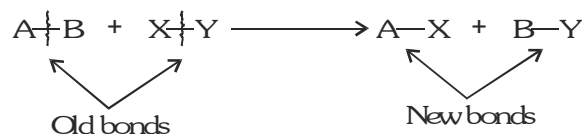


GENERAL ORGANIC CHEMISTRY

- ❑ **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.

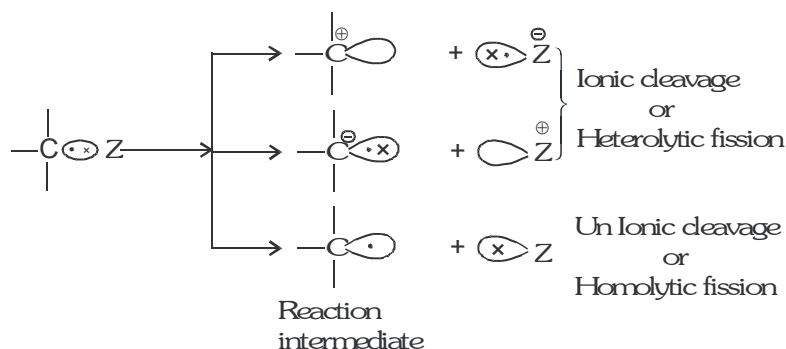
Species on which reagent is attacking is known as substrate or reactant.

Species which attack on substrate, is known as reagent.

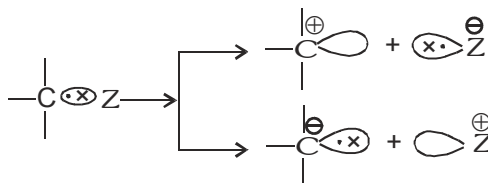
- ❑ **Type of cleavage of bond :**

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

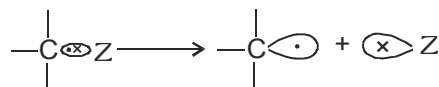
(B) **Homolytical cleavage/fission.**



- (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.

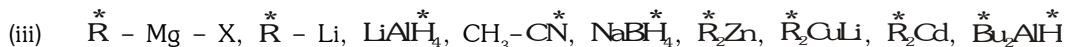


- (B) Cleavage in which equal distribution of e^- s takes place during the chemical reaction is known as homolytical cleavage.



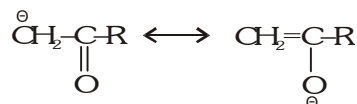
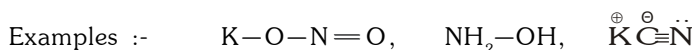
- ◆ Due to equally distribution of electrons, without charge unpaired electrons species is formed, which is known as free radical and cleavage is known as unionic cleavage/homolytical fission.
- ◆ By both cleavage [ionic/non ionic] three type of species are formed [One carrying positive charge, other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





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

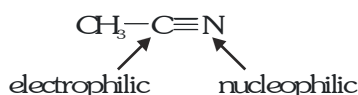
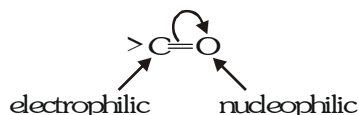
Ambident nucleophile : Nucleophiles which have two sites of electron rich centre or in which two or more atoms bear an unshared pair of electrons.



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.

For example :



| 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

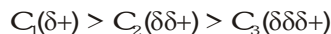
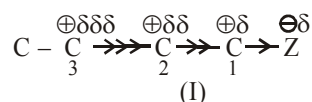
❑ INDUCTIVE EFFECT :

- ◆ 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 **Magnitude of I effect** $\propto \frac{1}{\text{distance}}$

- ◆ 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**.

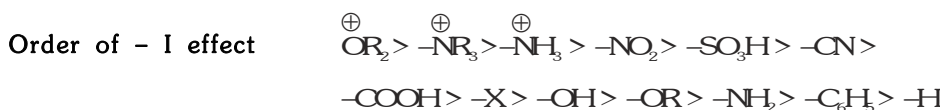
- ◆ If shifting of electron takes place from carbon chain to group or away from the carbon chain or towards the group, then it is known as **(-) I effects**.



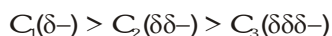
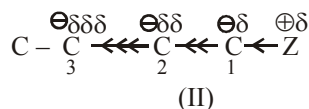
- ◆ Due to -I effect positive charge develops over carbon chain or carbon chain becomes electron deficient such type of carbon chain will be **more reactive towards nucleophile** or less reactive will be towards electrophile.

Group which shows (-) I are -

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

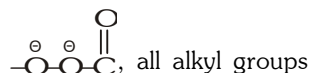


- ◆ Some groups are electron donor and therefore acquire partial positive charge by increasing electron density in the covalent bonds of a chain. Such groups exert **positive inductive (+ I) effect**.
- ◆ Or if shifting of electron takes place from group to carbon chain or away from the group or towards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

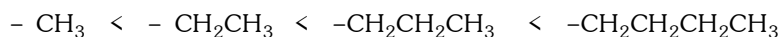


- ◆ Due to +I effect electron density increase on carbon chain or negative charge comes on carbon chain such type of carbon chain will be **more reactive towards electrophile** or will be less reactive towards nucleophile.

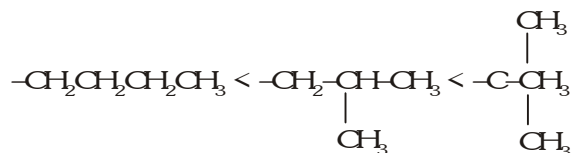
Group which shows +I effect are.



- ◆ In alkyl groups magnitude of **+I effect** \propto **size of alkyl group**



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



□ APPLICATION OF I-EFFECT

(1) Stability of carbocation :

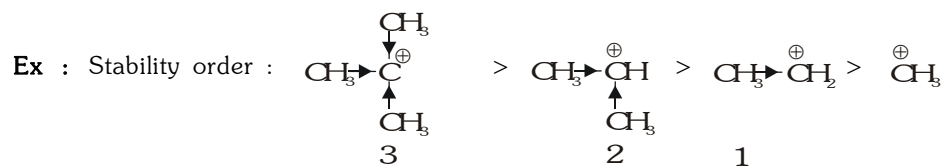
- If number of + I groups increases then stability of carbocation increases.
- If number of -I groups decreases then stability of carbocation increases.

(c) Therefore

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

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

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



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

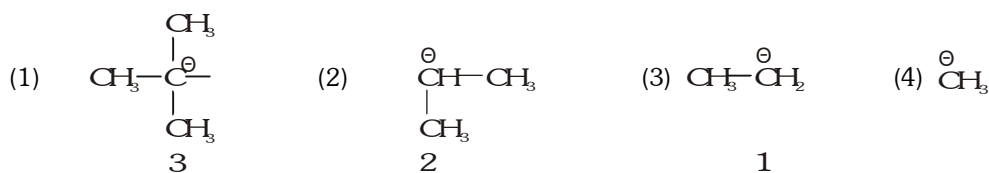
(2) Stability of carbanion :

- (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

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

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

Example :

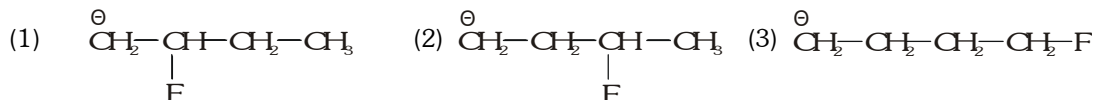


More No. of +I group.

Less stable carbanion.

So stability order $1 < 2 < 3 < 4$

Example :



Minimum distance of -F.

Maximum -I of -F.

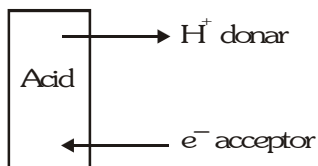
Minimum negative charge.

Maximum stable.

So stability order $1 > 2 > 3$

Acidic and basic strength :

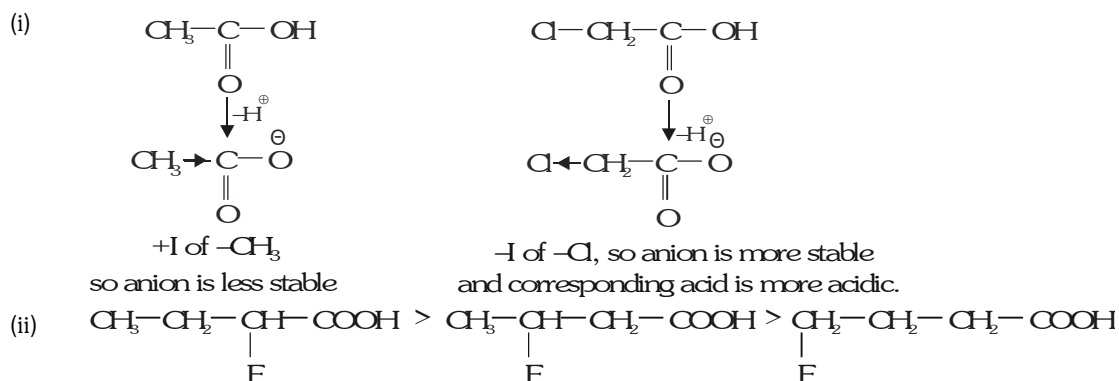
◆ **Acidic strength :**



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

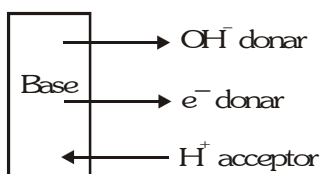
| |
|--|
| $\text{acidic strength} \propto \text{No. of -I groups} \propto \frac{1}{\text{No. of +I groups}}$ |
|--|

Example :



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

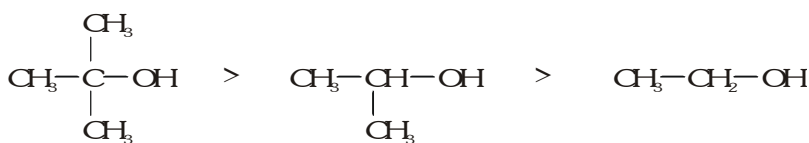
◆ **Basic strength :**



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

| |
|---|
| $\text{Basic strength} \propto \text{No. of +I groups} \propto \frac{1}{\text{No. of -I groups}}$ |
|---|

Example :



Maximum +I.

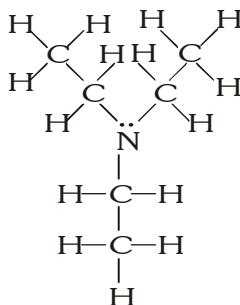
Maximum tendency to donate l.p.

Maximum basic.

Ex. Explain— Basicity order in aqueous solution and in liquid phase. $\text{Et}_2\text{NH} > \text{Et}_3\text{N} > \text{EtNH}_2$

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

Steric hindrance of three $-\text{C}_2\text{H}_5$ group protect the lone pair of nitrogen from the attack of H^+ .



But in gaseous phase basic order is $\text{R}_3\ddot{\text{N}} > \text{R}_2\ddot{\text{N}}\text{H} > \text{R}\ddot{\text{N}}\text{H}_2 > \ddot{\text{N}}\text{H}_3$

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

| Alkyl groups (R-) | Relative base strength |
|-------------------------------|---|
| (i) $\text{CH}_3 -$ | $\text{R}_2\text{NH} > \text{RNH}_2 > \text{R}_3\text{N} > \text{NH}_3$ |
| (ii) $\text{C}_2\text{H}_5 -$ | $\text{R}_2\text{NH} > \text{R}_3\text{N} > \text{RNH}_2 > \text{NH}_3$ |

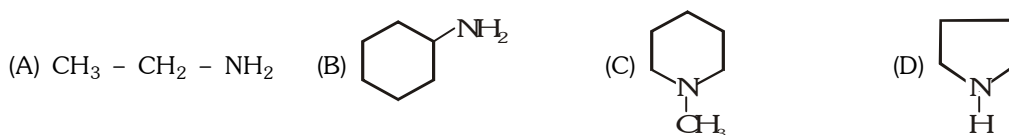
Ex. Ethyl amine is more basic than aniline, why ?

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

Ex. Cl-NH_2 is less basic than methyl amine, why ?

Sol. Due to - I effect of $-\text{Cl}$ group and $p_\pi-d_\pi$ conjugation.

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



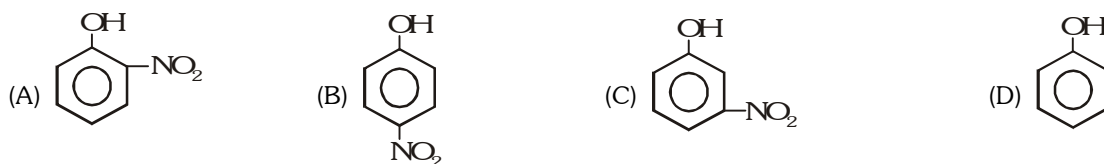
Sol. $(\text{C} > \text{D} > \text{B} > \text{A})$

Ex. Which is most basic among the following :



Sol. (D)

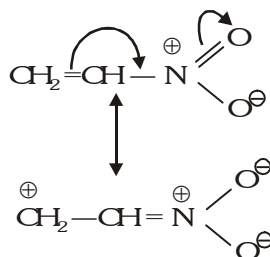
Ex. Which is most acidic compound -



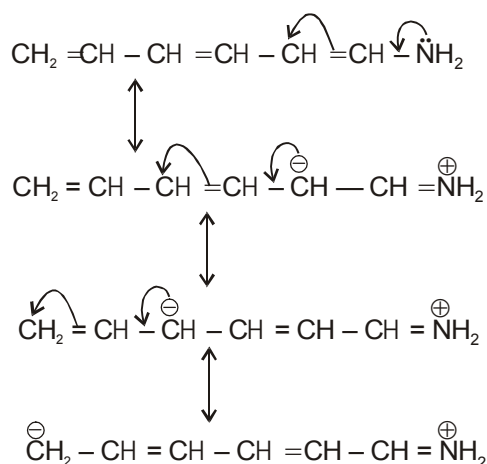
Sol. (B)

❑ 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.

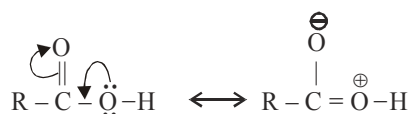


- ◆ For -M effect, group should have either be positive charge or should have vacant orbital.
- ◆ Due to -M effect positive charge comes over conjugate system or due to -M effect electron density decrease in conjugate system, such type of conjugate system will be more reactive towards nucleophile or will be less reactive towards electrophile.
- ◆ **Group which shows -M effect are -**
 $-\text{NO}_2$, $-\text{CN}$, $-\text{SO}_3\text{H}$, $-\text{CHO}$, $-\text{COR}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{COX}$, $-\text{CONH}_2$ etc.
- ◆ If transfer of non bonding electron takes place from group to conjugate system then it is known as **positive mesomeric (+M)** effect.

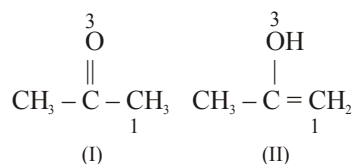


- ◆ For +M effect, group should have either be lone pair of electron or should have negative charge.
- ◆ Due to + M effect negative charge comes over conjugate system or electron density increase on conjugate system such type of conjugate system will be more reactive towards electrophile or will be less reactive towards nucleophile.
- ◆ **Group which shows + M effect are -**
 $-\text{O}^-$, $-\text{NH}^-$, $-\text{NR}_2^-$, $-\text{NHR}$, $-\text{NH}_2$, $-\text{OH}$, $-\text{OR}$, $-\text{SH}$ - SR , $-\text{F}$, $-\text{Cl}$, $-\text{NHCOR}$, $-\text{O}-\text{COR}$ 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 that's why we can say resonance phenomenon is the result of mesomeric effect or delocalisation.
- (i) Resonating structures 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.

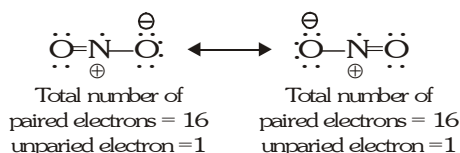


Positions of atomic nuclei in (I) and (II) are same.

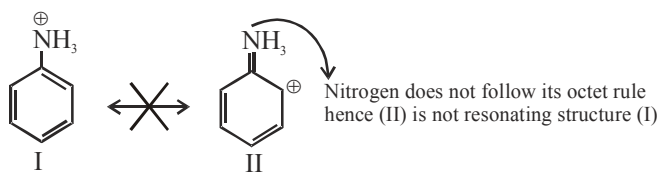


Position of hydrogen nuclei in (I) and (II) are different, hence (I) and (II) are not resonating structures, they are tautomer.

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



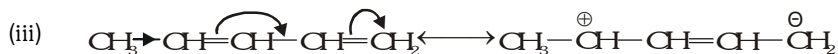
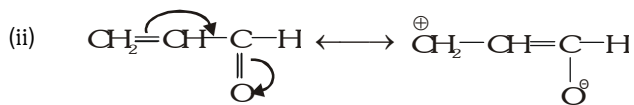
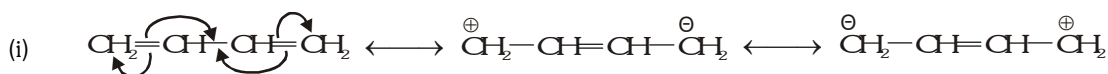
- ◆ The energy of the different resonating structures must be the same or nearly the same.
 - ◆ All atoms that are part of the delocalisation system must be in a plane or be nearly planar.
 - (v) All atoms of the resonating structure should follow the octet rule.
- For Example: All atoms follow octet rule.



□ Conditions for resonance :

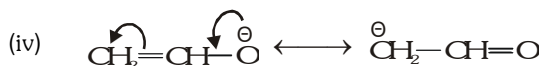
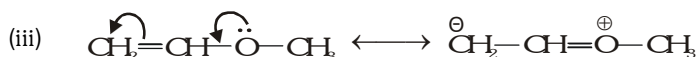
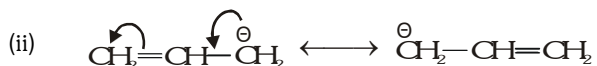
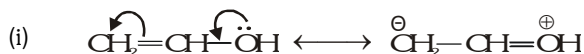
1. If there are two π bonds at alternate position then e^- of one π bond are transferred towards another π bond. (According to I-effect).

Example :



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

Example :



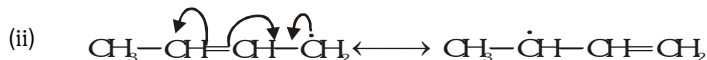
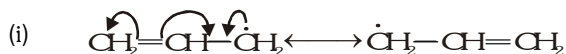
3. If there is one positive charge and one π bond are at alternate position then e^- of π bond are transferred towards positive charge.



Note : $\overset{+}{\text{CH}}_2-\text{C}(=\text{O})-\text{H}$ does not show resonance because due to more EN of oxygen πe^- are always transferred towards oxygen.

4. If there is one free e^- and one π bond are at alternate position.

Example :



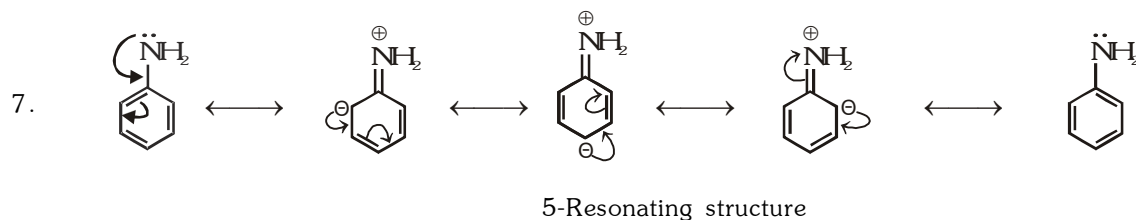
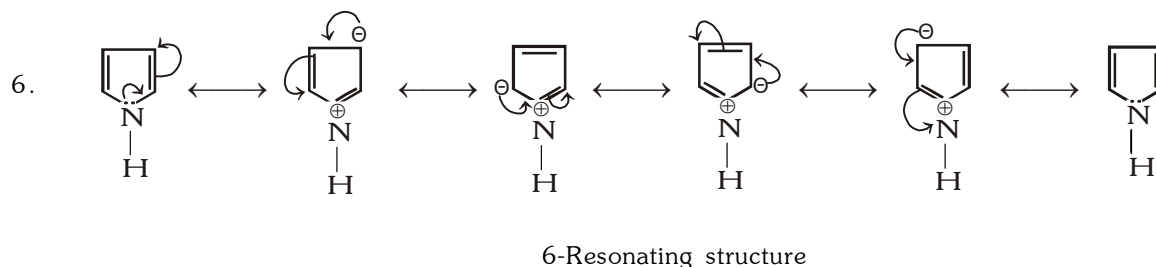
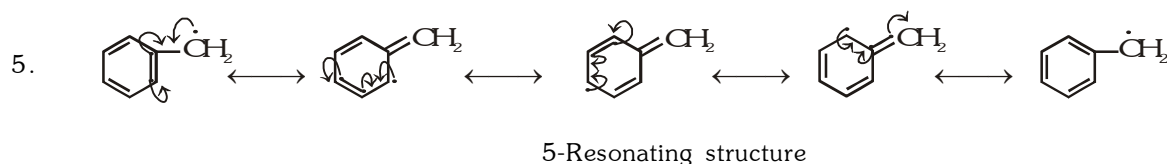
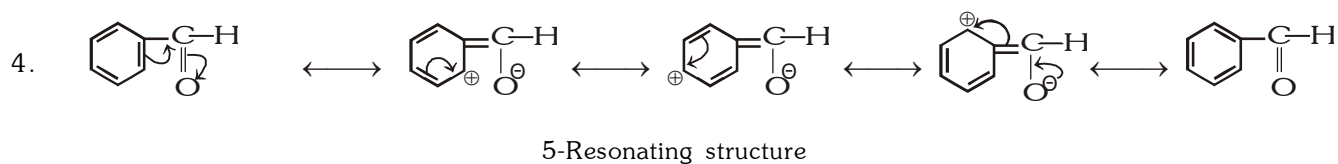
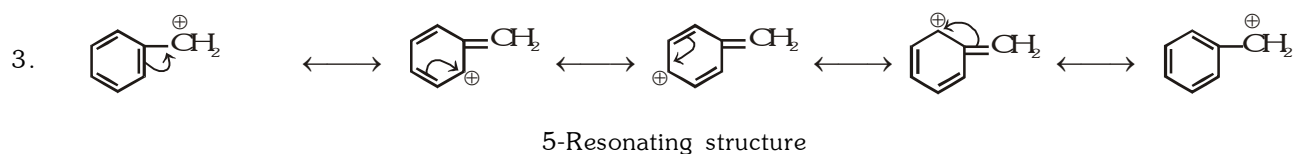
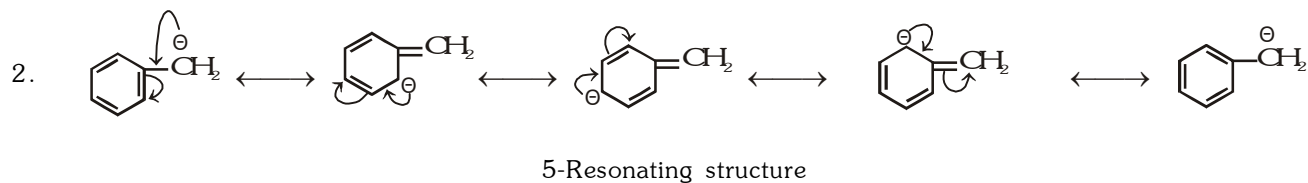
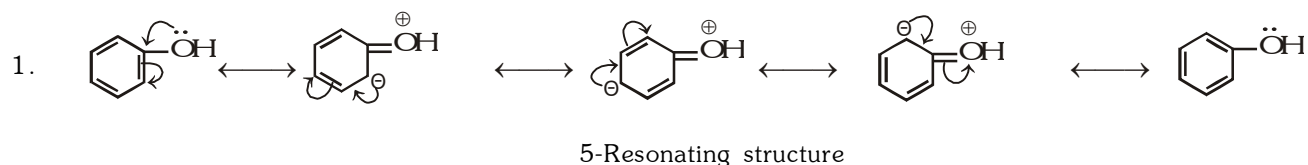
5. If there is one lone pair or negative charge and one positive charge are at adjacent atoms then e^- of lone pair or negative charge are transferred towards positive charge.



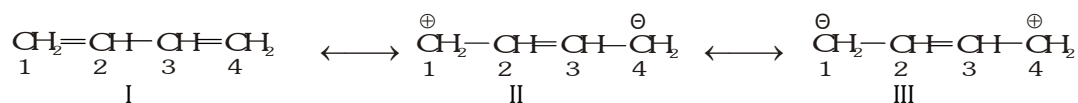
❑ Characteristics of Resonance :

- In resonance only e^- are transferred not atoms.
- The number of e^- or number of unpaired or paired e^- in all resonating structures should be same.
- The energy of resonating structures is almost same.
- It is permanent effect.
- All the resonating or canonical structures must confirm to Lewis structures.

□ Draw resonating structures :



□ Hybrid resonating structure :

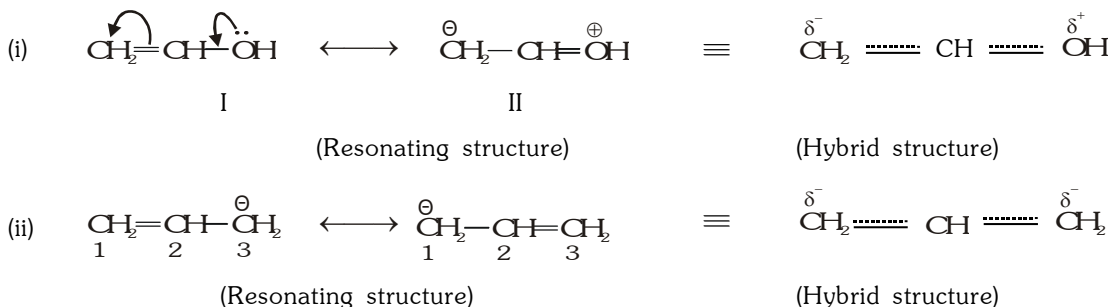


In the structure I C_1-C_2 has double bond while in II and III C_1-C_2 has single bond, so C_1-C_2 shows bond length in between single and double bond similarly in structure I C_2-C_3 has single bond. While in structure II and III C_2-C_3 has double bond, so C_2-C_3 shows bond length in between single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

So hybrid resonating structure from all its resonating structures is :



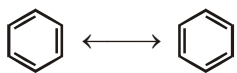
Example :



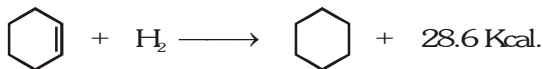
❑ Resonance energy :

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,

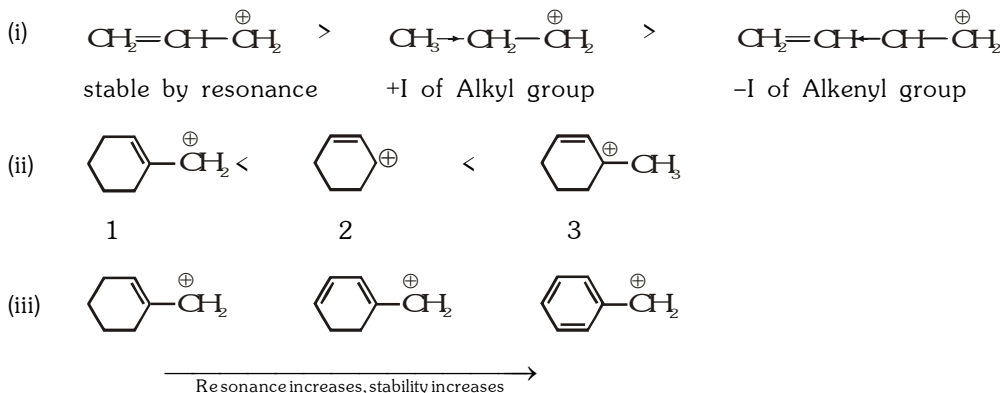
$$\begin{aligned} \text{Resonance energy} &= \text{Calculated value} - \text{Experimental value} \\ &= 85.8 - 49.8 = 36 \text{ Kcal.} \end{aligned}$$

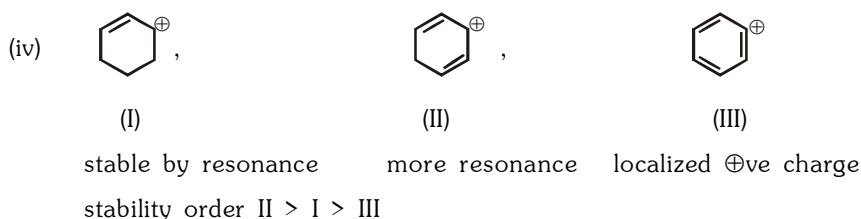
❑ APPLICATION OF M- EFFECT OR RESONANCE EFFECT :

◆ Stability of carbocation :

- (a) Stability of carbocation is increased by resonance.
- (b) Aromatic compound are more stable than non aromatic compound.

Example : Compare stability order of :-

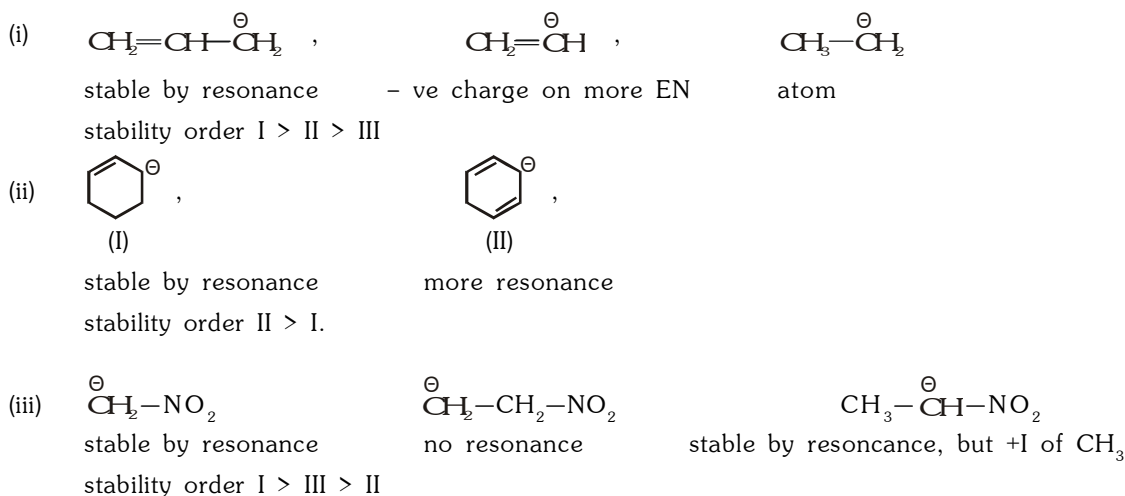




□ **Stability of carbanion :**

(a) Stability of carbanion is increased by resonance.

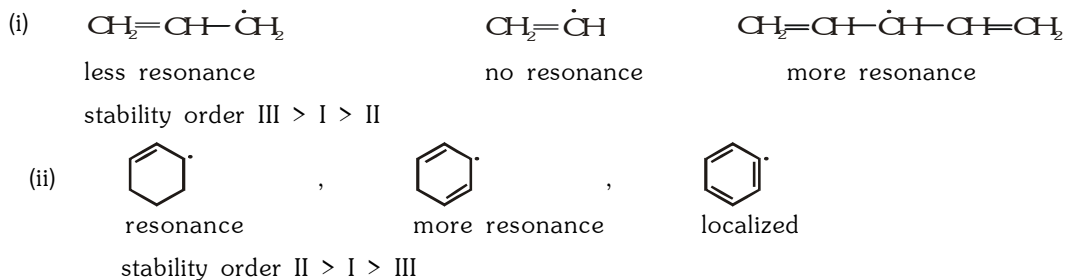
Example : Compare stability order of :



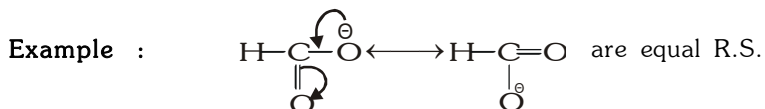
□ **Stability of free radicals :**

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

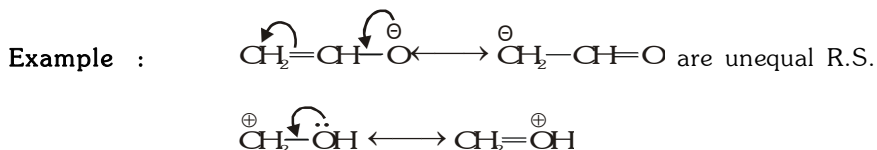
Example : Compare stability order of :



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



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.



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

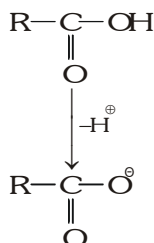
❑ Acidic and Basic strength :

(a) Acidic strength :

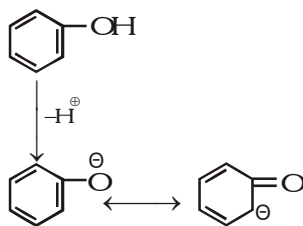
$$\text{Acidic strength} \propto -M \propto -I \propto \frac{1}{+M} \propto \frac{1}{+I}$$

Ex : Carboxylic acids are more acidic than phenols, why ?

Sol.



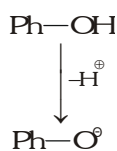
2, equal R.S. more stable anion
so corresponding acid is more acidic



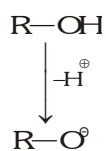
5, unequal R.S. less stable anion

Ex : Phenol is more acidic than alcohols why ?

Sol.



stable by resonance
So, it is more acidic.



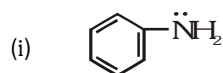
no resonance.

(b) Basic strength order :-

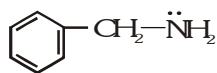
If there is more resonance of lone pair or negative charge then it will be more stable, means less basicity.

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

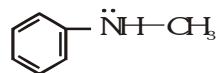
Ex : Give basic strength order :



l.p. is stabilized by
resonance

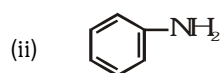


no resonance of l.p.
so maximum basic



l.p. is stabilized by resonance
stabilized and +I of CH₃

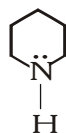
basic order — II > III > I



stable by
resonance



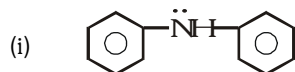
localized



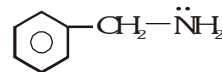
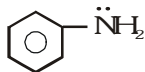
l.p. on more EN

basic order — III > II > I

Ex : Give basic strength order for :



diphenyl amine
more resonance



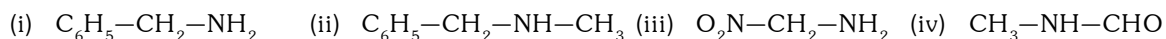
benzyl amine
no resonance

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 :



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

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

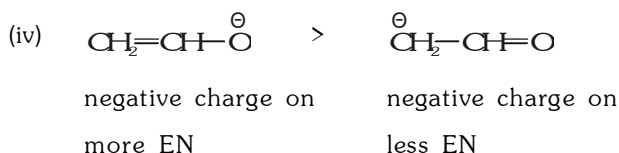
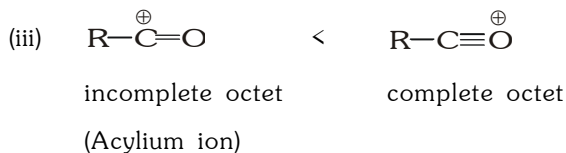
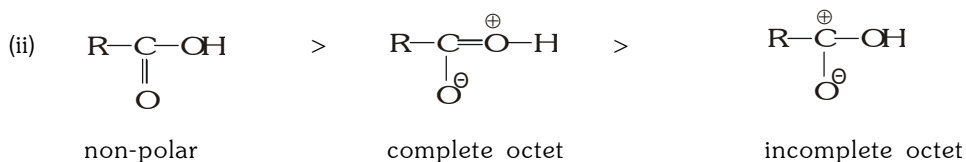
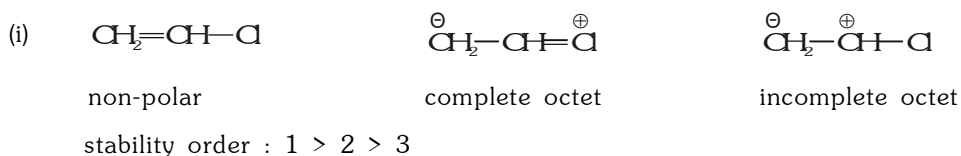


In benzene ring due to more electron density first attack will be of electrophile.

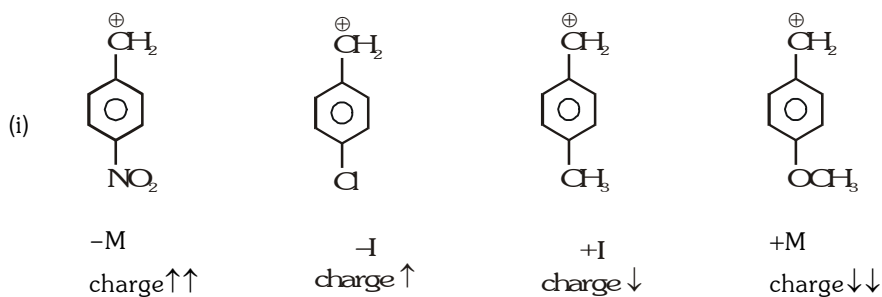
8. Rules for stability of resonating structure (R.S) :

- Non-polar R.S. is more stable than polar resonating structures.
- In polar R.S. complete octet is more stable than incomplete octet.
- For incomplete R.S. positive charge on more EN is less stable.

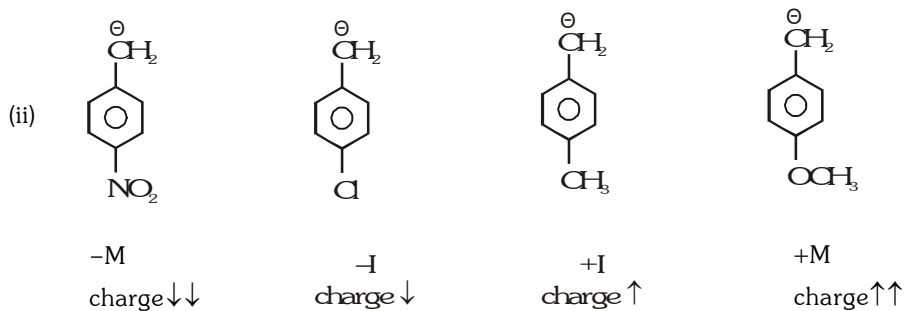
Example : Arrange the following for stability order.



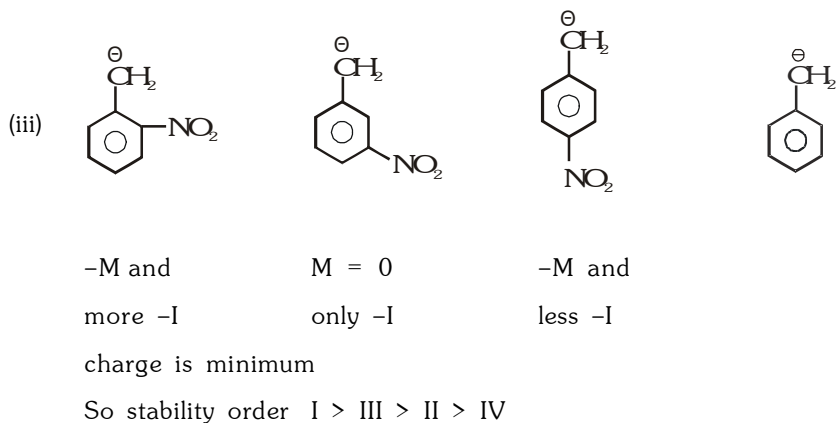
Ex : Give stability order of :



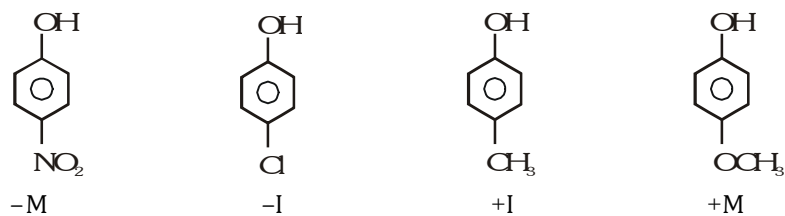
So stability order IV > III > II > I



Stability order I > II > III > IV



Ex. Give acidic strength order for :



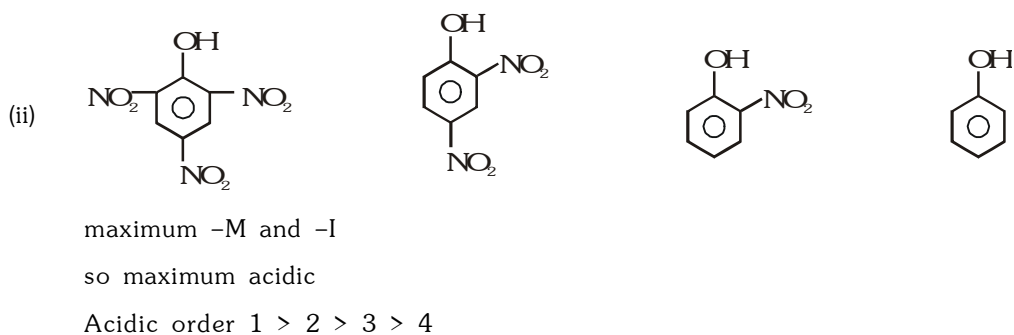
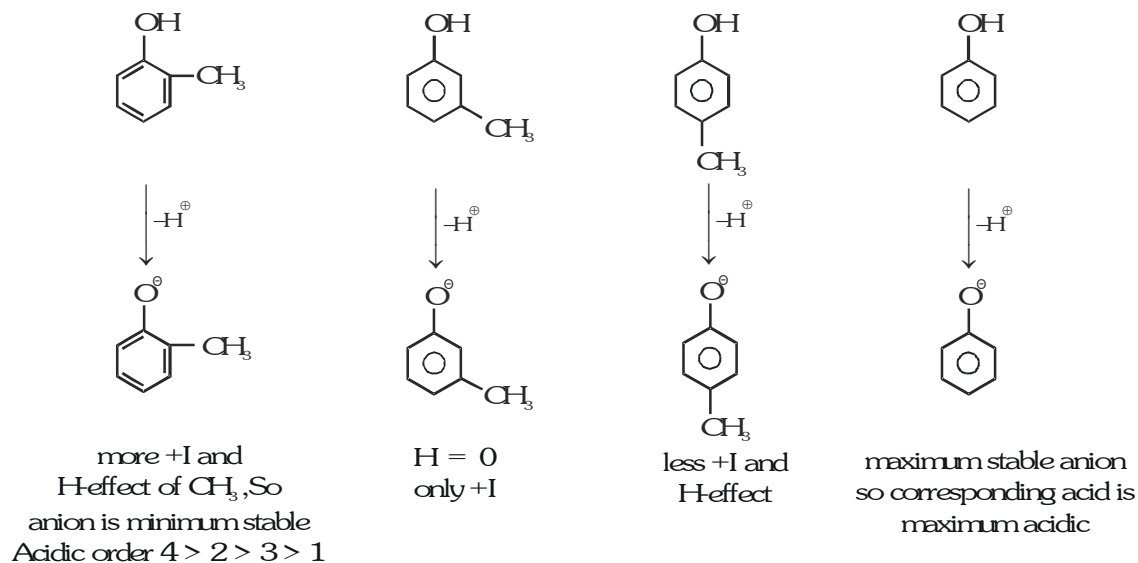
Sol. So acidic order is I > II > III > IV

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

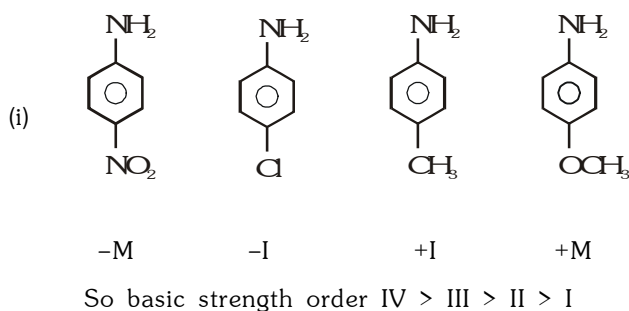
Sol. Ortho-nitrophenol is distilled out due to less B.P. of ortho-nitrophenol it is more volatile

Ex. Give acidic strength order for

(i)

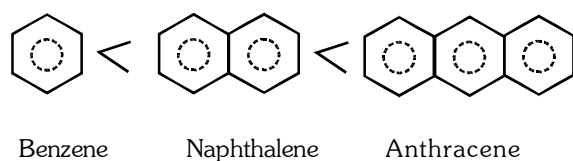


Ex : Give basic strength order for :

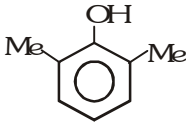
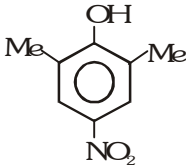
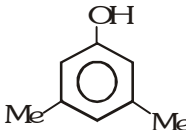
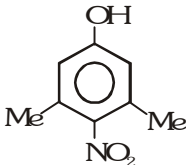


Ex : What is the increasing order of resonance stabilization of benzene, naphthalene and anthracene.

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.



Phenol : 9.98/1.10 10^{-10} pK_a/K_a value

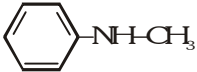
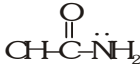
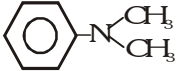
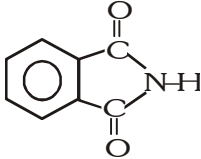
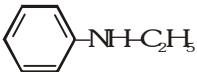
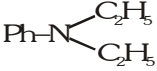
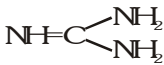
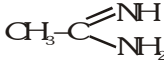
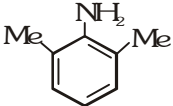
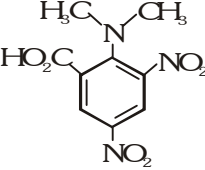
| Substituent | | O- | M- | P- |
|-------------|---|-----------------------|-----------------------|-----------------------|
| (i) | Me | 10.28/0.63 10^{-10} | 10.08/0.98 10^{-10} | 10.14/0.67 10^{-10} |
| (ii) | NO ₂ | 7.23/600 10^{-10} | 8.40/50 10^{-10} | 7.15/690 10^{-10} |
| (iii) | F | 8.81/15 10^{-10} | 9.28/5.2 10^{-10} | 9.98/1.1 10^{-10} |
| (iv) | Cl | 8.48/77 10^{-10} | 9.02/16 10^{-10} | 9.38/6.3 10^{-10} |
| (v) | CH ₃ -O | 9.98/1.05 10^{-10} | 9.65/2.24 10^{-10} | 9.38/0.62 10^{-10} |
| (vi) | OH | 9.48 | 9.44/3 10^{-10} | 9.96 |
| (vii) | NH ₂ | 9.71/2.0 10^{-10} | 8.16/68 10^{-10} | 10.30 |
| (viii) | Br | 41 10^{-10} | 14 10^{-10} | 5.6 10^{-10} |
| (ix) | I | 34 10^{-10} | 13 10^{-10} | 6.0 10^{-10} |
| (x) | 2,4- dinitrophenol | 4.00 | | |
| (xi) | 2,4,6-trinitro phenol | pKa = 0.71 | 10.50 10^{-2} | |
| |  | 10.60 | | |
| |  | 7.22 | | |
| |  | 10.17 | | |
| |  | 8.25 | | |


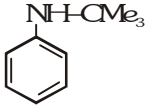

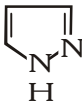

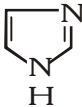
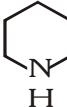
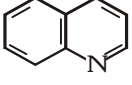
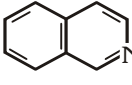
pK_a/Benzoic acid → 4.20

| Substituent | pK _a - | 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 (pK _a ¹) | 6.23 (pK _a ²) | | |
| Fumaric acid | 3.02 (pK _a ¹) | 4.38 (pK _a 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 ₂ N-CH ₂ -COOH | 1.68 | | | |
| Me ₃ N ⁺ -CH ₂ -COOH | 1.83 | | | |
| N≡C-CH ₂ -COOH | 2.47 | | | |
| EtOCOCH ₂ COOH | 3.35 | | | |
| MeO-CH ₂ -COOH | 3.58 | | | |

pK_a/K_a value-Aniline $\rightarrow 4.62$

| Substituent | 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 |  | ~ 0.5 |
|  | 5.06 |  | shown some acidic nature |
|  | 5.11 | | |
|  | 6.56 |  | 13.6 |
| Ph ₂ NH | 0.9 | | |
| Ph-NH-AC | 0.4 |  | 12.4 |
|  | 5.69 | (C ₂ H ₅) ₂ NH | 10.93 |
| | | Et ₃ N | 10.88 |
| | | Et-NH ₂ | 10.67 |
|  | 4.60 | NH ₃ | 9.25 |
| | | Me ₃ N | 9.80 |
| | | Me ₂ N | 10.77 |
| | | Me-NH ₂ | 10.64 |

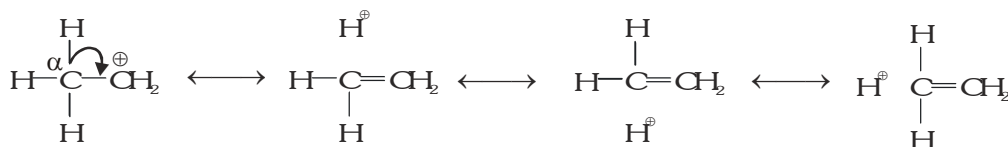
| | | | |
|---|-------|--|-------|
|  | 10.50 | Bu_3N | 9.87 |
|  | 7.1 | Bu_2NH | 11.28 |
|  | -0.27 | BuNH_2 | 10.61 |
|  | 2.53 |  | 5.23 |
|  | 7.03 |  | 11.22 |
| | |  | 4.94 |
| | |  | 5.2 |

❑ HYPERCONJUGATION EFFECT OR H-EFFECT :

Complete transfer of e^- of $-\text{C}-\text{H}$ 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 :

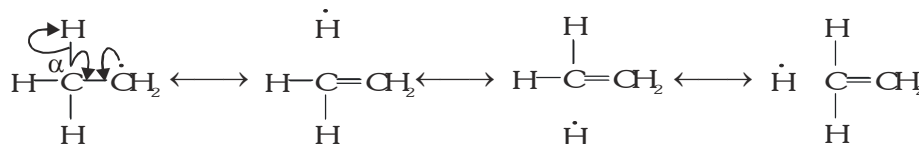
1. If there is one $\text{C}-\text{H}$ σ bond and one positive charge are at alternate position



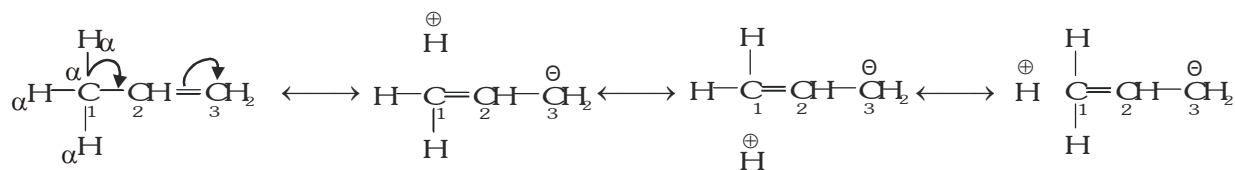
all are called as hyperconjugation structures or canonical structures.

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.

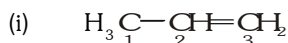
2. Carbon which is attached to sp^2 C is called as α -C and H which are attached to α -C are called as α -H. If there is one $-\text{C}-\text{H}$ σ bond and one free e^- are at alternate position then there will be H-effect.



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



Special point :

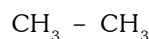
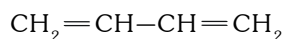


C_1-C_2 bond length = 1.54 Å

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



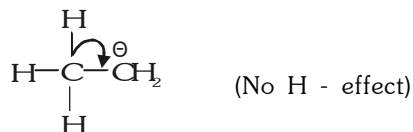
is III > II > I

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.



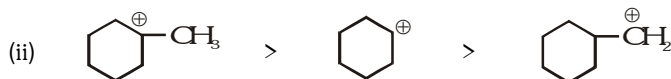
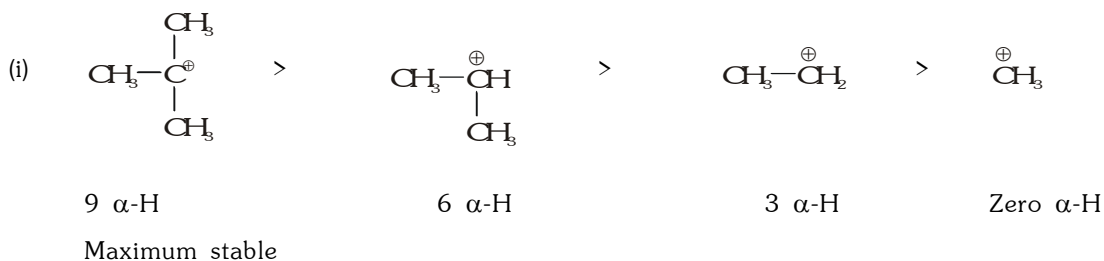
no shifting of $-C-H$ σ bond, because anion have complete octet. ($8e^-$)

□ APPLICATION OF H-EFFECT OR H-EFFECT :

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 \propto No. of canonical structures \propto No. of α H.

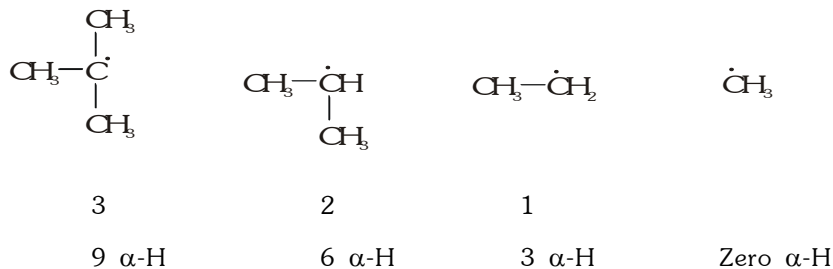
Ex. Give stability order for :-



❑ **Stability of carbon free radicals :**

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

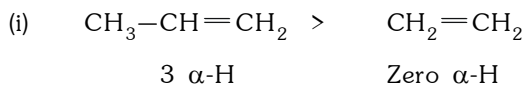
Ex : Give stability order for :-



Maximum stable

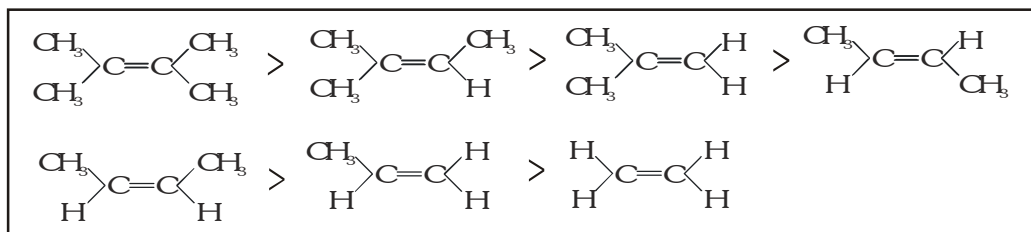
Stability order I > II > III > IV

❑ **Stability of alkenes :** More hyperconjugation structures (more α -H) more stable alkene.



more stable

(ii) Stability order of alkenes will be

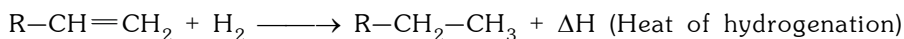


Ex : Which of the following alkene is maximum stable.

- (A) $\text{R}_2\text{C}=\text{CR}_2$ (B) $\text{R}-\text{CH}=\text{CR}_2$ (C) $\text{R}-\text{CH}=\text{CH}-\text{R}$ (D) $\text{R}-\text{CH}=\text{CH}_2$

Sol. (A) due to more substituted alkene.

❑ **Heat of hydrogenation :**



Heat evolved when any unsaturated hydrocarbon are hydrogenated is called heat of hydrogenation (ΔH)

If alkene is more reactive towards hydrogen then it will evolve more ΔH .

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

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.

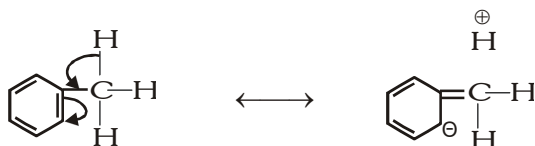
Actual ΔH - $60 > \Delta H > 30$ Kcal.

Ex : Which of the following is maximum stable.

- (i) Conjugated alkadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$)
 (ii) Isolated alkadiene ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$)
 (iii) Cumulated alkadiene ($\text{CH}_2=\text{C}=\text{CH}_2$)
 (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.

□ **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 substitution reaction order :



Maximum α -H.

So maximum H-effect

So maximum e^- density

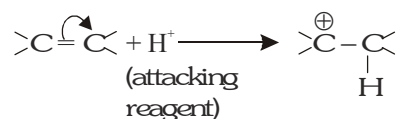
So maximum reactive

ESR order $\text{I} > \text{II} > \text{III} > \text{IV}$

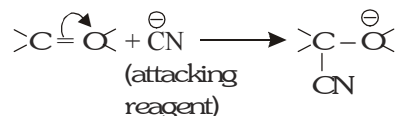
□ **ELECTROMERIC EFFECT : (E Effect)**

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 e^- 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 (\curvearrowright). There are two distinct types of electromeric effect.

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

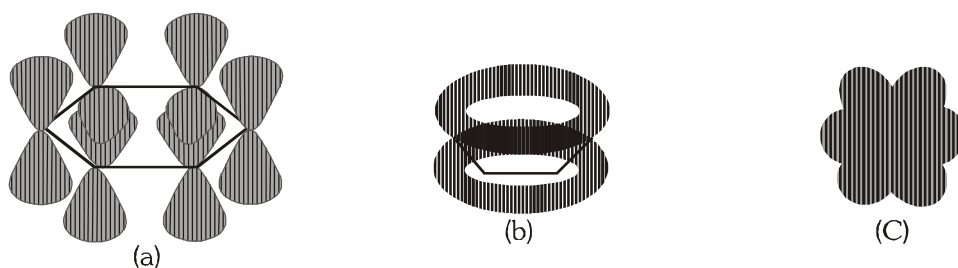


- (ii) **Negative Electromeric Effect (-E effect)** : In this effect the π - electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example.



□ AROMATICITY :

Many cyclic, conjugated compounds possess markedly different physical and chemical properties from those expected by comparison 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 π electrons above and below the plane of the ring, because its π -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 unusually 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 π 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 π electrons above and below the plane of the molecule (often called a π cloud).

For the π cloud to be cyclic, the molecule must be cyclic.

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

For the π 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 π cloud must contain an odd number of pairs of π electrons.

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

The German chemist Erich Huckel was the first to recognize that an aromatic compound must have an odd number of pairs of π 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 π cloud must contain $(4n + 2)$ π 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., π 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 π electron. Thus, Huckel's rule is just a mathematical way of saying that an aromatic compound must have an odd number of pairs of π electrons.

Cyclobutadiene has two pairs of π electrons and cyclooctatetraene has four pairs of π electrons therefore, these compounds are not aromatic because they have an even number of pairs of π 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.



Monocyclic hydrocarbons with alternating single and double bonds are called annulenes. 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.



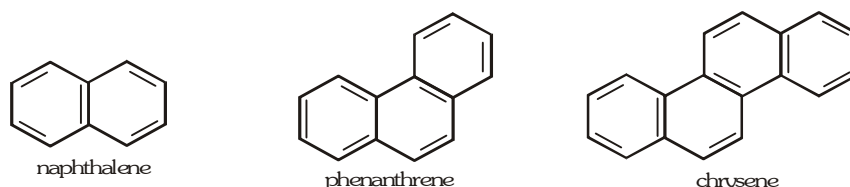
The cyclopropenyl cation is aromatic because it does have an uninterrupted ring of p orbital-bearing atoms and the π cloud contains one pair of delocalized π electrons. The cyclopropenyl anion is not aromatic because its π cloud has two (an even number) pairs of π electrons.



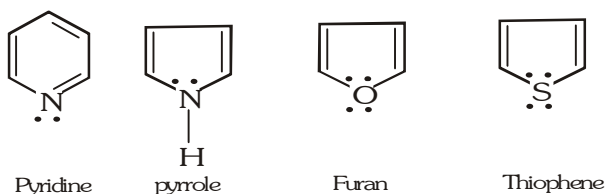
Cycloheptatriene is not aromatic. Although it has the correct number of pairs of π electrons to be aromatic (three pairs), it does not have an uninterrupted ring of p orbital-bearing atoms because one of the ring atoms is sp^3 hybridized. Cyclopentadiene is also not aromatic. It has an even number of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



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 pairs of π -electrons) and chrysene (nine pairs of π electrons) are aromatic.



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.



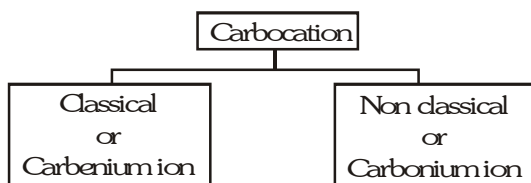
In pyrrole, furan and thiophene, the lone pairs are actually in sp^3 hybrid orbitals to form the aromatic sextet ($4n + 2$) π -electrons. In pyridine, the lone pair is in sp^2 hybrid orbital, which is not involved in delocalization. Thus, pyridine also has 6 π -electrons and is aromatic in nature.

❑ REACTION INTERMEDIATES :

In the study of organic chemistry following 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 deficient species act as electrophilic and lequid acid.



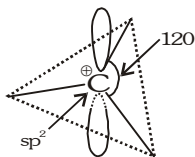
Note :

According to modern nomenclature accepted by IUPAC CH_3^+ , CH_3CH_2^+ etc. are termed as carbenium ion (but not carbonium ion). Although some authors still refers to CH_3^+ , CH_3CH_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 vacant 'p'orbital lies below and above the plane.

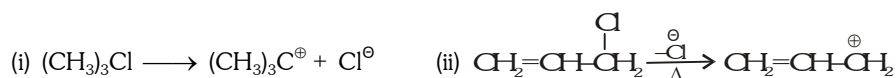


2. Stability : Carbocation are stabilised by :

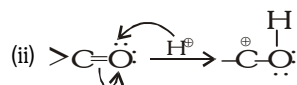
- (i) + I effect (ii) + M effect (iii) Hyper-conjugation

3. The generation of —C^+ (carbenium ion) :

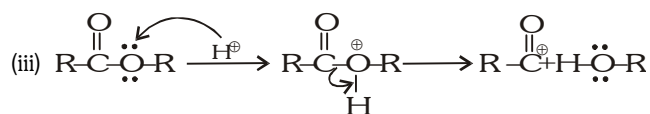
(a) By the direct ionisation : (In highly polar medium)



(b) By the protonation of unsaturated compound :



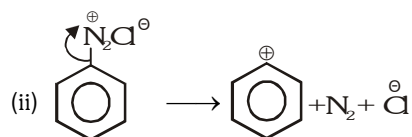
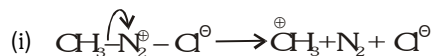
(c) By the protonation of lone pair of electron :



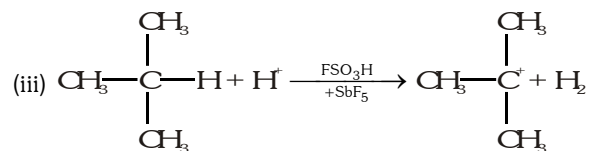
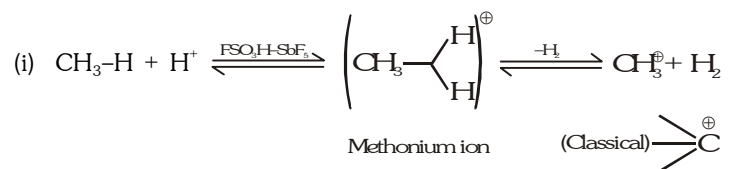
(d) By electrophilic attack on alkyl halide or acyl halide :



(e) By the decomposition of diazonium salt :

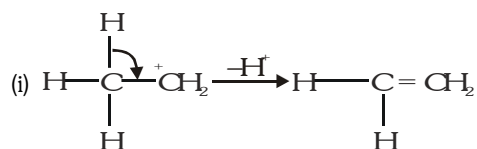


(f) By attack of super acid on alkane :

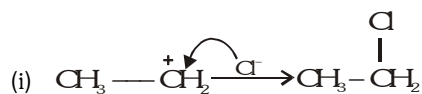
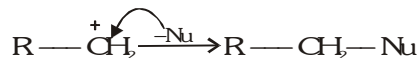


4. Reaction of Carbocation (carbenium ion) :

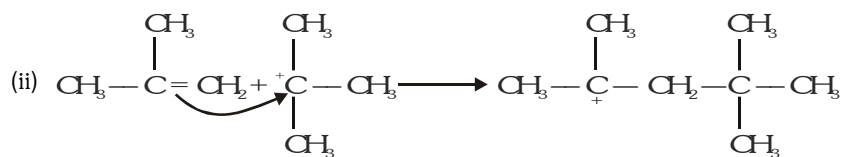
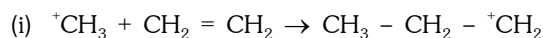
(a) Proton Loss : To form a multiple bond.



(b) Combination with Nucleophiles :

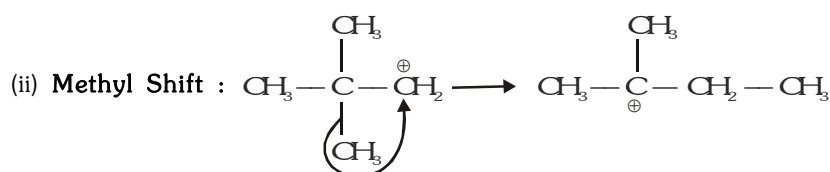
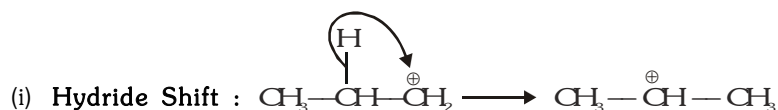


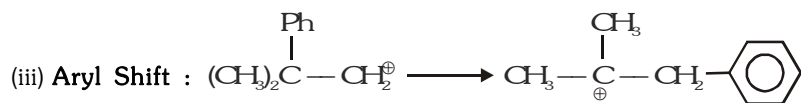
(c) Addition to an alkene :



(d) Molecular Rearrangement :

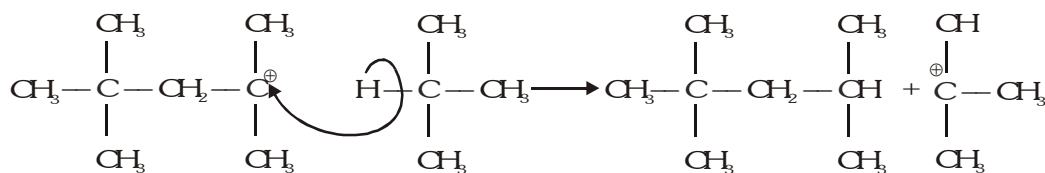
A carbocation would undergo a molecular rearrangement when it could produce a more stable carbocation e.g.





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

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



◆ **Carbanion** :

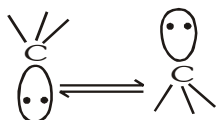
(1) A carbon intermediate which contains three bond pairs and a negative charge on it, is called carbanion.



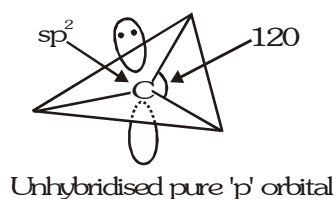
(2) **Structure and Hybridisation** :

On the basis of the structure carbanions are of two types

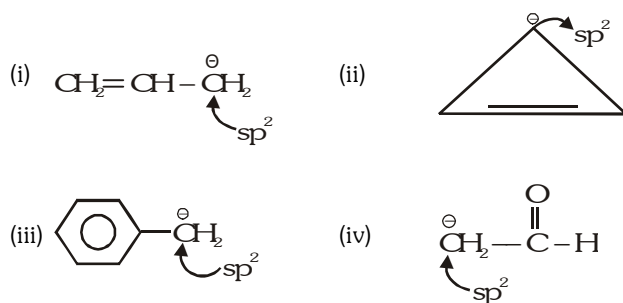
(a) Carbanion (sp^3) hybridised (pyramidal)



(b) Planar carbanion (sp^2) hybridised (–ve charge is attached to π bonded system)



Example :



(3) Stability of carbanion :

Carbanions are stabilised by electron withdrawing effects as

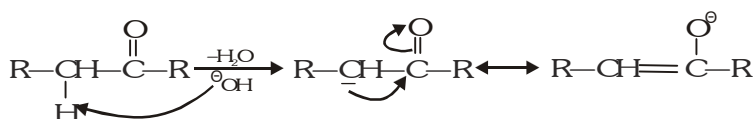
- (a) -I effect
- (b) -M effect
- (c) Delocalisation of charge
- (d) Aromatization

□ Generation of Carbanion :

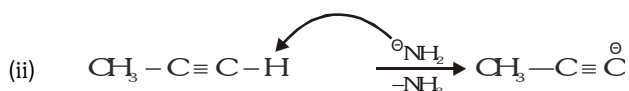
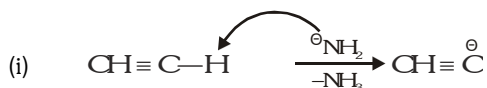
◆ By action of base on acidic hydrogen of C - H bond :

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

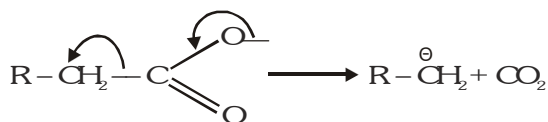
- (1) By attack of base on 'H' of $\begin{array}{c} \text{C}-\text{x}=\text{y} \\ | \\ \text{H} \end{array}$ system (E.N. $y > x$)



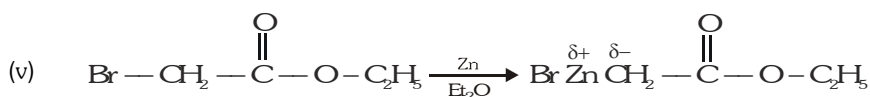
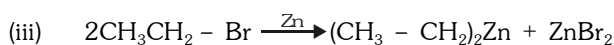
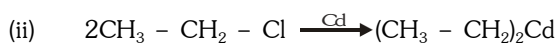
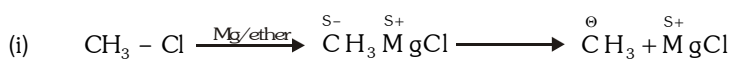
- (2) By attack of base on $\equiv \text{C}-\text{H}$:



◆ By decarboxylation of carboxylate ion :



◆ In the form of organometallic compound :

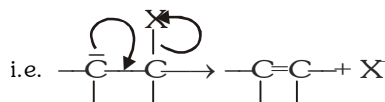


❑ Reactions of Carbanion :

(1) Attachment of H^+ : e.g. ${}^{\ominus}CH_3 + H^{\oplus} \rightarrow CH_4$ as

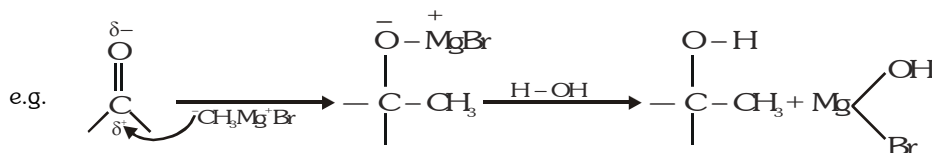
(2) Loss of Leaving Group :

In the system $\begin{array}{c} X \\ | \\ \ominus C - C \end{array}$ carbanion loses leaving group to form a π bond.



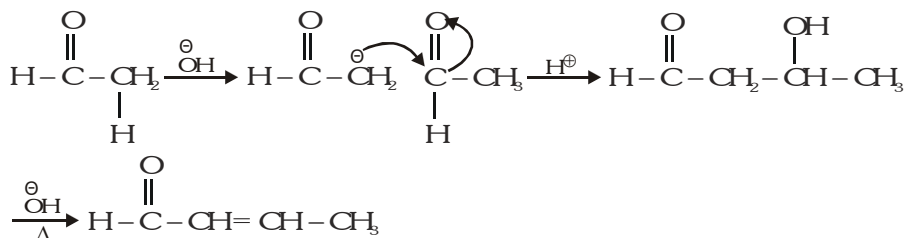
(3) Addition Reaction

Carbanion gives Nucleophilic addition reaction :

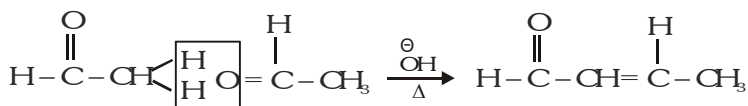


(4) Nucleophilic Addition plus condensation reaction :

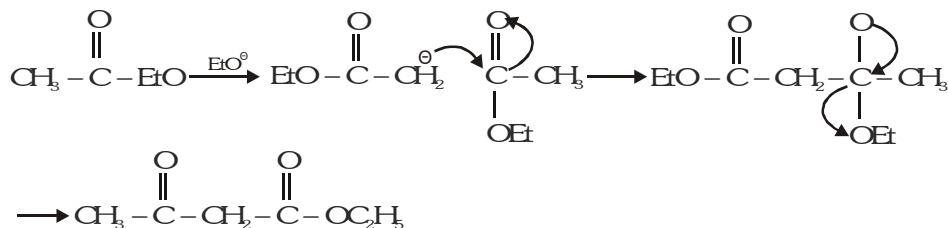
(i) Aldol condensation :



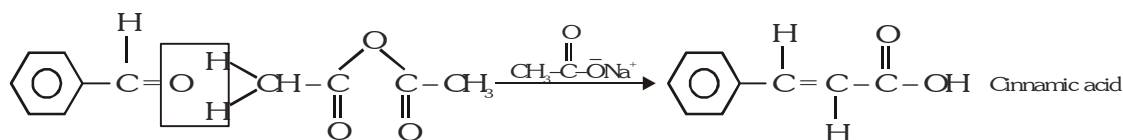
Shot cut :



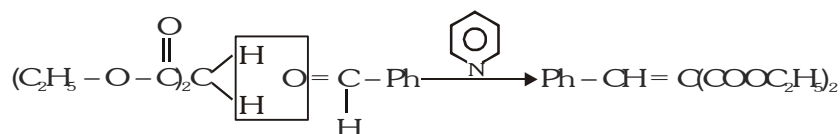
(ii) Claisen condensation :



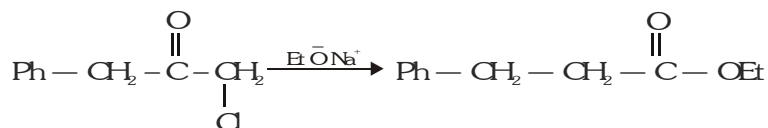
(iii) Perkin reaction :



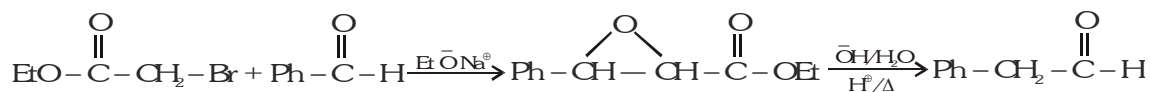
(iv) Knoevengel reaction :



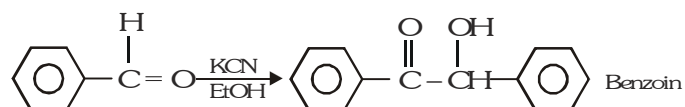
(v) Favorskii reaction :



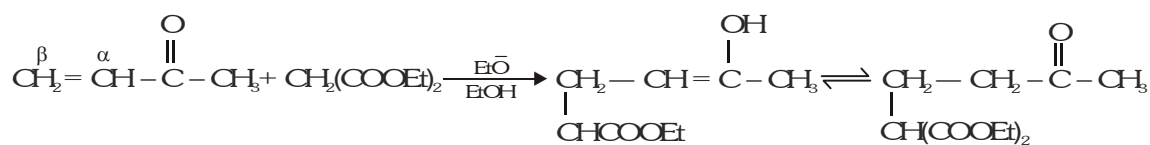
(vi) Darzen reaction :



(vii) Benzoin condensation :



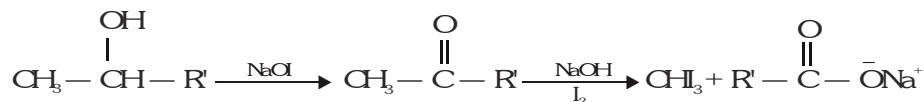
(viii) Micheal addition :



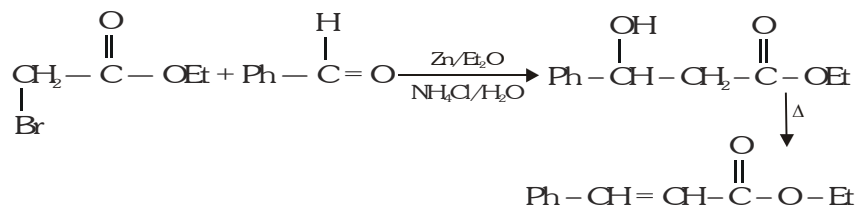
(ix) Wittig reaction :



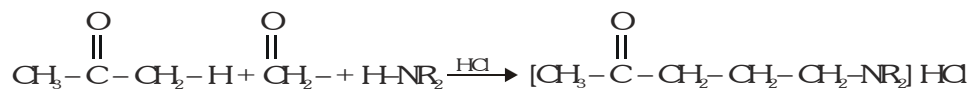
(x) Haloform reaction :



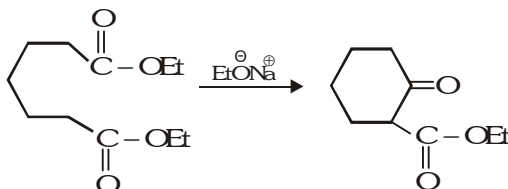
(xi) Reformatsky reaction :



(xii) **Mannich reaction :**



(xiii) **Dieckmann reaction :**



◆ **Carbon free Radical :**

- (1) Free radical is a species that contain an unpaired 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. $\overset{\cdot}{\underset{|}{\text{C}}}-$ unpaired electron.

- (2) **Structure and Hybridisation :** A free radical may considered as having :

Pyramidal structure which are rapidly interconverting, sp^3 hybridised.

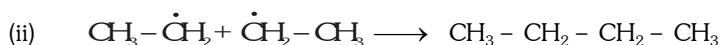
Planer structure ; sp^2 hybridised.

Note :

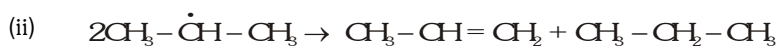
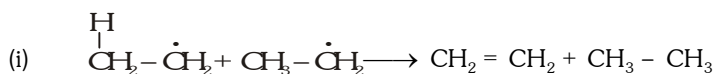
Although geometry of organic free radical is still controversial but recent studies revealed conclusive in the favour of planer structure.

- (3) **Reaction of Free Radicals :**

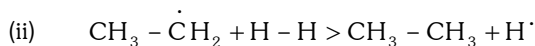
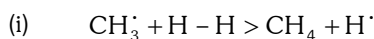
(a) **Recombination (coupling) :**



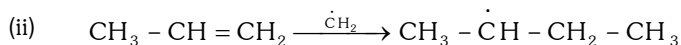
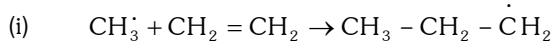
(b) **Disproportionation :**



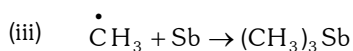
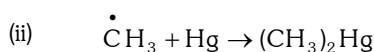
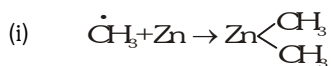
(c) **Reaction with hydrogen :**



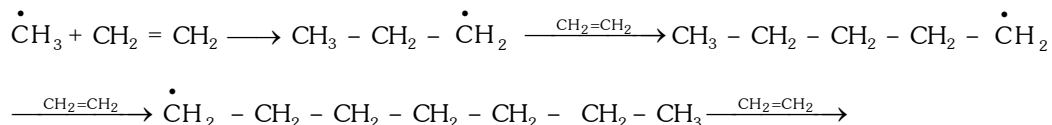
(d) **Reaction with unsaturated compound :**



(e) Reaction with metals :



(f) Polymerisation :

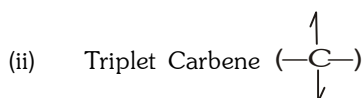


◆ **CARBENE :**

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

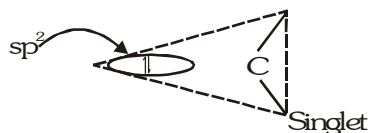


- (2) **Types of Carbene :** Carbenes are classified into two classes,



(a) Singlet Carbene :

- (i) Both non bonded electrons are present in the same sp^2 hybridised orbitals with opposite spin.
(ii) It has sp^2 hybridisation and bent structure.

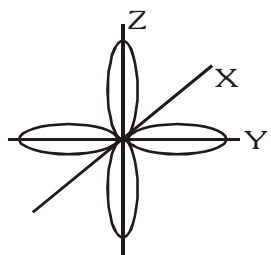


- (iii) It is an excited state of carbene
(iv) It is diamagnetic with magnetic moment zero.
(v) Multiplicity $M = 2S + 1$
But in this case $S = (+1/2) + (-1/2) = 0$ $M = 2 \quad 0 + 1 = 1$
(vi) It is a strong electrophile.

(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 structure.



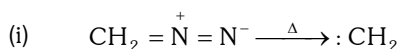
expected structure (But not real)

- (iii) It is ground state of carbene.
 (iv) It is paramagnetic with magnetic moment.

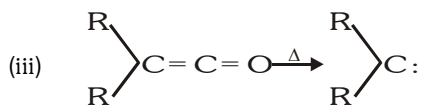
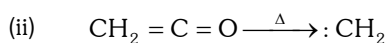
$$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = 2\sqrt{2} \text{ Bohr magneton.}$$

- (v) Multiplicity $M = 2S + 1 = 2(+1/2 + 1/2) + 1 = 3$
 (vi) It is strong electrophile.

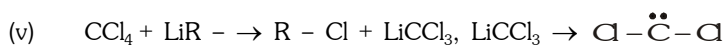
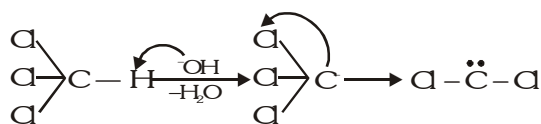
(3) Generation of carbene :



diazomethane

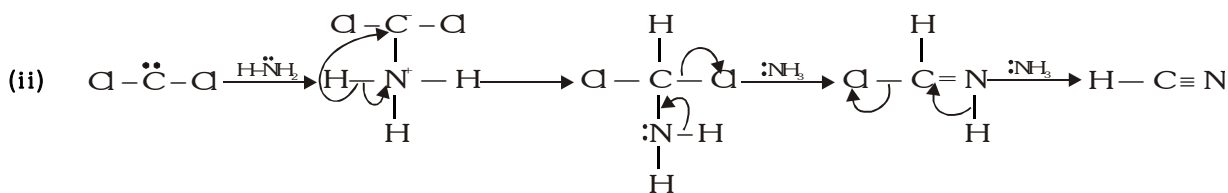
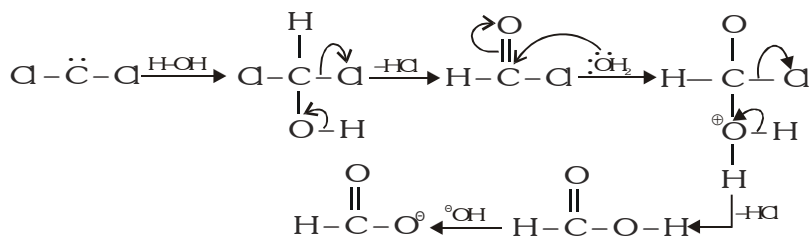


- (iv) By action of base of chloroform

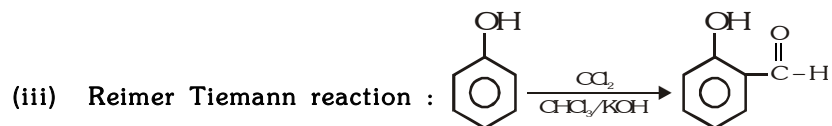
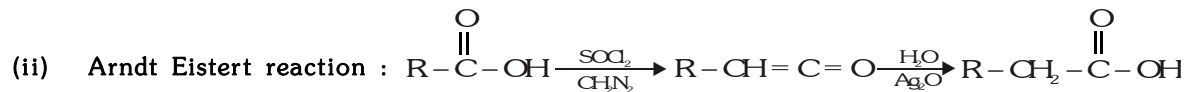
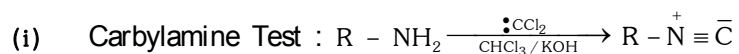


(4) Reactions of carbene :

- (i) Attachment with nucleophile :

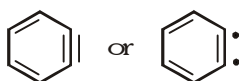


(5) CAR Reactions :



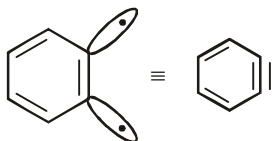
◆ BENZYNE :

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



(2) Structure and Hybridisation :

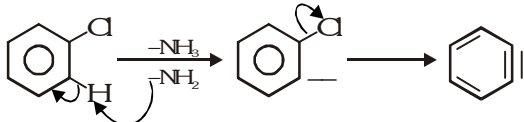
- (i) All carbon atoms in benzyne are sp^2 hybridised.



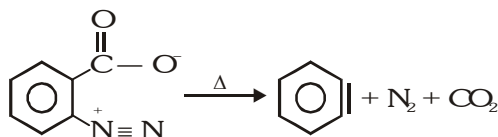
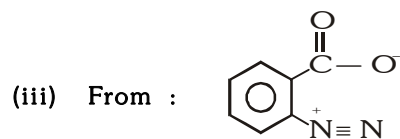
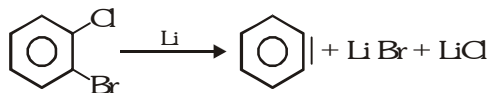
- (ii) Side way poor overlapping of sp^2 orbitals forms π bonds out side the ring and out of the plane of π system of the ring.

(3) Generation of Benzyne :

- (i) From chlorobenzene :

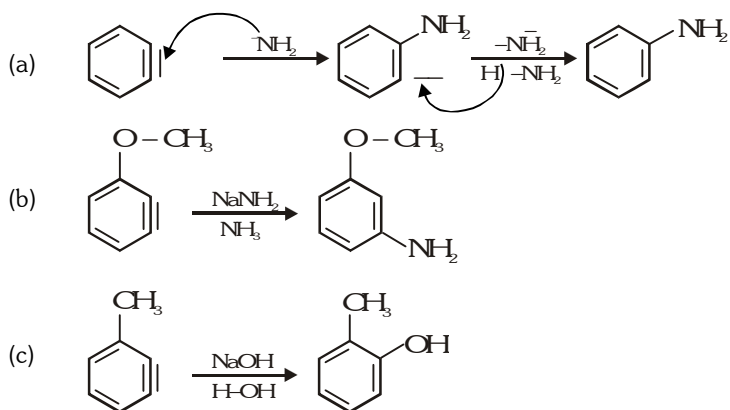


- (ii) From chloro bromo benzene :

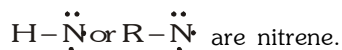
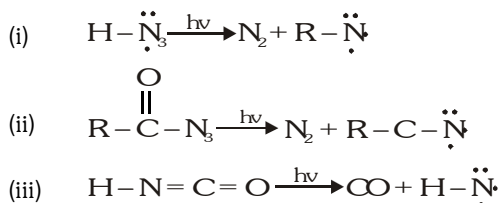
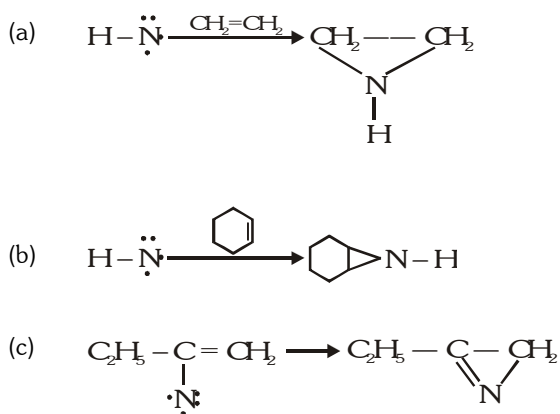
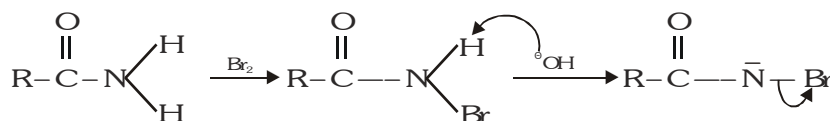


(4) Reactions of Benzyne :

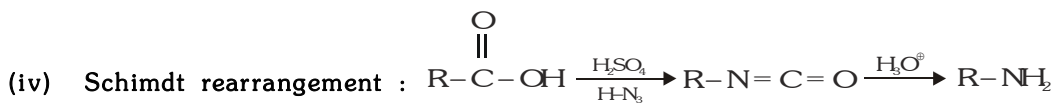
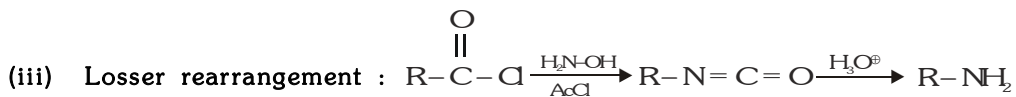
Benzyne are too unstable to be isolated and react with any nucleophile present in the solution.

◆ **NITRENE :**

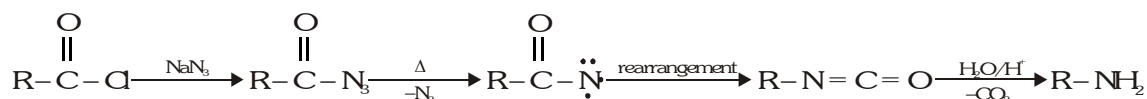
- (1) Nitrene may be defined as the electron deficient species in which nitrogen has a sextate of electrons. Nitrenes are analogues of carbene also known as unidogeh, azene, unene i.e.

**(2) Generation of Nitrene :****(3) Reactions of Nitrene :****(i) Addition to Olefine :****(i) Hofmann Bromoamide Degradation :**

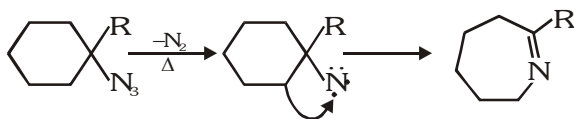
(ii) **Rearrangement reaction (HCLS reaction)** : This proceed via nitrene intermediate.



(b) **Curtius rearrangement** : This also proceed via nitrene but in this case nitrene is obtained from $\text{R}-\text{N}_3$ as :

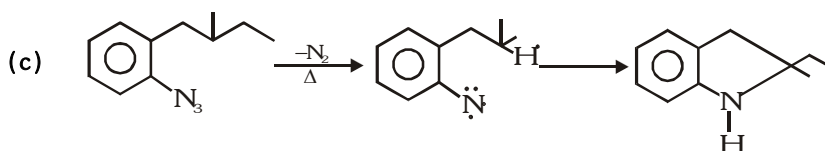
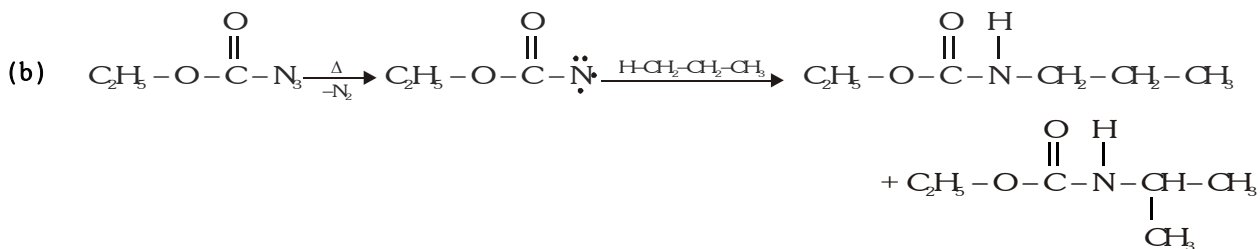
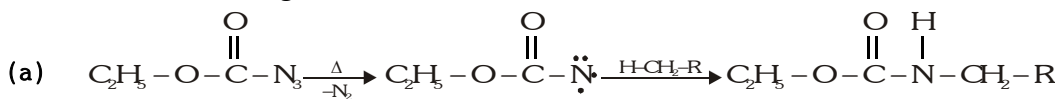


(c) **Cycloalkylazides gives ring expansion** :

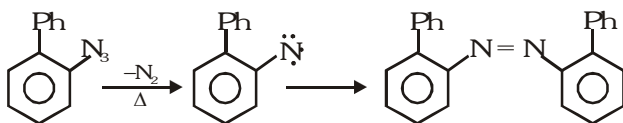


(iii) **Insertion Reaction** :

Nitrene can also give insertion reaction as :



(iv) **Recombination of Two Nitrenes** :



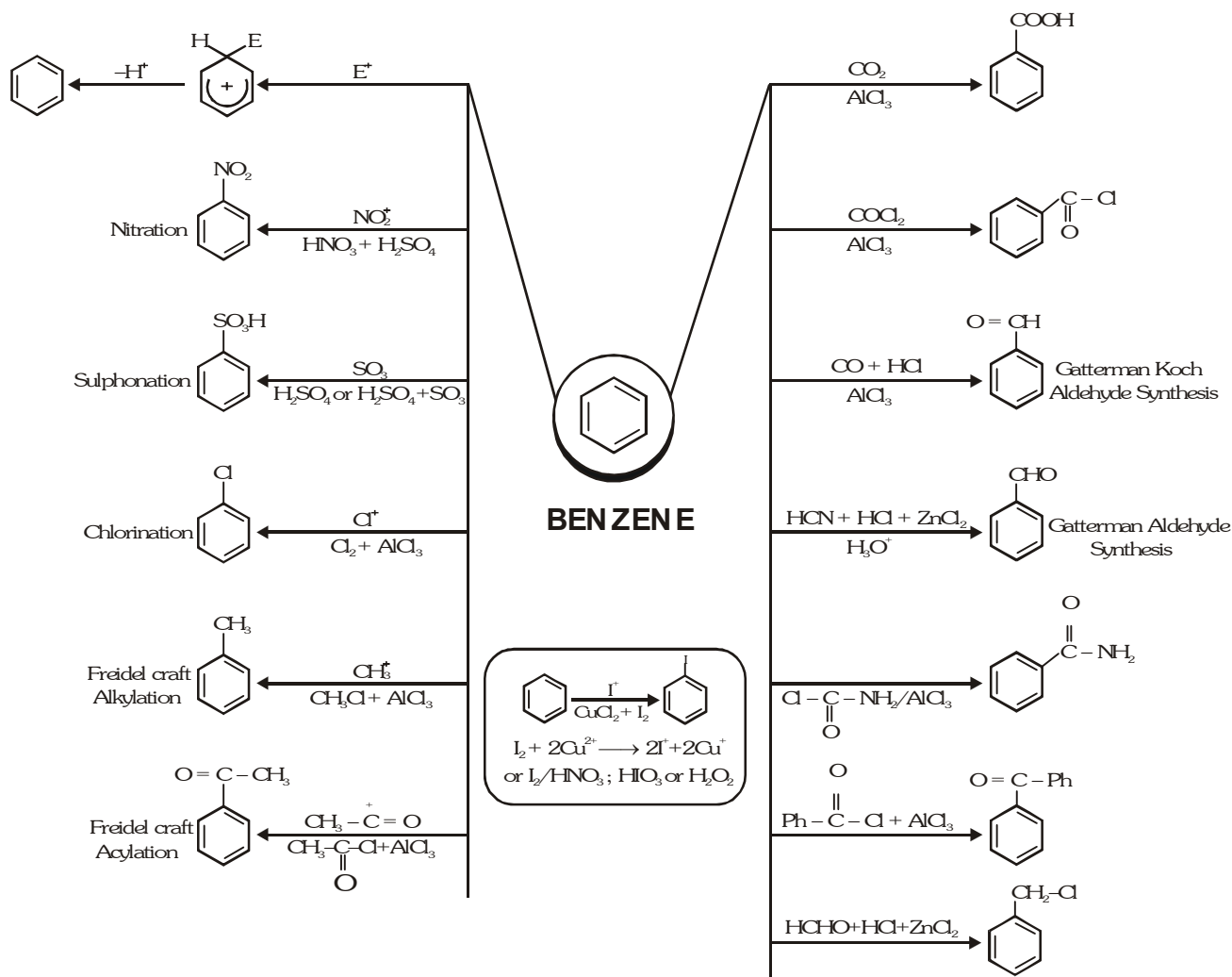
Types of Reactions

In organic chemistry the following types of reaction are more important,

- (I) Substitution reaction
- (II) Elimination reaction
- (III) Addition reaction
- (IV) Rearrangement reaction

(I) Substitution Reaction :

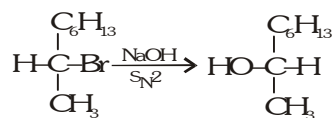
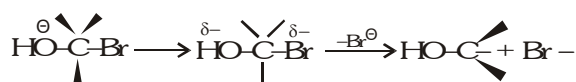
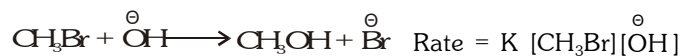
Electrophilic Substitution Reactions



Nucleophilic Substitution Reaction :

In secondary alkyl halide both types of reactions S_N1 or S_N2 occurs, depending upon the nature of solvent :

(1) S_N2 nucleophilic reaction : Mechanism and kinetics -



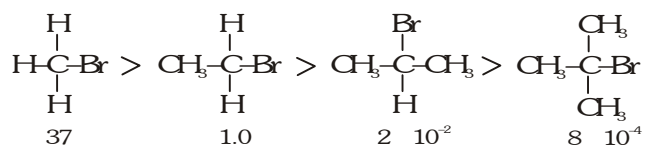
(RI > RBr > RCl > RF)

Less energy is required to break RI bond.

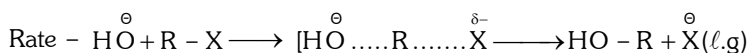
(-) 2-Bromo octane (Inversion of configuration).

An S_N2 reaction proceeds with complete stereo chemical inversion.

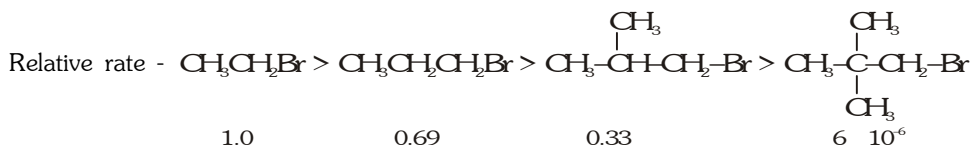
S_N2 reaction decreases with steric hindrance and increases by non protic solvent for example DMF and DMSO. S_N2 reaction decreases in the presence of protic solvent like CH_3OH , C_2H_5OH .



S_N2 reactivity $1 > 2 > 3$



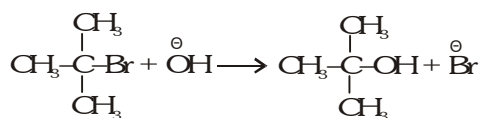
- As the size of alkyl group increases then chemical reactivity towards S_N2 decreases.



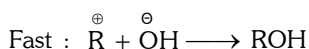
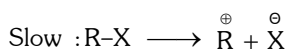
◆ Features of S_N2 Reaction :

- Occurs mainly in 1° alkyl halide.
- Order of reaction is 2, but total step = 1
- Speed of the reaction increases by non protic solvent ex. DMF and DMSO.
- Back attack of the nucleophile is there so that stereo chemical inversion occurs.
- Elemental effect so that RI is maximum reactive.
- No carbocation, so no molecular rearrangement. Only transition state is formed.

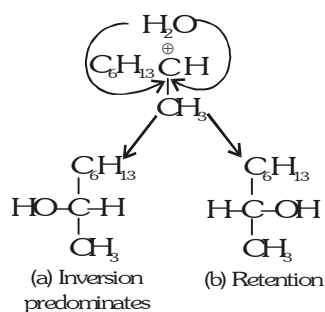
(2) S_N1 substitution reaction :



$$\text{Rate} = k [\text{RBr}]$$



Now nucleophilic attack can conceivably take place any time after the heterolysis and thus can involve any species from the initially formed ion pair to the free carbocation, attack on the free carbocation is random and yields the racemic modification. The anion clings to the side of the carbocation and thus shields this side from attack ; as result, back side attacks preferred to the extent, that attacks occurs before the ion pair has completely separated. Inversion of configuration competes with racemization.



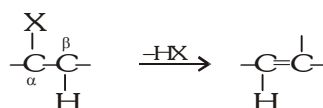
◆ **Features of S_N1 Reaction :**

- (i) Rate of reaction = $k[RX]$
Order = one, but occurs in two steps.
- (ii) Carbocation formation takes place so that molecular rearrangement may occur.
- (iii) Racemization takes place.
- (iv) Chemical reactivity $3 > 2 > 1$.
- (v) Elemental effect, so that RI are maximum reactive.

| Properties | S_N1 | S_N2 |
|--|---|--|
| Reactivity of halide leaving groups | $RI > RBr > RCl > RF$ | $RI > RBr > RCl > RF$ |
| Effect of structure | $R_3CX > R_2CHX > RCH_2X > CH_3X$ Rate is governed by stability of carbocation that is formed in ionization step. | $CH_3X > RCH_2X > R_2CHX > R_3CX$ Rate is governed by steric effect (crowding in transition state). |
| Effect of solvent | Rate increases with increasing polarity of solvent. | Rate depends on both nature and concentration of nucleophile. |
| Effect of nucleophile | Rate of substitution is independent of both concentration and nature of nucleophile by its dielectric constant ϵ . | Polar aprotic solvents give fastest rates of substitution; solvent of Nu^\ominus is maximum and nucleophilicity is greatest. |
| Stereochemistry | Not stereospecific ; racemization accompanies inversion when leaving group is present at a stereogenic centre | Stereospecific; 100 percent inversion of configuration at reaction site. Nucleophile attacks carbon from side opposite bond to leaving group. |

(II) **Elimination reactions :**

Elimination reactions, in which two groups are removed from a molecule, neither being replaced by another group, are the reverse of addition reactions. Usually they involve the loss of two substitutions from vicinal atoms resulting in the formation of a double or triple bond. Most commonly a proton is lost from one carbon whereas a nucleophile is lost from the adjacent carbon ; these two carbon atoms are usually to as β -and α -carbons, respectively.



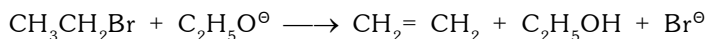
This type of elimination reaction is known β -elimination or 1, 2,-elimination reaction.

◆ **β -Elimination Reaction :**

In analogy with substitution reaction, β -elimination reactions are divided into E_1 (Elimination, unimolecular) and E_2 (Elimination, bimolecular) reactions.

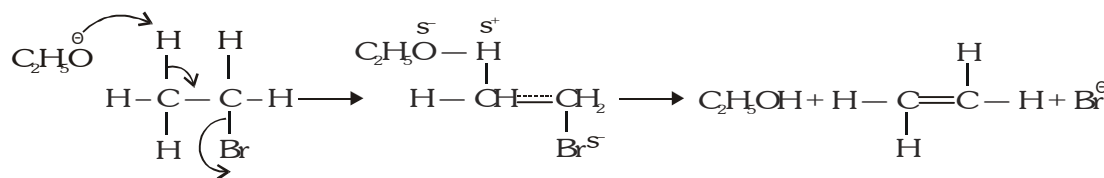
E_2 Reaction : The Bimolecular Mechanism :

Many elimination reactions are successful only when carried out in the presence of a strong base. The formation of ethylene on the treatment of ethyl bromide with sodium ethoxide is an example of this type. The rate of alkene formation is proportional to the concentrations of ethyl bromide as well as that of sodium ethoxide.

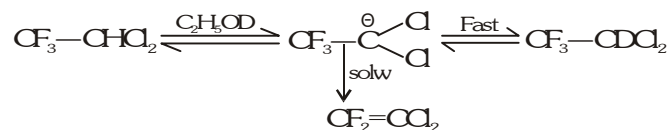


$$\text{Rate} = k [\text{CH}_3\text{CH}_2\text{Br}] [\text{C}_2\text{H}_5\text{O}^\ominus]$$

Two types of mechanism can be written both of which are in agreement with the kinetic data. In the first mechanism the base abstracts a proton from the β -carbon and simultaneously the leaving group departs from the α -carbon along with the pair of bonding electrons.

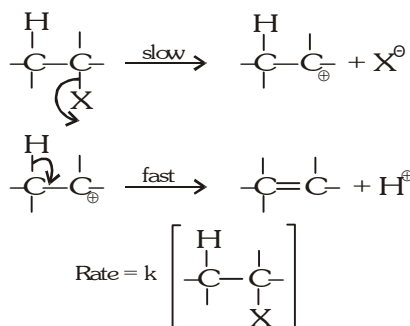


E_1 CB Reaction : Mechanism does operate under rather special circumstances 1, 1, 1 Trifluoro-2, 2 dichloroethane for instance, undergoes base-catalysed exchange of β -hydrogen atom with the solvent deuterium ethoxide faster than dehydrofluorination.



E_1 Reaction : The Unimolecular Mechanism :

The main feature of this mechanism is that under the influence of solvation forces, the electron attracting group ("leaving group") breaks away along with the bonding electrons. The resultant carbonium ion subsequently loses a proton to the solvent or to some other proton acceptor.

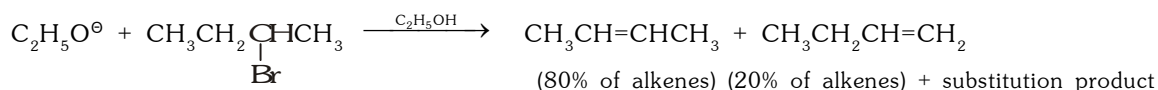
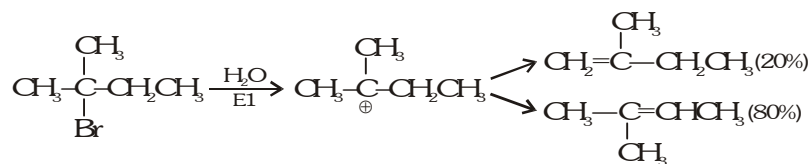


The reaction thus has two stages of which the first is the rate-determining step and as a result the reaction rate depends only on the concentration of the first reactant.

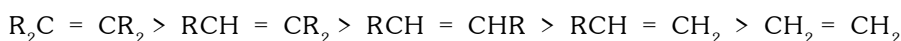
Orientation in elimination reactions :

The elimination reactions of unsymmetrical substrates usually yields mixtures of all possible products. There are two empirical rules governing the orientation in these reactions.

- (a) **The saytzeff Rule :** It states that neutral substrates (alkyl halides or sulphonates) capable of forming a double bond in either direction of the chain preferably yield that alkene in which there is greater number of alkyl groups attached to the double bond. This rule applies to E_1 reaction and to most of E_2 reactions. The following examples are typical.

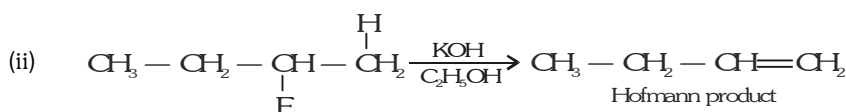
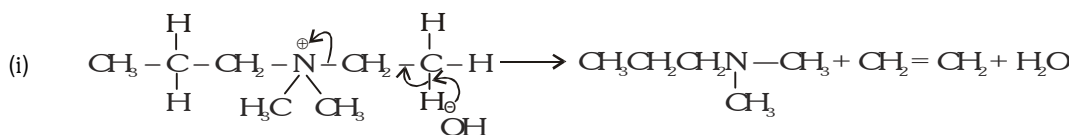


The preferential formation of more substituted alkenes in the above reactions can be correlated with the relative stability of various alkenes. Calculations from heats of combustion and hydrogenation establish that the stability of a double bond increases by alkyl substitution on the double-bonded carbon atoms. Thus the stabilities of alkenes follow the order :



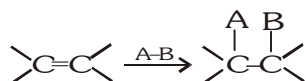
The greater stability of the more substituted alkene is sometimes explained on the basis of hyper conjugation.

(b) Hofmann Rule : Suggests usually less substituted products if leaving group are positively charged (NR_3^+ , SR_2^+ etc.) and fluorine, Actually more acidic β -hydrogen is abstracted to produce alkene.

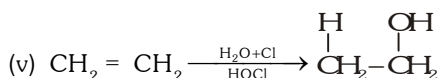
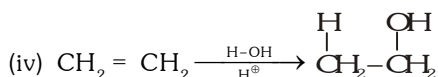
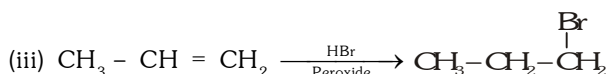
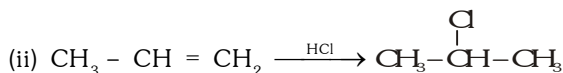
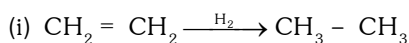


(III) Addition Reaction :

The reaction in which reagent adds to a multiple bonds to give less unsaturated or completely saturated product, are known as addition reactions. e.g.



Example :

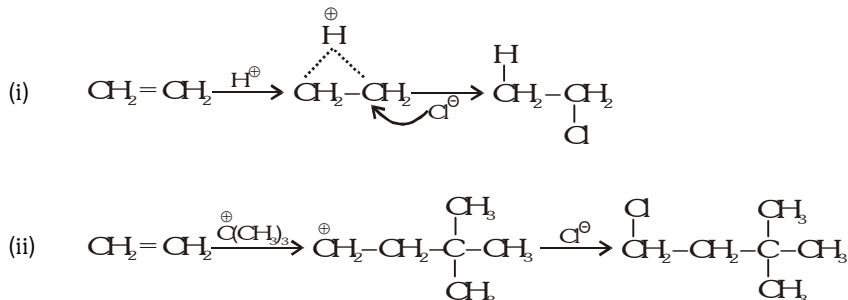


❑ Mechanism of addition reaction :

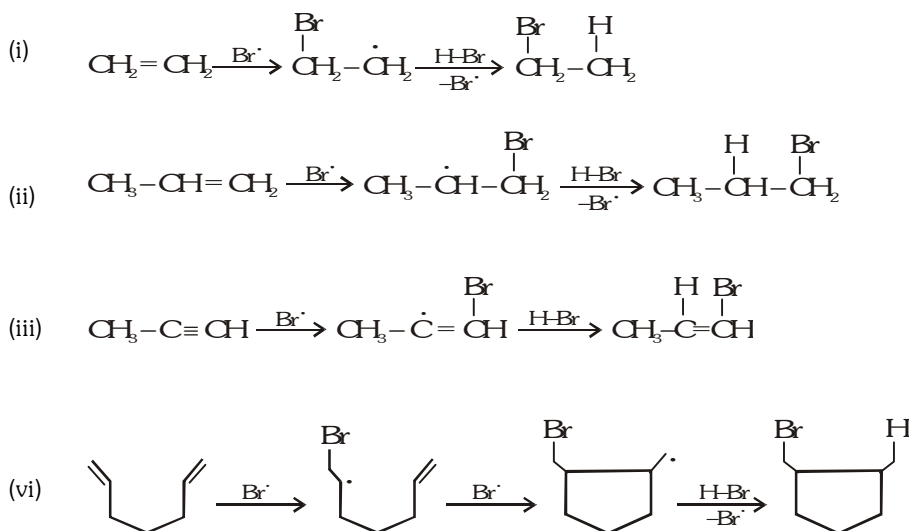
Mechanism of addition reactions can be classified in following ways :

- (A) Classification based on the type of attacking reagents.
- (B) Classification based on the fashion of addition.

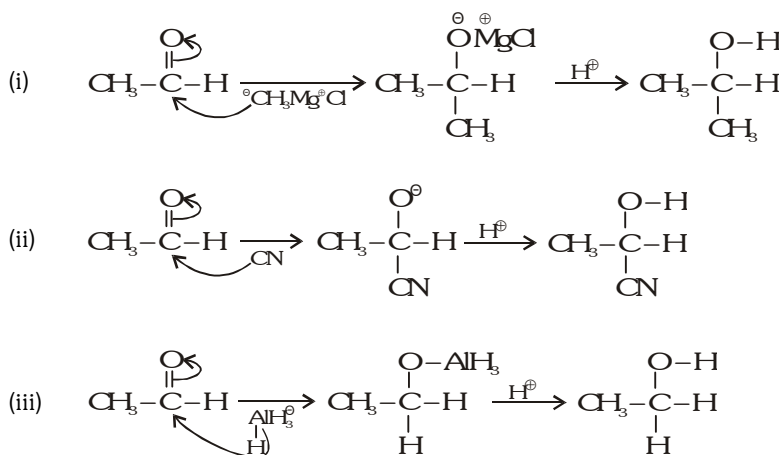
◆ Addition by cationic attack (Electrophilic addition) :

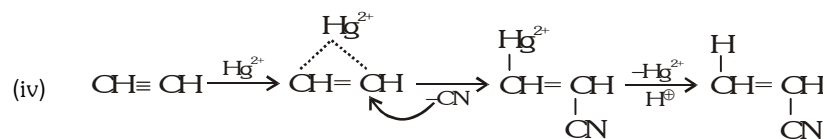


◆ Addition by free radical attack :

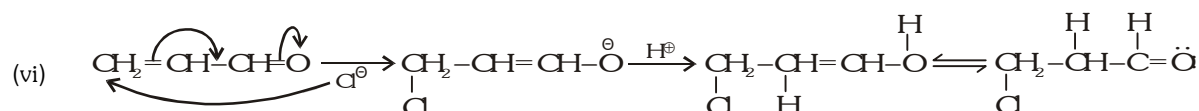
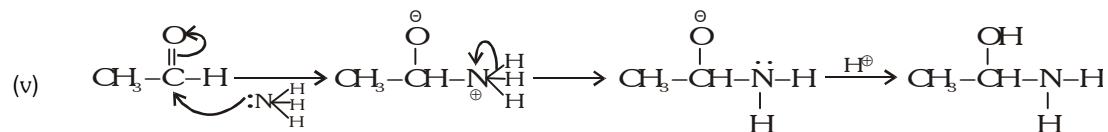


◆ Addition by anionic attack (nucleophilic addition) :

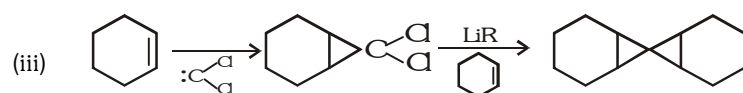
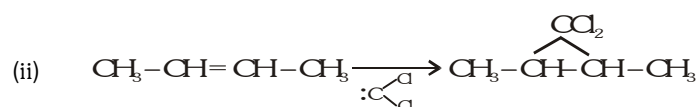
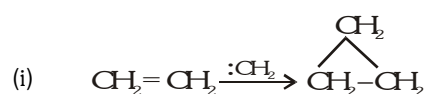




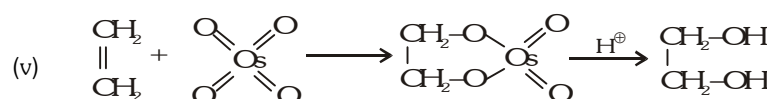
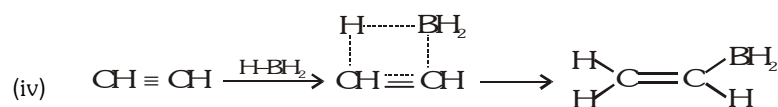
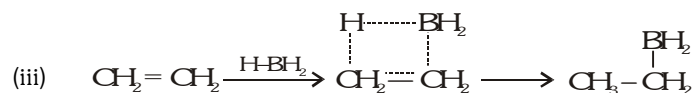
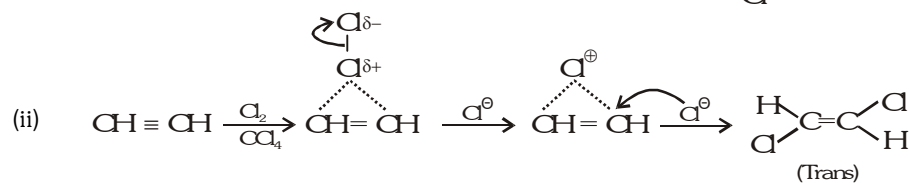
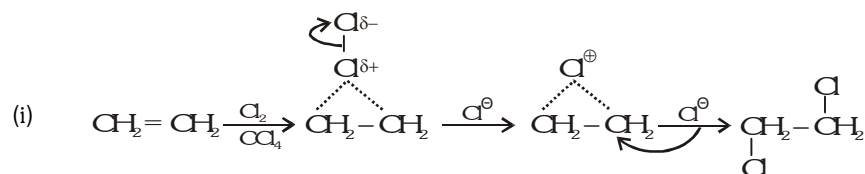
It is the example of nucleophilic addition reaction catalysed by Hg^{2+}



◆ Addition by carbene attack :

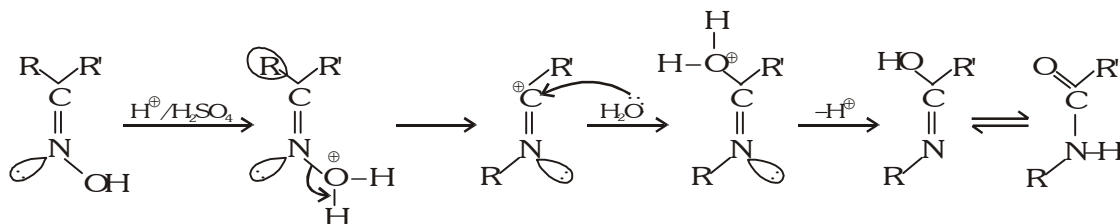


◆ Addition by molecular attack :



(IV) Rearrangement reaction :

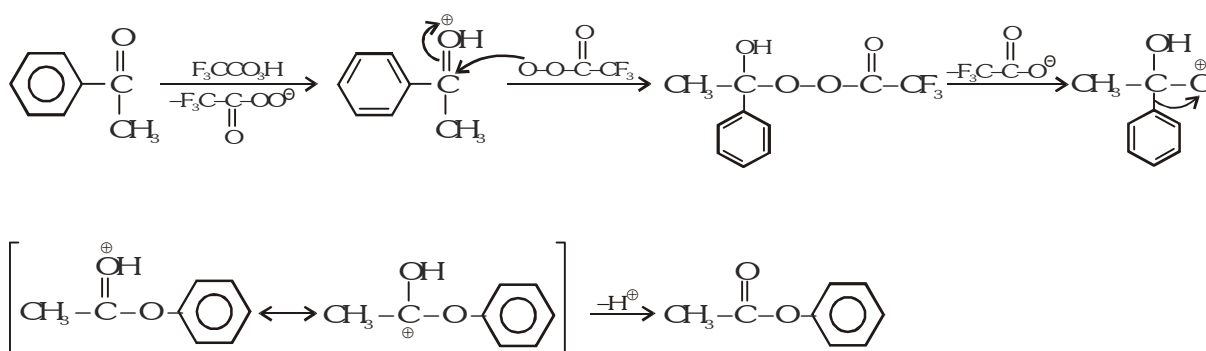
It may be defined as the reaction involving reshuffling of the sequence of atom to form a new structure :

◆ **Beckmann rearrangement :**

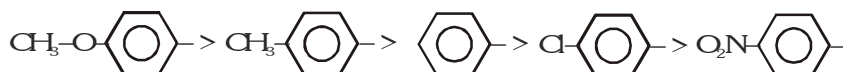
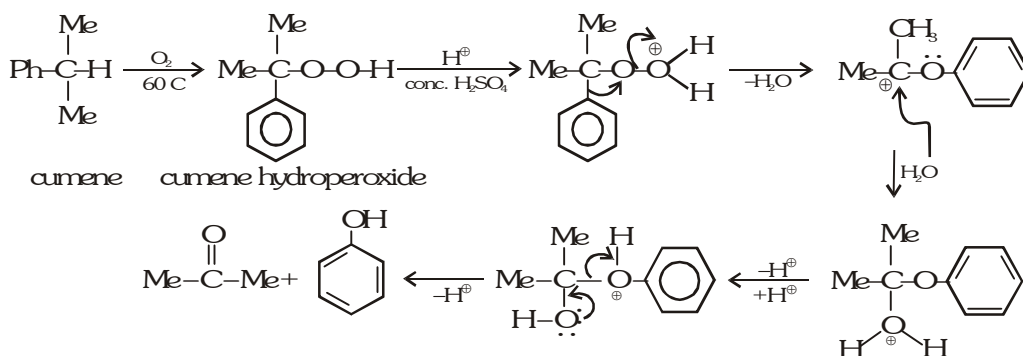
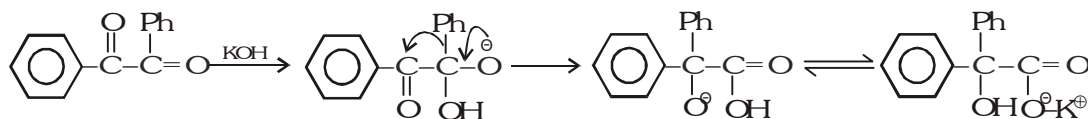
In this reaction ketoxime reacts with $\text{H}_2\text{SO}_4(\text{conc.})$ to give a product by alkyl migration.

◆ **Bayer-villiger rearrangement :**

The reaction involve the oxidation of ketone to ester by the treatment with peracids such as peracetic acid, perbenzoic acid, pertrifluoro acetic acid, etc. In this case best migratory group migrate to electron deficient oxygen.

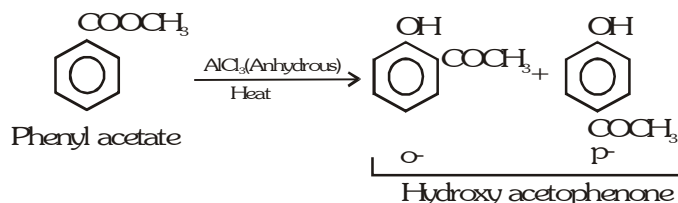


Migratory order : $3 > 2 > 1 > \text{CH}_3$

◆ **Acid-catalysed decomposition of cumene hydroxide :**◆ **Benzylic acid rearrangement :**

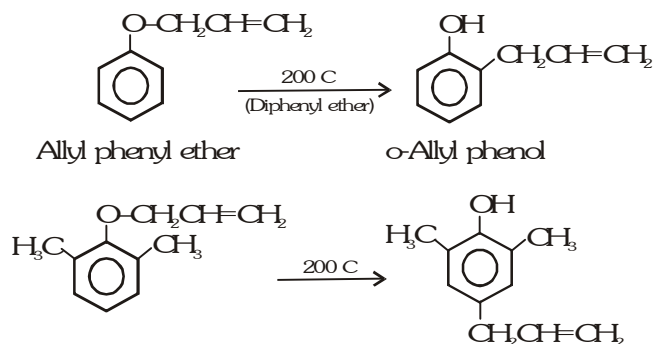
◆ **Fries rearrangement :**

The phenyl esters on treatment with anhydrous AlCl_3 undergo Fries rearrangement to give o - and p - hydroxy ketones.



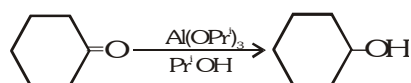
◆ **Claisen rearrangement :**

This is the rearrangement of allyl aryl ether to allyl phenols. No catalyst is required and it occurs when the substrate is heated alone to about 200 C or in some inert solvent like diphenyl ether. Allyl group migrates to ortho-position and if ortho-position is already occupied, para-isomer is obtained.

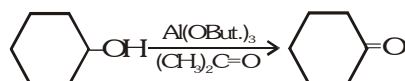


◆ **Hydride transfer reaction :**

(i) Meerwein ponndorf verley reduction :



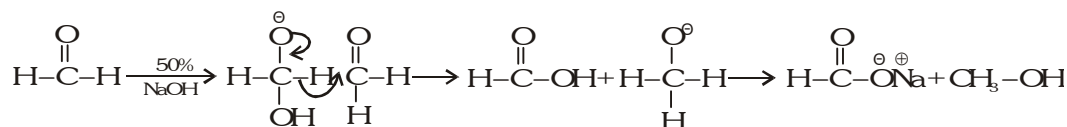
(ii) Oppenauer oxidation :



(iii) Tischenko Reaction :



(iv) Cannizzaro reaction :



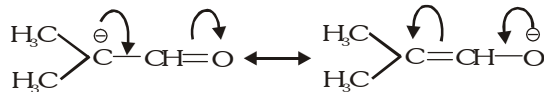
SOLVED EXAMPLES

Ex.1 If $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CHO}$ gives up proton the most-stable carbanion would be

- (A) $\overset{\ominus}{\text{CH}_2}-\underset{\text{CH}_3}{\text{CH}}-\text{CHO}$ (B) $\overset{\text{CH}_3}{\underset{\ominus}{\text{CH}_2}}-\text{CH}-\text{CHO}$ (C) $\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\overset{\ominus}{\text{CH}}-\text{CHO}$ (D) All the above

Sol. This carbanion shows resonance :

Ans.(C)



Ex.2 The most stable intermediate is :

- (A) $\text{BrCH}_2\text{CH}_2\dot{\text{C}}\text{H}_2$ (B) $\text{CH}_3-\underset{\text{Br}}{\text{CH}}-\dot{\text{C}}\text{H}_2$ (C) $\text{CH}_3-\dot{\text{C}}\text{H}-\text{CH}_2\text{Br}$ (D) All are equally stable

Ans. (C)

Ex.3 Which of the following is a true statement

- (A) RCOOH is more stable than RCOO^-
 (B) RCOO^- is more stable than RCOOH
 (C) RCOOH and RCOO^- do not show resonating structures
 (D) All of the above

Sol. RCOO^- is more stable than RCOOH due to resonance.

Ans.(B)

Ex.4 The electron attracting species in the following is -

- (A) $-\text{CN}$ (B) $-\text{NH}_2$ (C) $-\text{NHR}$ (D) $-\text{NHCOR}$

Sol. The groups having double or triple bonds are electron attracting. Hence $-\text{CN}$ is electron attracting and in rest of the species N-atom has lone pair of electrons.

Ans.(A)

Ex.5 Which carbanion is less stable than the other three -

- (A) $\overset{\ominus}{\text{CH}_2}-\text{NO}_2$ (B) $\overset{\ominus}{\text{CH}_2}-\text{CHO}$ (C) $\overset{\ominus}{\text{CH}_2}-\text{CH}_3$ (D) $\overset{\ominus}{\text{CH}_3}$

Sol. Due to + I effect of CH_3 group $\overset{\ominus}{\text{CH}_2}-\text{CH}_3$ is less stable.

Ans.(C)

Ex.6 Compound : on removal of proton gives a carbanion. The most stable carbanion should be

- (A) (B) (C) (D) All the above

Sol. In this case negatively charged carbon is present between two electron attracting groups. As such it is a stable carbanion.

Ans.(C)

Ex.7 $\overset{\oplus}{\text{C}}\text{H}_2\text{--O--H} \longrightarrow \text{CH}_2=\overset{\oplus}{\text{O}}\text{--H}$. The stability order of above structure is -

I
II