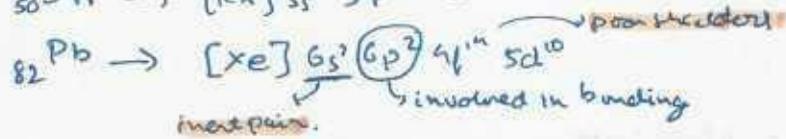
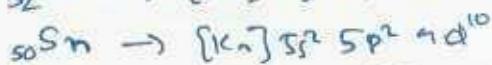
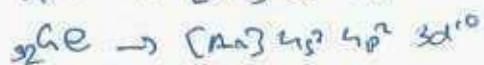
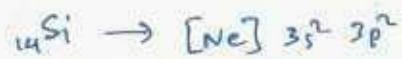




NAME: \_\_\_\_\_ STD.: \_\_\_\_\_ SEC.: \_\_\_\_\_ ROLL NO.: \_\_\_\_\_ SUB.: \_\_\_\_\_

# CARBON FAMILY

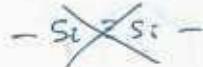
14<sup>th</sup> Group



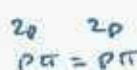
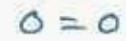
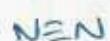
only possible in 2<sup>nd</sup> period element

Carbon, Catenation, Tetravalency ;  $\text{p}\pi-\text{p}\pi$  multiple bond

In silicon,  $\text{p}\pi-\text{p}\pi$  multiple bond not possible.



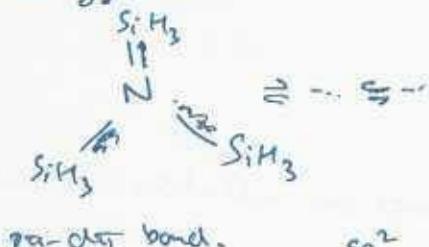
Si → can form  $\text{p}\pi-\text{d}\pi$  bond  
with F, O, N.



Because of large size of orbitals, they are far away from each other and thus  $\text{p}\pi$  bonding not possible.

→ sometimes with Cl.

$\text{N}(\text{SiH}_3)_3$ ,  
Tetrasilyl amine

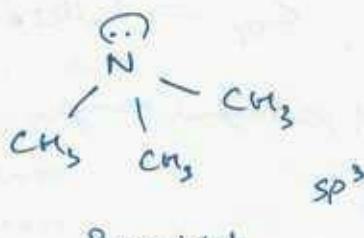


Triangular planar

back bonding

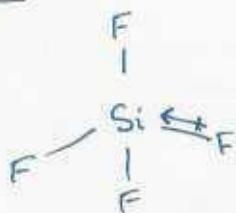
$\text{N}(\text{CH}_3)_3$ ,

Trimethyl amine



Pyramidal

$\text{SiF}_3$

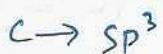


# INERT PAIR EFFECT

Stability of +4 oxidation state decreases.

## ALLOTROPIES

### Diamond



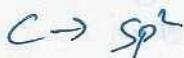
$$\rho = 3.5 \text{ g/ml}$$

Non conductor

Giant polymeric structure

High melting point.

### Graphite

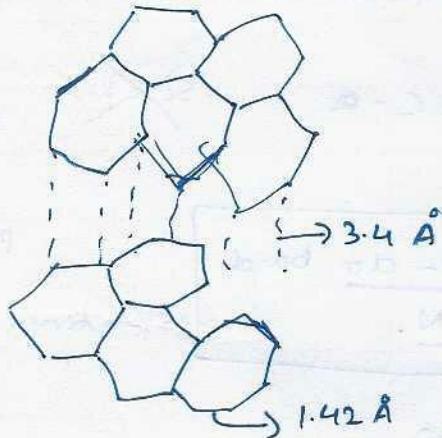


hexagonal sheet structure

Conductor

Less density

Thermodynamically more stable.



Soot:  $C_{60}$ ,  $C_{50}$ ,  $C_{56} \rightarrow$  Fullerenes

Hexagonal rings and pentagonal rings.

20 - hexagonal rings

12 - pentagonal rings

Pentagonal rings are attached to only hexagonal rings.

Hexagonal rings are attached to both.

## CARBIDES

Attached to less electronegative element: Binary compound

1. Salt like (Ionic) carbides
2. Covalent carbides
3. Interstitial carbides.

# SILICONES

Organic silicone polymers.



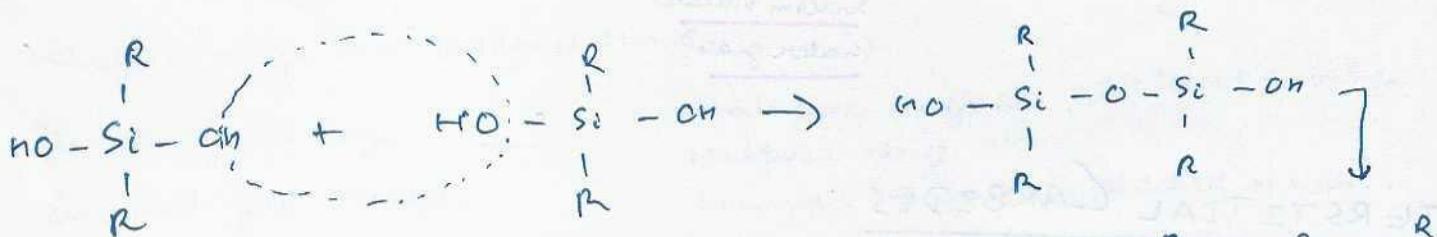
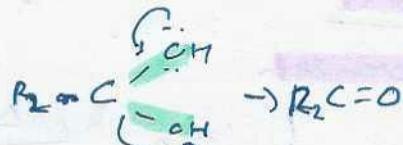
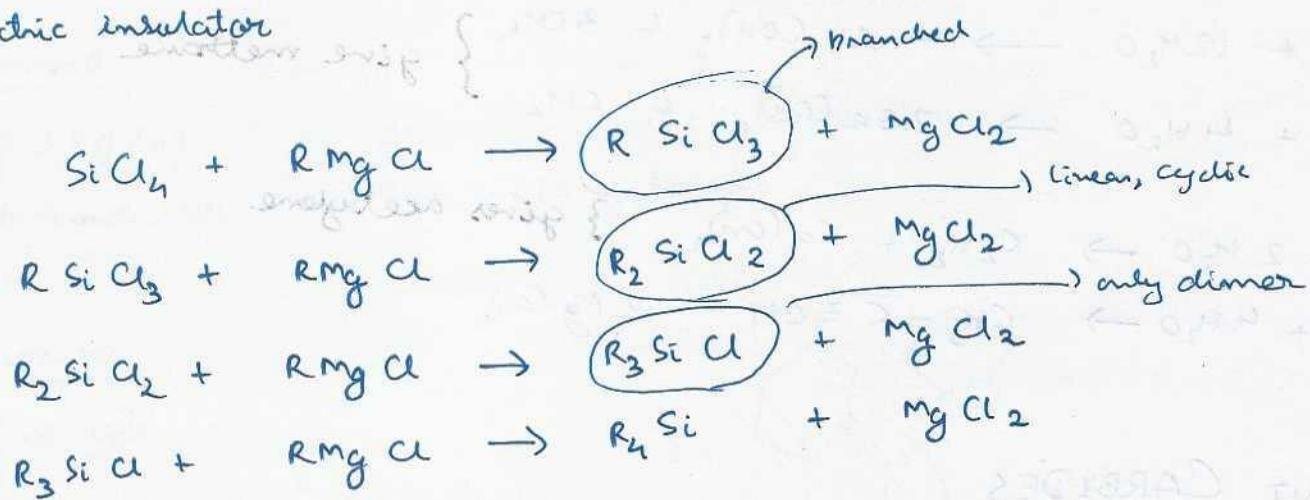
→ Inorganic polymer

water resistant

heat resistant

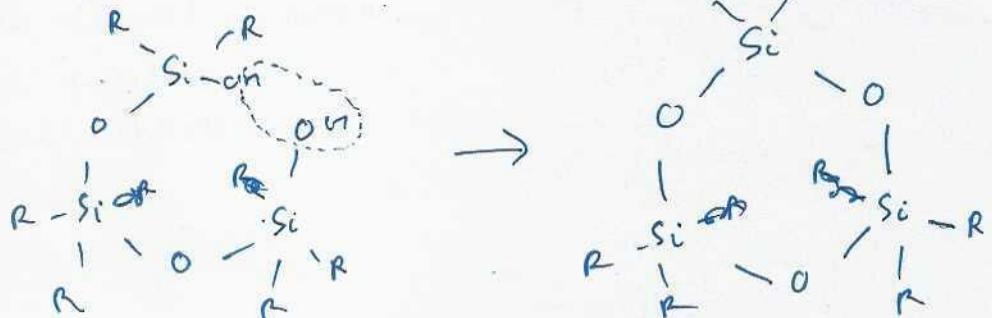
electric insulator

Backbone made with Si.



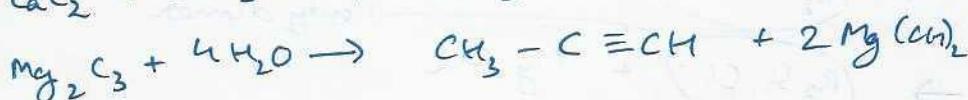
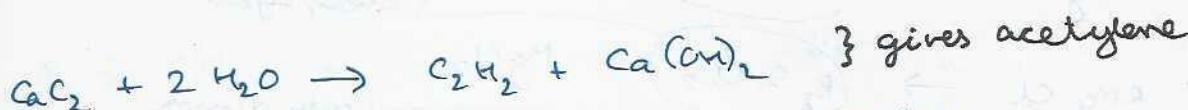
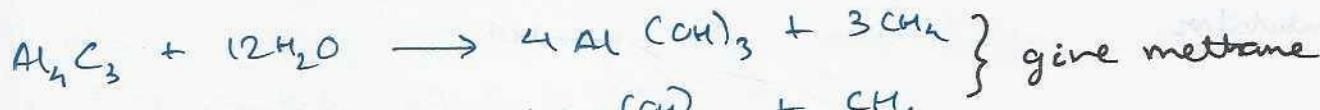
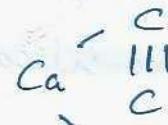
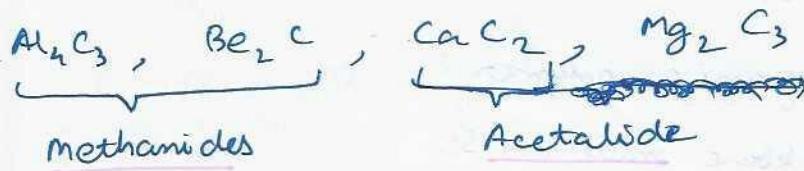
Linear polymers.

As they are surrounded by alkyl groups (hydrophobic)  
they are water resistant.

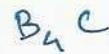


## IONIC CARBIDES

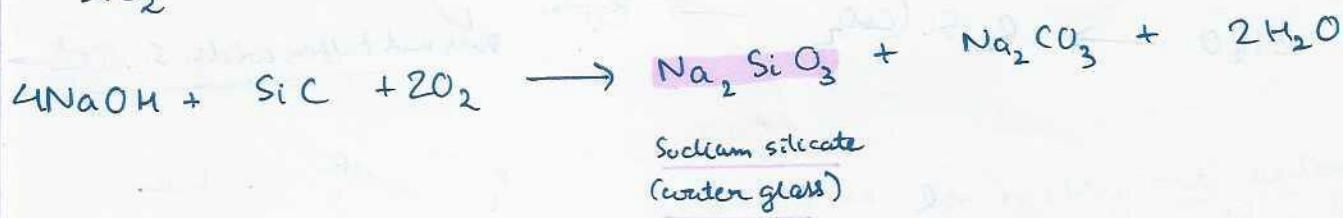
Formed by Be, Al, Ca, Mg



## COVALENT CARBIDES



Carborane dimer



## INTERSTITIAL CARBIDES

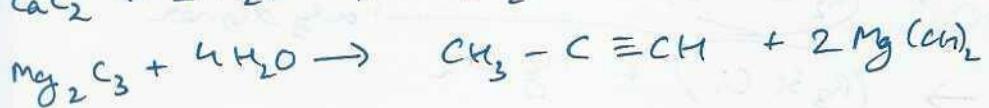
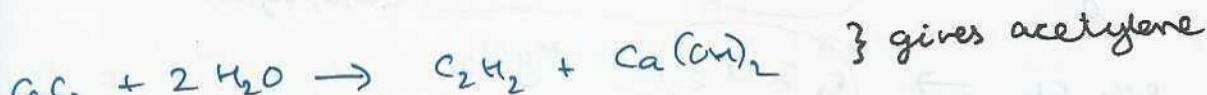
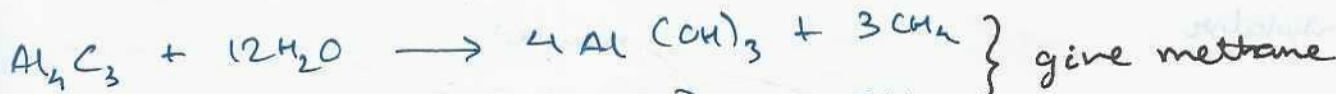
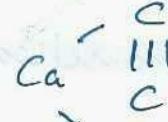
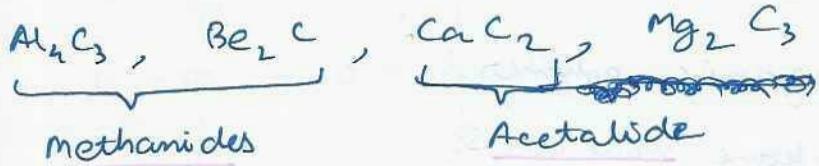
Formed by transition elements.

Carbon present in interstitial space.

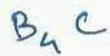
Octahedral voids.

## IONIC CARBIDES

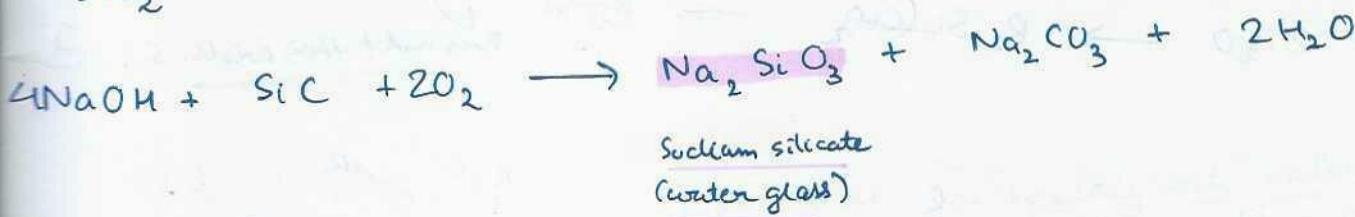
Formed by Be, Al, Ca, Mg



## COVALENT CARBIDES



Carborane



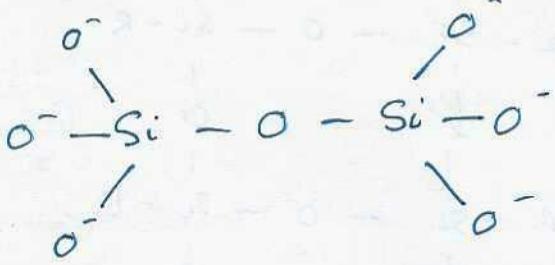
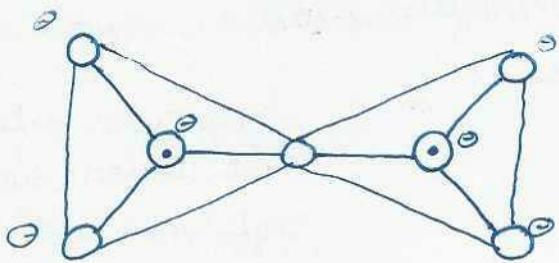
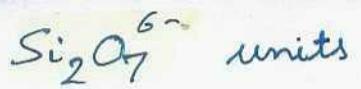
## INTERSTITIAL CARBIDES

Formed by transition elements.

Carbon present in interstitial space.

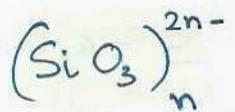
Octahedral voids.

## 2. Pyrosilicate

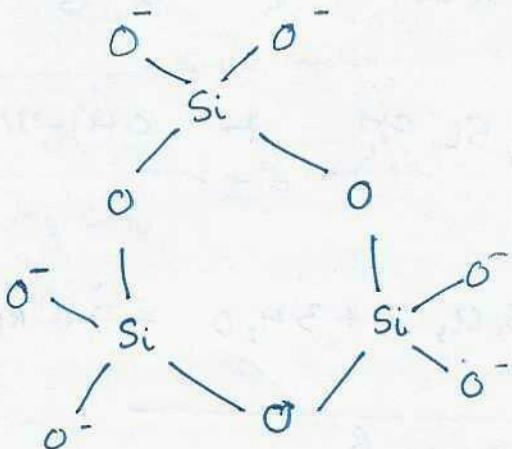
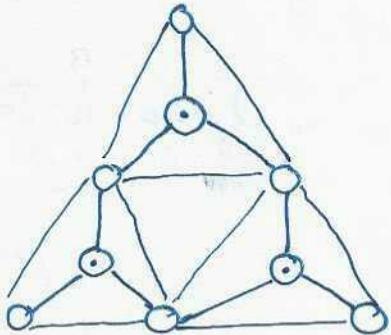
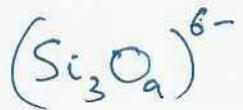


Per tetrahedron, one oxygen atom is shared.

## 3. Cyclic silicates

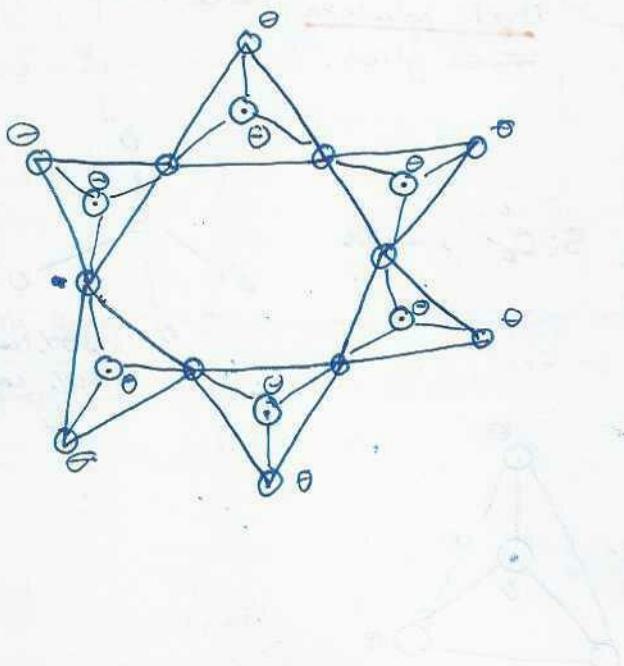
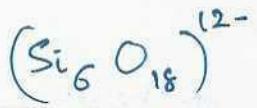


e.g. if  $n=3$

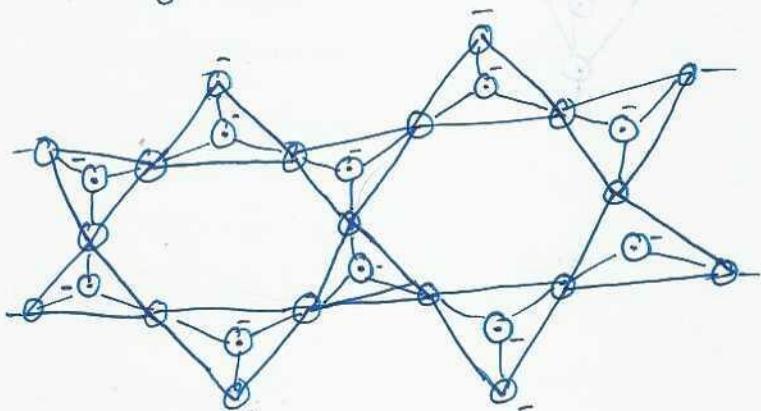
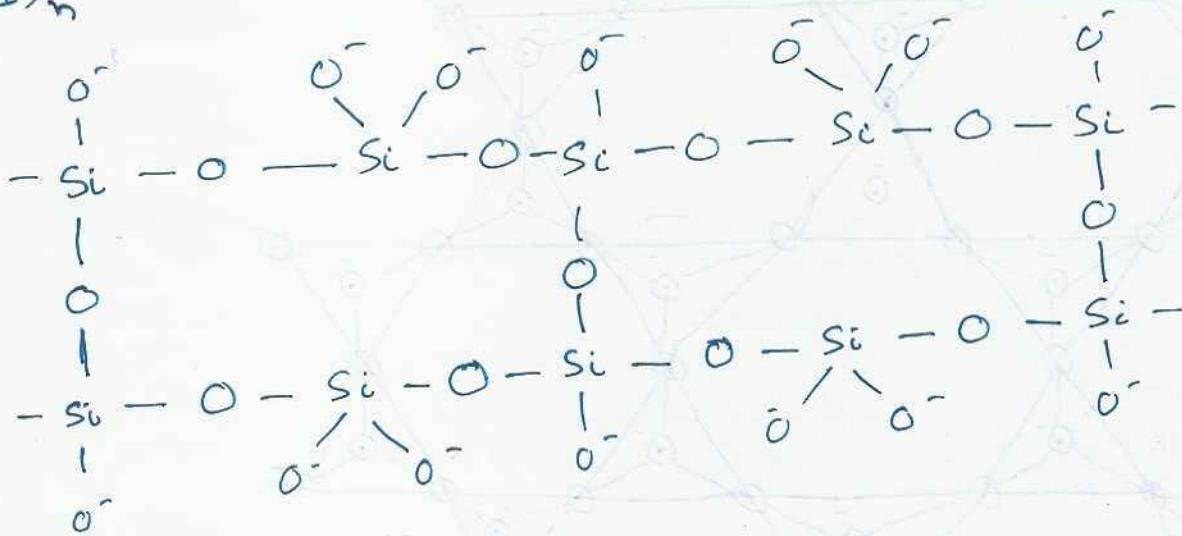
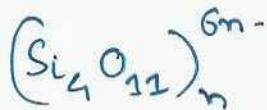
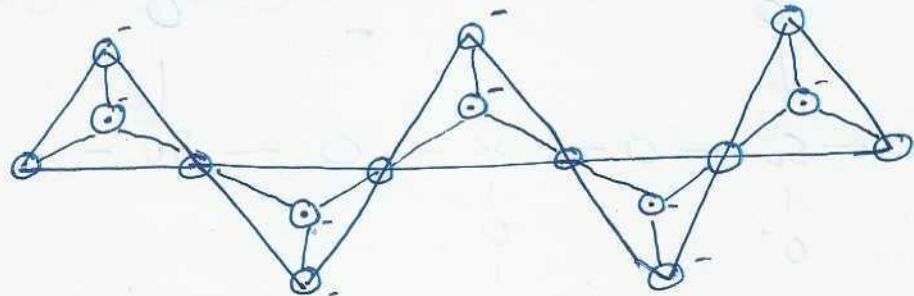
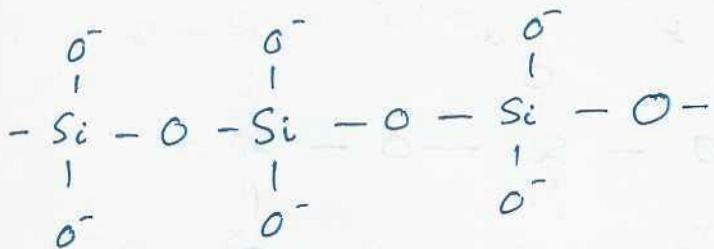
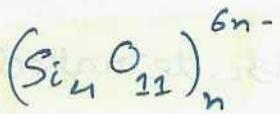
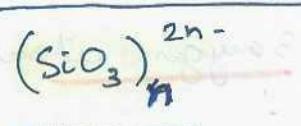


Each tetrahedron, two oxygen atoms are shared.

e.g. if  $n=6$

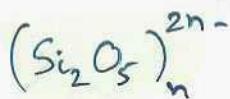


## 41. Chain Silicates

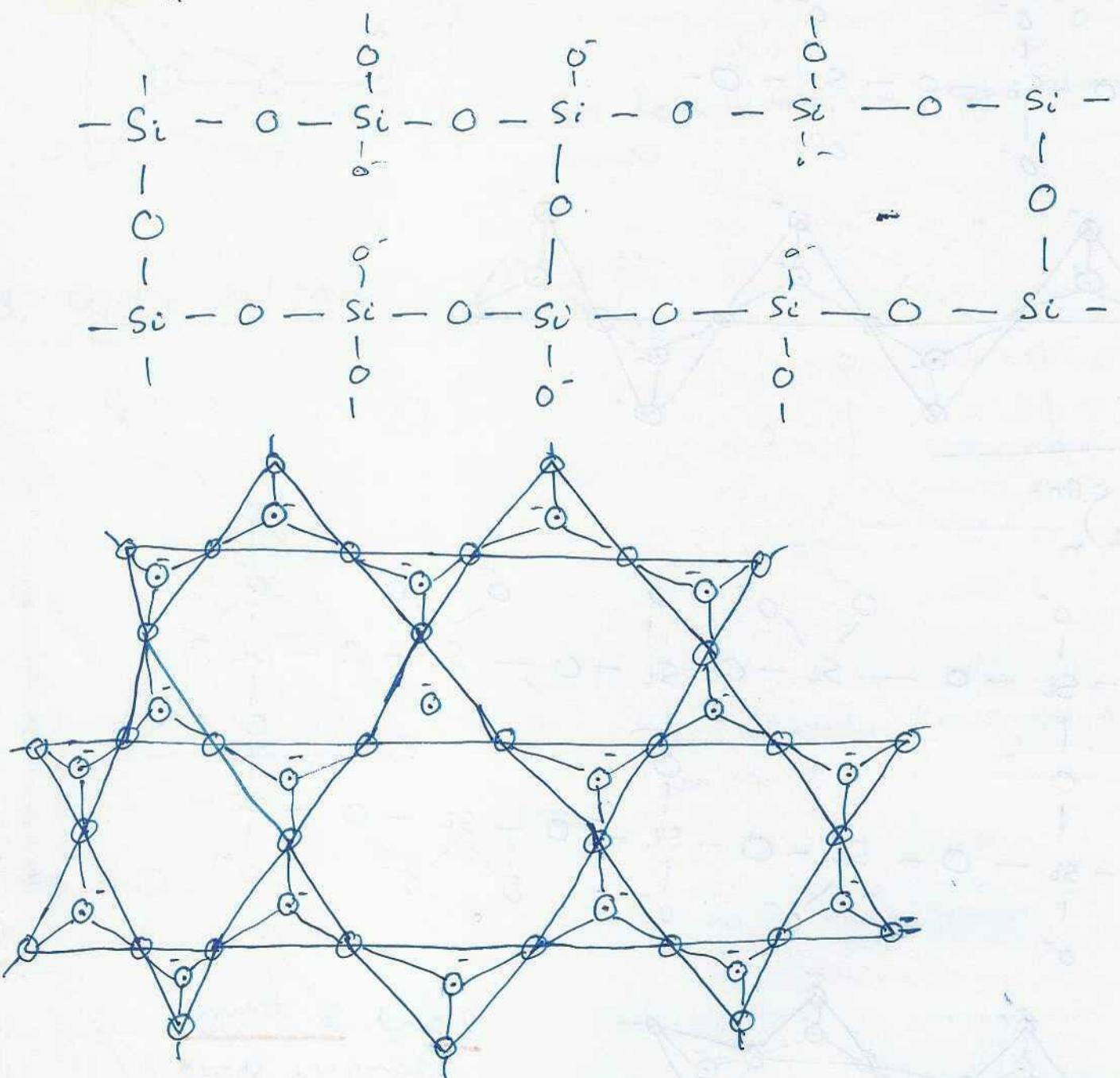


2 and 3 oxygen atoms are shared per tetrahedron.

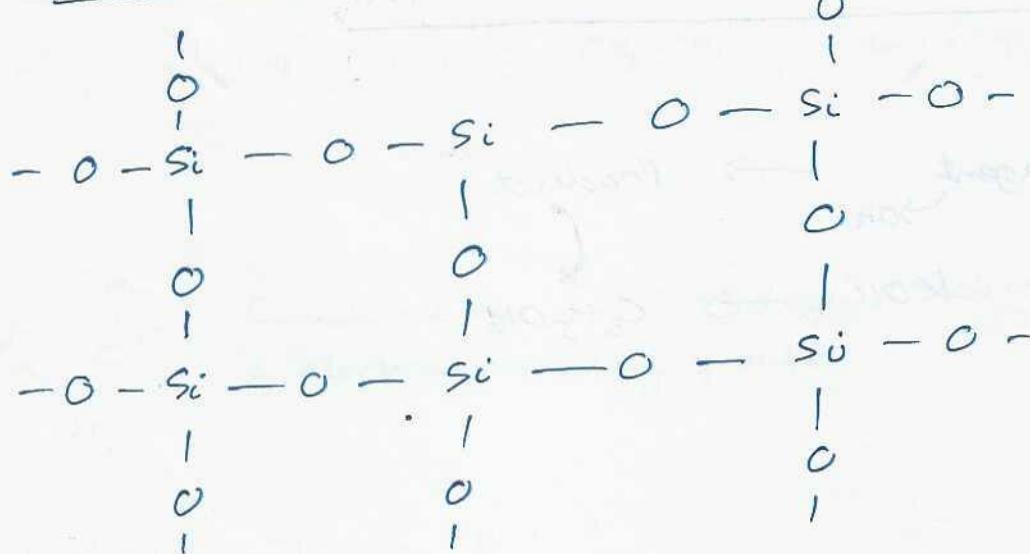
## 5. Sheet silicates



Per tetrahedron, 3 oxygen atoms are shared.



## 6. 3-Dimensional

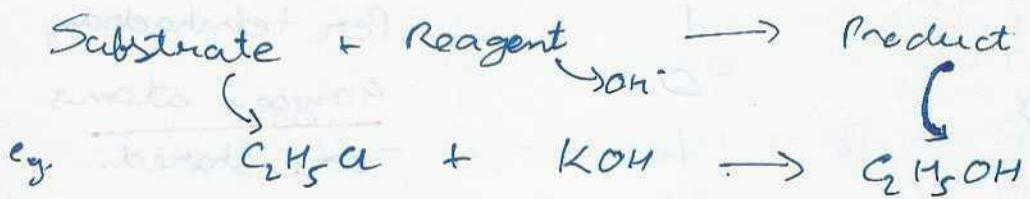


E.g. Gucontz,  
cysobalite.

Per tetrahedron,  
4 oxygen atoms  
are stored.



# GENERAL ORGANIC CHEMISTRY



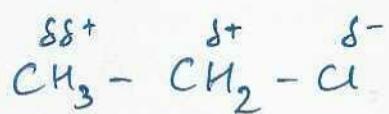
- Bond breaking
- Intermediates
- Electronic displacement.

## ELECTRONIC DISPLACEMENT

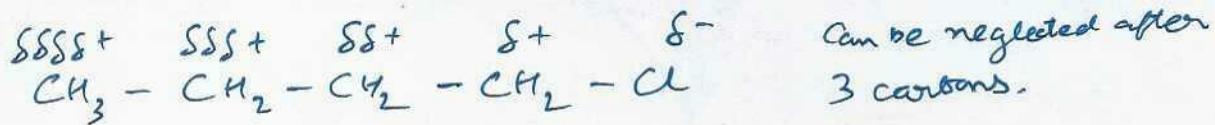
↳ Polarisation.

1. Inductive effect
2. Electromeric effect
3. Hyperconjugation
4. Mesomeric effect

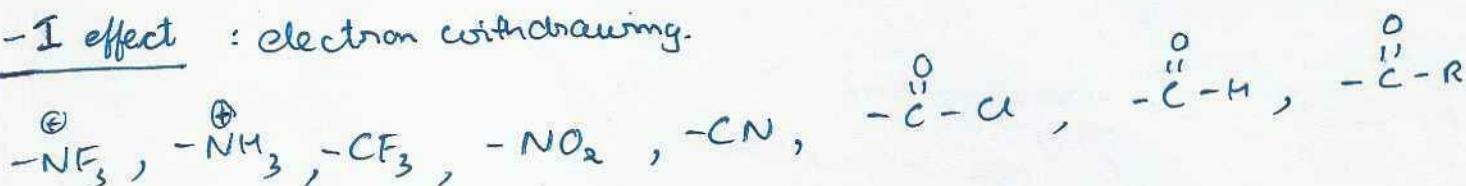
## INDUCTIVE EFFECT



- Permanent effect.
- Distance dependent.
- Operated in single direction.



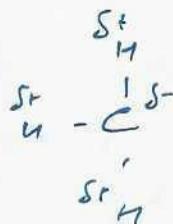
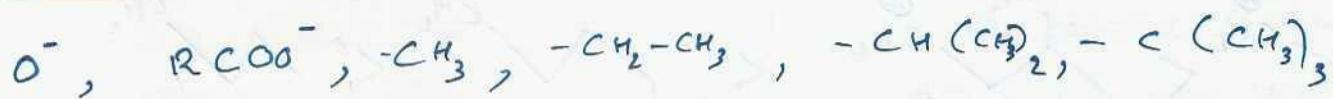
-I effect : electron withdrawing.



F, Cl, Br, I,



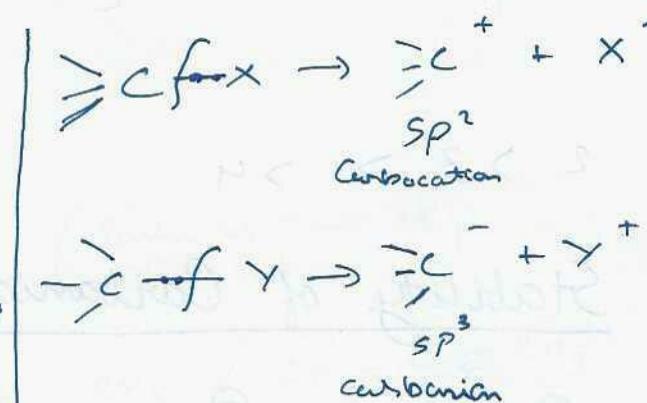
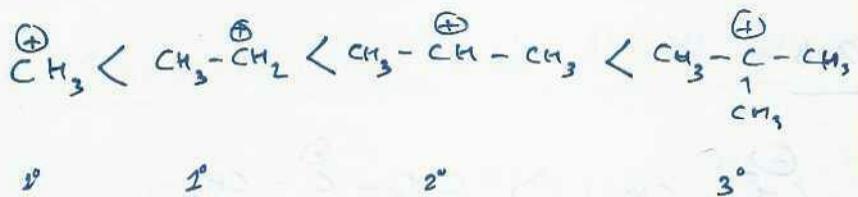
+ I effect : electron repelling or electron releasing



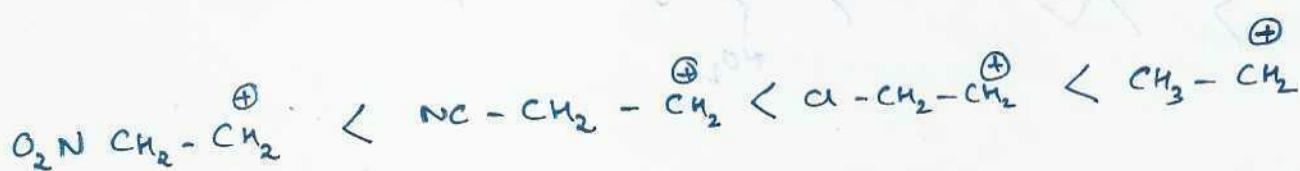
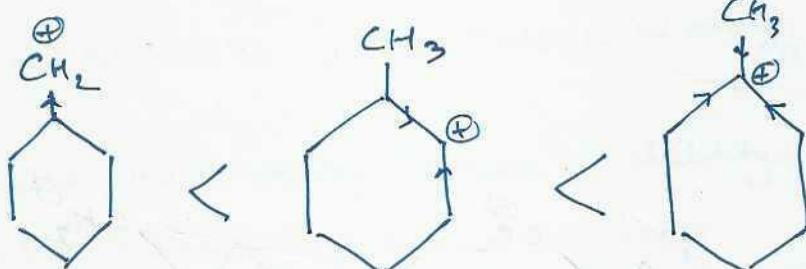
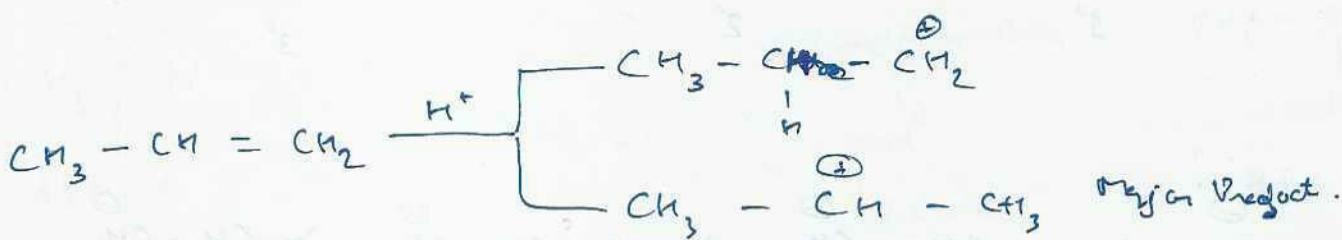
Cumulative effect of 3 hydrogens makes carbon an electron releasing group.

### Applications of Inductive Effect

#### 1. Stability of Carbocation

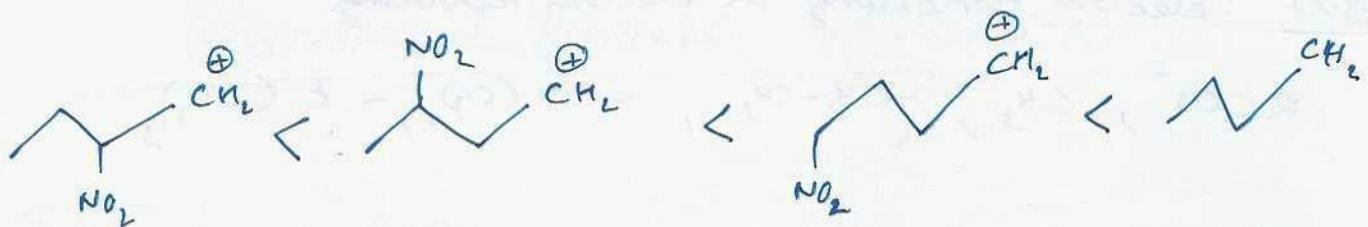


Stable carbocation is formed as intermediate during reaction.

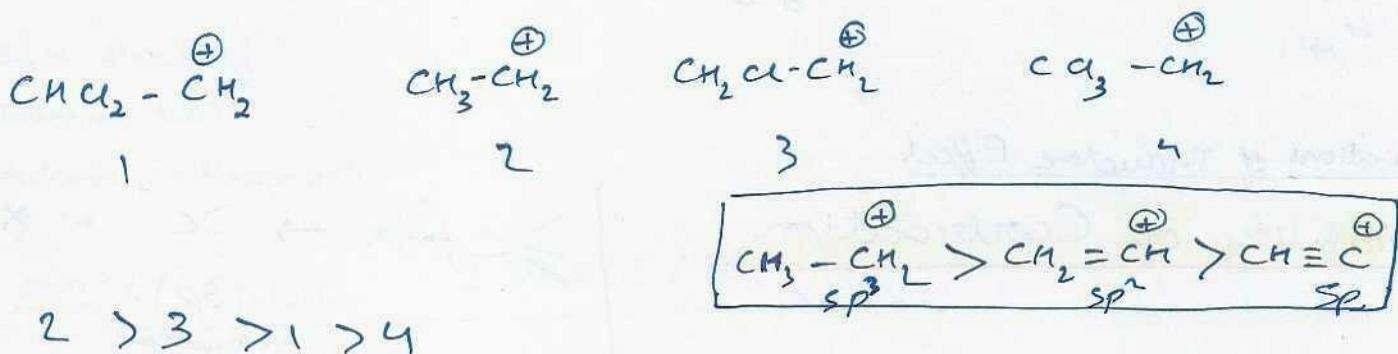


-I effect decreases stability

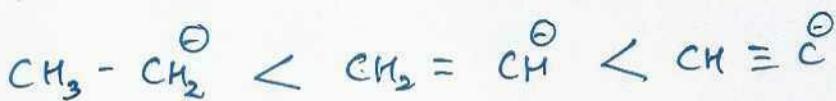
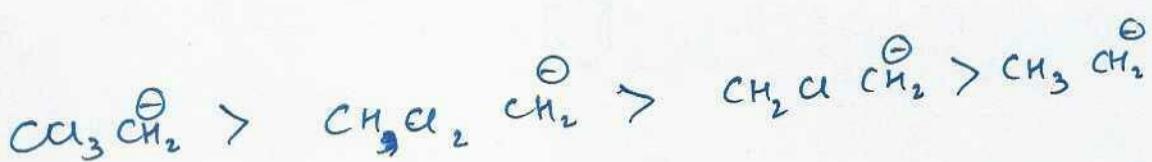
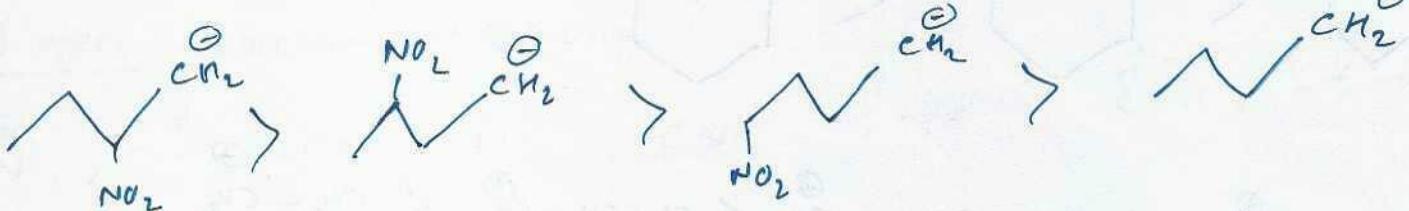
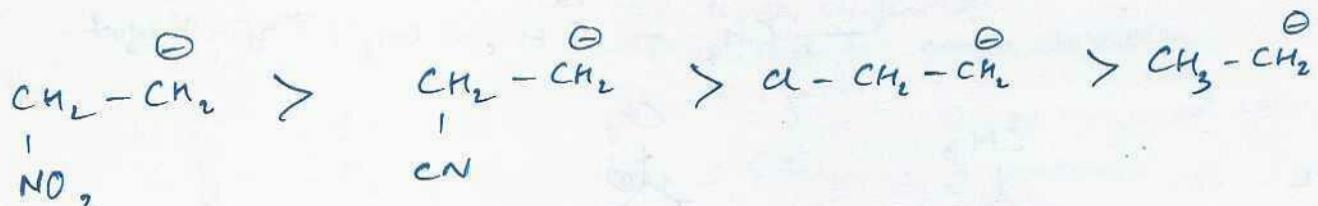
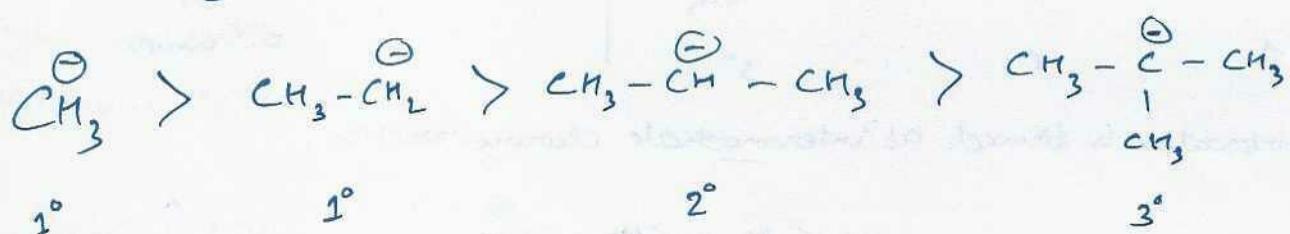
+I effect increases stability

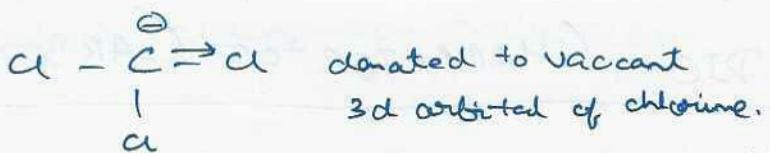


As distance increases Inductive effect decreases.



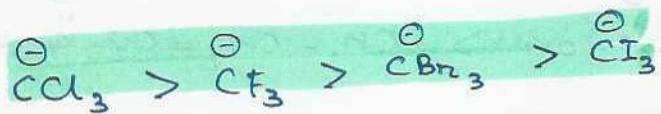
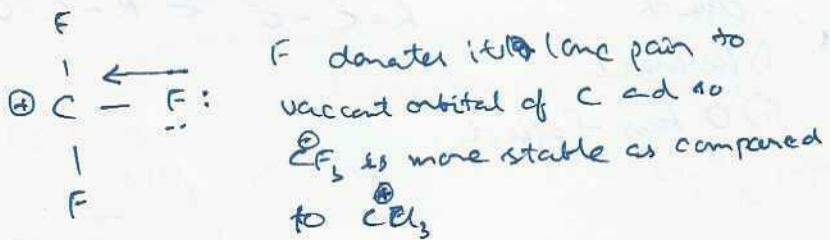
## 2. Stability of Carbanions





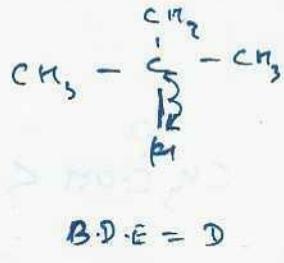
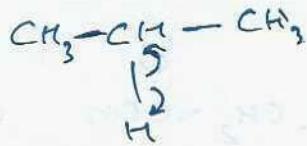
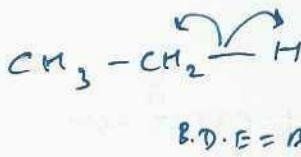
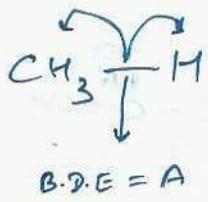
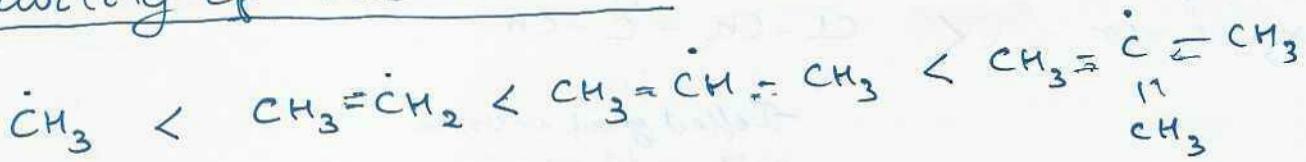
Thus it is more stable than  
 $\text{CF}_3^{\oplus}$

Acidic nature :  $\text{CHCl}_3 > \text{CHF}_3$



(Same as that of  
carbo cation)

### 3. Stability of Free Radicals



$A > B > C > D$ . } Bond dissociation energy (B.D.E) order.

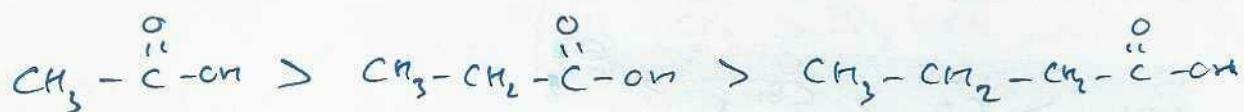
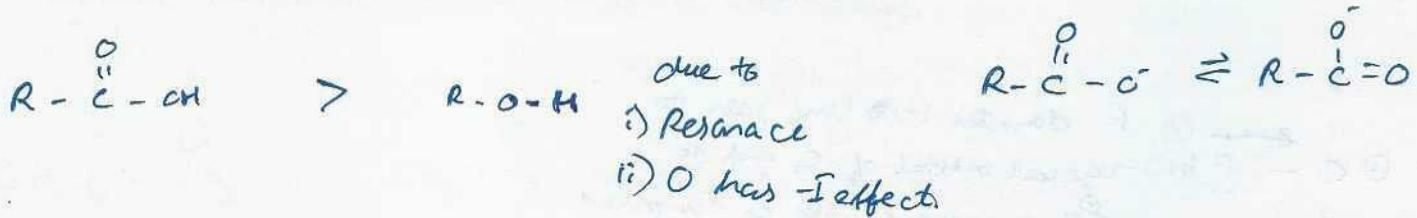
Electron withdrawing groups  $\downarrow$  stability.

Electron releasing groups  $\uparrow$  stability.

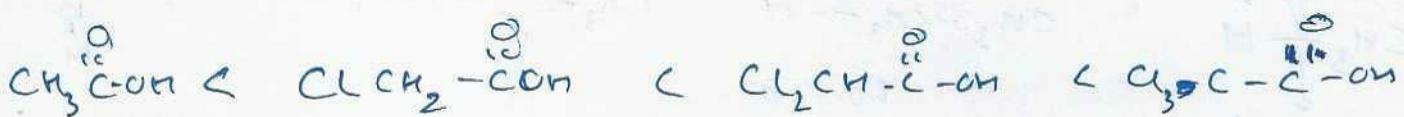
# ACIDIC CHARACTER OF CARBOXYLIC ACID



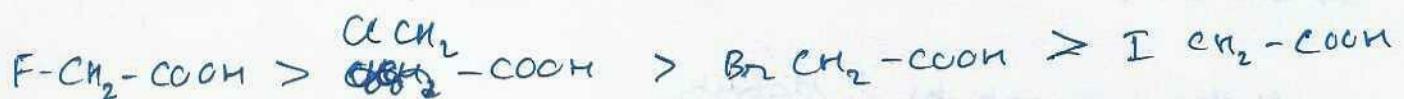
electron releasing group decreases acidic character



-I effect group increase acidic character.

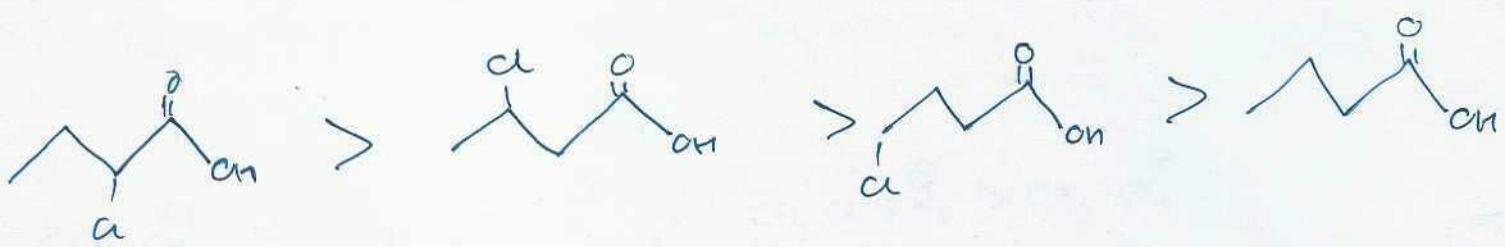


More the No. of -I groups, more increase in acidic character



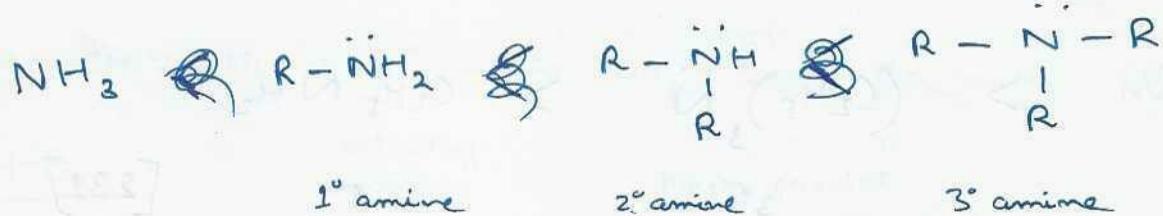
-I effect maximum

-I effect minimum

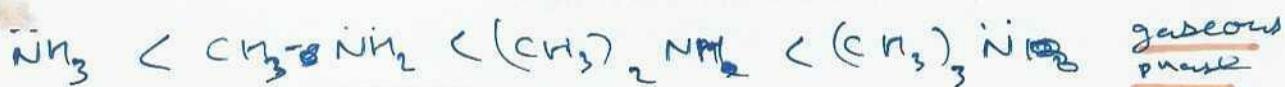




## BASIC CHARACTERS OF AMINES

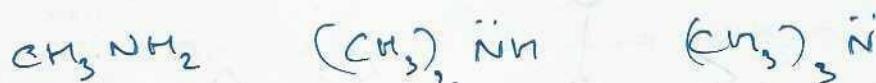


gaseous phase



gaseous phase

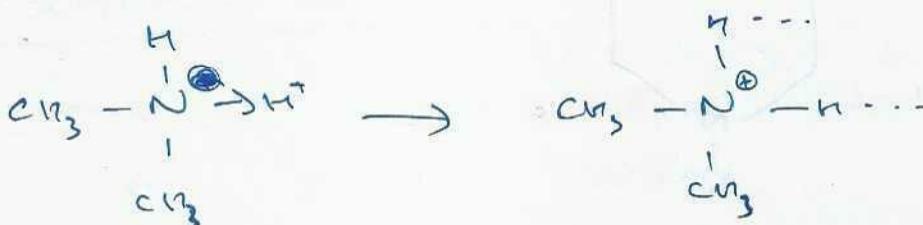
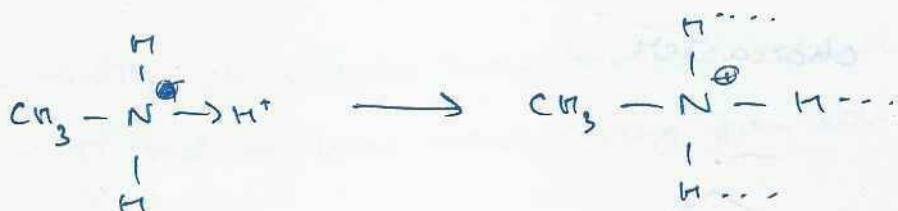
In aqueous medium



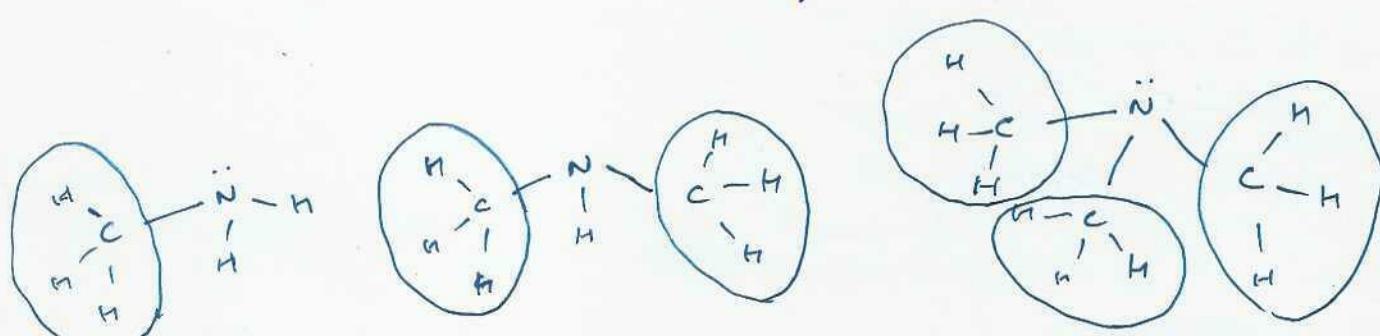
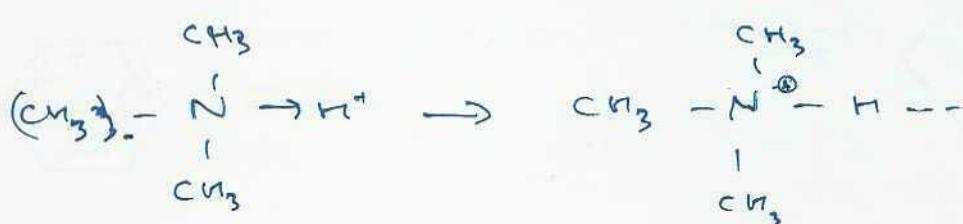
2° amine > 1° amine > 3° amine

[213] In aqueous medium due to Steric hindrance

methyl



Steric hindrance decreases basic character.

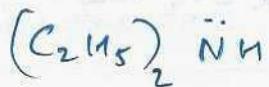


Steric hindrance arises due to steric repulsion.

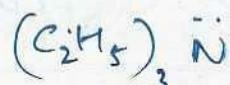
Steric hindrance is more.



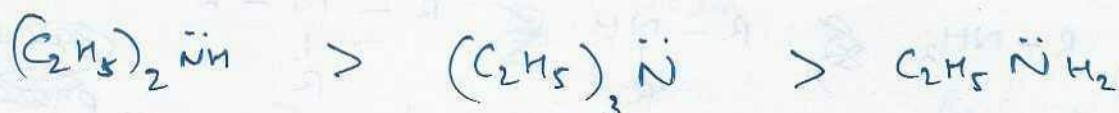
1° amine



2° amine



3° amine



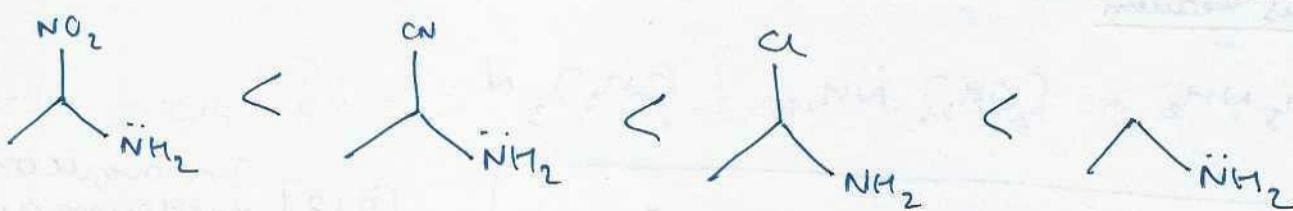
2° ~~aaa~~

3°

1°

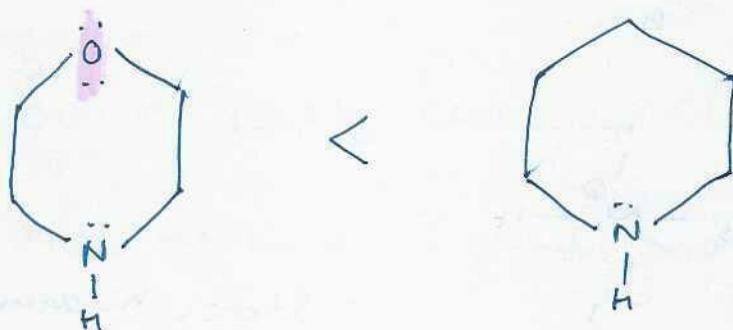
[231]

ethyl

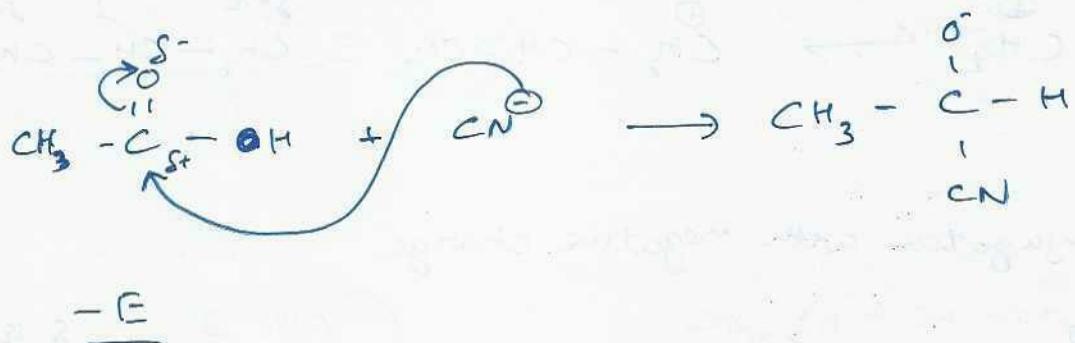
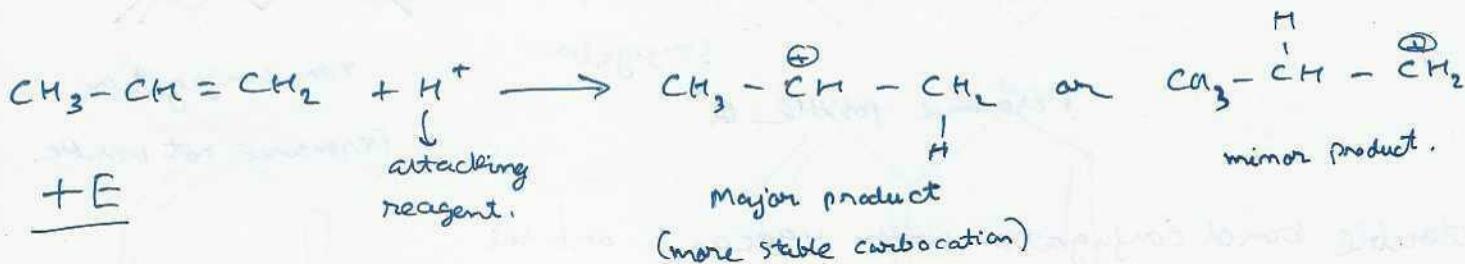
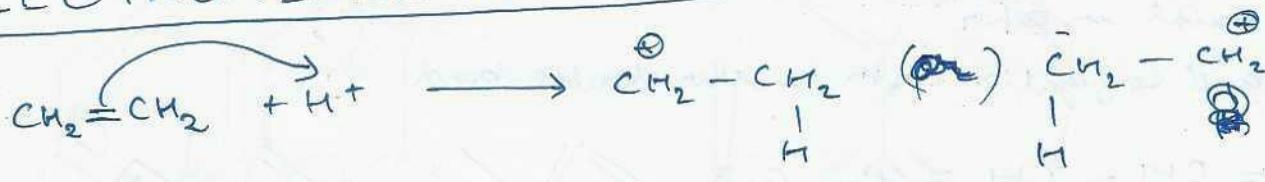


-I effect decreases basic character

+I effect increases basic character.



# ELECTROMERIC EFFECT (Temporary effect)



$+E \rightarrow \pi$  bond electrons move towards attacking reagent.  
 $-E \rightarrow \pi$  bond electrons move away from attacking reagent.

# MESOMERIC EFFECT

Resonance

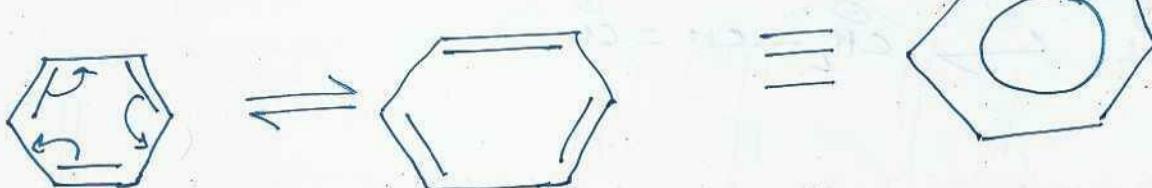


$$\text{C}-\text{C} \rightarrow 1.54 \text{ \AA}$$

$$\text{C}=\text{C} \rightarrow 1.34 \text{ \AA}$$

In benzene, experimentally

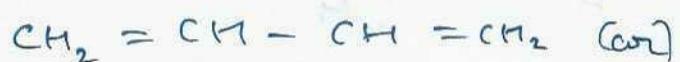
$$\text{C} \cdots \text{C} \rightarrow 1.39 \text{ \AA}$$



### Rules

→ do only exist in paper

→ double bond conjugation with another double bond



conjugation

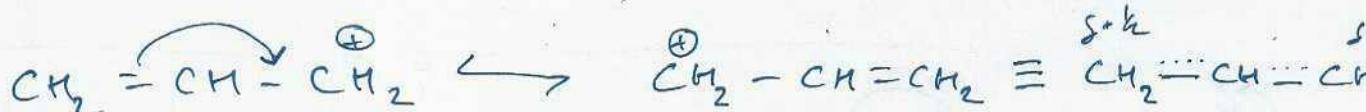
Resonance possible



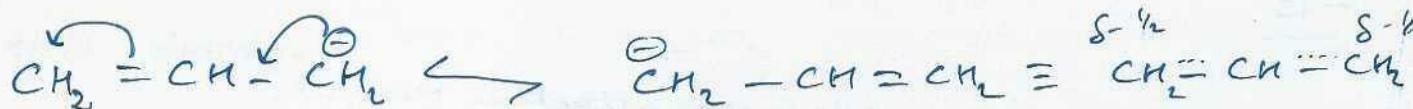
non-conjugation

Resonance not possible.

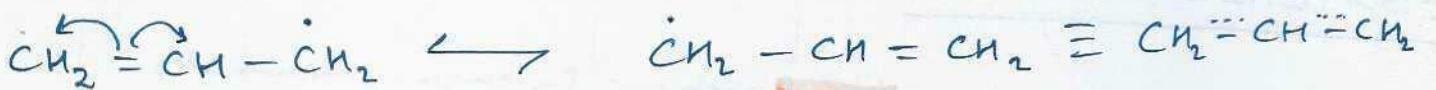
→ double bond conjugation with vacant orbital.



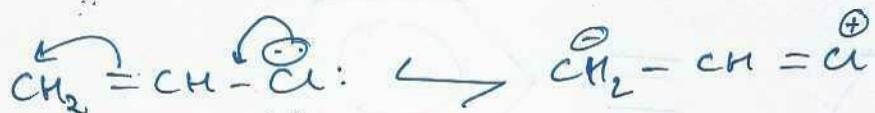
→ double bond in conjugation with negative charge.



→ π bond electron in conjugation with unpaired electron.

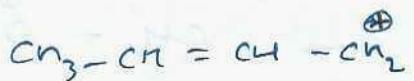
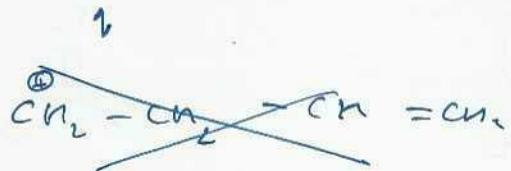
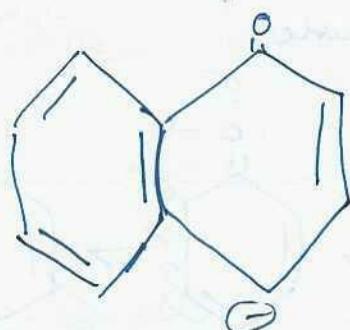
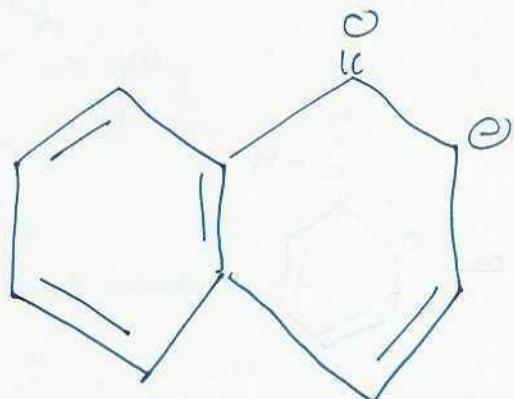
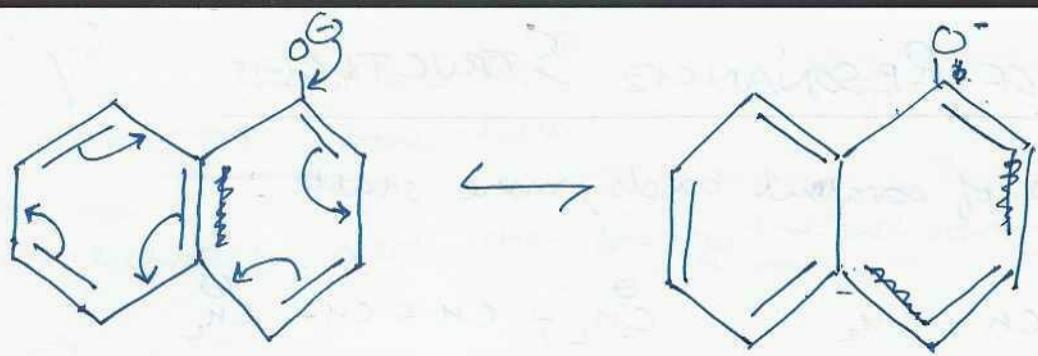


→ π bond electron conjugation with lone pair of electrons

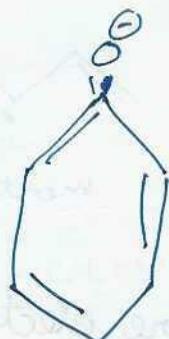
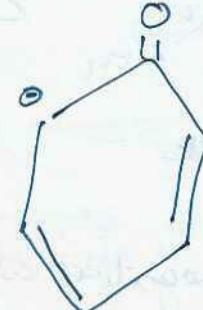
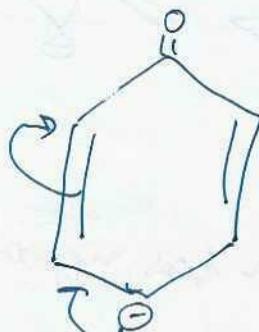
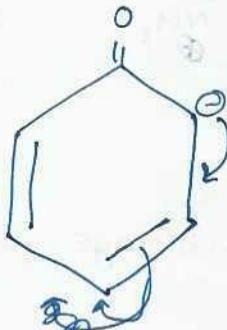
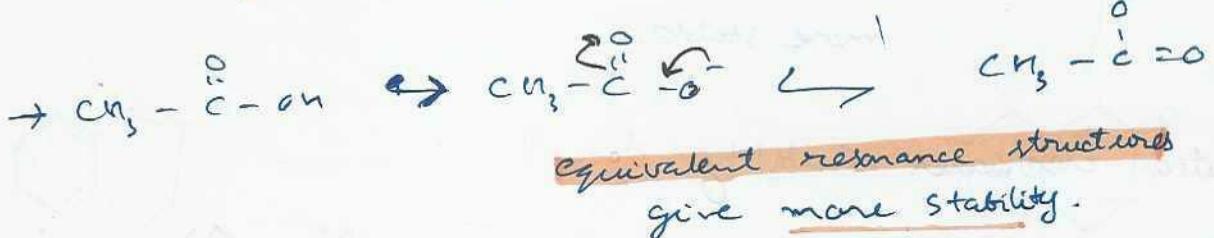


→ lone pair electron conjugation with vacant orbitals



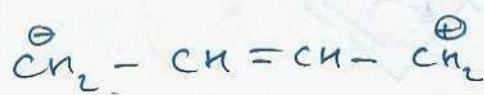


as atoms do not migrate  
their positions do not change.

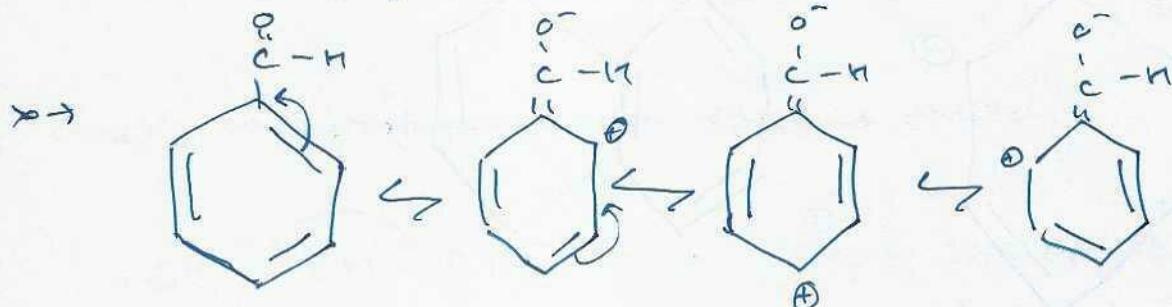


# STABILITY OF RESONANCE STRUCTURES

- More No. of covalent bonds, more stable.



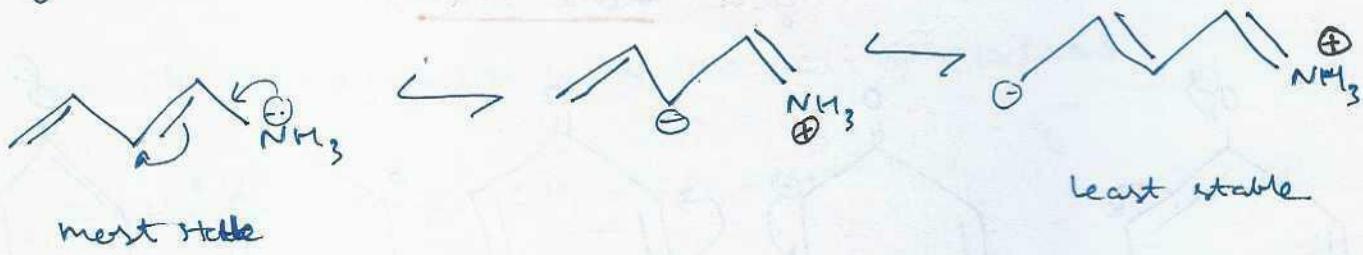
more stable



- More stable if octet is completed.



- Charge separation decreases stability

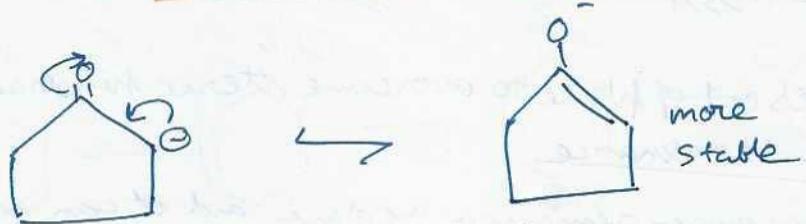


- More electronegative atom has negative charge, less electronegative has positive charge.

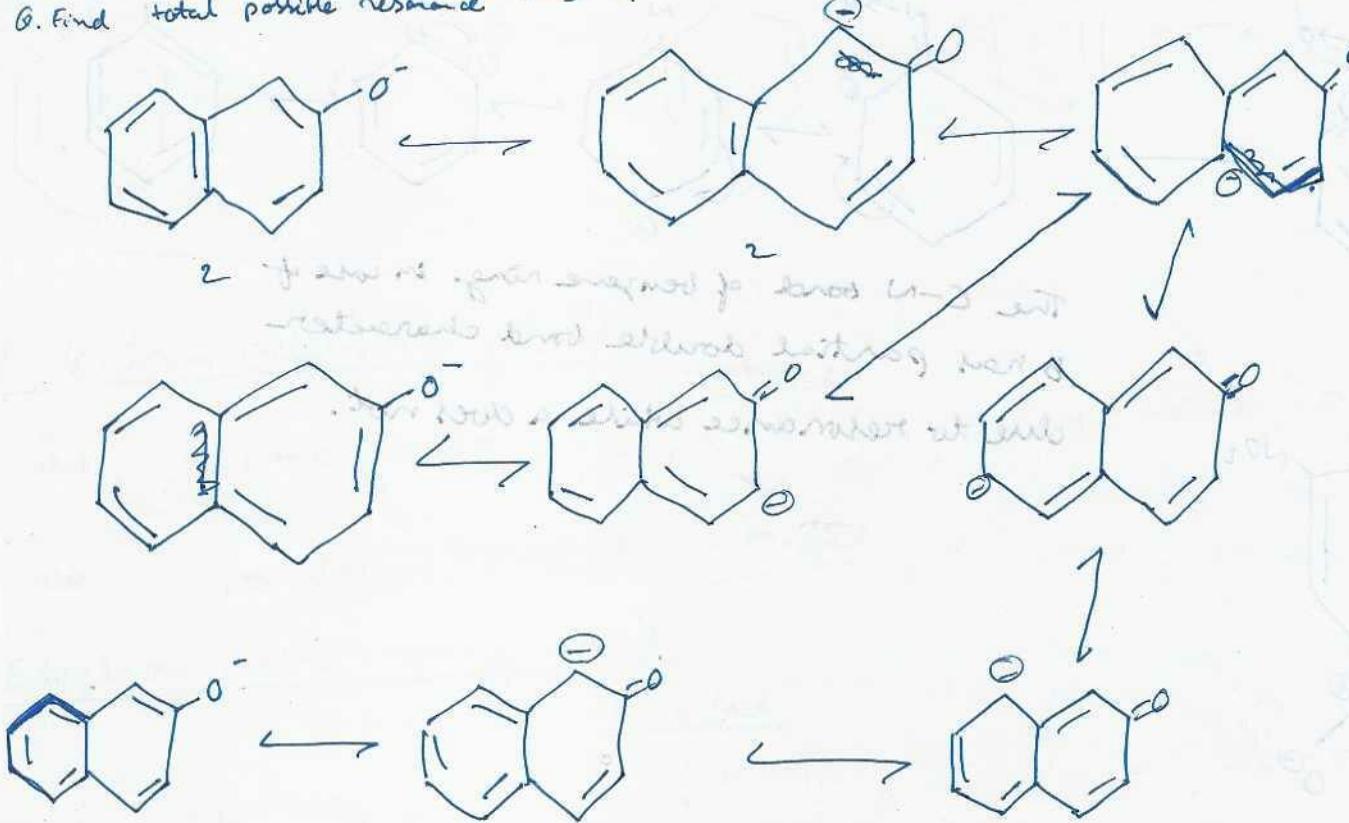




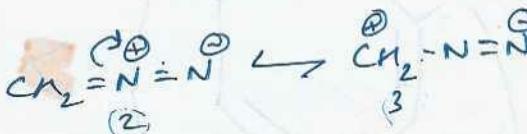
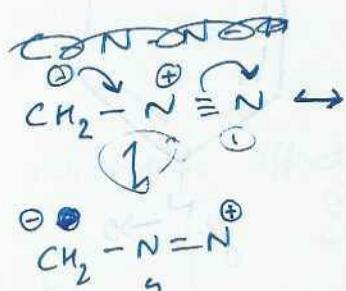
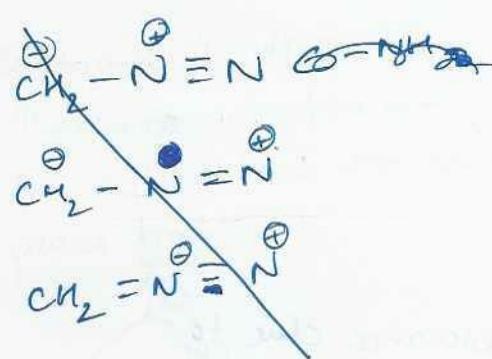
Note: First check for octet, then for negative and positive charge distribution



Q. Find total possible resonance  $\rightarrow 9$

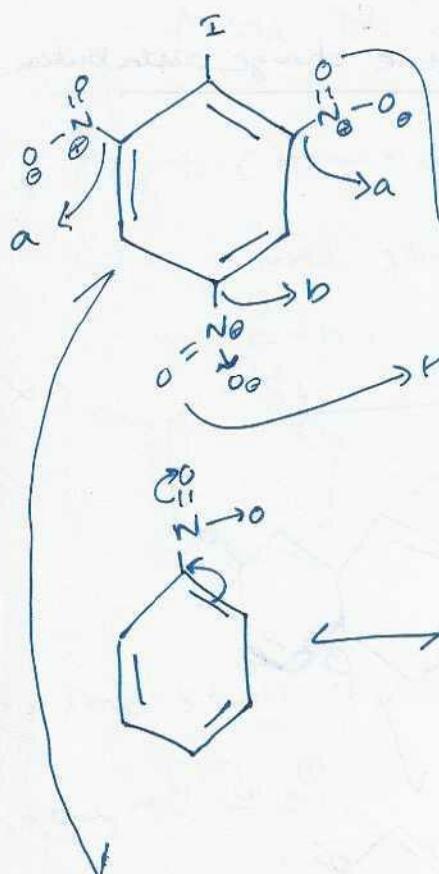


Q.  $\text{CH}_2\text{N}_2 \rightarrow 4$  structures



$2 > 1 > 3 > 4$

# STERIC INHIBITION OF RESONANCE (SIR)



C-N bond length

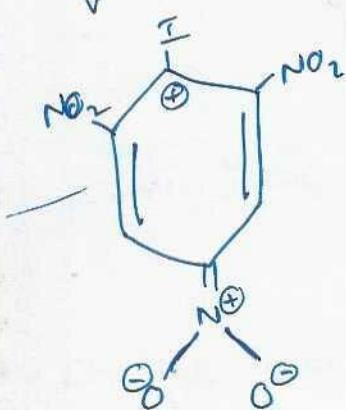
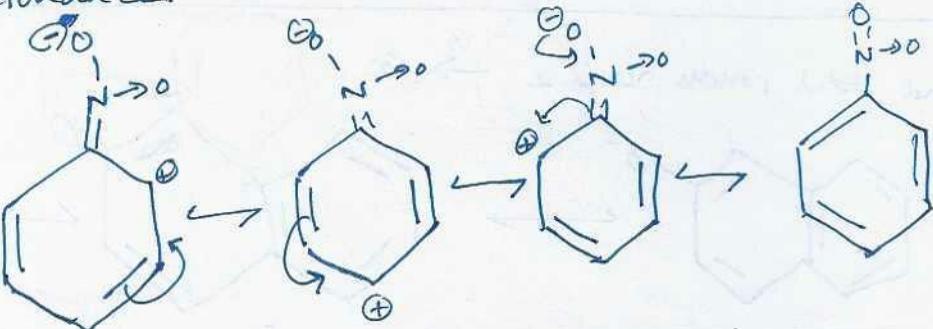
$$a = 1.45 \text{ \AA}$$

$$b = 1.35 \text{ \AA}$$

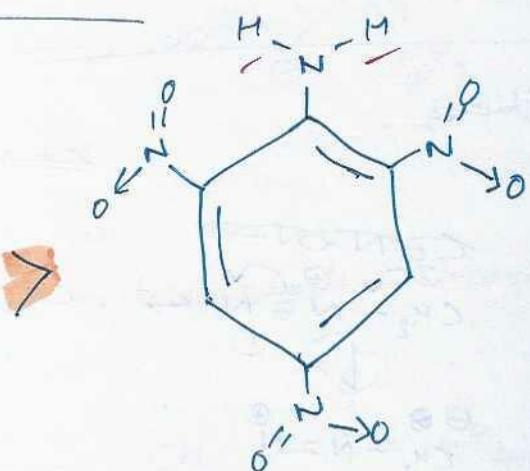
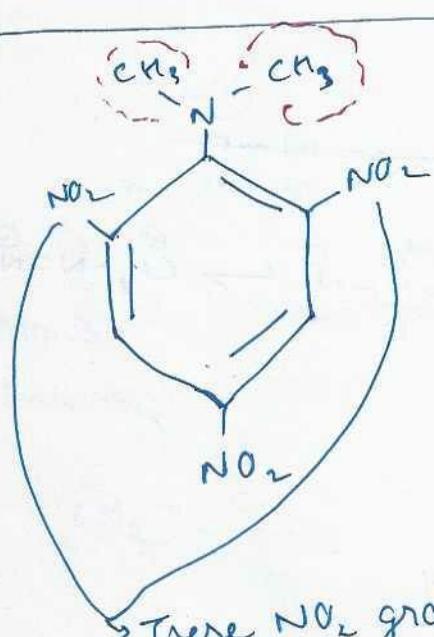
Steric hindrance: Repulsion or crowding between groups

Oxygen goes out of plane to overcome steric hindrance  
This prevents resonance

However this oxygen remains in the plane and it can be in resonance.



The C-N bond of benzene ring in case of b has partial double bond character due to resonance while a does not.

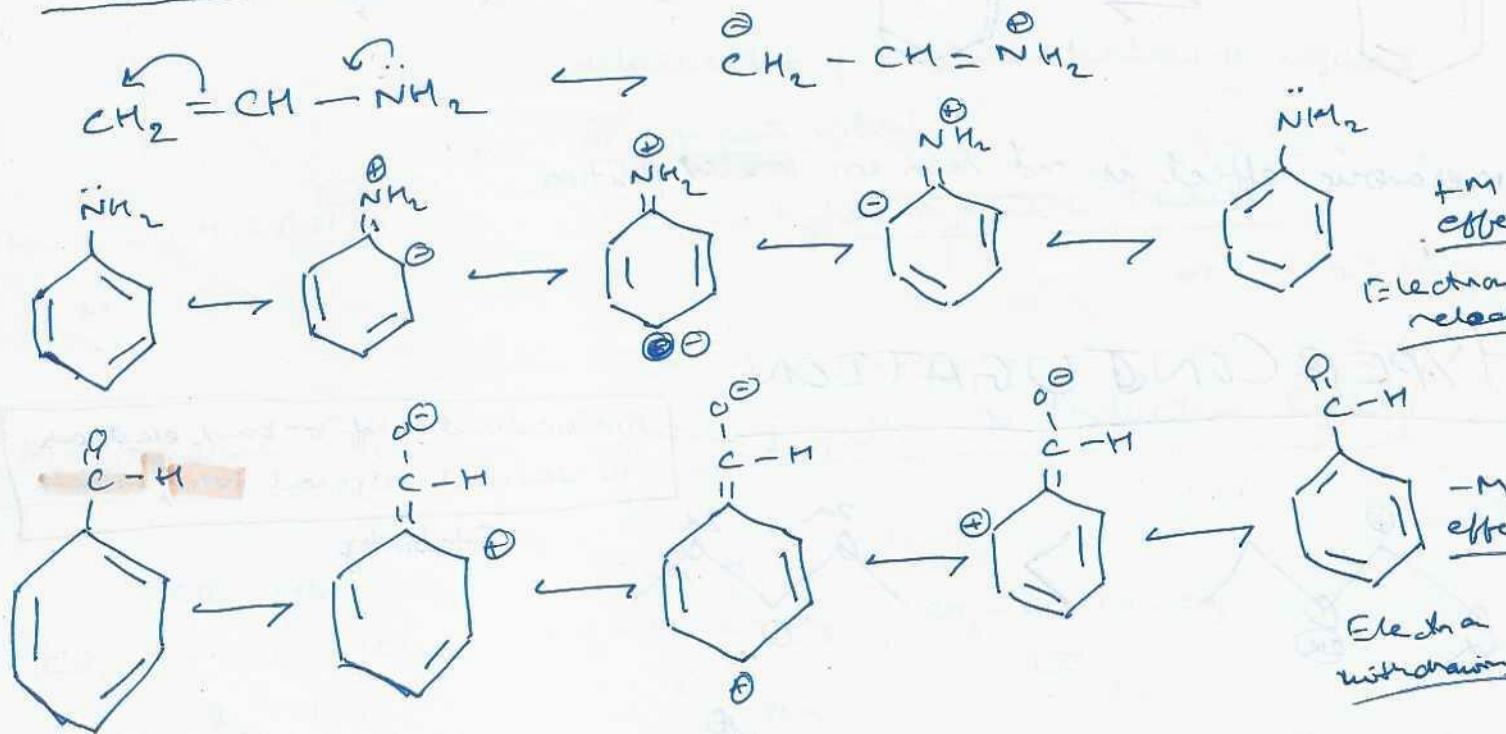


Basic character

These  $\text{NO}_2$  groups are not involved in resonance due to steric inhibition.

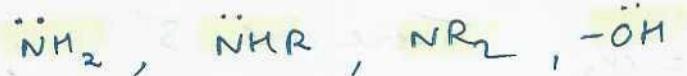
Thus  $\text{m}_{\text{eff}}$  is reduced and it is more basic

# MESOMERIC EFFECT

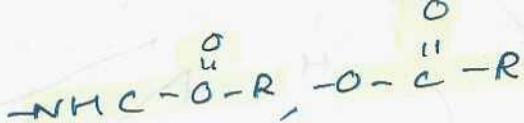


## Electron releasing groups

+M effect

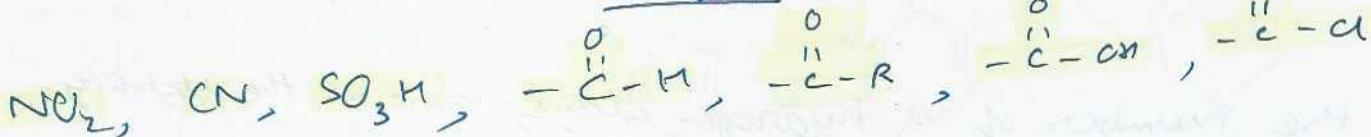


-M effect



## Electron withdrawing group

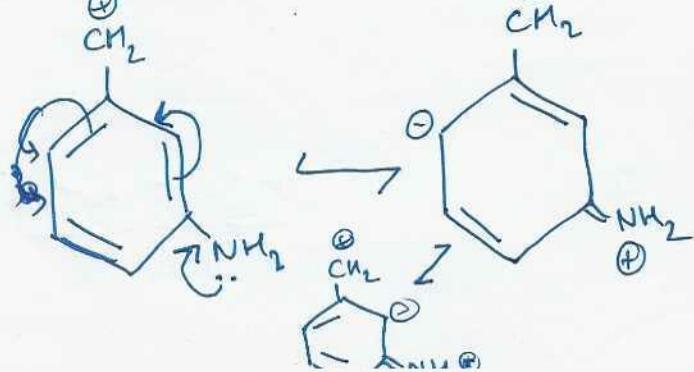
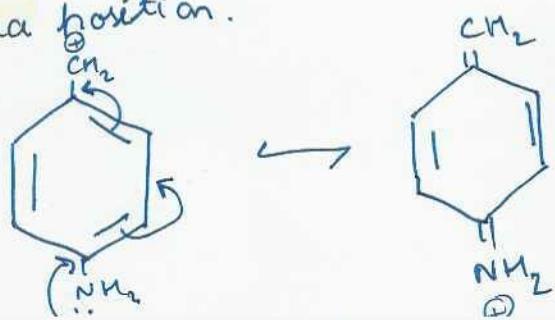
-M effect

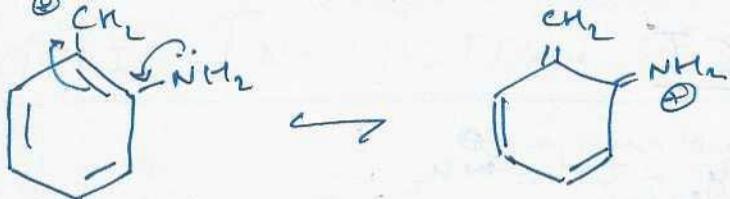


- Permanent effect.

- Distance independent.

- On substituted benzene, mesomeric effect can be seen at ortho and para position.



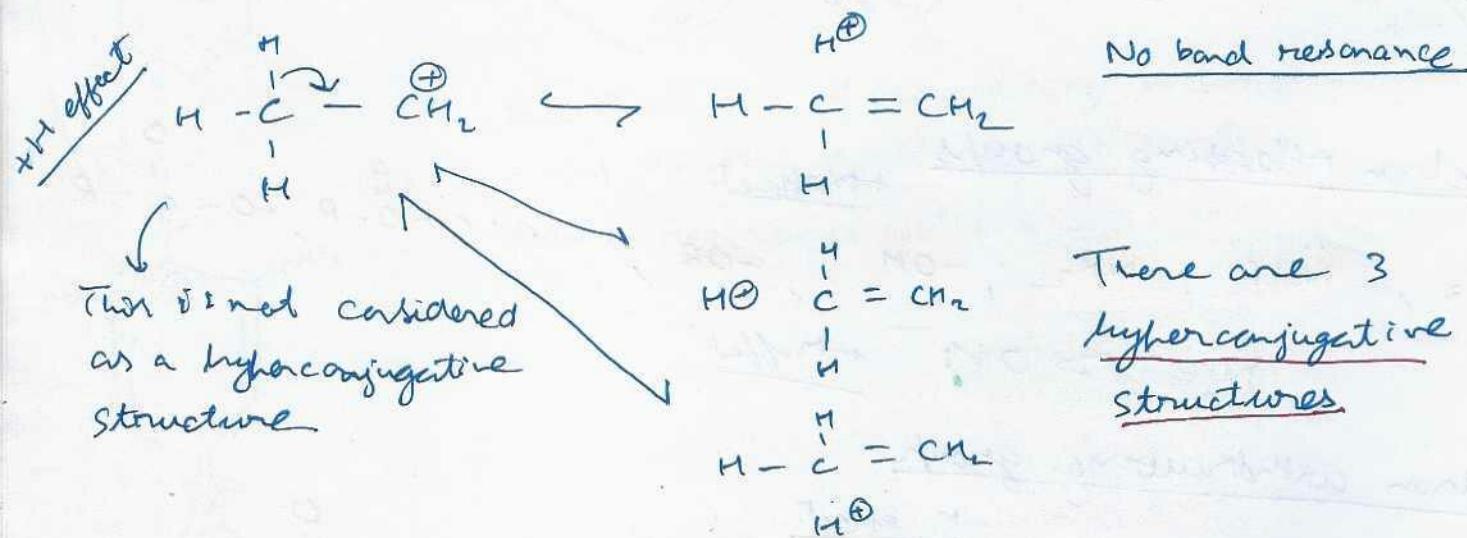


• Mesomeric effect is not seen in meta position.

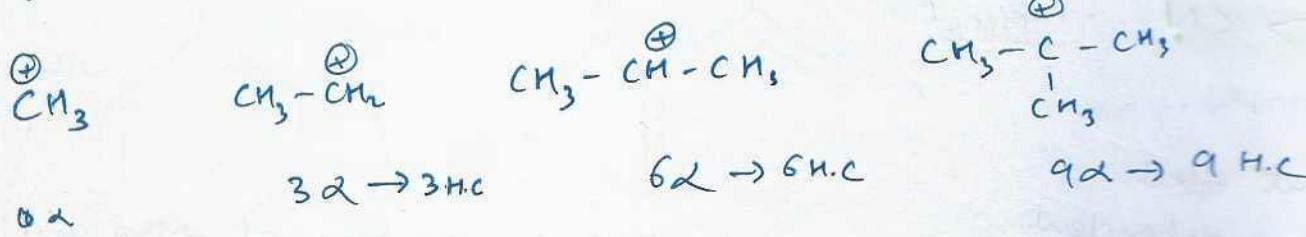
## HYPERCONJUGATION

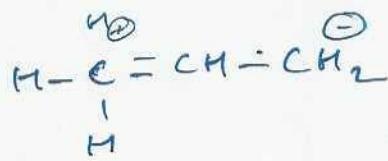
Delocalisation of  $\sigma$  bond electrons  
to vacant adjacent  $p_{\pi}$  orbitals

Stability

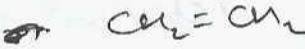


• More the number of  $\alpha$  hydrogen atoms, more is the stability of carbocation.

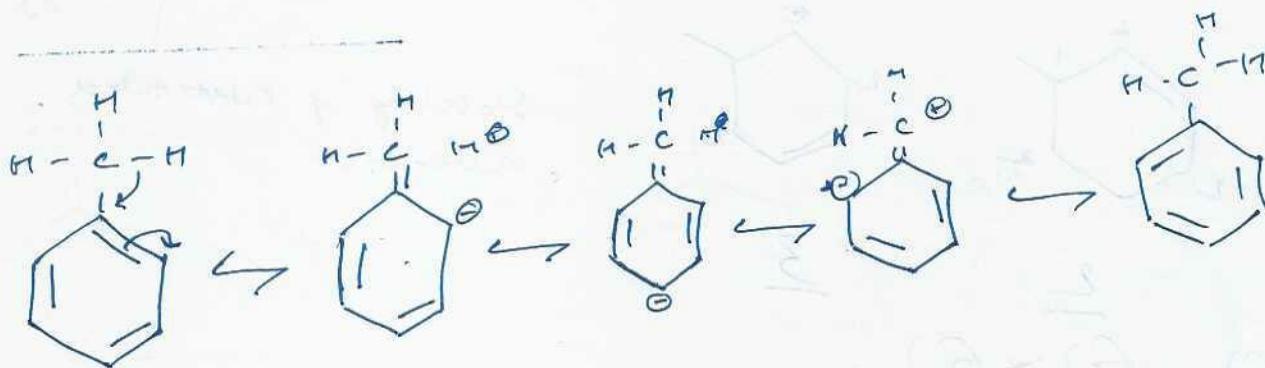
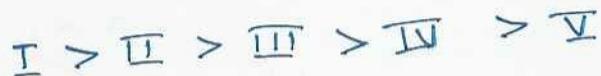
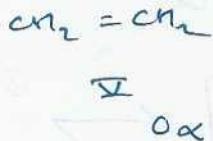
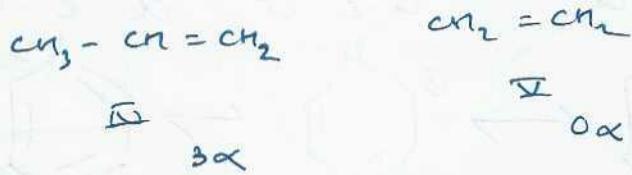
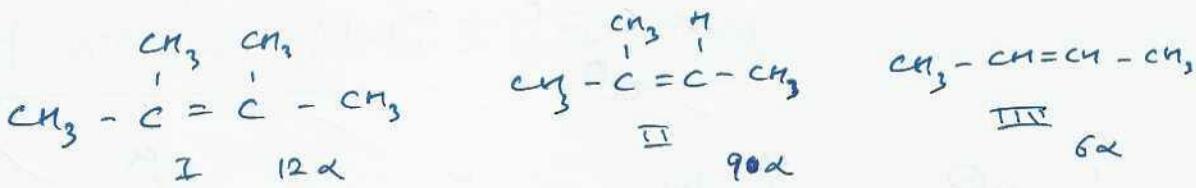




Thus no higher conjugative structures.

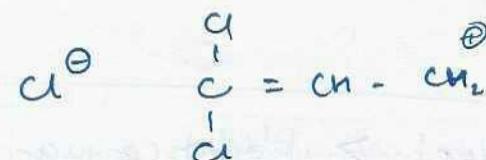
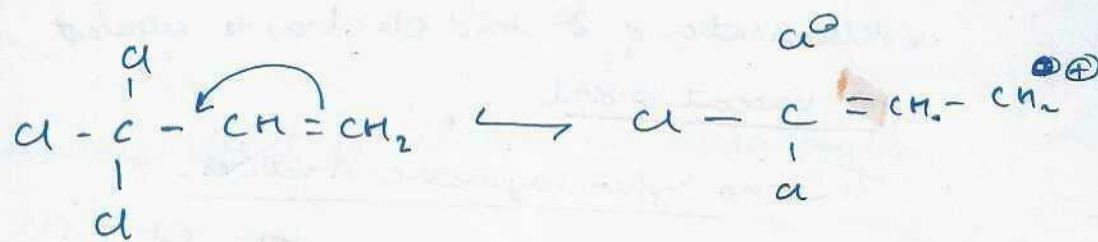


Mesomeric Effect > Hyperconjugation > Inductive Effect

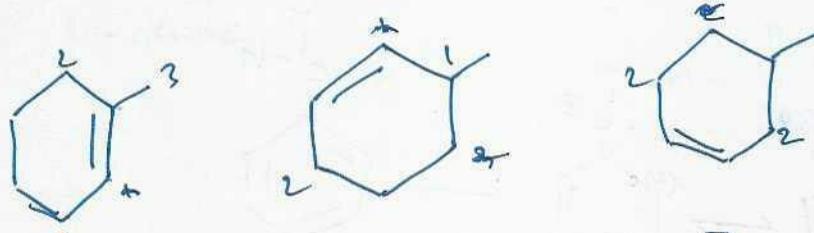
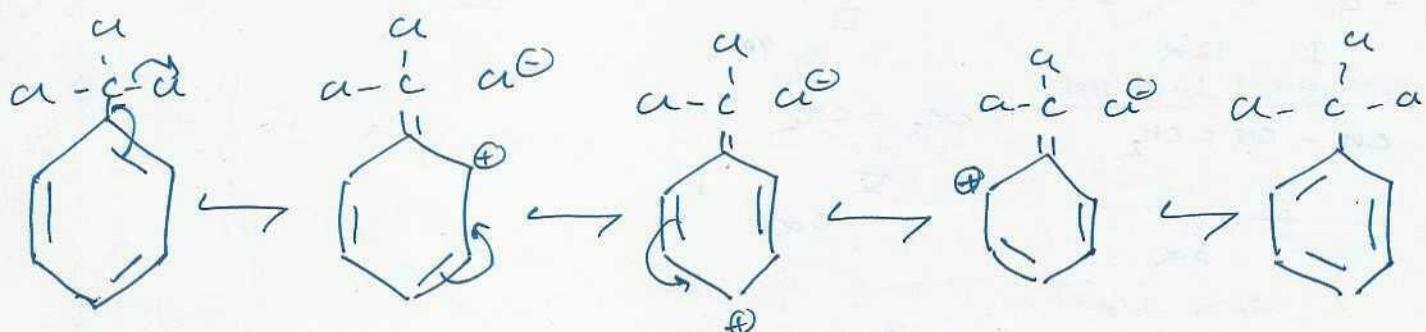
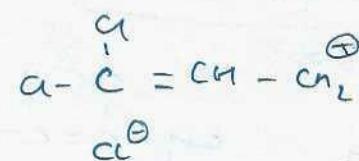


In meta position, hyperconjugation does not occur.

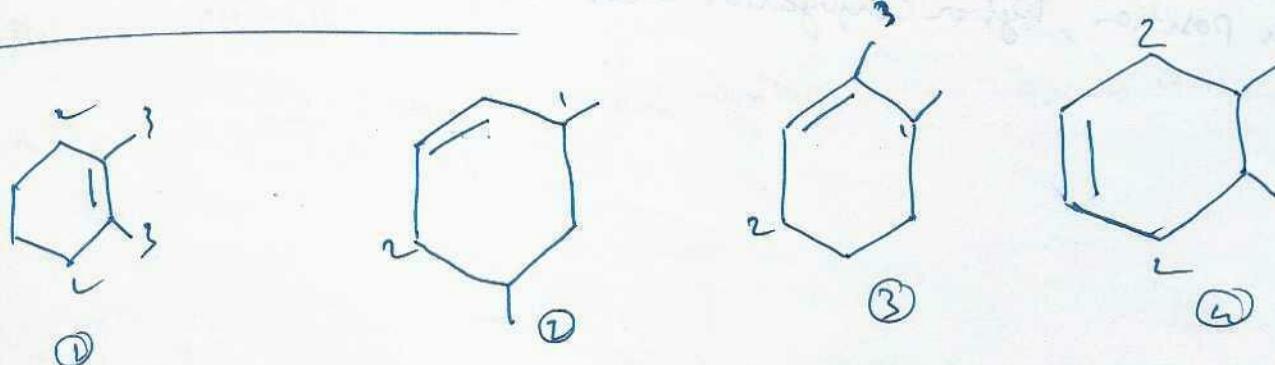
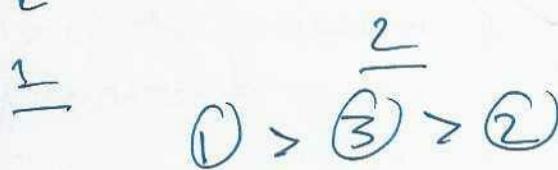
## Reverse Hyperconjugation (-n effect)

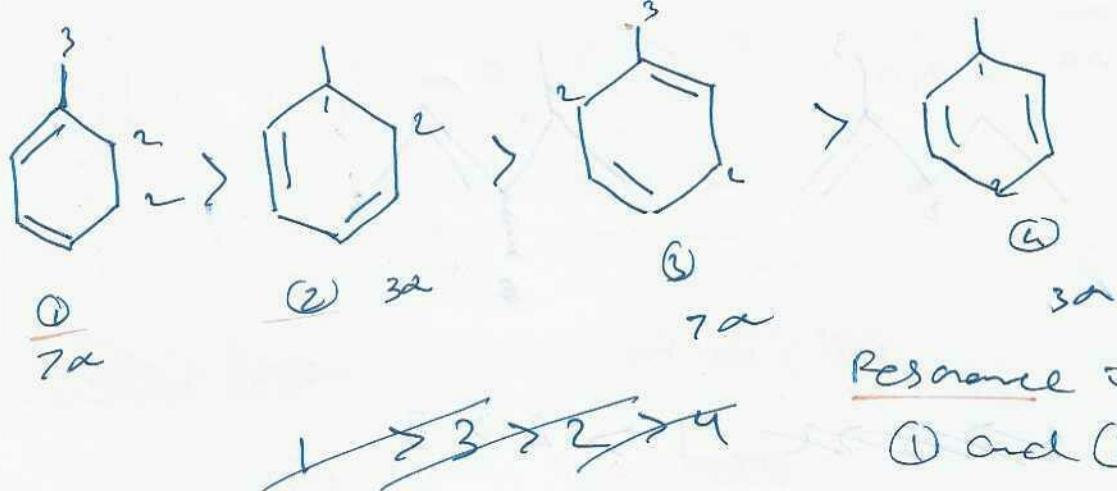


Decrease  
Stability



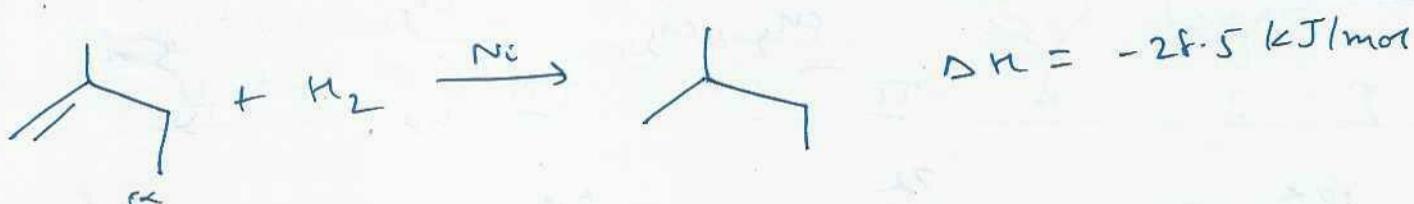
Stability of substituted alkenes -





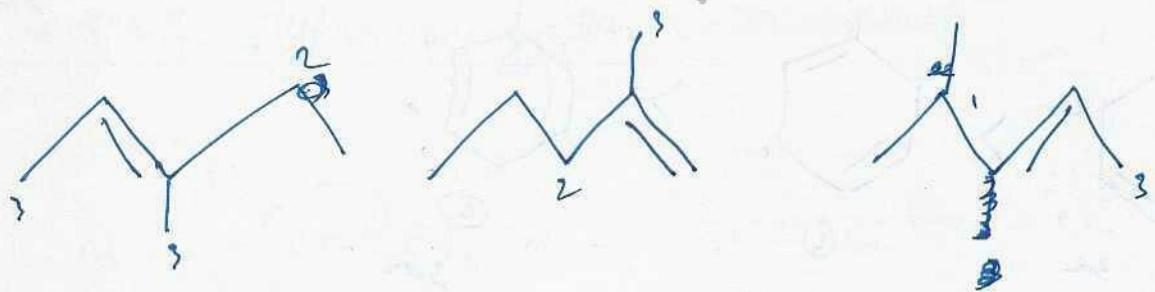
Resonance is possible in:  
① and ②

## HEAT OF HYDROGENATION



Stability of alkenes  $\propto$  No. of hyperconjugating structures

$$\alpha \frac{1}{\text{Heat of hydrogenation.}}$$

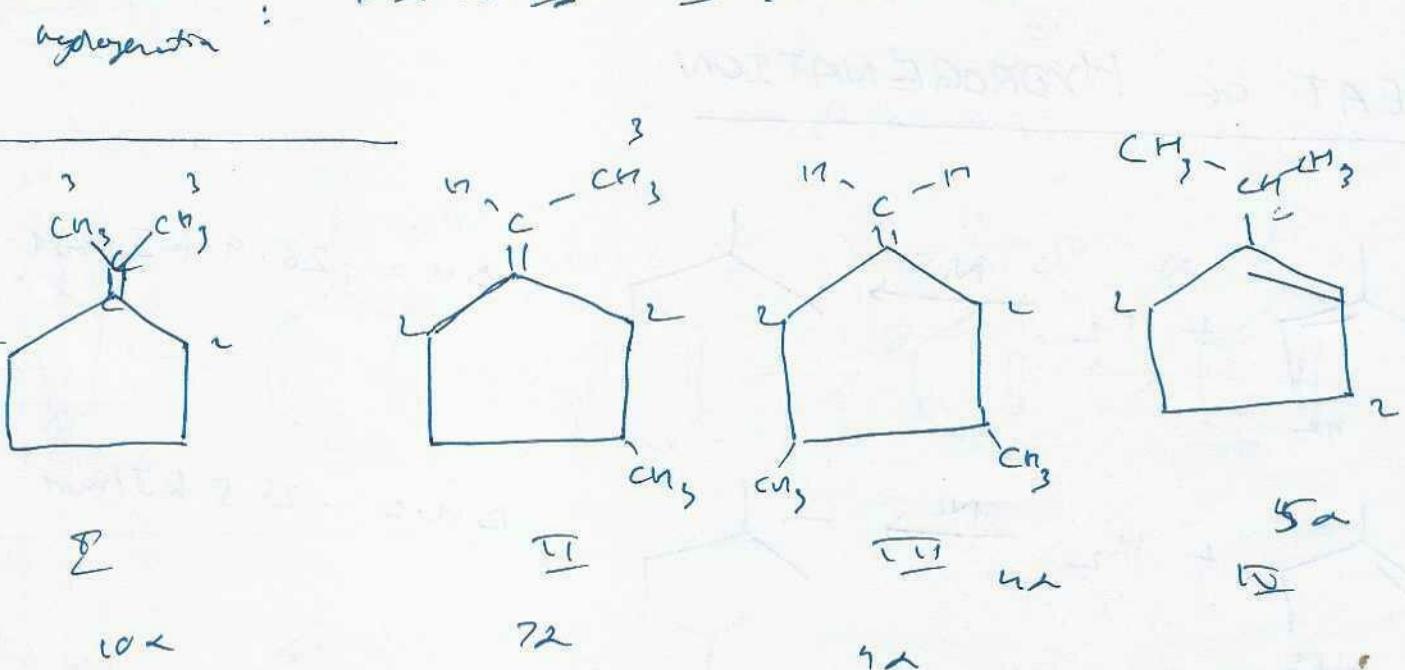


Stability



$$1 > 2 > 3$$

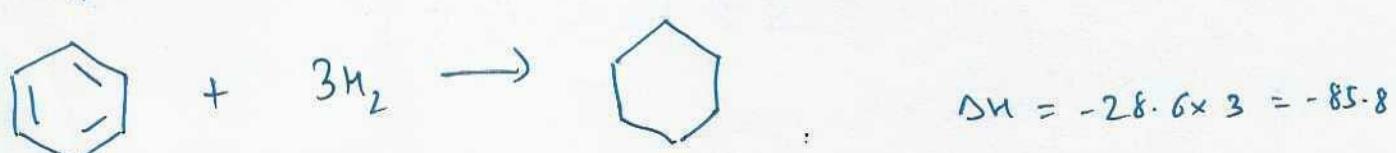
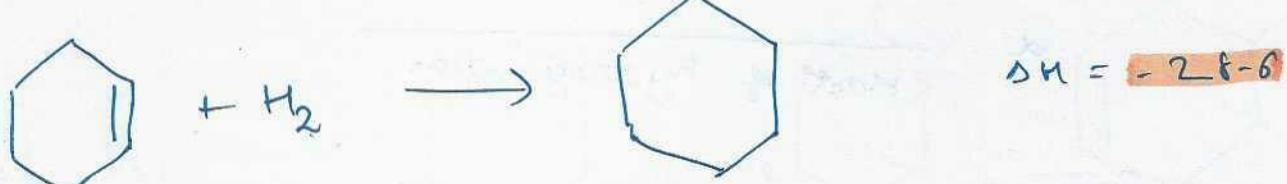
heat of  
hydrogenation



MON → Heat of hydrogenation.



## RESONANCE ENERGY



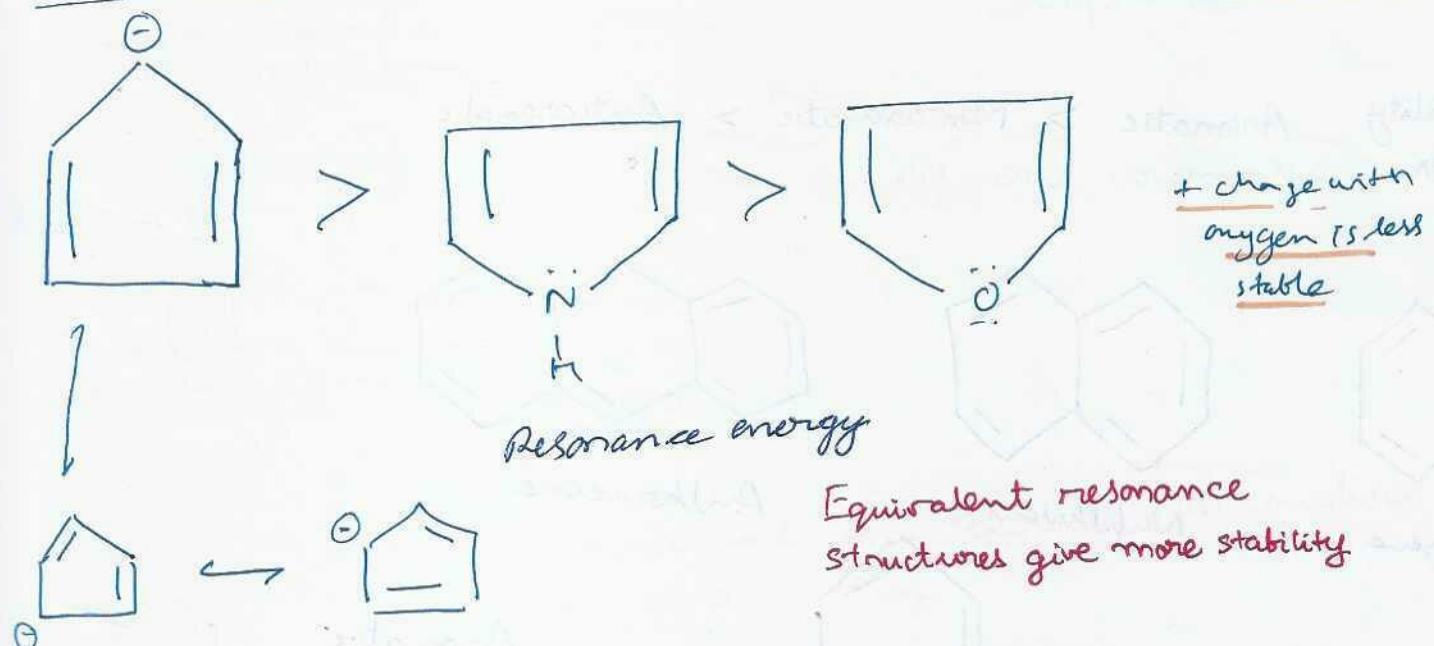
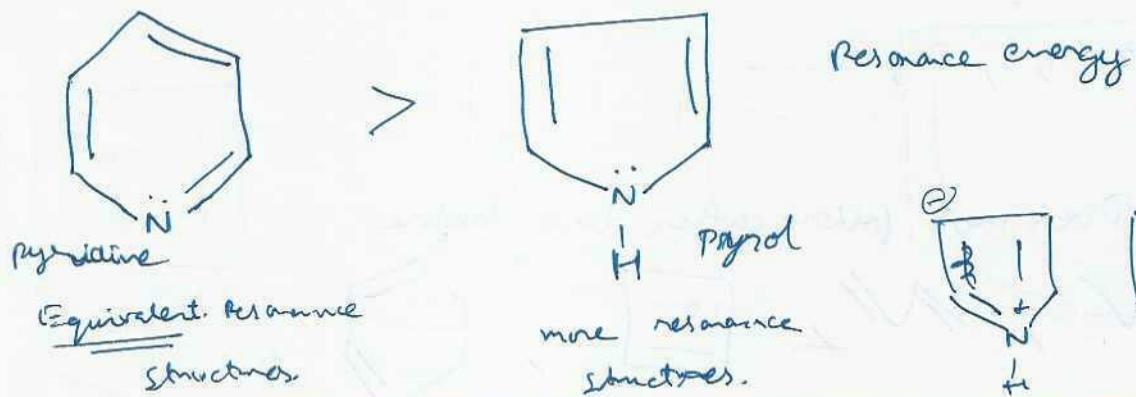


Calculated  $\Delta H_{\text{rxn}}$  - Experimental  $\Delta H_{\text{rxn}} = \Delta H$

$$\frac{85.1}{-49.8} = \frac{35.3}{36.0}$$

$$\Rightarrow \Delta H = -85.1 - (-49.8) = -35.3$$

## Equivalent Resonance structures



# Applications of Resonance Effect, Hyperconjugation & Inductive effect

## 1. Identification of AROMATIC COMPOUND

- Cyclic
- Planar ( $sp^2$  hybridisation)
- Complete delocalisation (conjugation)
- $(4n+2)\pi$  electrons } **Baeyer's Rule**  
↳ 2, 6, 10, 14, 18.....

Anti aromatic:  $(4n)\pi$  electrons

↳ 4, 8, 12, 16...

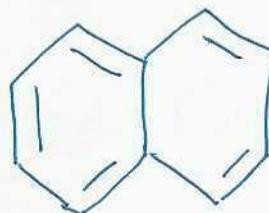
Non aromatic: Does not follow either two before.



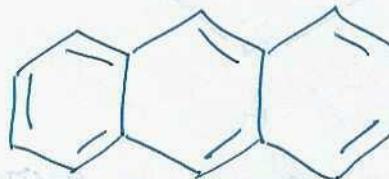
Stability order      Aromatic > Non aromatic > Anti aromatic



Benzene



Naphthalene

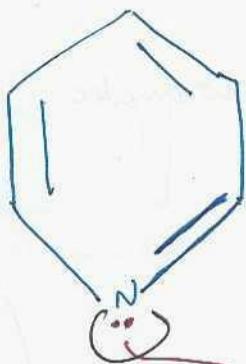


Anthracene



Phenanthrene

Aromatic



Lone pair electrons of N do not take part in delocalisation.  
 $\rightarrow$  N is  $sp^2$  hybridised.

Pyridine  $\rightarrow$  N = 7  
 not involved in delocalisation.

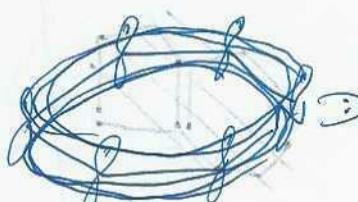
$1s^2 \ 2s^2 \ 2p^3$

$1s^2$

$1 \ 1 \ 1$

$sp^2$

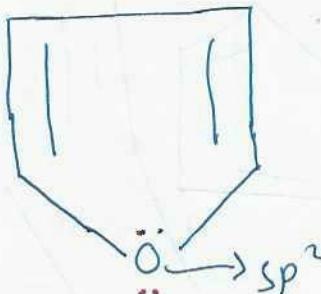
Lone pair involved in hybridisation



Aromatic

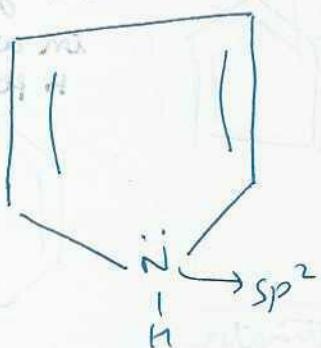
Structure is intrinsically stable

→ best structure determined by energy minimization

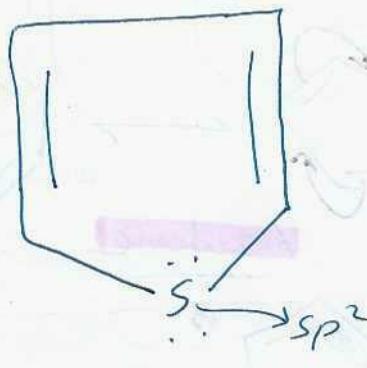


Furan

One lone pair involved in delocalisation



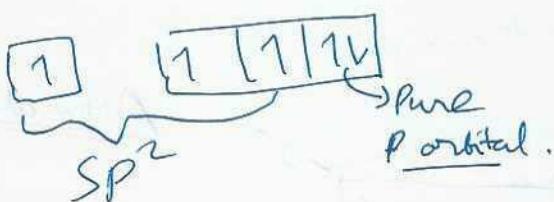
Pyrrole



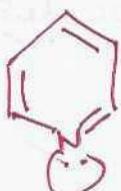
Triphenylene

N =  $1s^2$   $2s^2$   $2p^3$   
 $1 \ 1$   $1 \ 1 \ 1$

All are aromatic.

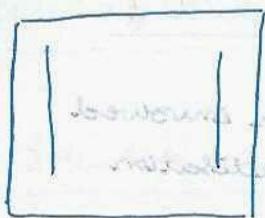


Pure P orbital.

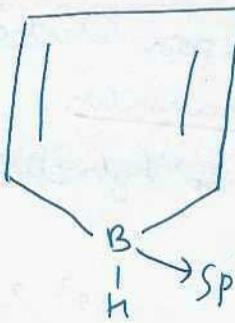


Hybridised lone pair is NOT involved in delocalisation.

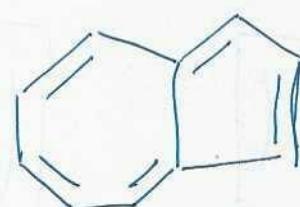
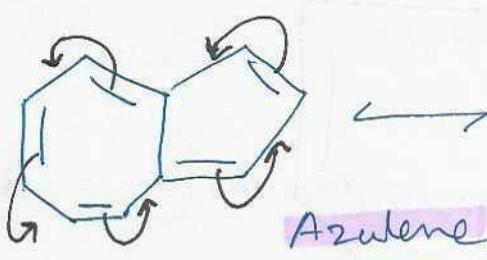
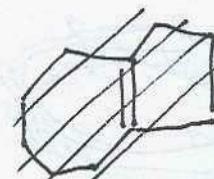
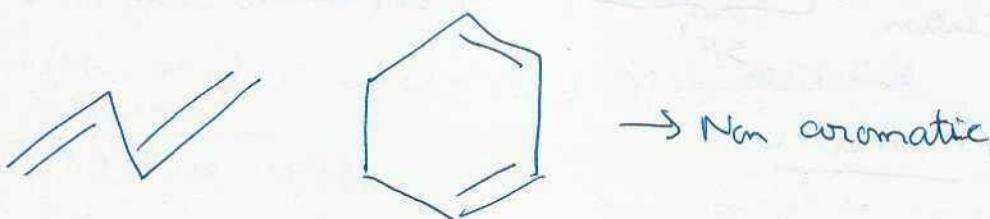
Unhybridised lone pairs are involved in delocalisation.



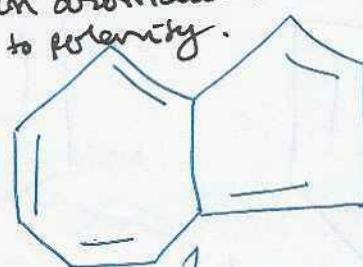
Anti aromatic



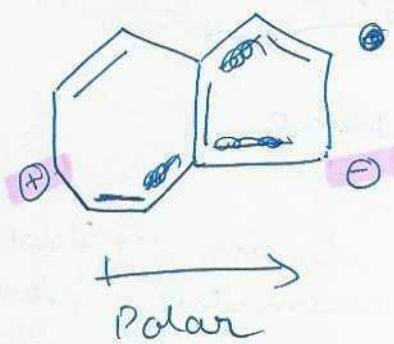
Anti aromatic



charge separation is present  
in aromatic structure leading  
to polarity.

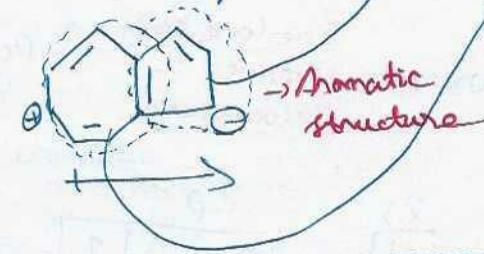


Aromatic



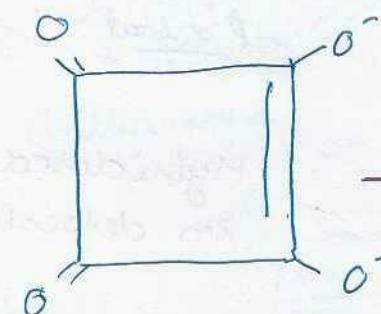
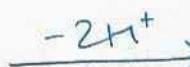
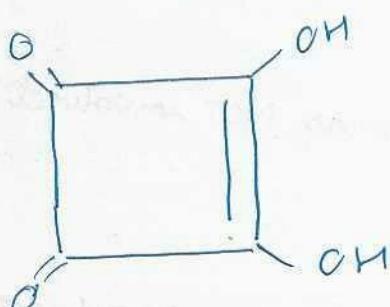
Polar

5 membered  
ring has higher  
electron density



→ Aromatic structure

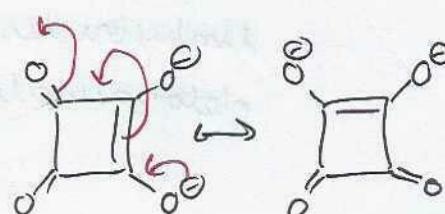
Squaric acid

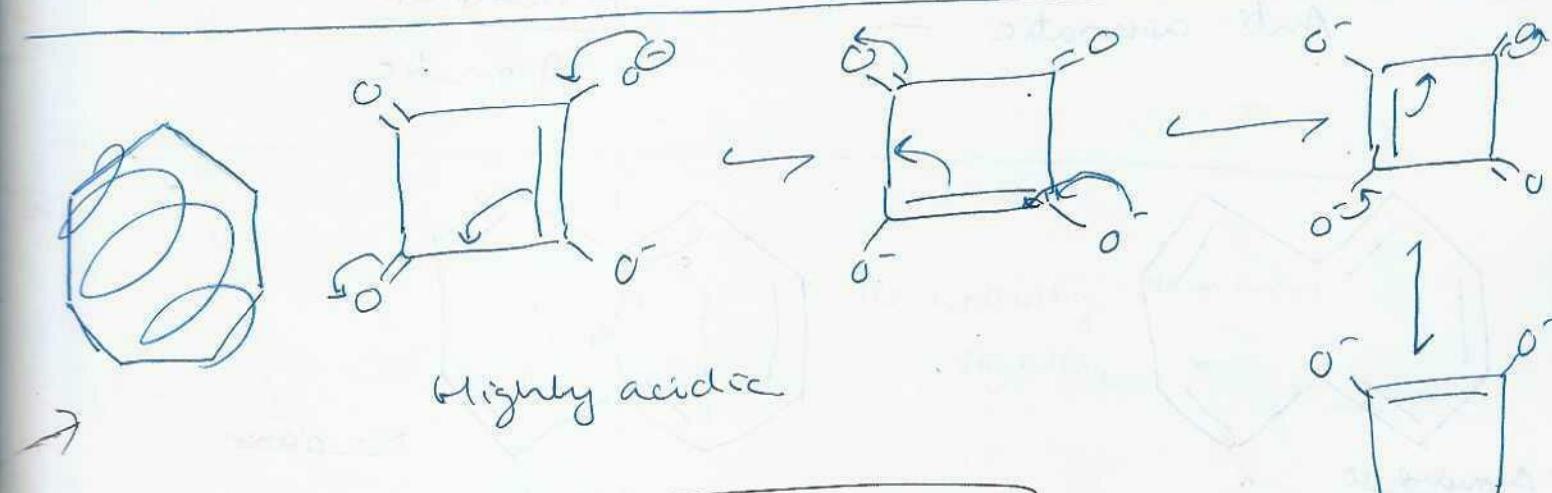
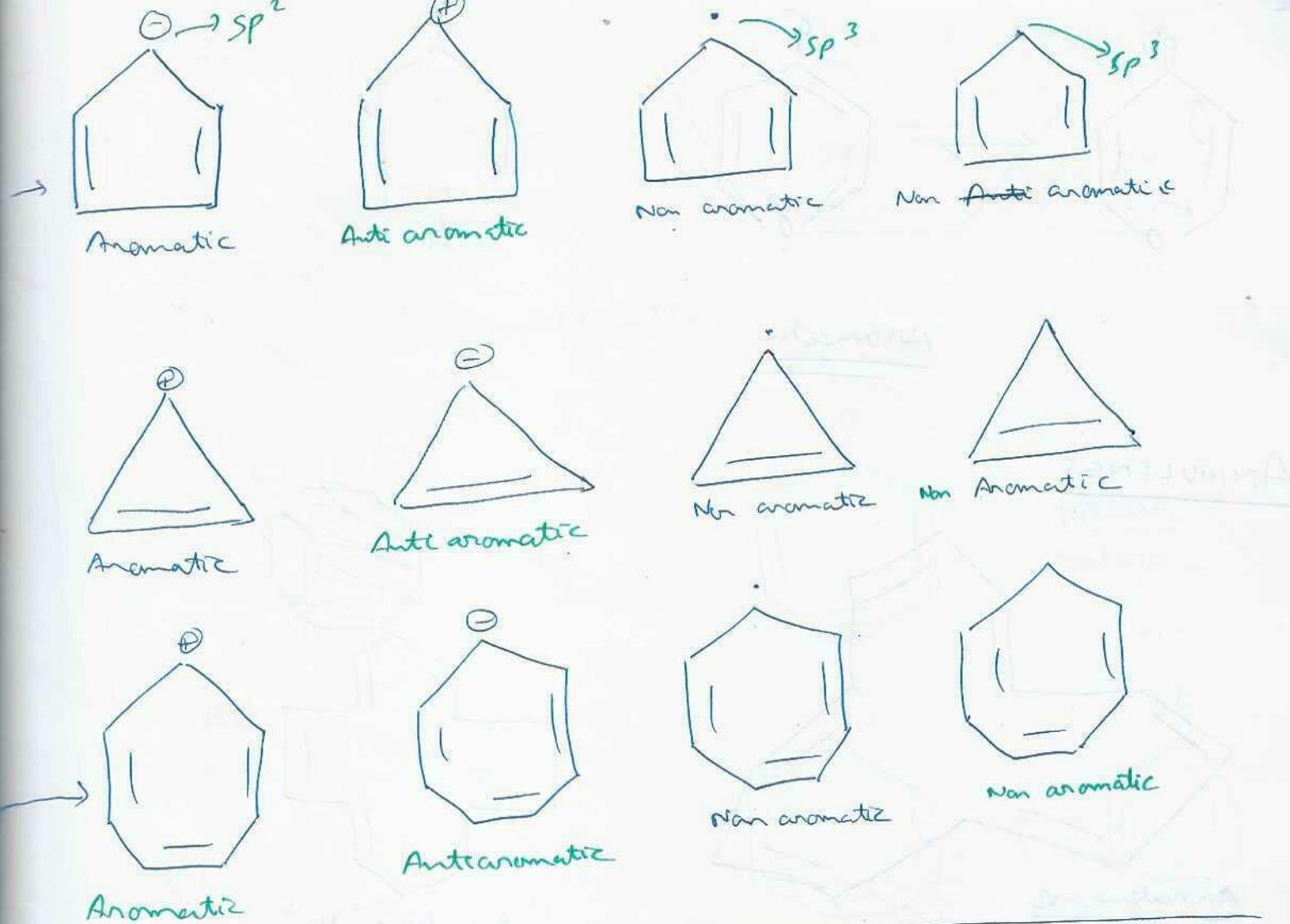


Aromatic

→ Complete  
delocalisation

↓  
Double bond  
Not delocalised

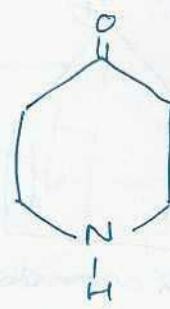
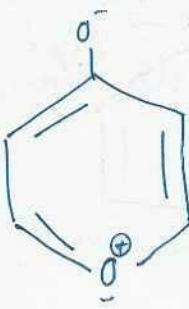
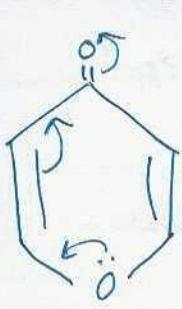




Free radical hybridisation -  $SP^3$

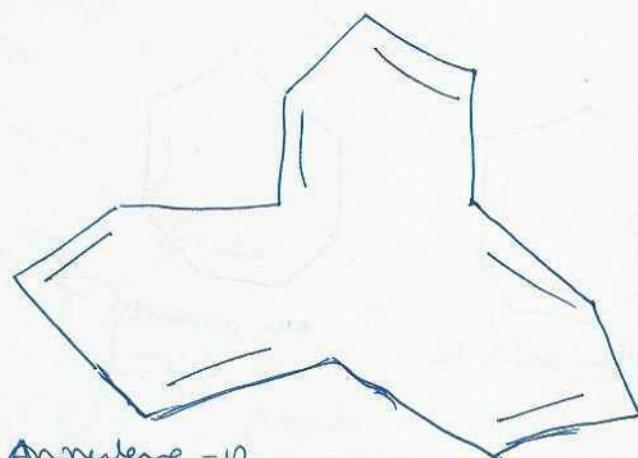
Carbocation and  
Carbanion  $\rightarrow SP^2$

Methyl free radical  $\rightarrow SP^2$



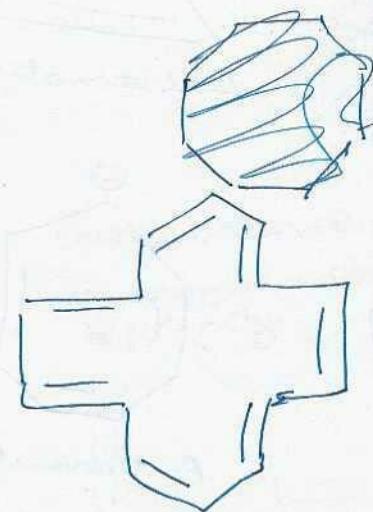
Aromatic

## ANNULENES



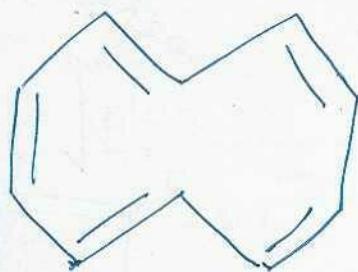
Annulene - 12

Anti aromatic



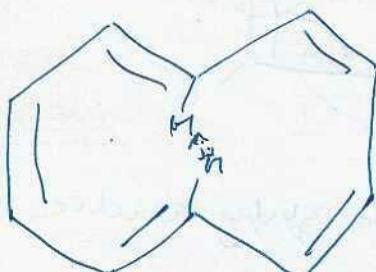
Annulene - 14

Aromatic



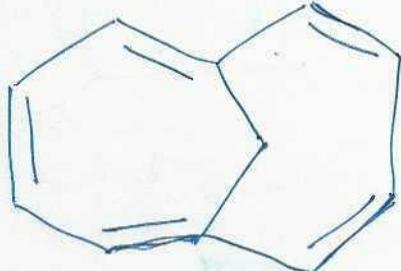
Annulene - 10

Non aromatic

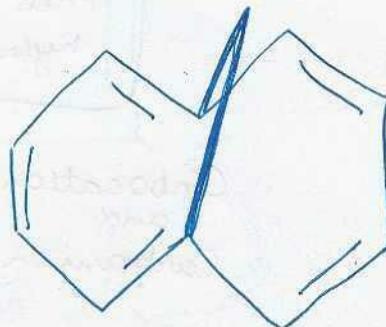


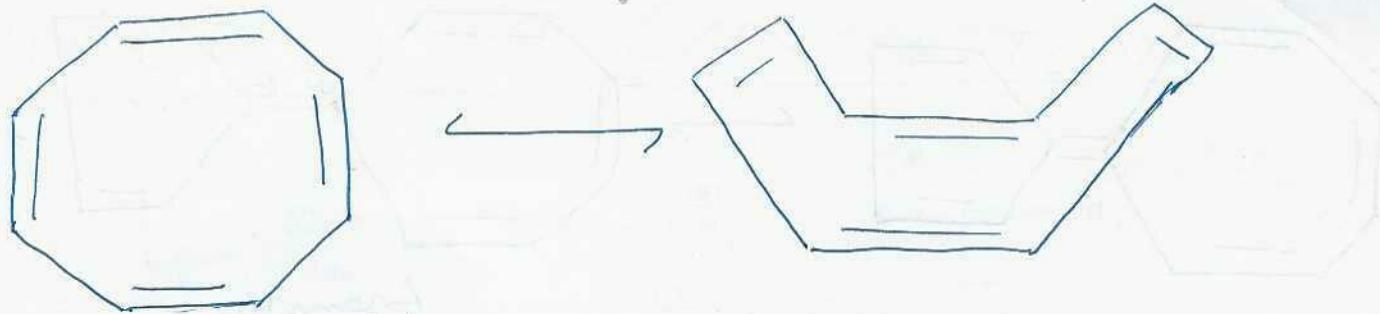
Non aromatic

Non planar

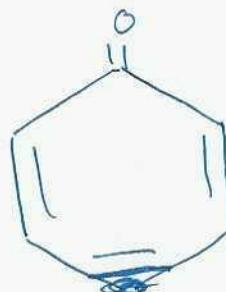
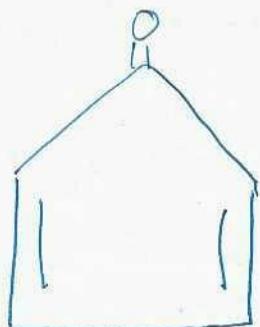


Aromatic



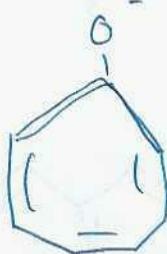
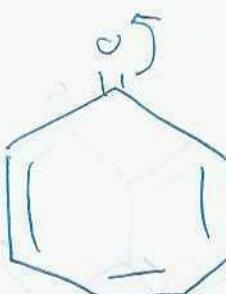
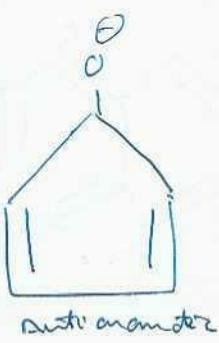


Non aromatic

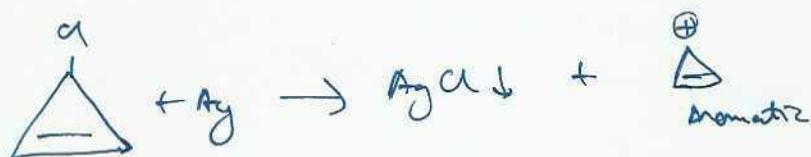
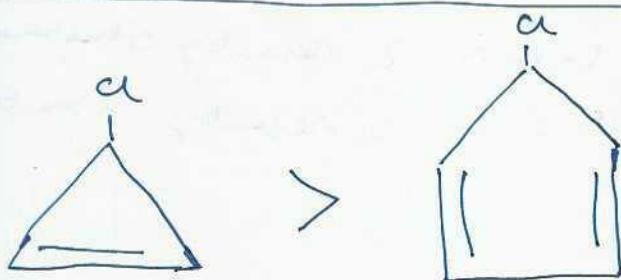


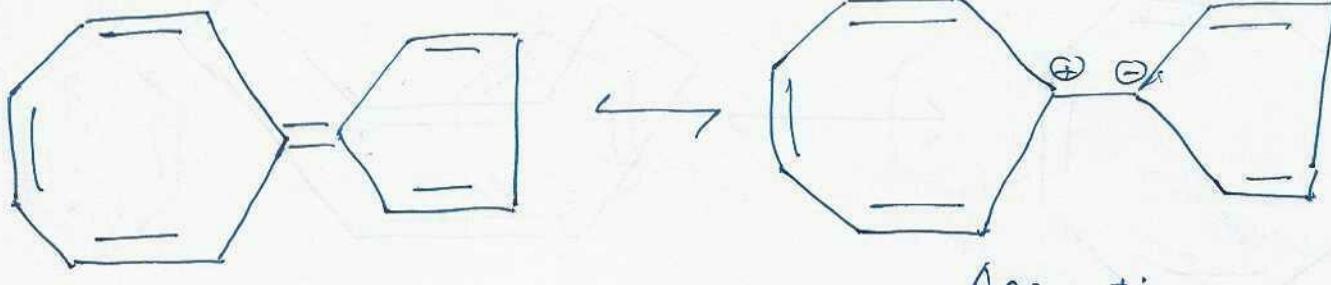
Polar  
Nature

Non polar  
(less polar)



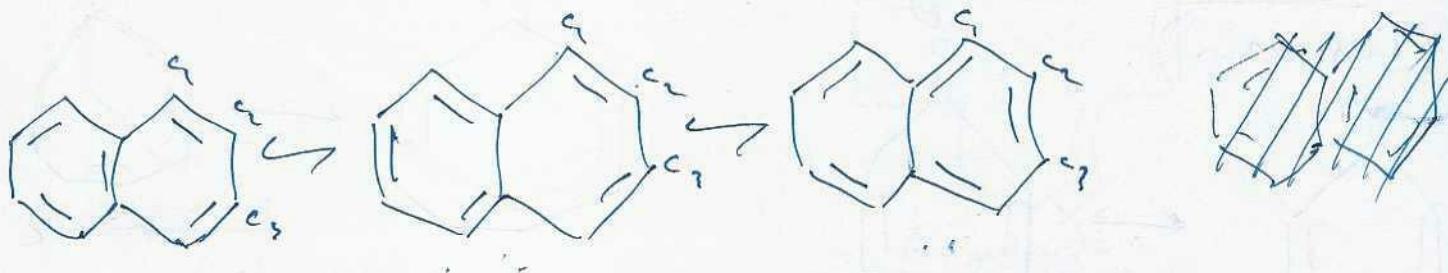
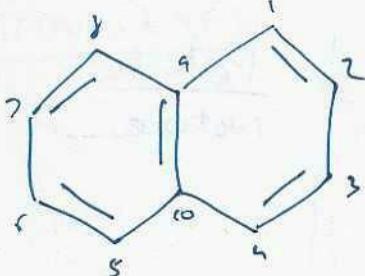
Reactivity towards  
 $\text{AgNO}_3$ .





Aromatic

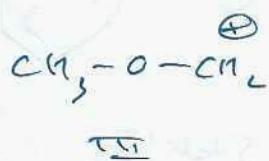
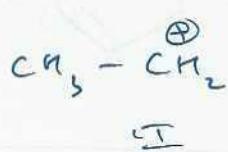
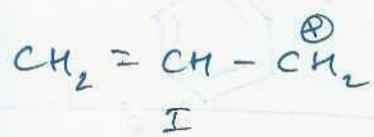
$C_1-C_2$  and  $C_2-C_3$ .



$C_1-C_2$  shorter than  $C_2-C_3$ .

~~$C_1-C_2$~~   $C_1-C_2$  has double bond on 2 resonance structures  
 $C_2-C_3$  has double bond on 1 resonance structure.

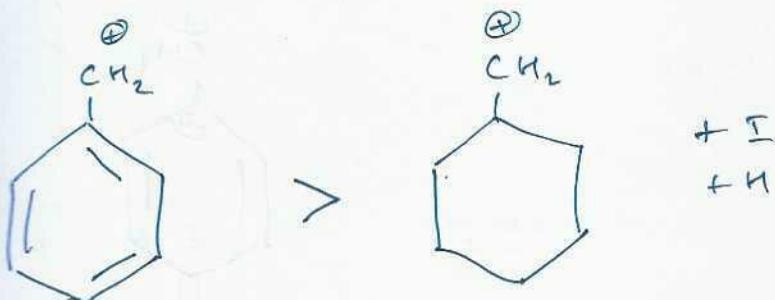
# STABILITY OF CARBOCATIONS



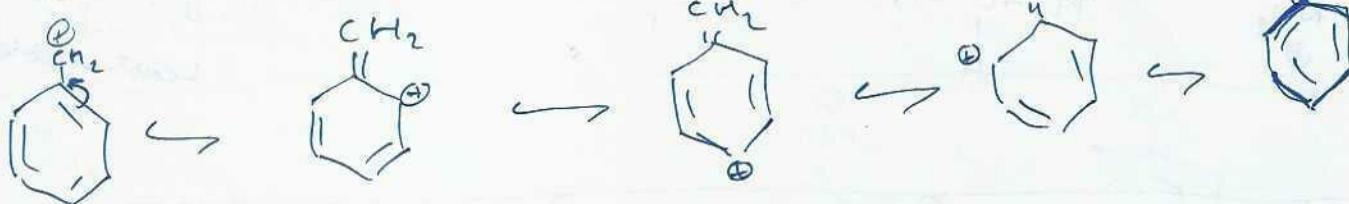
$\text{III} > \text{I} > \text{II}$   
 $+M, \text{Conjugate}, +I$

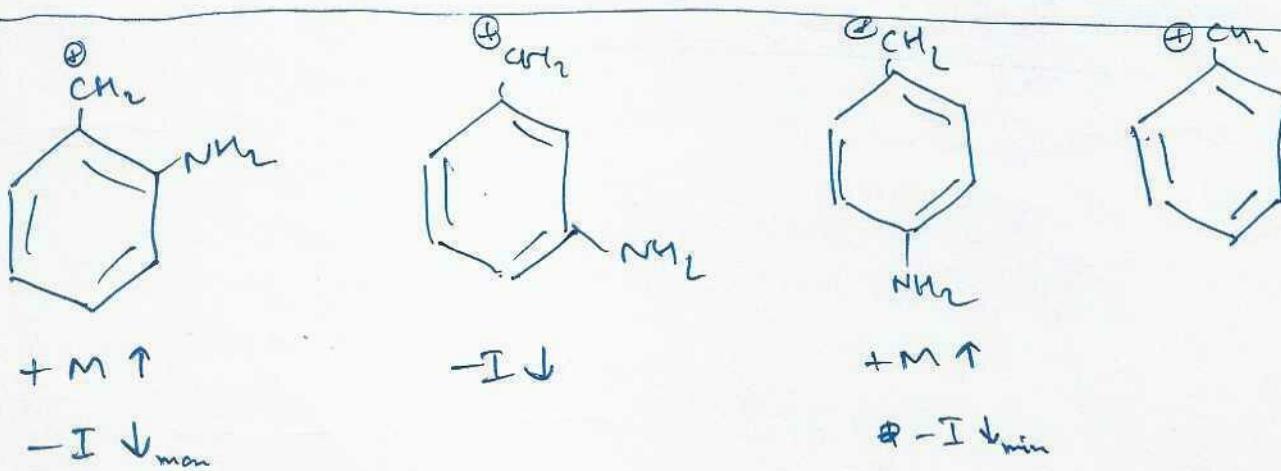
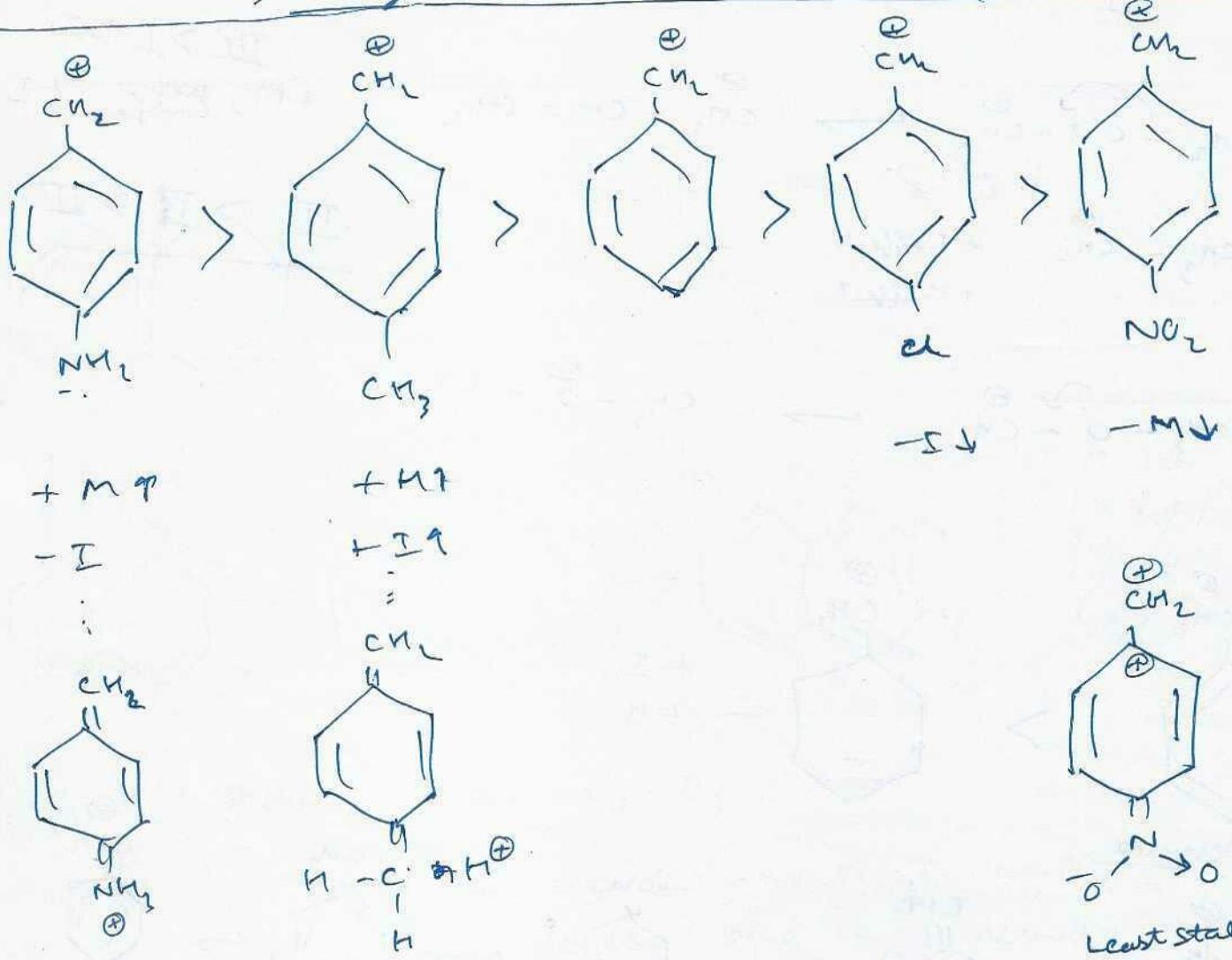
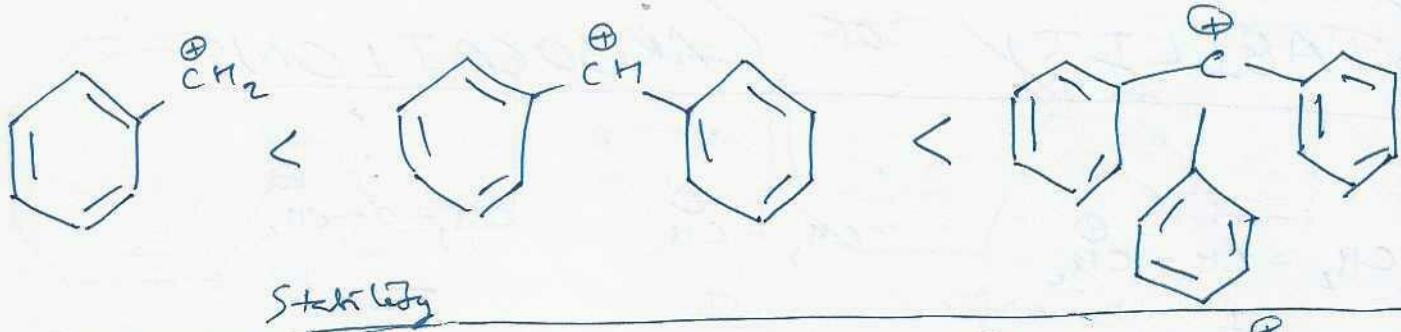


$\text{III} > \text{II} > \text{I}$



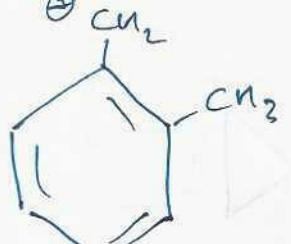
Resonance.





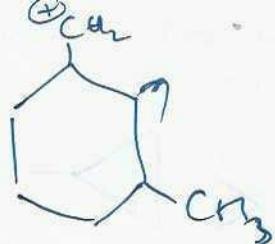
Para > Ortho > Benzyl > Meta

3,1,4,2



+ I<sub>para</sub>

+ H



+ I<sub>meta</sub>

.



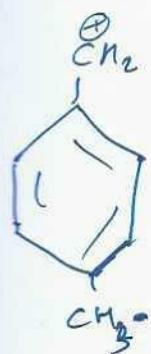
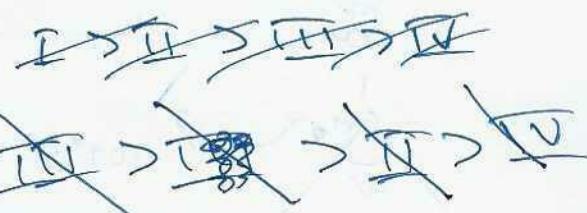
+ I<sub>ortho</sub>

+ H

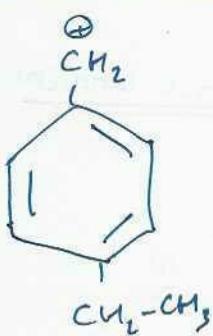


Ortho > Para > Meta > Benzyl.

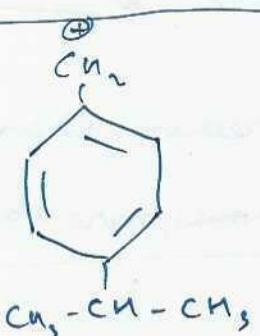
I > III > II > IV



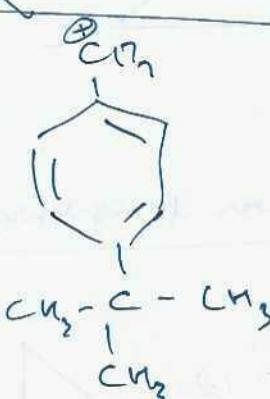
+ H → 3a



+ H → 2



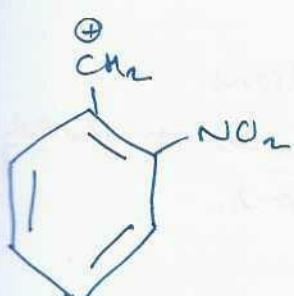
+ H → 2a



+ H X

I > II > III > IV

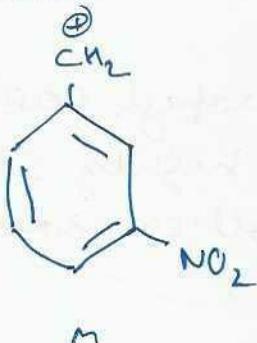
No. of  $\alpha$  hydrogen atoms.



O

- I<sub>meta</sub> ↓

- M ↓



M

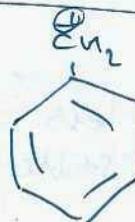
- I ↓



P

- I<sub>ortho</sub>

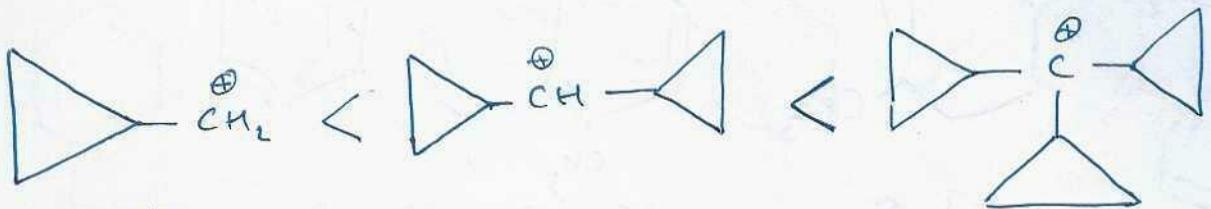
- M ↓



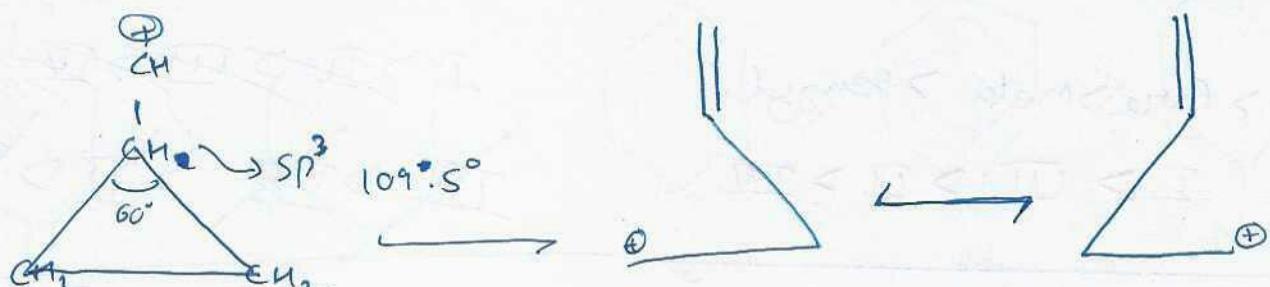
IV > II > III > I



Benzyl > meta > Para > Ortho

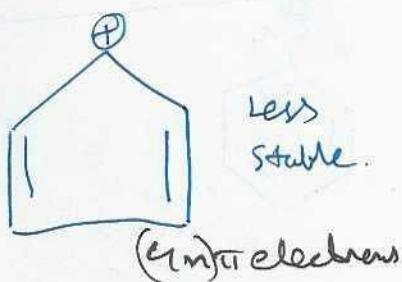
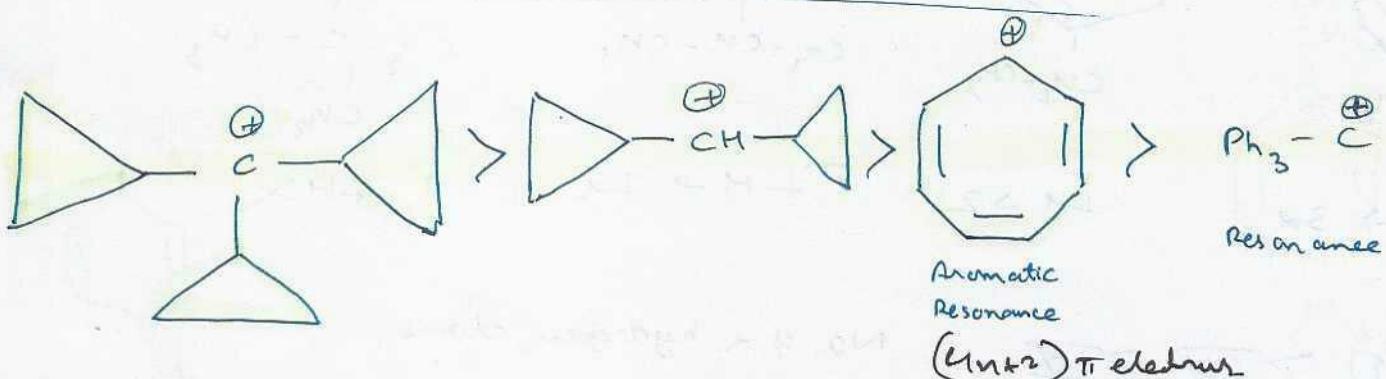


cycloproyl  
methyl  
carbocation.

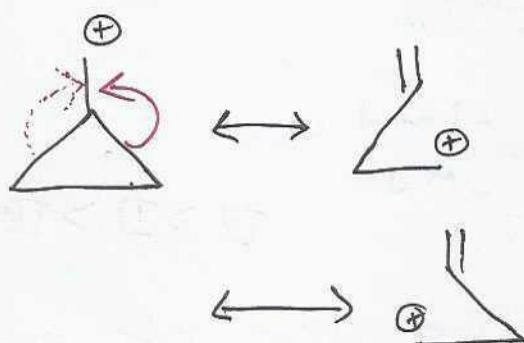


To reduce strain, bond breaks.

More number of cycloproyl groups, more stable.



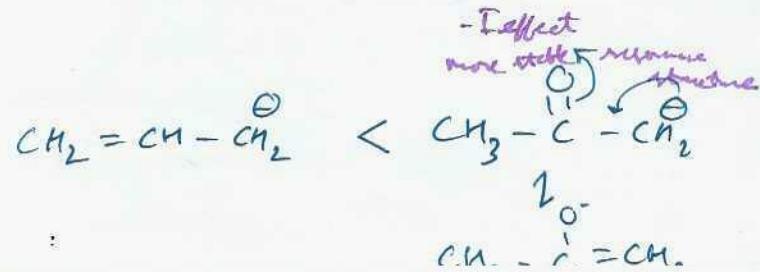
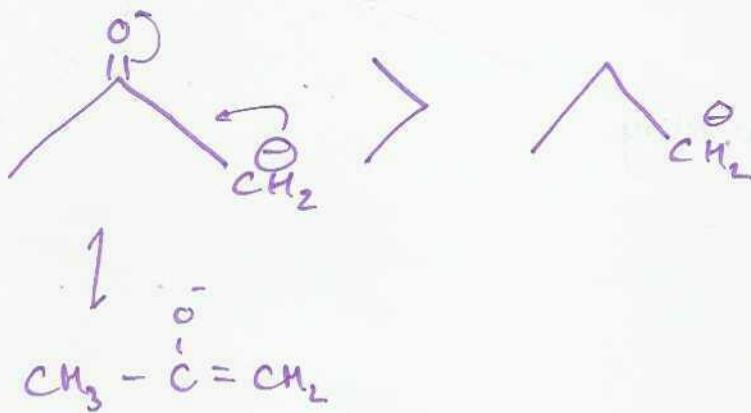
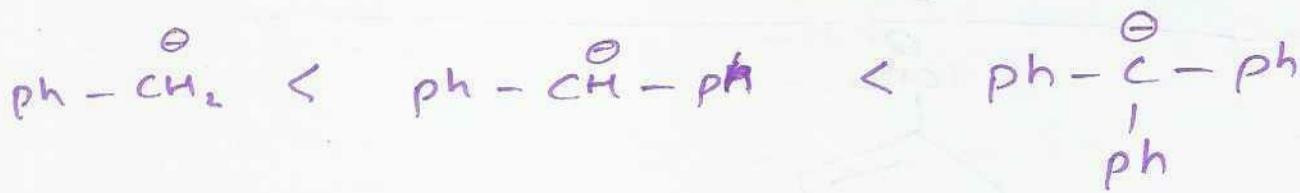
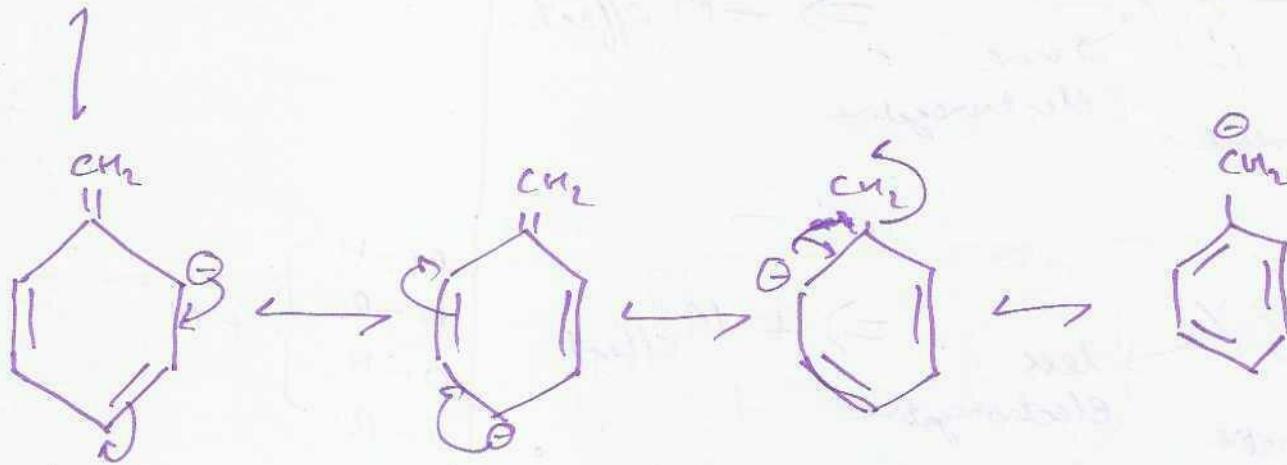
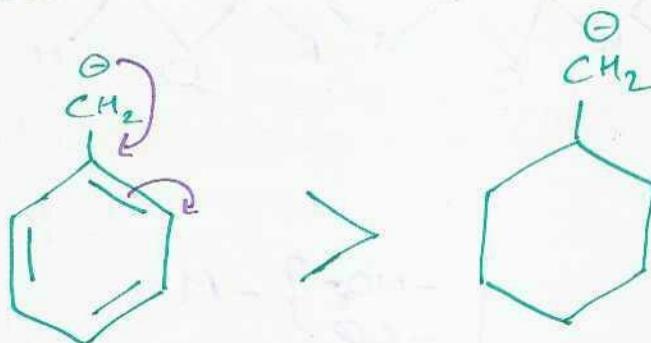
Cycloproyl carbocations are highly stable as compared to other carbocations.

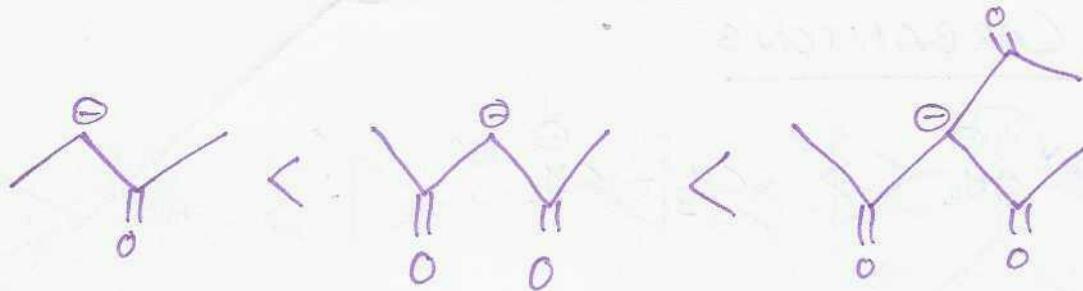


## STABILITY OF CARBANIONS

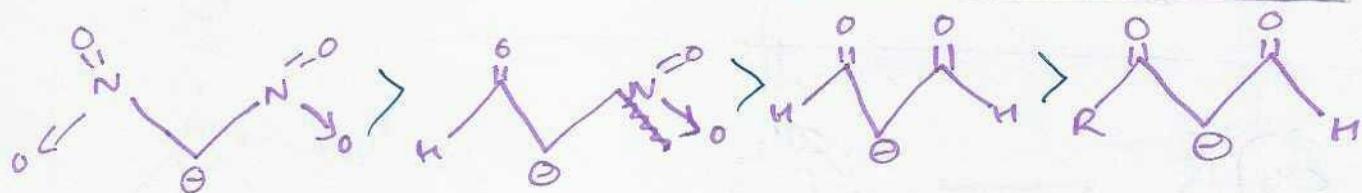


Equivalent Resonance structures

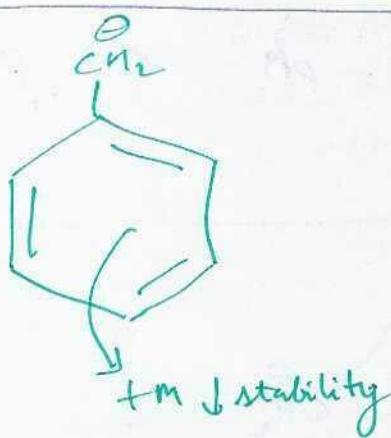
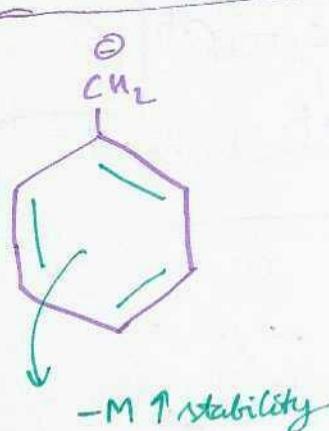
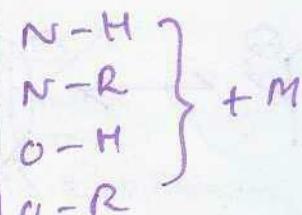
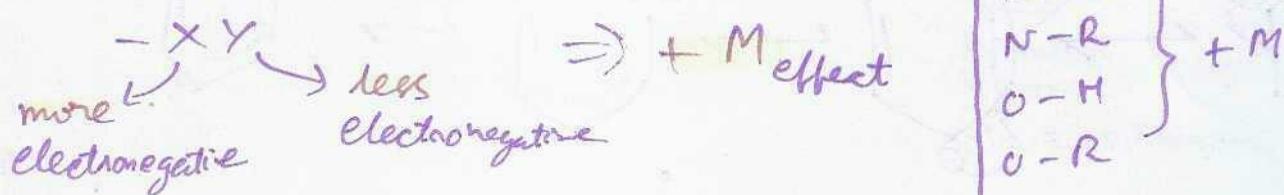
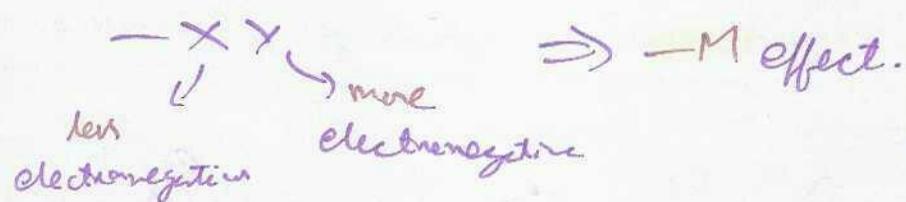


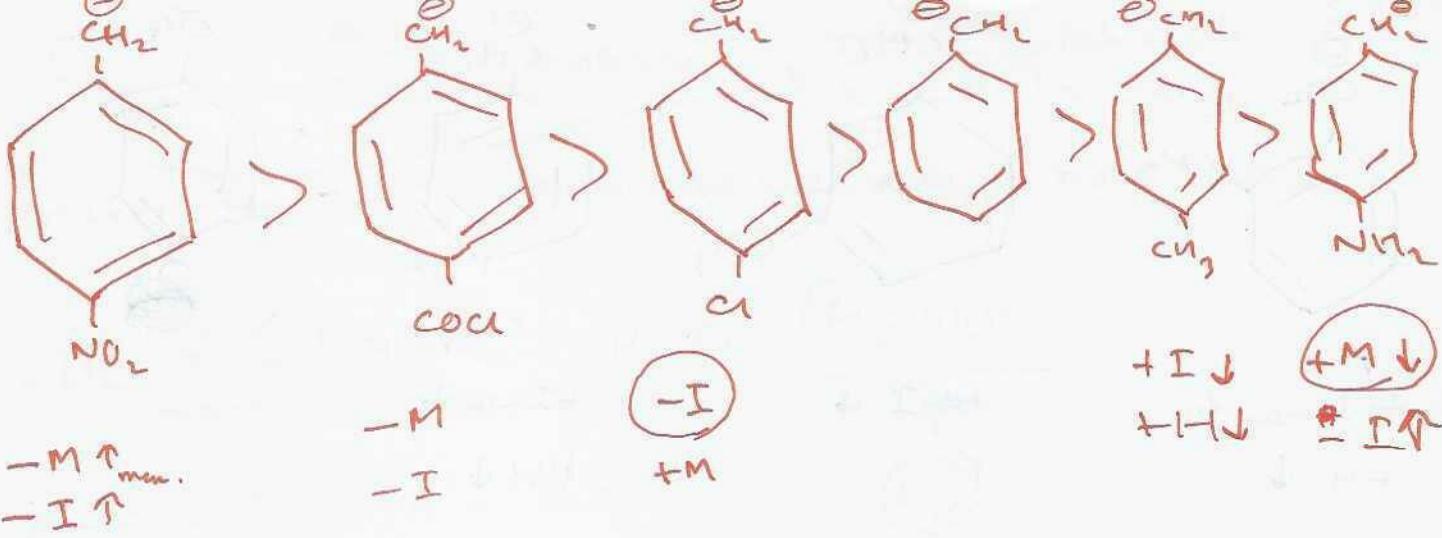


More No. of electron withdrawing groups  $\rightarrow$  More stable.

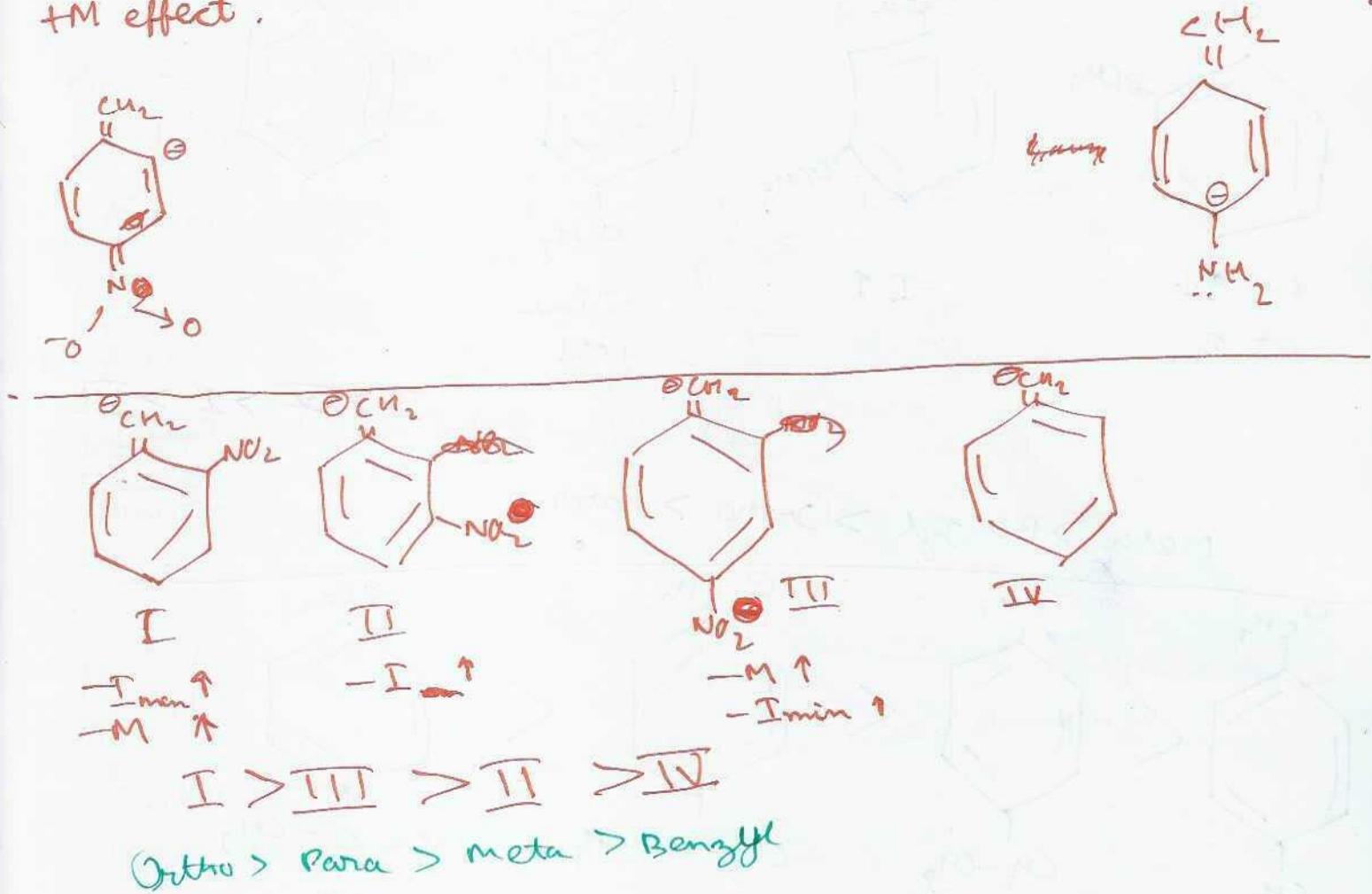


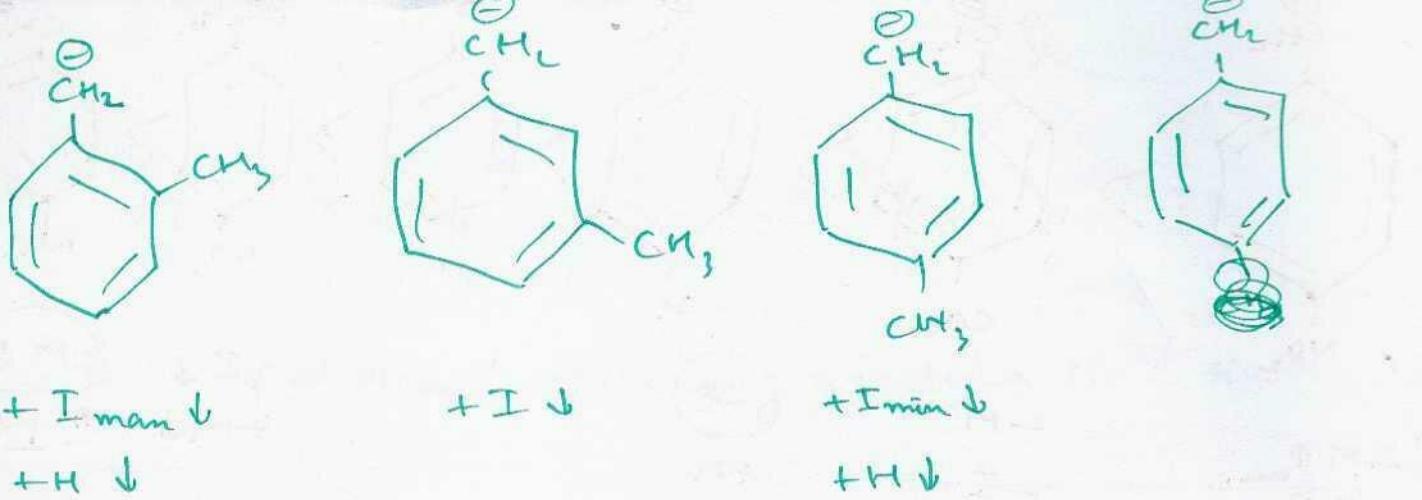
To determine  $-M$  or  $+M$





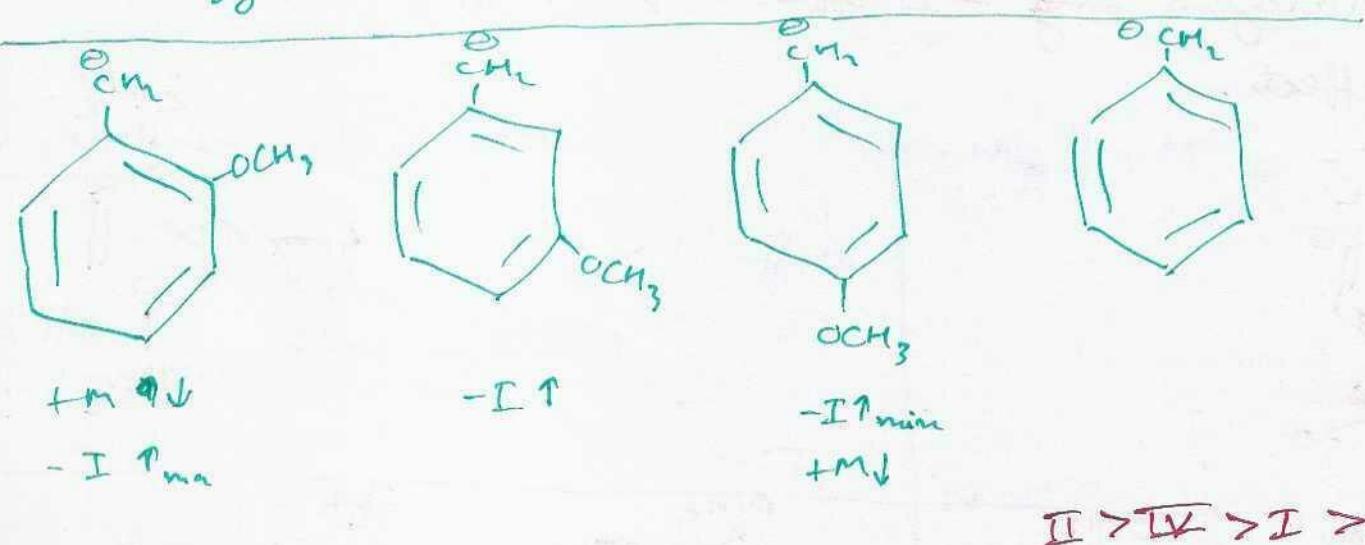
In Halogens only -I effect is generally dominating over +M effect.



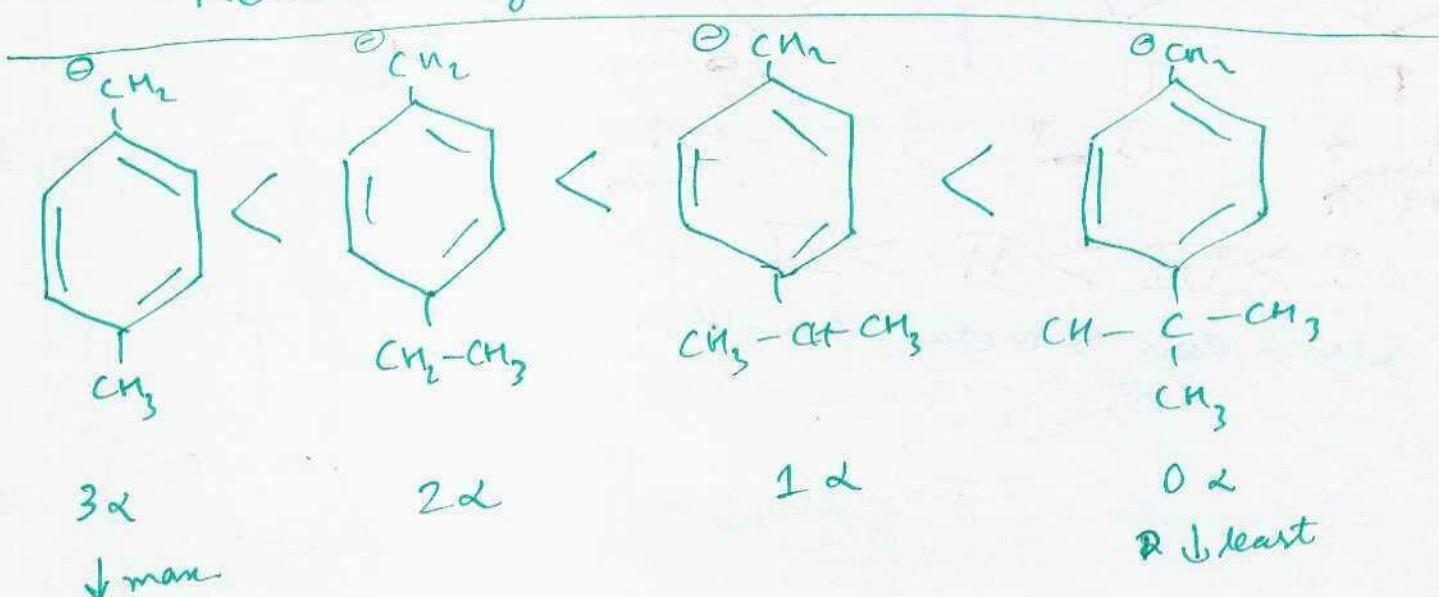


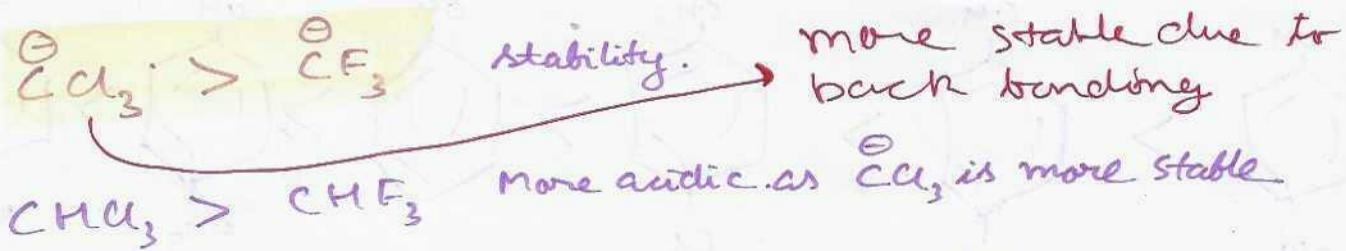
Benzyl > Meta > Para > Ortho.

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

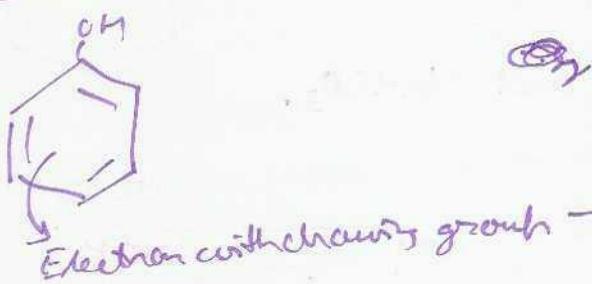
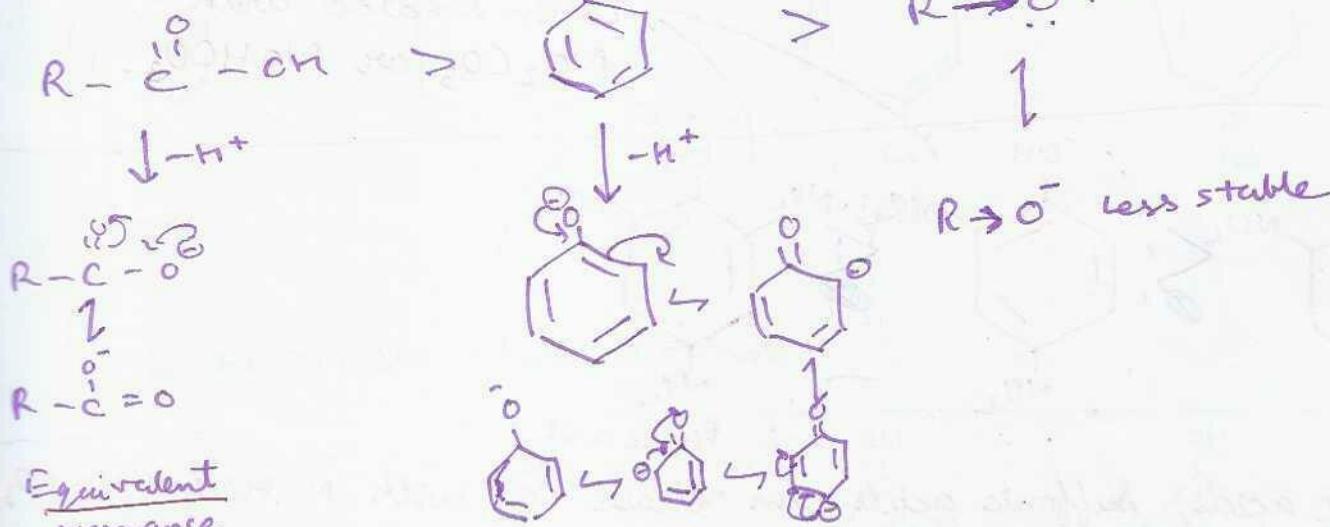
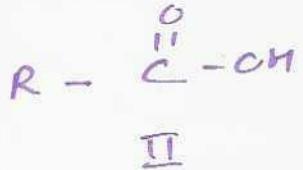
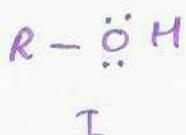


Meta > Benzyl > Ortho > Para

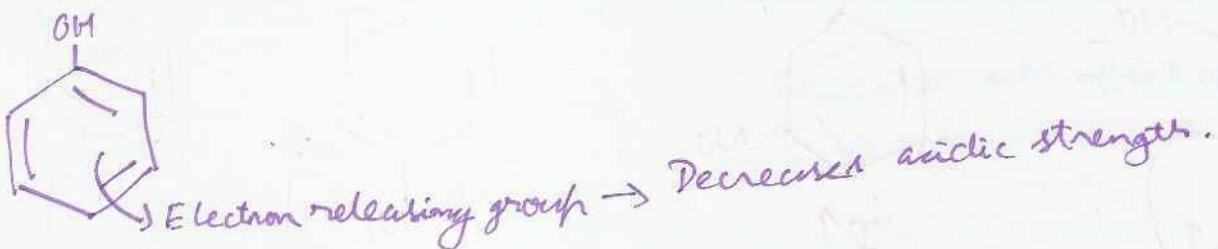


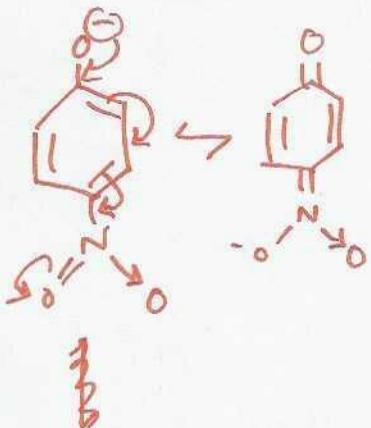
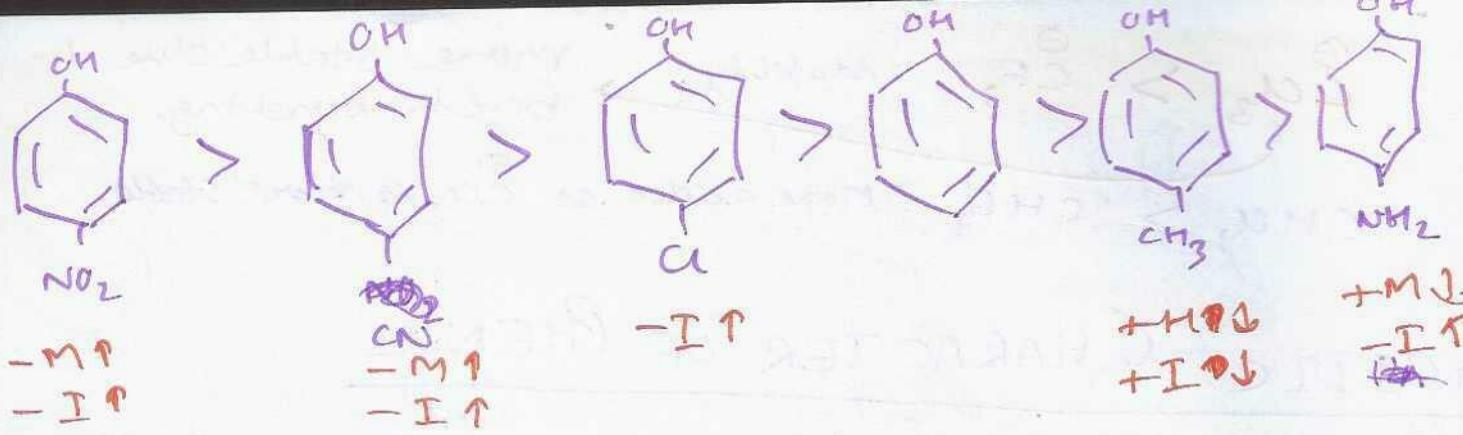


## ACIDIC CHARACTER OF PHENOL

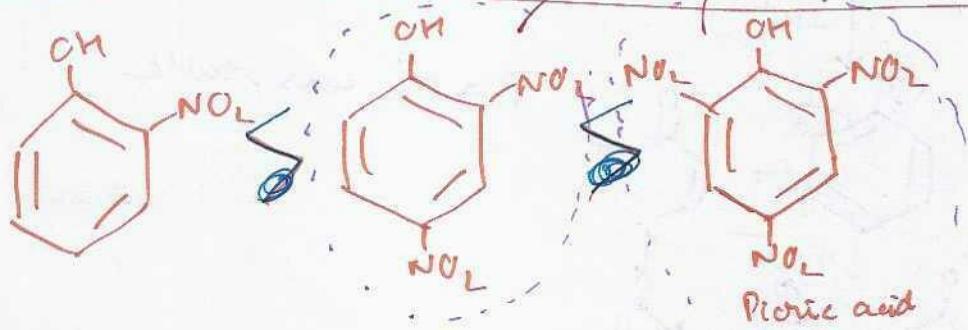


Electron withdrawing group → Increases acidic strength.



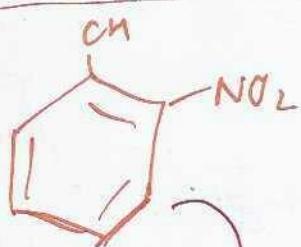


Can release  $\text{CO}_2$  when treated with  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$ .



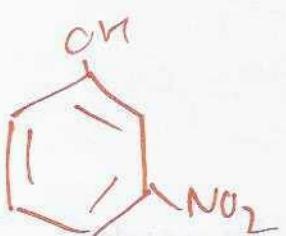
Carboxylic acids, sulfonic acids can release  $\text{CO}_2$  with  $\text{NaHCO}_3$  &  $\text{Na}_2\text{CO}_3$

Phenols do not release  $\text{CO}_2$  with  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ .  
However, the above two release  $\text{CO}_2$



-Iman $\uparrow$   
-M↑

Less acidic  
due to hydrogen  
bonding.



-I↑



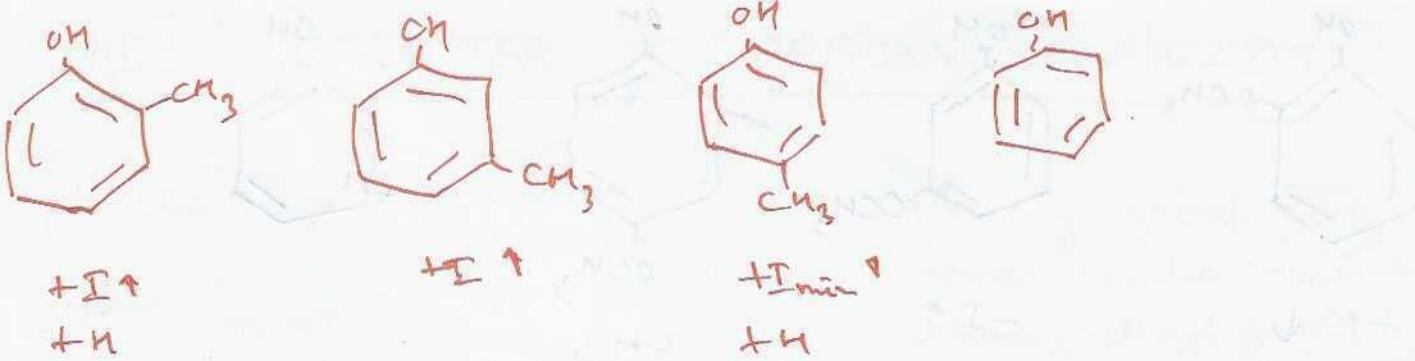
-I↑min  
-M↑



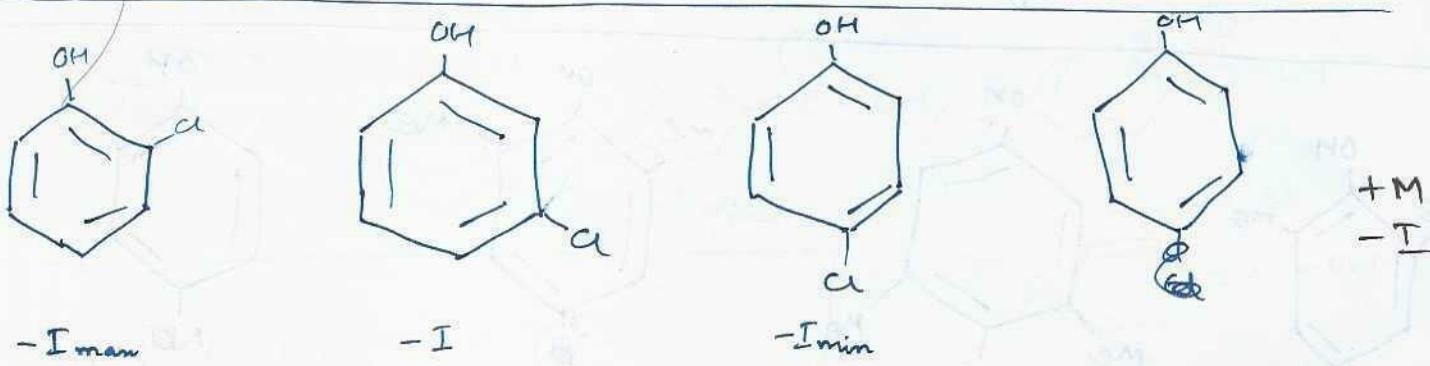
Most acidic  
of the four

B) Para  $>$  Ortho  $>$  Meta  $>$  Benzyl

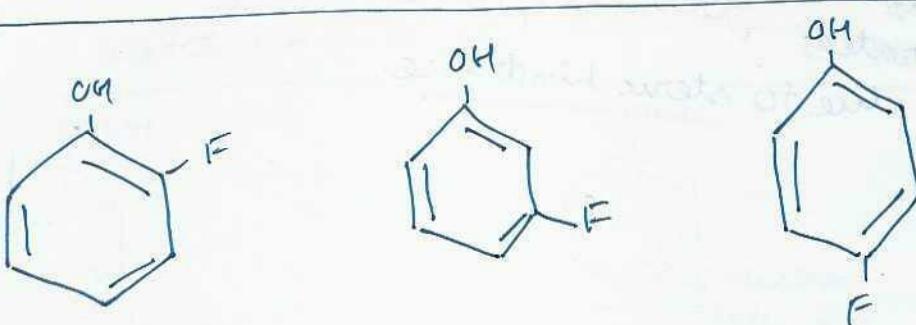
III  $>$  I  $>$  II  $>$  Benzyl



Benzyl  $\rightarrow$  Meta  $\rightarrow$  Para  $\rightarrow$  Ortho      IV  $>$  II  $>$  III  $>$  I



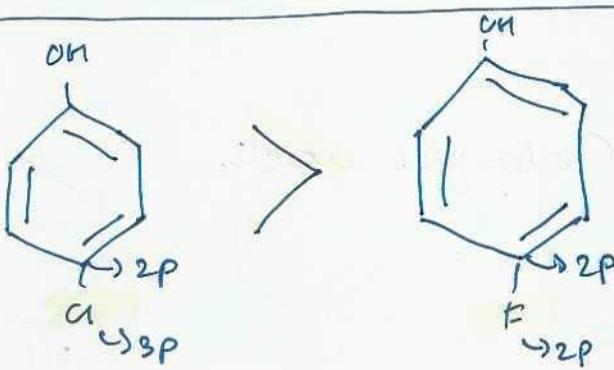
Ortho  $>$  Meta  $>$  Para  $>$  Phenol



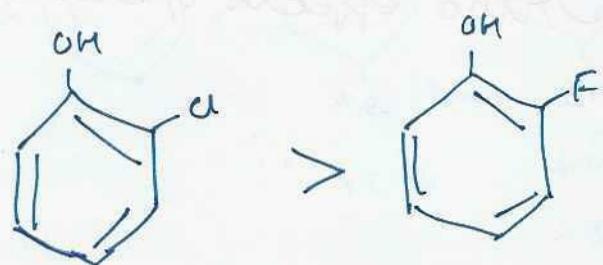
Ortho  $>$  Meta  $>$  Para  $>$  Phenol.

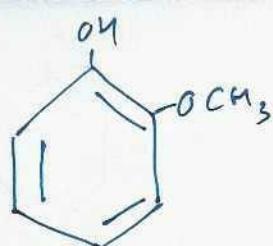
Hydrogen bonding does not have a big influence.

Hydrogen bonding influences when NO<sub>2</sub> group at ortho position.



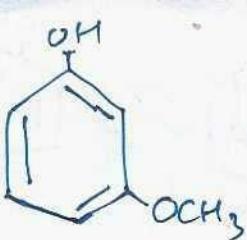
Because +M effect of F is more than Cl.



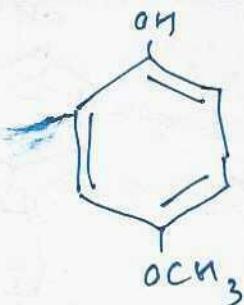


$+M \downarrow$

$-I^{\uparrow}_{\text{max}}$



$-I^{\uparrow}$

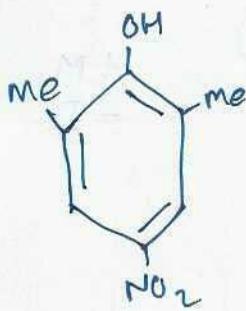


$+M \downarrow$

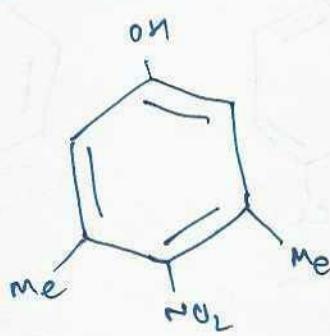
$-I^{\uparrow}_{\text{min}}$



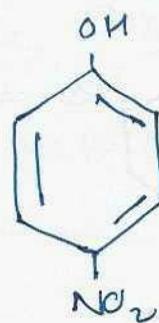
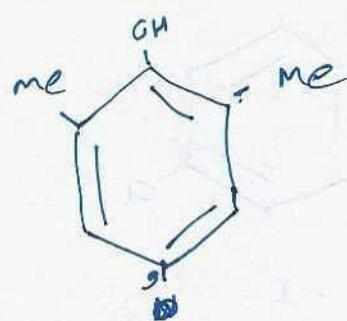
Meta > <sup>Phenol</sup> Benzene > Ortho > Para.



$+I$  effect  
does not have  
very big effect  
so is nearly equal  
to



$-I \downarrow$   
 $-M_{\text{eff}} \text{ is}$   
not operated  
here due to steric hindrance.



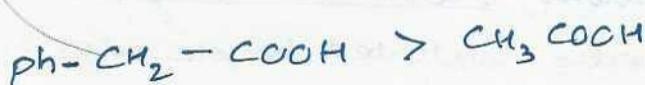
$4 \tilde{>} 1 > 2 > 3$

Ortho effects operates in Carboxylic acids.

# ACIDIC CHARACTER OF CARBOXYLIC ACIDS

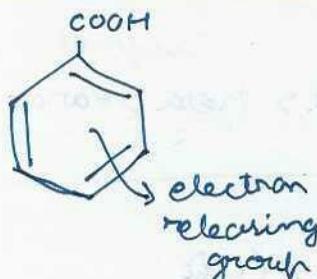
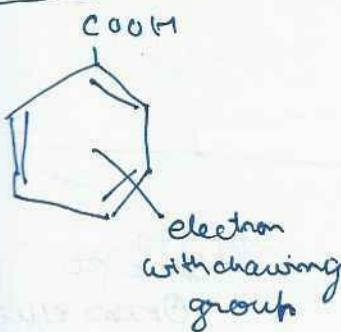
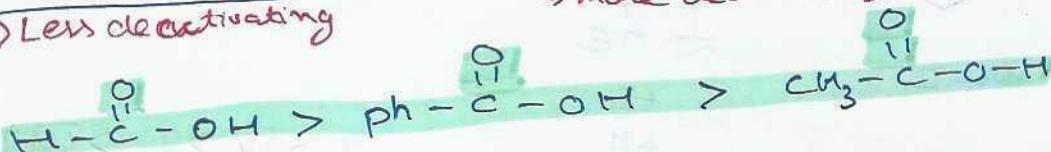
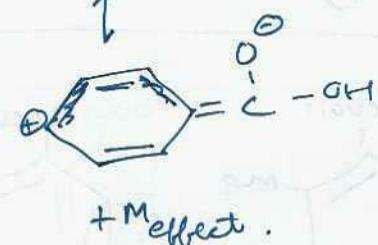
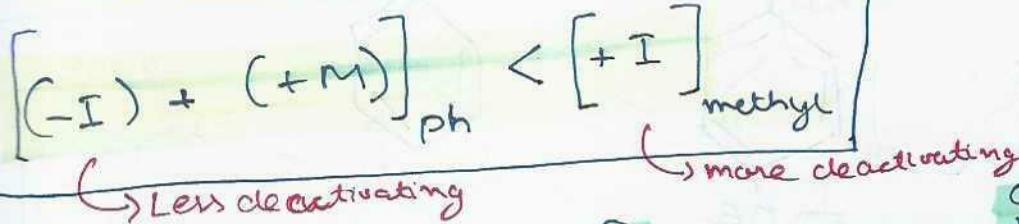
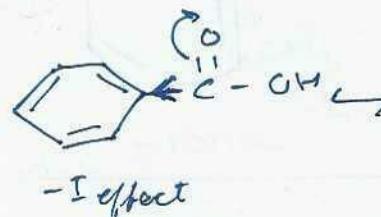
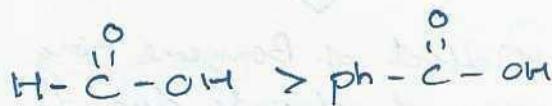


-I effect



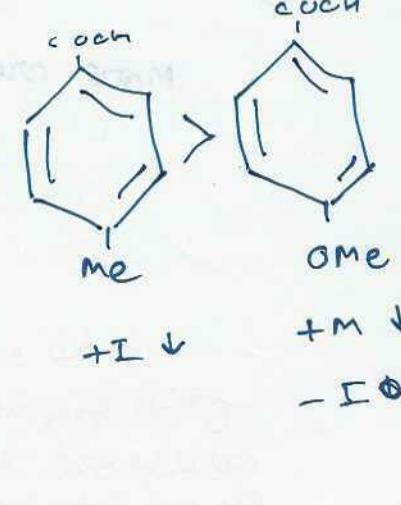
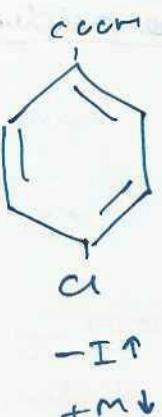
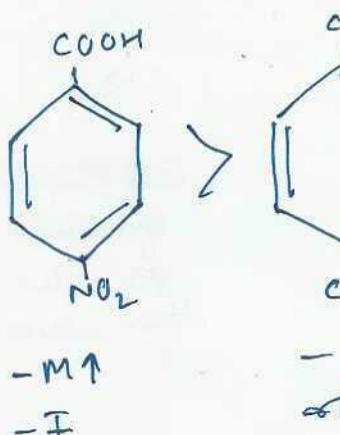
-I effect

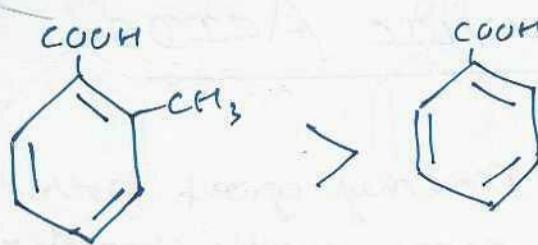
Phenyl group gives more acidic character than methyl group.



Decreases acidic character.

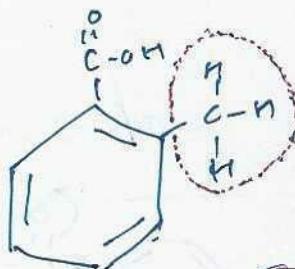
Increases acidic nature.





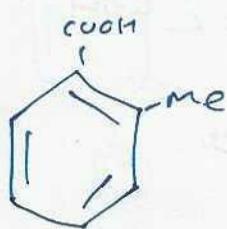
Benzene ring itself has a +M effect.

Ortho effect: Irrespective of substituent, electron releasing or withdrawing nature, ortho substituted benzoic acid is most acidic.



+M effect of Benzene ring does not operate due to steric hindrance.

Net applicable for  $\text{NH}_2$   
steric inhibition of protonation



Ortho effect



+I

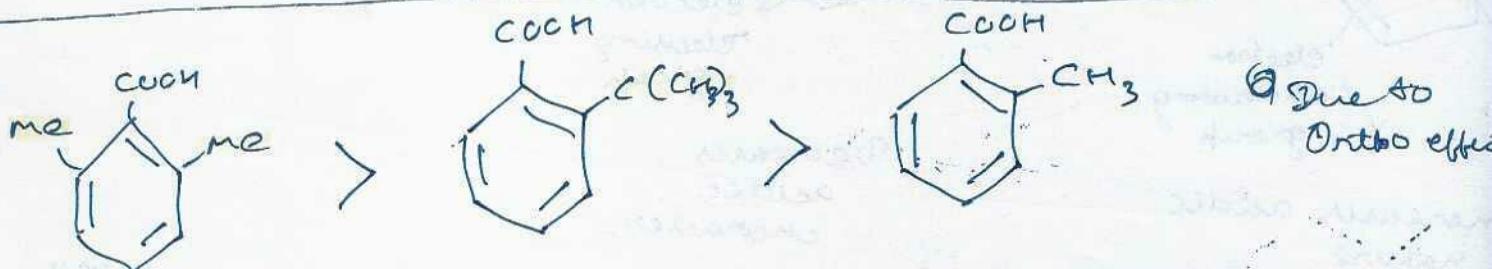


+I  
+H



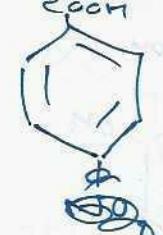
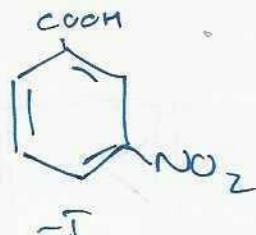
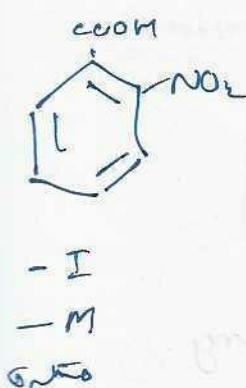
I > IV > II > III

Ortho > Benzoic acid > Meta > Para

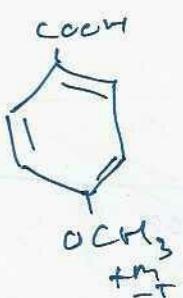
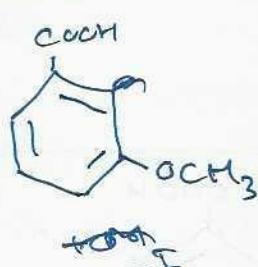
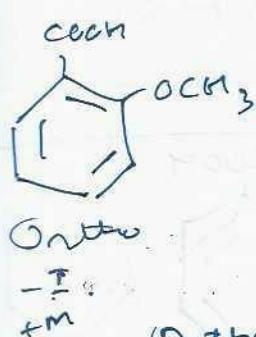


Due to Ortho effect

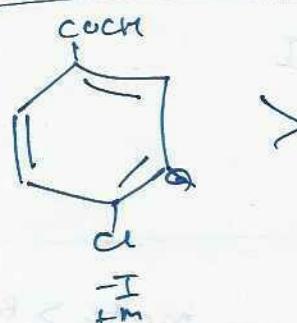
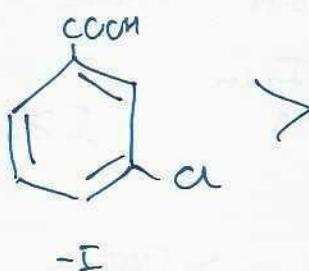
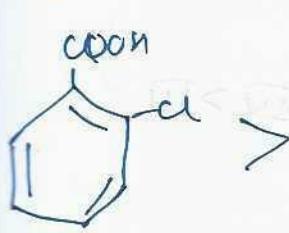
More crowding  $\rightarrow$  more acidic character.



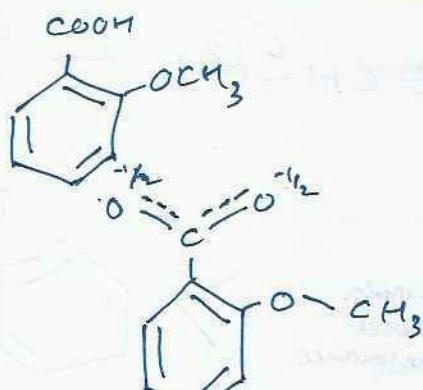
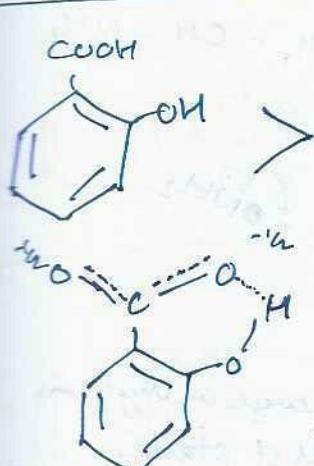
Ortho > Para > Meta > Benzoic



Ortho > Meta > Benzoic > Para



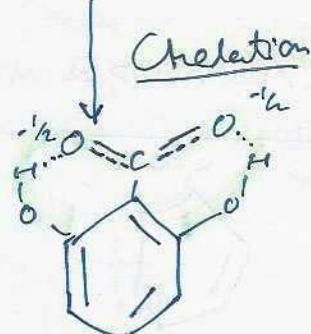
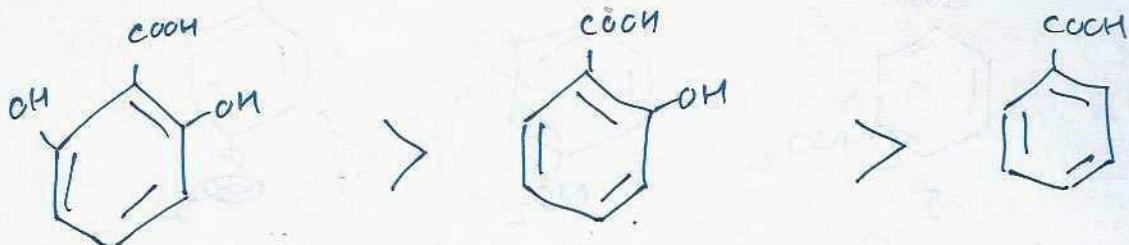
Ortho > Meta > Para > Benzoic



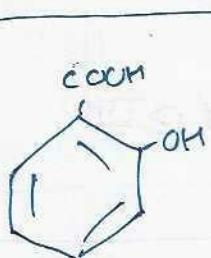
No hydrogen bonding is seen here.

Hydrogen bonding makes it more stable

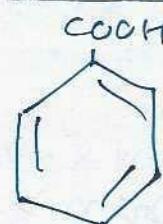
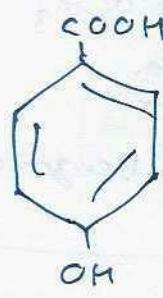
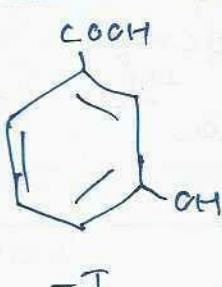
Hydrogen bonding takes place when OH group is attached to benzene ring. makes it more acidic as it stabilizes the anion formed after donation of H<sup>+</sup>.



Stabilised by hydrogen bonding.



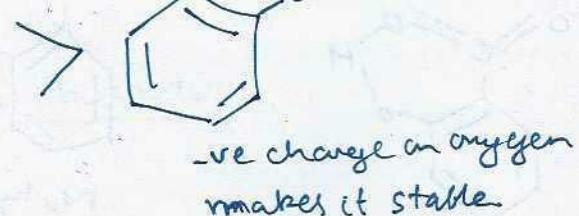
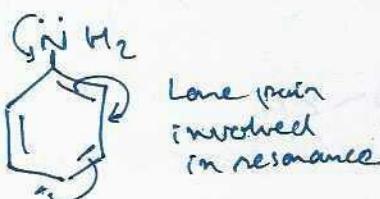
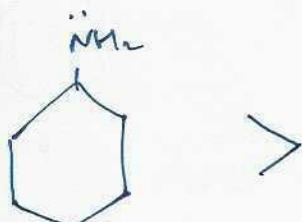
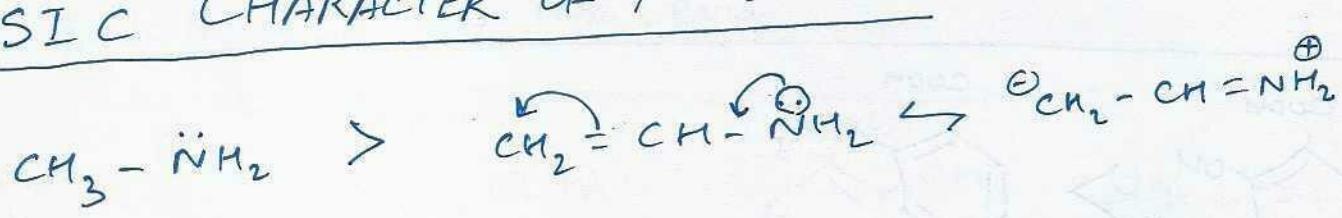
Ortho  
hydrogen bonding  
+ M  
≠ - I

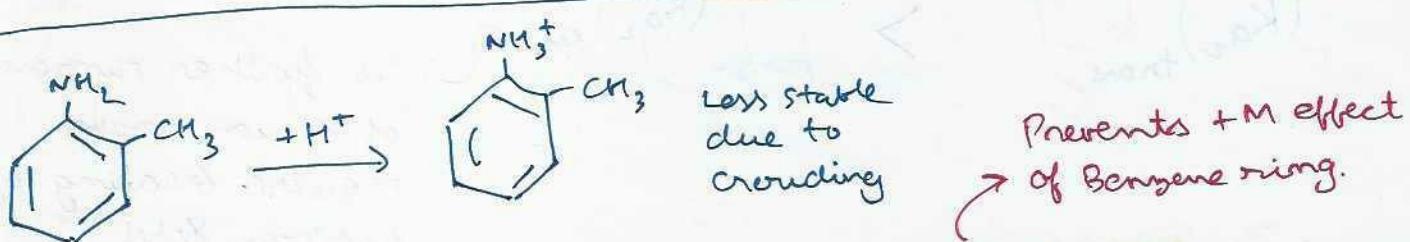
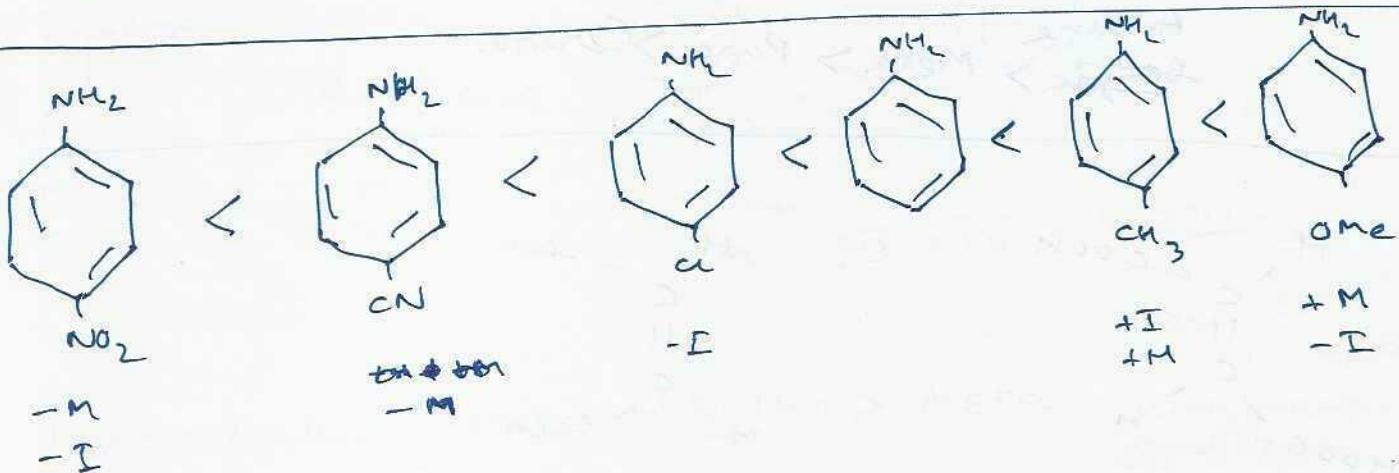
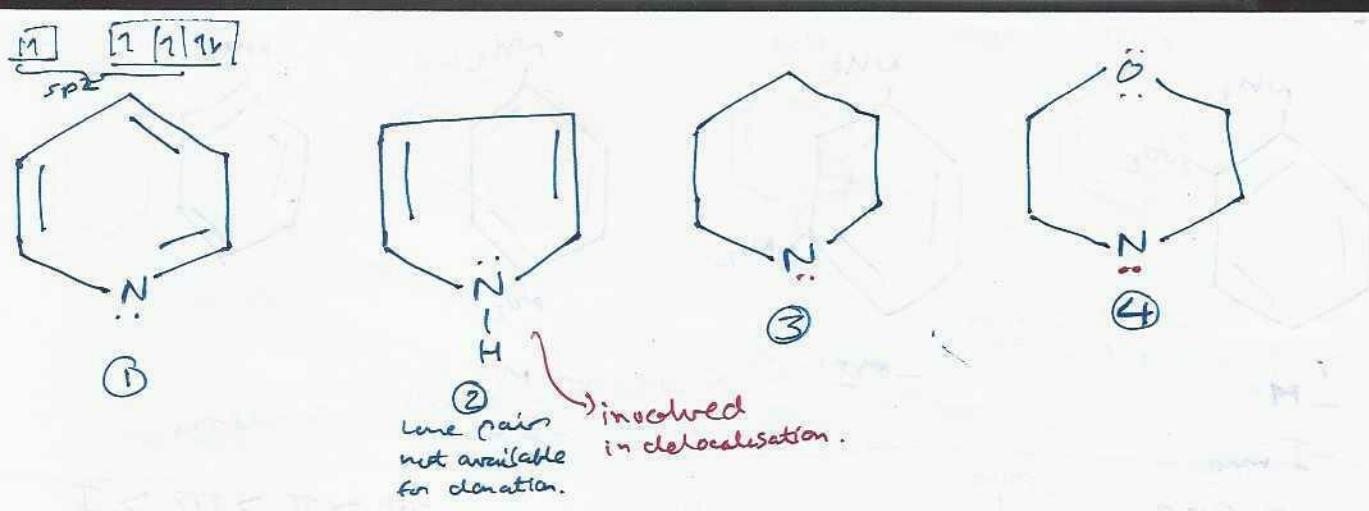


I > II > IV > III

Ortho > meta > Benzoic > Para

## BASIC CHARACTER OF AMINES



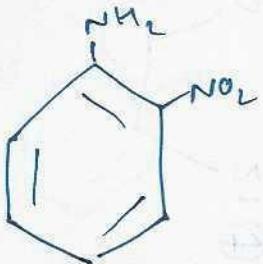


This is known as Steric Inhibition of Protonation.

Ortho isomers are least basic.

Not always.

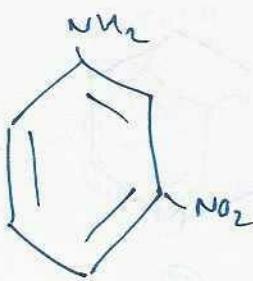
Ortho effect is always.



-M

-I max

~~extra SIP~~

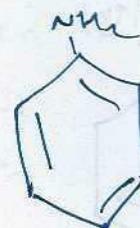


-~~M~~I



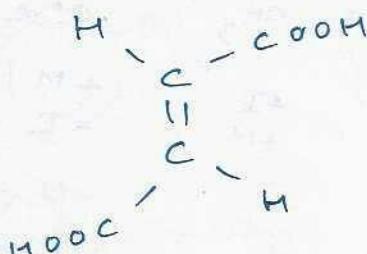
-M

-I min



IV > II > III > I

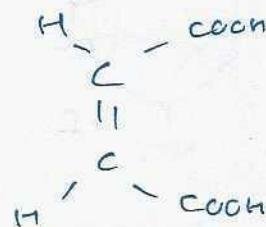
Aniline  
Benzac > Meta > Para > Ortho.



Fumaric

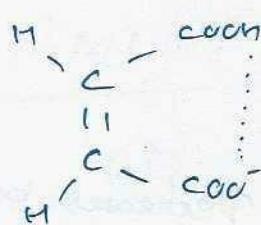
$(K_{a_1})_{\text{trans}}$

$\ominus <$



Malic

$(K_{a_1})_{\text{cis}}$



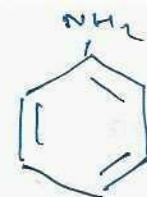
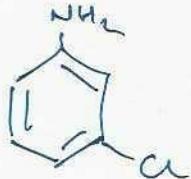
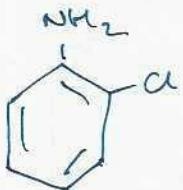
as it can form hydrogen bond after proton donation

$(K_{a_2})_{\text{trans}}$

$>$

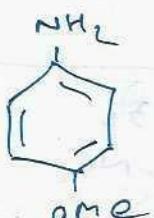
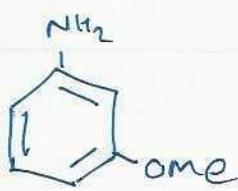
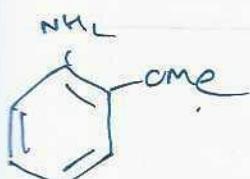
$(K_{a_2})_{\text{cis}}$

as further removal of  $\text{H}^+$  ion would require breaking of hydrogen bond.



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

Aniline > Para > Meta > Ortho



+M  
-I

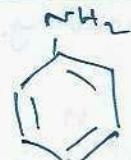
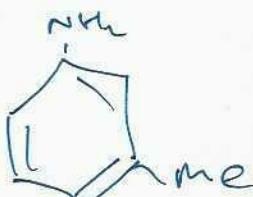
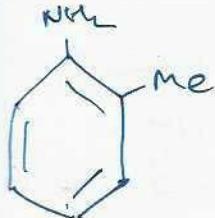
$\rightarrow \text{I}$

-I min  
+M

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

Here SIP  
does not make  
ortho isomer  
least basic.

Para > Aniline > Meta > Ortho > Meta



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

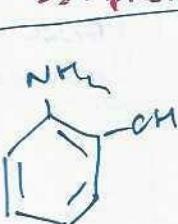
Me is tetrahedral

$\Rightarrow$  more crowding.

SIP prominent

Para > meta > Aniline > Ortho

Ortho effect: more prominent as Me is tetrahedral.



+M  
-I

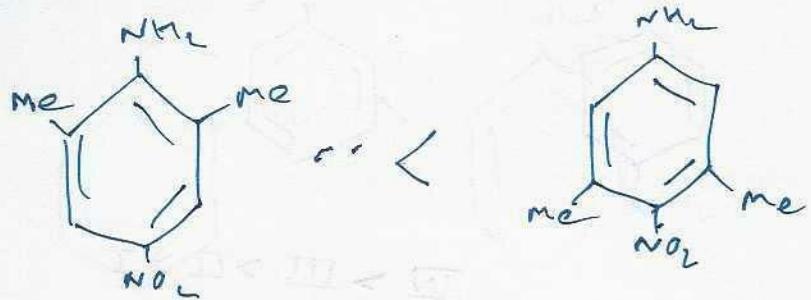
$\rightarrow \text{I}$

-I  
+M

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

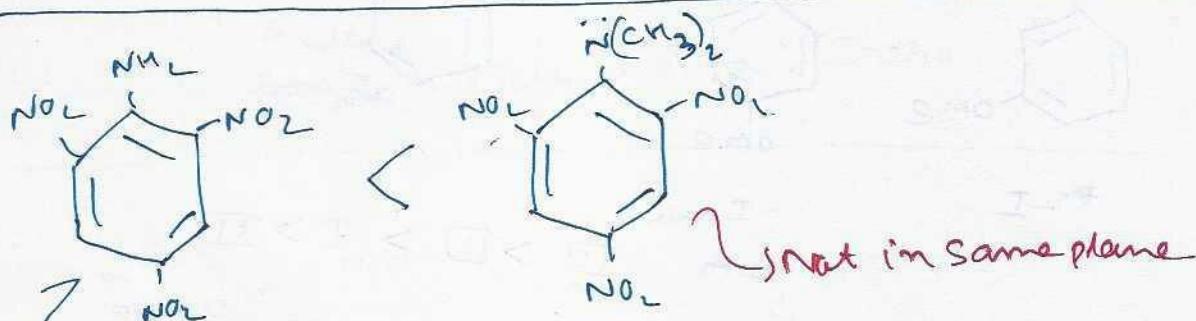
Para > Ortho > Aniline > Meta

Steric Inhibition is very less.



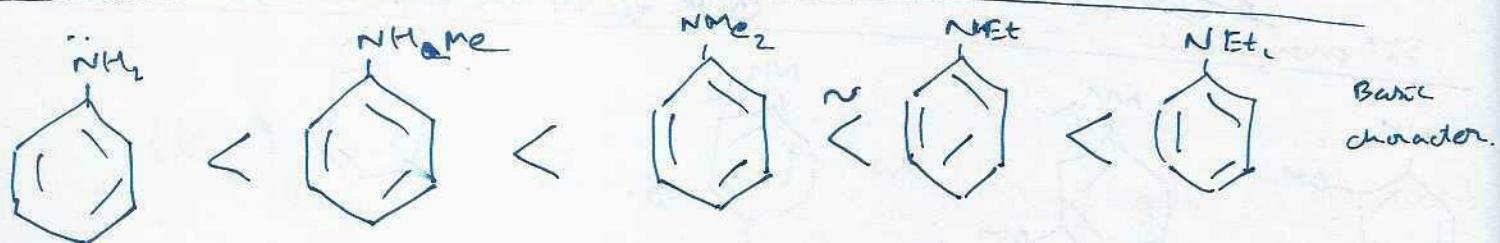
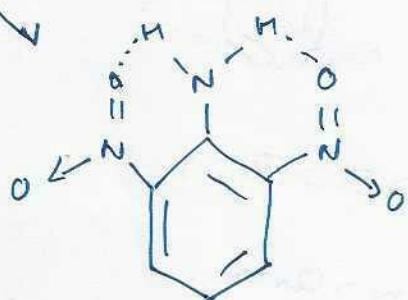
- M of  $\text{NO}_2$   
is operated

- M of  $\text{NO}_2$  is not  
operated (Steric inhibition of resonance)



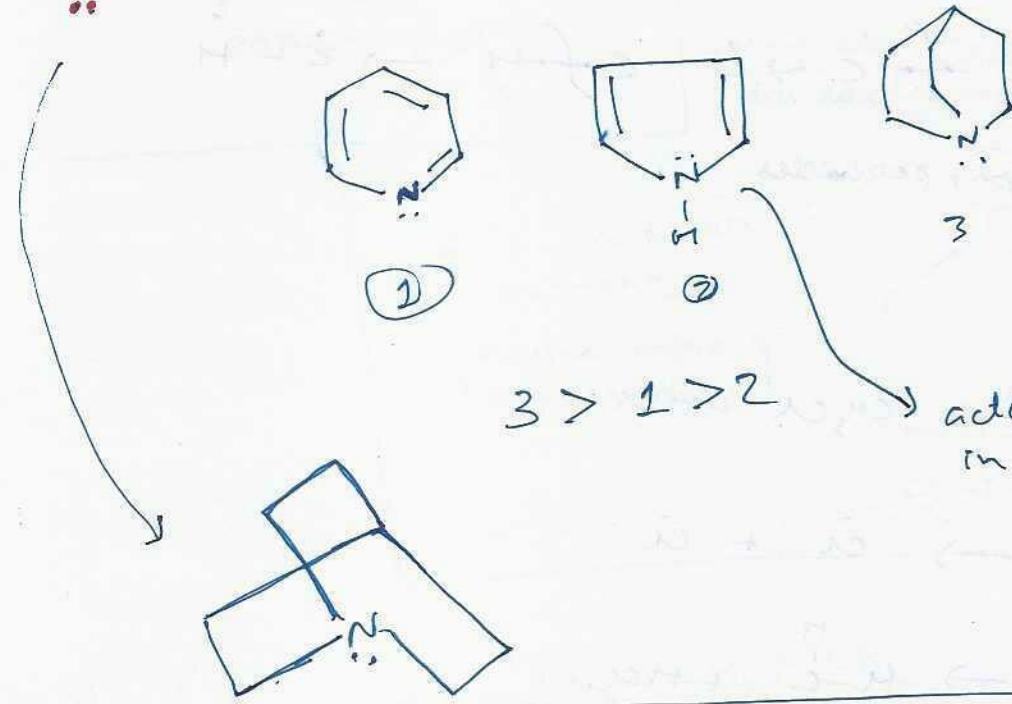
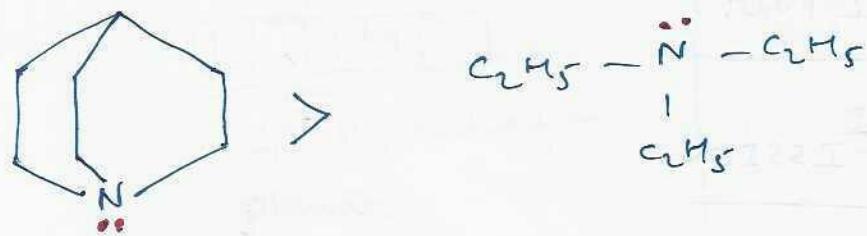
Remaining in  
Same plane due  
to hydrogen bonding.

-  $\text{NMe}_2$  does not involve  
in resonance due to  
steric inhibition of resonance.



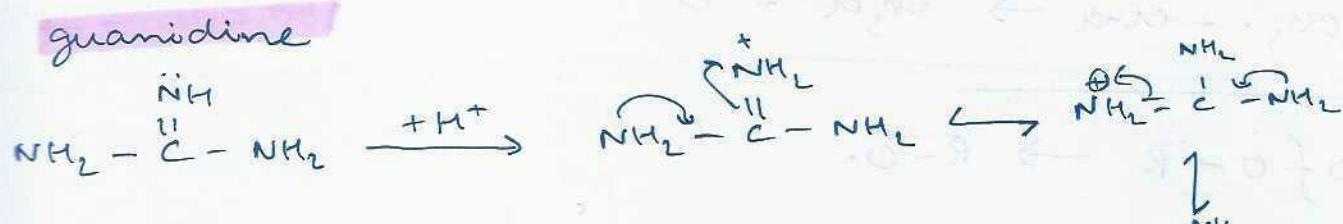
Basic  
character.

Resonance of lone pair is partially prevented by bulky groups due to steric crowding.



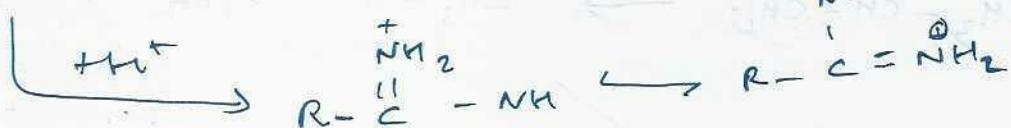
## NITROGENOUS BASE

guanidine



Strongest base  $\rightarrow pK_a = 13$

attraction



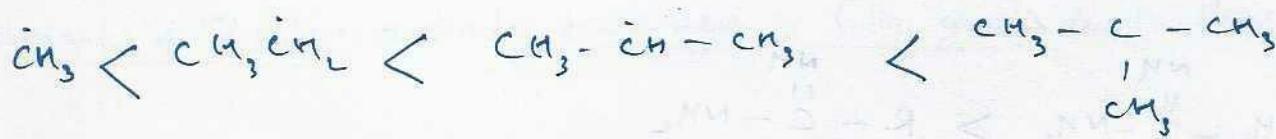
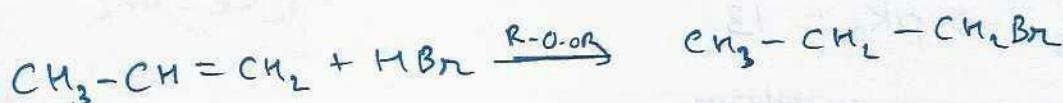
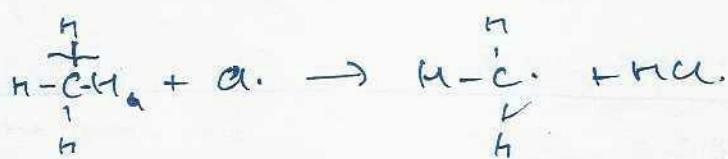
# BOND BREAKING

## HOMOLYTIC BOND FISSION

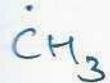


heat, electricity, light, peroxides

## FREE RADICALS



Stability



1	1	1
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$\text{sp}^2$  hybridisation.  
planar  
paramagnetic

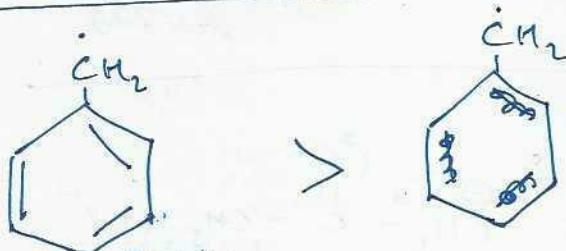
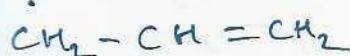
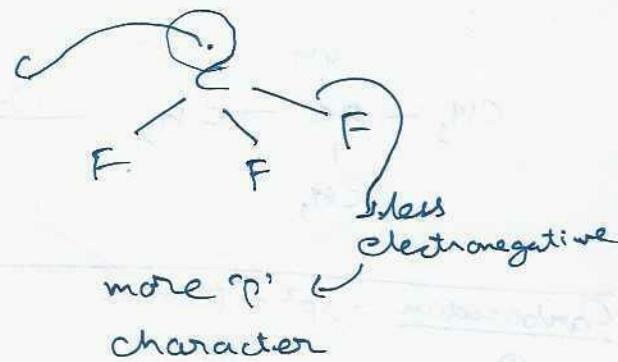


$\text{sp}^3$  hybridisation.

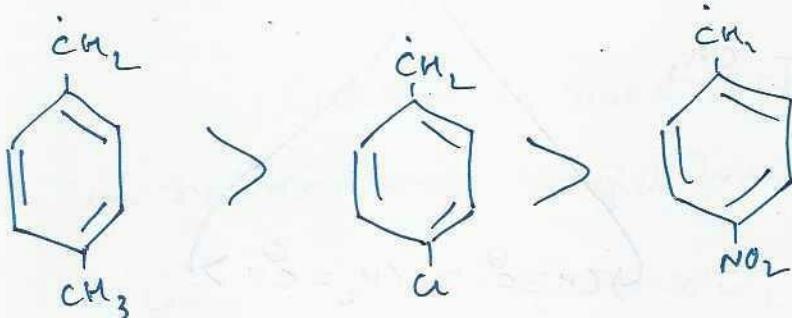
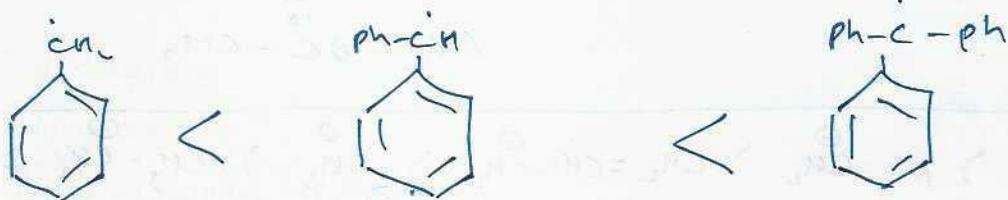
pyramidal geometry

$\therefore$  more electronegative atom occupies less electro negative orbital.

$\Rightarrow$  's' character is more (occupies more angular volume)



Stabilise through resonance

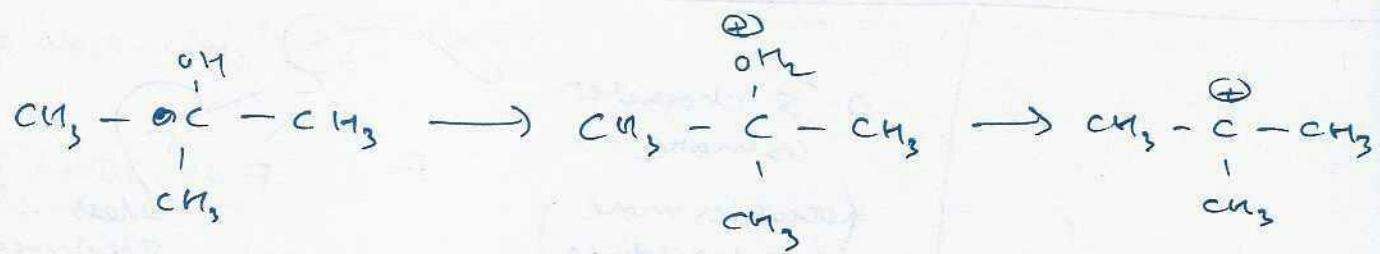


Electron releasing groups increase  $\uparrow$  stability of free radicals.

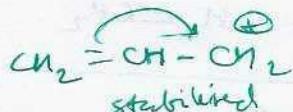
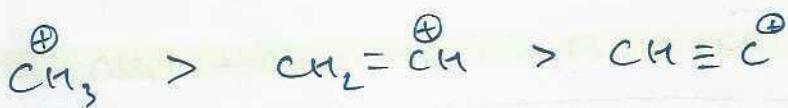
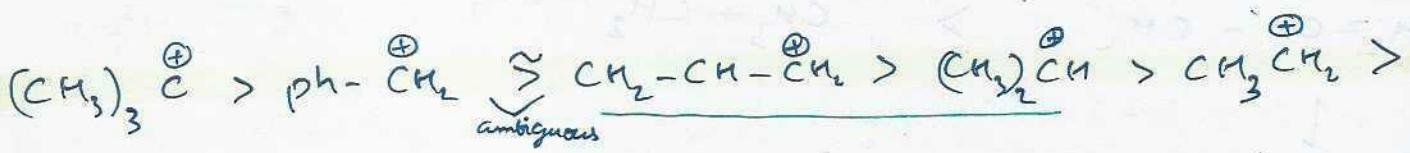
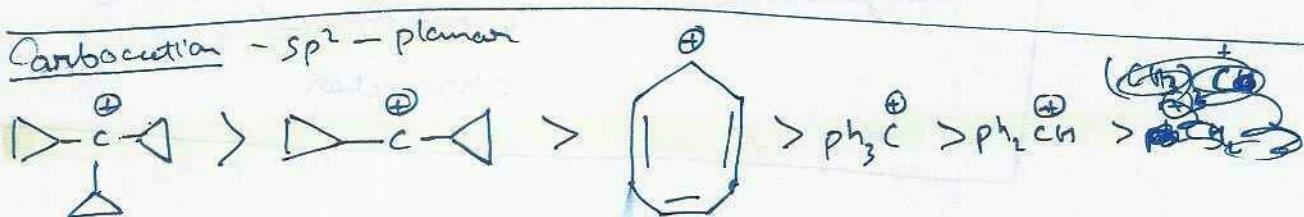
Electron withdrawing groups decrease  $\downarrow$  stability of free radicals.

# HETEROLYTIC BOND FISSION

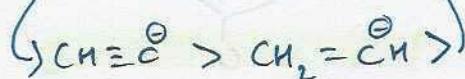
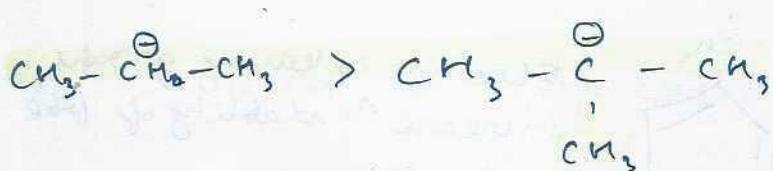
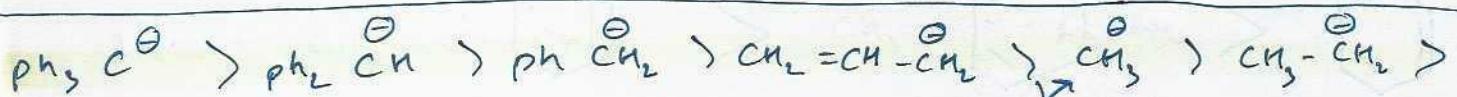
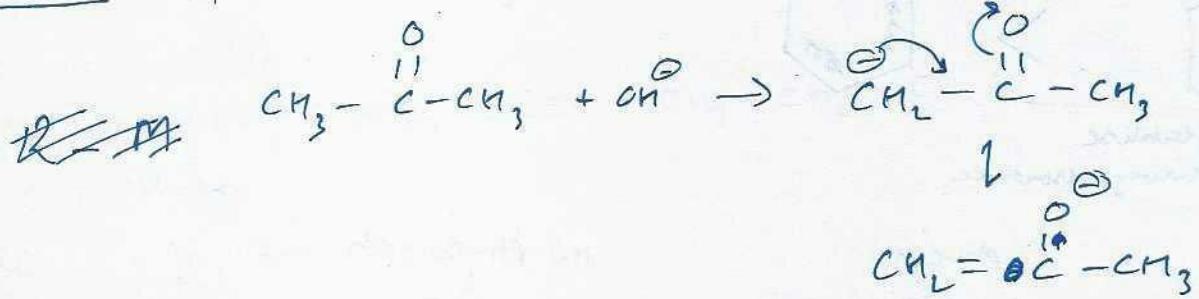
## Carbocations and Carbanions



Carbocation -  $sp^2$  - planar



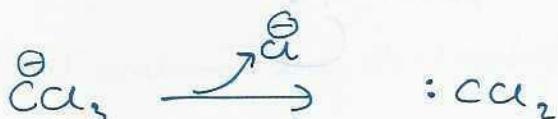
Carbanions -  $sp^3$



CARBENES      2 Bond pairs + 1 lone pair = Ge

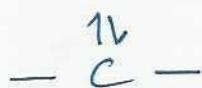
Neutral carbon compounds → intermediate

electrophile

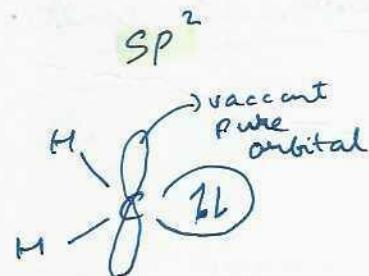


dichloro carbene

### Singlet Form



$e^-$  are paired

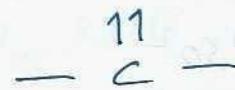


Diamagnetic

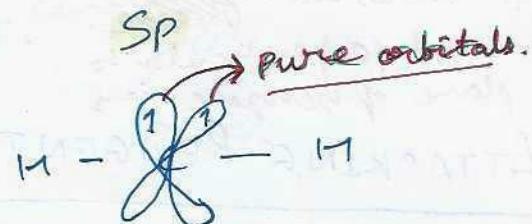
Angular

Bond pair - Lone pair repulsions

### Triplet Form



$e^-$  are unpaired



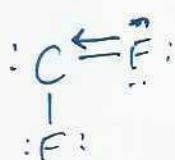
Paramagnetic

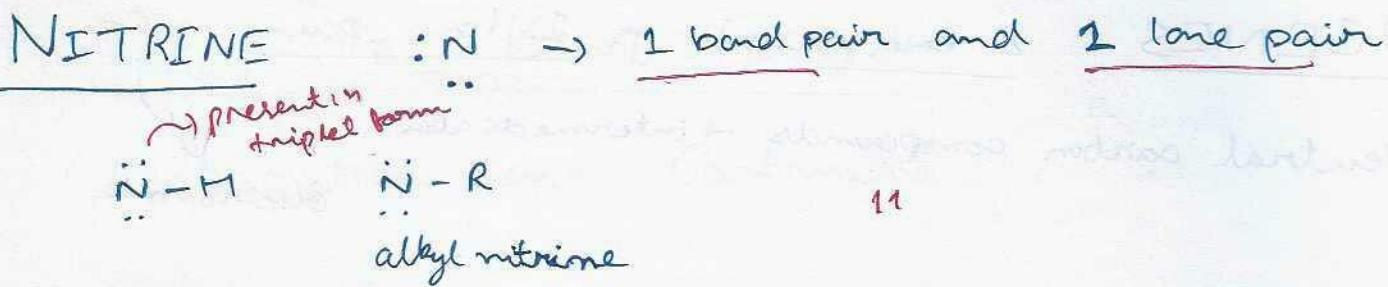
Linear

Bond pair - Bond pair repulsion.

Carbene is more stable in triplet form.

But in halocarbenes singlet form is more stable.



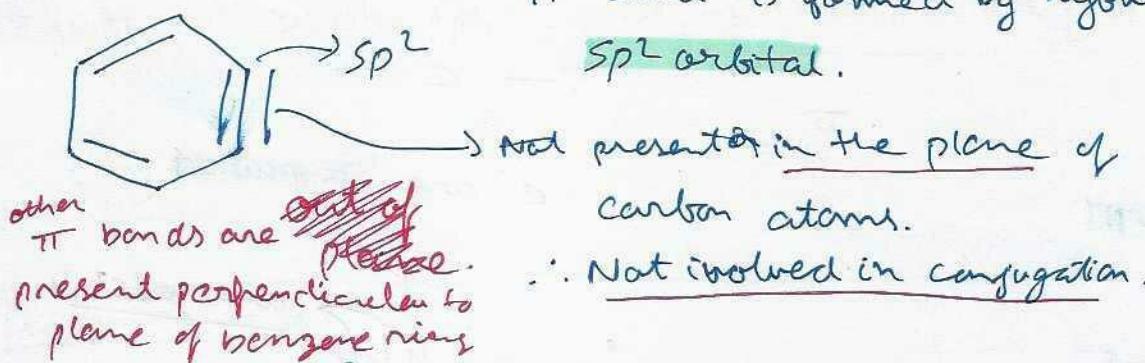


Triplet form more stable than Singlet Form



## BENZYNE

π bond is formed by hybridised SP<sup>2</sup> orbital.



## ATTACKING REAGENTS

① Electrophiles

② Nucleophiles

Addition

- Electrophilic addition
- Nucleophilic ~~addition~~ substitution
- Free radical

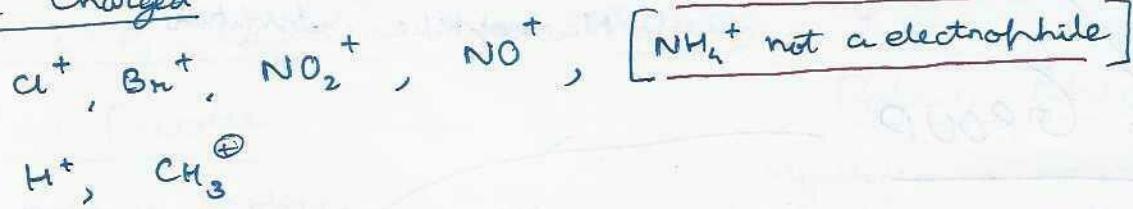
Substitution { :

Elimination

Rearrangement

# ELECTROPHILES

+ve charged



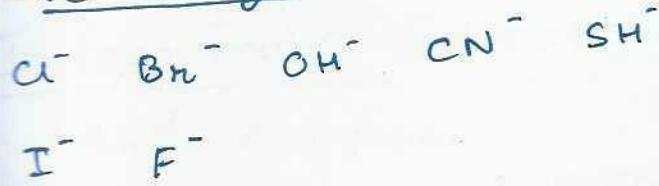
-Neutral



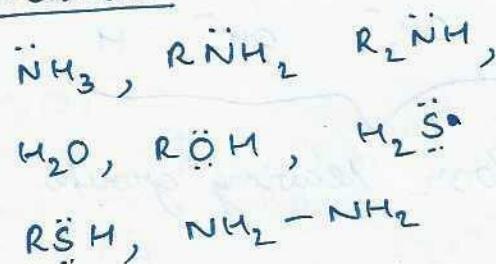
(all carbenes are electrophiles)

# NUCLEOPHILES

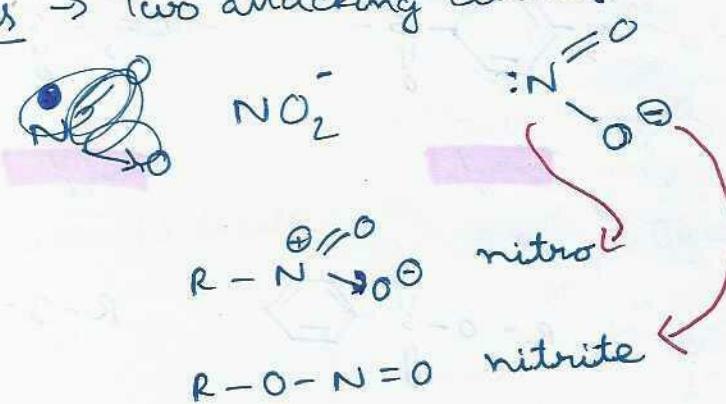
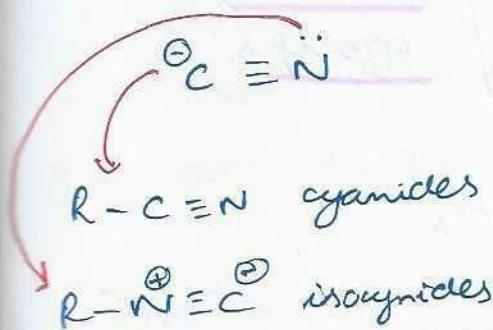
-ve charged

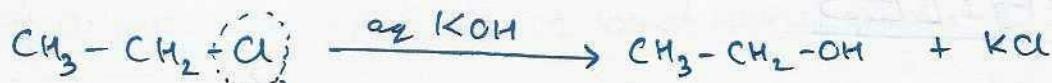


Neutral



Ambident Nucleophiles  $\rightarrow$  Two attacking centres.





Nucleophilic substitution

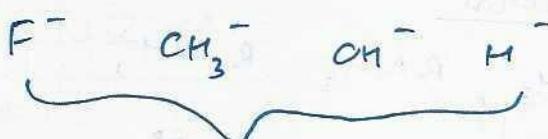
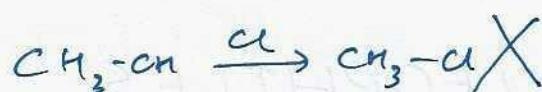
## LEAVING GROUP

Better leaving group  $\rightarrow$  faster reaction.

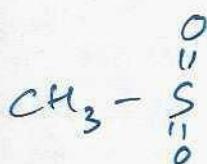
weak base  $\Rightarrow$  good leaving group. a pair of electrons.



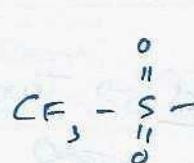
(poor leaving group)



Poor leaving groups.

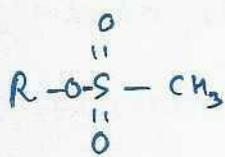


methyl

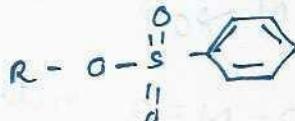


Triflyl

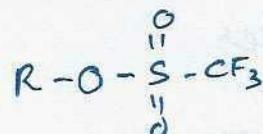
good  
leaving  
groups.



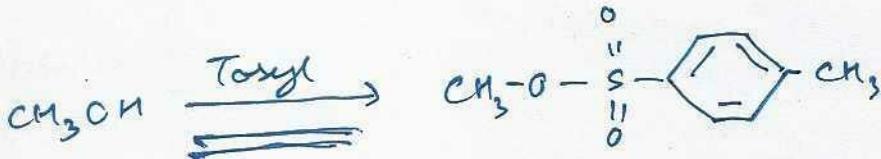
alkyl methylsulfonate



alkyl tosylate



alkyl triflate



$\bullet$   $\text{H}^-$  not stable..

Reaction is more towards backward direction.

$\text{N}^+ \equiv \text{N}$  very good leaving group.

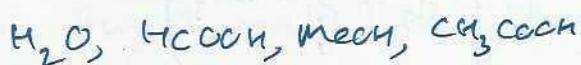
# NUCLEOPHILICITY

## Effect of solvent on nucleophilicity

### Polar Protic

Can produce protons.

Hydrogen directly attached to more electronegative atom.

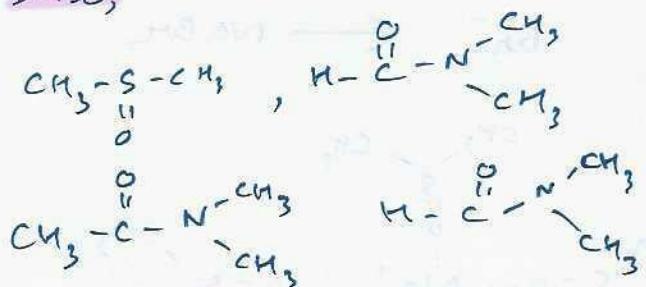


### Polar Aprotic

Hydrogen not directly attached to more electronegative atom.

Dimethyl formamide,  
Dimethyl acetamide

DMSO,



### In Polar Protic Solvent (e.g. in $\text{H}_2\text{O}$ )



Stronger nucleophile in protic solvent.

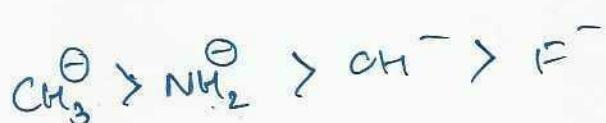
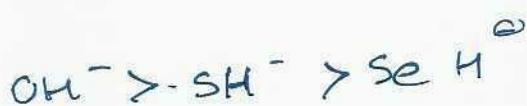
Nucleophilicity: tendency to attack

Highly solvated

Less solvated.

Nucleophilicity decreases.

Solvation decreases nucleophilicity.



Stronger basic character  
→ more nucleophilic.

- Negative charged species is more nucleophilic than corresponding neutral molecule

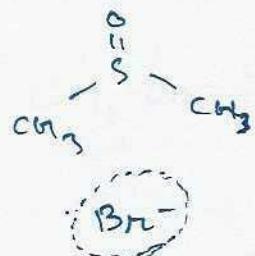
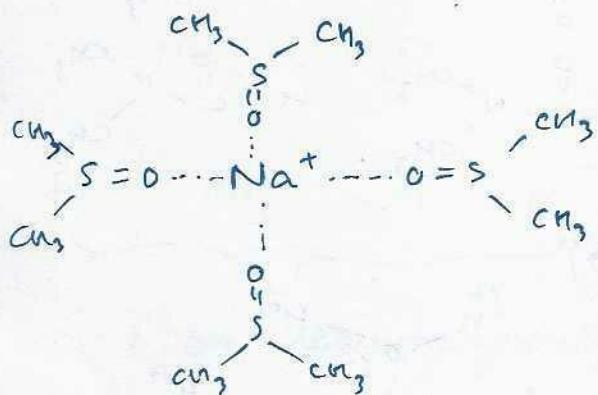
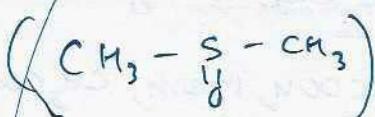


More the basic character  $\rightarrow$  more nucleophilic.



Ran < Me Cphon < CH<sub>3</sub>COOH < HNO<sub>3</sub>

## In Polar Aprotic Solvents



Nucleophilicity

$\hookrightarrow$  stronger nucleophile in  
aprotic solvent.

Order is reversed in  
protic and aprotic  
solvents.

# ISOMERISM

## Structural

1. Chain Isomerism
2. Position Isomerism
3. Functional Isomerism  
(Ring chain Isomerism)
4. Metamerism
5. Keto - enol Tautomerism

## Stereoisomers

### Configurational (meat bone)

#### Geometrical

#### Optical

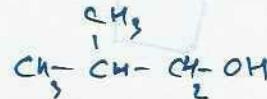
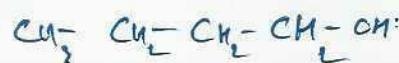
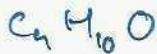
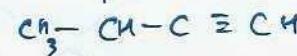
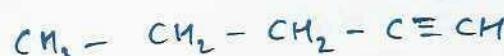
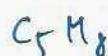
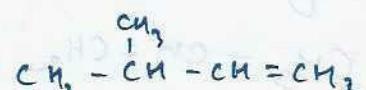
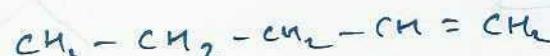
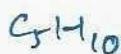
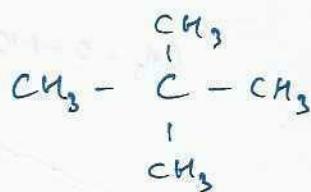
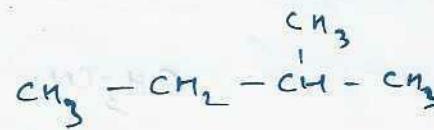
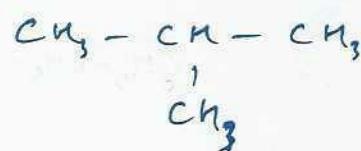
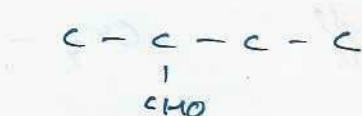
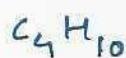
### Conformational (or free rotation)

## STRUCTURAL ISOMERS

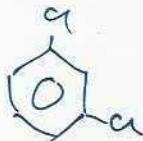
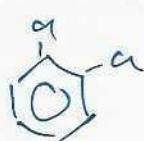
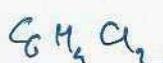
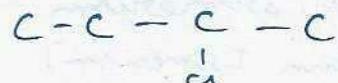
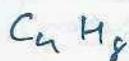
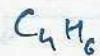
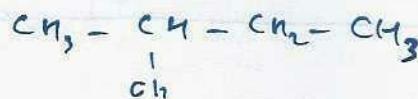
↳ Same Different structure.

### 1. Chain Isomerism

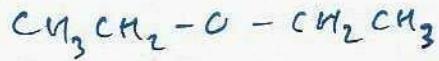
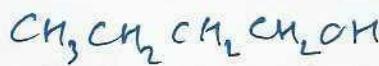
Difference in chain length.



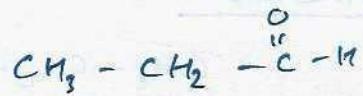
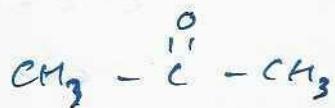
## 2 Positional Isomerism



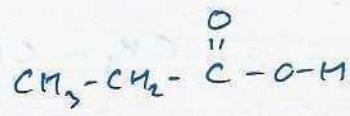
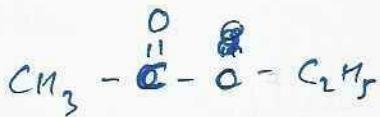
## 3 Functional Isomerism



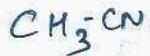
aldehyde  
& ketones



Ester  
& carbonylic acid



Cyanide  
& Mercaptide



Nitro  
& nitrites

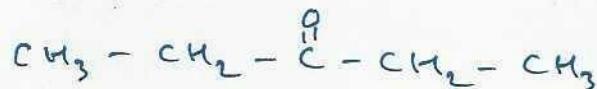
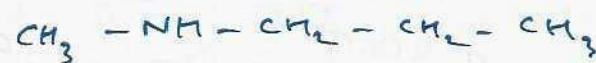
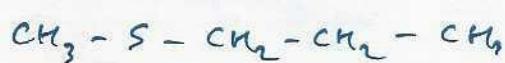


## Ring Chain Isomerism

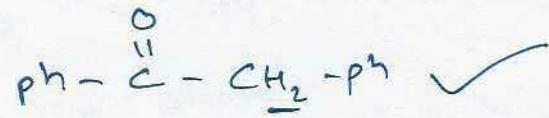
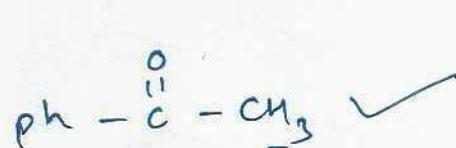
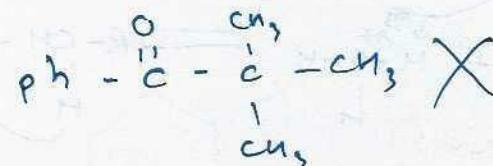
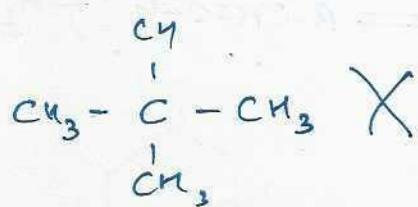


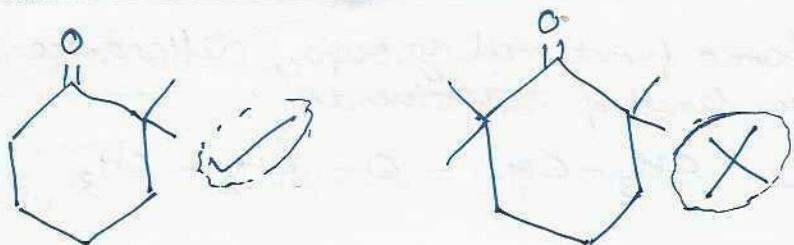
## 4. Metamerism

Same functional groups, difference in length of substituents.

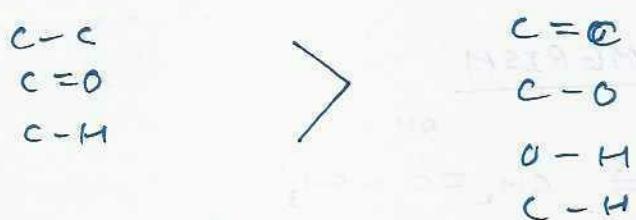


## 5. KETO AND ENOL TAUTOMERISM



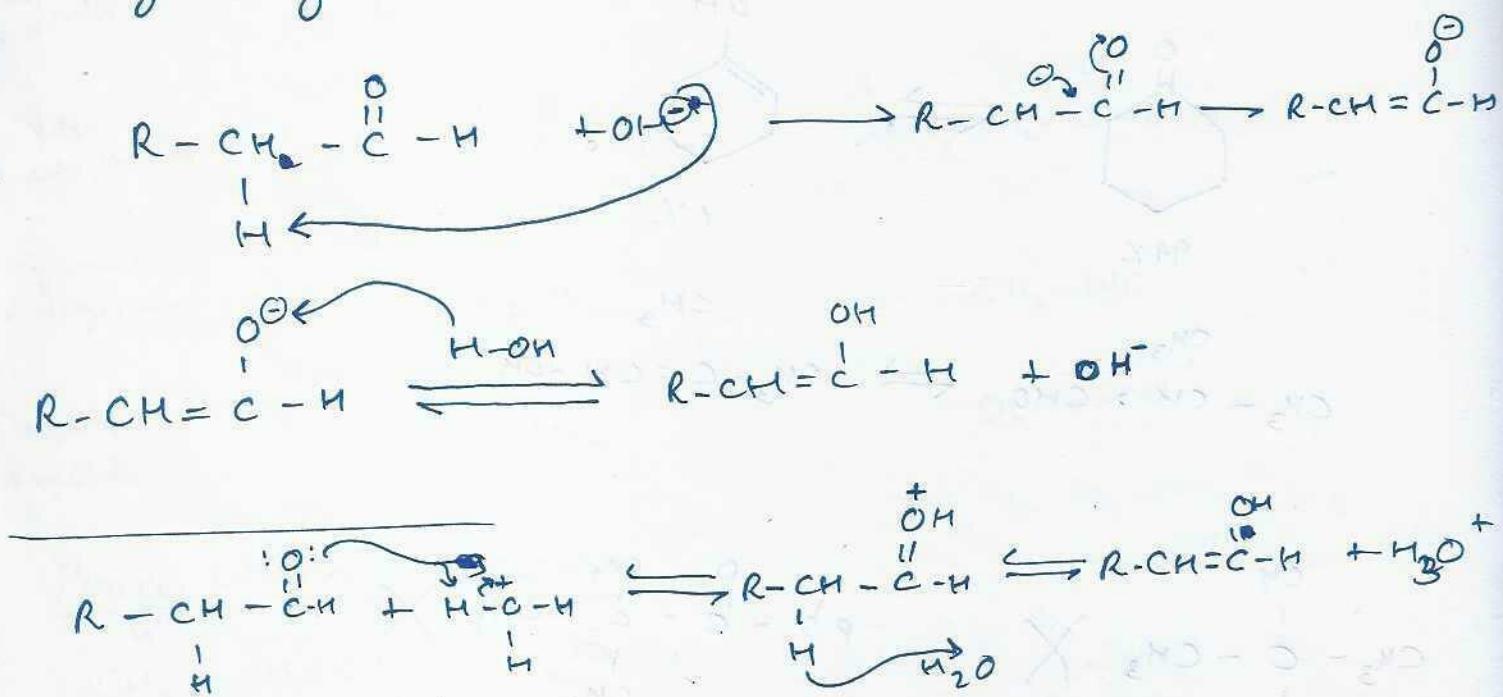


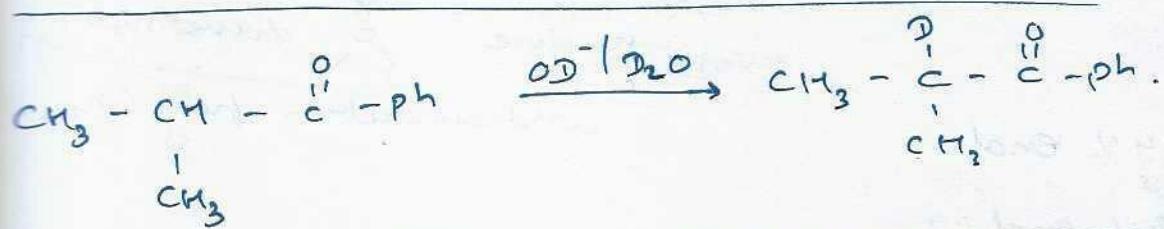
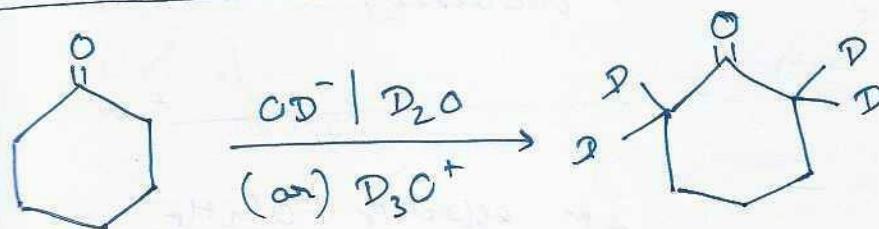
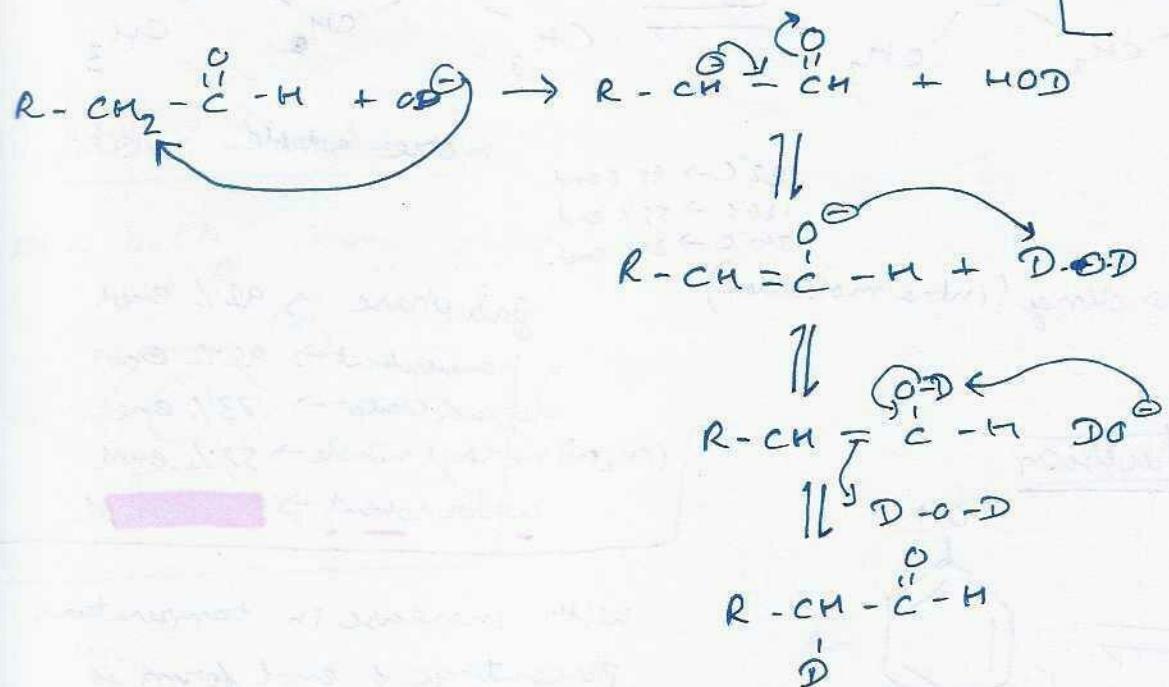
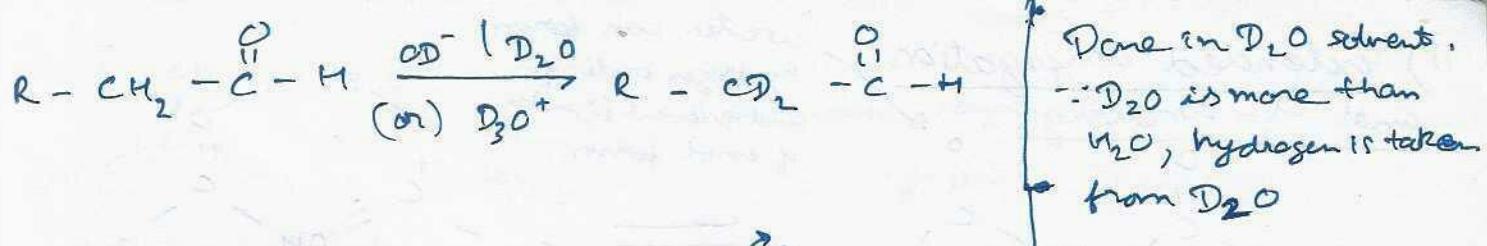
In most cases, keto form is more stable.



$\text{C=O} > \text{C=C}$  stability and bond dissociation energy

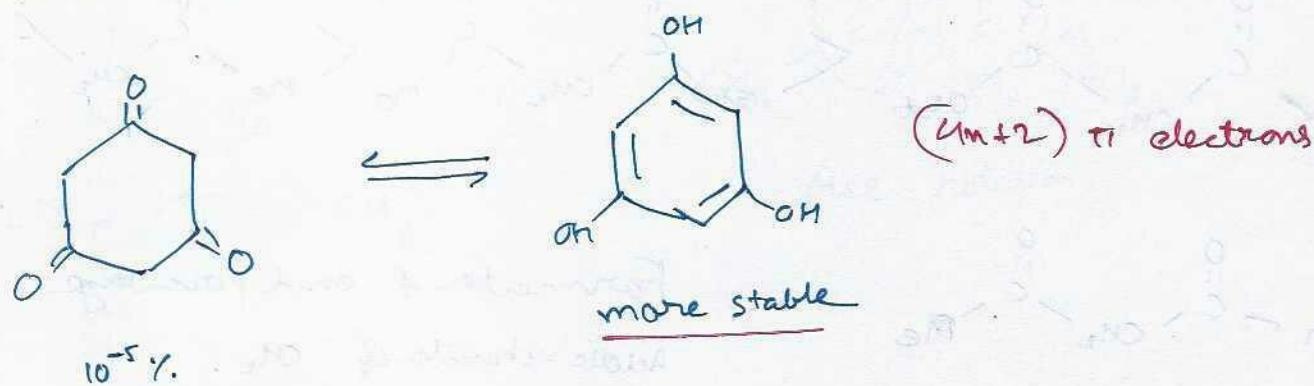
Catalysed by either  $\text{OH}^-$  or  $\text{H}_3\text{O}^+$



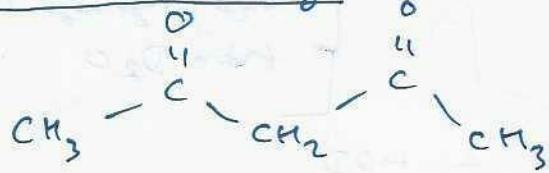


In certain cases enol form is dominating over keto form.

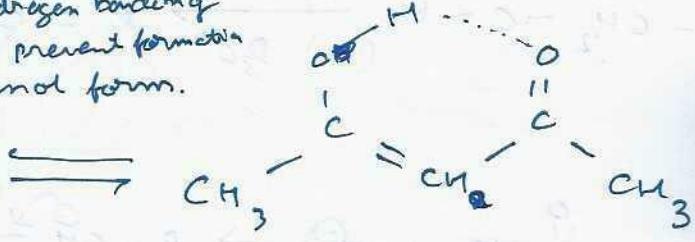
### i) Aromatic character



### ii) Extended conjugation and H-bonding



water can form hydrogen bonding and prevent formation of enol form.



more stable

→ Conjugation

→ Hydrogen bonding (intra molecular)

$22^\circ\text{C} \rightarrow 95\%$  enol  
 $180^\circ\text{C} \rightarrow 55\%$  enol  
 $260^\circ\text{C} \rightarrow 25\%$  enol.

gas phase  $\rightarrow 92\%$  enol

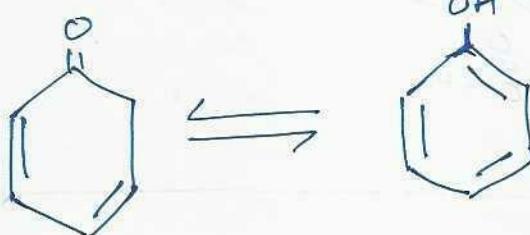
n-hexane solvent  $\rightarrow 92\%$  enol

liquid state  $\rightarrow 73\%$  enol

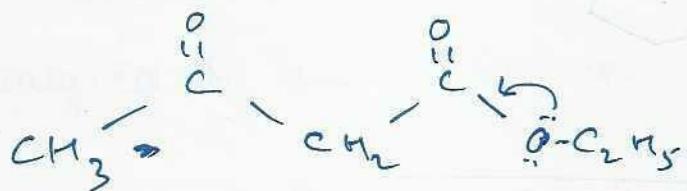
(CH<sub>3</sub>O)<sub>2</sub> methyl nitrate  $\rightarrow 52\%$  enol

water solvent  $\rightarrow 15\%$  enol

### iii) Steric Repulsion



With increase in temperature percentage of enol form is decreased.



+ m effect of  $-\ddot{\text{O}}\text{C}_2\text{H}_5$

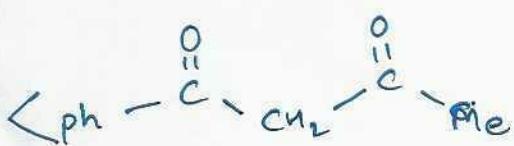
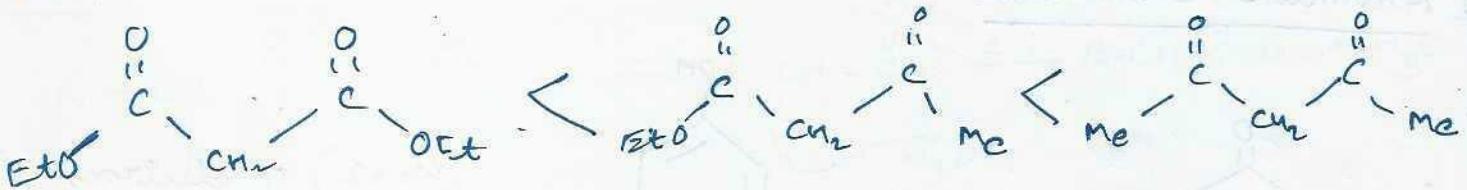
is operated

therefore  $\overset{\text{O}}{\underset{\text{H}}{\text{C}}}$  does not withdraw electron from CH<sub>2</sub>.

In water, 0.4% enol

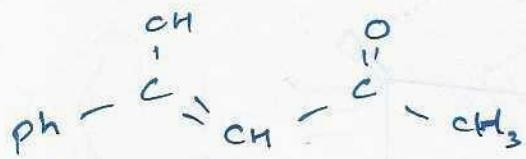
In toluene, 18% enol

Q



Formation of enol percentage

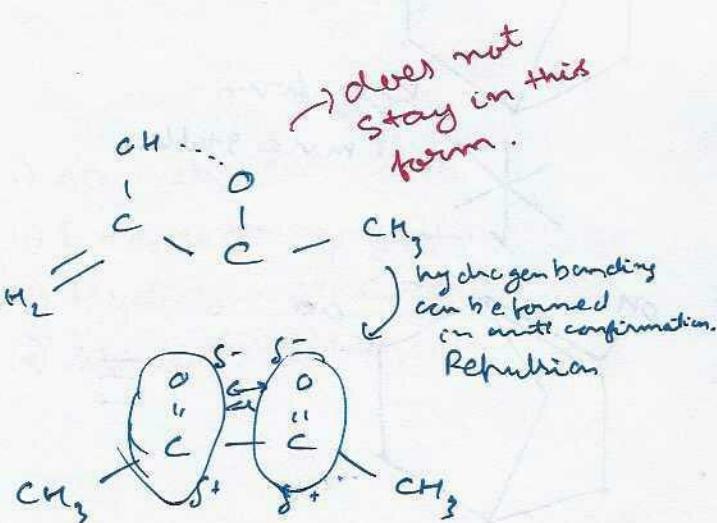
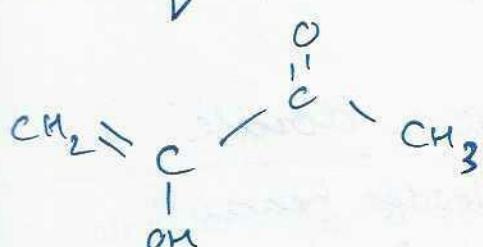
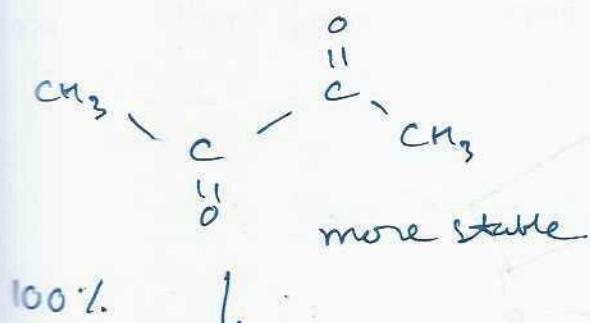
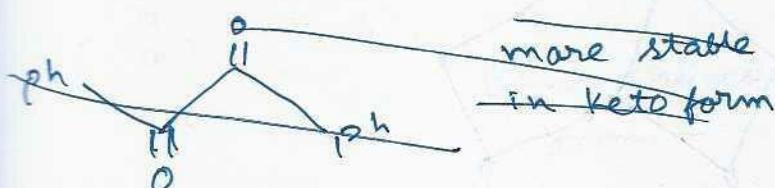
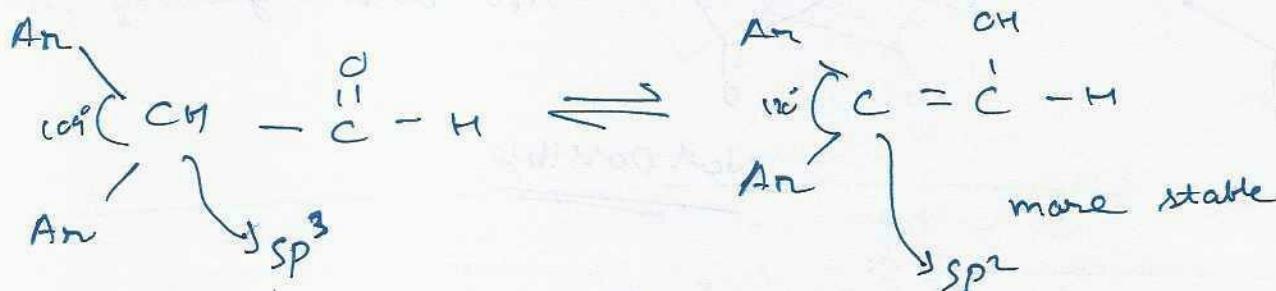
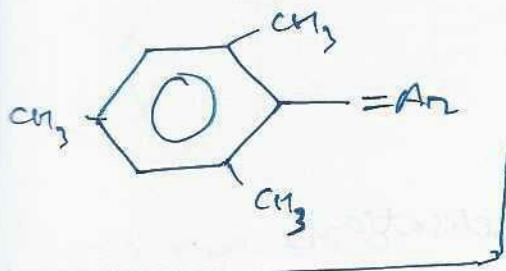
Acidic character of CH<sub>2</sub>.



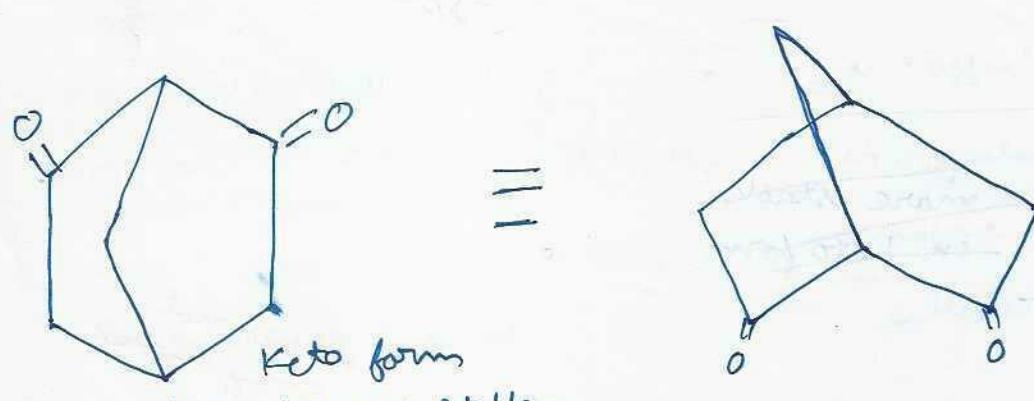
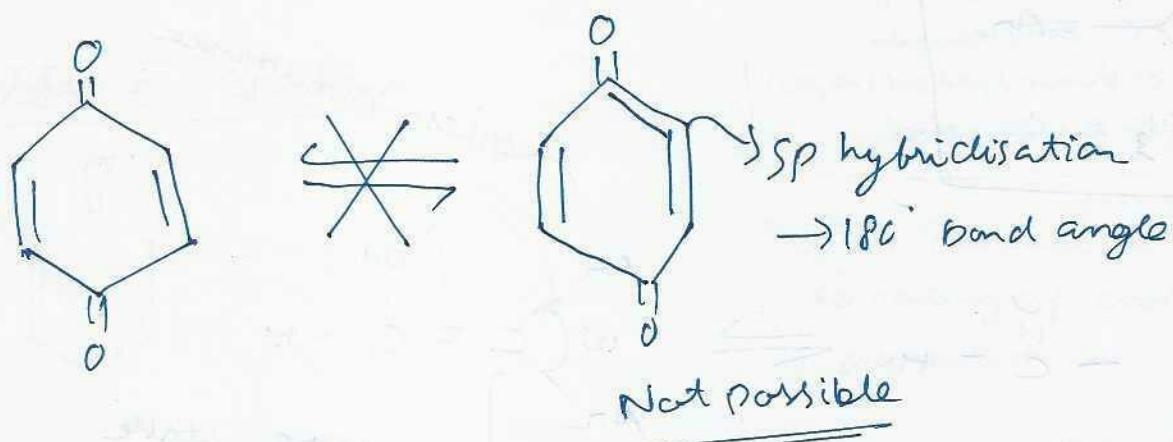
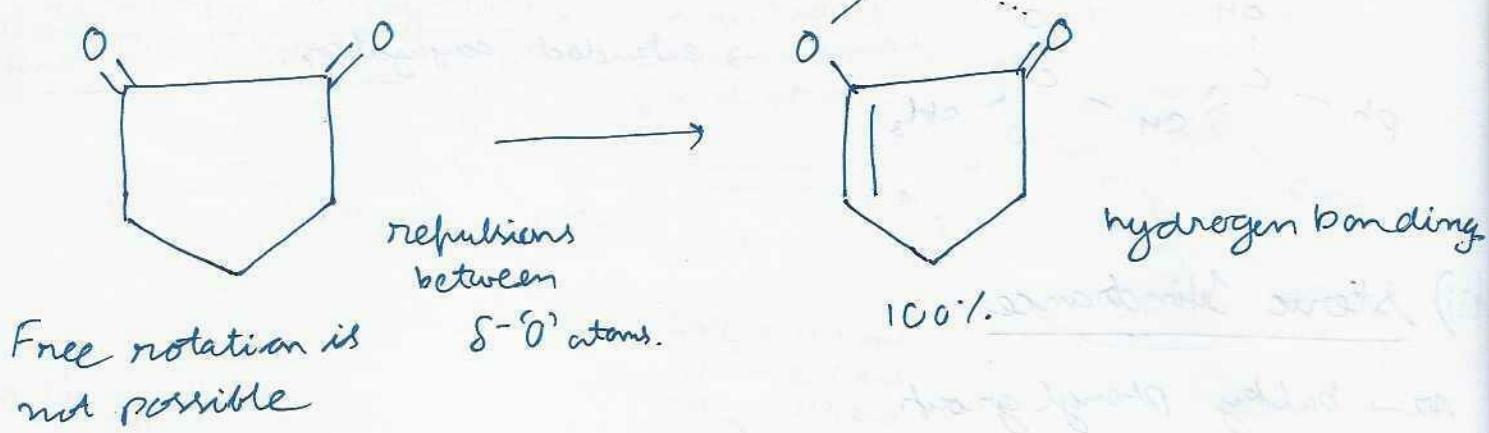
→ extended conjugation.

### iii) Steric Hindrance

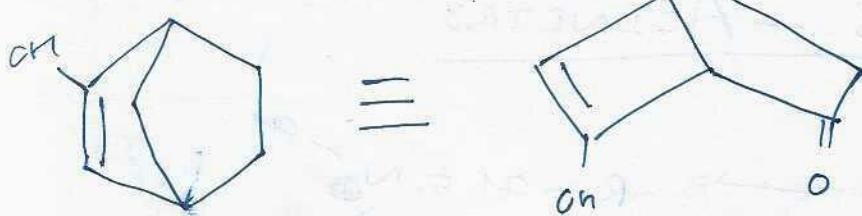
→ bulky phenyl group



free rotation.



Cannot give double bond to bridge head  
 $(\because$  It is not planar).

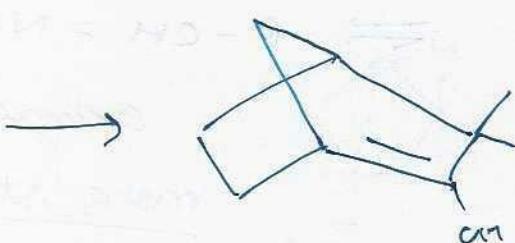


~~Possible~~ ~~stable~~  
Possible but less stable.

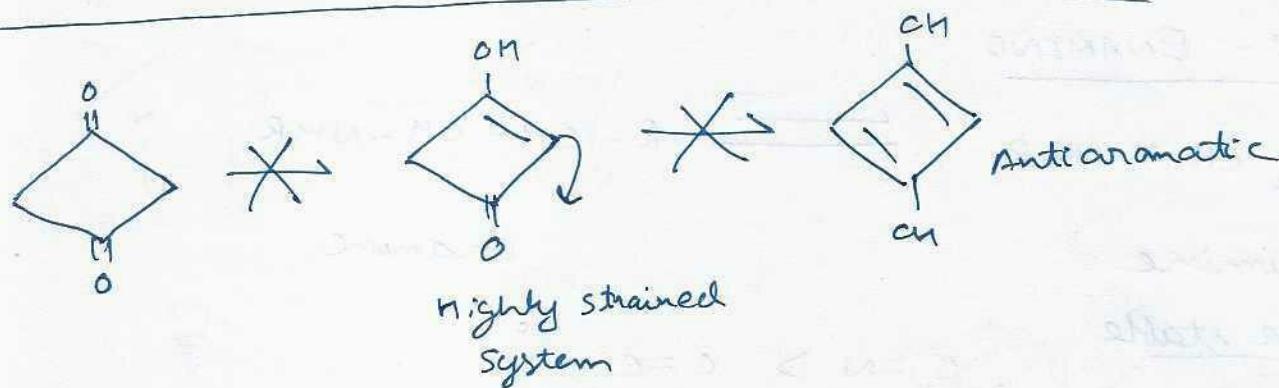


As double bond  
cannot be given  
to bridge head.

Does not show  
enol form.



Not possible

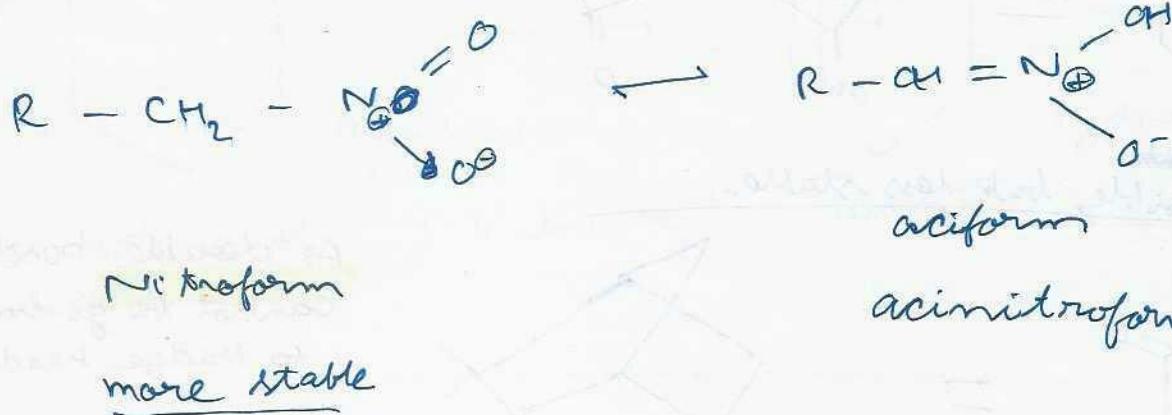


Antiaromatic

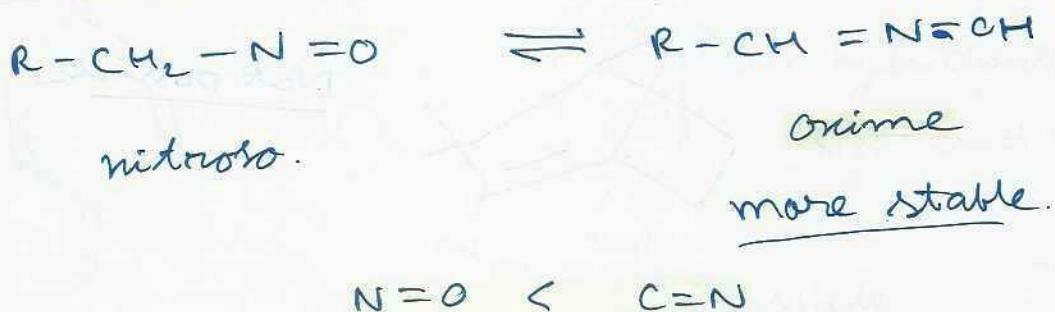
Enol form is more stable — i) Aromatic character  
ii) Extended conjugation  
iii) Hydrogen bonding.  
iv) Steric hindrance

Intramolecular hydrogen bonding does not increase boiling point.

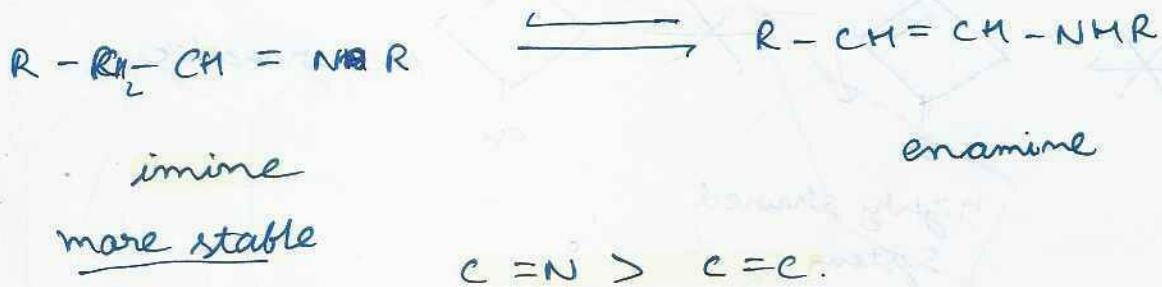
# NITRO COMPOUNDS - ACINITRO



## NITROSO



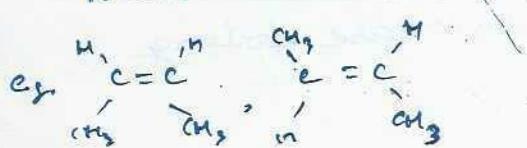
## IMINE - ENAMINE



## STEREOISOMERS

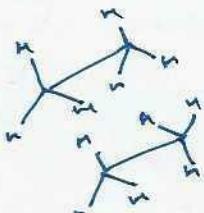
### Configurational isomerism

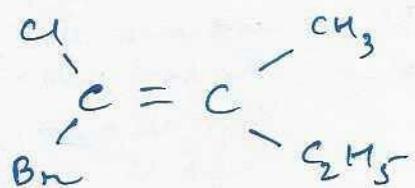
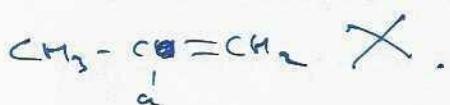
#### Geometrical



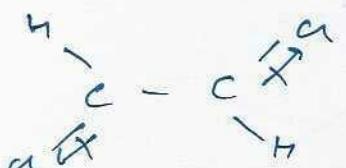
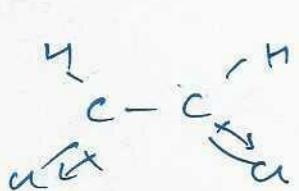
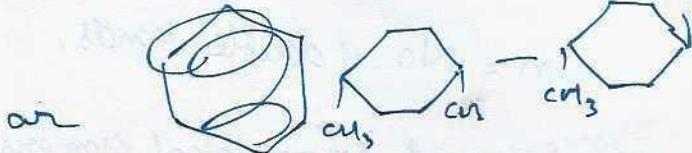
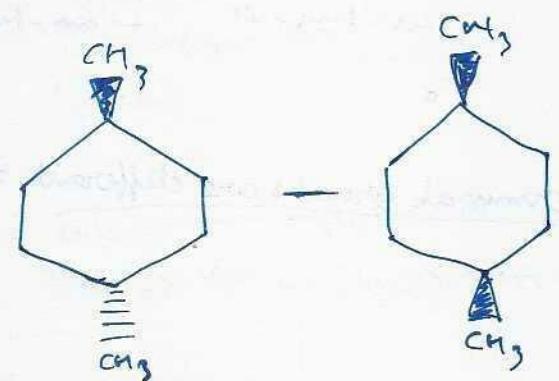
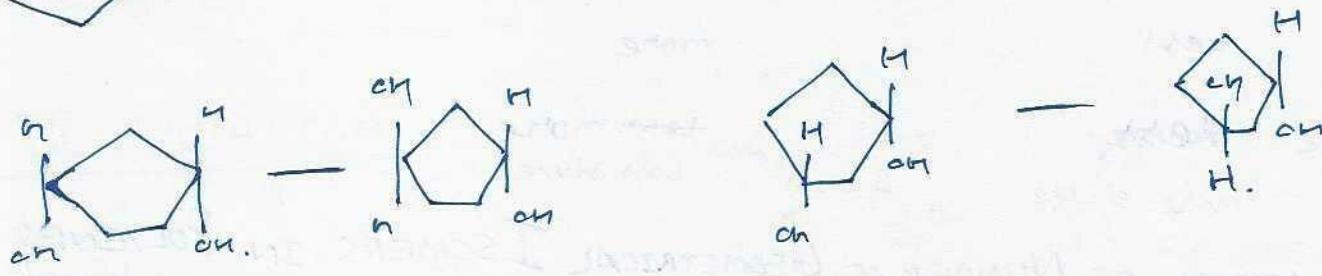
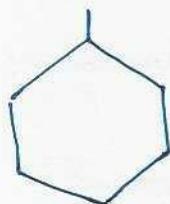
### Conformational isomers

C-C free rotation.





Can show geometrical isomerism depending on priority order



$$\mu \neq 0$$

Polar

Boiling Point

more boiling point

$$\mu = 0$$

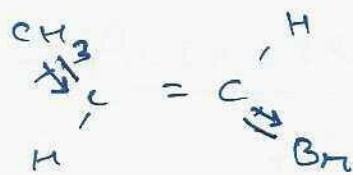
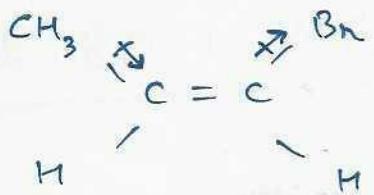
Non polar

melting point

Stability: Trans > Cis

Heat of hydrogenation: Cis > Trans.  
on combustion.

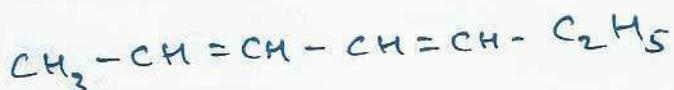
Solubility: Cis > Trans.



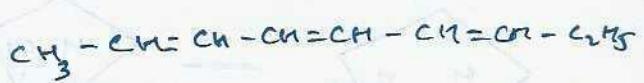
$M$	Less	more
Boiling point	less	more
melting point.	Less	more
Solubility	Less	more
$\text{HOC}_2\text{HOC}$	<del>less</del>	less more less stable.
	more stable	



## CALCULATION OF NUMBER OF GEOMETRICAL ISOMERS IN POLYENES



cis - cis  
cis - trans  
trans - trans  
trans - cis

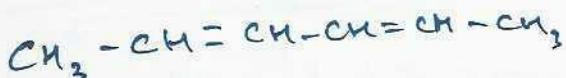


cis - cis - cis  
cis - cis - trans.  
cis - trans - trans.  
cis - trans - cis

trans - trans - trans  
trans - cis - cis.  
trans - cis - trans  
trans - trans - cis.

$n$  = No. of double bonds.

Total No. of geometrical isomers if terminal groups are different  $= 2^n$

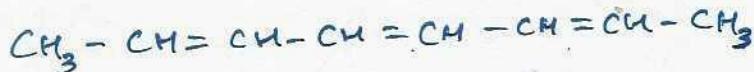


cis-trans  $\rightarrow$  same :: terminal groups are same.  
trans-cis  
trans-trans  $\Rightarrow 3$   
cis-cis

$n$  = No. of double bonds.  
(even)

Total No. of geometrical isomers if terminal groups are same

$$= \boxed{2^{n-1} + 2} \quad n \text{ is even.}$$



cis cis cis  
 cis trans trans  
 trans trans cis  
 trans trans cis  
 trans cis cis  
 cis cis trans

$$\begin{aligned}
 & 2^1 + 2^{\frac{n-1}{2}} \\
 & = 2^2 + 2^1 \\
 & = 6
 \end{aligned}$$

Total  $\Rightarrow 6$

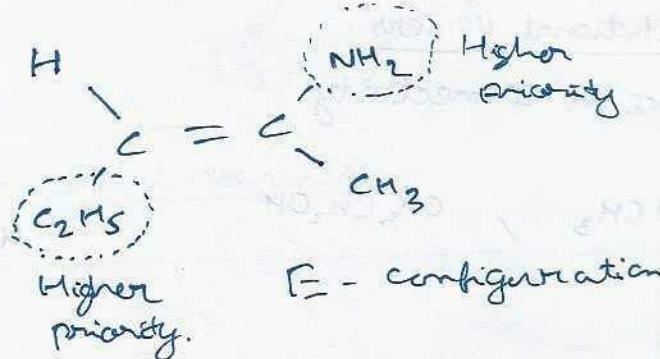
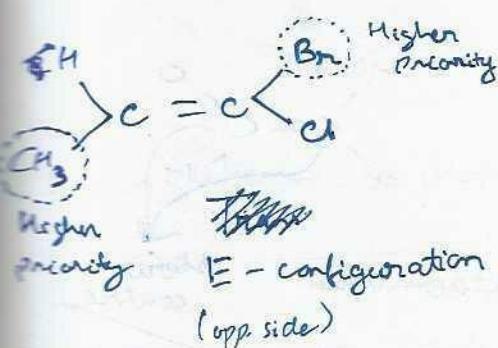
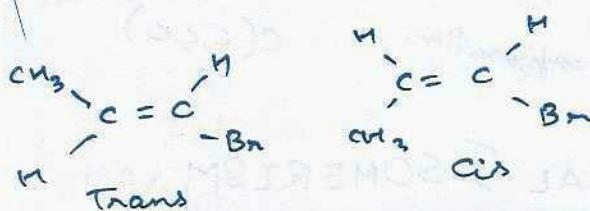
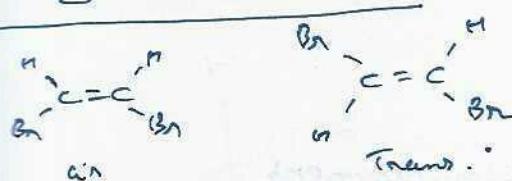
$n = \text{No. of double bonds (odd)}$

Terminal groups are same, then total geometrical isomers

$$= 2^{n-1} + 2^{\frac{n-1}{2}}$$

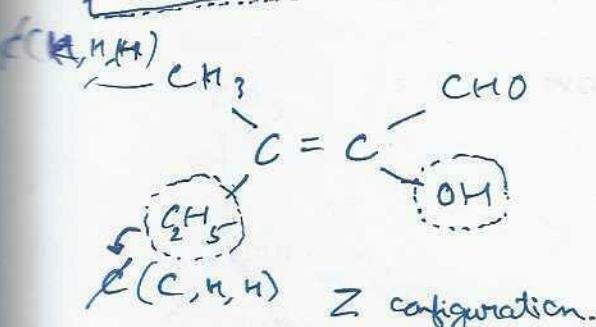
$n$  is odd.

### E-Z NOTATION



Opposite side  $\rightarrow$  E configuration  
Same side  $\rightarrow$  Z configuration

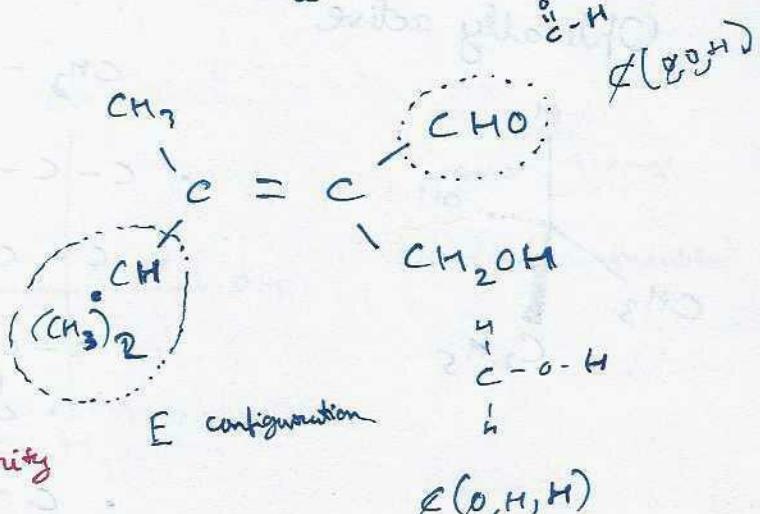
Z cis E trans

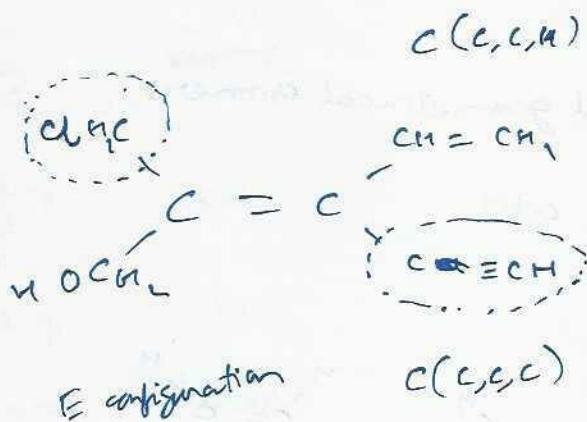
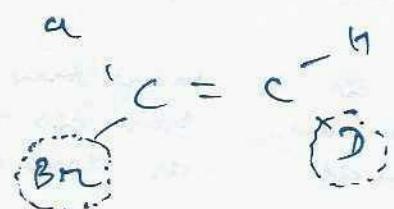
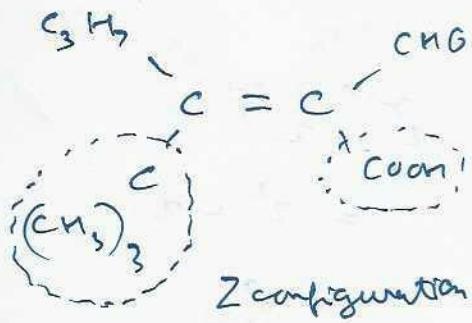


Higher atomic number  $\rightarrow$  higher priority

$\hookrightarrow$  If same, higher mass number.

Due to double bond, two oxygen atoms are considered.





- Higher atomic number & given priority
- In case of isotopes, mass numbers considered.

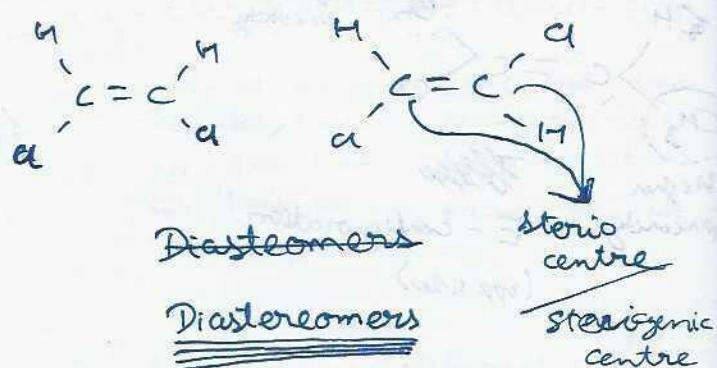
## OPTICAL ISOMERISM

### Constitutional isomers

Difference in connectivity

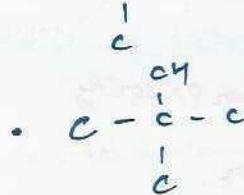
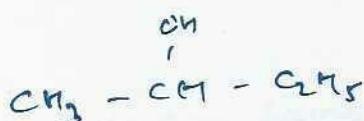
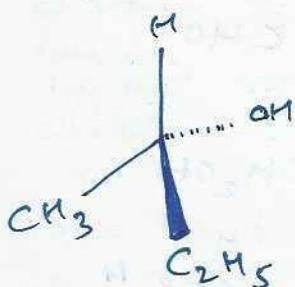


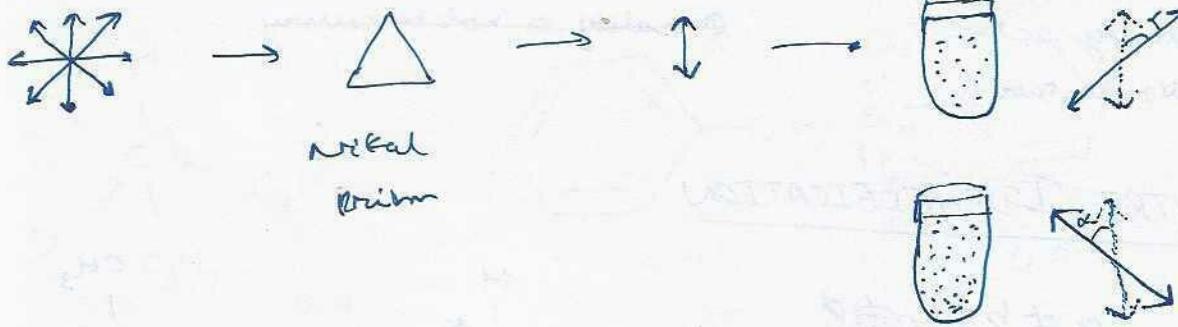
### Stereoisomers



## STEREICISMERS

### Optically active





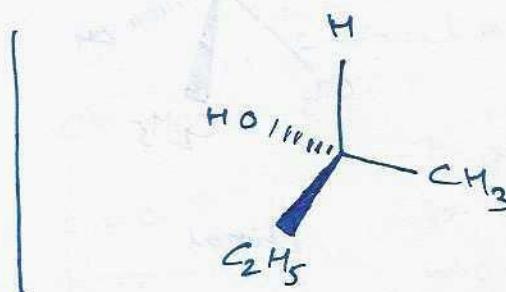
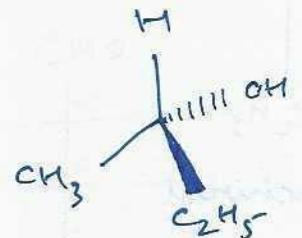
dextrorotatory → towards right

levorotatory → towards left.

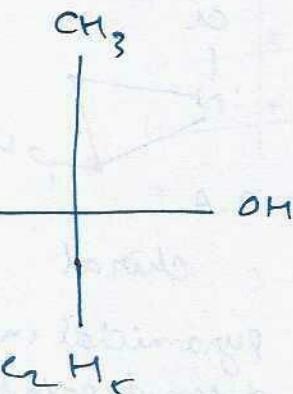
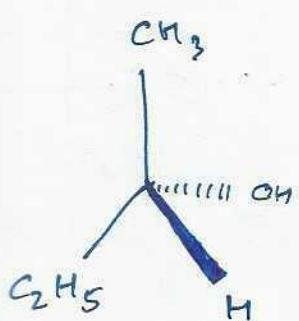
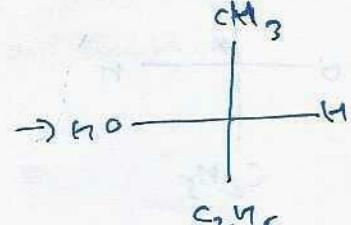
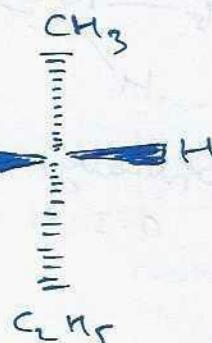
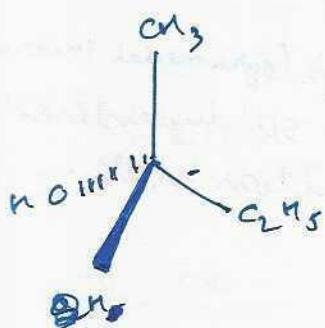
To show optical activity, chiral centre must be present: may be present.  
chiral carbon → attached to four different groups.

(asymteric carbon)

even though chiral carbon is not there, it can be optically active.



Shows difference in properties with chiral reagents.



mirror image

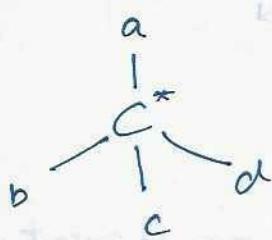
(non-superimposable)

resolvable  $\rightarrow$  optically active.

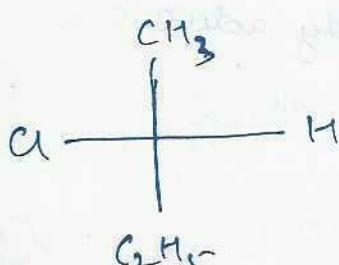
$\hookrightarrow$  into enantiomer pair

Chirality is not necessary

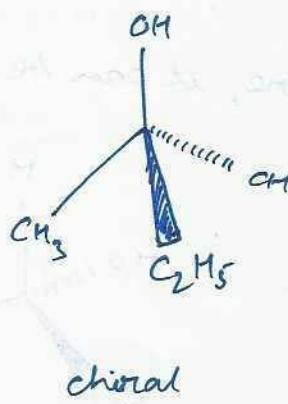
## CHIRAL CENTRE IDENTIFICATION



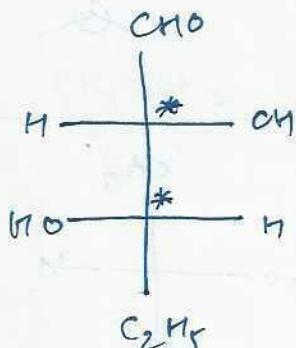
$$a \neq b \neq c \neq d$$



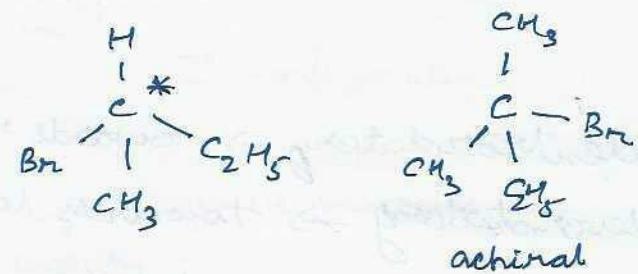
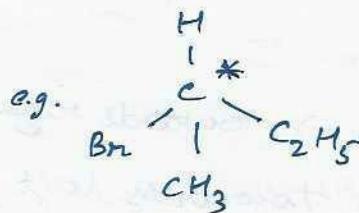
chiral



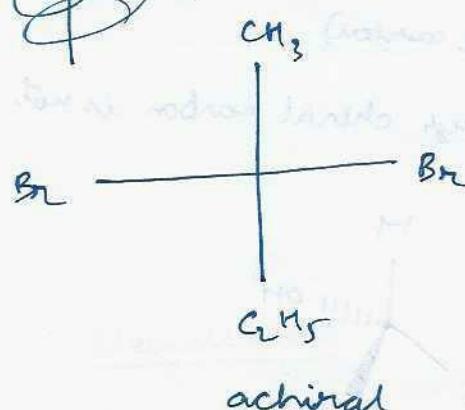
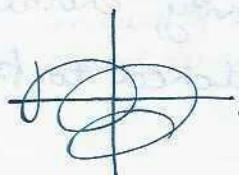
chiral



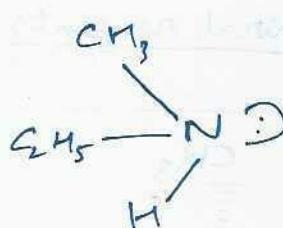
2 Chiral centres



achiral



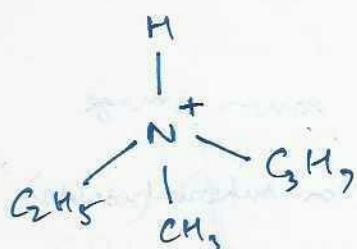
achiral



optically inactive, due to inversion. (Pyramidal inversion)  
O.I.A

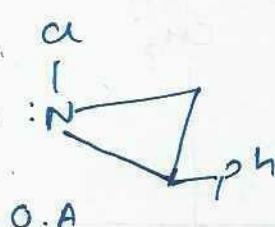
$\hookrightarrow$  by a  $sp^2$  hybridised transition state.

Pyramidal  
Pyramidal  
inversion



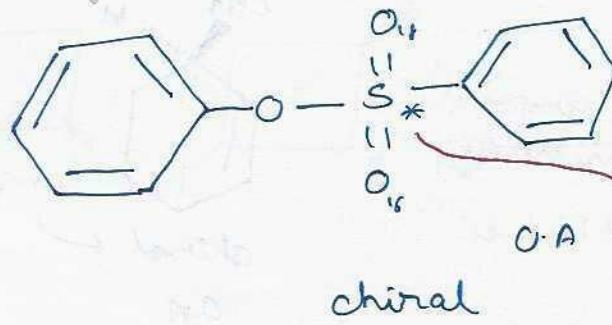
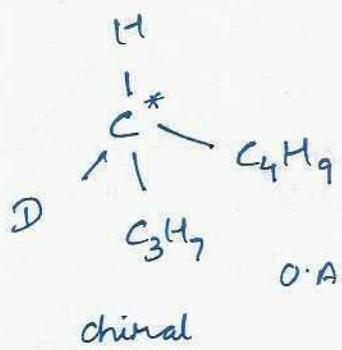
O.A

optically active.



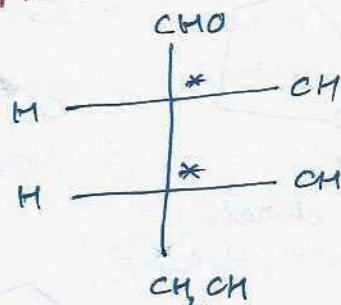
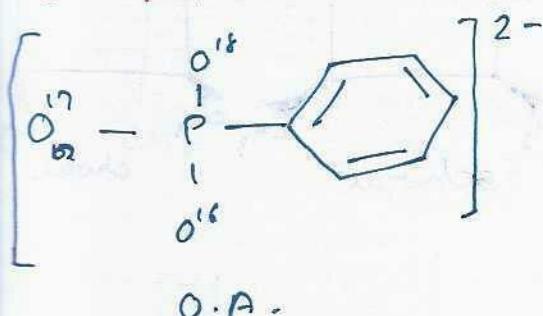
chiral

Pyramidal inversion  
does not possible due  
to cyclic structure.

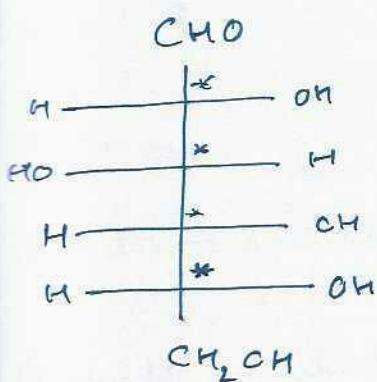


Hybridisation is  $sp^3$  even after double bond.

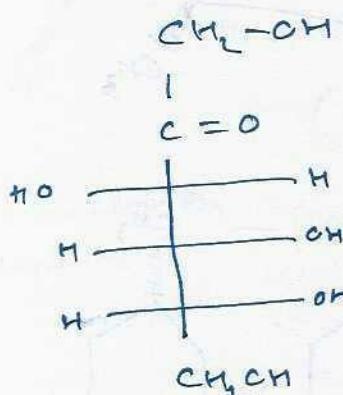
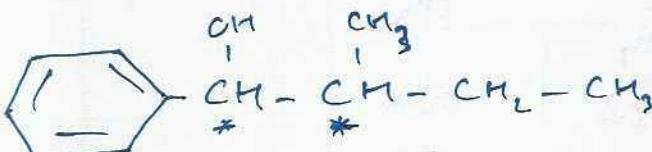
Isotopes are considered different groups.



2-chiral centres.



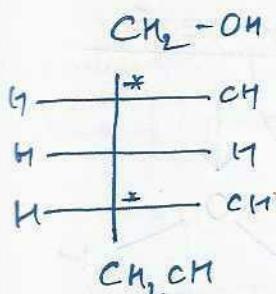
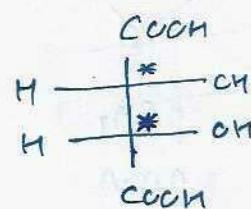
4-chiral centres



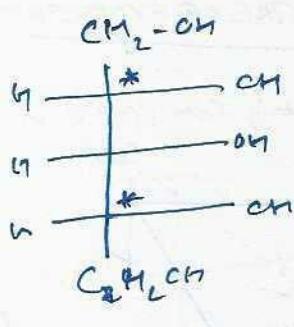
Double bonded oxygen to carbon can't show chirality.

Hybridisation changes from  $sp^3$  to  $sp^2$ .

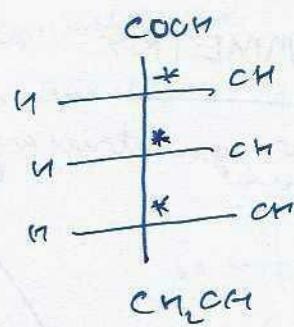
$sp^2$  chiral compounds 'can' exist.



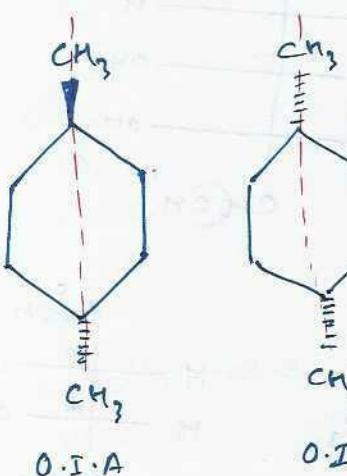
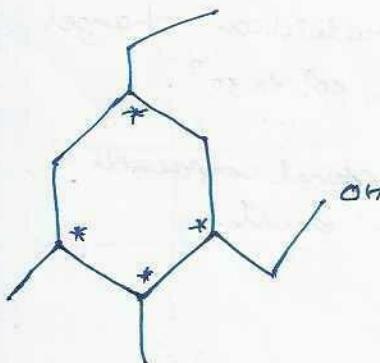
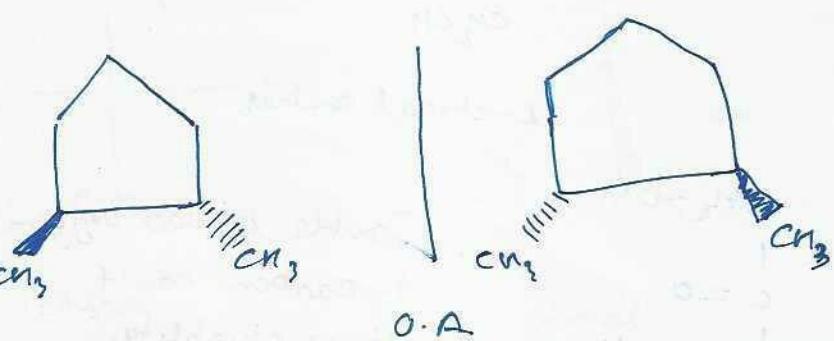
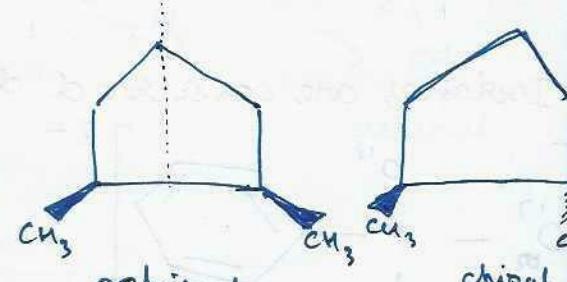
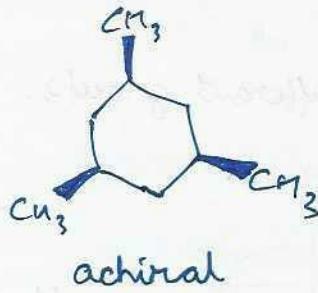
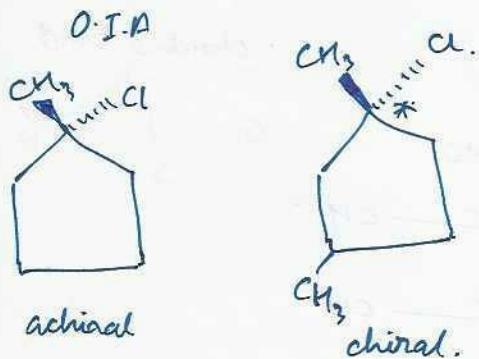
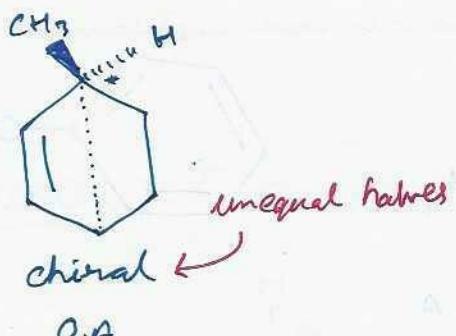
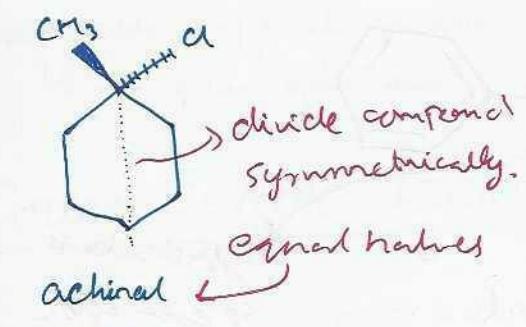
2-chiral



3,2-chiral

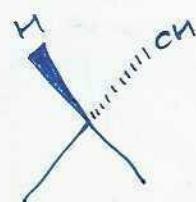


3-chiral



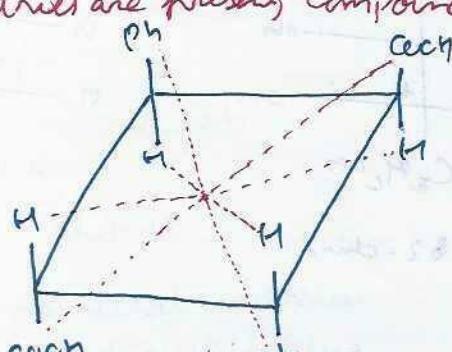
## PLANE OF SYMMETRY

If any of these symmetries are present compound is achiral



has plane of symmetry

## CENTRE OF SYMMETRY

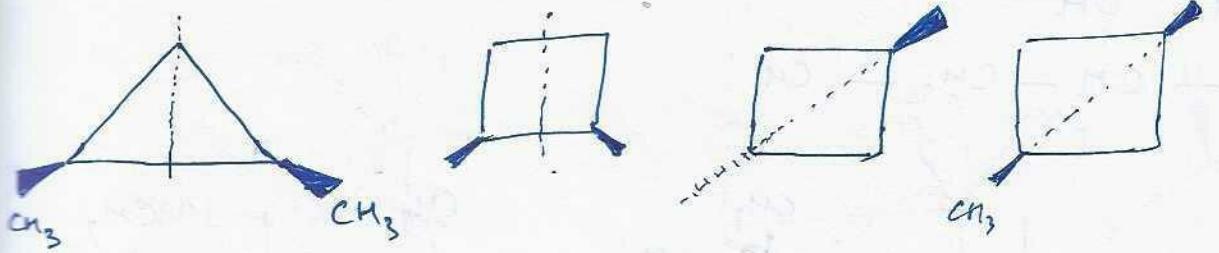


has centre of symmetry  
groups are situated at equal distance  
from a central point.

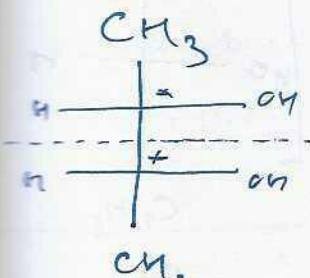
## ALTERNATE AXES OF SYMMETRY

$\text{N} < 360^\circ$   
Rotate the molecule through  
the axis. Same molecule  
is obtained.

can still be  
optically active.



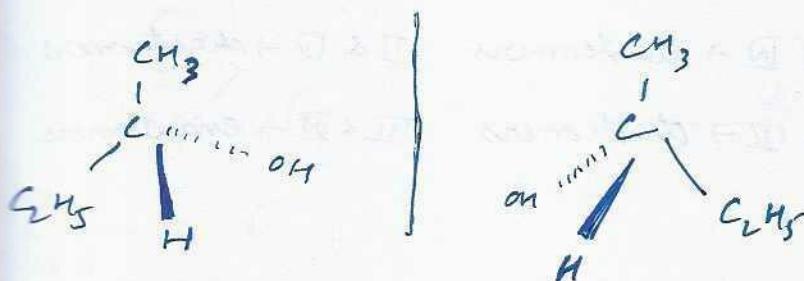
All have  
plane of  
symmetry.



2-chiral centres are there

But is optically inactive. → due to internal compensation.

Meso compounds  
↳ Rands. *Yinternal.*



Enantiomeric pair

Individually they are optically active

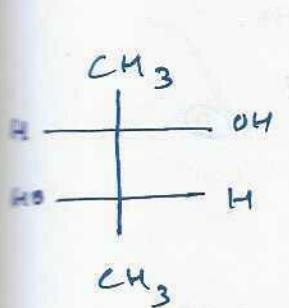
1:1 ratio mixture is optically inactive.

→ Racemic mixture

Optically inactive due to external compensation.

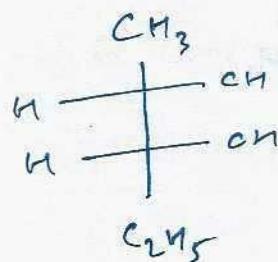
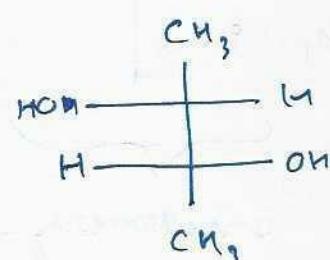
Resolution → separation of ~~race~~ enantiomer from racemic mixture.

Resolvable → optically active.



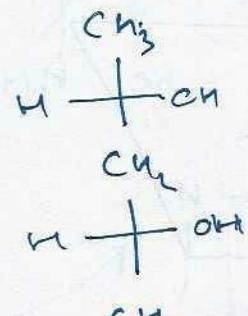
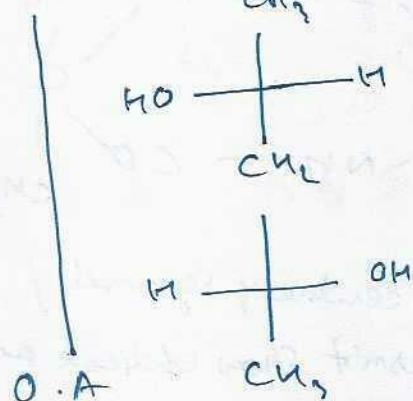
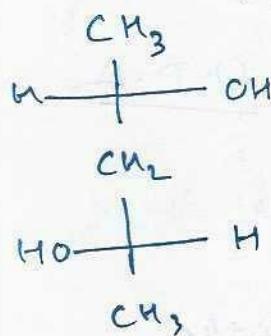
Optically active

No plane of symmetry

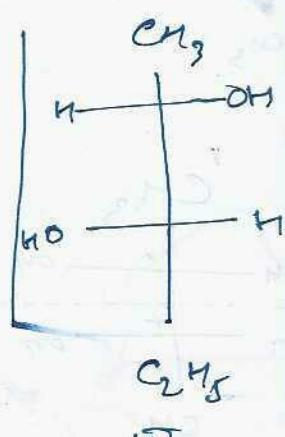
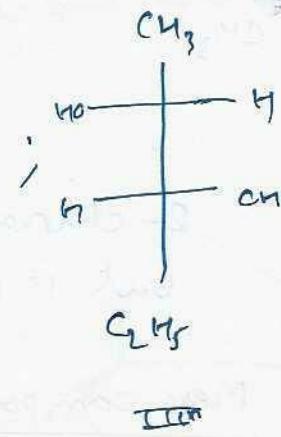
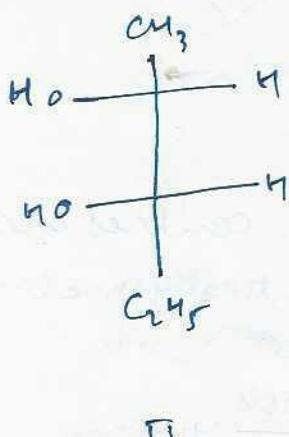
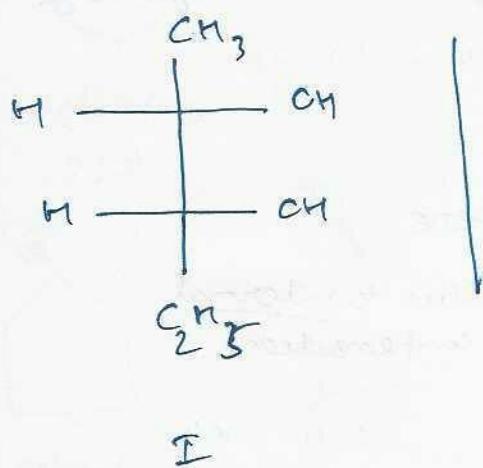
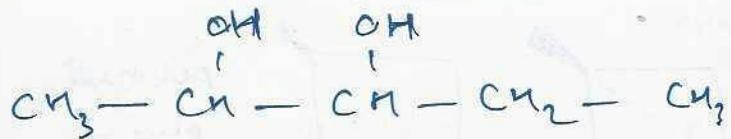


Optically active

No. plane of symmetry



O.I.A.



**I & II** → enantiomers

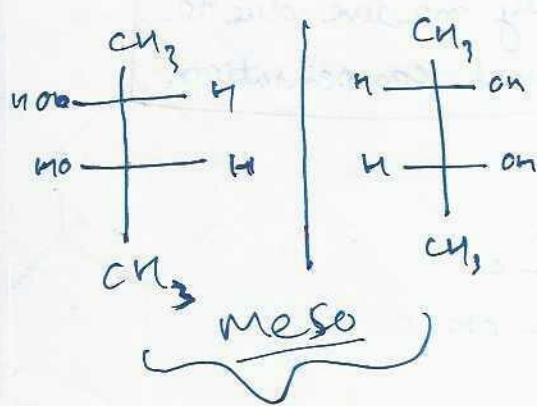
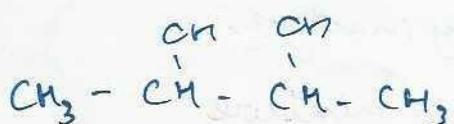
**I & IV** → diastereomers

**II & IV** → diastereomers

**I & III** → diastereomers

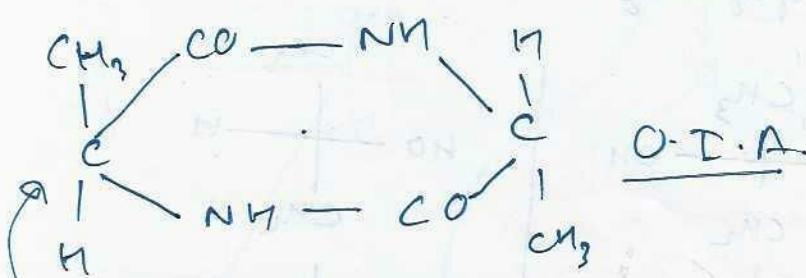
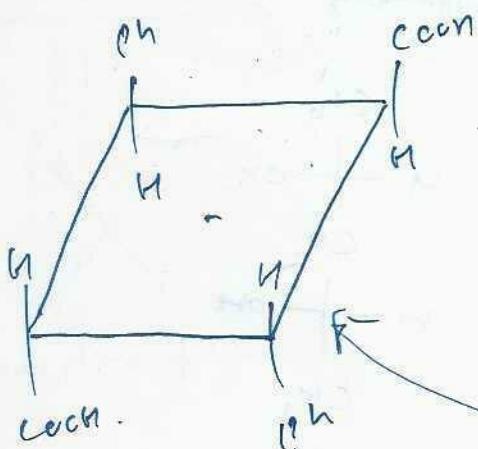
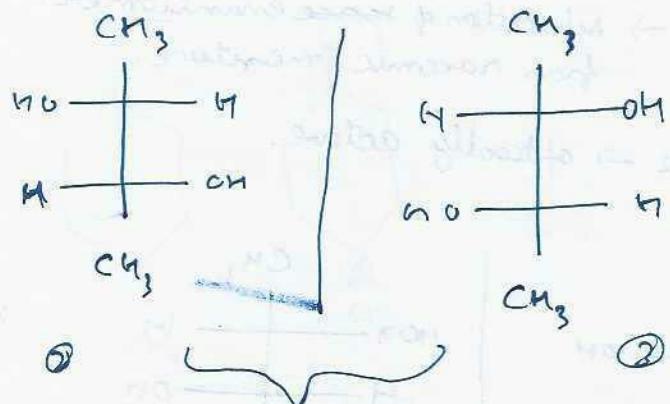
**II & III** → diastereomers

**III & IV** → enantiomers.

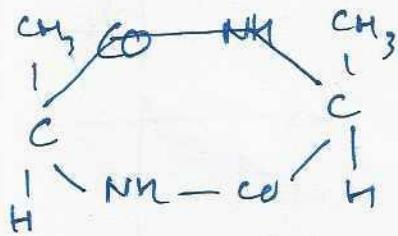


identical.

→ (1) compound

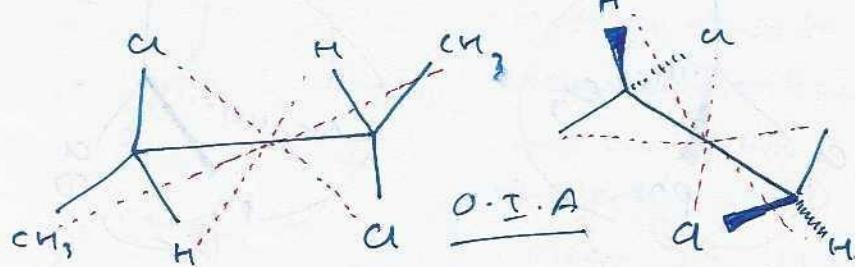


has centre of symmetry  
doesn't show optical activity



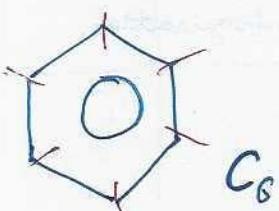
Does not have centre of symmetry

O.A.

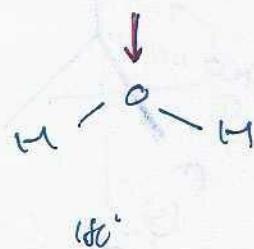


has centre of symmetry

has centre of symmetry



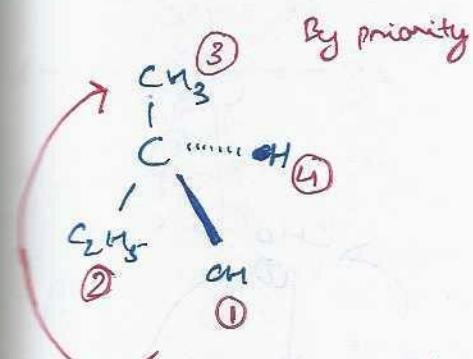
$$\frac{360}{60} = 6$$



Linear molecules have infinite number of axis of rotation.



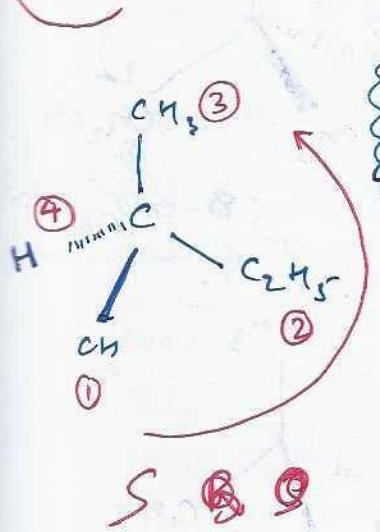
## R, S NOTATION



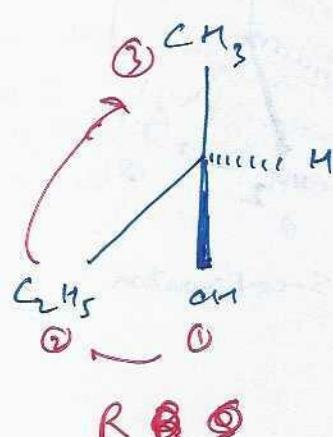
By priority

Clockwise  $\rightarrow$  R configuration

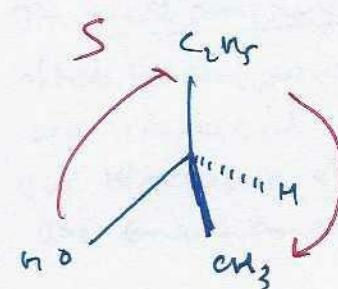
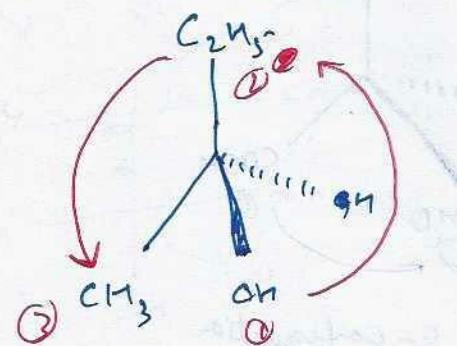
Anticlockwise  $\rightarrow$  S configuration



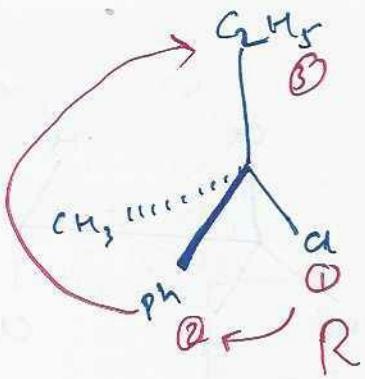
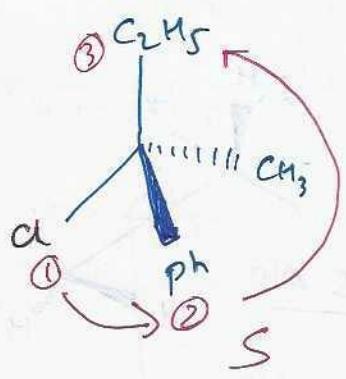
S



R

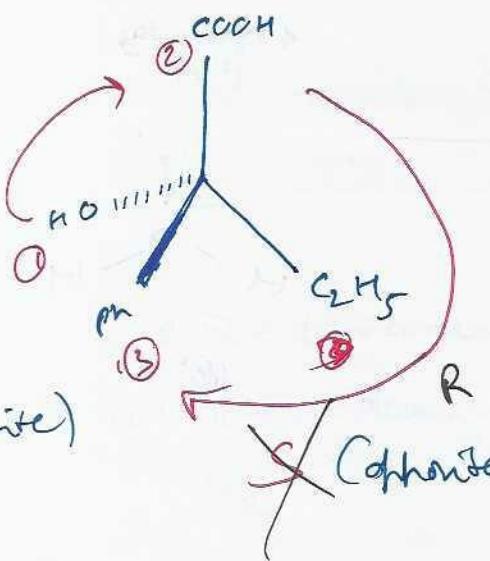
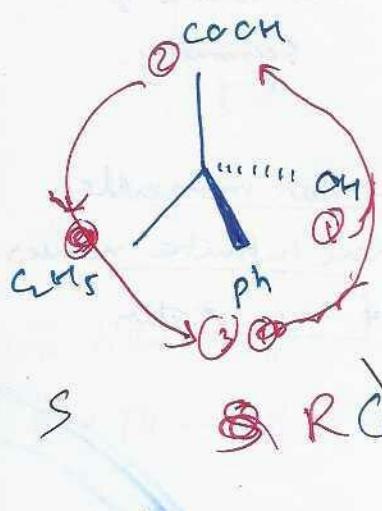


R



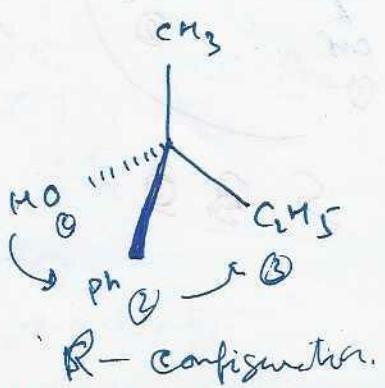
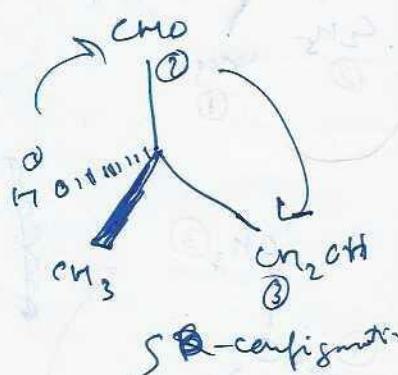
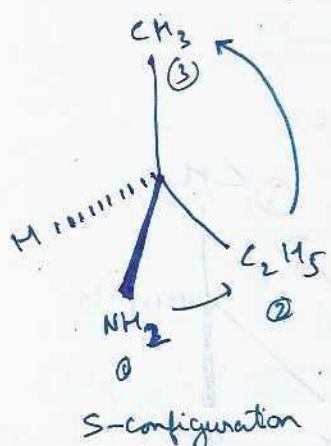
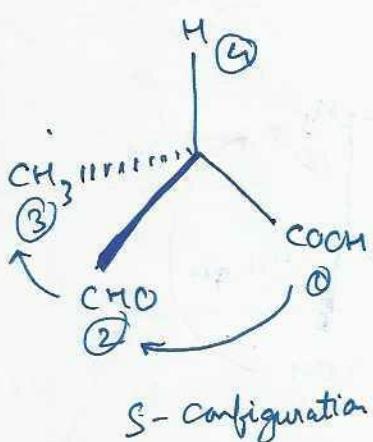
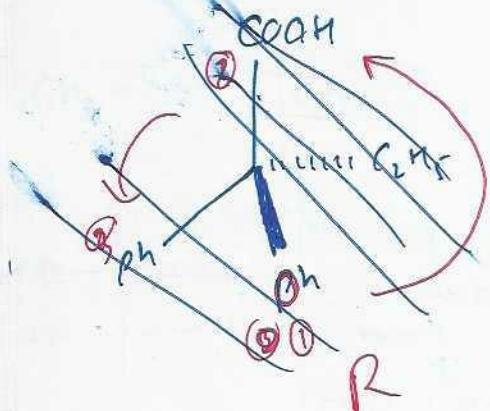
Lowest priority  
Should be present  
on the dashed  
line.

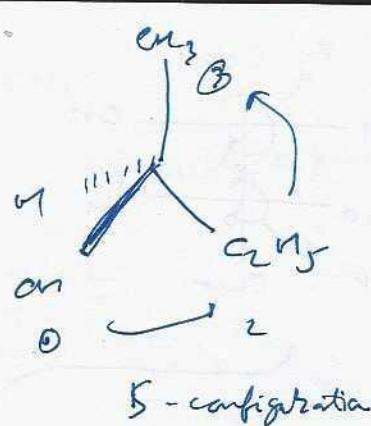
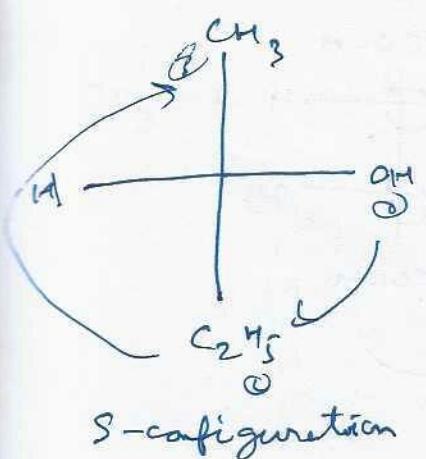
otherwise  
write reversed  
configuration.



~~S or R Cephurite)~~

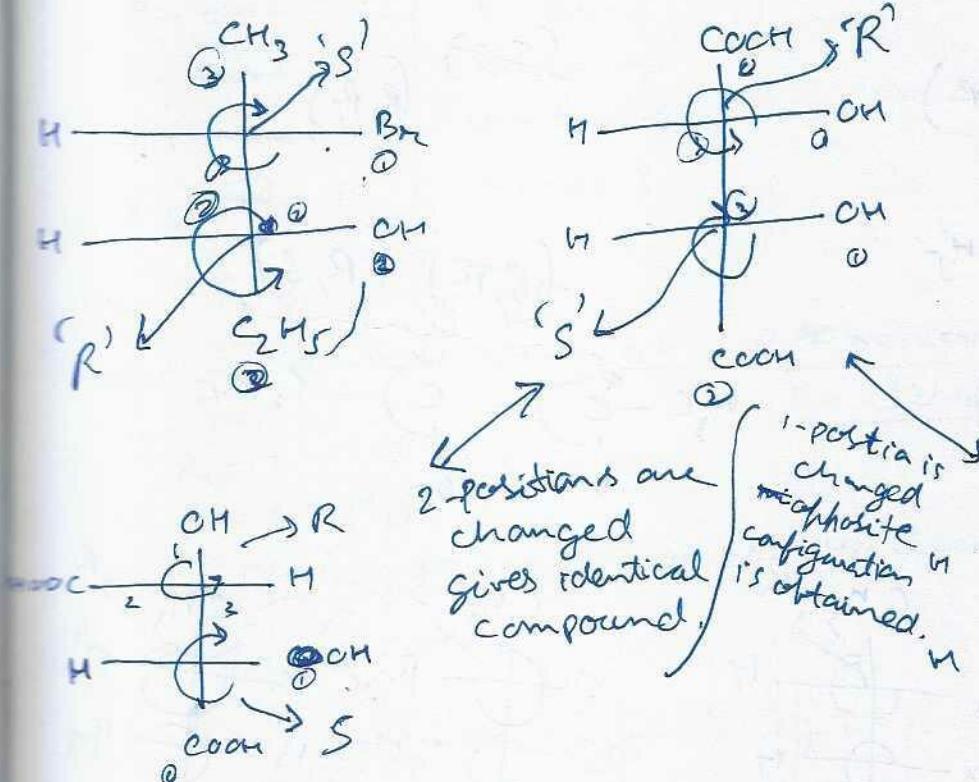
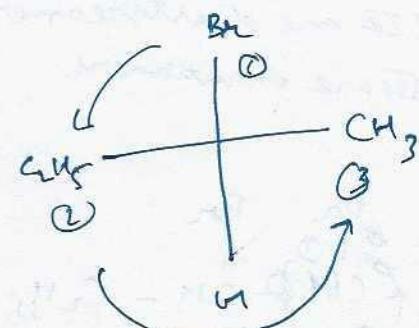
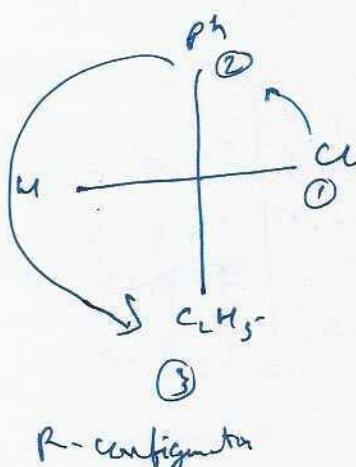
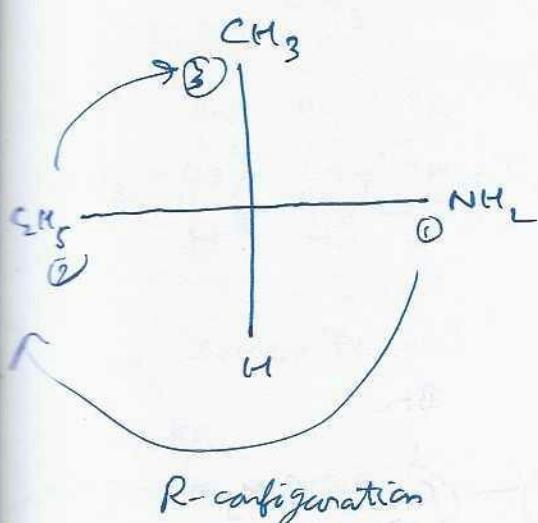
~~Cephurite)~~



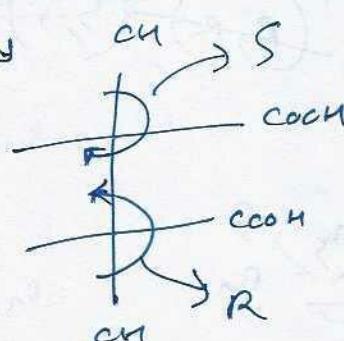


Hydrogen should be present on vertical line in Fischer Projector.

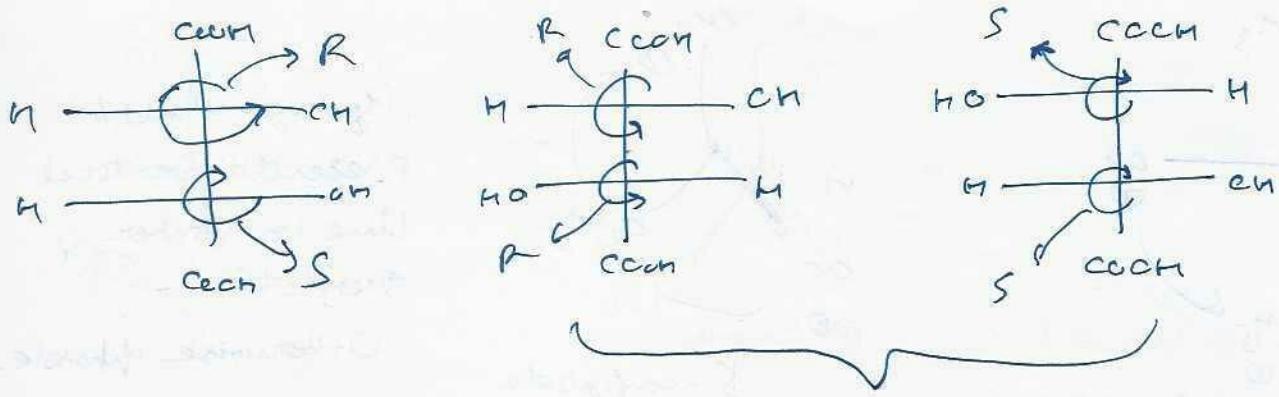
Otherwise phosphite.



Two chiral centres, having same groups has possibility of forming meso compounds.



In meso compounds, opposite configurations are identical. But otherwise they are enantiomers.

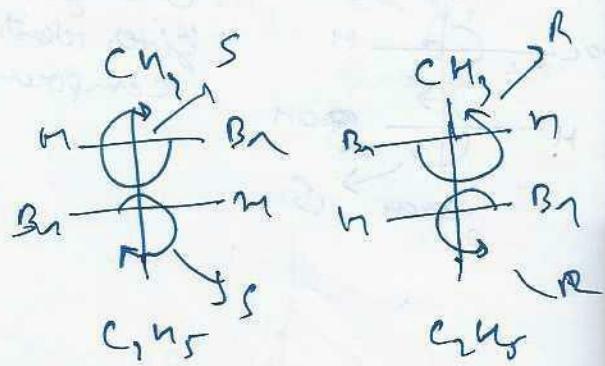
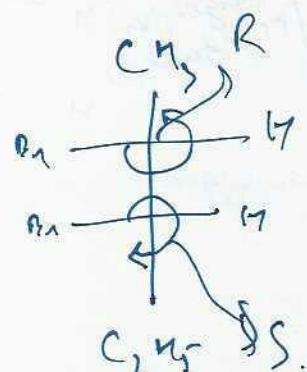
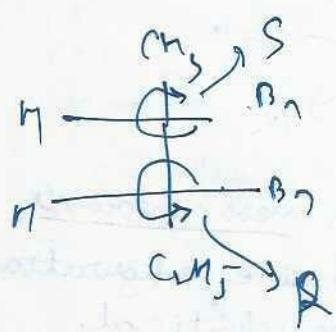
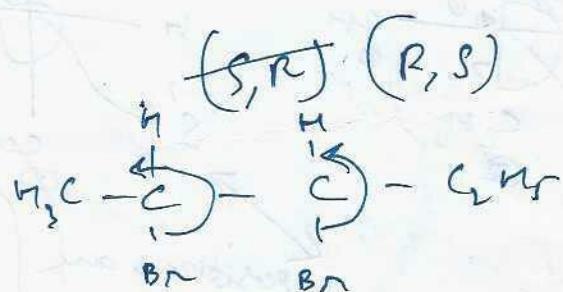
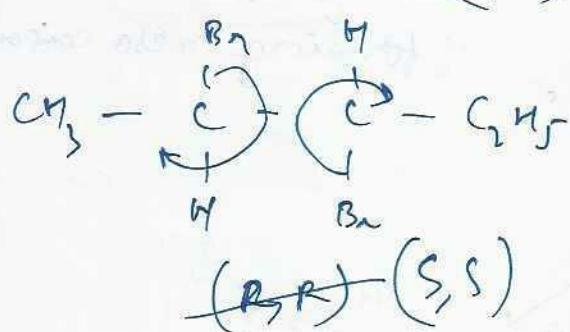
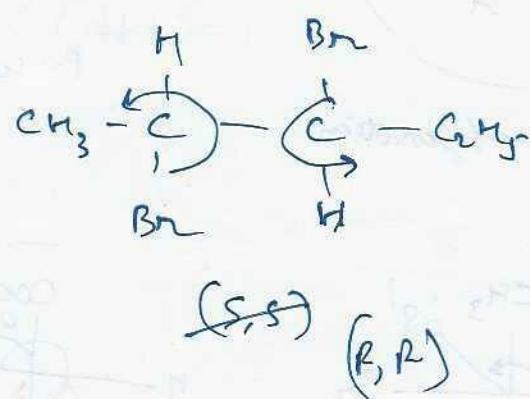
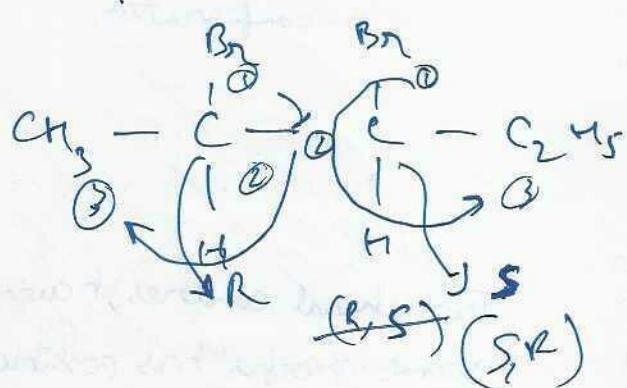
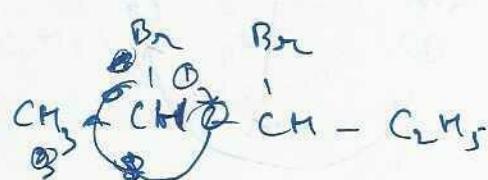


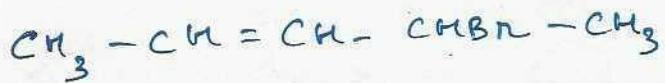
I and II are diastereomers

I and III are diastereomers

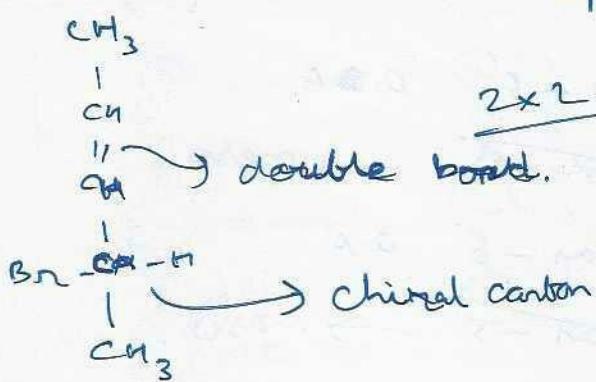
I and IV are enantiomers.

enantiomers



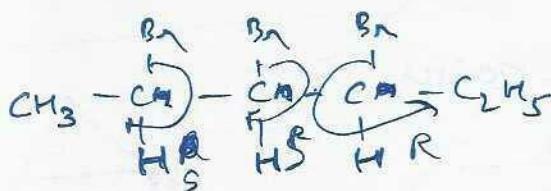


4 possible isomers (stereo)



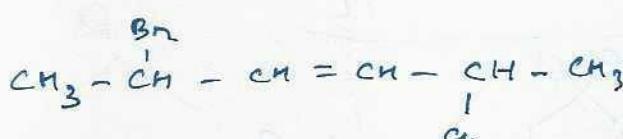
trans-S  
+ trans-R } enantiomers.

cis-S  
cis-R } enantiomers.

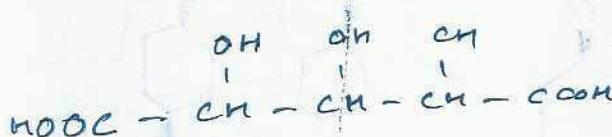


S-S-R	R-S=S
S-S-S	R-R-R
S-R-S	R-S-R
R-S-S-R	
S-R-R	R-S=S

8 isomers (stereo)



R-cis-R	S-cis-S
R-trans-R	S-trans-S
S-trans-R	R-trans-S
S-cis-R	R-cis-S



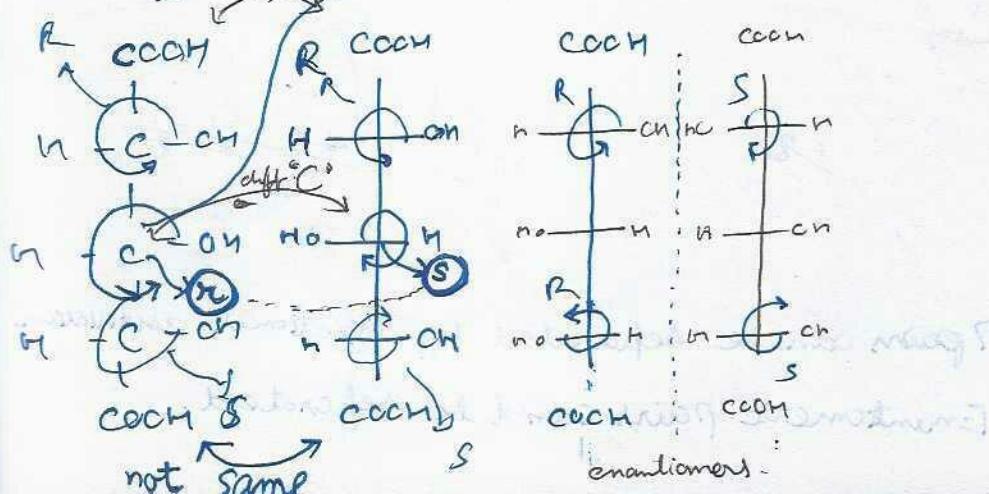
If two groups are same, highest priority given to 'R' group

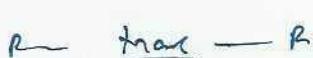
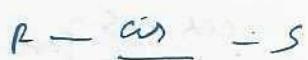
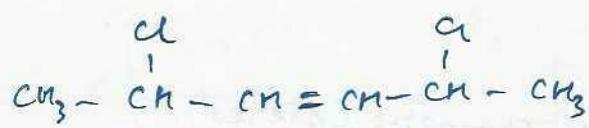
Pseudo symmetric compounds are represented by lower-case 's' and 'r'

$\frac{2}{4}$  meso compound.  
 $\frac{4}{4}$  stereoisomer.

R-R	S-S
R-S	R,S-R

a meso compound  $\rightarrow$  pseudo asymmetric chiral centre.





6 stereoisomers

enantiomers - 2 pairs

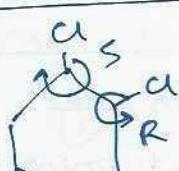
4 optically active.

meso compound - 2

$$\text{Diastereomers} = {}^6C_2 - 2 = 15 - 2 = 13 \text{ pairs.}$$

$$\frac{6 \times 5}{2} \\ 15$$

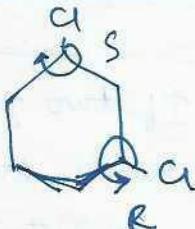
13



S; R

R; R

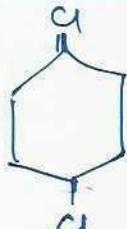
S; S



S; S, R

R; R

S; S



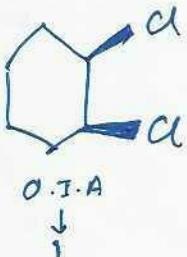
S; S

R; S

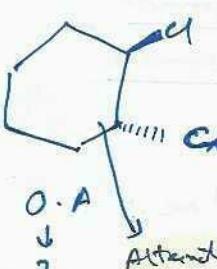


O.I.A

9



O.I.A  
↓ 1

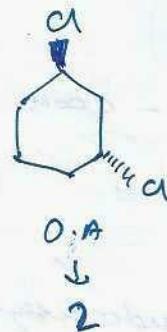


O.A  
↓ 2  
Altitude  
axis symmetry



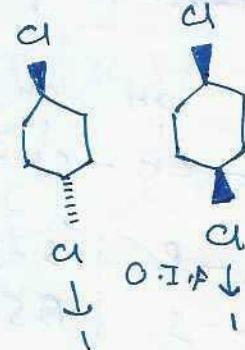
O.I.A

↓ 1



O.A

↓ 2



O.I.A  
↓ 1

+2

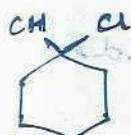
+2

+2 + 2

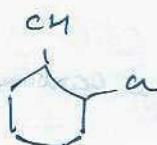
7 pairs can be separated by fractional distillation.

Enantiomeric pairs can't be separated.

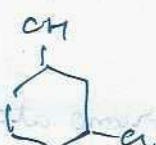
CH and Cl.



①



④

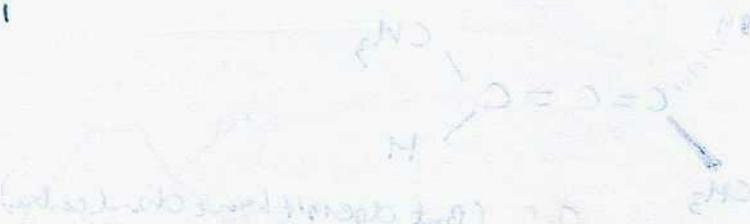
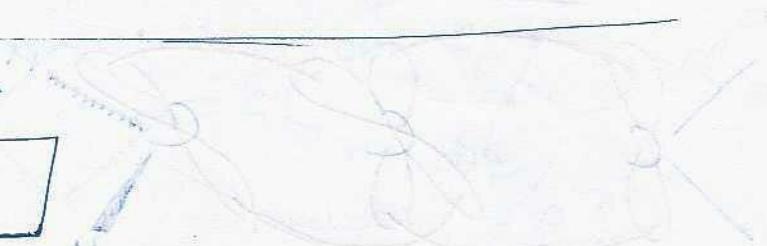
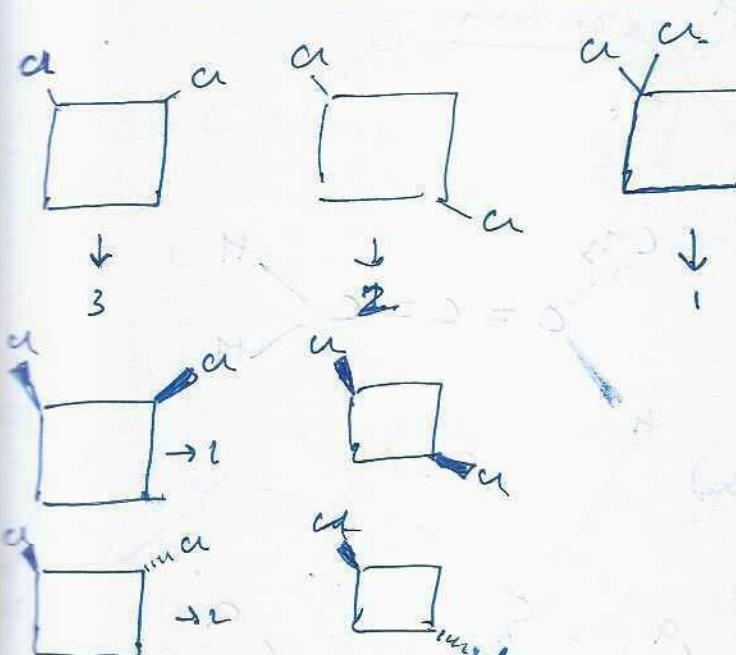
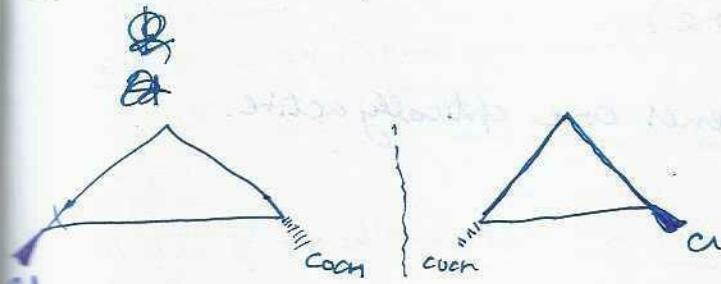
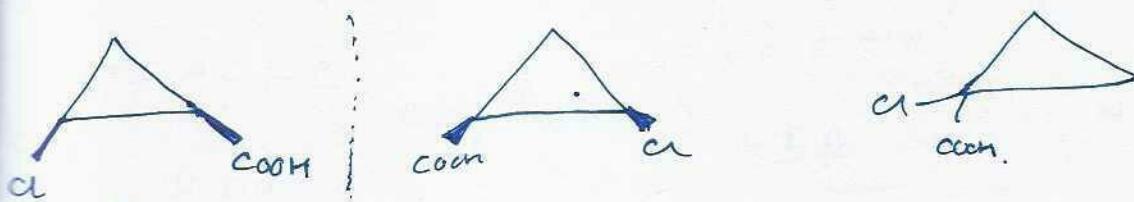
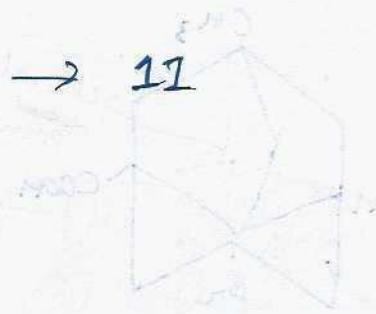


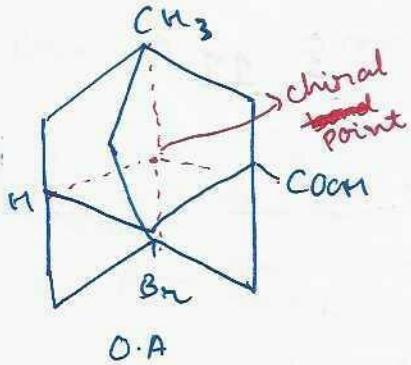
⑤



②

→ 11



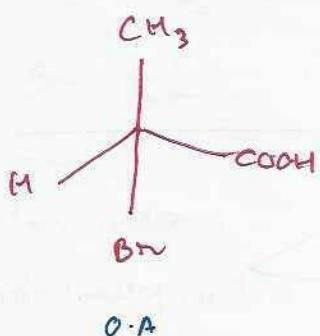


3-methyl-5-bromoatamantane carboxylic acid.

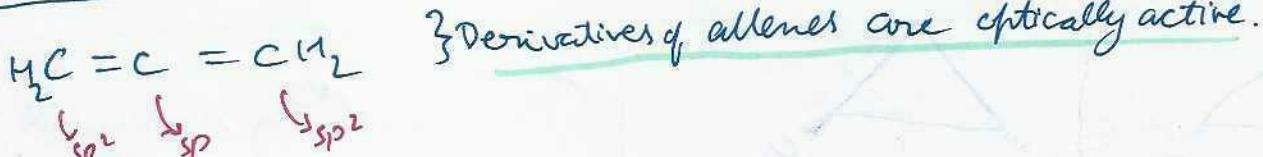
Chiral centres are there but doesn't form  $2^4$  stereoisomers.

Forms only 1 enantiomer pair.

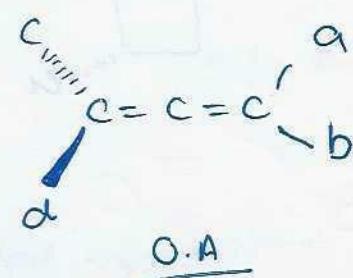
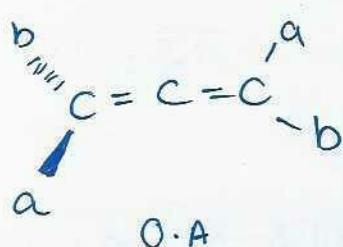
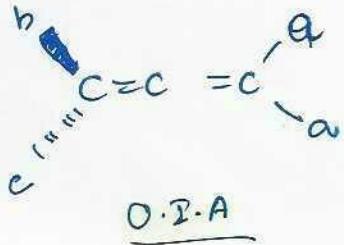
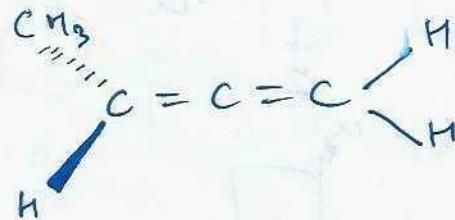
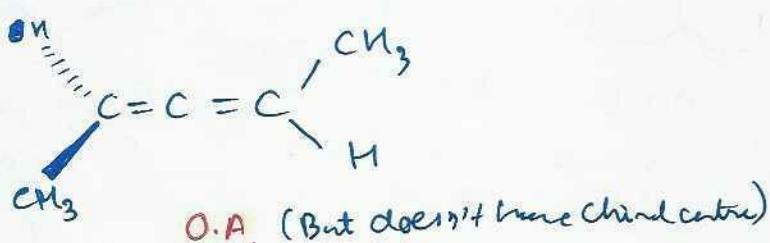
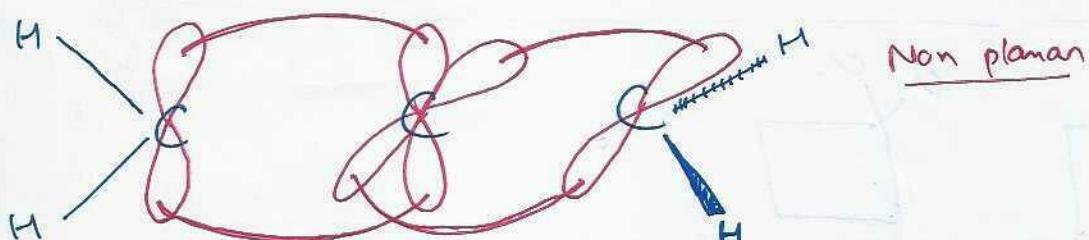
~~Because~~ Rotation is not possible due to complex structure.

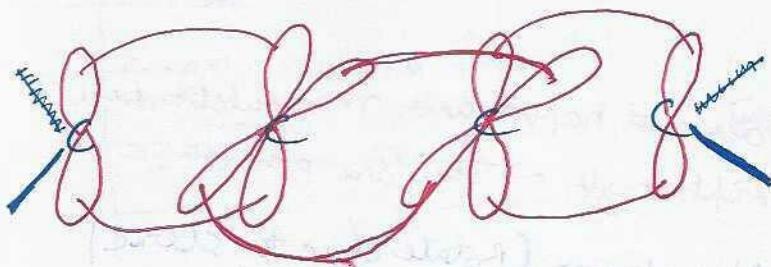
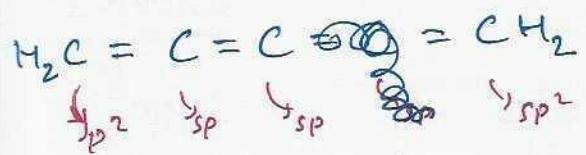


ALLENES (Do not have chiral centre)

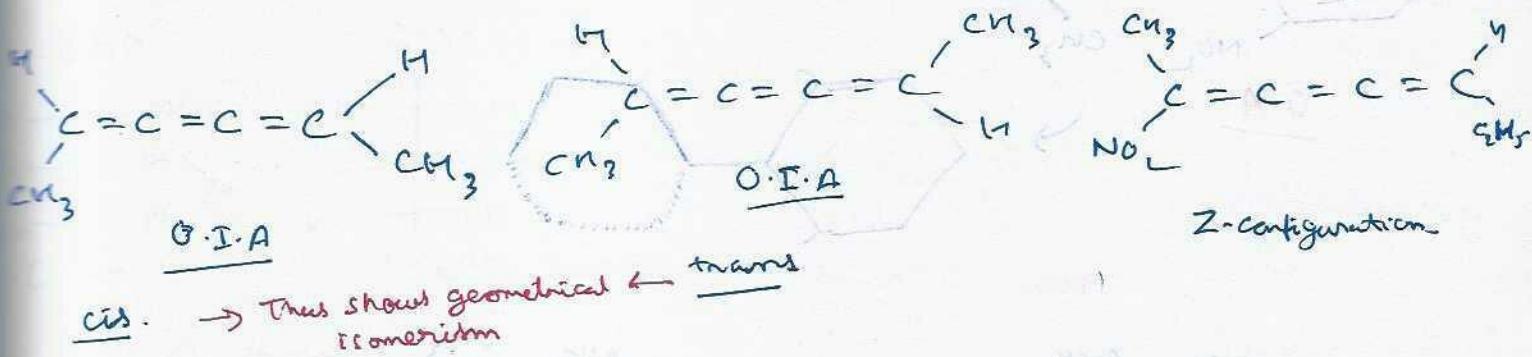
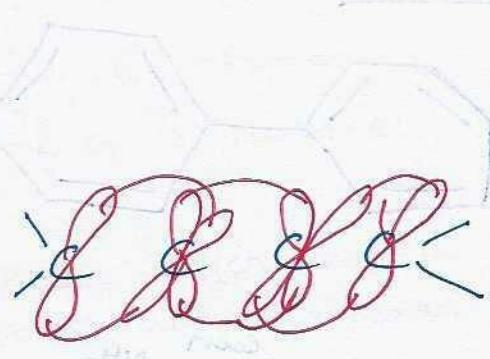


O.I.A



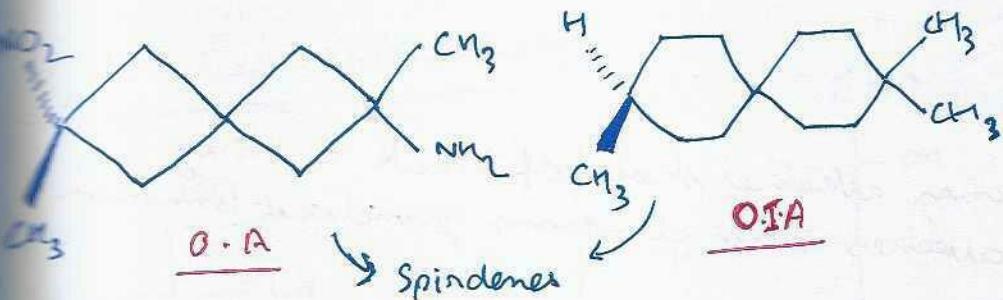
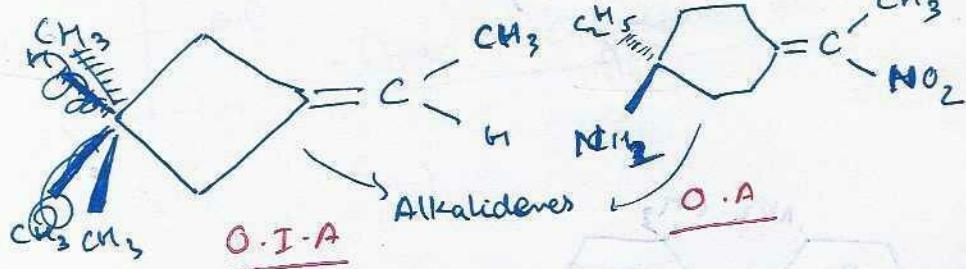
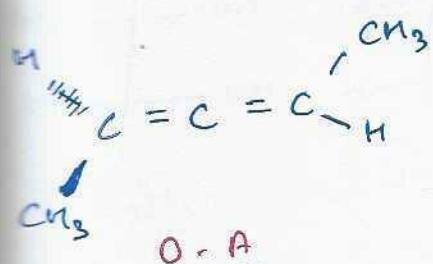


Planar

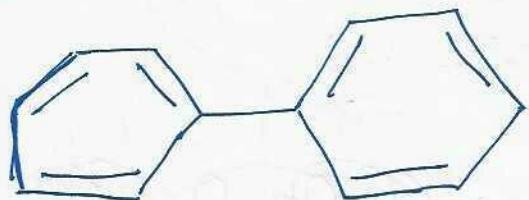


Even No. of double bonds are present → Shows optical isomerism

Odd No. of double bonds are present → Shows geometrical isomerism.



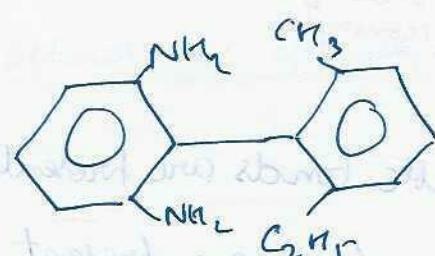
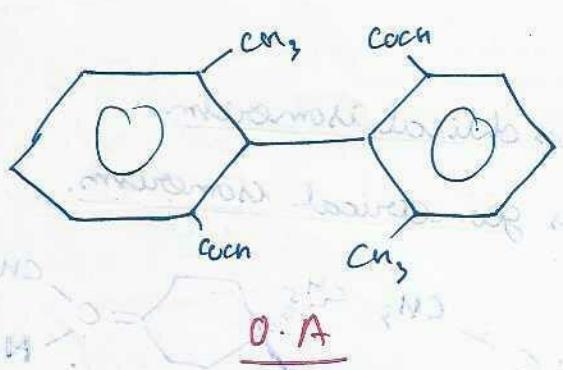
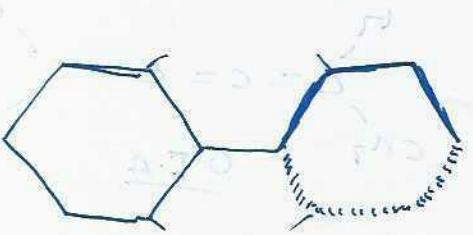
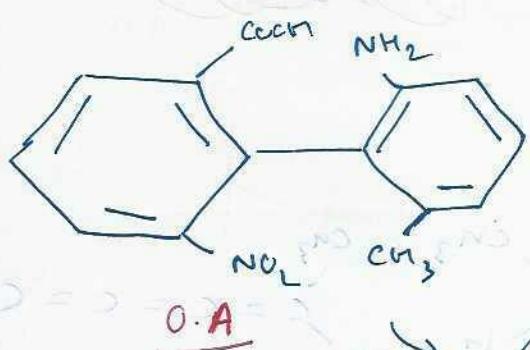
## BIPHENYLS



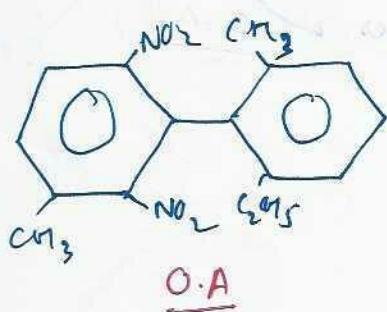
→ planar

Does not happen with monosubstituted biphenyls. → They are planar.

→ Non planar (rotate due to steric repulsion.)

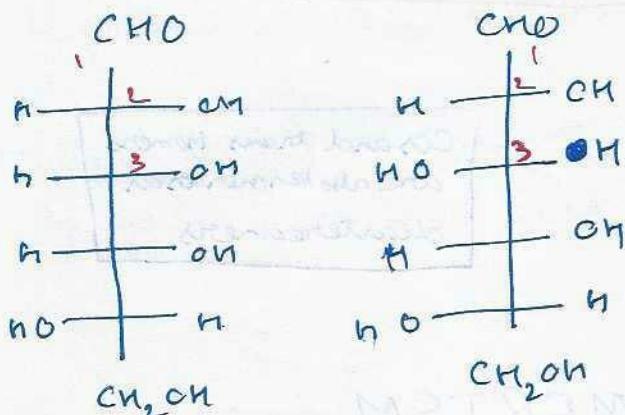


has plane of symmetry



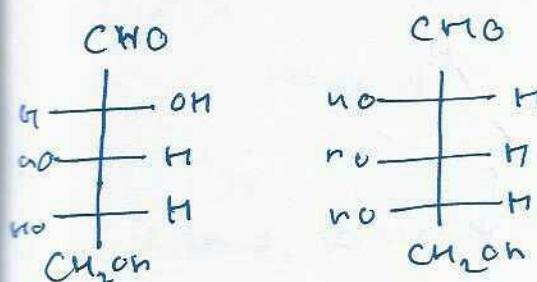
Non planar alkenes show optical activity.  
Planar alkenes show cis-trans geometrical isomerism.

# EPIMERS



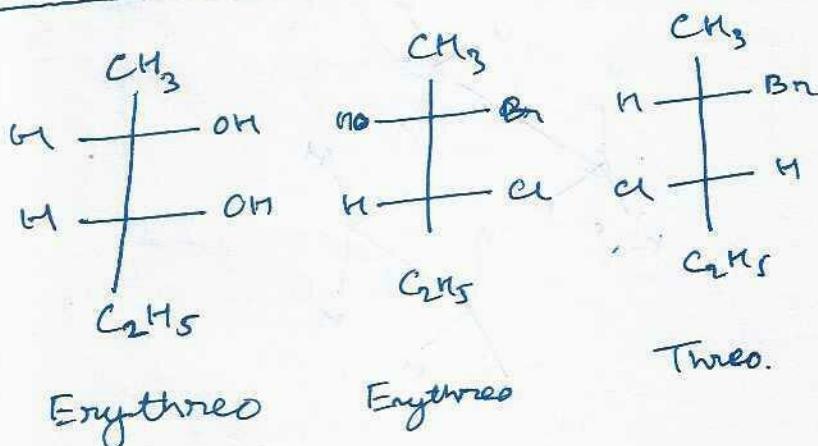
→ These are  $C_3$  epimers  
difference in 3rd carbon.

Epimer: Difference in position around 1 carbon atom.



$C_2$  epimers

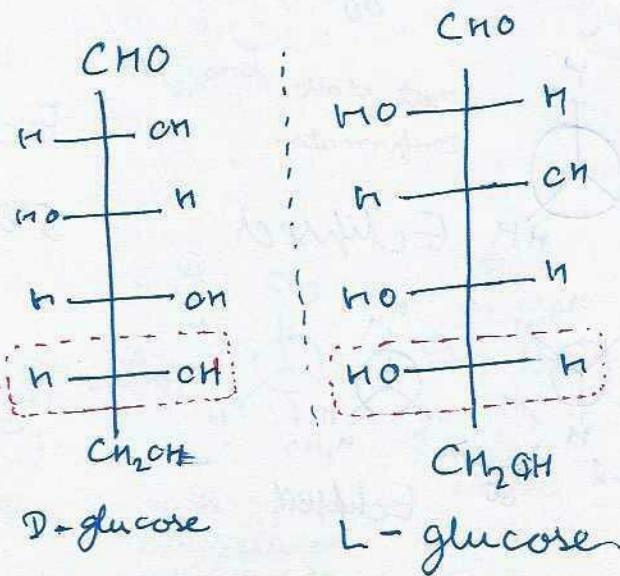
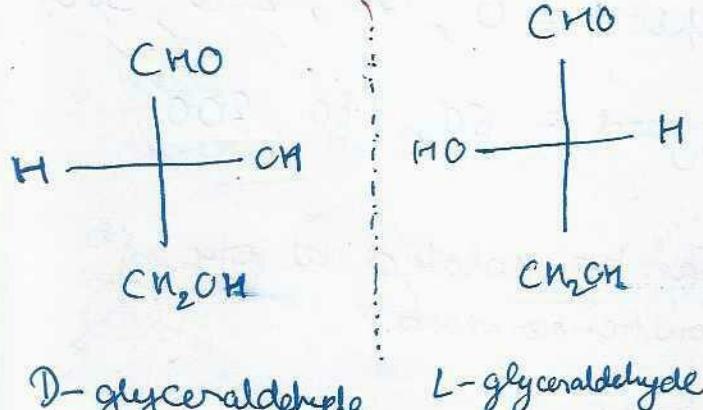
# ERYTHREO - THREO

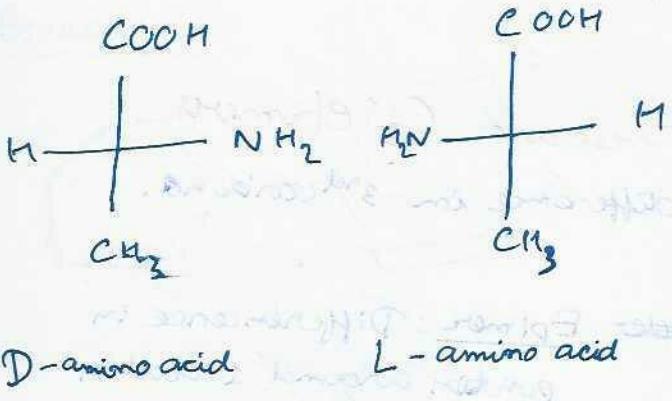


Erythro - Same side

Threo - Opposite side

# D, L CONFIGURATION



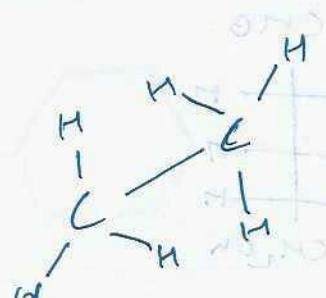
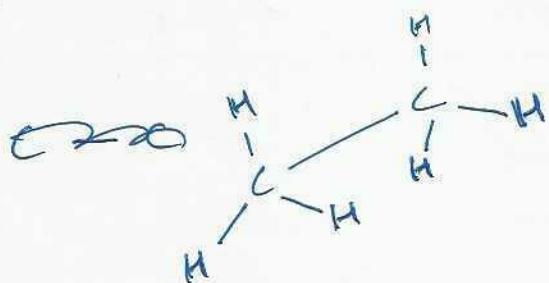


Resolution - Separation of enantiomer pairs

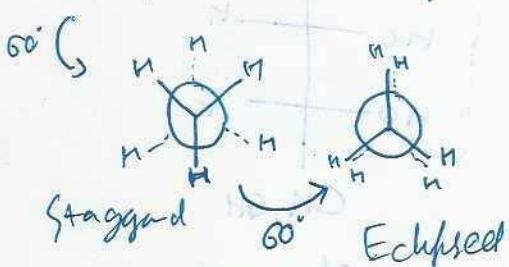
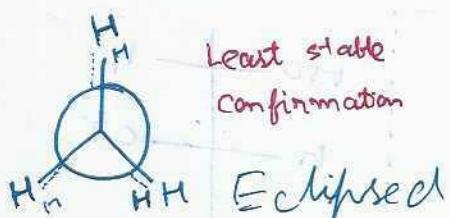
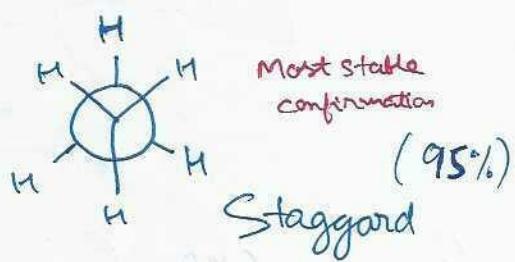
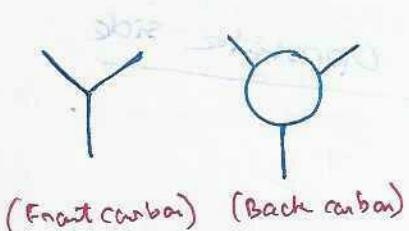
Cis and trans isomers are also known as diastereomers

## CONFORMATIONAL ISOMERISM

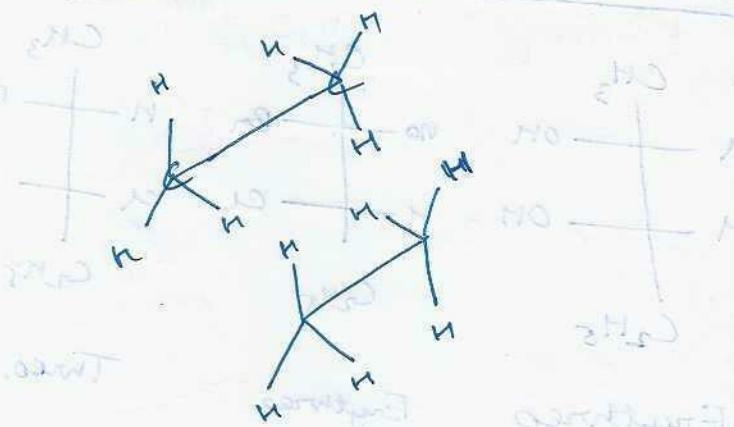
Does not involve bond breaking.



### NEWMAN PROJECTION



### SAWHORSE PROJECTION



Eclipsed = 0°, 120°, 240°, 360°

Staggered = 60°, 180°, 300°

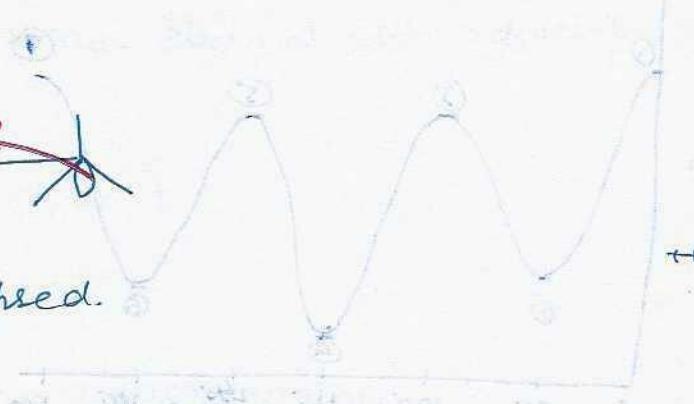
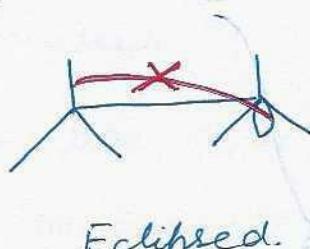
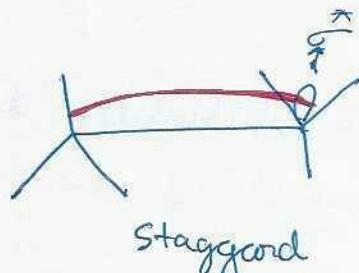
Can be isolated at very low temperatures.

Torsional strain  $\rightarrow$  Repulsion between hydrogen atoms.

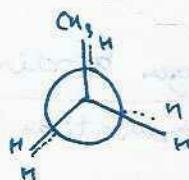
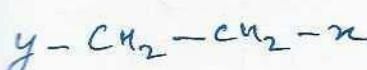
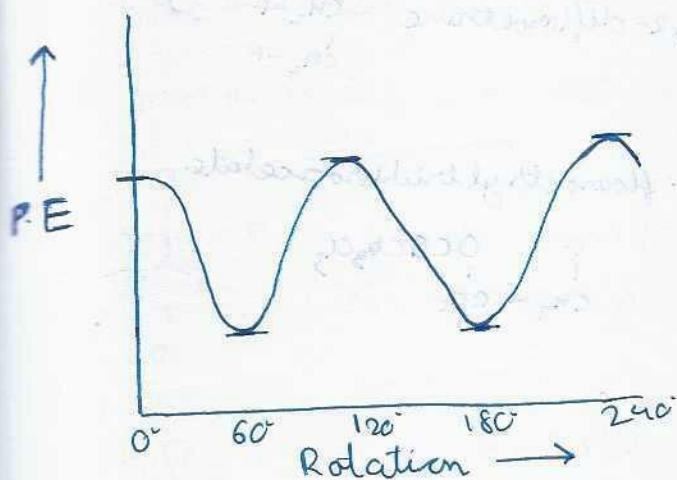
$\hookrightarrow$  contributes 10% (butane)

Filled  $\sigma'$  Bond electrons interaction with  $\pi$  orbital.

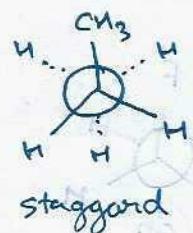
$\hookrightarrow$  contributes 90% (ethane)



In butane, torsional strain plays a bigger role.

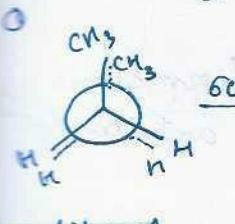
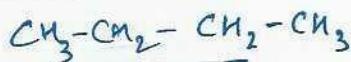


propane (eclipsed)

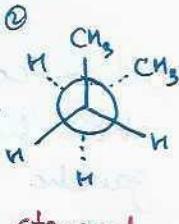


staggered

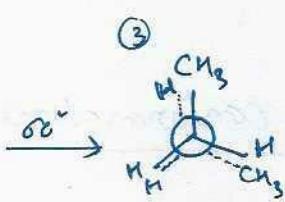
In  $n$ -butane



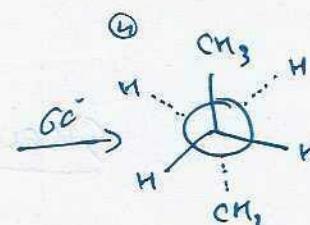
eclipsed  
syn-periplanar



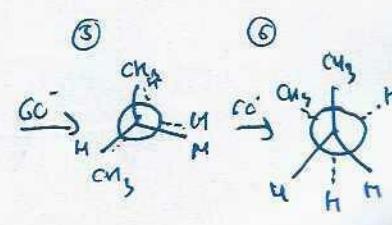
staggered  
gauche



partially eclipsed



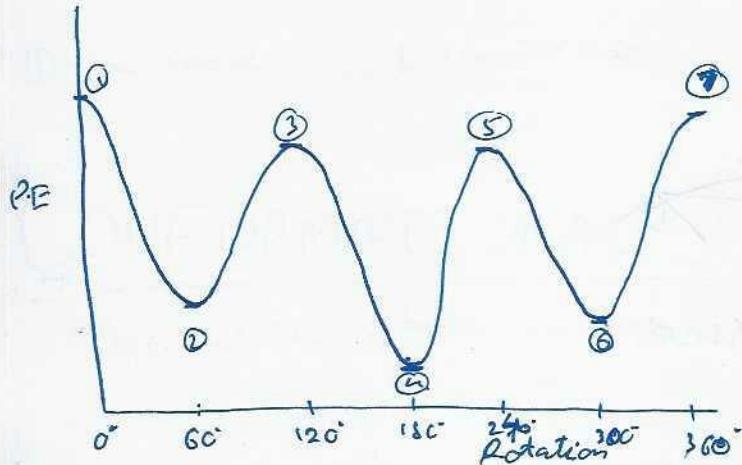
staggered  
anti-periplanar



eclipsed staggered

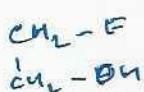
Stability: Anti > gauche > Partially eclipsed  $\gg$  syn-  
periplanar

$$④ > ② = ⑥ > ⑤ = ③ > ①$$

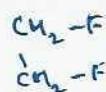


But in certain compounds, gauche conformation is more stable than anti conformation.

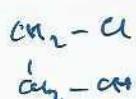
e.g. 2-Fluoroethanol



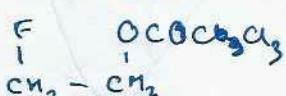
$1,2$ -difluoroethane



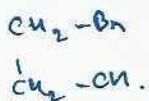
2-Chloroethanol



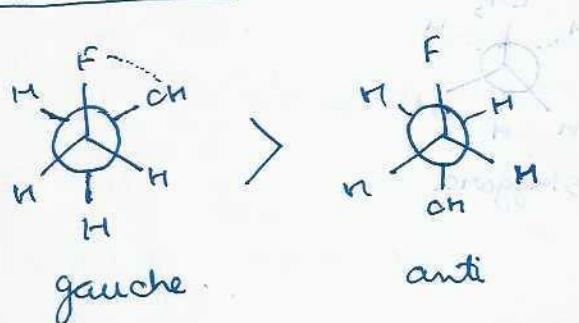
2-fluoroethyltrichloroacetate



2-Bromoethanol



### 2-Fluoroethanol

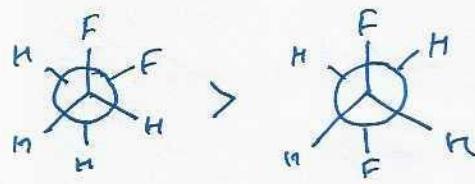


Hydrogen bonding gives gauche conformation more stability.

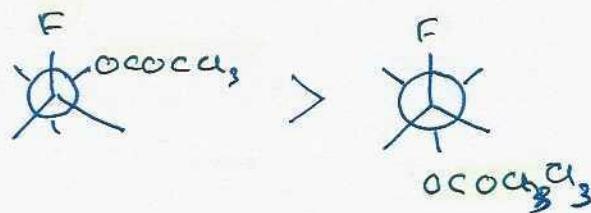
Skew conformations: other conformations apart from anti and gauche.

Their more fractions can be considered to be zero.

## 1,2-Difluoroethane



## 2-fluoroethyltrichloroacetate



**Gauche effect:** Interaction of lone pair electrons with adjacent atomic nucleus.

Not applicable for bulky atoms like Cl, Br, I ... .

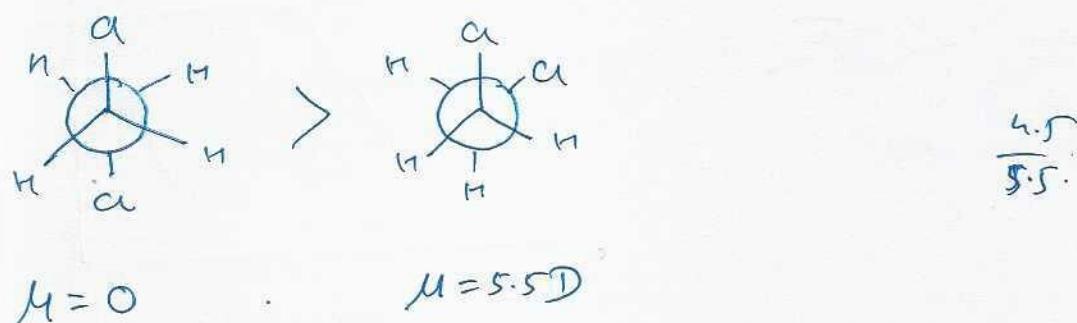
Applicable for Oxygen and Fluorine.

## CALCULATION OF MOLE FRACTIONS OF CONFORMATION

gauche conformation of 1,2-dichloroethane has  $\mu$  value 5.5 D

The  $\mu$  value of the molecule is 1 D.

Mole fraction of anti conformation is



$$\frac{\text{Gauge}}{5.5} = \frac{1}{5.5}$$

$$\mu_{\text{compound}} = (\chi_{\text{anti}} \times \mu_{\text{anti}}) + (\mu_{\text{gauge}} \times \chi_{\text{gauge}})$$

$$1 = (\chi_{\text{anti}} \times 0) + 5.5 \times \chi_{\text{gauge}}$$

$$\chi_{\text{gauge}} = \frac{1}{5.5} = 0.18$$

$$\chi_{\text{anti}} = \frac{4.5}{5.5} = 0.82$$

$$\frac{4.5}{5.5} = \frac{9}{11}$$

$$\frac{9}{11} \times \frac{1.22}{1.22 - 0.18} = \frac{9}{10}$$

# ELASTICITY

~~It is the property of matter due to which it regains its original configuration after removal of external deforming force.~~

Within elastic limit

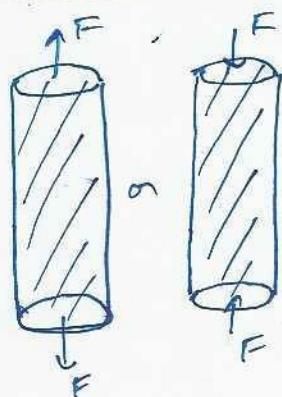
$$\vec{F}_{\text{ext}} = -\vec{F}_R$$

Under deformation of elastic body, it remains under stress.

$$\text{Stress} = \frac{\text{Internal Restoring force } \cancel{\text{from External deforming force}}}{\text{Area}}$$

Tensor

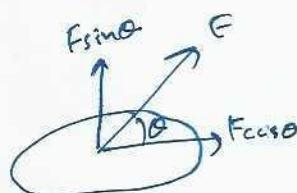
Normal stress



Tangential shear stress

$$S.T = \frac{F_{II}}{A}$$

$$N.S = \frac{F_1}{A}$$

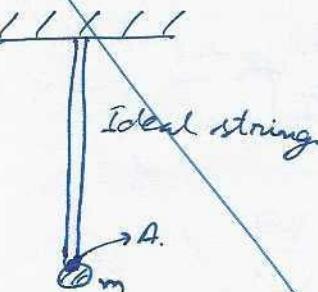


$$\text{Stress} = N.S + T.S$$

$$= \frac{F \cos \theta}{A} + \frac{F \sin \theta}{A}$$

## BREAKING STRESS

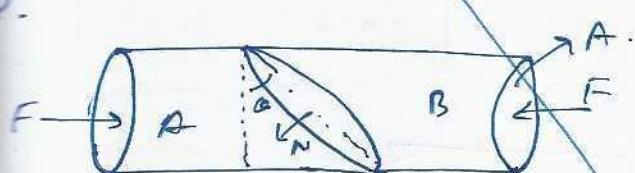
maximum stress without breaking.

Q. 

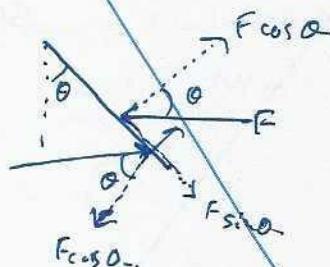
Find stress developed in string.

$$\text{Stress} = \frac{mg}{A}$$

Q.



Find stress developed at junction.



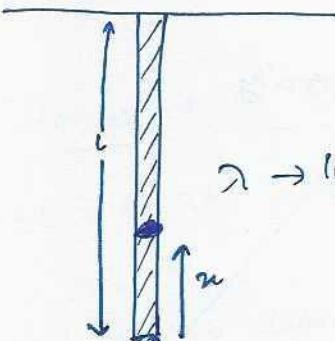
~~$$\frac{2F \cos \theta}{A \cos \theta} + \frac{2F \sin \theta}{A \sec \theta}$$~~

$$N \cos \theta = F$$

$$N = F \cos \theta$$

$$\text{Normal stress} = \frac{N}{\frac{A_{\text{cross}}}{\cos \theta}} = \frac{N \cos \theta}{A} = \frac{F}{A}$$

Q.

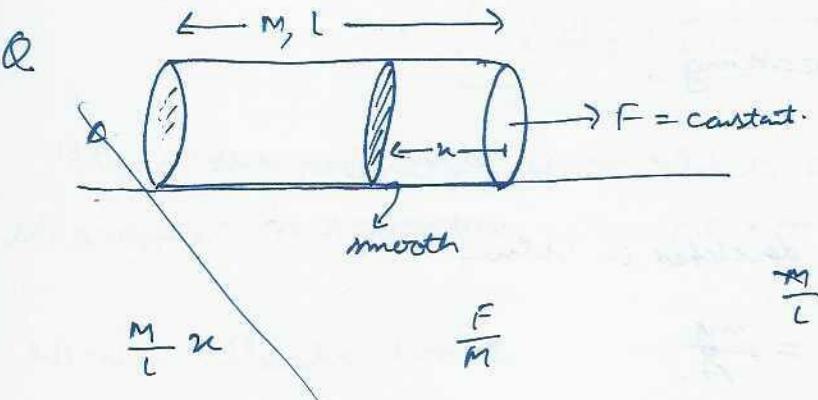


$\lambda \rightarrow$  linear mass density.

~~$$\lambda (dx)$$~~

~~$$\frac{\lambda \cdot g}{A}$$~~

$$\text{Stress} = \frac{\lambda \cdot g}{A}$$



$$\frac{\pi}{4} (1-\nu) \left( \frac{E}{\rho A} \right) = T$$

$$\text{Stress} = \frac{(1-\nu) F}{L A}$$

## STRAIN

Strain =  $\frac{\text{Change in Dimension}}{\text{Original Dimension}}$

Longitudinal  
 $\frac{\Delta L}{L}$

Volumetric  
 $\frac{\Delta V}{V}$

Shear strain =  $\theta$

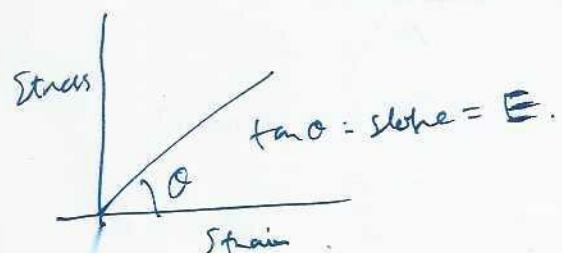
## HOOKE'S LAW

Within elastic limit stress and strain are proportional to each other.

$$\text{stress} = E \times \text{strain}$$

$E \rightarrow$  modulus of elasticity.

$$\Rightarrow E = \frac{\text{stress}}{\text{strain.}}$$



For perfectly rigid body

$$E = \infty$$

# TYPES OF MODULUS OF ELASTICITY

## Young's Modulus

$$\gamma = \frac{\text{Longitudinal stress}}{\text{Longitudinal strain}}$$

$$= \frac{F/A}{\Delta L/L}$$

$\gamma = \frac{FL}{A \Delta L}$

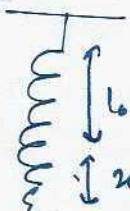


Notes:

- ① For ideal rigid body, Young's Modulus is infinite
- ② Defined for solids only ( $\approx 10^{11} \text{ N/m}^2$ )

$$③ F = \left( \frac{\gamma A}{L} \right) \Delta L = F_R$$

$\Rightarrow$  The equivalent spring constant of elastic wire is  $\left( \frac{\gamma A}{L} \right)$ .

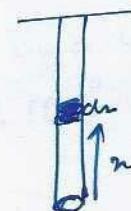


$$F_s = k_n = F.$$

## Elongation in the wire

Let  $s$  is the stress at a distance  $n$  from one end.

$$\Delta L = \frac{F \cdot n}{A \gamma}$$



If  $d\Delta L$  is the deformation in length  $dn$  due to this stress

then the stress

$$dn' = \frac{s dn}{\gamma}$$

$$\int dn' = \int \frac{s dn}{\gamma}$$

$\Rightarrow \Delta L = \frac{1}{\gamma} \int s dn'$

Q.

Stress at a distance  $x$  from lower end

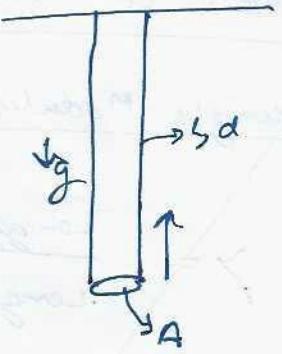
$$\text{Stress} = \frac{A \gamma d g}{A}$$

$$\Delta L = \frac{1}{2} \int_0^L \gamma d g \, dx$$

$$= \frac{1}{2} \gamma g \frac{L^2}{2}$$

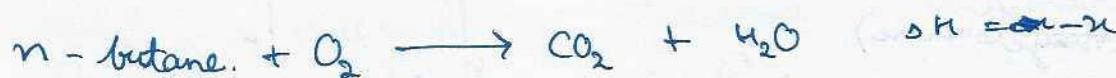
$$d = \frac{M}{AL}$$

$$\Rightarrow \Delta L = \frac{\gamma g L}{2 A Y}$$



# CONFORMATIONS IN CYCLOHEXANE

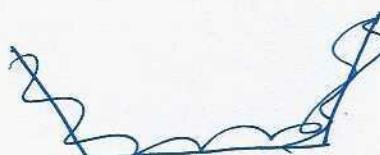
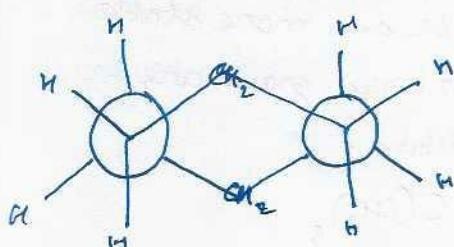
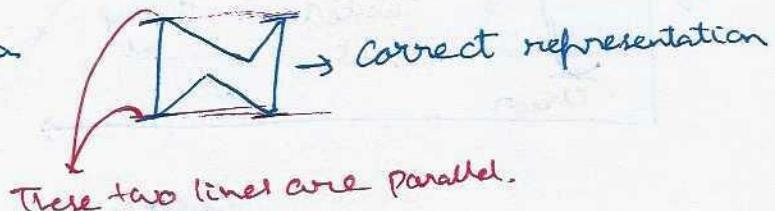
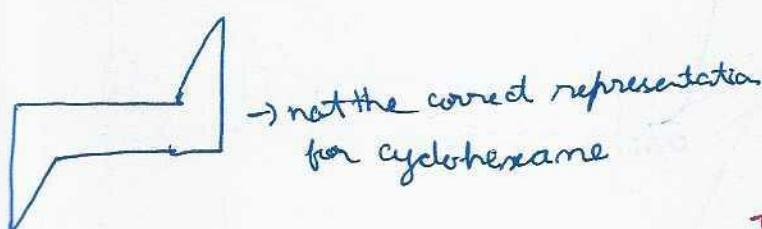
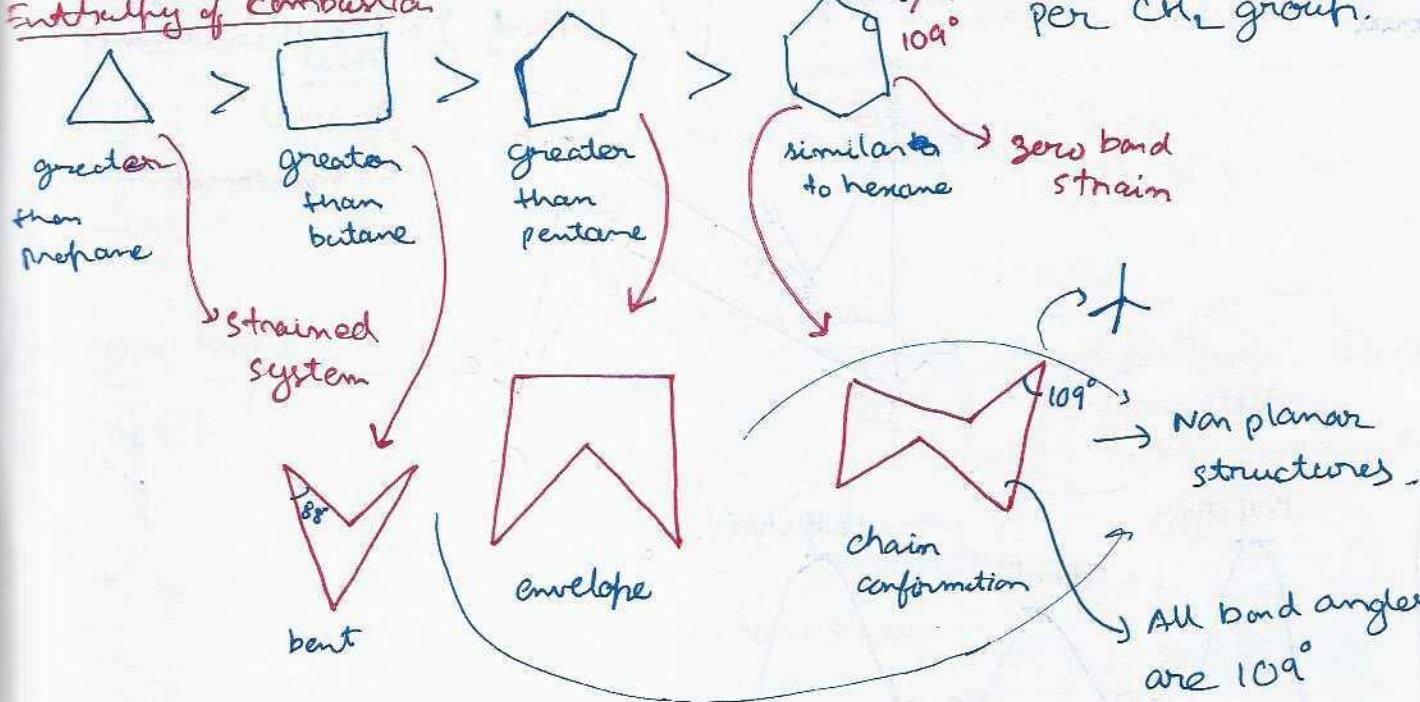
## Heat of Combustion and Stability of Compounds

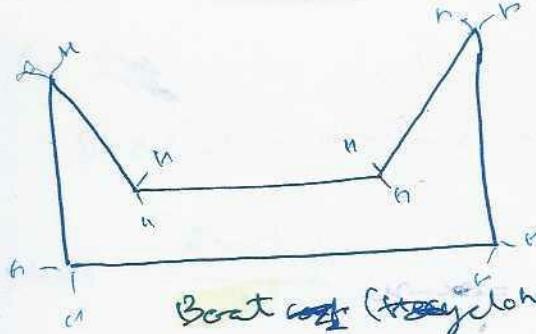


$x > y$ . Enthalpy of combustion of isobutane is less than  $n$ -butane.

isobutane  $>$   $n$ -butane : Stability.

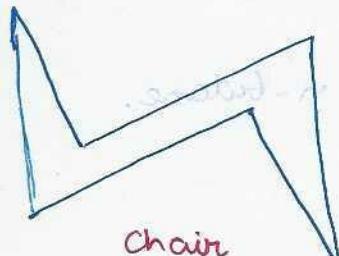
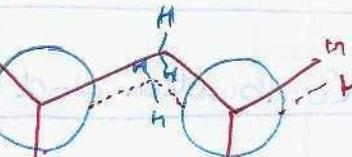
### Enthalpy of Combustion





Less stability

strains for pedantic



Axial  
Equatorial

a (up)

(down)

(up)

e (down)

a (down)

a (up)

e (up)

a (up)

(down)

(up)

e (down)

a (down)

a (up)

e (up)



Ring  
flipping

} axial becomes equatorial  
} a-equatorial becomes  
} axial.

a-axial

e-equatorial

Half chain.

Boat

Half chain.

Boat

Energy

(0.A)

(0.A)

(0.A)

(0.A)

Chair

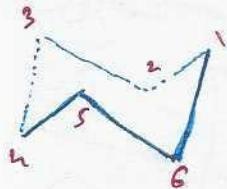
Twisted  
boat

Twisted  
boat

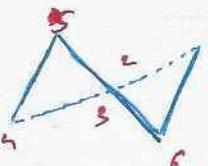
Conformation

) Can become more stable  
if two large groups are  
Substituted.  
eg.  $C(CH_3)_3$





Half-chair

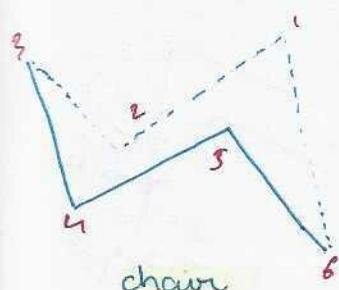


Twisted boat

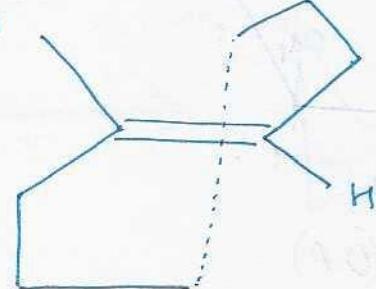
(O.A) chiral



Half-chair



Chair



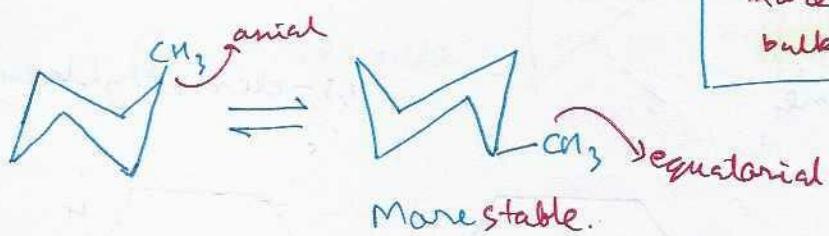
(O.A) chiral

Trans-2-octene

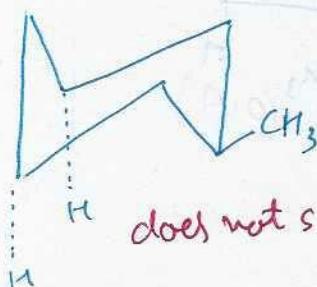
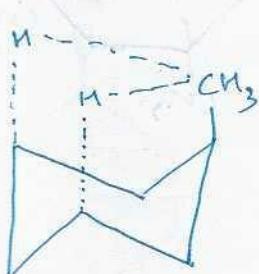


→ Twisted boat form

## MONOSUBSTITUTED CYCLOHEXANES



Equatorial position is more stable for bulky substituents

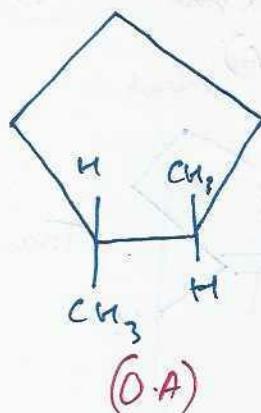
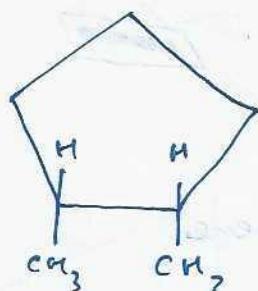


does not show interaction.

1,3 diaxial interactions decrease stability

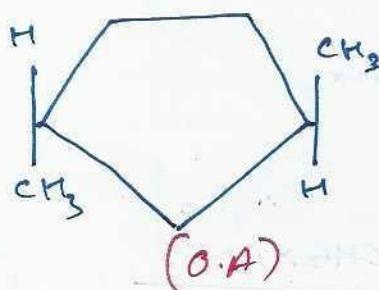
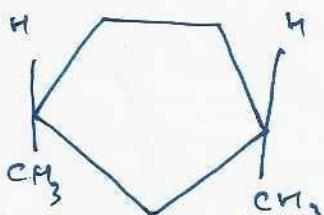
# DISUBSTITUTED CYCLOHEXANE

1,2-dimethylcyclohexane



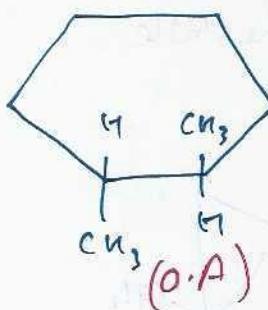
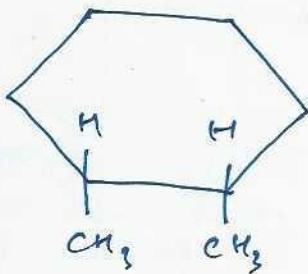
These structures  
are not planar.

1,3-dimethylcyclohexane

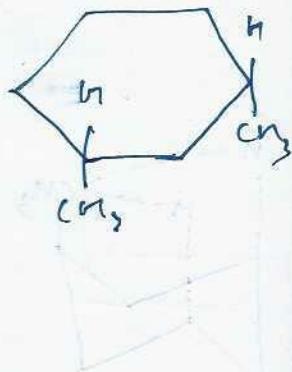
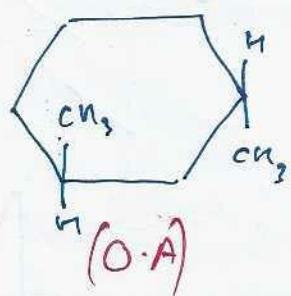


Trans is  
optically active.

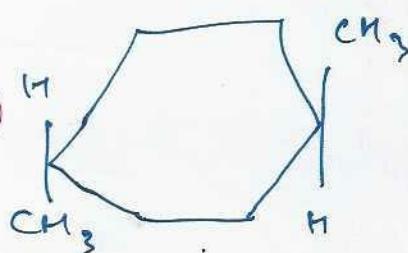
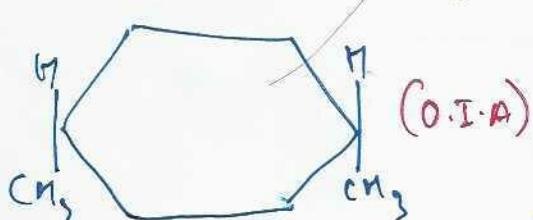
1,2-dimethylhexane



1,3-dimethylhexane

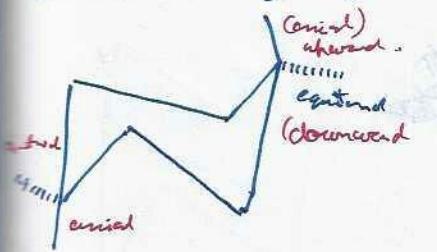


1,4-dimethylcyclohexane

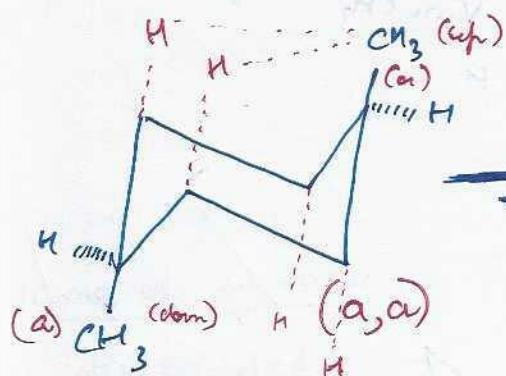


Both are  
optically inactive.

### 1,4-dimethyl cyclohexane



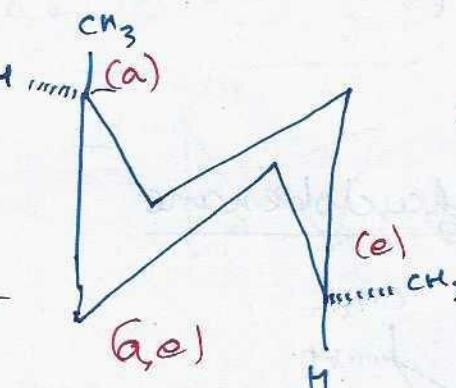
Upward and downward positions are seen for classification into cis and trans.



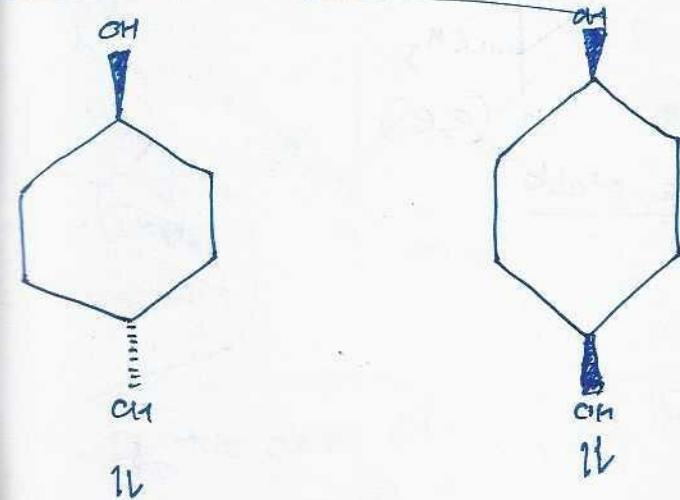
### trans-1,4-dimethylcyclohexane

Two trans isomers are possible.

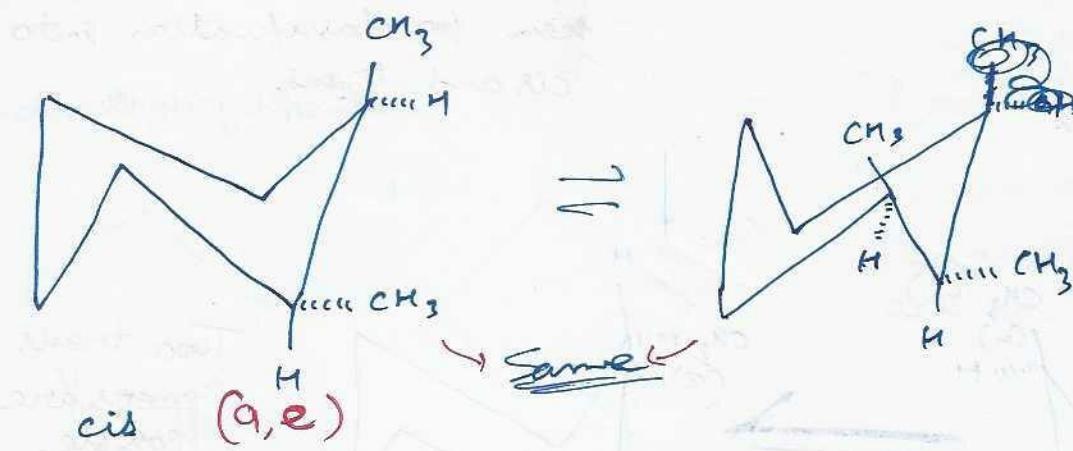
More stable (95%)



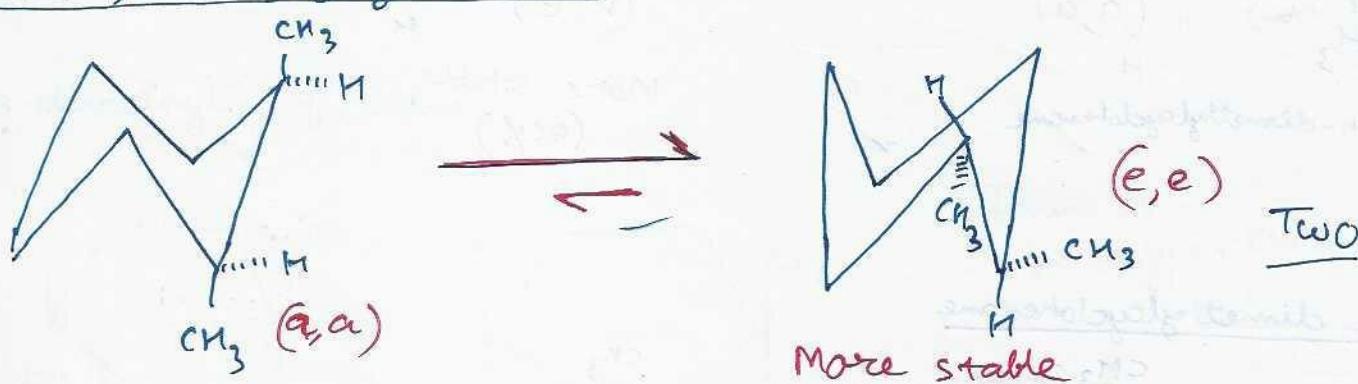
One isomer



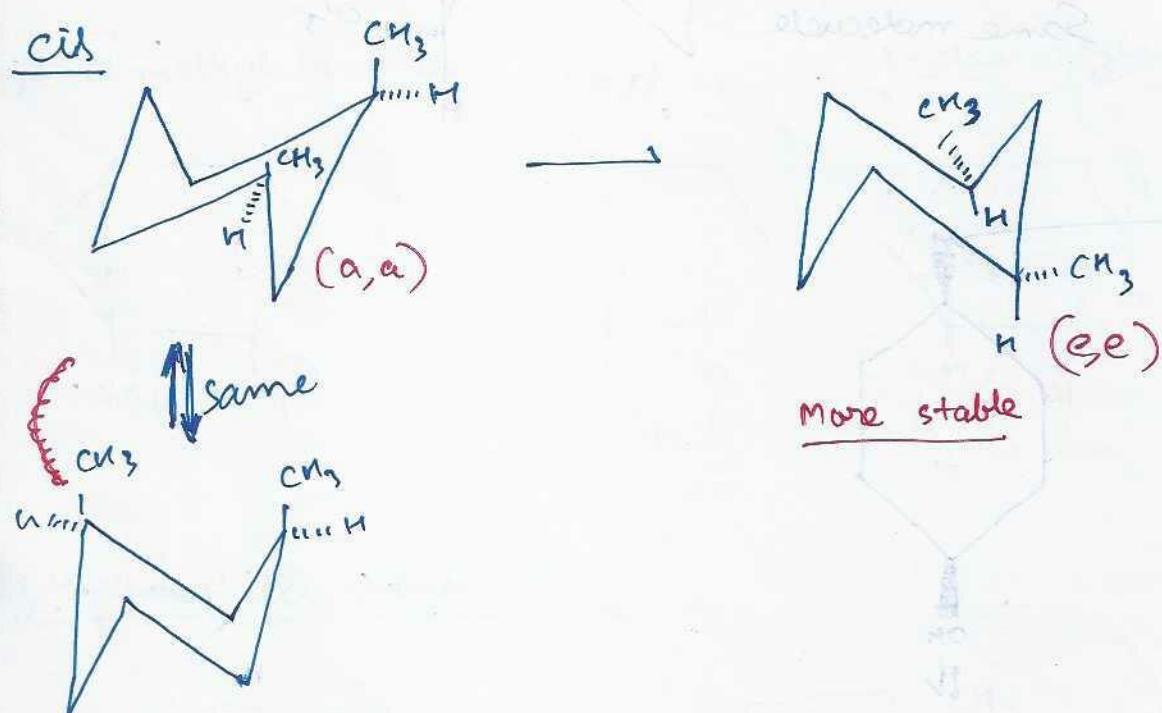
### 1,2-dimethylcyclohexane



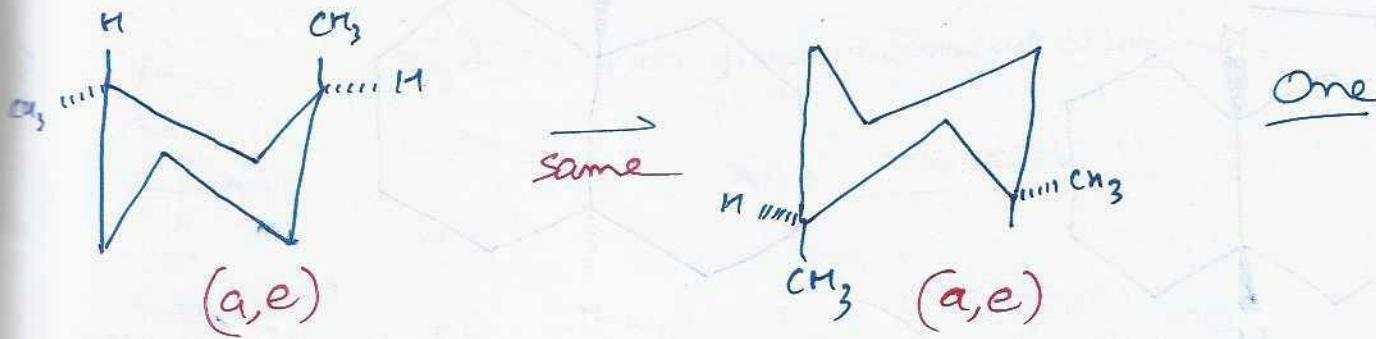
### trans-1,2-Dimethylcyclohexane



### 1,3-dimethylcyclohexane



## trans - 1, 3-Dimethylcyclohexane



### Name of isomer

1,2-disubstituted  
(or)

1,4-disubstituted

1,3-disubstituted

### Isomer

cis

trans

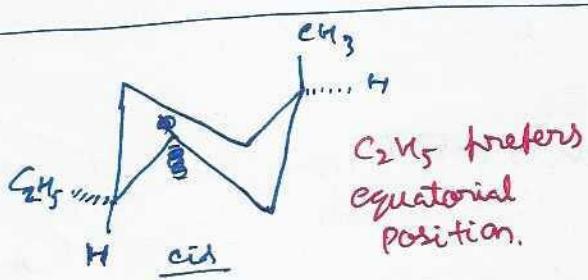
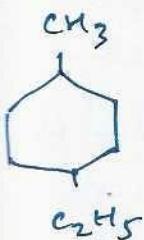
### Position

(a,e) or (e,a) → One isomer

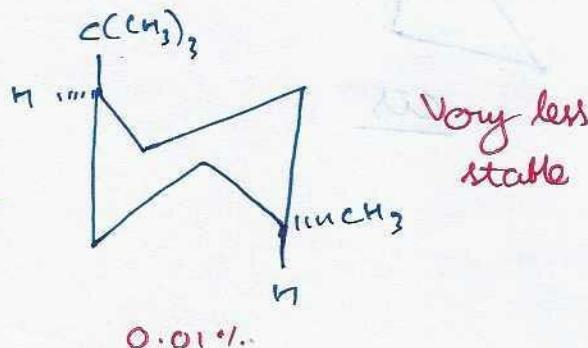
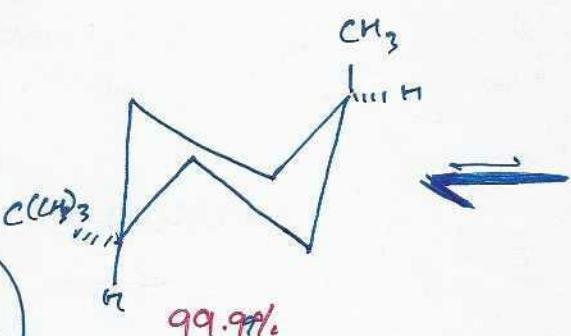
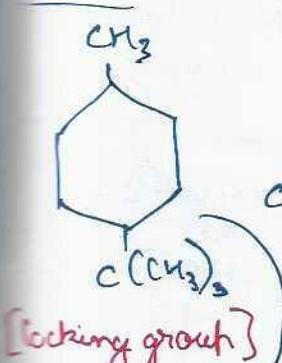
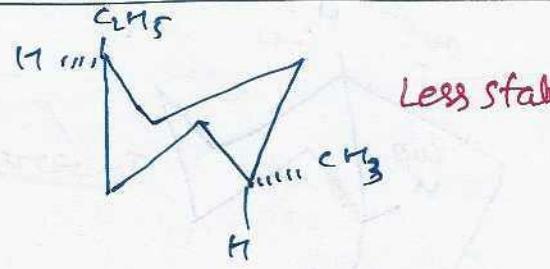
(e,e) or (a,a) → Two isomers

(a,a) or (e,e) → Two isomers

(a,e) or (e,a) → One isomer

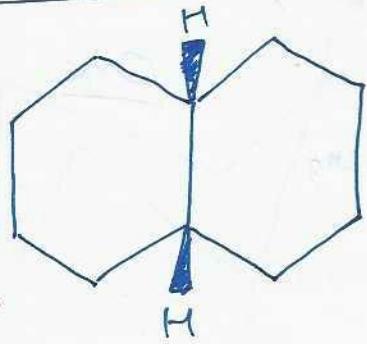


cis  
trans

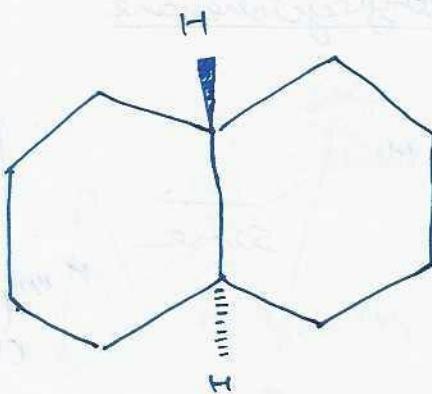


→ If two are  $C(CH_3)_3$ , → They give twisted boat conformation.

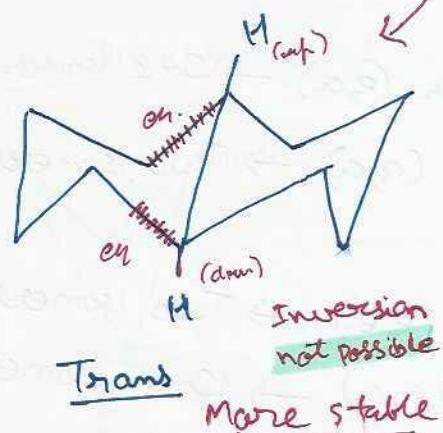
# DECALIN



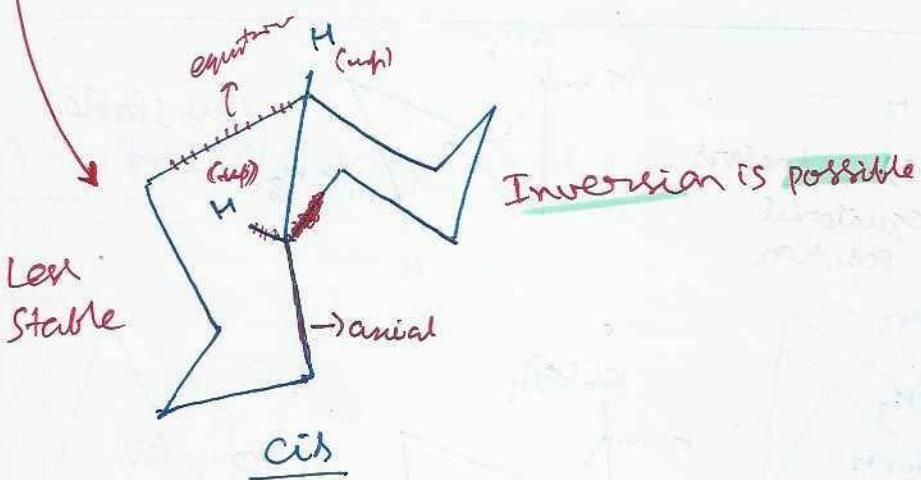
cis decalin



trans decalin



Trans More stable



Inversion is possible

Less Stable

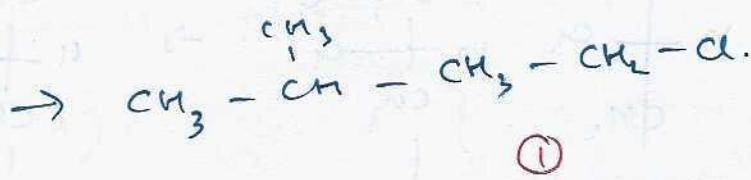
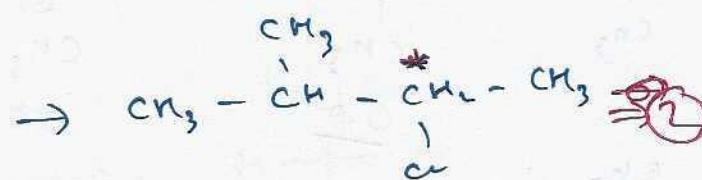
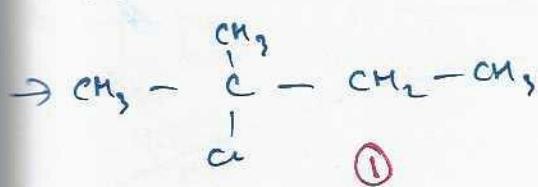
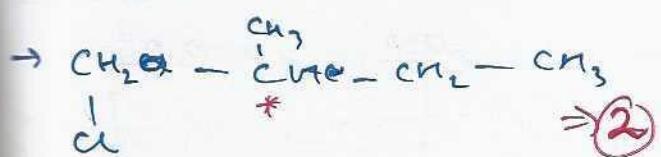
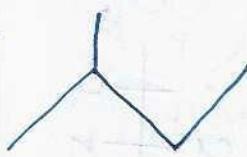
cis

DISQ

Q.

Find No. of no. of mono substituted chlorine.

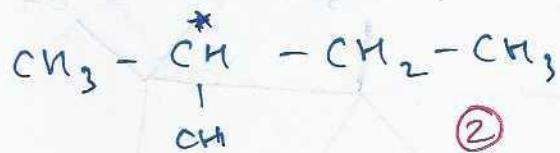
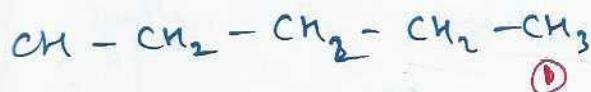
$\Rightarrow$  6 isomers



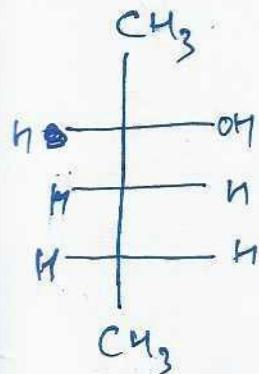
Q.

(CH<sub>3</sub>)

$\Rightarrow$  3 isomers

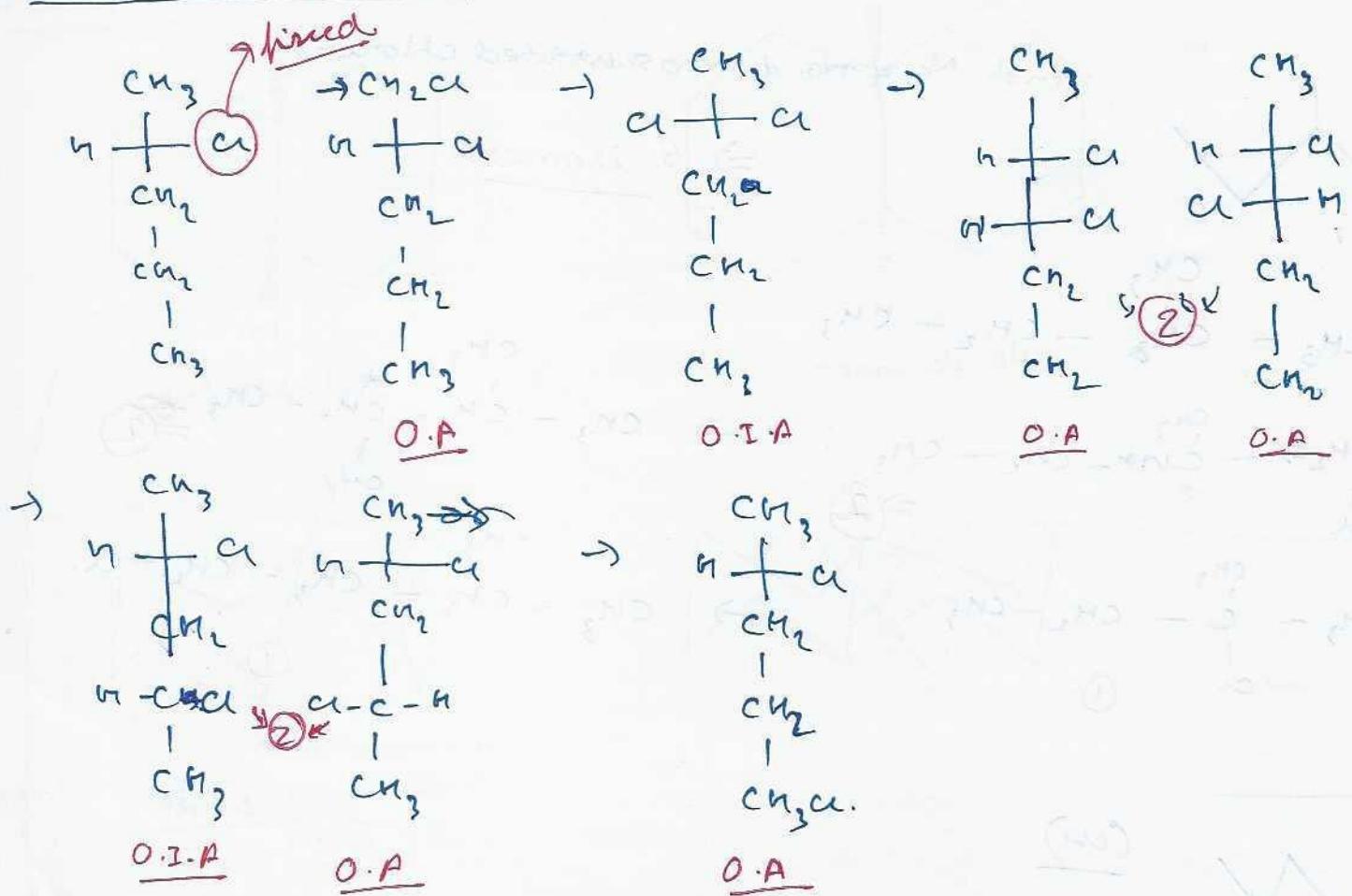


S-2-hydroxypentane

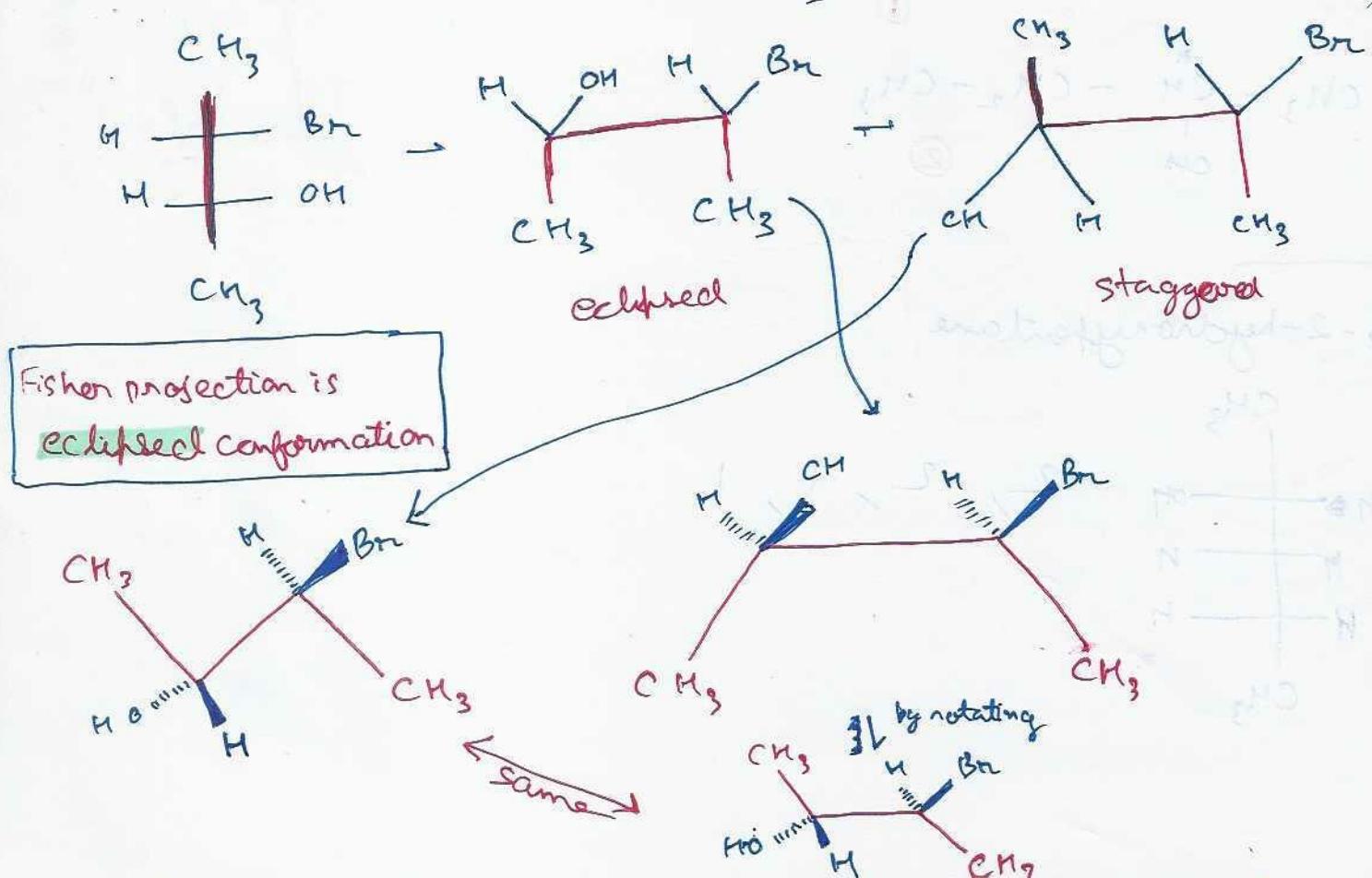


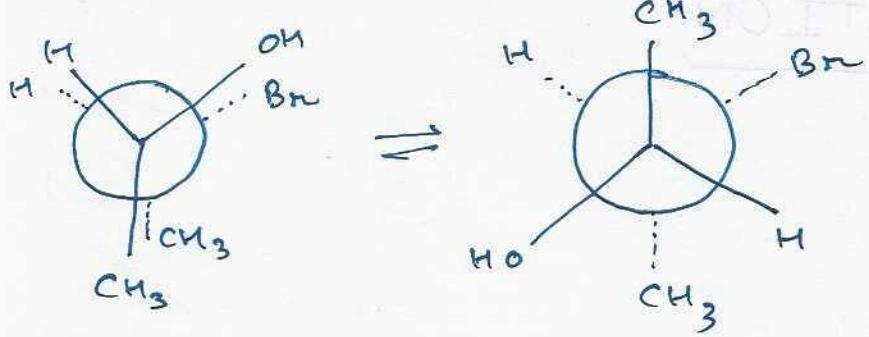
2, 2, 1, 1

## S-2-chloropentane



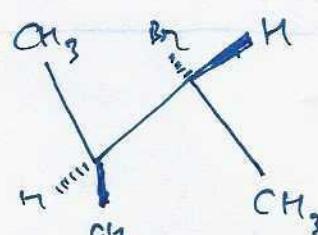
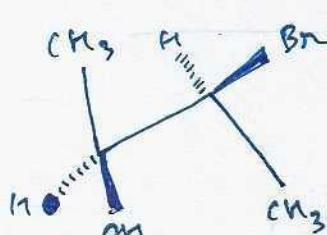
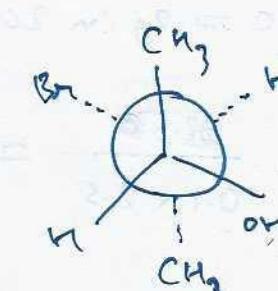
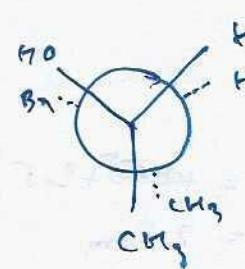
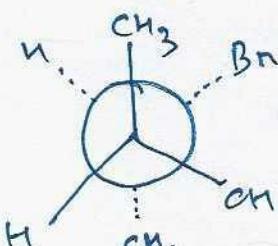
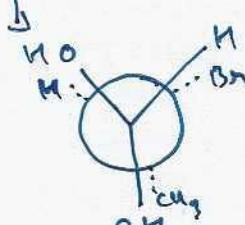
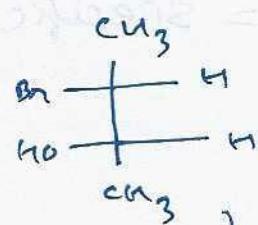
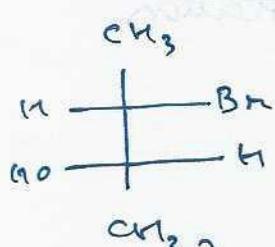
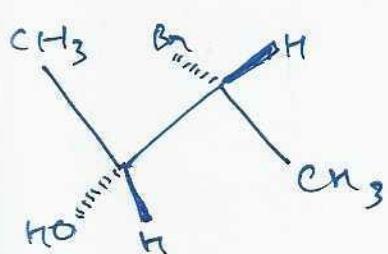
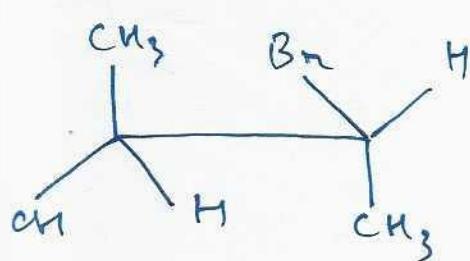
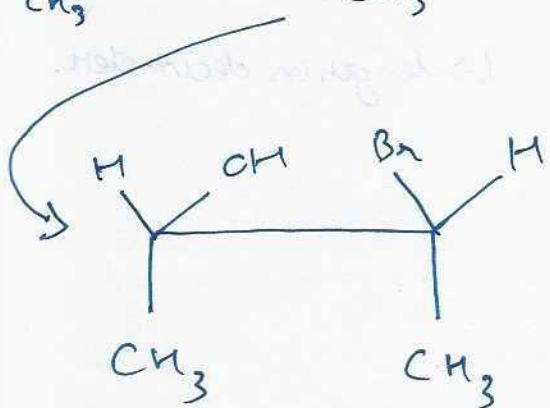
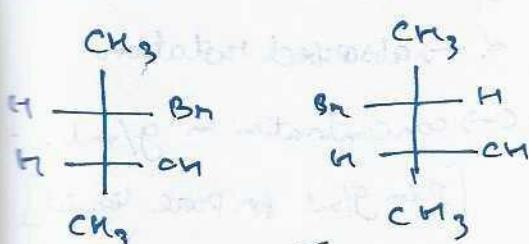
## CONVERSION





eclipsed

staggered



# SPECIFIC ROTATION

For same component

$$[\alpha]_D^{25} = \frac{\alpha}{c \times l}$$

$$[\alpha]_D^{25^\circ C} = \text{specific rotation}$$

D = 589 nm

$\alpha$  → absorbed rotation

c → concentration in g/ml.

[ρ in g/ml for pure liquid]

l → length in decimeter.

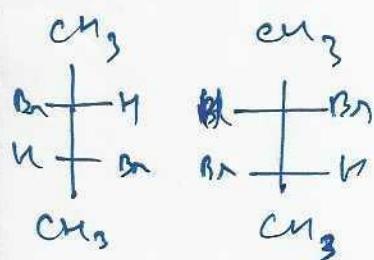
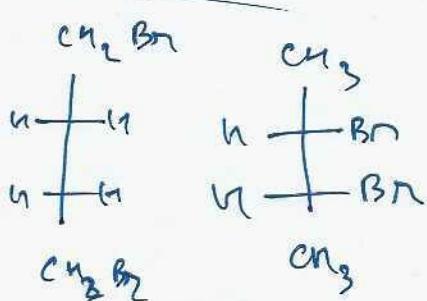
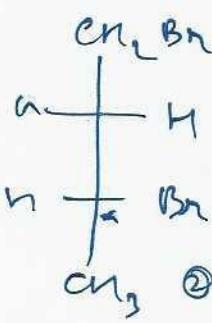
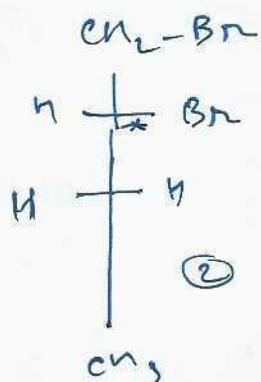
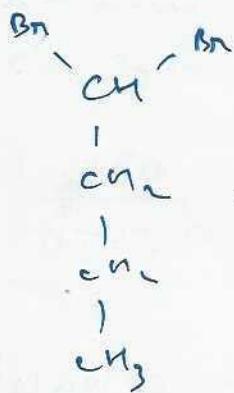
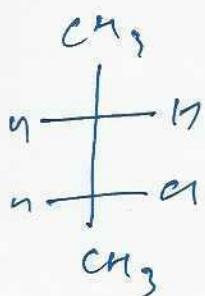
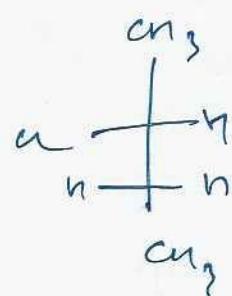
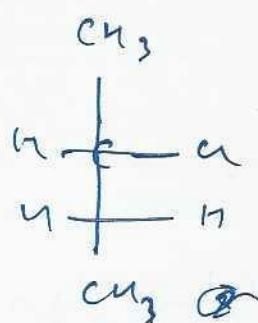
Q.  $\alpha = +25^\circ + 2.5$

$l = 25\text{ cm}$

$c = 2\text{ g in } 20\text{ ml.}$

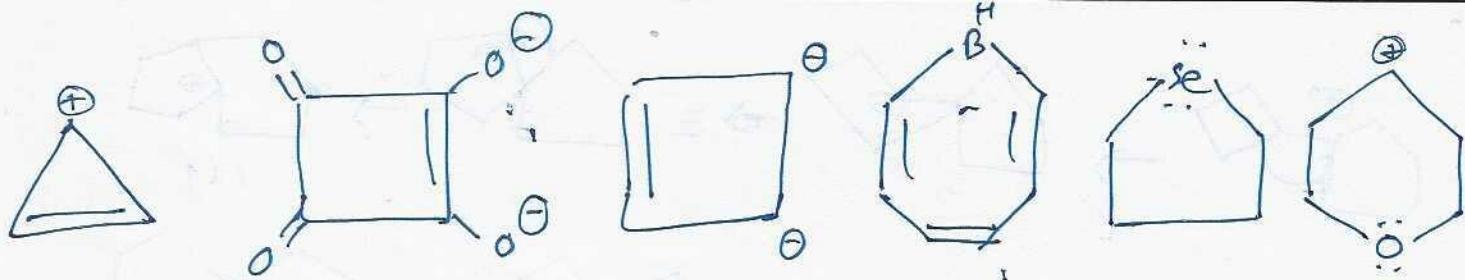
$$\frac{82.50}{0.1 \times 2.5} = +100$$

# ENANTIOMERIC EXCESS

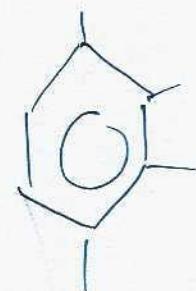


→ 10 isomers

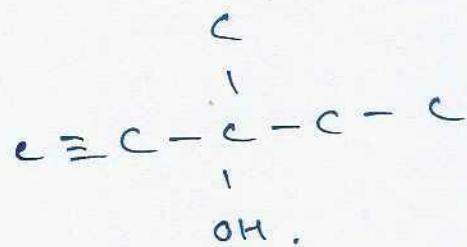
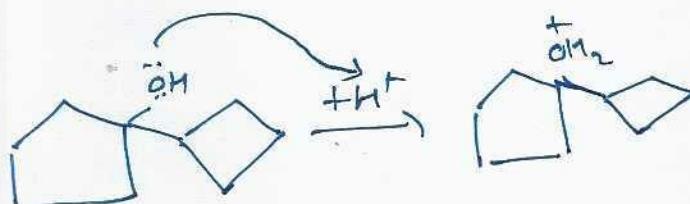
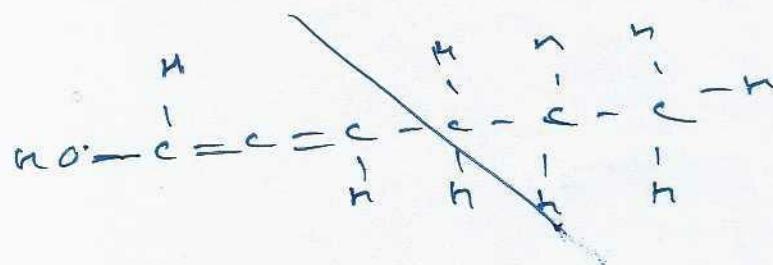
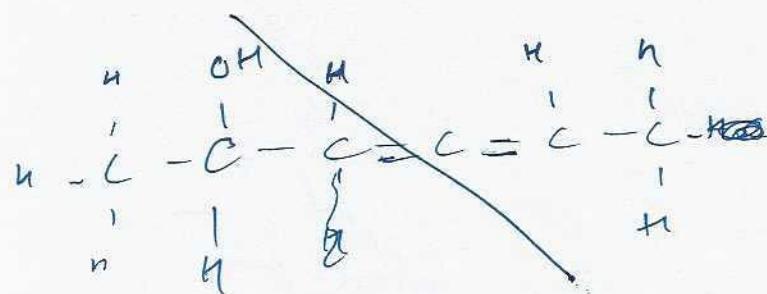
∴ fractions can be separated.



All are aromatic.



3.



v < v\_e

### Conservation of Angular Momentum

$$\{\vec{L}_g\}_{co} = \text{const.}$$

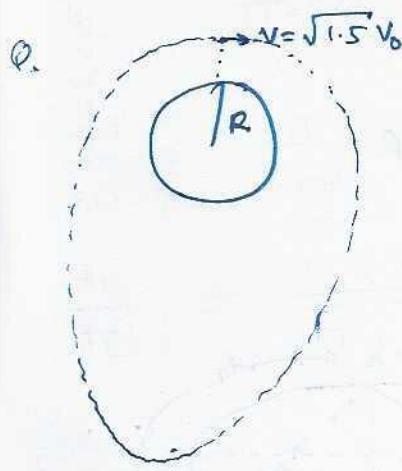
Case 1

$$\text{If } \frac{mv_{\min}^2}{R+h_{\min}} = F_c \Rightarrow F_g \rightarrow \text{required force.}$$

$$F_g = \frac{GMm_s}{R+h_{\min}}$$

- If  $F_g = F_c \Rightarrow$  particle revolve in circular orbit.

- If  $F_g \neq F_c$ 
  - $F_g > F_c \Rightarrow$  hit earth surface with trajectory elliptical.
  - $F_g < F_c$



$$\frac{1}{2} m (1.5 v_0^2) - \frac{GM}{R} = \frac{1}{2} m v_{\min}^2 + \frac{GM}{R+h}$$

$$\sqrt{1.5} v_0 R = v_{\min} (R+h)$$

$$v_{\min} = \frac{\sqrt{1.5} v_0 R}{R+h}$$

$$\frac{1}{2} (1.5 v_0^2) - \frac{GM}{R} = \frac{1}{2} \frac{1.5 v_0^2 R^2}{(R+h)^2} - \frac{GM}{R+h}$$

$$\Rightarrow \frac{1}{2} (1.5 v_0^2) - \frac{GM}{R} = \frac{1}{2} \frac{1.5 v_0^2 R^2}{R^2 + h^2 + 2Rh} - \frac{GM}{R+h}$$

$$\frac{3}{2} \frac{GM}{R} - \frac{GM}{R} = \frac{v_{\min}^2}{R^2} - \frac{GM}{R+h}$$

$$GM \left[ \frac{1}{R+h} - \frac{1}{4R} \right] = \frac{v_{\min}^2}{R^2} = \frac{1.5 v_0^2 R^2}{2R(R+h)^2} = \frac{1.5 GM R}{4(R+h)^2}$$

$$\frac{3R-h}{(R+h)(2R)} = \frac{3R}{a(R+h)}$$

$$3R^2 = (3R-h)(R+h)$$

$$h = 2R$$

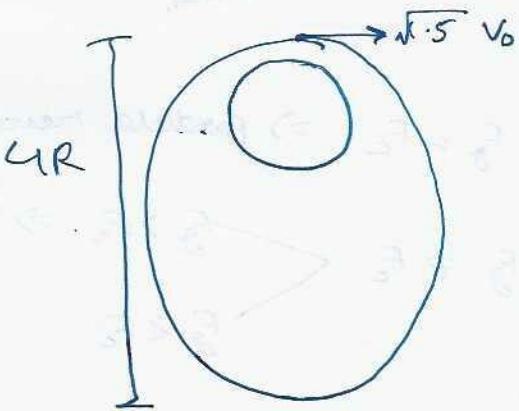
$$E_{\text{ext}} = -\frac{GMm}{2a}$$

$$\frac{1}{2} \gamma h \left( \frac{3}{2} \frac{GM}{R} - \frac{GMm}{R} \right) = -\frac{GMm}{2a}$$

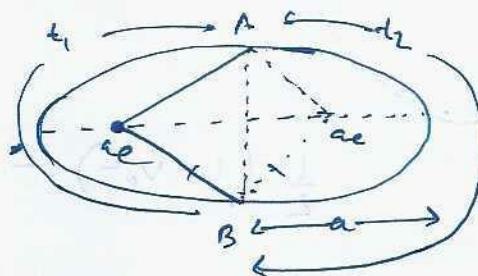
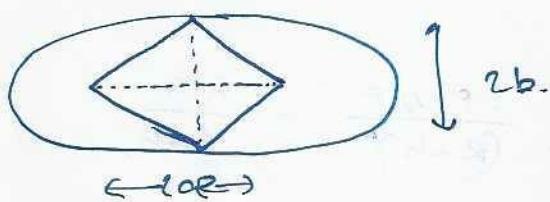
$$-\frac{1}{2} \gamma h = -\frac{1}{2} a$$

$$\Rightarrow 2a = 4R$$

$$R_p = \frac{v^2}{g} = \frac{3}{2} \frac{GM}{Rg} = 1.5R$$



$$\text{Q. Find } \frac{t_1}{t_2} = \frac{T-t_2}{T}$$



$$\text{Or } \left( \frac{4\pi^2}{GM} \right) a^3$$

$$2ae \times b \quad 2ab^2$$

$$\frac{1+2abe}{1}, \quad 1+2abe.$$

$$\frac{dA}{dt} = \frac{L}{2m}$$

$$\Rightarrow \frac{\frac{\pi ab}{2} + eab}{t_2} = \frac{mv\sqrt{\frac{GMb^2}{a}}}{2\pi}$$

$$\frac{\left(\frac{\pi}{2} + e\right)a}{t_2} = \frac{1}{2} \sqrt{\frac{GM}{a}}$$

$$\Rightarrow \frac{\left(\frac{\pi}{2} + e\right)a^2}{t_2^2} = \frac{1}{4} \frac{GM}{a}$$

$$t_2^2 = \frac{4a^3}{GM} \left(\frac{\pi}{2} + e\right)^2$$

$$= \frac{T^2}{\pi^2} \left(\frac{\pi}{2} + e\right)^2$$

$$t_2 = \frac{T}{\pi} \left(\frac{\pi}{2} + e\right)$$

$$\frac{T}{t_2} = \frac{2\pi}{\pi + 2e}$$

$$\frac{t_1}{t_2} = \frac{2\pi}{\pi + 2e} - 1$$

$$\frac{t_1}{t_2} = \frac{\pi - 2e}{\pi + 2e}$$