T.R.R GOVERNMENT DEGREE COLLEGE(A), KANDUKUR

DEPARTMENT OF CHEMISTRY

CLASS NOTES

II B.SC (Hons) CHEMISTRY

MAJOR/MINOR C-5- FUNDAMENTALS IN ORGANIC CHEMISTRY

UNIT-1

CLASS: SEMESTER-III B. Sc. (HONS) CHEMISTRY

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COURSE 4: FUNDAMENTALS IN ORGANIC CHEMISTRY

UNIT-I STRUCTURAL THEORY IN ORGANIC CHEMISTRY (9 Hrs.)

Types of bond fission and organic reagents (Electrophilic, Nucleophilic, and free radical reagents).

Reaction intermediates – Carbocations, carbanions & free radicals. Bond polarization: Factors influencing the polarization of covalent bonds, inductive effect – Application of inductive effect (a)Basicity of amines (b) Acidity of carboxylic acids (c) Stability of carbonium ions. Resonance or Mesomeric effect, application to (a) acidity of phenol, and (b) acidity of carboxylic acids. Hyperconjugation and its application to stability of carbonium ions, Free radicals, and alkenes

Electrophiles and Nucleophiles: Detailed Notes

1. Definitions

Electrophile (Electron-loving species):

- **Definition:** A species that seeks electrons and accepts an electron pair.
- **Nature:** Electron-deficient (positive charge or partial positive).
- **Function: Accepts** electron pairs during a chemical reaction.
- **Acts as: Lewis acid** (electron pair acceptor).

Nucleophile (Nucleus-loving species):

- **Definition:** A species that donates an electron pair to an electrophile.
- **Nature:** Electron-rich (negative charge or lone pairs).
- **Function: Donates** electron pairs during a chemical reaction.
- **Acts as: Lewis base** (electron pair donor).

Category	Electrophiles	Nucleophiles
Neutral	SO_3, BF_3, $AlCl_3$, CO_2	H_2O, NH_3, ROH (alcohols), RSH
Cations	H^+, NO_2^+, Br^+, Cl^+, CH_3^+	OH^-, CN^-, Cl^-, Br^-, I^-, RO^-

🔬 3. Mechanistic Roles in Organic Chemistry

🔹 *Electrophiles* participate in:

- **Electrophilic Addition Reactions**
  - Example: Alkene + HBr → Bromoalkene
- **Electrophilic Substitution Reactions**
  - Example: Benzene + Br_2 (with $FeBr_3$) → Bromobenzene

🔹 *Nucleophiles* participate in:

- **Nucleophilic Substitution Reactions**
  - SN1 and SN2 mechanisms
  - Example: $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$
- **Nucleophilic Addition Reactions**
  - Example: Aldehyde + CN^- → Cyanohydrin

🟪 4. Characteristics of Good Electrophiles and Nucleophiles

Д **Electrophiles:**

- Positive or partially positive atoms (δ+).
- Incomplete octet (e.g., carbocations, BF_3).
- Easily attacked by electron-rich species.

Д **Nucleophiles:**

- Lone pair or π electrons.
- Negative charge often makes them stronger.
- Ability to form new bonds with electrophilic carbon.

📊 5. Factors Affecting Strength

Σ) *Nucleophile Strength Depends on:*

1. **Charge:** Anions > neutral molecules.
2. **Electronegativity:** Less electronegative atoms donate electrons more easily.
3. **Solvent:**
   - **Polar protic solvent**: Weakens nucleophiles (hydrogen bonding).
   - **Polar aprotic solvent**: Enhances nucleophilicity.
4. **Steric hindrance:** Bulky nucleophiles are less reactive.

- ***Electrophile Strength Depends on:***

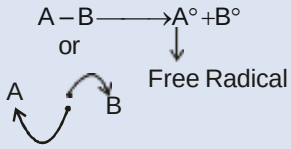
1. **Charge:** More positive = stronger electrophile.
2. **Leaving group:** Good leaving groups make carbon more electrophilic.
3. **Electron-withdrawing groups:** Increase electrophilicity by reducing electron density.

- **Conceptual Summary**

Feature	Electrophile	Nucleophile
Electron status	Deficient	Rich
Type of species	Lewis acid	Lewis base
Action	Accepts electrons	Donates electrons
Charge	Often +ve or partial +ve	Often – ve or lone pair
Examples	H^+, NO_2^+, BF_3, carbocation	OH^-, NH_3, CN^-, alkene

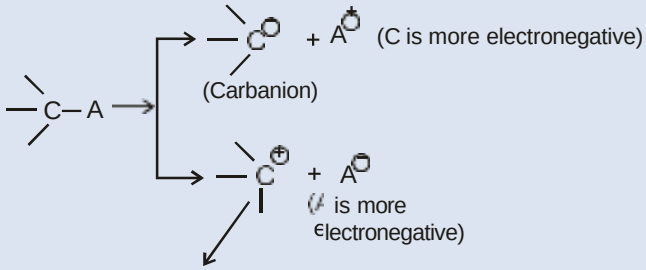
HOMOLYTIC BOND FISSION HOMOLYSIS

The bond cleavage in which each bonded atom gets their own contribution

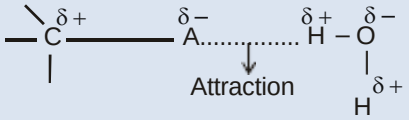


- Cleavage takes place due to
  HELP (H = Heat, E = Electricity, L = light, P = Peroxide)
- Favoured when E.N. difference is less or zero.
- Cleavage favoured in non polar solvent.

HETROLYTIC BOND FISSION



- It is formed when the electronegativity difference between the bonded atom is more
- formation is favoured by polar solvent



+ve charge of the solvent attracts the –ve pole of compound and the – ve pole of the solvent attracts +ve pole of compound and the bond breaks.

INTERMEDIATES OF ORGANIC COMPOUNDS

		Free Radical	Carbocation	Carbanion
(1)	Lone pair	0	0	1
(2)	Bond pair	3	3	3
(3)	Unpaired e^-	1	×	×
(4)	Bond Angle	120º	120º	107º
(5)	Hybridisation	sp^2	sp^2	sp^3
(6)	Shape	Trigonal planer	Trigonal planer	Pyramidal
(7)	Magnetic property	Para magnetic	Diamagnetic	Dia magnetic)
(8)	Stability order (As per inductive effect)	3º > 2º > 1º	3º > 2º > 1º	1º > 2º > 3º
(9)	e^- rich/deficient/poor	ED(Deficient)	ED	ER(Rich)
(10)	Reactivity order	1º > 2º > 3º	1º > 2º > 3º	3º > 2º > 1º

(11)	+I/−I (stablized)	+I	+I	I

ELECTRONIC DISPLACEMENT EFFECT

The displacement of electrons with in the same molecule is known as electronic displacement. These effects affect the stability of a species or compound and it also affect the acidic & basic strength.

Electronic Displacement Effect is divided into two parts:–

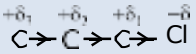
(1) Permanent effect
(2) Temporary effect

(1) Permanent effect
(i) Inductive effect
(ii) Mesomeric (resonance) effect
(iii) Hyperconjugation

(2) Temporary effect:
(i) Electromeric effect
(ii) Inductomeric effect

(i) Inductive effect:

It is an effect in which permament polarisation arises due to partial displacement of σ-electrons along carbon chain or partial displacement of sigma-bonded electron toward more electronegative atom in carbon chain.

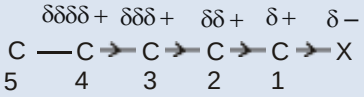


Magnitude of partial positive charge

$+\delta_1 > +\delta_2 > +\delta_3 = \delta^-$ (net charge remain constant in a molecule having inductive effect)

Inductive effect

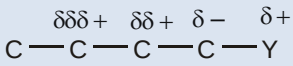
It is a permament effect



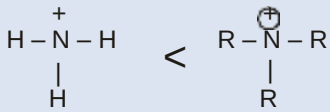
if X i.e more electronegative

(After carbon No. 3 the effect disappears)

(–I effect of X)



(+ I effect of Y)

*  (– I effect order)

* $O^- < O < O^+$ (–I effect order)

- It is a permament effect
- It is caused due to electronegative difference.
- It operates via σ bonded electron.
- It is distance dependent effect.

As distance increases, its effect decreases.

- It can be negalected after third carbon.
- It is a destablising effect.
- It is divided into 2 parts. (On the basis of electronegativity w.r.t. hydrogen atom)
  (1) +I effect
  (2) – I effect

If any atom or group having electronegativity greater than that of hydrogen. than it is considered as – I effect and vice-versa.

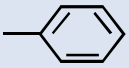
	+I effect	– I effect
(i)	e^- releasing group	(i) e^- accepting group
(ii)	EN less than H	(ii) EN greater than H
(iii)	Those group which are showing + I effect, disperses partial – ve charge on the C-chain	(iii) Those group showing –I effect disperses + ve charge on the C-chain

Eg. $CH_3 - CH_2 - Cl$ (–I of Cl)

Eg. $CH_3 - CH = CH_2$ (–I of $-CH=CH_2$ & +I of $-CH_3$)

Eg. $CH_3 - CH_2 - C \equiv CH$ (–I of $-C \equiv CH$ & + I of $-CH_2-CH_3$)

Eg. I – Cl
+I I

Eg. $CH_2 = CH$  (–I of –ph)

Order of –I effect showing group:

$$-\overset{\oplus}{N}F_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -CN > -\overset{O}{\overset{\|}{C}}-H > -\overset{O}{\overset{\|}{C}}-R > -\overset{O}{\overset{\|}{C}}-OH > -F > -Cl > -Br > -I$$

(–I order) $-C \equiv CH > -CH = CH_2$

$-CH = CH_2 <$

Order of + I effect showing group

$$-\overset{\ominus}{C}H_2 > -\overset{\ominus}{N}H > -\overset{\ominus}{O} > -CMe_3 > -CHMe_2 > -CH_2Me > CT_3 > CD_3 > CH_3 > T > D > H$$

Bond Strength : $CT_3 > CD_3 > CH_3$ (+ I of T > D > H)

Q. Why carbon - hydrogen bond is longer than C - T bond

Ans. As the mass increases, vibration decreases as a result of which the heavier isotope will be more closer to the C-atom for a longer time. There for C – T bond is stronger C – T > C – D > C – H
Which implies that C – H bond has longest bond

<u>APPLICATION OF INDUCTIVE EFFECT</u>

To compare the stability of intermediates.

Intermediates

These are reals reparable species having measurable stability formed during coversion of reactant to product. (After bond cleavage and before bond formation).

6 types of intermediates:

(i) Free radical (ii) Carbocation (iii) Carbanion

(iv) Carbene (v) Nitrene (vi) Benzyne

They are formed by homolytical and heterolytical cleavage.

MESOMERIC EFFECT (RESONANCE EFFECT)

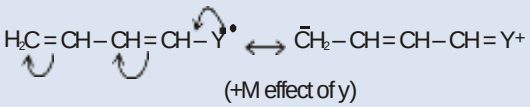
Mesomeric effect is valid only for conjugated system.

Types

1 + M effect (+R)

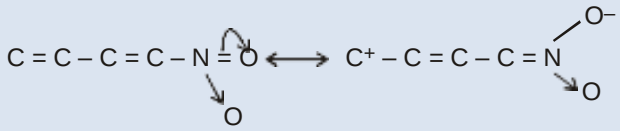
2 – M Effect (–R)

* Consider the following conjugated system



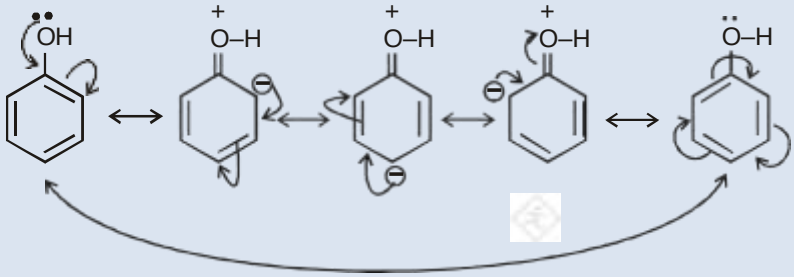
(+M effect of y)

* Consider another conjugated system

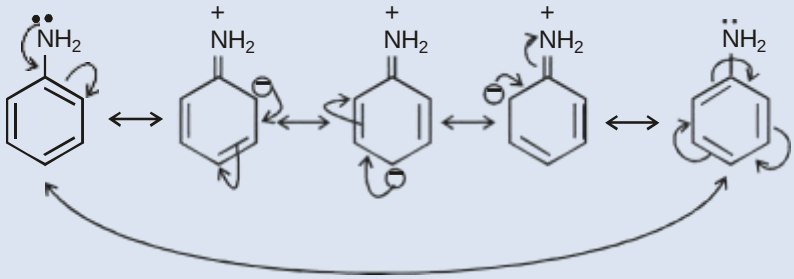


(– M effect of NO_2)

MESOMERIC EFFECT IN PHENOL (+ M EFFECT)



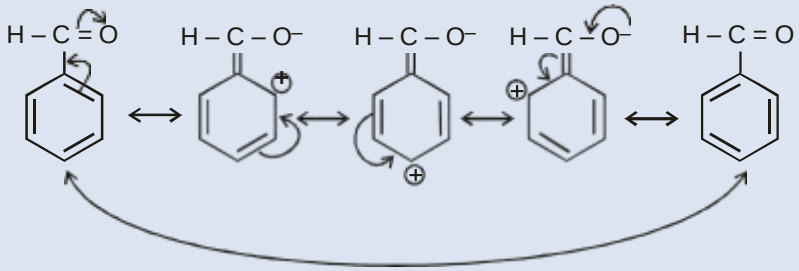
+M effect in aniline



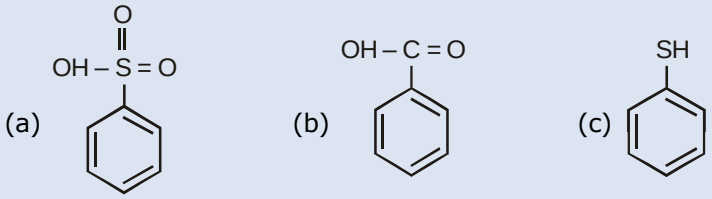
if more of e^- towards ring ⇒ (+M effect)

⇒ This effect increases the electron density over benzene ring.

* –M effect in Benzaldehyde



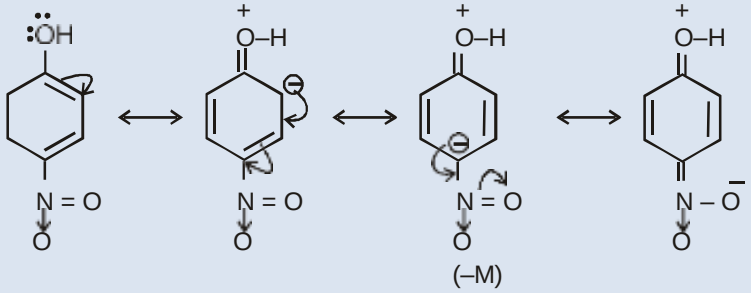
Ex.23 Idenfity the compound showing +M or –M seperately



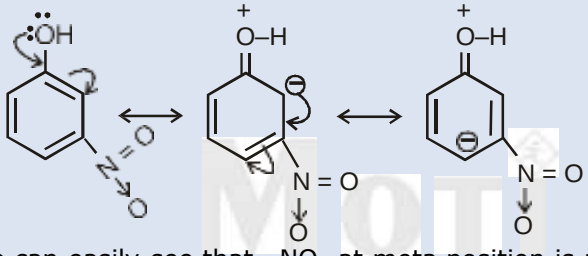
Sol. (a) (–M) (b) (–M) (c) +M

* +M group increases electron density of ring while – M decreases the electron density of benzene ring.

* if NO_2 is present on the ortho or para position then along with its –I effect, It will also show –M effect.



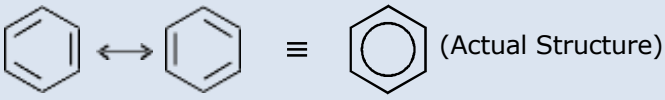
* Above comound have +M of –OH and –M of NO_2 group.



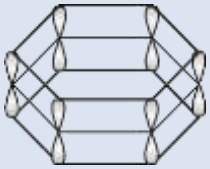
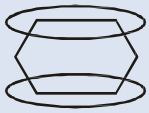
as we can easily see that $-NO_2$ at meta position is not attracting e^- density towards it self and that's why it will not show –M effect at m-position

RESONANCE

Delocalisation of π-electrons in conjugation is known as resonance.



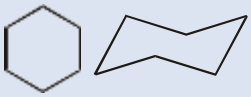
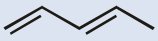
(resonating structures) (Resonance hybrid)

 in this form 

CONDITION FOR SHOWING RESONANCE

1. Molecule should be planer, nearly planer or a part of it is planar

Q.1 Which are planer

(A) (B)  *(C)  *(D) 

Becouse they are sp^2 hybridised.

Q.2 Molecule should posses conjugated system.

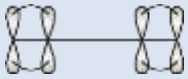
Conjugated system:–

Continous unhybridised p-orbital parallel to each–other.

Types of conjugated system:–

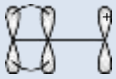
(1) π-bond aternate to π-bond

$CH_2 = CH - CH = CH_2$



(2) π-bond alternate to + charge

$CH_2 = CH - \overset{+}{C}H_2$



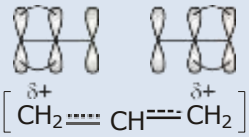
Eg. $CH_2 = \overset{\curvearrowright}{CH} - CH = CH_2$

$\overset{\ominus}{C}H_2 - CH = CH - CH_2$ R.S. CH_2 CH CH CH_2

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

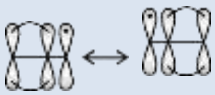
Eg. $\overset{\curvearrowright}{CH_2} = CH - \overset{\curvearrowright}{CH_2}$ 

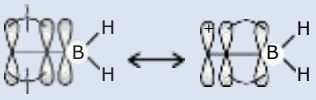
$\ominus CH_2 - CH = CH_2 \equiv \left[\overset{\delta-}{C}H_2 = CH = \overset{\delta-}{C}H_2\right]$

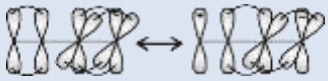
Eg. $CH_2 = CH - \overset{\oplus}{C}H_2$ 

$\overset{\ominus}{C}H_2 - CH = CH_2$ $\left[\overset{\delta+}{C}H_2 \cdots CH \cdots \overset{\delta+}{C}H_2 \right]$

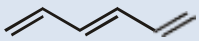
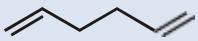
(4) $CH_2 = CH - \ddot{N}H_2 \longleftrightarrow \overset{\ominus}{C}H_2 - CH = \overset{\oplus}{N}H_2$

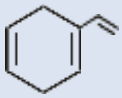
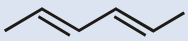
(5) $CH_2 = CH - \dot{C}H_2$ 

(6) $CH_2 = CH - BH_2$ 

(7) $CH_2 = CH - C \equiv CH \longleftrightarrow \overset{\oplus}{C}H_2 - CH = C = \overset{\ominus}{C}H$ 

(2) Resonance takes place due to delocalization of πe^-.

(a)  Resonance (b)  Resonance absent

(c)  Resonance (d)  Resonance

(3) Position of the atoms remains the same, only delocalization of πe^- takes place.

Note:- $CH_3 - \overset{\overset{O}{\|}}{C} - NH_2 \longleftrightarrow CH_3 - \overset{\overset{OH}{|}}{C} = NH$ [They are net resonating structure rather they are tautomer]

(4) Bond pair get converted into lone pair and l.p. get converted into b.p.

$CH_3 = C - \ddot{N}H_2 \longleftrightarrow \overset{\ominus}{C}H_2 - C = \overset{\oplus}{N}H_2$

(5) In Resonance No. of unpaired e^- remains the same

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

(They are not resonating structure)

Resonating structure :

(1) Hypothetical strtucture exist on paper

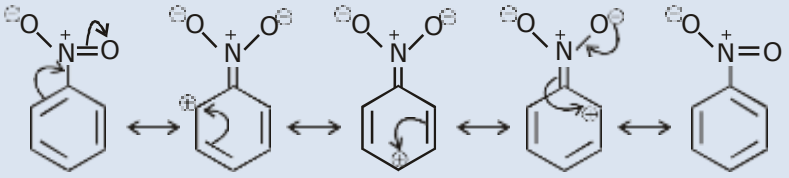
(2) The energy difference b/w different resonating structure is very small.

(3) All R. S. contribute twoards the formation of resonance hybrid (Their contribution may different)

(4) A single R. S. Can't explain each & every property of that particular compound

Draw the resonating structures : –

Q.1 

Q.2  –m of NO_2 group

Resonance hybrid : –

It is a real structure which explain all the properties of a compound, formed by the contribution of different R. S. Pt has got maximum stability as compared R. S.

Resonance Energy : –

It is the diffrence b/w theoriticle value of H.O.H & experimental value.

Or

It is the difference b/w more stable R.S. & R. H.

* More the resonance energy, more stable will be the molecule.

* Cyclohexane is thermodynamically more stable than benzene, even though resonance energy of benzene is more.

* Resoance energy is a absolute term.

CONTRIBUTION OF DIFFERENT R. S. TOWARDS RESOANCE HYBRID

(1) Non-polar R. S. contribute more than polar R. S.

(a) $CH_2 = CH - CH = CH_2$ (b) $^{+}CH_2-CH = CH - CH_2$ (c) $CH_2 - CH = CH - CH_2^{+}$

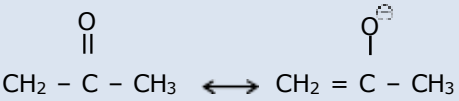
a > b = c stability

(2) Polar R. S. With complete octet will contribute more as compared with the one with incomplete octet

$CH_3 - CH^{+} - OCH_3 \longleftrightarrow CH_3 - CH = :O^{+} - CH_3$

Incomplete octet Complete octet

(3) In polar R. S. The –ve charge should be on more electro – ve atom & +ve charge should be more electro + ve atom

(a) 

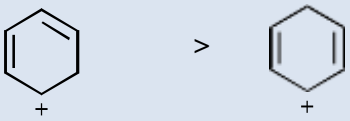
(b) 

(4) Compound with more covalent bond will contribute more

(5) Unlike charges should be closer to each other whereas like charges should be isotated.

(6) Extended conjugation contribute more than cross conjugation.

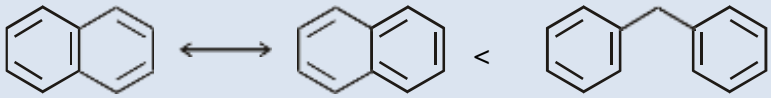
Cross conjugation < Extended conjugation



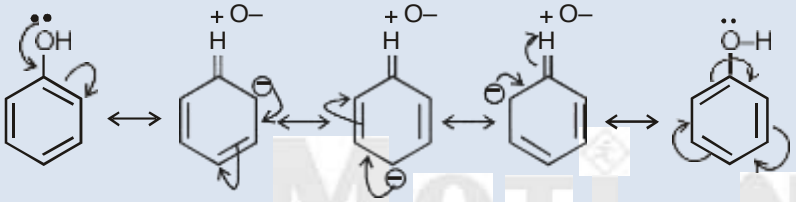
(Extended) (cross)

Fries Rule :–

Compound with more benzenoid structure are more stable as their Resonance energy is greater than those in which lesser no. of benzenoid structure are present.

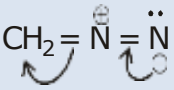
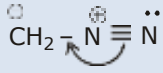
R. E. is 

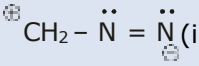
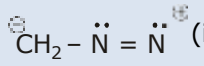
* If double bond is participating in resonance then it will aquire partial single bond character as a result of which bond length increase & bond strength decreases.
If a single bond is involved in resonance then it will aquire partial doulbe bond character. As a result of which bond length decreases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

Q.1 

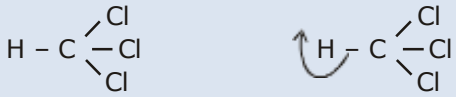
(a) (b) (c) (d) (e)

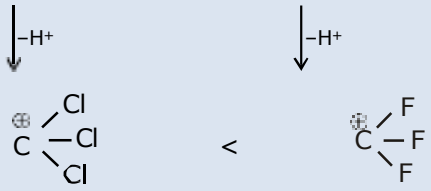
a = e > b = d > c

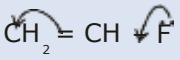
Q.2 (a)  (b) 

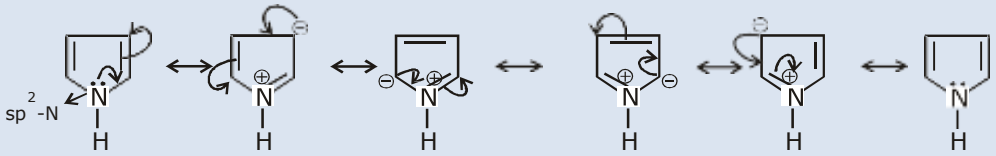
(c)  (incomplete) (d)  (incomplete)

a > b > c > d

Q.3 

Stability  <

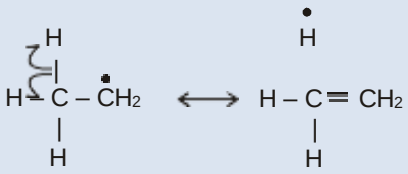
Q.4 (a)  (b) $CH_2 - CH = F^+$ a > b (stability)

(3) 

Note:–When lone pair as well as double bond as present in some atom. Then only π bond will participating resonance. Where as lone pair remains sp^2 hybridises orbital.
When an atom two and more then two known a lone pair of e^- will participet. Then only one lone pair remins sp^2 hybridised.

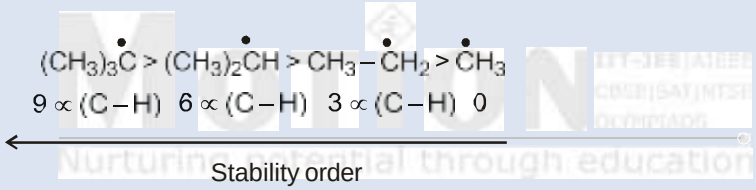
HYPER CONJUGATION

Permanent polarisation caused by displacement of σ-electrons into π-molecular orbital is known as hyperconjugation



Hyper conjugation is called No bond Resonance

* More α C – H bond, more will be the no bond resonating structure (Hyper conjugation)
• More α (C – H) bond, more will be the stability of free radical.



Properties of Free Radical
1. It is a neutral species.
2. It has one upaired electron that's why paramagnetic in nature.

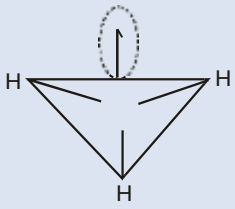
Structure :

$\dot{C}H_3$ → methyl free Radical

$CH_3\dot{C}H_2$ → ethyl free radical

3. its hydridisation is sp^2 and triangular planer shape.

Note : unpaired electron is not counted while calculating the hybridisation state.



(unpaired electron stay perpendicular to the plane)

Stability of free Radical :
Its stability can be determined with the help of hyperconjugation as well as Resonance effect

ALLYLIC FREE RADICAL

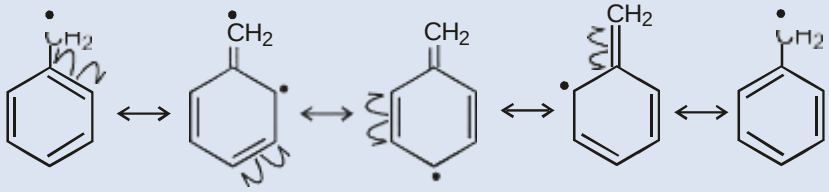
$CH_2 = CH - \dot{C}H_2 \longleftrightarrow \dot{C}H_2 - CH = CH_2$
(Homolysis)

(Free Radical is on next carbon to doubly bonded carbon atoms)

Effect of Resonance > Hyper conjugation

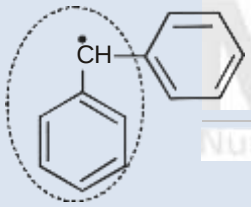
$\dot{C}H_2 - CH = CH_2 > (CH_3)_3\dot{C}$
(stability)

BENZYLIC FREE RADICAL



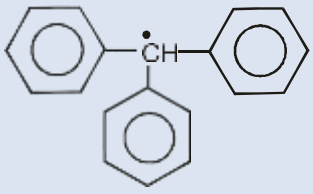
(4 Resonating structure)

* More Resonating structure, more will be the stability of the free Radical.



(di-benzylic free Radical)

No. of Resonating structure = 7



(Tribenzylic free Radical)

No. of Resonating structure = 10

Stability Order :

$$ph_3\dot{C} > ph_2\dot{C}H > ph\dot{C}H_2 > CH_2 = CH - \dot{C}H_2 > (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3 - \dot{C}H_2 > \dot{C}H_3$$

Ex.1 Compare the stability of the following free Radical.

(a) $CH_3 - \dot{C}H_2$ (b) $CH_2 = \dot{C}H$ (c) $CH \equiv \dot{C}H$

Sol. (a) $CH_3 - \dot{C}H_2$ will be most stable due to hyper conjugation

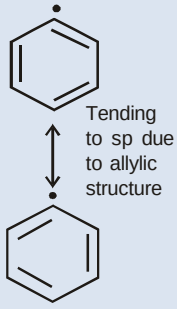
between $CH_2 = \dot{C}H$ and $CH \equiv \underset{\downarrow}{\dot{C}}$ (sp)

⇒ more s-character
⇒ more electronegative
⇒ e^- density maximum
⇒ more repulsion
⇒ less stable

Ans. a > b > c

* More repulsion, less stability

Ex.2 Compare the stability of the following free Radicals

(a) 

(very unstable)

(b) $CH = \dot{C}H$ (sp^2)

(c) $CH \equiv \dot{C}$ (actual sp)

⇒ More repulsion
⇒ less stability

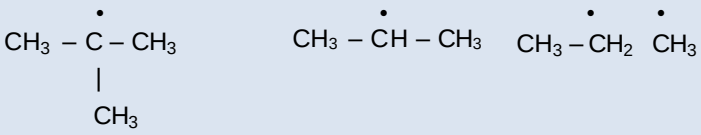
(Therefore this resonating structure is not possible)

Sol. b > a > c

Ex.3 (a) $CH_3 - \overset{*}{C}H - CH_3$ with CH_3 branch (b) $CH_3 - \overset{*}{C}H_2 - CH_3$ (c) $CH_3 - \overset{*}{C}H_3$ (d) $\overset{*}{C}H_4$

Compare the $\overset{*}{C} - H$ bond energy of the above compounds.

Sol. After forming free radical from the compound



(3°) (2°) (1°) methyl free radical

(a) (b) (c) (d)

(most stable)

⇓

therefore will have more

tendency to come in this form

⇓

And C – H bond will break very readily

⇒ bond energies will be very less.

a < b < c < d < (bond energies order)

* $\text{Bond energy} \propto \frac{1}{\text{stability of free Radical}}$

* $\text{Bond length} \propto \text{stability of free Radical}$

Ex.4 Compare the potential energy of the following compounds (above compounds)

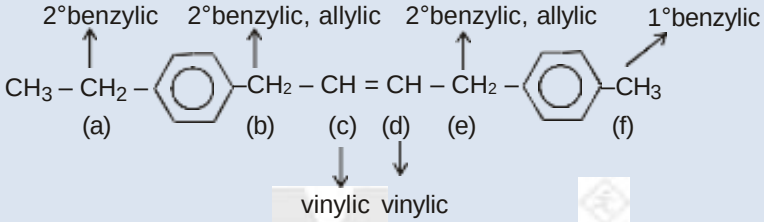
Sol. If compound after being in free Radical form is very stable (i.e., less energy) it mean it would have possessed more energy initially i.e. it potential energy will be most

a < b < c < d

* Potential energy ∝ stability of free Radical

Ex.5 Compare the bond energies of C – H bond

(at a, b, c, d, e and f position)



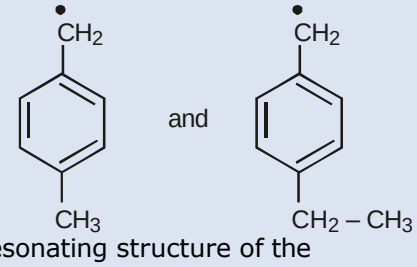
e > b > a > f > c = d

Stability order of free Radical that might be formed after removal of H (Homolytically) from the given carbon.

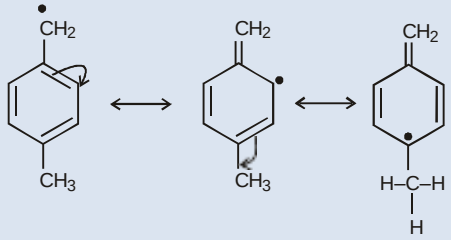
⇒ e < b < a < f < c = d

(C – H bond energies)

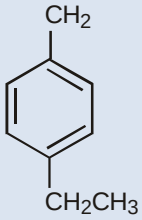
• In the above compound while comparing 2° benzylic allylic stability at two given position



while drawing the resonating structure of the

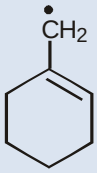


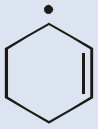
(Here inspite of Resonace three α (C – H) bond are available for no bond Resonance.

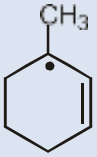
⇒ Therefore extra stable than  which have only two α (C – H) bond for Hyper conjugation.

Therefore 2° benzylic allylic corresponding to structure (a) is more stable than that of structure (b)

Ex.6 Compare the stability of the following free Radical


(a)

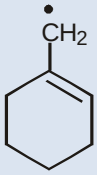

(b)

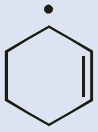

(c)

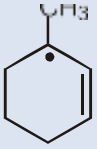
$CH_2 = CH - \dot{C}H_2$

(d)

Sol.


(a)


(b)

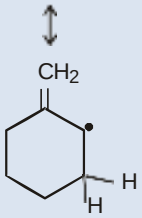

(c)

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

(d)

1° allylic 2° allylic + 2αH 3° allylic + 5αH

$\dot{C}H_2 - CH = CH_2$ (only resonance)


(Resonance + 2αH)

(d)

⇒ c > b > a > d

Ex.7 Compare the potential energy of $CH_3 - CH_3$, $CH_2 = CH_2$ $CH \equiv CH$

Sol. After making free Radical of the above compounds

$CH_3 - \dot{C}H_2$ (most – stable), $CH_2 = \dot{C}H$ $CH \equiv \dot{C}$ (least stable)

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

(a) (b) (c)

a > b > c

CARBOCATION

$\overset{+}{C}H_3 \rightarrow$ Carbonioum ion

$CH_3 - \overset{+}{C}H_2 \rightarrow$ Methyl carbonium ion

$CH_3 - \underset{\underset{CH_3}{|}}{CH} - \overset{+}{C}H_2 \rightarrow$ Isopropyl carbonium ion

Properties of Carbocation :

1. it is positivly charged species
2. it has sixtet of electrons i.e. diamanetic
3. it is formed by heterolysis
4. it is generally formed due to polar solvent

Structure :

(sp^2) Triangular planer

Stability :

Its stability can be determined with the help of Inductive effect, Hyper conjugation and Resonance effect.

Stability of Carbocation :

$\overset{+}{C}H_3$, $CH_3 \rightarrow \overset{+}{C}H_2$ (+ I effect)

$\text{charge} \propto \frac{1}{\text{Stability}}$

$\overset{+}{C}H_3 <$ $CH_3 \rightarrow \overset{+}{C}H_2$ (stability order)

Stability of carbocation can also be determined by Hyper conjugation (no bond Resonance)

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

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\oplus}{C}} - CH_3 > CH_3 - \underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}H > CH_3 - \overset{\oplus}{C}H > \overset{\oplus}{C}H_3$$

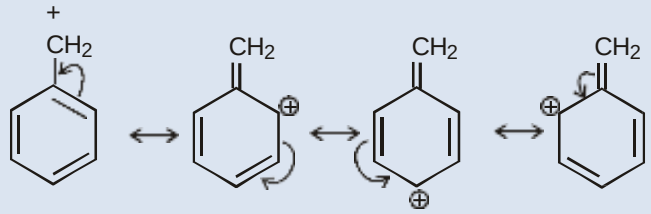
9α C – H bond 6α C – H bond 3α C – H bond

ALLYLIC CARBOCATION

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

allylic carbocation Actual Resonance

BENZYLIC CARBOCATION



$ph_2\overset{+}{C}H \rightarrow$ 7 Resonating strucutre

$ph_3\overset{+}{C} \rightarrow$ 10 Resonating strucutre

$$ph_3\overset{+}{C} > ph_2\overset{+}{C}H > (CH_3)_3\overset{+}{C} > ph\overset{+}{C}H_2$$

Ex.8 Compare the stability of th following carbocation

(a) $CH_3 - \overset{+}{C}H_2$ (b) $CH_2 = \overset{+}{C}H$ ($\downarrow$ sp^2) (c) $CH \equiv \overset{+}{C}$ ($\downarrow$ sp)

⇒ more electronegativity

⇒ +ve charge on more electronegative element is symbol of unstability.

a > b > c

Ex.9 Compare the stability of the following compounds

(a) $\overset{+}{C}H_2 - CF_3$ (b) $\overset{+}{C}H_2 - CCl_3$ (c) $\overset{+}{C}H_2 - CBr_3$ (d) $\overset{+}{C}H_3$

Sol. d > c > b > a

F being most electron attracting group decreases the e^- density from positively charged C-atom and decreases the charge density and makes the carbo cation less stable.

Ex.10 Compare the stability of the following carbocation :

(a) $\overset{+}{C}H_2 - F$ (b) $\overset{+}{C}H_2 - Cl$ (c) $\overset{+}{C}H_2Br$ (d) $\overset{+}{C}H_2 - I$

Sol. due to greater size of Iodine, its L.P. will not be available for coordinate bond. Therefore L.P. would not stabilize corbocation.

In case of F due to its small size its lone pair can be easily coordinated to $\overset{+}{C}$ making it most stable

a > b > c > d (Stability)

* By coordination the carbocation completes its octet and structure having complete octet of its atom is supposed to be most stable.

$$\overset{\oplus}{C}H_2 - \ddot{F}: \leftrightarrow \overset{\oplus}{C}H_2 \leftarrow F \cong CH_2 = \overset{\oplus}{F}$$

(Each atom has its full octet)

* $\overset{\oplus}{C}-A$ > $ph_3\overset{\oplus}{C}$

(stability)

Note : In Rasonating Structure of $ph_3\overset{+}{C}$, at least one C gets sixtet of e^- and hence less stable than coordinated compound.

Ex.11 Compare the stabilities of the following corbocation

(a) $\overset{+}{C}H_2NH_2$ (b) $\overset{+}{C}H_2 - OH$ (c) $\overset{+}{C}H_2 - F$

Sol. N, O, F belongs to same period

⇒ In period Electronegativity of the atom is deciding factor

⇒ F being most electronegative, holds its e^- pair very firmly.

⇒ Its L.P. will not be easily available for coordination.

⇒ Stability by it will be minimum.

a > b > c

Ex.12 Compare the following corbocation in order of their stability.

(a) $\overset{+}{C}H_2 - Cl$ (b) $\overset{+}{C}H_2 - OH$

Sol. If periods of atoms which have to donate their electrons for coordination (for stability) is different then atomic size will be deciding factor. The atom whose size is greater will be unable to make it e^- pair available for coordination.

b > a

Ex.13 Compare the stability of the following compounds

(a) $CH_3 \rightarrow \overset{+}{C}H_2 = CH_2$ (b) $CH_2 = CH - \overset{+}{C}H_2$ (allylic) (c) $CH \equiv \underset{\downarrow}{C} - \overset{+}{C}H_2$ (sp) (d) $ph \leftarrow \overset{+}{C}H_2 - CH_2$

Sol ⇒ more s-character

⇒ more e.n.

⇒ attracts e^-

⇒ reduces, stability

b > a > d > c

CARBANION

1. it is a –ve charged species
2. it has octet of electrons.
3. diamagnetic

Strucutre :

* if –ve charge is in Resonance then the hybridisation of carbanion is sp^2 (Triangular planer shape)
* If –ve charge is not in Resonance then the hybridisation of carbanion is sp^3 (pyramidal)

Stability :

Its stability can be determined with the help of

(1) Inductive effect (2) Resonance effect

Ex.14 $\overset{\ominus}{C}H_3$, $CH_3\overset{\ominus}{C}H_2$

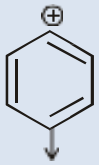
(a) (b)

a > b (stability)

* Stability of the carbanion is as follows

$$ph_3\overset{\ominus}{C} > ph_2\overset{\ominus}{C}H > ph\,\overset{\ominus}{C}H_2 > CH_2 = CH - \overset{-}{C}H_2 > CH \equiv \overset{-}{C} > CH_2 = \overset{-}{C}H > CH_3\overset{-}{} > CH_3 - \overset{\ominus}{C}H_2 > (CH_3)_2\overset{-}{C}H > (CH_3)_3\overset{-}{C}$$

Ex.15 Compare the stability of the following carbacation

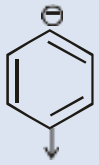
(a)  tending to sp

(b) $CH \equiv \overset{+}{C}$ actual(sp)

(c) $CH_2 = \overset{+}{C}H$ sp^2

Sol. c > a > b

Ex.16 Compare the stability of the following carbanion

(a)  tending sp

(b) $CH \equiv \overset{\ominus}{C}$ (sp) –ve change is attracted sp hybridised carbon (most electronegative) ⇒ become more stable

(c) $CH_2 = \overset{\ominus}{C}H$ sp^2

Sol. b > a > c

Ex.17 Compare the stability of the following carbanion

(a) $\overset{\ominus}{C}H_2 - CF_3$ (b) $\overset{\ominus}{C}H_2 - CCl_3$ (c) $\overset{\ominus}{C}H_2 - CBr_3$

Sol. a > b > c

Ex.18 Arrange the following anion order of their stability

(a) Cl^-, (b) Br^- (c) F^- (d) I^- (maximum size)

⇒ maximum dispersion –ve charge

⇒ max stability

Sol. d > b > a > c

Ex.19 Compare the stability of the following

(a) $\overline{C}H_3$ (b) $\overline{N}H_2$ (c) $\overline{O}H$ (d) F^-

Sol. Same period element (C, N, O, F)

⇒ Stability ∝ E.N. of the atom

d > c > b > a

Ex.20 Compare the acidic strength

(a) HC_1 (b) HF (C) HBr (D) HI

Sol. Acidic strength ∝ stability of the anion formed (conjugate base)

as we know I^- > Br^- > Cl^- > F

⇒ H I > HBr > HCl > HF

Ex.21 Compare the Acidic strength of the following

(a) NH_3 (b) pH_3 (c) AsH_3 (d) SbH_3 (e) BiH_3

Sol. Anion formed from there acids are

$\overline{N}H_2 < \overline{P}H_2 < \overline{A}sH_2 < \overline{S}bH_2 < \overline{B}iH_2$

(Stability)

⇒ acidic strength e > d > c > b > a

Ex.22 Compare the acidic strength of the following comounds
CH_4, NH_3, H_2O, HF

Sol. The conjugate base of the given acid is as follows

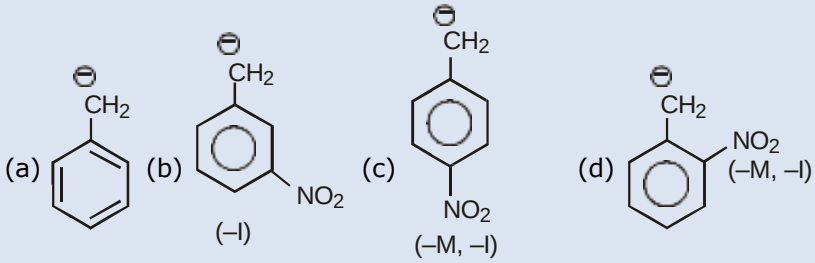
$\overline{C}H_3, \overline{N}H_2, \overline{O}H, F^{\ominus}$

we have already proved that

$F^- > OH^- > \overline{N}H_2 > \overset{\ominus}{C}H_3$ (Stability)

$\Rightarrow$ HF > H_2O > NH_3 > CH_4 (acidic strength)

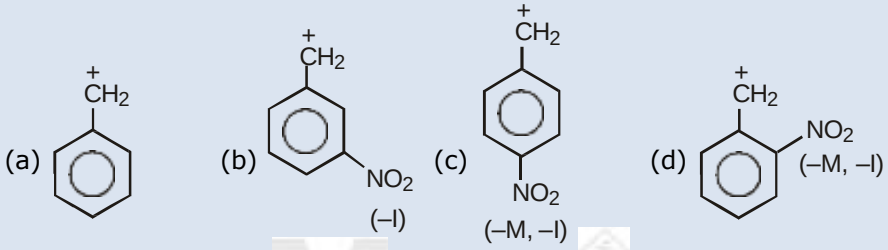
Ex.24 Compare the stability of the following carbanion.



Sol. d > c > b > a

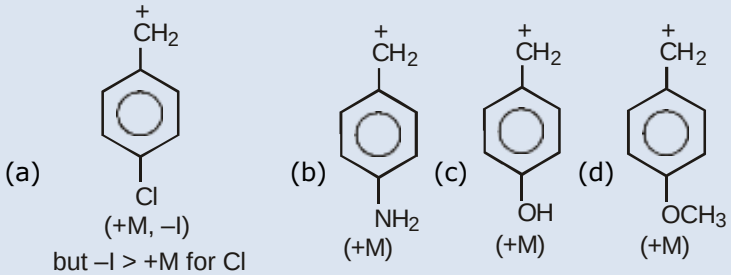
* +M or –M is not distance dependent

Ex.25 compare the stability of the following carbocation



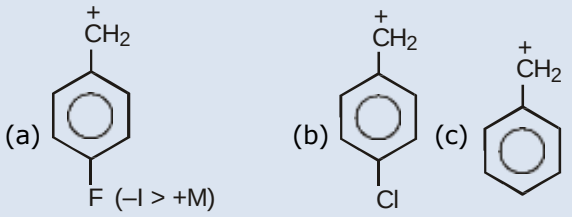
Sol. a > b > c > d

Ex.26 Compare the stability of the following carbocation.



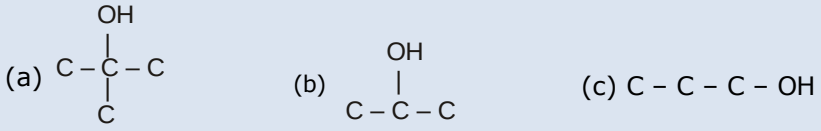
Sol. +M (OH) > +M (OCH_3)
b > c > d > a

Ex.27 Compare the stability of the following carbocation

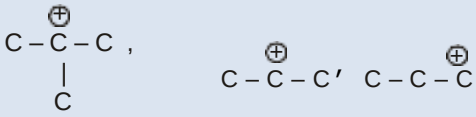


Sol. c > a > b

Ex.28 Compare order of dehydration of the following alcohols :



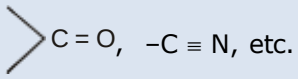
Sol. After formation of carbocation



Since 3° carbocation is most stable therefore it will show greatest tendency to lose water as after lose of water it comes in stable form.

<u>TYPES OF REAGENT</u>

1. Electrophilic reagent : All electron deficient atom or group of atoms is known as Electrophilic reagent, the electrophile attacks at the electron rich centre.
   (a) all positively charqed species are electrophile
   H^+, NO_2^+, Br^+, Cl^+, etc.
   (b) The compound in which the octet of central atom is not complete
   BF_3, $AlCl_3$, $ZnCl_2$, etc.
   (c) all the compound in which the central atom can expand its octet
   $SnCl_4$, $SiCl_4$, etc.
   (d) all polarising functional group are electrophile as well as nuelophile

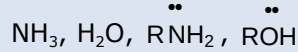


Nucleophile :

All electron rich compounds are nucleophile and attack at the electron deficient centre.

(a) all negatively charqed species
H^-, Cl^-, NO_2^-, Br^-, CH_3^- etc.

(b) the compound in which the central atom has lone pair of electron.



(c) all organometallic compounds are nucleophile

R – Mgx, RLi, R_2Cd

(d) The compound having π e⁻ density, $CH_2 = CH_2$,  etc.

Nucleophilicity :

The power of nucleophile is known as nucleophilicity .

⇒ The nucleophilicity of negative charge is greater than the nucleophilicity of lone pair

$\overline{O}H > H_2O$

$CH_3\overline{O} > CH_3OH$

⇒ If lone pair or –ve charge is present on the different atom then less electronegativity, more will be the nucleophilicity.

CH_3^-, NH_2^- , OH^-, F^-

Nucleophilicity $\overset{-}{C}H_3 > \overset{-}{N}H_2 > OH^- > F^-$

⇒ $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$ (Nucleophilicity)

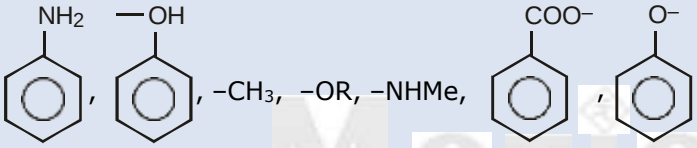
⇒ If –ve charge or lone pair of electron is present on the same atom then the less stable –ve charge will be the better nucleophile

OH^-, $CH_3\overline{O}$, CH_3COO^-

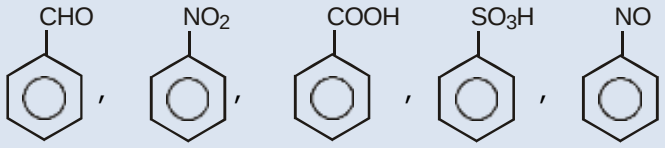
$CH_3O^- > OH^- > CH_3COO^-$ (nucleophilicity)

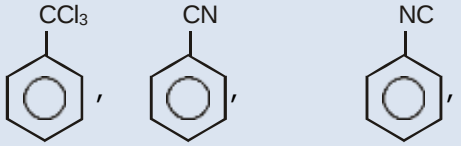
ACTIVATOR & DEACTIVATOR

The groups in benzene which show +M effect or +I effect Increases the electron density on benzene it means they activate the ring towards electrophile and known as activator.



The groups which shows –M or –I effect (resultant) decreases the e⁻ density from benzene ring. It means they deactivate the ring towards electrophile

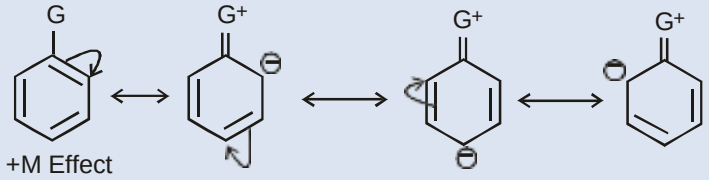




etc.

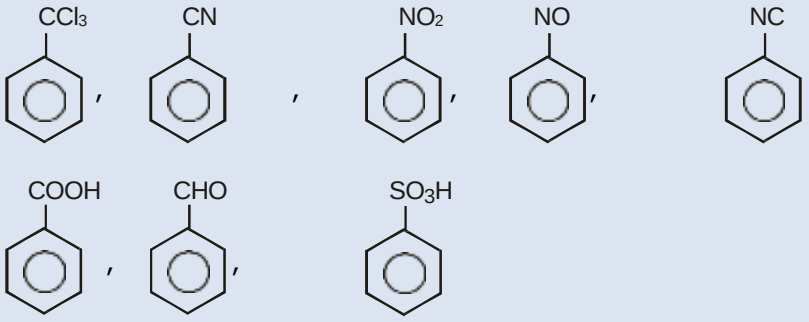
ORTHO PARA & META DIRECTOR

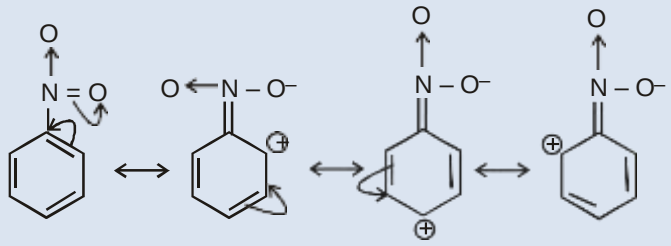
The groups which shows +I (resultant) or +M effect then negative charge is developed at the ortho & para position. Therefore electrophile attack at the ortho & para position and the groups are known as OP director.



+M Effect

- The groups which shows –M effect or – I effect (resultant) then +ve charge is developed at the ortho & para position this means electron density is minimum at the ortho & para positions and electronphile will attack at the meta position the groups are known as meta director.





HEAT OF HYDROGENATION(H.O.H)

It is the amount of energy realeased when one mole of H_2 is added to any unsaturated system.

$$CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3 + \text{energy}$$

HOH is exothermic process $\Delta H = -ve$

*HOH $\propto$ No. of π-bonds in compound

If no. of π-bonds is same then

$$*HOH \propto \frac{1}{\text{stability of compound}}$$

$\therefore$ In case of alkene

$$**HOH\ \alpha\ \frac{1}{\text{stability of compound}}\ \alpha\ \frac{1}{\text{No.of } \alpha H}$$

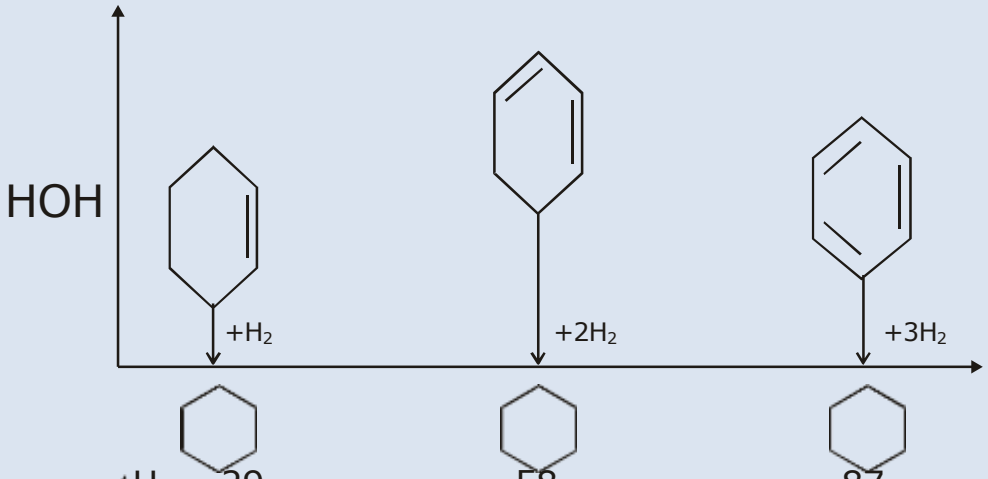
Ex. a  + H_2 ⟶  + 29 kcal

b  + 2 H_2 ⟶  + 58 kcal ⟹ 55 kcal
(expected) (actual)

c  + 3 H_2 ⟶  + 87 k cal ⟹ 51 k cal
(expected) (actual)

b > c > a

Energy



ΔH=– 29 58 87

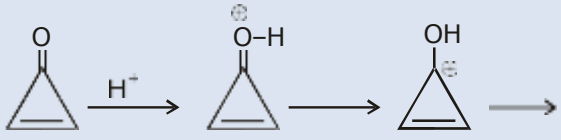
ΔH=– 55 ΔH=– 51

RE = 3 k Cal RE = 36 k Cal

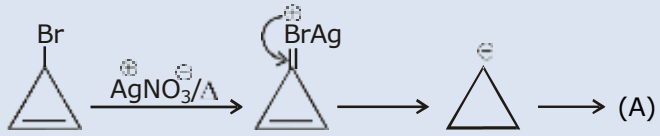
Some examples of Arromatic(A), Non-arromatic(NA) and Anti-arromatic(AA)

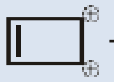
(1)  (A) (2) (AA) (3) (AA)

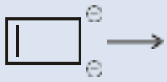
(4)  (NA) (5)  (AA) (6)  (A)

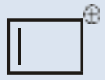
(7) 

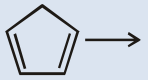
(A)

(8) 

(9)  (A) ⟶ (2πe)

(10)  (A) ⟶ (6πe)

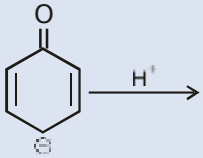
(11)  (NA)

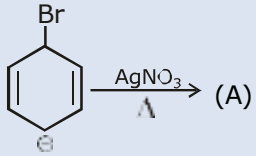
(12)  (NA)

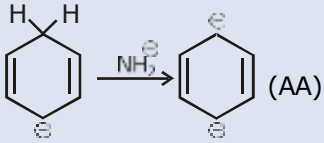
(13)  (AA) ⟶ (4πe)

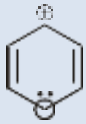
(14)  (A)

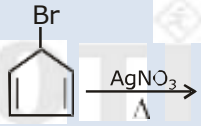
(15)  (NA)

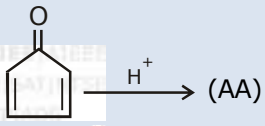
(16) 

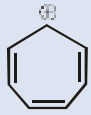
(17) 

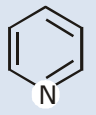
(18) 

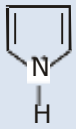
(19)  (A)

(20) 

(21) 

(22)  (AA)

(23) 

(24) 

QUESTION BANK

Unit 1: Structural Theory in Organic Chemistry

Long Answer Questions (10 Marks)

1. Explain the different types of bond fission in organic reactions and their significance.
2. Discuss the concept of resonance and its application to the acidity of phenols and carboxylic acids.
3. Describe the factors influencing the polarization of covalent bonds.
4. What is hyperconjugation? Discuss its role in the stability of carbocations and free radicals.
5. Explain the inductive effect and its application in the basicity of amines and the acidity of carboxylic acids.

Short Answer Questions (5 Marks)

1. Define the concept of free radicals and provide examples.
2. What is the role of carbocations in organic reactions?
3. State the effect of hyperconjugation on the stability of alkenes.
4. What is the application of resonance in organic chemistry?
5. Discuss the concept of bond polarization and its importance in organic reactions.

4

GENERAL PRINCIPLES OF ORGANIC REACTION MECHANISM

INDUCTIVE EFFECT

Q. 1. What is inductive effect? *(Marathwada, 2003; Madurai, 2004; Guwahati, 2005; Nagpur, 2008; Patna, 2010)*

Ans. Inductive effect: When a covalent bond ininvolves two atoms of different electronegativities, the shared pair of electrons is displaced towards the more electronegative element. As a result, the more electronegative atom gets a small negative charge and the other atom gets equal small positive charge. For example, consider a chain of carbon atoms joined to a chlorine atom

$$— C_3 — C_2 — C_1 — Cl$$

Chlorine has a greater electronegativity than carbon, therefore the electron pair forming the covalent bond between the chlorine atom and C_1 will be displaced towards the chlorine atom. This causes the chlorine atom to acquire a small negative charge, $-\delta$ and C_1 a small positive charge, $+\delta$ as shown below :

$$— C_3 — C_2 — \overset{+\delta}{C_1} — \overset{-\delta}{Cl}$$

Since C_1 is slightly positively charged, it will attract towards itself the electron pair forming the covalent bond between C_1 and C_2. This will cause C_2 to acquire a small positive charge but the charge will be smaller than that on C_1 because the effect of the chlorine atom has been passed through C_1 to C_2.

$$— C_3 — \overset{+\delta}{C_2} — C_1 — \overset{-\delta}{Cl}$$

Similarly C_3 acquires a positive charge which will be less than that on C_2. **This type of electron shift or displacement along a carbon chain is known as inductive effect.** Inductive effect is permanent and decreases rapidly as the distance from the source (Cl) increases. Practically it is almost negligible beyond two carbon atoms from the active atom or group. The important thing to note is that the electron pairs although permanently displaced, remains in the same valency shell. The inductive effect is shown by a line marked with arrow head ($\rightarrow$) pointing towards the electron attracting atoms or groups.

Types of Inductive Effect

1. Negative Inductive Effect: If the atom or group of atoms attached to a carbon atom is such that it attracts the shared pair of electrons towards itself it is said to exert negative or –I effect. The decreasing order of the –I effect of some atoms or groups is:

$$NO_2 > CN > COOH > F > Cl > Br > I > OCH_3 > C_6H_5$$

2. Positive Inductive Effect: If the atom or group of atoms attached to the carbon atom is such that it pushes the electrons away from it, it is said to exert positive or +I effect. The decreasing order of + I effect of some groups is:

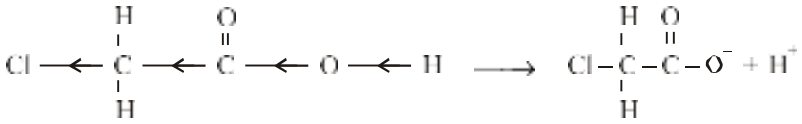
$$(CH_3)_3C > (CH_3)_2CH > CH_3CH_2 > CH_3$$

For comparison of inductive effect hydrogen (H) is chosen as the standard. Atoms or groups with –I effect are more electron withdrawing than H while with +I effect are less electron withdrawing than H or in other words they more electron releasing than H.

Q. 2. Define inductive effect. Explain with the help of this effect that chloroacetic acid is stronger than acetic acid. (*Kerala 2000*)

Ans. (*i*) For inductive effect see Q. 1.

(*ii*) Chloroacetic acid is stronger than acetic acid because of the inductive effect of chlorine.



Chlorine exerts negative inductive effect, as a result of which, the electron displacement takes place away from carboxy hydrogen. This facilitates the removal of hydrogen as proton.

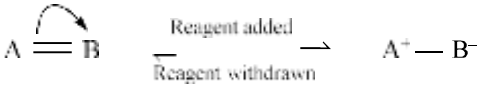
ELECTROMERIC EFFECT

Q. 3. Explain clearly electromeric effect.

(*Meerut, 2000; G. Nanakdev, 2000; Awadh 2000*)

Ans. It is temporary effect which involves a complete and instantaneous transfer of a shared pair of electrons to one or the other atom joined by multiple bond at the requirement of an attacking reagent.

The electromeric effect is represented by a curved arrow beginning at the original position of the electron pair and ending where the pair has migrated. Let us consider a molecule AB having a double bond between atoms A and B. In the presence of attacking reagent, one of the shared pair of electrons is completely transferred to one of atoms (say B) as shown below :

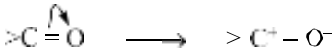


Thus A becomes positively charged while B becomes negativily charged,. The removal of the attacking reagent causes the charged molecule to revert to its original condition.

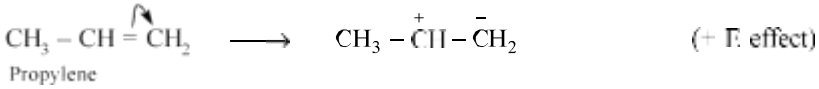
Electronegativity plays an important role in knowing the direction of the transfer of the shared pair of electrons to one of the atoms.

For example,

(*i*) In a carbonyl group > C = O, present in aldehydes or ketones, the displacement is towards the oxygen atom. This is due to greater electronegativity of oxygen than carbon.



(*ii*) In propylene, the displacement of shared electron pair is towards the carbon atom which is away from methyl group. This is due to the inductive effect of methyl group which is electron repelling.



Thus the electromeric effect is of two types. When the electron displacement is away from the group, it is denoted by +E and when the displacement is towards the group, it is denoted by —E.

RESONANCE OR MESOMERIC **EFFECT**

Q. **4. Describe resonance or mesomeric effect.** Give conditions necessary for resonance.
(Shivaji, 2004,' West Bengal, 2004,' Panjab, 2005,' Banaras, 2004, Purvanchal 2007, Patna, 2010, Pune, 2010)

Ans. Resonance and Resonance **effect**

Sometimes it is found that a single structural formula cannot satisfactorily explain all the properties of a given compound. In such a case the compound is represented by two or more structural formulae which differ only in the arrangement of electrons. None of the structural formula alone can explain all the observed properties of the compound. The compound is then said to show resonance. The various structures are called resonating structures or canonical **structures.** The true structure of the molecule is not represented by any of the resonating structures but is considered to be a resonance hybrid (intermediate) of the various resonating structures.

For example, the most frequently used Lewis structure for carbon dioxide molecule is

$$:O::C::O: \qquad \text{or} \qquad O=C=O \quad \text{(I)}$$

On the basis of this structure, the heat of formation of carbon dioxide from its elements should have been 1463 kJ/mole and C = O bond length should have been 1.21 &. But the experimental value for the heat of formation of CO_2 is 1588 kJ/mole and C = O bond length is 1.15a. Thus, structure I for CO_2 cannot explain its properties completely. Structures II and III contain triple bonds which have shorter bond lengths,. But they have shorter bond lengths than 1.15a. Thus structures II and III also fail to account for all the observed properties of carbon dioxide.

$$O:::O: \qquad \text{or} \qquad 0-C=0 \quad \text{(II)}$$

and

$$:0::C:0": \qquad \text{or} \qquad O=C-O \quad \text{(III)}$$

In the light of the above concept, CO_2 is regarded as a resonance hybrid of the structures I, II and III, *i.e.,*

$$O=C=O \;(\text{I}) \longleftrightarrow O-C=O \;(\text{II}) \longleftrightarrow O=C-O^{*} \;(\text{III})$$

Resonance is also called mesomerism.

Conditions for resonance

Main conditions for resonance are:

(i) The positions of the nuclei (of each atom) in each structure must be the same.

(ii) The number of unpaired electrons in each structure must be the same.

(iii) Each structure must have about the same internal energy.

(iv) The contributing structures, which involve separation of positive and negative charges are of high energy and hence contribute slightly towards the resonance hybrid.

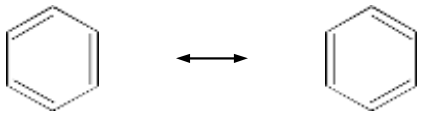
(v) The greater the number of contributing structures, the greater will be the stability of the molecule.

(vi) The larger the number of bonds in the contributing structure, the greater is its stability.

Consequences of resonance

(*i*) **Bond length.** The bond length in actual molecule is different from that of any of the contributing structures.

Let us consider the example of benzene molecule. Had I or II been the structure of benzene then it should have shown two bond lengths, *i.e.*, three C = C double bonds should have been 1.34 Å long and three C — C single bonds should have been 1.54 Å long. But the X-ray analysis of benzene shows that all the carbon-carbon bond lengths are identical and equal to 1.39 Å. This can be explained if we consider benzene to be a resonance hybrid of two Kekule's structures I and II.



I II

In other words, the real structure of benzene is neither represented by Kekule structure I nor by II but is somewhat in between these two structures. This means that any two adjacent carbon atoms of the benzene molecule are joined neither by a pure single bond nor by a pure double bond. As a result, all the carbon-carbon bond lengths should not only be equal but should also lie in between C = C bond length of 1.34 Å and C — C bond length of 1.54 Å. This is in excellent agreement with the experimental value of 1.39 Å.

(*ii*) **Stability.** A resonance hybrid is always more stable than any of its canonical structures. For example, the observed heat of formation of carbon dioxide is 125 kJ/mole than the value calculated on the basis of structure O = C = O. This implies that the internal energy of CO_2 is less than the calculated value by 125 kJ/mole. In other words the real molecule of CO_2 is 125 kJ/mole more stable than the Lewis structure O = C = O.

The magnitude of stability conferred on a molecule as a result of resonance is expressed in terms of **resonance energy or delocalization energy.** It is defined as the difference between the actual energy of the molecule capable of exhibiting resonance and the energy calculated for the resonating structures.

Q. 5. By what electronic effect can you explain the low reactivity of halogen atom in vinyl bromide.

Or

On the basis of resonance, how will you explain low reactivity of vinyl bromide as compared to ethyl bromide?

Ans. Low reactivity of halogen in vinyl bromide can be explained on account of the phenomenon or resonance or mesomerism.

Halogen compounds generally give nucleophilic substitution reactions, in which the halogen is removed as halide ion.

But in the case of vinyl bromide, resonance takes place as illustrated above. This creates a double bond between carbon and bromine. Removal of bromine thus becomes difficult. Moreover, bromine, acquires a positive charge and hence cannot be substituted by a nucleophile. That is why vinyl bromide shows low reactivity.

Q. 6. Which of the following canonical forms would contribute most towards resonance? Explain

$$\underset{(a)}{CH_2=CH-CH=CH_2} \longleftrightarrow \underset{(b)}{\overset{-}{C}H_2-CH=CH-\overset{+}{C}H_2} \longleftrightarrow \underset{(c)}{\overset{-}{C}H_2-\overset{+}{C}H_2-CH=CH_2}$$

(*Delhi 2006*)

Ans. The resonance structures fulfilling the following conditions are more stable :

1. Greater number of covalent bonds
2. Less separation of charges
3. Negative charge on electronegative atom
4. Position charge on electropositive atom
5. More dispersal of charges

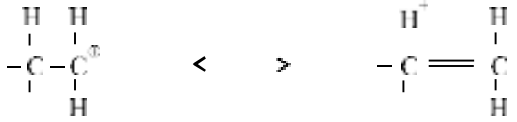
Structure (*b*) takes care of dispersal of charge. Hence, it is more stable and contributes more towards resonance.

HYPERCONJUGATION

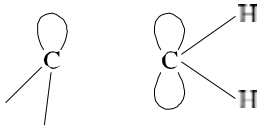
Q. 7. What is meant by hyperconjugation? Why is it also termed no-bond resonance?

(*Kerala 2001; Manipal, 2002; Punjabi, 2003; Nagpur, 2008; Patna, 2010, Andhra, 2010*)

Ans. It is a special type of resonance which involves the overlapping of σ-orbital with a π-orbital or *p*-orbital. Hyperconjugation takes place in the following carbonium ion as depicted



(I) (II)



Since in structure (II), there is no bond between H^+ and C, hyperconjugation is also referred to as no-bond resonance.

Q. 8. In what ways a covalent bond can be fissioned and what are its results?

Or

Explain :

(*i*) Homolytic fission

(*ii*) Heterolytic fission

(*Kerala 2001; Delhi 2003; Nagpur 2003; Goa 2004; Garhwal 2010*)

Ans. Consider a covalent bond between atoms A and B.

A : B or A — B

The cleavage (or breaking) of this bond can take place in three possible ways depending upon the relative electronegativities of A and B.

(*i*) $A : B \longrightarrow A\bullet + B\bullet$ (A and B of equal electronegativity)

(*ii*) $A : B \longrightarrow \overset{-}{A} : + \overset{+}{B}$ (A more electronegative than B)

(*iii*) $A : B \longrightarrow \overset{+}{A} + : \overset{-}{B}$ (B more electronegative than A)

The first type of cleavage is called *homolytic fission* or homolysis and leads to the formation of very reactive species called '*free radicals*' (atoms or groups of atoms containing odd or unpaired electrons).

In homolytic fission the covalent bond breaks in such a way that each fragment carries one unpaired electron.

The second and third types of cleavage is called *heterolytic fission* and leads to the formation of ionic species. These ionic species are also very reactive and carry charges on carbon. Cationic species carrying positive charge on a carbon atom are called *carbonium ions* or *carbocations.* Anionic species carrying negative charge on carbon atom are called *carbanions.*

In heterolytic fission the covalent bond breaks in such a way that the pair of electrons stays on the more electronegative atom.

Q. 9. What is meant by reaction intermediates? List all of them.

(*Kerala 2000; Nagpur 2003*)

Ans. In organic reactions, reactants do not change into products in one step. The change normally takes place via an intermediate product, which is short-lived. From the intermediate product, the reaction passes on to the products. Various reaction intermediates that we come across in the study of organic reactions are:

(*i*) Carbonium ion (or carbocation) (*ii*) Carbanion (iii) Free radial

(*iv*) Carbene (*v*) Nitrene

FREE RADICALS

Q. 10. What are free radicals? Discuss their characteristics, structure and stability.

(*G. Nanakdev, 2000; Garhwal, 2000; Meerut, 2000; Kanpur 2001; Magadh, 2002; Nagpur 2008*)

Ans. Free radical is an atom or group of atoms containing odd or unpaired electron. Methyl free radical ($CH_3\bullet$), ethyl free radical $CH_3—CH_2\bullet$), chlorine free radical ($Cl\bullet$) are some of the examples.

Characteristics of Free Radicals

(1) Free radicals ae electrically neutral and highly reactive species formed by homolytic fission of a covalent bond.

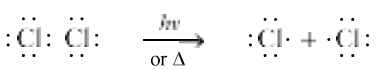
(2) They are paramagnetic in nature due to the presence of odd electrons.

(3) They are extremely reactive since they have tendency to complete the octet of the atom carrying the unpaired electron.

(4) They have short life period.

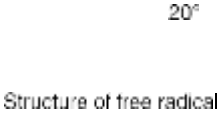
(5) They are usually formed in reactions which are carried out at very high temperatures or under the influence of ultraviolet light or in the presence of radical initiators such as peroxides.

For example,



Structure of an Alkyl Free Radical

The carbon atom of an alkyl free radical is sp^2 hybridised. Its three hybridised orbitals are bonded to three atoms or groups of atoms. Thus free radicals have planer structures and have bond angles of 120°. The unpaired electron is present in unhybridised *p*-orbitals as shown in the figure.



Structure of free radical

Stability of Free Radicals

The bond dissociation energies for various alkanes are given below:

$$CH_4 \longrightarrow \bullet CH_3 + H\bullet \qquad \Delta H = +426 \text{ kJ}$$

$$C_2H_6 \longrightarrow \bullet CH_2 - CH_3 + H\bullet \qquad \Delta H = 406 \text{ kJ}$$

A primary free radical

$$CH_3 - CH_2 - CH_3 \longrightarrow CH_3 - CH_2CH_2\bullet + H\bullet \qquad \Delta H = 406 \text{ kJ}$$

A primary free radical

$$CH_3 - CH_2 - CH_3 \longrightarrow CH_3 - \dot{C}H - CH_3 + H\bullet \qquad \Delta H = 393 \text{ kJ}$$

A secondary free radical

$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - CH_3 \longrightarrow CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle \bullet}{\overset{|}{\underset{|}{C}}}} - CH_3 + H\bullet \qquad \Delta H = 380 \text{ kJ}$$

Tert. free radical

It is obvious from the above that tertiary alkyl radical is more stable than secondary alkyl radical which in turn is more stable than primary alkyl radical.

The order of stability is:

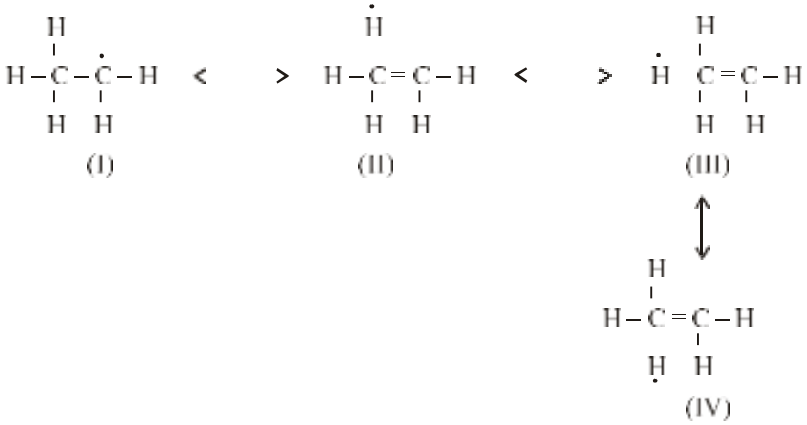
$$\text{Tert. alkyl radical} > \text{Sec. alkyl radical} > \text{Prim. alkyl radical} > \dot{C}H_3$$

Q. 11. Arrange the following free-radicals in increasing order of stability and explain your answer.

$$\dot{C}_2H_5, \quad (C_2H_5)_2\dot{C}(C_2H_5), \quad (C_2H_5)_2\dot{C}H, \quad \dot{C}H_3$$

Ans. The order of stability can be given considering the hyperconjugation phenomenon.

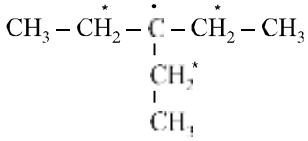
(*i*) Ethyl radical is a hybrid of four resonating structures.



(I) (II) (III) (IV)

Thus no. of resonating structures is one more than the no. of hydrogen atoms on the neighbouring carbon atoms.

(*ii*) $(C_2H_5)_2\dot{C}(C_2H_5)$ is a hybrid of seven resonating structures, as there are six hydrogens marked * which can participate in hyperconjugation.



(*iii*) $(C_2H_5)_2\dot{C}H$ is a hybrid of five resonating structures.

(*iv*) There is one and only one structure of $\dot{C}H_3$

Greater the no. of resonating structures of a species, greater is the stability. Hence the order of increasing stability is

$$\dot{C}H_3 < CH_3\dot{C}H_2 < (C_2H_5)\dot{C}H < (C_2H_5)_2\dot{C}(C_2H_5)$$

Q. 12. Arrange the following free-radicals in order of increasing stability.

$CH_3-\dot{C}H_2$, $(CH_3)_2\dot{C}H$, $\dot{C}H_3$ and $(CH_3)_3\dot{C}$. Explain your answer.

(Kurukshetra, 2001)

Ans. Proceed as explained in Q. 11.

CARBOCATIONS (CARBONIUM IONS)

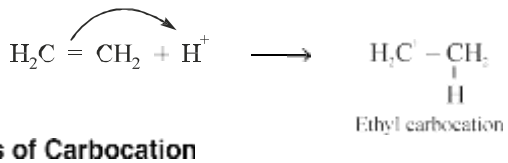
Q. 13. What are carbocations? Discuss their characteristics, stability and structure.

(Delhi 2005; Purvanchal 2007; Nagpur 2008; Andhra 2010; Garhwal, 2010)

Ans. A species which has a carbon atom bearing only six electrons and having a positive charge is called *carbonium ion* or *carbocation.*

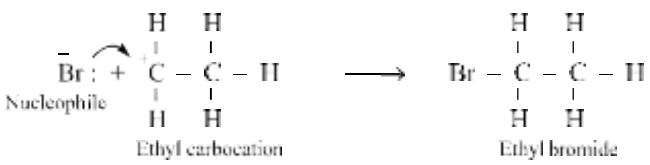
For example,

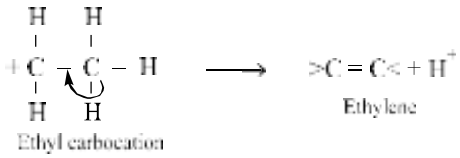
When a proton adds to a carbon-carbon double bond, a carbonium ion gets formed.



Characteristics of Carbocation

1. Carbocations have a very strong tendency to complete the octet and consequently they are exceedingly reactive. Either they combine with nucleophiles such as OH^-, CN^- ions, or may lose a proton to form an alkene. The loss of proton takes place from the adjacent atom.

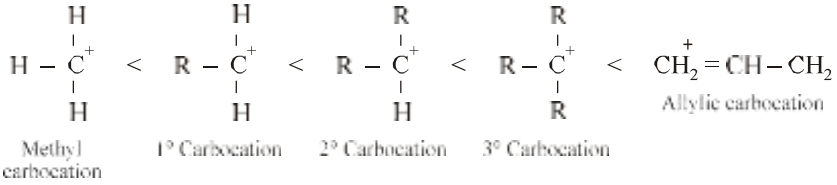




2. They are short lived.

Stability of Carbocations

Like free radicals, the relative stabilities of carbocations is of the following order.

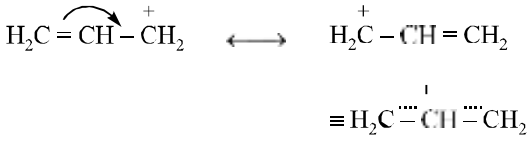


Any factor (Inductive effect, Resonance or both) which helps in the dispersal of the charge increases the stability of the carbocation.

The above mentioned order can be easily explained in terms of the electron releasing (+I) inductive effect of the alkyl groups. An alkyl group attached to the positively charged carbon atom of the carbocation tends to release electrons to the positively charged carbon. As a result, the +ve charge on the carbon atom decreases. In other words, positive charge on the carbon atom gets dispersed. According to the laws of electrostatics, dispersal of the charge leads to the stability of the ionic species. *Thus, greater the number of alkyl groups, greater in the dispersal of the +ve charge and hence greater is the stability of the carbocation.*

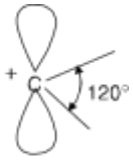
This explains why 3° carbocation with three alkyl groups are more stable than 2° carbocation with two alkyl groups which in turn are more stable than 1° carbocation with one such group. A methyl carbocation which does not contain any alkyl group is, the least stable.

The resonance stabilisation of allylic carbocation enhances its stability (delocalisation of π electrons).



Structure of Carbocations

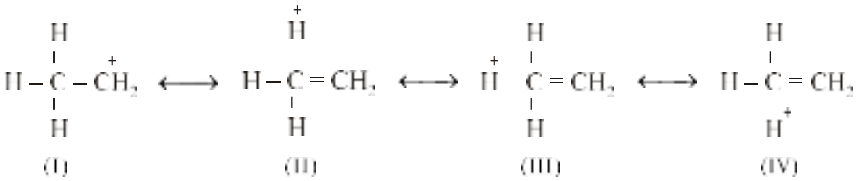
The carbon atom of a carbocation is sp^2 hybridized. The three sp^2 orbitals form three σ-bonds with the three substituents. The unhybridized *p*-orbital which is perpendicular to the plane of the three σ-bonds, however, remains empty. *Thus, carbocations are planer chemical species having all the three σ-bonds in one plane with a angle of 120° between them* as shown in the figure.



Structure of carbocation ion.

Q. 14. Explain why ethyl carbocation ($CH_3 - \overset{+}{C}H_2$) is more stable than n-propyl carbocation ($CH_3 - CH_2 - \overset{+}{C}H_2$)? *(Delhi 2006)*

Ans. Greater the number of hyperconjugation structures of a carbocation, greater is the stability



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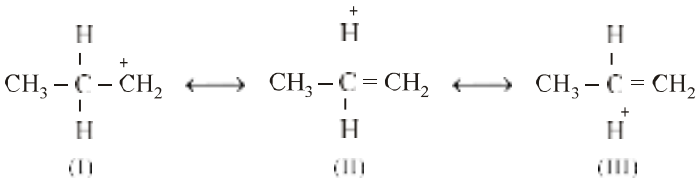


(I) (II) (III)

We find that ethyl carbocation has four hyperconjugative structures while *n*-propyl carbocation has three. Thus, ethyl carbocation is more stable .

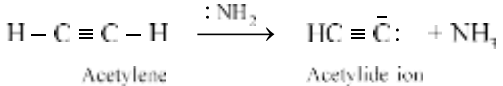
CARBANIONS

Q.15. What are carbanions? Discuss their formation, stability and structure.

(G. Nanakdev 2000; M. Dayanand 2000; Kerala, 2003; Osmania, 2003, Sri Venkateswara, 2003; Guwahati, 2005, Nagpur, 2005)

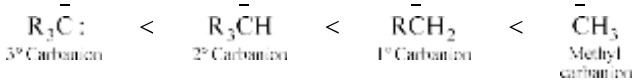
Ans. An organic anion with the negative charge on carbon is known as *carbanion.* It is generated by the removal of an atom or group of atoms from a molecule without the bonding electrons.

Formation of Carbanion



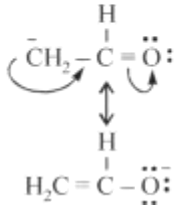
Acetylene — Acetylide ion (Carbanion)

Stability of carbanion. The relative stability of carbanions is just the opposite of carbonium ions. Thus $\bar{C}H_3$ (Methyl carbanion) is the most stable among 1°, 2° and 3° carbanions.



3° Carbanion < 2° Carbanion < 1° Carbanion < Methyl carbanion

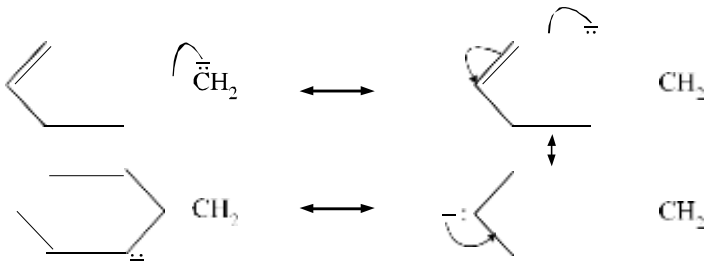
This is due to the fact that electron releasing alkyl groups tend to intensify the negative charge and hence destabilize the carbonium ions while electron withdrawing substituents such as > C = O and –C ≡ N groups enhance the stability of carbonium ion due to the dispersal of –ve charge (delocalisation).



They can be stabilized by resonance involving the unshared pair and an adjacent unsaturated system.

For example,

$\bar{C}H_2$ is more stable than $CH_3 - \bar{C}H_2$: because of resonance as shown:



Structure of Carbanions

The negatively charged carbon atom of simple carbanions is sp^3-hybridized. Three of the sp^3 orbitals form three σ-bonds with the three substituents whereas the fourth contains the non-bonding pair of electrons. Thus, *carbanions are isoelectronic with ammonia.* Like NH_3, *they appear to have pyramidal structure.*

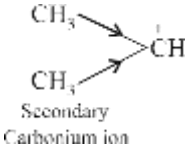
Structure of carbanion

Q. 16. Define carbonium ion and carbanion and explain that a secondary carbonium ion is more stable than primary but a secondary carbanion is less stable than primary.

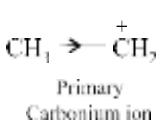
(*Dayanand, 2000*)

Ans. For the definition of carbonium ion and carbanion, see Q. No. 13 and 15.

A secondary carbonium ion is more stable than primary carbonium ion because in secondary carbonium ion, the positive charge is dispersed by the inductive effect of two methyl groups.



Secondary Carbonium ion



Primary Carbonium ion

In primary carbonium ion, the dispersal of charge takes place to a smaller extent as there is only one alkyl group.

However, when we go to carbanions, the situation is just opposite.

Here the alkyl groups tend to destabilize the carbanion. Instead of dispersal of charge, there is rather concentration of charge on the carbanion. Two alkyl groups will destabilize carbanion more than one alkyl group. Hence secondary carbanion is less stable than primary carbanion.

CARBENES

Q. 17. What are carbenes? Discuss their formation and structure.

(*Meerut, 2000; Kurukshetra, 2001; Kerala 2001; Punjab 2003; Delhi 2006; Nagpur 2008*)

Ans. Carbenes are neutral divalent chemical species which contain a carbon atom having six electrons in their valence shell out of which two are unshared. The simplest carbene is methylene : CH_2, other examples are : CCl_2 dichlorocarbene, : CBr_2 dibromocarbene, : $C(C_6H_5)_2$ diphenyl carbene etc.

Formation of Carbenes. Carbenes are obtained by the following methods:

(*i*) Methylene : CH_2 is obtained by the action of UV light on diazomethane

$$\underset{\text{Diazomethane}}{CH_2N_2} \xrightarrow[\text{light}]{\text{UV}} : CH_2 + N_2$$

It is also obtained by the action of UV light on ketene

$$CH_2 = C = O \xrightarrow[\text{light}]{\text{UV}} : CH_2 + CO$$

(*ii*) Dichloro carbene is obtained by the action of chloroform on sodium ethoxide

$$HCCl_3 + C_2H_5ONa \longrightarrow \underset{\text{Dichloro carbene}}{: CCl_2} + C_2H_5OH + NaCl$$

Types of carbenes. Depending upon whether the two electrons on carbene are paired or not, they can be classified into two types.

Singlet carbenes are those in which the unshared electrons are paired. Singlet carbene may be written as

$$\uparrow\downarrow CH_2$$

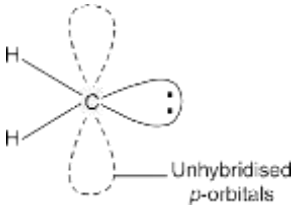
Triplet carbenes are those in which the unshared electrons are unpaired, it may be represented as

$$\uparrow\uparrow CH_2$$

Triplet carbenes are lower in energy and hence more stable than singlet carbenes.

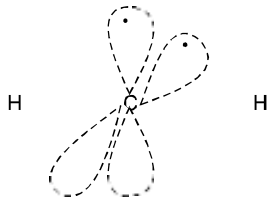
Structure of Carbene

The structures of two types of carbenes are different : Singlet carbenes have their carbon in sp^2 hybridised state. Of the three sp^2 hybrid orbitals, two are used in forming two single bonds with monovalent atoms or groups attached to carbon. The unshared pair of electrons is present in the third sp^2 hybrid orbital and the unhybridised *p*-orbital is emtpy.



Singlet methylene

Triplet carbene has its carbon in *sp* hybridised state. The two *sp* hybrid orbitals form two bonds with monovalent atoms or groups attached to carbon. The two unhybridised *p*-orbitals contain one electron each.



Triplet methylene

Q. 18. Describe different types of reaction that we come across.

(*Kerala 2001, Delhi 2003, Nagpur 2008*)

Ans. Organic reactions may be classified into four main types:

(*a*) Substitution reactions

(*b*) Addition reactions

(*c*) Elimination reactions

(*d*) Rearrangements.

These are separately described as under.

(*a*) Substitution reactions: A substitution reaction is one in which a part of one molecule is replaced by other atom or group without causing a change in the rest of the molecule. Following are some examples of substitution reactions.

(*i*) $\underset{\text{Methane}}{CH_4} + Cl_2 \longrightarrow \underset{\substack{\text{Methyl}\\ \text{chloride}}}{CH_3Cl} + HCl$

(*ii*) $C_2H_5Br - KOH \longrightarrow C_2H_5OH + KBr$

(*iii*) $\underset{\text{Benzene}}{C_6H_6} + Cl_2 \xrightarrow{FeCl_3} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + HCl$

The substitution reactions may be brought about by free-radicals, nucleophilic or electrophilic reagents.

(*b*) Addition reactions: When two molecules of same or different substances combine together giving rising to a new product, it is a addition reaction. Examples of addition reactions are:

$\underset{\text{Ethene}}{CH_2 = CH_2} + Br_2 \longrightarrow \underset{\text{Ethylene dibromide}}{CH_2BrCH_2Br}$

$\underset{\text{Acetaldehyde}}{CH_3CHO} + HCN \longrightarrow \underset{\text{Acetaldehyde cyanohydrin}}{CH_3CH(OH)CN}$

Addition reactions could be brought about by free-radical, electrophilic or nucleophilic reagents.

(c) **Elimination** reactions: These reactions involve the removal of atoms or groups from a molecule to form a new compounds containing multiple bonds. Dehydrohalogenation of alkyl halides is a common example of this type of reaction.

$$\underset{\text{n-Propy1 chloride}}{CQ—CJCJCl} + KOH \qquad CACH=CQ + KCl + JO \quad \underset{\text{Propene}}{}$$

(d) Rearrangement reactions: Rearrangement reactions involve the migration of an atom or a group from one atom to the other within the same molecule.

It is interesting to note that the first organic compound, *i.c.*, urea synthesized in the laboratory by Wohler actually involved a rearrangement reaction.

$$\underset{\text{Amm. cyanate}}{NH,CNO} \xrightarrow{\Delta} \underset{\text{Urea}}{NH_2 - CO - NH_2}$$

Another important example of such reactions is *Hoffmann broniamide reaction.* This reaction involves the migration of an alkyl groups from the carbon to the nitrogen atom of an amide with the simultaneous elimination of CO as carbonate ion under the influence of Br;/KOH.

$$\underset{\text{Acetamide}}{CQ—CONT} + Br_2 + 4KOH \longrightarrow \underset{\text{Methy lamine}}{CQ—NQ} + SCO, + 2KBr + 2JO$$

Similarly maleic acid, when heated in a sealed tube, is converted into fumaric acid.

$$\begin{array}{ll} H—C—COOH & —+ \quad H—C—COOH \\ H—C—COOH & \quad HOOC—C—H \\ \text{Maleic acid} & \quad \text{Fumaric acid} \end{array}$$

Q. 19. Write notes on:

(a) Nucleophilic reagents

(b) Electrophilic reagents. *(Kerala 2000, Nagpur 2005, Patna 2010)*

Ans. *(a)* Nucleophilic reagents or nucleophiles

A nucleophilic reagent is a reagent with an atom having an unshared or lone pair of electrons. Such a reagent is in search of a point where it can share these electrons to form a bond. Nucleophiles are of two types:

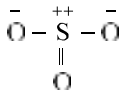
(r) Neutral nucleophiles. These are the nucleophiles which are neutral in charge. But they carry some unshared electrons which they like to share with some positive centre or electron deficient centre. Ammonia NH , water H_2O and alcohols R —O —H are examples of neutral nucleophiles.

(ii) Negative nucleophiles. These are the nucleophiles which carry negative charge. Examples of this type of nucleophiles are hydroxyl ions (OH), halide ion (X), alkoxide ion (RO) and cyanide ion (CN). Carbanions also come in the category of negative nucleophiles.

(b) Electrophilic Reagents or Electrophiles

An electrophile is a reagent containing electron deficient atoms. Such species have a tendency to attach themselves to centres of high electron density. There are two types of electrophiles:

(r) Neutral electrophiles. These electrophile don't carry any net charge. Lewis acids like AlCl;, $FeCl_3$ and BF_3 belong to this category of electrophiles. Sulphonium ion (SO) carries no net charge, but it acts as an electrophile for sulphonation in benzene rings. This is because of its structure.



As the positive charge is concentrated and the negative charge is scattered, it acts as an electrophile. Substances like $SnCl_4$ which have vacant *d*-orbitals would like to accommodate electrons in them. Thus such substances also act as electrophiles.

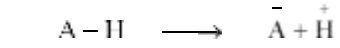
(*ii*) Positive electrophiles. These electrophiles carry a net positive charge. Examples of this category of electrophiles are hydrogen ion (H^+), hydronium ion (H_3O^+), nitronium ion (NO_2^+), and chloronium ion (Cl^+). In the halogenation and nitration of aromatic systems, these electrophiles are involved.

STRENGTH OF AN ORGANIC ACID

Q. 20. What are the factors that determine the strength of an organic acid?

(*Kerala 2000*)

Ans. (*i*) Nature of the atom holding the hydrogen atom. According to Arrhenius and Bronstead-Lowry concepts an acid is a substance which gives out protons. The strength of an acid is determined by the concentration of hydrogen ions. Strength of the acid actually depends upon the capacity of the atom holding the protons, to accommodate the electrons after, hydrogen has been released Greater the electronegativity and size of the atom holding hydrogen, greater will be the strength of the acid.

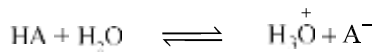


Thus A must be highly electronegative in order that A – H exhibits strong acidic properties.

(*ii*) Inductive and resonance effects in the molecules. Presence of groups which give rise to the above effects influence the strength of the acid. We observe that electron withdrawing groups like $–NO_2$, –CN etc. increase the strength of the acid electron donating groups like alkyl groups decrease the strength.

Q. 21. What is meant by K_a and pK_a values of an acid?

Ans. Consider the dissociation of an acid HA as given below



For this reaction in equilibrium

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

Water is taken in large excess, so its concentration $[H_2O]$ may be taken as constant

$$K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

or

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

where K_a is dissociation constant of the acid. Higher the value of K_a, stronger is the acid.

These days, the strength of an acid is represented as pK_a where

$$pK_a = -\log K_a$$

consider the case of acetic acid. Its K_a value is 1.75×10^{-5}. pK_a value of acetic acid will be given by

$$\begin{aligned} pK_a &= -\log K_a \\ &= -\log (1.75 \times 10^{-5}) \\ &= 4.75 \end{aligned}$$

It may be noted that a higher value of K_a signifies a stronger acid, but a higher value of pK_a signifies a weaker acid.

STRENGTH OF A BASE

Q. 22. What are the factors that determine the strength of a base? *(Kerala, 2000)*

Ans. The following factors determine the strength of a base:

(*i*) Nature of the atom holding the lone pair of electrons. If the atom holding the lone pair of electrons has smaller electronegativity, smaller size and a negative charge, the electron pair will be more easily available for reaction. Consequently, the base will be a strong base.

(*ii*) Magnitude of negative charge or no. of lone pairs of electrons. Greater the magnitude of negative charge or greater the no. of lone pairs of electrons, greater will be the basic strength.

(*iii*) Inductive or resonance effects. Presence of groups exhibiting inductive or resonance effects influence the basic strength. Groups having electron donating effect increase the basic strength whereas groups which show electron withdrawing effect decrease the basic strength.

Q. 23. What is meant by K_b and pK_b value of a base?

Ans. The dissociation of a base can be represented as

$$B + H_2O \rightleftharpoons \overset{+}{B}H + \overset{-}{O}H$$

The equilibrium constant of this reaction is given by

$$K = \frac{[B^+H][OH^-]}{[B][H_2O]}$$

or

$$K\,[H_2O] = \frac{[B^+H][OH^-]}{[B]}$$

Water is taken in large excess, so its concentration may be taken as constant, therefore, the product of K and $[H_2O]$, which are both constants may be taken as K_b, another constant K_b is called the dissociation constant of the base, higher the K_b value of a base, greater is the basic strength.

These days the basic strength is represented by pK_b.

where $$pK_b = -\log K_b$$

For example for methylamine $K_b = 4.4 \times 10^{-4}$

$$\begin{aligned} pK_b &= -\log K_b \\ &= -\log (4.4 \times 10^{-4}) \\ &= 3.36 \end{aligned}$$

It is noteworthy that a greater value of K_b signifies greater basic strength whereas a greater value of pK_b signifies smaller basic strength.

Q. 24. Classify the following as nucleophiles and electrophiles: H_3O^+, NH_3, $AlCl_3$, ROH, BF_3, CN^-, SO_3.

Ans.

Nucleophiles	**Electrophiles**
NH_1	H_3O'
ROH	$AlCl_3$
CN-	BF,
	SO (Sulphenium ion)

Q. 25. Pick up from the following, the electrophiles and nucleophiles:

AICl,, PH,, HNO_3, @N

Ans. Electrophiles: AlCl , $HNO_,$.

Nucleophiles: PH,, R_3N.

Q. 26. Pick up from the following, the electrophiles and nucleophiles:

BF,, NH_3, ROH, SnCl4.

Ans. Electrophiles : BF,, $SnCl_4$.

Nucleophiles : NH , ROH.

ASSIGNING FORMAL CHARGE

Q. 27. Discuss the method **for** assigning **formal** charges on intermediates **and ionic** species.

Ans. Formal charge on a intermediate or an ionic species is calculated from Lewis structure. The main features of this method are given below

1. The average electrons around an atom in a given species is equal to half the number of electrons present in bond pairs plus the number of non-bonding electrons.

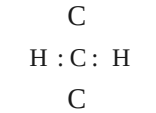
$$\text{Average electrons} = \frac{1}{2} \times \text{No. of electrons in bond pairs} + \text{No. of non-bonding electrons.}$$

2. If the no. of average electrons present around an atom is equal to the no. of valence electrons in the neutral atom, there is no charge on the species.
3. If the average electrons present around an atom is less than the no. of valence electrons in the neutral atom, the species carries a positive charge.
4. If the average electrons on an atom in a species is more than the valence electrons on that atom, the species carries a negative charge.

The examples that following will illustrate the point.

Average Charge on Methane

The Lewis structure of methane is :



There are four C —H bonds. Each bond means one pair of electrons shared between carbon and hydrogen. In each one electron is possessed by carbon and one electron is possessed by hydrogen.

Thus electrons possessed by carbon = $1 \times 4 = 4$

The no. of valence electrons in carbon atom = 4. Since the two values are the same, there is no net charge on the carbon.

UNIT-III

UNSATURATED HYDROCARBONS (ALKENES AND ALKYNES)

General methods of preparation, physical and chemical properties, Saytzeff and Hoffmann eliminations (with mechanism), Electrophilic Additions, (H2, HX) mechanism (Markonikoff's/ Anti Markonikoff's addition) with suitable examples-syn and anti-addition. addition of X2, HX. Oxymercuration demercuration, ozonolysis, hydroxylation, Diels Alder reaction,1,2- and1,4-addition reactions in conjugated dienes. Reactions of alkynes; acidity, electrophilic and nucleophilic additions, hydration to form carbonyl compounds, Alkylation of terminal alkynes

General methods of preparation, physical and chemical properties:

Alkenes (C_nH_{2n})

- Definition: Hydrocarbons containing at least one C=C double bond.
- Hybridization: Each carbon in the double bond is sp^2 hybridized, planar geometry (~120°).
- Bonding: One σ-bond (overlap of sp^2 orbitals) + one π-bond (sidewise overlap of p orbitals).
- General formula: C_nH_{2n} (acyclic, one double bond).

. General Methods of Preparation of Alkenes

(A) From Alkyl Halides (Dehydrohalogenation)

- Reagent: **Alcoholic KOH**, heat.
- Reaction:

$$R{-}CH_2{-}CH_2X \xrightarrow[\Delta]{\text{alc.KOH}} R{-}CH{=}CH_2 + HX$$

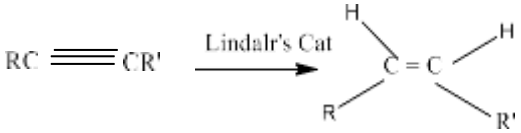
(B) From Alcohols (Dehydration)

- Reagent: **Conc. H_2SO_4** or **H_3PO_4**, heat.
- Reaction:

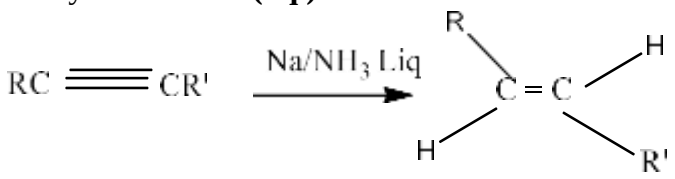
$$R{-}CH_2{-}CH_2OH \xrightarrow[\Delta]{\text{conc.}H_2SO_4} R{-}CH{=}CH_2{+}H_2O$$

C) By Partial Hydrogenation of Alkynes

- Catalyst: **Lindlar's catalyst → cis-alkenes**.



- Catalyst: **Na / NH_3 (liq.) → trans-alkenes**.



D)From Geminal or Vicinal Dihalides
Reagent: Zn/alcohol or $NaNH_2$.
Reaction: R-CHX-CHX-R' → R-CH=CH-R' + 2HX

2. Physical Properties of Alkenes

State: C_2–C_4 gases; C_5–C_{17} liquids; higher → waxy solids.
Boiling point increases with molecular mass; cis isomers have higher b.p. than trans due to dipole moment.
Insoluble in water (nonpolar), soluble in organic solvents.
Density < 1 (lighter than water).
Lower alkenes have a faint sweet odour.

Saytzeff's Rule (Zaitsev's Rule)

Saytzeff's Rule, also known as Zaitsev's Rule, is an empirical rule formulated by Russian chemist Alexander Zaitsev that predicts the major product in elimination reactions. The rule states that in an elimination reaction, the alkene formed in greatest amount is the one that corresponds to removal of hydrogen from the β-carbon having the fewest hydrogen substituents[1][2]. This results in the formation of the most substituted and thermodynamically stable alkene as the major product

Definition and Statement

The rule can be formally stated as: "When more than one elimination product is possible, the most substituted alkene is formed as the major product" The stability order of alkenes follows: monosubstituted < disubstituted < trisubstituted < tetrasubstituted

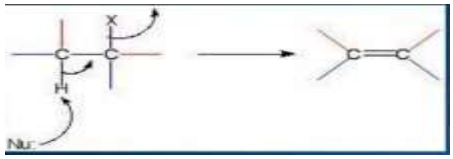
Mechanism of Saytzeff's Rule

Saytzeff's rule applies to both **E1 and E2 elimination mechanisms**

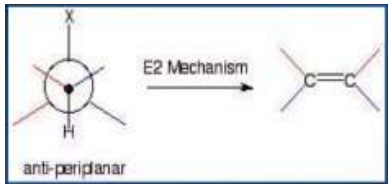
E2 Mechanism (Bimolecular Elimination)

The E2 mechanism involves a **concerted, one-step process** where bond breaking, and formation occur simultaneously

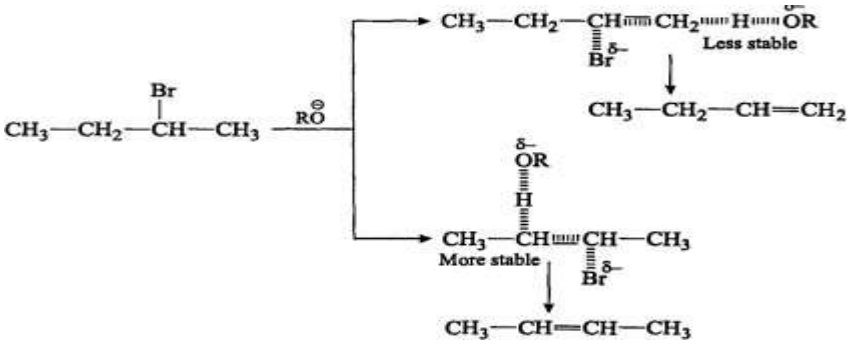
1. **Concerted Process**: A strong base removes a β-hydrogen while the leaving group departs simultaneously



2. **Stereochemical Requirement**: The β-hydrogen and leaving group must be **antiperiplanar** (180° apart) for optimal orbital overlap



3. **Rate Law**: Second-order kinetics: Rate = k[RX][Base]
4. **Product Formation**: The more substituted alkene forms preferentially due to its greater thermodynamic stability. The Transition state has Double bond character which lowers energy and gives stable alkene

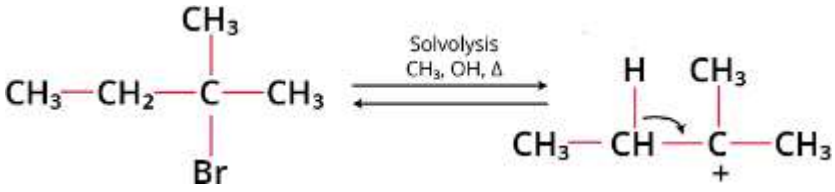


E1

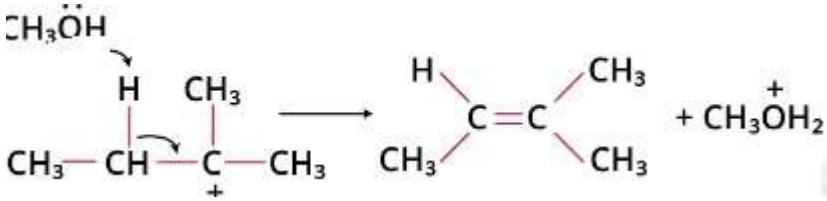
Mechanism (Unimolecular Elimination)

The E1 mechanism follows a **two-step process** involving carbocation formation

1. **Step 1 (Rate-determining)**: Loss of leaving group to form a carbocation intermediate



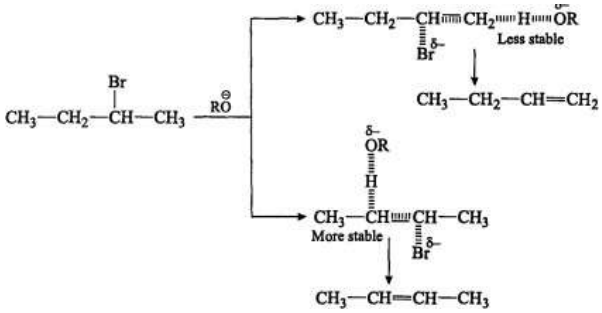
2. **Step 2**: Base removes a β-hydrogen from the carbocation, forming the alkene



3. **Carbocation Stability**: Tertiary > Secondary > Primary carbocations
4. **Rate Law**: First-order kinetics: Rate = k[RX]

Example of Saytzeff's Rule

When **2-bromobutane** undergoes dehydrohalogenation with alcoholic KOH



Major product: 2-butene (disubstituted, more stable)

Minor product: 1-butene (monosubstituted, less stable)

The **2-butene is favoured** because it has two alkyl groups attached to the double bond, making it more substituted and thermodynamically stable

Hofmann's Rule

Hofmann's Rule represents the opposite trend to Zaitsev's rule and applies specifically to elimination reactions involving quaternary ammonium salts The rule states that the major alkene product is the least substituted and least stable product

Definition and Statement

Hofmann's Rule: In eliminations involving quaternary ammonium salts or other bulky leaving groups, **the** least substituted alkene becomes the major product due to steric hindrance effects

Mechanism of Hofmann Elimination

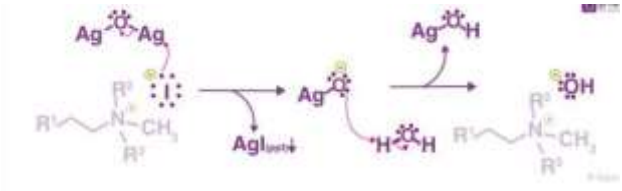
The **Hofmann elimination** (also called **exhaustive methylation**) occurs through a multi-step process

Step 1: Exhaustive Methylation

1. **Primary, secondary, or tertiary amine** reacts with **excess methyl iodide (CH_3I)**
2. **Complete methylation** occurs, forming a **quaternary ammonium iodide salt**
3. **SN2 mechanism**: Each methylation follows nucleophilic substitution

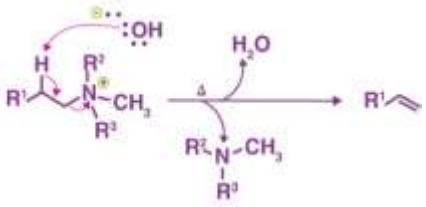
Step 2: Anion Exchange

1. **Silver oxide (Ag_2O)** treatment replaces iodide with hydroxide
2. **AgI precipitates** as an insoluble salt
3. **Quaternary ammonium hydroxide** is formed



Step 3: E2 Elimination

1. **Heating (100-200°C)** initiates the elimination
2. **Hydroxide acts as base**, abstracting β-hydrogen
3. **Trimethylamine (NR_3) leaves** as the leaving group
4. **Antiperiplanar requirement** still applies, but steric effects dominate



Why Hofmann Rule Gives Less Substituted Products

The **steric bulk** of the quaternary ammonium leaving group causes the base to preferentially abstract hydrogens from **less hindered positions**

1. **Steric Hindrance**: The bulky NR_3^+ group creates unfavourable interactions with alkyl substituents
2. **Conformational Effects**: The conformation required for Zaitsev product formation becomes energetically unfavourable
3. **Accessibility**: β-hydrogens on less substituted carbons are more accessible to the base

Example of Hofmann Elimination

Propylamine exhaustive methylation

1. **$CH_3CH_2CH_2NH_2$ + excess CH_3I → $CH_3CH_2CH_2N^+(CH_3)_3I^-$**
2. **Ag_2O/H_2O treatment → $CH_3CH_2CH_2N^+(CH_3)_3OH^-$**
3. **Heat → $CH_2{=}CHCH_3$** (propene) **+ $N(CH_3)_3$**

The **propene** (less substituted) forms as the major product rather than a more substituted alternative[22].

Key Differences Between Saytzeff and Hofmann Rules

Aspect	Saytzeff Rule	Hofmann Rule
Product Preference	Most substituted alkene[25][26]	Least substituted alkene[25][26]
Stability	More stable product[25][3]	Less stable product[25][22]
Leaving Groups	Halides, hydroxyl groups[1][2]	Quaternary ammonium salts[16][17]
Mechanism	E1 and E2 both applicable[3][5]	Primarily E2[17][20]
Driving Force	Thermodynamic stability[2][3]	Steric hindrance effects[18][20]

Exceptions to Saytzeff's Rule

Several important exceptions exist to Zaitsev's rule

1. Bulky Bases

When **bulky bases** like **tert-butoxide** are used with bulky substrates, the **Hofmann product** becomes favored due to steric hindrance

2. Poor Leaving Groups

Fluoride and other poor leaving groups can lead to non-Zaitsev products

3. Conformational Constraints

In **cyclohexane rings**, E2 elimination requires **antiperiplanar geometry**, which may not be available for the most substituted pathway

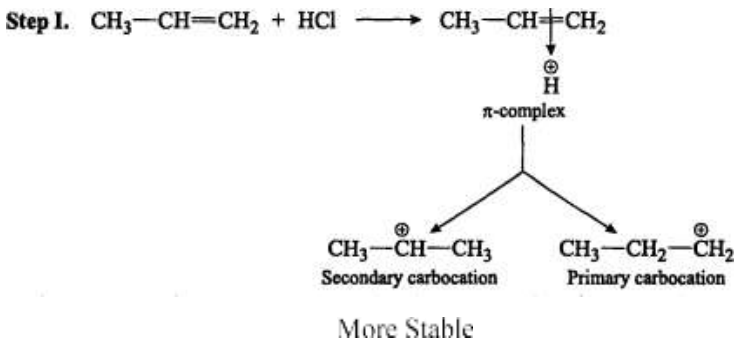
4. Conjugation Effects

When **conjugated systems** can form, they may override the normal substitution preference

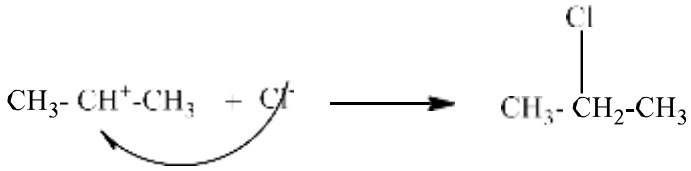
Markovnikov's Addition: In the ionic addition of HX to an alkene (no peroxides), the hydrogen attaches to the carbon with more hydrogens, and the halogen attaches to the more substituted carbon. This outcome is controlled by carbocation stability.

Mechanistic Steps

1. Step 1: Protonation of double bond — π electrons attack H of HCl; bond between H–Cl breaks, generating Cl^-. Intermediate: Carbocation on more substituted carbon.



2. Step 2: Nucleophilic attack — Cl^- attacks the carbocation, forming the alkyl halide product.



Reaction Conditions that Favor Markovnikov

- Acidic ionic conditions.
- HX (HCl, HBr, HI) with no peroxides or radical initiators.
- More stable carbocation intermediate determines regiochemistry.
- Hyperconjugation and resonance stabilize carbocations.

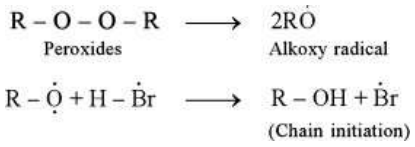
Example Reactions

- CH3CH=CH2 + HBr → CH3CHBrCH3 [HBr, no peroxides]
- CH2=CHCH3 + HCl → CH3CHClCH3 [HCl]
- CH3CH=CHCH3 + HI → CH3CHI–CH2CH3 [HI]

  Anti-Markovnikov's Addition: In the radical addition of HX to an alkene (with peroxides, light, or radical initiators), the regiochemistry is reversed: the halogen attaches to the less substituted carbon. This is due to radical stability controlling the reaction pathway.

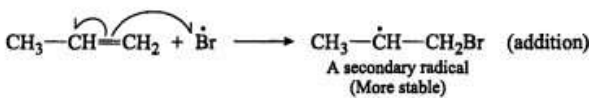
Mechanistic Steps

1. Initiation: Peroxide decomposes into radicals (RO·). RO· abstracts H from HBr to create Br· radical.



1. Propagation Step 1: Br· radical attacks double bond and new C–Br bond on less substituted carbon; carbon radical forms on more substituted carbon. halogen bonds to less substituted carbon to maximize stability of intermediate radical.

2.



3. Propagation Step 2: Carbon radical abstracts H from HBr and the product is (anti-Markovnikov) + Br· radical regenerated.

$$CH_3 - \dot{C}H - CH_2Br + H - Br \longrightarrow CH_3 - CH_2 - CH_2Br + \dot{B}r$$

(Chain propagation) 1-Bromopropane

4. Termination:

Two radicals combine (minor pathways).

$$\dot{R} + \dot{R}' \longrightarrow R - R'$$

$$\dot{B}r + \dot{B}r \longrightarrow Br_2$$

This was supported by small addition of H_2O_2 can influence a large no of molecules on Alkene and it can be inhibited by addition of Hydroquinone or Diphenyl Amine

Conditions that Favour Anti-Markovnikov

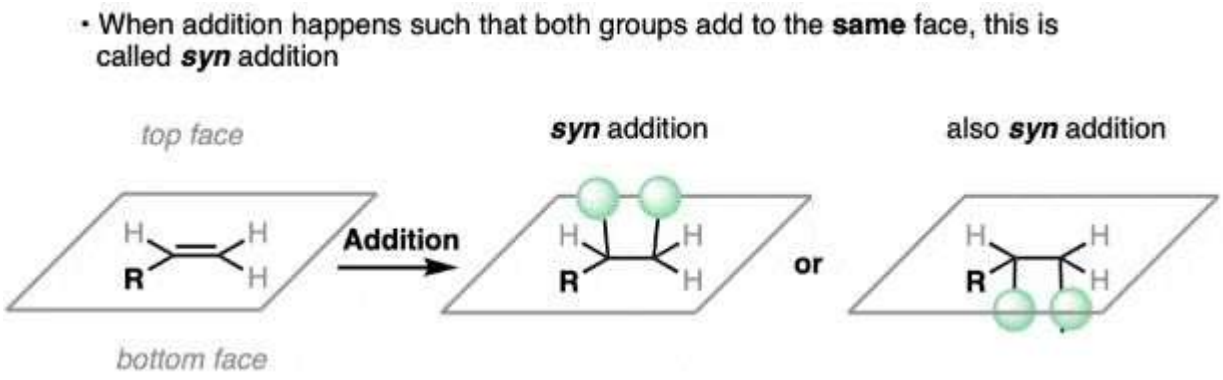
- Presence of peroxides (RO–OR).
- Radical initiators or light (hv).
- radical stability under radical conditions
- The peroxide effect is observed only in addition of HBr but not observed in addition of HCI and H-1.

Example Reactions

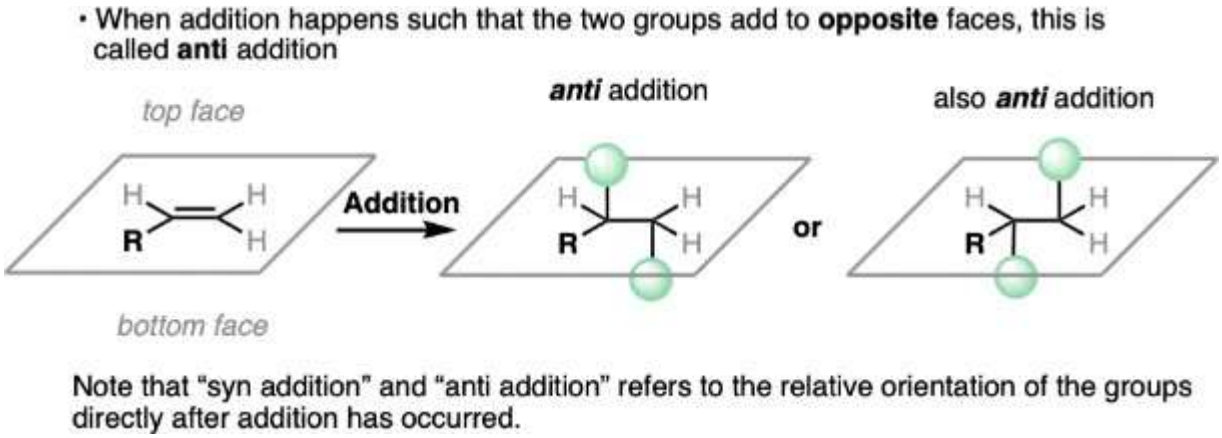
- CH3CH=CH2 + HBr → CH3CH2CH2Br [HBr, peroxides]
- CH2=CHCH3 + HBr → CH3CH2CH2Br [HBr, ROOR]

Syn and Anti Addition in Alkenes

Syn Addition: This is an addition reaction where **two groups/atoms are added to the same side (or face) of a double bond** in an alkene. As a result, both substituents are oriented in the same direction in the resulting product



- **Anti Addition**: Here, **the two groups/atoms are added on opposite sides (or faces) of the double bond**. The substituents end up on different sides, leading to a trans orientation in the product

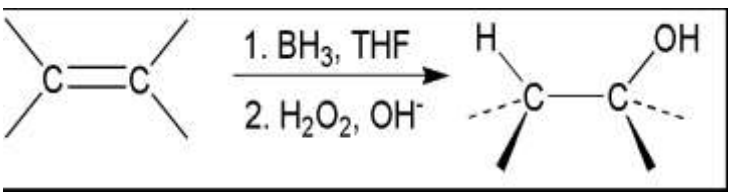


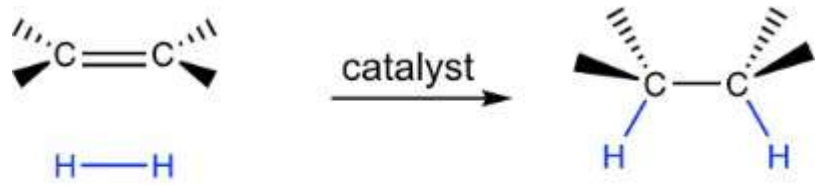
Key Differences

Criteria	Syn Addition	Anti Addition
Definition	Addition to **same side/face** of double bond	Addition to **opposite sides/faces** of double bond
Stereochemistry	Leads to **cis/isomers** or groups together	Leads to **trans/isomers** or groups apart
Common Examples	Hydroboration-oxidation, catalytic hydrogenation, dihydroxylation with OsO_4 or $KMnO_4$[2][3][4][5]	Halogenation (e.g., Br_2), oxymercuration-demercuration, epoxidation then ring opening[2][3][4][6]

Mechanistic Insight & Examples

- **Syn Addition**:
  - Both substituents add from the same side of the π-bond.
  - Examples:
    - **Hydroboration-Oxidation**: Addition of BH_3 followed by oxidation (adds H and OH syn to each other).





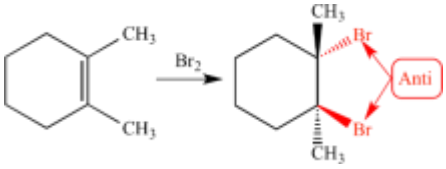
catalytic hydrogenation: syn addition

Catalytic Hydrogenation: Addition of H_2 using metal catalysts (Pd, Pt, Ni) — both hydrogens add to the same face.

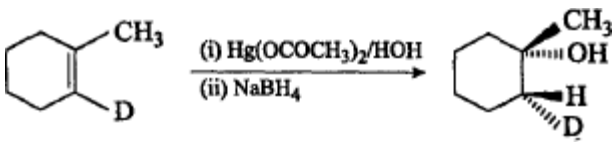
- **Dihydroxylation**: Using OsO_4 or cold, dilute $KMnO_4$, both OH groups add to the same side.

Anti- addition: One group adds from one side of the π-bond, while the other adds from the opposite side. In **anti addition**, the first group blocks one face, so the second must add from the opposite face, causing a trans or anti spatial relationship

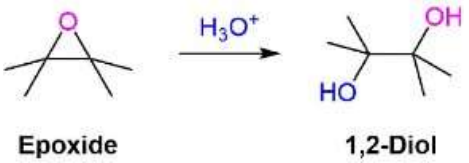
- **Halogenation**: When Br_2 adds to an alkene, a three-membered bromonium ion intermediate is formed; then the Br^- attacks from the opposite side — yielding anti addition and a trans product.



- **Oxymercuration-Demercuration**: Adds OH and Hg(OAc), often in anti fashion.

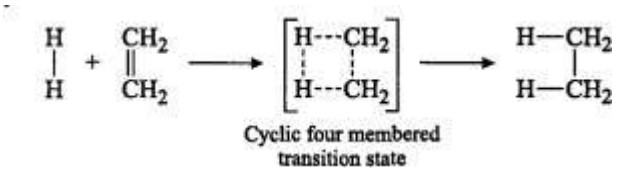


- **Epoxidation followed by Acidic Ring Opening**: Produces trans/anti-diol.

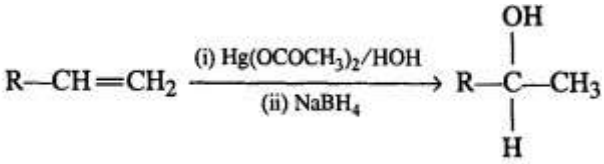


Mechanism

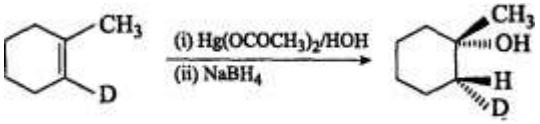
- In **syn addition**, both groups are delivered to the same face of the alkene's plane.



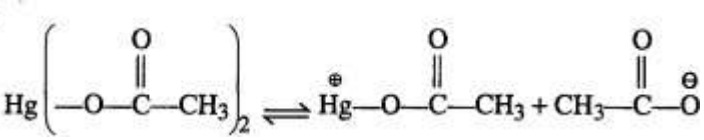
Oxymercuration demercuration: Addition of alkene with mercuric acetate in the presence of water is called oxymercuration reaction. In this case product formation takes place by the formation of bridged carbocation as reaction intermediate. The adduct on reduction with sodium borohydride gives alcohol. This step is known as demercuration, and the overall reaction is also called oxymercuration reduction.



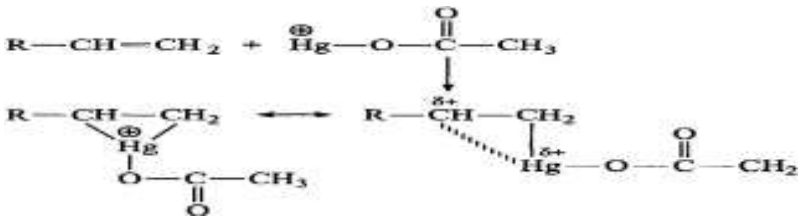
Experimentally it has been found that the product of the reaction is result of the anti addition reaction.



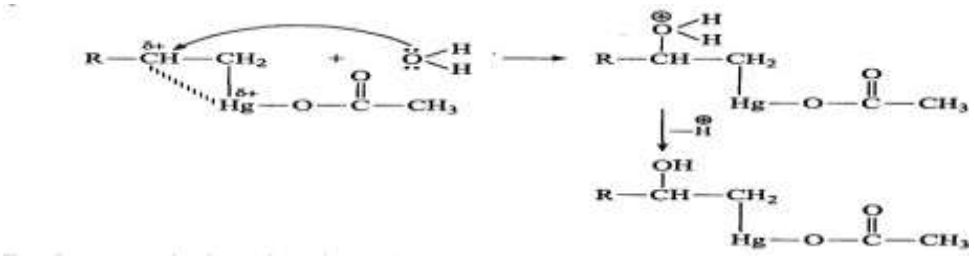
Mechanism:



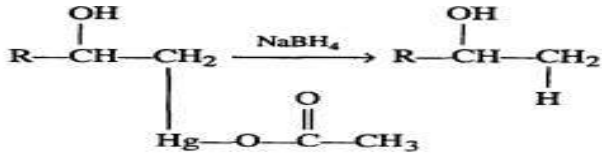
First step:



Second step : In the second step nucleophile attacks on the opposite face of the Hg. Nucleophile will attack on the carbon which has more carbocation character.

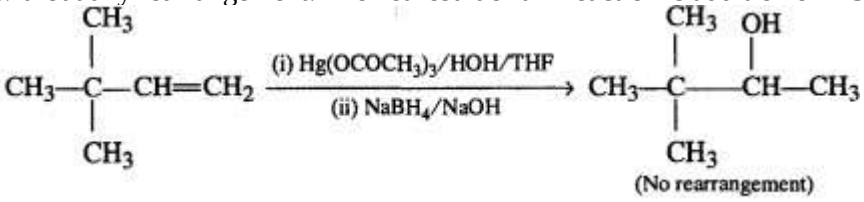


Third step: Sodium borohydride converts carbon-mercury bond into a carbon-hydrogen bond. Because the reaction results in the loss of mercury. it is called demercuration.



In the product both -OH and H are anti to each other.

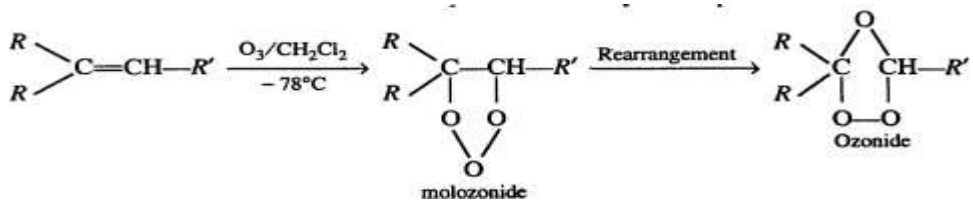
Note 1. Oxymercuration-demercuration .llows the Markovnikov addition of -H and -OH without any rearrangement. The net result of th¢ reaction is addition of HOH.



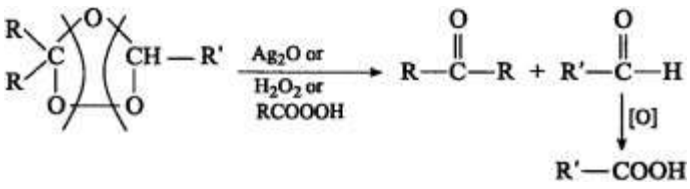
OZONOLYSIS

Ozone undergoes a reaction with olefins in an inert solvent at low temperatures to yield unstable addition compounds called 'ozonides'. These ozonides are not easily isolated and yield carbonyl compounds on further treatment either with boiling water and Zn or zinc and acetic acid.

This overall reaction is called as Ozonolysis.



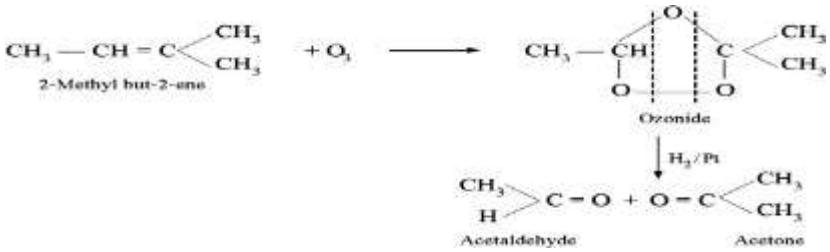
Ozonide converts into carbonyl compound by the addition of reducing agents or oxidizing agents



In this sequence of reactions doubly bonded carbon having no hydrogen converts into keto group

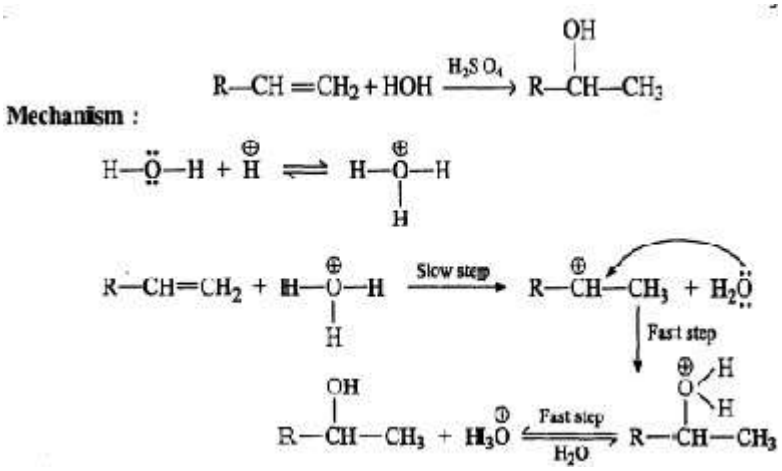
and doubly bonded carbon having hydrogens converts into aldehydes and further aldehydes oxidized into carboxylic acids

Examples



Hydration of Alkenes : Addition of water

Alkenes give addition reaction with water only in the presence of acid as catalyst. The catalyst of the reaction is sulphuric acid.

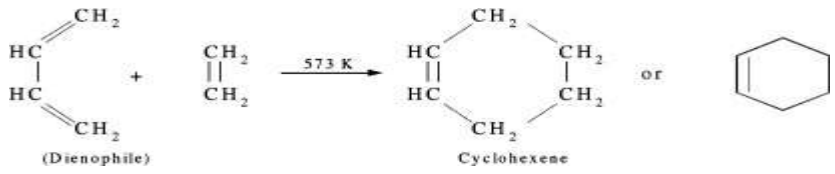


Diels–Alder Reaction

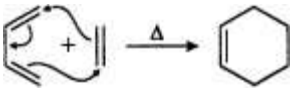
This reaction involves the formation of a six membered ring by the1, 4-addition of an alkene to a conjugated diene. Alkene used in this reaction is generally referred as dienophile and the product formed is called Diels-Alder adduct

Key Features

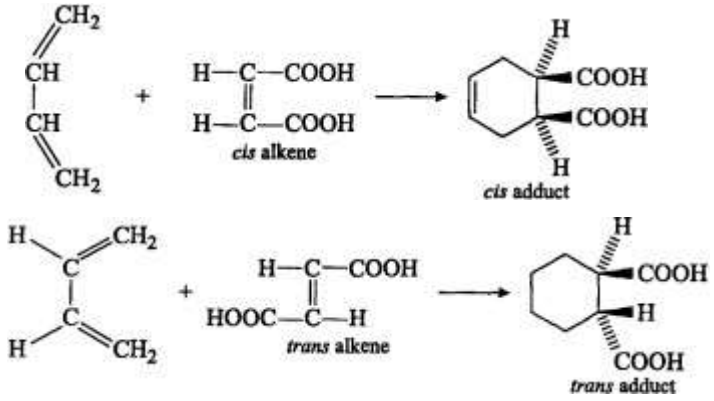
- Type: [4+2] cycloaddition
- Concerted: all bonds form/break in one step
- Pericyclic: cyclic transition state, no intermediates



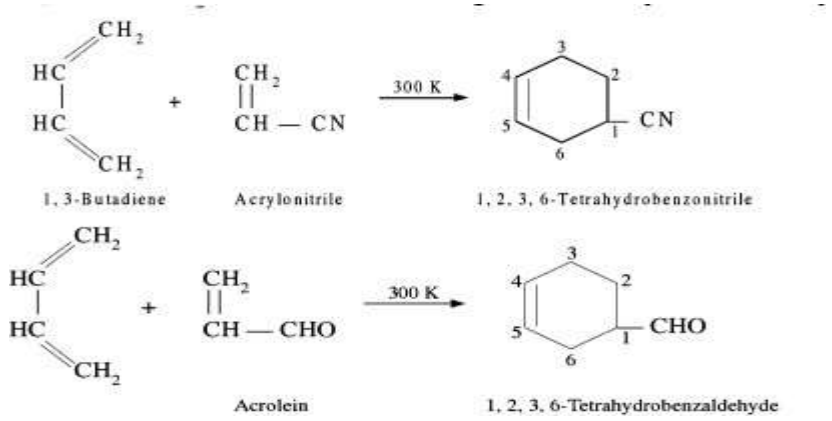
Or



The Diels-Alder reaction is highly stereospecific. The stereochemistry of the diene and dienophile are preserved during adduct formation. This can be seen when cis and trans disubstituted alkenes are used as dienophile



This reaction proceeds faster when the dienophile has electron withdrawing substituents such as -COOH, CHO-NO, and - CN. Thus following reactions take place at low temperatures.



1,2- and1,4-addition reactions in conjugated dienes

1,2-Addition in Alkenes

1,2-addition refers to the addition of a reagent (like HX, H_2, or other electrophiles) to an alkene, where the addition occurs at the **first and second carbon atoms** of the double bond.

- **Mechanism**:
  In 1,2-addition, the double bond of the alkene reacts with the reagent, breaking the pi bond and creating a carbocation intermediate at the more stable position (or the position of least steric hindrance). The electrophile (or nucleophile, depending on the reaction) then attacks the carbocation, leading to the formation of the product.

- **Example**:
  Consider the addition of HBr to but-2-ene:
  $CH_3CH=CHCH_3+HBr \rightarrow CH_3CH_2CHBrCH_3$

  In this case, the HBr adds to the first and second carbons of the double bond, resulting in 1-bromobutane (a 1,2-addition product).

- **Product Structure**:
  The product of a 1,2-addition generally retains the original placement of the substituents on the carbons involved in the double bond. The major product in this case is often the one where the electrophile adds to the carbon of the double bond that forms the more stable carbocation intermediate.

1,4-Addition in Alkenes

1,4-addition, also known as **conjugate addition**, occurs when the reagent adds to the **1st and 4th carbons** of a conjugated system (like a diene or a compound with a conjugated double bond system).

- **Mechanism**:
  In a conjugated diene system (such as buta-1,3-diene), the double bond is shared between two carbon atoms (C1 and C2) and the conjugated system has additional possibilities for electrophilic attack. In **1,4-addition**, the reagent adds to the C1 (where the double bond starts) and the C4 (the terminal carbon of the conjugated system).
- **Example**:
  Consider the addition of HBr to buta-1,3-diene:

  $CH_2=CHCH=CH_2+HBr \rightarrow CH2CHBrCH_2CH_3$

  In this case, HBr adds to C1 and C4, leading to **3-bromo-1-butene** (a 1,4-addition product).

- **Product Structure**:
  The 1,4-addition product places the new substituent (e.g., Br) on the terminal carbon of the conjugated diene, which may lead to a more stable product depending on the reaction conditions.

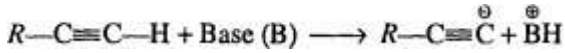
Key Differences Between 1,2- and 1,4-Addition:

1. **Position of Addition**:
   - 1,2-addition occurs directly at the two carbons of the original double bond.
   - 1,4-addition occurs between the first carbon and the fourth carbon of a conjugated system.
2. **Reaction Conditions**:
   - 1,2-addition is typically favoured in conditions where the reaction occurs quickly and with strong electrophiles.
   - 1,4-addition tends to be favoured in conditions with weaker electrophiles or under conditions that stabilize the intermediate anion (e.g., in the presence of a stabilizing solvent or at lower temperatures).
3. **Stability of Products**:

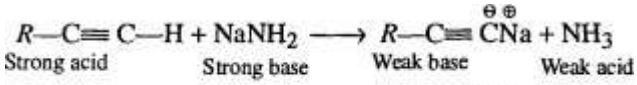
In conjugated systems, 1,4-addition can lead to a more thermodynamically stable product due to conjugation, while 1,2-addition can be a kinetic product

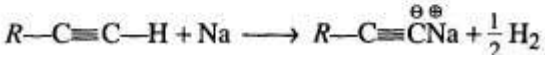
Acidity of Alkynes

The hydrogens in terminal alkynes are relatively acidic because they readily donate proton to strong bases.



When terminal alkynes are treated with sodarnide in liquid ammonia or passed over molten sodium they convert into the corresponding carbanions.

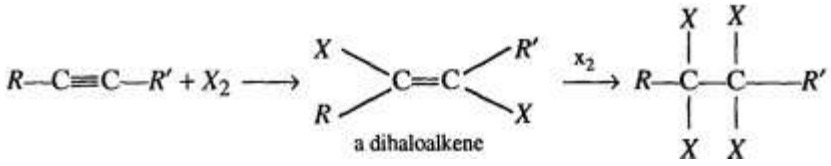




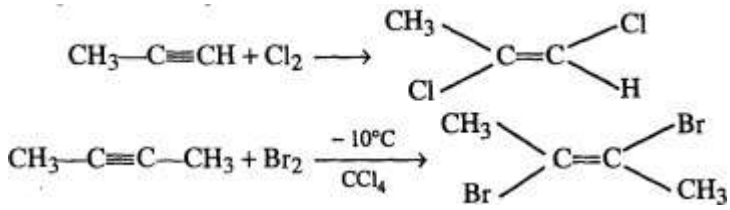
The above two reactions suggest the acidic character of hydrogen in l-alkynes.
Carbon atoms in l-alkynes are sp hybridized, hence have more s character than in
As s electrons are closer to the nucleus than p electrons, s orbitals are more electronegative than p orbitals Therefore, increasing the s character of a hybrid orbital makes the orbital more electronegative and hence they are acidic

ALKYNES ELECTROPHILIC ADDITION REACTIONS

Alkynes undergo addition reactions with 2 molecules of chlorine or bromine



A dihaloalkene is an intermediate in this reaction dihaloalkenes can be prepared by adding calculated amount of halogen (1 mole) to the alkyne at low temperatures. This addition of halogen to an alkyne is predominately an anti-addition.



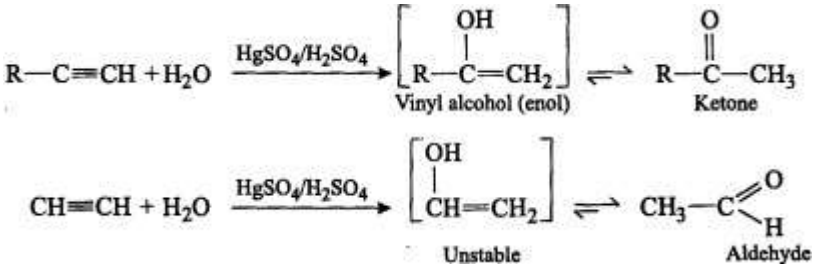
ALKYNES NUCLEOPHILIC ADDITION REACTIONS

Alkynes undergo nucleophilic addition reactions because of the greater stability of the resulting carbanion is more stable formed by the attack of nucleophile . Since the rate determining step involves the formation of vinylic (Sp^2) carbanion

HYDRATION TO FORM CARBONYL COMPOUNDS

Hg metal ions form some sort of complex with alkyne by coordinating with the electrons of the pie (n) bonds This complex formation decreases the electron density around the triply bonded carbon atoms and thus helps in the attack by the nucleophilic reagent

Water adds to carbon-carbon triple bond in the presence of mercuric sulphate and sulphuric acid to form a vinyl alcohol (enol) which readily tautomerizes to the corresponding carbonyl compound. the addition follows Markovnikov rule



Important Questions (Long Answer)

1. Describe the mechanism of electrophilic addition in alkenes, focusing on the Markovnikov's and Anti-Markovnikov's additions.
2. Discuss the Saytzeff and Hoffmann eliminations with suitable examples.
3. Explain the mechanism and importance of ozonolysis in alkenes.
4. Discuss the reactions of alkynes, including their acidity, electrophilic additions, and nucleophilic additions.
5. Explain the Diels-Alder reaction with mechanisms and its significance in organic synthesis.

Important Questions (Short Answer)

1. What is the mechanism of electrophilic addition in alkenes?
2. Write a note on the hydration of alkynes to form carbonyl compounds.
3. Describe the process of syn and anti-addition in alkenes.
4. What is the significance of ozonolysis in organic chemistry?
5. Explain the 1,2- and 1,4-addition reactions in conjugated dienes.

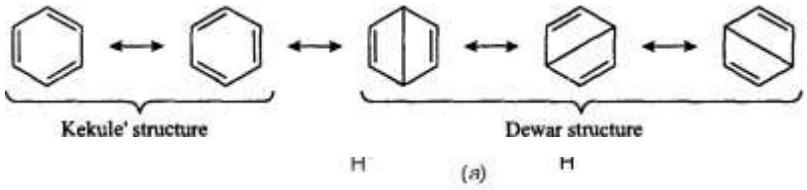
UNIT-IV:BENZENE AND ITS REACTIVITY(9 Hrs.)

Structure of Benzene – Preparation - polymerization of acetylene and decarboxylation- Properties - mechanism of electrophilic aromatic substitution of Friedel- Craft's alkylation and acylation. halogenation and nitration.

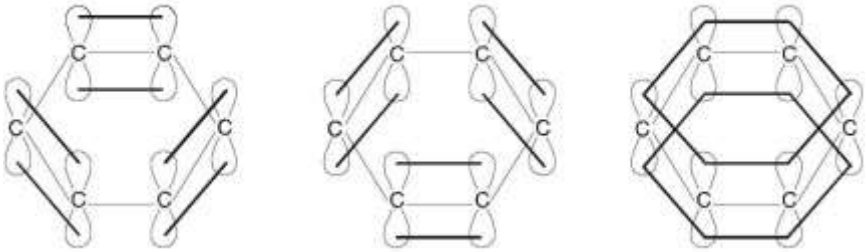
Structure of Benzene: Bonding and Resonance

Benzene: C_6H_6, planar hexagonal ring.

Real structure: resonance hybrid, delocalized π cloud above and below plane.

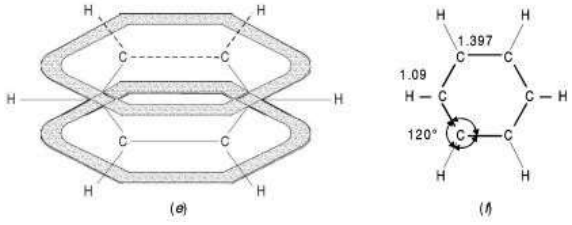


(a)



(b) (c) (d)

Orbital structure. Structure of benzene can be best described by using the orbital concept. Each carbon atom in benzene is sp^2 hybridized and thus forms three bonds, two with adjacent carbon atoms and one with hydrogen. Thus, all the six carbons and six hydrogen atoms lie in the same plane and the angle between two adjacent & bonds is 120° Each carbon is still left with an unhybridized p-orbitals lying above and below the plane of benzene ring. Each one of these p-orbitals overlap sideways on either sides to form two sets of π-electron clouds. [Figs. (b) and (c)]. π electrons are delocalized as these can move over all the six carbon atoms [Fig. (d)]. As a result of this delocalization two continuous ring like electron clouds one above and the other below the plane of carbon atoms [Fig. (e)] are formed. Bond angles and bond lengths in the molecule of benzene are depicted in [Fig. (/)].



(e) (f)

Experimental Evidence:

Bond lengths: All C–C equal (1.39 Å) by X-ray diffraction.

Hydrogenation energies: Cyclohexatriene would release ~360 kJ/mol; benzene releases ~208 kJ/mol

→ resonance energy ~152 kJ/mol.

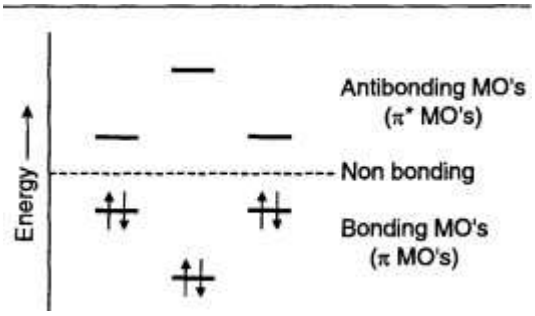
Spectroscopy: NMR shows ring current, equal deshielding.

Molecular Orbital Description:

6 p-orbitals overlap, forming 6 π MOs.

Energy levels: three bonding (π_1, π_2, π_3), three antibonding (π^*).

Filling: 6 π electrons fully occupy bonding orbitals.



Physical Properties

Non-polar liquid, bp = 80 °C, mp = 5.5 °C.

Insoluble in water, soluble in organic solvents.

Density: 0.88 g/cm³.

Toxic, carcinogenic; handle with care.

Preparation of Benzene

1. From Acetylene (Polymerization)
   [red hot Fe tube, 600 °C]

C_2H_2 → C_6H_6
(acetylene)

Mechanism: trimerization via radical intermediates.

Formation of the First Radical

Acetylene molecules are activated by either high temperature, UV irradiation, or catalytic surfaces, resulting in the formation of a carbon-cantered acetylene radical

CH≡CH → ·C≡CH

The acetylene radical reacts with another acetylene molecule to form a butadiyne-type radical intermediate ·CH = C-C≡CH

The butadiyne-type radical intermediate reacts with a third acetylene molecule to form a six-carbon linear radical

CH≡CH + ·CH = C-C≡CH → ·CH2-CH = CH-CH=CH- CH2 ·

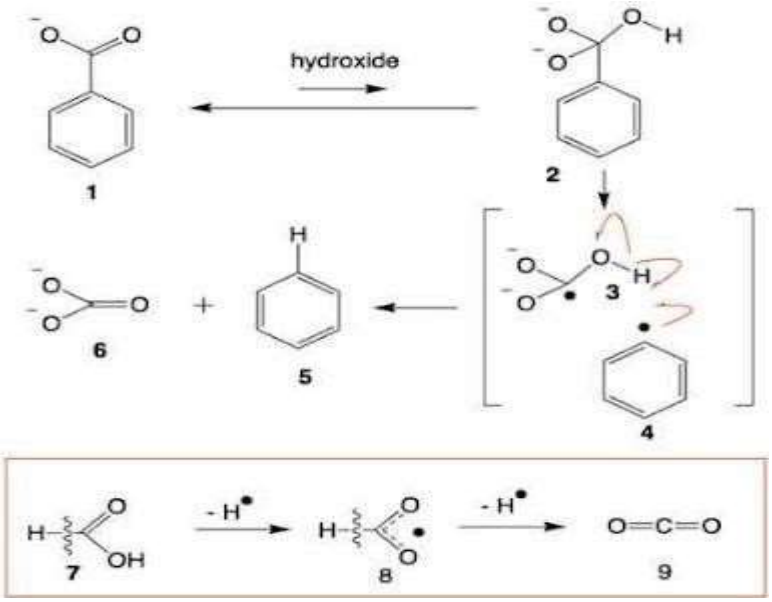
The six-carbon radical undergoes intramolecular radical cyclization, forming a cyclohexatriene radical intermediate

further The cyclohexatriene radical intermediate undergoes hydrogen shifts and electron rearrangement, resulting in aromatization and formation of the benzene ring

2. Decarboxylation of Benzoic Acid

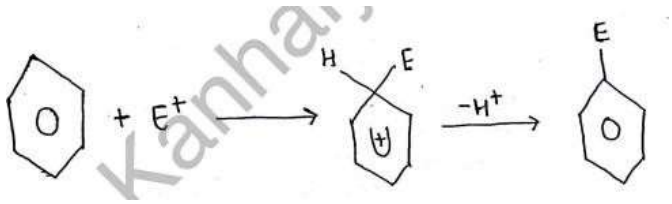
$$C_6H_5COONa + NaOH \xrightarrow{[CaO,\ \Delta]} C_6H_6 + Na_2CO_3$$

Mechanism: carboxylate → carbanion → decarboxylation.
addition of hydroxide to the carbonyl group of the benzoate anion 1 occurs to form adduct 2. Bond dissociation of 2 leads to phenyl radical 4 and radical 3

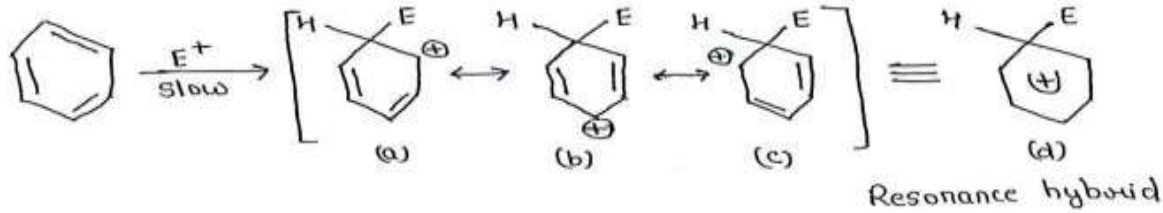


Electrophilic Substitution Mechanism:

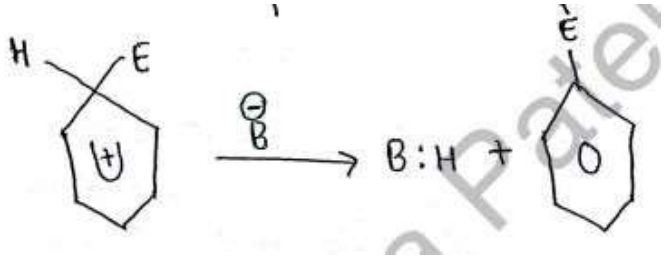
Electrophilic substitution is a type of replacement reaction where a hydrogen atom or any other radical attached to a benzene nucleus is replaced by an electrophilic reagent. The mechanism of all electrophilic substitution reactions is approximately the same. When an electrophilic reagent approaches a benzene ring, the equal distribution of electron density in the ring is disturbed. This disturbance leads to the formation of two centers: one with high electron density (δ-) and another with low electron density (δ+).The electrophile, being electron-deficient, links with the carbon atom that has high electron density (δ-), forming an intermediate compound. This intermediate compound then loses a proton (H+) in the presence of a base, resulting in the formation of a mono-substituted compound is formed. Electrophilic Substitution is a bimolecular (E2) reaction in which formation of intermediate Compound is a rate determining step



This reaction takes place in two steps :-
(i) In first step electrophilic reagent attacks any Carbon of benzene ring and forms intermediate Complex which is a resonance hybrid of a,b and c.

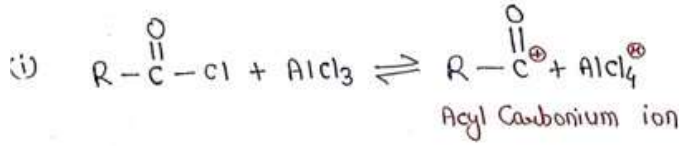


Out of 6π-electrons of benzene ring, 2π electrons are used in bond formation with electrophilic reagent and remaining 4π electrons are delocalized on 5 Carbon atoms. delocalized positive charge remains on all five Carbon atoms (d) and thus, intermediate Compound is formed.
And (ii) In Second step this intermediate Compound in presence of any base loses proton and change into benzenoid form a substitution product is formed



Friedel - Grafts alkylation:
In this reaction reacted with an aromatic hydrocarbon is an alkyl halide in the presence of anhydrous aluminum chloride.
For example

Mechanism:
The reaction begins with the generation of an electrophile, an alkyl carbocation. This occurs when the alkyl halide (R-Cl) reacts with a Lewis acid, such as anhydrous aluminum chloride ($AlCl_3$). The Lewis acid accepts the lone pair of electrons from the chlorine atom, forming a complex that facilitates the departure of the chloride ion, leaving behind a carbocation (R^+) and a tetra chloroaluminate anion ($AlCl_4^-$).

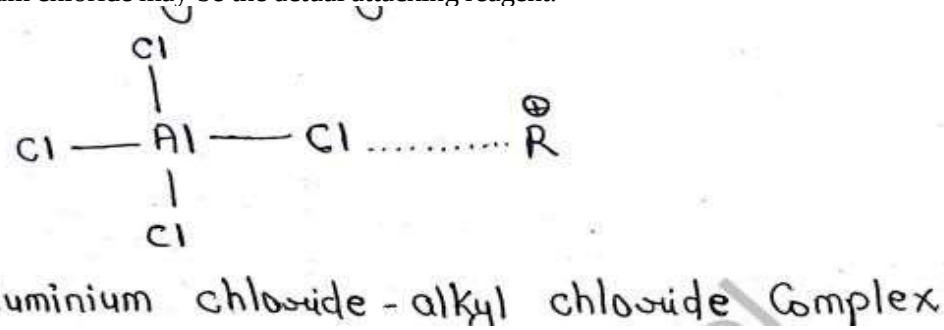


The generated carbocation (R+), acting as an electrophile, attacks the electron-rich aromatic ring. This step is typically the slow, rate-determining step of the reaction. The π electrons of the aromatic ring attack the carbocation, forming a new C-C bond and disrupting the aromaticity of the ring, leading to

the formation of a resonance-stabilized carbocationic intermediate known as a sigma complex or arenium ion. This intermediate is stabilized by resonance, with the positive charge delocalized over the ring.

A proton is removed from the arenium ion, restoring the aromaticity of the ring and forming the alkylbenzene product, while also regenerating the Lewis acid catalyst.

It is also possible that the free alkyl Carbonium may not exist. Complexes of alkyl chloride and the aluminum chloride may be the actual attacking reagent.



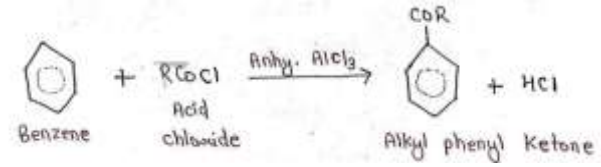
Limitation of Friedel Craft alkylation

- Vinyl and aryl halides do not generate stable carbocations. As a result, they are ineligible for use in the Friedel-Crafts alkylation procedure.
- Aromatic rings with deactivating groups may not be ideal for Friedel-Crafts alkylation because the deactivating groups remove the electron density from the benzene ring, making a nucleophilic attack on the benzene ring impossible.
- The aniline amine group interacts with anhydrous aluminum chloride to generate a compound that deactivates the ring. As a result, the response is incomplete.
- Alkylation occurs on the benzene ring when it combines with an alkyl halide in the presence of anhydrous Lewis acid, however, polyalkylation may occur due to the activating nature of the alkyl group. To avoid this problem, a considerable amount of aromatic samples must be taken.
- The Lewis acid catalyst AlCl3 frequently binds with aryl amines, rendering them inactive.
- Isomerization and disproportionation can occur in the presence of excess catalysts and at high temperatures.

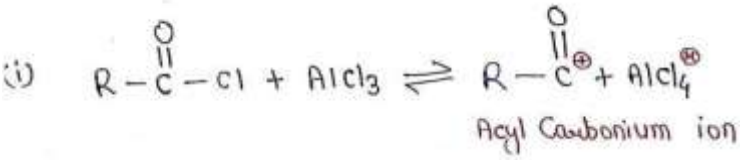
Friedel - Crafts Acylation :

In this reaction an aromatic hydrocarbon reacts with an acid halide or acid anhydride in the Presence of anhydrous aluminum chloride to form alkyl aryl ketone.

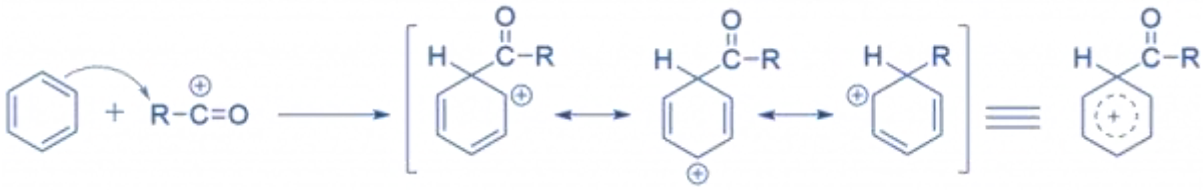
for example



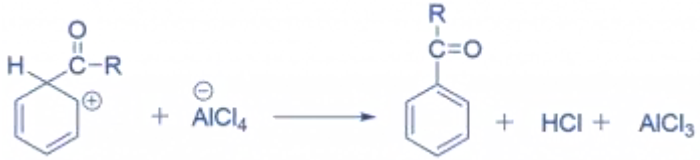
In this reaction, Lewis's acid $AlCl_3$ polarizes the acid chloride to form also Known electrophilic an acyl Carbonium ion.



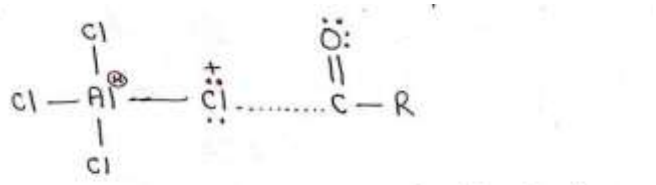
This ion as the acylium ion makes attack an on the benzene nucleus. When RCO^+ attacks an aromatic ring, an arenium ion or sigma complex is formed. Another carbon in this arenium ion has gone through sp3 hybridization. This arenium ion achieves stability in a resonance configuration. Because electron delocalization occurs at the sp3 hybridized carbon,' the aromatic property of the sigma complex or intermediate ion' is lost.



The intermediate complex is now deprotonated, restoring the ring's aromaticity. A chloride ion extracts the proton from the complexed Lewis acid, creating HCl. The $AlCl_3$ catalyst has been regenerated.



In this reaction, instead of RCO^+, the actual attacking reagent may be the acyl chloride aluminum chloride Complex.



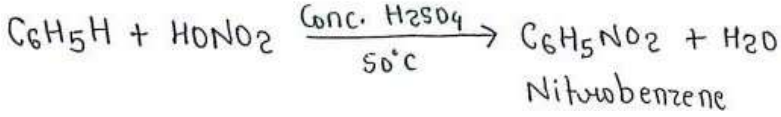
Aluminium chloride - acyl chloride Complex

Limitation of Friedel Craft acylation

- Acylation can only produce ketones. Because of the reaction circumstances, HCOCl decomposes into CO and HCl.
- The Lewis acid catalyst AlCl3 frequently binds with aryl amines, rendering them inactive.
- Instead of the required ring acylation, amines, and alcohols can produce competing N or O acylation.
- Because they are the least reactive, compounds like mono halo benzenes do not respond or participate in the Friedel-Crafts acylation reaction.

Nitration :-

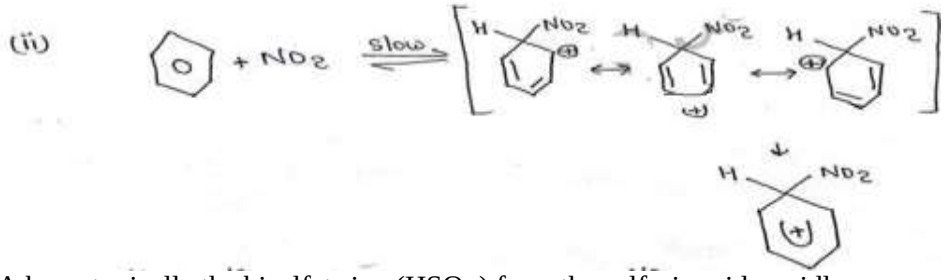
On heating benzene with mixture of Conc. HNO_3 and Conc. H_2SO_4 (nitrating mixture), nitrobenzene is formed



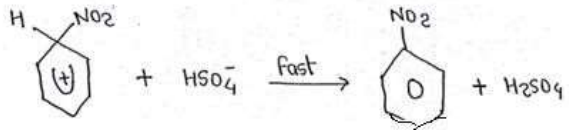
Mechanism :- This reaction takes place by electrophilic nitronium ion (NO^+_2).

Nitric acid $HONO_2$ reacts with sulfuric acid (H_2SO_4) to generate the nitronium ion (NO^+_2), which is the active electrophile in this reaction.

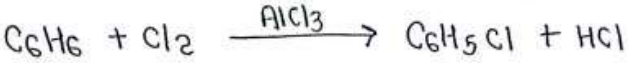
The nitronium ion (NO^+_2) attacks the electron-rich benzene ring in a slow, rate-determining step, forming a resonance-stabilized carbocation intermediate known as the arenium ion or sigma complex. This involves the breaking of aromaticity in the benzene ring.



A base, typically the bisulfate ion (HSO_4^-) from the sulfuric acid, rapidly removes a proton from the arenium ion. This step restores the aromaticity of the ring and forms nitrobenzene, along with regenerating sulfuric acid.

iii) 

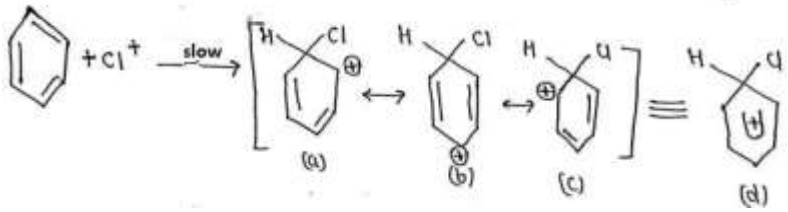
Halogenation :-
When aromatic hydrocarbons react with halogen at room temperature in dark and in presence of any halogen Carrier ($AlCl_3$, BF_3 Iron, J_2,etc.) aryl halide is formed. For example: benzene forms chlorobenzene with chlorine in presence of halogen carrier



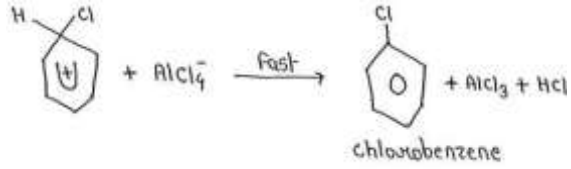
If halogen is in excess, Further halogenation proceeds and mixture of 0- and P-dichlorobenzene is formed.

Mechanism :- Halogenation takes place by electrophilic reagent chloronium ion or in general halonium ion. chlorine molecule reacts with Catalyst with Catalyst and Cl^+ is formed

(ii) chloronium ion attacks on double bond of benzene ring an addition product Carbocation is formed. It is hybrid of 3 structures (a. b and c) a resonance



In presence of $AlCl_3$, Carbocation loses one proton and now Structure becomes Chlorobenzene



Unit 4: Benzene and its Reactivity

Long Answer Questions (10 Marks)

1. Explain the structure of benzene and its resonance properties.
2. Describe the mechanism of electrophilic aromatic substitution with examples of Friedel-Crafts alkylation and acylation.
3. Discuss the polymerization of acetylene and its role in organic chemistry.

4. Explain the decarboxylation of benzene derivatives with examples.
5. Discuss the electrophilic aromatic substitution reactions with a focus on nitration and halogenation.

Short Answer Questions (5 Marks)

1. What is the mechanism of Friedel-Crafts alkylation?
2. Write a short note on the polymerization of acetylene.
3. Discuss the halogenation reaction of benzene.
4. What is the decarboxylation of benzene derivatives?
5. Explain the concept of aromaticity and its importance in organic chemistry.

UNIT-V: Orientation of aromatic substitution (9 h)

Concept of aromaticity, Huckel's rule - application to Benzenoid (Benzene, Naphthalene) and Non - Benzenoid compounds (cyclo propenyl cation, cyclopentadienyl anion and tropylium cation) Orientation of aromatic substitution - ortho, para and meta directing groups. Ring activating and deactivating groups with examples (Electronic interpretation of various groups like NO2 and Phenolic). Orientation of (i) Amino, methoxy and methyl groups (ii) Carboxy, nitro, nitrile, Carbonyl and sulphonic acid groups (iii) Halogens

Concept of aromaticity: Aromatic compounds are those which resembles benzene like chemical behaviour and are extremely stable cyclic molecules due to their unique electron delocalization

Characteristics.

(1) Although their molecular formulae suggest a high degree of unsaturation, yet they fail to give to characteristic tests of unsaturated compounds (Bayer's test).

(ii) They undergo readily certain electrophilic substitution reactions such as nitration, halogenation, sulphonation, Friedel-Crafts alkylation, and acylation, etc.

(iii) Their molecules are flat or nearly flat as shown by physical methods such as X-ray and electron diffraction methods

Huckel's rule:

According to Huckle a compound is said to be aromatic if it satisfies the following conditions:

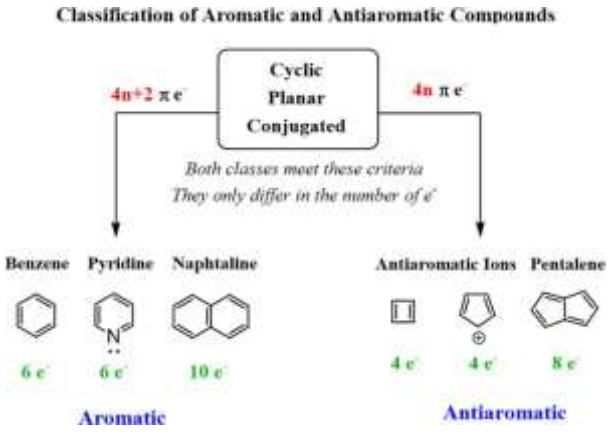
1. Planar (all atoms lie in one plane).
2. Cyclic conjugation (continuous overlap of p-orbitals).
3. Complete delocalization of π-electrons.
4. Huckel's rule: it must contain (4n + 2) π electrons (n = 0, 1, 2, …).

If a ring has 4n π electrons, it is antiaromatic (unstable). If it does not have continuous conjugation, it is non-aromatic

Why 4n+2 Electrons?

According to Huckel's Molecular Orbital Theory, a compound is particularly stable if all of its bonding molecular orbitals are filled with paired electrons. This is true of aromatic compounds, meaning they are quite stable

Examples :



Benzenoid and Non-Benzenoids:

Aromatic compounds can be broadly divided into two categories: benzenoids (those containing a benzene ring) and non-benzenoids (those not containing a benzene ring)

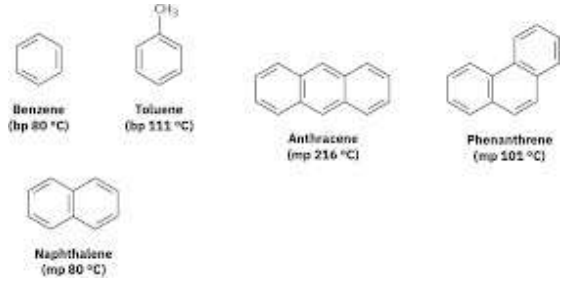
Benzenoid Compounds"

Definition: Compounds containing at least one benzene ring (C_6H_6) with aromatic character.

Characteristics:

- Planar, cyclic, conjugated π-system.
- Follow Huckel's rule (4n+2 π electrons).
- Highly stable due to resonance.
- Undergo electrophilic aromatic substitution (EAS).

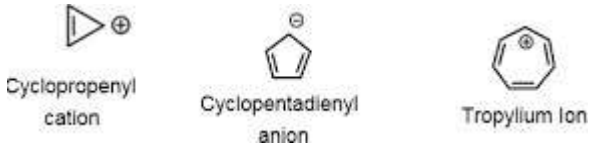
Examples: Benzene, Toluene, Naphthalene, Anthracene, Phenanthrene.



Non-Benzenoid Compounds

Definition: Compounds that do not contain a benzene ring but obeys Huckel's rule and aromatic are called Non-benzenoid

Cyclopropenyl cation ($C_3H_3^+$), Tropylium ion ($C_7H_7^+$), Cyclopentadienyl anion ($C_5H_5^-$).all follows Huckel's rule (4n+2 π e-).



Benzenoid	Non-Benzenoids
Contain benzene ring	No benzene ring
Always aromatic	May be aromatic, non-aromatic, or anti-aromatic
Stable (4n+2 π electrons)	Stability varies
Examples: Benzene, Naphthalene	Examples: Tropylium ion, Cyclobutadiene, Cyclooctatetraene

Orientation of aromatic substitution:

The substituents already attached to the benzene ring not only govern the orientation of further substitution but also affect the reactivity of the benzene ring.

the nature of the group already attached to benzene ring determines the position of the incoming group. In general, groups have been classified into two categories:

(a) Ortho-para directing groups. The groups which direct the incoming group towards ortho, and para positions are called ortho-para directing groups. Groups such as -R, $-C_6H_5$-OH, -SH, -OR, $-NH_2$, NHR, NR_2, Cl, Br, I, etc. are all ortho-para directing groups.

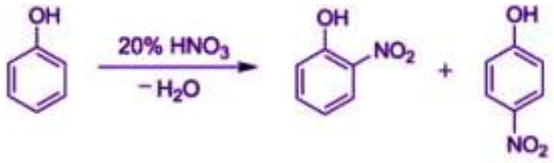
(b) Meta directing groups. The groups which direct the incoming groups towards meta position are called meta directing groups. Groups such as -COOH, -CHO, CN, $-NO_2$, COR, $-SO_3H$, etc., are all meta directing groups.

It may be mentioned that groups which contain double or triple bond are usually meta directing while those which do not contain multiple bonds are ortho-para directing.

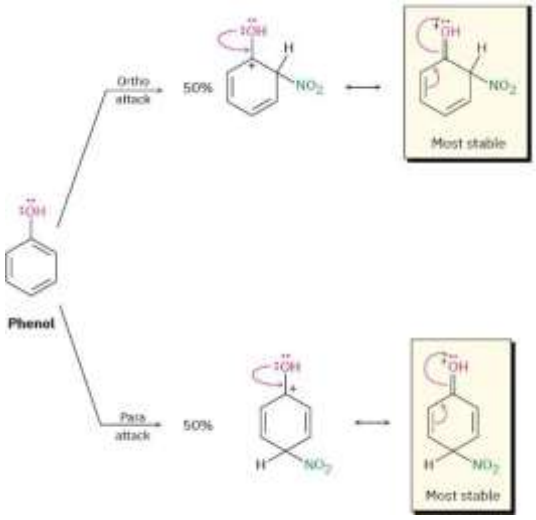
Ring activating and Ring deactivating :

Reactivity of the benzene ring in electrophilic substitution reactions depends upon the tendency of the substituent group already present in the benzene ring to release or withdraw electrons. A group that releases electrons activates benzene ring while the one which draws electrons deactivates the benzene ring. It is found that except halogens all ortho-para directing groups activate the ring and all meta directing groups deactivate the ring towards further electrophilic substitution.

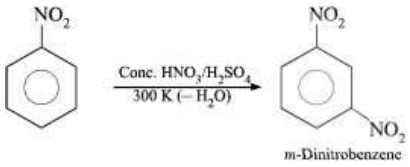
Thus, nitration of Phenol (ring activating) can be carried out at room temperature



Phenolic OH has a strong, electron-donating resonance effect(+M effect) that outweighs a weaker electron-withdrawing inductive effect(-I effect) and tend to decrease the positive charge on the carbocation and thus stabilize the ion. As a result, the rate of the reaction increases.



the nitration of nitrobenzene requires more drastic conditions.



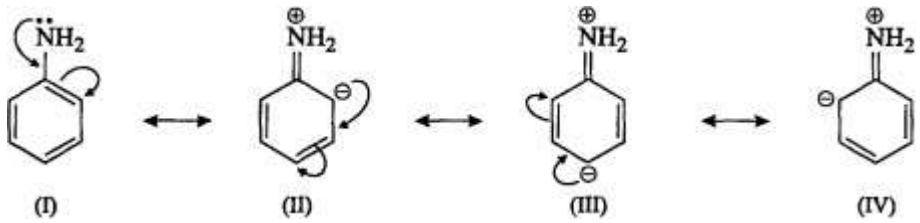
The NO_2 group destabilize the carbocation through high electronegativity and -I effect by intensifying the positive charge on it. Consequently, the rate of further electrophilic substitution reaction decreases

It may be mentioned that release or withdrawal of electrons may occur due to Inductive effect or Resonance effect or Hyperconjugation or Mesomeric effect

Orientation of (i) Amino, methoxy and methyl groups (ii) Carboxy, nitro, nitrile, Carbonyl and sulphonic acid groups (iii) Halogens**:**

Amino NH_2 Group:

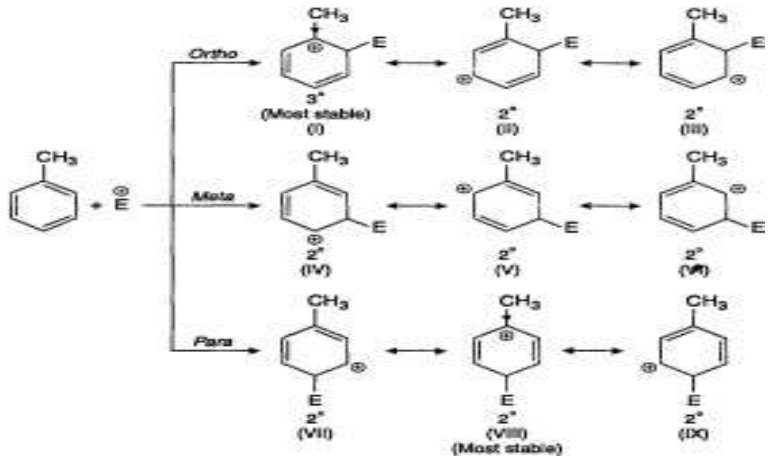
The lone pair of electrons present on oxygen atom is in conjugation with the pi electrons of the ring and exhibits a strong + R effect, thus increasing the overall electron density on the benzene ring. Although the -I effect opposes the + R effect but latter predominates because resonance effect is primary where inductive effect is secondary in nature. Also, the relative increase of electron density is greater at 0- and p-positions due to nature of conjugation .hence the substitution occurs at ortho and para positions.



Methyl CH_3 Group:

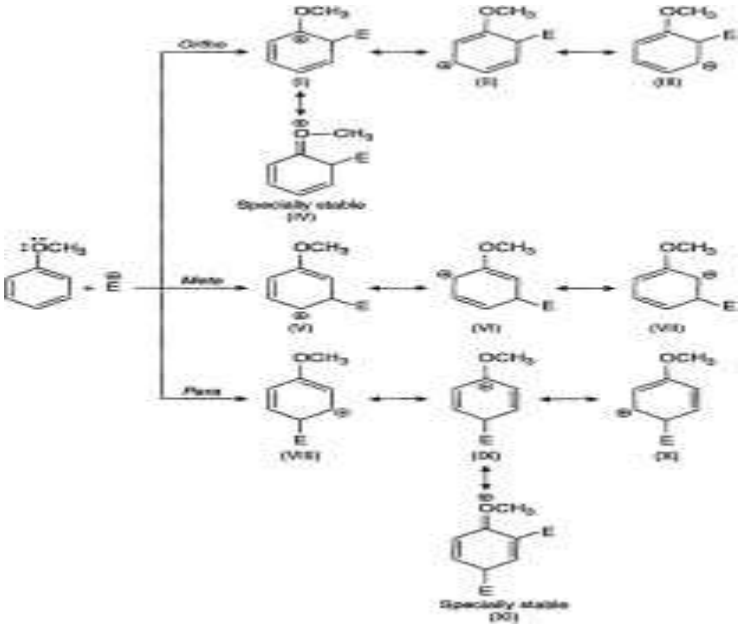
When a substituted benzene undergoes an electrophilic substitution reaction, one is formed depends on the relative stabilities of the carbocations. In the case of ortho and para substitution of toluene, however, the positive charge is spread over two secondary (2°)carbons and one tertiary (3°) Methyl carbon donates electrons by inductive effect, the indicated resonance contributors, (I) and (VIII) are most stable This is because the substituent is attached directly to the positively charged carbon, which

it can stabilize by inductive electron donation. Therefore, the most stable carbocation is obtained by directing the incoming group to the ortho and para position



Methoxy OCH_3 Group:

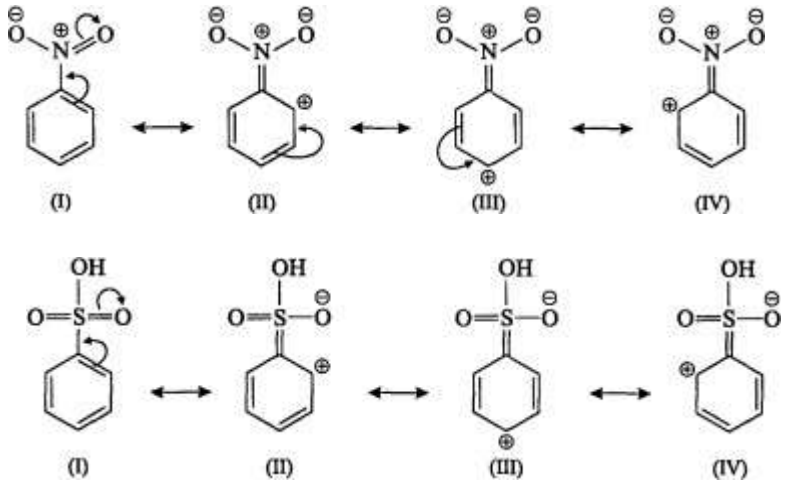
If a substituent donates electrons by resonance, the carbocation formed by putting the incoming electrophile on the ortho and para positions have a fourth resonating structure as a result of resonance electron donation by the substituent . This is a specially stable resonance contributor because it is the only one whose all atoms have complete octets. Therefore, all groups that donate electrons by resonance are ortho/para directors.



Nitro NO_2 Group:

The groups like -N02, -CHO, -CN, -COOH, etc. have a pi bond conjugated to the benzene ring and strongly electron attracting atom linked to the key atom through this multiple bond. Due to conjugation electron attracting atom causes withdrawal of electrons away from the ring and towards the group by a - R effect, this deactivates the nucleus. However, the effect is more pronounced at 0-

and p- positions leaving m- position as point of relatively high electron density. The - I effect assists the - R effect As the molecule is' a resonance hybrid of various contributing structures, there is small positive charge at the ortho and para position (structures II-IV). The meta positions remain the position of relatively high electron density and attract electrophiles resulting in m- substitution.



Halogen Groups:

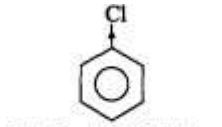
Halogens are ortho/para directing groups but are deactivating groups

(1) The halogens are strongly electronegative and withdraw electron from a carbon atom through the sigma bond (- I effect).

(2) The halogens have non-bonding electrons that can donate electrons through pi bonding (+ R effect)

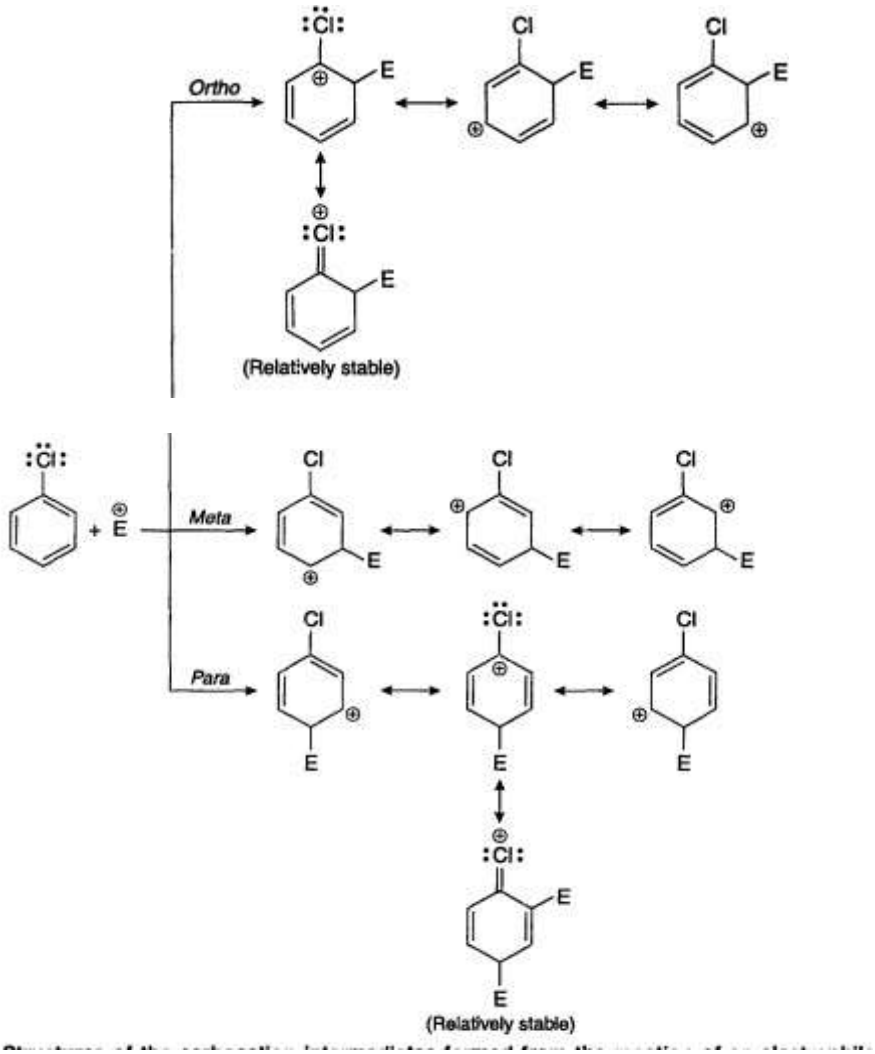
their electron withdrawing inductive effect influences reactivity and their electron donating resonance effect governs orientation.

Thus, we would expect a chlorine atom to withdraw electrons from the benzene ring and thereby deactivate it.



Inductive effect of chlorine atom deactivates ring

when electrophilic attack does take place, the chlorine atom stabilizes the carbocation (arenium cation) resulting from ortho and para-attack relative to that from meta-attack. The chlorine atom does this by donating an unshared pair of electrons. These electrons give rise to relatively stable resonance structures (with octet)



Unit 5: Orientation of Aromatic Substitution

Long Answer Questions (10 Marks)

1. Explain the concept of aromaticity and Huckel's rule with examples from benzenoid and non-benzenoid compounds.
2. Discuss the orientation of aromatic substitution in terms of electron-donating and electron-withdrawing groups.
3. Describe the effect of activating and deactivating groups on the orientation of aromatic substitution.
4. Discuss the electronic interpretation of groups like NO2 and phenolic on aromatic substitution.
5. Explain the effects of amino, methoxy, and methyl groups on the orientation of aromatic substitution.

Short Answer Questions (5 Marks)

1. What is Huckel's rule? Explain its application to benzene.
2. Discuss the effect of halogen groups on aromatic substitution.
3. Explain the concept of ortho-para and meta-directing groups in aromatic substitution.
4. What are activating and deactivating groups in the context of aromatic substitution?
5. Discuss the role of methyl and methoxy groups in the orientation of aromatic substitution