}{C}-CH_3\rightleftharpoons\underset{\underset{CH(COOEt)_2}{|}}{CH_2}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

### (ix) Wittig reaction

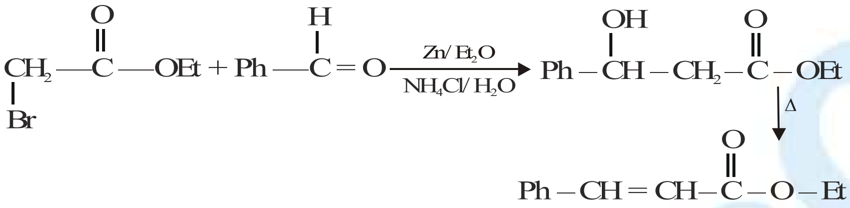
$$CH_3-\overset{\overset{CH_3}{|}}{C}=O \quad CH_2=PPh_3\xrightarrow{DMSO}CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2+Ph_3P=O$$

### (x) Haloform reaction



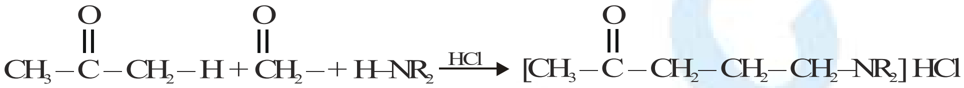
$$CH_3-\overset{OH}{\overset{|}{C}H}-R' \xrightarrow{NaOI} CH_3-\overset{O}{\overset{\|}{C}}-R' \xrightarrow[I_2]{NaOH} CHI_3 + R'-\overset{O}{\overset{\|}{C}}-\overset{-}{O}Na^+$$

### (xi) Reformatsky reaction



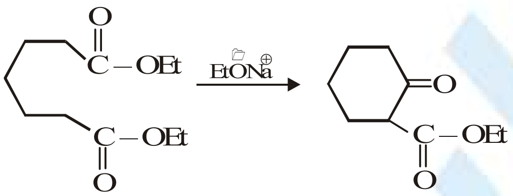
$$\underset{\underset{Br}{|}}{CH_2}-\overset{O}{\overset{\|}{C}}-OEt + Ph-\overset{H}{\overset{|}{C}}=O \xrightarrow[NH_4Cl/H_2O]{Zn/Et_2O} Ph-\overset{OH}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow{\Delta} Ph-CH=CH-\overset{O}{\overset{\|}{C}}-O-Et$$

### (xii) Mannich reaction



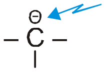
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-H+\overset{O}{\overset{\|}{C}H_2}-+H-NR_2 \xrightarrow{HCl} [CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-NR_2]\,HCl$$

### (xiii) Dieckmann reaction

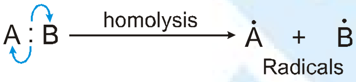


## Carbon free Radical

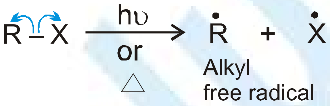
**(1)** Free radical is a species that contain an unparied electron in valance shell of one of its atom and if the atom is carbon atom the free radical is known as CARBON FREE RADICAL. It has three bond pairs and one unpaired electron i.e.


unpaired electron.

Homolysis of covalent bond results into free radical intermediates possessing the unpaired electrons.



It is generated in presence of Sun light, Peroxides or High temperature

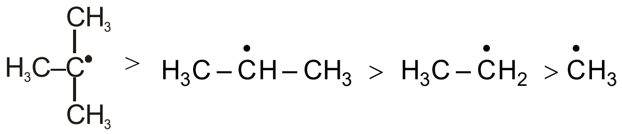


**Free Radical :** An uncharged intermediate which has three bond pair and an unpaired electron on carbon atom.

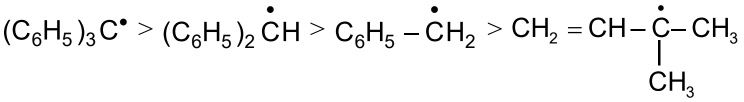
### EDUBULL KEY POINTS

- (i) It is Neutral species with odd $e^-$
- (ii) It is paramagnetic in nature due to odd $e^-$
- (iii) No rearrangement is observed generally.
- (iv) Carbon atom having odd electron is in $sp^2$ hybridised state
- (v) Any reaction if it is carried out in the presence of sunlight, peroxide or high temperature it generally proceeds via free radical intermediate.

**Stability of free radical :** It is stabilised by resonance, hyperconjugation and + I groups.

**Ex.** 

$(CH_3)_3C^{\bullet} > H_3C-\dot{C}H-CH_3 > H_3C-\dot{C}H_2 > \dot{C}H_3$ (Stability order)

**Ex.** 

$(C_6H_5)_3C^{\bullet} > (C_6H_5)_2\dot{C}H > C_6H_5-\dot{C}H_2 > CH_2=CH-\dot{C}(CH_3)-CH_3$ (Stability order)

**(2)** **Structure and Hybridisation :** A free radical may considered as having :
Pyramidal structure which are rapidly interconverting, $sp^3$ hybridised.
Planer structure ; $sp^2$ hybridised.

**Note**
Although geometry of organic free radical is still controversial but recent studies revealed conclusive in the favour of planer structure.

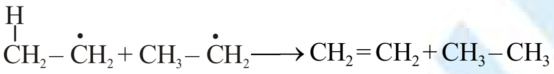
### (3) Reaction of Free Radicals

#### (a) Recombination (coupling)

(i) $\dot{C}H_3 + \dot{C}H_2CH_2\text{–}CH_3 \longrightarrow CH_3CH_2CH_2\text{–}CH_3$

(ii) $CH_3-\dot{C}H_2 + \dot{C}H_2-CH_3 \longrightarrow CH_3-CH_2-CH_2-CH_3$

#### (b) Disproportionation

(i) 

$\overset{H}{C}H_2-\dot{C}H_2 + CH_3-\dot{C}H_2 \longrightarrow CH_2=CH_2 + CH_3-CH_3$

(ii) $2CH_3-\dot{C}H-CH_3 \qquad CH_3-CH=CH_2 + CH_3-CH_2-CH_3$

#### (c) Reaction with hydrogen

(i) $\dot{C}H_3 + H-H > CH_4 + H^{\bullet}$

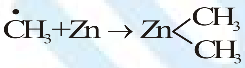
(ii) $CH_3-\dot{C}H_2 + H-H > CH_3-CH_3 + H^{\bullet}$

#### (d) Reaction with unsaturated compound

(i) $\dot{C}H_3 + CH_2=CH_2 \rightarrow CH_3-CH_2-\dot{C}H_2$

(ii) $CH_3-CH=CH_2 \xrightarrow{\dot{C}H_3} CH_3-\dot{C}H-CH_2-CH_3$

#### (e) Reaction with metals

(i) 

$\dot{C}H_3 + Zn \rightarrow Zn(CH_3)_2$

(ii) $\dot{C}H_3 + Hg \rightarrow (CH_3)_2Hg$

(iii) $\dot{C}H_3 + Sb \rightarrow (CH_3)_3Sb$

#### (f) Polymerisation

$$\dot{C}H_3 + CH_2=CH_2 \longrightarrow CH_3-CH_2-\dot{C}H_2 \xrightarrow{CH_2=CH_2} CH_3-CH_2-CH_2-CH_2-\dot{C}H_2$$

$$\xrightarrow{CH_2=CH_2} \dot{C}H_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3 \xrightarrow{CH_2=CH_2}$$

## Carbene

**(1) Carbenes are neutral species containing a carbon atom with two bonds and two non bonded electrons**

i.e. $\ddot{\text{C}}$ (Carbene)

**(2) Types of Carbene :** Carbenes are classified into two classes,

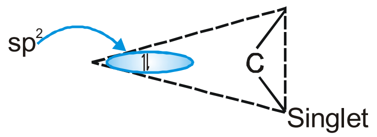
(i) Singlet Carbene $(-\overset{\uparrow\downarrow}{\text{C}}-)$

(ii) Triplet Carbene $(-\overset{\uparrow}{\underset{\downarrow}{\text{C}}}-)$

**(a) Singlet Carbene**

(i) Both non bonded electrons are present in the same $sp^2$ hybridises orbitals with opposite spin.

(ii) It has $sp^2$ hybridisation and bent structure.



(iii) It is a exited state of carbene

(iv) It is dimagnetic with magnetic moment zero.

(v) Multiplicity M = 2S + 1

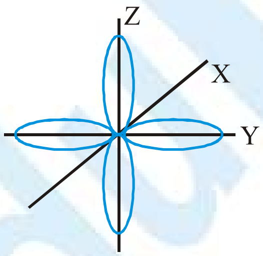
But in this case S = (+1/2) + (–1/2) = 0 M = 2 × 0 + 1 = 1

(vi) It is stronge electrophile.

**(b) Triplet Carbene**

(i) Both non bonded electrons are present in two different 'p' orbitals with parallel spin.

(ii) It has 'sp' hybridisation but Linear strucuture.



expected structure (But not real)

(iii) It is ground state of carbene.

(iv) It is paramagnetic with magnetic moment.

$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = 2\sqrt{2}$ Bohr magnaton.

(v) Multiplicity M = 2S + 1 = 2 (+1/2 + 1/2) + 1 = 3

(vi) It is stronge electrophile.

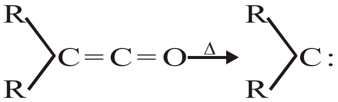
## (3) Generation of carbene

(i) $CH_2 = \overset{+}{N} = N^- \xrightarrow{\Delta} :CH_2$

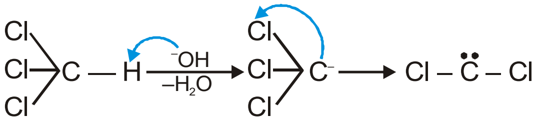
diazomethane

(ii) $CH_2 = C = O \xrightarrow{\Delta} :CH_2$

(iii)



(iv) By action of base of chloroform

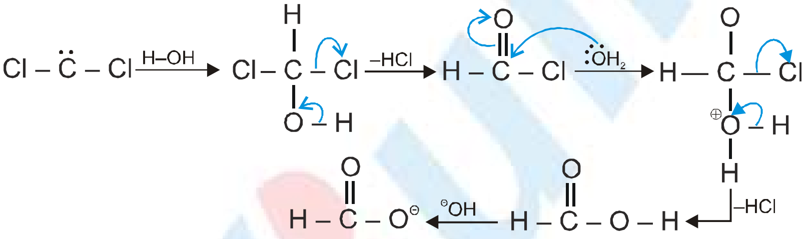


(v) $CCl_4 + LiR \dashrightarrow R-Cl + LiCCl_3, LiCCl_3 \rightarrow Cl-\ddot{C}-Cl$

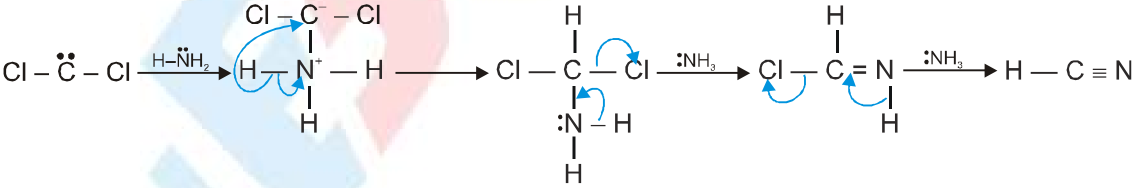
(vi) $CH_2Cl_2 \xrightarrow{LiR} :CHCl$

## (4) Reactions of carbene

### (a) Attachment with nucleophile



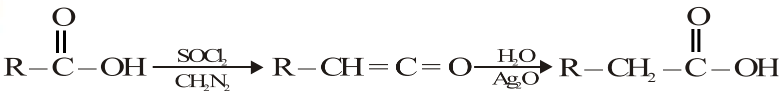
**(b)**



## (5) CAR Reactions

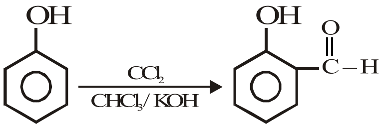
**(a) Carbylamine Test :** $R-NH_2 \xrightarrow[CHCl_3\,/\,KOH]{:CCl_2} R-\overset{+}{N}\equiv\overline{C}$

**(b) Arndt Eistert reaction :**



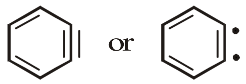
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[CH_2N_2]{SOCl_2} R-CH=C=O \xrightarrow[Ag_2O]{H_2O} R-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

**(c) Reimer Tiemann reaction :**



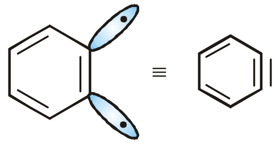
## Benzyne

**(1)** Benzyne may be defined as a neutral reactive intermediate in which the aromatic character are not markeldy disturbed. Benzyne can be represented as :



### (2) Structure and Hybridisation

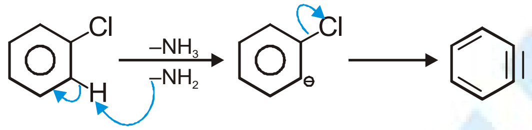
(i) All carbon atoms in benzyne are $sp^2$ hybridised.



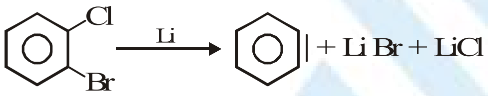
(ii) Side way poor overlaping of $sp^2$ orbitals forms π bonds out side the ring and out of the plane of π system of the ring.

### (3) Generation of Benzyne

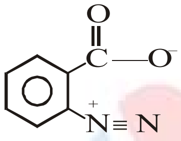
**(a) From chlorobenzene**

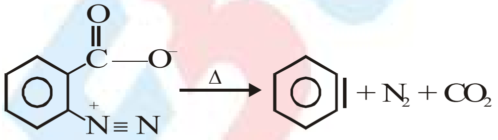


**(b) From chloro bromo benzene**



**(c) From :**

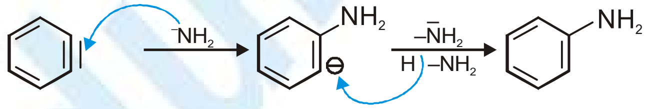




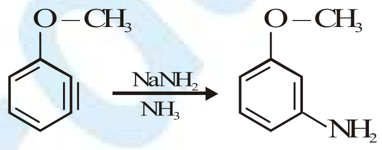
### (4) Reactions of Benzyne

Benzynes are too unstable to be isolated and react with any nucleophile present in the solution.

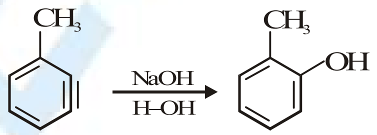
**(a)**



**(b)**



**(c)**



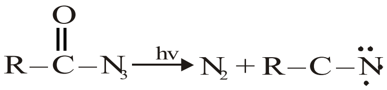
## Nitrene

**(1)** Nitrene may be defined as the electron deficient species in which nitrogen has a sextate of electrons. Nitrenes are analogoues of carbene also known as unidogeh, azene, unene i.e.

$H-\ddot{\underset{\cdot}{N}}\cdot$ or $R-\ddot{\underset{\cdot}{N}}\cdot$ are nitrene.

**(2) Generation of Nitrene**

(i) $H-\ddot{N}_3 \xrightarrow{hv} N_2 + R-\ddot{\underset{\cdot}{N}}\cdot$

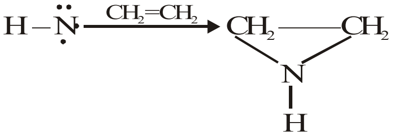
(ii) 

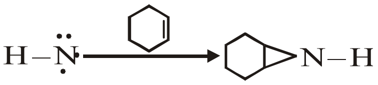
$R-\overset{O}{\overset{\|}{C}}-N_3 \xrightarrow{hv} N_2 + R-C-\ddot{\underset{\cdot}{N}}\cdot$

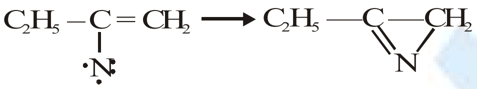
(iii) $H-N=C=O \xrightarrow{hv} CO + H-\ddot{\underset{\cdot}{N}}\cdot$

**(3) Reactions of Nitrene**

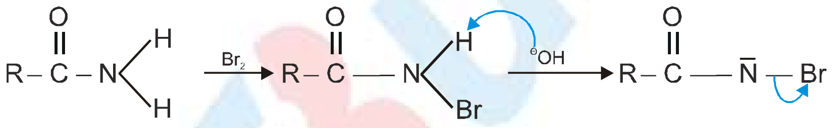
**(a) Addition to Olefine**

(i) 

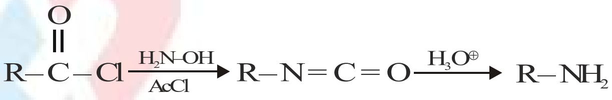
(ii) 

(iii) 

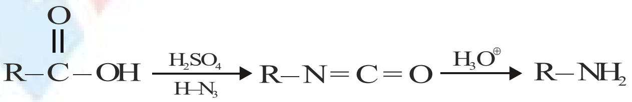
**(b) Hofmann Bromoamide Degradation**



**(c) Rearrangement reaction (HCLS reaction) :** This proceed via nitrene intermediate.

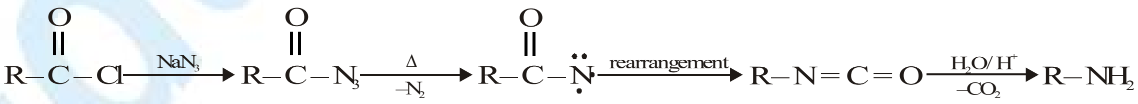
**(d) Losser rearrangement :** 

$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[AcCl]{H_2N-OH} R-N=C=O \xrightarrow{H_3O^{\oplus}} R-NH_2$

**(e) Schimdt rearrangement :** 

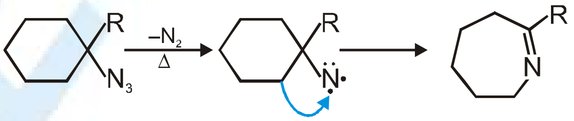
$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H-N_3]{H_2SO_4} R-N=C=O \xrightarrow{H_3O^{\oplus}} R-NH_2$

**(f) Curtius rearrangement :** This also proceed via nitrene but in this case nitrene is obtained form $R-N_3$ as :



$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{NaN_3} R-\overset{O}{\overset{\|}{C}}-N_3 \xrightarrow[-N_2]{\Delta} R-\overset{O}{\overset{\|}{C}}-\ddot{\underset{\cdot}{N}} \xrightarrow{rearrangement} R-N=C=O \xrightarrow[-CO_2]{H_2O/H^+} R-NH_2$

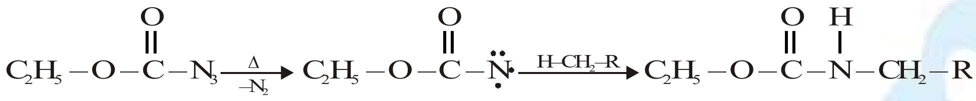
**(g) Cycloalkylazides gives ring expansion**



**(h) Insertion Reaction**

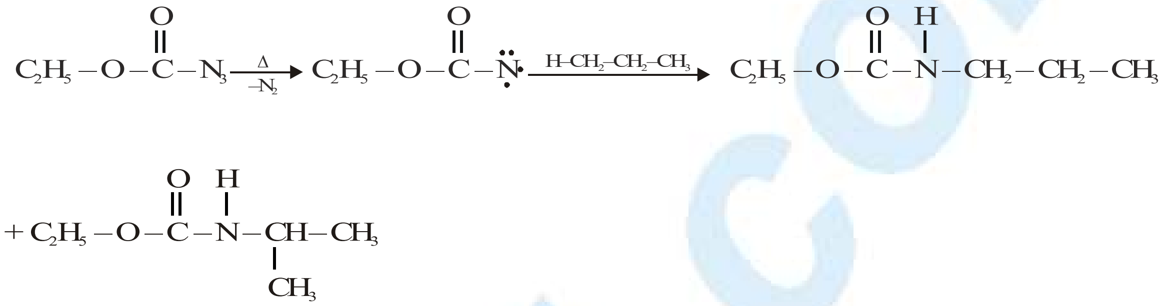
Nitrene can also give insertion reaction as :

(i)



$$C_2H_5-O-\overset{O}{\overset{\|}{C}}-N_3 \xrightarrow[-N_2]{\Delta} C_2H_5-O-\overset{O}{\overset{\|}{C}}-\ddot{N}\cdot \xrightarrow{H-CH_2-R} C_2H_5-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-CH_2-R$$

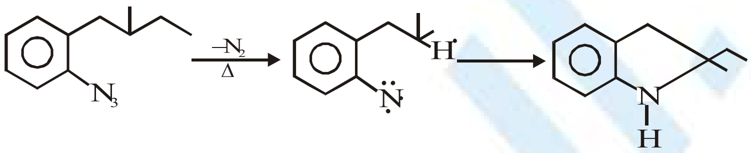
(ii)



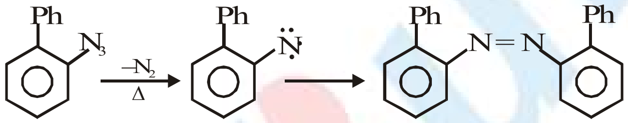
$$C_2H_5-O-\overset{O}{\overset{\|}{C}}-N_3 \xrightarrow[-N_2]{\Delta} C_2H_5-O-\overset{O}{\overset{\|}{C}}-\ddot{N}\cdot \xrightarrow{H-CH_2-CH_2-CH_3} C_2H_5-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-CH_2-CH_2-CH_3$$

$$+\,C_2H_5-O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

(c)



**(iv) Recombination of Two Nitrenes**



## TAUTOMERISM

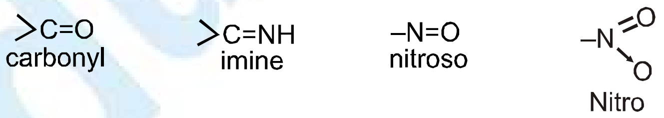
### Definition

Tautomerism is a phenomenon by which a single compound exists in two or more readily interconvertible structures that differ in the relative positions of at least one atomic nucleus, generally hydrogen.

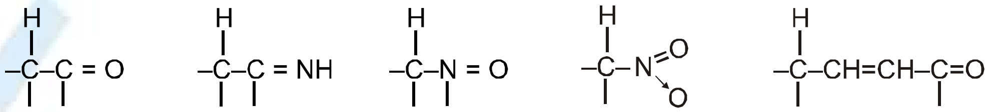
These two isomers remain in dynamic equilibrium and can be isolated also give different lab test.

**Conditions**

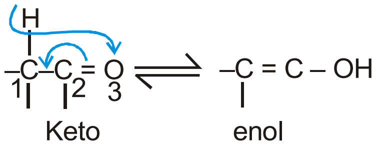
**1.** Usually present in the following functional groups



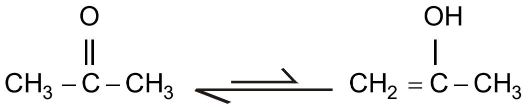
**2.** Basic need for its existence is attachment of these groups with the sp$^3$ hybridised C-atom having atleast one hydrogen atom as –



To get tautomer of above structures α-hydrogen atom is shifting to more electronegative atom attached to double bond (i.e. hydrogen atom from 1st atom to 3rd atom) and double bond is developed between 1,2-atom from 2,3-atom. This can be represented as :

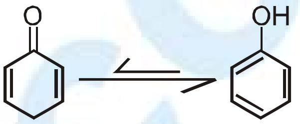


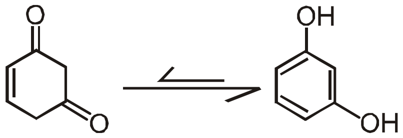
These two forms (remain in equilibrium) are called tautomers of each other. The interconvertibility of tautomers is a chemical reaction which involves making and breaking of bonds.

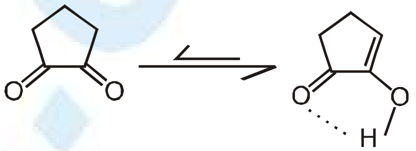
**Ex.** (a) 

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

(I) (II)

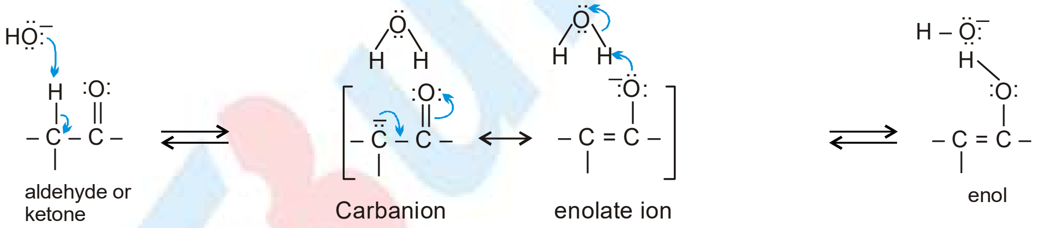
(b) 

(c) 

(d) 

## Keto-enol Tautomerisation

### (A) Base-catalyzed enolization

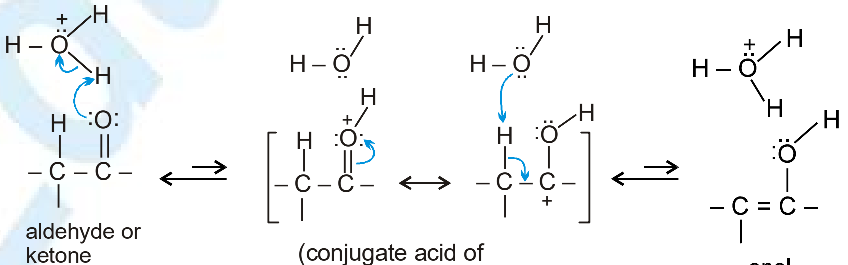


(conjugate base of both carbonyl compound and enol)

Protonation of the carbanion by water on the α-carbon gives back the carbonyl compound. Protonation on oxygen gives the enol. Notice that the enolate ion is the conjugate base of both the carbonyl compound and the enol.

### (B) Acid-catalyzed enolization

Involves the conjugate acid of the carbonyl compound. Recall that this ion has carbocation characteristics. Loss of the proton from oxygen gives back the starting carbonyl compound ; loss of the proton from the α-carbon gives the enol. Notice that an enol and its carbonyl isomer have the same conjugate acid.

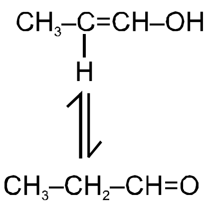


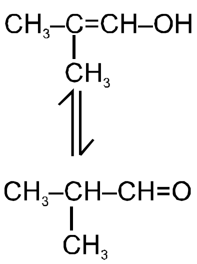
(conjugate acid of both carbonyl compound and enol)

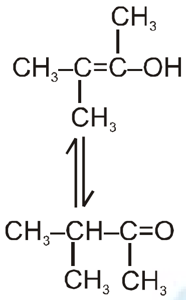
## % ENOL CONTENT IN THE CARBONYL COMPOUNDS

(a) For monocarbonyl % Enol is very less

(b) Enol content increases with increase in the stability of enol by resonance, hyperconjugation, hydrogen bonding etc.

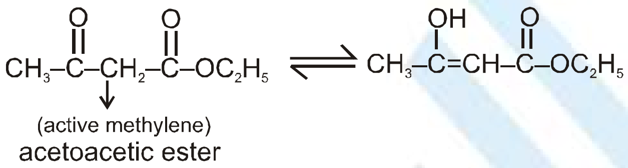

(1)

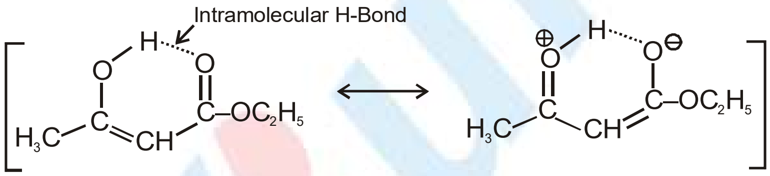

(2)


(3)

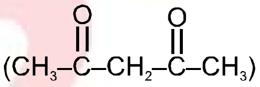
Decreasing order of enol content for above carbonyl compounds is : 3 > 2 > 1.

(c) For a carbonyl compound having active methylene group percentage of enol content will be more because enolic form has intramolecular H-bonding and also it will be stabilised by resonance.





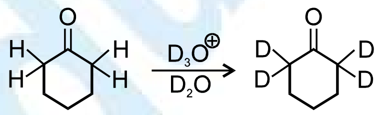
(d) If active methylene group is more acidic then enol content will be more.

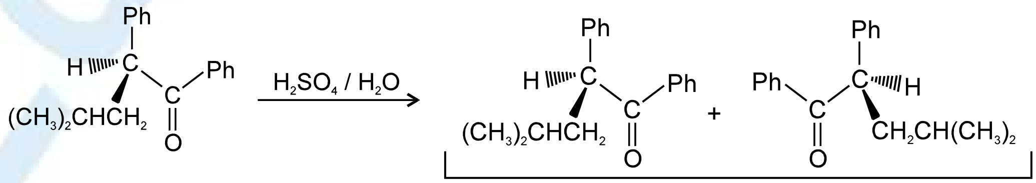
For example in **acetyl acetone** ($CH_3-\overset{\overset{O}{||}}{C}-CH_2-\overset{\overset{O}{||}}{C}-CH_3$) enolic content is 75–76% while it is 7–8% in **acetoacetic ester** because ester group shows less electron withdrawing nature than keto group.

(e) Percentage of enol content is more in non-polar media while % of keto form is more in polar media.

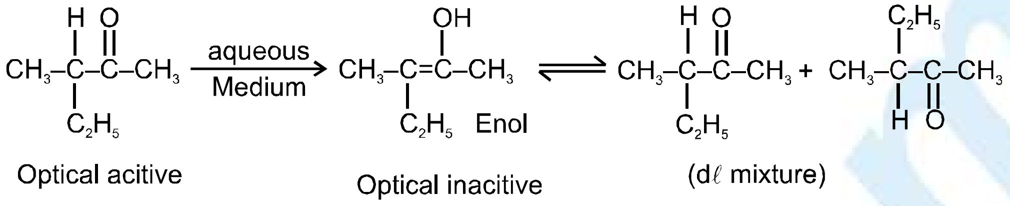
## Racemisation and D-exchange

Exchange of α-hydrogen from deuterium as well as racemization at the α-carbon are catalyzed not only by bases but also by acids due to the phenomenon of tautomerisation.

1.  (D-exchange)

2. 

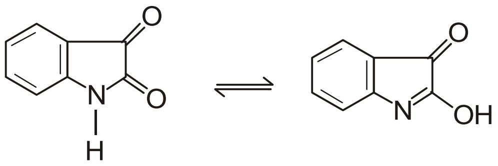
racemate

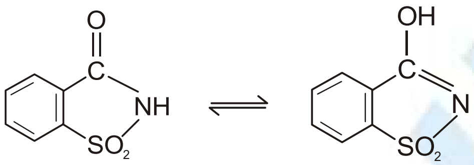
3. 

$$CH_3-\underset{C_2H_5}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{Medium}]{\text{aqueous}} CH_3-\underset{C_2H_5}{C}=\overset{OH}{C}-CH_3 \rightleftharpoons CH_3-\underset{C_2H_5}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\underset{H}{\overset{C_2H_5}{C}}-\underset{O}{\underset{\|}{C}}-CH_3$$

## Other examples of Tautomers

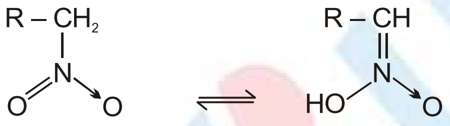
### Lactam-Lactim system





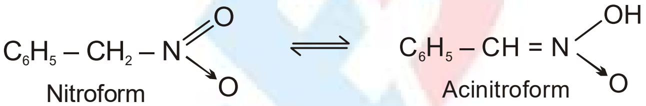
### Nitro-Acinitro system

The acidic nature of the nitro compounds gives rise to the belief that the nitro compounds exist in two forms, a more stable or normal nitro form and the less stable acinitro form.



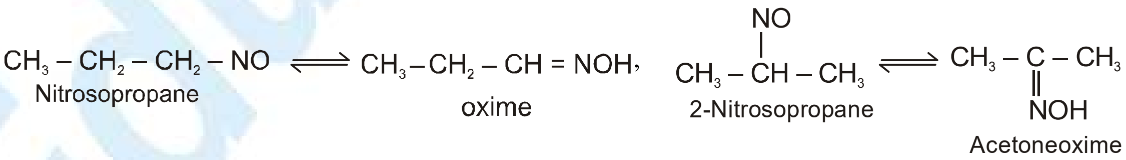
Nitroform Acinitroform

The stability of the nitro form is more as compared to the acinitro form because it is stabilised by resonance.



### Nitroso-Isonitroso system

Like primary and secondary nitro compounds, primary and secondary nitroso compounds also exhibit tautomerism with their more stable isonitroso or oxime form.



$$CH_3-CH_2-CH_2-NO \rightleftharpoons CH_3-CH_2-CH=NOH, \quad CH_3-\overset{NO}{\overset{|}{CH}}-CH_3 \rightleftharpoons CH_3-\underset{NOH}{\underset{\|}{C}}-CH_3$$

### Imine - Enamine system

$$R_2CH-CR=NR \rightleftharpoons R_2C=CR-NH-R$$

Imine Enamine

Among these two tautomers, enamines are stable only when there is no hydrogen on the nitrogen, otherwise the imine form predominates.

**1.** All the +ve charge species are electrophile except $H_3O^+$ and $NH_4^+$.

**2.** Relative electron withdrawing order (–1 order)

$$-NO_2 > -CN > -COOH > -F > -OR > -OH > -C_6H_5 > -CH = CH_2$$

**3.** + I order

$$-NO^- > -O > -COO^- > 3° \text{ alkyl} > 2° \text{ alkyl} < 1° \text{ alkyl}$$

**4.** Greater the number of α-Hydrogen, more stable is carbocation and free radical due to hyperconjugation.

**(A) Carbocation**

$$> (Ph)_3\overset{+}{C} > (Ph)_2\overset{+}{C}H > Ph-\overset{+}{C}H_2 > CH_2=CH-\overset{+}{C}H_2$$

$$(CH)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3 > CH_2=\overset{+}{C}H > CH\equiv\overset{+}{C}$$

**(B) Free radical**

$$(Ph)_3\dot{C} > (Ph)_2\dot{C}H > Ph\dot{C}H_2 > CH_2=CH-\dot{C}H_2 >$$

$$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2$$

**(C) Carbanion**

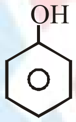
$$(Ph)_3\overset{\ominus}{C} > (Ph)_2\overset{\ominus}{C}H > Ph-\overset{\ominus}{C}H_2 > CH_2=CH-\overset{\ominus}{C}H_2 > \overset{\ominus}{C}H_3 >$$

$$CH_3\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$$

## Acidic Strength

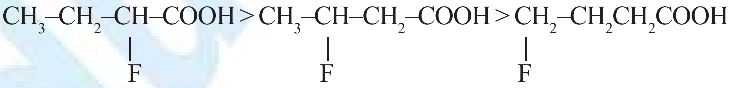
(i) $H_2O > CH\equiv CH > NH_3$

(ii) $CH\equiv CH > CH_2=CH_2 > CH_3-CH_3$

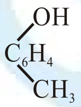
(iii) $R-SO_3H > R-COOH >$  $> R-OH$

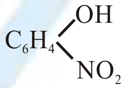
(iv) $HCOOH > CH_3COOH > CH_3CH_2COOH$

(v) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$

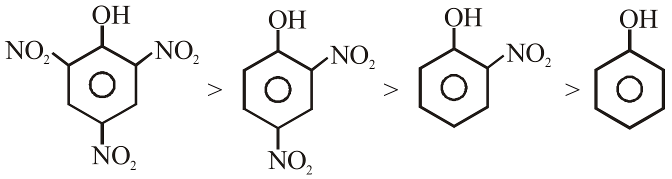
(vi) 

$$CH_3-CH_2-\underset{|}{\underset{F}{CH}}-COOH > CH_3-\underset{|}{\underset{F}{CH}}-CH_2-COOH > \underset{|}{\underset{F}{CH_2}}-CH_2CH_2COOH$$

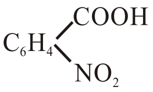
(vii)  Phenol > m > p > 0

(viii)  p > o > m > Phenol

(ix)

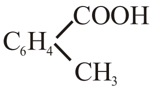


(x)



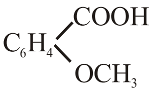
$C_6H_4(COOH)(NO_2)$ o > p > m > benzoic acid

(xi)



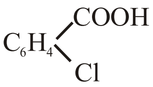
$C_6H_4(COOH)(CH_3)$ o > benzoic acid > m > p

(xii)



$C_6H_4(COOH)(OCH_3)$ o > m > benzoic acid > p

(xiii)



$C_6H_4(COOH)(Cl)$ o > m > p > benzoic acid

## Basic strength of amine

R $\Rightarrow -CH_3$ $2° > 1° > 3° > NH_3$

R $\Rightarrow -CH_2CH_3$ $2° > 3° > 1° > NH_3$

$\Rightarrow$ decreasing order of reactivity towards nucleophile (NAR)

(i) $HCHO > CH_3CHO > (CH_3)_2CO$

(ii) $CCl_3CHO > CHCl_2CHO > CH_2ClCHO$

(iii) Reactivity order towards acyl nucelophilic substitution.

Acid chloride > anhydride > carboxylic acid > ester > amide

## Order of electronic effect

Mesomeric > Hyperconjugation > Inductive effect

## Stability of alkene

$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 > RCH=CH\text{–}R$

$R\text{–}CH=CH_2 > CH_2=CH_2$