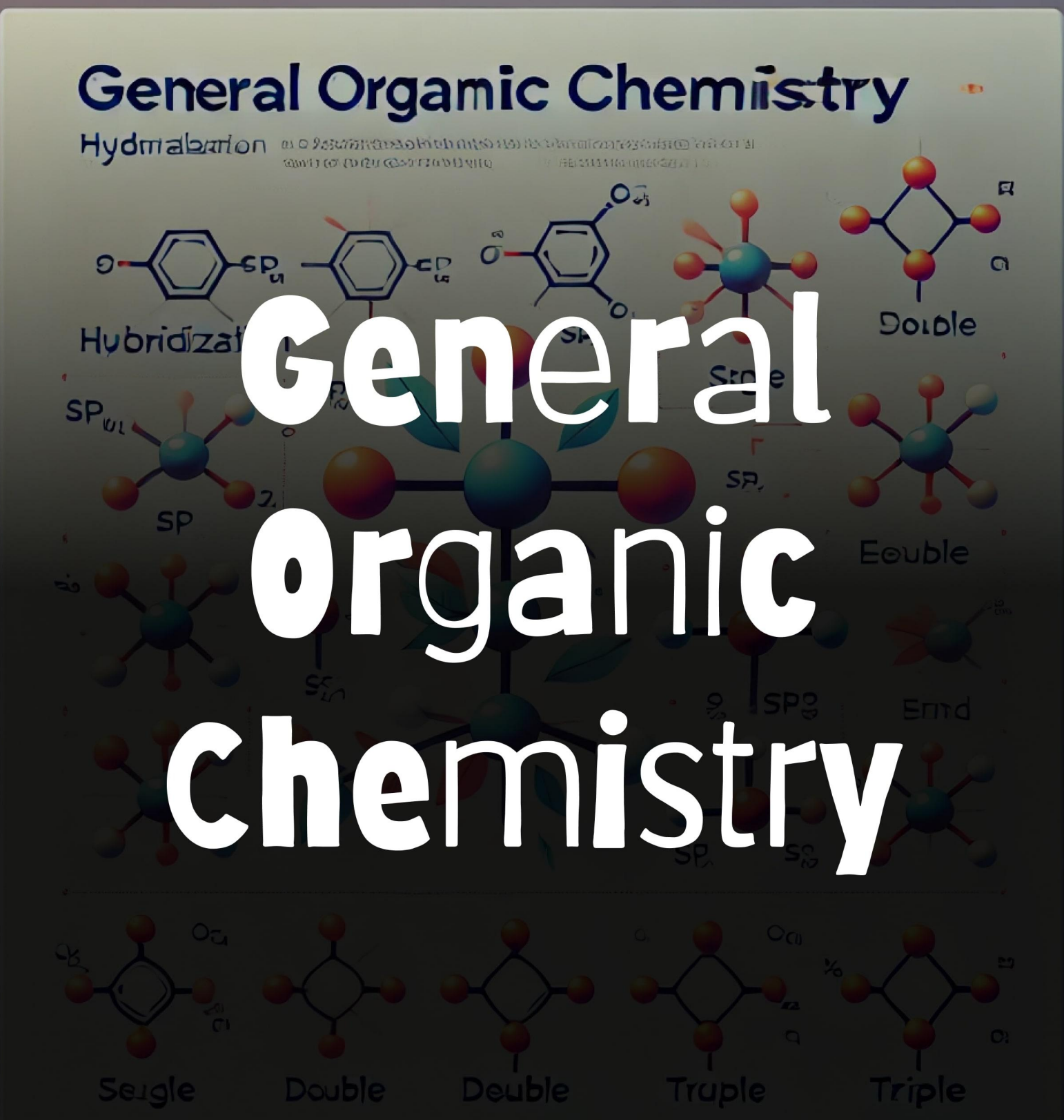
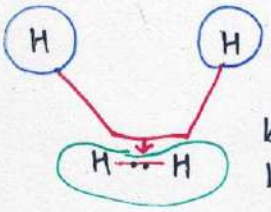


General organic Chemistry

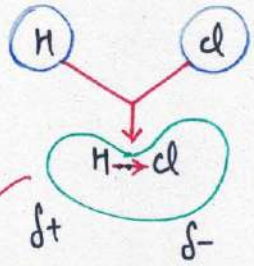
GENERAL ORGANIC CHEMISTRY

INDUCTIVE EFFECT



both the H atoms have same EN

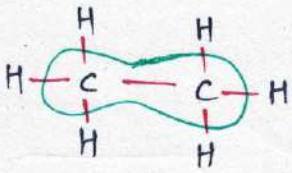
homoatomic molecule
non-polar bond



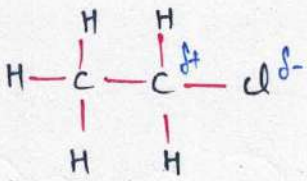
Cl is more EN than H

Bond moment is towards Cl

Polar covalent bond
(unequalled distributed e⁻ cloud)



non-polar



Polar

Poles are created

+ve pole

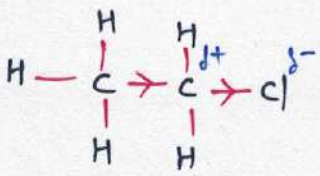
-ve pole

unequally distributed → polarised

$Fe < Fe^{+2} < Fe^{+3}$ [electronegativity]

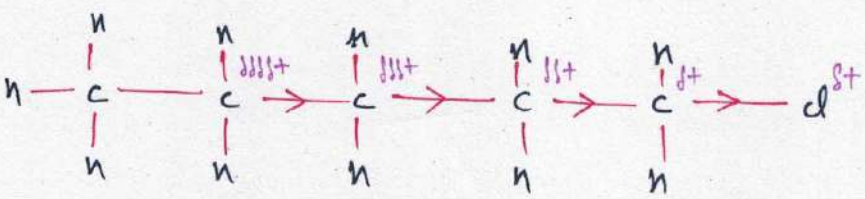
Fe^{+3} have deficiency of $3e^{\ominus}$, it is hungry of $e^{\ominus}$ so, it has more e⁻ attracting capacity

- Mov is the +ve charge on element, more is the electronegativity.
- $Sn^{+2} < Sn^{+4}$
- $Pb^{+2} < Pb^{+4}$
- $Cu < Cu^{+1} < Cu^{+2}$ [e_{CoNo}]



[I effect always travels through sigma bond only]

- Inducing the polarisability of a bond by adjacent sigma bond is known as inductive effect.
- It is transmitted through σ bond.
- Inductive effect is maxᵐ transmitted upto 3-4 sigma bonds only.



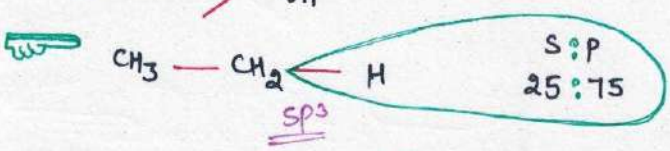
I effect

- +I effect (Releasing, giving e^-)
- -I effect (withdrawing, taking, gaining e^-)

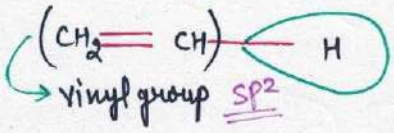
ORDER OF -I EFFECT

As EN increases, -I effect ↑↑ses

- -F > -Cl > -Br > -I
- -OH > -SH
- -OH > $-NH_2$
- -F > -OH

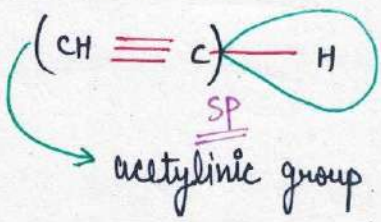


alkyl C–H



S : P
33.33 : 66.7

Vinyl C–H



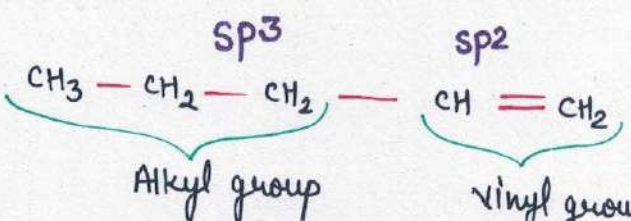
S : P
50 : 50

Acetylinic C–H

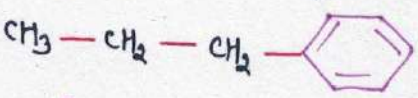
Size of carbon — $Csp < Csp^2 < Csp^3$

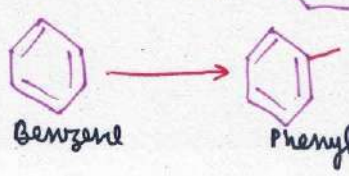
Size is less, e^- are more attracted towards nucleus $\left[F \propto \frac{1}{\text{size}}\right]$

EN — $Csp > Csp^2 > Csp^3$

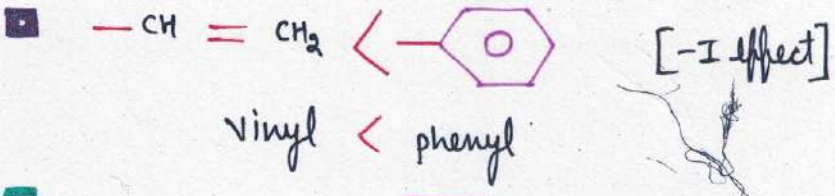


Alkyl group will always show +I effect.
Vinyl group will always show -I effect.

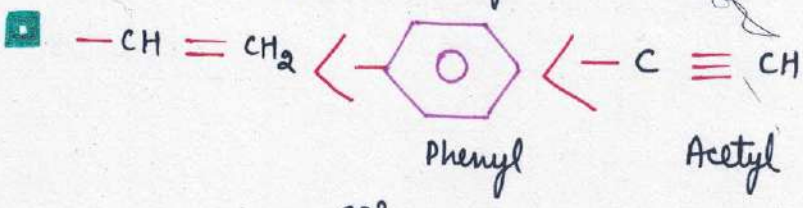




in Benzene ring all 6 carbon atoms sp^2 hybridised



Vinyl < phenyl



Phenyl Acetyl

sp^2 more C atoms $sp^2 < sp$

$R-CH_2-NH_2 \rightarrow$ amine

$R-CH=NH \rightarrow$ imine

$CH_3-CH_2-CH_2-\underset{sp^2}{CH}=\underset{sp^2}{CH_2}$

$CH_3-CH_2-CH_2-\underset{sp^2}{CH}=\underset{sp^2}{NH}$

$CH_2-CH_2-CH_2-\underset{H}{C}=O$

first hyb. is same look for next atom.

$-CH=CH_2 < -CH=NH < -CH=O$

vinyl imine aldehyde

$CH_3-CH_2-CH_2-C\equiv CH$

$CH_3-CH_2-CH_2-C\equiv N$

$CH_3-CH_2-CH_2-N^{\oplus}\equiv C^{\ominus}$

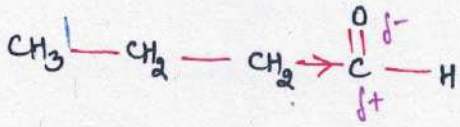
Acetylinic Nitrile isocyanide

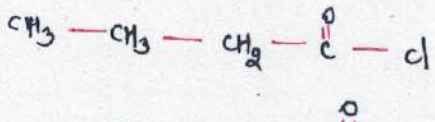
[+ve are more hungry]

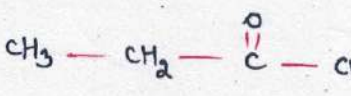
$-C\equiv CH < -C\equiv N \ll -N^{\oplus}\equiv C^{\ominus}$

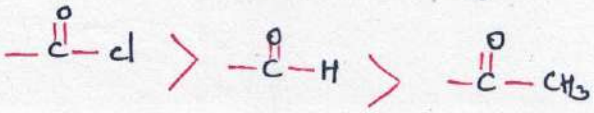
acetylinic cyanide isocyanide

[N is more EN than C] [+ve charge on first atom $\Rightarrow$ -I effect]







-I effect 

(nitroso $-\ddot{N}=O$)

$CH_3-CH_2-CH_2 \rightarrow \ddot{N}=O$

(+I)

nitroso

$CH_3-CH_2-CH_2-N^{+}(=O)-O^{-}$

-I effect

$[-N^{+}(=O)-O^{-}$ +ve are more hungry$]$

- $-N^{+}(=O)-O^{-} > -\ddot{N}=O$
- $CH_3-CH_2-CH_2-C(=O)-OH$ carboxylic

  $CH_3-CH_2-CH_2-S(=O)-OH$ sulphinic

  $CH_3-CH_2-CH_2-S(=O)_2-OH$ sulphonic

-I effect

$-C(=O)-OH < -S(=O)-OH < -S(=O)_2-OH$

- $CH_3\ CH_2\ CH_2\ F$

  $CH_3\ CH_2\ CH_2\ CF_3$

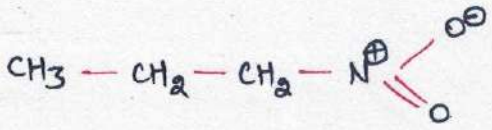
  $-F < CF_3$; $-Cl < -CCl_3$; $-Br < CBr_3$;

  $-I < CI_3$
- $CH_3-CH_2-CH_2-O-H$

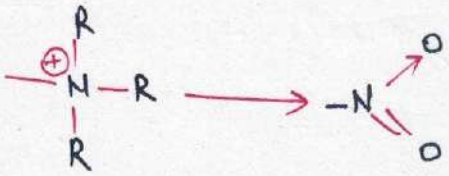
  $CH_3-CH_2-CH_2-O-C(=O)-R$ acyl (upon acylation -I effect ↑)

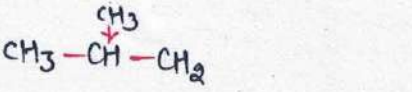
  $CH_3-CH_2-CH_2-O^{+}(H)-H$

  $-O^{+}H_2 > O-C(=O)-R > -OH$
- $-S^{+}H_2 > S-C(=O)-R > -SH$ (same story)
- $-N^{+}H_3 > NH-C(=O)-R > -NH_2$
- $CH_3-CH_2-CH_2-N^{+}(CH_3)(CH_3)-CH_3$ (net +ve charge on N)

D 

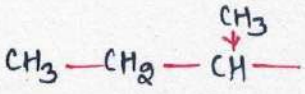
[Net charge = 0]



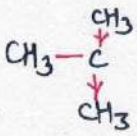


n - butyl

iso butyl



Secondary - butyl

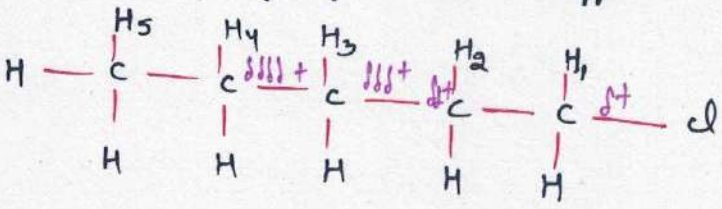


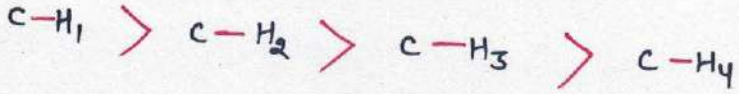
tertiary - butyl

t butyl > sec - butyl > iso - butyl > n butyl

[+I effect]

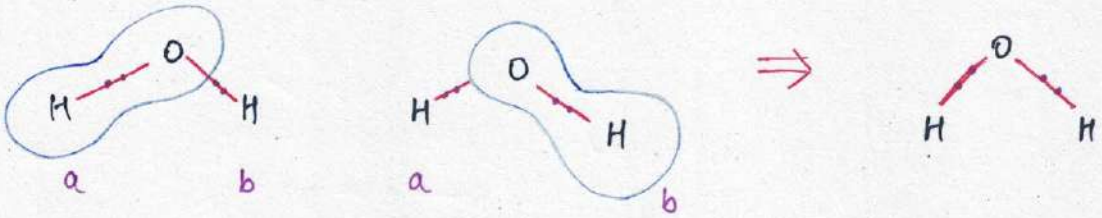
All Alkyl groups show +I effect.





[Polarizability of C-H bond]

RESONANCE

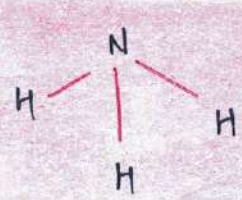


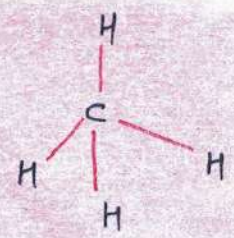
Localised bonding orbital

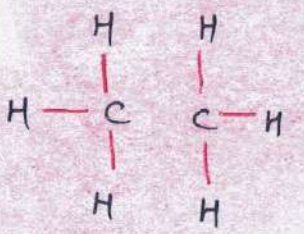
Localised bonding orbital

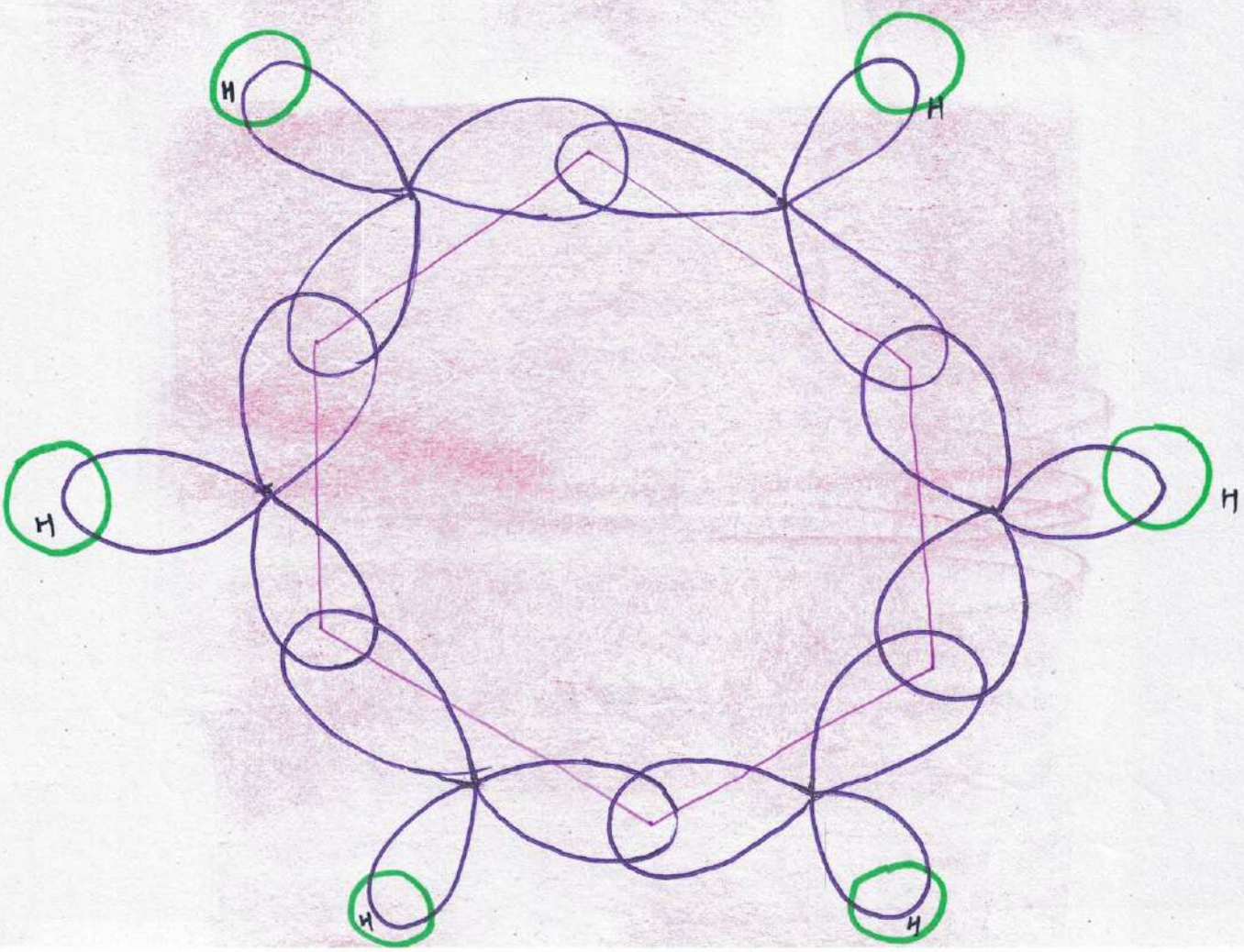
whenever orbitals are localised bonding orbital, the structure can be written by a single Lewis structure.

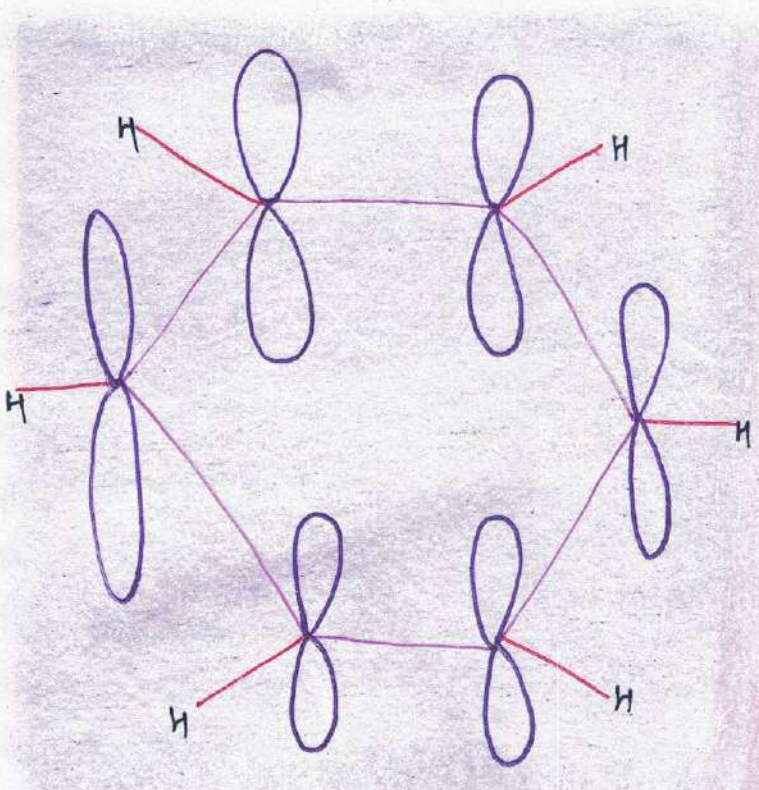
only sigma bonds → one single

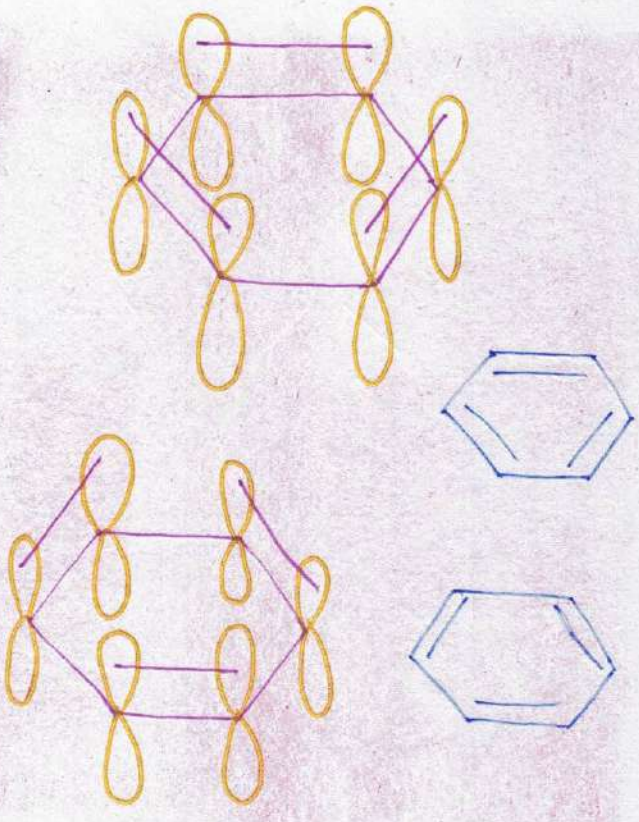












Delocalisation of bonding orbitals is known as Resonance.

→ Structure can be written as 2 or more Lewis structure.

- The molecular which have only sigma bond will not show resonance.

Conditions for Resonance.

- Planar molecule
- conjugated pie bonds.

The different structures of the molecule due to resonance are called resonating / canonical structure.

They are hypothetical structures. They do not exist.

A hybrid possessing the combined characteristic of resonating structure exist

→ Resonance hybrid

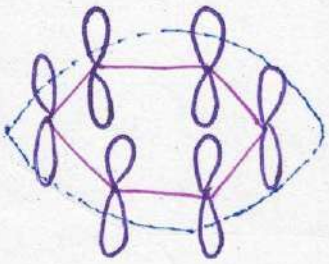
They are not in equilibrium
They do not exist.
Then what exist ?

⇓

A resonance hybrid

In Resonance position of atom do not change

In Resonance position of bonding orbitals will change.

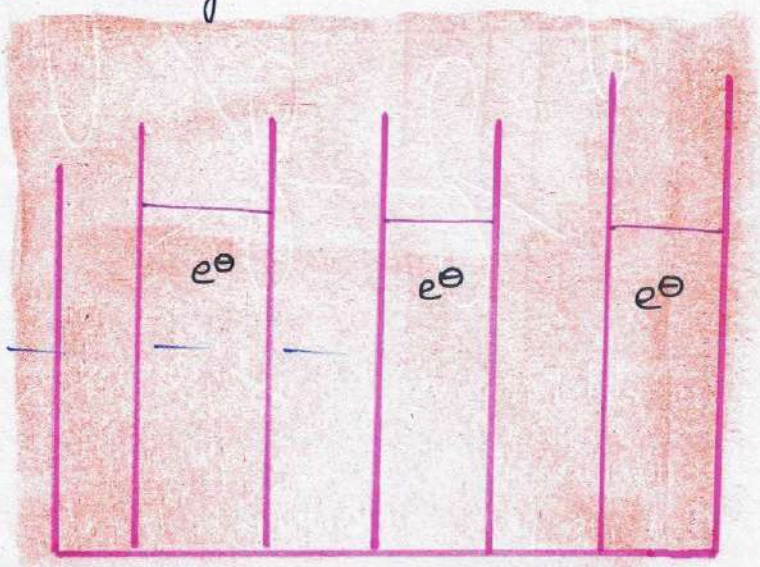


Resonance hybrid

⚠ Resonating structure are not in equilibrium.

Why Resonance Occurs?

Ans :- Stability



$P_r = h f_g$

$P_s = \frac{h}{2} f_g$

After delocalisation P decreases.

☞ Delocalisation of bonding orbitals. lowers the potential energy of the molecule. Hybrid will have bond P.E.

$$P.E. \propto \frac{1}{\text{Stability}}$$

☞ The energy difference between a resonance hybrid and cannonical structure is known as Resonance energy.

☞ Loss in P.E. due to delocalisation of bonding orbital is known as Resonance energy.

☞ Additional stability acquired due to the delocalisation of bonding orbitals is also known as Resonance energy.

☞ Resonance energy is energy lost [exothermic process]. R.E. will have (-)ve sign.

☞ Resonance energy cannot be measured. but can be calculated.

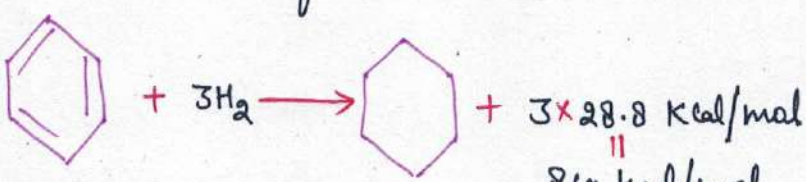
Heat of hydrogen-ation

Resonance energy can be calculated by heat of hydrogenation.

$CH_2=CH_2 + H_2 \longrightarrow CH_2(H)-CH_2(H)$; Δ Heat ΔH -28.8 k cal./mol

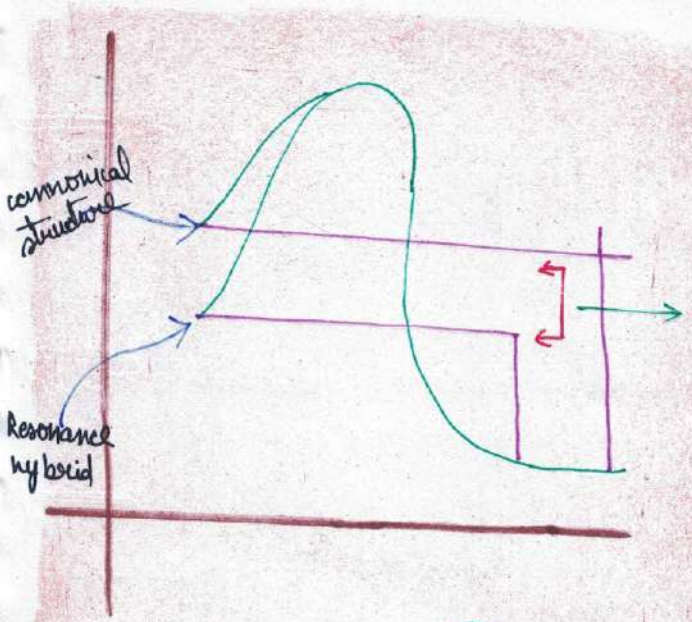
($CH_2=CH_2$: π; H_2: σ; 2σ)

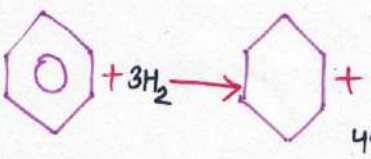
Addition reaction is always exothermic.



$+ 3H_2 \longrightarrow$ + 3×28.8 Kcal/mol

= 85.8 Kcal/mol



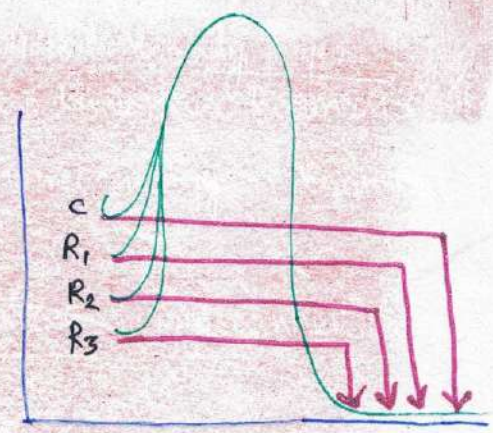


49.8 Kcal/mol

Resonance energy

Heat of hydrogenation

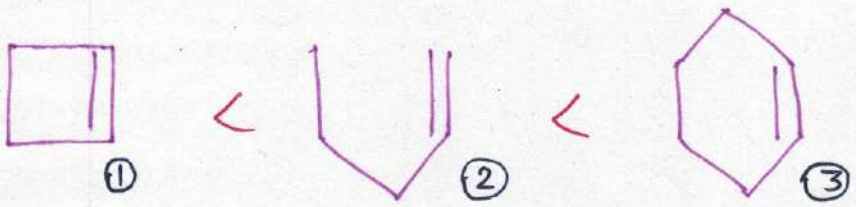
diff = 85.8 − 49.8 = 36.0 Kcal/mol



IMPORTANT

Less stable ⇒ more heat of hydrogenation

More stable ⇒ less heat of hydrogenation

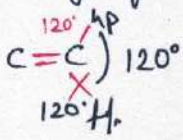


(Stability)

L = 90° Angle < 120° Angle ≃ 120°

① > ② > ③ (Heat of hydrogenation)

sp^2 B.A. 120°

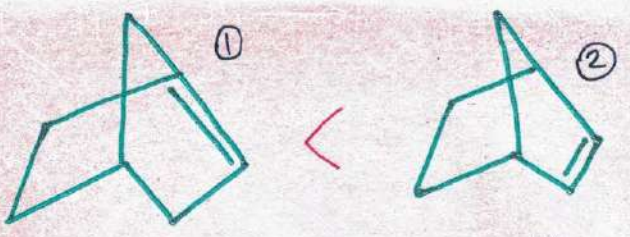


if BA increases of decreases from 120° strain on bond occurs

⇒ Less stability

Stability - ① < ②

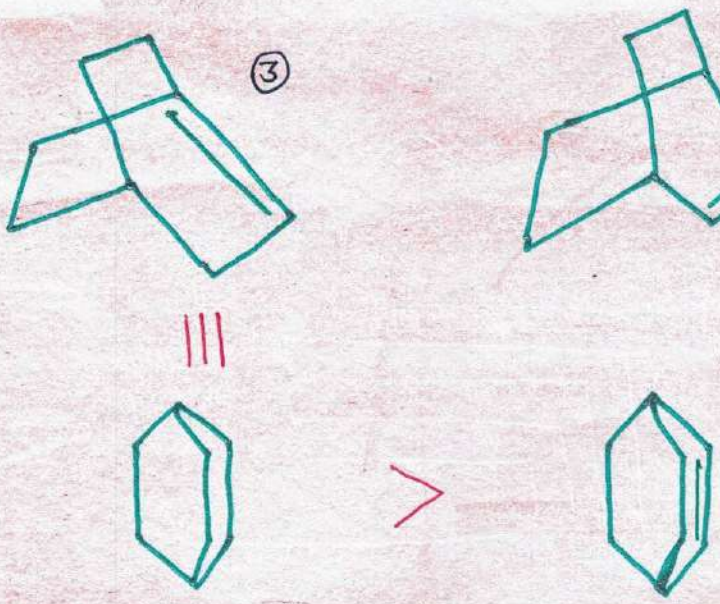
Heat of hydro - ① > ②



stability

(can be written as)

Heat of hydrogenation



Stability ③ < ④

Heat of hydrogenation

STABILITY

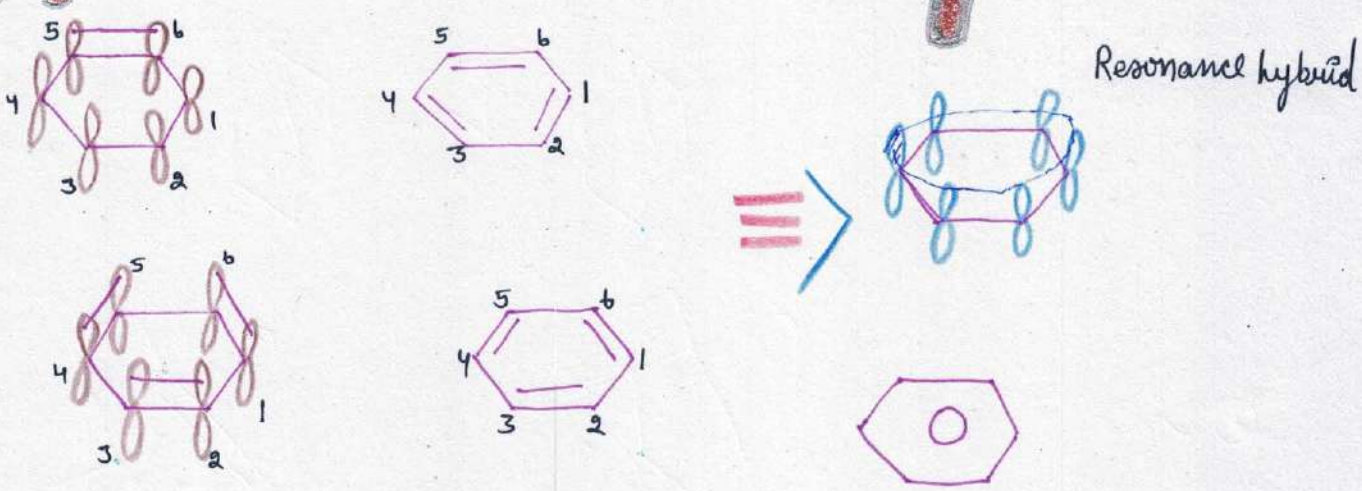
④ > ② > ③ > ①

④ < ② < ③ < ①

TYPES OF DELOCALISATION

1. Delocalisation in aromatic system
2. Delocalisation in conjugated system
3. Delocalisation of pie bond with adjacent vacant p or d orbital.
4. Hyperconjugation

Aromatic system



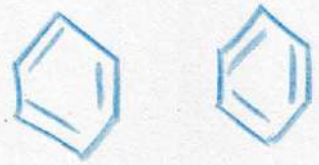
The resonance hybrid is a combination of all connonical structure.
The relative stability of resonature structure will determine the contribution of individual str. in hybrid.

$$B.O. = \frac{2+1}{2} = \frac{3}{2} = 1.5$$

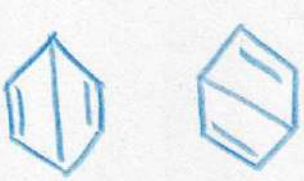
All bonds in benzene have equal bond order = 1.5

Bond length of Benzene 1.4 A°

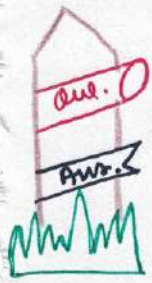
	B.O	B.h
CH_3-CH_3	1	1.54
Benzene	1.5	1.40 A°
$CH_2=CH_2$	2	1.34 A°



Kekule's Structure 94%



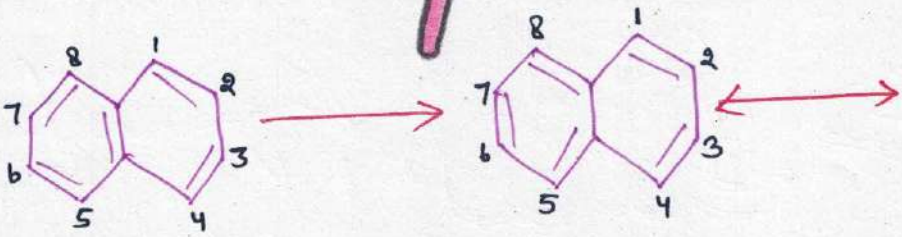
Dewar's Structure



In Benzene all C-C bonds are identical ?

Benzene is a resonance hybrid. All bonds have bond order 1.5 and bond length 1.4 A°.

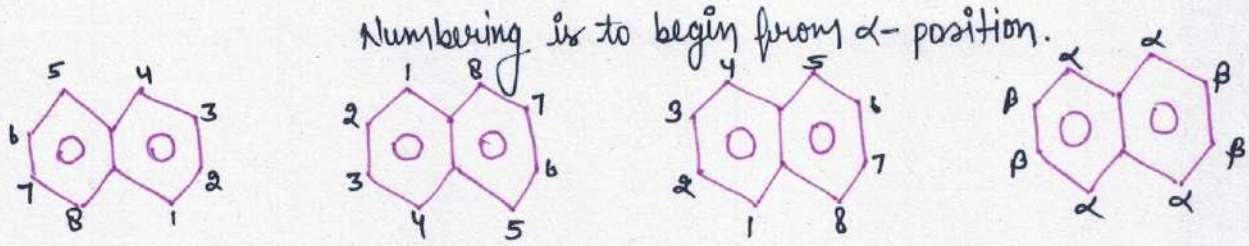
Napthalene

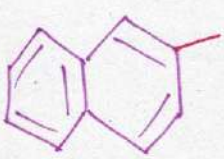


I II III

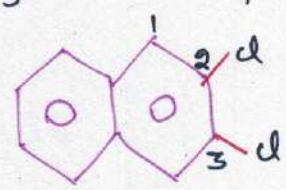
(bicyclic compound)

Numbering is to begin from α- position.





1,2 - dichloro napthalene



2,3 - dichloro napthalene

Always start numbering from α - position

of the several canonicals / resonance structure, the structure having more benze-noid rings is more stable.

Structure I of napthalene is most stable in Napthalene, all bonds are not identical. α-β bonds are shorter and β-β bonds are longer.

1-2 bond is shorter
2-3 bond is longer

B.O → 1-2 bond $\frac{2+2+1}{3} = 1\frac{2}{3}$

2-3 bond $\frac{1+1+2}{3} = 1\frac{1}{3}$

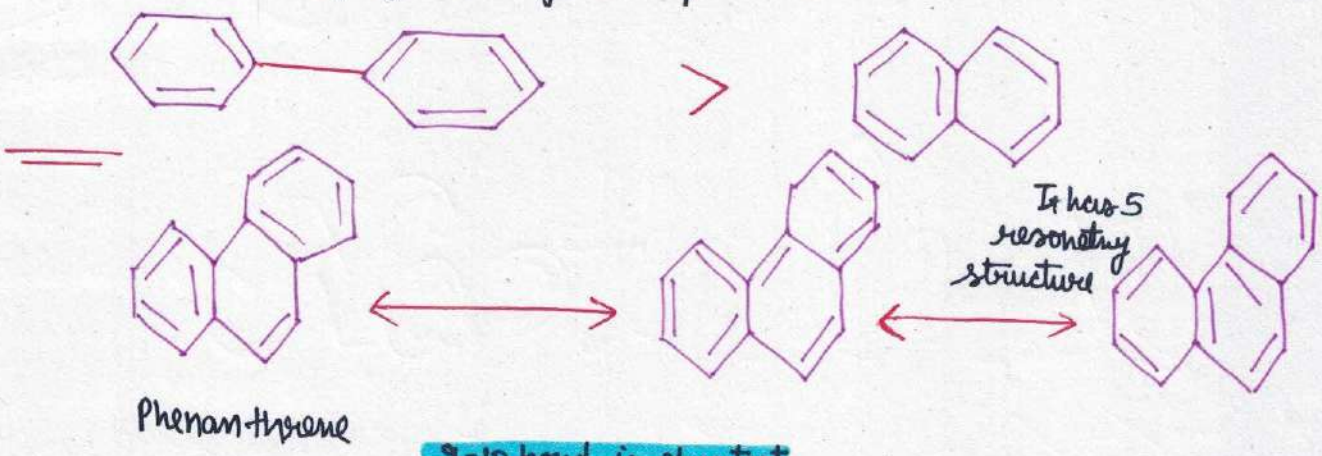
Resonance energy of napthalene = 50 kcal/mol

≠ 36×2 [2 × RE Benzene]

All rings are not benzenoid.

Maxm double bond position has shortest bond length.

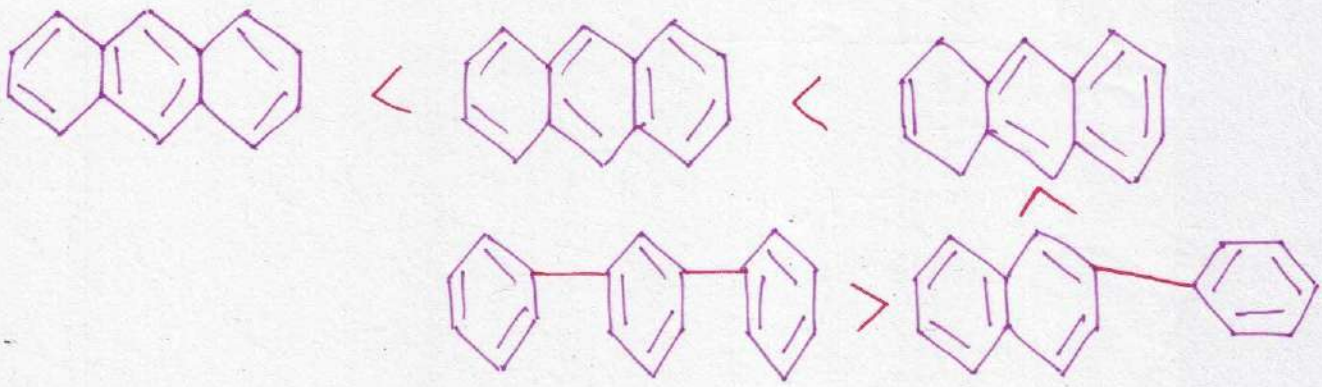
Resonance energy of biphenyl > Napthalene



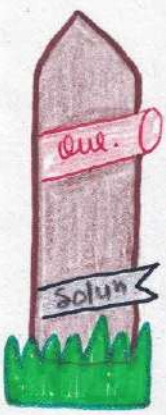
Phenanthrene

It has 5 resonating structure

9-10 bond is shortest



Resonance Energy



Which of the following have all e⁻c bonds identical?

(A) Napthalene (B) Anthracene (C) Phenanthrene

(D) Benzene

(D) Benzene

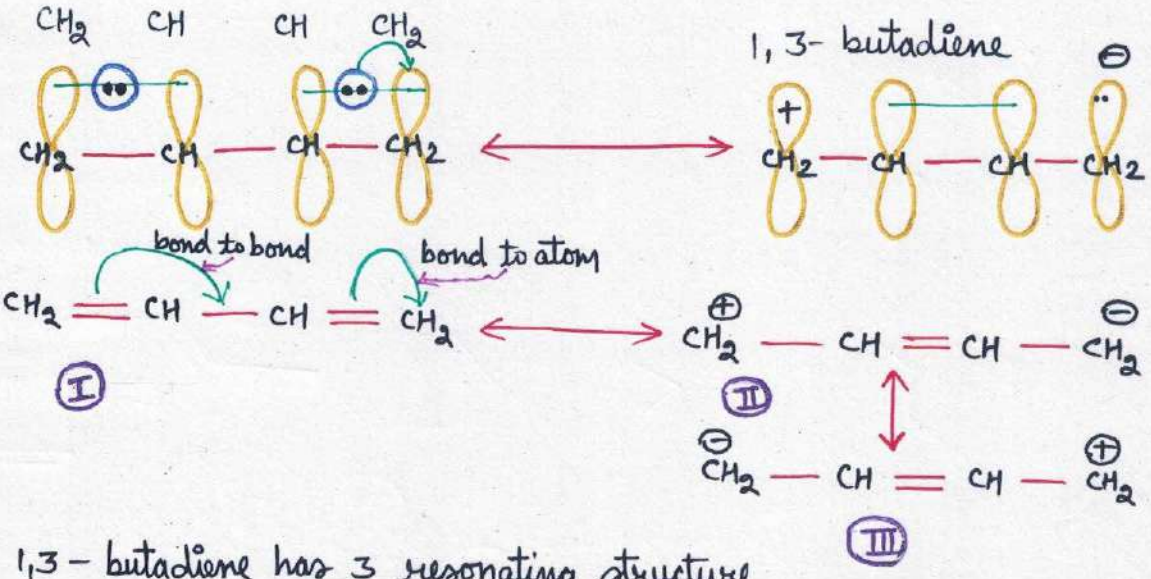
9-10 bond of Phenanthene is shortest....

α-β bond of Naphthalene is shortest....

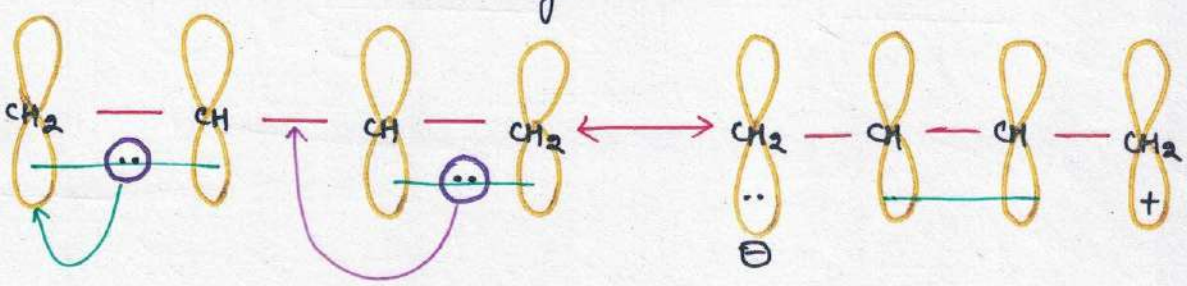
β-β bond of Napthalene is shortest....

α-β bond of Anthracene is shortest.....

DELOCALISATION IN CONJUGATED SYSTEM



1,3 – butadiene has 3 resonating structure

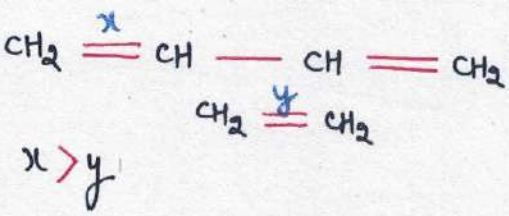


Real structure is Resonance hybrid.

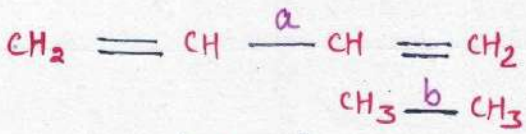
B.O. 1-2 → 1.8
2-3 → 1.4
3-4 → 1.8

- of the several resonance structures, the structures having more bond pair is more stable.
- of the several resonance structures, the structure having no charge separation is most stable.
- Sum of the total charge on all resonance structures must be equivalent.

Most stable structure is represented. while writing a compound, structure whenever in a planar molecule, pie e⁻ are in conjugation, resonance occurs.



B.O.Y > B.O.X
(bond length)

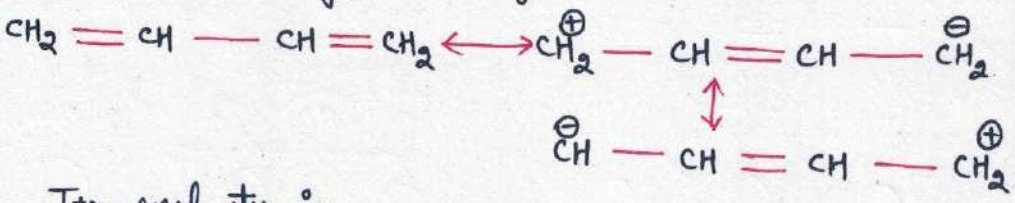


b > a (bond length)

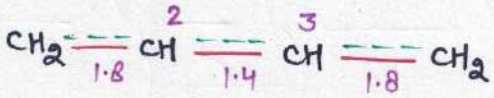
B.O @ > B.O. (b)

1,3 -butadine then is a single bond between 2 and 3 but its Bond distance is less than C-C bond distance of ethane, explain?

Butadine has following resonating structures



Its real sty. is

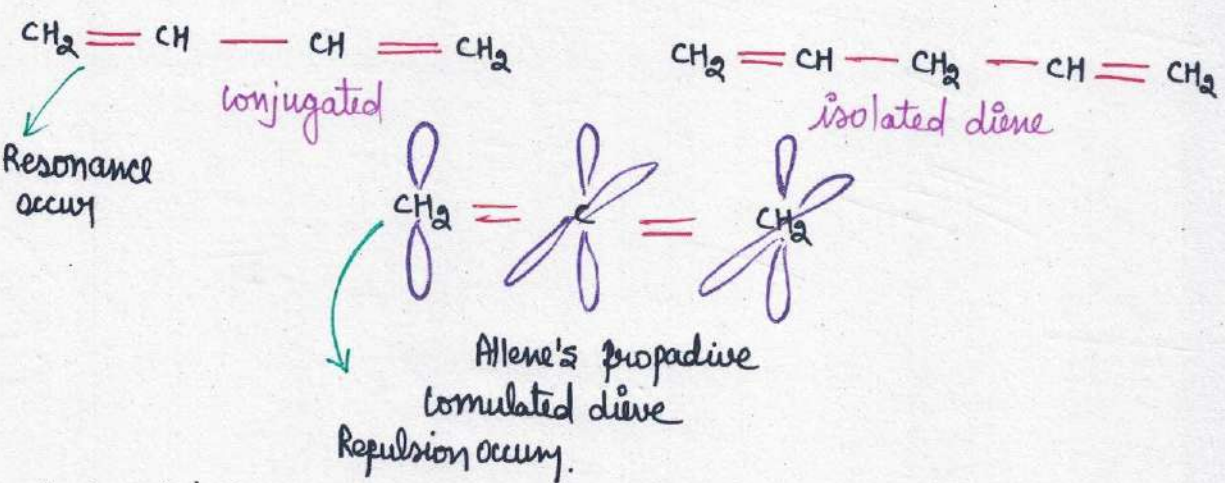


Its 2-3 bond order.

= 1.4

1.4 > 1

Hence. 2-3 bond is smaller than in ethane.

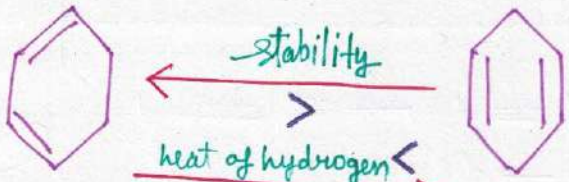


Conjugated diene > isolated > cumulated

[stability]

< < [heat of hydrogenation]

[heat of hydrogenation $\propto \frac{1}{\text{stability}}$]



1-3 cyclohexadiene → conjugated

1,4 - cyclohexdiene → isolated

$CH_2=CH-CH=CH_2$

It is difficult to break this bond as it is more stable. so we get resultant in less quantity.

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

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

III $CH_2=C=CH-CH_2-CH_3$

QUES. Which is most stable isomer? (C_5H_8)

ANS. I > II > III stability

I < II < III heat of hydroge

$$C_xH_y + \left(x+\frac{y}{4}\right) O_2 \longrightarrow xCO_2 + \frac{y}{2} H_2O$$

$C_xH_y \longrightarrow xC + yH - \Delta H$

$O=O \longrightarrow 2O - \Delta H$

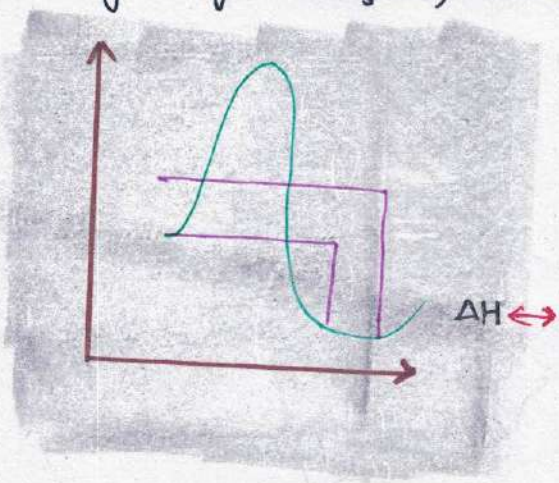
$C + 2O \longrightarrow CO_2 + \Delta H$

$2H + O \longrightarrow H_2O + \Delta H$

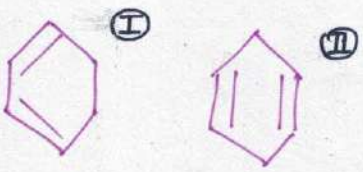
To compare the heat of esydrogenation, compound must posses same no. of unsaturation.

For comparing heat of combustion, the compounds should be isomers.

P.E.



$\Delta H \leftrightarrow$ Heat of combustion.



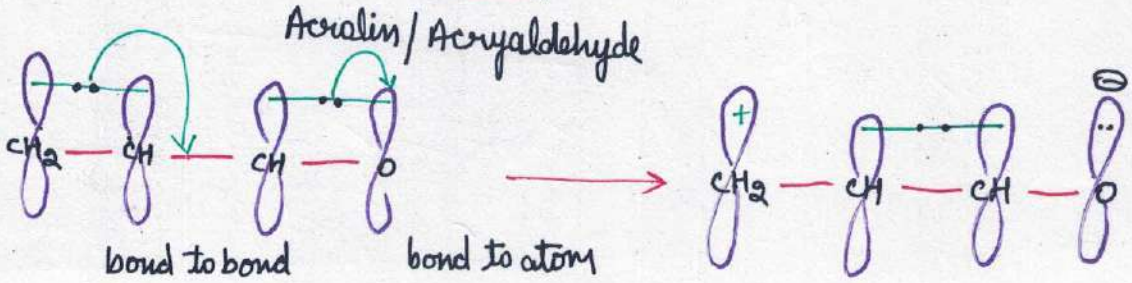
I > II stable

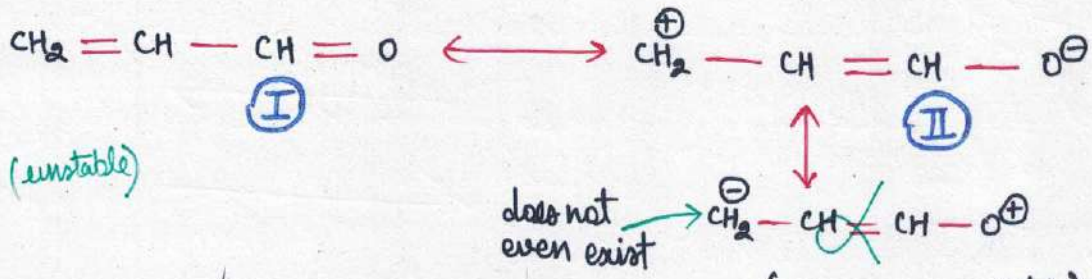
I < II heat of hydrog

I < II heat of combustion

$CH_2=CH-CH=O$

Acrolin / Acryaldehyde



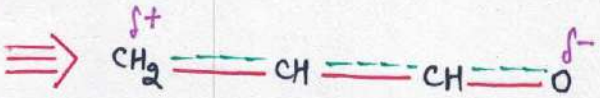


(unstable)

(very very unstable)

Acrolin has only 2 resonance structures.

Resonance hybrid



Stability :- I > II

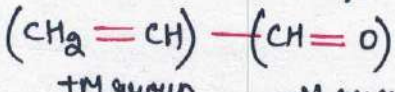
When molecule is in resonance, if there is an accumulation of charge at one end and depletion of charge at another end, the resonance is known as mesomeric resonance.

The group which is accumulating is called -M group.

+M → D (Dega) -M → L (Large)

The group which is releasing is called +M group.

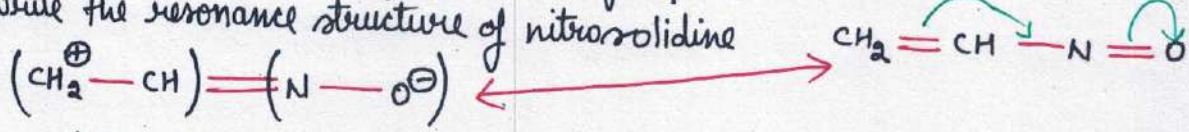
Group having pie bond along with more electronegative atom and attached to another pie system can show -M effect.



+M group -M group

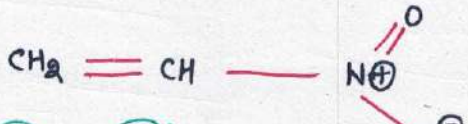
Que Write the resonance structure of nitrosolidine

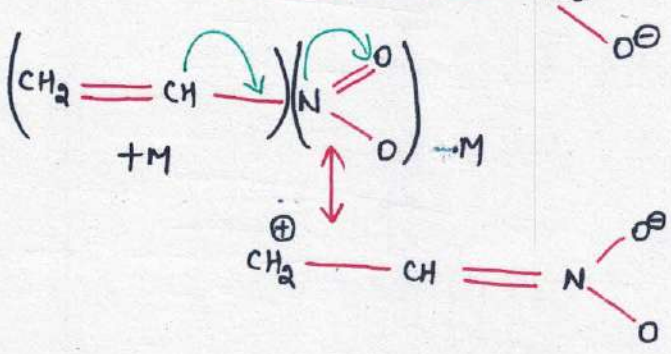
Ans.



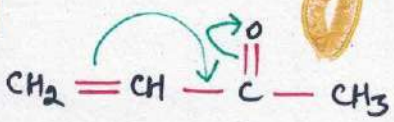
+M group -M group

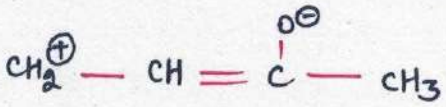
Nitroethene





Methyl vinyl ketone

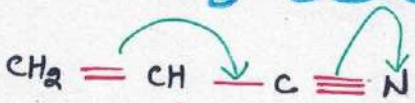


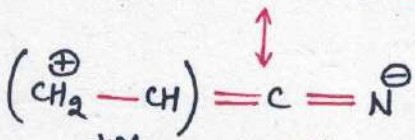


+M -M

$CH_2=C-$
vinyl group

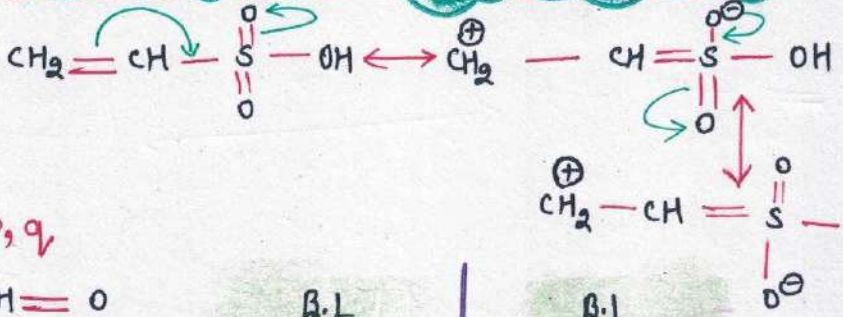
Acrylo nitrile





+M -M

Sulphinic acid



Compare x, y and p, q

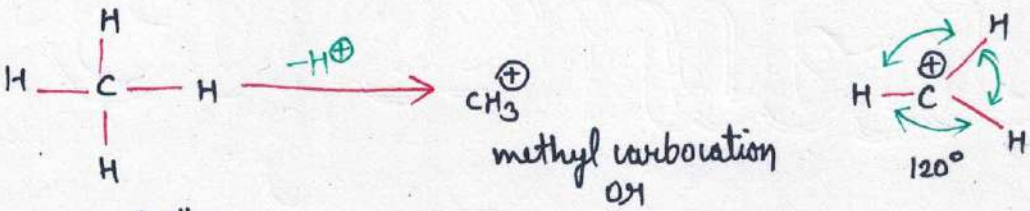
I. $CH_3-CH_2-\overset{x}{-}CH=O$

II. $CH_2=CH-\overset{y}{-}CH-\overset{p}{=}O$

III. $H-\underset{H}{\overset{|}{C}}-\overset{q}{=}O$

B.L	B.L
$x > y$	$p > q$
	B.D $\simeq$ <2 2

Delocalisation of π-bond with adjacent P or D orbital



Methane

methyl carbocation
or
carbonium ion.

Carbocations have —
- sp^2 hybridisation ion
- trigonal planar geometry
- diamagnetic nature

$CH_2 = CH - CH_2 - H$ allyl

$CH_2 = CH - CH_2 -$ Allyl group

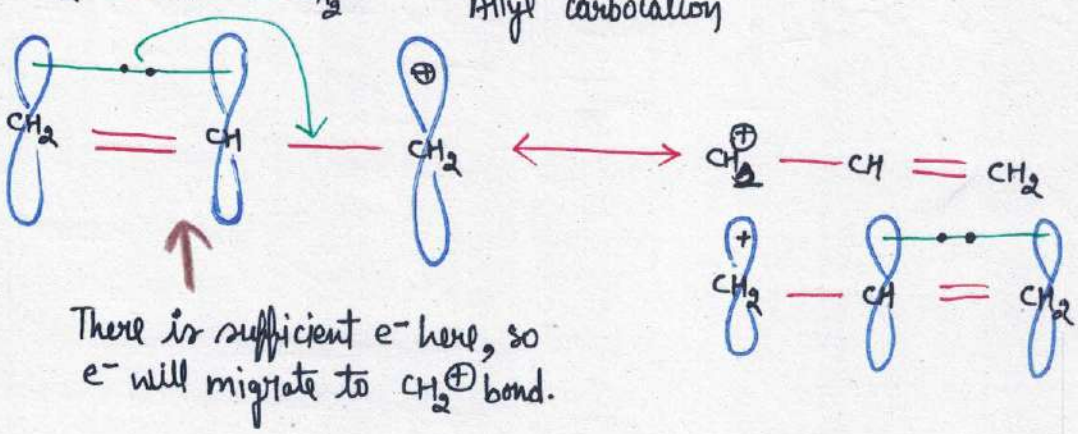
$CH_2 = CH - CH_2 - Cl$ Allyl chloride

$- Br$ Allyl bromide

$- OH$ Allyl alcohol

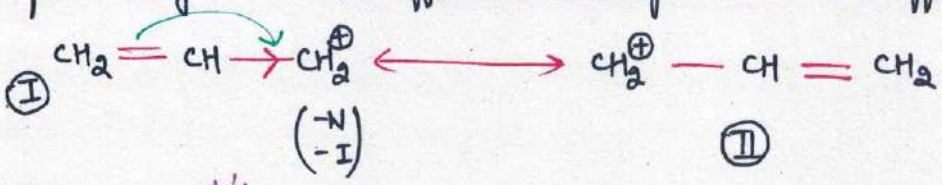
$- NH_2$ Allyl amine

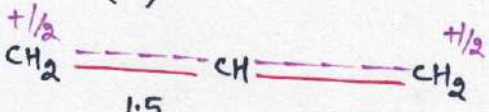
$CH_2 = CH - CH_2^{\oplus}$ Allyl carbocation

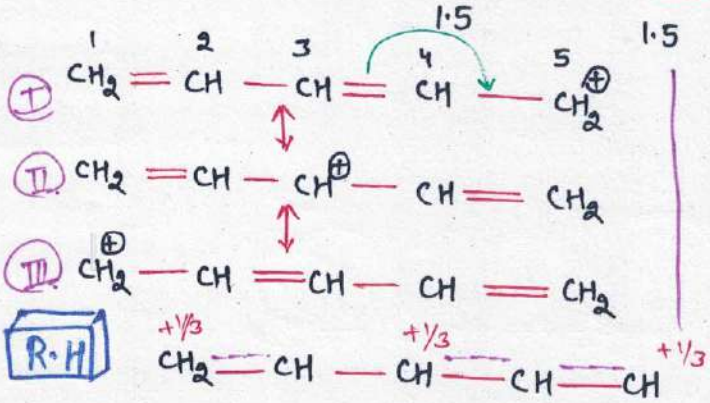


There is sufficient e^- here, so e^- will migrate to $CH_2^{\oplus}$ bond.

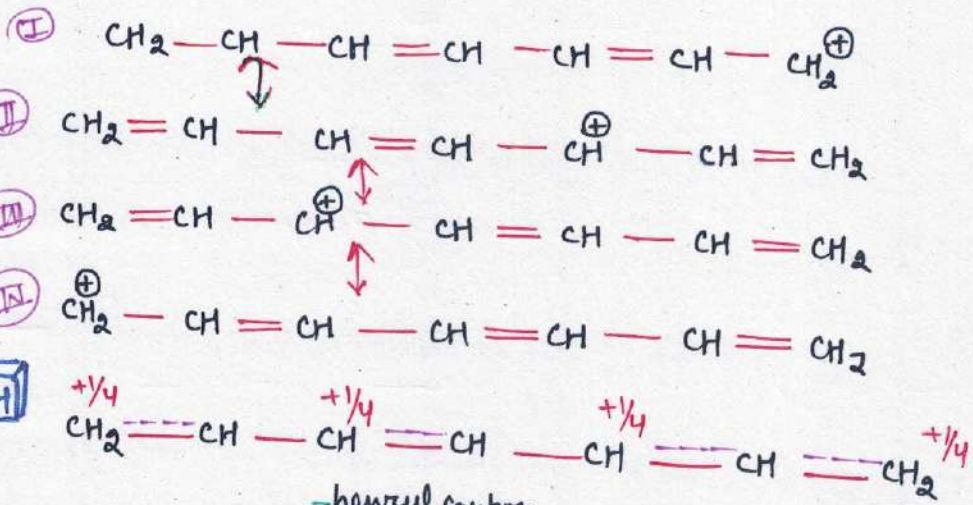
Any group showing -M effect will always show -I effect.

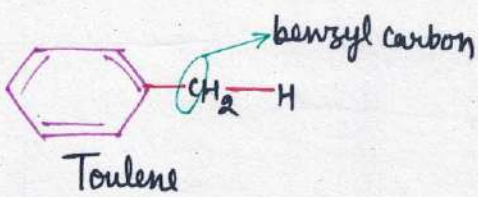






1,3,5 are electron deficient position (carryings +ve charge in resonance)



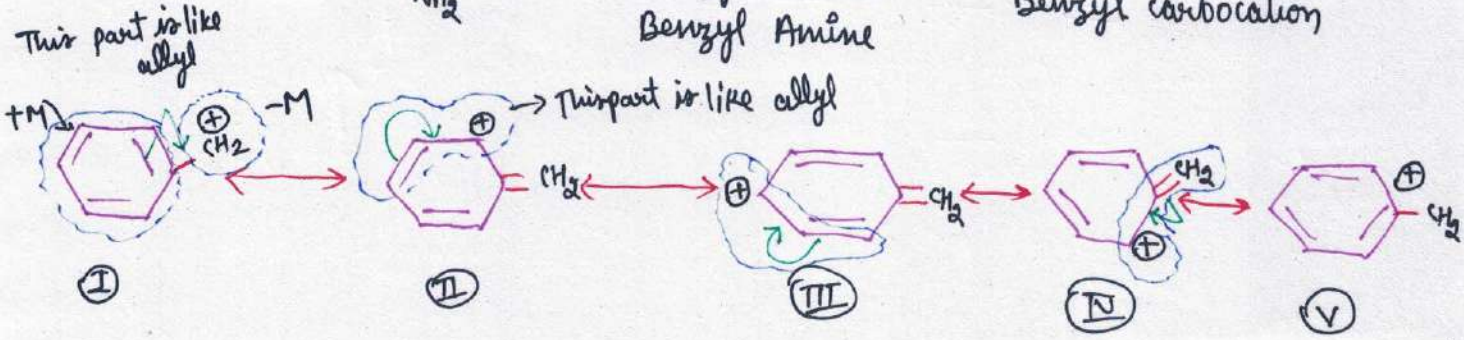


Toulene

A carbon adjacent to the benzene ring is called benzyl carbon.

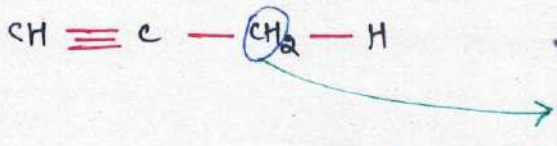
CH_2-Cl — Benzyl chloride
$-Br$ — Benzyl Bromide
$-I$ — Benzyl Iodide
$-OH$ — Benzyl Alcohol
$-NH_2$ — Benzyl Amine

Benzyl carbocation

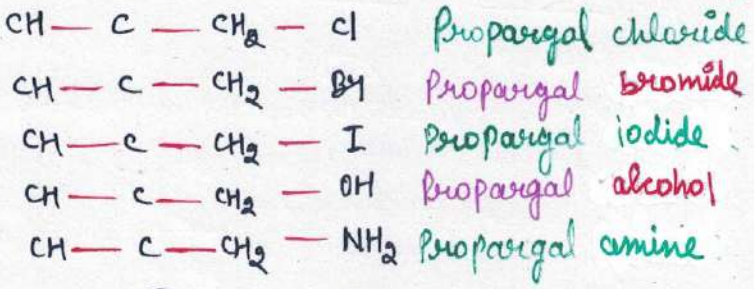


Resonance effect transfer through ortho-para position only

Ring is showing +M

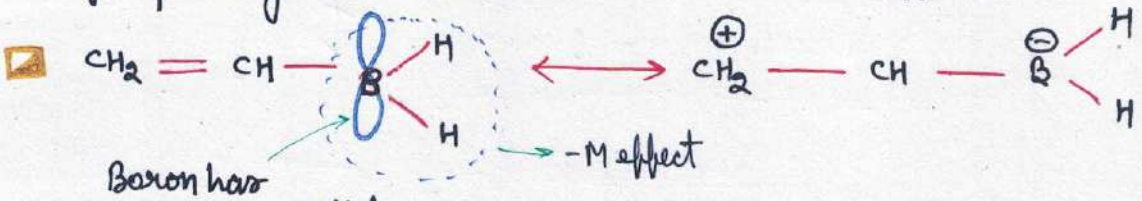


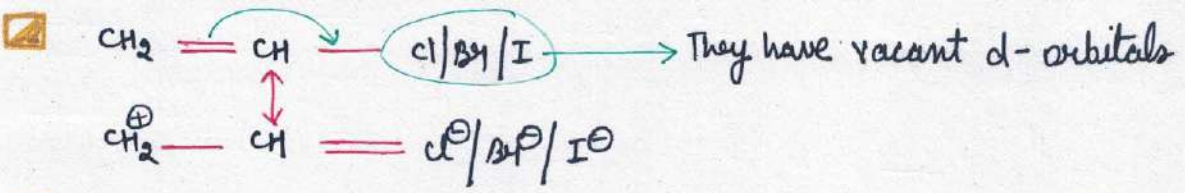
A carbon adjacent to triple bond is called Propargyl carbon propargal.

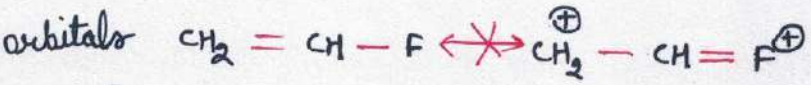


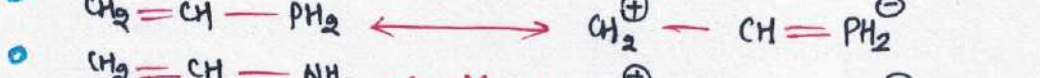
propargyl carbocation

A group having vacant orbitals will show -M effect.



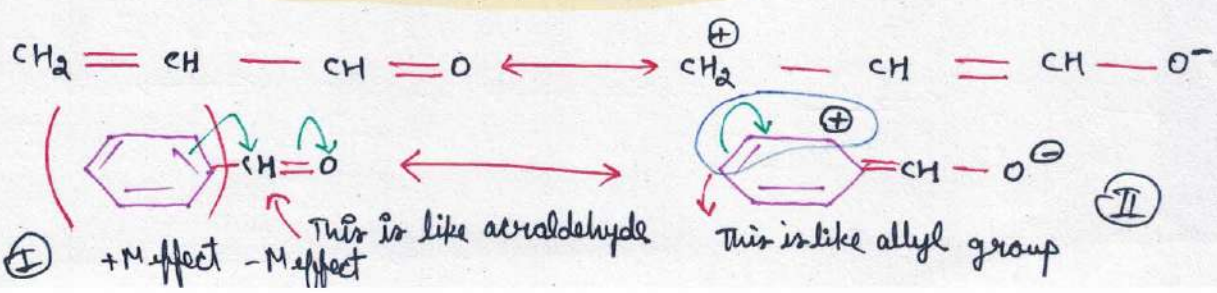


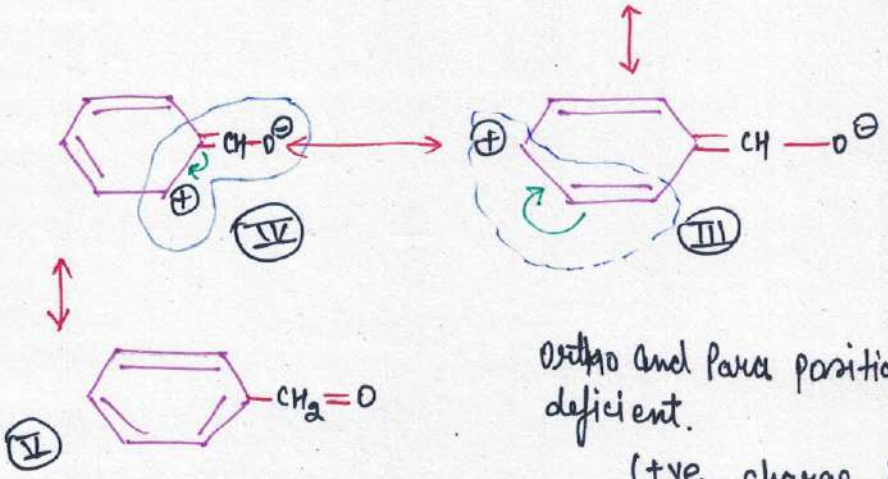
F does not have vacant d orbitals 



II Period elements will not show -H effect. They do not have vacant orbitals.

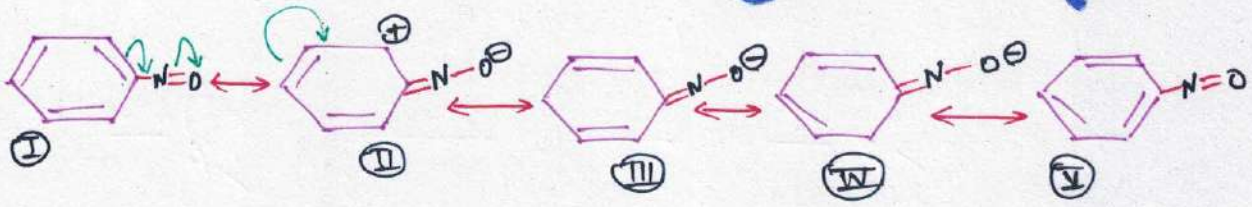
B has vacant p-orbitals



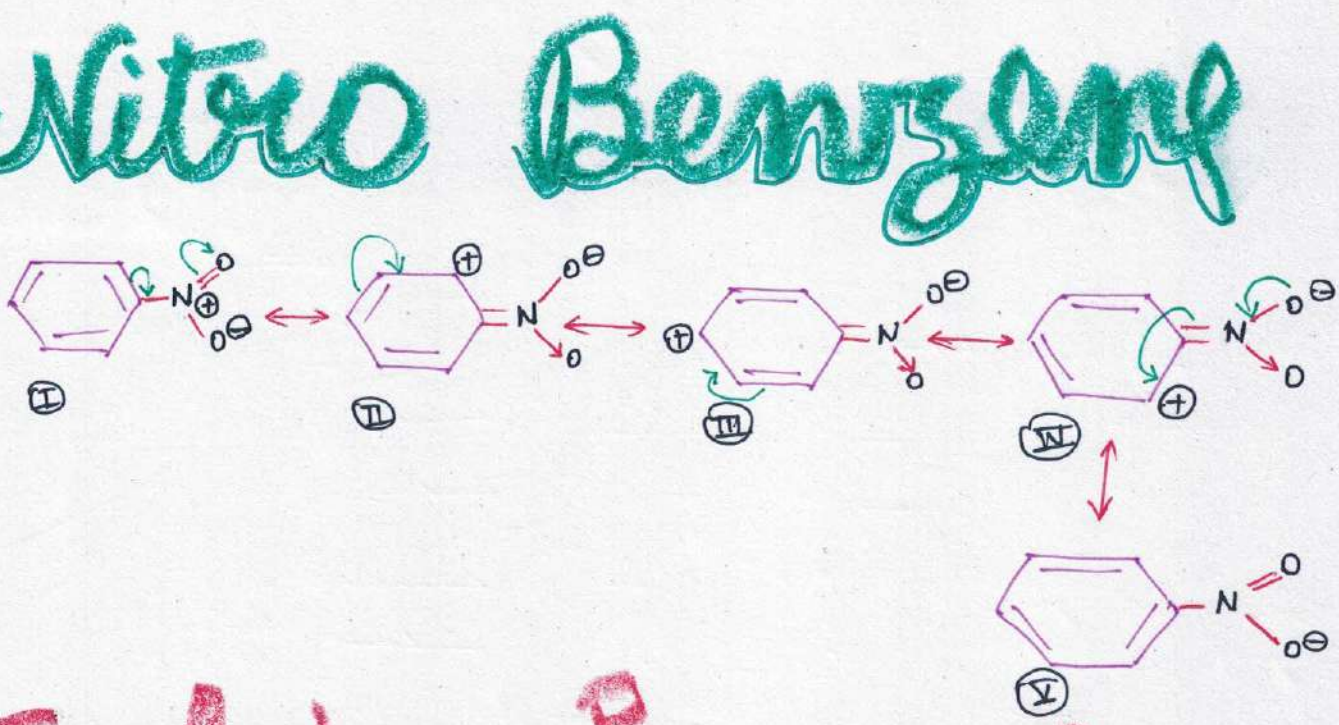


Ortho and Para position are electron deficient.
(+ve charge is there)

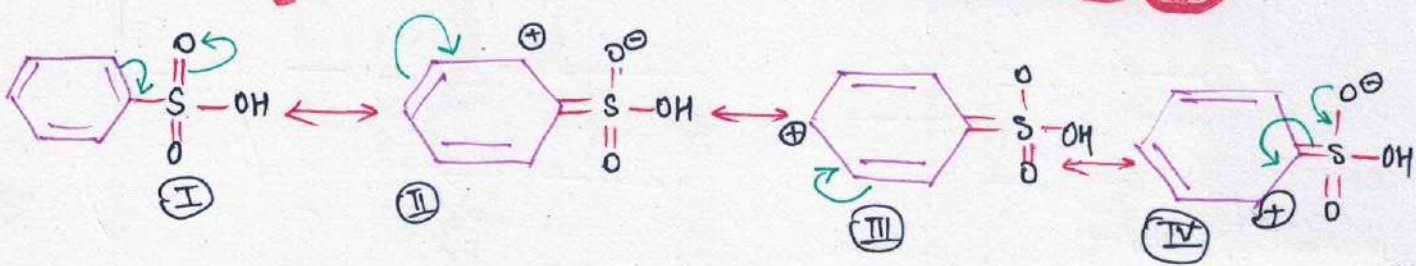
Nitroso Benzene

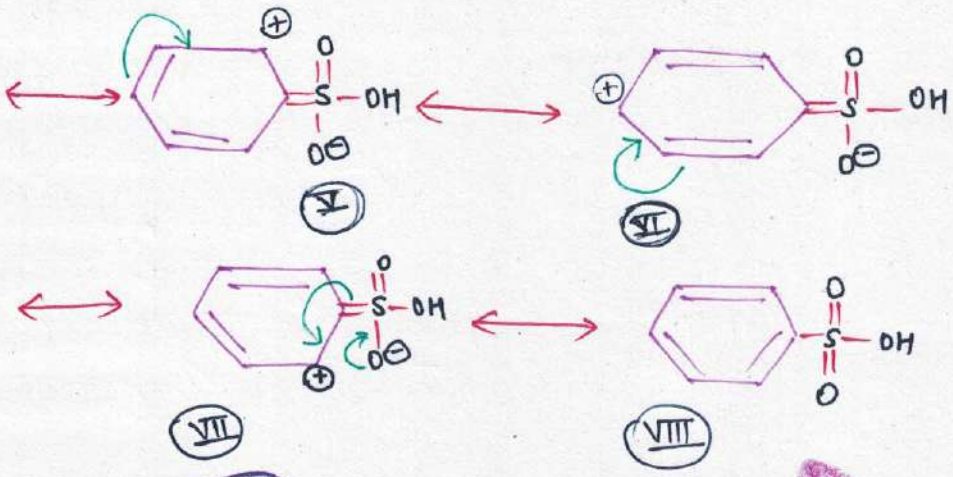


Nitro Benzene

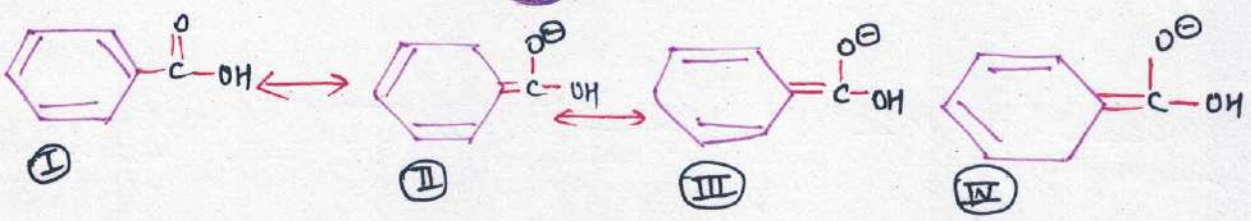


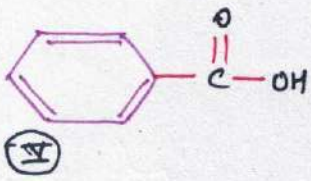
Sulphonic acid



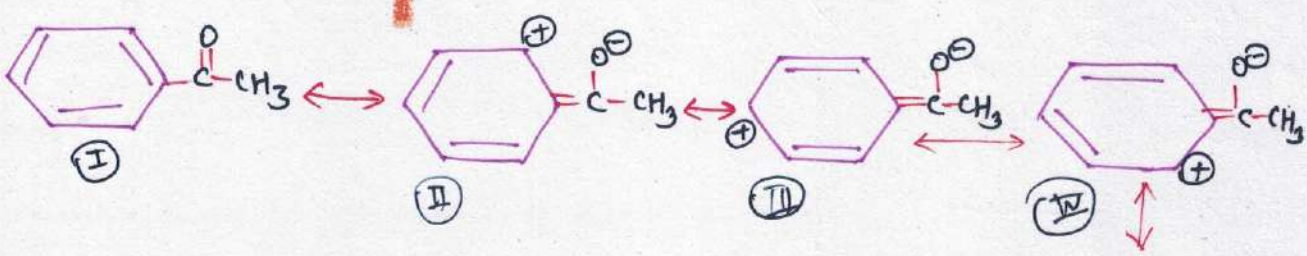


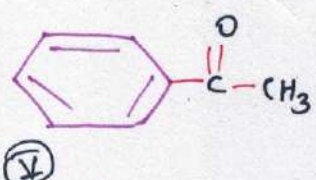
Benzoic Acid



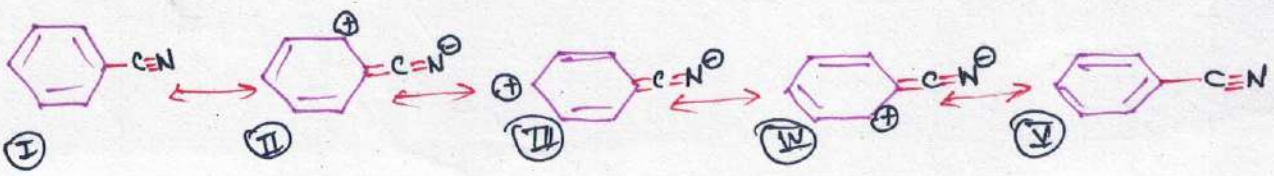


Acetophenone

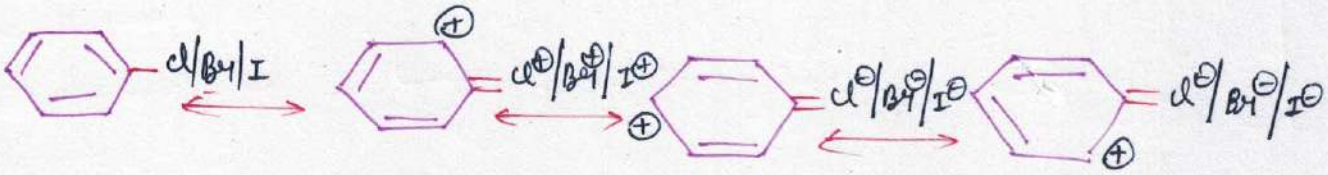


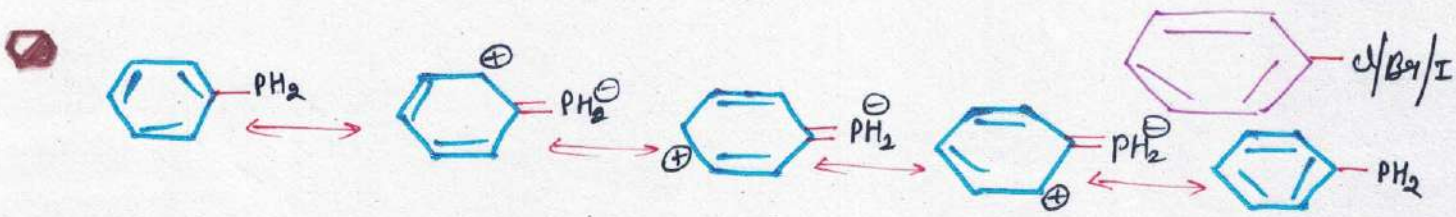


Benzene Nitrile



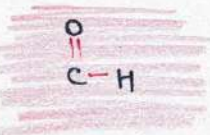
Benzyl chloride Bromide/Iodide

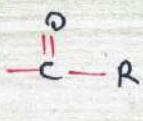


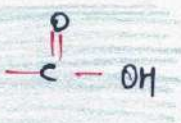


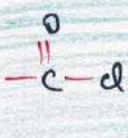
GROUPS SHOWING -H EFFECT

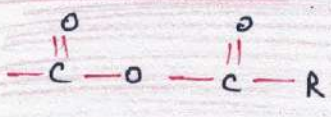
They have π bond with more EN atom

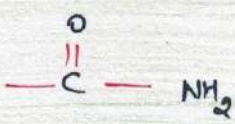


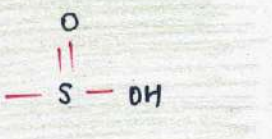


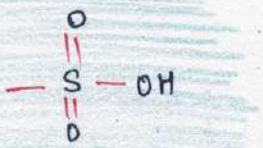


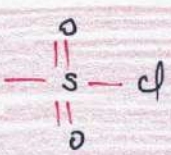


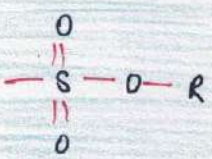


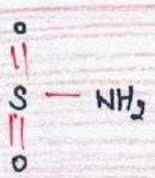


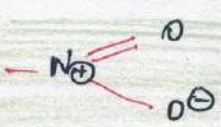






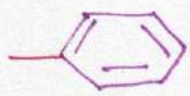






$-Cl$ $-Br$ $-I$ $-SH$ $-S-R$ $-PH_2$ $-CH_2^{\oplus}$ $PH_3^{\oplus}$ $SH_2^{\oplus}$

They have vaccant orbital

$-CH=CH_2$ $-C\equiv CH_2$ 

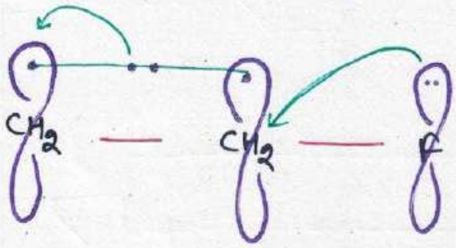
They show both +M and −M effect

- $-N(=O)(\to O^{\ominus})$ with $N^{\oplus}$ > $-N=O$
  (−I) (−I) ∴ NO_2 is strong withdrawing group than −NO.
  also
  (+M) (−M)

- $\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H-\overset{5}{C}H=\overset{6}{O}$ 1,3,5 are electron deficient positions.
  ($\delta+$ at 1, 3, 5)

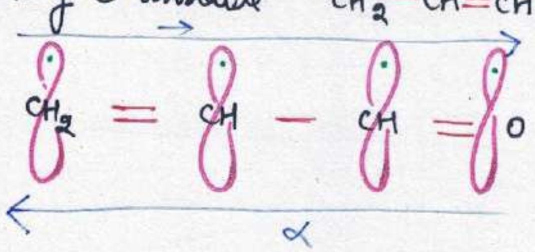
Delocalisation of π-bond with adjacent orbital having lone pair...

$CH_2=CH-\ddot{F}: \longleftrightarrow (\overset{\ominus}{C}H_2)(CH=\overset{\oplus}{F}:)$ 8e⁻ octel of F complete
(−M) (+M)



But → $CH_2=CH-CH=\ddot{O}:$

very very ⊖ unstable $CH_2-CH=CH-\ddot{O}^{\oplus}$ 6e⁻ octel incomplete



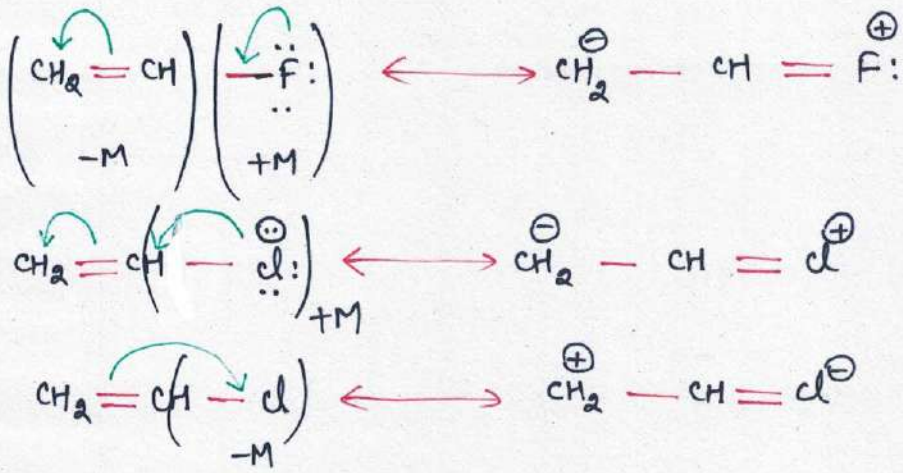
$CH_2=CH-\ddot{G}$
↕
$\overset{\ominus}{C}H_2-CH=G^{\oplus}$

So double bond can show +M as well as −M effect.

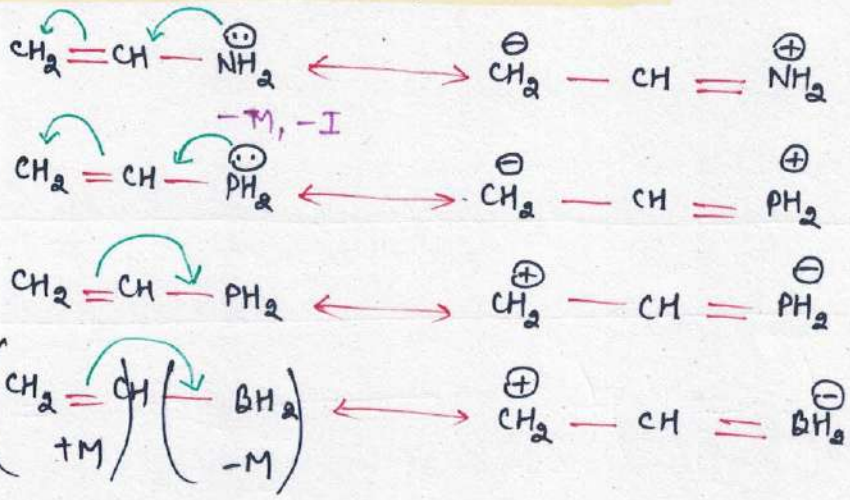
$(CH_2=CH)-CH=O \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH-O^{\ominus}$
(+M)

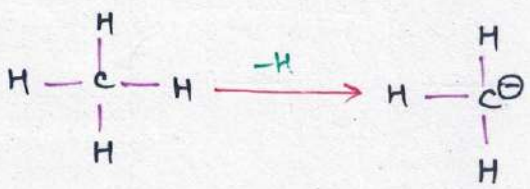
$(CH_2=CH)(\ddot{F}:) \longleftrightarrow \overset{\ominus}{C}H_2-CH=\overset{\oplus}{F}$
(−M) (+M)

$(CH_2=CH)(\ddot{O}-CH_3) \longleftrightarrow \overset{\ominus}{C}H_2-CH=\overset{\oplus}{O}-CH_3$
(−M) (+M)

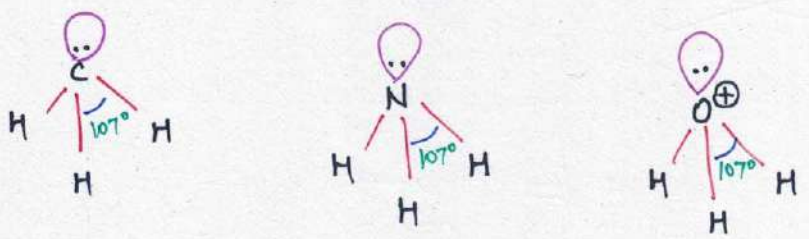


Cl/Br/I shows −M, +M, −I





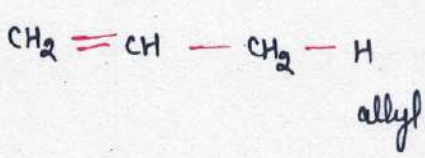
$CH_3^{\ominus}$ methyl carbanion



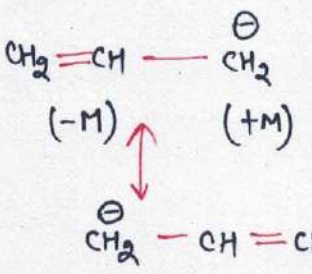
sp3 trigonal pyramidal

6 + 1 = 7 = 8 − 1

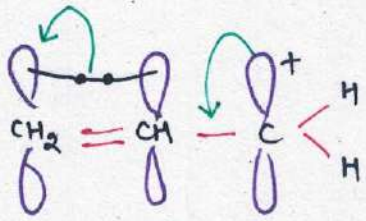
Carbanium, ammonium, hydronium ion are isoelectronic & isostructure.

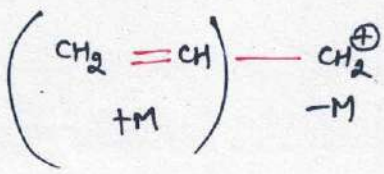


allyl

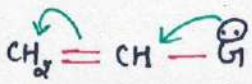


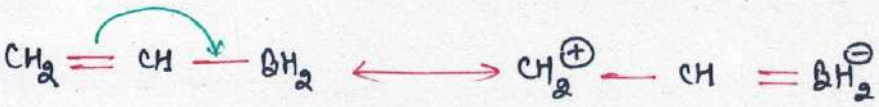
Allyl carbanium

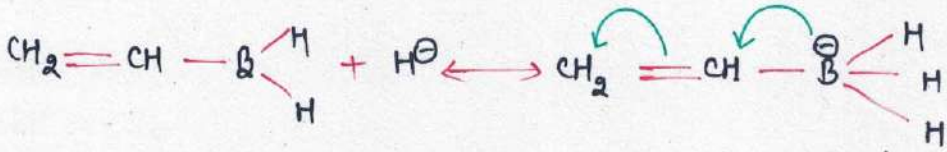




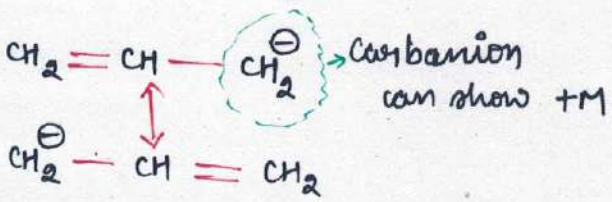
Any group having lone pair has to show +M effect always. (No exception)

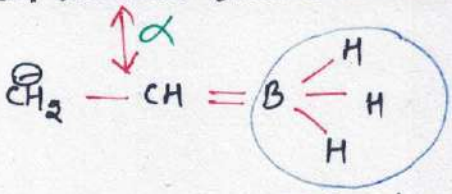




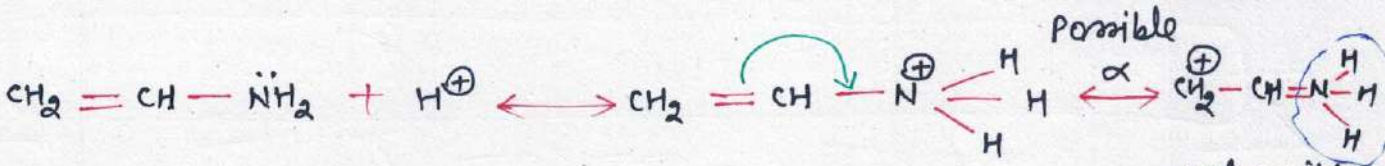


This molecule will not show resonance effect.

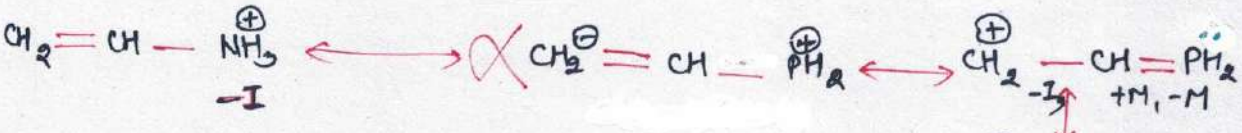


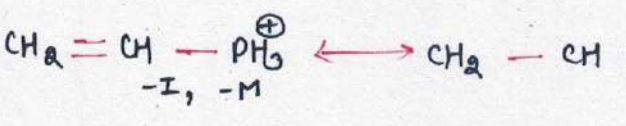


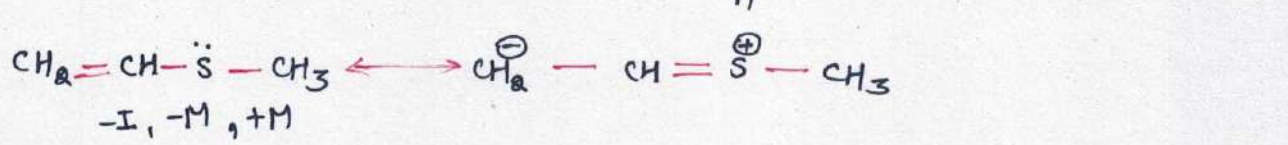
5 bonds not possible

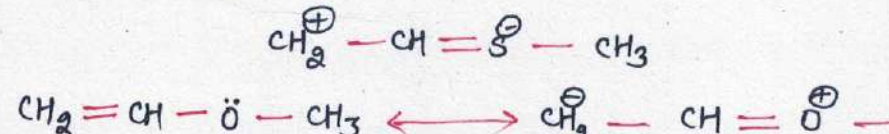


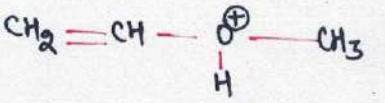
not possible



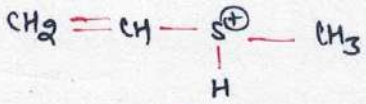


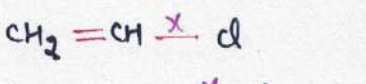


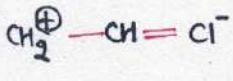




(no resonance effect)

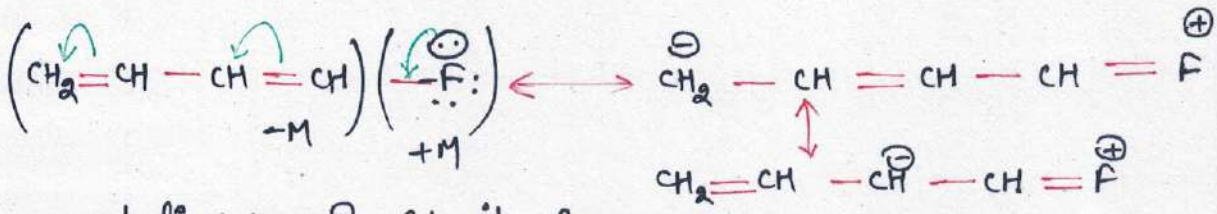




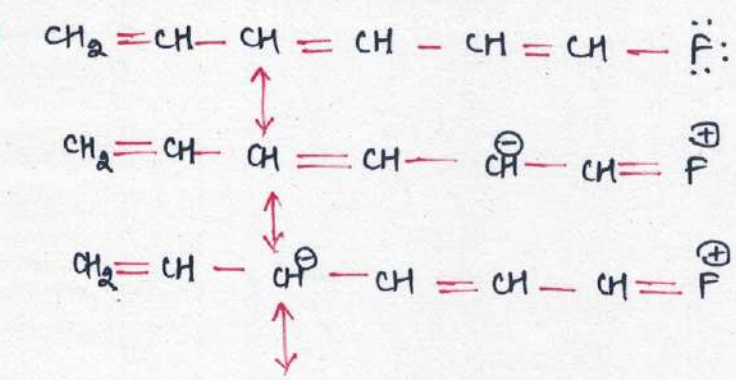


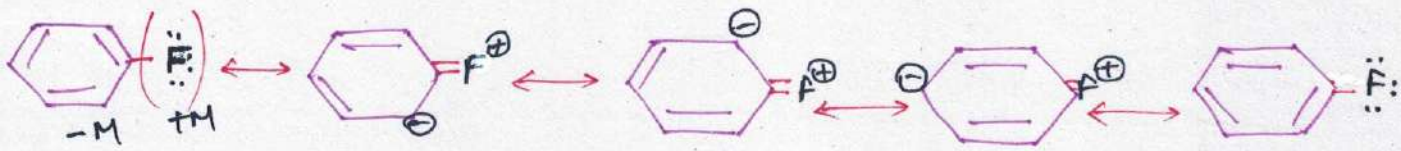
-I, -M

x is stronger than Y due to resonance (Partial double bond character).

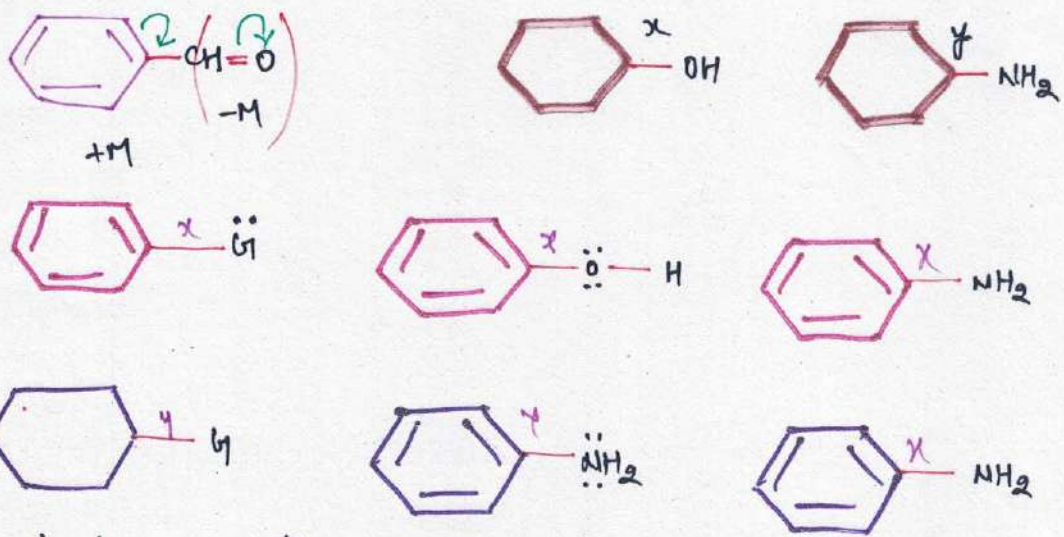


underline the $e^{\ominus}$ rich sites in



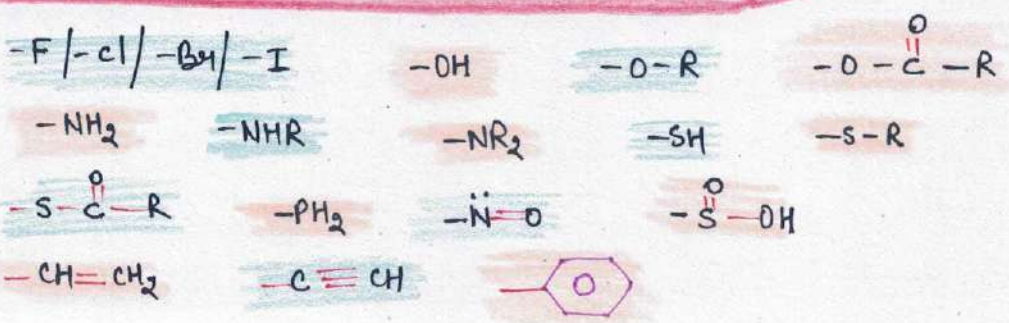


whether +M effect or -M effect resonance effect always transfer to ortho and para positions.

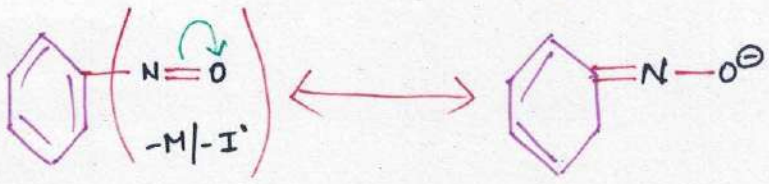


x is always shorter & stronger than Y

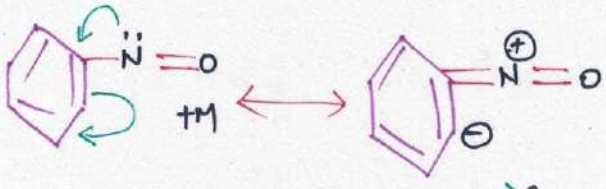
GROUPS SHOWING +M EFFECT

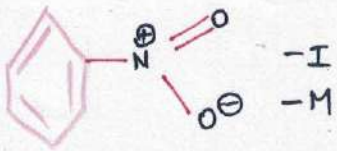


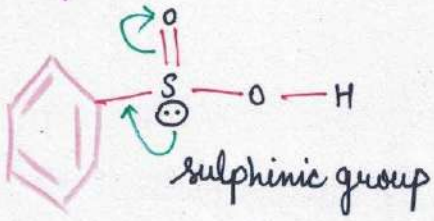
A group which shows −M, always show −I



☞ N=O group can show +M, −M and −I effect

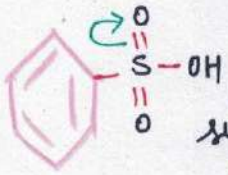






sulphinic group

+M, −M, −I



sulphonic group

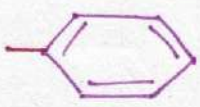
−M, −I

A group having more e⁻ v atom as well as having lone pair can show +M, −M and −I effect.

Groups showing −I, −M, +M effect

−Cl −Br −I −S−H −S−R $-PH_2$ −N=O −S(=O)−OH

$-CH=CH_2$ $-C\equiv CH$



−I EFFECT = −F > −Cl > −Br > −Br > −I

+M EFFECT = −F > −Cl > −Br > −I

2P − 2P mixing > 2P − 3P > 2P − 4P > 2P − 5P

Resonance energy / stability ⇒ −F > −Cl > −Br > −I

Heat of Hydrogenation ⇒ I > Br > Cl > F

STABILITY

$CH\equiv CH-F$ > $CH_2=CH-Cl$ > $CH_2=CH-Br$ > $CH_2=CH-I$

Vinyl fluoride Vinyl chloride Vinyl bromide Vinyl iodide

if −I > +M, the group is said to be withdrawing group.

if −I < +M, the group is said to be releasing group.

in all halogens, $-I > +M \Rightarrow$ halogens are always withdrawing group.

$CH_2=CH-\ddot{O}-CH_3$ All Alkoxy group will show +M releasing group.

$-I < +M$

$(CH_2=CH)\rightarrow X$

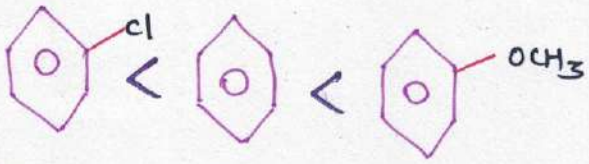
electron deficient

$CH_2=CH_2$

$(CH_2=CH)-O-CH_3$

electron rich

What is the rate of eqxn?



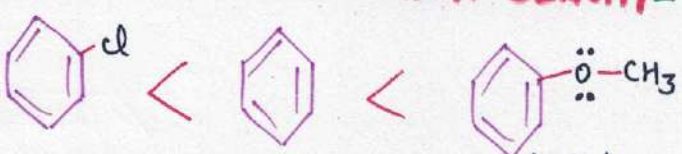
$CH_2=CH_2\rightarrow \ddot{Cl}:$

$-I > +M$

$CH_2=CH_2$

$CH_2=CH-\ddot{O}-CH_3$

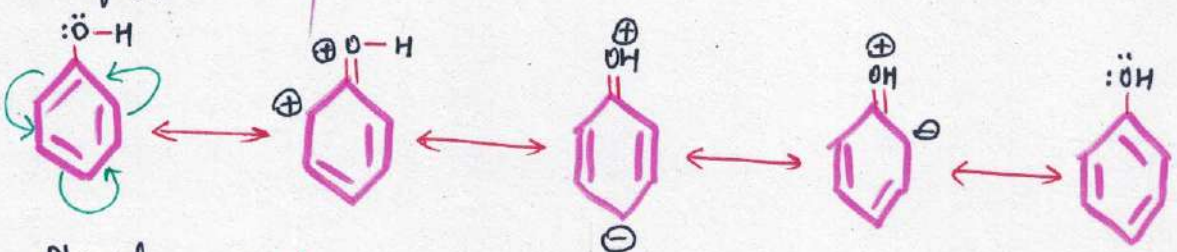
ELECTRON DENSITY = ① < ② < ③



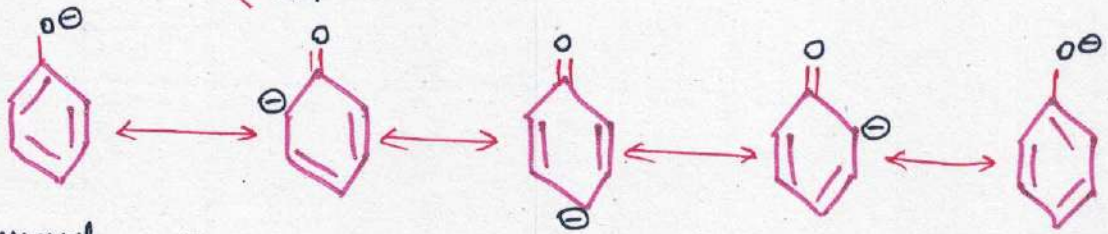
[Electron density]

The one having highest charge density will react with electrophile fast.

it reacts with $\overset{\oplus}{NO_2}$ mixture fastest



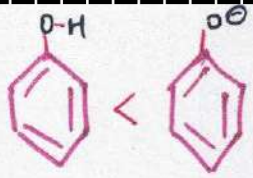
Phenol $-I < +M$

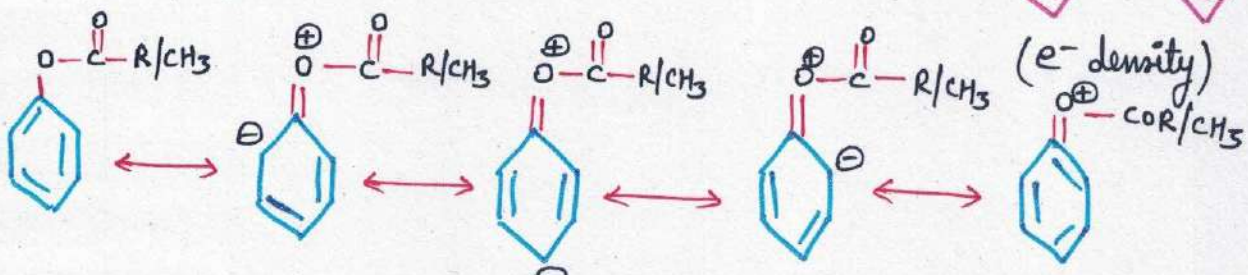


Phenoxyl $-I \ll +M$

+M effect = $O^{\ominus} > OH$

Phenoxyl will react faster than phenol with NO_2 mixture





(e⁻ density)

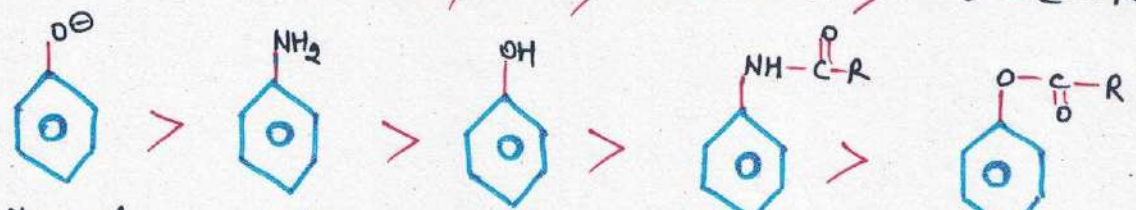
+M Effect = $-O^{\ominus} > -OH > -O-\overset{O}{\overset{\|}{C}}-R$

—Ö— have to disperse its e⁻ density between  and $-\overset{O}{\overset{\|}{C}}-R$

+M Effect $-S^{\ominus} > -SH > -S-\overset{O}{\overset{\|}{C}}-R$

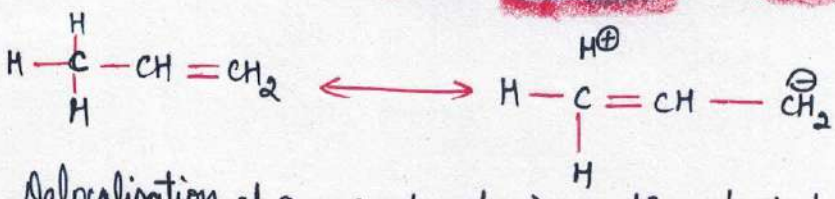
+M Effect $-NH^{\ominus} > -NH_2 > NH-\overset{O}{\overset{\|}{C}}-R > \overset{\oplus}{N}H_2$

+M Effect $-O^{\ominus} > -NH_2 > -OH > -NH-\overset{O}{\overset{\|}{C}}-R > -O-\overset{O}{\overset{\|}{C}}-R$

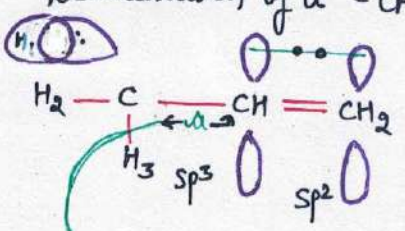


Phenoxyl > Aniline > Phenol > Acetanilide > Anisole

HYPER CONJUGA-TION

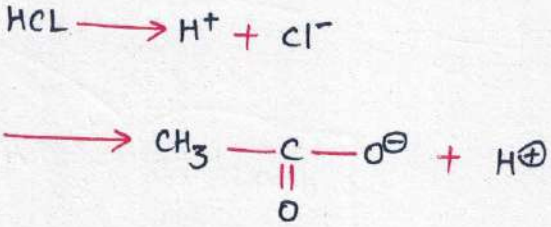


Delocalisation of a -CH bond with adjacent pie bond is known as hyperconjugation.

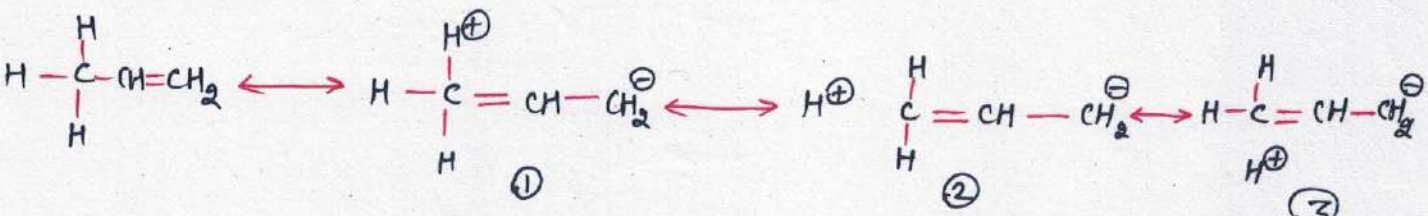


Electrons move from less EN(sp^3) to more EN(sp^2).

This bond can rotate. Sometimes H_1 will lie in plane, sometimes H_2, sometimes H_3.

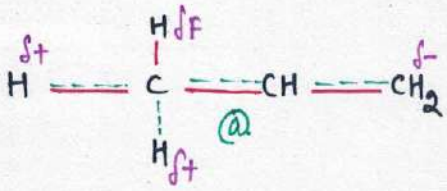


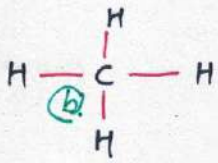
In hyperconjugation, there is no bond with one H^+. Therefore, it is called as no bond resonance.



no. of hyperconjugation structure = α-structure

$CH_3-CH=CH_2$ has 3 hyperconjugation structure.





(a) is longer and weaker bond than (b).

(a) < (b) (bond order) bond order of b=1

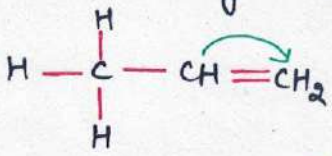
(a) < 1

A C–H bond if involved in hyperconjugation has bond order less than 1.

$CH_3 \overset{x}{-} CH_2 - CH_3$ B.O $x<Y$

$CH_3 \overset{Y}{-} CH = CH_2$ B.L $x>Y$

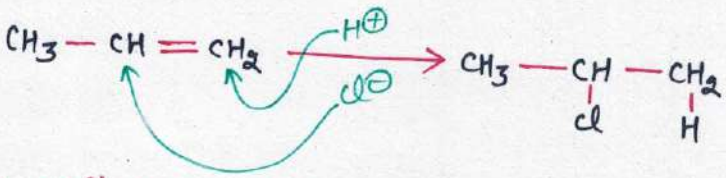
terminal carbon of the double bond is more basic.



Terminal c is more basic, it will accept $H^{\oplus}$

$CH_3 - CH = CH - CH_3$

no. of hyp. sty = 6



Q. Write the no. of hyper. sty. of the compounds.

- $CH_2 = CH_2$ → Zero
- $CH_3 - CH = CH_2$ → 3
- $CH_3 - CH = CH - CH_3$ → 6
- $CH_3 - C(CH_3) = CH - CH_3$ → 9
- $CH_3 - C(CH_3) = C(CH_3) - CH_3$ → 12

STABILITY

Tetra alkyl alkens > Tri > Di > mono

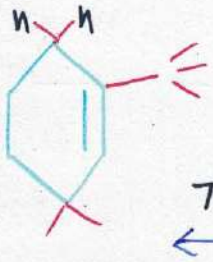
more hyper. sty., more stable

Heat of hyderogenation $\propto \frac{1}{\text{stability}}$

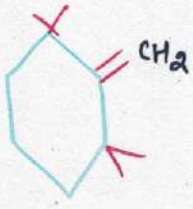
Heat of Hydrogenation ↓

- $CH_3 - CH = CH_2$ — 3α-H
- $CH_3 - CH_2 - CH = CH_2$ — 2α-H
- $CH_3 - CH(CH_3) - CH = CH_3$ — 1α-H
- $CH_3 - C(CH_3)_2 - CH = CH_2$ — 0α-H

stability ↑



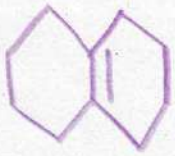
7-α-H



4α-H

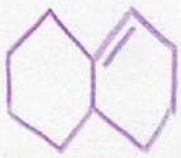
(heat of hydrogenation)

stability



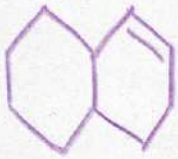
I

8α-H



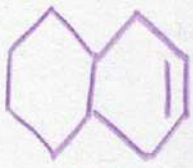
II

5α-H



III

3-αH

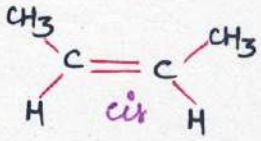


IV

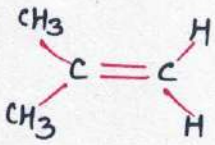
4α-H

Stability - I > II > IV > III

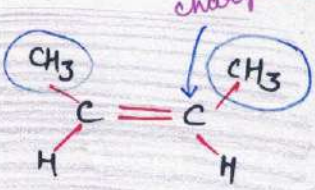
C_4H_8 isomers

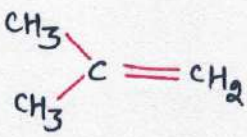


cis



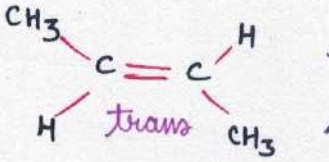
charge density



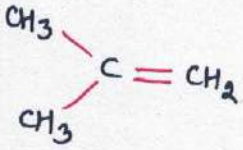


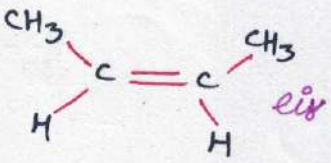
2. methyl propene

Stability



trans

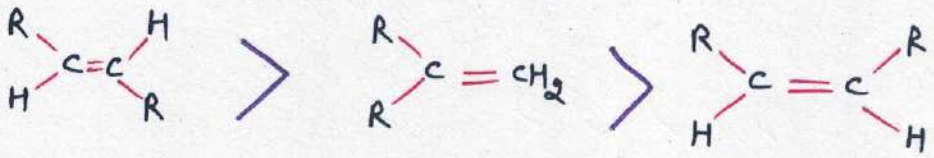




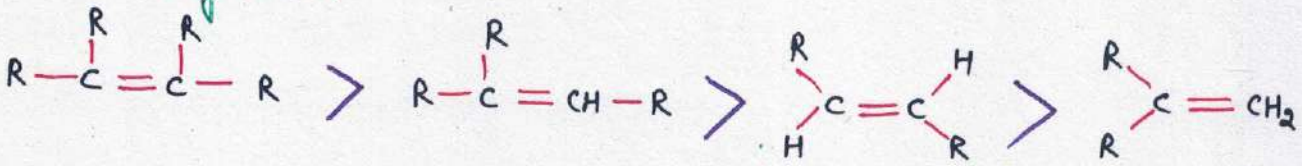
cis

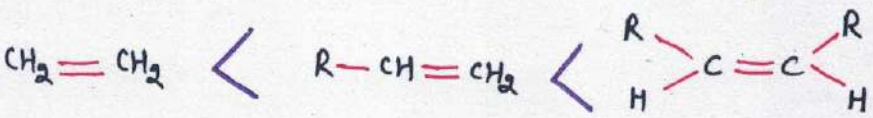
Reverse order for heat of hydrogenation / combination

$CH_3-CH_2-CH=CH_2$



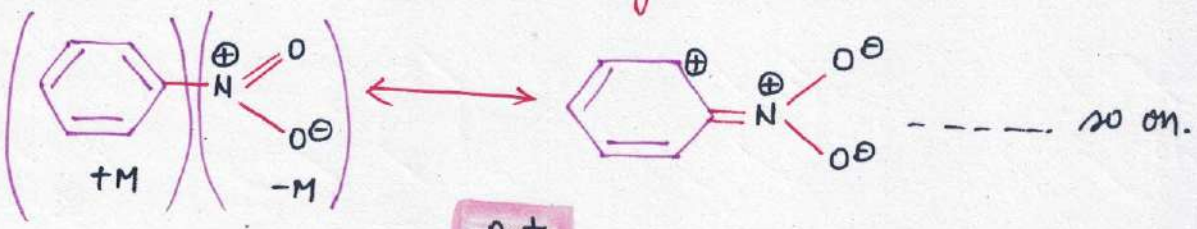
Stability order



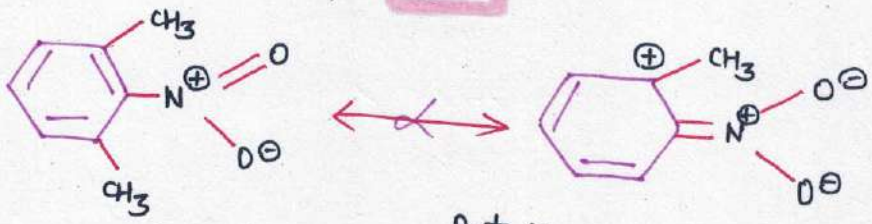


STERIC INHIBITION OF RESONANCE

Inhibition of Resonance between 2 groups due to adjacent bulky / crowded atoms is known as steric inhibition of resonance.

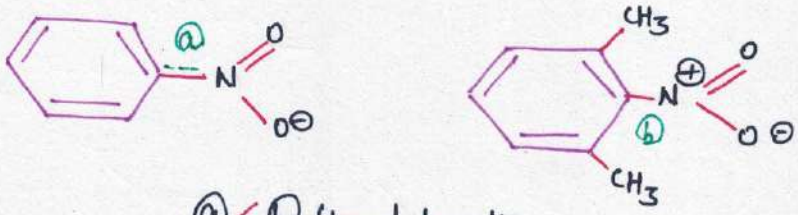


But



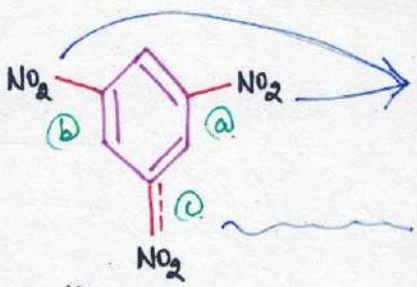
Condition of Resonance
→ Planar molecule

But they are never in same plane
→ steric Inhibition



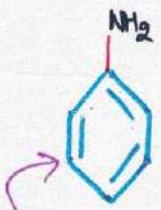
strong bond → @ > b

@ < b (bond length)

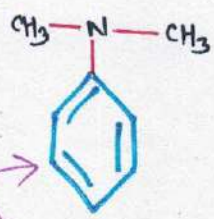


No Resonance will occur here (steric inhibition) Bond length
@ = b > @

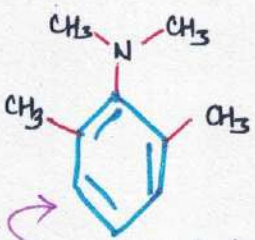
Resonance will occur here



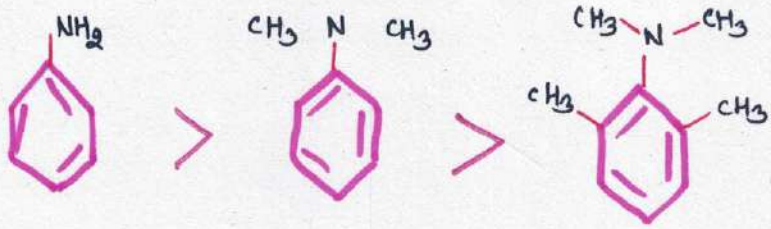
Resonance



partial inhibition



steric inhibition



(Stability)

HyperConjugation

Just decide by the no. of α-hydrogen.
More the no. of α-hydrogen, more is the stability.

E.g.

(i) $CH_3-CH=CH_2$ ⟶ No. of α-H = 3

(ii) $H_3C-CH=CH-CH_3$ ⟶ No. of α-H = 6

(iii) $CH_2=CH_2$ ⟶ No. of α-H = 0

(iv) $CH_3-C(CH_3)=C(CH_3)-CH_3$ ⟶ No. of α-H = 12

Stability (iv) > (ii) > (i) > (iii)

Compare the heat of hydrogenation for the following

(i) $CH_3-CH(CH_3)-CH=CH_2$

(ii) $CH_3-CH=CH_2$

(iii) $CH_3-C(CH_3)_2-CH=CH_2$

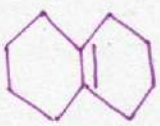
(iv) $CH_3-CH_2-CH=CH_2$

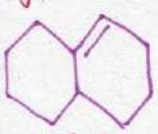
(i) ⟶ 1 (ii) ⟶ 3 (iii) ⟶ 0 (iv) ⟶ 2

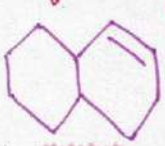
Stability → (ii) > (iv) > (i) > (iii)

Heat of hydrogenation → (iii) > (i) > (iv) > (ii)

Compare the stability order for the following.


(I)


(II)


(III)

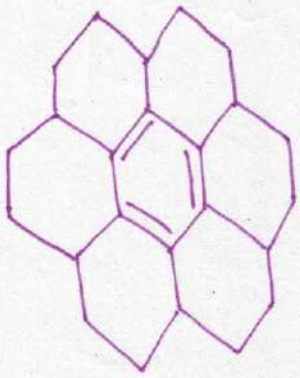

(IV)

(I) ⟶ 8α H (II) ⟶ 5α H (III) ⟶ 3α H (IV) ⟶ 4α H

Thus, stability order (I) > (II) > (IV) > (III)

QUE.

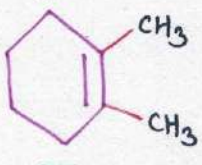
Find the no. of hyperconjugation structures for:-



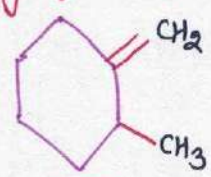
ANS... → (b)

QUE

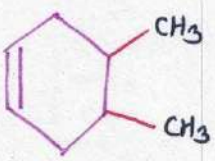
compare the stability of the following compounds:-



(a)



(b)



(c.)

ANS

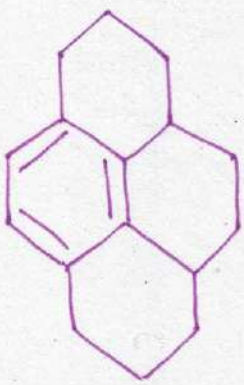
(a) → 10

(b) → 3

(c.) → 4

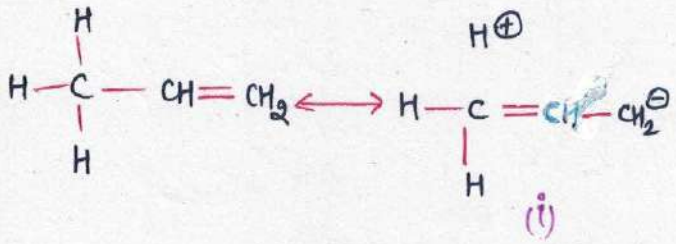
Stability a > b > c

Total number of hyperconjugation structures for:-

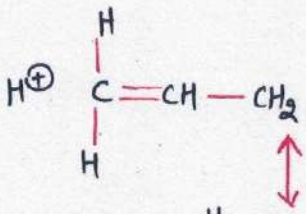


QUE. What is hyperconjugation ?

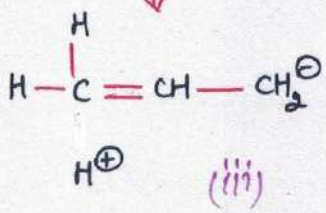
ANS. Delocalisation of a-CH bond with adjacent π-bond is known as hyperconjugation.



(i)



(ii)



(iii)

No. of hyperconjugation str. = No. of α-H

AROMATICITY

+ Br_2 / CCl_4 ⟶ no. reaxⁿ

36 Kcal very high Resonance energy

$CH_2=CH_2$ + Br_2 / CCl_4 ⟶ $CH_2(Br)-CH_2(Br)$

Compounds like benzene having very high Resonance energy resist to undergo addition reaxⁿ. (inspite of having unsaturation) shows aromaticity.

Conditions for a compound to be aromatic

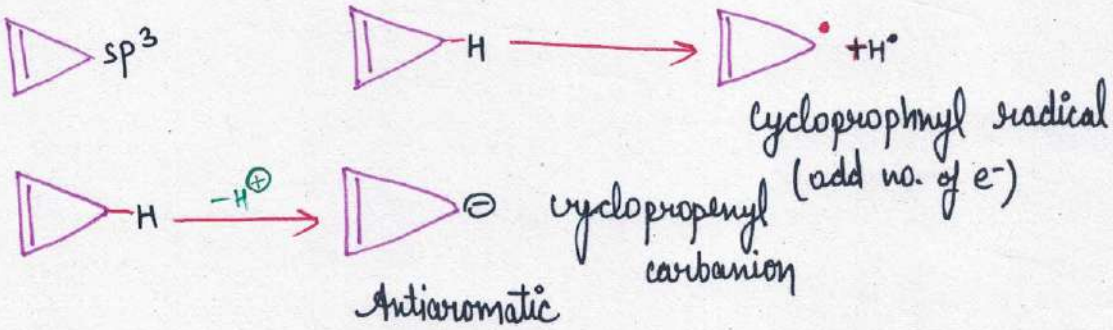
1. It should be cyclic
2. It should be planar
3. It should be have $(4n+2)\pi e^-$

$n = 0, 1, 2, 3$

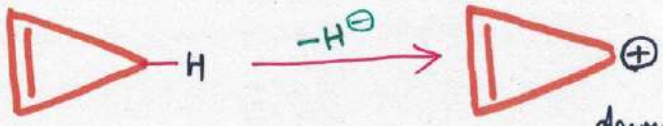
HUCKE'S RULE

A cyclic planar molecule possessing $(4n+2)\pi e^-$ is always aromatic.

If any one of the three is not satisfied, the compound is not aromatic.

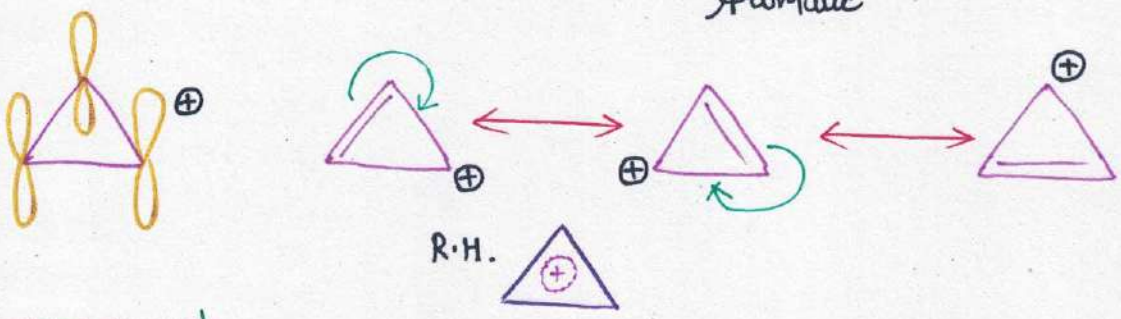


A Planar molecule (ion having $4n\pi\ e^{\ominus}$ is always antiaromatic.



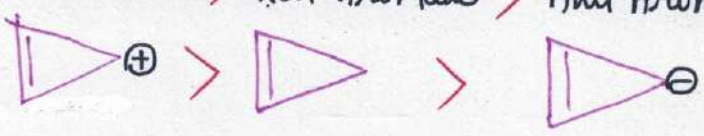
cyclopropenyl carbocation

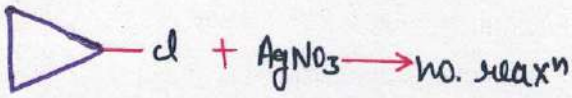
Aromatic



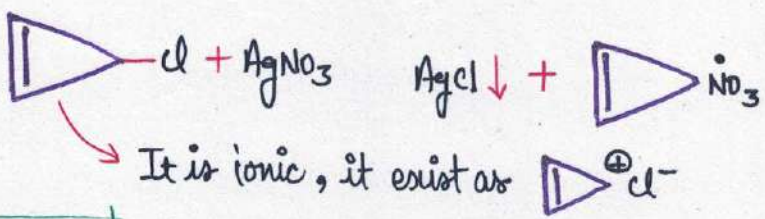
STABILITY

Aromatic > Non Aromatic > Anti Aromatic

Therefore,  (Stability)

1. 

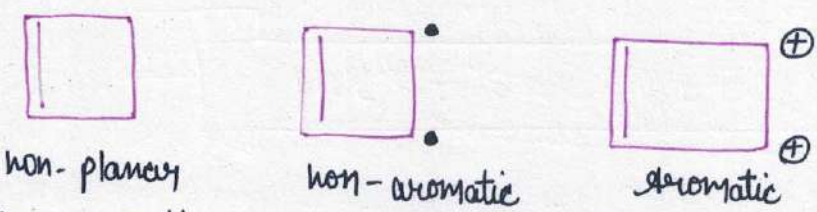
→ no. reaxn

2. 

It is ionic, it exist as

SOLUBILITY ② > ① reactivity with $AgNO_3$ ② > ①

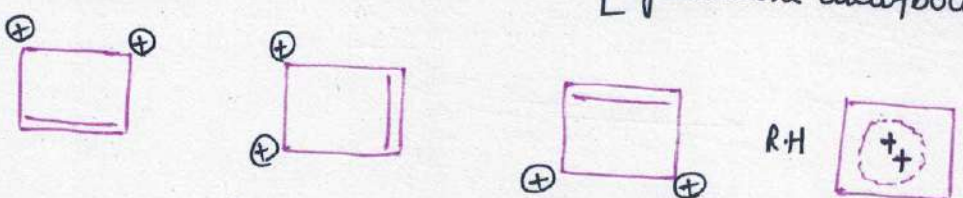
dipole moment ② > ① same order of m.p. b.p.

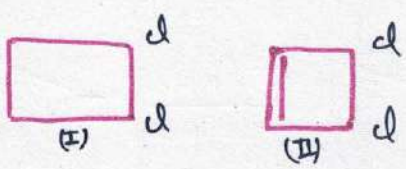


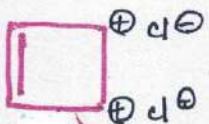
non-planar
non-aromatic

non-aromatic

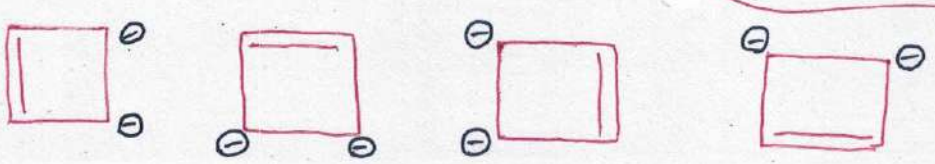
Aromatic
[cyclobutene dicarbocation]





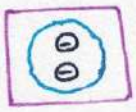
it exists as 

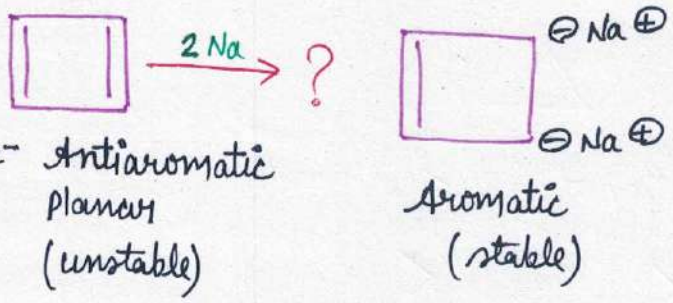
(II) Aromatic
(I) Non Aromatic



stability ② > ①

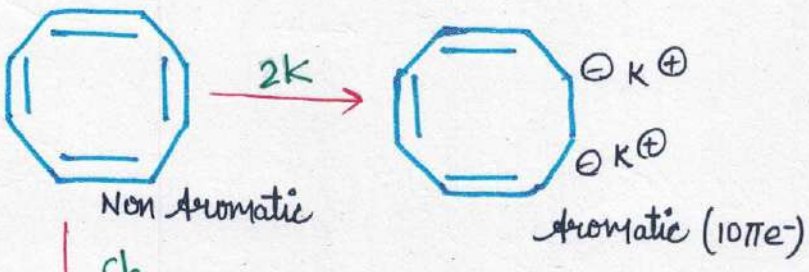
→ Cyclobutene dicarbanion (Aromatic) $6\pi e^-$ planar cyclic

R.H.  A 4 numbered ring will have 4 resonating structures



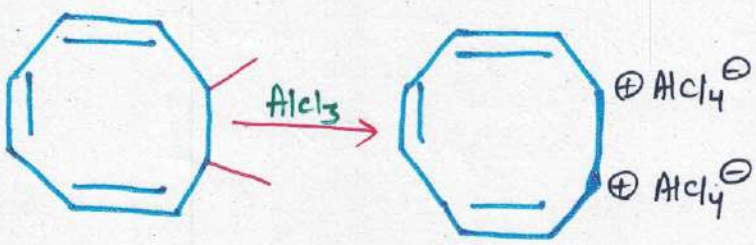
$4\pi e^-$ Antiaromatic Planar (unstable)

Aromatic (stable)

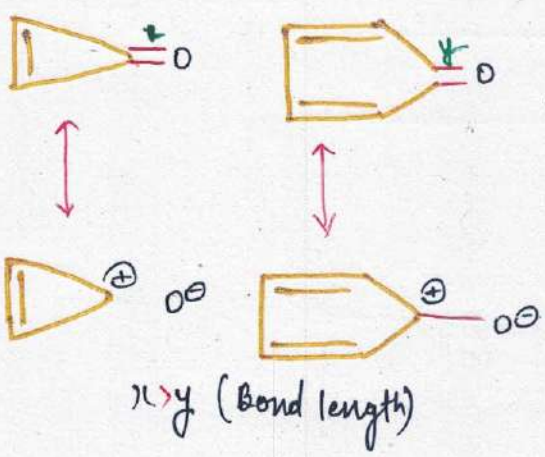


Non Aromatic

Aromatic ($10\pi e^-$)

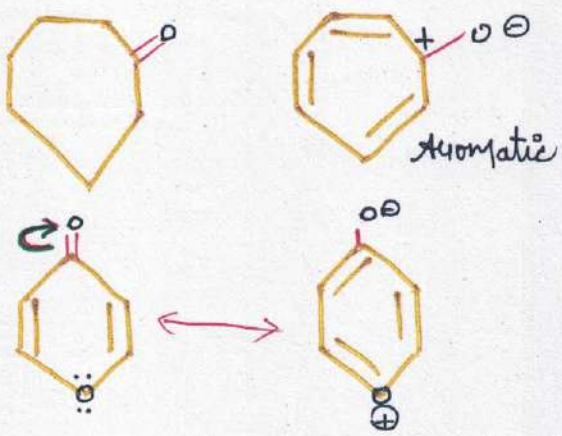


$6\pi e^-$ (Aromatic)

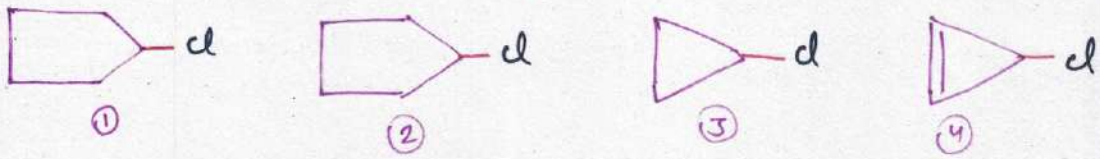


$x > y$ (Bond length)

Aromatic Antiaromatic



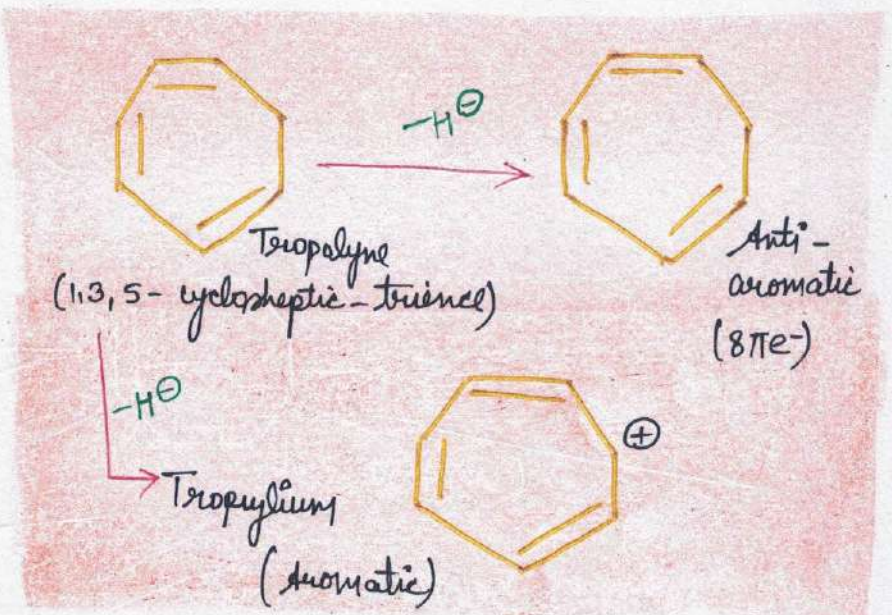
Which will react first with $AgNO_3$ resolive?

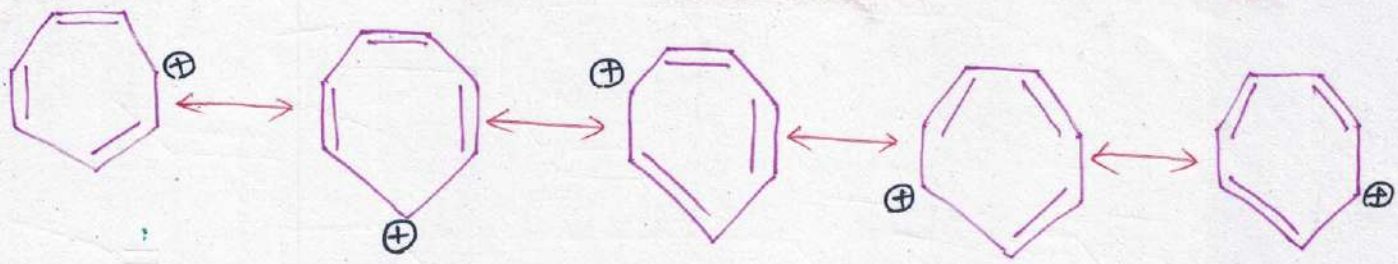


4.

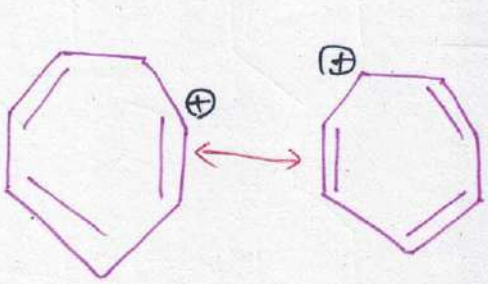
Benzene
(Aromatic)

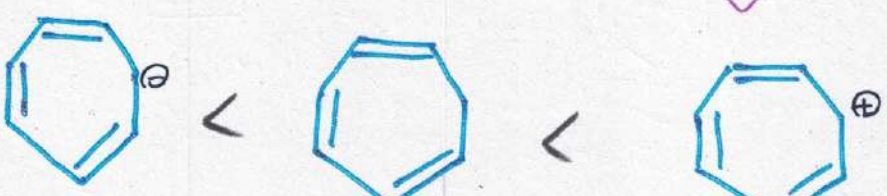
7 member ring will have
7 resonating structures.





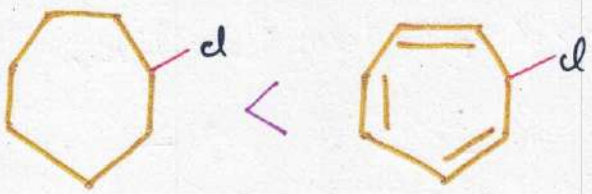
7 Resonating structures of
Tropylium





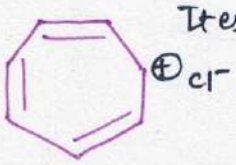
Anti Aromatic < Non-aromatic < Aromatic

stability

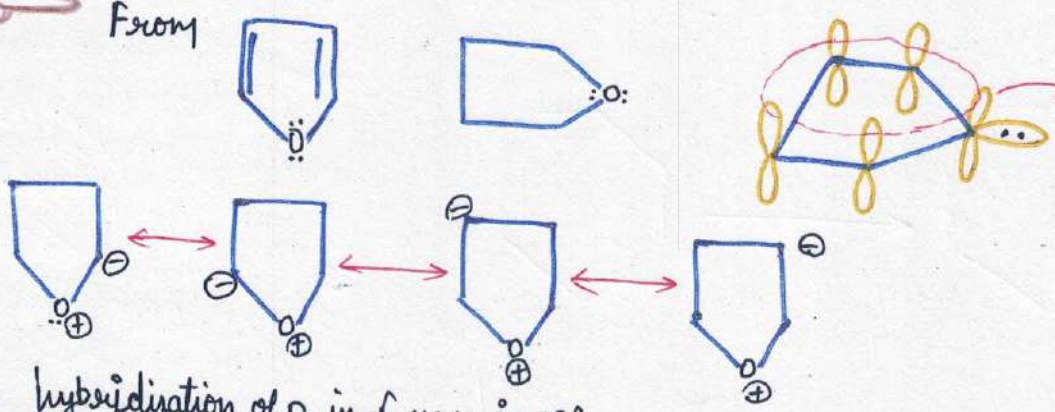


[m.p., b.p. dipole moment, reactivity with $AgNO_3$]

It exist as

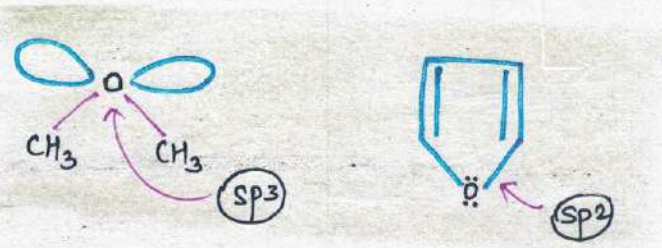


From



This lone pair is not involve in delocalisation

hybridisation of O in furan is sp^2.

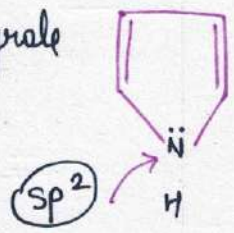


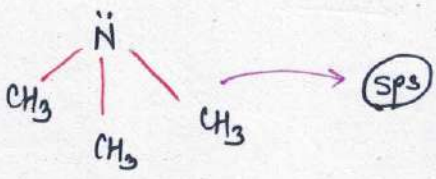
The lone pair inside will be participating in resonance.

no. of $\pi e^- = 6$

(Aromatic compound)

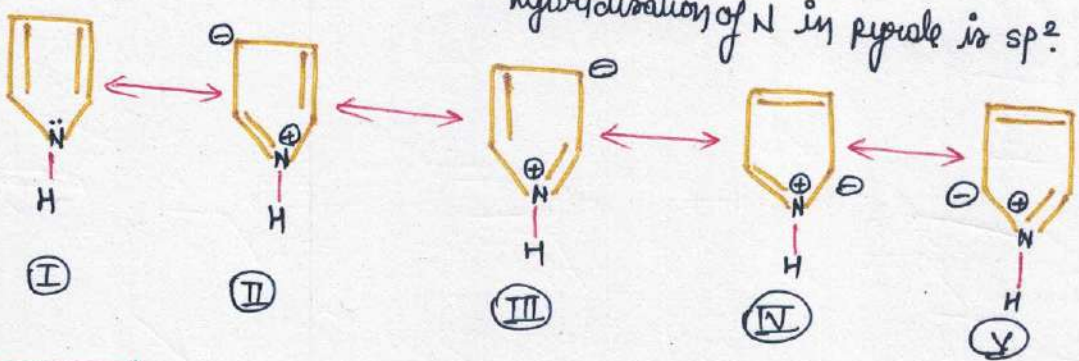
Pyrole





Pyramidal

hybridisation of N in pyrole is sp^2.

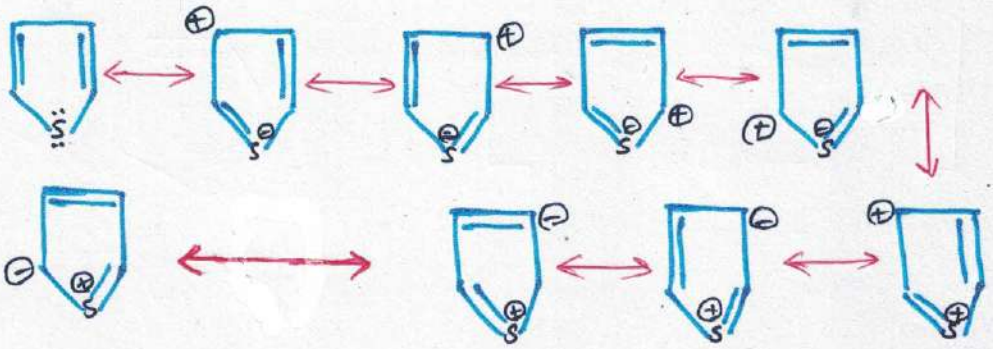


Stability

Pyrole > furan (Resonance energy)

+ve charge on N is more stable than +ve charge on O

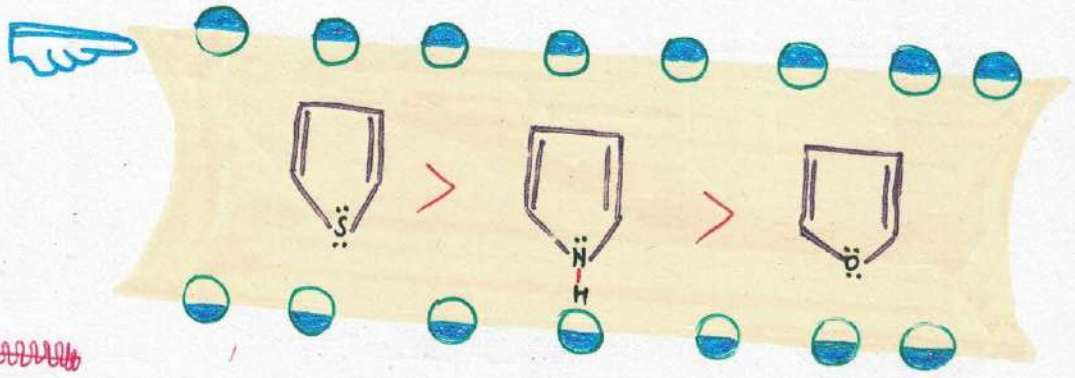
Thiophene

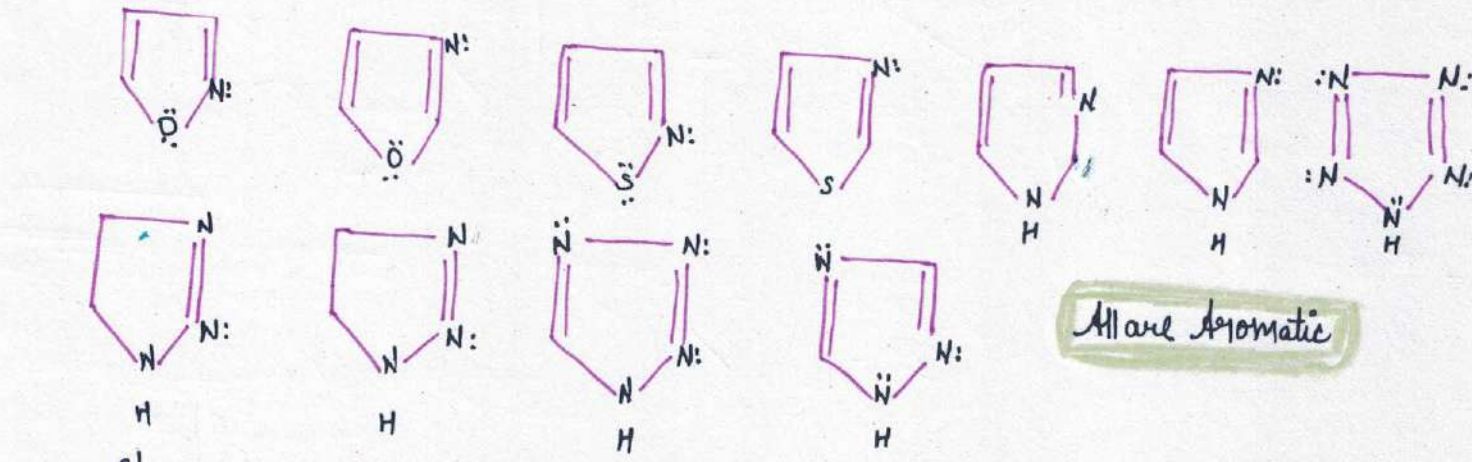


Thiophene has 9 resonating structure

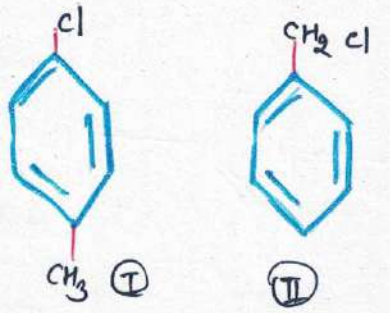
Stability

Thiophene > pyrole > furan

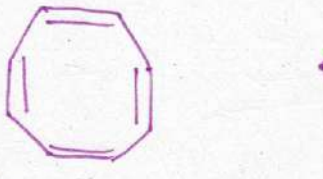




All are Aromatic



III will react with $AgNO_3$ fast.

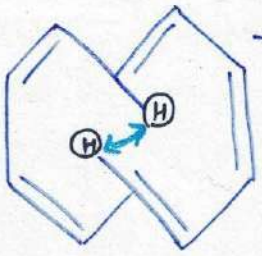


[8] - Annulene

Non Aromatic

Boat like structure

[cyclooctatriene is non-aromatic]

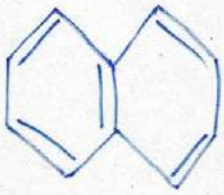


→ Its R.E is less. The H atom repel each other so, both rings will not lie in same plane.

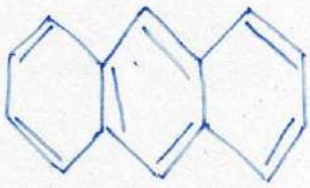
[10] - Annulene ↔ Non aromatic

Mono cyclic → single ring

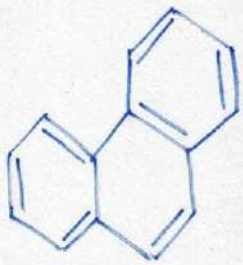
carbocyclic compounds → All atom are carbon



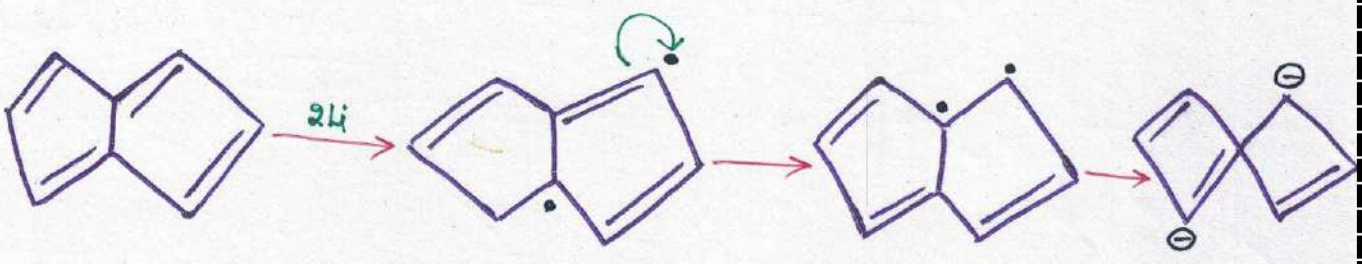
Napthalene → carbocyclic bicyclic compound



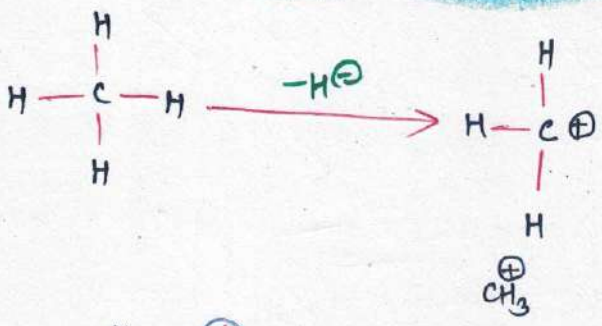
Anthracene → carbocyclic Tricycle compound



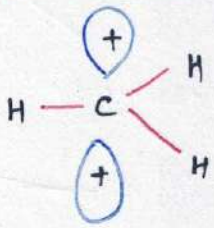
Phenanthrene



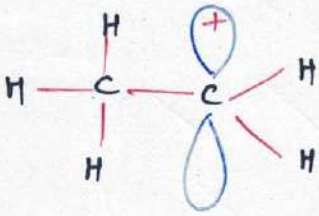
STABILITY OF CARBOCATION

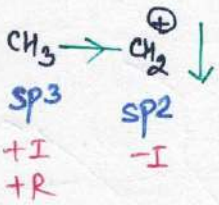


methyl carbocation



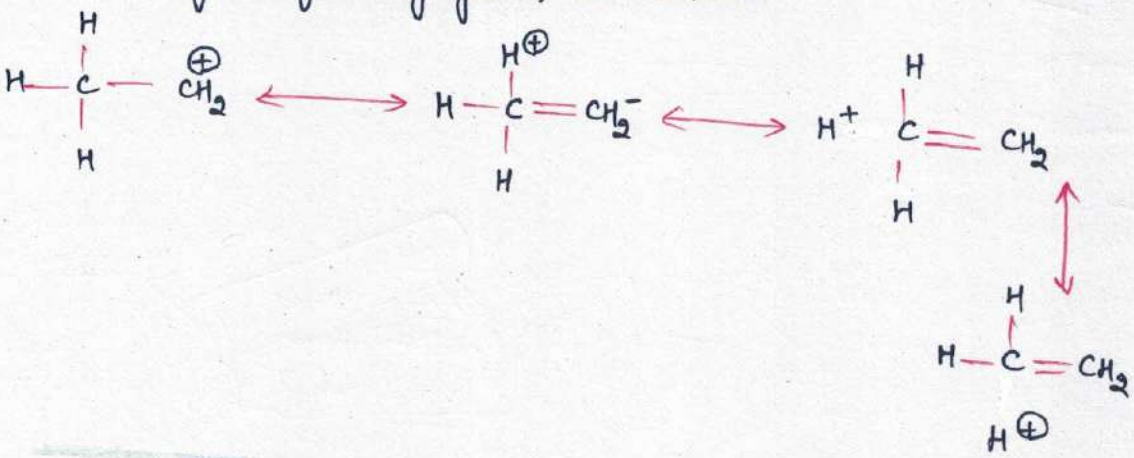
sp^2, diamagnetic

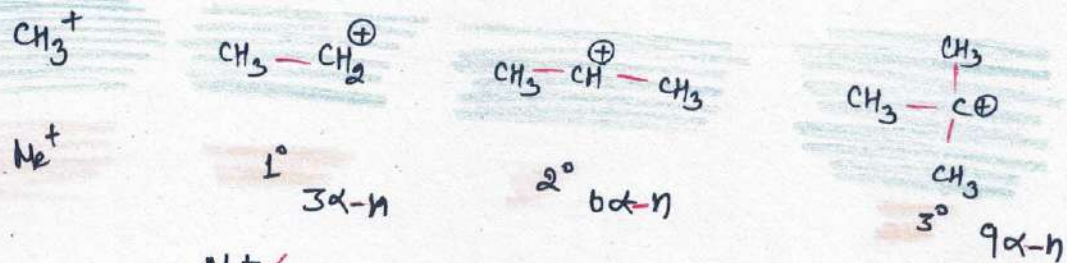




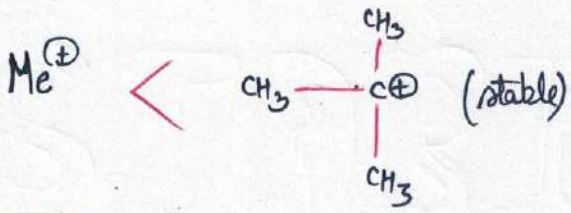
+I effect is decreasing charge intensity.

carbocation also undergoes hyperconjugation like alkenes.



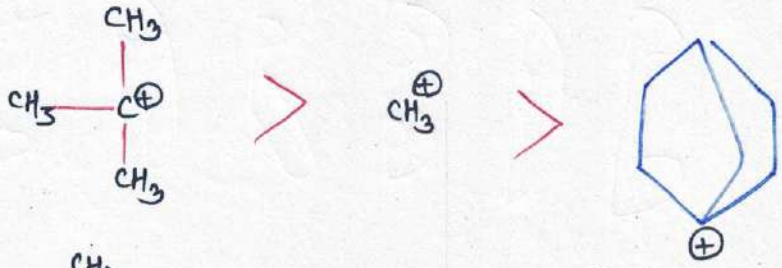


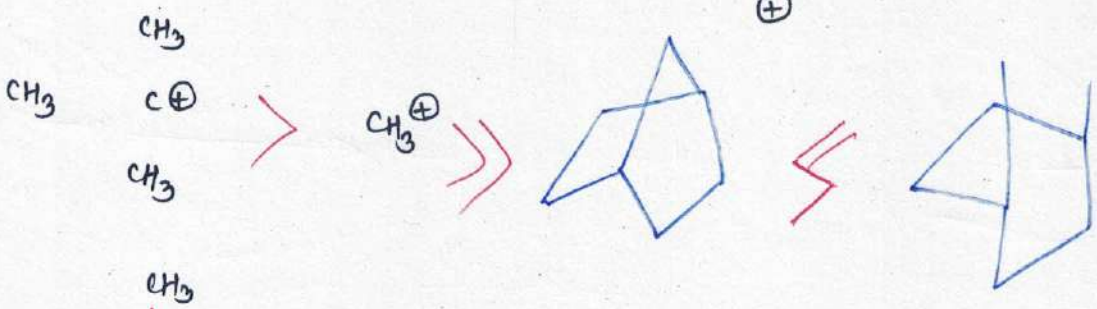
$Me^+ < 1° < 2° < 3°$ carbocation (stability)

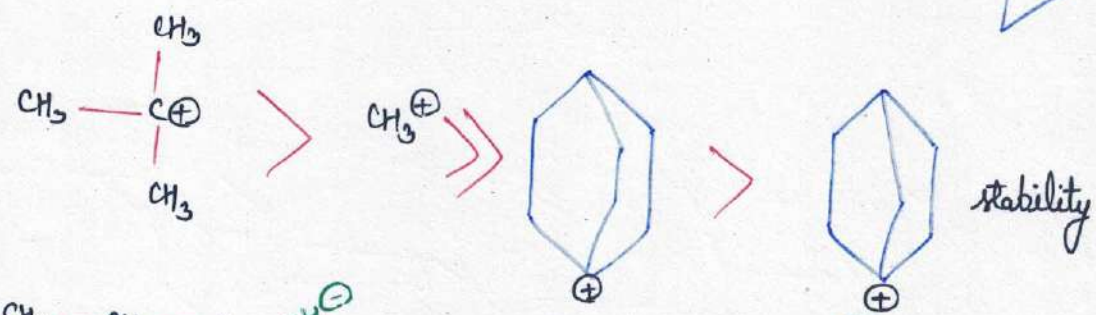


Carbocation at bridgejection is unstable.

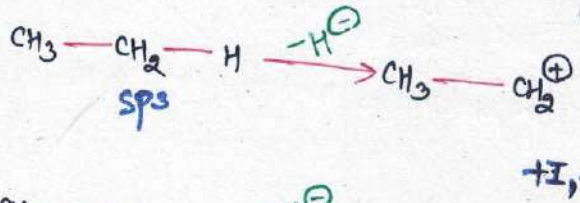
Non-planar carbocations are unstable.

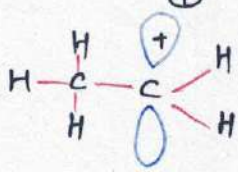




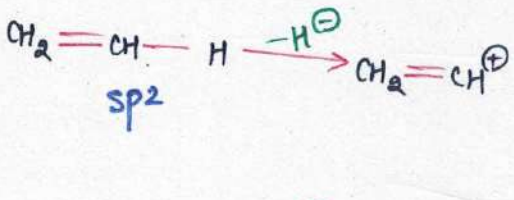


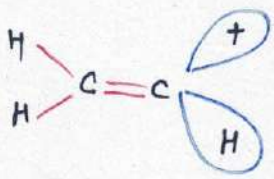
stability



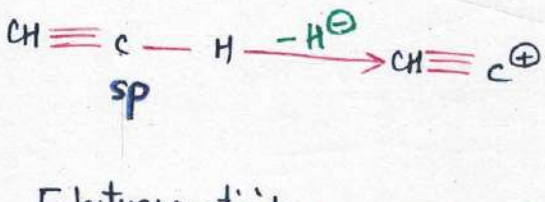


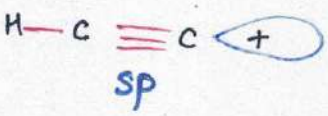
Resonance occur





sp2 No Resonance



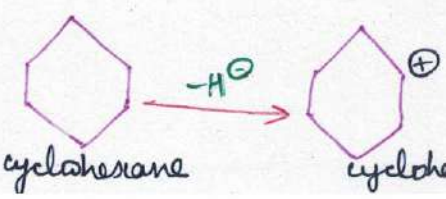


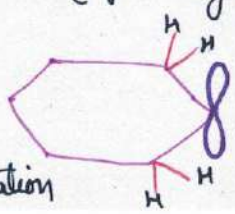
No Resonance

Electronegativity :- $sp > sp^2 > sp^3 > p$

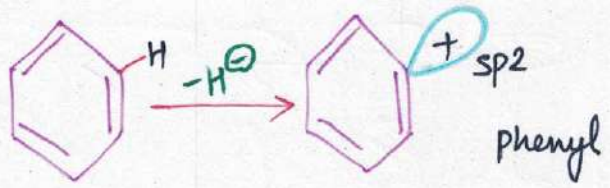
$CH_3-CH_2^{\oplus} > CH_2=CH^{\oplus} > CH\equiv C^{\oplus}$ (stability)

Stabilised by resonance (hyper conjugation)



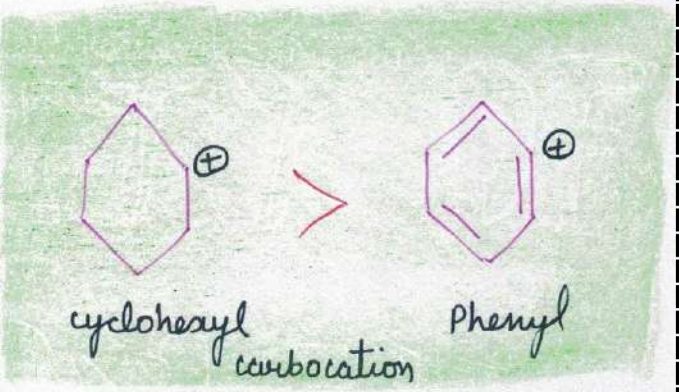


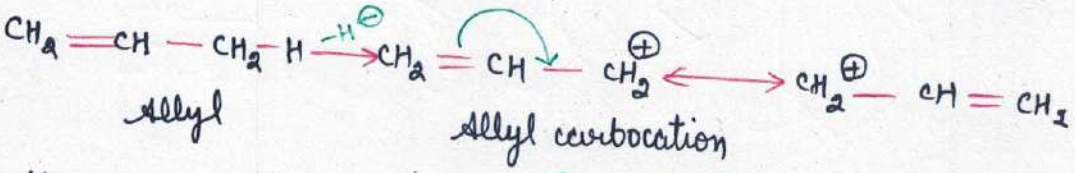
+I, +R

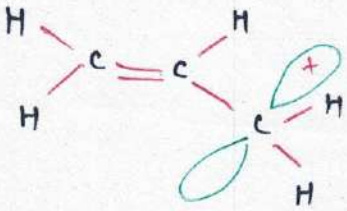


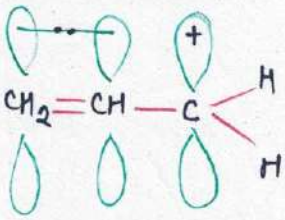
phenyl

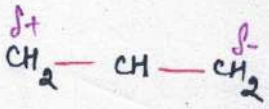
(no resonance)



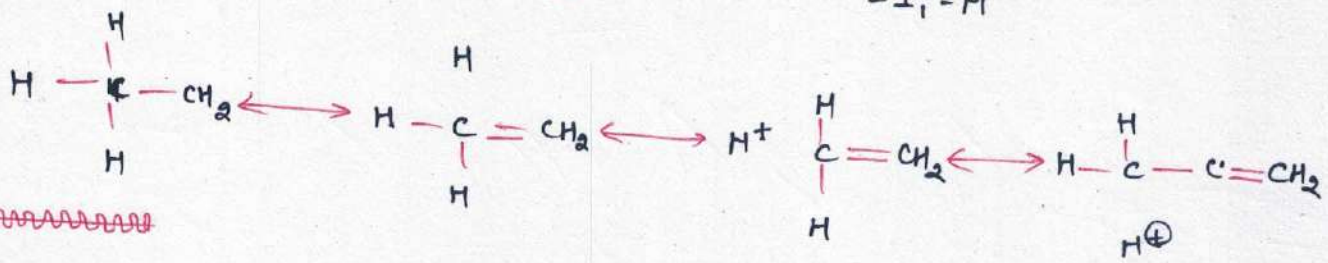


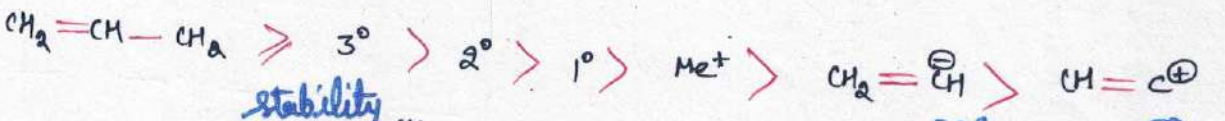


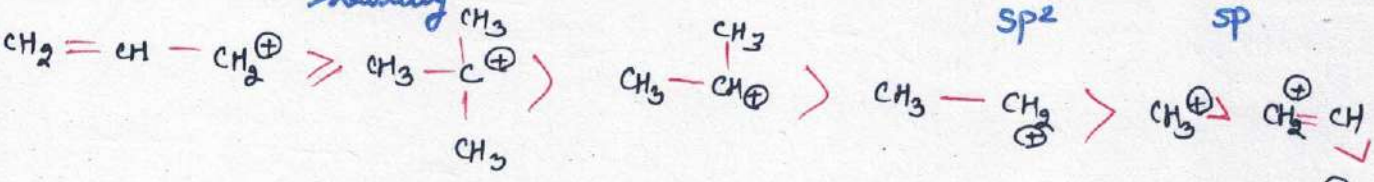




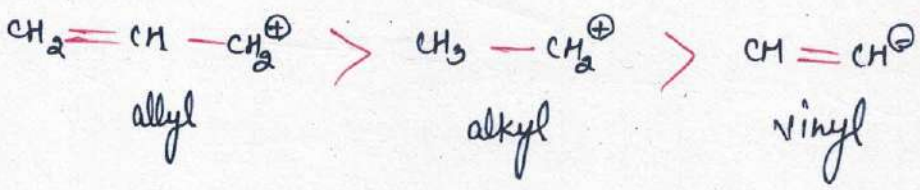
$-I, -M$

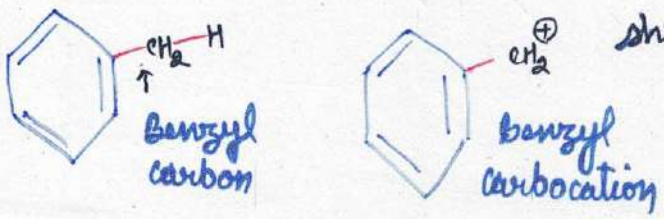




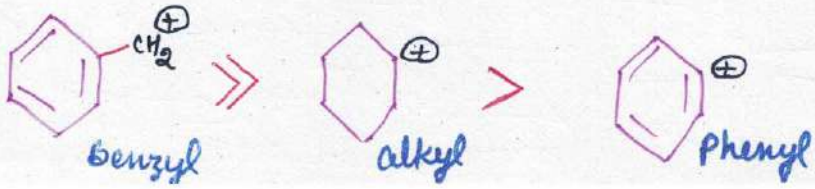


Stability acquired by mesomeric effect is more than that of hyperconjugation.



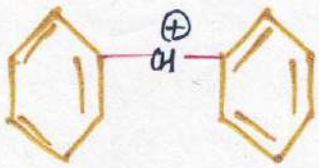


shows mesomeric effect



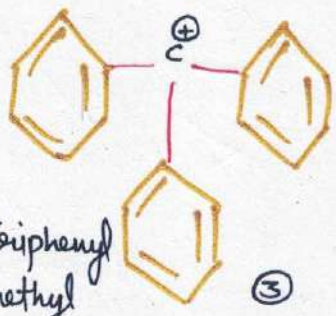
Benzyl
or Phenyl-methyl

①



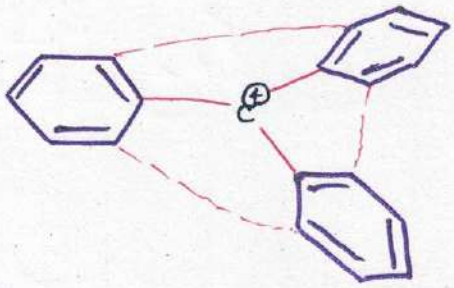
Diphenyl methyl

②



Triphenyl methyl

③



stability ④ > ③ > ② > ①

ring is not able to rotate

$CH_3-\overset{\oplus}{C}H_2$ < $CH_3-\overset{\oplus}{C}H-\ddot{O}-CH_3$ (stability)

$CH_3-CH=\overset{\oplus}{O}-CH_3$ ← octet complete (more stable)

alkoxy group → when in resonance → releasing group (-I, +M)(+M, +T)

when not in resonance → withdrawing group (-I)

$CH_3-\overset{\oplus}{C}H-OCH_3$ > $CH_3-\overset{\oplus}{C}H_2$ > $\overset{\oplus}{C}H_2-CH_2-OCH_3$

resonance — hyper. — no resonance

$CH_3-\overset{\oplus}{C}H_2$ ①

$CH_3-\overset{\oplus}{C}H-NH-CH_3$ ↔ $CH_3-CH=\overset{\oplus}{N}H-CH_3$ ②

$\overset{\ominus}{C}H_2-CH_2-NH-CH_3$ ③

Stability :- ② > ① > ③

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

-I > +M — -I

$CH_3-\overset{\oplus}{C}H_2$ ①

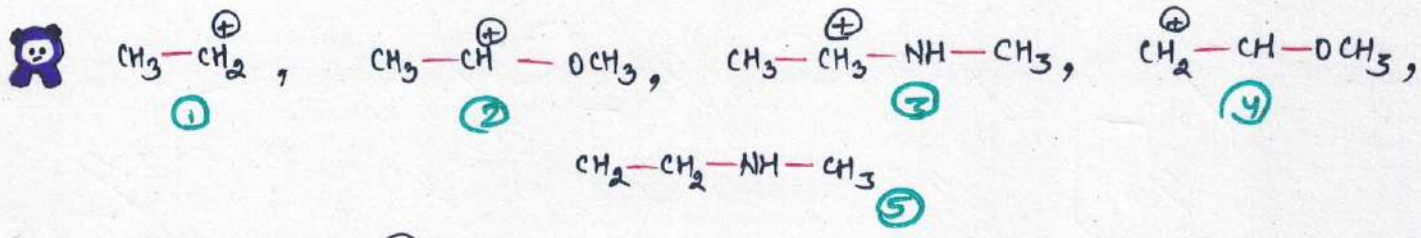
$CH_3-\overset{\oplus}{C}H-OCH_3$ ②

$CH_3-\overset{\oplus}{C}H-NH-CH_2$ ③

$CH_3-\overset{\oplus}{C}H-Cl$ ④

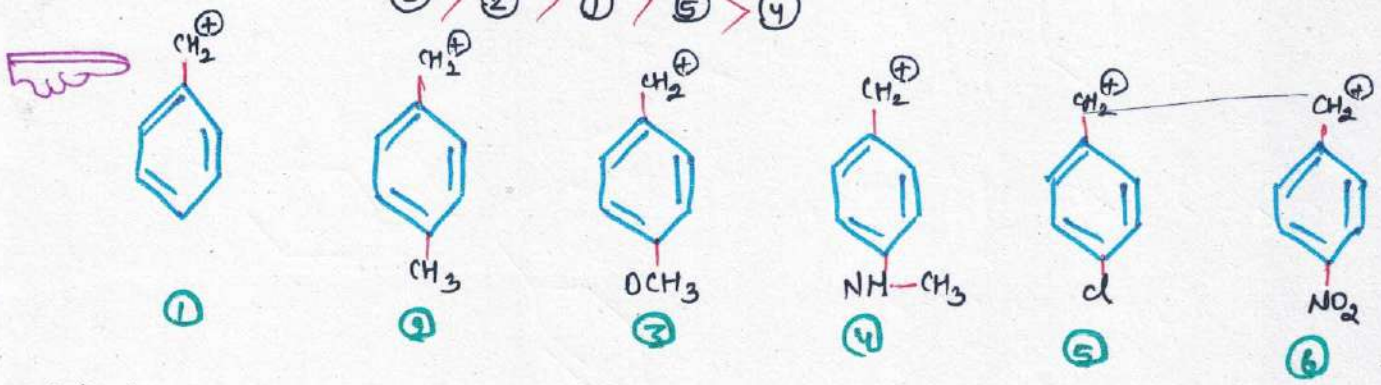
③ > ② > ① > ④

stability



(1) (2) (3) (4) (5)

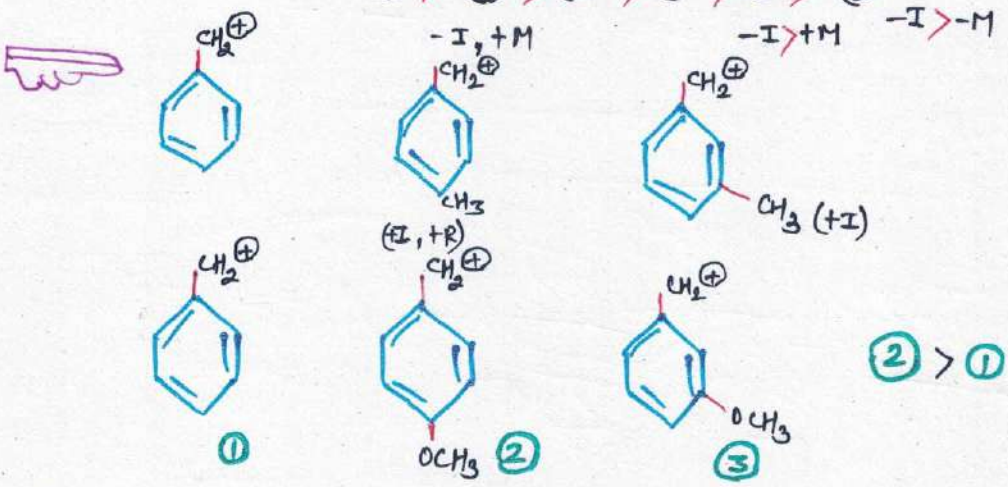
③ > ② > ① > ⑤ > ④



(1) (2) (3) (4) (5) (6)

Releasing group stabilisis the carbocation, withdrawing group destabilish carbocation.

④ > ③ > ② > ① > ⑤ > ⑥



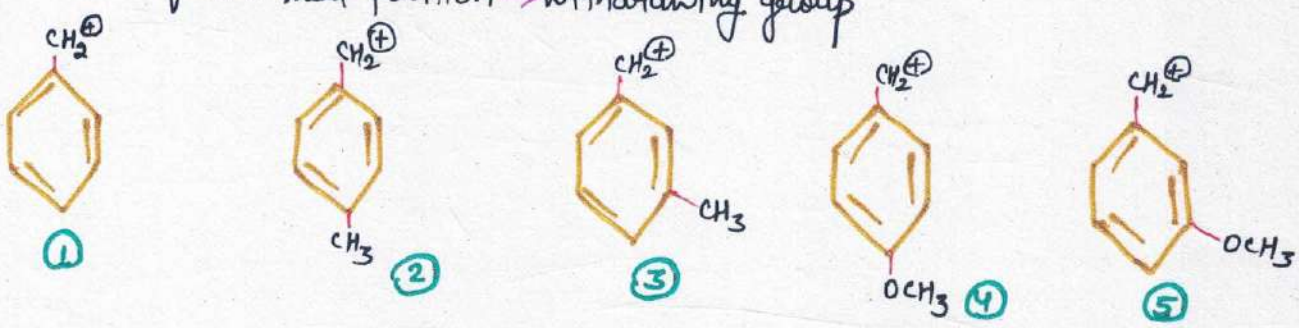
(1) (2) (3)

② > ① > ③

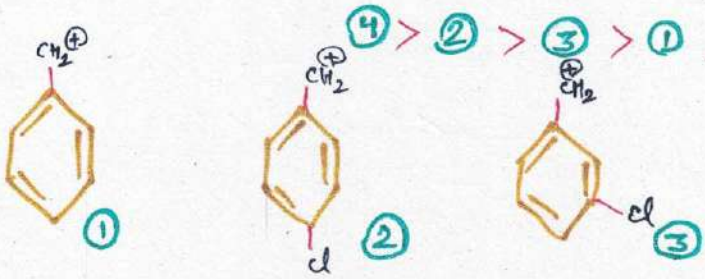
(Alkoxy)

OCH_3 from para position → releasing group

from meta position → withdrawing group



(1) (2) (3) (4) (5)

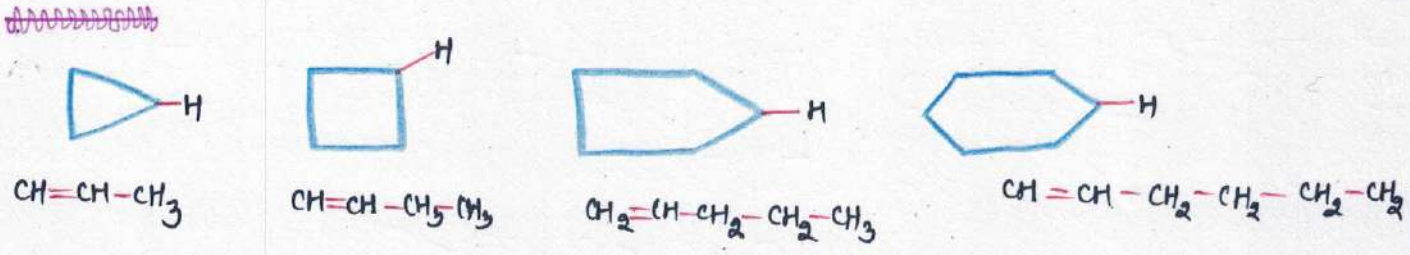


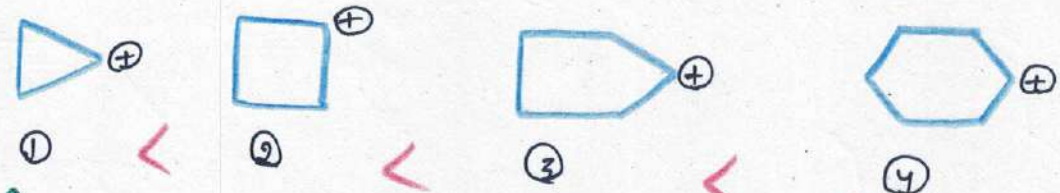
(1) (2) (3)

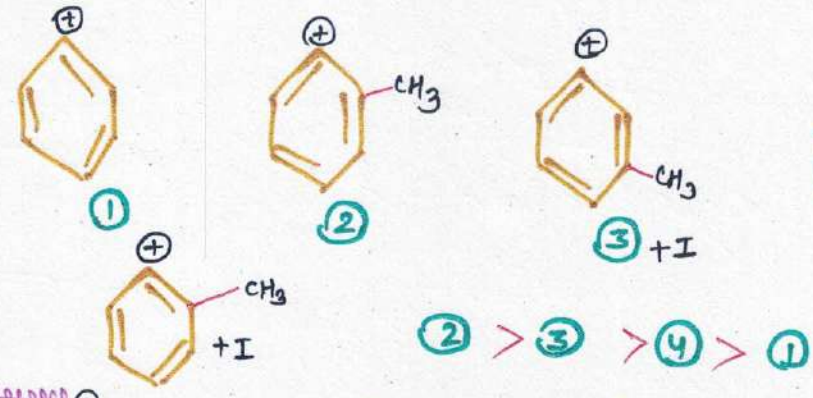
④ > ② > ③ > ① > ⑤

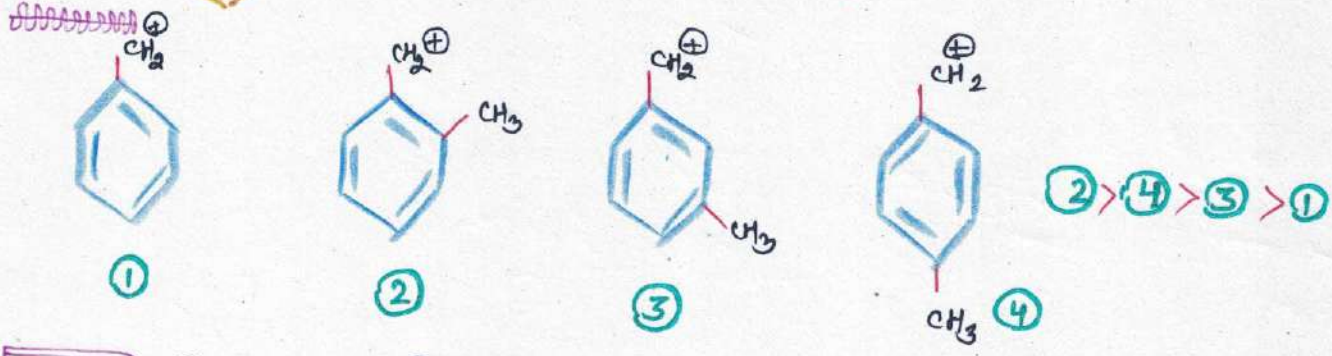
① > ② > ③

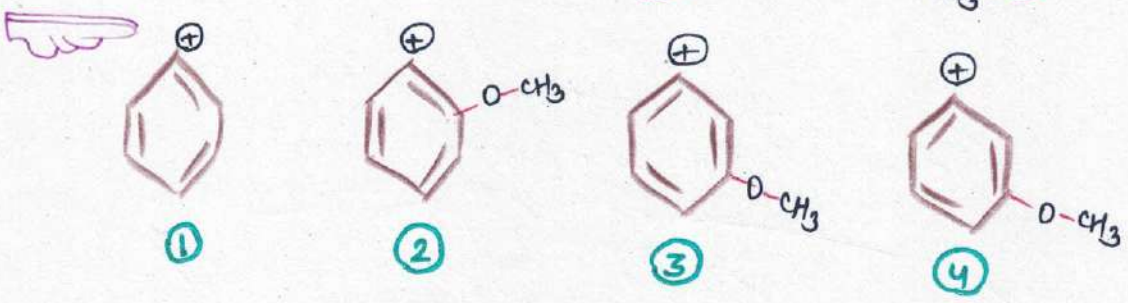
(-I > +M)

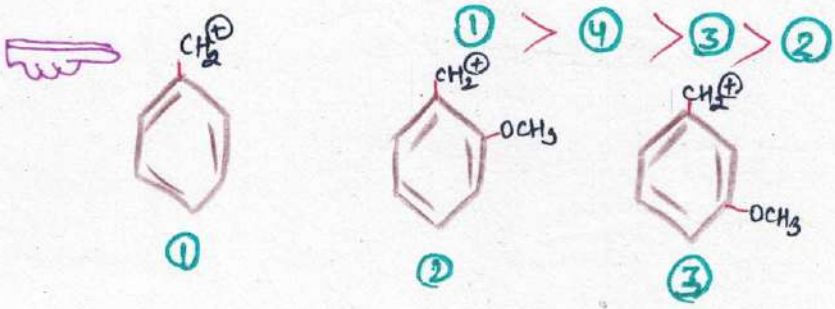


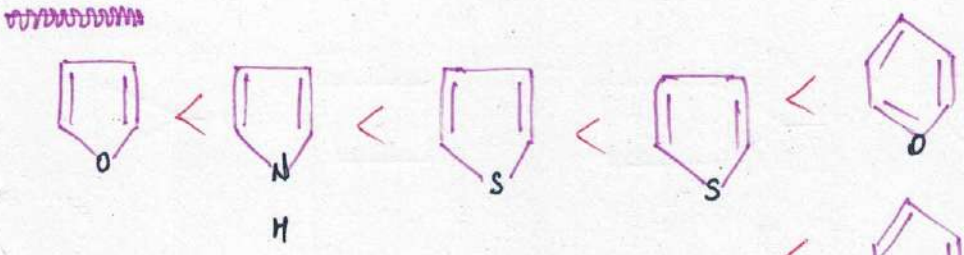


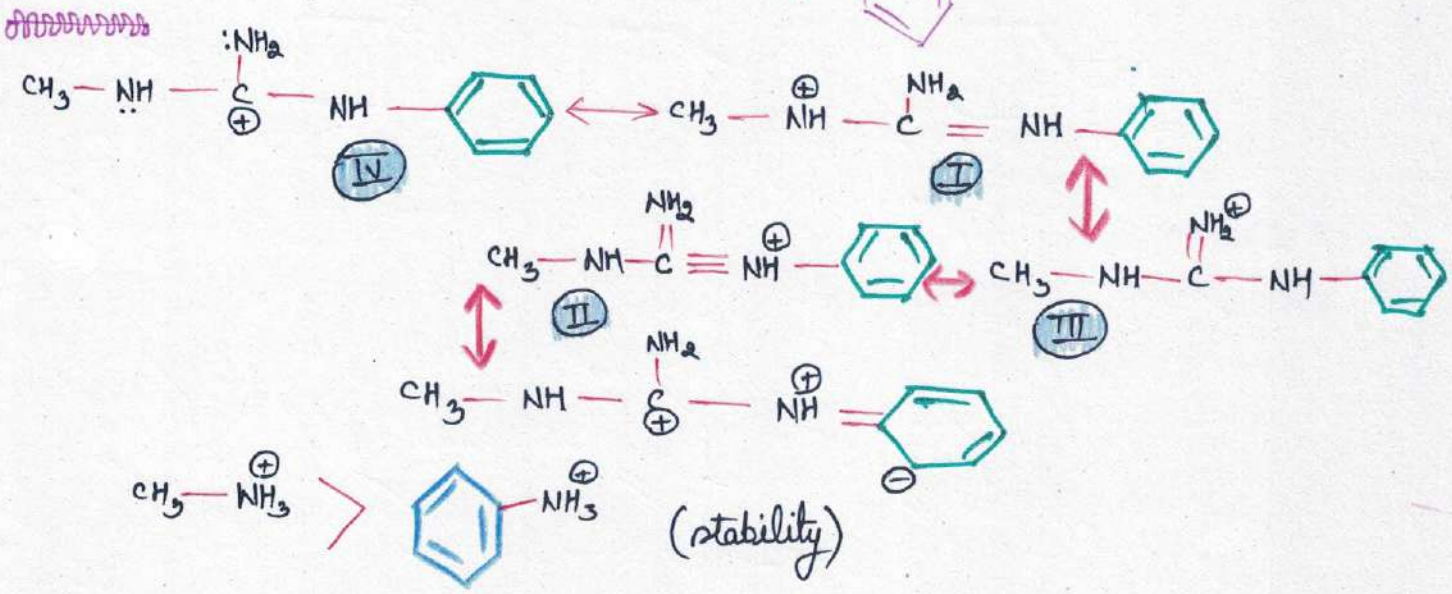


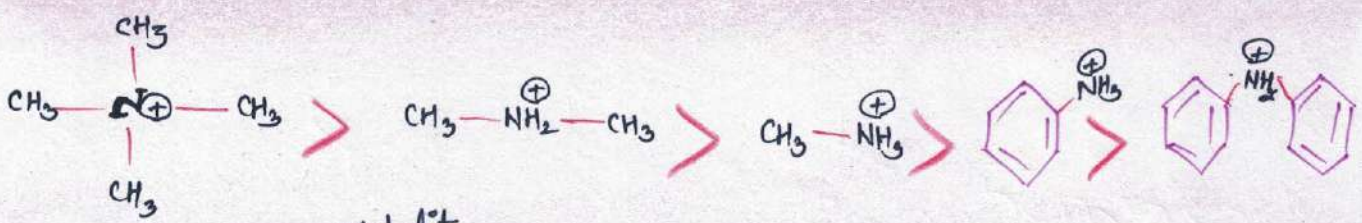




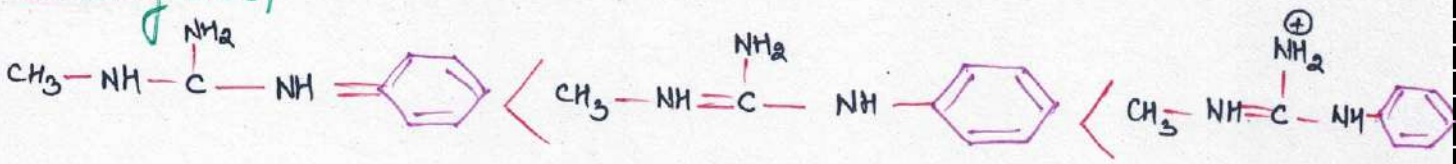


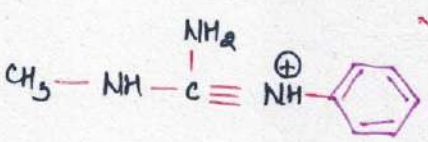


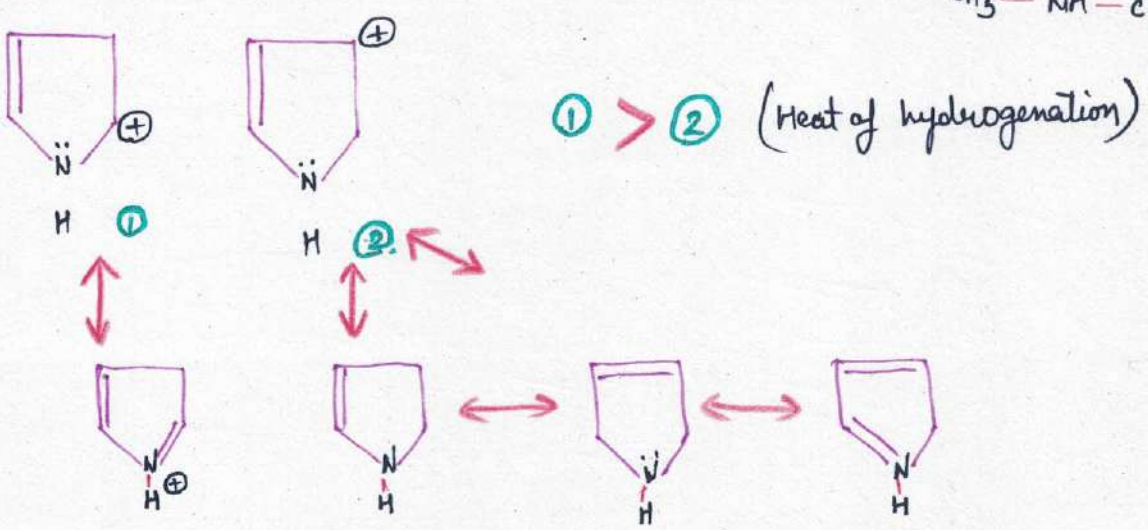


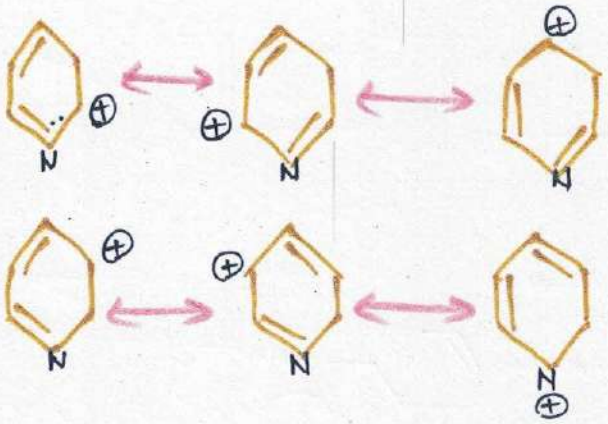


Stability Order



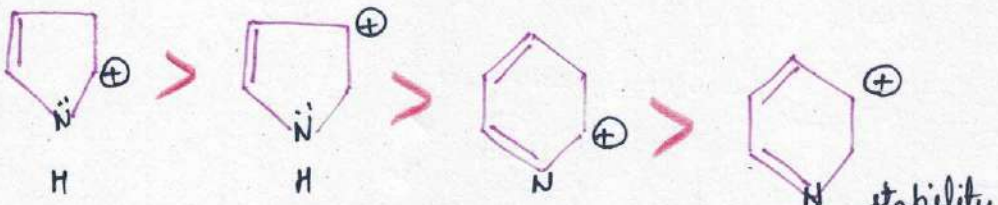




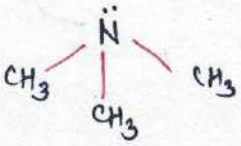


I > II

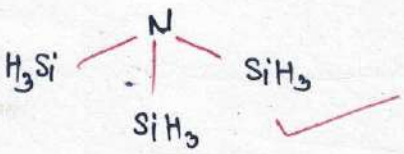
(nitrogen +ve charge unstable)



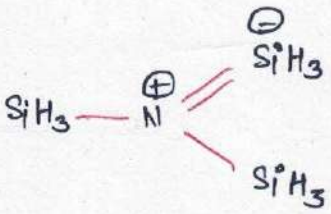
stability



sp^3 trigonal pyramidal [no resonance]

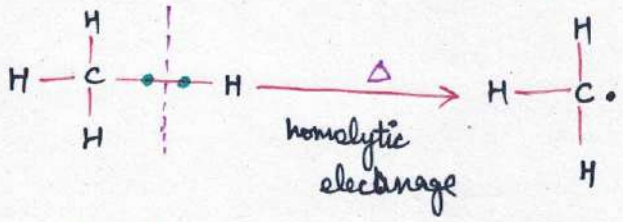


(sp^2 planar)

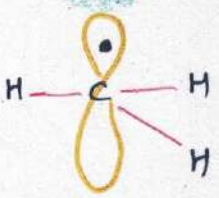


[Resonance Si has vaccant d-orbitals]

STABILITY OF RADICALS



Radical



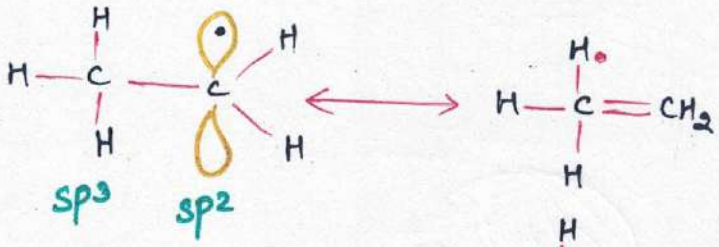
sp^2 hybrid

Carbocation → Cationic electron deficient

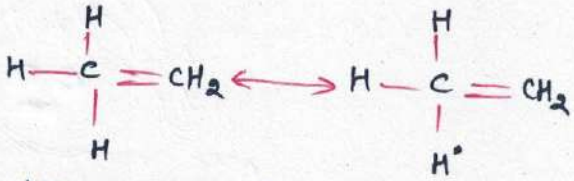
Radical → neutral electron deficient

Planar

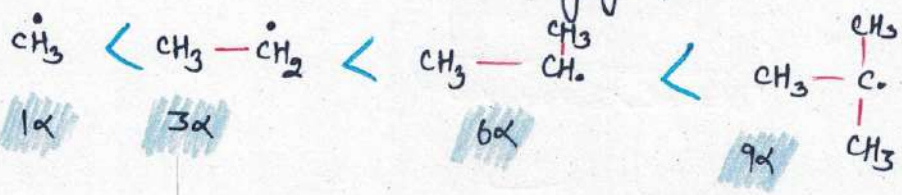
paramagnetic



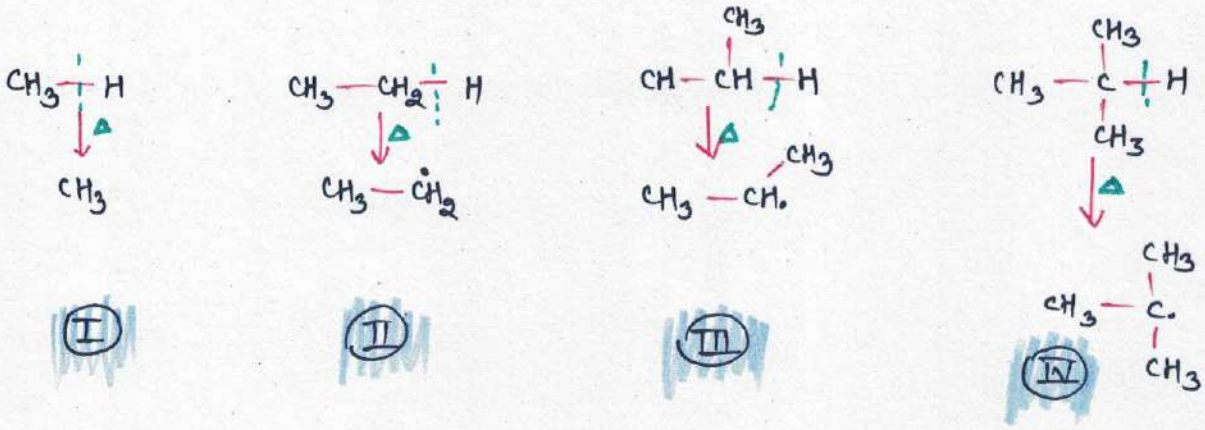
Radical also undergoes hyperconjugation



Carbocation and Radical stability go parallel



$3^\circ > 2^\circ > 1^\circ > \dot{C}H_3$ (stability)



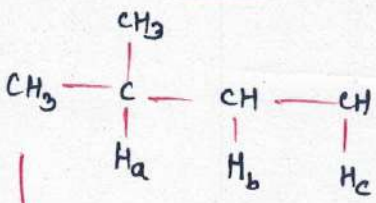
(I) (II) (III) (IV)

Tertiary C–H < Secondary C–H < Primary C–H < Me C–H

Tradical is stable ⇒ it is easy (Bond energy) to break t_{C-H} bond. (bond energy less)

BOND DISTANCE

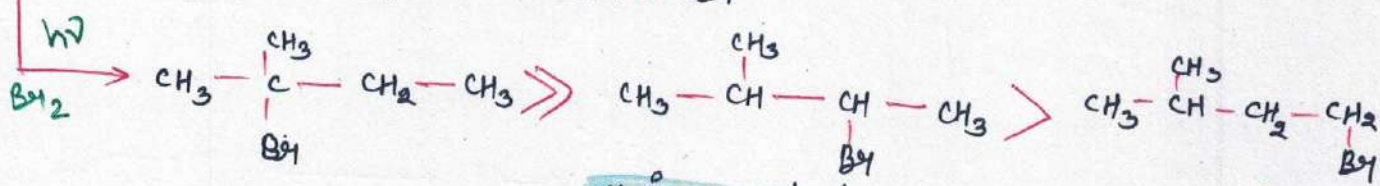
$t_{C-H} > S_{C-H} > P_{C-H} > Me_{C-H}$



B.L. $C-H_a > C-H_b > C-H_c$

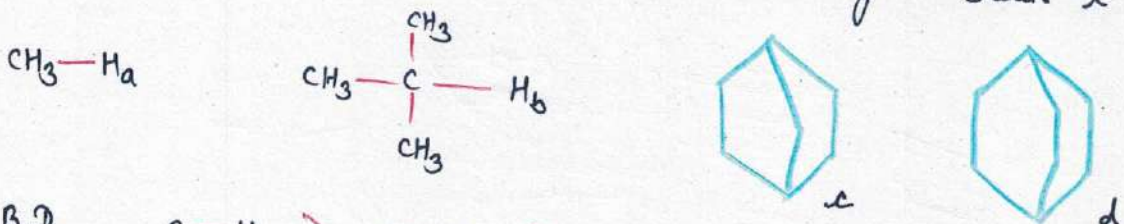
B.E. $C-H_a < C-H_b < C-H_c$

$R-H + Br_2/h\nu \rightarrow R-Br + HBr$



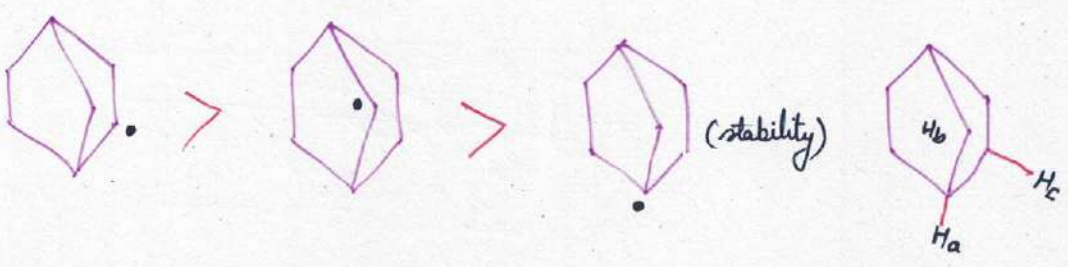
major product

Tertiary bromide will be most stable as it easy to break t-bond.



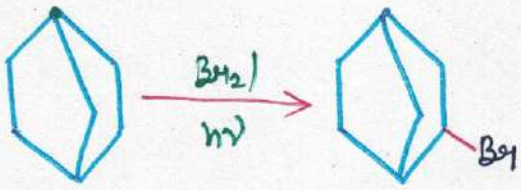
B.D. $C-H_b > C-H_a > C-H_d > C-H_c$

B.E.

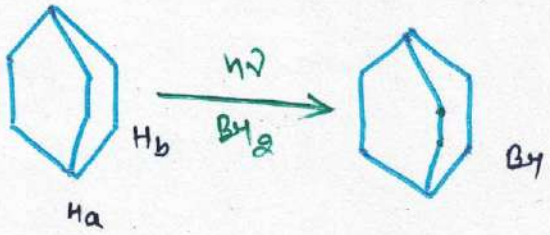


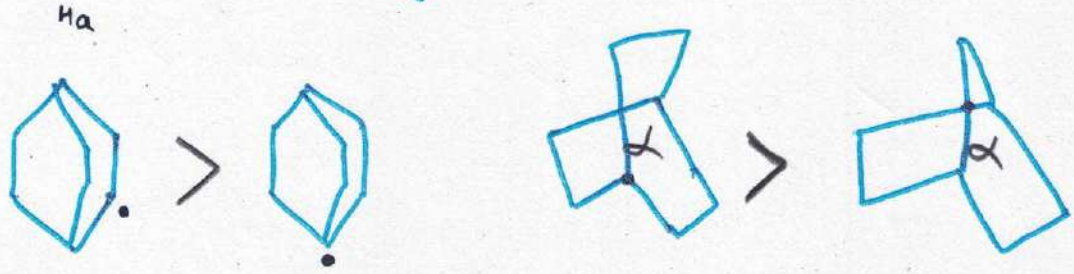
(stability)

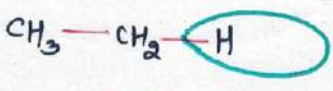
B.D.
B.E. $c > b > a$



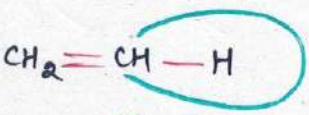
(major product)







sp^3



sp^2

sp^2

Size of carbon :- $C_{sp^3} > C_{sp^2} > C_{sp}$

B.D. $C_{sp^3} - H > C_{sp^2} - H > C_{sp} - H$

B.E. $C_{sp^3} - H < C_{sp^2} - H < C_{sp} - H$

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

alkyl radical > vinyl radical > allyl radical

(as like carbocations na)

bond is weak, bond is long → radical stable

bond is strong, bond is short → radical unstable

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

allyl

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

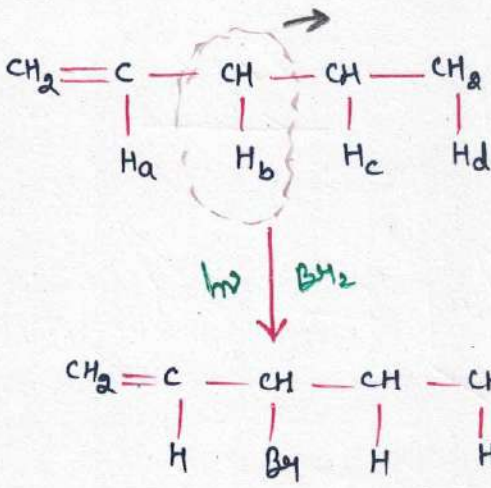
I II

I > II

$CH_2 = CH - \overset{\oplus}{C}H_2 \simeq$ 3 > 2 > 1 > Me > $CH_2 = \overset{\oplus}{C}H$ > $CH \equiv \overset{\oplus}{C}H$

mesomeric hyper ✗ ✗ ✗

no resonance

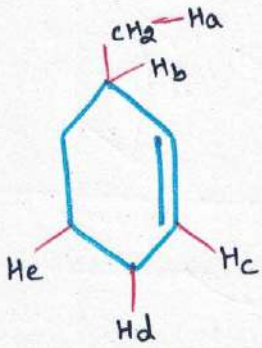


B.D :- b > c > d > a

B.E. :- b < c < d < a

b is longest

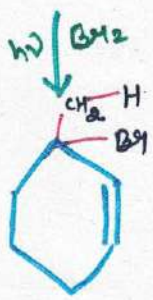
3° > 2° > 1° (stability)

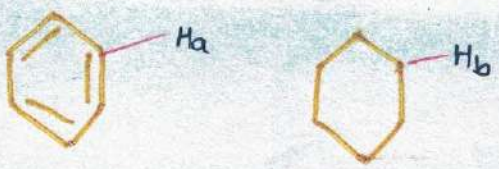


H_b allyl as well as tertiary

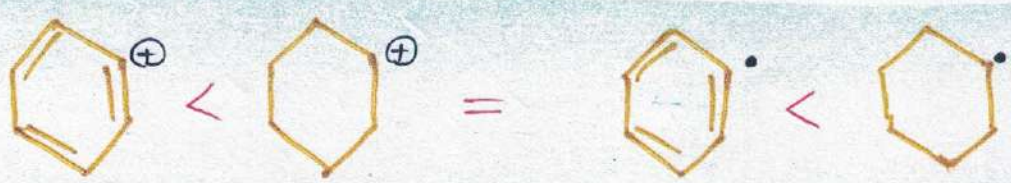
$H_b > H_d > H_e > H_a > H_c$

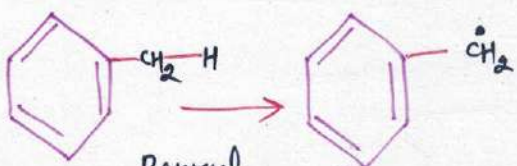
H_b: allyl tertiary; H_d: allyl; H_e: 2°; H_a: 1°; H_c: Vinyl





do same as carbocation





Benzyl radical

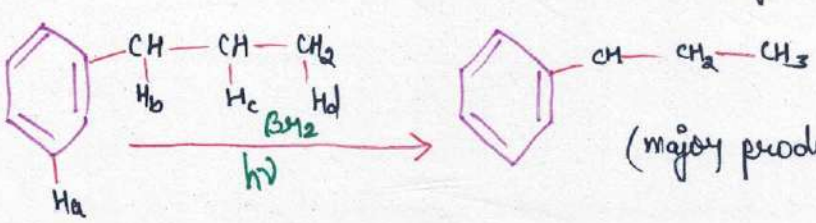
Benzyl C–H

Benzyl ≃ 3 > 2 > 1 > Me > Vinyl

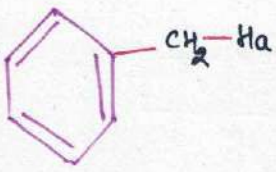
CH ≡ C°

$H_b > H_c > H_d > H_a$

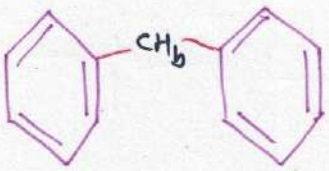
H_b: allyl; H_c: 2°; H_d: 1°; H_a: Vinylic



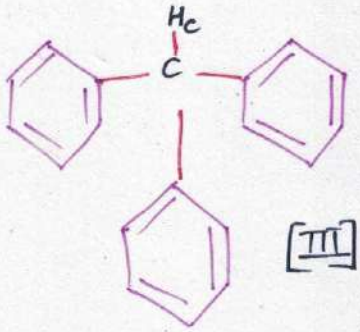
(major product)



[I]



[II]

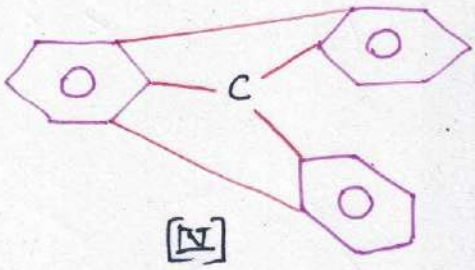


[III]

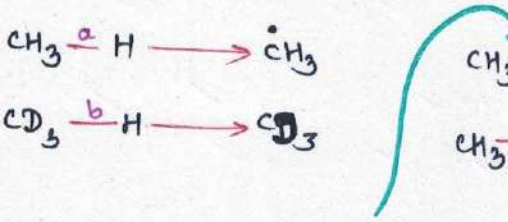
B.D. [I] [II] [III] [IV]

(rate of bromination/stability)

B.E. I > II > III > IV

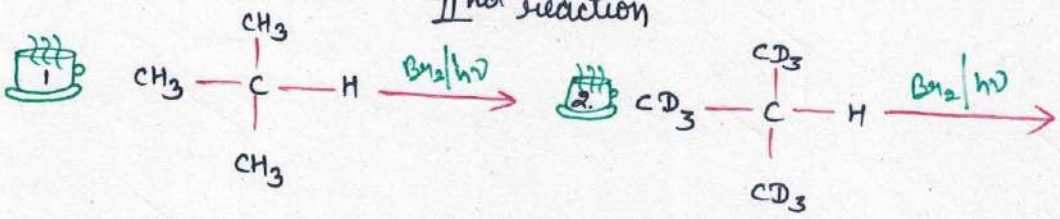


[IV]



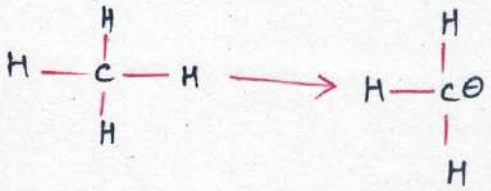
This reaxn is 12 times faster than $CH_3 > CD_3$ (stability)

IInd reaction

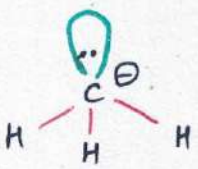


rate of reaxn (1) > (2)

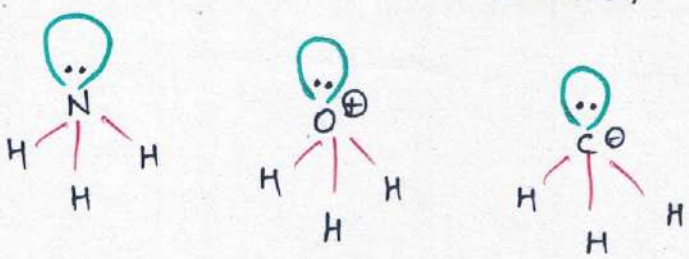
STABILITY OF CABANION



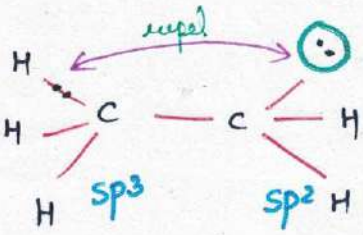
methyl carbanion

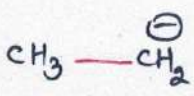


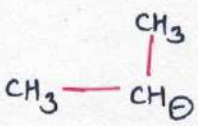
sp^3 Trigonal pyramidal diamagnetic



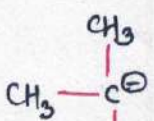
isostructural, isoelectronic





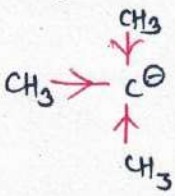


isopropyl



carbanion

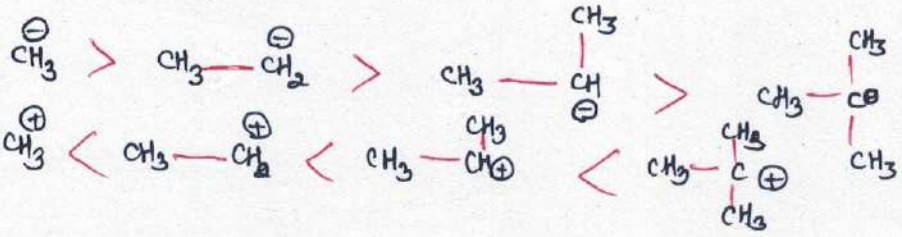
Hyperconjugation is not possible in carbanion. It is possible in carbocation & radical



unstable already -ve on C
CH_3 are releasing also

BO, stability order

$3° < 2° < 1° < Me$

Stability 

Whereas

$CH_3-CH_2-H \xrightarrow{-H^{\oplus}} CH_3-CH_2^{\ominus}$ sp^3

$CH_2=CH-H \xrightarrow{-H^{\oplus}} CH_2=CH_2^{\ominus}$ sp^2

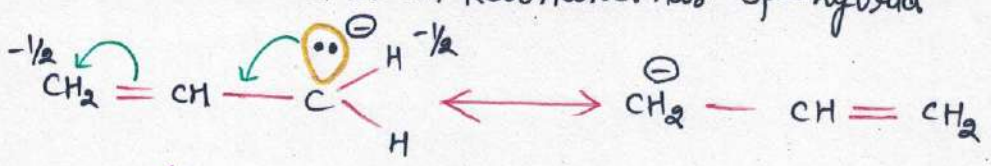
$CH\equiv C-H \xrightarrow{-H^{\oplus}} CH\equiv C^{\ominus}$ sp

-ve charge on more EN → stable

$CH_3-CH_2^{\ominus} < CH_2=CH^{\ominus} < CH\equiv C^{\ominus}$ (stability)

$CH_2=CH-CH_2-H \xrightarrow{-H^{\oplus}} CH_2=CH-CH_2^{\ominus}$

A carbanion which is in Resonance has sp^2 hybrid



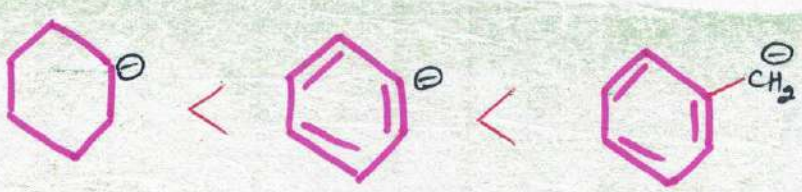
So allyl group

$CH_2=CH-CH_2^{\ominus}$ This is in resonance

$CH_2=CH-CH_2^{\oplus}$

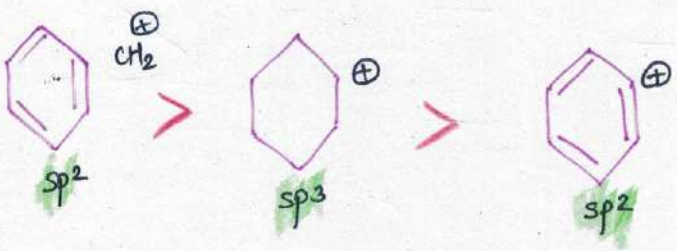
$CH_2=CH^{\ominus} > CH_3-CH_2^{\ominus}$ no resonance

$CH_3-CH_2^{\oplus} > CH_2=CH^{\oplus}$



sp³ while

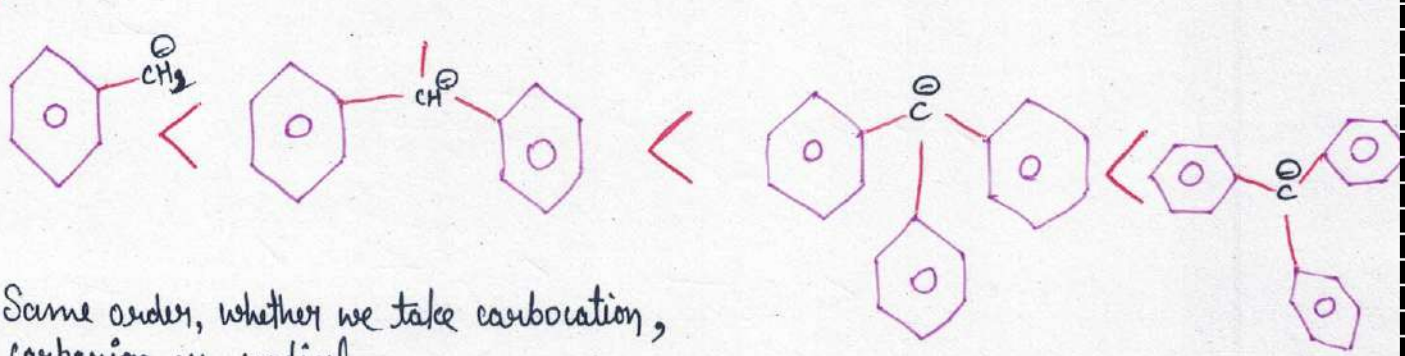
cyclo alkyl < Phenyl < benzyl



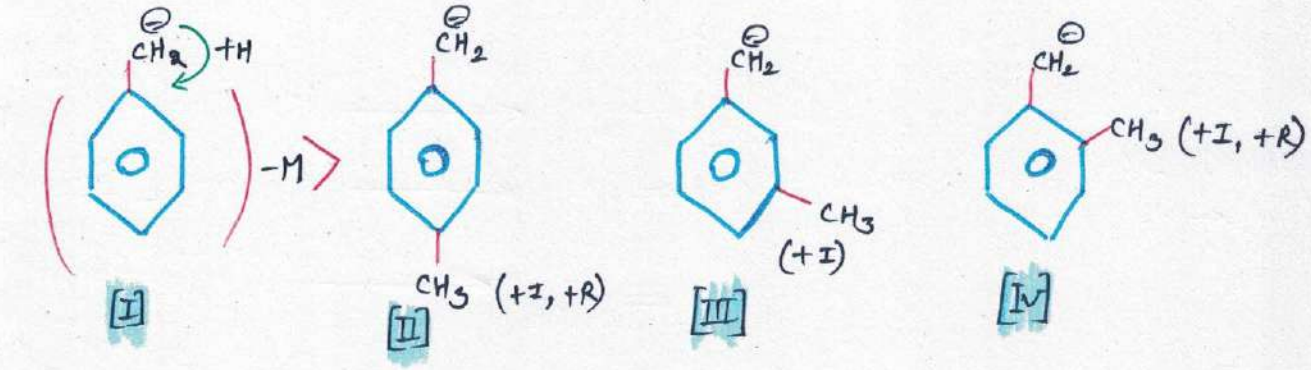
sp^2 sp^3 sp^2

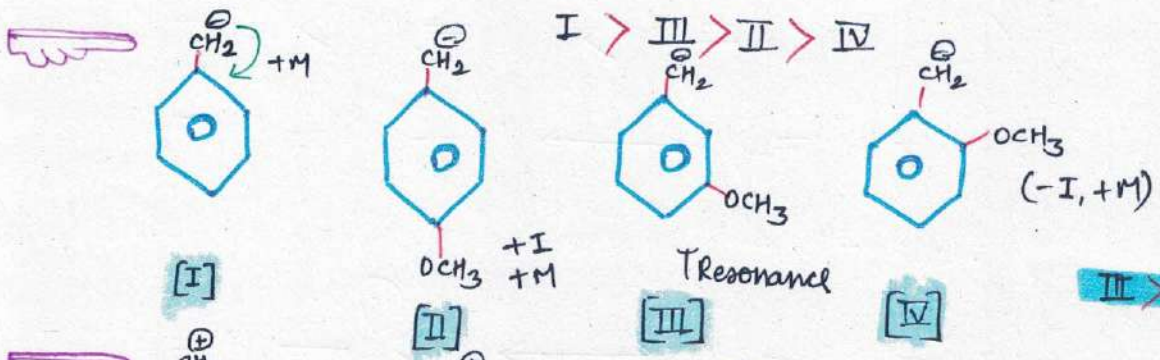
sp^2 → +ve unstable

sp^3 → stable



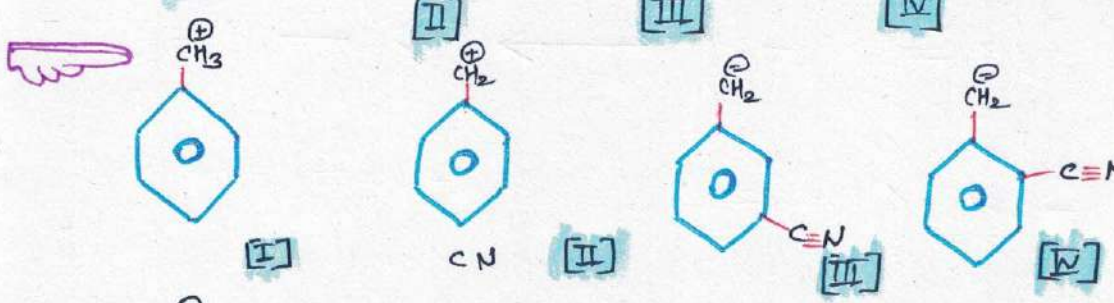
Same order, whether we take carbocation, carbanion or radical.



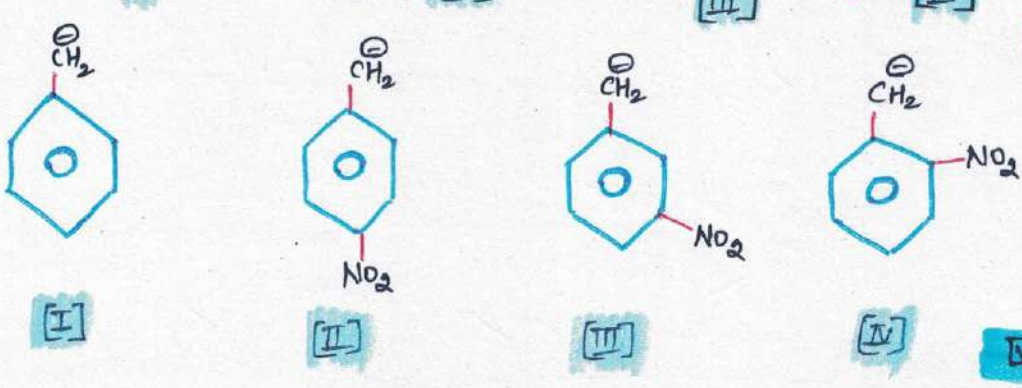


I > III > II > IV

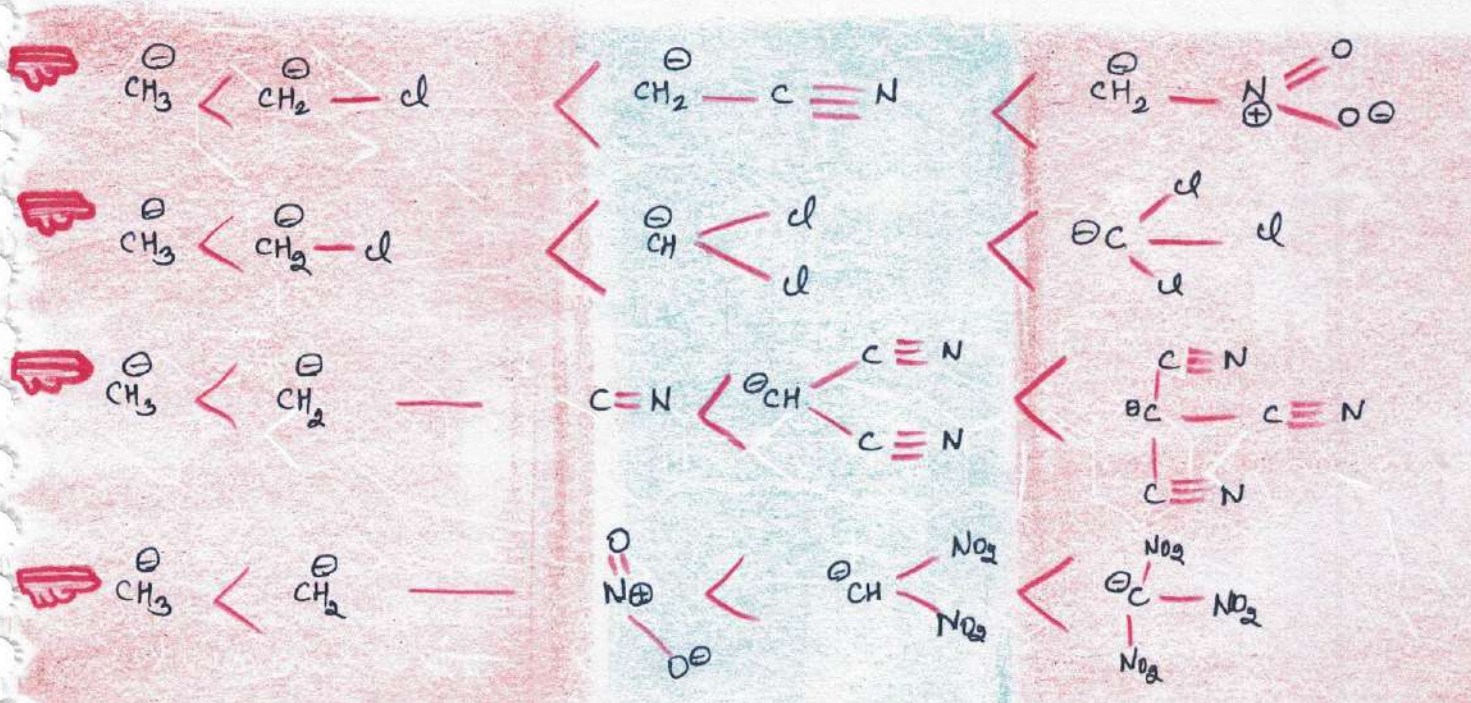
III > I > IV > II

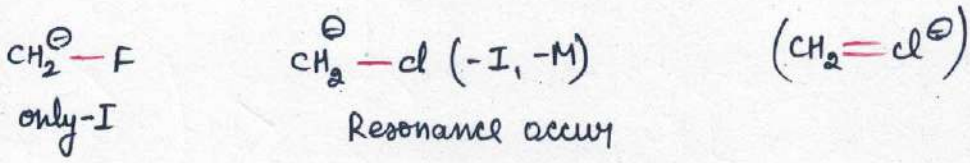


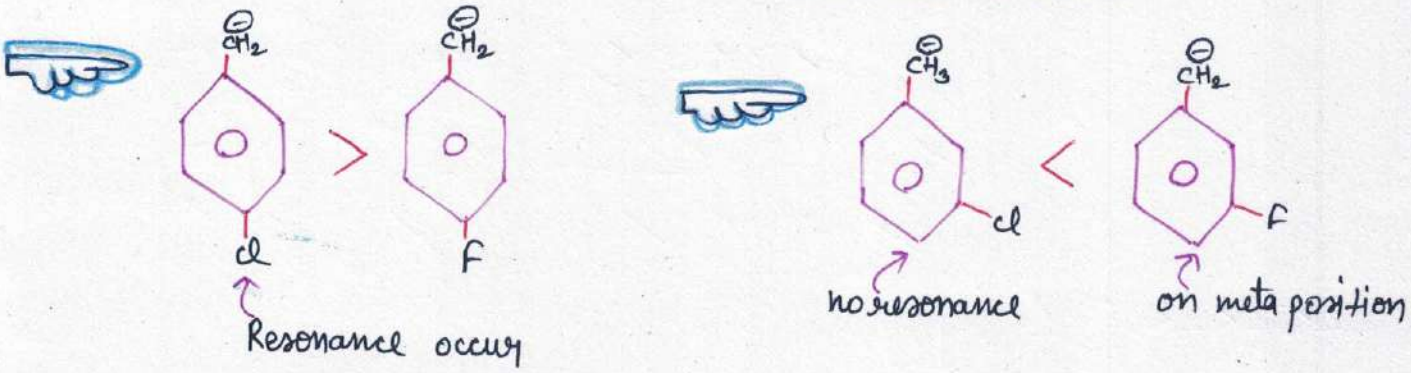
IV > II > III > I

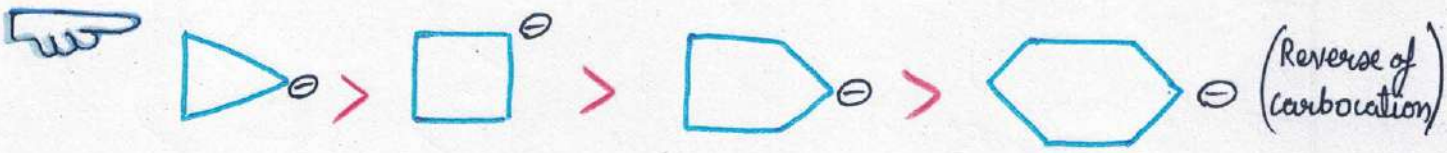


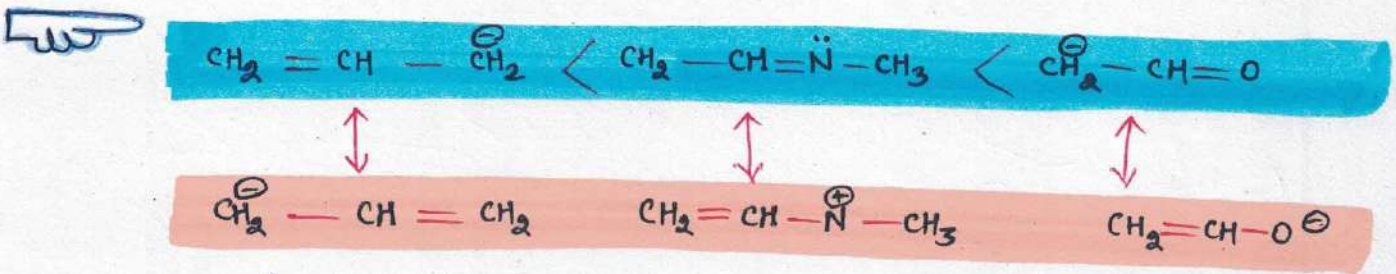
IV > II > III > I



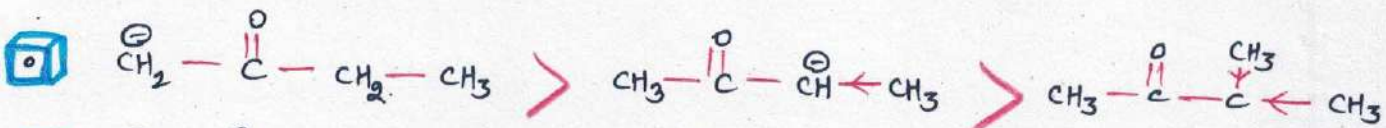


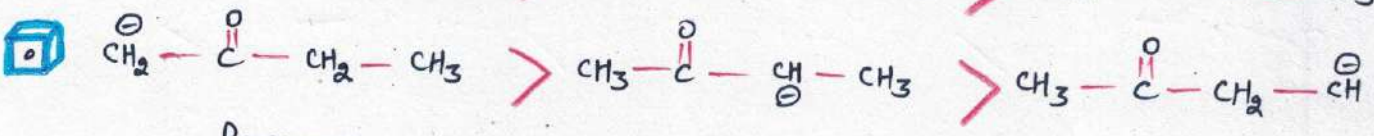




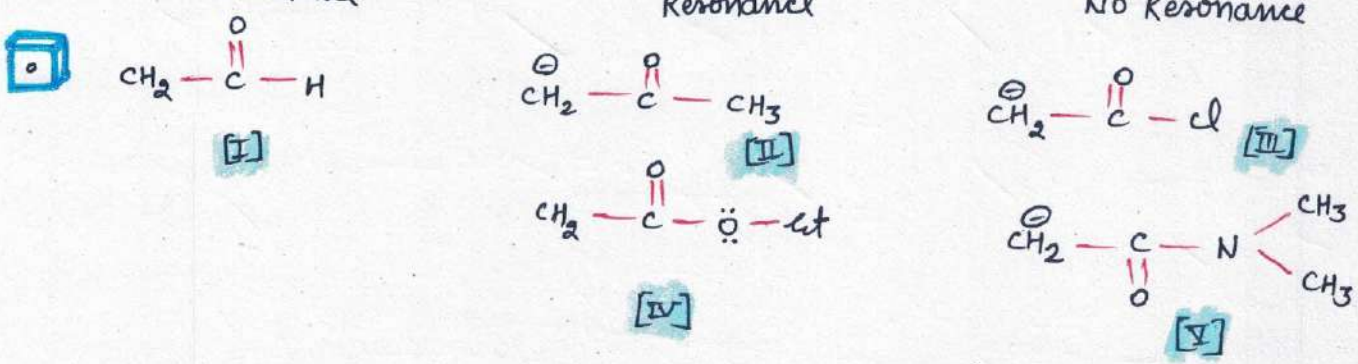


of the several canonical structures, the str. having -ve charge on more EN atom is more stable.

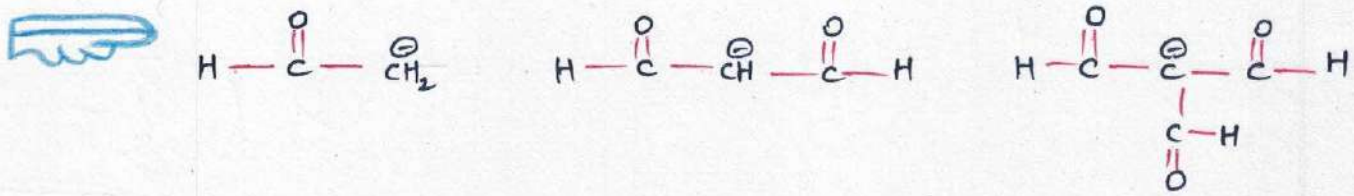


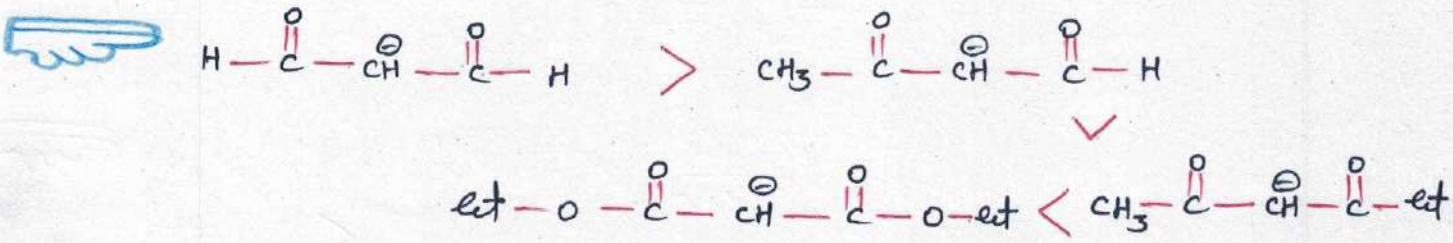


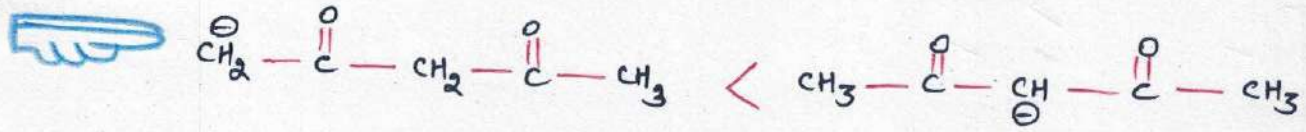
Resonance | Resonance | No Resonance

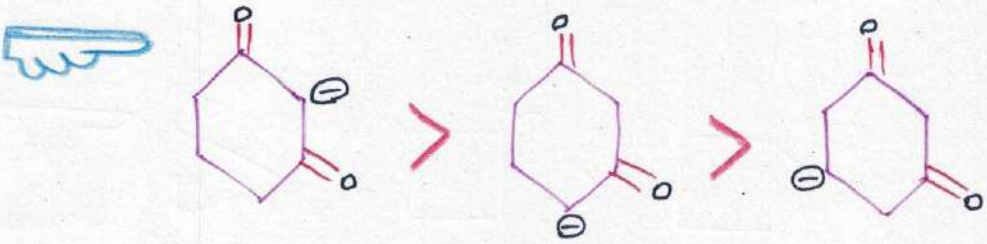


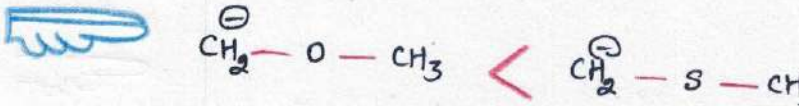
III > I > II > IV > V

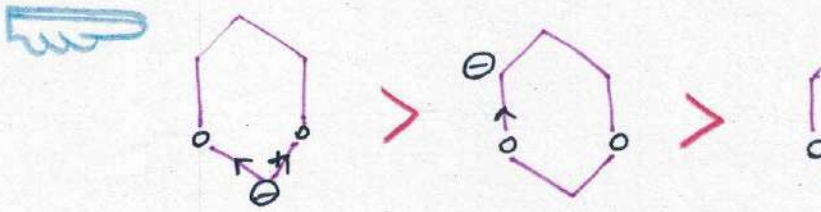


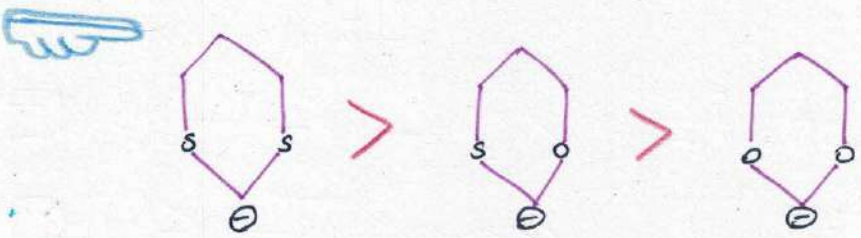


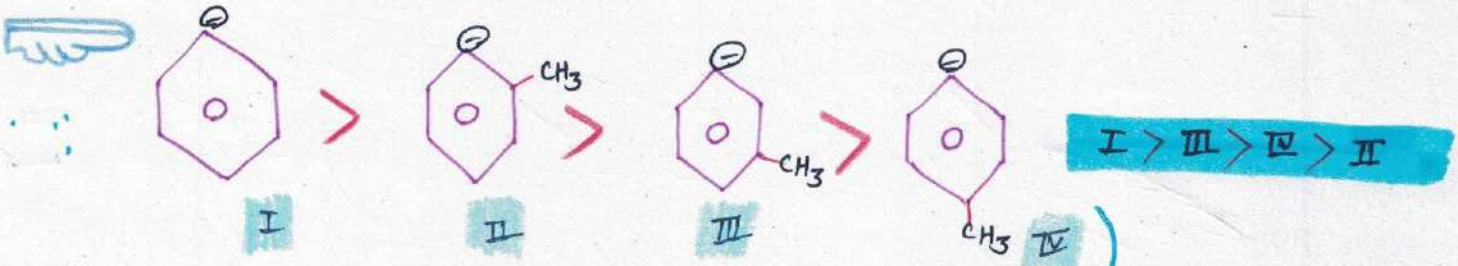


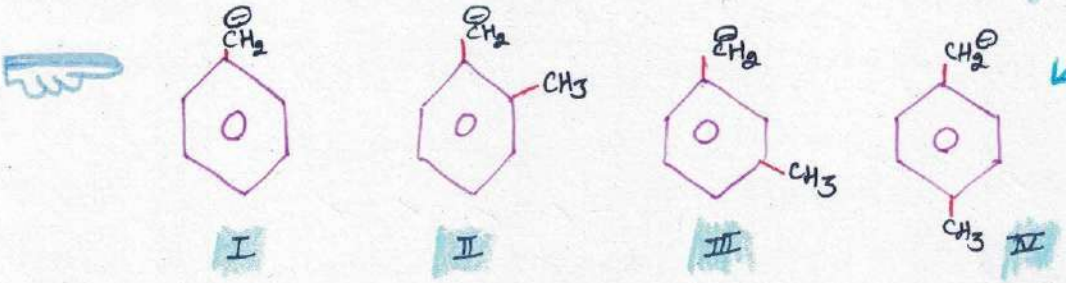


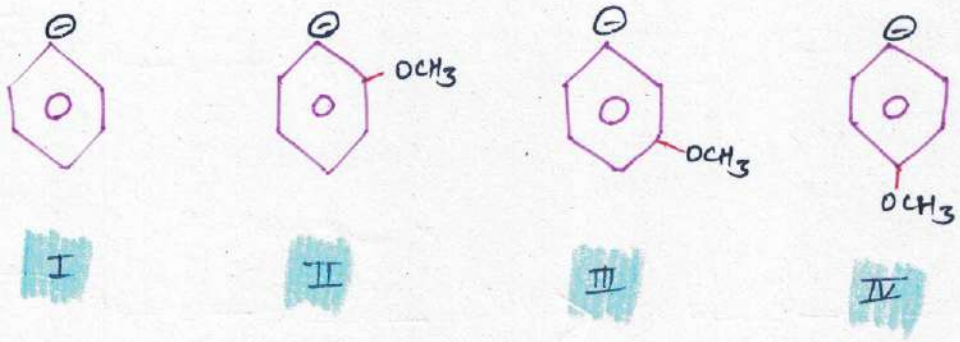






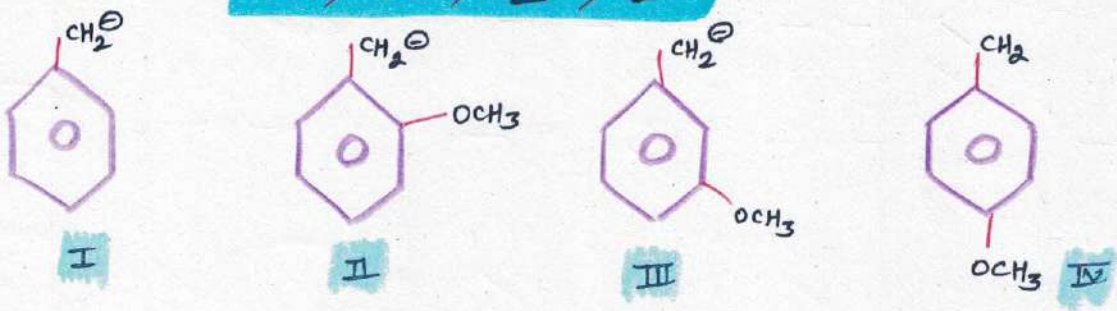






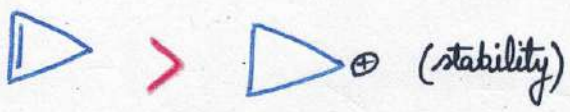
I II III IV

II > III > IV > I

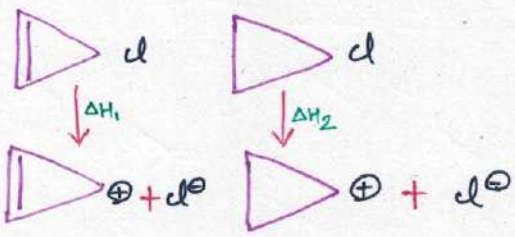


I II III IV

I > III > II > IV



(stability)



$\Delta H_2 > \Delta H_1$

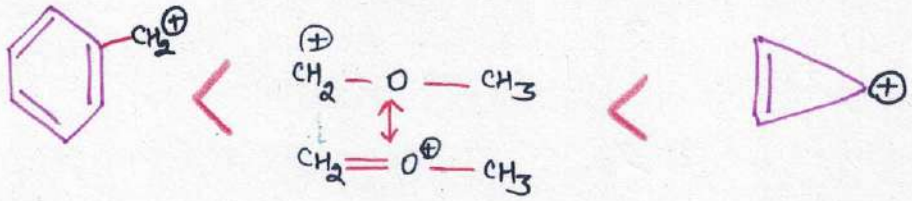
$CH_3-Cl \xrightarrow{\Delta H_1} CH_3^+ + Cl^\ominus$

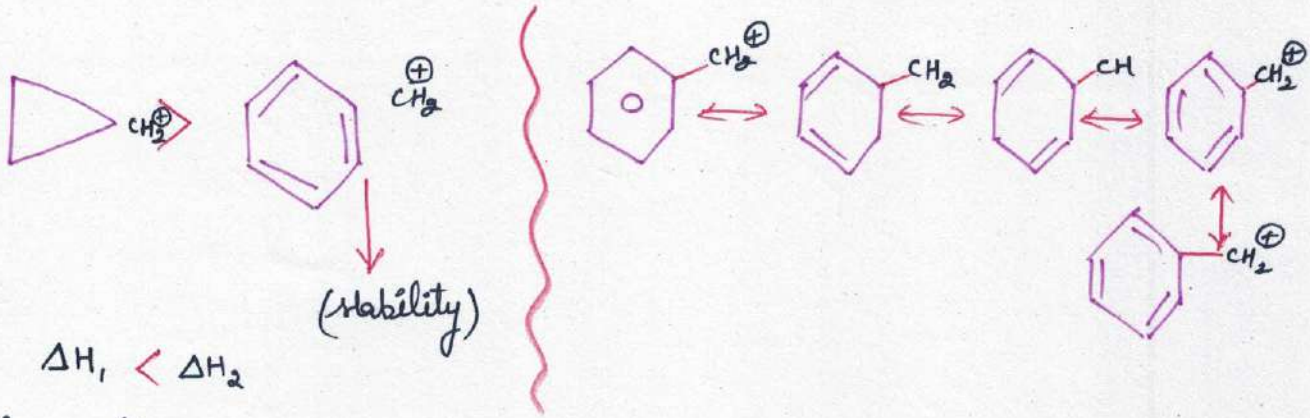
$CH_3-CH_2-Cl \xrightarrow{\Delta H_2} CH_3-CH_2^\oplus + Cl^\ominus$

$CH_3-CH(CH_3)-Cl \xrightarrow{\Delta H_3} CH_3-CH^\oplus(CH_3) + Cl^\ominus$

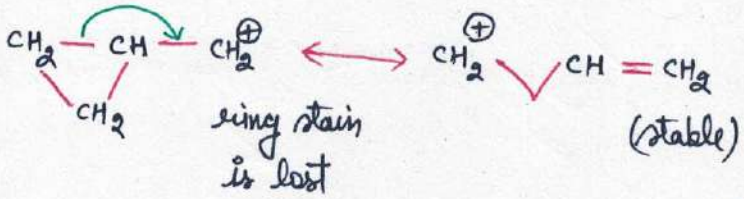
$CH_3-C(CH_3)_2-Cl \xrightarrow{\Delta H_4} CH_3-C^\oplus(CH_3)_2 + Cl^\ominus$

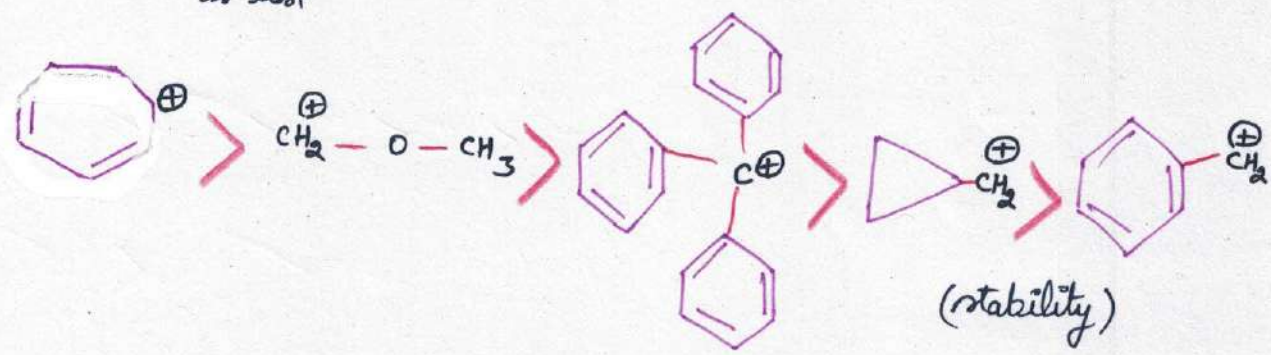
$\Delta H_1 > \Delta H_2 > \Delta H_3 > \Delta H_4$





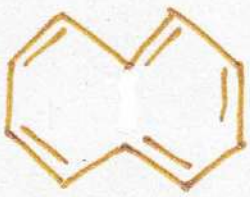
So cyclopropyl methyl carbocation is more stable than benzyl carbocation.





Non- aromatic

but



Aromatic

because exist in same plane $-CH_2$ can be replaced by $-O-$, $-NH_2$, all are aromatic.

NOMEN-CLATURE

ACID HALIDE

FUNCTIONAL GROUPS

$-COX$ or $-\overset{O}{\overset{\|}{C}}-X$ (where X → F, Cl, Br, I)

Base name – Alkanoyal halide

E.g.

1. $H-\overset{O}{\overset{\|}{C}}-Br$

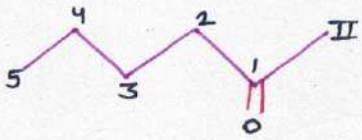
IUPAC → Methanoyal bromide
C.N → Formyl bromide

2. $CH_3-\overset{O}{\overset{\|}{C}}-Cl$

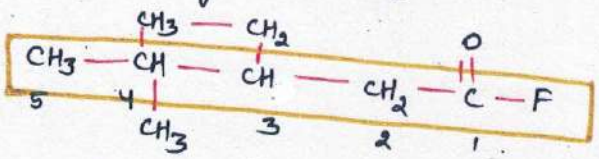
IUPAC → ethanoyal chloride
C.N → Acetyl chloride

3. $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-Cl$

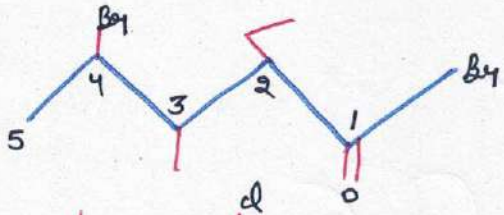
Propanoyal chloride

4. 

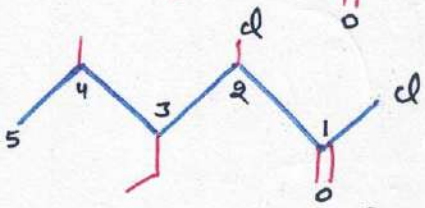
Pentanoyal iodide

5. 

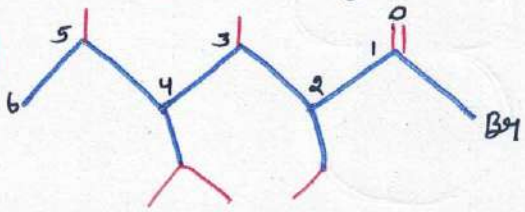
3-ethyl – 4-methyl
Pentanoyal fluoride

6. 

4- bromo
2- ethyl – 3 – methyl
Pentanoyal bromide

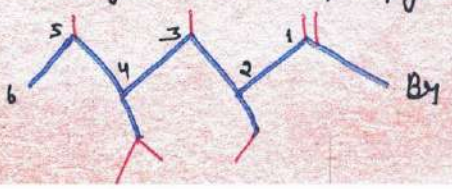
7. 

2- chloro 3- ethyl
4- methyl pentanoyal chloride

8. 

2-4diethyl -3, 5-dimethyl

Hexanoyal bromide

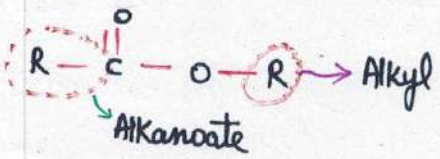
9. 

2 ethyl – 4- isopropyl OR -3,5 – dimethyl hexanoyal bromide
2 ethyl -3, 5 dimethyl
4-(1- methyl ethyl), hexanoyal bromide

ESTER

FUNCTIONAL GROUP

$-COOR$ or $-\overset{O}{\overset{\|}{C}}-O-R$



Base name :- Alkyl Alkanoate

(1) $H-\overset{O}{\overset{\|}{C}}-OCH_3$

IUPAC → methyl methanoate
C.N. → methyl formate

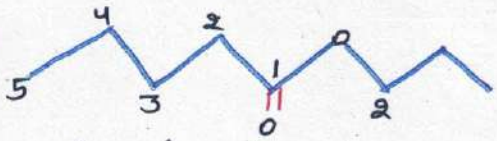
(2) $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$

IUPAC → methyl ethanoate
C.N. → methyl acetate

(3) $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$

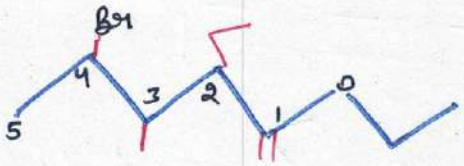
ethyl ethanoate

(4)



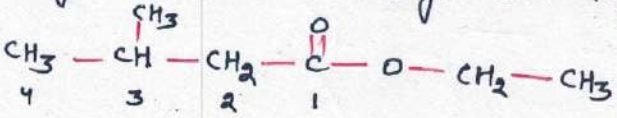
Propyl pentanoate

(5)



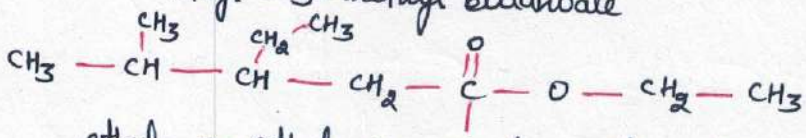
methyl 4-bromo-2-ethyl-3-methyl pentanoate

(6)



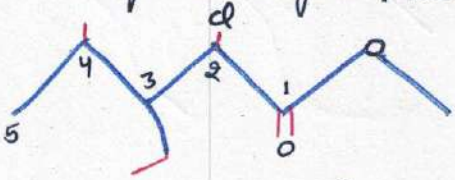
ethyl-3-methyl butanoate

(7)



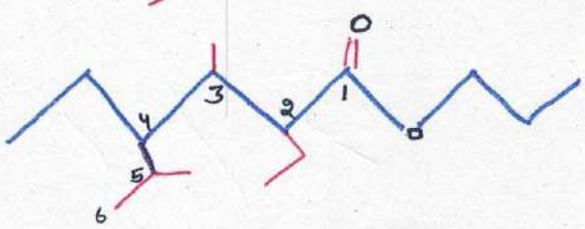
ethyl-3-ethyl-4 methyl pentanoate

(8)

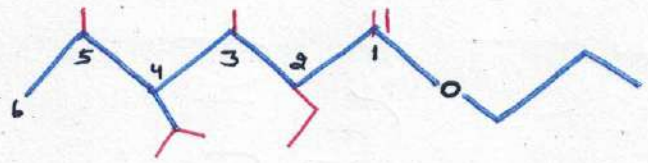


Methyl 2-chloro-3-methyl-4-ethyl Pentaanoate

(9)



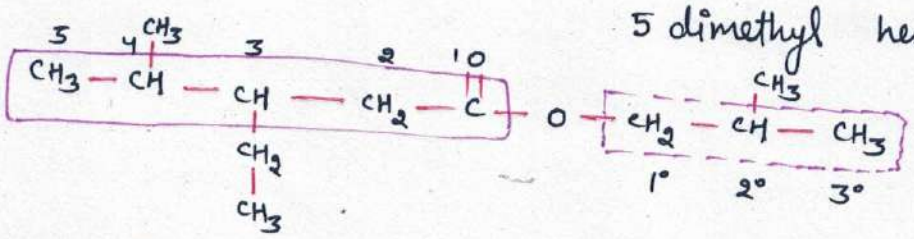
Propyl 2,4-diethyl 3,5 dimethyl hexanoate



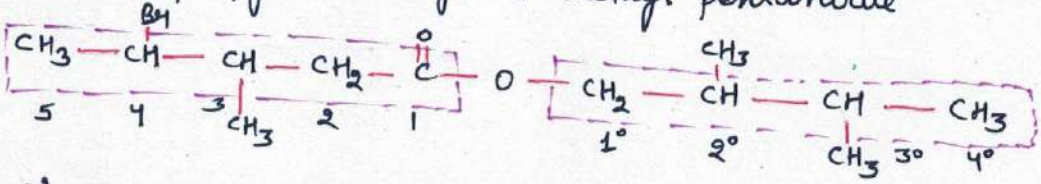
Propyl 2-ethyl-3, 5-di methyl (1-methyl ethyl) hexanoate

OR

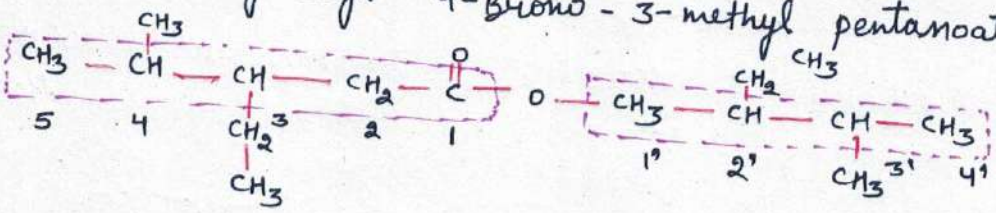
Propyl 2-ethyl-4-isopropyl-3, 5 dimethyl hexanoate



2 methyl propyl 3-ethyl-4-methyl pentanoate



2', 3' dimethyl butyl 4-Brono-3-methyl pentanoate



2'-ethyl-3'-methyl butyl 3-ethyl-4 ethyl pentanoate

2'-ethyl, 1-methyl, butyl 3 Bromo-2-ethyl-5-methyl hexanoate

AMIDE

1° Amide ($-\overset{O}{\overset{\|}{C}}-NH_2$) 2° Amide ($-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-R$) 3° Amide ($-\overset{O}{\overset{\|}{C}}-N\begin{matrix}R\\R\end{matrix}$)

NAMING OF 1° AMIDE

G.F. → $-\overset{O}{\overset{\|}{C}}-NH_2$

Base name → Alkanamide

$H-\overset{O}{\overset{\|}{C}}-NH_2$

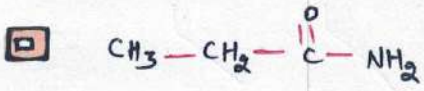
IUPAC → Methanamide

C.N. → formamide

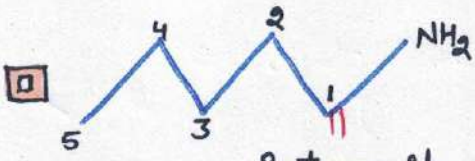
$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$

IUPAC ethanamide

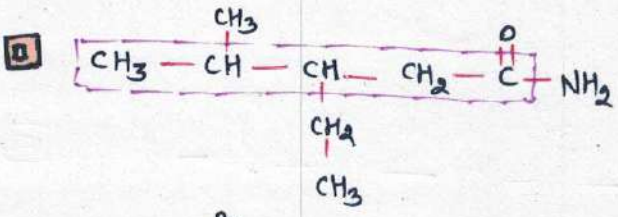
C.N. Acetamide



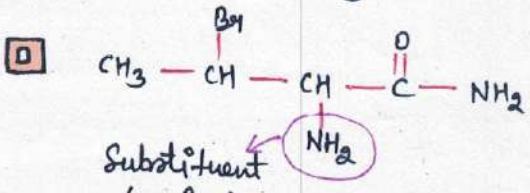
Propanamide



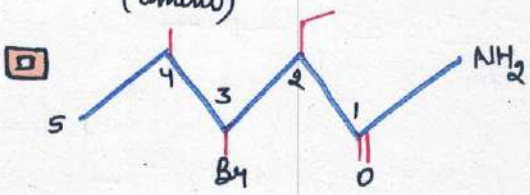
Pentanamide



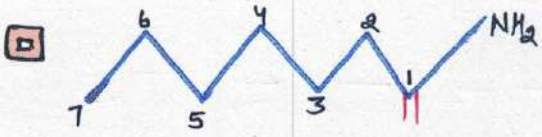
3 - ethyl, - 4 - methyl Pentanamide



2 - Amino - 3 Bromo - butanamide

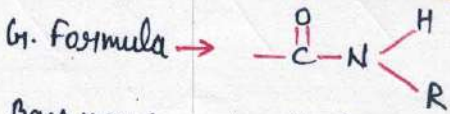


3 - bromo - 2 - ethyl - 4 - methyl pentanamide

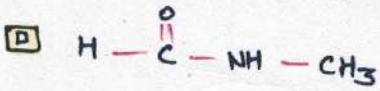


Heptanamide

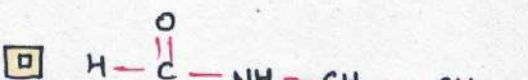
NAMING OF 2° AMIDE



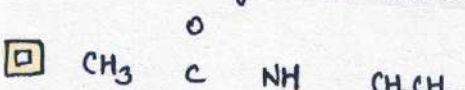
Base name → N- alkyl alkanamide



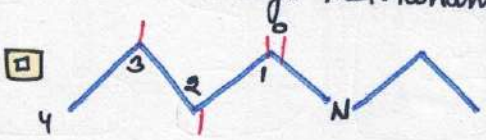
N- methyl methanamide



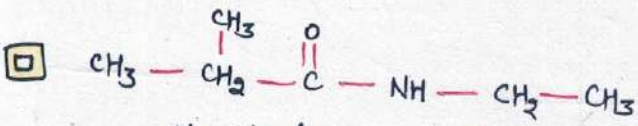
N- ethyl methanamide



N- ethyl ethanamide

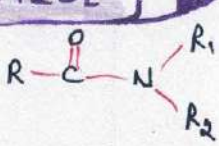


N- ethyl 2,3- dimethyl butanamide



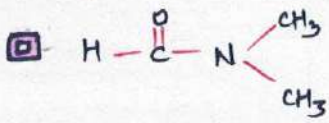
N- ethyl 2- methyl propanamide

NAMING OF 3° AMIDE



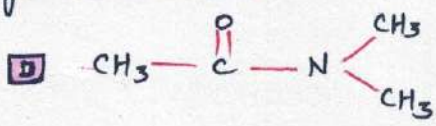
1. if $R_1 \neq R_2$, base name N-alkyl, N-alkyl alkanamide

2. if $R_1 = R_2$, base name N,N-dialkyl alkanamide



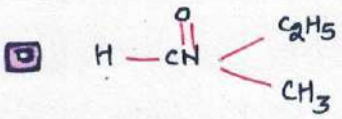
IUPAC → N, N-dimethyl methanamide

C.N. → N, N-dimethyl formamide (DMF)

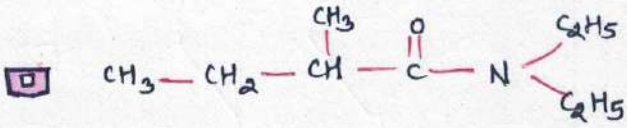


IUPAC → N, N-dimethyl ethanamide

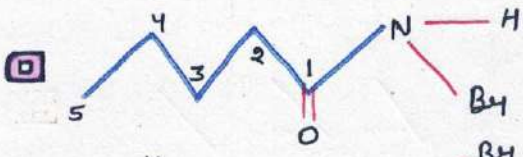
C.N. → N, N-dimethyl acetamide (DMA)



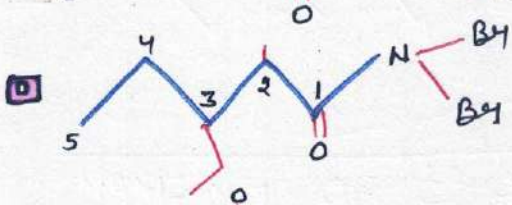
N-ethyl-N methyl methanamide



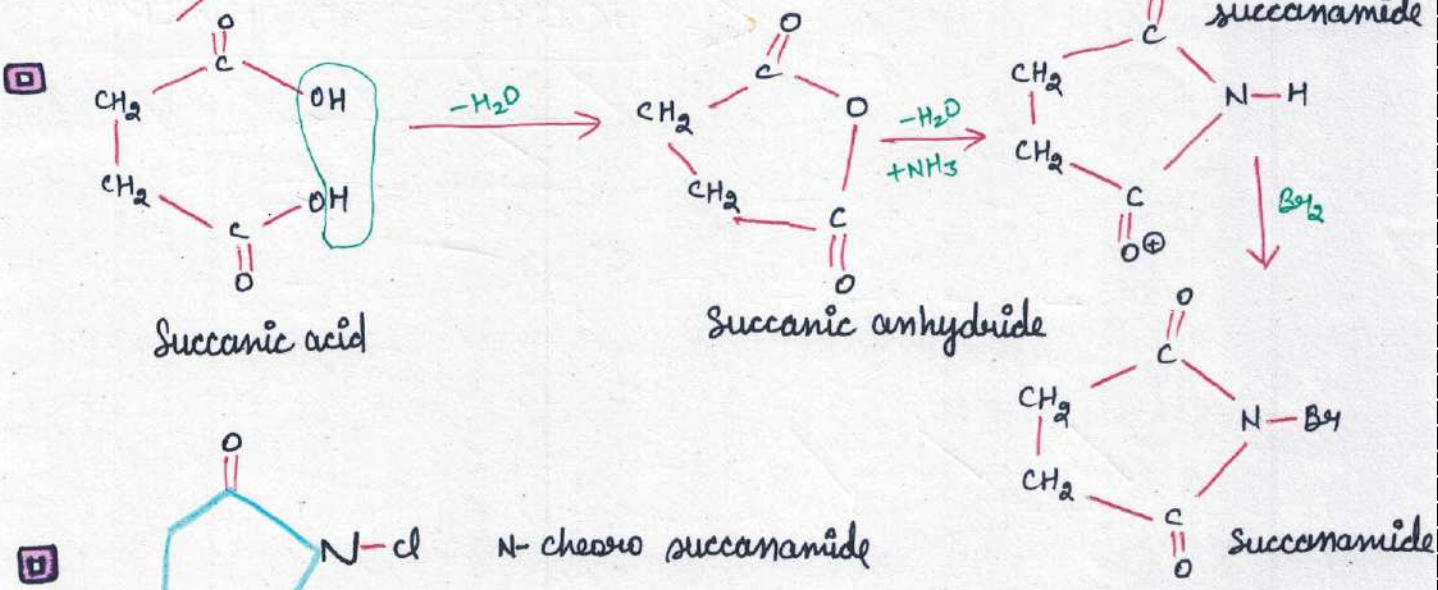
N,N-diethyl 2-methyl butanamide



N-Bromo-2-ethyl-3-methyl pentanamide



N,N-dibromo-3-ethyl-2 methyl pentanamide



Succanic acid

Succanic anhydride

succanamide

Succonamide

N-chloro succanamide

Naming of organic compounds having monovalent functional groups which has first atom other than carbon

E.g. $-OH$, $-SH$, $-SO_3H$, $-NC$

ALCOHOLS

Gen. formula (-OH)

Base name Alkanol

- CH_3-OH
  - IUPAC methanal
  - C.N. methyl alcohol
  - D.N. carbinal

- C_2H_5OH
  - IUPAC ethanal
  - C.N. ethyl alcohol
  - D.N. methyl carbinal

- $\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-OH$
  - IUPAC → propanal
  - C.N. → n-propyl alcohol
  - D.N. → ethyl carbinal

- $CH_3-\overset{\overset{2}{OH}}{\underset{1}{C}H_2}-\underset{3}{C}H_3$
  - IUPAC → 2-propanal
  - C.N. → isopropyl alcohol
  - D.N. → dimethyl carbinal

- $CH_3-\overset{\overset{2}{CH_3}}{\underset{3}{C}}(\overset{1}{CH_3})-OH$
  - IUPAC → 2-methyl propan-2-ol
  - C.N. → Terbutyl alcohol
  - D.N → Trimethyl carbinal

Rules for numb-ering

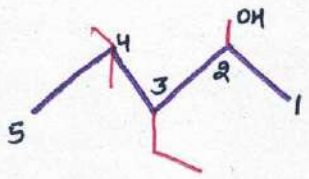
First apply REPD on main functional group

⇓ if not decided

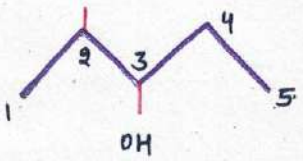
Apply RFPD on substituents

⇓

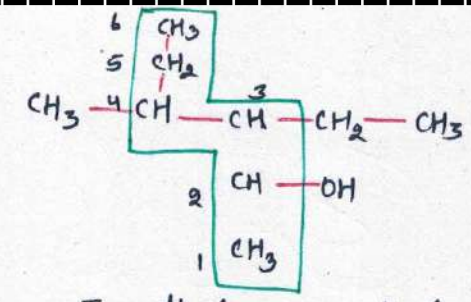
Go by alphabetical order



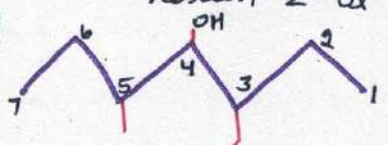
3- ethyl - 4, 4 dimethyl
Pentan - 2 - ol



2- methyl pentan - 3 - ol



3 - ethyl - 9 - methyl
hexan - 2 - ol

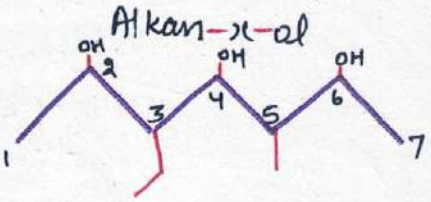


3 - ethyl - 5 - methyl
heptan - 4 - ol

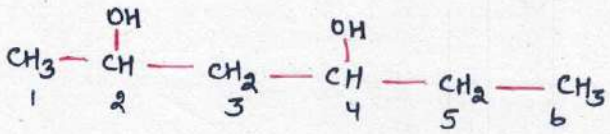
- if more than 2 (-OH) group is present

1-OH
x - alkanal or
Alkan-x-al

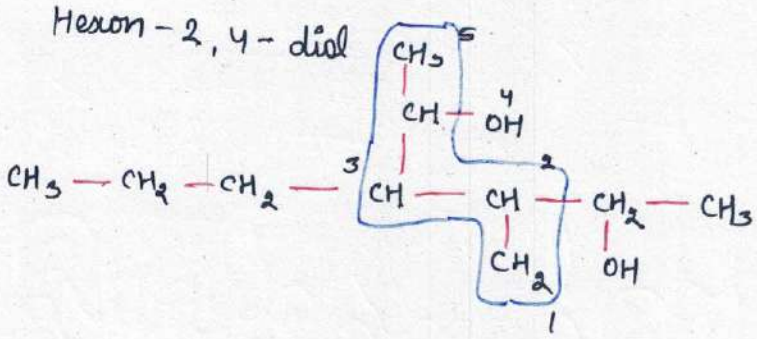
2-OH
x,y - Alkanal or
Alkan-x,y-al



3- ethyl - 5- methyl
hepton - 2, 4, 6 - trial



Hexan - 2, 4 - diol



2 ethyl - 3 propyl
Pentan - 1, 4 - diol

ISONITRILE

ISOCYANIDE

Functional group → -NC or -N≡C or $-\overset{+}{N}\equiv C^{-}$

B.N → Alkane isonitrile

(1) CH_3-NC

IUPAC - Methane isonitrile
C.N. - Methyl isocyanide

(2) CH_3-CH_2-NC

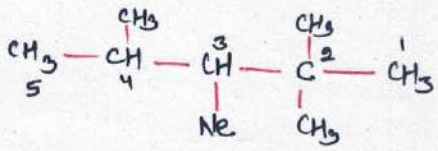
IUPAC - ethane isonitrile
C.N - ethyl isocyanide

(3) $CH_3-CH_2-CH_2-NC$

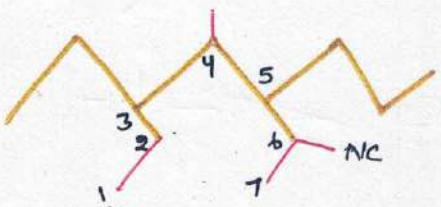
IUPAC - ethane isonitrile
C.N - ethyl isocyanide

(4) $CH_3-CH(NC)-CH_3$

Propane - 2 - isonitrile
isopropyl isonitrile

(5) 

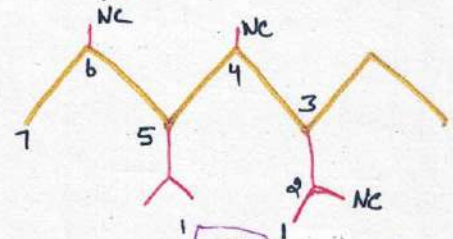
2,2,4 trimethyl pentan-2-isonitril

(6) 

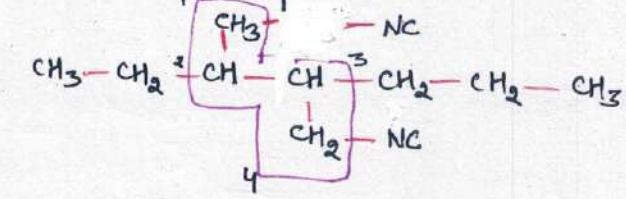
3 - ethyl - 5 - methyl hepton - 4 - isonitrile

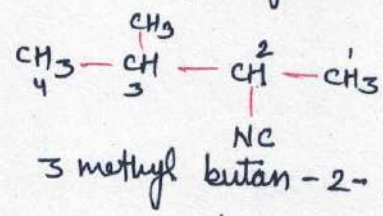
(7)

3 - ethyl - 5 - propyl - 4 - methyl hepton - 2, 6 - diisonitrile

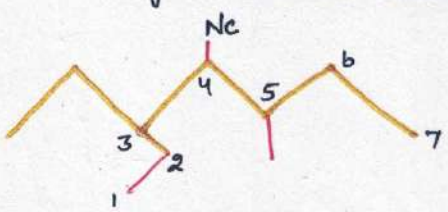
(8) 

3 ethyl - 5 - isopropyl hepton - 2, 4, 6 - tri-isonitrile

(9) 

(10) 

3 methyl butan - 2 - isonitrile

(11) 

3 - ethyl - 5 - methyl hepton - 4 - isonitrile

AMINE

$-NH_2$

Primary amine / 1° amine → $(-NH_2)$
Secondary amine / 2° amine → $(-N(R)(H))$
Tertiary amine / 3° amine $(-N(R_1)(R_2))$

1° Amine

($-NH_2$)

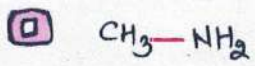
Base name → Alkanamine

1 → x- Alkanamine or Alkane -x- amine

2 → x,y- Alkanamine or Alkane -x,y- diamine

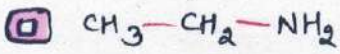
3 → x,y,z- Alkanamine or Alkane -x,y,z- triamine

E.g.



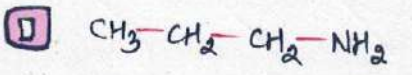
IUPAC - Methanamine

C.N - Methyl amine



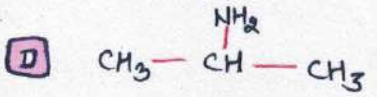
IUPAC- ethanamine

C.N - ethyl amine



propan -1- amine

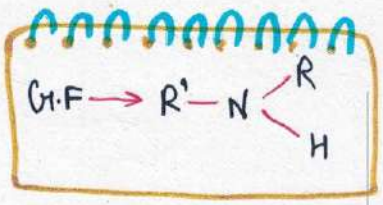
C.N- n- propyl amine



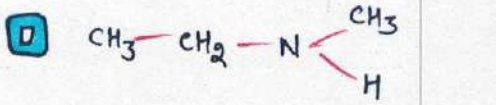
propan -2- amine

isopropyl amine

Naming of 2° Amine



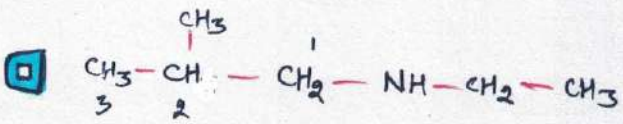
N- alkyl alkanamine



N- methyl ethanamine

$CH_3-CH_2-NH-CH_3$

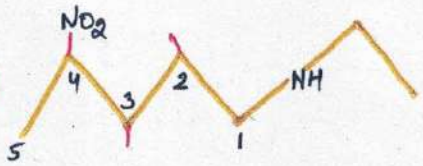
ethyl methyl amine



N- ethyl 2- methyl -1- propanamine

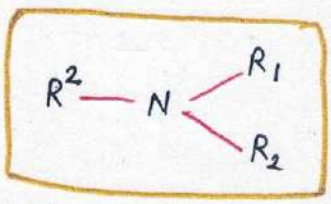
$CH_3 - NH - CH_3$

N - methyl methanamine
Dimethyl amine



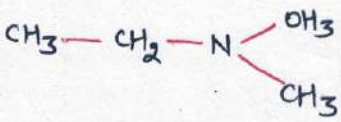
N- ethyl -2, 3-dimethyl
4- nitro penta 1-amine

Naming of 3° Amine

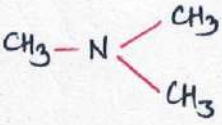


if $R_1 \neq R_2$ — N- alkyl -N- alkyl alkanamine

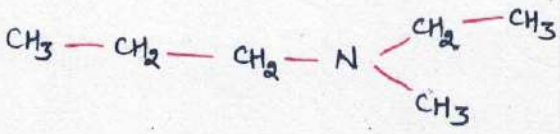
if $R_1 = R_2$ — N, N - dialkyl alkanamine



N, N -dimethyl - ethanamine
CN → ethyl dimethyl amine



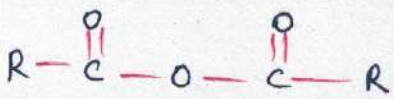
N, N- dimethyl methanamine
C.N → Trimethyl amine



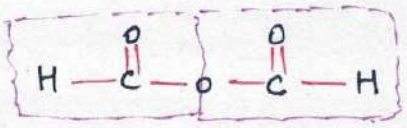
N- ethyl N- methyl propan - 1- amine
C.N → ethyl methyl n- propyl amine

ANHYDRIDE

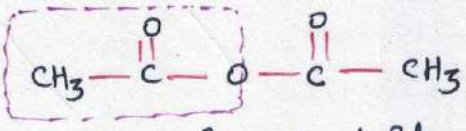
Symmetrical Anhydride



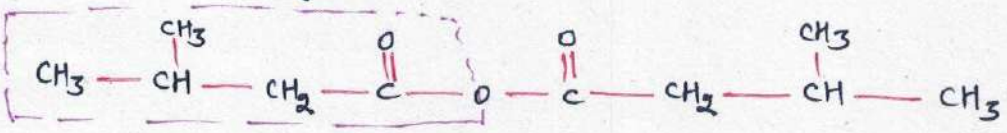
B.N → Alkanoic anhydride

(a) 

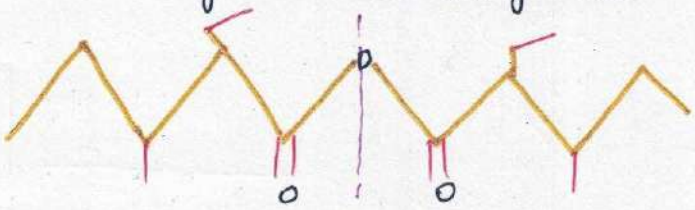
→ Methanoic anhydride
C.N → Formic anhydride

(a) 

→ ethanoic anhydride
C.N → Acetic anhydride

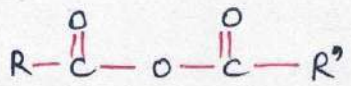
(b) 

3 methyl butanoic anhydride

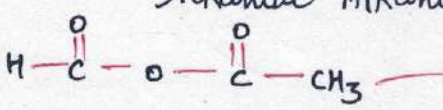
(b) 

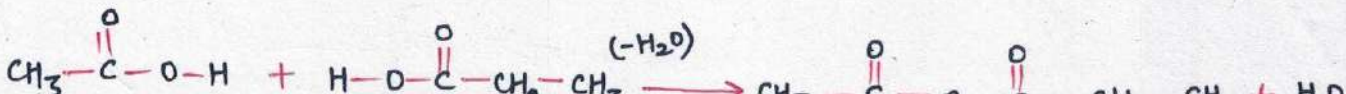
2 ethyl - 3- methyl
Pentanoic anhydride

ASYMMETRIC ANHYDRIDE

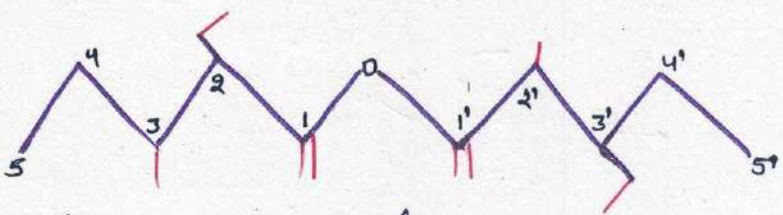


Alkanoic Alkanoic anhydride

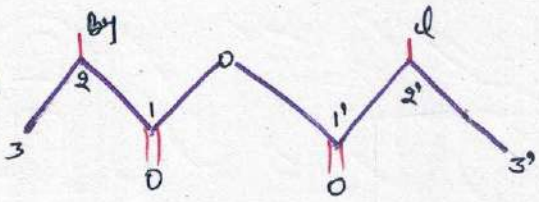
(c)  → Ethanoic Methanoic anhydride

(c) 

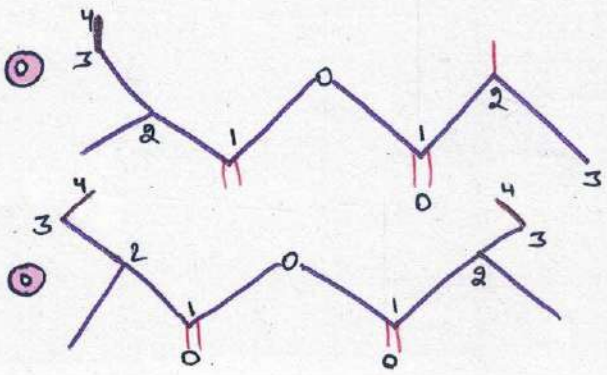
ethanoic propanoic anhydride

(c) 

2 - ethyl - 3- methyl pentanoic
3' - ethyl - 2'- methyl
Pentanoic anhydride

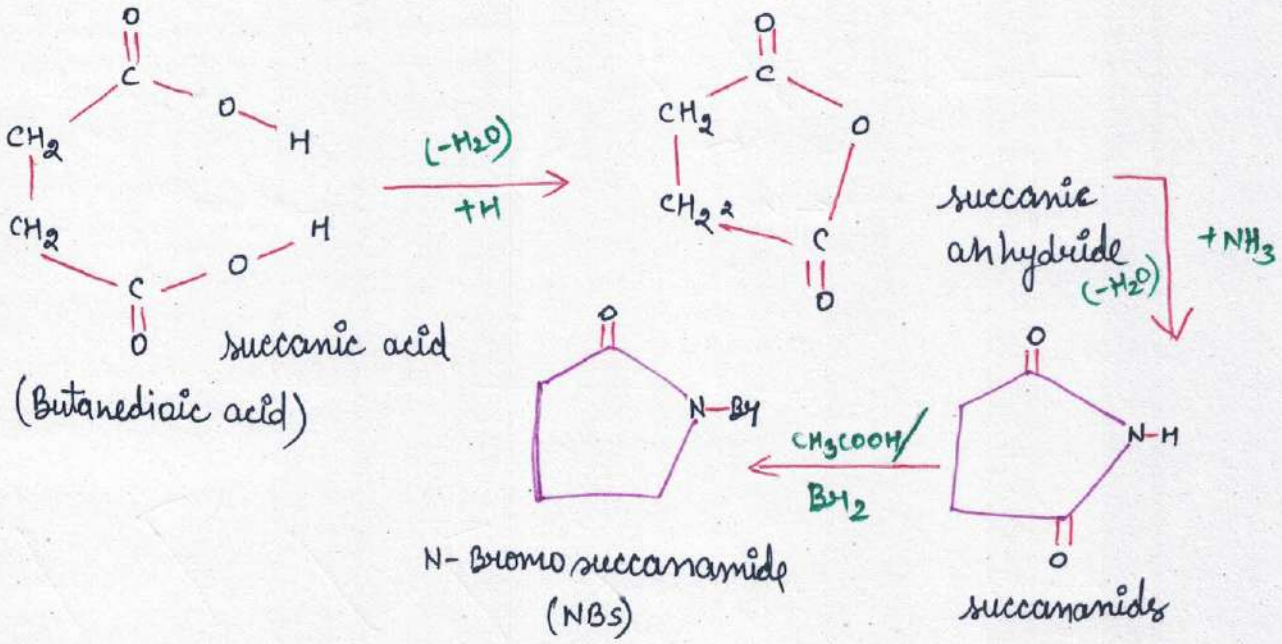
(c) 

2 -Bromo propanoic
2' - chloro propanoic anhydride

(c) 

2 - methyl butanoic
2- methyl propanoic anhydride

2- methyl butanoic anhydride



ETHER

-O-

Symmetrical ether ⟶ R–O–R

Assymmetrical ether ⟶ R–O–R'

B.N ⟶ Alkoxy alkane

◎ CH_3-O-CH_3

Methoxy methane

C.N ⟶ dimethyl ether

◎ $CH_3-CH_2-O-CH_3$

Methoxy ethane

C.N ⟶ ethyl methyl ether

◎ $CH_3-CH_2-CH_2-O-CH_3$

1-Methoxy propane

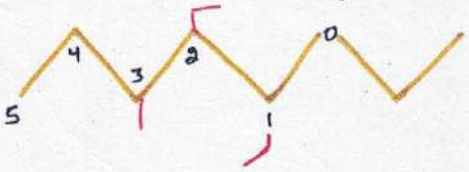
C.N ⟶ methyl n-propyl ether

◎ $CH_3-CH(CH_3)-O-CH_3$

2-Methoxy propane

C.N ⟶ Methyl iso-propyl ether

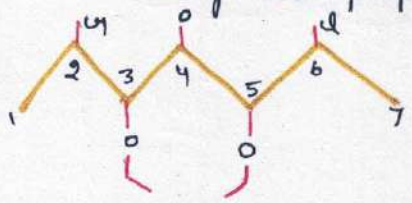
◎



1- ethoxy, 2- ethyl

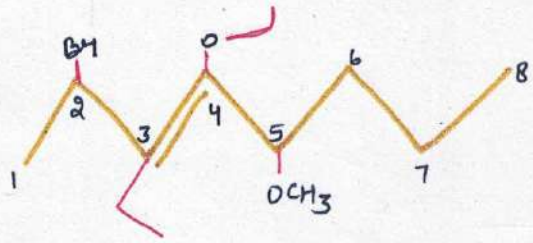
3- methyl pentane

◎



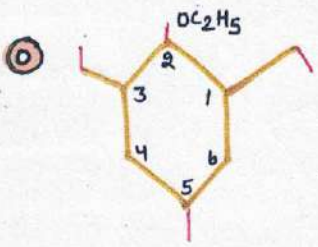
2- Bromo-6-chloro-4-ethoxy

3,5- dimethoxy heptone

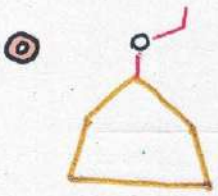


2- Bromo - 4 - ethoxy
3 - ethyl - 5 - methoxy
Oct - 3 - ene

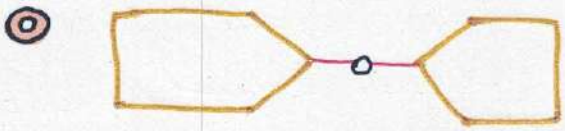
Methoxy cyclohexane
C.N → Cyclohexyl methyl ether



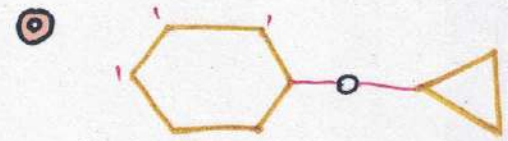
2 - Ethoxy - 3, 1 - diethyl -
3 - ethyl cyclo hexane
C.N → cyclo.



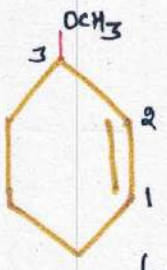
ethoxy cyclo pentane
C.N → Cyclo pentyl ethyl ether



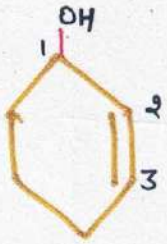
cyclopentoxy cyclopentane
C.N → Diclopentyl ether



Cyclopropoxy cyclo hexane
C.N → cyclohexyl cyclopropyl

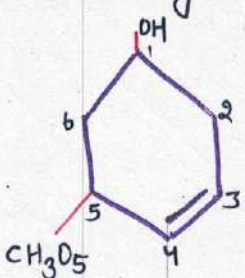


3 - Methoxy
cyclohex - 1 - ene
(-O-R-)

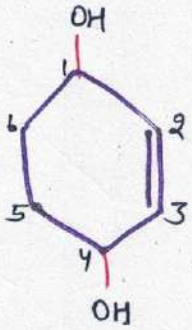


cyclohex - 2 - ene
1 - ol

Alkoxy is also treated as substituent and is not given priority while numbering.

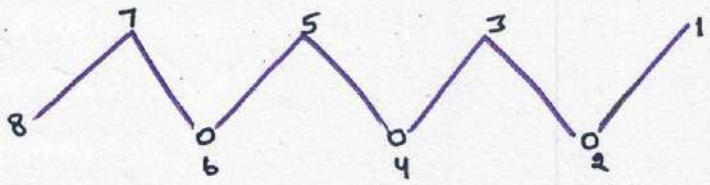


5 - Methoxy cyclohex - 5 - ene - 1 - ol

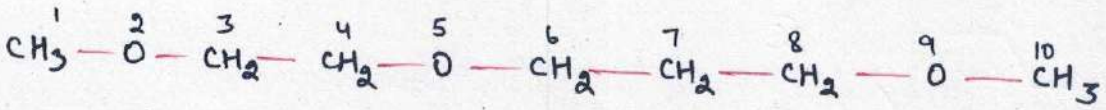


cyclohex - 2 - ene - 1, 4 - ol

Polyether



2, 4, 6 - trioxa octant

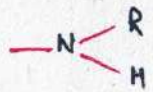
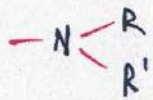
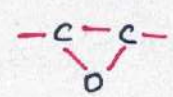


2, 5, 9 - trioxadecane

POLYFUNCTIONAL COMPOUND

Priority Order

	Functional Group	class	Base Name (suffix)	Prefix
1		Carboxylic acid	Alkanoic acid - oic acid	carboxy
2		Sulphonic acid	Alkane sulphonic acid	sulpho
3		Acid Anhydride	Alkanoic Anhyonide	
4		ether	Alky Alkanoate	Alkoxy carbonyl or Alkyl carboxylate
5		Acid Halide	Alkanoyl halide	Halocarboxy or Haloformyl
6		Amide	Alkanamide	Carbomoyal
7		Nitrile / cyanide	Alkane nitrile	cyano
8		isonitrile / isocyanide	Alkane - isonitrile	Isocyano
9		Aldehyde	Alkanal - al	formyl / oxo / Aldo
10		Ketone	Alkanone - one	Keto / oxo
11		Alcohol	Alkanol - ol	Hydroxy
12.		Thio alcohol	Alkanethiol - thiol	Mercapto

13.	$-NH_2$	Amine (1° Amine)	Alkanamine	Amin
14.		2° Amine	N- Alkyl amine	–
15.		3° Amine	N-alkyl-N-alkyl or N,N-alkyl amine	–
16.		Alkene	Alk-x-ene	Alkenyl
17.	$-C\equiv C-$	* Alkyne	Alk-x-yne *	alkynyl *
18.	$-O-R$	ether	–	Alkoxy
19.		episide	–	Epoxy
20.	$-X$	Halogen compounds	–	Halo
21.		Nitrile or nitro compounds	–	Nitro
22.	$-N=O$	Nitroso	–	Nitroso
23.	$-N=N-$	Azo compounds	–	Azo

☞ No priority as like function group. They are simply treated a substituite

Functional groups which are treated as substituents as below:-

ARYL GROUP

Phenyl

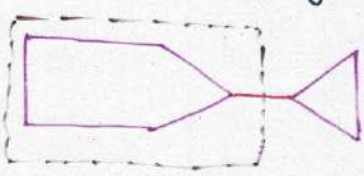
Benzyl

Benzal

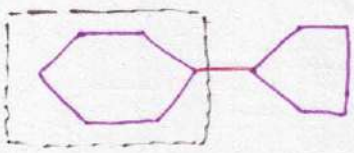
Benzo

BICYCLIC COMPOUND

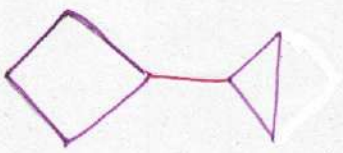
Case-I if both cyclic ring has no common atom Hence.
Bigger ring → parent chain, smaller chain → substituent



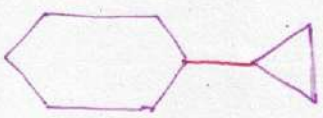
Cyclopropyl cyclopentane



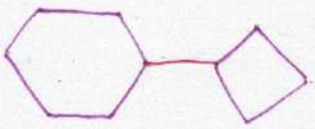
Cyclopentyl cyclohexane



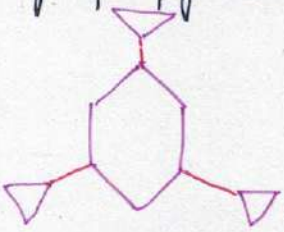
cyclopropyl cyclobutane



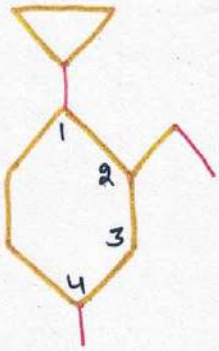
cyclopropyl chclohexane



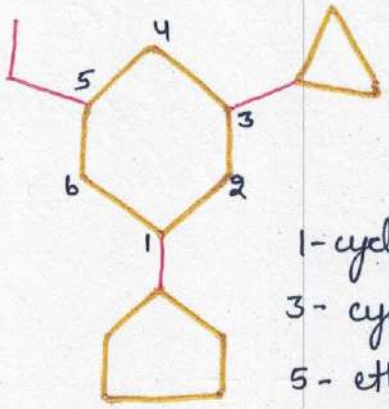
Cyclobutyl cyclohexane



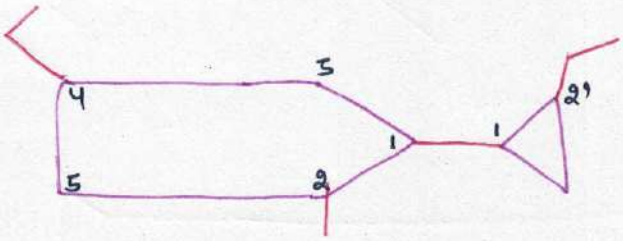
1,3,5- tricyclo-propyl cyclohexane



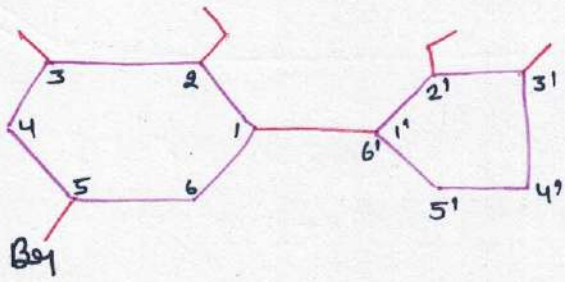
1- cyclopropyl-
2- ethyl - 4- methyl
cyclohexane



1- cyclopentyl
3- cyclopropyl
5- ethyl
cyclohexane



4 - ethyl -
1 - [2' ethyl] cyclopropyl - 2 - methyl
cyclopentane



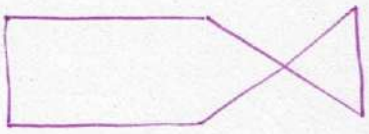
5 - Bromo
1 - [2 - ethyl , 3- methyl]
cyclopentyl - 2- ethyl - 3 - methyl
cyclohexane

Case-II

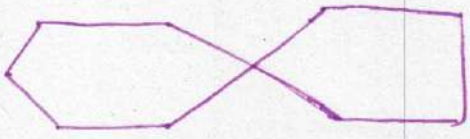
SPIRO COMPOUND

Bicyclic compound in which only one carbon atom is common in both cyclic rings is called as Spiro compounds.

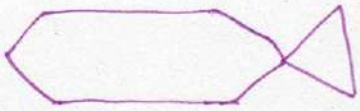
PRIORITY - smaller ring > Bigger ring



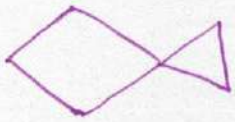
Spiro [2,4] heptane



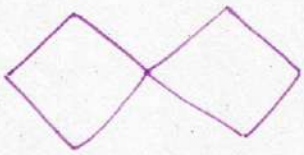
spiro [4.5] decane



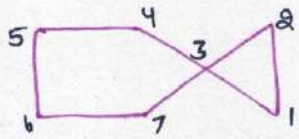
spiro [2,5] octane



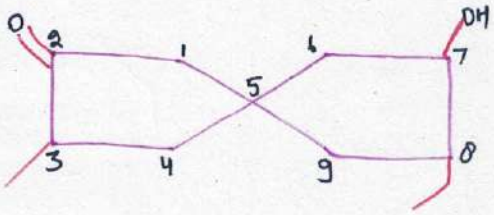
spiro [2,3] hexane



Spiro [3, 3] heptane



5-ethyl spiro [2,4] heptane

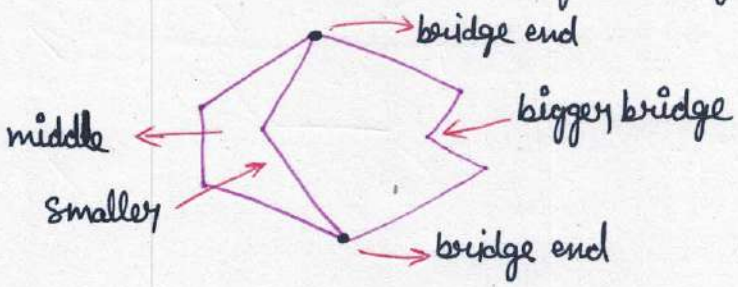


8 ethyl - 7- hydroxy - 3 methyl spiro [4,4] nonan - 2 - one

BICYCLO COMPOUNDS

The compounds which have 2 or more than 2 common carbon in both cyclic rings are known as **bicyclo compounds.**

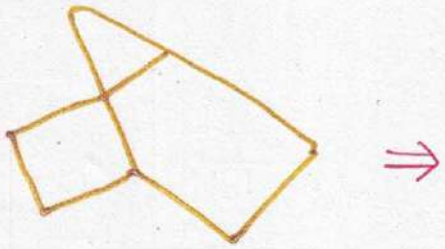
The two common carbon atoms in cyclic ring are known as bridge head carbons.



Priority Order :- Bigger > middle > smaller

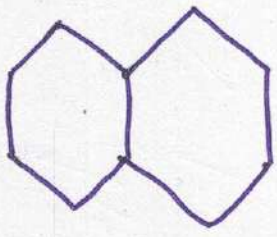
IUPAC name :- Bicyclo [3,2,1] octane

Bicyclo [2,2,1] heptane



Bicyclo [2,2,1] hepton

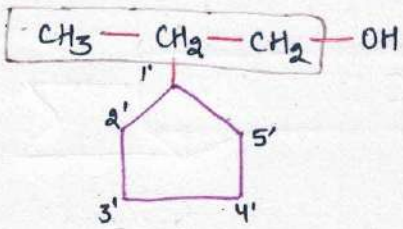
Bicyclo [2,2,0] hexane



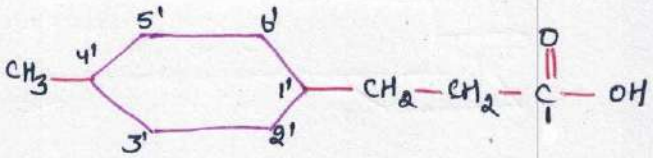
Bicyclo [4,4,0] decane

RULES FOR NAMING ALICYCLIC COMPOUNDS

If the ring contains a multiple bond and the side chain contains a functional group, then the ring is treated as a substituent and the compound is named as the derivative of the side chain.

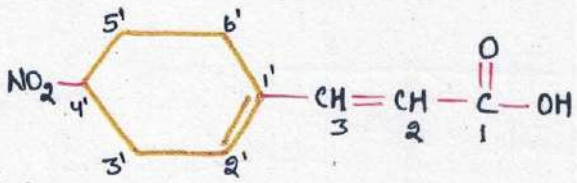


2-(cyclo-3'-pentyl)-propan-1-al

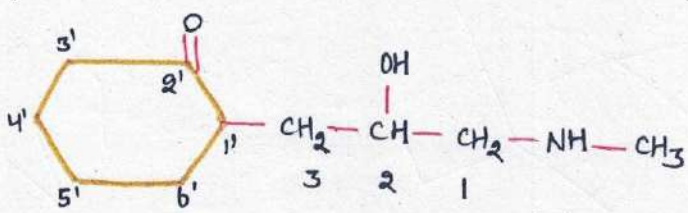


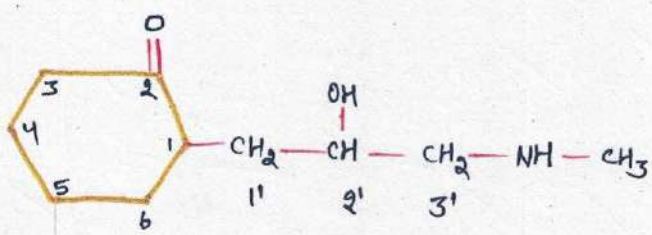
3-[4'-methyl, cyclo hex-2'-enyl] propan-1-oic acid

If the ring as well as side chain contains functional group. the compound is named as a derivative of the side chain or the ring as according to the one containing the principal functional group [i.e. the group with more priority]



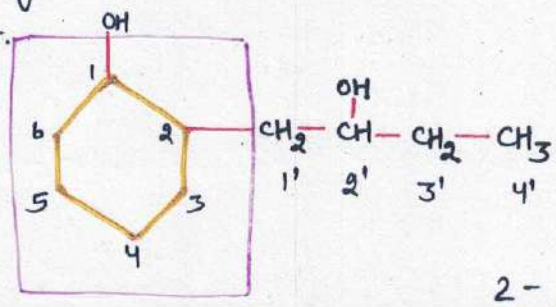
3-(4' nitro cyclohex-1'-enyl) prop-2-en-1-oic acid



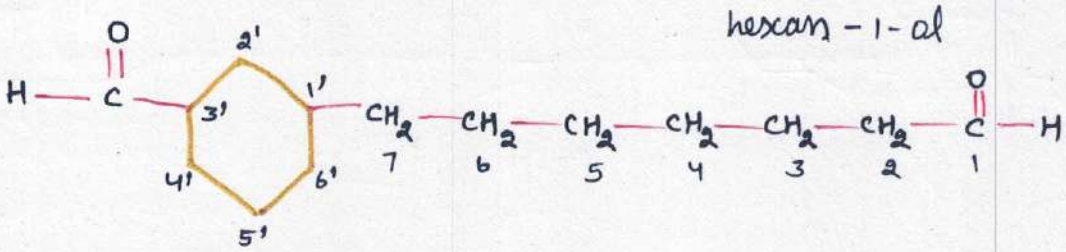


1-[3'-aminomethyl, 2'-hydroxy propyn] cyclohexan-2-one

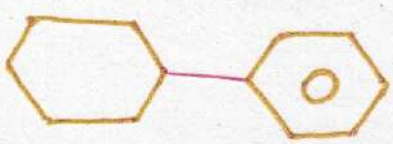
Case-III If the alicyclic ring and the side chain contains the same functional group, the compound is name as the derivative of the ring or side chain which contains higher number of carbon-atoms.



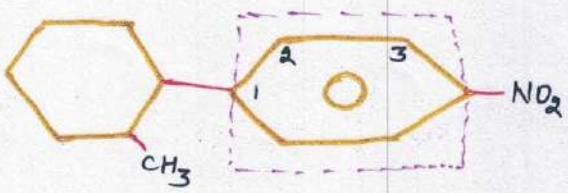
2 - [2' hydroxy butyl] - cyclo hexan - 1 - ol



Case-IV If the compound contains alicyclic ring, directly linked with benzene ring. it is named as derivative of benzene.

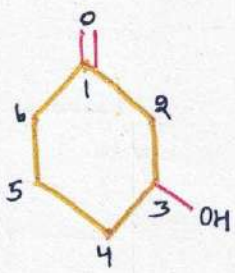


cyclohexyl benzene

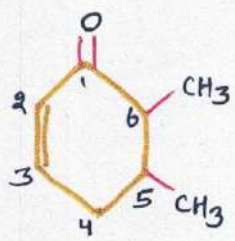


cyclohexyl 4 - nitro benzene

Case-V If some functional group along with other substituents are present in the ring, it is indicated by same appropriate prefix or suffix or its position is indicated by numbering the carbon atom of ring in such a way that the principal functional group gets the lowest no.



3 - hydroxy cyclohexa - 1 - one

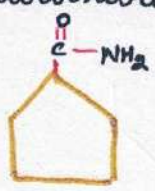


5, 6 - dimethyl cyclohex - 2 - ene - 1 - one

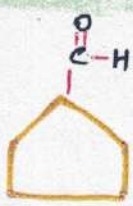
Case-VI In an alicyclic ring is directly attached to a carbon-containing functional group, the carbon atom of the functional group is not included in the parent chain or base name of alicyclic system. Therefore, for such systems the following prefix and suffix are used:-

FUNCTIONAL GROUP	SUFFIX	PREFIX
$-COOH$	carboxylic acid	carboxy
$-CHO$	carbaldehyde	formyl
$-\overset{O}{\overset{\|}{C}}-X$	carbonoyal halide	Halo carbonyl
$-\overset{O}{\overset{\|}{C}}-O-R$	Alkyl carboxylate	Alkoxy carbonyl or carbalkoxy
$-\overset{O}{\overset{\|}{C}}-NH_2$	carboxamide	carbamoyal
$-CN$	carbonitrile	Cyano

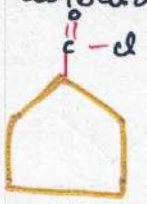
cyclohexane carbonitrile



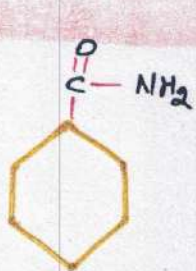
cyclopentane carboxamide



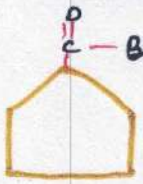
cyclopentane carbaldehyde



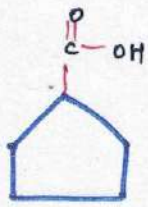
cyclopentane carbonoyal chloride



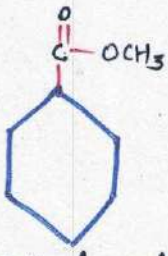
cyclohexane carboxamide



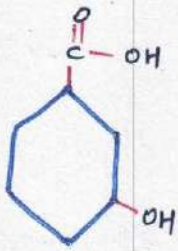
cyclopentane carbonoyal bromide



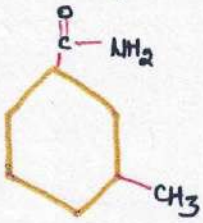
Cyclopentane carboxylic acid



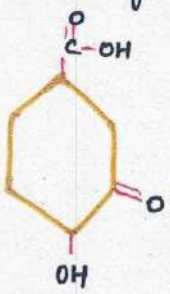
Methyl cyclohexane carboxylate



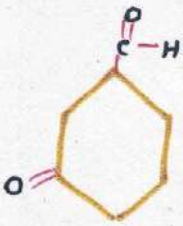
3- Hydroxy cyclohexane carboxylic acid



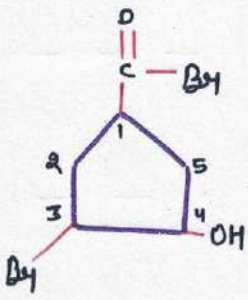
3- methyl cyclohexane carboxamide



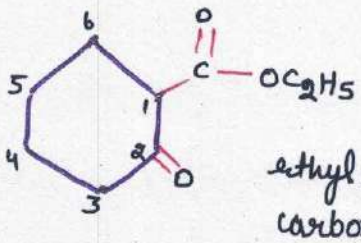
4- Hydroxy-3- keto cyclohexane carboxylic acid



3- keto cyclohexane carbaldehyde



3- Bromo - 4- hydroxy cyclohexene carbonoyl bromide



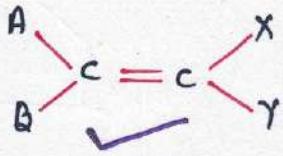
ethyl 2- keto - cyclohexane carboxylate

GEOMETRICAL ISOMERISM

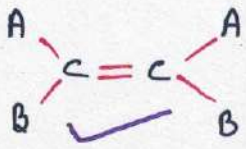
C_4H_8 ⟶ 4 isomers 4 fraction

To show geometrical isomers;

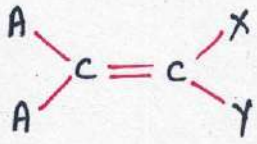
a.



b.

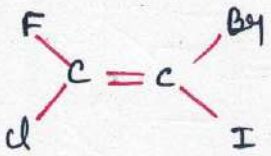


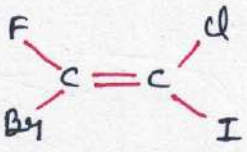
c.

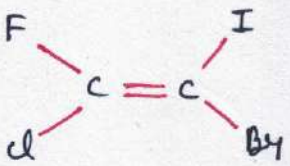


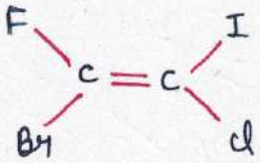
X ⟶ will not show

No. of isomers of $C_2BrClFI$ = 6









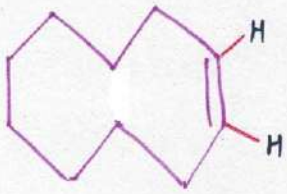
+ 2 more (Fix one and make other three to more).

Generally 'trans' is more stable than "cis" (Linear) If cis trans

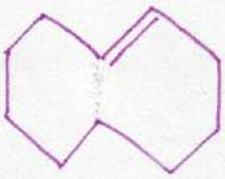
HOC ⟶ cis > Trans

- All geometrical isomers are "diastereoisomers." stereoalso. which are not mirror images are called as "diastereoisomers."
  All geometrical isomers are not mirror images.

Cyclodecene



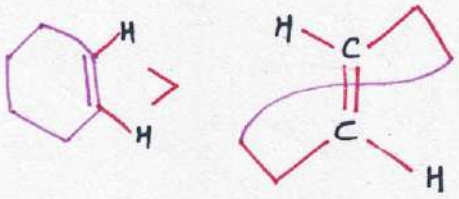
(Cis)



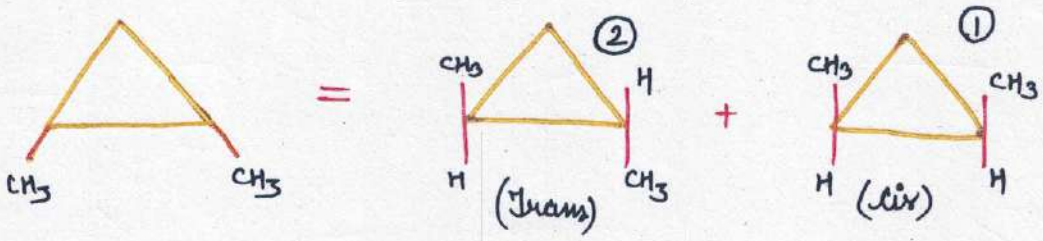
(Trans)

Cyclohexene

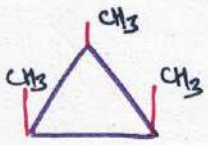
cis is most stable Trans doesn't exist.



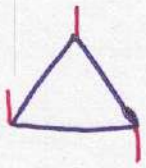
Trans cycloalkenes exist after the cyclooctenes.



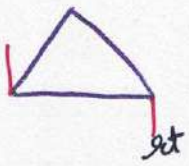
- For a molecule to show geometrical isomer, there must be restricted rotation about a bond.



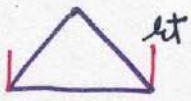
and



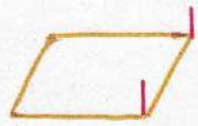
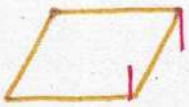
are G.I

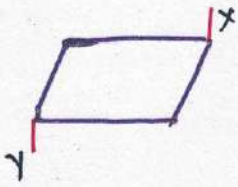
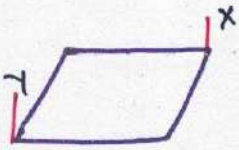


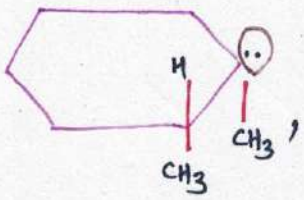
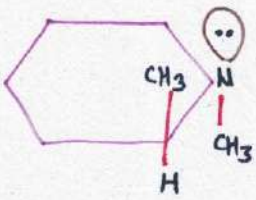
and

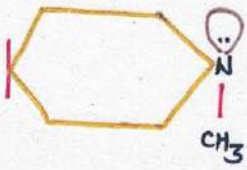
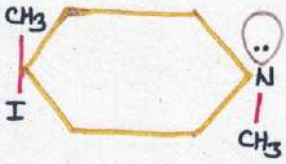


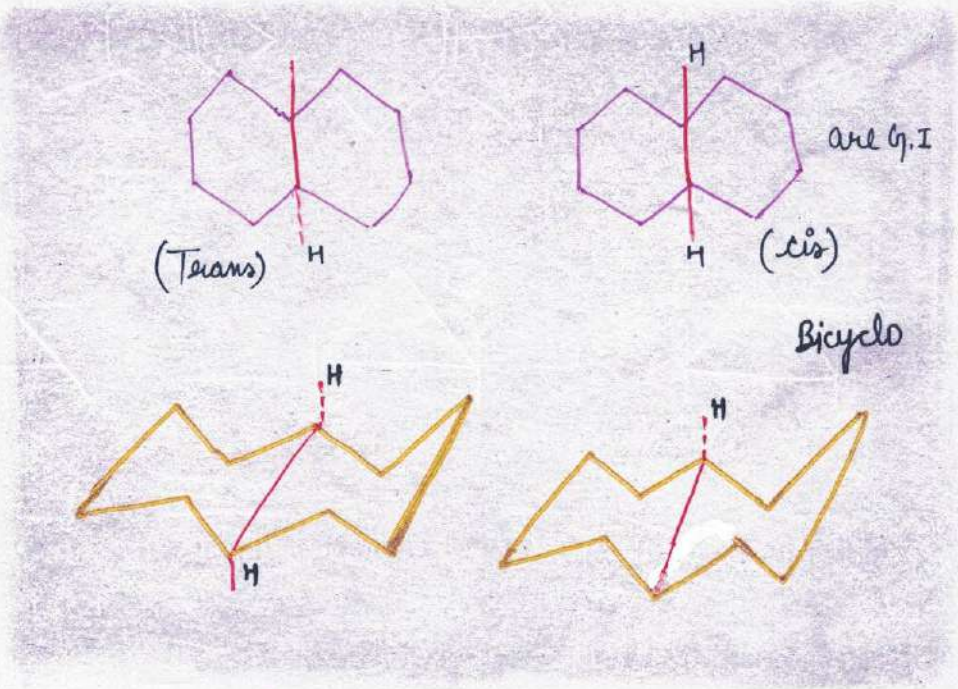
are G.I.

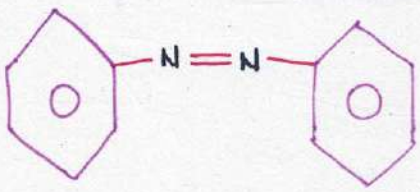
-  and  are G.I.

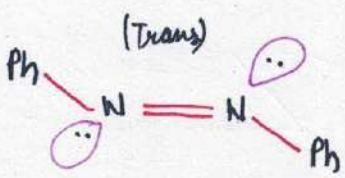
-  ,  are G.I.

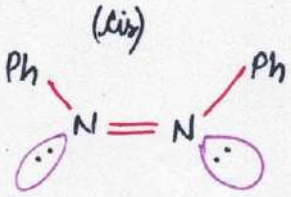
-  ,  are G.I.

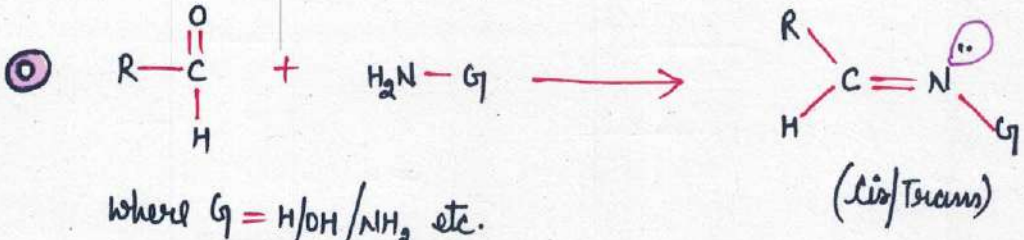
-  ,  are G.I.



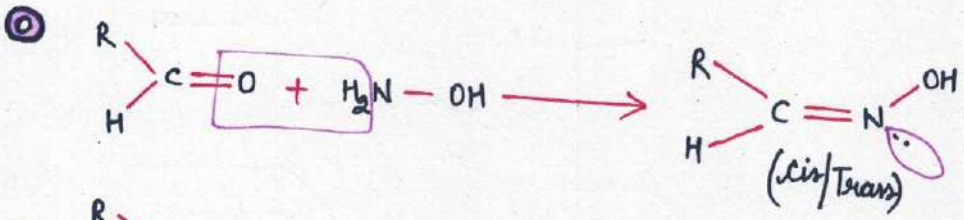
-  All Azocompounds show G.I.

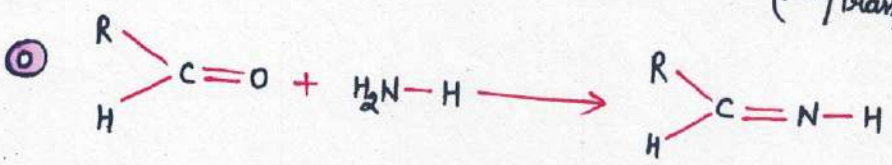




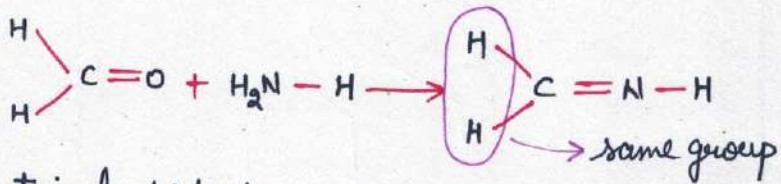


Where G = H/OH/NH_2 etc.

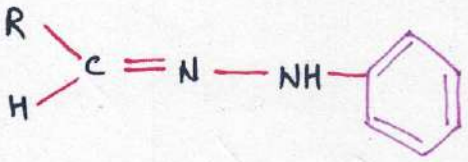


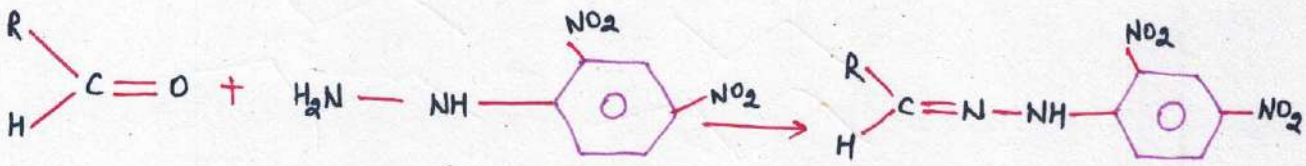


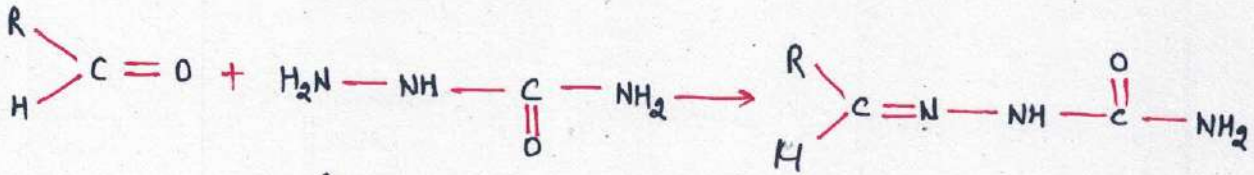
- Imines of all aldehydes except formaldehydes show G.I.
- Imines of all unsymmetrical ketons show G.I
- All oxims of unsymmetrical ketons/aldehydes show G.I.

In case of formaldehyde 

All hydrozones of unsymmetrical ald./ketons show G.I.


(Phenyl hydrozones)


(2,4 DNP)

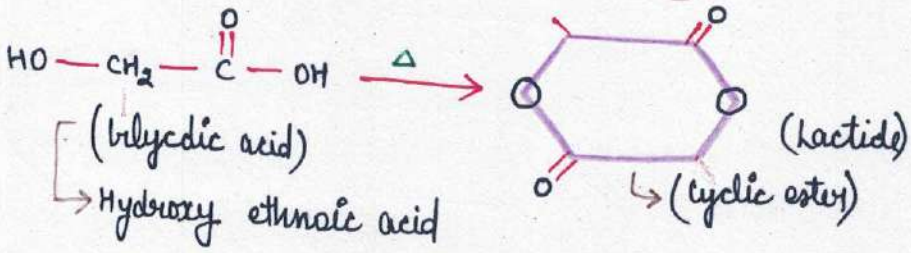

(Semi-carbozyls) (Semi-carbozones)

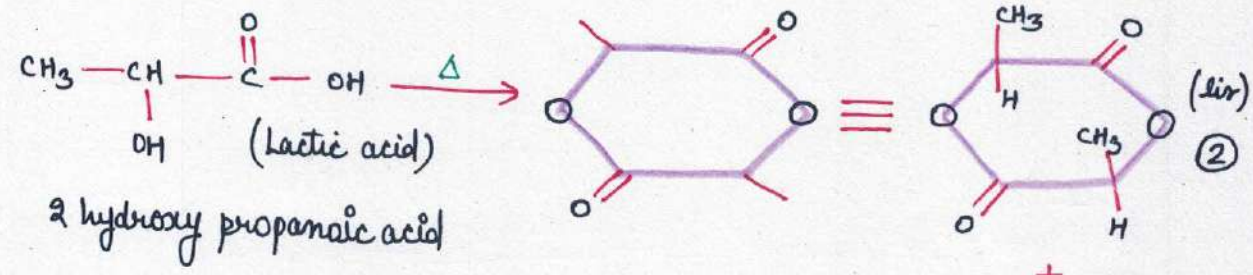
Semi-carbonones of all unsymmetrical ald./ketons show G.I.

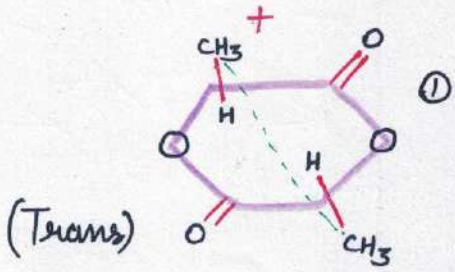
Ammonia derivatives of all aldehydes except formaldehydes show G.I. same for unsymmetrical ketons.

- HNO_3 → Nitric acid HNO_2 → Nitrous acid, $H_2N_2O_2$ (Dimer) → Hyponitrous acid

  $H_2N_2O_2$ is unstable (it has a azo group) → shows G.I.

- 

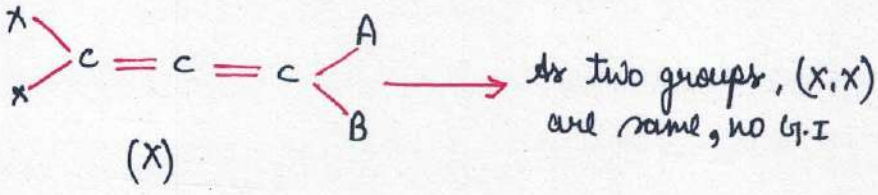
- 



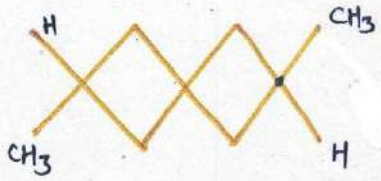
Lactides of all α-hydroxy acids except glycolic acid will show geometrical isomerism.

Imp. Trick

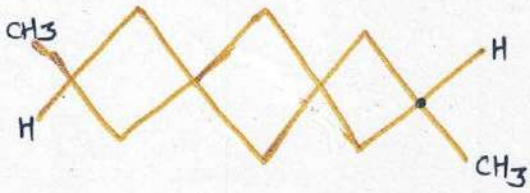
- If Σ(Double Bond Rings) = even, no G.I. (non-planar)
- If Σ(Double Bond Rings) = odd, G.I. is possible (They are planar)



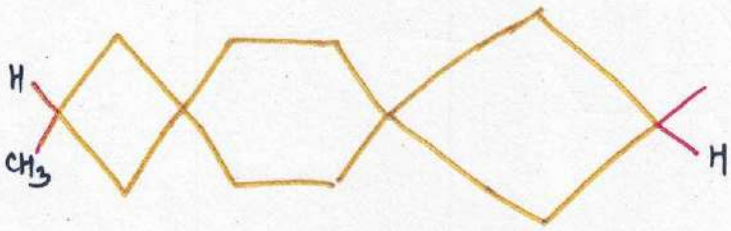
→ As two groups, (X, X) are same, no G.I



(X)



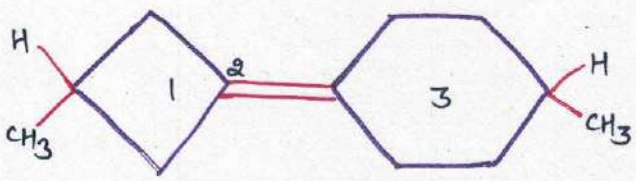
(✓)



(✓)

Spiro

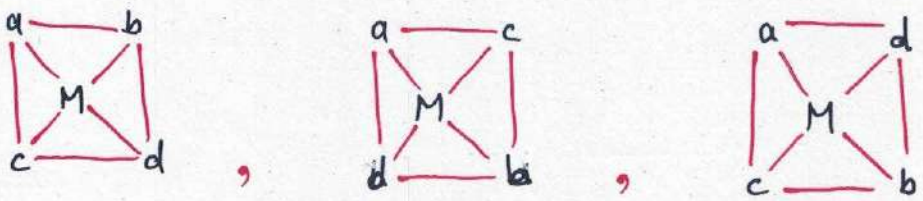
The rings must be symmetric, non-5-membered



(✓)

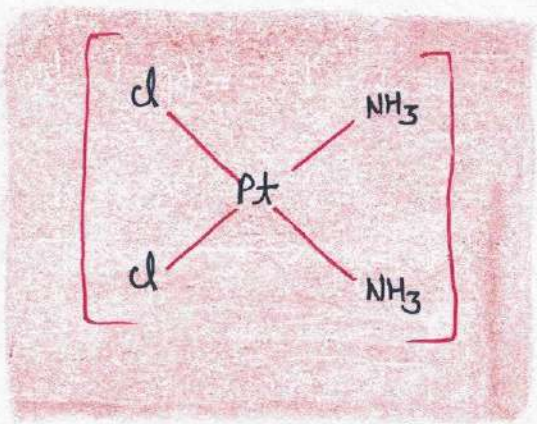
Tetrahedral complex don't show G.I. (Mabcd)

Square planar will show G.I. (Mabcd)

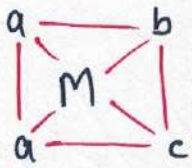


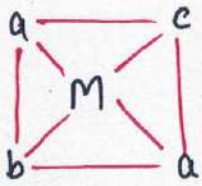
3 isomers are possible

Ma_2b_2 → (Sq. planar) → E.g. :- Cisplation → used for cancer treat



- Ma_2bc (sq. planar)

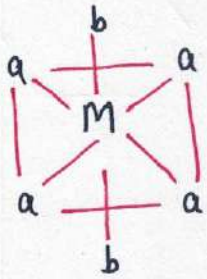


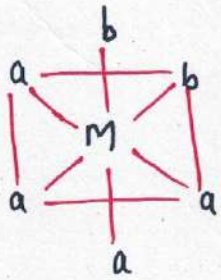


(2 isomers)

- Ma_3b (sq. Planar) No. G.I

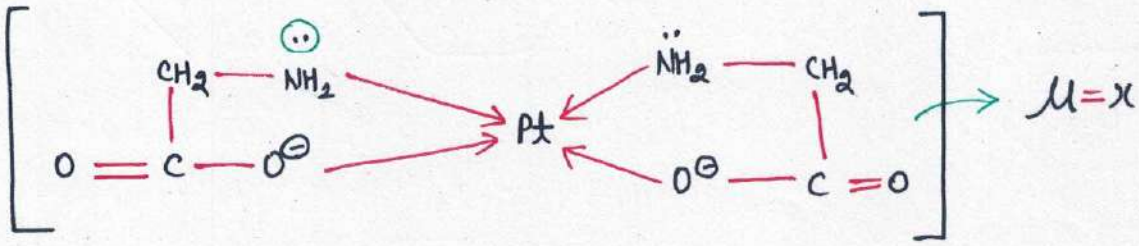
- Ma_4b_2

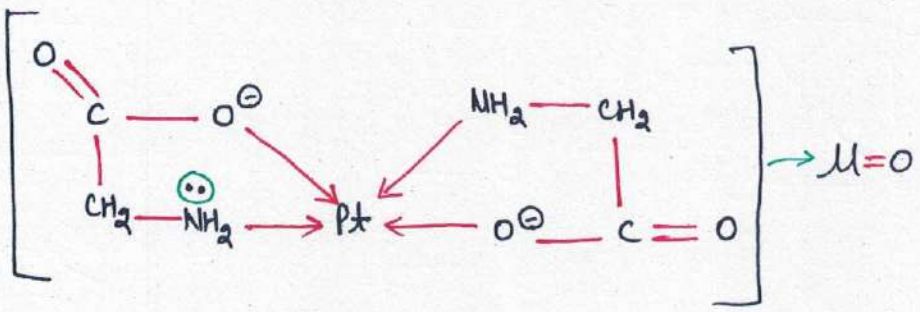




shows G.I (octahedral)

- $[Pt(\ddot{N}H_2\ CH_2\ CO^{\ominus})_2]$





- Inorganic compounds can also show geometrical isomeric.

ACID AND BASE CONCEPT

- $H_2O \longrightarrow H^{\oplus} + OH^{\ominus}$
  $H_2S \longrightarrow H^{\oplus} + SH^{\ominus}$
  $H_2Se \longrightarrow H^{\oplus} + SeH^{\ominus}$
  $H_2Te \longrightarrow H^{\oplus} + TeH^{\ominus}$

  size ↓ acidic ↓ basic ↑

  acidic nature $H_2Te > H_2Se > H_2S > H_2O$

- $NH_3 \longrightarrow H^{\oplus} + NH_2^{\ominus}$
  $PH_3 \longrightarrow H^{\oplus} + PH_2^{\ominus}$
  $AsH_3 \longrightarrow H^{\oplus} + AsH_2^{\ominus}$
  $SbH_3 \longrightarrow H^{\oplus} + SbH_2^{\ominus}$

  size ↓ acidic ↓ basic ↑

  acidic nature $NH_3 < PH_3 < AsH_3 < SbH_3$

- $H-CH_3 \xrightarrow{-H^{\oplus}} CH_3^{\ominus}$
  $H-NH_2 \xrightarrow{-H^{\oplus}} NH_2^{\ominus}$
  $H-OH \xrightarrow{-H^{\oplus}} OH^{\ominus}$
  $H-F \xrightarrow{-H^{\oplus}} F^{\ominus}$

  STABILITY $CH_3^{\ominus} < NH_2^{\ominus} < OH^{\ominus} < F^{\ominus}$

Acidic Nature :- $HCH_3 < HNH_2 < HOH < HF$

Left to right, acidic nature of hydrides increases. NaOH is strong base NaF is neutral.

HCl, HBr, HI ↓ acidic

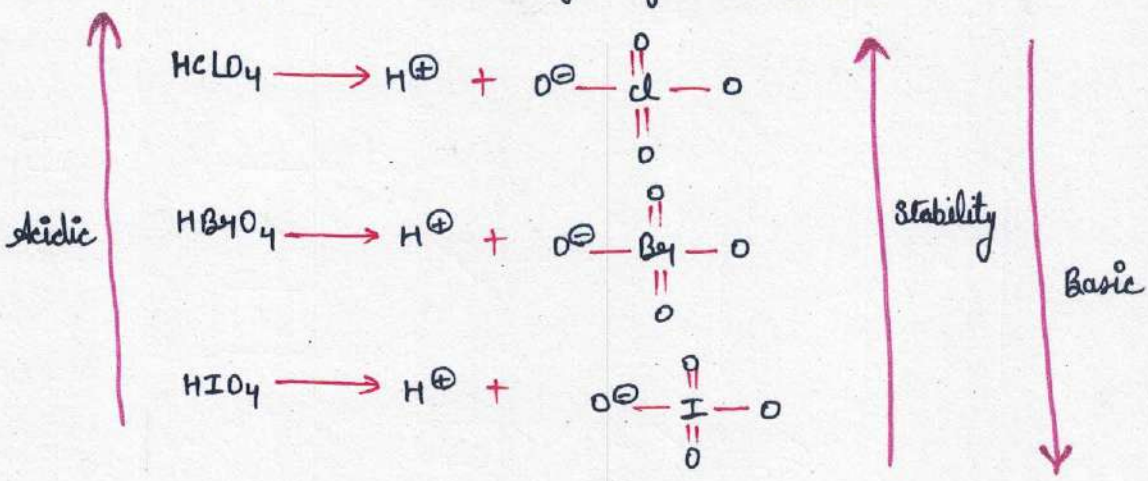
$HOCl \longrightarrow H^{\oplus} + O^{\ominus}-Cl$ $(+I|-M)$
$HOBr \longrightarrow H^{\oplus} + O^{\ominus}-Br$
$HOI \longrightarrow H^{\oplus} + O^{\ominus}-I$

Stability $CH_3^{\ominus} < NH_2^{\ominus} < OH^{\ominus} < HF$

ACIDIC NATURE :- HOCL > HOBr > HOI

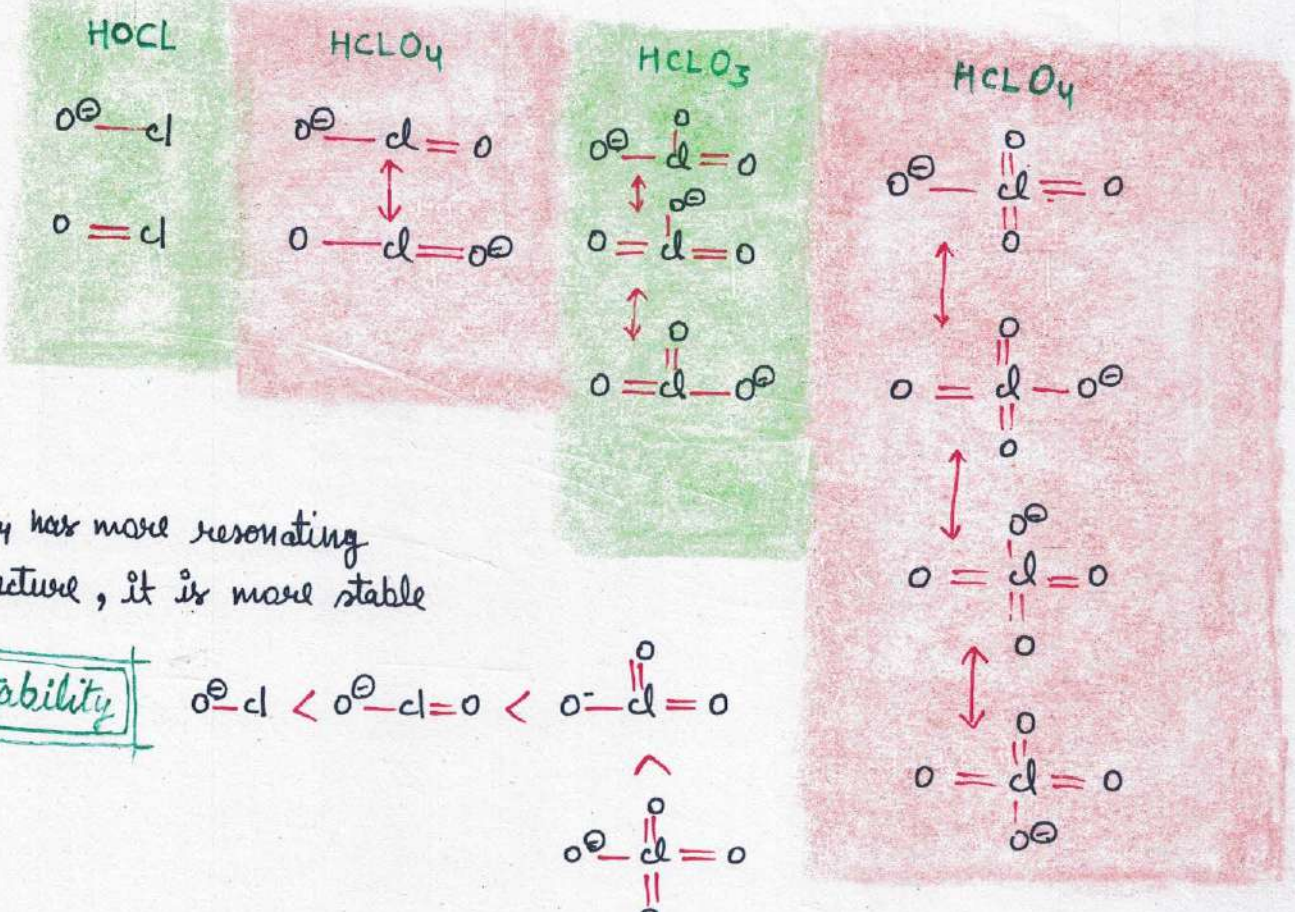
BASIC NATURE :- HOCL < HOBr < HOI

Down the group, acidic nature of oxyacids decrease



ACIDIC NATURE :- $HClO_4 > HBrO_4 > HIO_4$

Similarly $H_3PO_4 > H_3AsO_4 > H_3SbO_4$ [acidic nature]



$HClO_4$ has more resonating structure, it is more stable

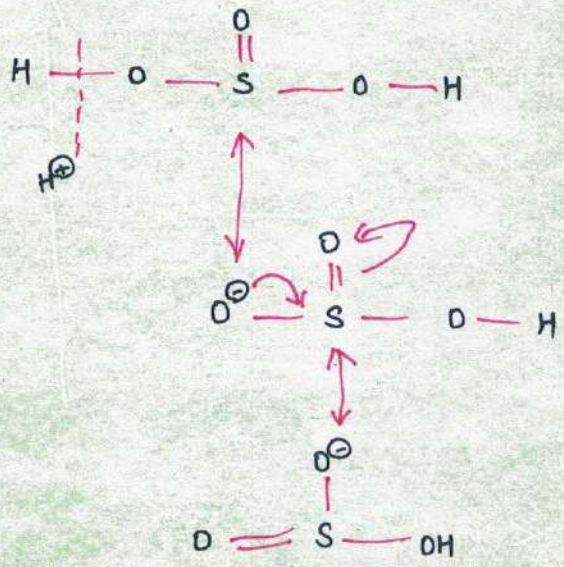
Stability $O^{\ominus}-Cl < O^{\ominus}-Cl=O < O-Cl(=O)=O$

ACIDIC NATURE :- $HOCL < HO_2Cl < HClO_3 < HClO_4$

↓ Give O_2 easily

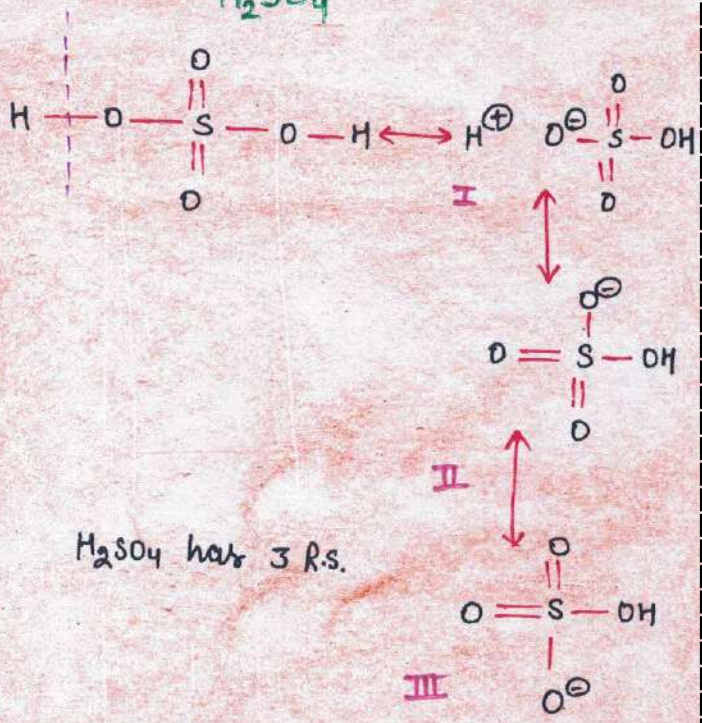
As % of oxygen increases, acidic nature increases

H_2SO_3



H_2SO_3 has 2 R.S.

H_2SO_4

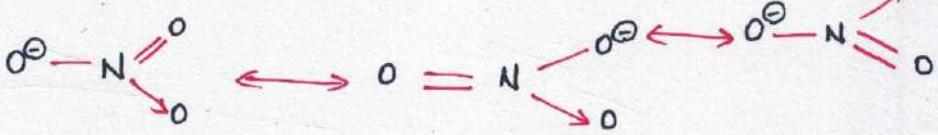


H_2SO_4 has 3 R.S.

ACIDIC NATURE :- $H_2SO_3 < H_2SO_4$

- HNO_2

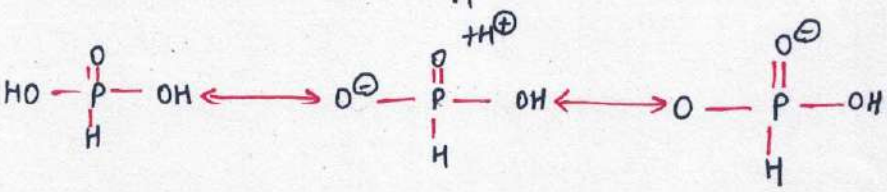
- HNO_3

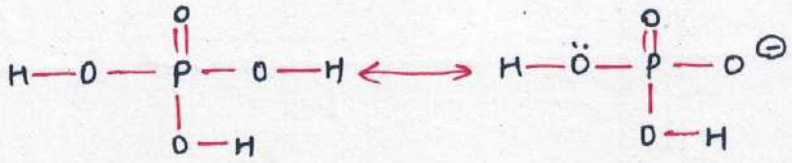


ACIDIC NATURE :- $HNO_2 < HNO_3$

- H_3PO_2

- H_3PO_4



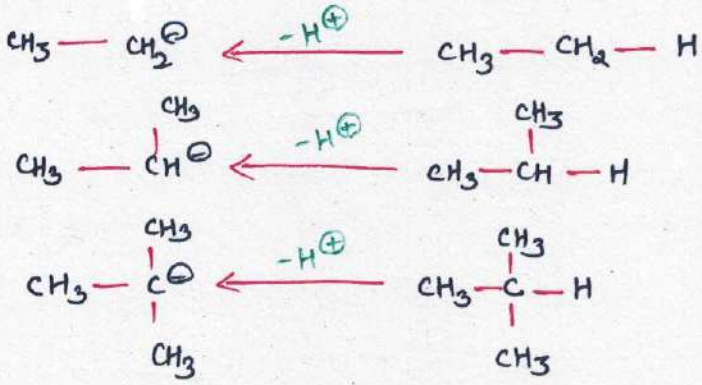
H_3PO_4 

ACIDIC NATURE :- $H_3PO_2 > H_3PO_3 > H_3PO_4$

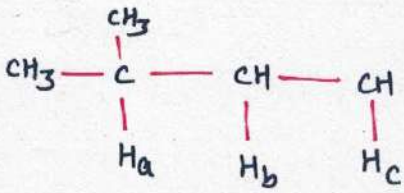
- H_3PO_2 → No counter resonance
- H_3PO_3 → 1 counter resonance
- H_3PO_4 → 2 counter resonance

$HX \longrightarrow H^+ + X^\ominus$ stable

(stable) $CH_3^\ominus \xleftarrow{-H^\oplus} CH_3-H$ (strong)



$t_{C-H} < S_{eH} < P_{C-H}$ (Me)

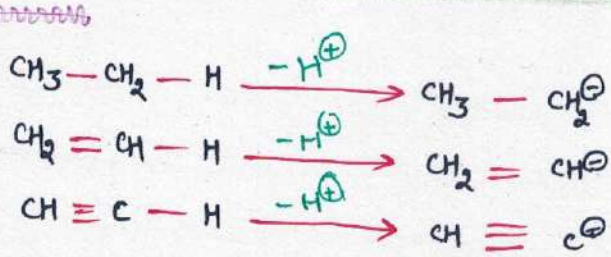


Acidic :- $C-H_c > C-H_b > C-H_a$

BD :- $C-H_a > C-H_b > C-H_c$

BE :- $C-H_c > C-H_b > C-H_a$

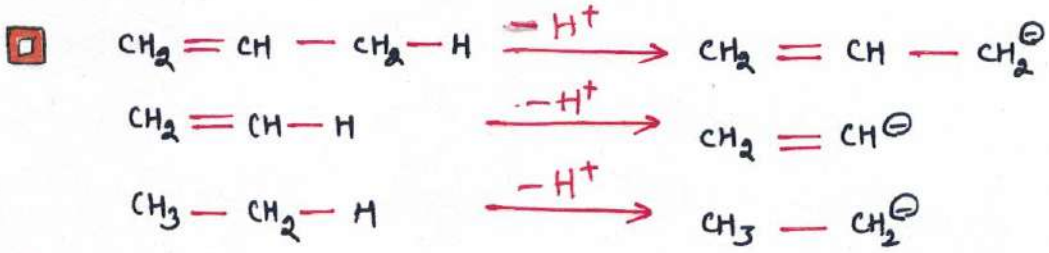
BASIC NATURE :- $CH_3-\overset{CH_3}{\underset{CH_3}{C}}{}^\ominus > CH_3-\overset{CH_3}{CH}{}^\ominus > CH_3-CH_2^\ominus > CH_2^\ominus$



Stability :- $CH \equiv C^\ominus > CH_2 = CH^\ominus > CH_2-CH_2^\ominus$

Acidic nature :- $CH \equiv C-H > CH_2=CH-H > CH_3-CH_2-H$

Basic nature :- $CH \equiv C^\ominus < CH_2=CH^\ominus < CH_3-CH_2^\ominus$

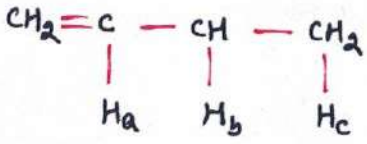


Stability $CH_2=CH-CH_2^{\ominus} > CH_2=CH^{\ominus} > CH_3-CH_2^{\ominus}$

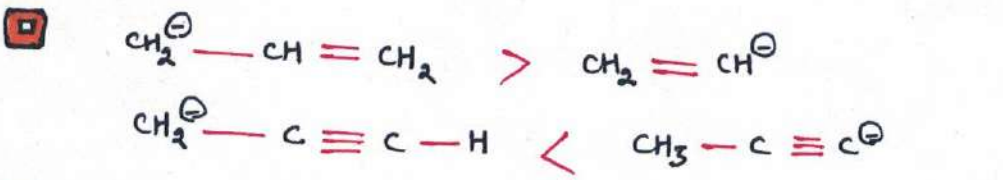
Basic nature :- $CH_2=CH-CH_2^{\ominus} < CH_2=CH^{\ominus} < CH_3-CH_2^{\ominus}$

Acidic nature :- $CH_2=CH-CH_3 > CH_2=CH-H > CH_3-CH_2-H$

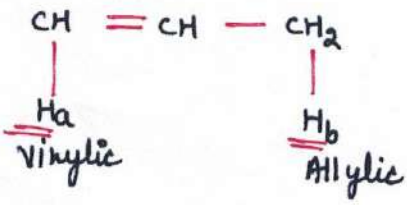
Allylic $_{C-H}$ > Vinyl $_{C-H}$ > Alkyl $_{C-H}$ (acidic)



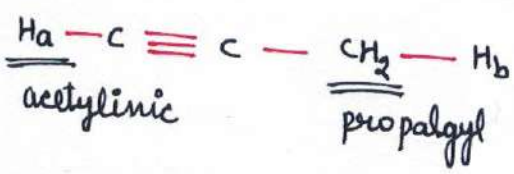
$C-H_b > C-H_a > C-H_c$ (acidic)



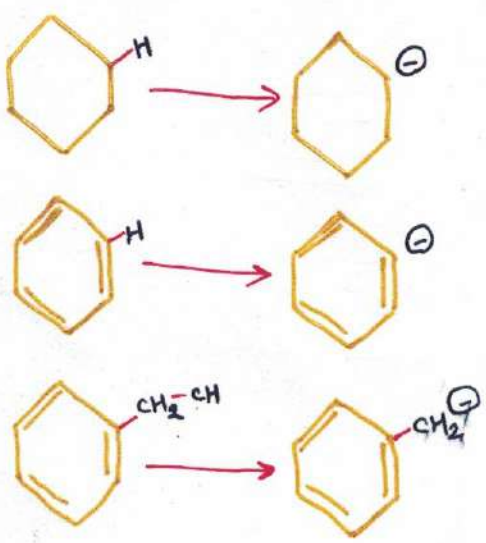
$C-H_b > C-H_a$



$C-H_b > C-H_a$

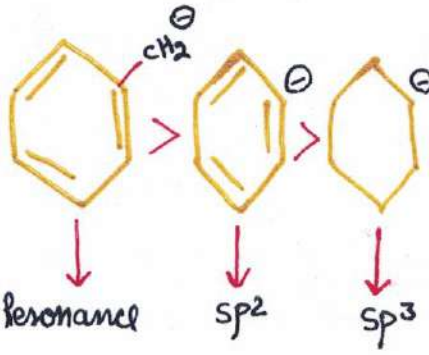


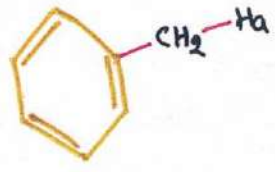
$C-H_a > C-H_b$

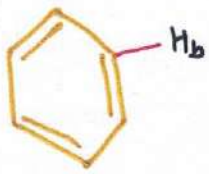


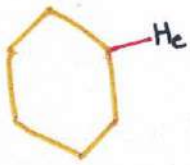
acidic nature

Stability

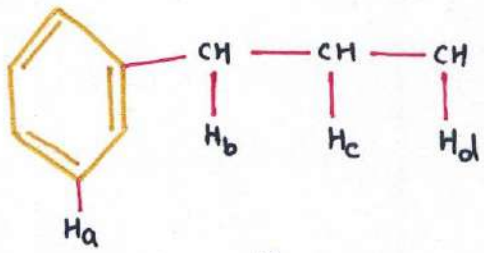




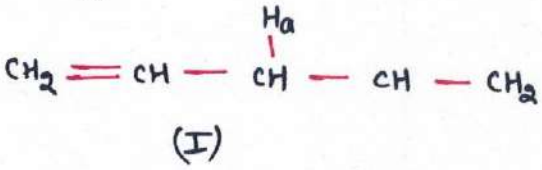




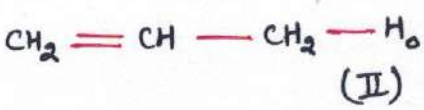
Benzylic C-H > Phenylic C-H > Alkyl C-H



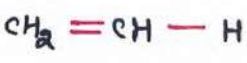
C-Hb > C-Ha > C-Hd > C-Hc



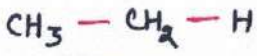
(I)



(II)

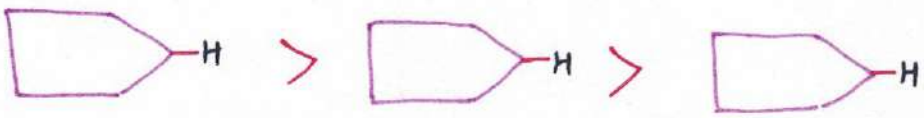


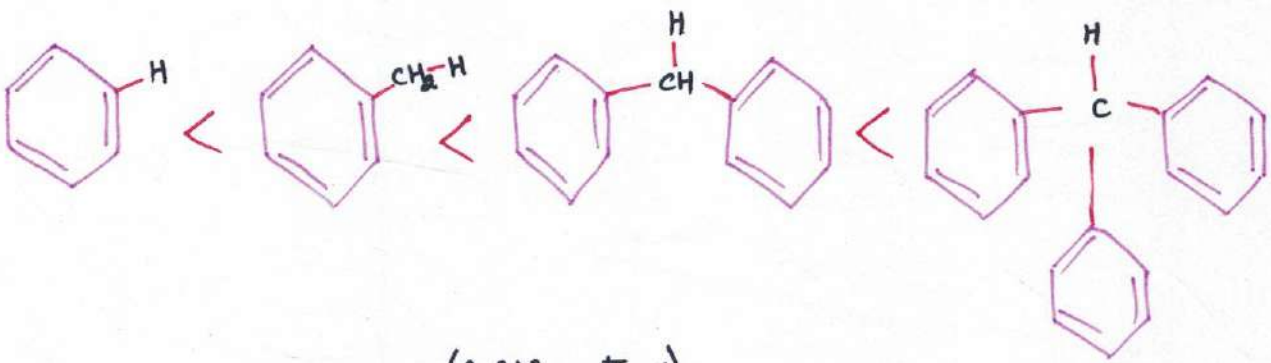
(III)



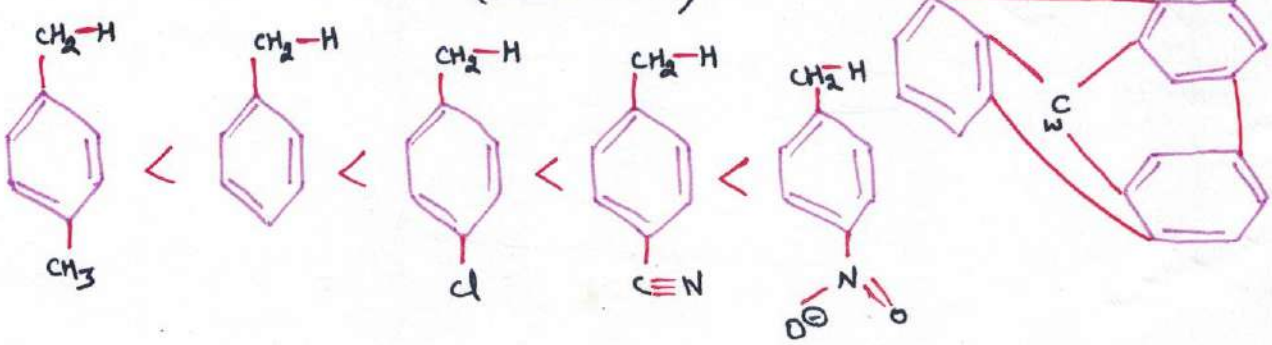
(IV)

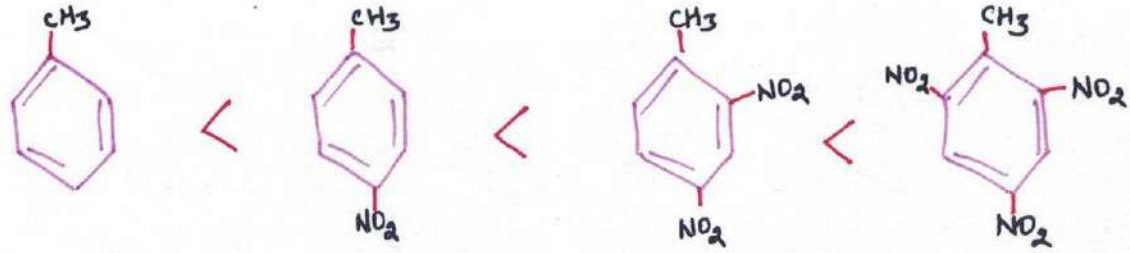
I > II > III > IV (acidic)

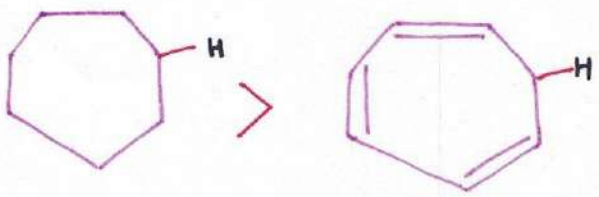




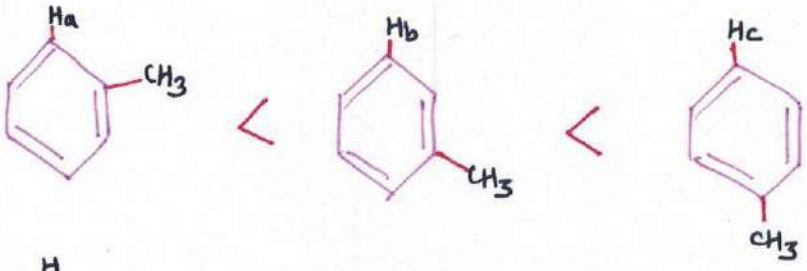
(Acidic natural)

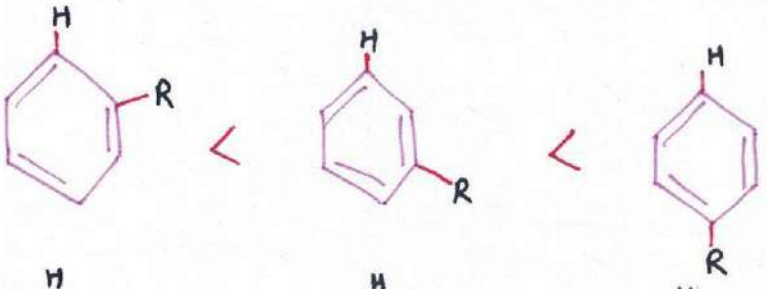


- 

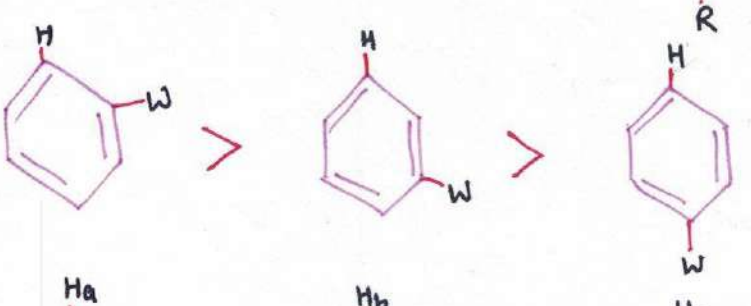
- 

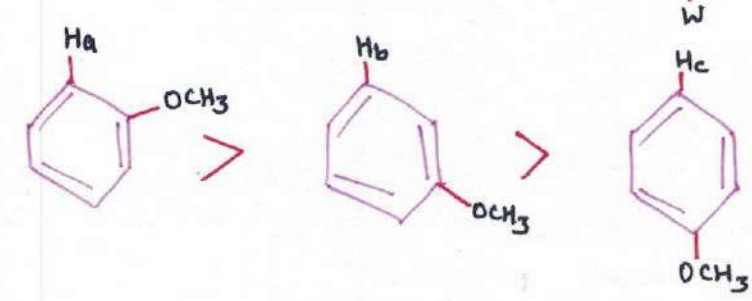
I^st is non-cyclic
II^nd is AA

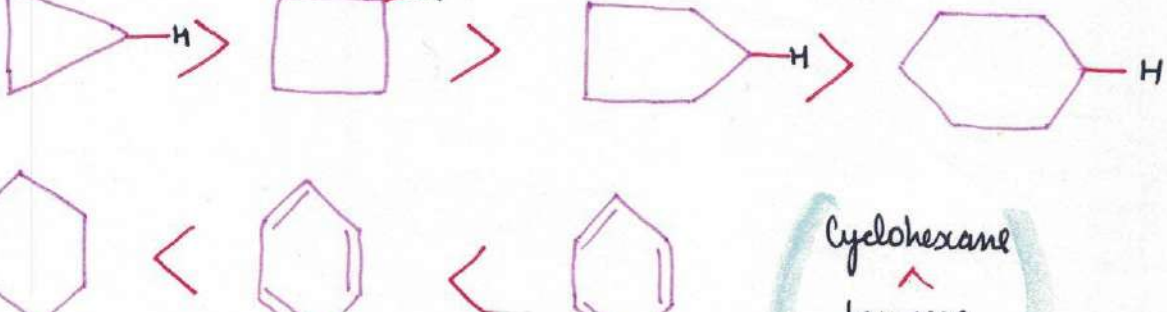
- 

- 

R is releasing group

- 

- 

- 

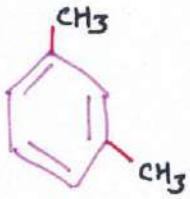
-

Cyclohexane
^
benzene
^
Toluene

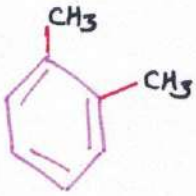
D

I

II (+I, +M)



III



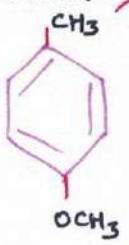
IV

I > III > II > IV

toluene > M-xylene > p-xylene > O-xylene

D

I



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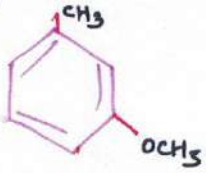

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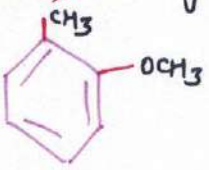
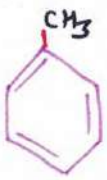


IV

III > I > II > IV

D



I

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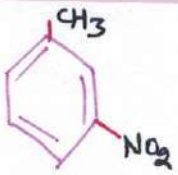

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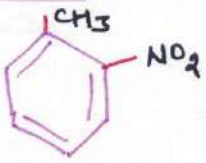
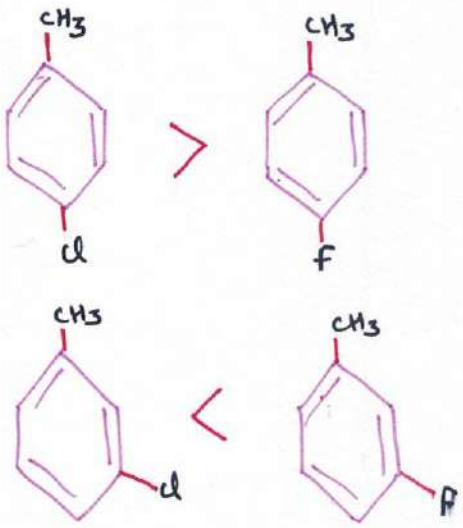
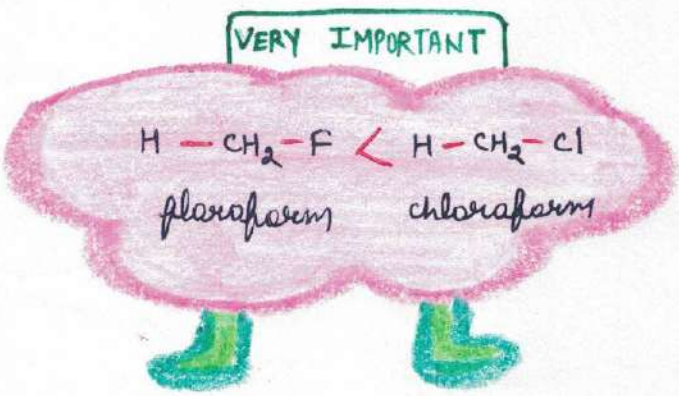


IV

IV > II > III > I

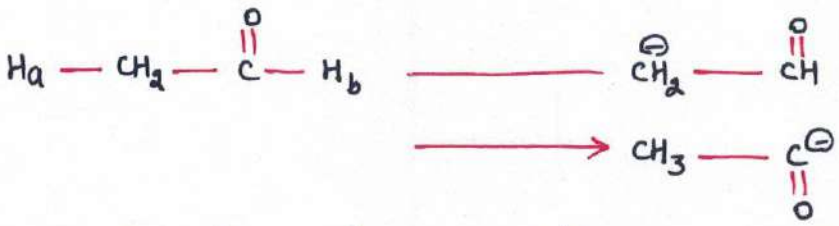




$CH_2F_2 < CH_2Cl_2$

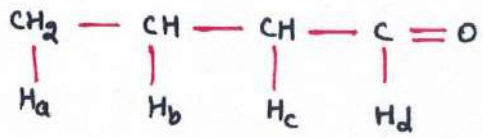
$CHF_3 < CHCl_3$

$CH_2^{\ominus} - Cl$ (-I/-M)

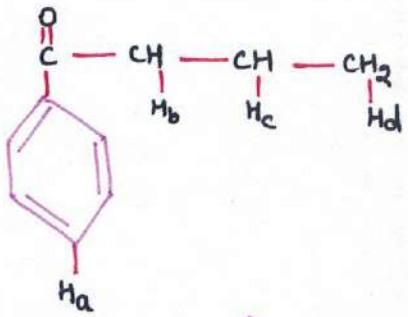


α- hydrogen is more acidic than aldehyde hydrogen.

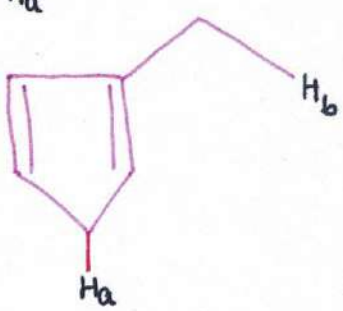
$C-H_a > C-H_b$

(1) 

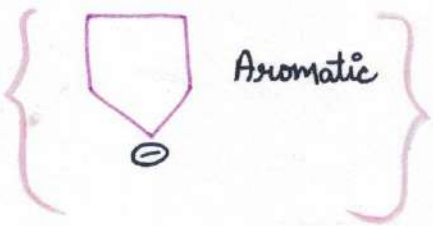
$C-H_c > C-H_d > C-H_a > C-H_b$

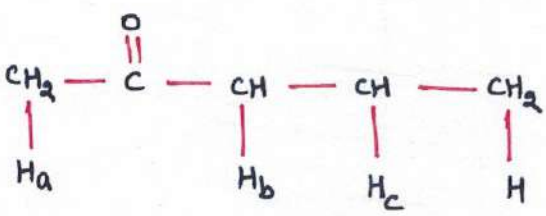
(2) 

$C-H_b > C-H_a > C-H_d > C-H_c$

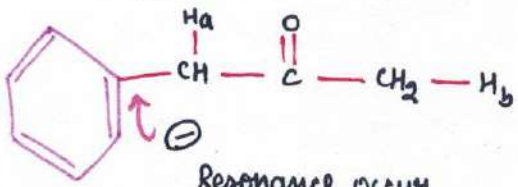
(3) 

$H_a > H_b$



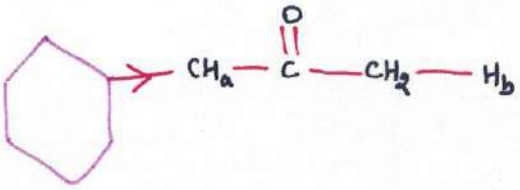
(4) 

$C-H_a > C-H_b$

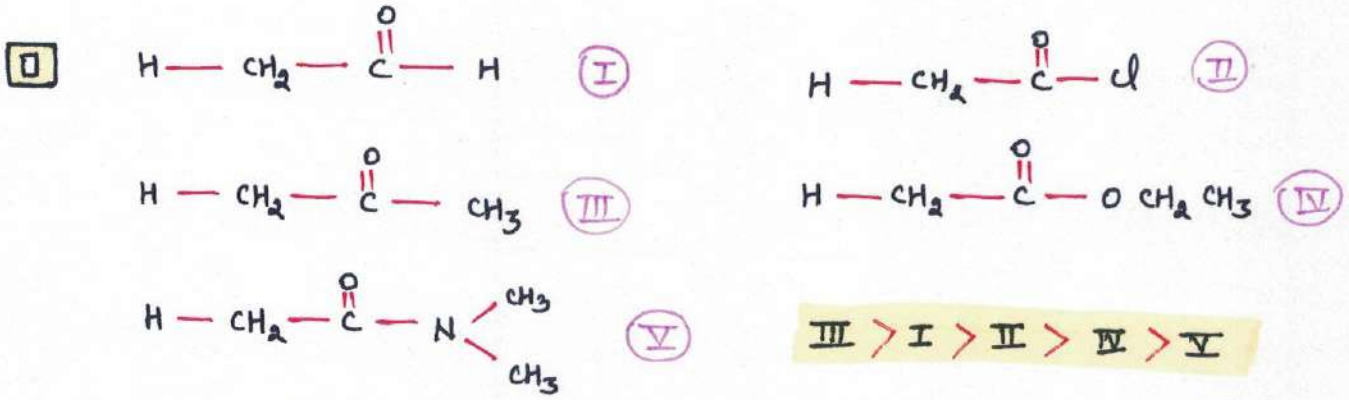
(5) 

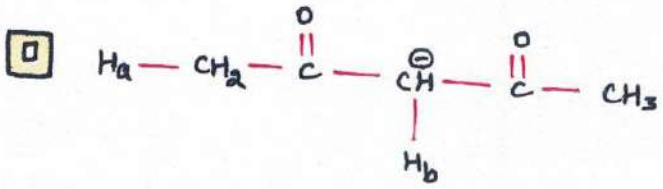
Resonance occur

$C-H_a > C-H_b$

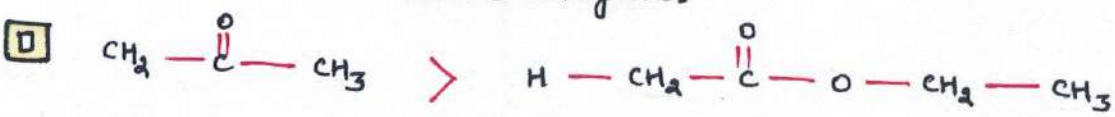
(6) 

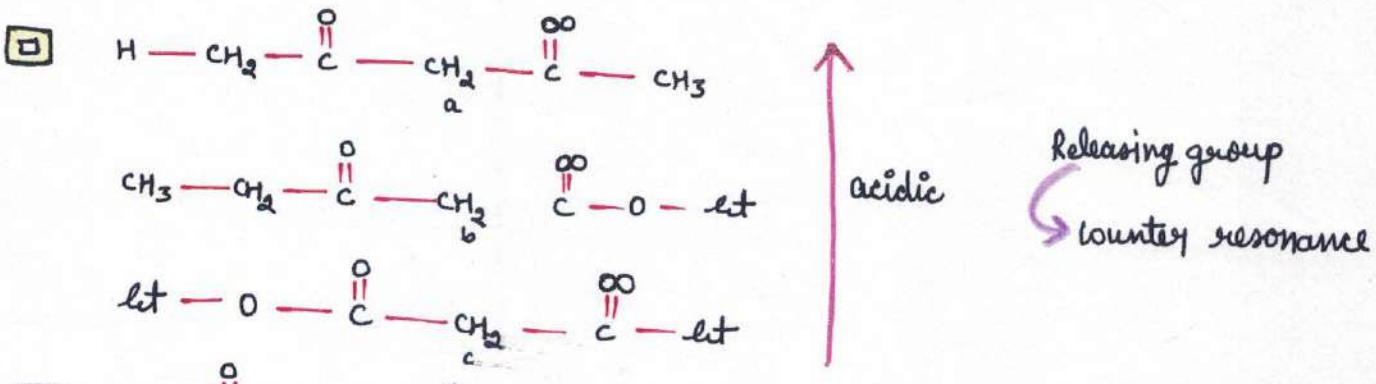
$C-H_b > C-H_a$

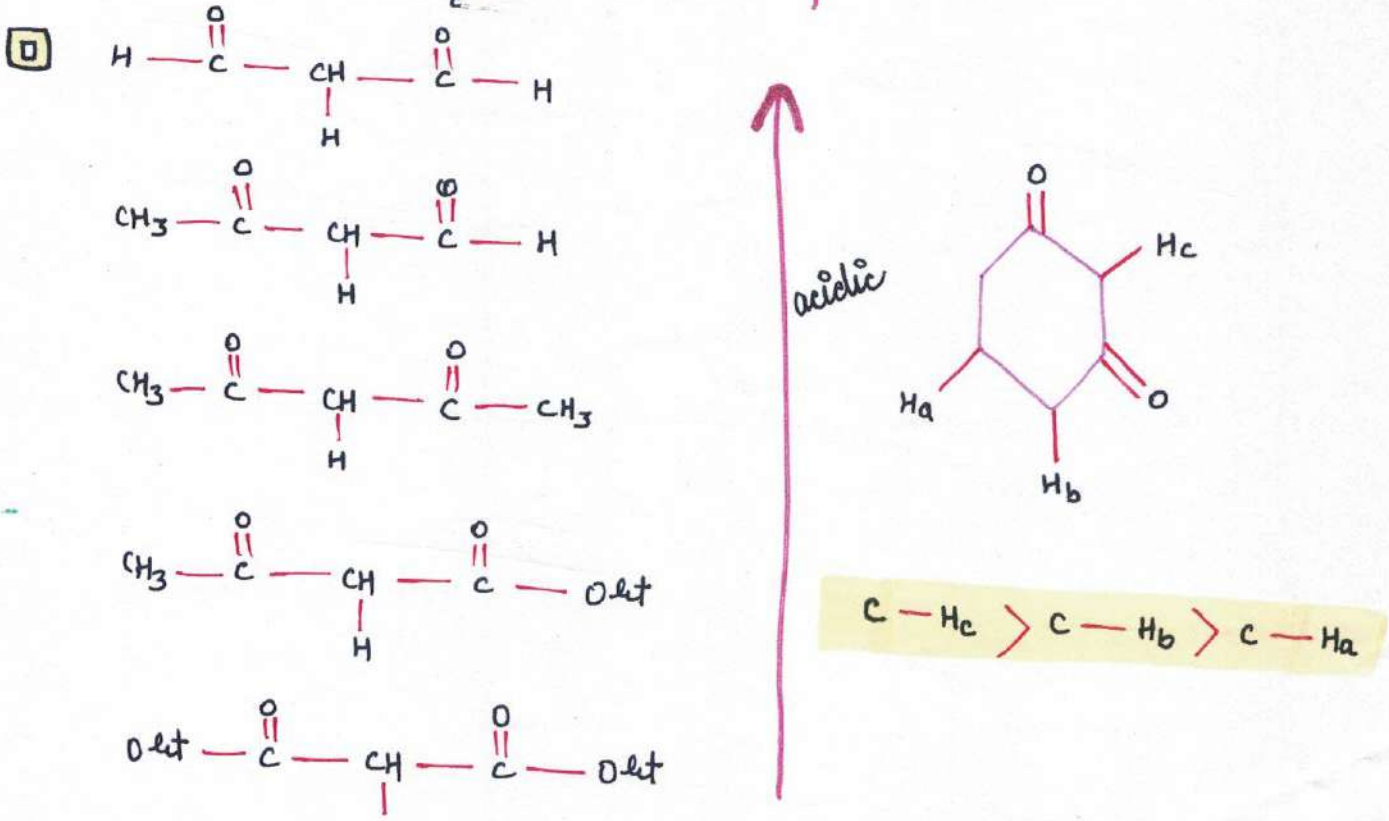


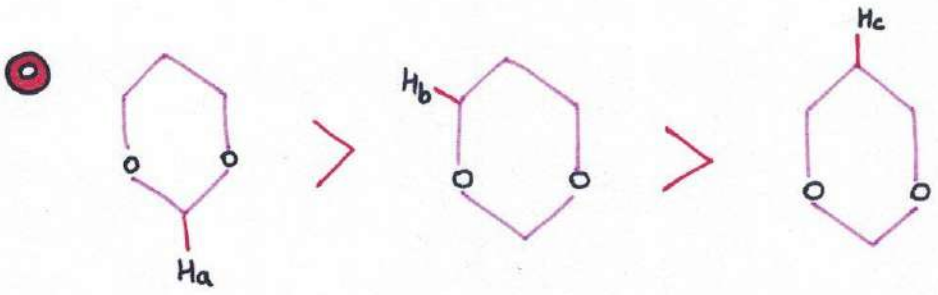


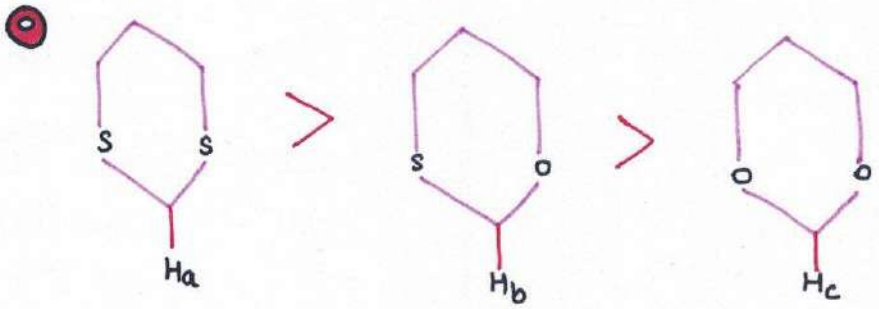
Reactive Methylenes











- $CHCl_3 < CH(CN)_3 < CH(NO_2)_3$
- $CH_3-NO_2 < CH_2(NO_2)_2 < CH(NO_2)_3$
- $H-O-H \longrightarrow OH^{\ominus} + H^{\oplus}$

  $R-O-H \longrightarrow R-O^{\ominus} + H$ (+I)

  $R-OH < H_2O$ (acidic)

$CH_3-OH > CH_3-CH_2-OH > CH_3-CH(CH_3)-OH > CH_3-C(CH_3)_2-OH$

(acidic nature)

MeOH > 1° alcohol > 2° > 3° (stability)

$CH_3-O^{\ominus} < CH_3-CH_2-O^{\ominus} < CH_3-CH(CH_3)-O^{\ominus} < CH_3-C(CH_3)_2-O^{\ominus}$

(Basic nature)

$CH_3-CH_2-OH + NaOH \not\longrightarrow CH_3-CH_2-O^{\ominus}Na^{\oplus} + H_2O$

This reaction does not occur

$OH^{\ominus}$ weak base stable

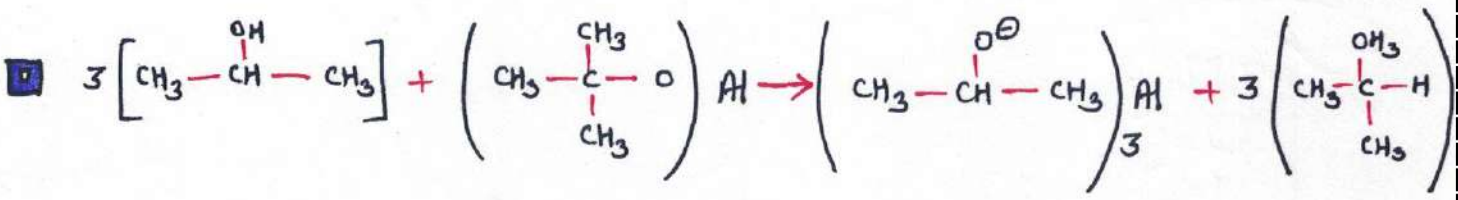
$CH_3-CH_2-O^{\ominus}$ strong base unstable

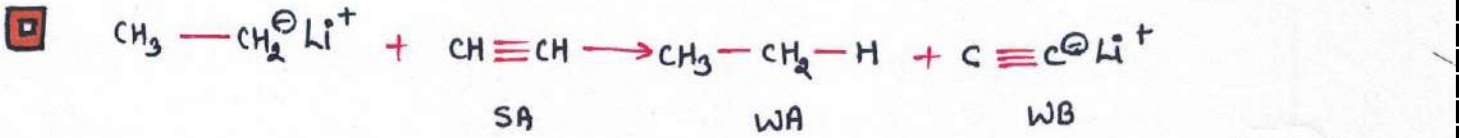
$CH_3-CH_2-OH + NaOH \longleftarrow CH_3-CH_2-O^{\ominus}Na^{\oplus} + H_2O$

$X + NaOH \longrightarrow W.B. + W.A \quad H_2O$

SA SB

Any compound X will react with NaOH which is more acidic than NaOH.

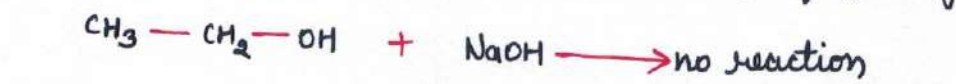


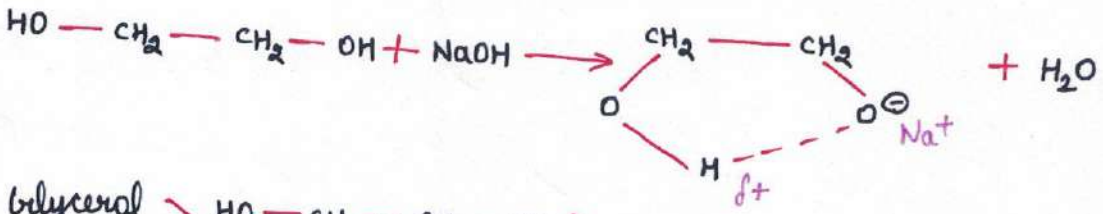


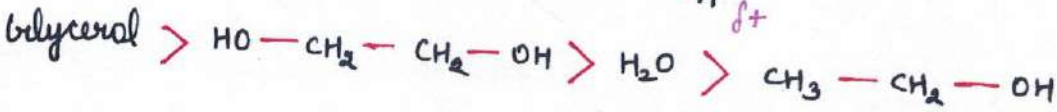
SA WA WB

$CH_3-CH_2^{\ominus} > CH\equiv C^{\ominus}$ (basic)

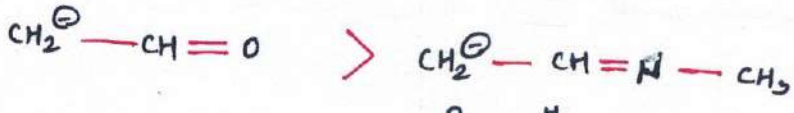
Alcohols do not react with NaOH but polyhydroxy alcohols can.







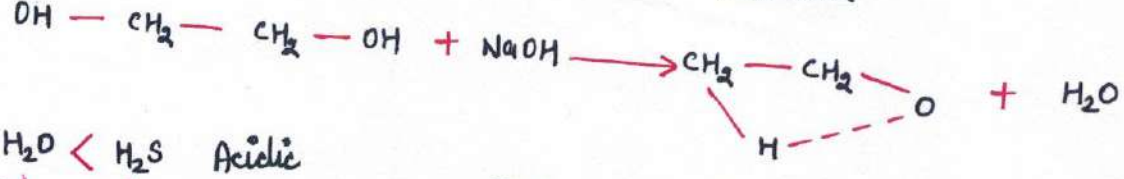
Polyhydric alcohols are more acidic than H_2O Hydrogen bonding stabilises them.

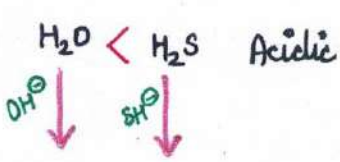


$H_a < H_b$ (acidic)

With NaOH, a stronger acid than H_2O will react.

unstable





$S^{\ominus}$ is more stable
$S^{\ominus}$ is bigger

$OH^{\ominus} < SH^{\ominus}$ acidic

$NaOH > NaSH$ (basic)

$S^{\ominus} > O^{\ominus}$ (stable)

$CH_3-CH_2-OH < H_2O < CH_3-CH_2-SH$

Alcohols are weaker acid than H_2O but thioalcohols are stronger acid than H_2O.

$CH_3-CH_2-OH + NaOH \longrightarrow$ no reaction because $CH_3-CH_2-O^{\ominus}Na^{\oplus}$ unstable

$CH_3-CH_2-SH + NaOH \longrightarrow CH_3 \; CH_2 \; S^{\ominus} \; Na^{\oplus} \quad H_2O$ (stable)

$CH\equiv CH + NaOH \not\longrightarrow CH\equiv C^{\ominus} Na^{\oplus} + H_2O$

$O^{\ominus} > C^{\ominus}$

- Stable • unstable
- Weak base • Strong base

Weak base will not give strong base, Reaction will not occur. But reverse reaction occur.

$H_2O > CH\equiv CH > CH_2=CH_2 > CH_3-CH_2^{\ominus}$ (acidic H)

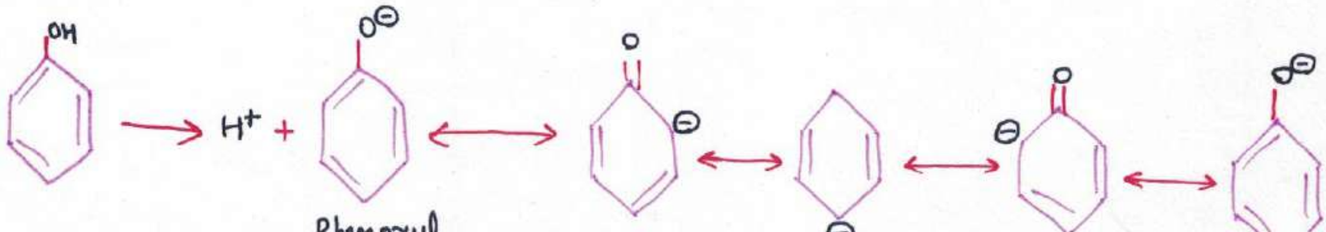
$CH\equiv CH + Na^{\oplus}O^{\ominus}CH_2-CH_3 \not\longrightarrow CH\equiv C^{\ominus} Na^{\oplus} + CH_3-CH_2-OH$

Que. which of these compounds react with NaOH?

(a) $CH\equiv CH$ (b) CH_3-CH_2-OH (c) CH_3-CH_2-SH

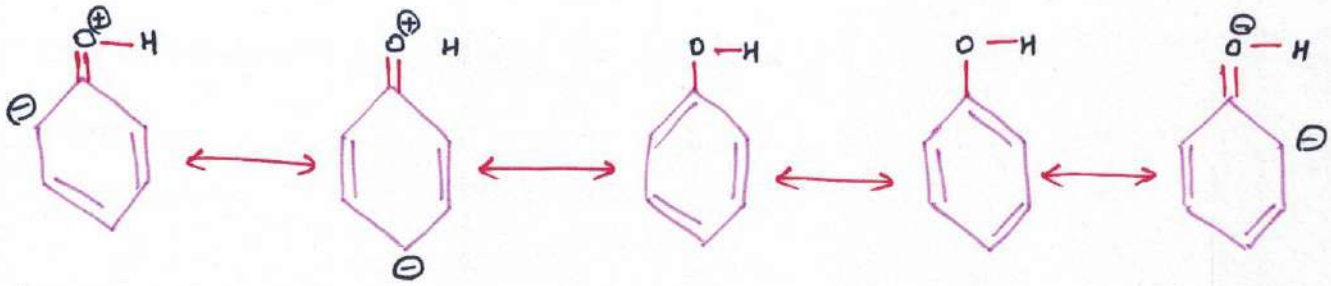
(d) $HO-CH_2-CH_2-OH$ (e) $HO-CH-CH-CH_2-OH$ (with OH on the third carbon)

Ans. c, d, e because they all are more acidic than H_2O. so, can react with NaOH.



Phenoxyl

(acidic) PhOH > H_2O [because $O^{\ominus} > OH^{\ominus}$] stable



whose conj base is more stabilised than acid will give H^+

- Phenol is an acid.

Phenoxyl ion is more stable than phenoxide ion.

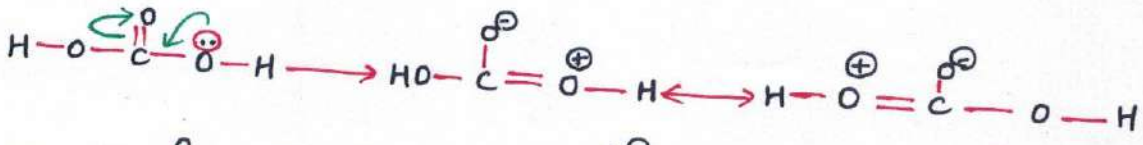
Phenoxyl → no charge separation, more stable conj base of phenol.

Phenol < Phenoxyl (stable)

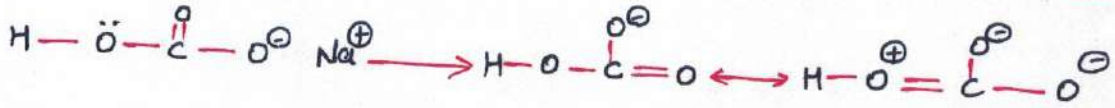
Hence, phenol is an acid.

Phenoxyl has 5 resonance structure.

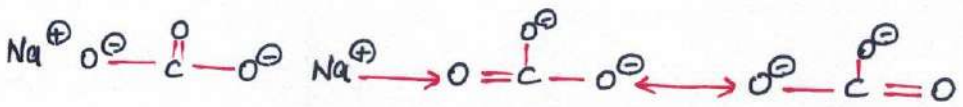
H_2CO_3



$NaHCO_3$



Na_2CO_3



In ionic compounds, there is no charge separation when in resonance while in covalent compounds charge separation occurs.

covalent < ionic (stability)

PhOH (Phenol) is more acidic than water, it will react with NaOH.

Electronegativity :- $C_{sp} > N > C_{sp^2} > C_{sp^3}$

∵ Csp is more EN than nitrogen

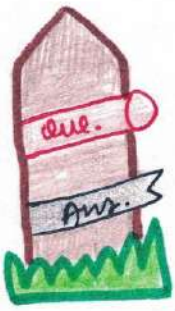
$CH \equiv CH$ (strong acid) $\longrightarrow NH_3$ (weak acid)

$CH_2 = CH_2 + NaNH_2 \longrightarrow$ no reaction

$N > C_{sp^2}$ (stable)

$PhOH > H_2O > EtOH > CH \equiv CH > NH_3 > CH_2 > CH_3 - CH$

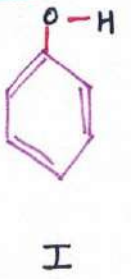
$CH \equiv CH$ will react with $NaNH_2$; CH_2 and $CH_3 - CH$ will not react



in O_2 (x) which will react with $NaNH_2$?

All

(a)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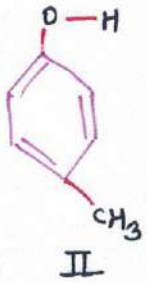
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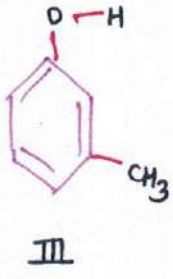
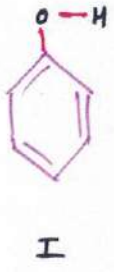
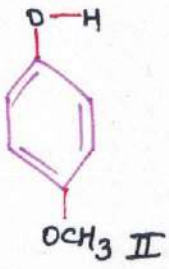

III

I > III > II


I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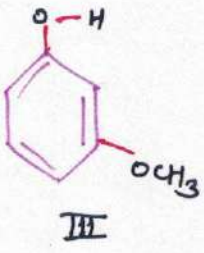
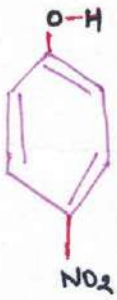

III

III > I > II

(b)


I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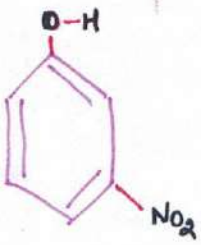
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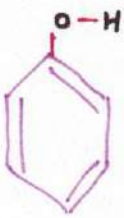
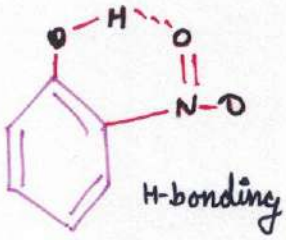
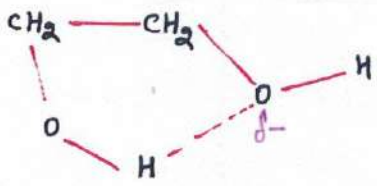
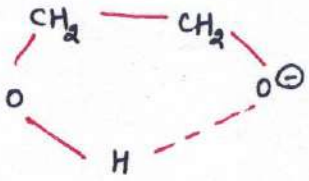
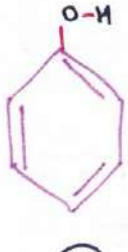

IV

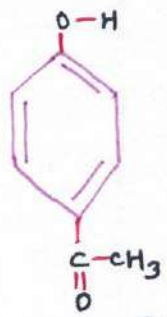


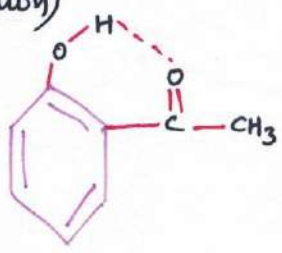
II > IV > III > I


Weak H-bonding
(before dissociation)

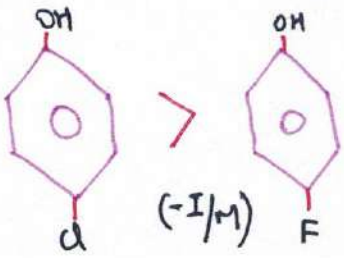

strong H-bonding
after dissociation

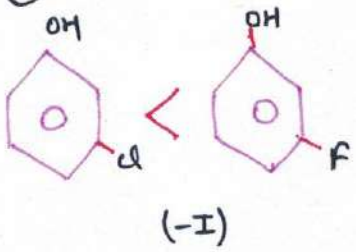

③


①

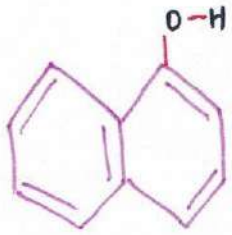

②

Acidic native

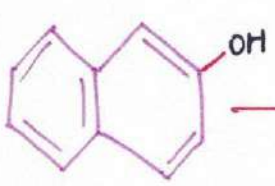




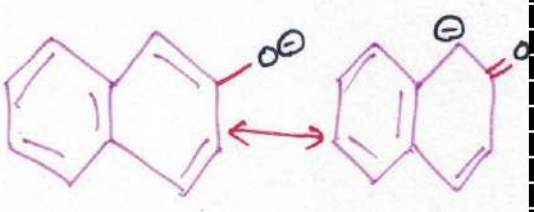
$CHCl_3 > CHF_3$

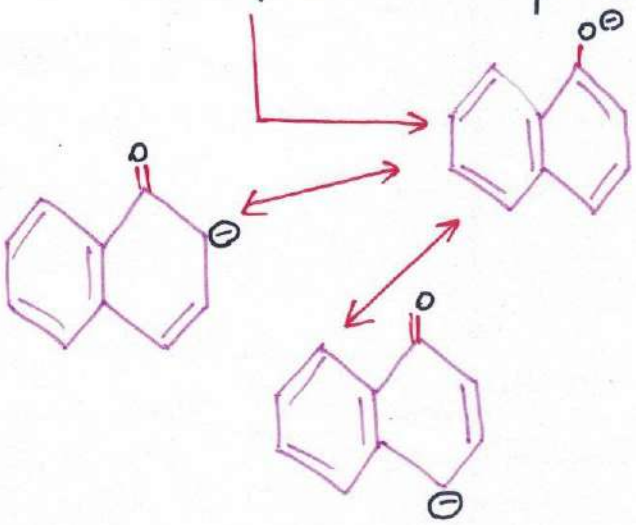


α - Napthol



β - Napthal

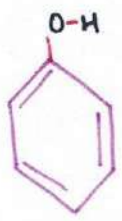


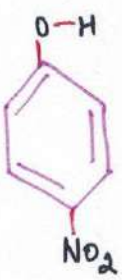


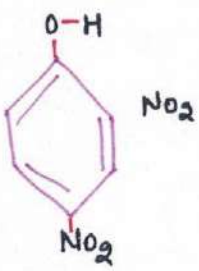
α - Napthol is stronger acid than β - Napthol. [α has 3 R.S, β has 2 R.S (without disturbing benzene ring)]

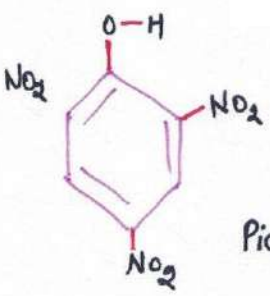
2,4,6 - tri nitro phenol is known as picric acid

[Picric acid is an acid without any carboxylic group.]



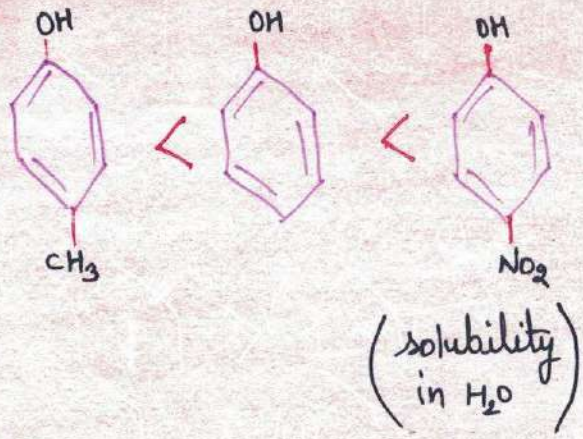




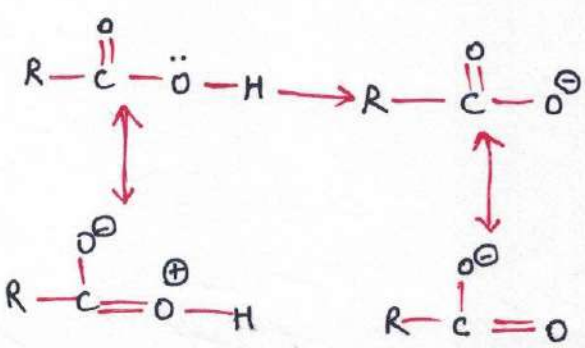


Picric acid

STRONG ACID → more it will dissociate more it will break into ions, more ionic, more soluble strong acid has more solubility in H_2O.



(solubility in H_2O)



Carboxylic acid is an acid because conjugate base is more stabilised than acid (due to no charge separation)

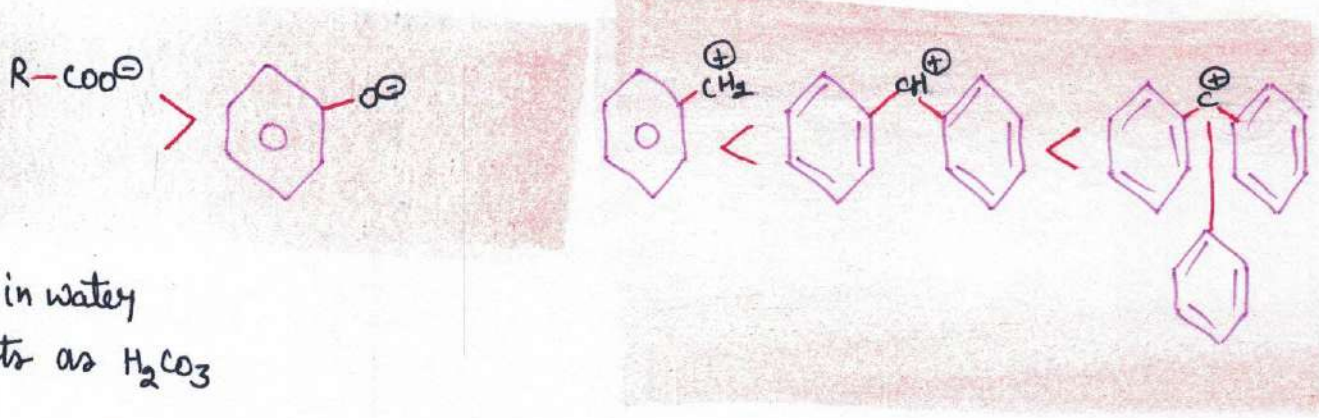
In a carboxylic acid, both C-O bonds are not equal but in a carboxylate both C-O bonds are equal.

Case I in carboxylic acid, carboxylate has only 2 resonating structure but both contribute equally.

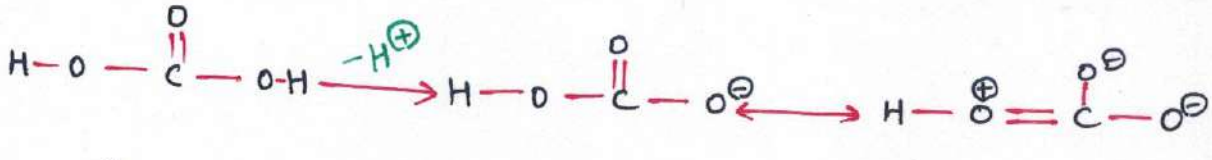
Case II in phenal, phenoxyl has 5 resonating structure but all is not contribute equally.

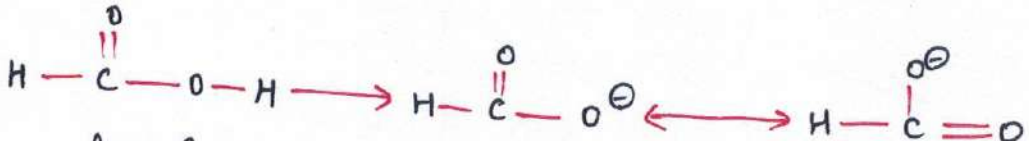
So carboxylic acid > phenol (acidic)

$RCOOH > PhOH$



CO_2 in water exists as H_2CO_3

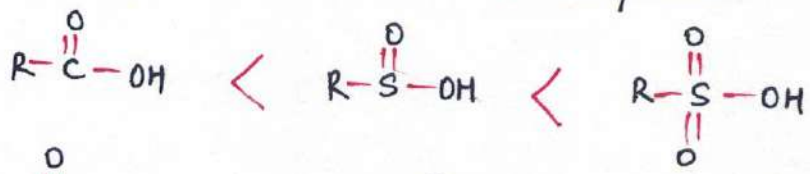




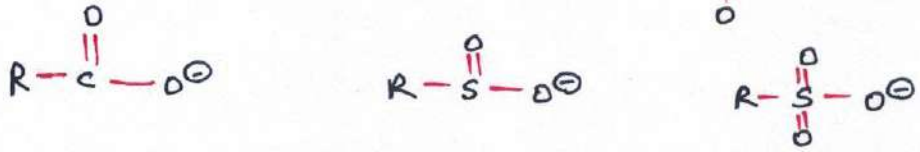
formic acid

$HCOOH > RCOOH > CO_2 > PhOH$

Carboxylic < sulphinic < sulphonic



[acidic nature]



$RSO_3H > RSO_2H > RCO_2H > CO_2 > PhOH > H_2O > ROH > CH \equiv CH$

(RCO_2H ← $NaHCO_3$; $PhOH$ ← $NaOH$; ROH ← $NaOEt$)

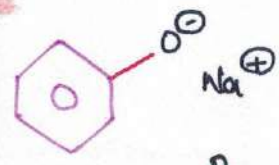
$CH_3-CH_3 < CH_2=CH_2 < NH_3$ (NH_3 → $NaNH_2$)

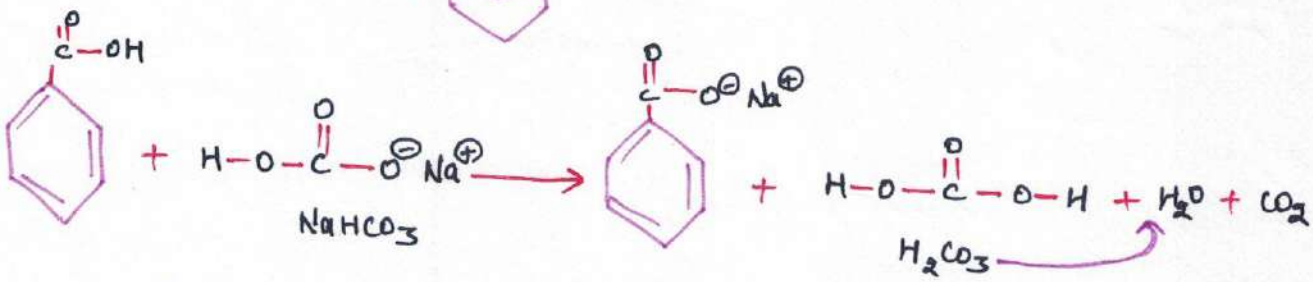
Arrange in basic nature :-

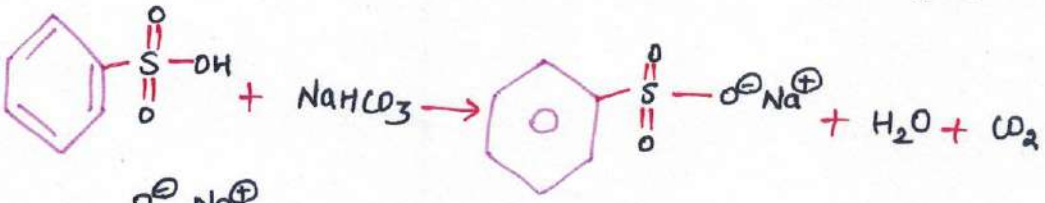
$CH_3-CH_2^{\ominus} > CH_2=CH^{\ominus} > NH_2^{\ominus} > CH \equiv C^{\ominus} > R-O^{\ominus} > OH^{\ominus}$

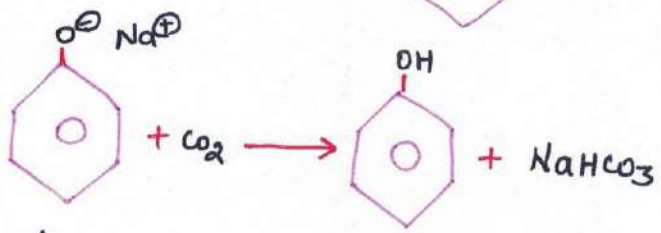
$RCOO^{\ominus} < HCO_3^{\ominus} < Ph-O^{\ominus}$

Arrange in basic nature :-

$CH_3COONa < NaHCO_3 <$ 





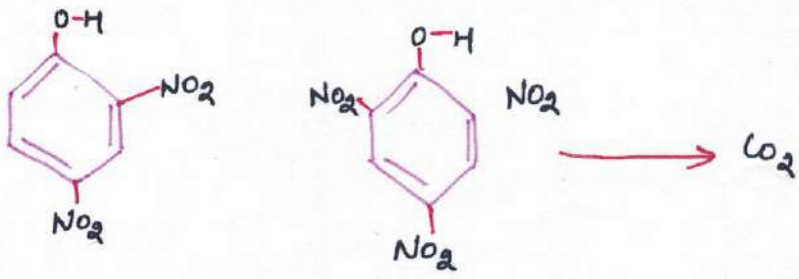


we can distinguish phenols and benzoic acid reaction $NaHCO_3$.

Phenols does not react with $NaHCO_3$.

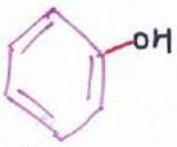
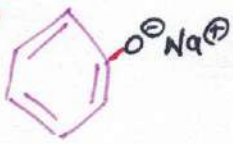
Benzoic acid gives CO_2 (effervescence) with $NaHCO_3$.

dinitro phenol and trinitro phenols react with $NaHCO_3$ and librate CO_2.



(Picric acid)

Ques. How many of the following react with

(i) $NaHCO_3$ (ii)  (iii)  (iv) $NaNH_2$

(v) $NaOH$

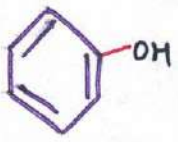
(a) $CH_3 \equiv CH$ (b) CH_3-CH_2-OH (c) CH_3-CH_2-C-H (d) $HO-CH_2-\overset{OH}{\underset{|}{CH}}-CH_2$

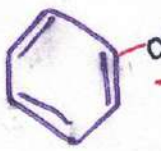
(e) $HO-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-OH$ (f) CH_3-COOH (g) CO_2

(h) CH_3-SO_2H (i) CH_3-SO_3H

Anr.

(i) $NaHCO_3$ → (f), (h), (i)

(ii)  → (f), (g), (h), (i) [-δ-h > -OH poly]

(iii)  → (f), (g), (h), (i), (c), (d), (e)

$NaNH_2$ → All except (a), (b)

$NaOH$ → All except (a), (b)

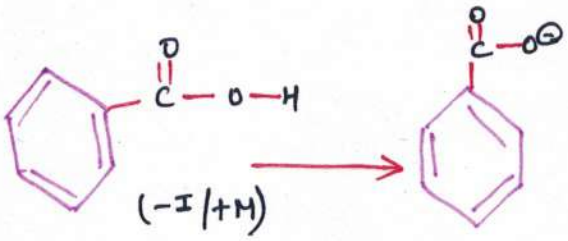
$H-\overset{O}{\overset{||}{C}}-O-H \rightleftharpoons H-\overset{O}{\overset{||}{C}}-O^{\ominus} + H^{\oplus}$ $\quad \alpha = 17 \times 10^{-5}$

$b > a$

$CH_3-\overset{O}{\overset{||}{C}}-O-H \longrightarrow CH_3-\overset{O}{\overset{||}{C}}-O^{\ominus} + H^{\oplus}$ $\quad \alpha = 1.7 \times 10^{-5}$

$R \rightarrow \overset{O}{\overset{||}{C}}-O-H$ weaker acid

$\omega \rightarrow \overset{O}{\overset{||}{C}}-O-H$ stronger acid

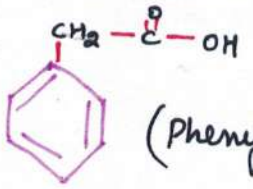


$\alpha = 6.5 \times 10^{-5}$

(+M decreases acidic nature)

- $HCOOH > Ph-COOH > CH_3COOH$

formic acid benzoic acid acetic acid.

- CH_3-CHO (acetic acid) $<$  (Phenyl acetic acid)

(only -I)

- $F-CH_2-CHO > Cl-CH_2-CHO > Br-CH_2-CHO$

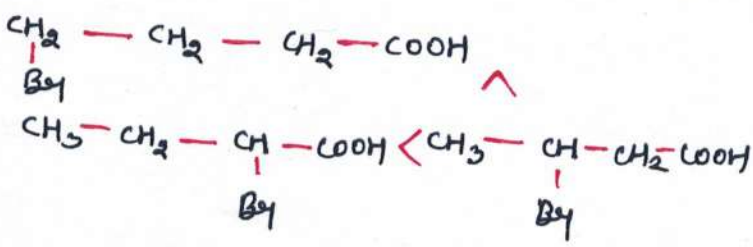
$CH_3-CHO < I-CH_2-CHO$

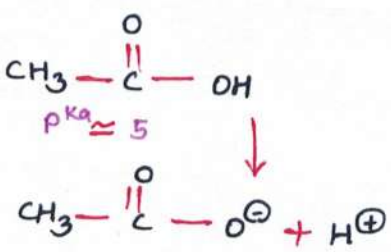
- $CCl_3-COOH > CHCl_2-COOH > CH_2Cl-COOH > CH_3-COOH$

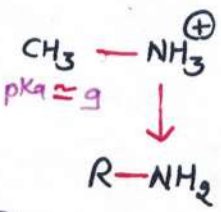
- $NO_2-CH_2-COOH > NC-CH_2-COOH > Cl-CH_2-COOH >$

CH_3-COOH

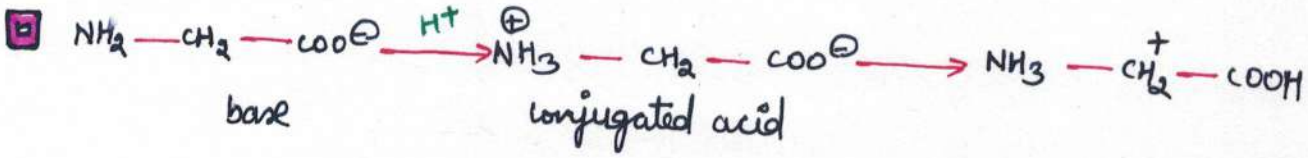
- $CH_3-COOH > CH_3-CH_2-COOH > CH_3-CH(CH_3)-COOH > CH_3-C(CH_3)_2-COOH$

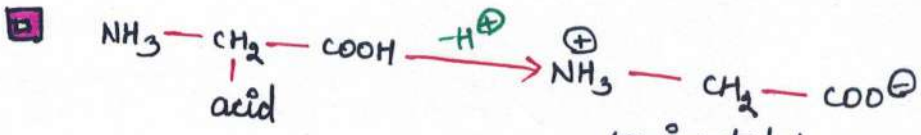
- $CH_3-CH_2-CH_2-COOH <$ 

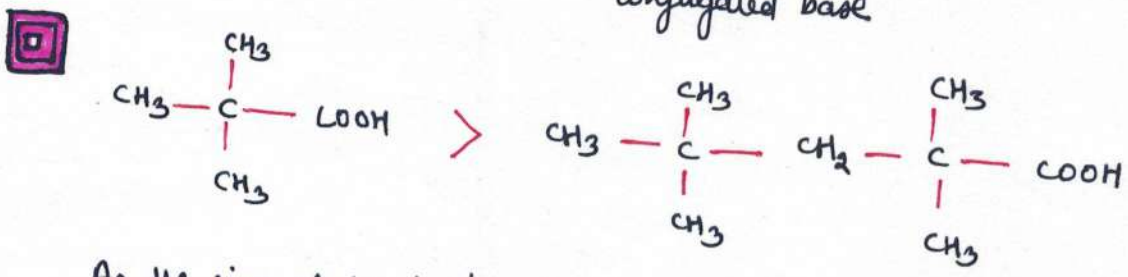




$CH_3COO^- < R-NH_2$ (basic natural)

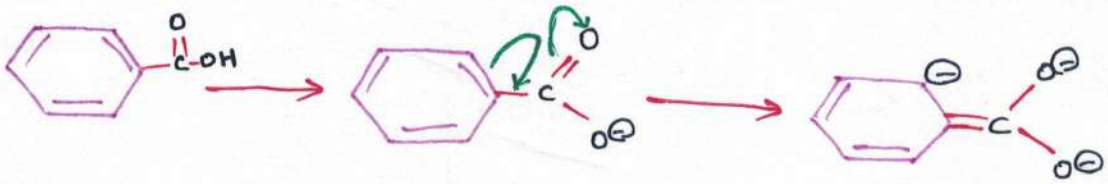




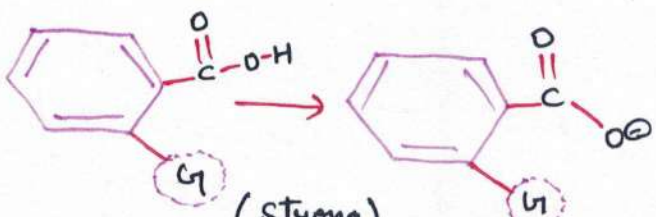


As the size of the hydrophobic group increases acidic nature decreases due to the lack of hydration

ORTHO EFFECT



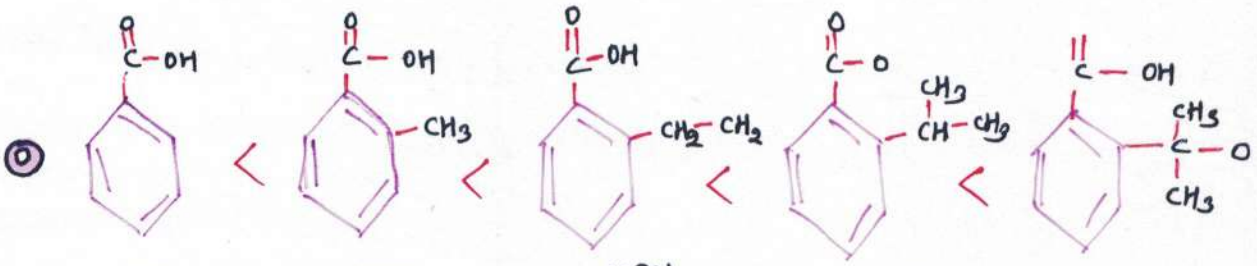
Benzoate
(strong Base)

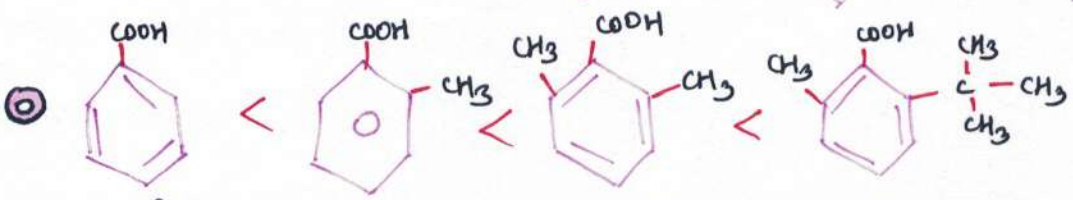


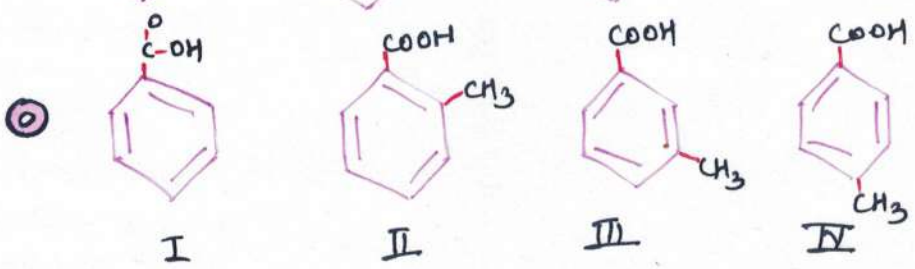
REMEMBER

ortho - substituted benzoic acids are always more acidic than benzoic acid. Always !

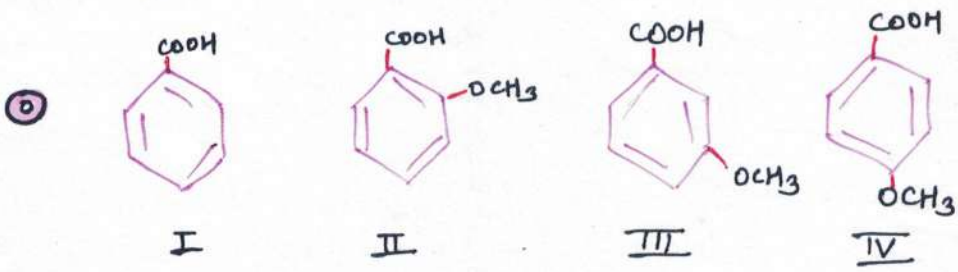
irrespective of the +I or -I, +M or -M effect of the group attached.







II > I > III > IV



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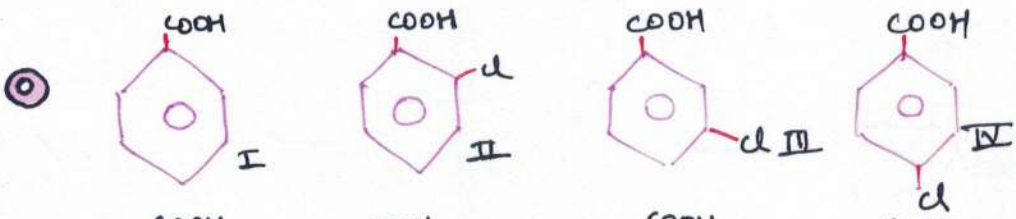
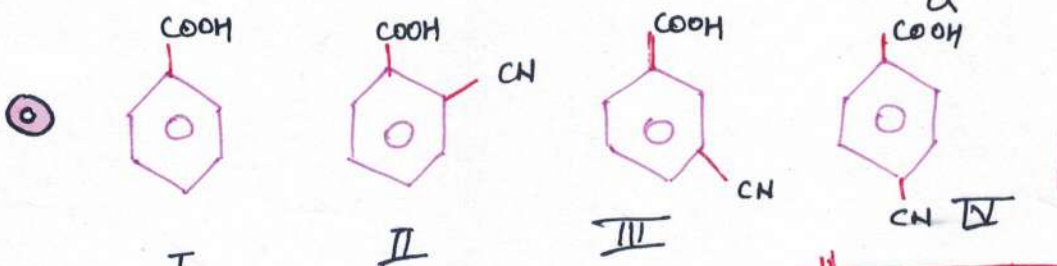
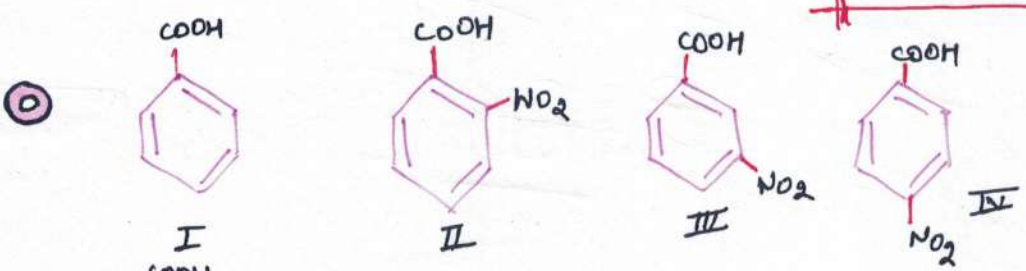


II > III > IV > I

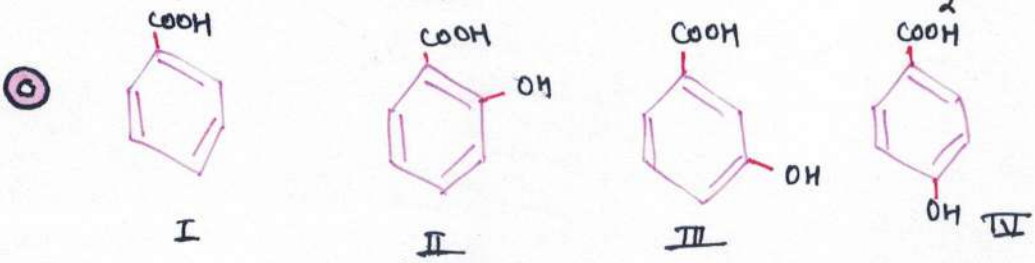


II > IV > III > I

Acidic Nature

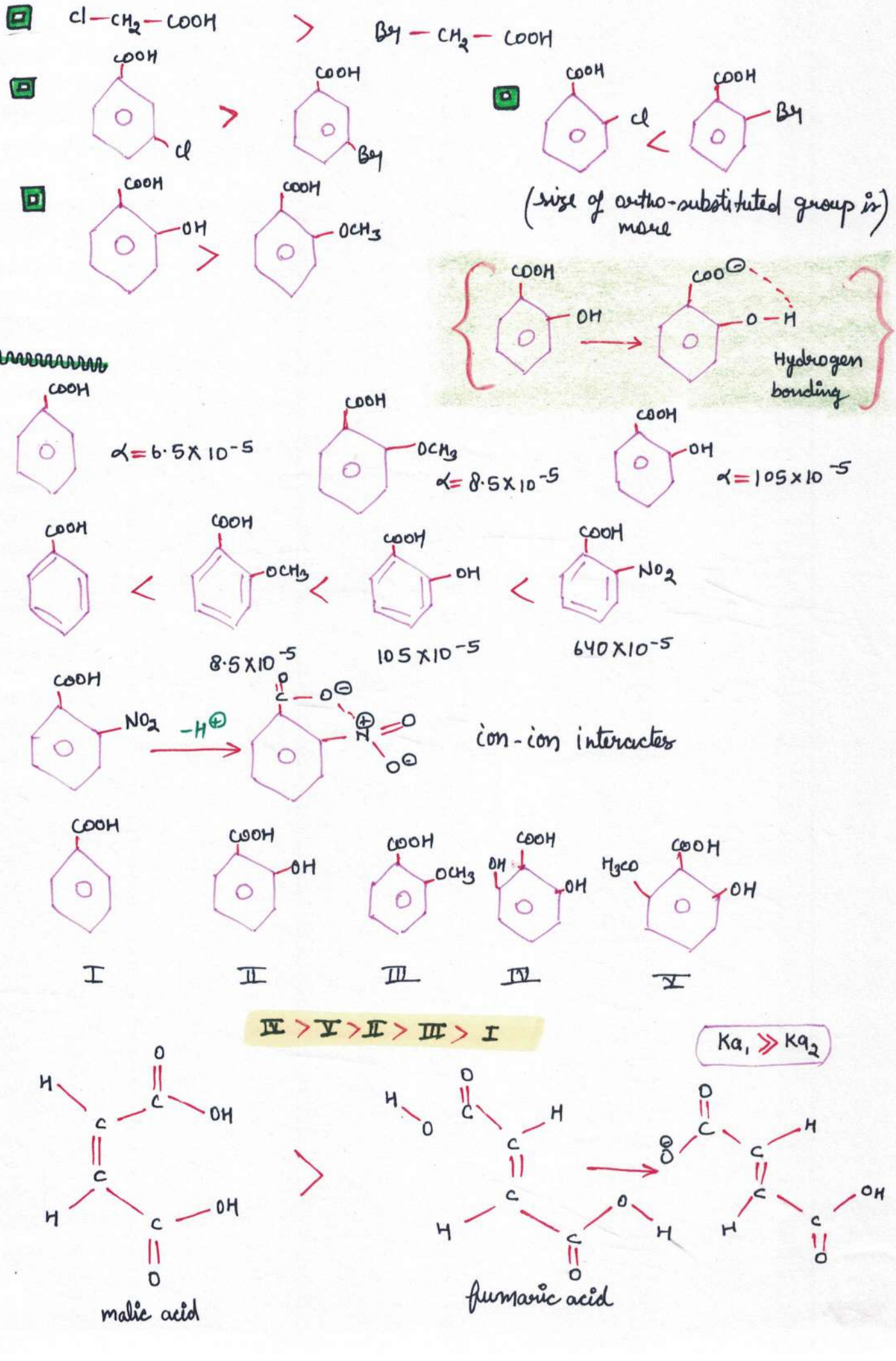


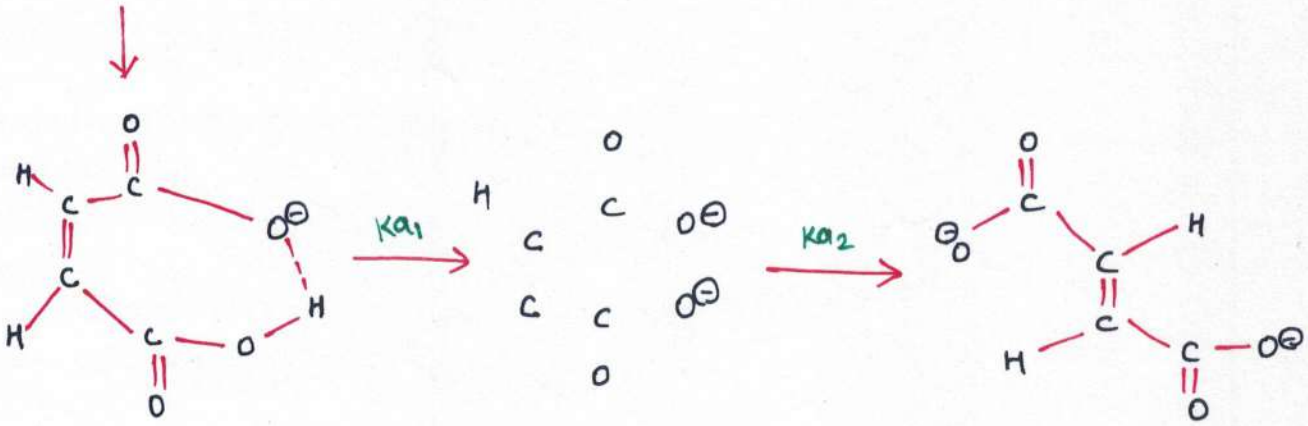
II > IV > III > I



Here -H- bonding in the ans:

II > III > I > IV



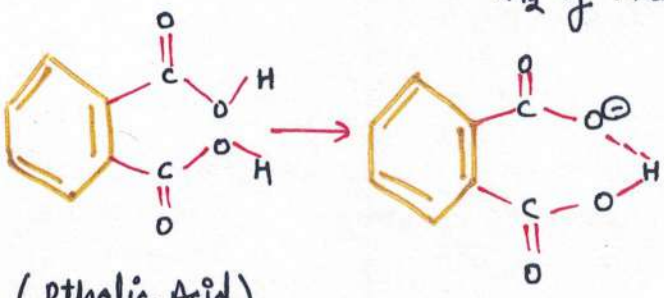


(Hydrogen bonding)

Ka_1 of malic > Ka_1 of fumaric

Ka_2 of malic < Ka_2 of fumaric

1.



Acidic nature depends on Ka_1

(Pthalic Acid)

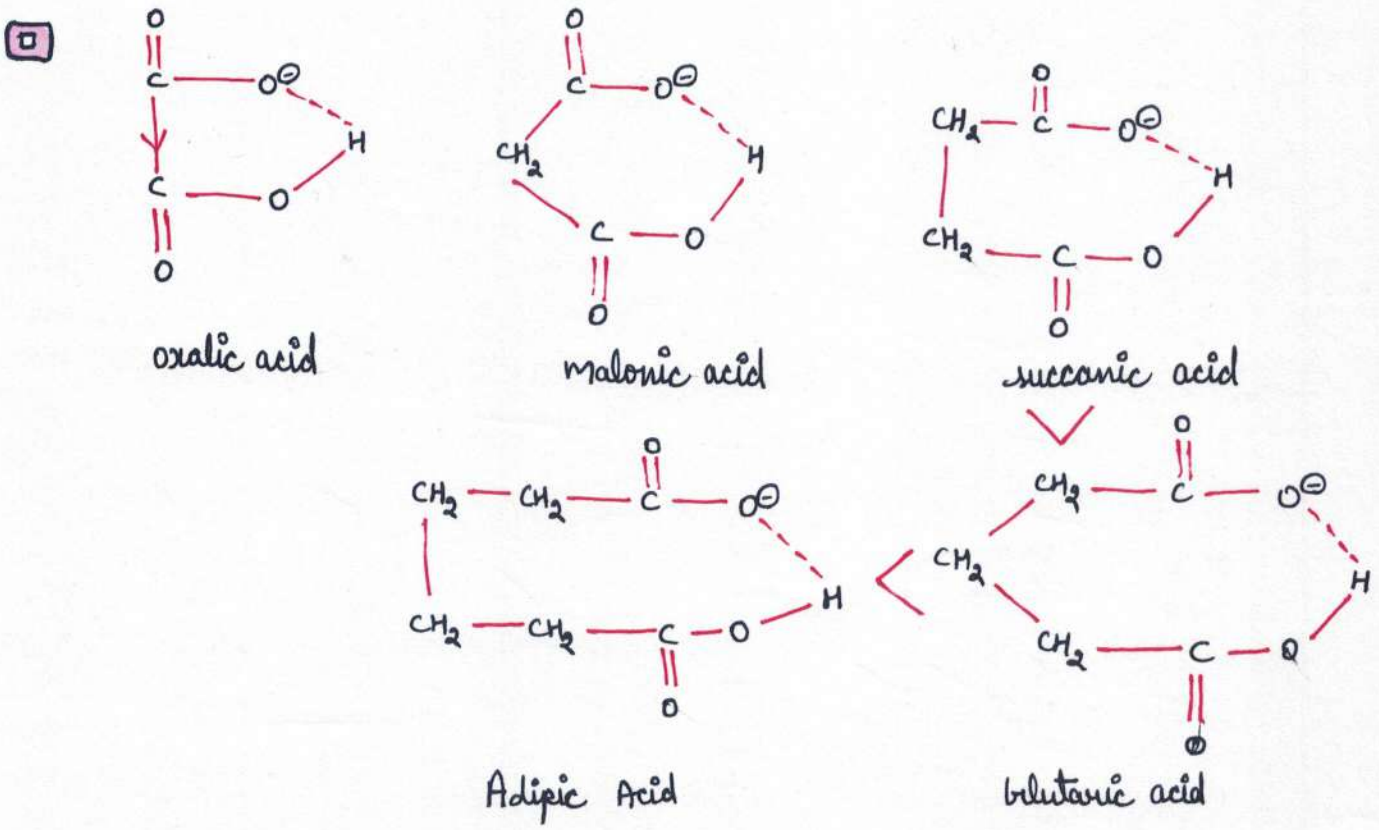
2.

[Iso-pthalic acid]

$Ka_1 1 > Ka_1 2$

$Ka_2 1 < Ka_2 2$

If acid is dicarboxy acid, then Ka_1 of first acid is more than second.



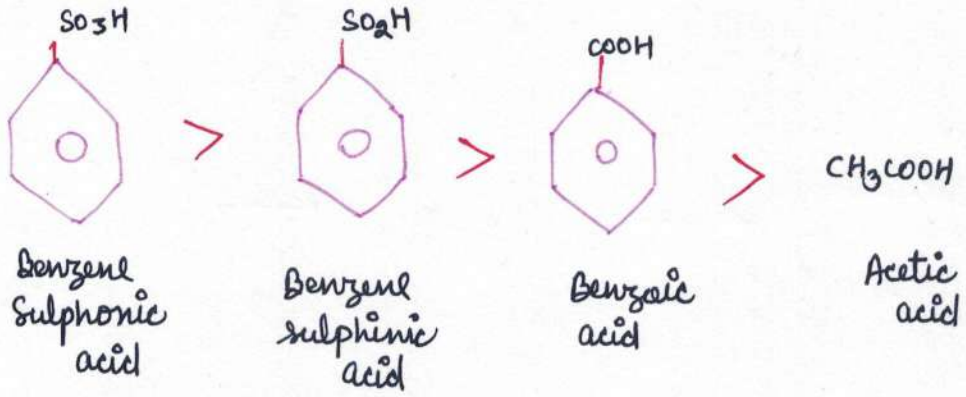
oxalic acid

malonic acid

succonic acid

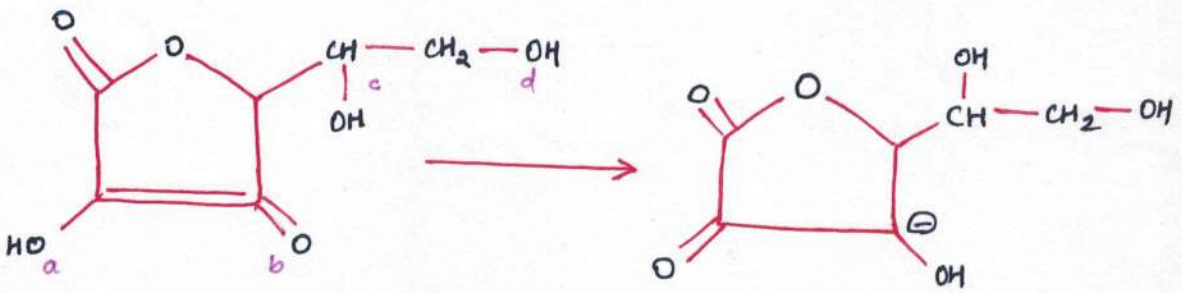
Adipic Acid

glutaric acid

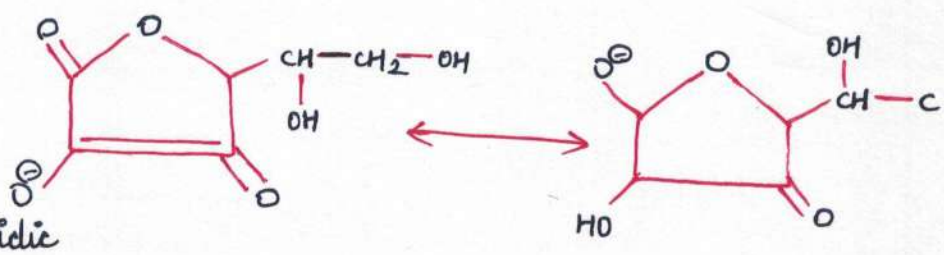


Benzene Sulphonic acid > Benzene sulphinic acid > Benzoic acid > Acetic acid

IMPORTANT

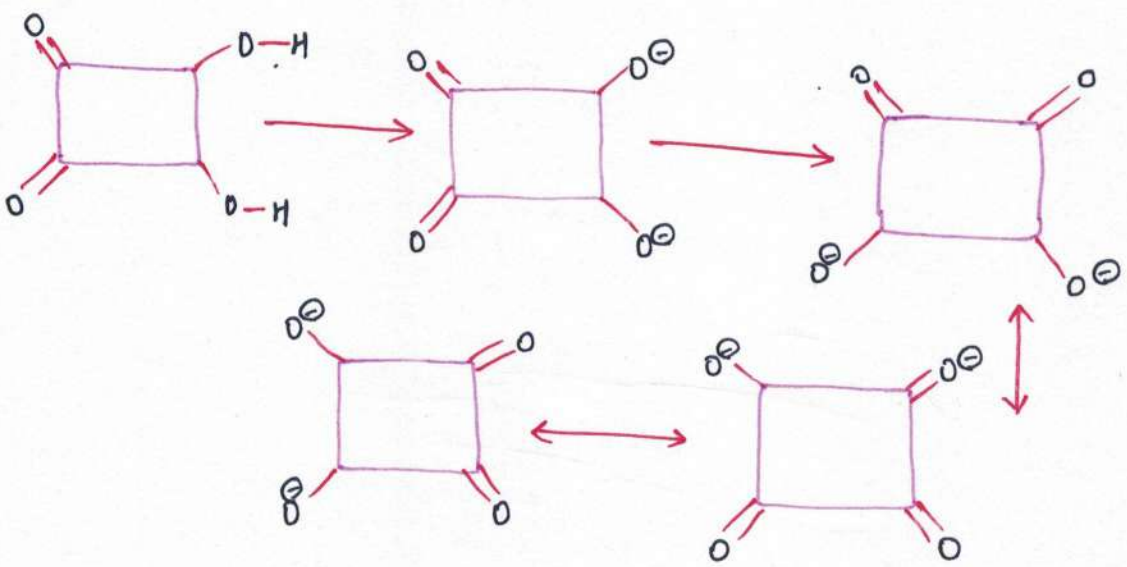


Ascorbic Acid (Vitamin c)

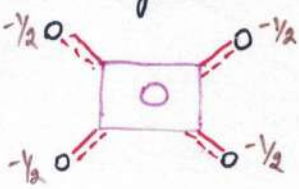


b is most acidic

b > a > c > d



Squaric acid dianion has all the c-c bond length and c-o bond length equal. All are equivalent resonating structure.



> RCOOH

BASE

$B: + H^{\oplus} \rightleftharpoons BH^{\oplus}$

strong Base — stable → weak acid

in acids $HX \rightarrow H^+ + X^-$

acid — stable → weak base

$NH_3 \xrightarrow{H^{\oplus}} NH_4^{\oplus}$ strong base — stable (weak acid)

$H_2O \xrightarrow{H^{\oplus}} H_3O^{\oplus}$ weak base — unstable (strong acid)

Basic Nature

$NH_3 < CH_3-NH_2 < CH_3-\underset{CH_3}{NH} < CH_3-\underset{CH_3}{\overset{CH_3}{N}} \rightarrow CH_3-\overset{\oplus}{NH}(-CH_3)_2$ (stable weak base)

$NH_3 \rightarrow NH_4^+$

$CH_3-NH_2 \rightarrow CH_3-\overset{\oplus}{N}H_3$

$CH_3-\underset{CH_3}{NH} \rightarrow CH_3-\overset{\oplus}{N}H_2(CH_3)$

E.g.

$NH_3 < R-NH_2 < R_2NH < R_3N$

$H_2O \quad H_2S \quad H_2Se \quad H_2Te$

acidic nature →

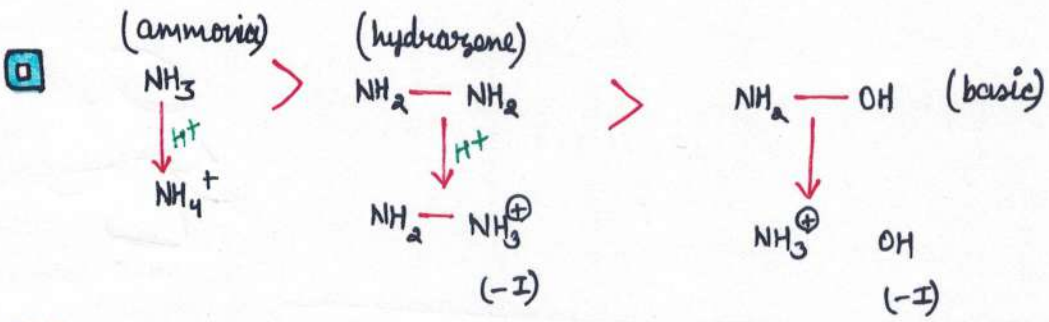
← basic nature

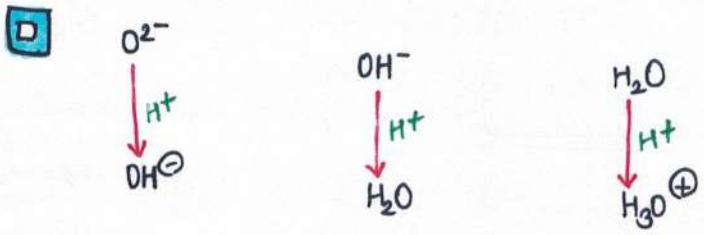
(H_2O strong base)

$NH_3 \quad PH_3 \quad AsH_3 \quad SbH_3$

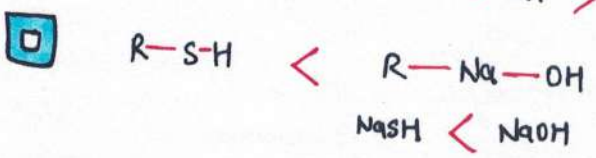
acidic →

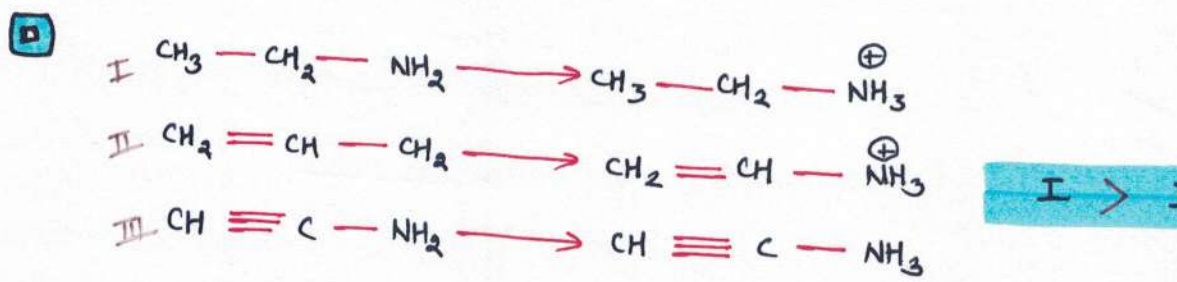
← basic



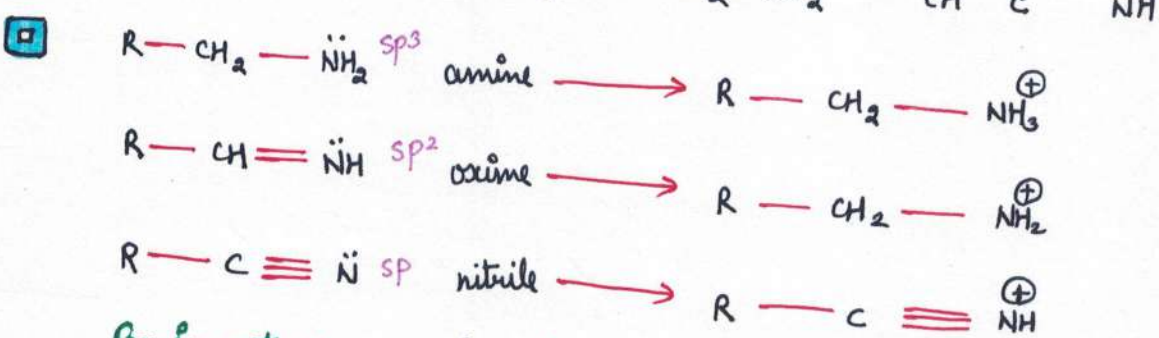


Basic Nature :- $O^{2-} > OH^- > H_2O$

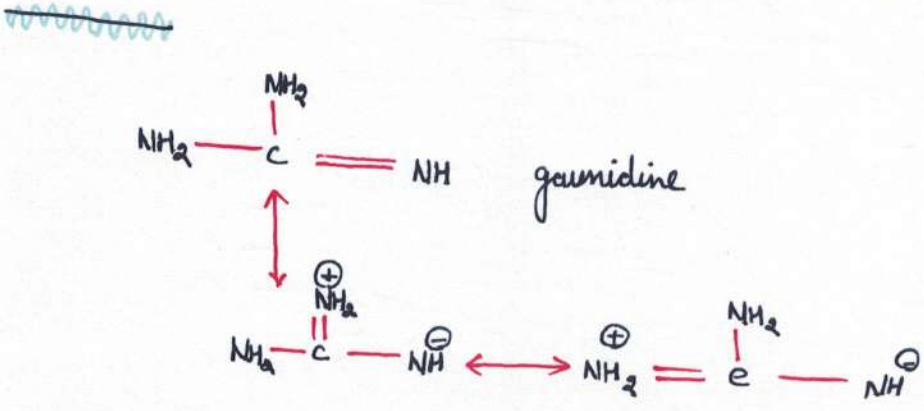


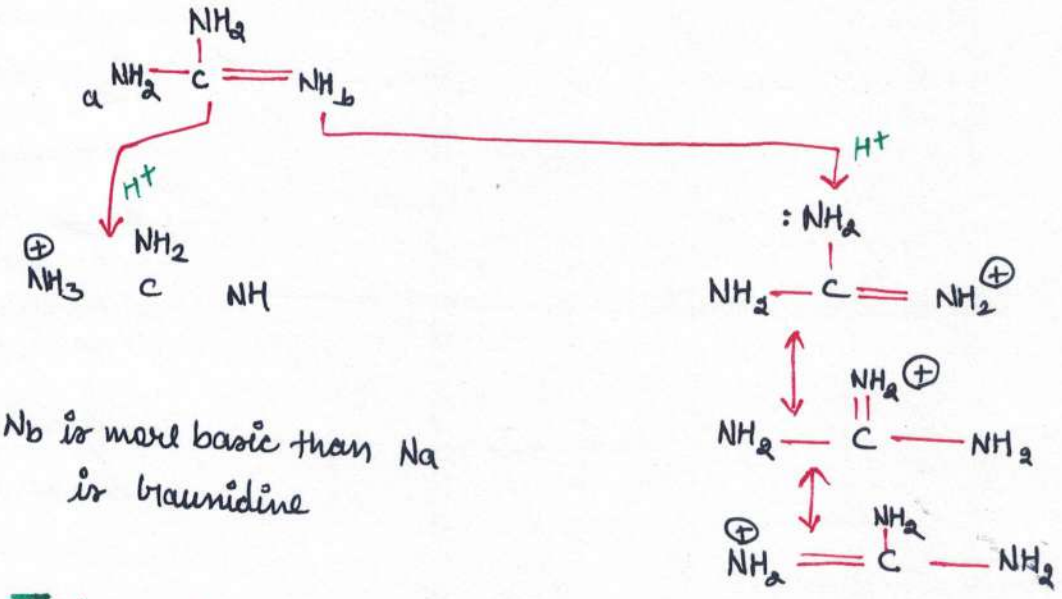


I > II > III



Basic nature :- amine > Imine > nitrile

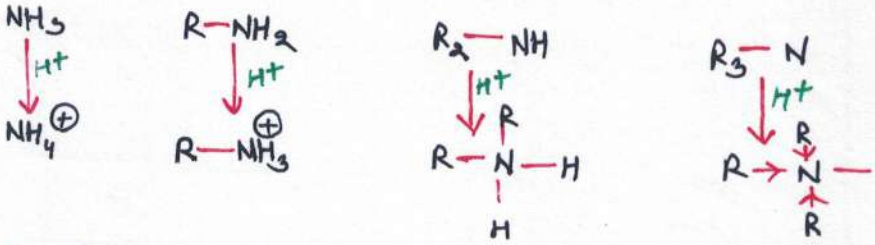




Nb is more basic than Na
is guanidine

△ In Gas phase :- $NH_3 < R-NH_2 < R_2-NH < R_3-NH$

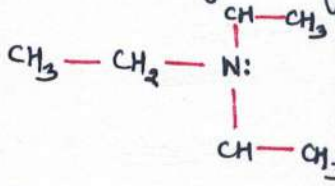
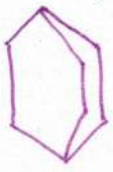
△ In aqueous phase :-



△ In aq. phase :- 2° amine > 1° amine > NH_3 > 3 amine

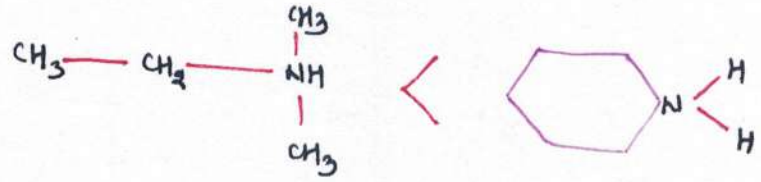
Et_2NH > $EtNH$ > NH_3 > Et_3N (basic)

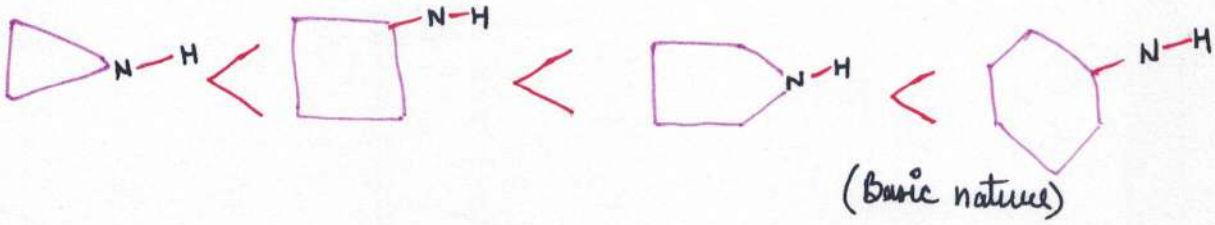
The 3° amine very strong base in gas phase becomes very weak base.

△  < NH_3 <  quanaclidine

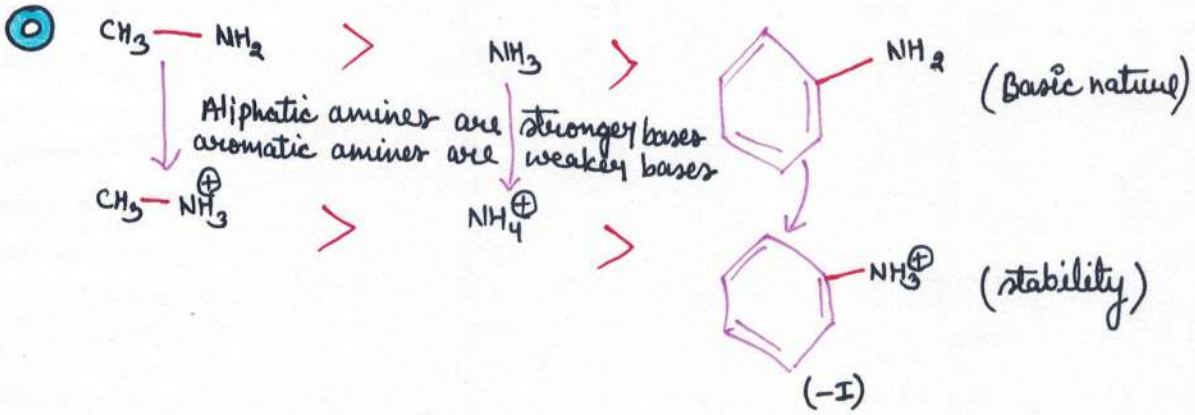
Space around the ground for hydration is less.

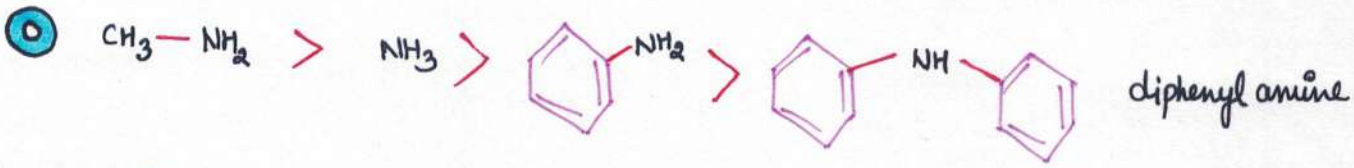
This is tritery amine but have more area for hydration (stablised more by hydration)

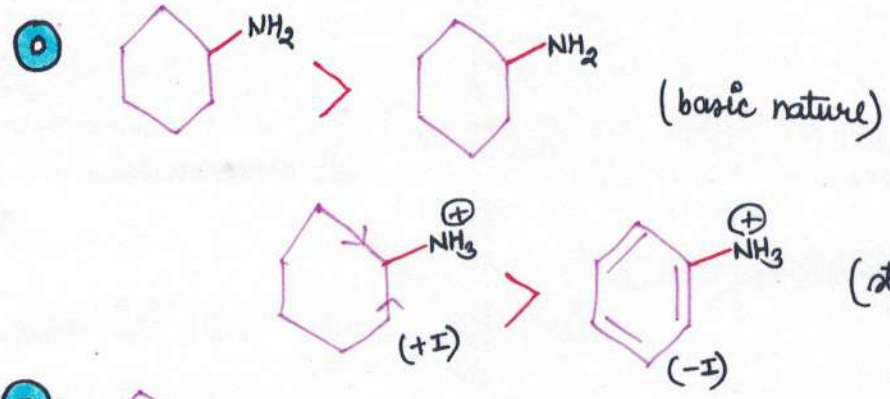
△ 

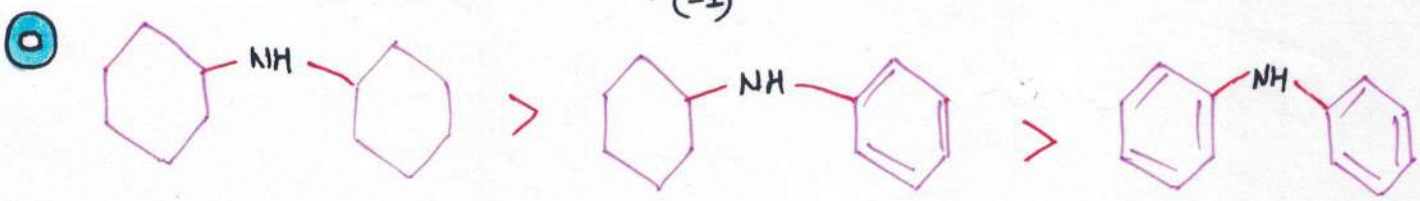
△ 

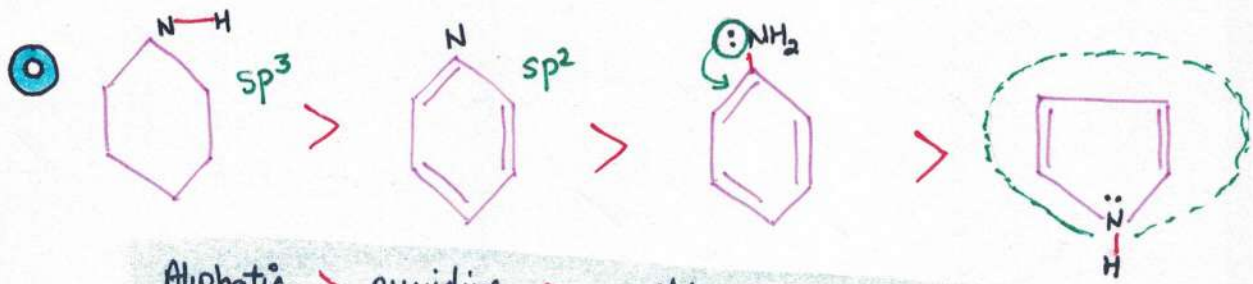
(Basic nature)











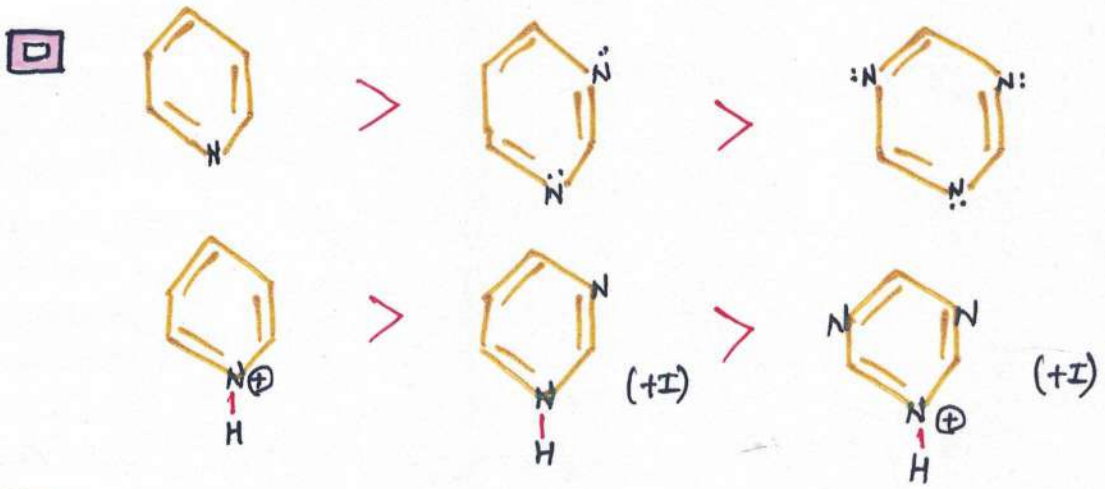
Aliphatic > pyridine > aniline > pyrrole
(basic nature)

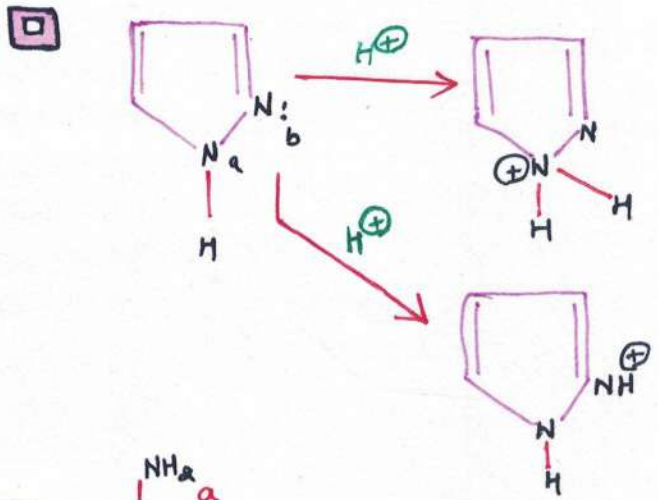
H_2SO_4 > H_3PO_4 (acidic)

more H does not mean more acidic

$\ddot{N}H_3$ > $\ddot{N}H_2 - \ddot{N}H_2$

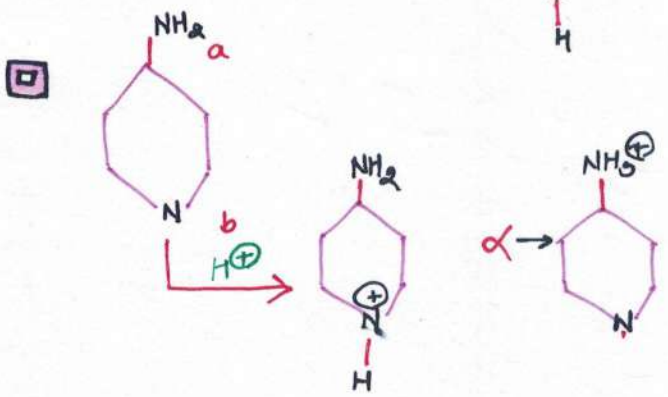
more lone pair does not mean more basic.

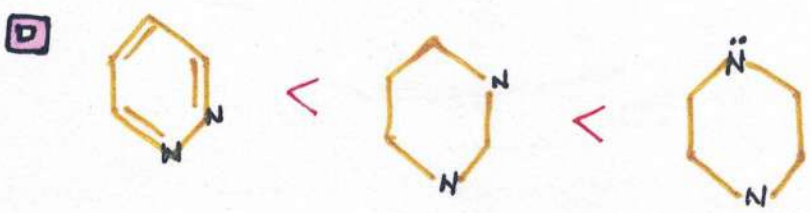




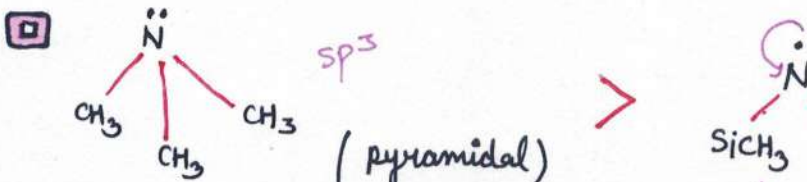
Pyridine on protination does not loose aromatically.

Pyrole on protination looses aromatically.

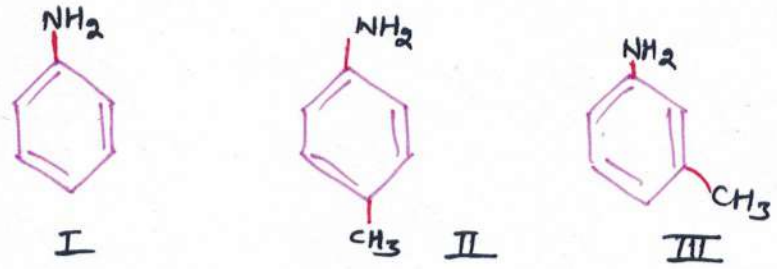




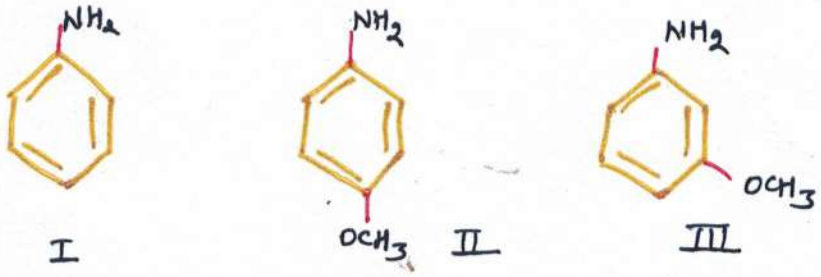
(-I effect will be more in I^st one
-I effect will be less in last one)



Its lone pair is in delocalisation, not ready for protination (Backbonding occurs).

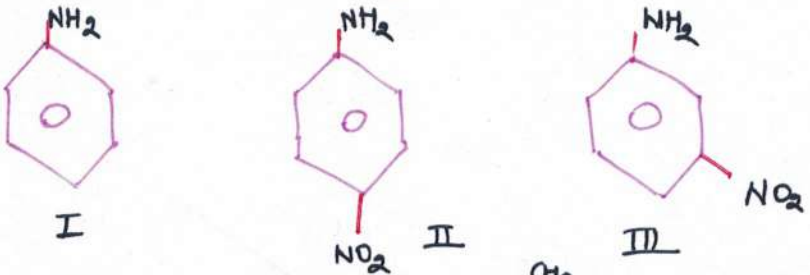
(a) 

I > II > III

(b) 

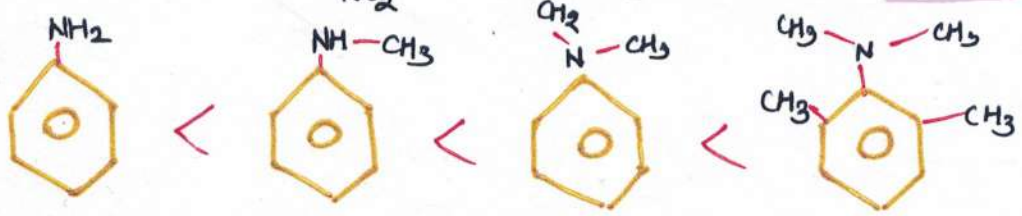
(+M, −I)

II > I > III

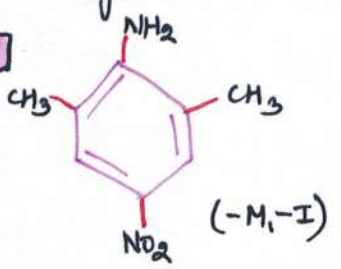
(c) 

(−I, −M)

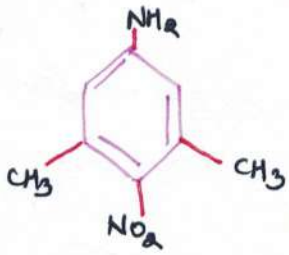
I > III > II

(d) 

whatever may be the medium, in case of aromatic group attached, always 3° amine is more basic.

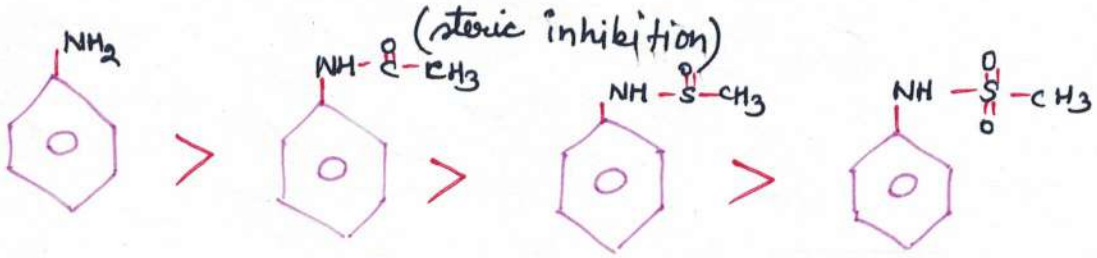
(e) 

(−M, −I)

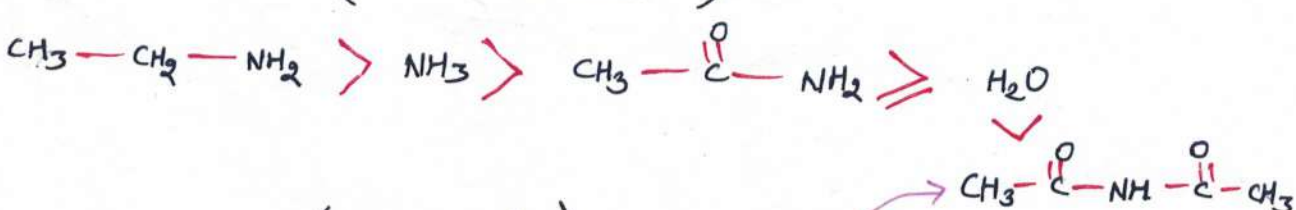


(−M, −I)

(steric inhibition)

(f) 

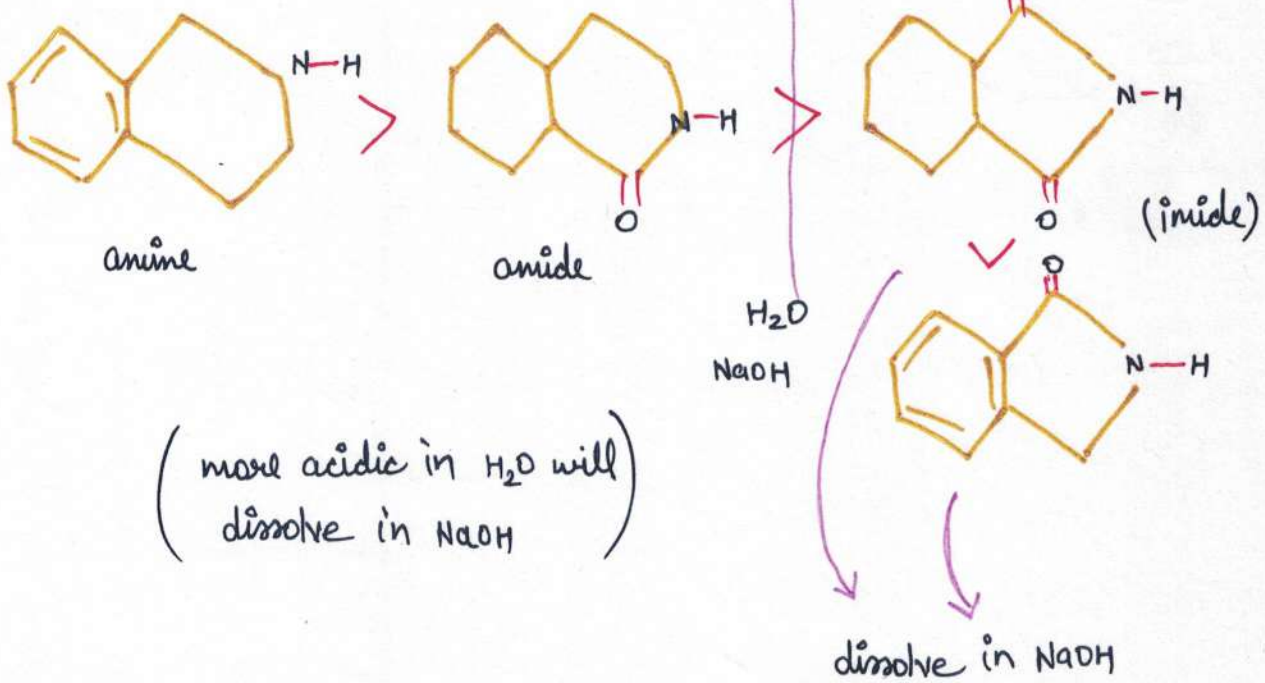
(Resonance acid −I)

(g) 

(more acidic in H_2O)

dissolve in NaOH

(a)



(more acidic in H_2O will dissolve in NaOH)

HYDROGEN BONDING

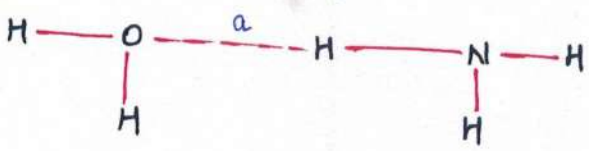
Hydrogen bonding is a kind of dipole-dipole interaction in which Hydrogen forms a bridge between 2 electro (-ve) atoms one by dipole bond and other by electro-static att^n.

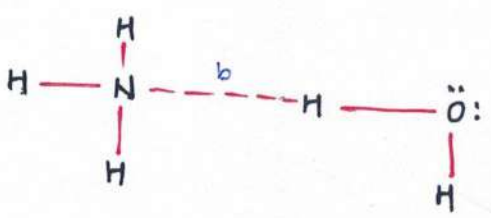
The electrostatic att^n is called as the **Hydrogen bond.**

Strength of H-bond gradually varies between 3-6 kcal/mol.

Strength depends on EN of A and basic nature of B

E.g.





Strength in b > a, N > O (basicity), O > N (EN)

$CH_3I > CH_3-Br > CH_3-Cl > CH_3-F$ (BP)

$H-F > H-Cl > H-Br > H-I$ (BP)

H-bond strength

H–F > H–Ö: > H–N̈

No. of H-bonds = (No. of H) or (L.P) × (2)

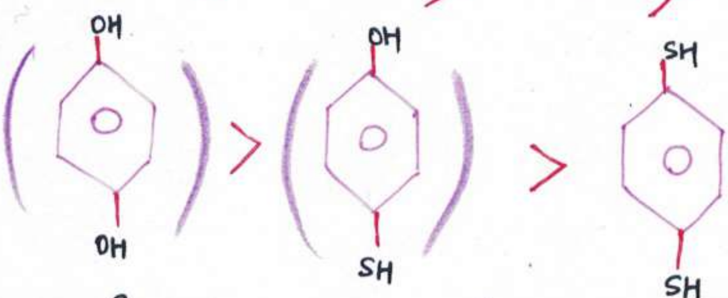
$H_2O > H_2Te > H_2Se > H_2S$ (BP)

$SbH_3 > AsH_3 > NH_3 > PH_3$ (BP)

$CH_4 < SiH_4 < SnH_4 < PbH_4$ (BP)

- HF is gas but H_2O is a liquid because in H_2O, it make H-bonds pre molecule but HF make 2 bond

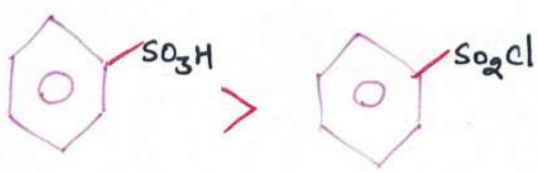
- $R-NO_2 > R-OH > R-Cl > R-H$ (H-bond)

- 

(B.P)

- $HO-S(=O)_2-OH > HO-S(=O)_2-Cl$ [B.P]

- $R-C(=O)-OH > R-C(=O)-Cl$ [B.P]

- 

[B.P]

- $CH_2(OH)-CH_2-OH > CH_2(OCH_3)-CH_2-OH$ [B.P]

- $C_3H_9N \longrightarrow$ 3 isomers, $C_7H_9N \longrightarrow$ 5 isomers

- $KF + HF \longrightarrow KHF_2 \longrightarrow [K^+][HF_2^-]$

str. of $HF_2 \longrightarrow F^{\ominus}$- - - H — F

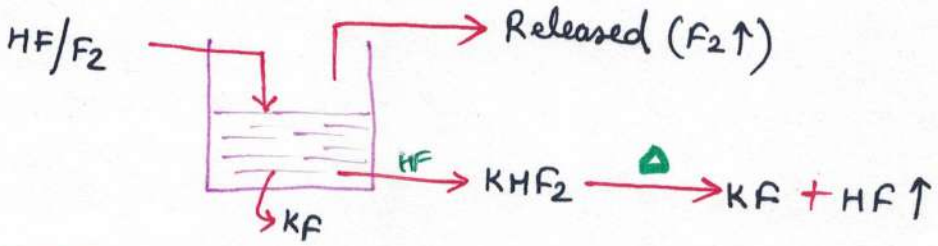
50 kcal mol., Possess 1σ, 1H-bond, BO = ½

9. Which of the tail has H-bond in its str?

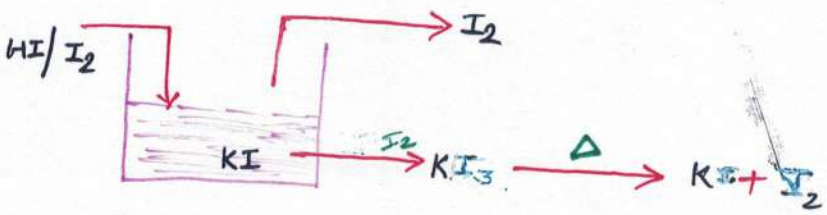
(a) HF_2^{-1} (b) HCO_3^{-1} (c) HSO_4^{-1} (d) HSO_3^{-1}

Ans (a) HF_2^{-1}

▷ **Separating HF and F-1**

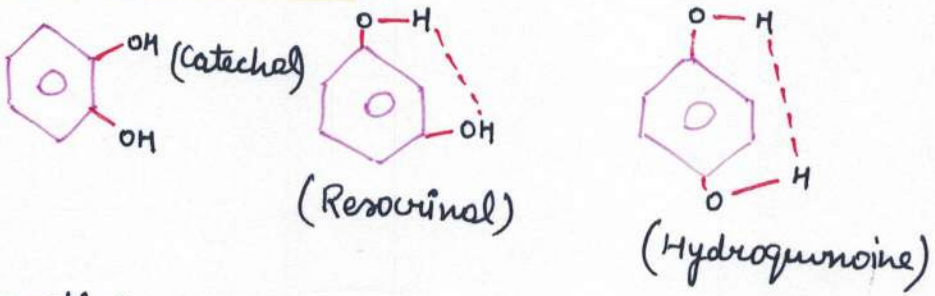


▷ **Separating HI and I_2**



$K^+ I_3^{-1} \longrightarrow I_3^{-1} = sp^3d$

▷ **Intramal H-bond**



▷ If a particular compound doesn't have five or six membered rings, then intramolecular H-bonds is not possible.

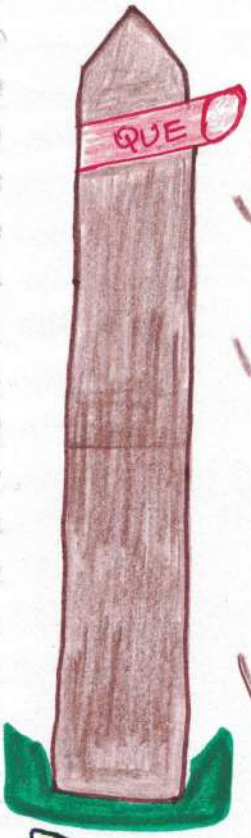
▷ Meta and para involve in intermal H-bonding while ortho invdves in intramal H-bonding.

▷ V.P of the molecule having intramal. H-bonding is very high. Thus, ortho has very high V.P.

MP of para is always greater,

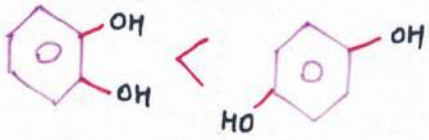
▷ ortho > Meta > Para (V.P)

Para > Meta > ortho (BP)

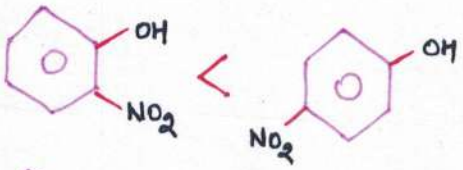


Arrange in mentioned qualities :-

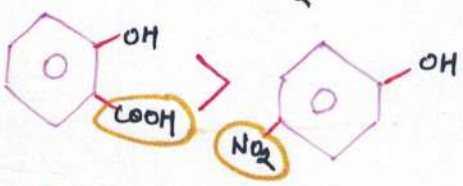
a. B.P



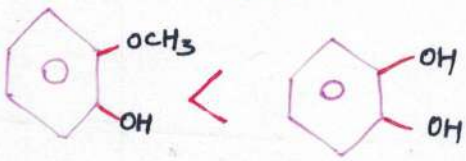
b. M.P



c. Sol.



d. BP.



▷ Suppression of a component having high V.P form a component having low vapour pressure by passing steam is called as "steam Distillation."

▷ Thus all orthoisomers which are intramolecular H-bond undergo steam distillation. while meta and para don't.

▷ % of enol → n-hexane > Benzene > CH_3OH > H_2O. Enol % is more in non-polar solvents while less in polar solvents ketone is vice-versa.

▷ $\left(CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3\right) > \left(CH_3-\overset{O}{\overset{\|}{C}}-CH_3\right)$

(Enol content)

OPTICAL ISOMERISM

when plane polarised light is passed and it comes out without any change, the compound is optically inactive.

where there is deviation, then it is optically active.

when light is deviated to left, it is leavo (l-).

when light is deviated to right, it is dextro (dt).

D/L → they are mirror images and they don't superimpose. these are mirror images isomers and they are called "enantiomers." → optically active.

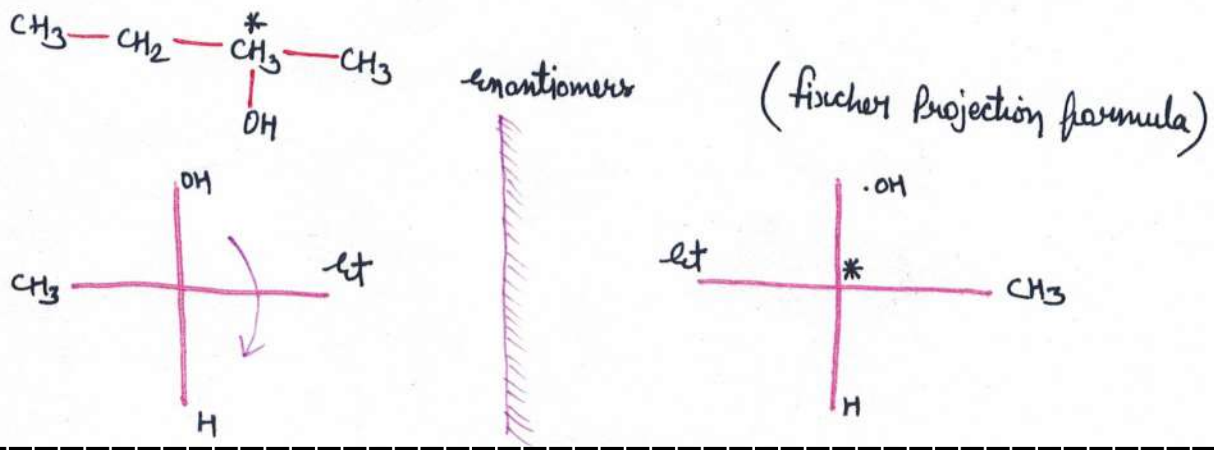
The molecules which are mirror images and they superimpose, they will be optically inactive. whenever there is a plane of symmetry, their mirror images superimpose, thus, optically inactive.

when molecule has only 1 asymmetric centre, their mirror images don't superimpose, thus, optically active.

The angle of rotation is measured by "Polarimeter".

"Magnitude" of rotation by the D/L of the compound will be same but in the opposite direction.

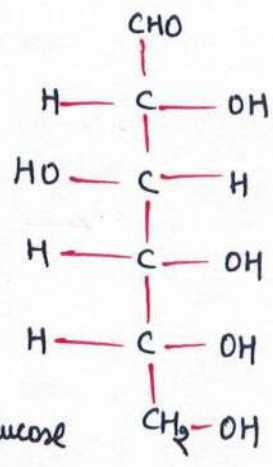
D



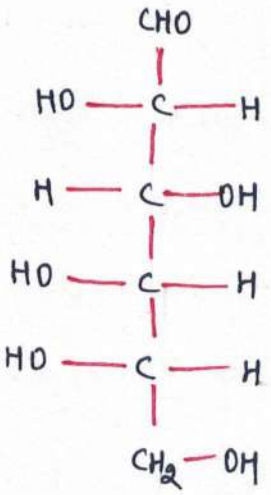
In Fischer formula, horizontal groups are out of the plane (towards us, out of paper) (◁)

In Fisher formula, vertical groups are in the plane. (away from us) (|||)

Enantiomers are mirror image isomers, and their images don't superimpose. They have same and absolutely identical physical properties. Thus, they can't be isolated. only 1 fraction will be obtained. They have the same angle of rotation (magnitide), they have different directions of rotation. They have same and identical chemical properties too except with the bioactive reagents such as enzymes.



(D+)glucose

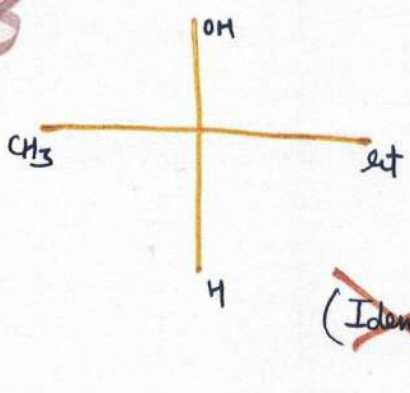


(L-) glucose

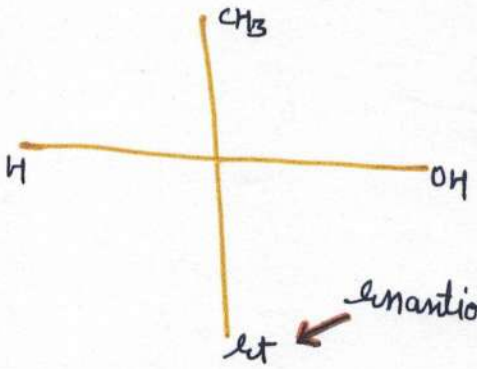
Nature only produces Dextro, never levo.

Starch can be digested but cellulose can't be digested.

IMPORTANT

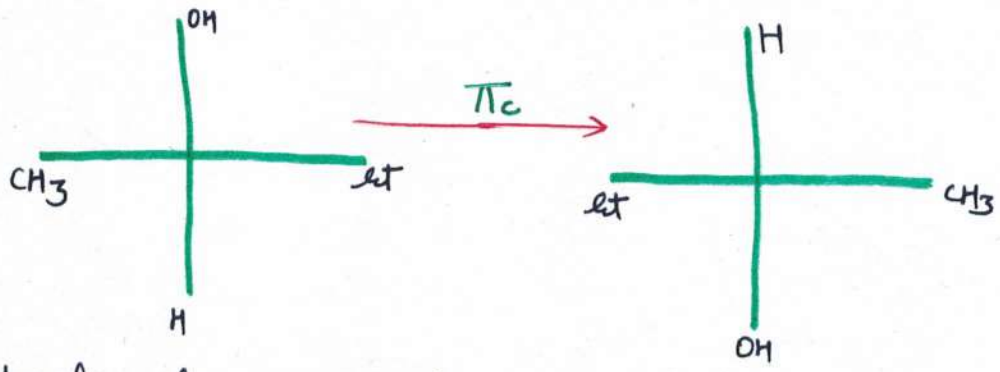


(Identical)

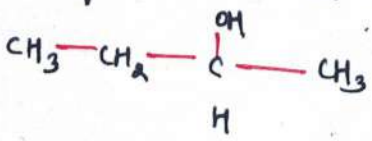


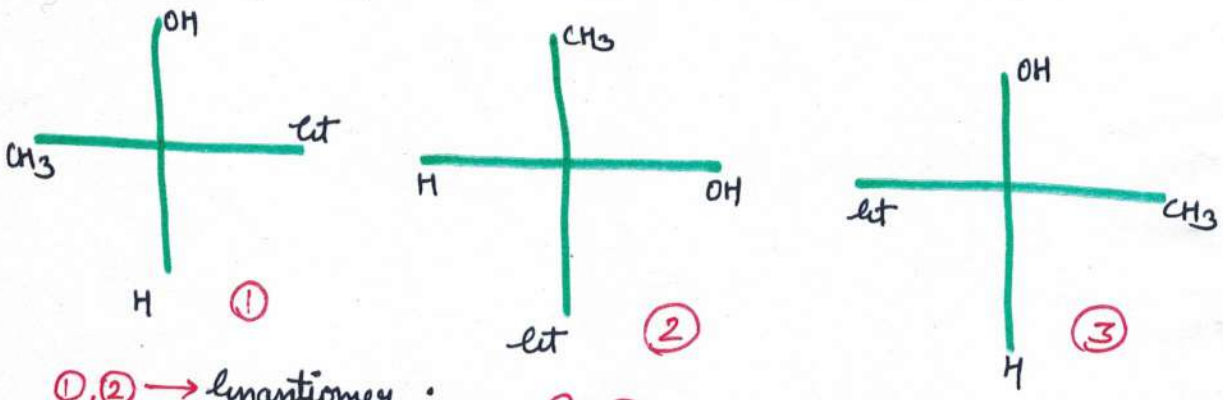
Enantiomers

- Whenever even no. of exchanges → Identical
  Odd no. of exchanges → Enantiomers
- Fisher formula can't be rotated by 90°. Thus, when we rotate it by 90°, we get enantiomers (mirror images don't superimpose).



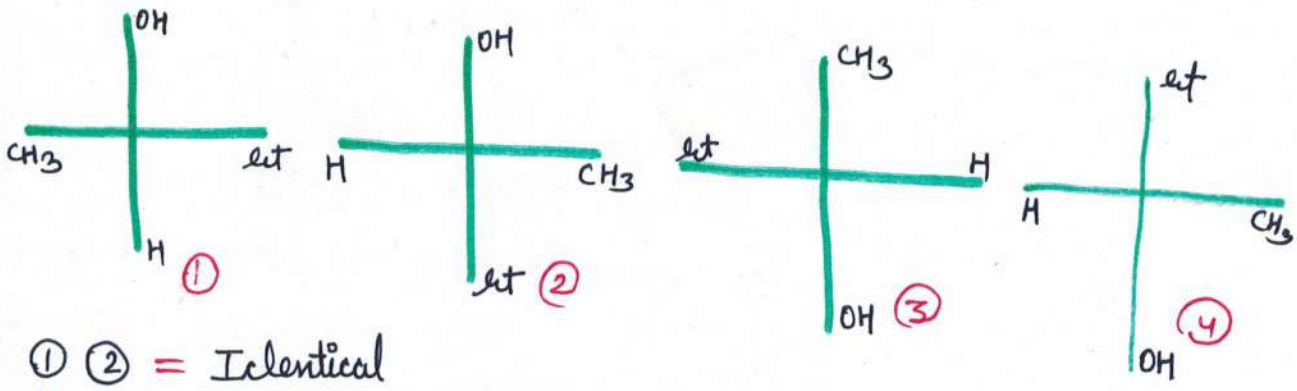
Fisher formula can be rotated by "$n\pi$" to get the identical compounds.





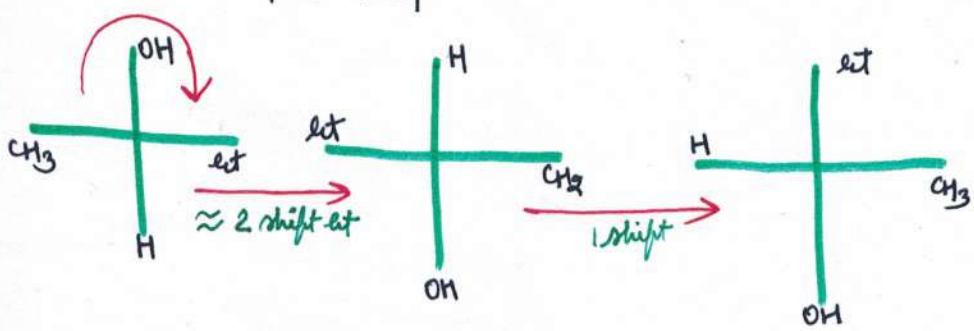
①, ② → Enantiomer ; ①, ③ → Identical

Que. Find the relation w.r.t ①



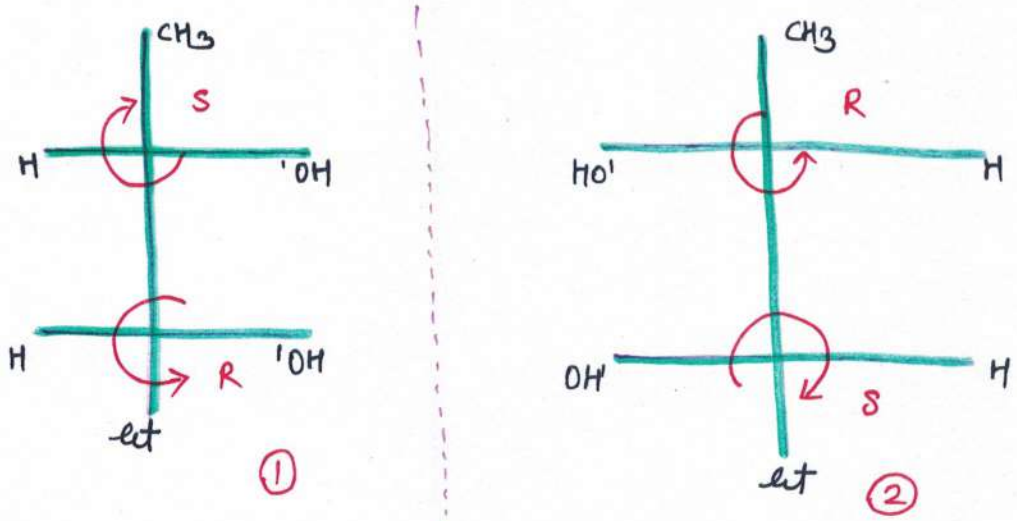
Ans.

① ② = Identical
② ③ = Enantiomers
① ④ = Enantiomer



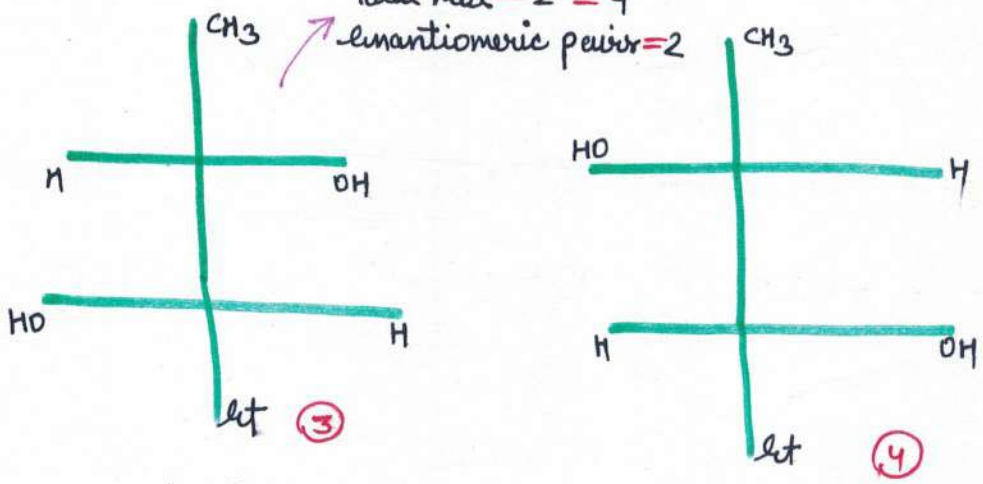
Thus ①, ④ are enantiomers
As 3 shift required.

(c) $CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$



Total mol $= 2^n = 4$

enantiomeric pairs $= 2$



{1,2}, {3,4} are enantiomers.

▷ Itereoisomers which aren't mirror images are called diastereoisomers. All G.I are diastereoisomers.

▷ Diastereoisomers differ in physical properties. Thus they form 2 diffey fraction. They can be isolated.

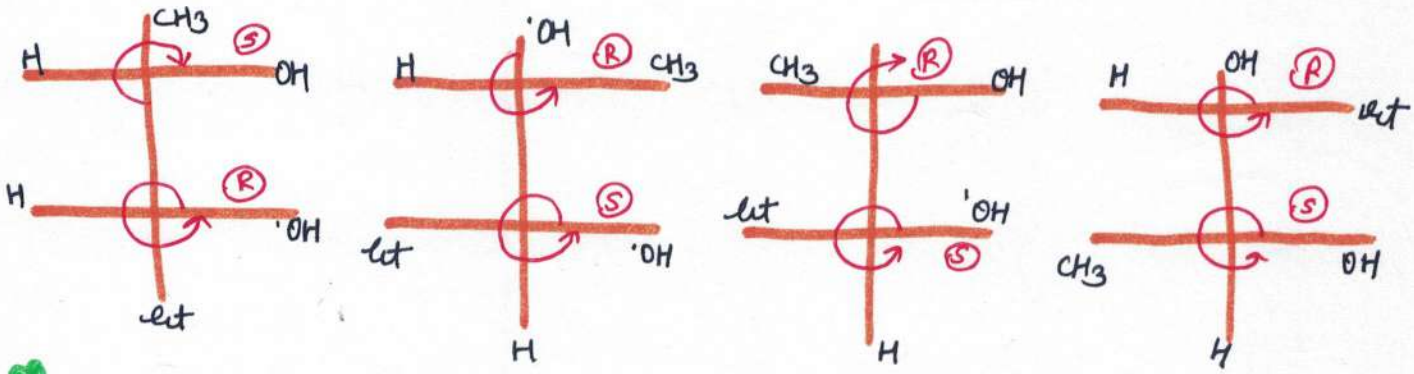
In ①, the two –OH are in same plane. The two bulky groups are in same plane, thus, more repulsion. The intramol H-bonding ↓. Thus, the amount of intermol H-bond ↑.

In ③, the two -OH are in diff. plane. The two bulky groups are in diff. plane, thus, less repulsion. The mitramol H-bonding ↑. Thus the internal H-bond ↓

B.P. of ① > B.P of ③

- when there are no plane of symmetry, then the no. of total isomers $= 2^n$
  enantiomeric pair $= 2^{n-1}$

IMPORTANT



Identify relation unit ①

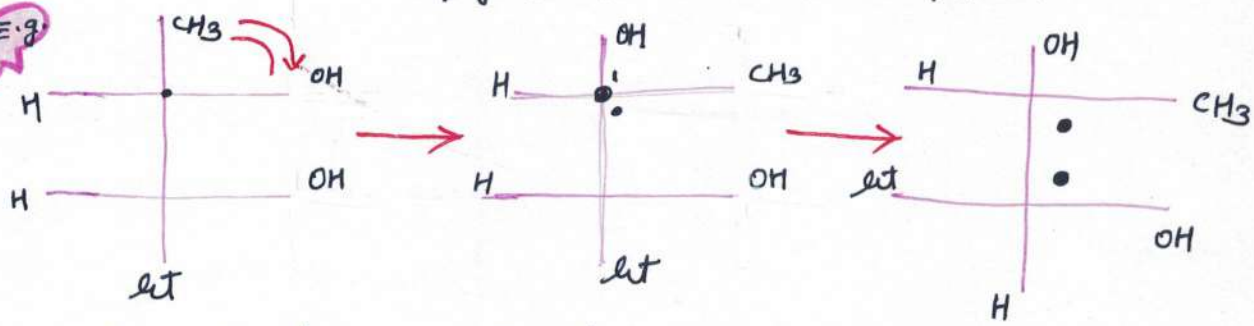
①, ② → Enan

②, ③ → Identical

①, ② → Enantiomers

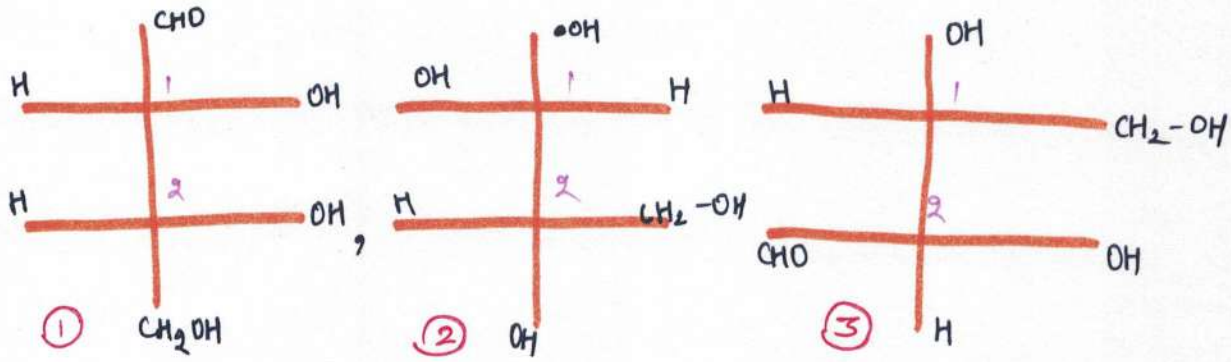
Total exchanges don't matter on a single carbon, even no. of exchanges must be done so that the configuration doesn't become inverse.

E.g.



one more exchange must be done on "1" so that the config remains

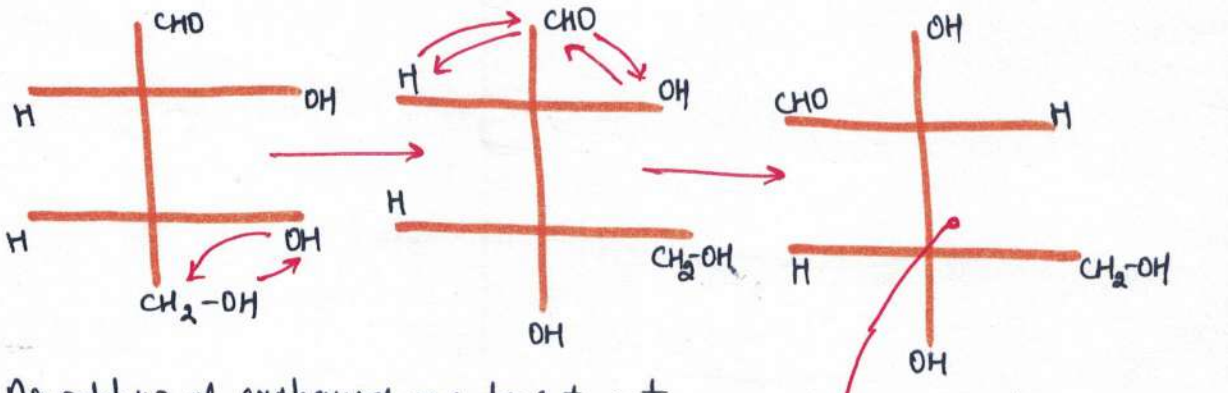
①, ② - enantiomers as both carbons are inverted due to change in configuration.



As C_2 is inverted

① ② → Diastereoisomers

① ③ → Identical

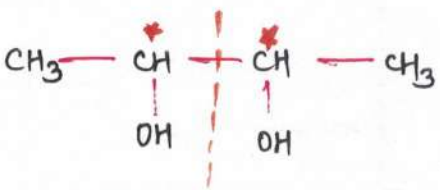


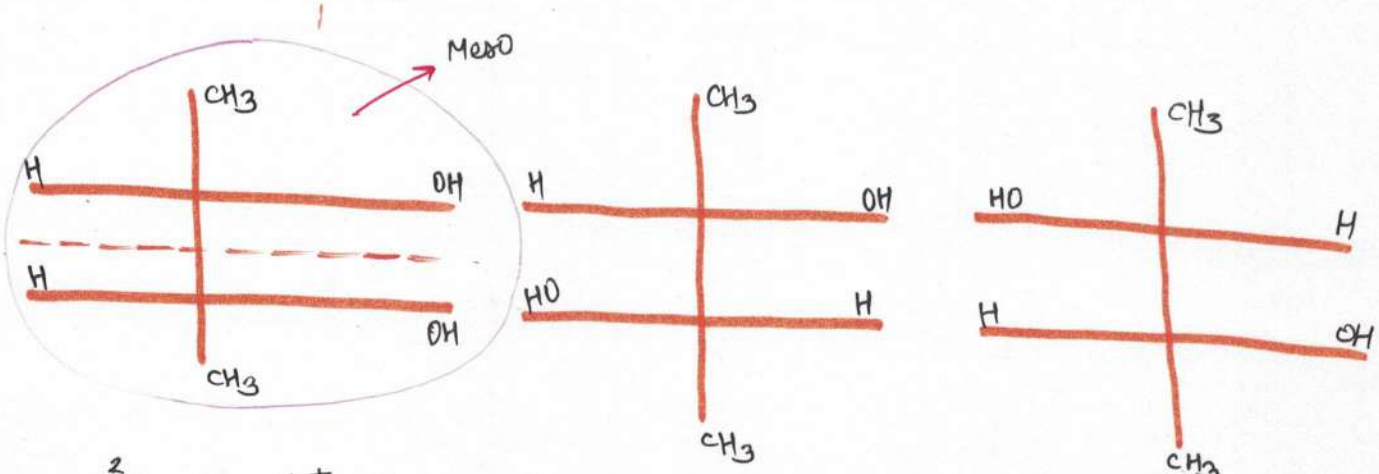
As odd no. of exchanges are done to get this confign.

(Inverted confign. - carbon)

▷ In glucose, $2^4 = 16$ isomers. we have, thus, 8 pairs of enatiomers

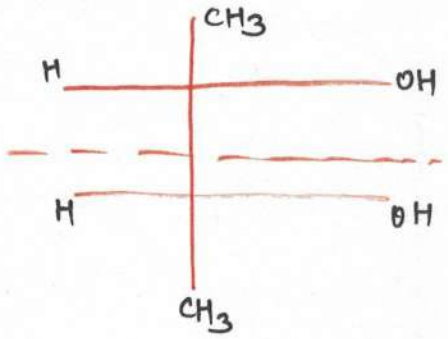
▷ In fructose, $2^3 = 8$ isomers, we have, thus 4 pair of enantiomers.



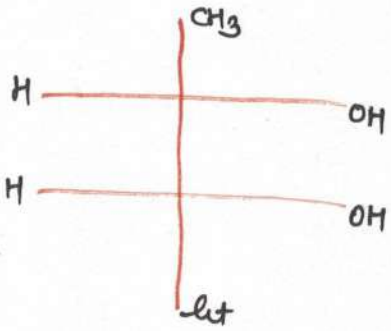


$2^2 - 1$ 3 enatiomers, 2 pair of enantiomers

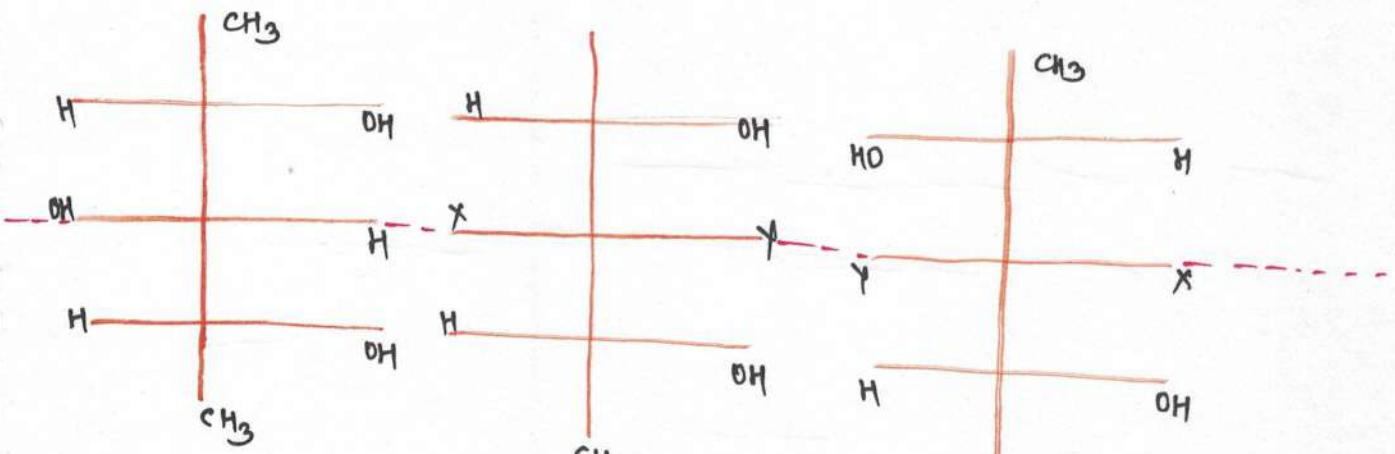
Meso isomers are optically inactive, inspite of having assymetric centres, as they posses plane of symmetry. Their imagers are non-superim posable.



(Meso) Inactive



(Active)



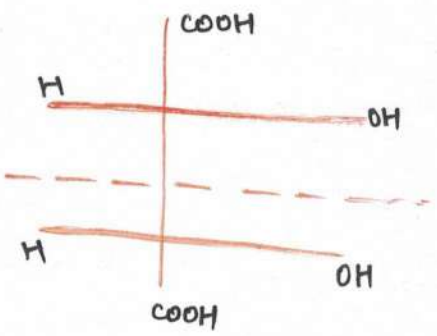
Meso – (Inactive)

Inactive

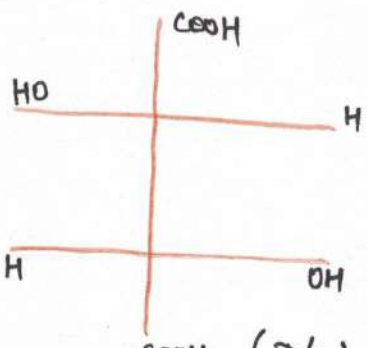
Active

Tartaric acid

(3 iso.)



Inactive (Meso)

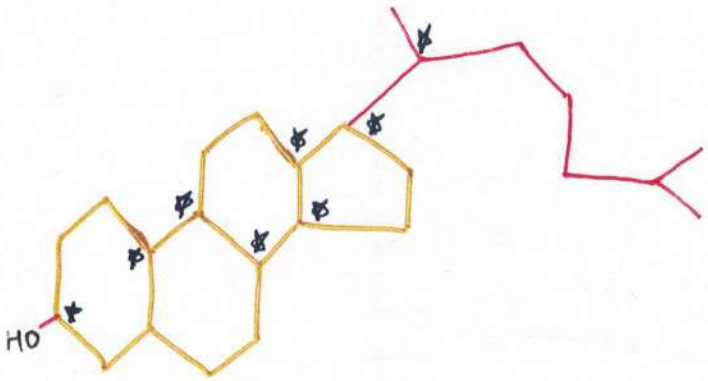


(Active) (D/L)

▷ C_3H_6OCl

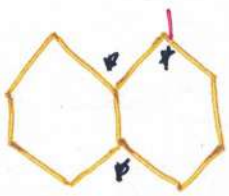
Total stereoisomers = 6

▷



2^8 enantiomers
2^7 enantiomeric pairs

▷



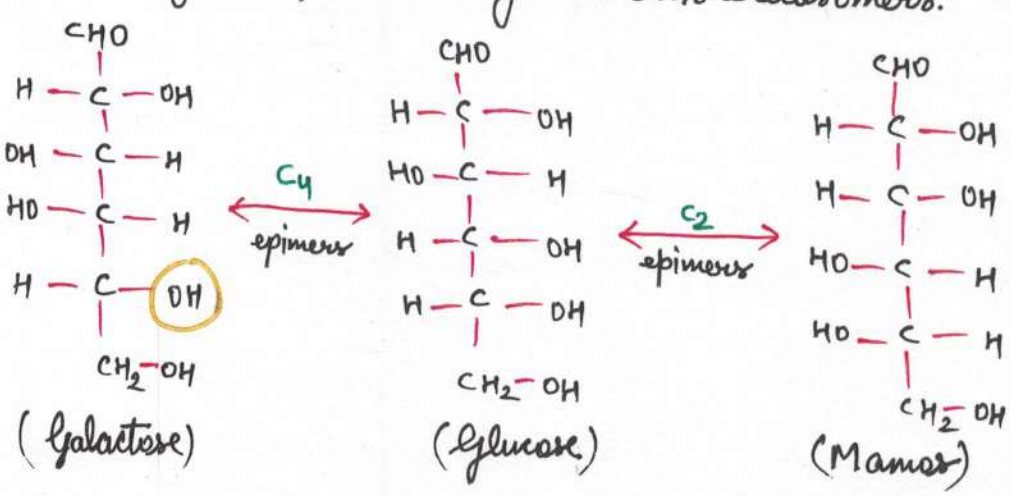
Total stereoisomers = $2^3 = 8$

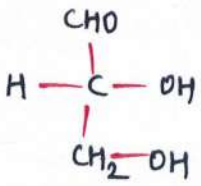
⊙ If there are n- stereogenic centres and is mirror images, if the config is opposite in all, then they are enantiomers.

⊙ If there are n- stereogenic centres and in mirror images the config is opposite only in some (not all), they are diastereoisomers.

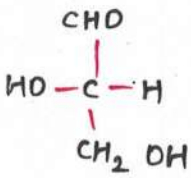
⊙ If there are n-stereogenic centres and the config^n is opp. only in one centre, they are epimers. they are diastereoisomers.

⊙

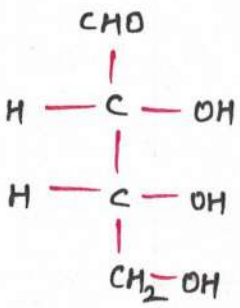




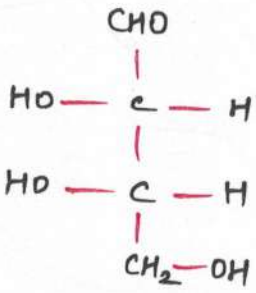
is named as D(+) - glyceraldehyde



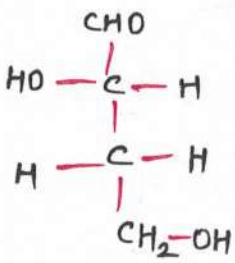
is named as L(-) - glyceraldehyde



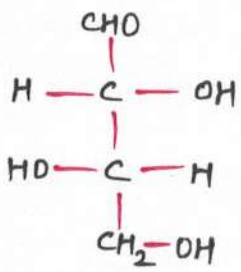
D(+) erythrose



L(-) erythrose

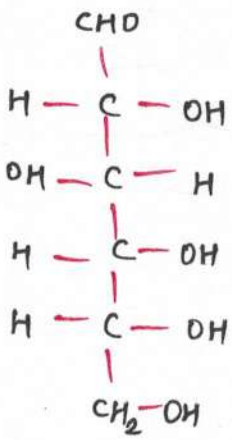


D(+) threose

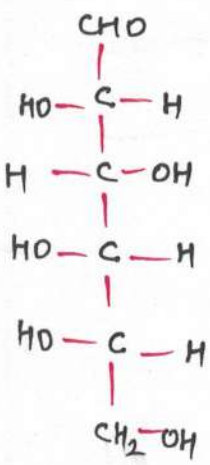


L(-) Threose

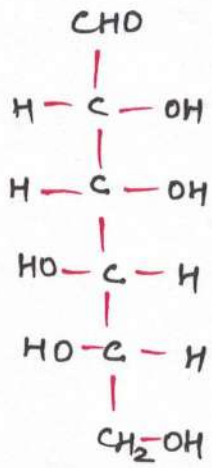
BOTTOMOST:- "-OH will decide the configuration."



D(+) glucose

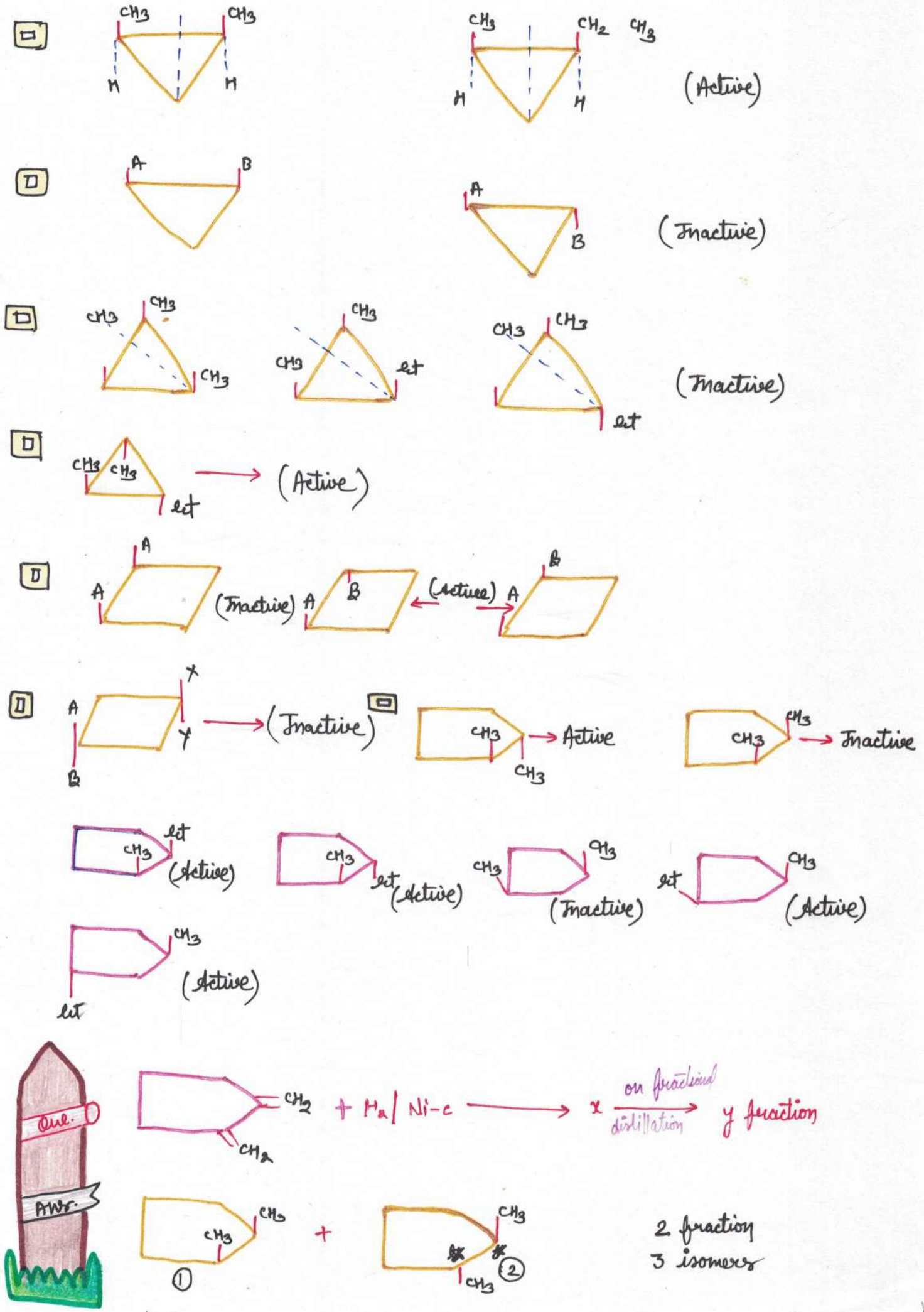


L(-) glucose

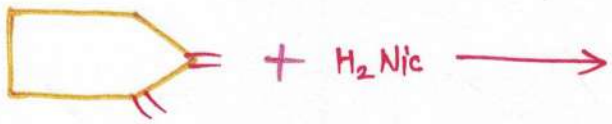


D+ -(manos)

Mamose & galactose are simply diastereo-isomers



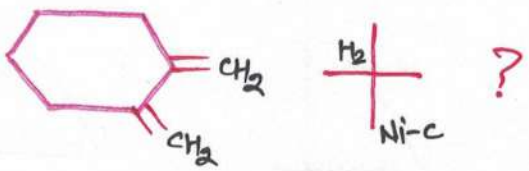
QUE



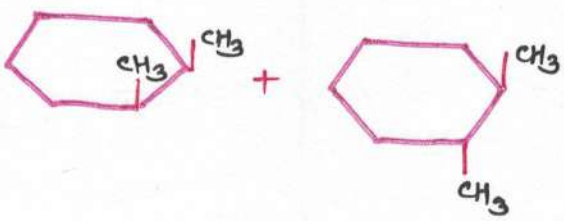
ANS.

2 fractional
4 isomers

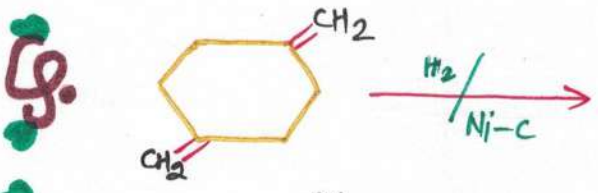
QUE



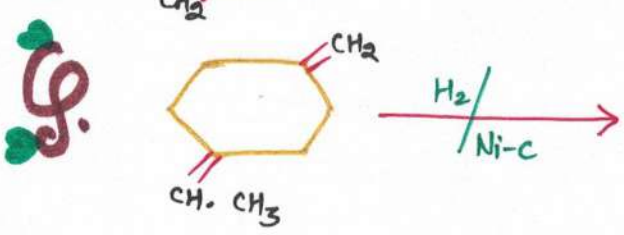
ANS.



3 isomers
2 fractional



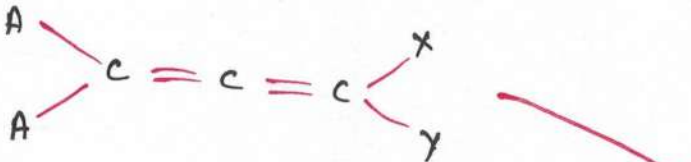
2 fractional
2 isomers



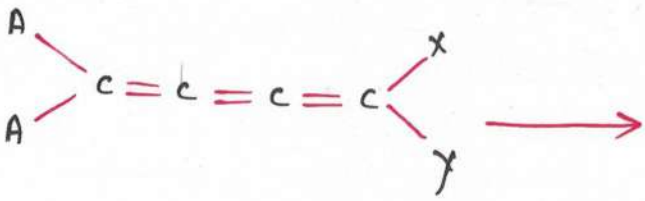
2 fractional
2 isomers

(o)

shows optical as it is non-planar.



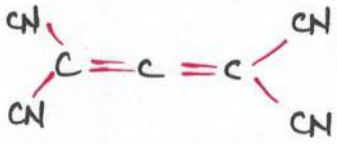
No optical iso

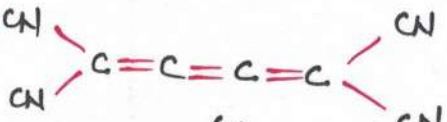


No iso

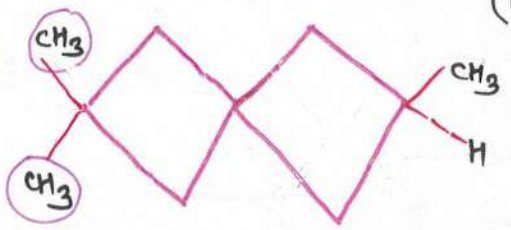
⊙ $C(CN)_4$ ⟶ Never planar

$C_2(CN)_4$ ⟶ Planar

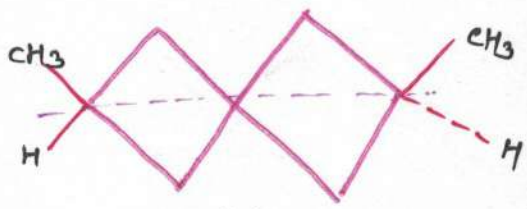
$C_3(CN)_4$ ⟶  (Non planar)

$C_4(CN)_4$ ⟶ 

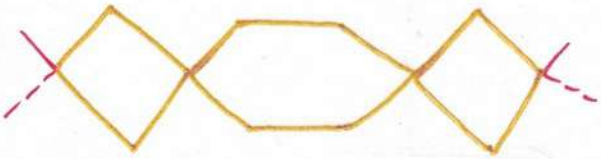
(Planar)

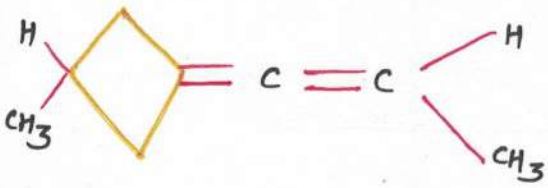
⊙ 

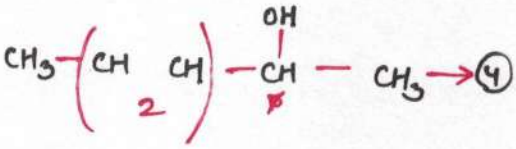
Inactive



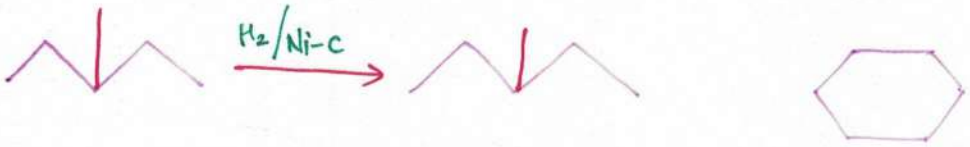
Active

⊙  (Inactive)

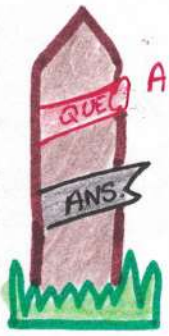
⊙  (Active)

⊙ 

A (C_6H_{12}) Active $\xrightarrow[Ni\text{-}C]{H_2}$ C_6H_{14} (Inactive) DU = 1



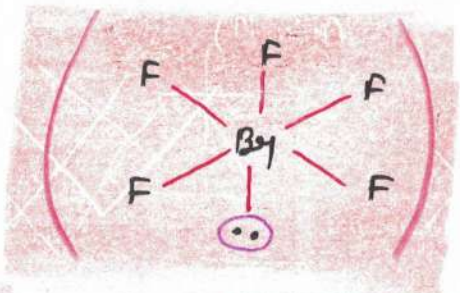
A (C_6H_{12}) $\xrightarrow[H^{\oplus}]{KMnO_4}$ B $(C_5H_{10}O_2)$ $\xrightarrow{}$ CO_2

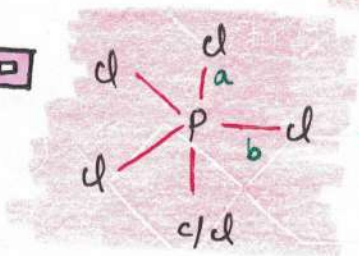


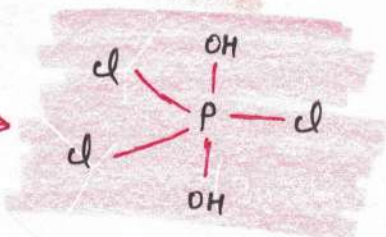
A $(CH_3-C\equiv C-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH-CH_3)$ $\xrightarrow[Pd-CaCO_3]{Active}$ $CH_3-CH=CH-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH-CH_2$

cis $\xrightarrow{Cis}$ D/L mixture

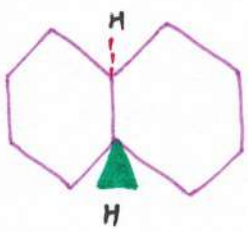
- **BrF5 :-** In sp^3d^2, there is no axial or equatorial. All are identical.



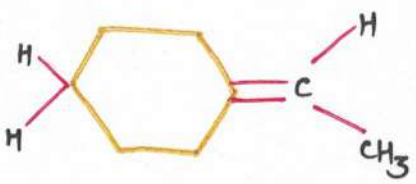
- 

$\xrightarrow{H_2O}$ 

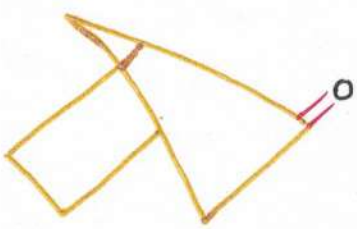
$\longrightarrow POCl_3 + HCL$

- 

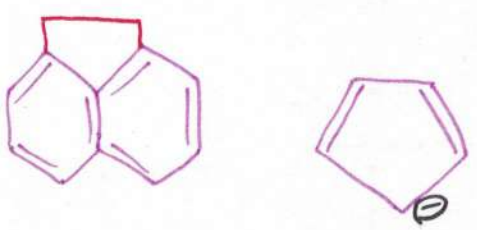
→ only shows geometrical isomerism
Not optical isomerism.

- 

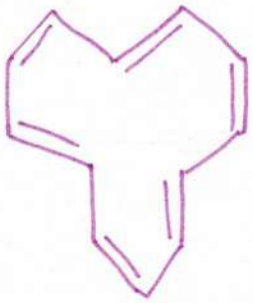
→ No O.I. as the terminal is (H,H).

- 

→ shows O.I.

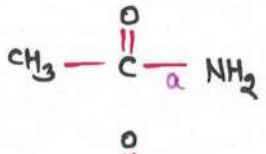
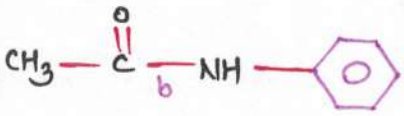
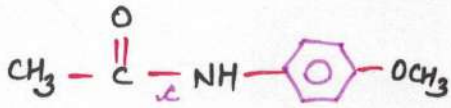
- 

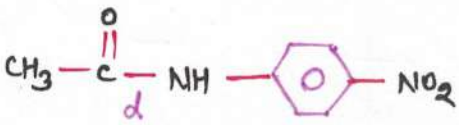
→ Aromatic



→ Non Aromatic

→ Anti-Aromatic

(a)  ,  , 



Bond length

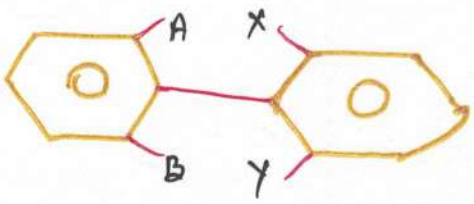
(a < c < b < d)

(b) $CO_2 \longleftrightarrow O=C=O \longleftrightarrow O^{\oplus}\equiv C-O^{\ominus} \longleftrightarrow O^{\ominus}-C\equiv O^{\oplus}$

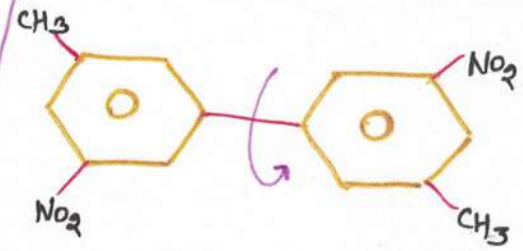
Q4. Which is most stable carbene?

a : CF_2 b : CCl_2 c : CBr_2 d : $C(Br)Cl$

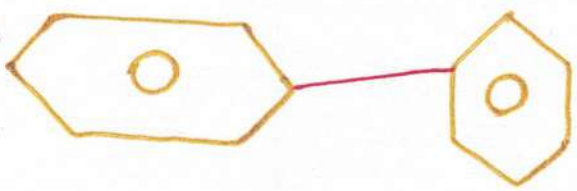
Q7. a : CF_2

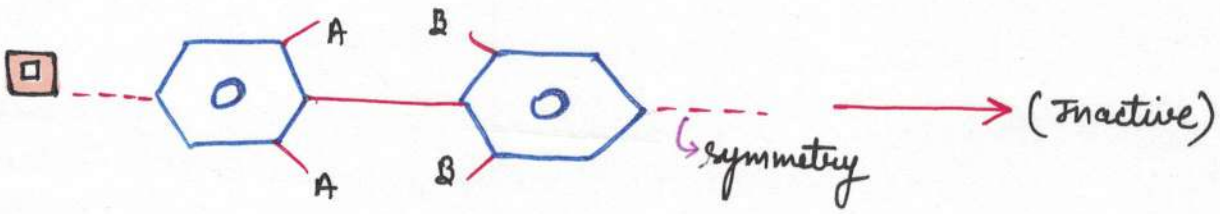
(a) 

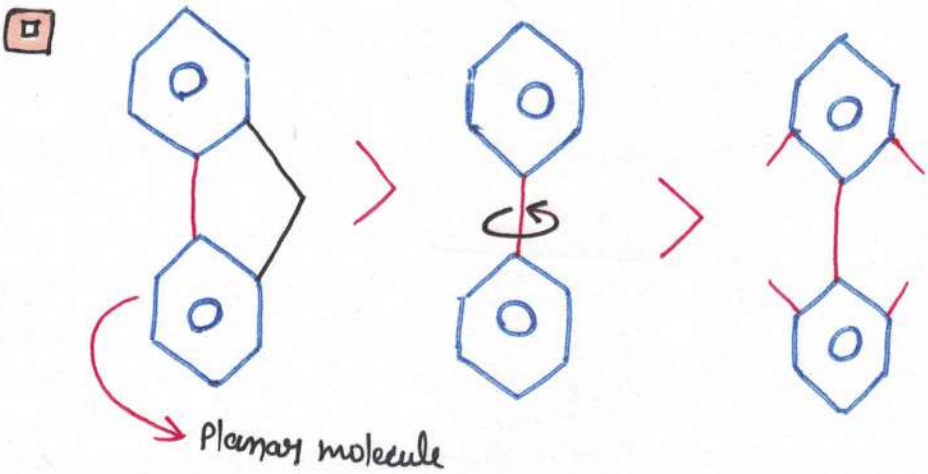
Will show optical activity if the groups are crowded hindering the free relation.

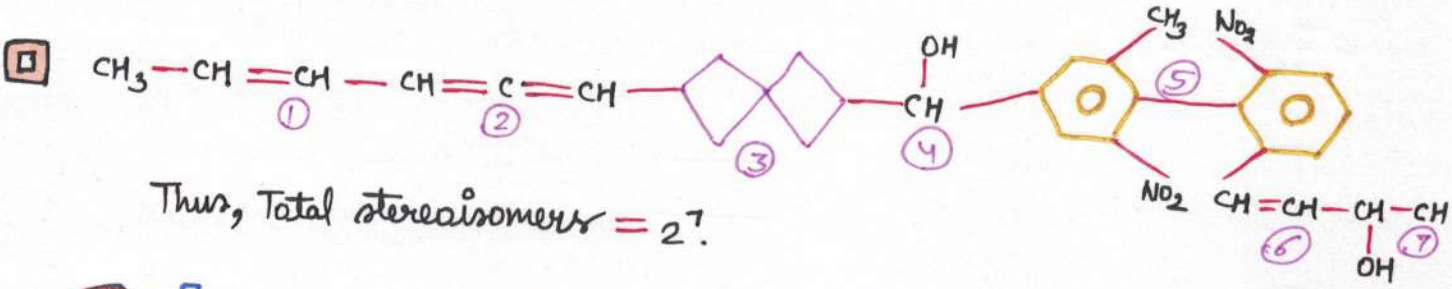
(b) 

(Inactive)



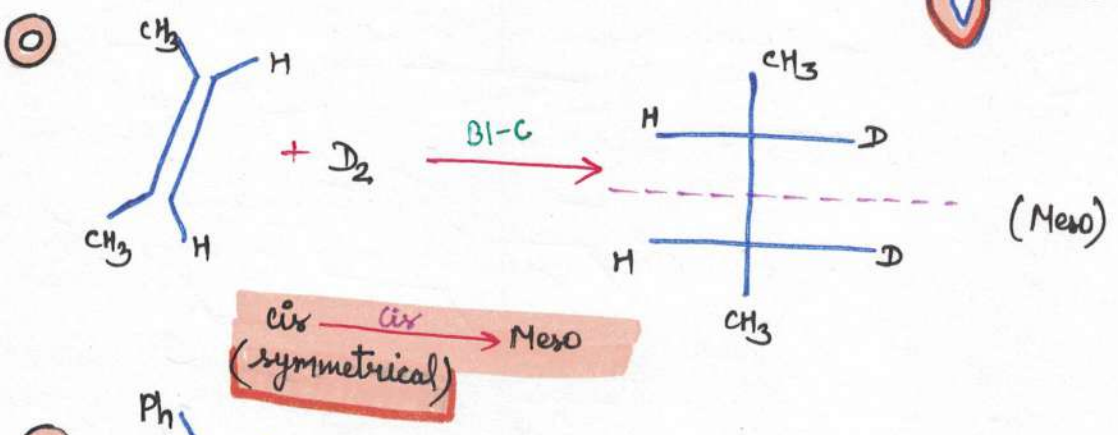


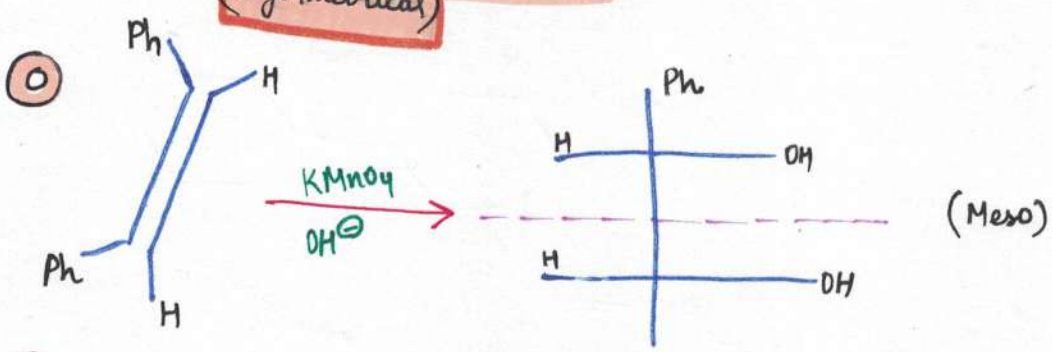




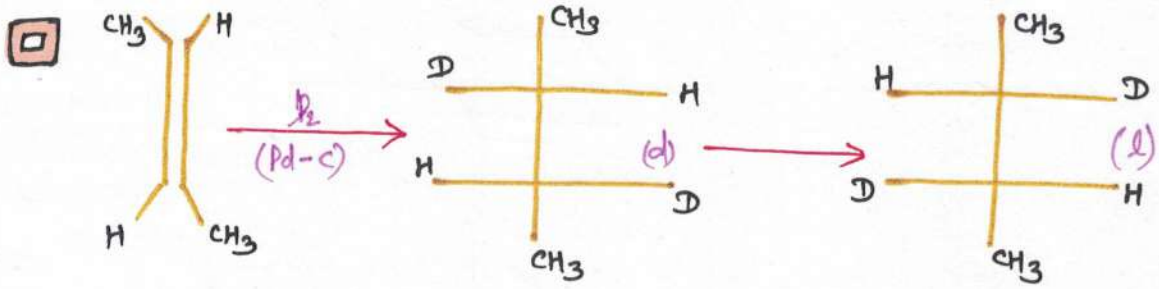
Thus, Total stereoisomers = 2^7.

Stereochemistry Addition



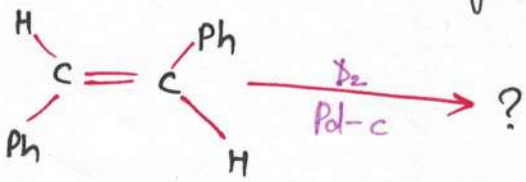


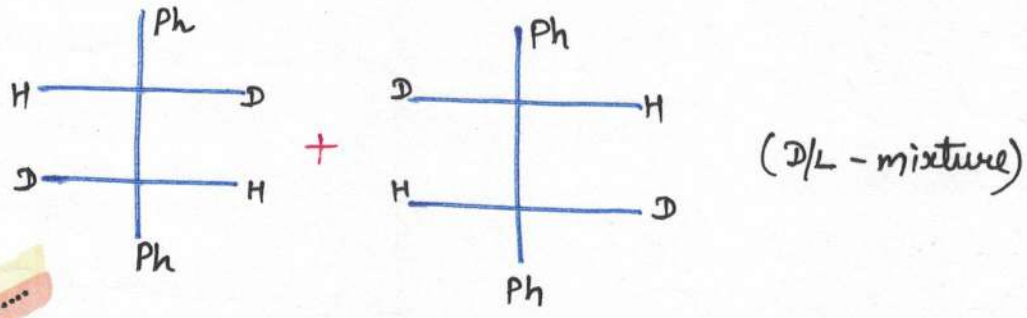
◎ of the several stereoisomers, one of the isomers is formed as a major product then reaction is 'stereoselective- reaction. product decides whether stereo-selective or not.



Trans $\xrightarrow{H_2/Pd-C}$ D/L mixture
Symmetrical

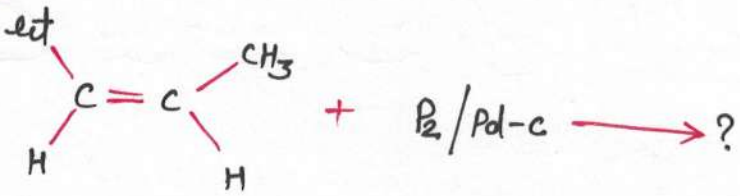
D/L is formed as a major stereo

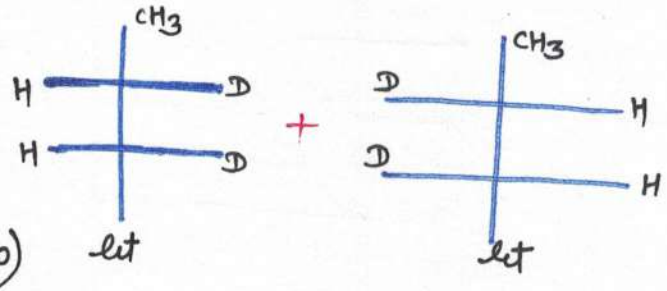




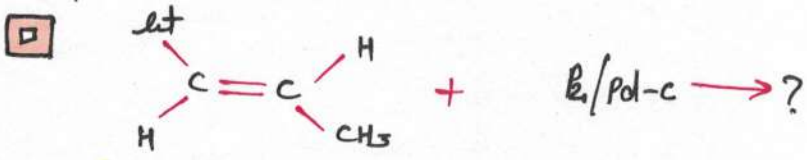
(D/L - mixture)

IMP.....

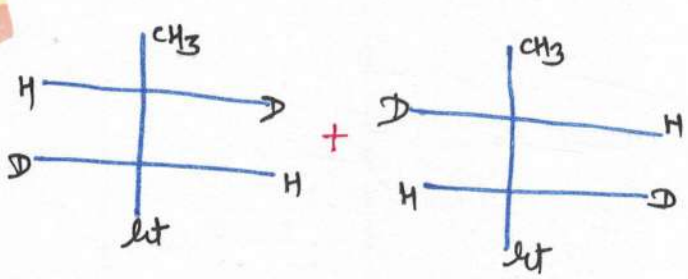




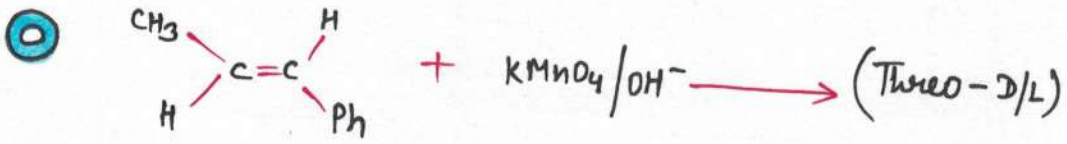
(Erythro D/L)

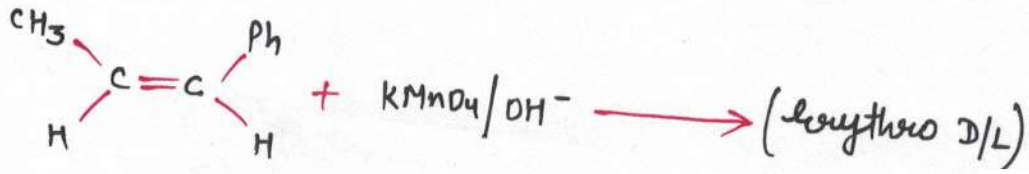


IMP..

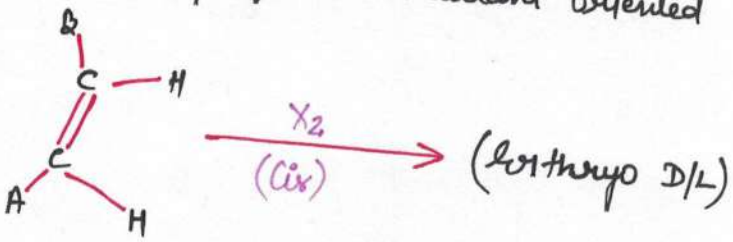


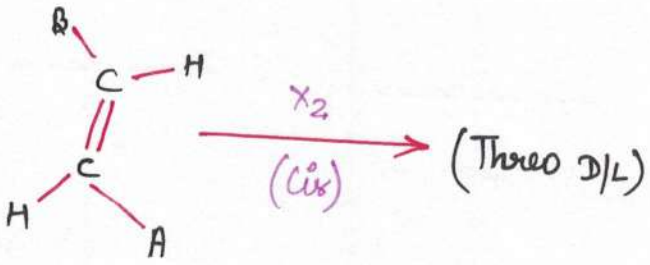
(Threo D/L)





- Stereoselective — Product oriented
- Stereospecific — Reactant oriented

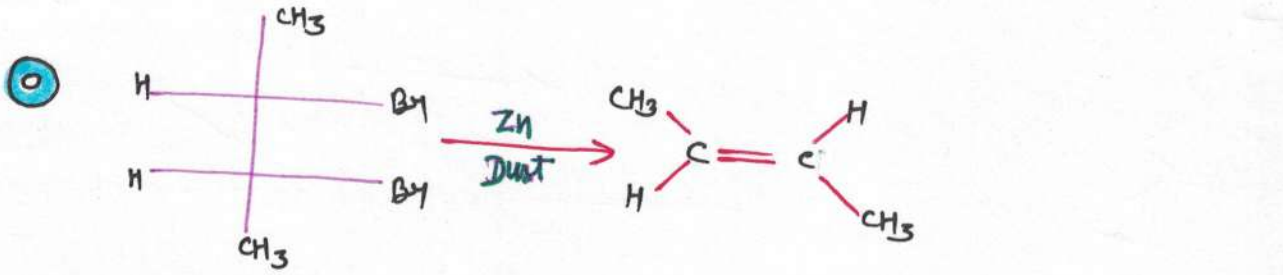


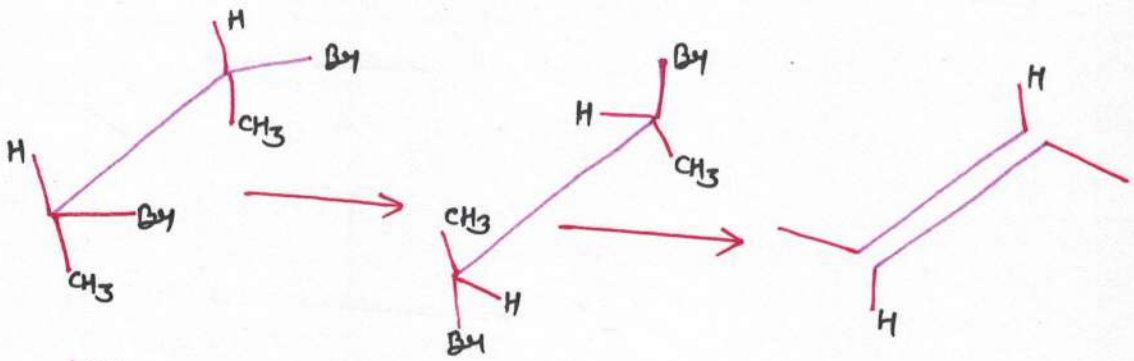


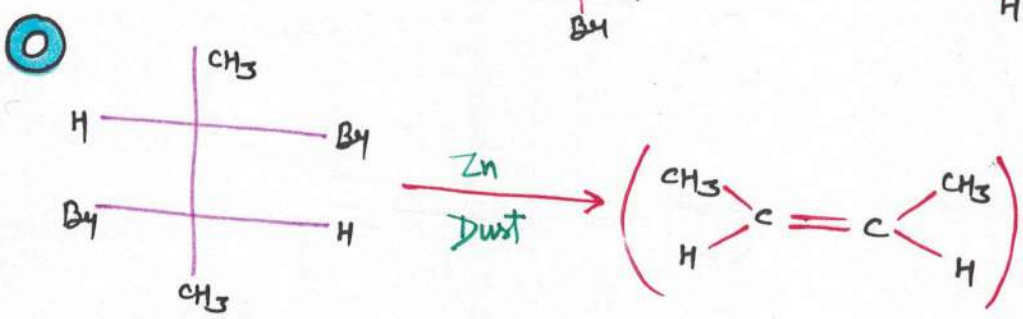
- Trans (symmetrical) —Cis→ (D/L)
- Trans (symmetrical) —Trans→ Meso
- Trans (unsymmetrical) —Trans→ Erythro d/L
- Trans (unsymmetrical) —Cis→ Threo d/L

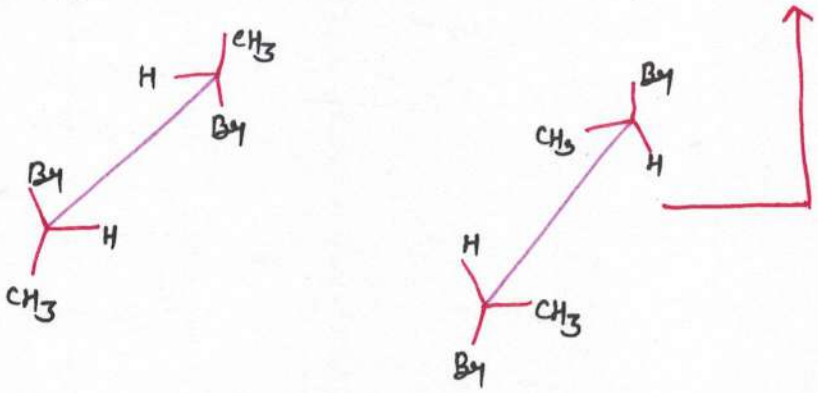
Stereochemistry - Elimination

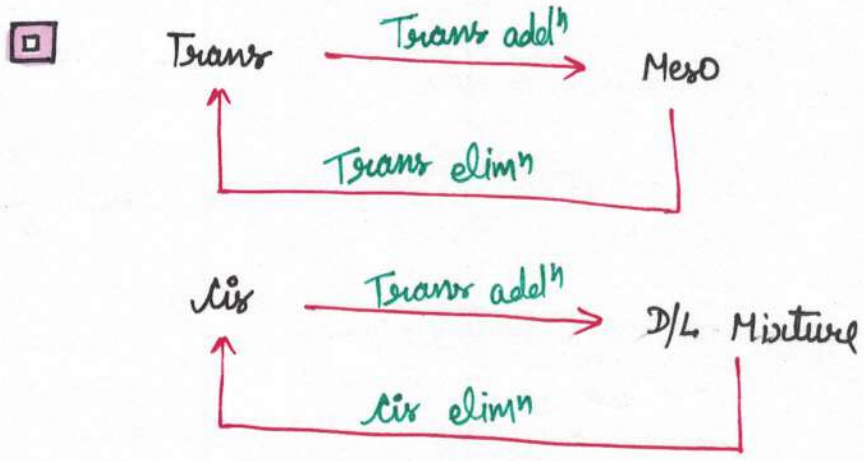
a. TRANS ELIMINATION

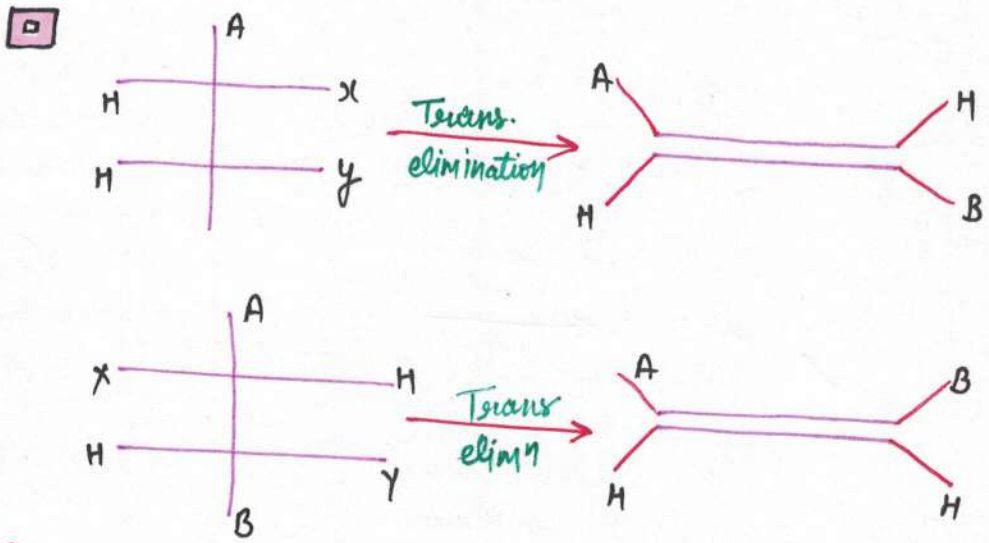


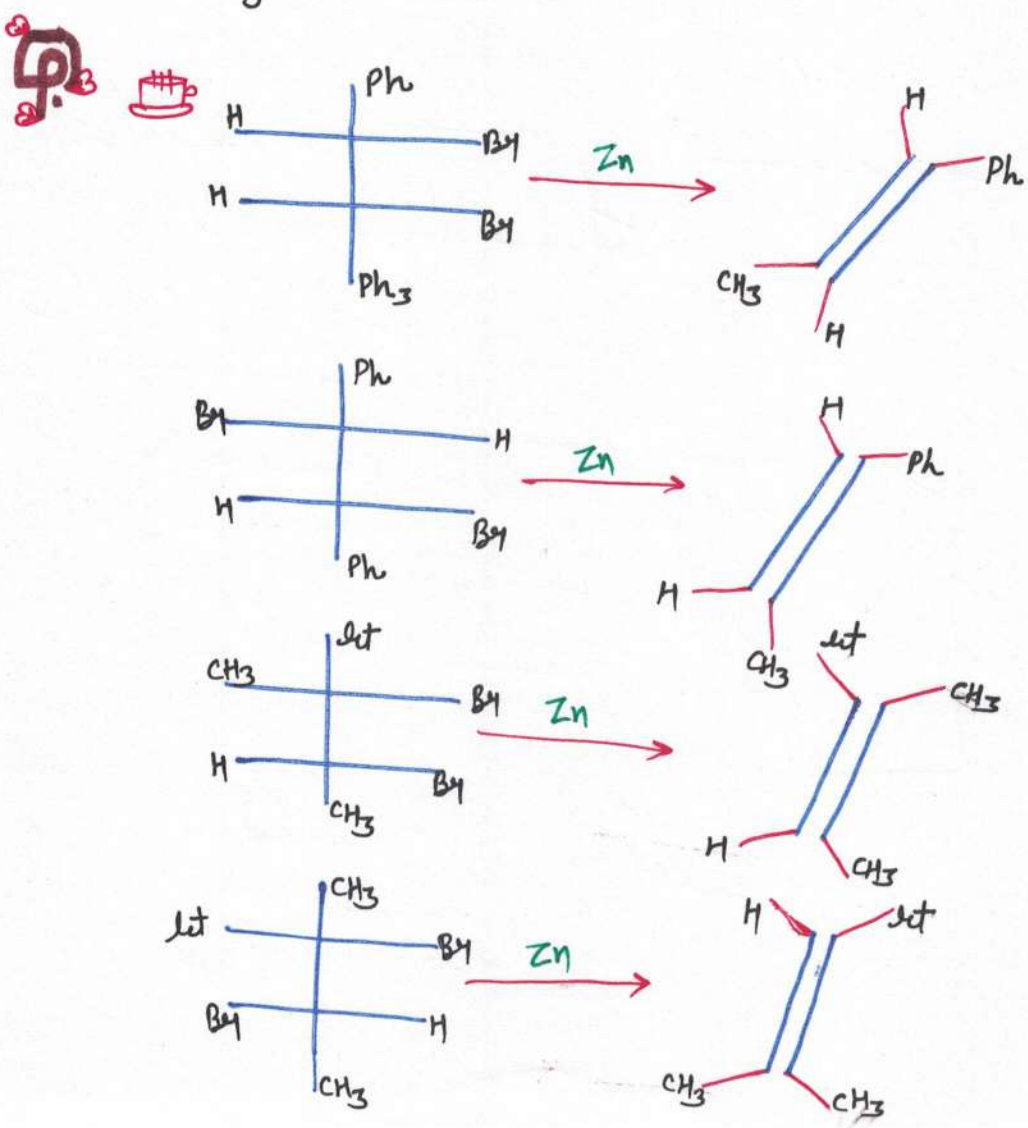


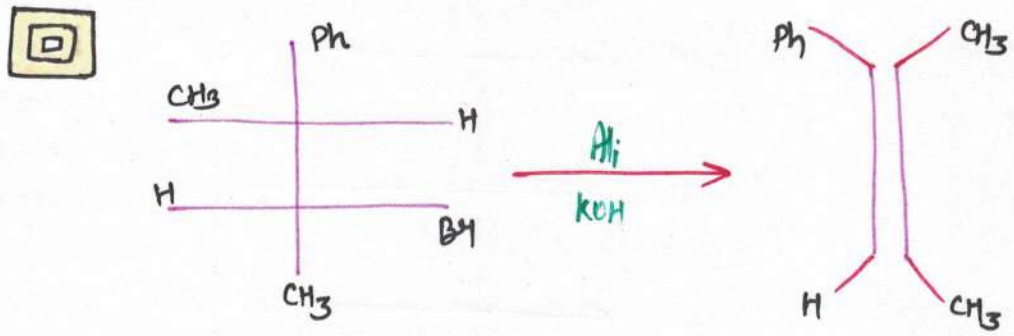


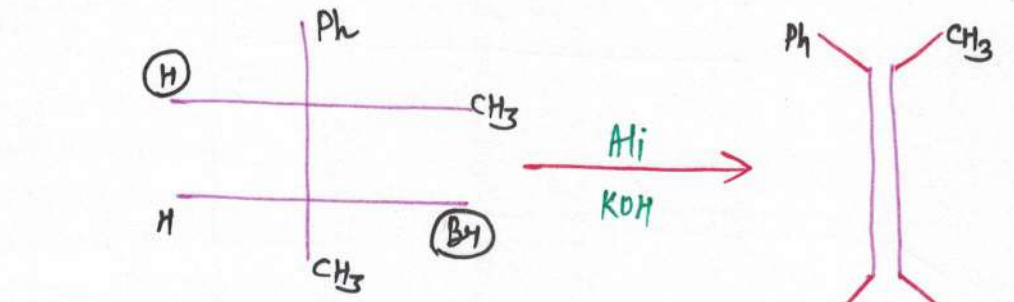


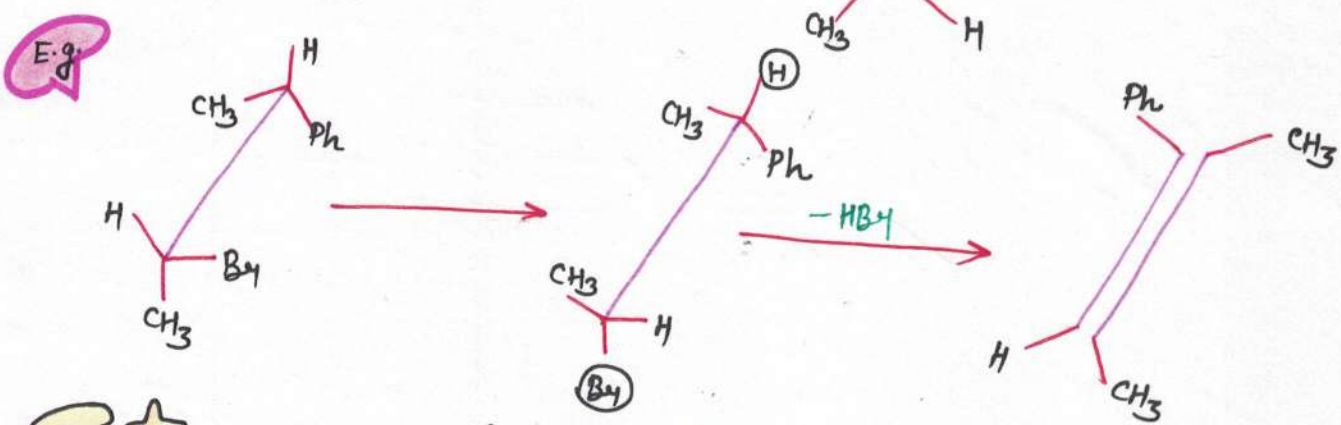




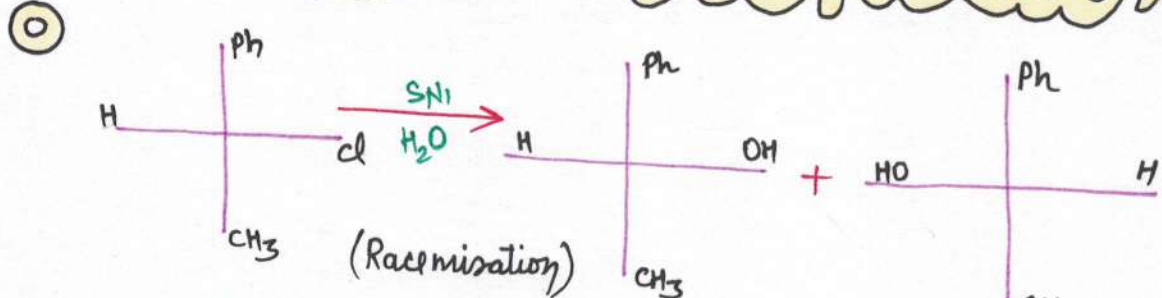


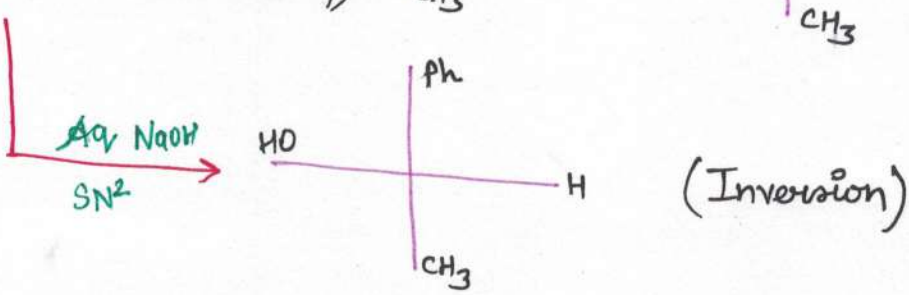




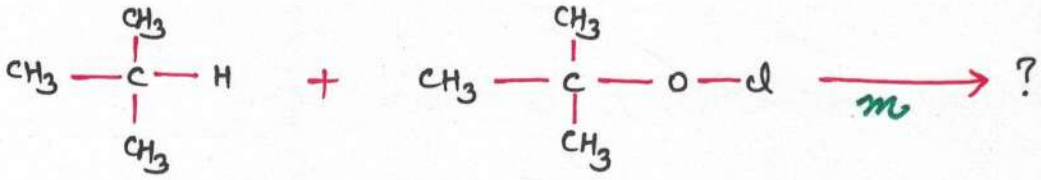


Stereochemistry – Substitution

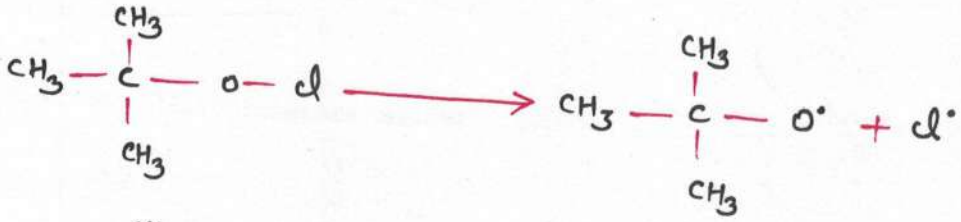




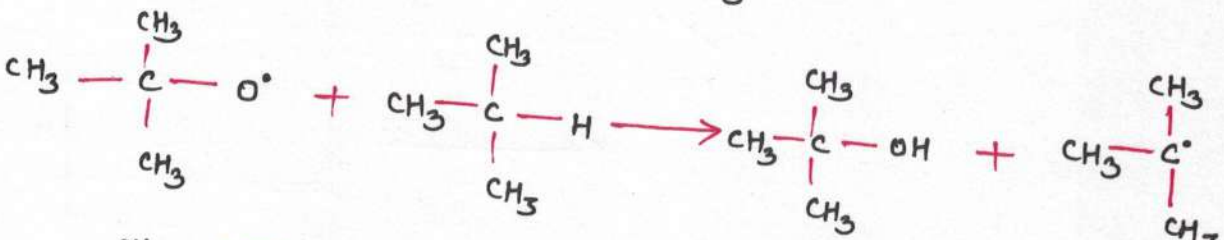
(D)



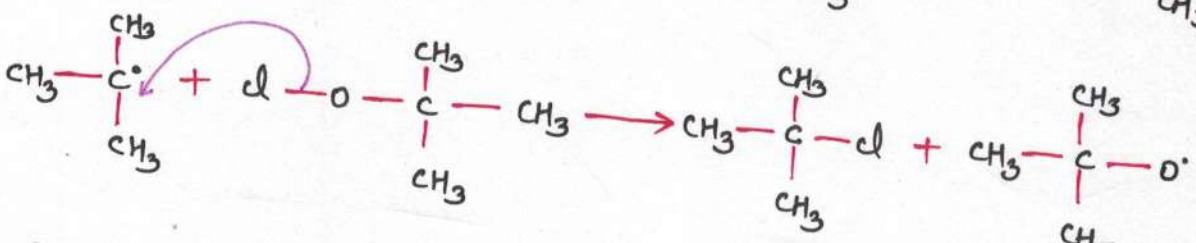
(a)



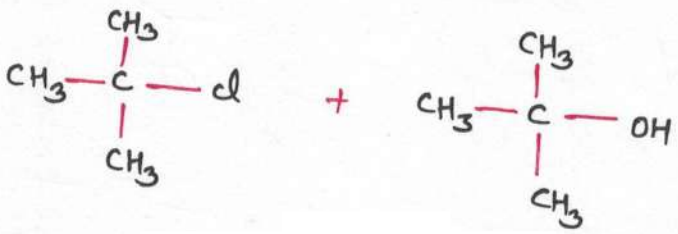
(b)



(c)



(d) Products in the reaction are :—



STRUCTURAL ISOMERISM

ISOMERISM

- Structural Isomerism
  - Positional Isomerism
  - chain Isomerism
  - Ring chain Isomerism
  - functional Isomerism
  - Meta-merism
  - Tauto-merism
- Stereoisomerism
  - Geometrical Isomerism
  - optical Isomerism

Part (I) Part (II) Part (III)

POSITIONAL ISOMERISM + CHAIN ISOMERISM

Many students are confused between the two. I'll let you understand the difference just by taking a simple example.

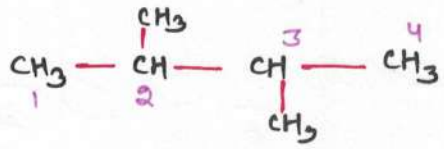
Draw all possible structural isomers for n-hexane

Ans

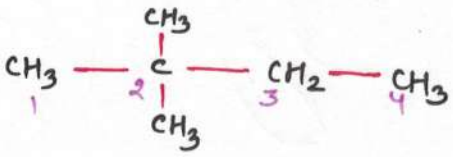
i) $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ (n-hexane)

ii) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-CH_3$ (2-methyl pentane)

iii) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$ (3-methyl pentane)

(iv) 

(2,3 - dimethyl butane)

(v) 

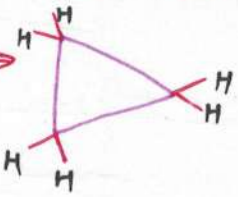
(2,2 - dimethyl butane)

[(ii)(iii)] ⟶ Positional isomers ⟵ [(iv)(v)]

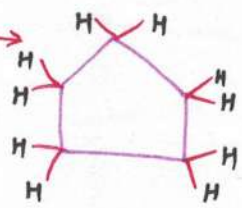
[(i)(ii)] [(ii)(iv)] [(i)(iii)] etc. are chain isomers.

RING CHAIN ISOMERISM

(i) Propene ⟶ $CH_3 - CH = CH_2$ (D.V=1); C_3H_6

cyclopropane ⟶  (D.V=1); C_3H_6

(ii) 1- Pentene ⟶ $CH_2 = CH - CH_2 - CH_2 - CH_3$ (D.V=1); C_5H_{10}

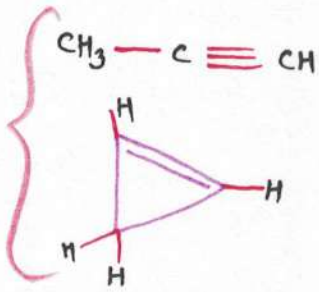
cyclopentane ⟶  (D.V=1); C_5H_{10}

Thus, alkenes (D.V=1) and cycloalkanes (D.V.=1) are ring - chain isomers.

Similarly

alkynes (D.V=2) and cycloalkenes (D.V=2) are ring - chain isomers.

E.g.

(i) 

(Propyne); C_3H_4 D.V=2

(Cyclopropene); C_3H_4 D.V=2

(Ring chain isomers)

PART-II

STRUCTURAL ISOMERISM

FUNCTIONAL ISOMERISM :- The compounds have the same molecular formula but possess different functional groups.

E.g. (i) $H_3C-CH_2-CH_2-CH_2-OH$ (1-butanal) Alcohol

(A) $C_4H_{10}O$ (ii) $H_3C\ CH_2\ O\ CH_2\ CH_3$ (diethyl ether) Ether

Thus, (i) and (ii) are functional isomers.

(i) $H_3C\ CH_2\ CH_2\ OH$ (1-Propanal) Alcohol

(B) C_3H_8O

(ii) $CH_3\ O\ CH_2\ CH_3$ (methoxy ethane) Ether

Thus, (i) and (ii) are functional isomers.

(i) $CH_3\ C(=O)\ CH_3$ (Acetone) Ketone

C_3H_6O

(ii) $CH_3\ CH_2\ C(=O)\ H$ (Propionaldehyde) Aldehyde

Thus i and ii are functional isomers.

(Alcohols and ethers); (ketones and aldehyde) are functional isomers.

(i) $CH_3-CH_2-CH_2-C(=O)-OH$ (Butanoic acid) carboxylic acid

C_4H_8O

ii $CH_3-CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3$ (Ethyl ethanoate) ester

Thus carboxylic acids and esters are functional isomers.

METAMERISM

E.g i $\left(CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3\right)$ 2 pentanone

$\left(CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3\right)$ 3-pentanone

- Metamerism exists due to the unequal distribution of carbon atoms on either side of the functional groups. They can show positional isomerism too.
- The isomers are known as metamers.

$CH_3-C\equiv C-CH_2-CH_2-CH_3$ (2-hexyne)

$CH_3-CH_2-C\equiv C-CH_2-CH_3$ (3-hexyne)

The isomers are mekamers and positional isomers.

$CH_3-CH=CH-CH_2-CH_2-CH_3$ (2-hexene)

$CH_2=CH_2-CH_2-CH_2-CH_2-CH_3$ (Hexene)

The isomers are metamers and positional isomers.

(PART- III)

STRUCTIONAL ISOMERISM

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

  (Keto) (enol)

- $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$ Draw the tautomers

  i. 

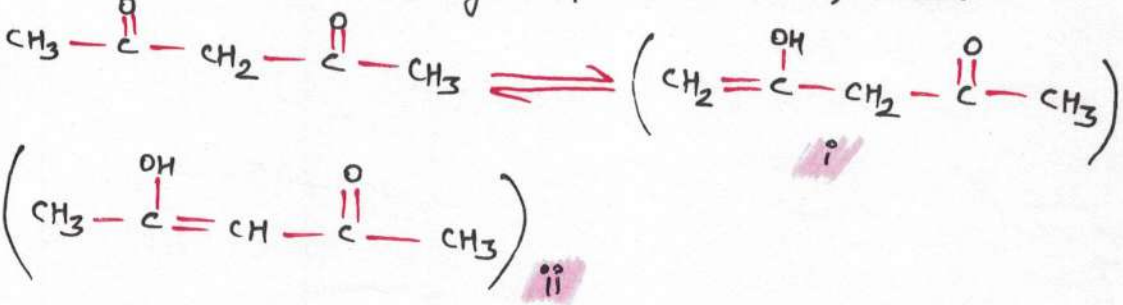
  ii. 

  Thus ii is more stable than i

- 

  (Keto) (Phenol)

  In phenol; the aromatically is present. Thus, stable.

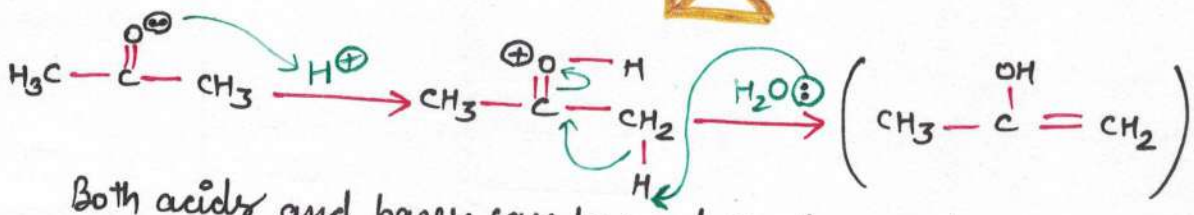
- 

ii is more stable form of enol.

o Thus, the tautomers are in equilibrium.

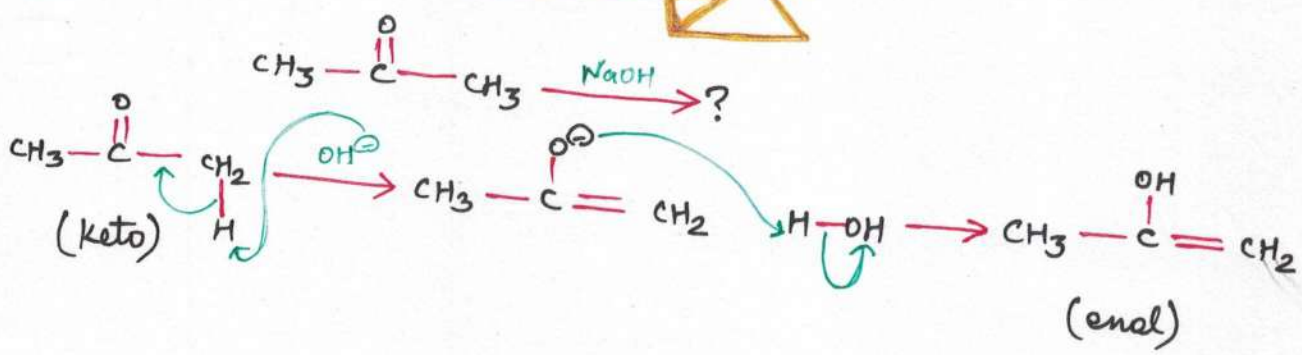
The resonance structures aren't in equilibrium.

ACID CATALYSED TAUTOMERISM



Both acids and bases can be used to form tautomers.

BASE CATALYSED TAUTOMERISM



DIPOLE MOMENT

It measures ionic character in covalent compounds or bond polarity [bond moment] in a covalent compound.

Dipole moment is a vector quantity.

E.g H Cl E·N of Cl E·N of H

Bond pair of e⁻ shifted towards Cl atom. Cl acquire partial -ve charge (δ-) and H acquires partial +ve charge (δ+).

$\overset{\delta+}{H}\!-\!\overset{\delta-}{Cl}$ (EN of Cl > EN of H)

$|\vec{\mu}| = q \times l$

	CGS	MKS
charge =	4.8×10^{-10} esu	1.6×10^{-19} C
l =	$1A^\circ = 10^{-8}$ cm	$1A^\circ = 10^{-10}$ cm

$\mu = n \times e \times l$

$\mu = n \times 4.8 \times 10^{-1}$ esu $\times\ l \times 10^{-8}$ cm

$4.8 \times n \times l \times 10^{-18}$ esu · cm

$4.8 \times n \times l \times$ Debye

Q. $\mu_{LiCl} = ?$ $Li-Cl \Rightarrow (l) = 1.2A^\circ$

n = charge on C.A. 1

$\Rightarrow 4.8 \times n \times l \times D \Rightarrow 4.8 \times 1 \times 1.2 \Rightarrow 5.76\,D$

QUE $\mu_{NaCl} = ?$

$NaCl = (l) = 1.5 A^\circ$

$\eta =$ change on C.A. $= L$

$\mu = 4.8 \times 1 \times 1.5$

$= 7.200 D$

QUE $\mu_{BeCl_2} = ?$

$Be-Cl = 1.5$

$\eta = 2$

$\mu = 4.8 \times 2 \times 1.5$

$4.8 \times 3 = 14.4 D$

FACTORS AFFECTING DIPOLE MOMENT

ELECTRO NEGATIVITY

$\mu \propto \Delta EN$

$H-F > H-Cl > H-Br > H-I$

$C-F > C-Cl > C-Br > C-I$

STRUCTURE OF MOLECULE

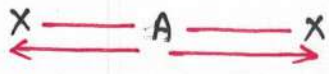
SYMMETRICAL STRUCTURE

μ of all diatomic (homoatomic) molecule is equal to zero.

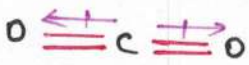
$H_2, F_2, O_2, Cl_2, Br_2, N_2$

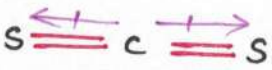
(ii) (a) μ of AX_2 type molecule is 0. (sp^2 hybridisation if no lone pair present on central atom)

Dipole moment of all symmetrical str. 0 if central atom has no lone pair of $e^{\ominus}$.

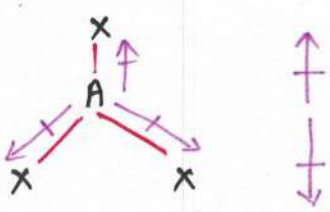


(linear)

E.g. 



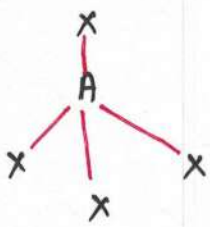
(b) A X_3 type



$\mu = 0$ (Trigonal planar)

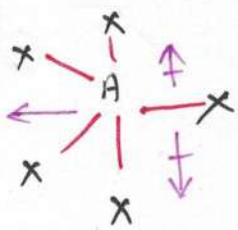
E.g. BF_3, SO_3, BCl_3

(c) AX_4 type



(tetrahedral)

(d)

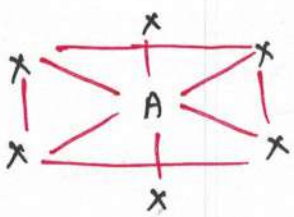


Maxial 0 Meq 0

(trigonal bipyramidal)

(e) AX_6 Type

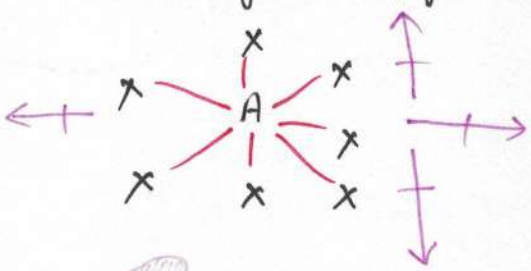
(octahedral)



E.g. SF_6

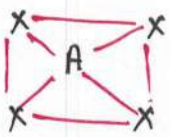
(f) AX_7 type

str. Pentagonal bipyramidal



E.g. IF_7 $\mu = 0$

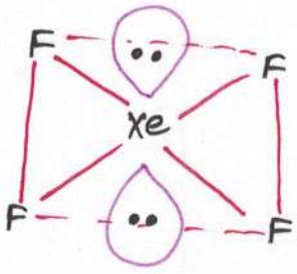
(g) AX_4 (dsp^2)



square planar

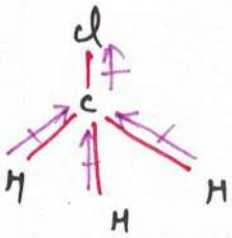
(h) AX_4L_2

XeF_4



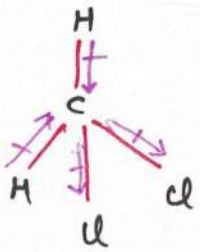
$\mu = 0$

(B) Dipole moment of asymmetrical structure is not equal to zero.



$\mu = 1.98\ D$

>



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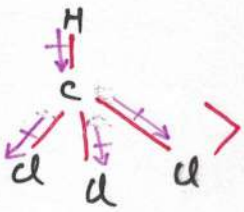

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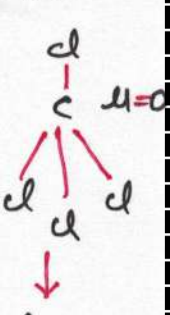


AX_4 type

$(\mu = 0)$

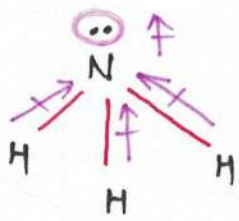
$\mu_{CH_3Cl} > \mu_{CHCl_3}$

Direction of dipole moment

- Less EN to more EN
- central atom to lone pair

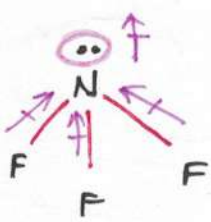
$CH_3Cl > CH_2Cl > CHCl_3 > CCl_4$

(C) If lone pair present on central atom, μ 0 as no. of lone pair increases on central atom μ also increases.



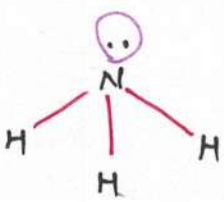
$\mu = 1.12\ D$

>



$\mu = 0.12\ D$

$\mu_{NH_3} > \mu_{NF_3}$



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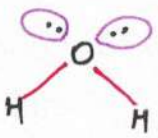
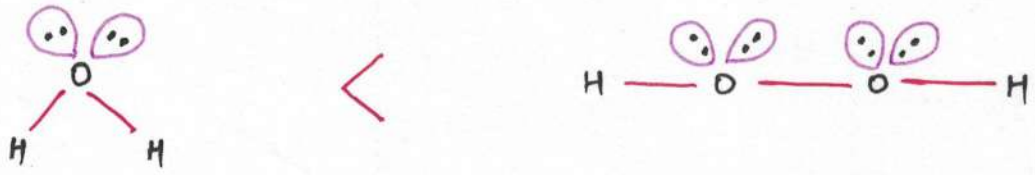
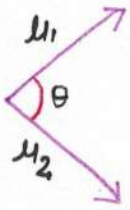


as no of l.p. increases
μ increases



BOND ANGLE

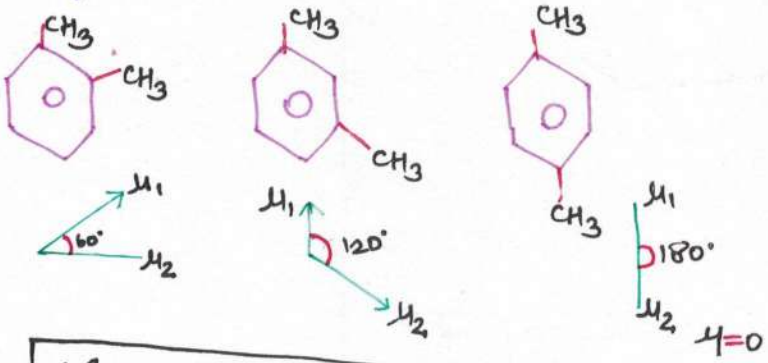
Generally $\mu \propto \frac{1}{\text{Bond Angle}}$



$$\mu_R = \sqrt{\mu_1^2 \; \mu_2^2 \; 2\mu_1\mu_2\cos\theta}$$

$$\mu \propto \frac{1}{\theta}$$

Position of substituents



$$\mu_e = \sqrt{\mu_1^2 + \mu^2 + 2\mu_1\mu_1 \cos 60^\circ}$$

$$= \sqrt{3}\mu$$

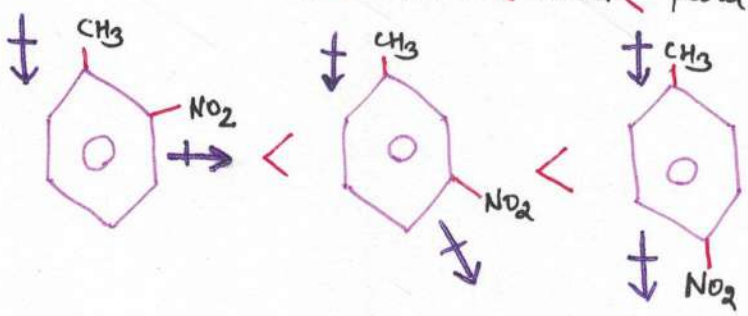
$\mu - \mu$

When same group attached on Benzene ring. (ERG/EWG)

μ = ortho > meta > para

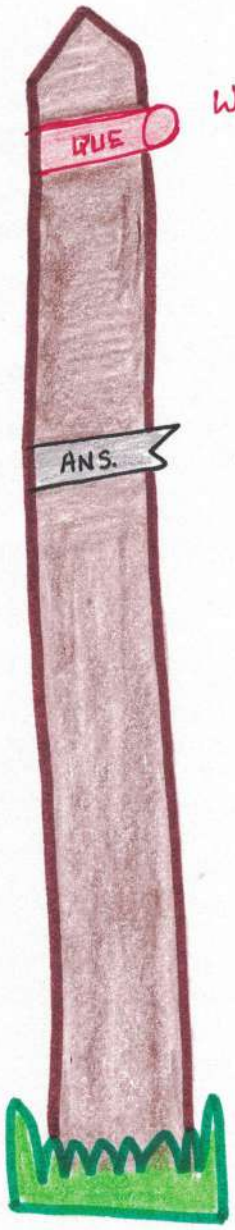
But when opposite group, attached on Benzene group (ERG and EWG)

μ = ortho < meta < para

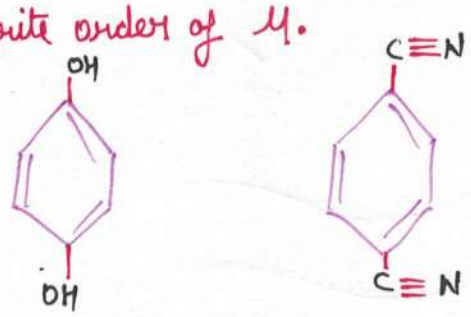


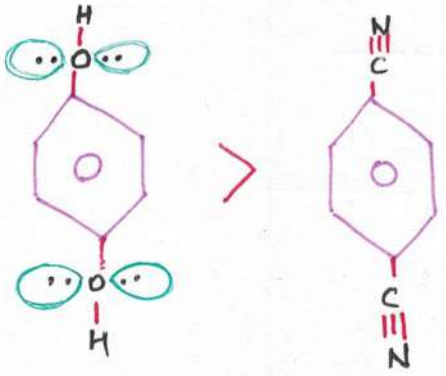
CH_3 is ERG

NO_2 is EWG



Write order of μ.



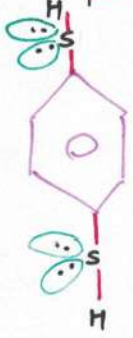


(C≡N is line on str.)

$\mu \neq 0$

$\mu \neq 0 \Rightarrow$

$\mu = 0$



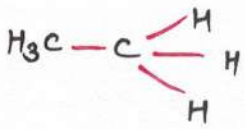
$\mu \neq 0$

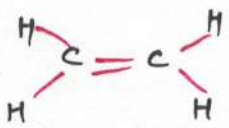
HYBRIDISATION

As % of s character increase in hybridisation dipole moment decreases.

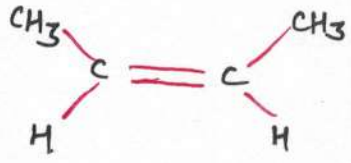
sp^3 > sp^2 > sp

Alkane Alkene Alkyne





generally dipole moment of cis isomer is more than trans isomer.



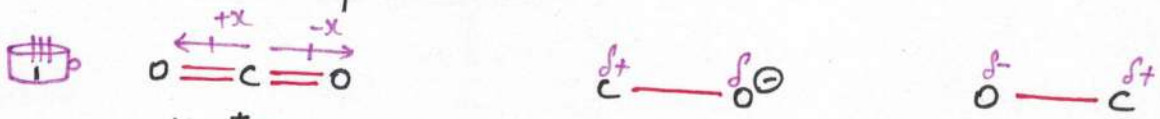
cis

trans

$\mu_{cis} > \mu_{trans}$

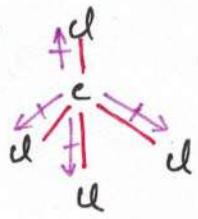
APPLICATION OF DIPOLE MOMENT

1. Polar and Non-polar compounds for finding the polarity of a compound we check its dipole moment.



μ net = $+x - x$ = zero

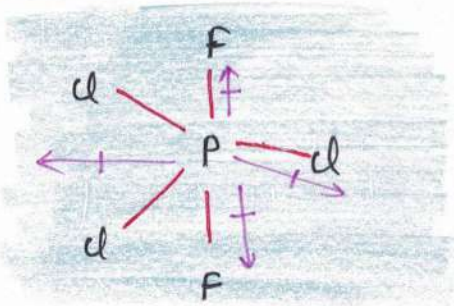
non-polar compound having polar bond.

2. 

μnet Zero

(due to symmetrical structure non-polar compound)

3. PCl_3F_2



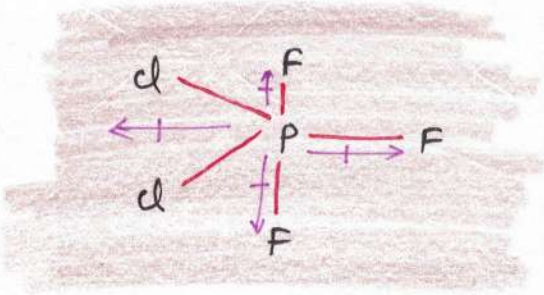
$\mu_{eq} = 0$

$\mu_{eq} = 0$

$\mu_{net} = 0$

non-polar compound

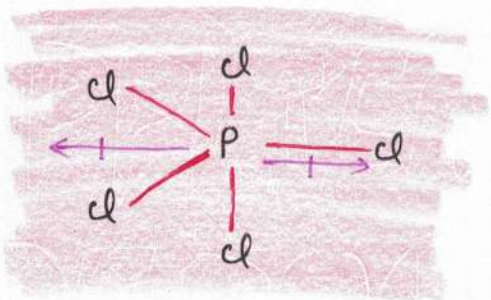
4. PF_3Cl_2



μ_{axial} = zero
(F-F will be 0)

$\mu_{eq} = x - y$ $\quad \mu_{net} \neq 0$
polar compound

5. PCl_5

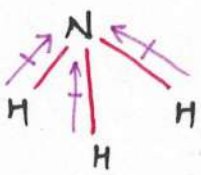


$\mu_{axial} = 0$
$\mu_{eq} = 0$
μ_{net} = zero
non polar compound

if $\mu_{net} = 0$, compound is non-polar.
if $\mu_{net} \neq 0$, compound is polar.

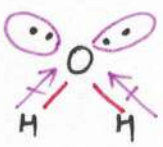
if net dipole moment of molecule is equal to zero, compound is non-polar.
But if $\mu_{net} \neq 0$, compound is polar.

6.



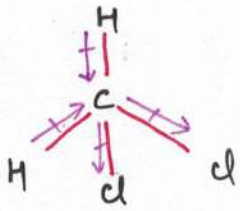
$\mu \neq 0$ unsymmetrical
polar compound

7.



$\mu \neq 0$
polar compound
(H_2O)

7. CH_2Cl_2



$\mu \neq 0$ (μ_{net} is not balanced)
Polar compound

Polar comp. means the one in which (net) electron density shifts towards one dirn. electron density ↓ $\delta+$, electron density ↑ $\delta-$.

% age ionic character in covalent compound.

$$\mu_{theoritical} = 4.8 \times n \times l \text{ Debye}$$
$$= 16 \times 10^{-18} c \times n \times l \times 10^{-10} m$$

% ionic character $= \frac{\mu \text{ observed}}{\mu \text{ theoritical}} \times 100$

μ observed $= \mu$ given $= \mu$ experimental

calculate the % ionic character in NaCl, if l 1.5A° and $\mu_{ob} = 6D$

$\mu_{ob} = 4.8 \times 1 \times 1.5\ D$

$= 7.20$

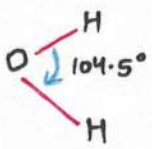
% ionic character $= 6 \times 100$

$= 2.2$

$= \frac{6000}{72}$

$= 83.33\%$.

BOND MOMENT



$\mu_e = 1.85D$

$\mu_{OH} = ?$

$\cos 52.25 = 0.6189$

$\mu_R^2 = \mu^2 + \mu^2 + 2\mu^2 \cos 104.5°$

$\mu_R^2 = 2\mu^2 + 2\mu^2 \cos(110)$

$\mu_R^2 = 2\mu^2 (1 + 0)$

$\mu_R^2 = 2\mu^2$

$(1.85)^2 = 2\mu^2$

$1 + \cos 2A = 2\cos^2 2A$

$\frac{1.85 \quad 1.85}{2(1 + \cos 1.10)} = \mu^2$

$\mu = \frac{1.85}{\sqrt{2\ (1 + \cos 104.5)}} = \frac{1.85}{\sqrt{2} \cdot \cos 52.25}$

$\mu = \frac{0.925}{0.6189 + 2} = \frac{0.925}{0.6189\sqrt{2}}$

$\mu = \frac{0.925}{0.6189 \times 1.414} = \frac{0.925}{0.7} = 1.43 \simeq 1.5$

To decide position of substituents

if same group is attached on benzene ring, $\mu_{ortho} > \mu_{meta} > \mu_{para}$.

But if opposite group is attached, then

$$\mu_{para} > \mu_{meta} > \mu_{ortho}$$

OPPOSITE GROUP :- one is electron releasing group and one is electron with drawing group.

QUE

correct increasing order of dipole moment of

i. CH_3F, CH_3Cl, CH_3Br, CH_3I

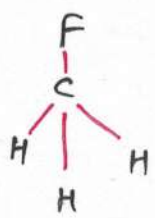
ii. NH_3, NF_3, BF_3

iii. PF_3, PH_3

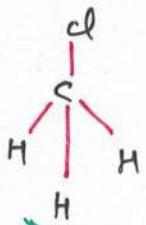
iv. CO, NO, CN

ANS...

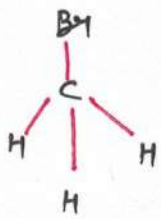
i. CH_3F



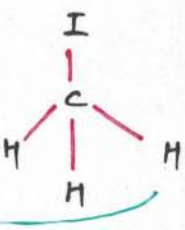
CH_3Cl



CH_3Br



CH_3I



$\mu \propto l$

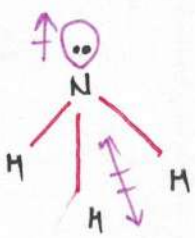
bond length of C-F is small.

$\mu \propto$ EN of bonded atom

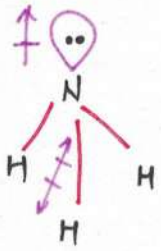
Exception:- EN is dominating over bond length.

$CH_3F < CH_3Cl$

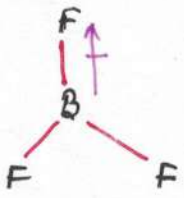
ii.



$\mu_R = 1.12\ D$

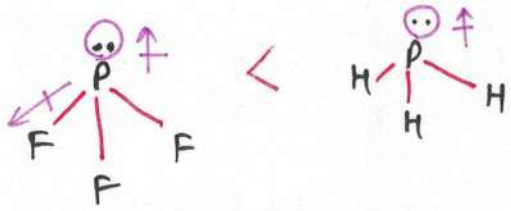


$\mu_R = x - y = 0.12\ D$



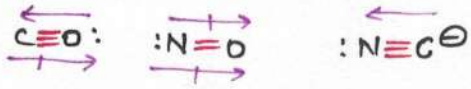
$\mu = 0$ symmetrical

(iii) PF_3 < PH_3



$\mu = x - y$ $\quad\quad$ $\mu = x + y$

(iv) CO, NO^+, CN^-



$CN^{\ominus}$ >

B.O = 3 3 3

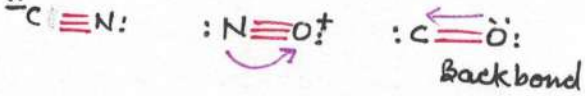
are isoelectronic species

$B.l \alpha \frac{1}{B.O}$

B.l ↓

Order $\quad$ CN^- $\quad$ NO^+ $\quad$ CO

0.51 D $\quad$ .22 D $\quad$ 0.15 D



Backbond