



# General Organic Chemistry

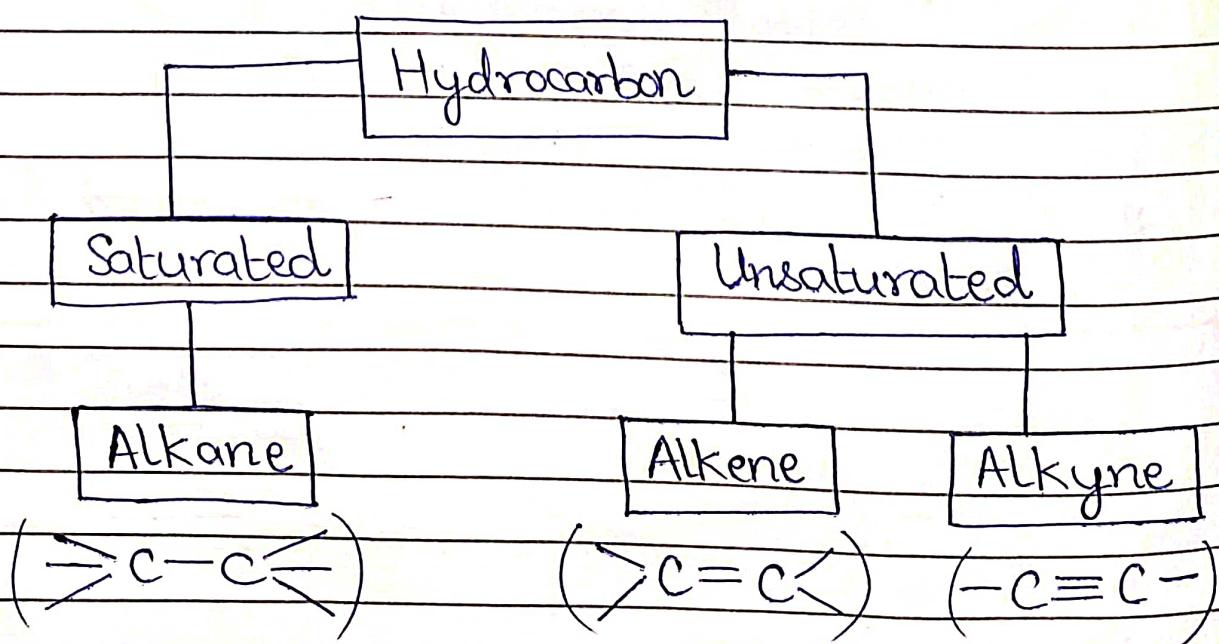
Organic Comps - Hydrocarbons and their derivatives are called organic comp's.

Eg:  $\text{CH}_4$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{CH}_3$ , ...

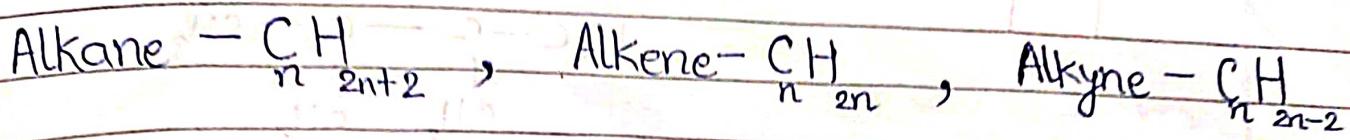


$\text{CCl}_4$  is organic

Carbides, carbonates & bicarbonates are inorganic.

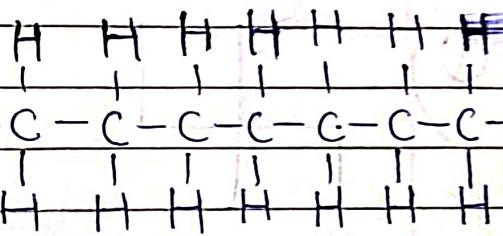


General Formula:



Representation

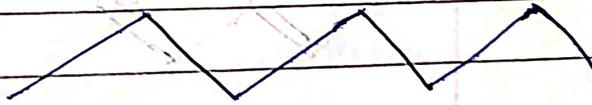
1) Molecular formula. Eg -  $\text{C}_7\text{H}_{16}$



2) Complete Structural. Eg -  $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ | \quad | \quad | \quad | \quad | \quad | \quad | \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ | \quad | \quad | \quad | \quad | \quad | \quad | \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$

3) Condensed Structural. Eg -  $\begin{array}{ccccccccc} \text{CH} & \text{CH} & \text{CH} & \text{CH} & \text{CH} & \text{CH} & \text{CH} \\ 3 & 2 & 2 & 2 & 2 & 2 & 3 \end{array}$

4) Bond Line Notation. Eg -



$$\boxed{\left( \begin{matrix} \# \text{ invisible} \\ \text{H atoms} \end{matrix} \right) = \left( \begin{matrix} \text{Valency} \\ \text{of Atom} \end{matrix} \right) - \left( \begin{matrix} \text{No. of} \\ \text{Visible bonds} \end{matrix} \right)}$$

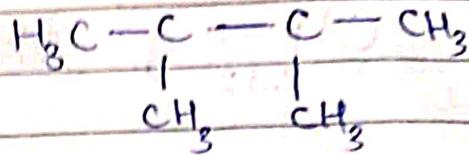
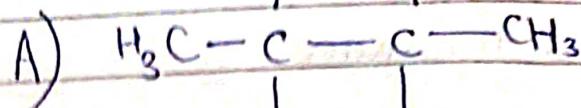
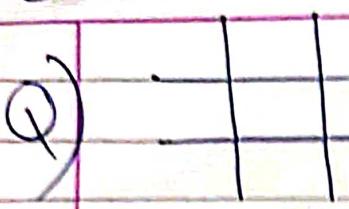
66

## Bond Line

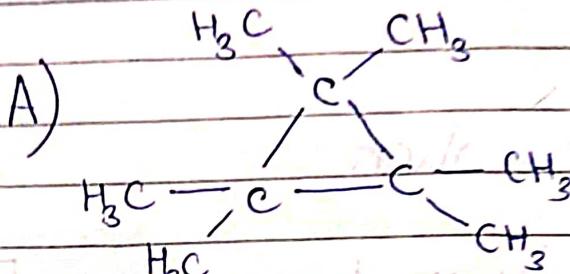
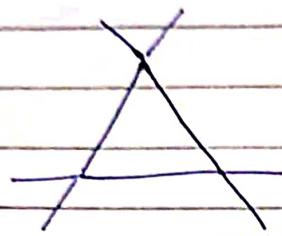
## Condensed

DATE \_\_\_\_\_  
PAGE \_\_\_\_\_

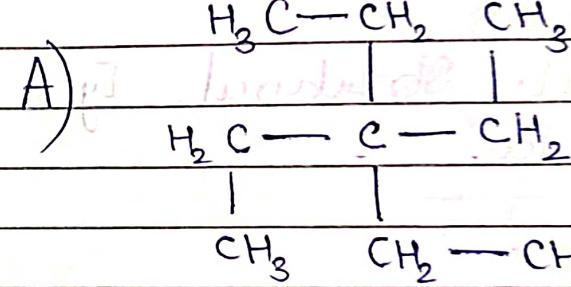
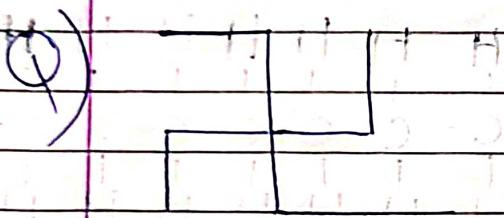
Q)



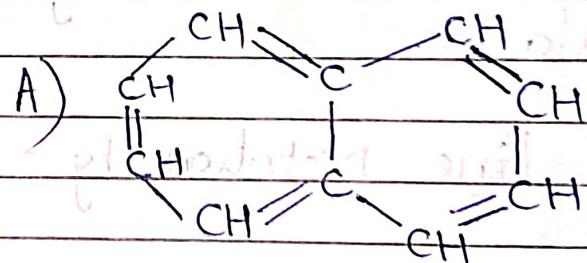
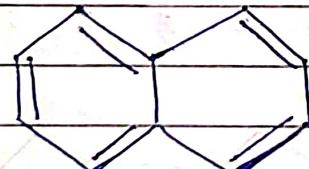
Q)



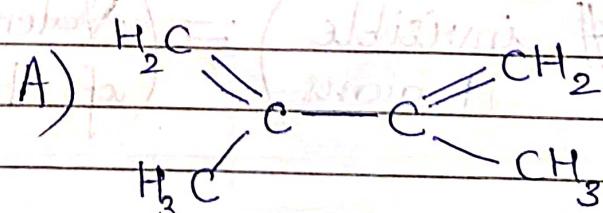
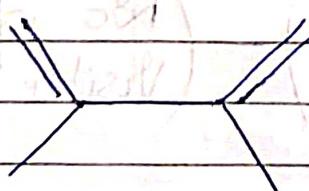
Q)



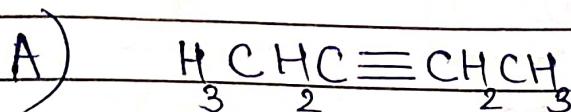
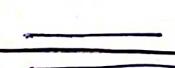
Q)



Q)



Q)

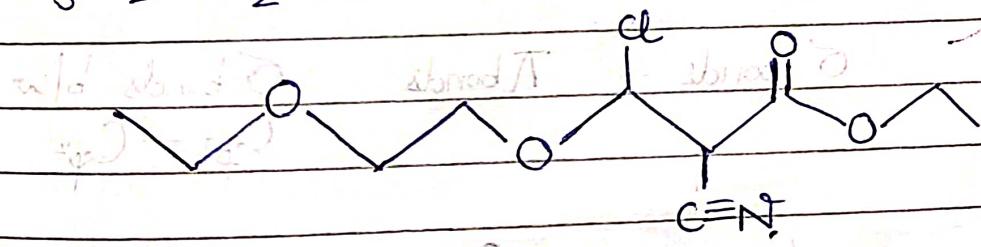
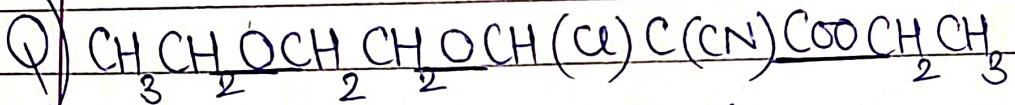
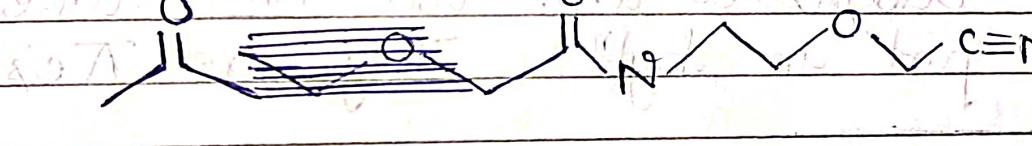
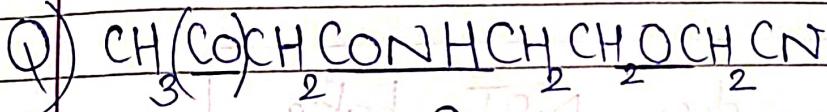
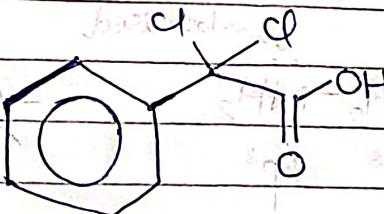
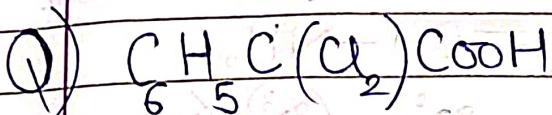
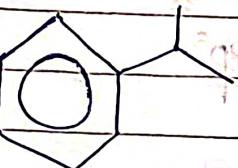
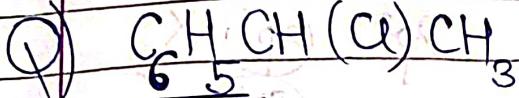
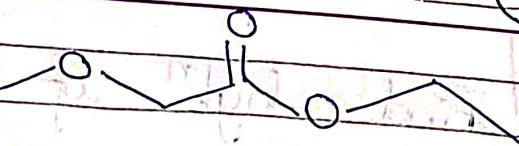
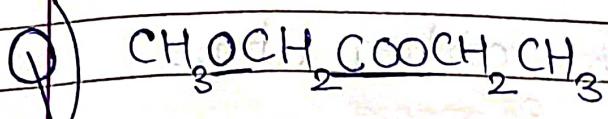


# Condensed

# Bond Line

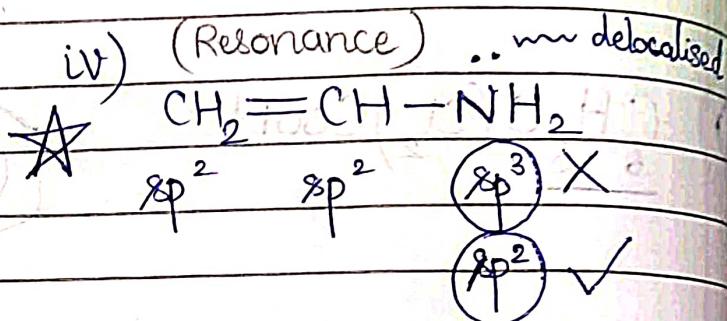
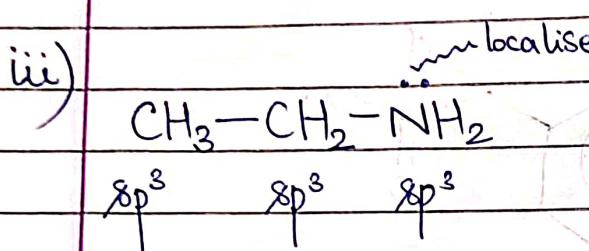
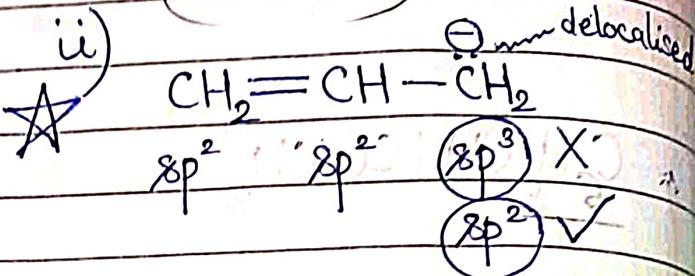
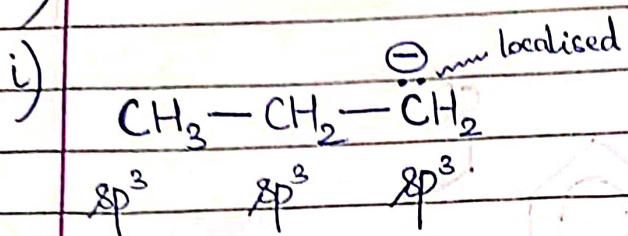
DATE  
PAGE

61



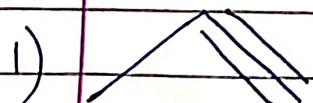
★ () → Out of carbon chain

Q) Find hyb<sup>n</sup> of each carbon atom:  
 (Resonance)



\* Delocalised l.p. does NOT take part in hyb<sup>n</sup>. They are  $\pi$  electrons.

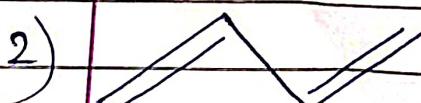
Q) Structure       $\sigma$  bonds       $\pi$  bonds       $\sigma$  bonds b/w  
 $\text{C}_{\text{sp}^2}-\text{C}_{\text{sp}^2}$



6

2

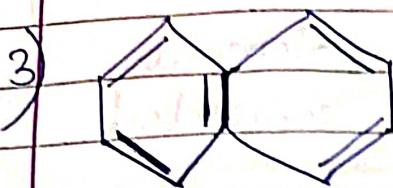
0



9

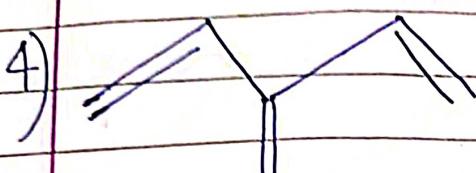
2

3



19

5



3

5

### Degree of Carbon & Hydrogen

Primary C ( $1^\circ$ ): C connected to 0 or 1 other C atom.

Secondary C ( $2^\circ$ ): C connected to 2 other C atoms

Tertiary C ( $3^\circ$ ): C connected to 3 other C atoms

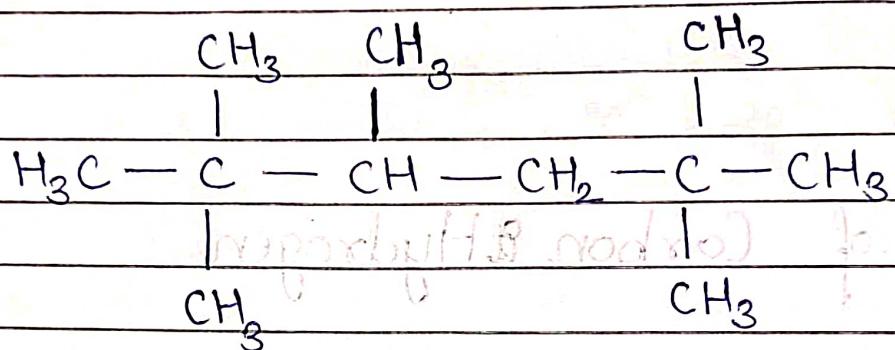
Quaternary C ( $4^\circ$ ): C connected to 4 other C atoms

10

Degree of H: Degree of H atom is degree atom connected to that H atom.

Eg: In  $\text{CH}_4$ ,  $\exists$  4  $1^\circ$  H atoms.

(Q)

 $1^\circ$ 

: 7

 $2^\circ$ 

: 1

 $3^\circ$ 

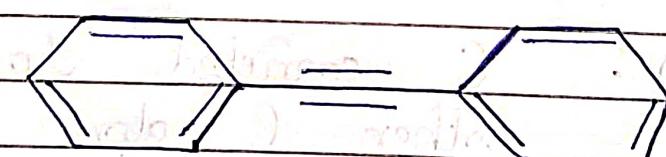
: 1

 $4^\circ$ 

: 2

 $1^\circ$  : 21 $2^\circ$  : 2 $3^\circ$  : 1

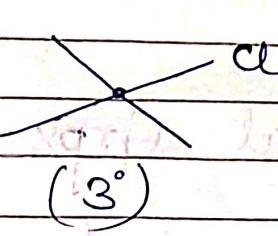
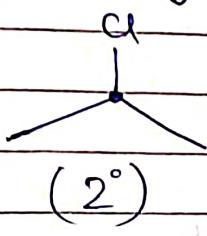
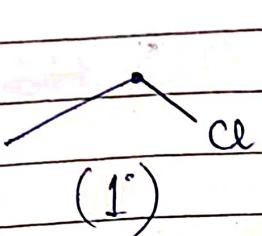
(Q)

 $C -$  $1^\circ$  : 1 $2^\circ$  : 11 $3^\circ$  : 3 $4^\circ$  : 0 $H -$  $1^\circ$  : 3 $2^\circ$  : 9 $3^\circ$  : 0

Degree of Alkyl Halide — R-X

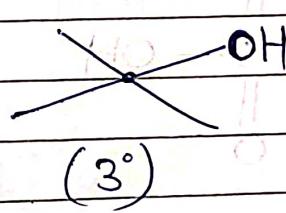
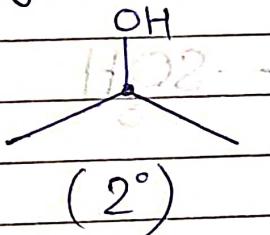
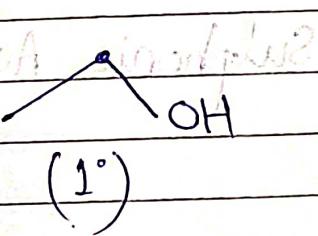
Degree of Alkyl Halide is degree of C bonded to halogen atom.

Eg:

Degree of Alcohol — R-OH

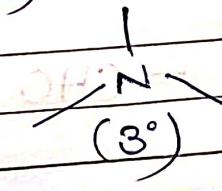
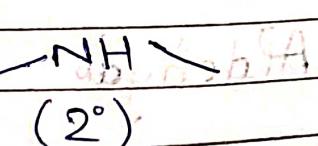
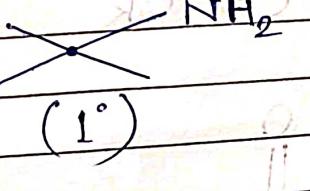
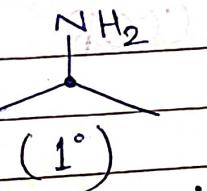
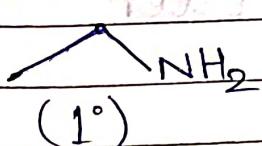
Degree of Alcohol (His) is degree of C bonded to hydroxyl group.

Eg:

Degree of Amines — R-NH<sub>2</sub>

Degree of Amines is no. of C atoms bonded to N atom of amine.

Eg:

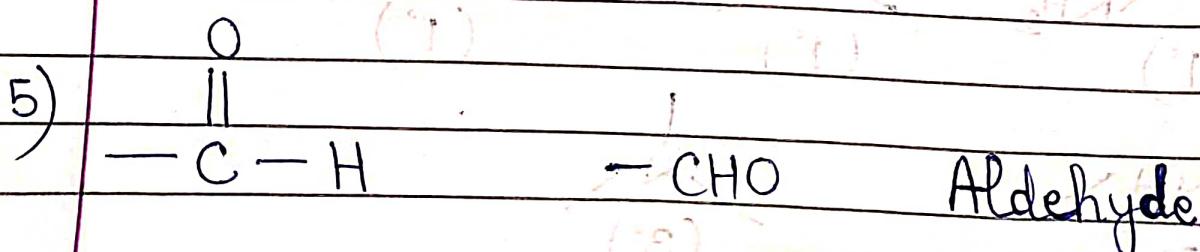
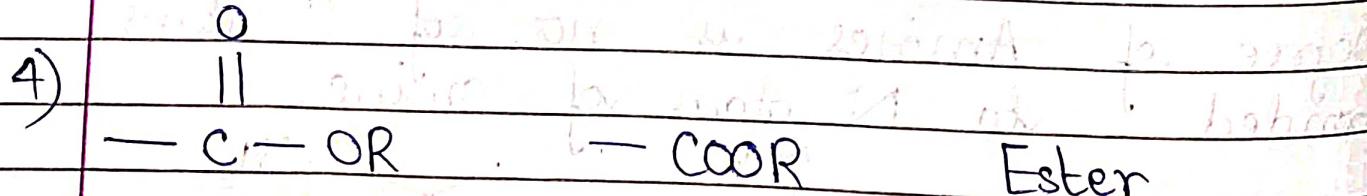
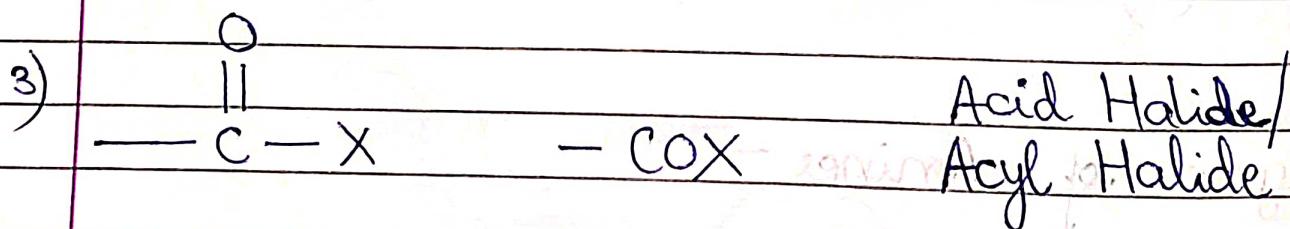
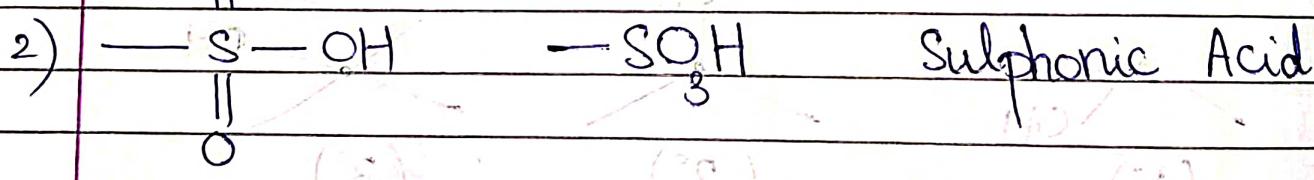
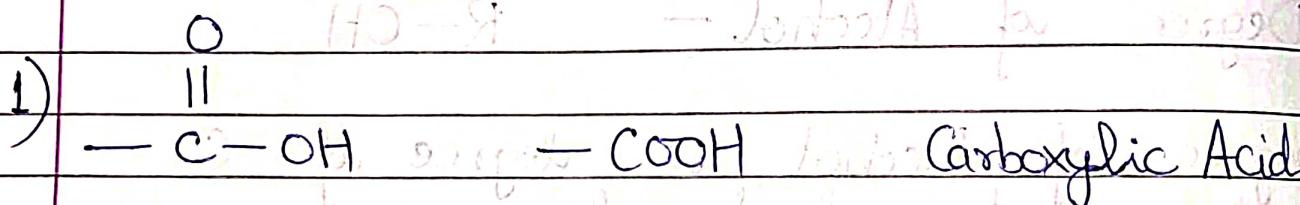


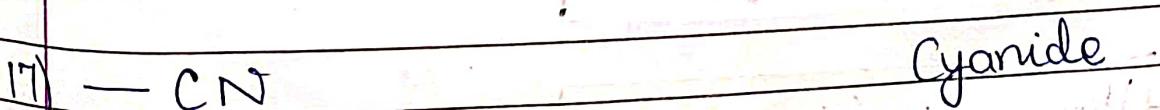
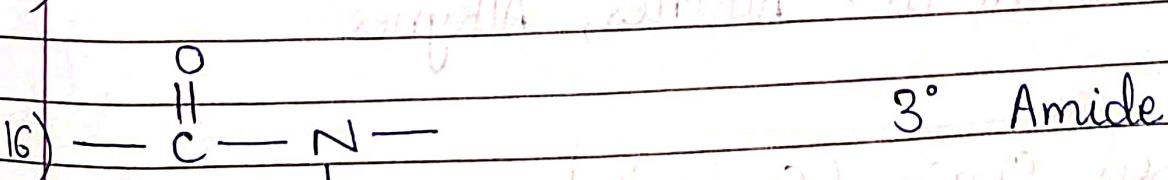
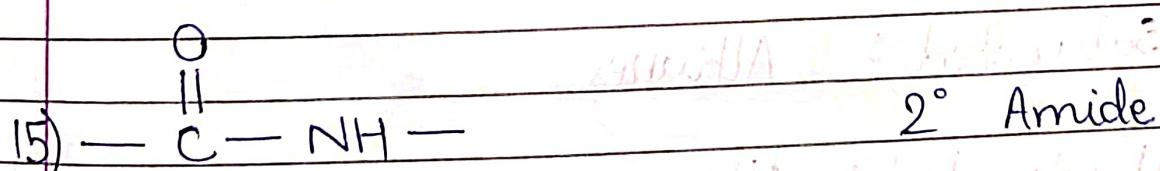
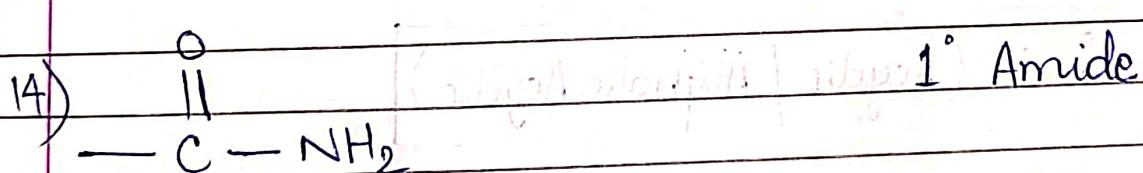
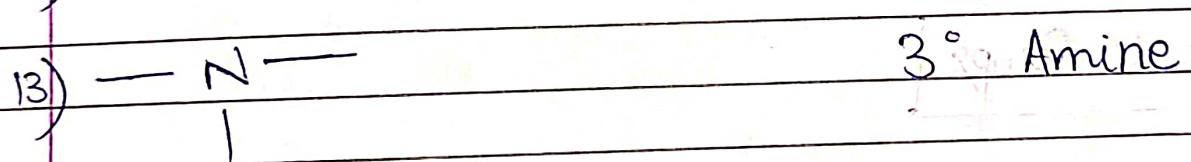
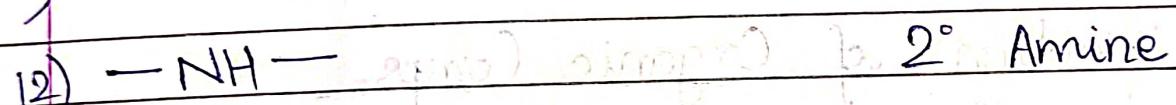
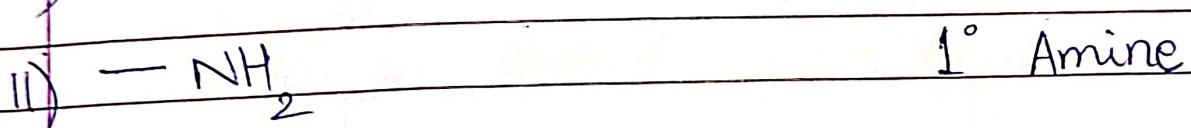
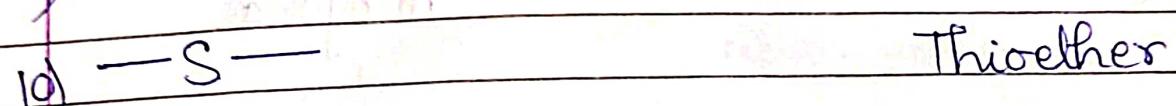
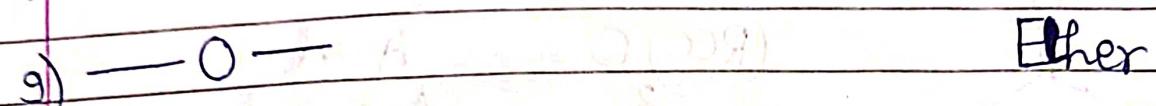
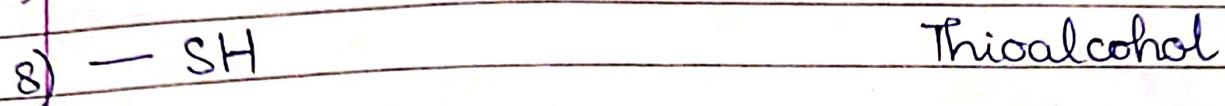
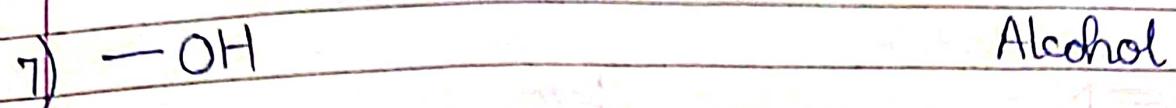
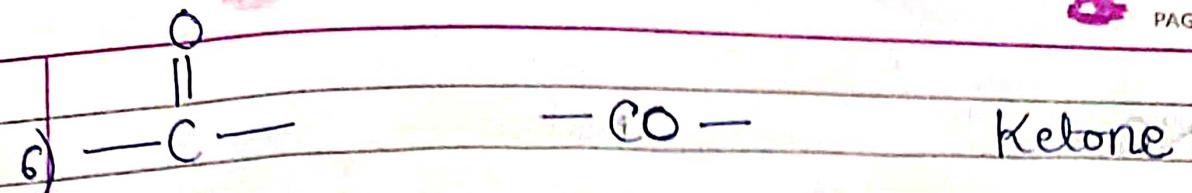


$1^\circ$ ,  $2^\circ$ ,  $3^\circ$  amines are Seperate  
'fxnal' grps.

### Fxnal Grps

Grps which decide a molecule's physical or chem. prop's.

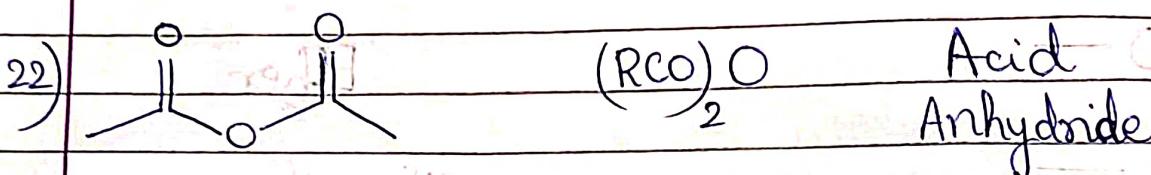




19)  $-NO_2$  Nitro

20)  $-X$  Halide

21)  $-N=N-$  Azo



## Classification of Organic Comps.

### Organic Comps.

Open Chain (Acyclic / Aliphatic Acyclic)

Saturated: Alkanes

Unsaturated: Alkenes, Alkynes

Closed Chain (Cyclic)

Homocyclic (Carbocyclic)



+ Aliphatic Cyclic/ Alicyclic

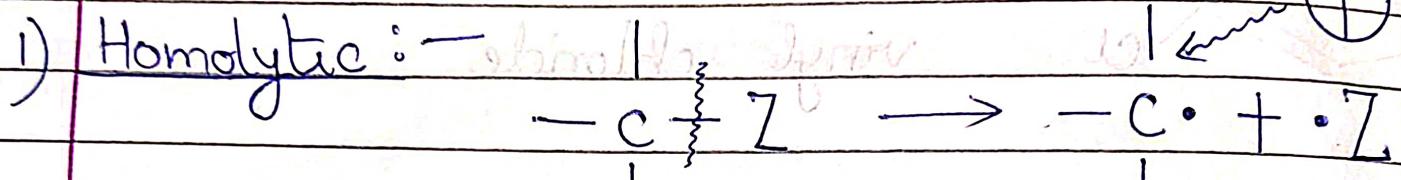
+ Aromatic

Heterocyclic

+ Aliphatic Cyclic/ Alicyclic

+ Aromatic

## Bond Fission

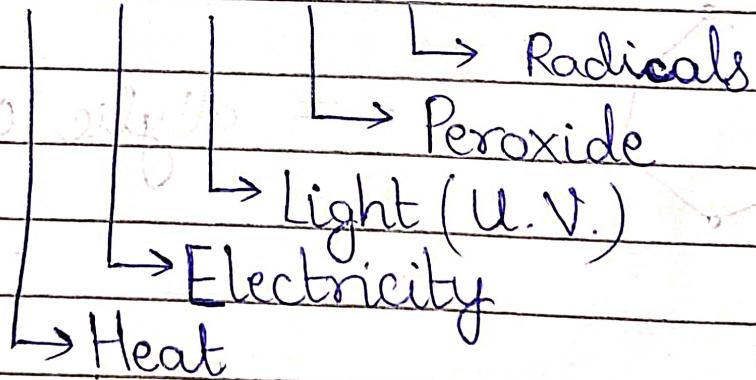


$\text{sp}^2$

free  
Radicals

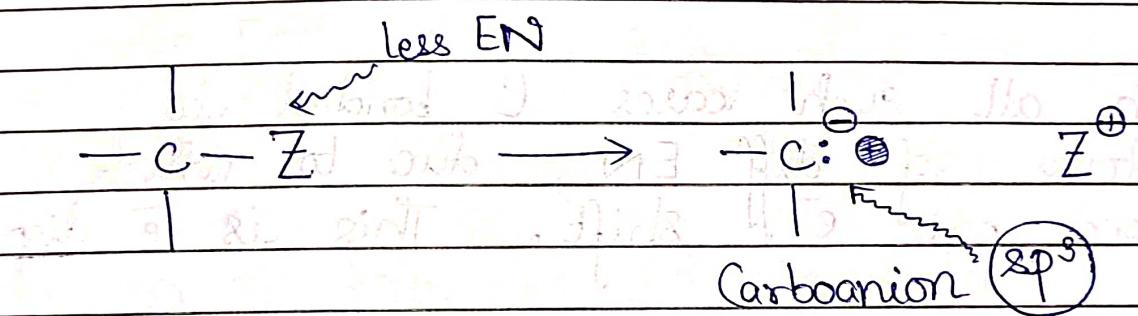
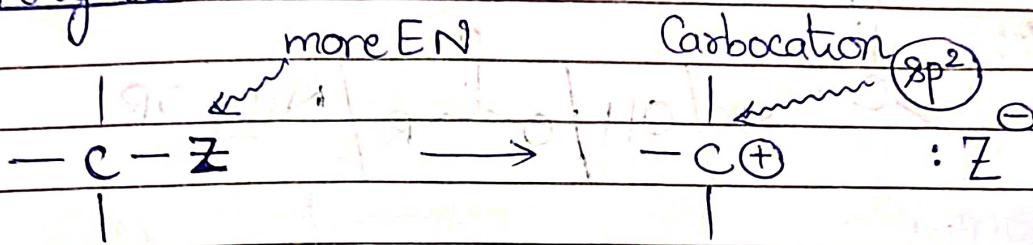
Cond's

H E L P R



The fission in which there is equal distribution of  $\bar{e}s$  during chem. rxn is known as homolytic bond fission

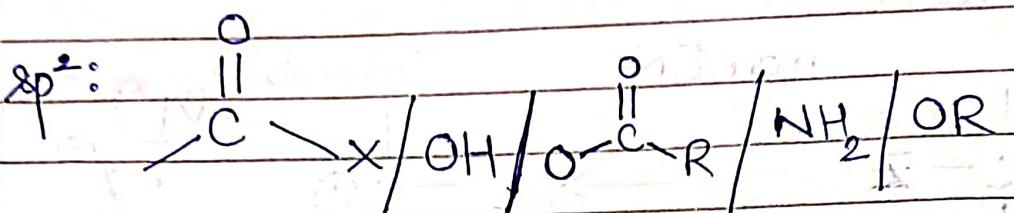
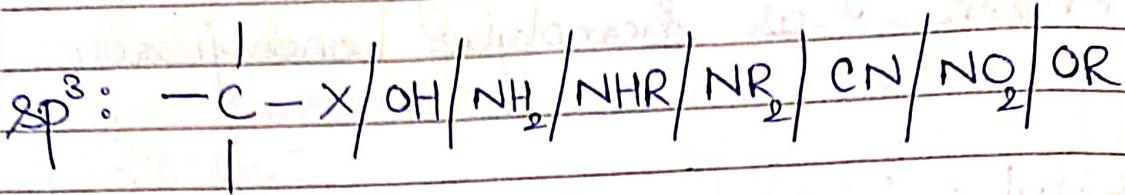
## 2) Heterolytic :-



The fission in which there is unequal distribution of  $\bar{e}s$  during chem. rxn is known as heterolytic bond fission.

It is also called ionic fission as ions are formed.

## Electronic Disp. Effects

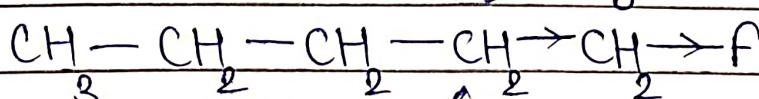
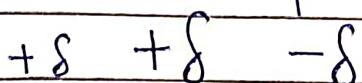
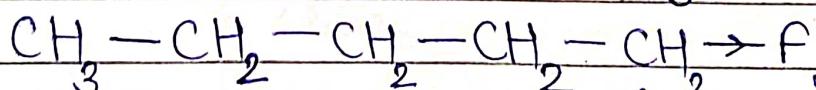
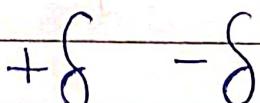


In all such cases — C bonded to atoms of diff. EN, due to which bond pair  $e^-$  shift. This is  $\bar{e}$  disp.

- Inductive Effect      — Resonance (Mesomeric Effect)
- Hyperconjugation      — Electromeric Effect

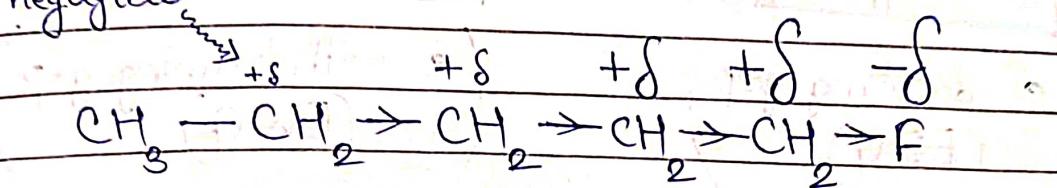
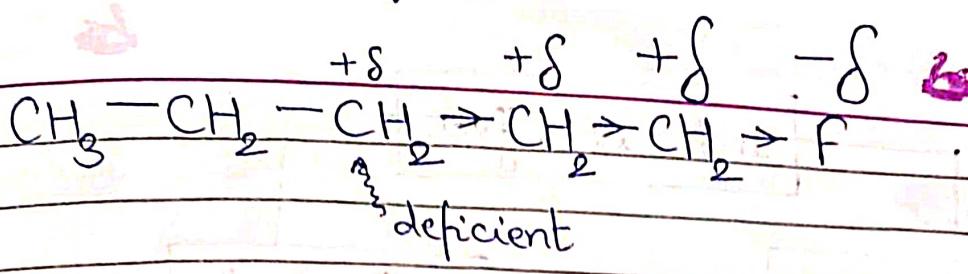


### Inductive Effect



deficient





Polarisation of bonds under influence of more EN atom / group of atoms.

OR

Permanent disp. of  $\sigma$  e<sup>-</sup>s along the carbon chain towards more EN atom / group of atoms.

- i) It is a permanent effect.
- ii) It is also called transmission effect.
- iii) Reduces ~~dist.~~ with dist. Vanishes after 4th C atom
- iv) It causes polarisation of bonds.
- v) Operates thru  $\sigma$  e<sup>-</sup>s

99

DATE  
PAGE

## Inductive Effect

+ I effect

( $e^-$  donating grp  
(EDG))

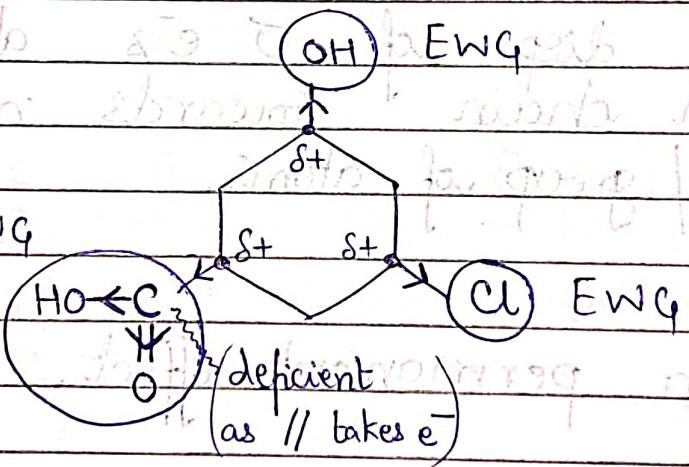
- I effect

( $e^-$  withdrawing grp  
(EWG))

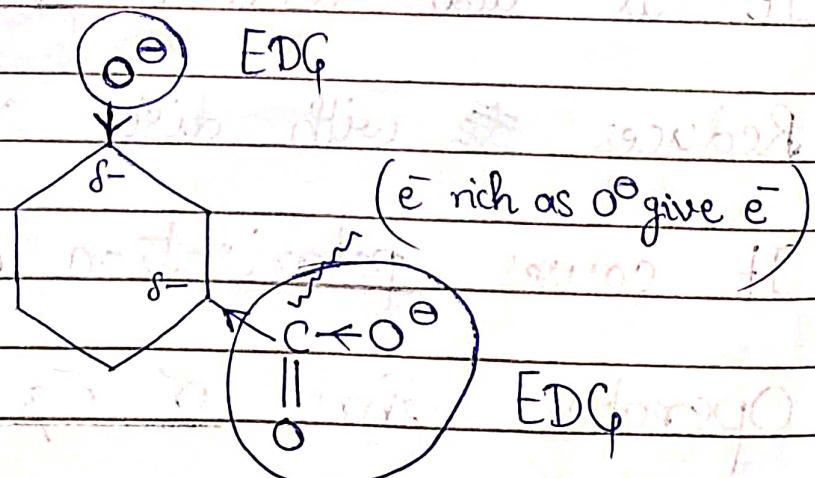
for finding EDG or EWG, we take  
H atom form reference.

$$EN(EWG) > EN(H) > EN(EDG)$$

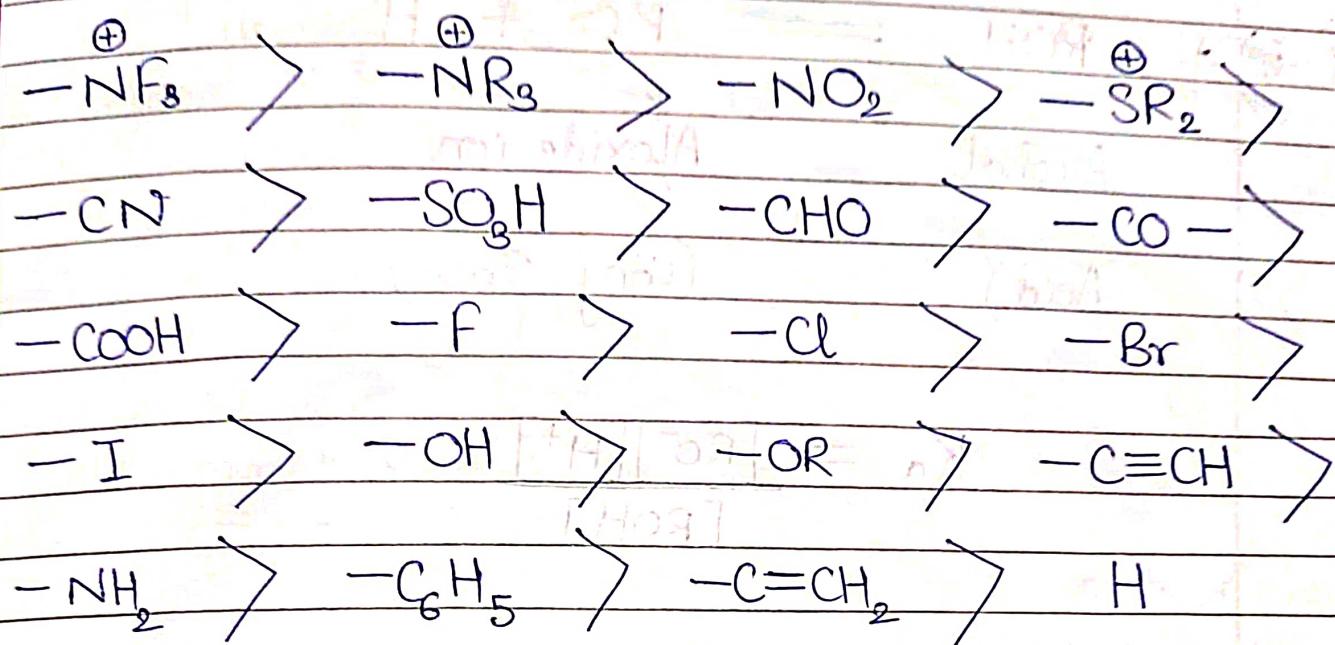
Eg:



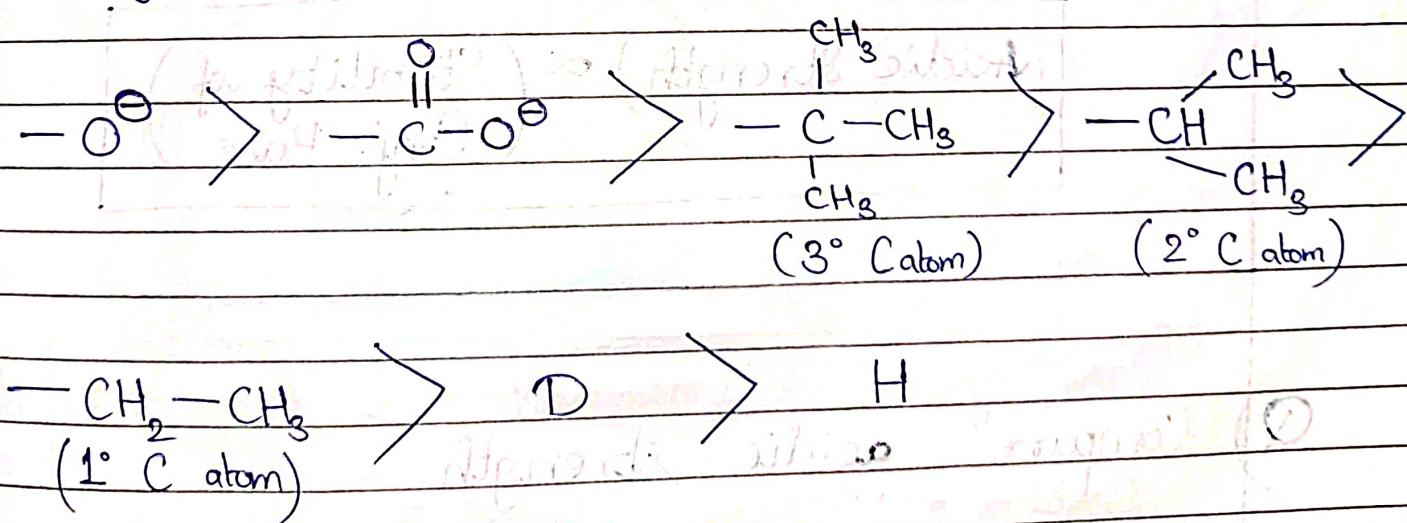
Eg:



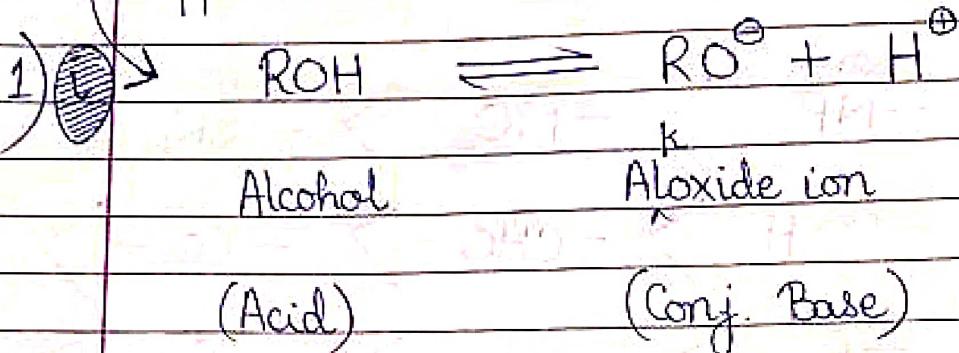
Strength of  $-I$  effect :-



Strength of  $+I$  effect :-



## Application :-

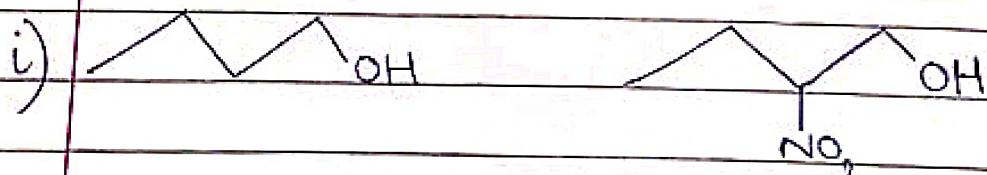


$$K_a = \frac{[R\bar{O}][H^+]}{[ROH]}$$

(Strong  $\text{Acid}$ )  $\rightleftharpoons$  (Ka more)  $\rightleftharpoons$  (Rx<sup>n</sup> more frwd)  $\rightleftharpoons$  (Conj. base more stable)

(Acidic Strength)  $\propto$  (Stability of  
Conj. Base)

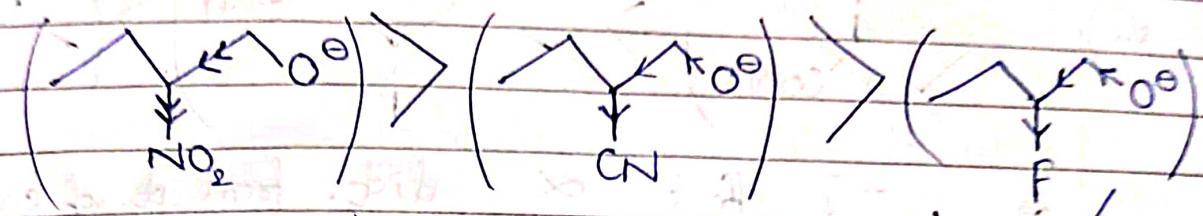
Q) Compare acidic strength.



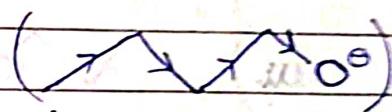
A)

Make  $\text{conj. base}$ . Ignore effect due grp. on which we are finding effect. In this case ignore  $+I$  due to  $\text{O}^\ominus$ .

Stability:



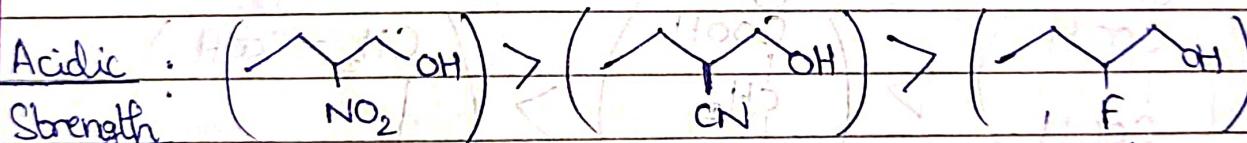
(more  $\ominus$  dispersed  
 $\Rightarrow$  more stable)



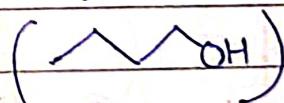
(Alkyl grp shows  
 $+I$  effect)

We have applied effect ON  $\text{O}^\ominus$

Acidic



Strength

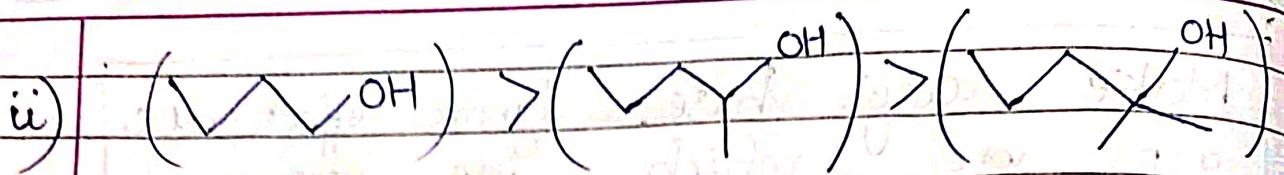


No need to make  $\text{conj. base}$  every time.

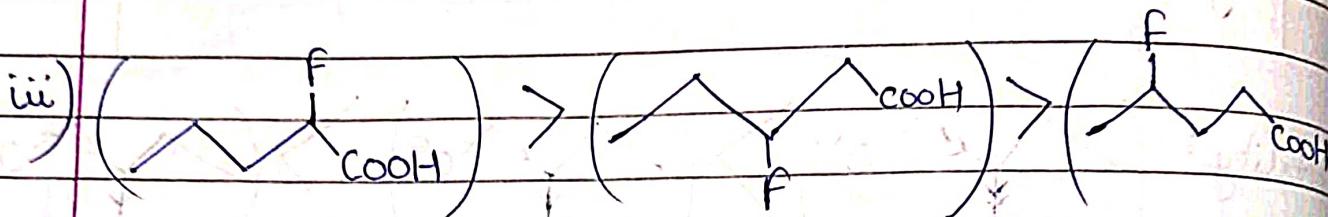
(Lesser the  $\bar{\epsilon}$  density on  $-\text{OH}$ ,  $-\text{COOH}$ , ... )  $\rightarrow$  (More acidic strength)

due to  $-I$  effect

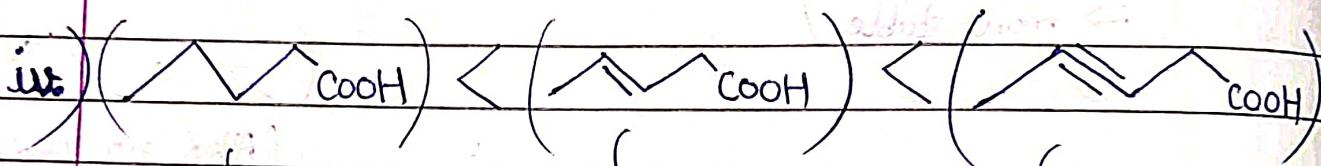
96

DATE \_\_\_\_\_  
PAGE \_\_\_\_\_

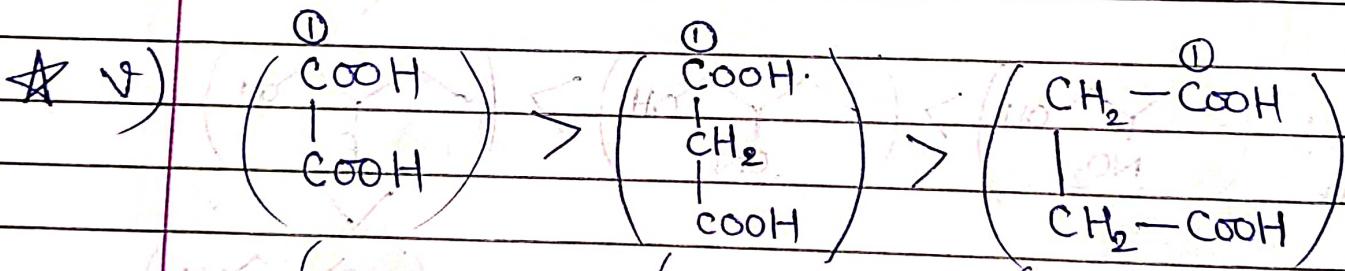
as + I effect of  $3^\circ > 2^\circ > 1^\circ$



as - I effect  $\propto$  dist. from pt. of calc.



as + I effect  $\downarrow$  - I effect  $\downarrow$  - I effect  $\downarrow$   
 on - COOH on - COOH on - COOH



as ~~effect~~ direct on  
 ① COOH

only 1 C  
 show + I  
 on COOH

2 C atoms

show + I  
 on COOH

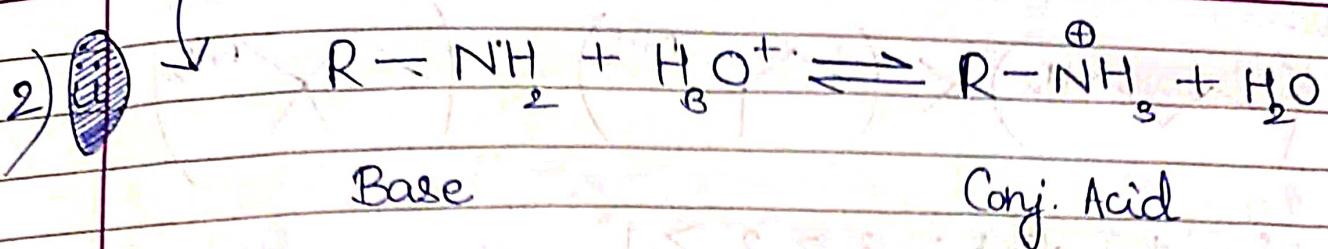
1 C b/w

① COOH st. COOH

b/w ① COOH  
 st. COOH

★ In such Q, pick one grp. &  
 find effect of others on that grp.

## Basic Strength:



$$K_b = \frac{[R-NH_3^+]}{[R-NH_2][H_3O^+]}$$

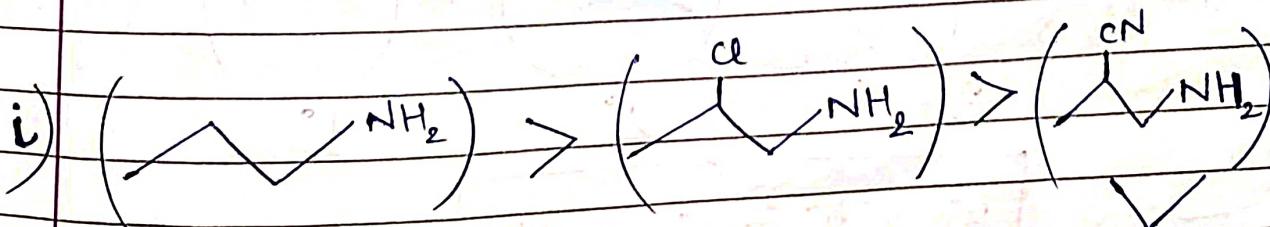
(Strong Base)  $\Leftrightarrow$  ( $K_b$  more)  $\Leftrightarrow$  (Rx<sup>n</sup> more fwd)  $\Leftrightarrow$  (Conj. Acid more Stable)

$$(\text{Basic Strength}) \propto (\text{Stability of Conj. Acid})$$

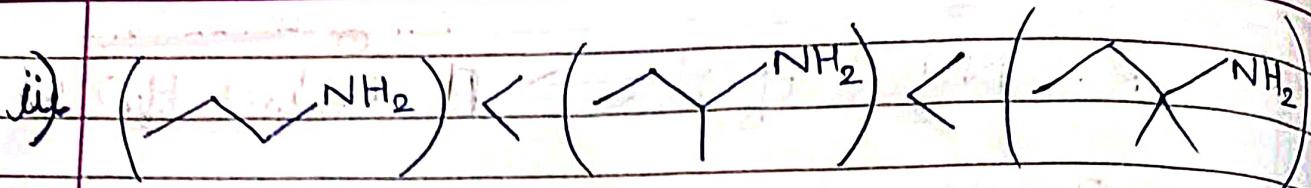
①) Compare basic strength.

★ No need to make conj. acid every time.

(More the  $\bar{e}$  density)  $\Rightarrow$  (More basic & strength)  
on  $- \ddot{\text{N}}\text{H}_2$

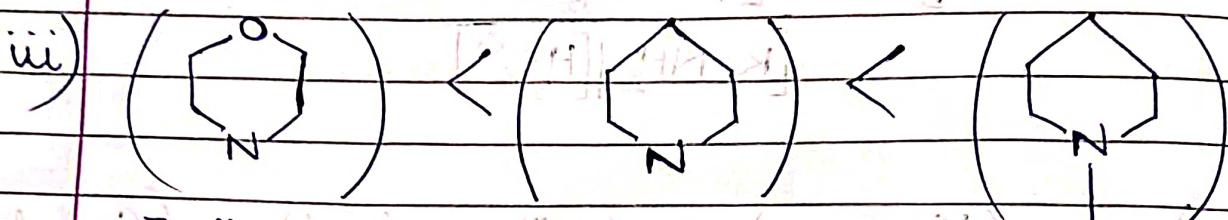


as -I effect:  $\text{Cl} < \text{CN} < \text{NO}_2$

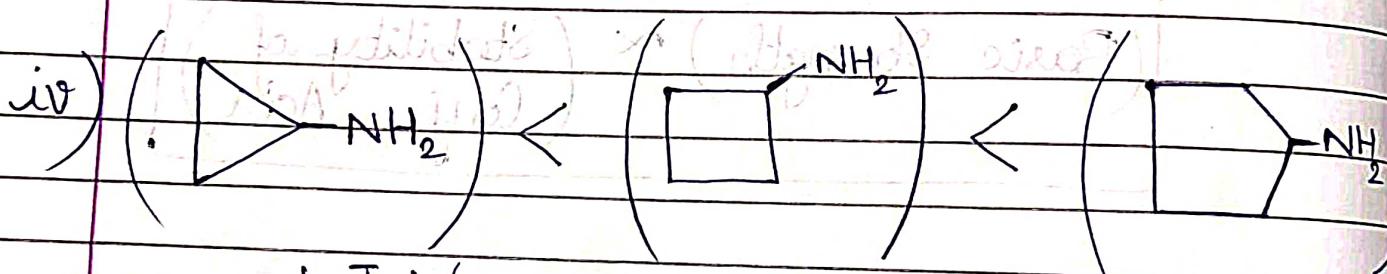


as + I effect:  $3^\circ > 2^\circ > 1^\circ$

$$K_b = [E_3\text{NH}_2 - \text{H}_3\text{N}^+]$$

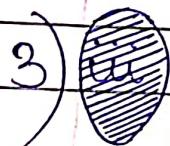


- I effect + I effect: ( $\propto$  more C atoms)



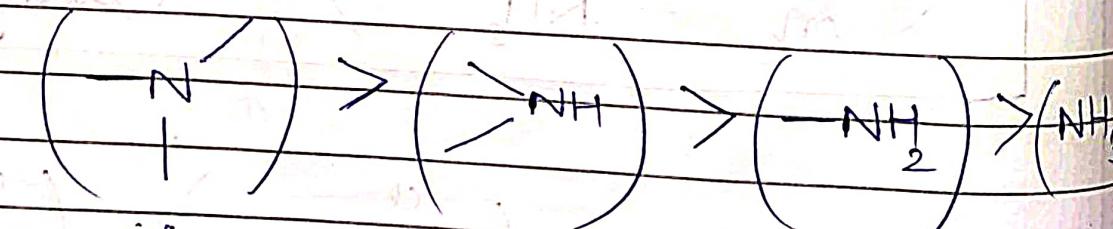
as + I: ( $\propto$  no. of C atoms)  
effect

### Basic Strength of Amines:



3) C1:— In vapour state,

Basic strength:

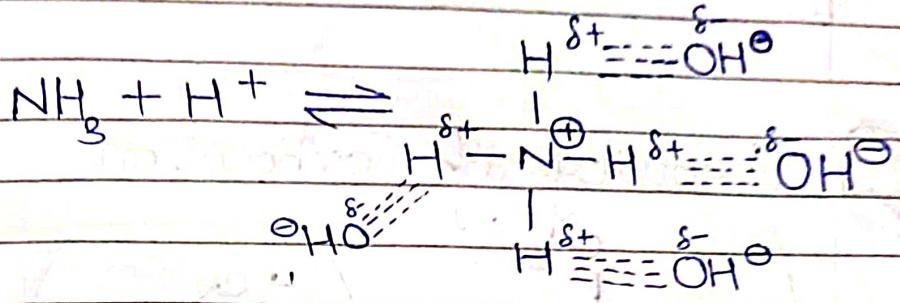


$$3^\circ > 2^\circ > 1^\circ > \text{NH}_3$$

C2 :- In aqueous state, (if nothing specified, assume aq. form)

Acc. to I. effect,  $(-\text{N}^-) > (>\text{NH}) > (-\text{NH}_2) > (\text{NH}_3)$

Acc. to solvation,



$\oplus$  charge

$\Rightarrow$  ~~density~~ ion N decreases.

$\Rightarrow$  More stable conj. acid  $\Rightarrow$  Stronger ~~base~~ base

$\therefore$  Acc to solvation,  $(\text{NH}_3) > (-\text{NH}_2) > (>\text{NH}) > (-\text{N}^-)$

Practically, we get

$$2^\circ > 1^\circ > 3^\circ > \text{NH}_3$$

if alkyl grps ~~Methyl~~.

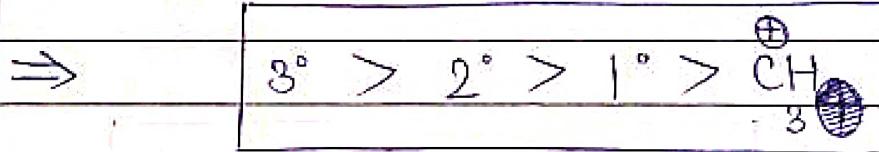
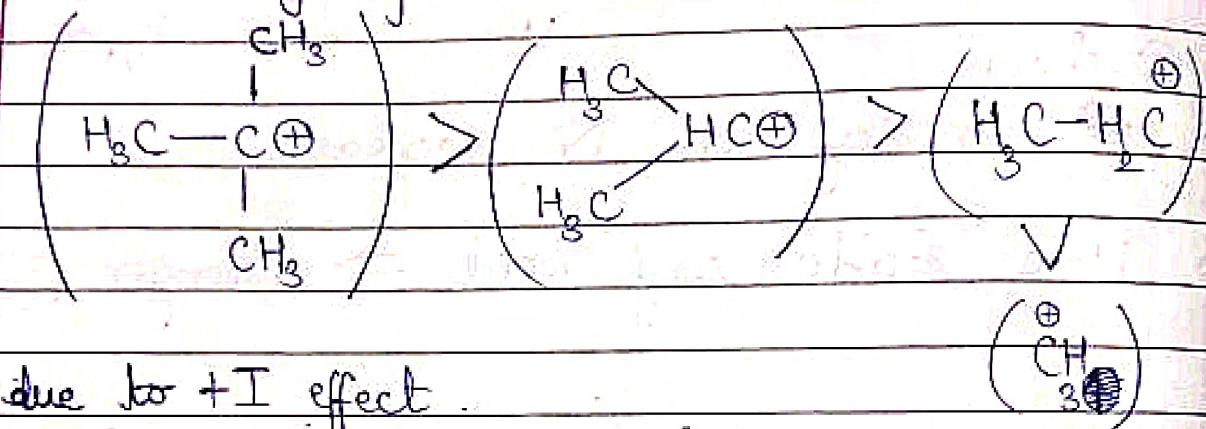
Practically, we get.

$$2^\circ > 3^\circ > 1^\circ > \text{NH}_3$$

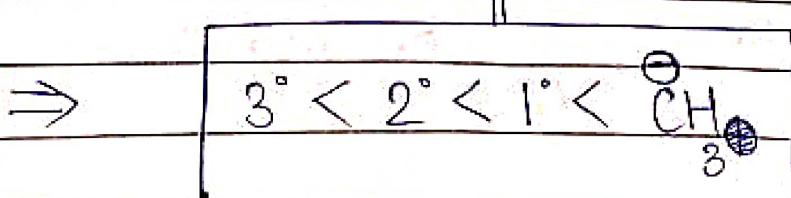
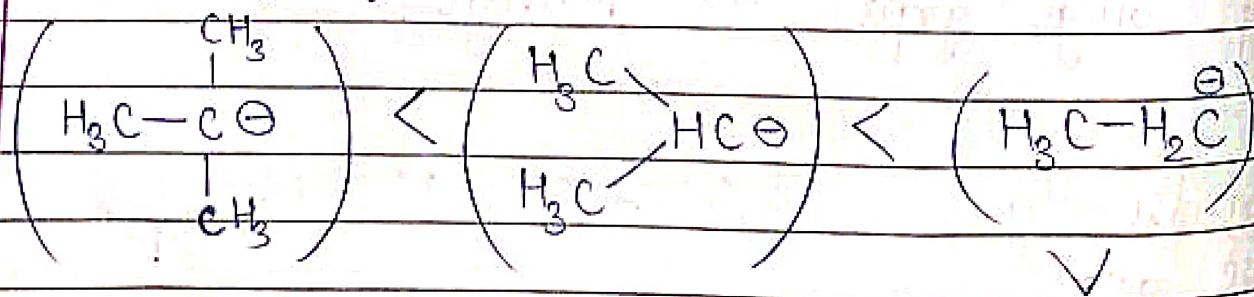
if alkyl grps ~~ethyl or higher~~.

★ If diff. alkyl grp's around N  
 (eg.  $\text{NH}_2$ ) , then  $2^\circ$  most basic.

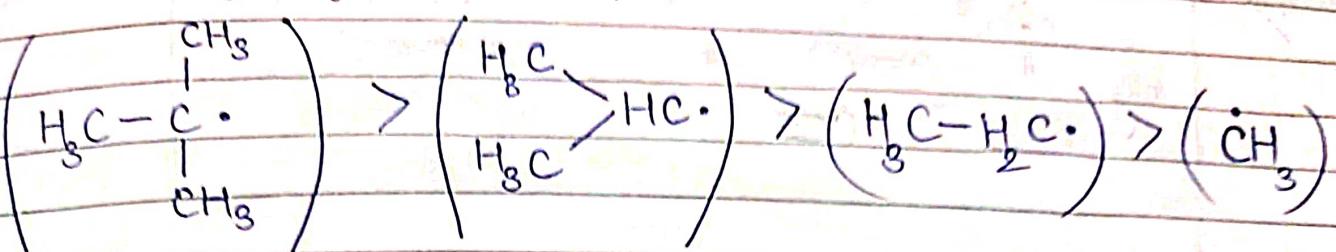
#### 4) Stability of Carbocation:



#### 5) Stability of Carbanions:

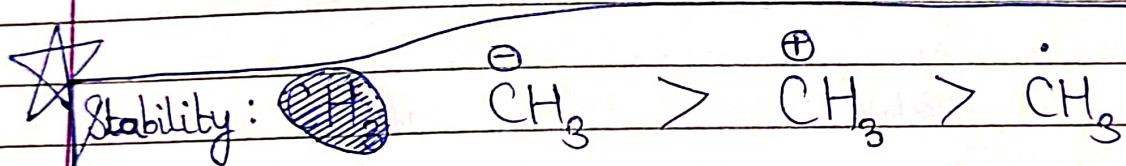


### 6) Stability of Carbon free radical :



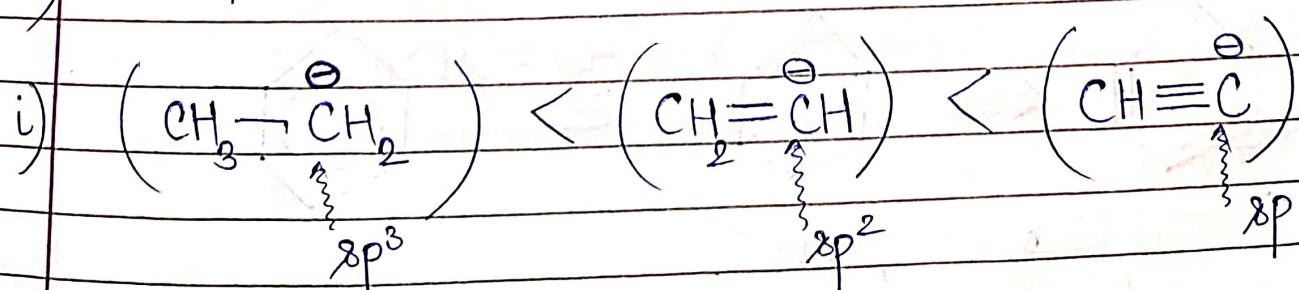
$$\Rightarrow 3^\circ > 2^\circ > 1^\circ > \cdot\text{CH}_3$$

Carbon free radical are  $e^-$  deficient species bcoz C has incomplete octet.

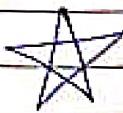


free radicals are highly energetic.

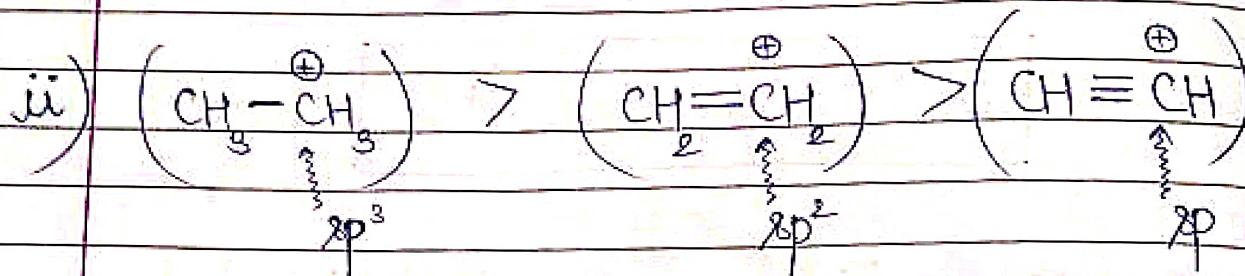
Q) Compare stability of species.



as EN ( $\text{sp} > \text{sp}^2 > \text{sp}^3$ ) and atom with  $\uparrow \text{EN}$  can tolerate  $\uparrow \ominus$  charge.



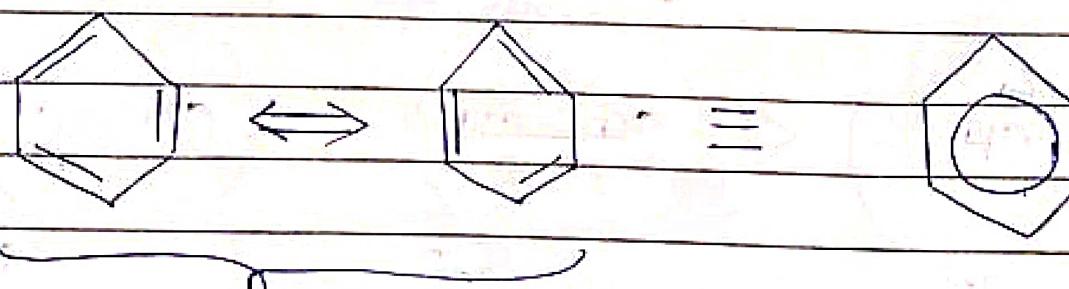
We can't apply I effect bcoz  
I effect is created  
by  $-C\equiv C-$  or  $>C=C<$   
NOT  $C\equiv$  or  $C=$



EN  $\uparrow \Rightarrow \ominus$  charge Stable  $\Rightarrow \oplus$  charge Unst.

## Resonance (Mesomeric Effect)

Generally, localisation of  $\pi e^-$  when there is contradiction b/w theoretical & practical data.



Resonance /  
Canonical  
Structures

Resonance  
Hybrid

(Res. inc. stability as charge  
is dispersed.)

DATE \_\_\_\_\_  
PAGE \_\_\_\_\_

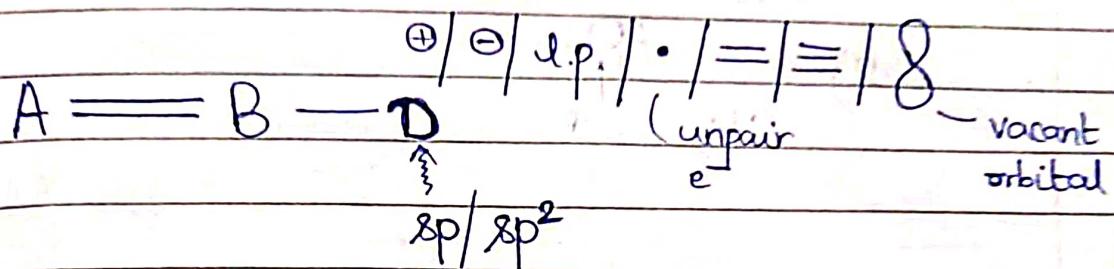
103

Cond'n's :-

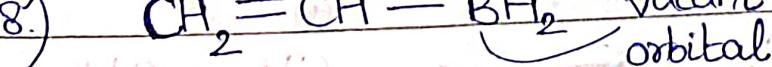
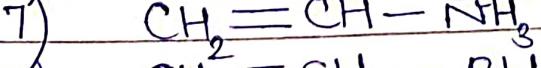
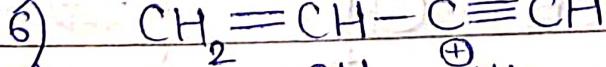
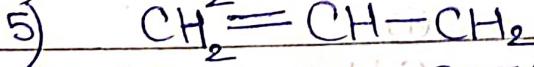
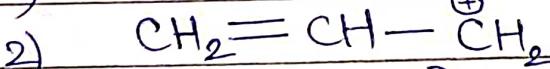
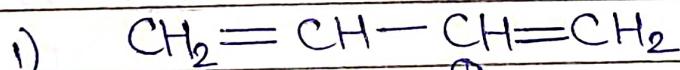
Planar (part of molecule showing resonance)  
should be planar

Conjugation :-

C1:

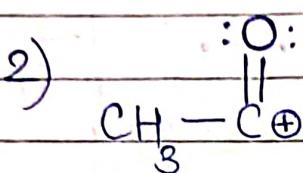
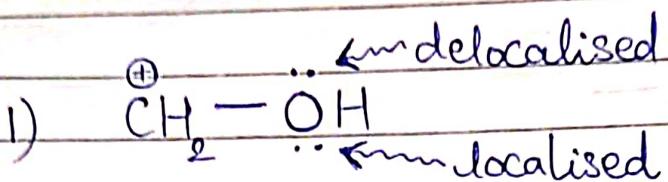
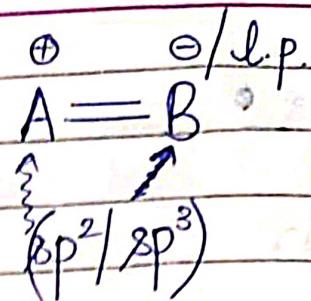
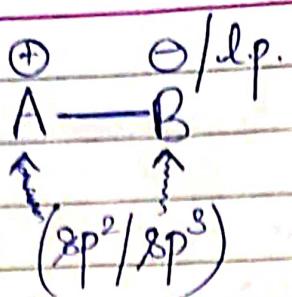
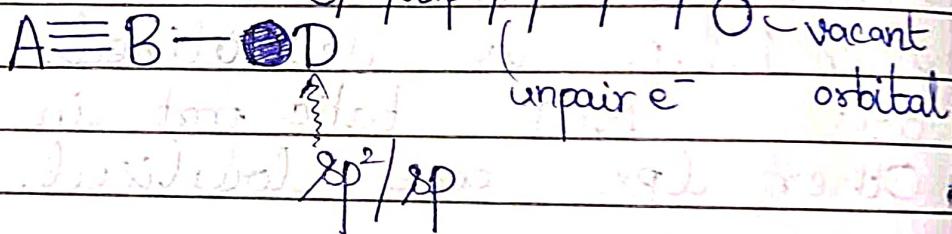


When 'D' has a  $\geq 1$  l.p. (i.e.  $D:$ )  
then 1 l.p. is delocalised, i.e. it  
does NOT take part in hyb.  
Other l.p.s. are localised.



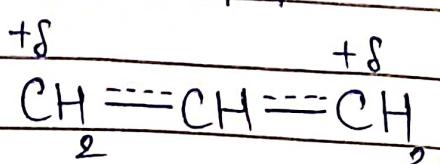
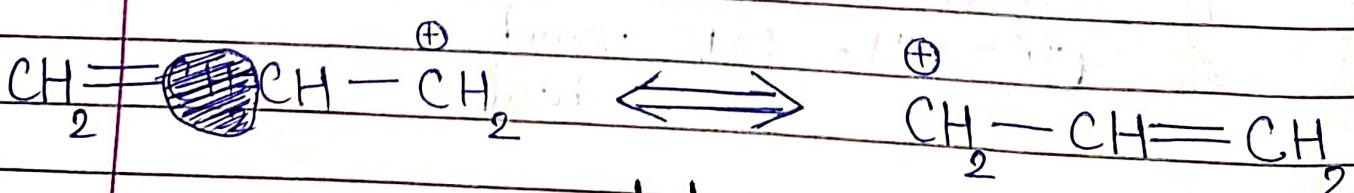
104

C2:

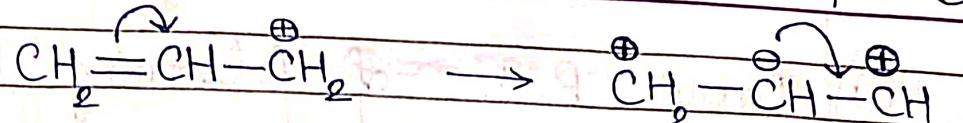
C3:  $\text{A}^+/\text{B}^-/\text{l.p.}/\text{..} = \equiv / 8$ 

## Resonating Structures

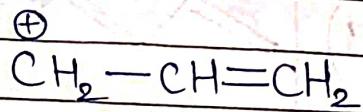
C1:



Working :



$\oplus \text{ & } =$   
exchange



Resonance Energy :

$$(\text{Resonance Energy}) = (\text{Energy of most stable canonical structure}) - (\text{Energy of Resonance Hybrid})$$

Lower energy of R.H.



More resonance energy



More stability



Energy ↑

most stable C.S.

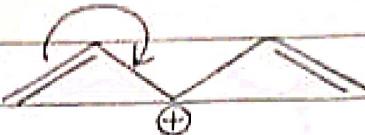
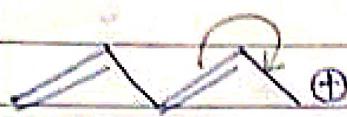
Resonance Energy

R.H

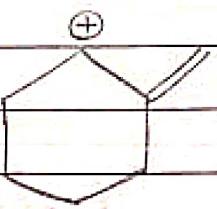
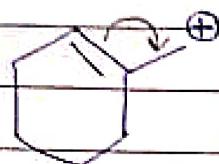
$$(\text{Resonance Energy}) \propto (\text{Stability})$$

Q) Draw R.S. of following species.

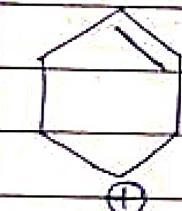
1)

 $\oplus$ 

2)

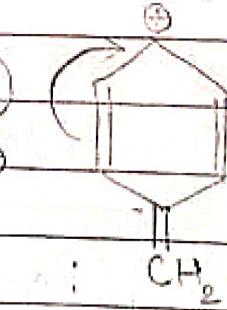
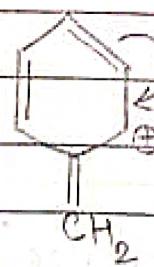
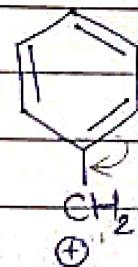
 $\oplus$ 

3)

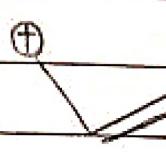
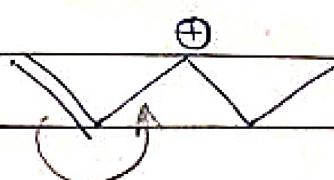


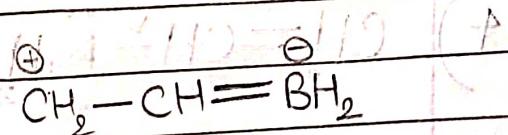
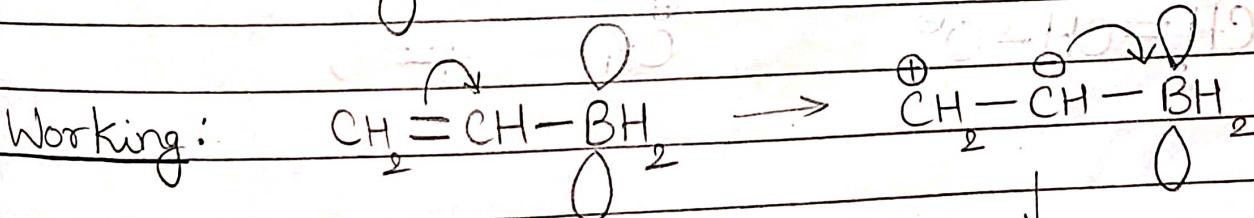
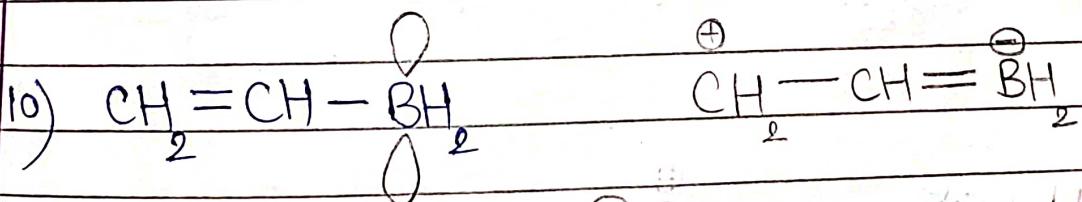
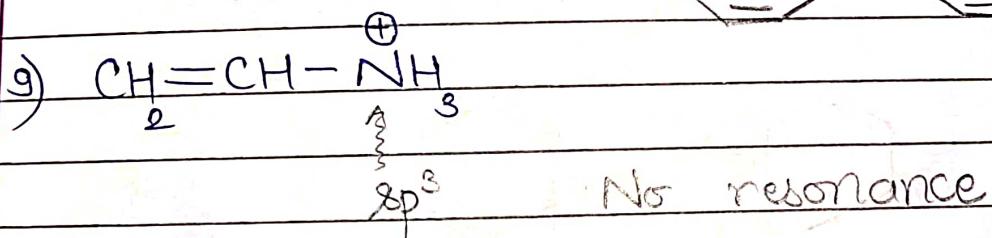
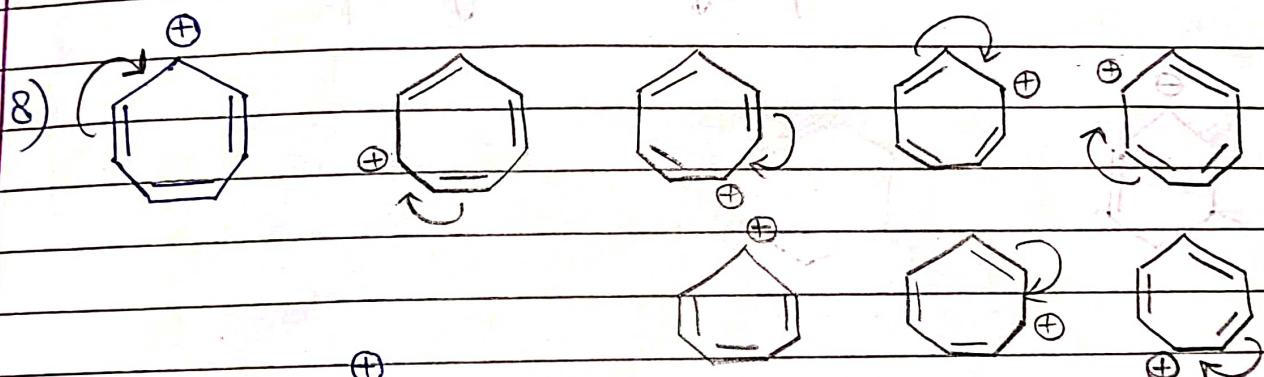
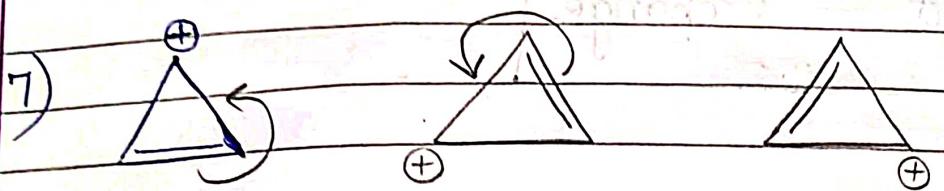
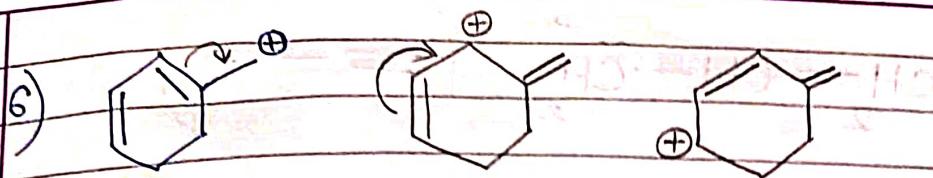
No Resonance

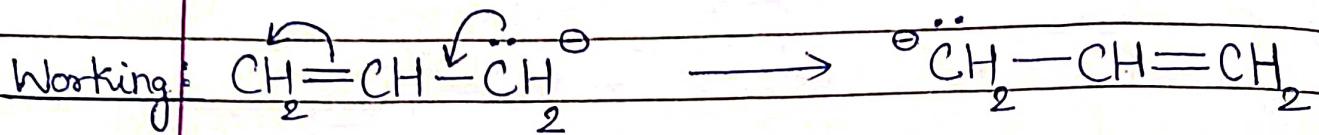
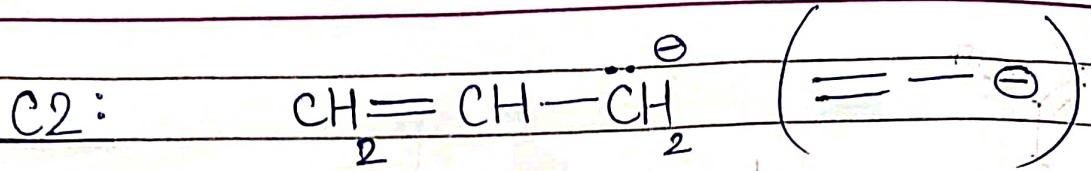
4)



5)

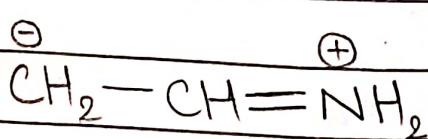
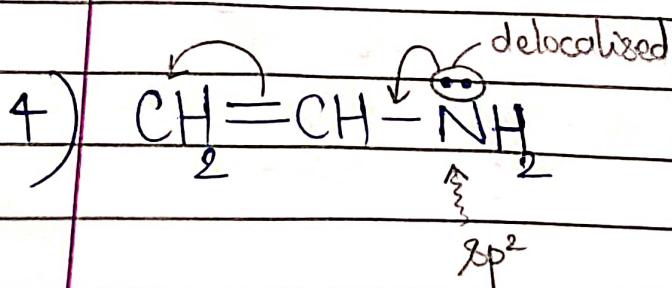
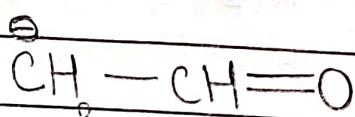
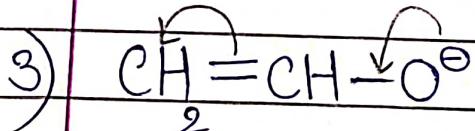
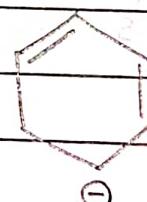
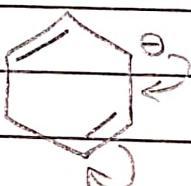
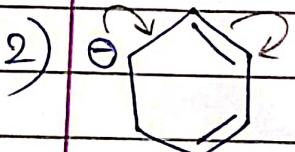
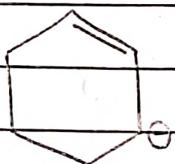
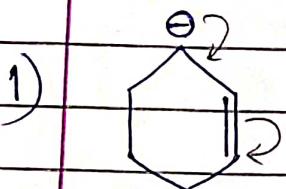




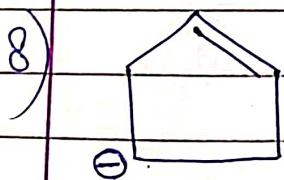
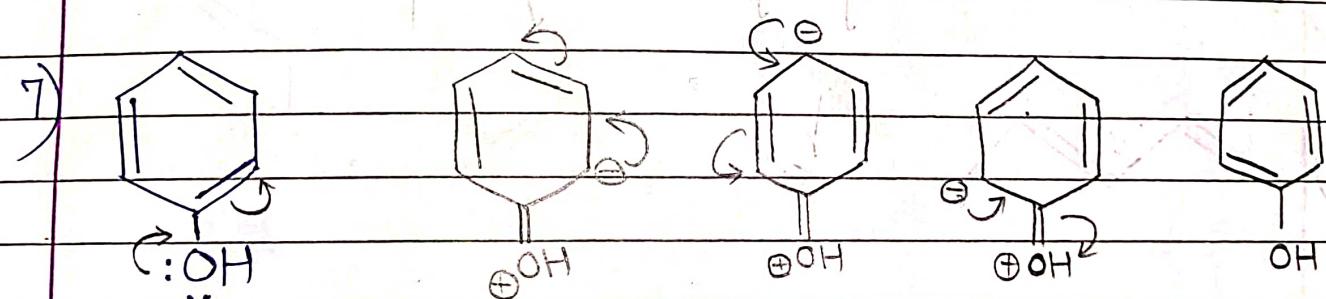
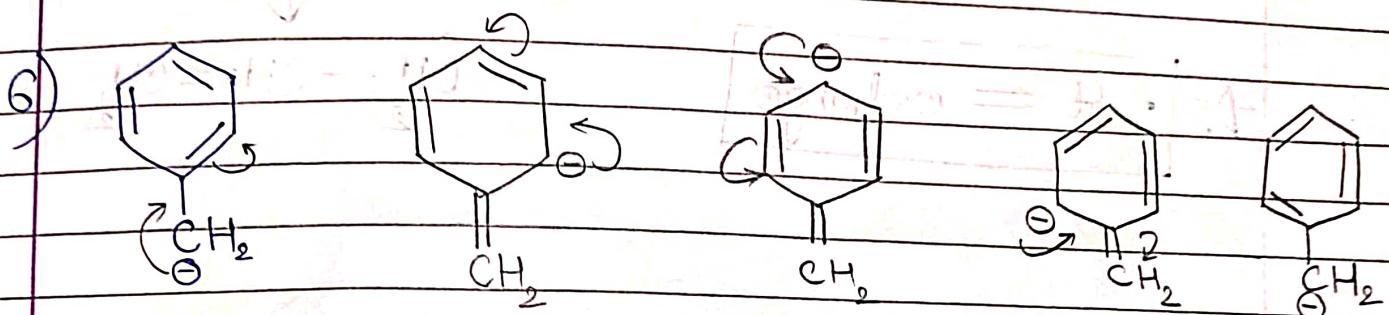
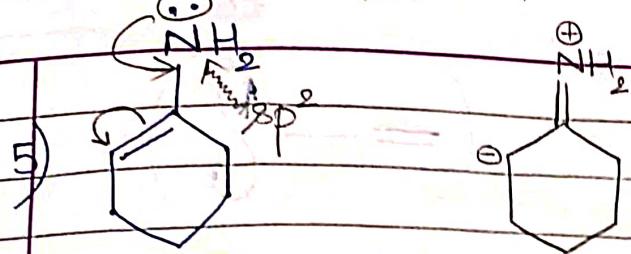


★  $\ominus$  it = exchange

Q) Draw R.S. of following species.



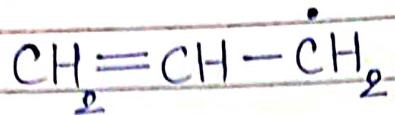
delocalized



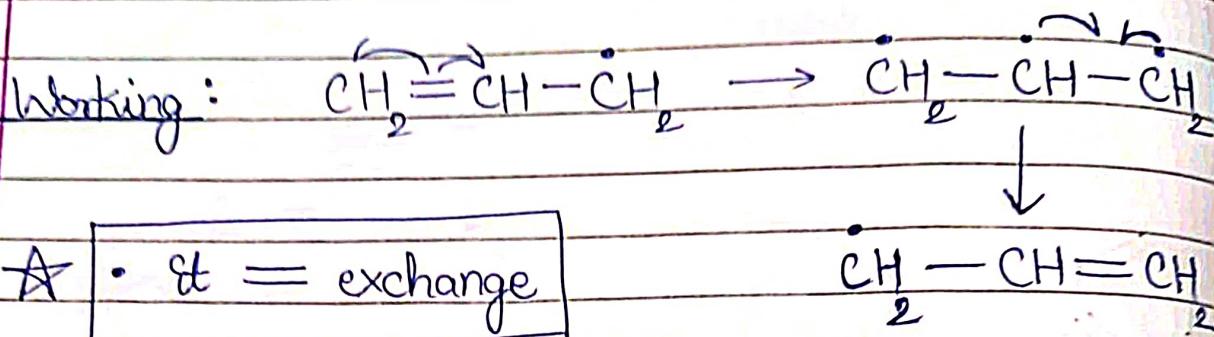
110

DATE  
PAGE

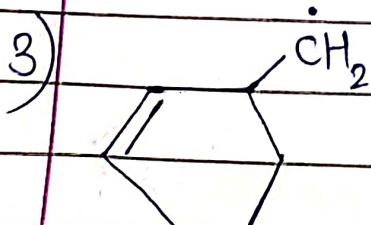
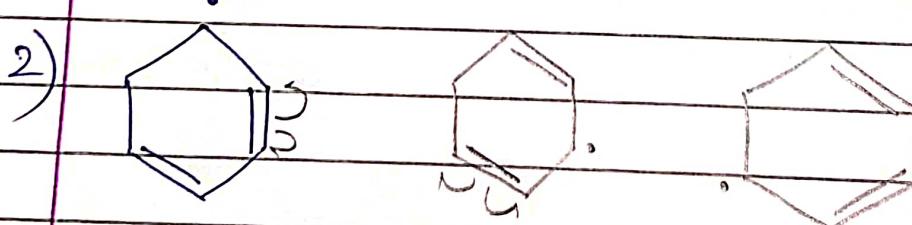
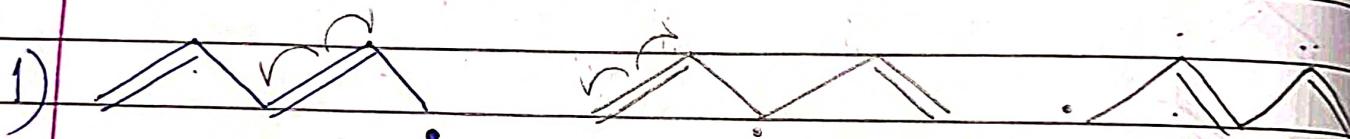
C3:

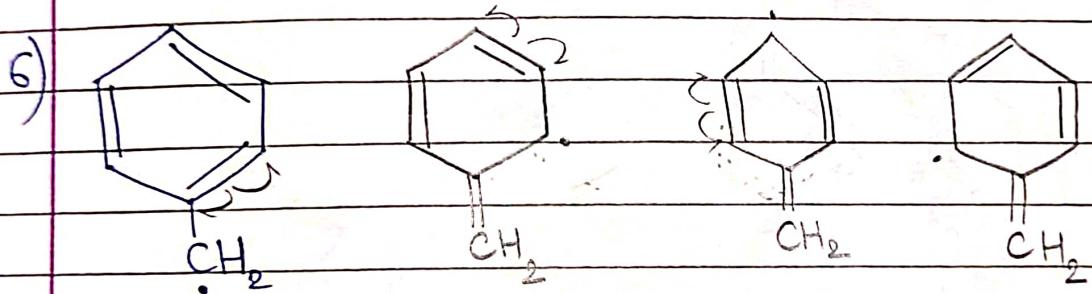
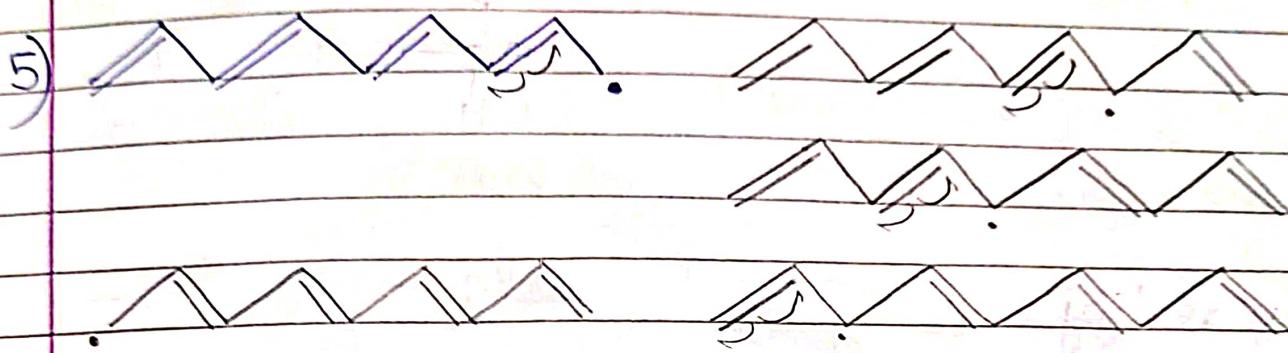
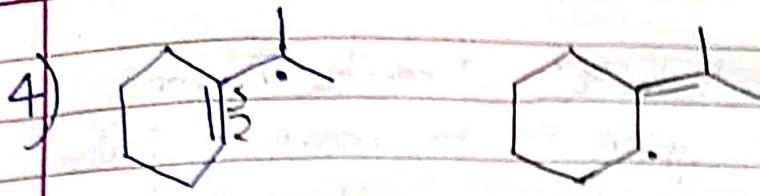


( = - 8 )

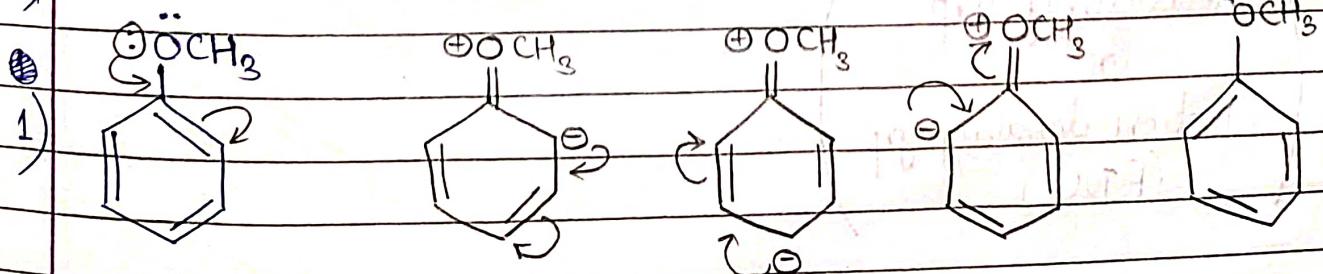


①) Draw R.S. of following species.

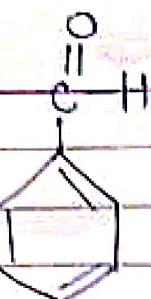




Q) Draw R. S. of following species.

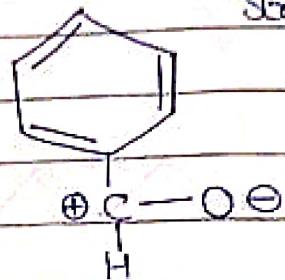


(★2)

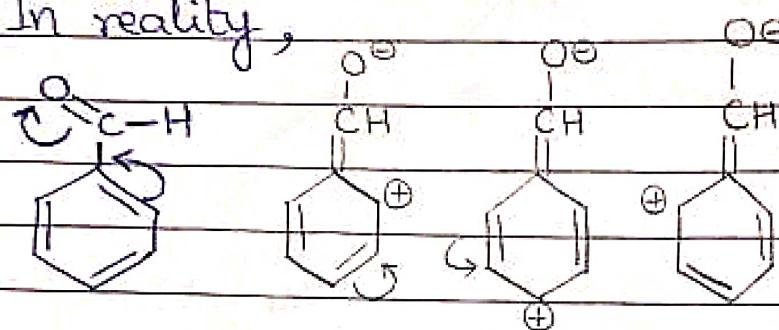


Short Trick: Break  $\pi$ -bond  
it give  $\Theta$  to more EN atom

Hypothetical  
Structure



In reality,



### Resonance Effect

+M effect

-M effect

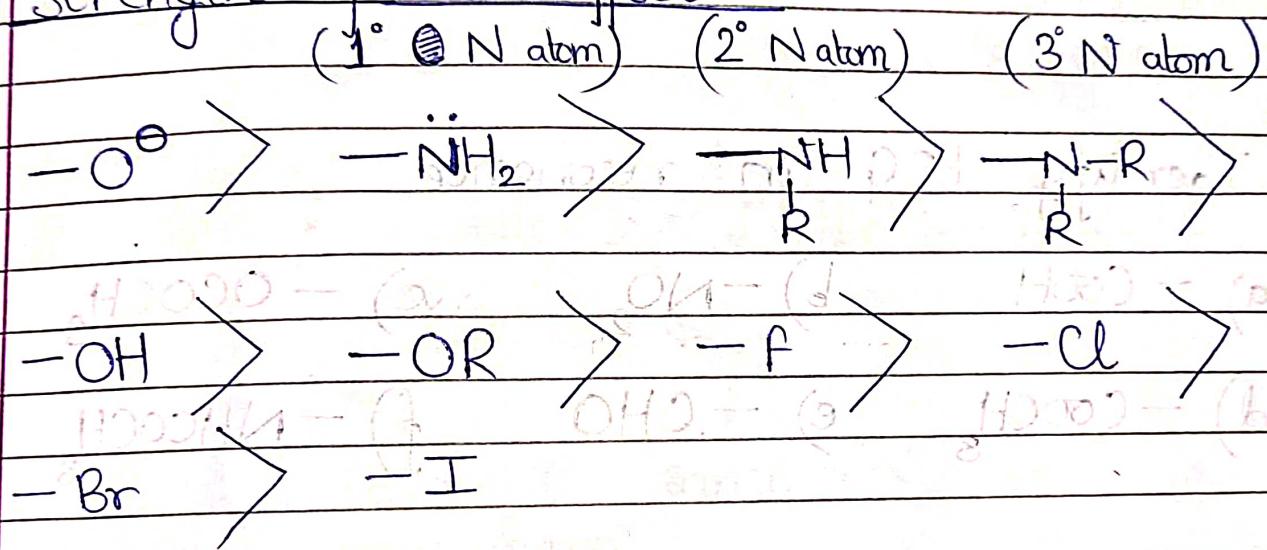
Activating grp  
or

Electron donating grp  
(EDG)

$+M$  effect:—  $e^-$  donated in ring/chain.  
*(only)*

For showing  $+M$  effect, grp. must have at least 1 l.p. without having multiple bond with more EN atom.

Strength of  $+M$  effect:—



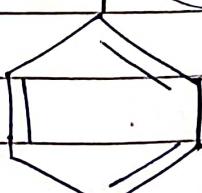
$-M$  effect:—  $e^-$  taken from ring/chain.

for showing  $-M$  effect, grp. must be multiple bonded to atom with greater EN & it not having l.p.

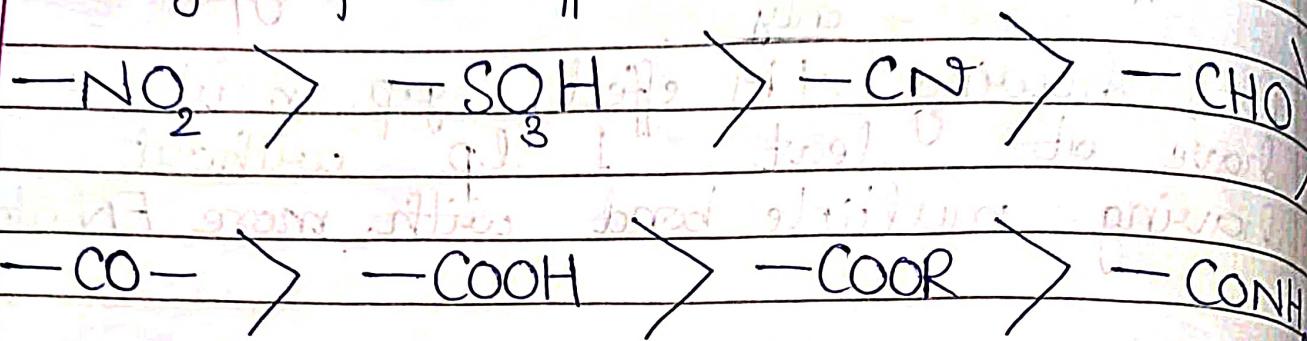
$$x = y$$

*(no l.p.)*

$$\text{at } \text{EN: } y > x$$

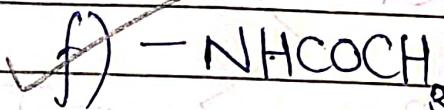
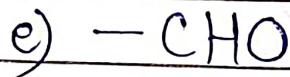
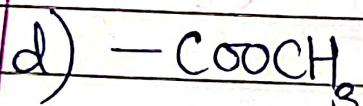
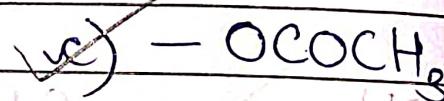
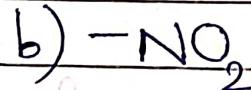
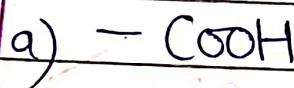


Strength of  $-M$  effect:



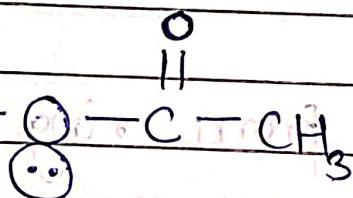
(Q)

Identify EDG in resonance



A)

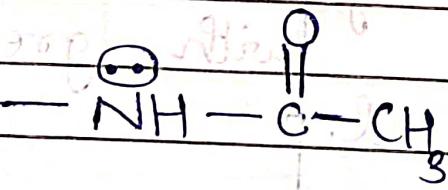
c)



l.p. It no multiple bond

 $\Rightarrow +M$  effect

f)

 $\Rightarrow +M$  effect

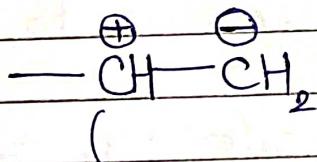
Q) Which can show both +M & -M effect.

- a)  $\text{NO}_2$       b)  $\text{NO}$       c)  $\text{CH}=\text{CH}_2$   
 d)  $\text{CHO}$       e)  $\text{NH}_2$       f)  $\text{N}=\text{NH}$

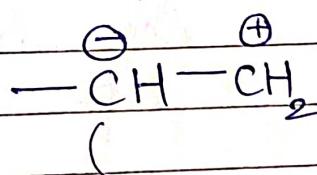
A) b)  $\text{N}=\text{O}$  Both l.p. & multiple bond with more EN atom

⇒ +M effect due to l.p. &  
 ⇒ -M effect due to double bond.

c) Since both C same EN, bond can break anywhere.



takes  $\bar{e}$  from chain/ring



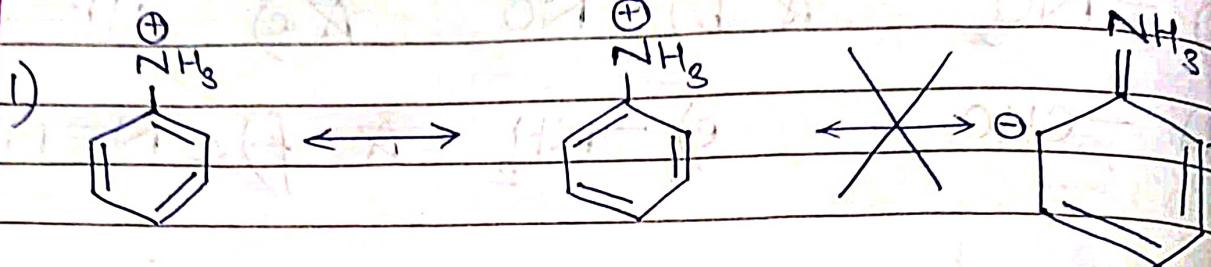
donate  $\bar{e}$  in chain/ring

⇒ -M effect      ⇒ +M effect

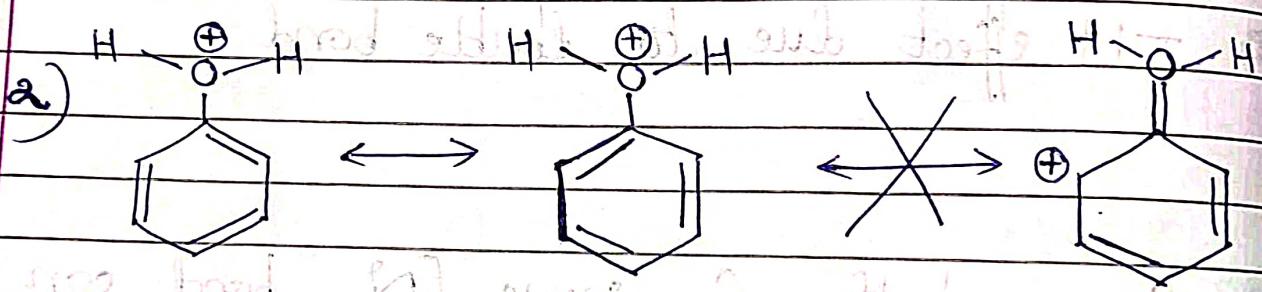
f) same as c).



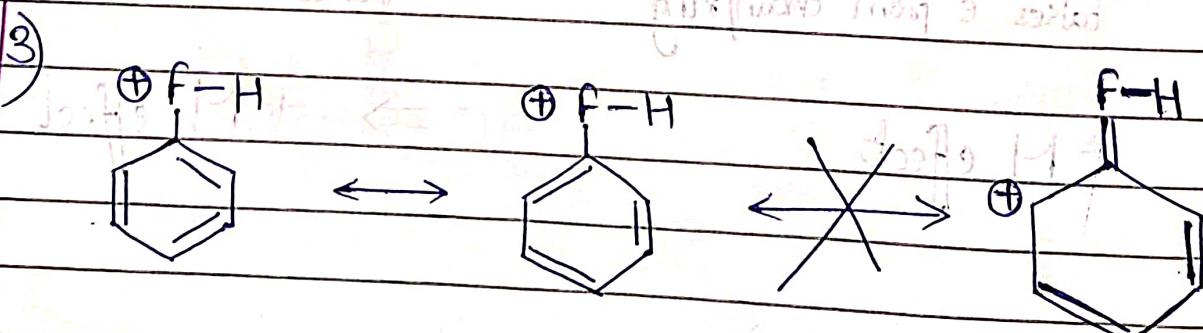
## Resonance Structures



as in last structure N is making 5 bonds which is impossible.



as O not have vacant orbital to accept l.p. from ring.



as F not have vacant orbital to accept l.p. from ring.

# Aromatic, Anti-aromatic & Non-aromatic

## Aromatic —

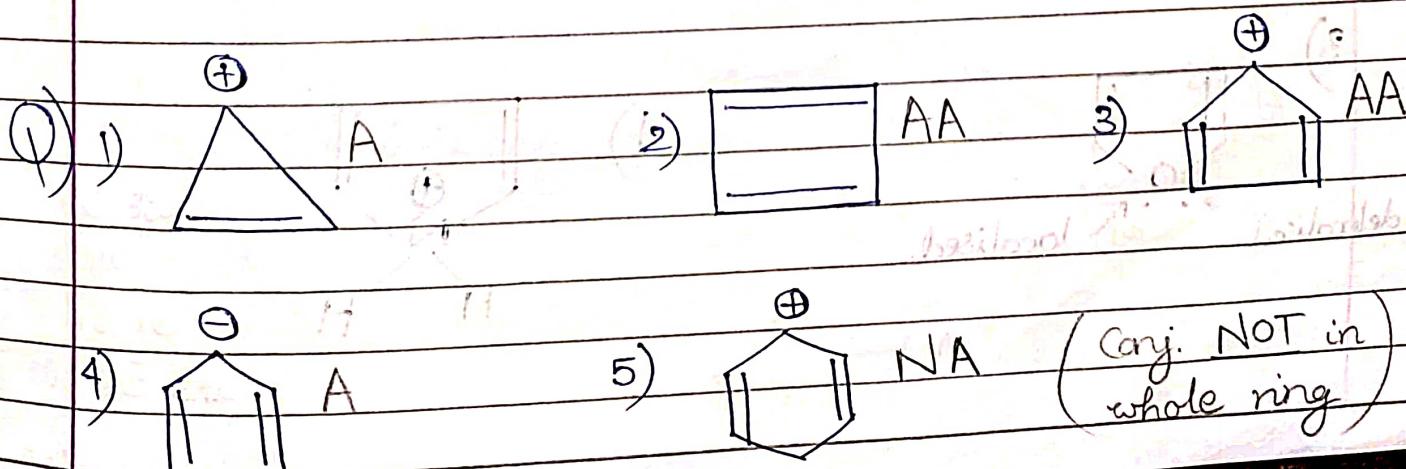
- 1) Cyclic
- 2) Planar
- 3) Every atom  $sp/sp^2$
- 4) Conjugation in whole
- 5) follow Hückel's Rule :  
 $(4n+2)\pi$  delocalized  $e^-$  ( $n \in \mathbb{Z}$ )  
at Periphery.

## Anti-aromatic —

- 1) Cyclic
- 2) Planar
- 3) Every atom  $sp/sp^2$
- 4) Conjugation in whole
- 5)  $(4n)\pi$  delocalised  $e^-$  ( $n \in \mathbb{N}$ )  
at Periphery.

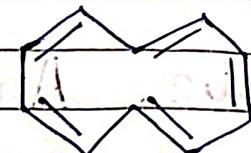
## Non-aromatic —

Neither aromatic nor anti-aromatic



Real Structure:

(Q) 1)

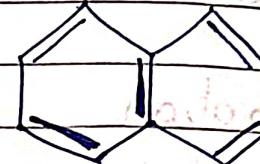
NA (not isomers)  
(NOT planar)

NA (NOT planar)

3)

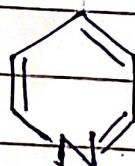


4)

★ 1) In general,  $\geq 8C \Rightarrow$  Non-planar structure.

2) If it contains any molecule, if even 1 ring is aromatic then whole molecule (is) aromatic.

(Q) 1)



A

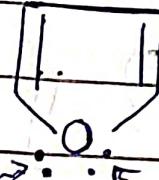
l.p. NOT in  
conj. as they  
lie above plane

2)



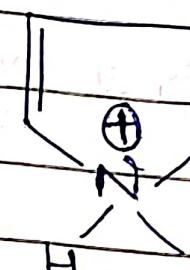
delocalised

3)



A

4)

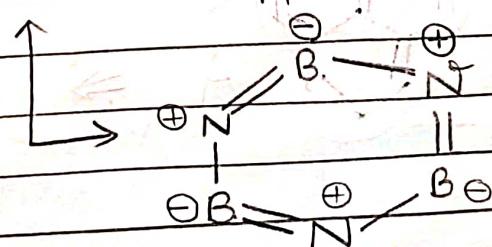
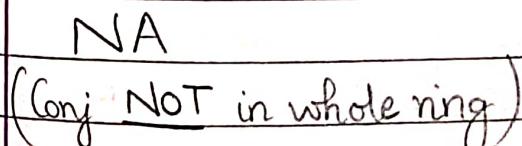
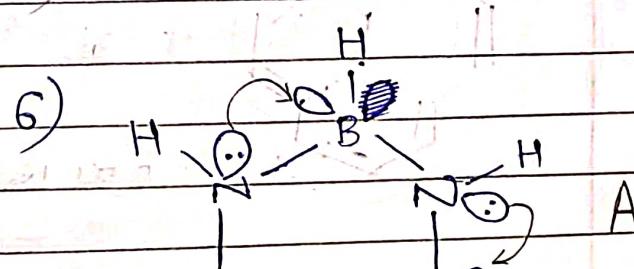
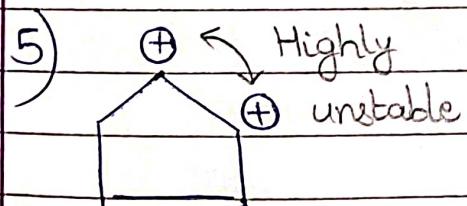
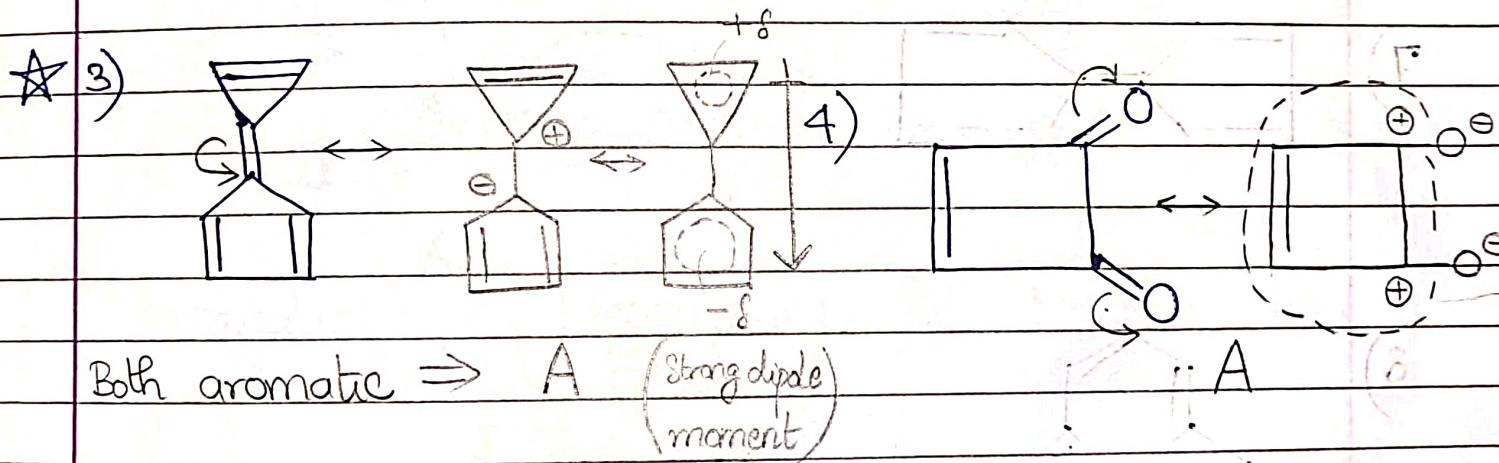
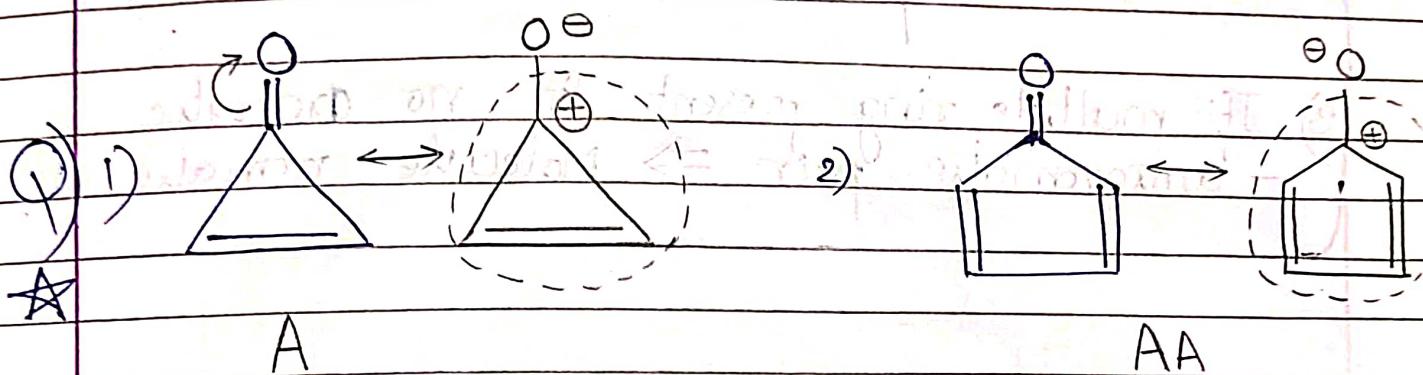
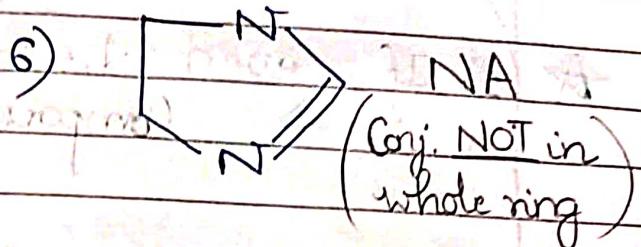
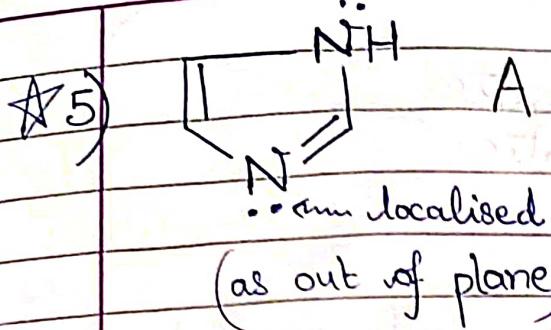


NA

delocalised

localised

N NOT in  
conj. as  
it can't  
make 5 bond

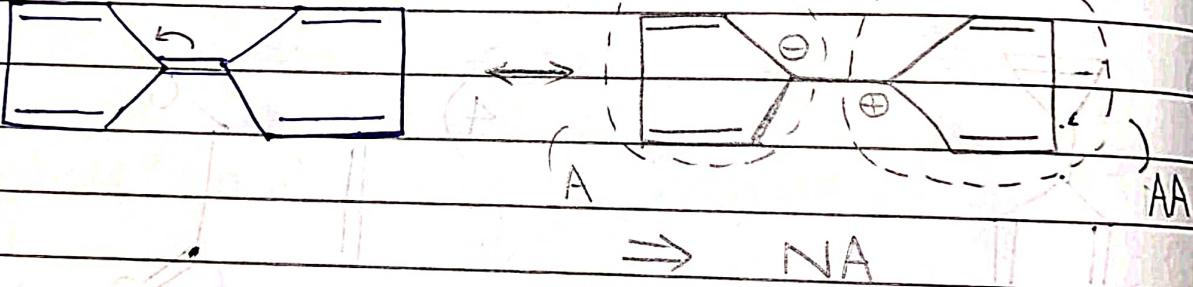
unlocalised

20

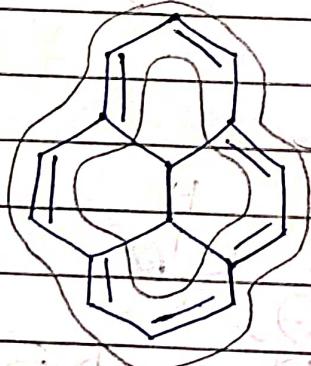
DATE  
PAGE

- resonance
- ★ 1) If even 1 substituent aromatic  $\rightarrow$  Compound aromatic.
  - 2) If multiple bond & l.p. both present  $\rightarrow$  l.p. localised.
  - 3) If multiple ring present & no aromatic - antiaromatic pair  $\Rightarrow$  Molecule aromatic.

7)



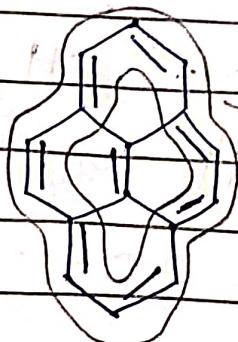
8)



$14\pi$  delocalised  $e^-$   
at PERIPHERY

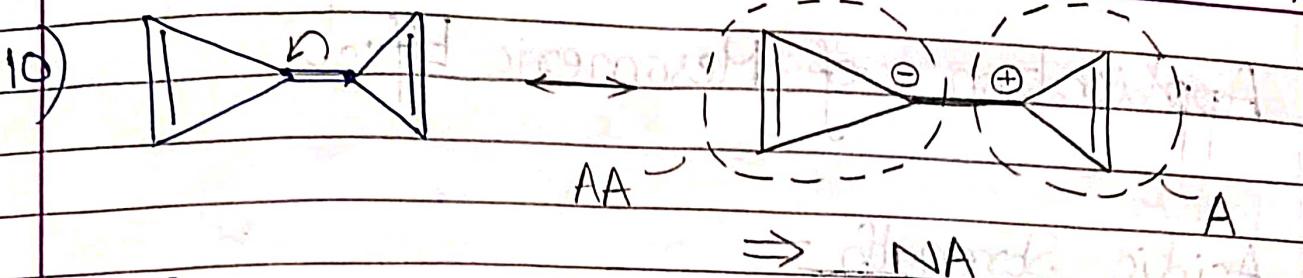
AA

9)

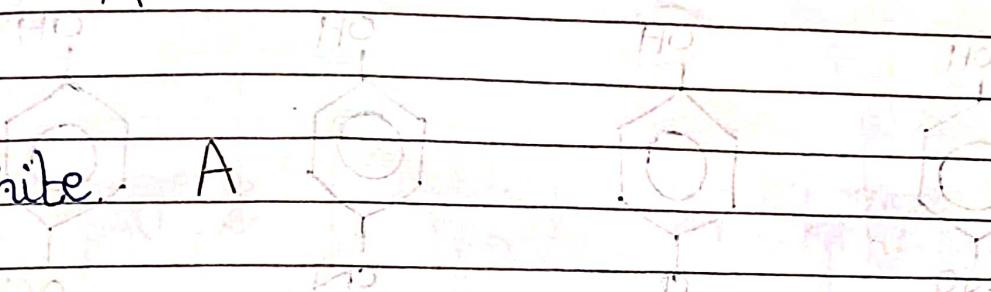


$14\pi$  delocalised  $e^-$   
at PERIPHERY

AA



★ 11)  $C_{60}$  A



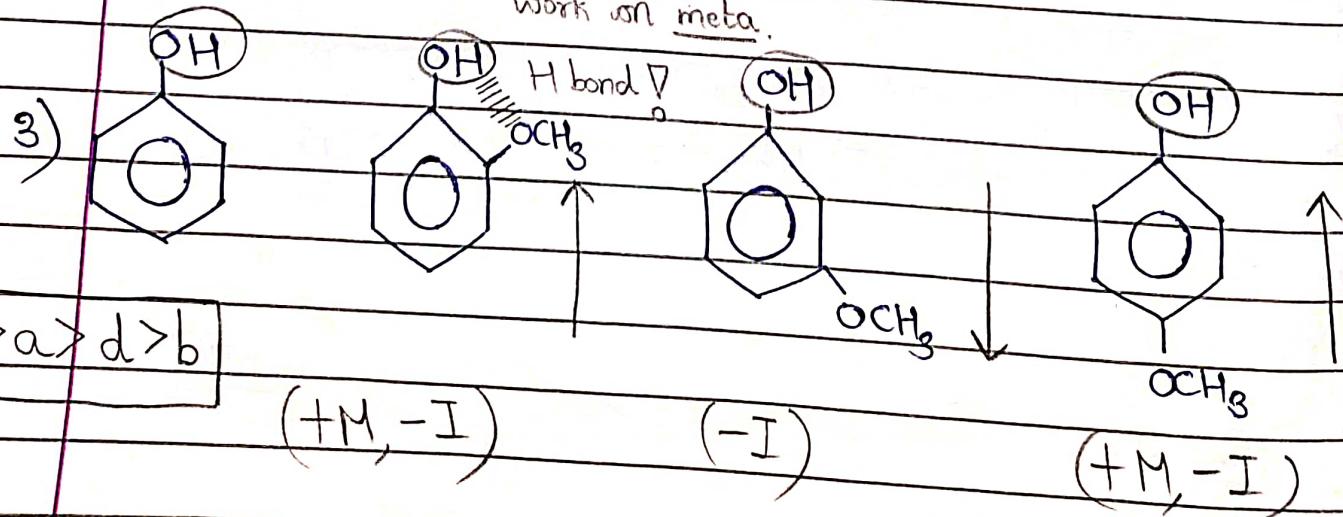
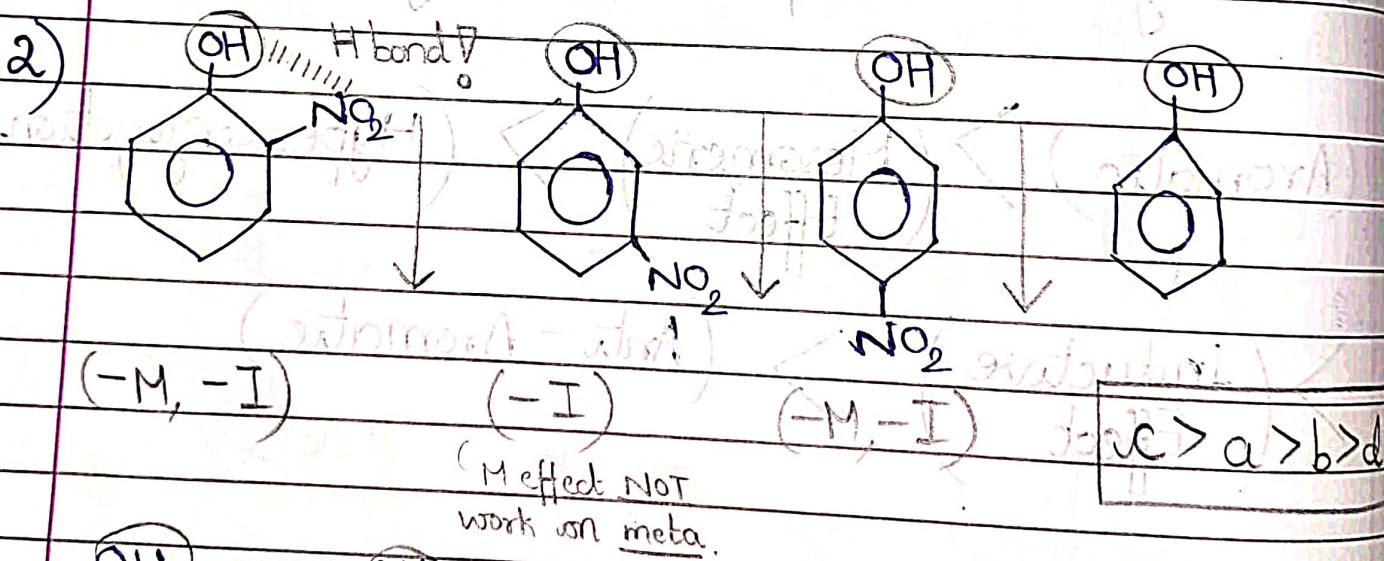
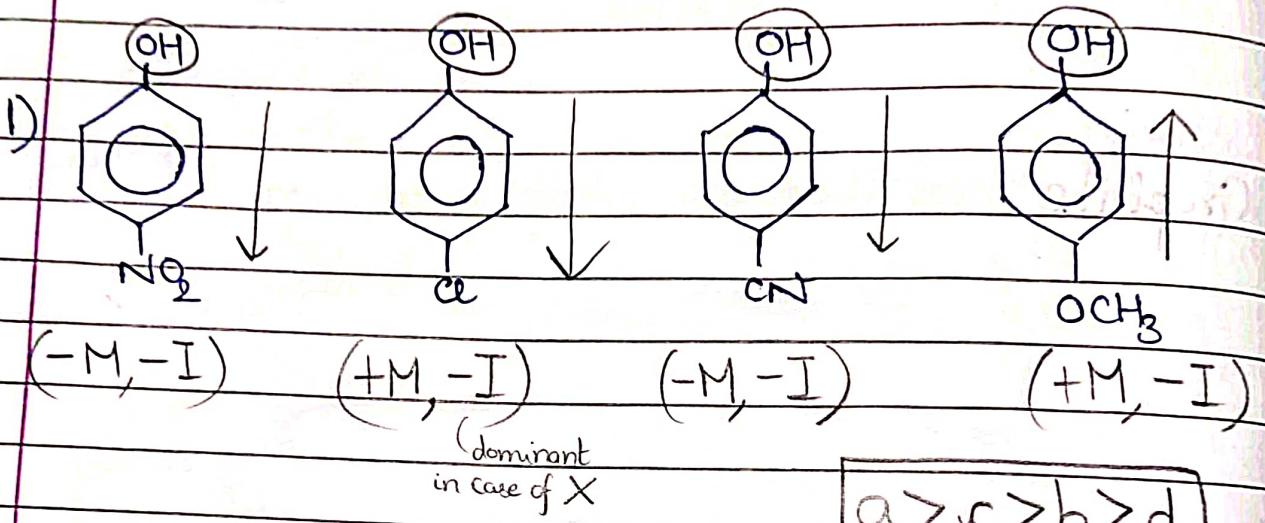
★ 12) Graphite A

## Priority Order for Q solving

(Aromatic)  $>$  (Mesomeric Effect)  $>$  (Hyperconjugation)  
 $>$  (Inductive Effect)  $>$  (Anti-Aromatic)

# Application of Mesomeric Effect.

## 1) Acidic Strength -



(-I)

(-I)

(-I)

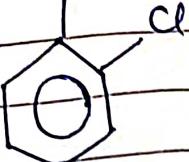
OH

OH

OH

OH

4)



Ignore M effect as Halogen.

$$a > b > c > d$$

\* i) for Halogens  
(except F)

(Inductive Effect)  $\rightarrow$  (Mesomeric Effect)

2) Mesomeric Effect does NOT work  
on Meta post. as there is no resonance  
stability.  $\pm$  charge does NOT appear on meta post.

3) When no. of M & I effect same,  
look for H bond. It will reduce H release.

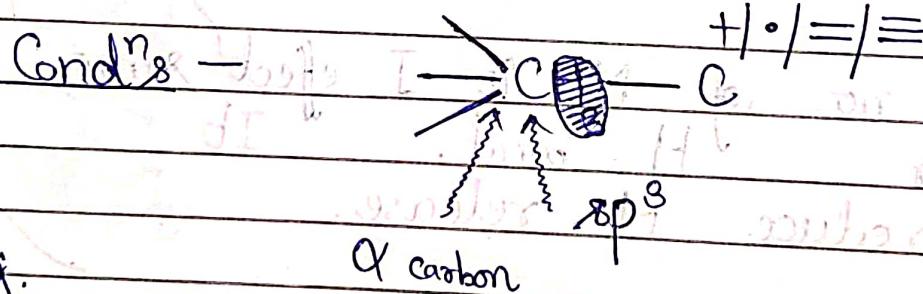
## Hyperconjugation

- Baker & Nathan Effect
- No bond resonance
- $\sigma$  bond resonance

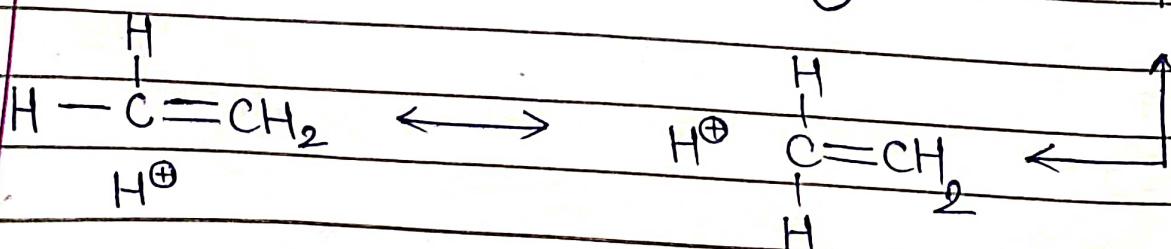
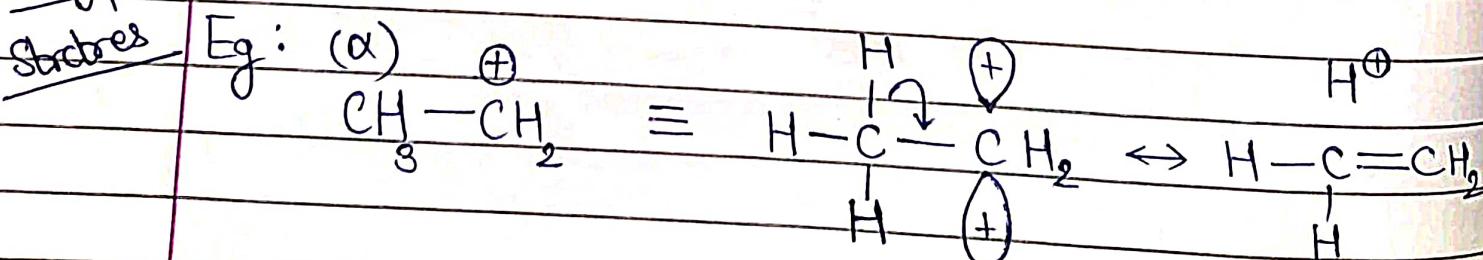
It explains the stability of

Alkene & Carbon free Radical

It involves bond conju. with adj. empty or partially filled p orbital, or  $\pi$  bond



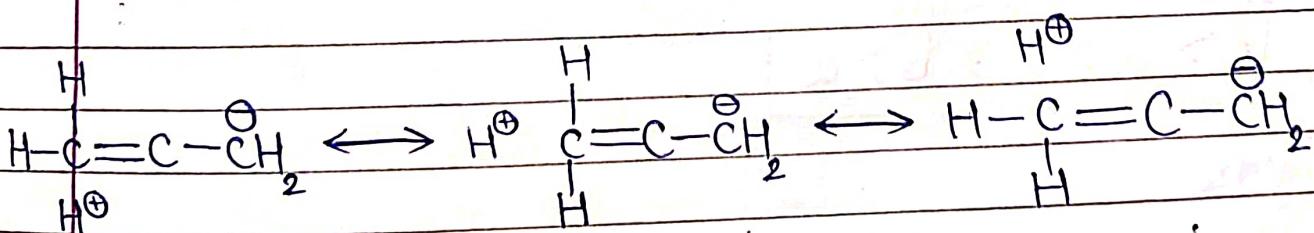
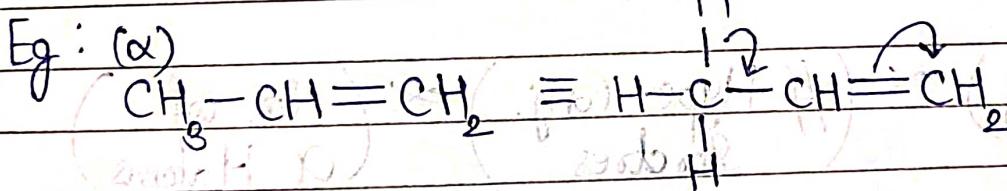
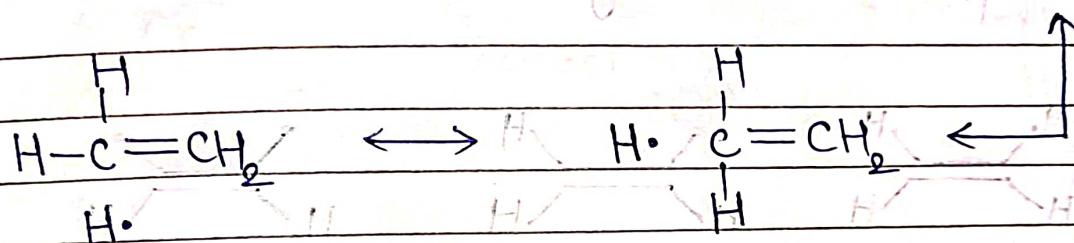
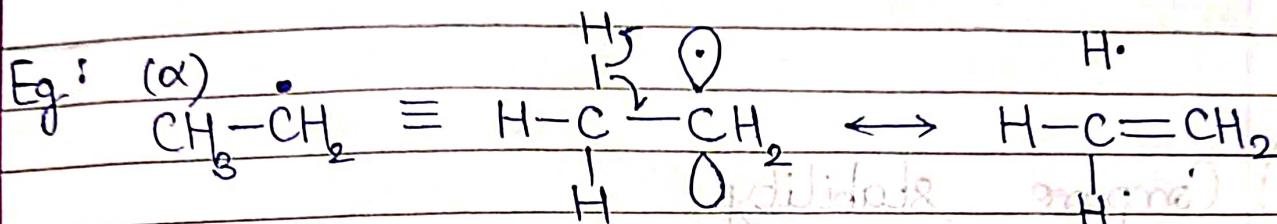
Hyperconj.



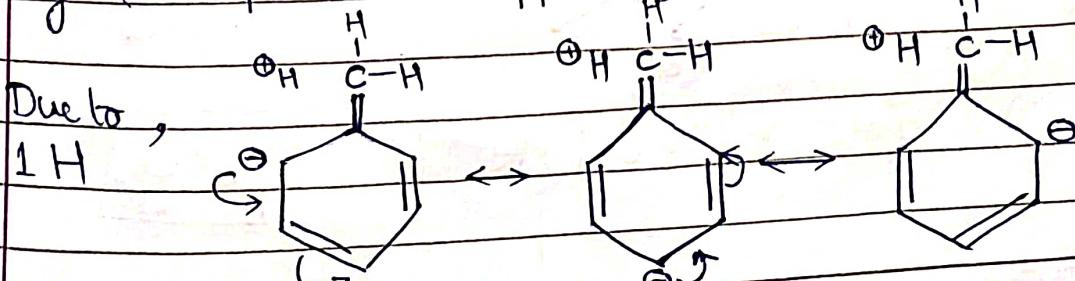
$(\alpha \text{ H atom}) = \text{H atoms connected}$   
 $\text{to } \alpha \text{ C atom}$

125  
 DATE \_\_\_\_\_  
 PAGE \_\_\_\_\_

$$(\# \text{ Hyperconj. structures}) = (\text{No. of } \alpha \text{ H atoms}) + 1$$



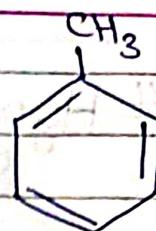
Eg: (Above formula NOT applicable)  $(\# \text{ Hyperconj. structures}) = 10$



126

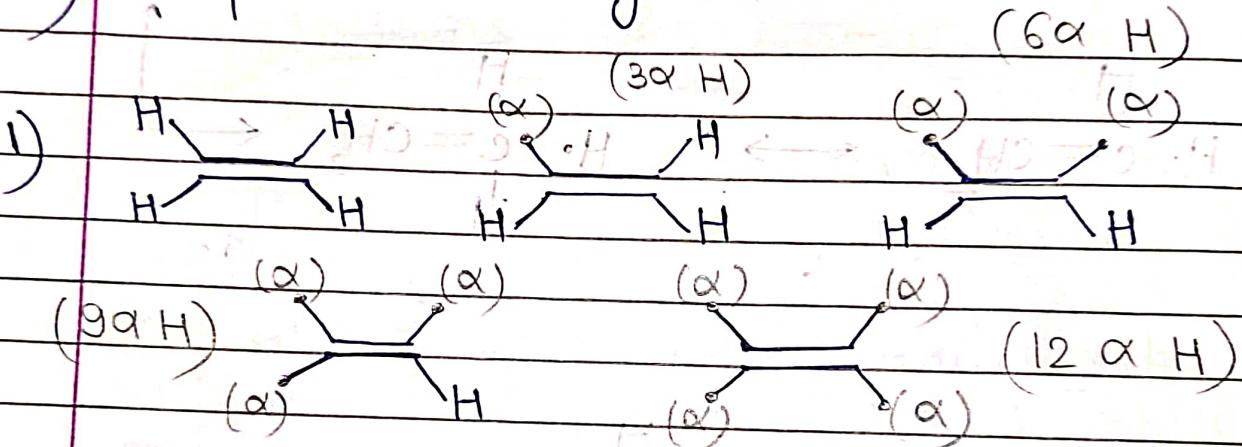
DATE  
PAGE

Observe that

are Resonance structures, NOT Hyperconj. structures.

Q)

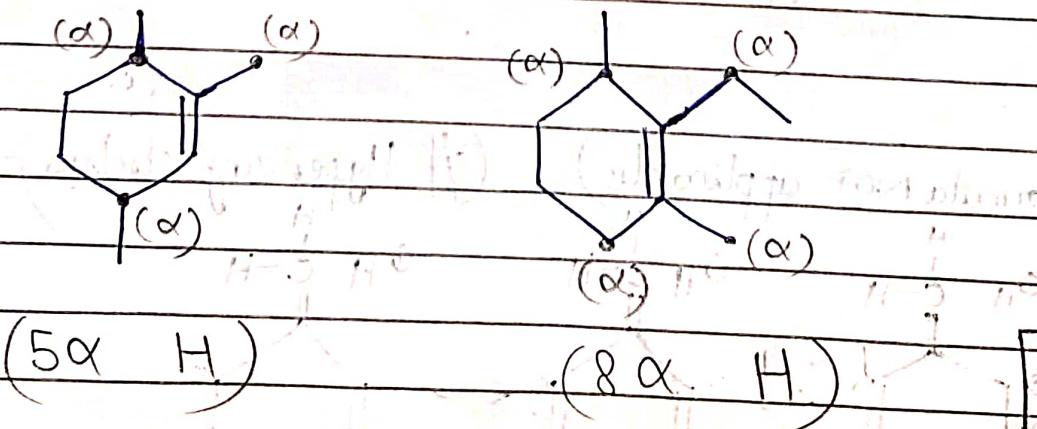
Compare stability.

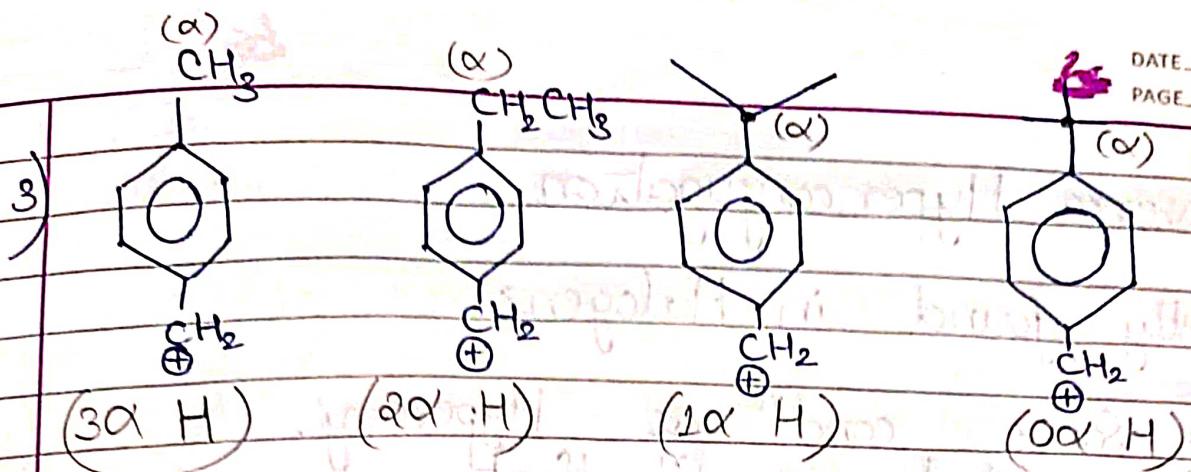


A) (Stability)  $\propto$  (# HyperConj.)  $\propto$  (No. of  $\alpha$  H atoms)

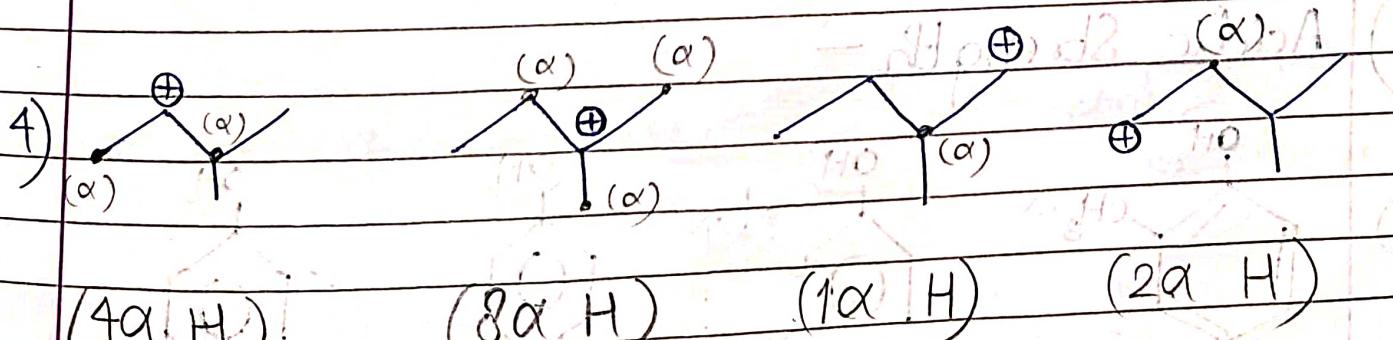
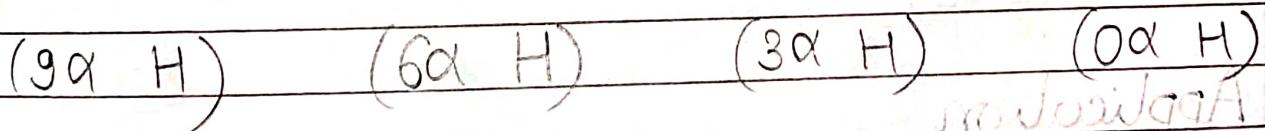
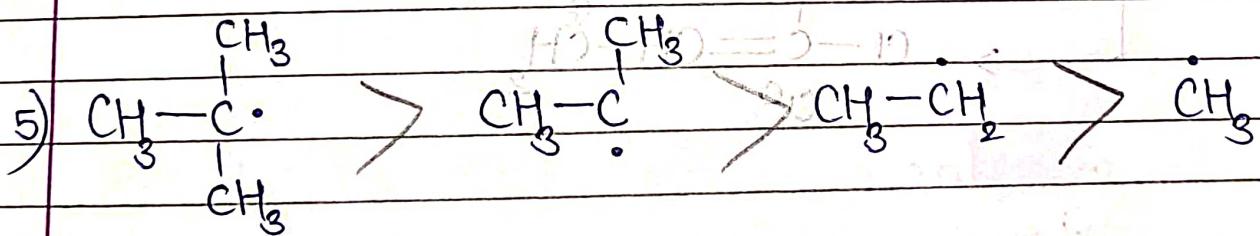
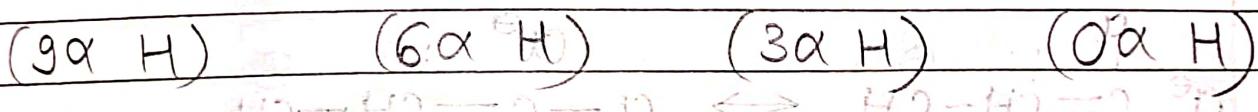
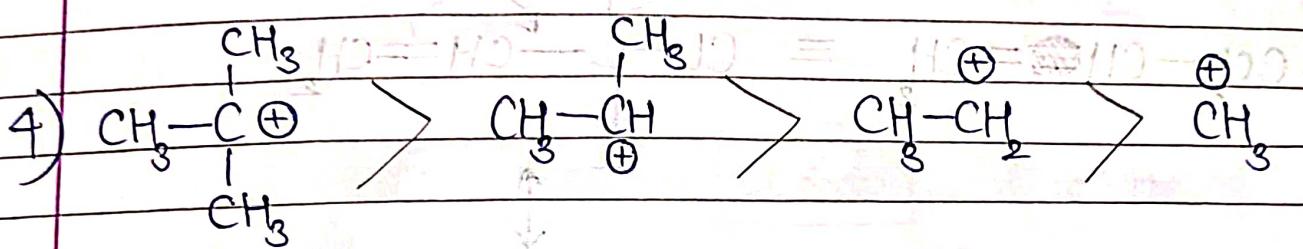
$$e > d > c > b > a$$

2)





$$a > b > c > d$$

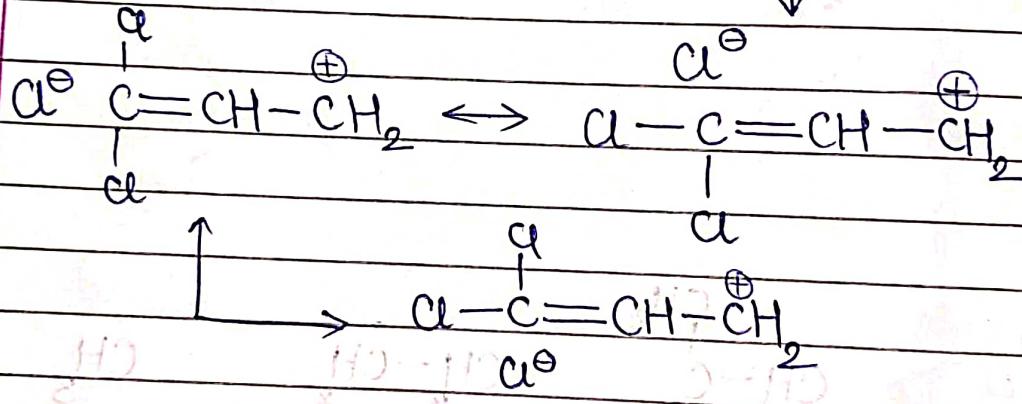
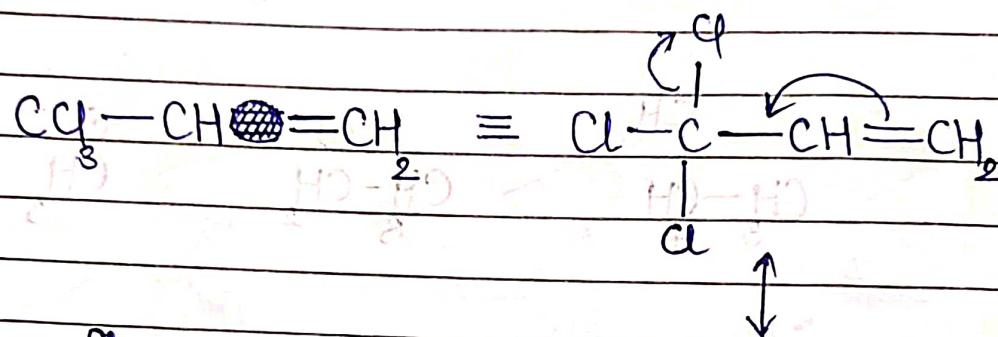


$$b > a > d > c$$

## Reverse Hyperconjugation

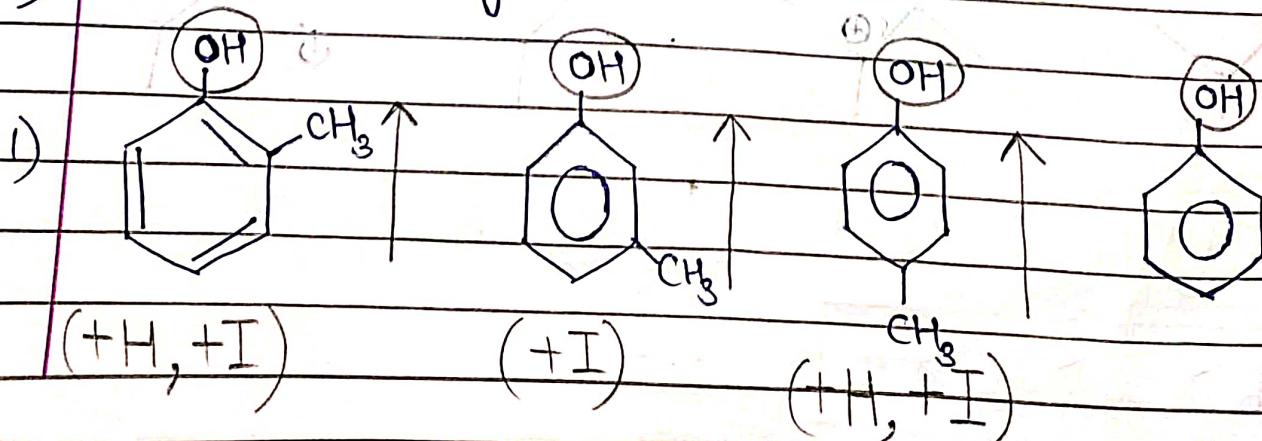
Mostly found in Halogens.

Same cond'n as Hyperconj.  
with added cond'n that  
halogens ion  $\alpha$  carbon.



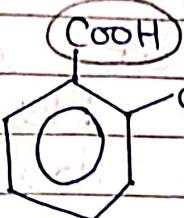
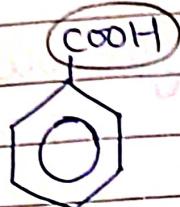
## Application

### 1) Acidic Strength -

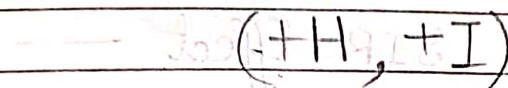


$$d > b > c > a$$

2)



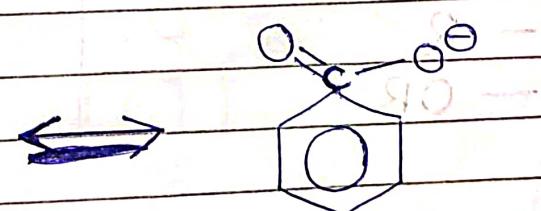
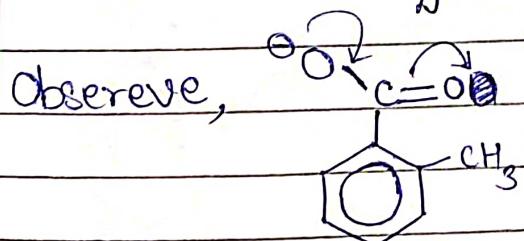
$$a > b$$



But in this case  $a < b$  due to  
Ortho Effect.

Reason:  $\text{COOH}$  &  $\text{CH}_3$  out of each other's plane  $\Rightarrow \text{COOH}$  NOT in conj. with

$\Rightarrow +\text{H}$  effect NOT operate.



are only res. structures  $\Rightarrow$  Their contribution in res. hybrid more.

And as they contain  $\ominus$  on more EN atom  $\Rightarrow$

More stable.

## Ortho Effect

Also called SIR (Steric Inhibition Resonance)

Ring ~~it~~ grps. at ortho post. go out  
of plane  $\Rightarrow$  Mesomeric effect  
does NOT occur.

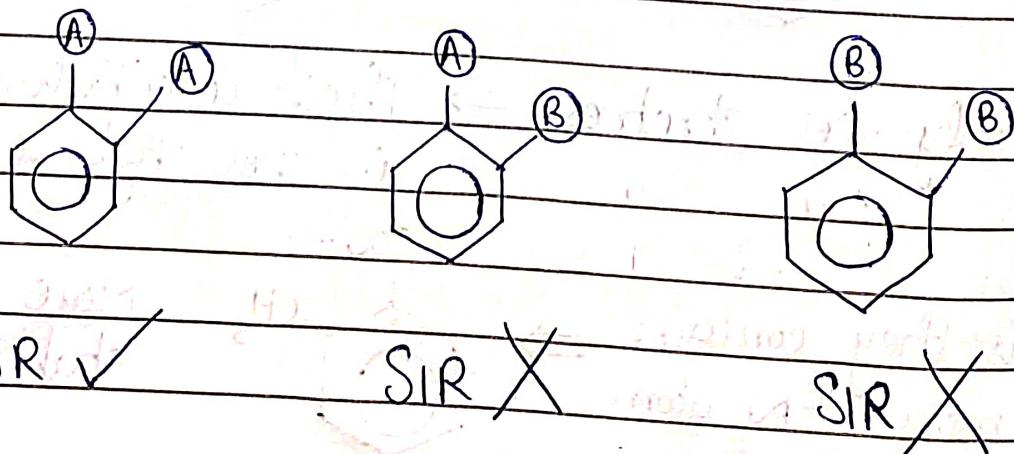
Grps. showing SIR Effect —

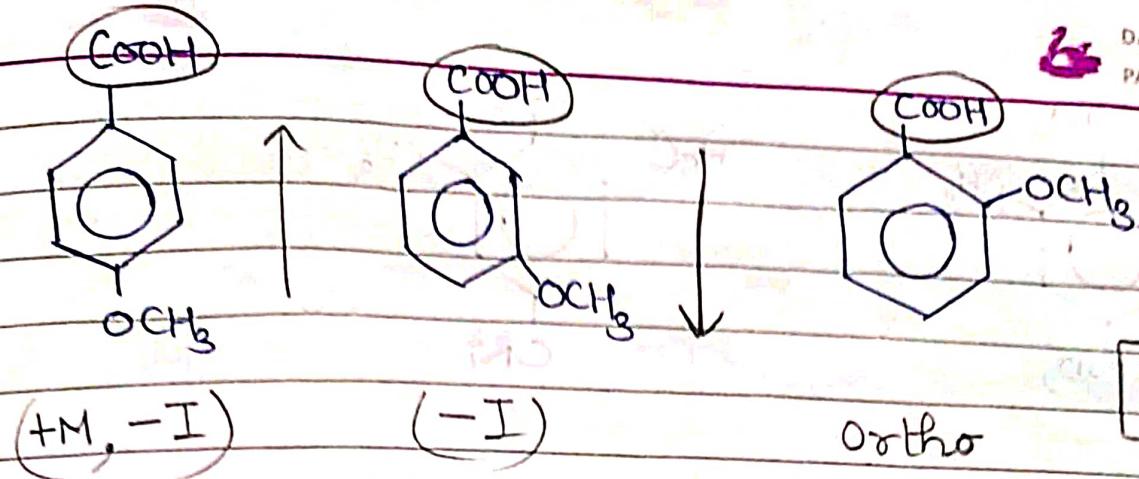
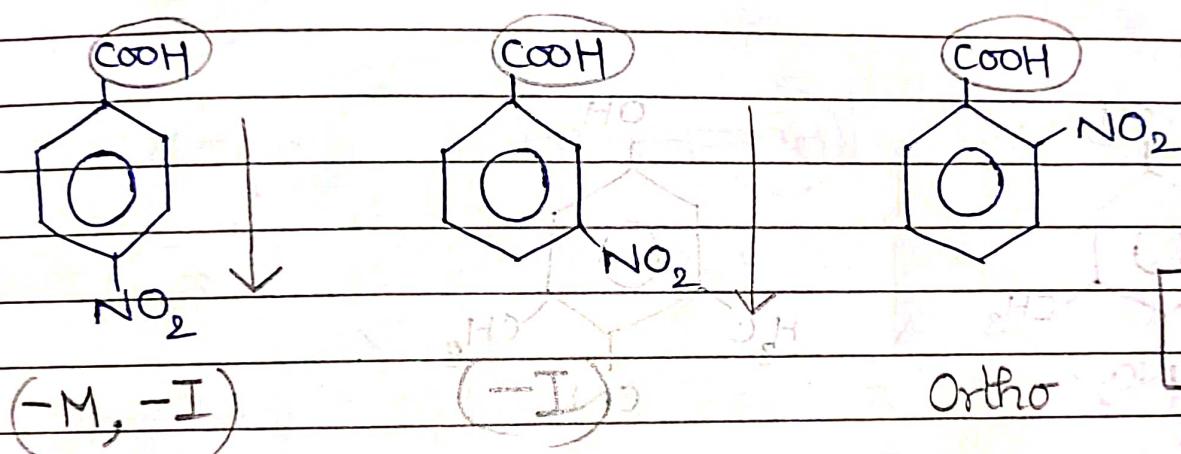
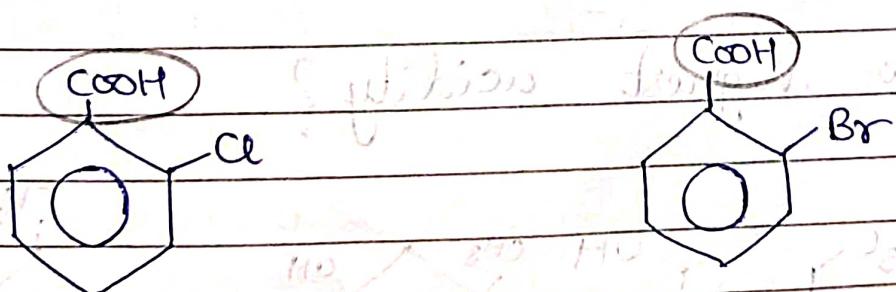
Grp. A

- NR<sub>2</sub>
- COOH
- COX
- CONH<sub>2</sub>
- Cl
- Br
- I
- NO<sub>2</sub>
- R
- OR

Grp. B

- F
- NH<sub>2</sub>
- CN
- OH



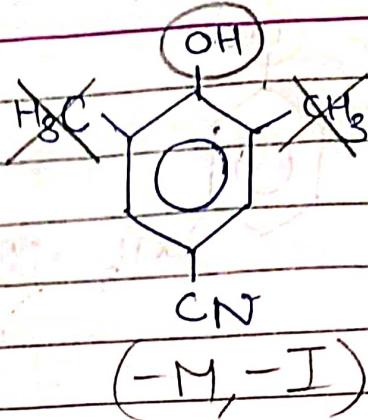
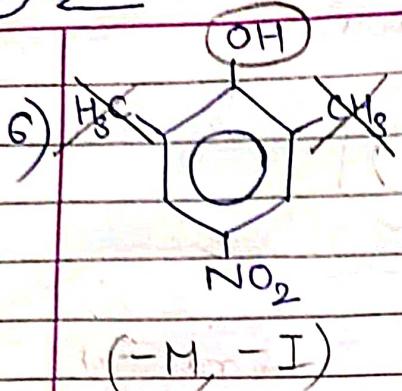
 $c > b > a$  $c > a > b$ 

Both show Ortho effect. But Br more bulky than Cl  $\Rightarrow$  More deviation  $\Rightarrow$  Weaker resonance

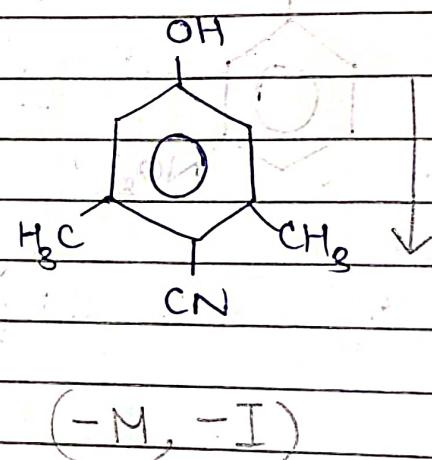
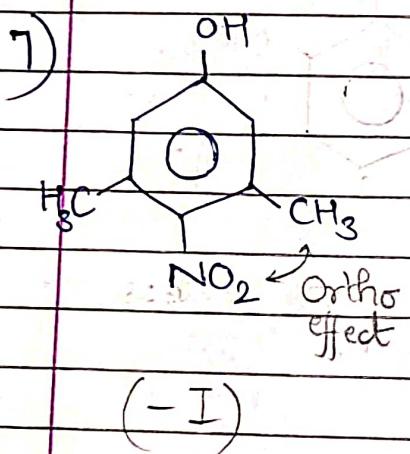
139

(Decide  
Mostly)

acc. to one with higher power.  
prefer EWG.

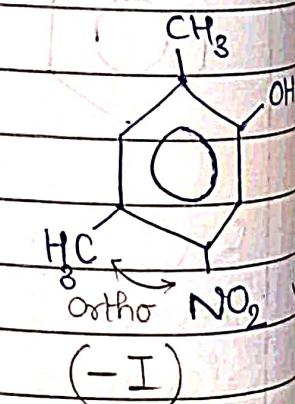
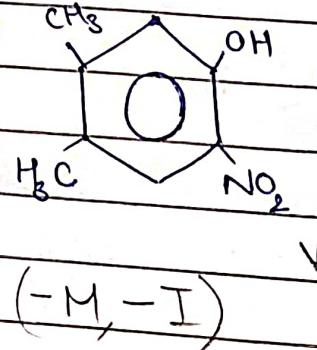
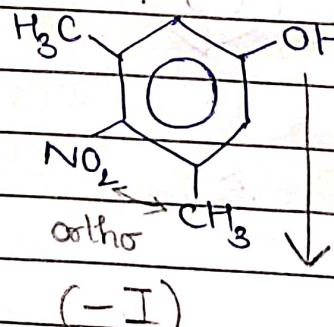
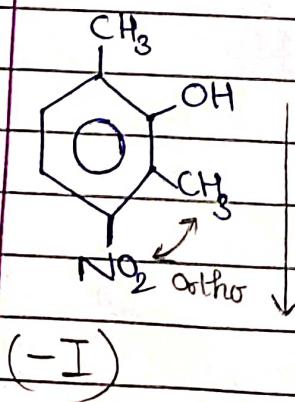


$a > b$



$b > a$

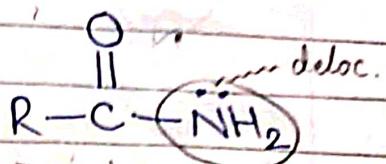
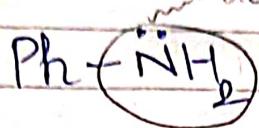
8) Which show highest acidity?



$c > d > a > b$

(CH<sub>3</sub> jiada donor) (NO<sub>2</sub> donor)

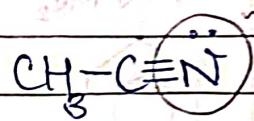
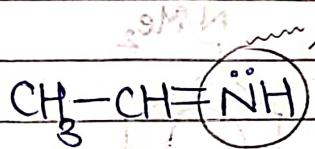
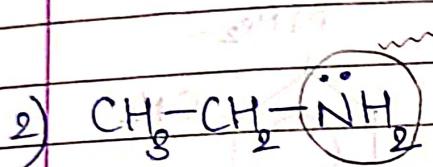
## 2) Basic Strength. -



Loc. l.p.  $\Rightarrow$  Able to give more  
Deloc. l.p.  $\Rightarrow$  Able to give less.

In its res. structures,  
 $\ominus$  on O (more EN) atom  
 $\Rightarrow$  More stable comp.  
 $\Rightarrow$  Less reactive  
 $\Rightarrow$  Less basic

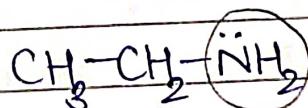
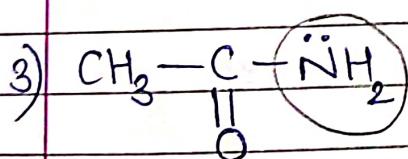
$$\boxed{a > b > c}$$



Can't apply M or I effect  $\Rightarrow$  Think Hyb<sup>n</sup>!

EN:  $\text{sp} > \text{sp}^2 > \text{sp}^3$

EN  $\uparrow \Rightarrow$  NOT release l.p. easily



In its res. structures,

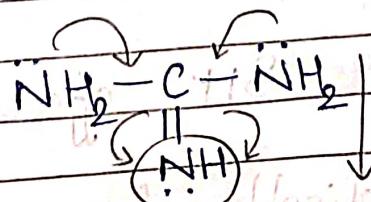
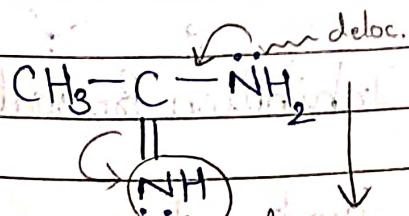
$\ominus$  on O (more EN) atom

$\Rightarrow$  More stable comp.

$\Rightarrow$  Less basic

(+I)

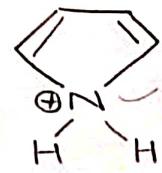
$$\boxed{d > c > b > a}$$



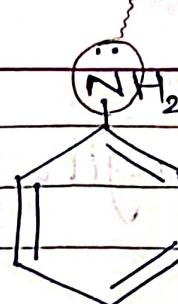
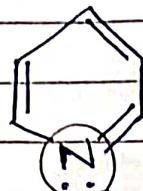
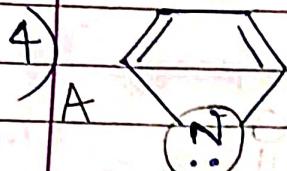
(+M)

(+2M)

134


 $\text{sp}^3 \Rightarrow \text{N.A.}$ 

deloc.

DATE  
PAGE

After gaining  
 $\text{H}^+$ , comp.

becomes N.A.

$\Rightarrow$  Conj. acid less  
 $\Rightarrow$  Less basic. stable

Can give  
easily

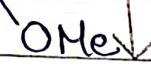
$b > c > a$

5)

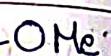
deloc.


 $(+M, -I)$ 

deloc.


 $(-I)$ 

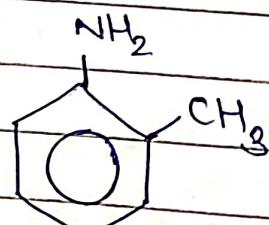
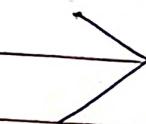
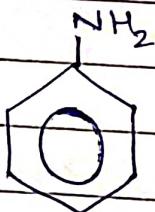
deloc.


 $\text{Ortho}$ 

$c > a > b$



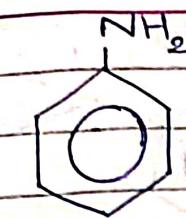
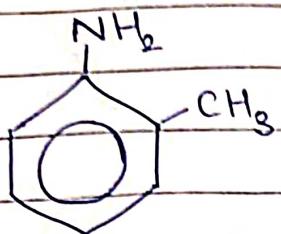
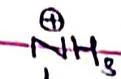
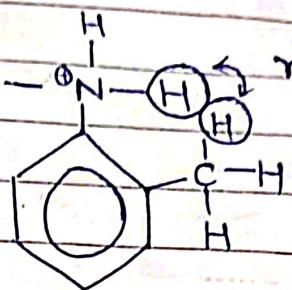
6)



Reason :

SIP effect (Steric Inhibition Protonation)

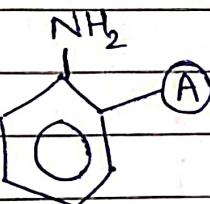
Only applicable for  $-\text{NH}_2$  that too if gap. present at ortho.

 $H^{\oplus}$  $H^{\oplus}$ 

⇒ Less basic base.



1) SIP works when



bulky grp.

2) If  $\ominus$  charge on more EN atom in ~~any~~ any res. strctre of comp., then no. of res. strctre does NOT matter. It will be more stable.

3) Ring Strain -  $sp^2$  C wants  $120^\circ$ .

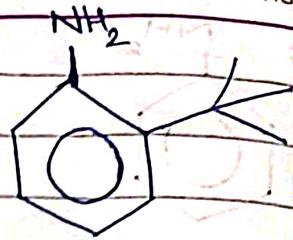
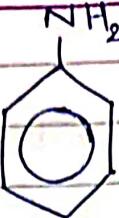
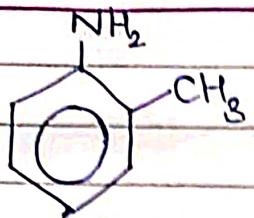
∴ 6 membered ring more stable

4) In basicity, first check if l.p. localised or delocalised.

136

DATE  
PAGE

7)



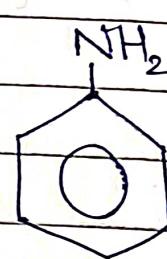
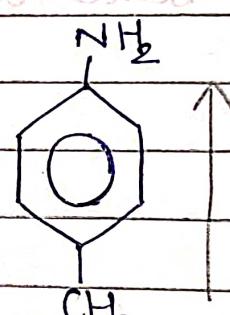
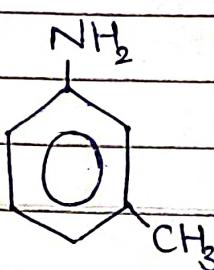
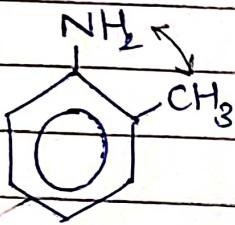
T SIP ✓

H SIP X

SIP ✓

$$b > a > c$$

8)



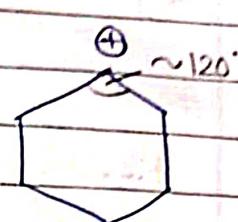
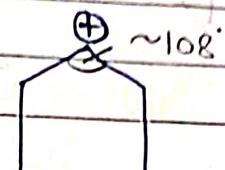
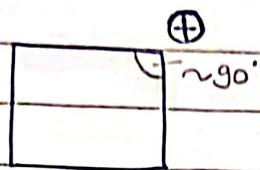
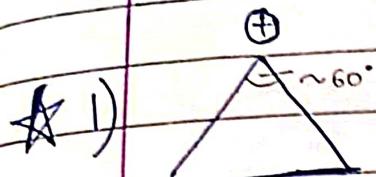
SIP ✓

(+I)

(+M, +I)

$$c > b > d > a$$

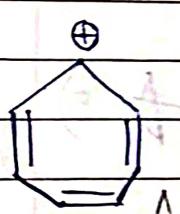
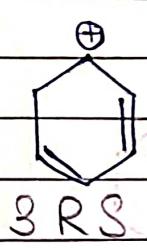
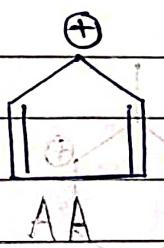
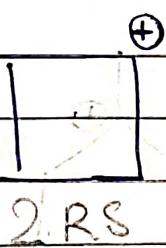
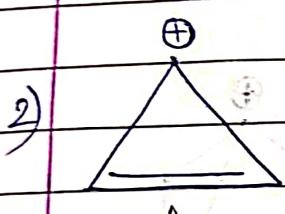
### 3) Stability of Carbocation —



The  $\text{C}^+$  is  $sp^2$   $\Rightarrow$  It wants to have  $120^\circ$

$\left( \begin{array}{l} \uparrow \text{Deviation} \\ \text{from } 120^\circ \end{array} \right) \Rightarrow \left( \begin{array}{l} \uparrow \text{Ring /} \\ \text{Angular Strain} \end{array} \right)$

$$d > c > b > a$$



A.

2 RS

AA

3 RS

A

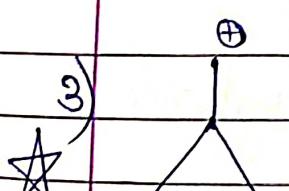
Less conj.

$\Rightarrow$  Less stable

More conj.

$\Rightarrow$  More stable

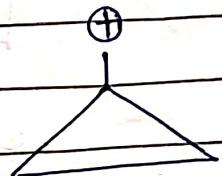
$$e > a > d > b > c$$



Expected:  $b > a$   
Actual:  $a > b$

Cyclopropyl methyl carbocation

A) Reason :

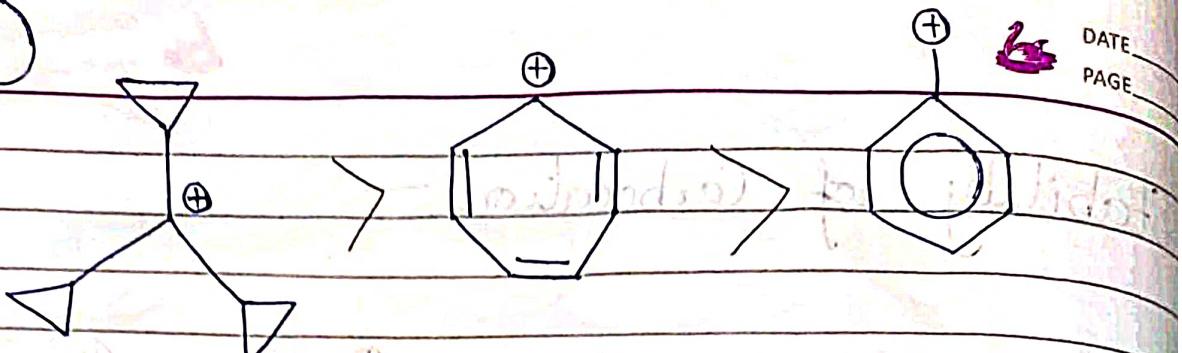


~~It shows~~ Dancing Resonance

38

DATE \_\_\_\_\_  
PAGE \_\_\_\_\_

4)



Dancing Res.

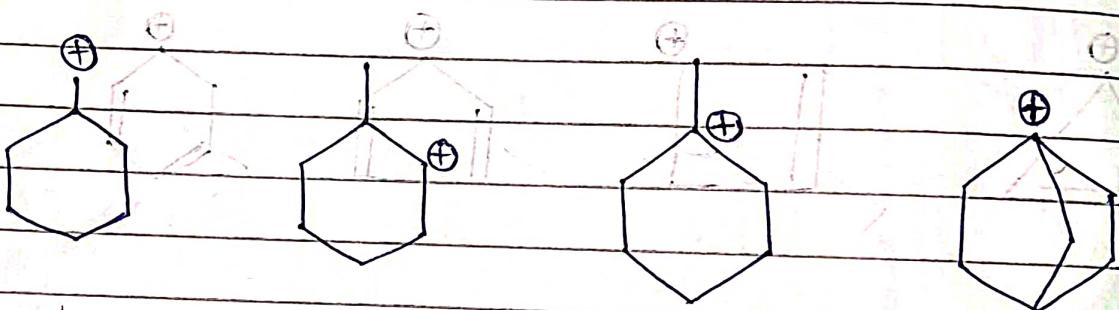
More res.

structures

Less res.

structures

5)

 $(\alpha H)$   
atomsExpected -  $c > d > b > a$ 

Bredt's

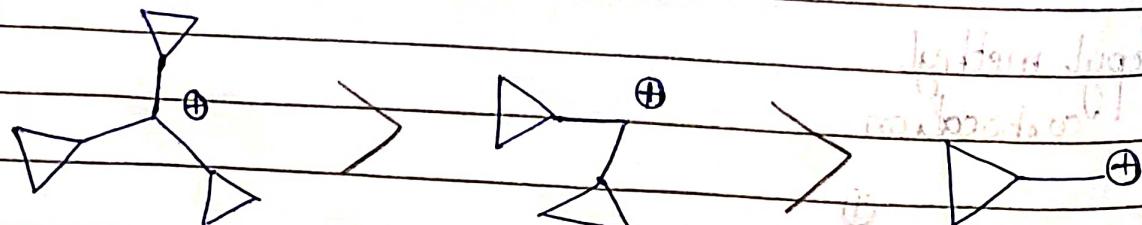
Rule

Actual -  $c > b > a > d$ 

d &lt; b : hindrance



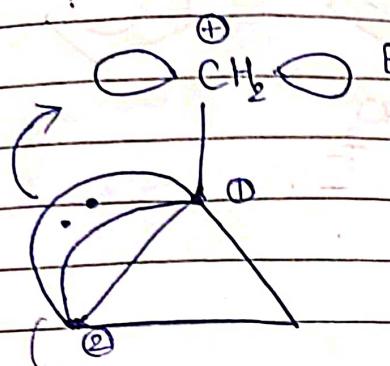
6)



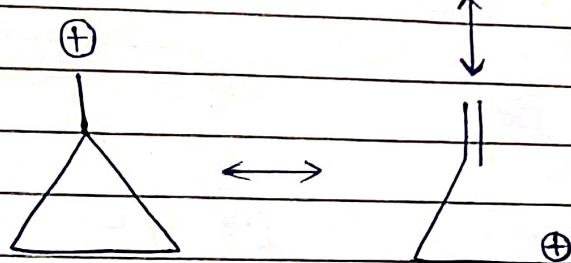
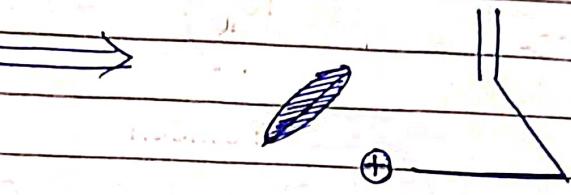
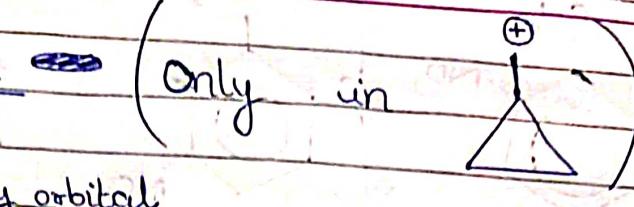
Most Dancing Resonance!

Least Dancing Resonance

## Dancing Resonance (Only in)



①-② bond's  
actual structure



This is HIGHLY stable. (Greater than even Aromatic!!)

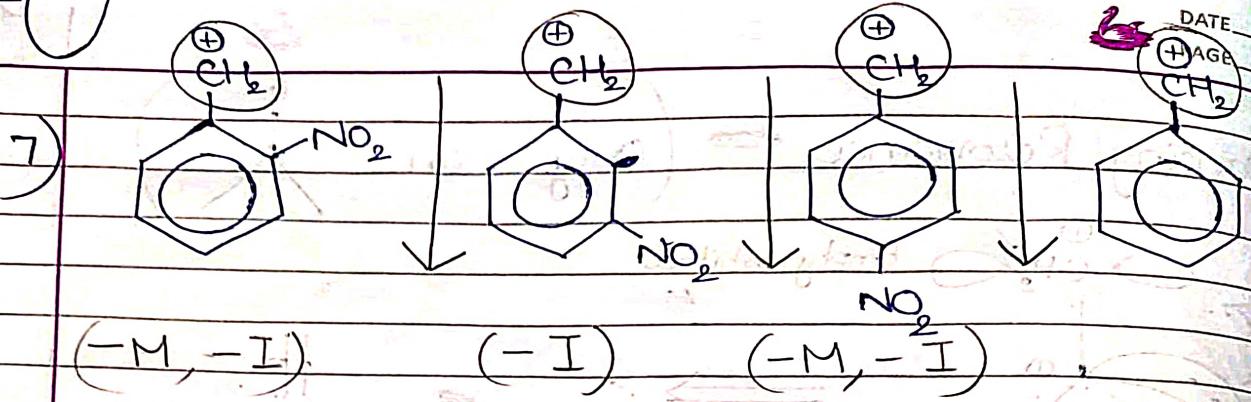
In this  $\sigma$  e<sup>-</sup> show resonance.

## Bredt's Rule

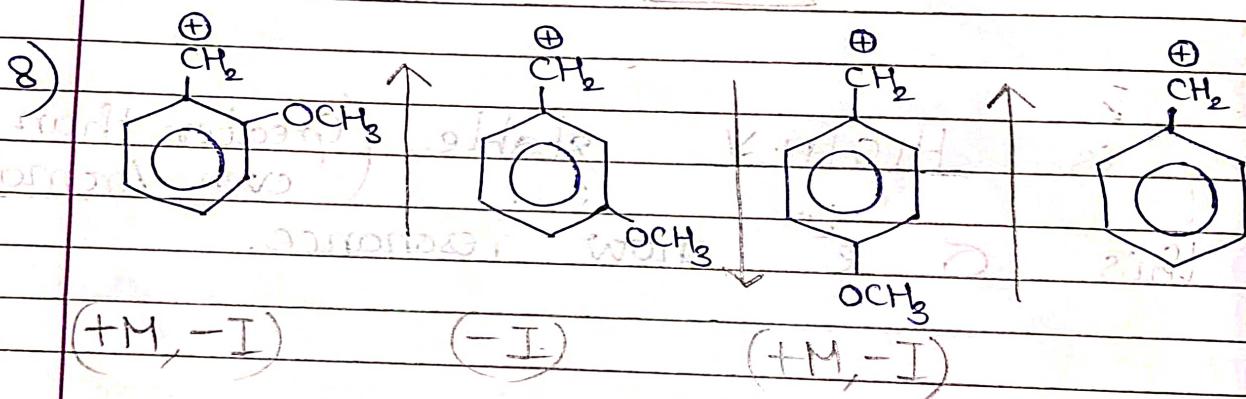
Bridge head C having  $sp^2$

hybrid. is highly unstable, as it loses its planarity.

140

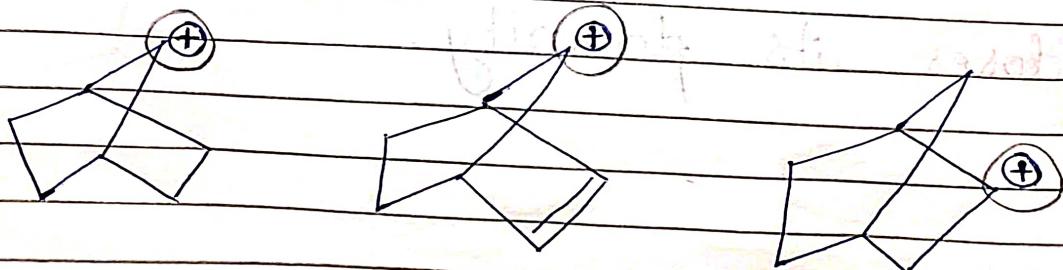


$$d > b > c > a$$

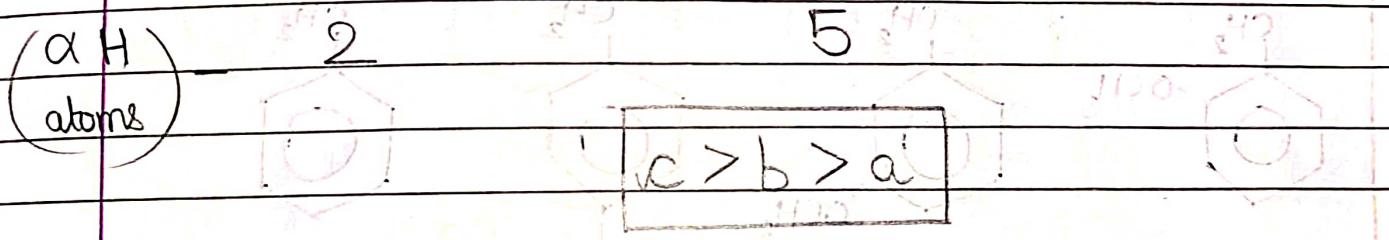
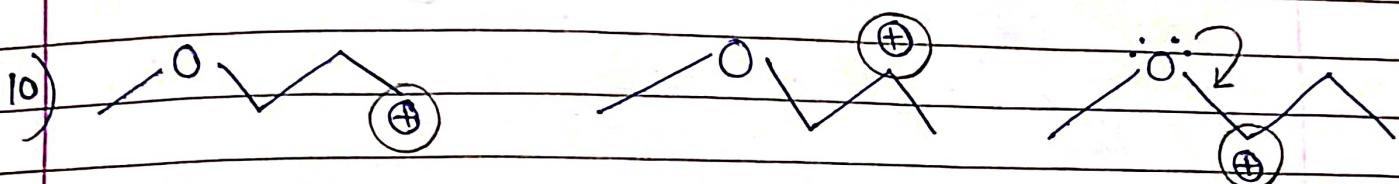
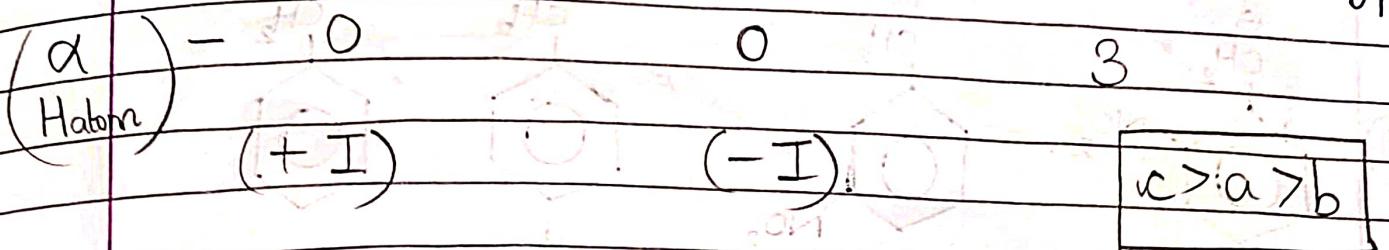


$$c > a > d > b$$

9)



A) Bridge Head Carbon can NOT have bond  $\Rightarrow$  It can't be  $\alpha$  C in Hypercong.



★ 1) In above Q, we could apply +H effect on  $\text{CH}_2^+$  as it is caused by  $\alpha$  H atoms, just presence of  $\text{C}^+$  is req.

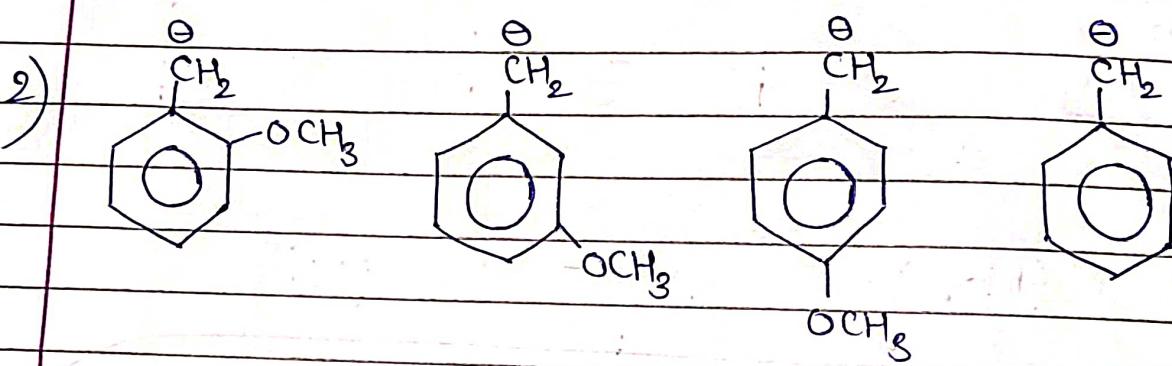
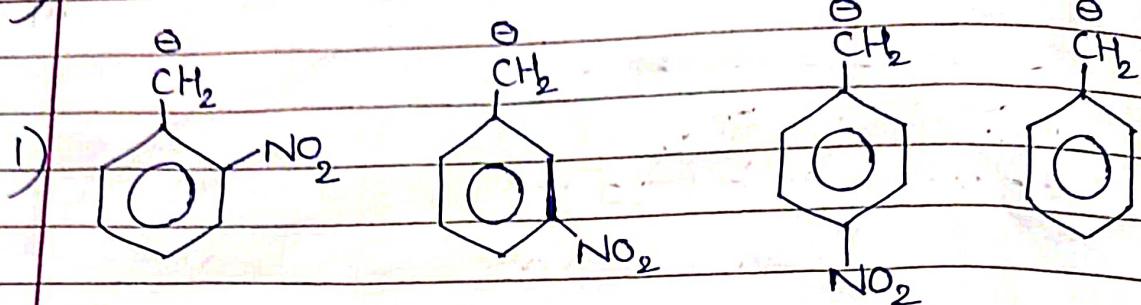
2) Ortho effect NOT operate on  $\text{C}^+$  &  $\text{C}^-$ .

3) When // or / present, check hyb<sup>n</sup> of atoms.

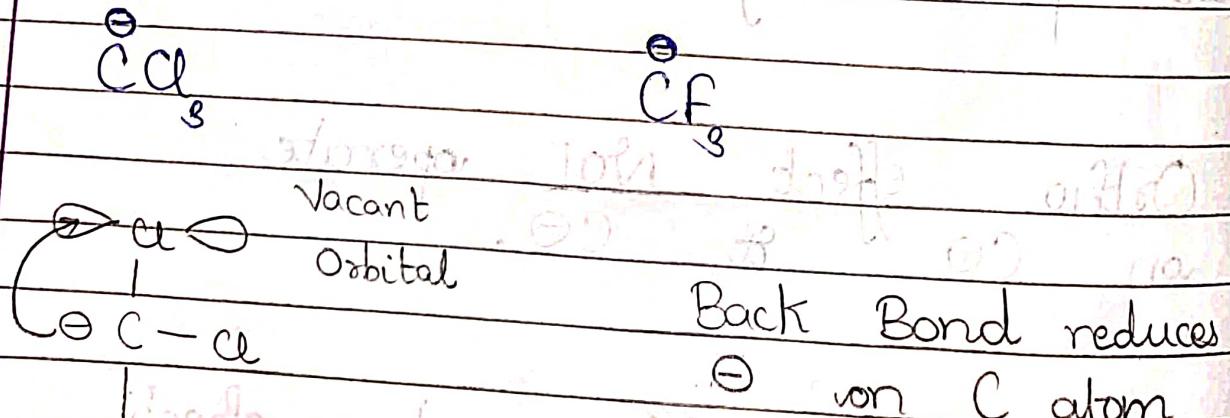
149

DATE  
PAGE

## 4) Stability of Carboanion

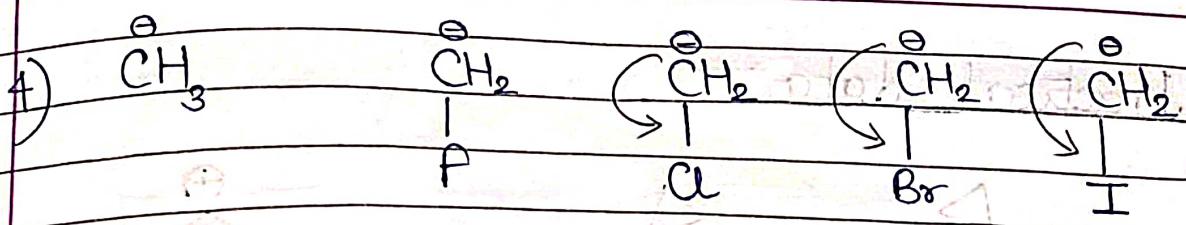


★ 3)



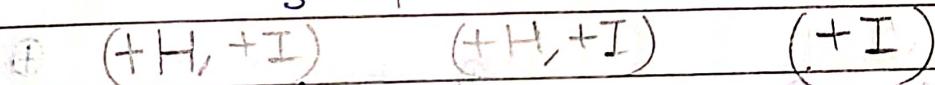
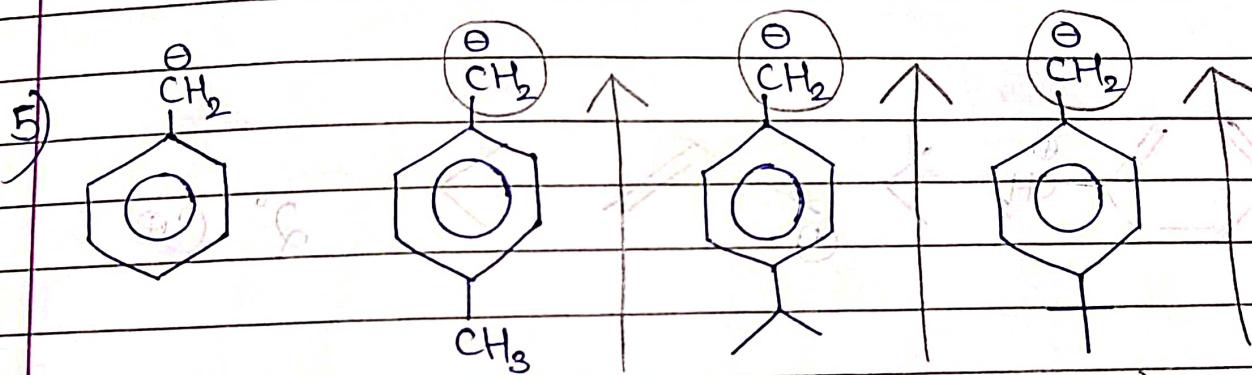


(-I)



$$v_c > d > e > b > a$$

very weak back bond



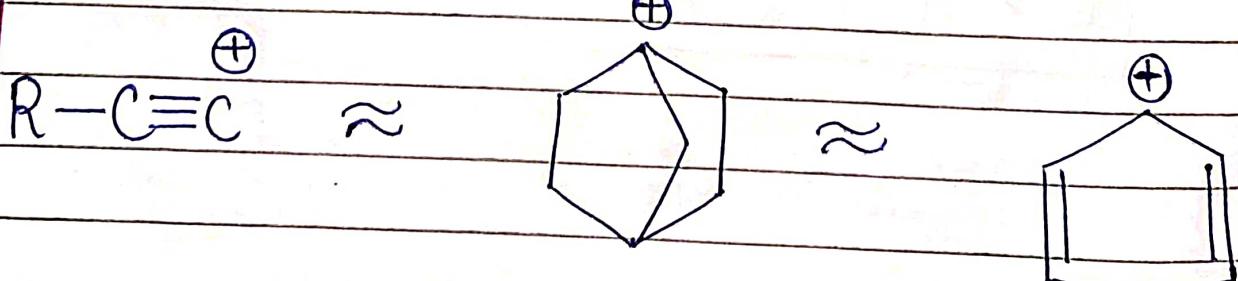
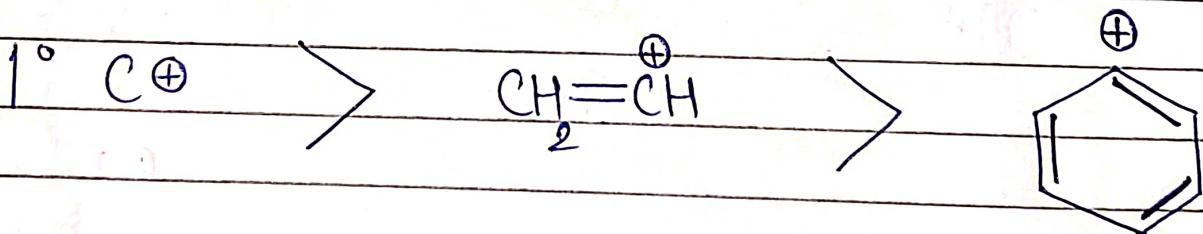
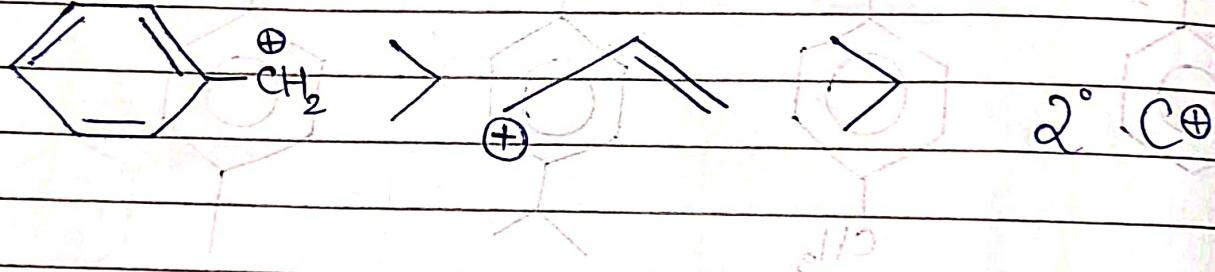
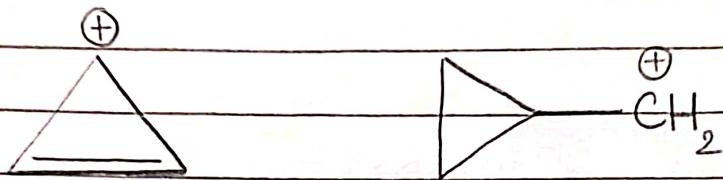
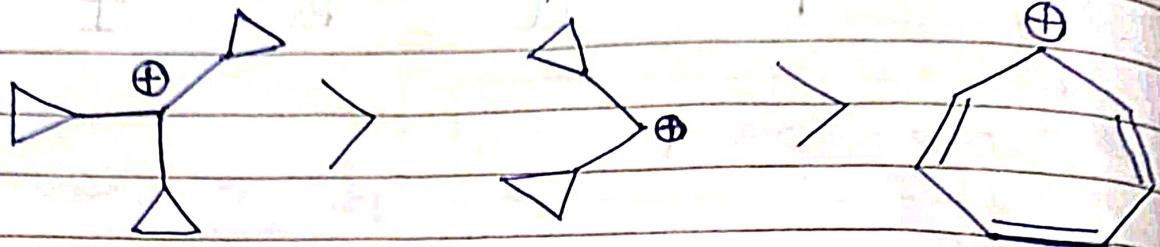
$(\alpha \text{ H})$   
atoms

$$a > d > c > b$$

144

DATE  
PAGE

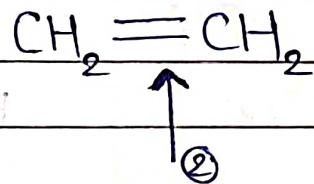
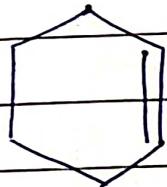
## Practical data



## Bond Length, Bond Order & Bond Diss. Energy

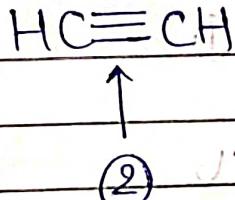
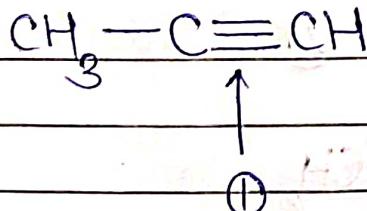
$$\text{B.O.} \propto \text{B.E.} \propto \frac{1}{\text{B.L.}} \propto \text{Stability}$$

In which of the following, indicated bond has less bond energy.



Due to Hyperconj. in ①, it is partial //.

$$\Rightarrow \text{B.O. - } ① < ② \Rightarrow \text{B.E. - } ① < ②$$

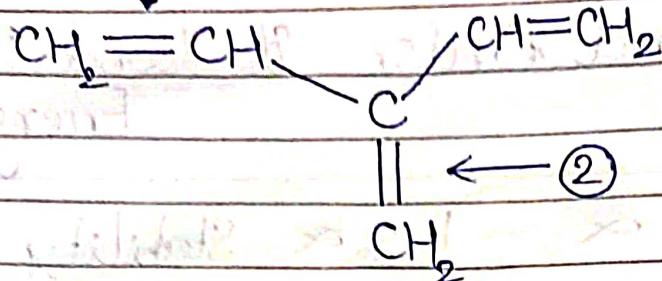


Due to Hyperconj.  $\text{B.E. - } ① < ②$

$$\text{B.O. - } ① < ②$$

46

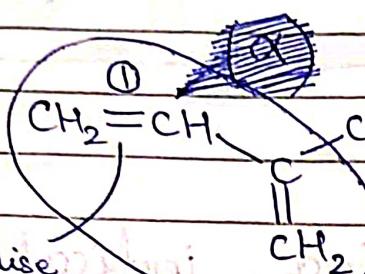
g)



$$\text{B.O.} - ① > ②$$

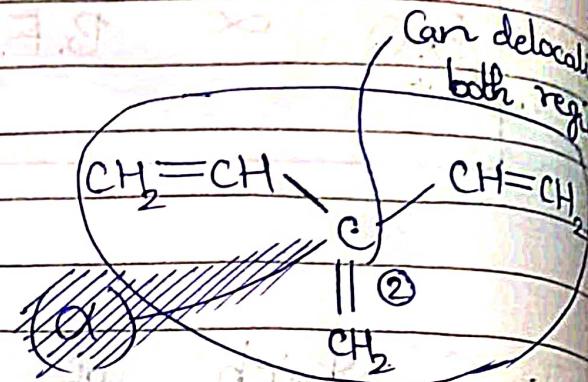
$$\Rightarrow \text{B.E.} - ① > ②$$

A)



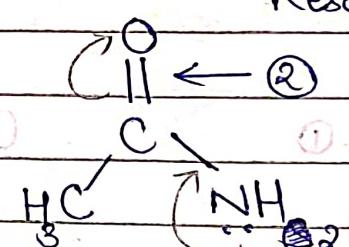
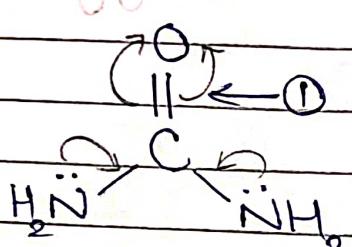
Can delocalise  
only in this  
region

Less Resonance



More Resonance

4)



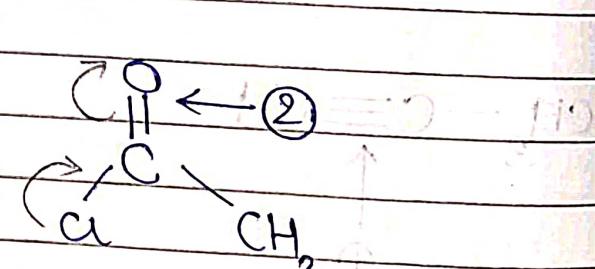
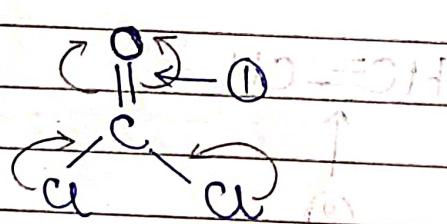
A)

$$\text{B.O.} - ① < ②$$

$$\Rightarrow \text{B.E.} - ① < ②$$

More res. in ① than ②  $> ① - 0.8$

5)

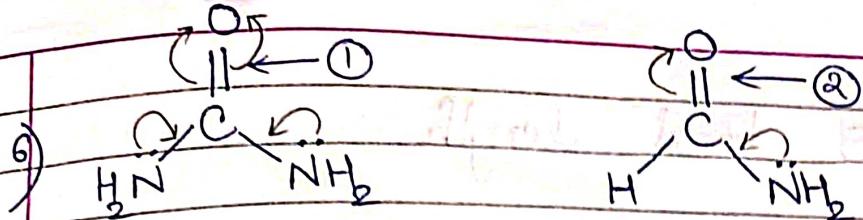


A)

$$\text{B.O.} - ① < ②$$

$$\Rightarrow \text{B.E.} - ① < ②$$

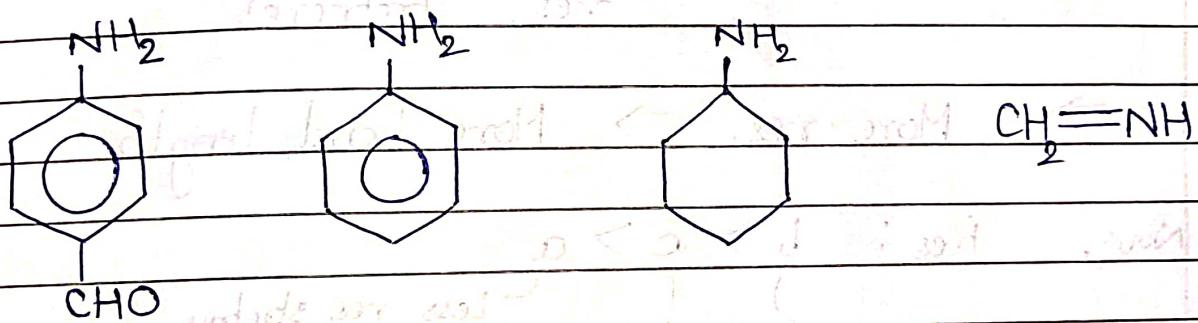
More res. in ① than ②.



A) B.O. - ① < ②  $\Rightarrow$  B.E. - ① < ②

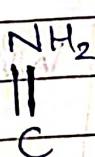
More res. in ① than ②.

Q) Compare CN bond length



- A) (c) has pure single bond.  
 (d) has pure double bond.

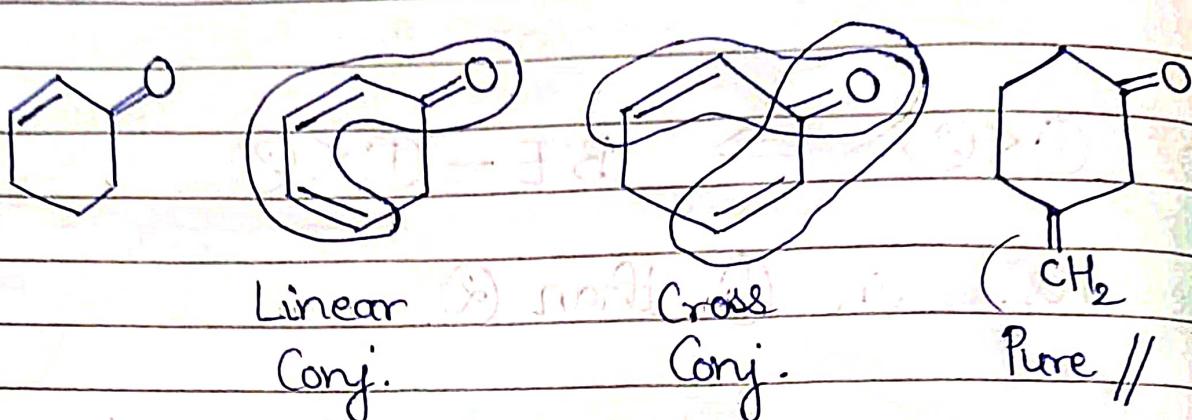
Now, in (a) shows (-M, -I) effect

$\Rightarrow$  More res. structures, each with 

$\Rightarrow$  (B.O. of C-N)  $\bullet$  (a) > (b)

$\Rightarrow$  B.L. - c > b > a > d

Q) Compare CO bond length.



Here, res.  $\leftrightarrow$  // change into / in  
res. structures

More res.  $\rightarrow$  More bond length.

Now, Res.: b > c > a

) ( Less res. structures  
Linear conj.      Cross conj.

$$\Rightarrow \boxed{B.L. - b > c > a > d}$$

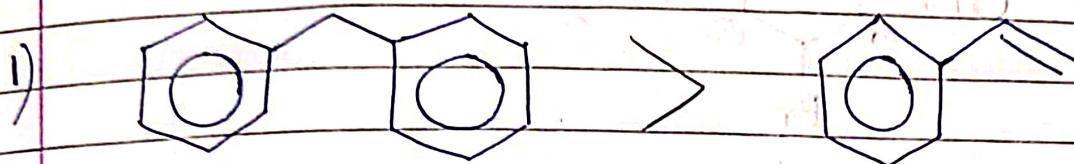
$\star$  When no. of res. structures same,

Stability -

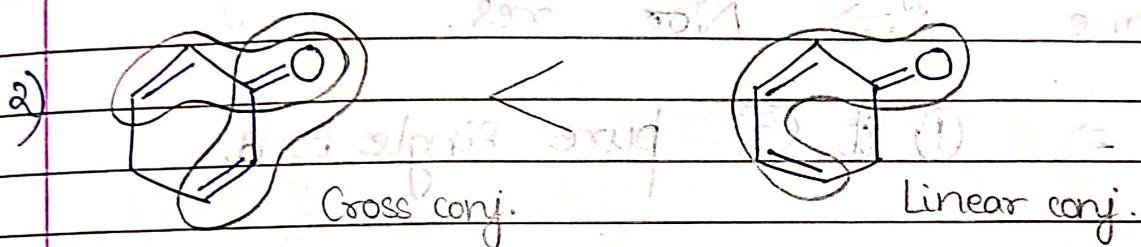
$$\boxed{\begin{array}{c} (\text{Linear}) \\ \text{Conj.} \end{array}} > \boxed{\begin{array}{c} (\text{Cross}) \\ \text{Conj.} \end{array}}$$

$$b < c < d < a$$

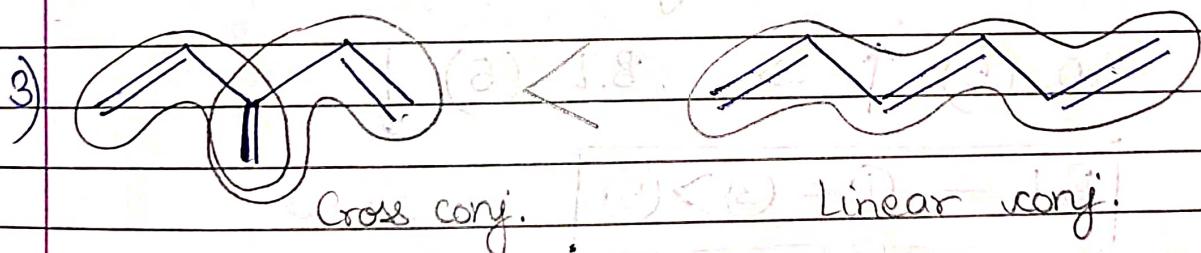
Misc. Q8

Q) Compare res. energy.  $\propto$  (Stability)

Stability - 1 &gt; 2 as more aromatic rings



Stability - 1 &lt; 2 as 29.6 kcal/mole (2) is resonance off



Stability - 1 &lt; 2

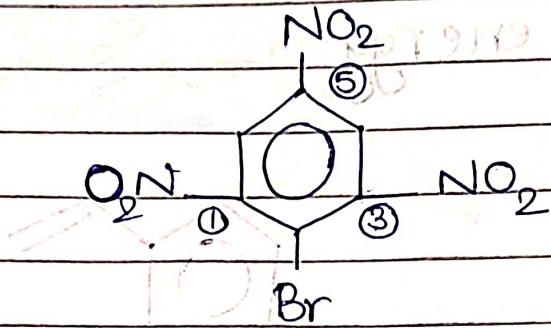
★ 1) If in comparing acidity or basicity, if f'x'al grp diff, then compare using f'x'al grp.

2) Basicity dec. both along period & down grp.

150

DATE  
PAGE

Q) Compare bond lengths of CN.



A) By Ortho effect, ① & ③ out of plane  $\Rightarrow$  Non res.  
 $\Rightarrow$  ① & ③ pure single bond

However, ⑤ shows res. with res. strctres having  $C-N \rightsquigarrow C \equiv N$

$\Rightarrow$  B.O. (5)  $\uparrow \Rightarrow$  B.L. (5)  $\downarrow$

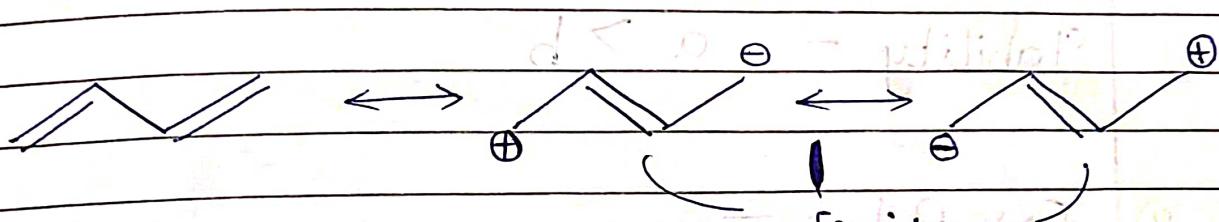
$$\Rightarrow B.L. - ① = ③ > ⑤$$

## Stability of Res. Structures

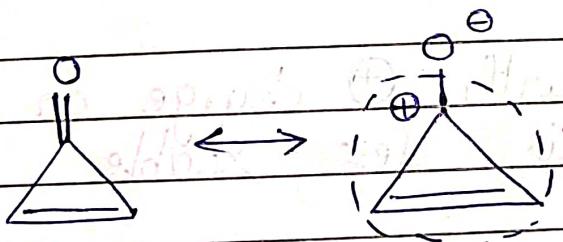
If these rules ~~were~~ NOT apply, then use earlier given priority.

i) Generally, (Neutral molecule) more stable than (Charged molecule)

Eg -



Stability -  $a > b = c$



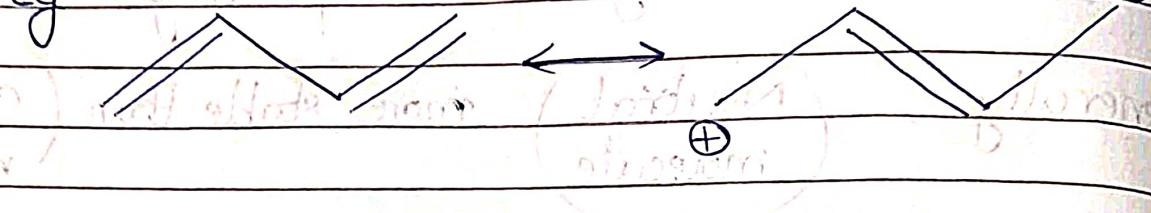
i) Aromatic

$\Rightarrow$  Stability -  $b > a$  even though charges in  $b$

So above rule NOT followed.

2) Res. structure having more no. of covalent bonds is more stable.

Eg - nitroso & nitrogen nitroxyl

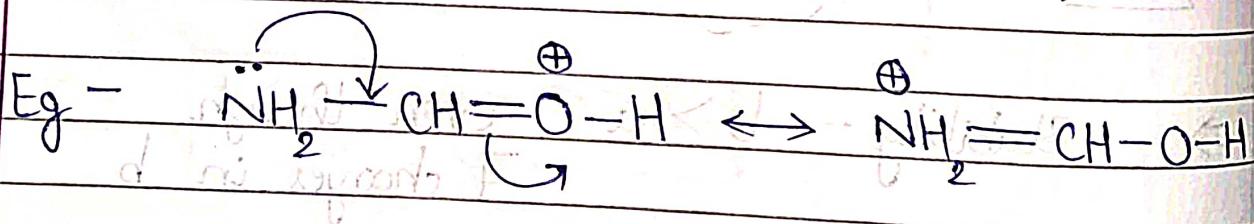


Stability -  $a > b$

3) EN Rule -

Res. structure, with  $\ominus$  charge on more EN atom, is more stable.

Similarly, R.S. with  $\oplus$  charge on more EN atoms is less stable.

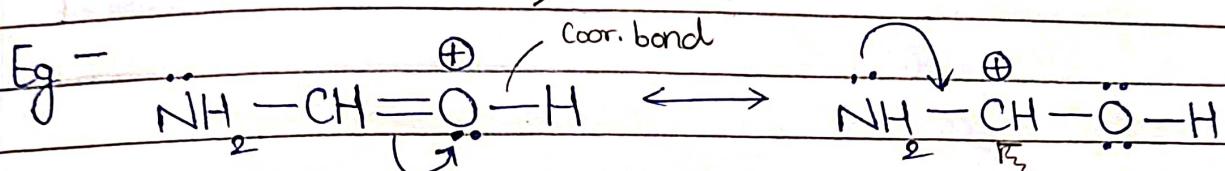


Stability -  $b > a$

## 4) Octet Rule -

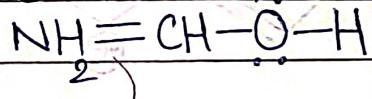
R.S. in which all atoms have complete octet (or duplet) is more stable.

$\Rightarrow$  O octet ✓

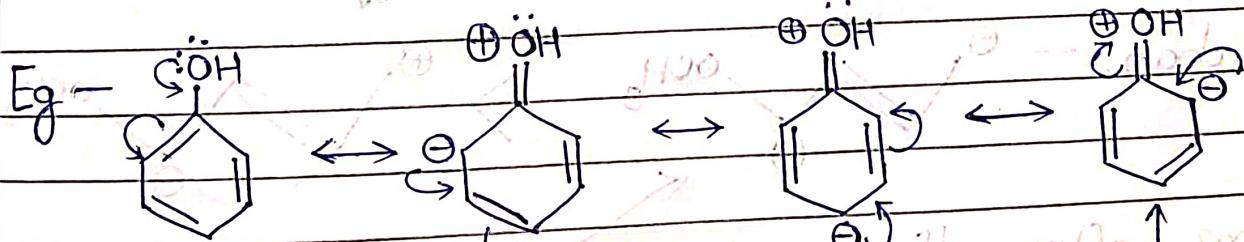


Stability -  $c > a > b$

EN Rule:



coor. bond  $\Rightarrow$  N octet ✓

5) More charge sep.  $\Rightarrow$  Lesser stability

Stability -  $a = e > b = d > c$

Charge sep.



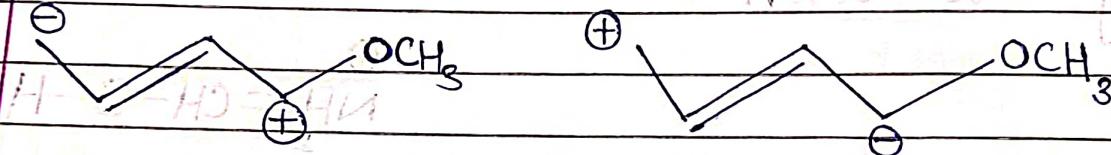
Priority Order —

Aromatic > Mesomeric > Neutral {1,2} >

Octet > EN > Charge Sep.

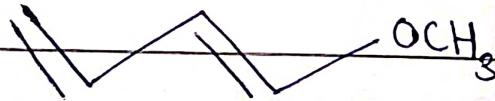
(Q)

Which is more stable?



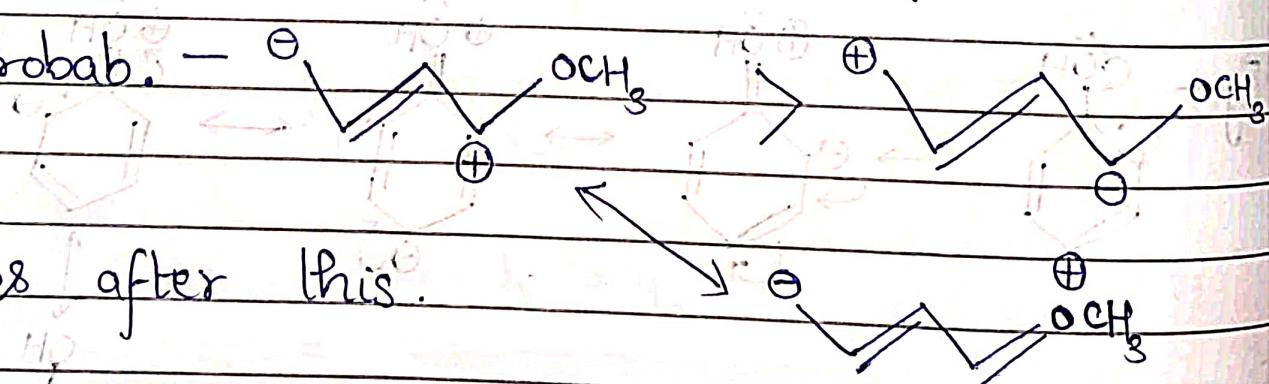
A)

Both res. structures of



Since  $-OCH_3$  show +M effect,

Probab.



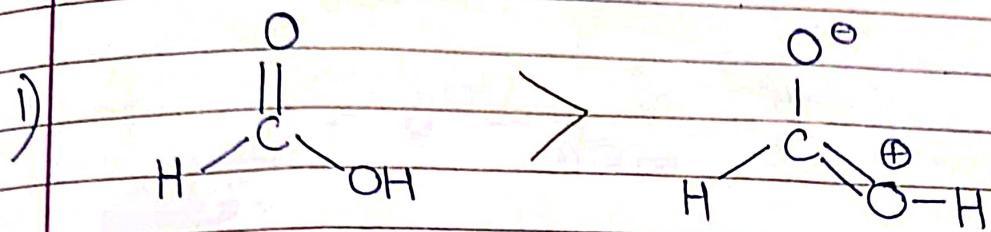
bcoz after this.

Since 'b' not follow Mesomeric effect,

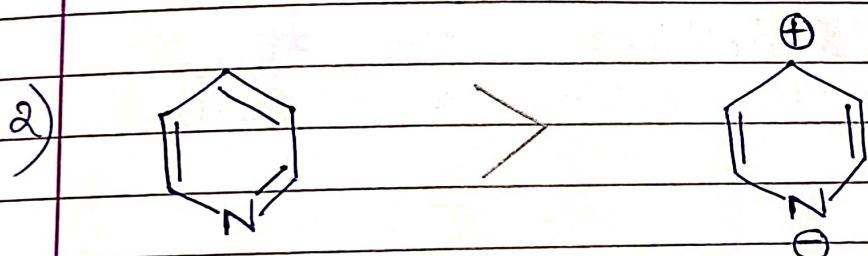
Stability —

$$a > b$$

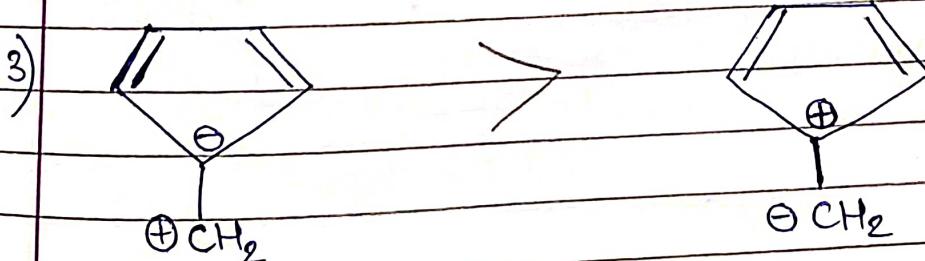
Q) Which is more stable?



Neutral

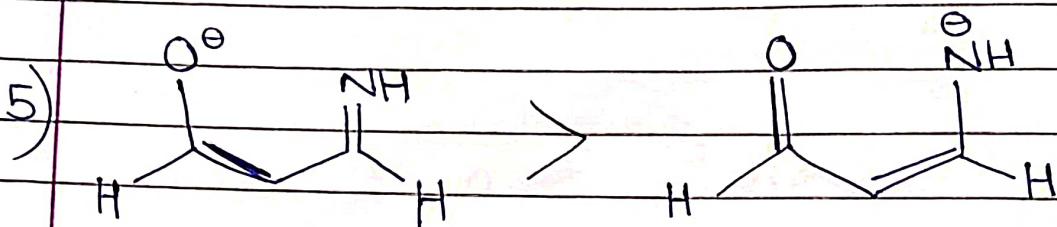
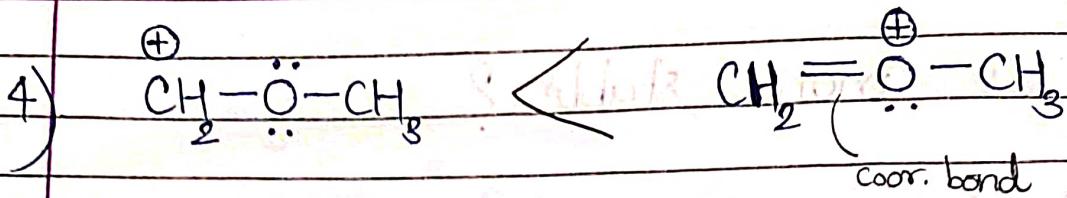


Neutral

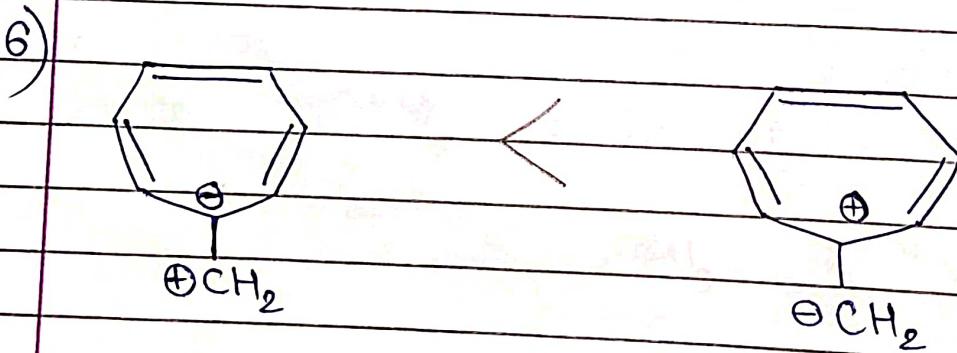


Aromatic

156

DATE  
PAGE

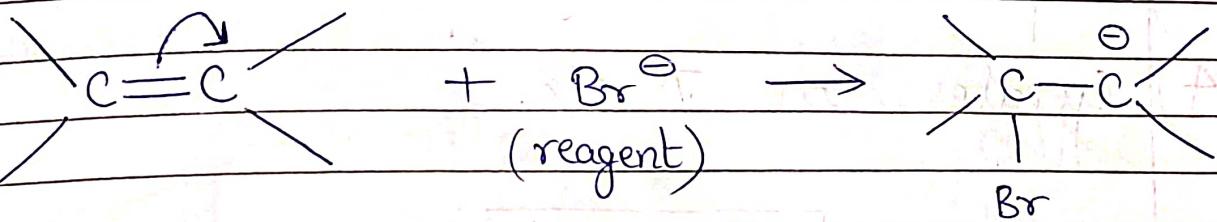
En Rule



Aromatic

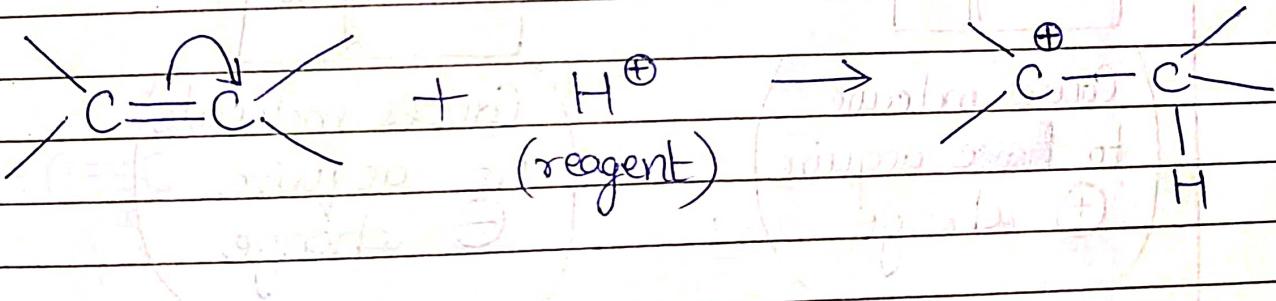
## Electromeric Effect

Shifting of  $\pi e^-$  cloud in presence of reagent to one of the bonded atoms is known as electromeric effect.



Since, reagent attack on atom from which  $e^-$  cloud is AWAY

$$\Rightarrow -E$$



Since, reagent attack on atom TOWARDS which  $e^-$  cloud shifts

$$\Rightarrow +E$$

## Characteristics -

- 1) Temporary effect.
- 2) NOT transmitted (like I effect)
- 3) Depends on reagent.
- 4) Operates on  $\pi$  electrons.

### Electromeric Effect

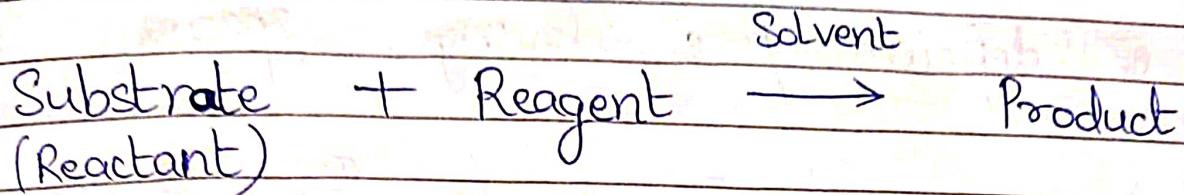
+E effect

-E effect

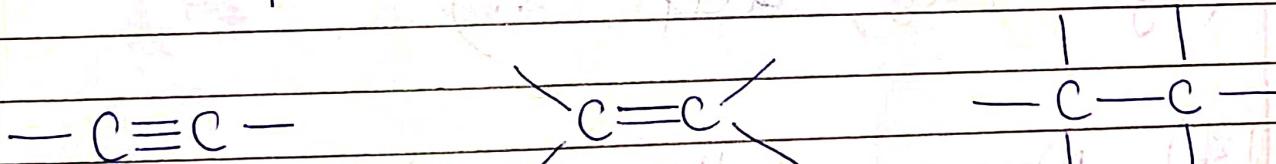
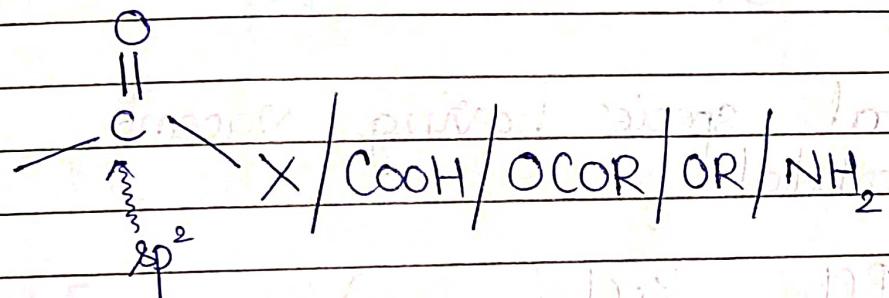
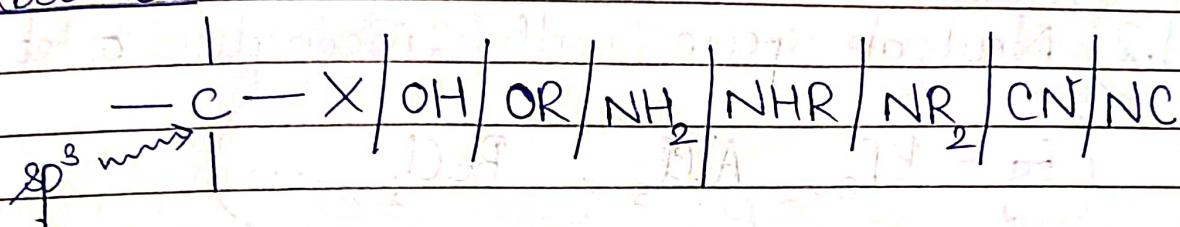
Causes molecule  
to ~~acquire~~  
 $(+)$  charge

Causes molecule  
to acquire  
 $(-)$  charge

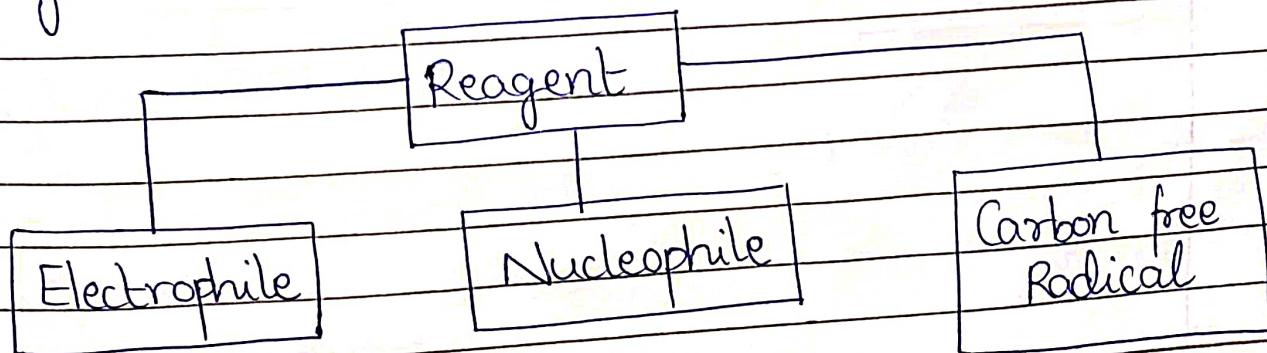
# Reaction Mechanism



Substrate -



Reagent -



1) Electrophile :-

$e^-$  deficient /  $e^-$  loving species.

1.1)  $\oplus$  charged species. (Eg -  $\text{CH}_3^+$ ,  $\text{H}^+$ ,  $\text{Cl}^+$ , ...)

1.2) Neutral species with incomplete octet.

(Eg -  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{BeCl}_2$ , ...)

1.3) Neutral species having vacant d-orbital.

(Eg -  $\text{PCl}_5$ ,  $\text{SiCl}_4$ , ...)

1.4) Non-metallic oxides.

(Eg -  $\text{CO}_2$ ,  $\text{SO}_3$ , ...)

Nucleophile :-

e<sup>-</sup> rich / nucleus loving species.

2.1)  $\Theta^-$  charged species. (Eg - Cl<sup>-</sup>, CH<sub>3</sub><sup>-</sup>, ...)

2.2)  $\oplus$  charged Neutral species having at least 1 lp.

(Eg - PCl<sub>3</sub>, NH<sub>3</sub>, H<sub>2</sub>O, NH<sub>2</sub> NH<sub>2</sub>, ...)

2.3) Multiple bonded system.

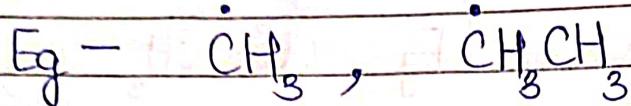
(Eg - Alkene, Alkyne, Benzene derivatives, ...)

Nucleophilicity & Basicity will be discussed later in chapter.

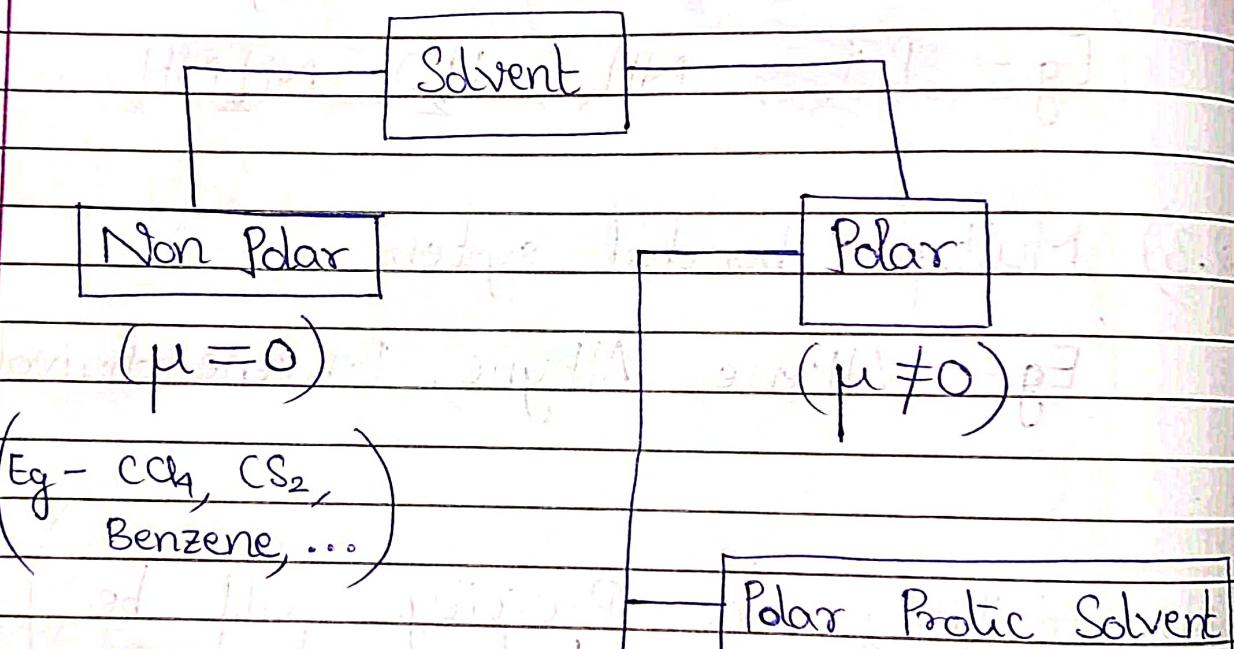
Nucleophile  $\neq$  Base

3) Carbon free radical :-

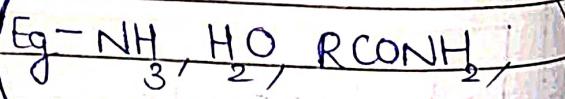
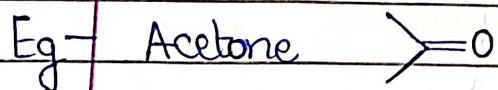
Neutral species having unpair  $e^-$ .  
Formed by homolytic bond fission.



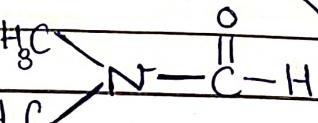
Solvent -



Polar Aprotic Solvent



Dimethyl Sulphoxide (DMSO)



N,N-Dimethylformamide (DMF)

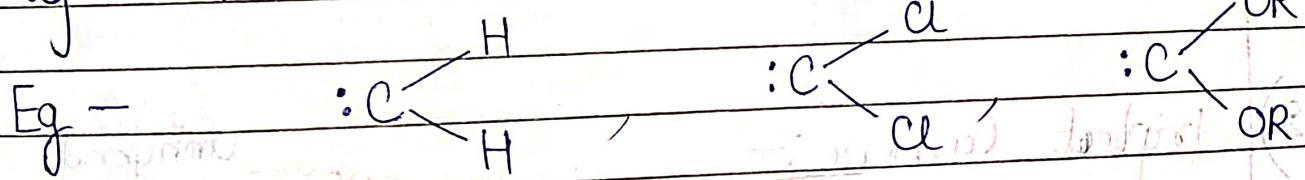
## Reaction Intermediates

They are formed by breaking of covalent bonds. They are short lived, highly unstable & reactive.

- 1) Carbocation
- 2) Carboanion
- 3) Carbon free radical
- 4) Carbene
- 5) Nitrone
- 6) Benzyne

### Carbene

These species are neutral with sextet of  $e^-$ .



They are electron deficient (C has only 6  $e^-$ )

$\Rightarrow$  Electrophiles

Types :-

1) Singlet Carbene :-

Spin multiplicity

$$= 2|s| + 1$$

$$= \textcircled{1} \quad (\text{as } S=0)$$

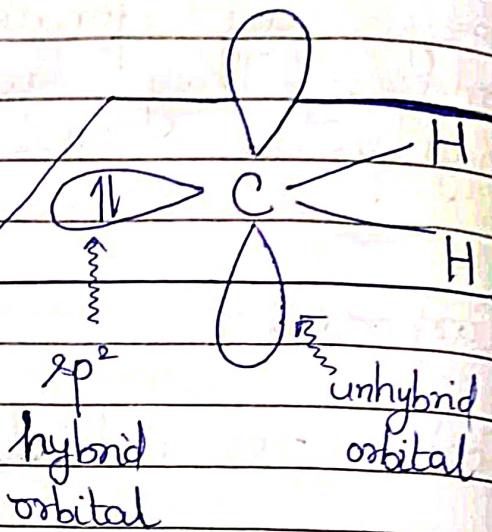
$$C = \boxed{1L} \quad \boxed{1} \quad \boxed{1} \quad \boxed{1}$$

2s      2p

Hyb<sup>n</sup>

$\text{sp}^2$

2p



$\Rightarrow$  No unpair  $e^-$

2) Triplet Carbene :-

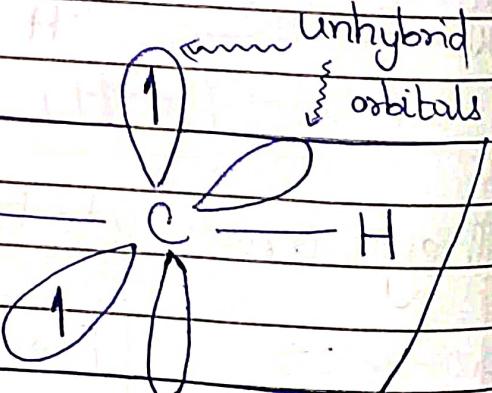
$$C^* \quad \boxed{1} \quad \boxed{1} \quad \boxed{1} \quad \boxed{1}$$

2s      2p

Hyb<sup>n</sup>

$\text{sp}$       2p      2p

H    L    H    L



$\Rightarrow$  2 unpair  $e^-$

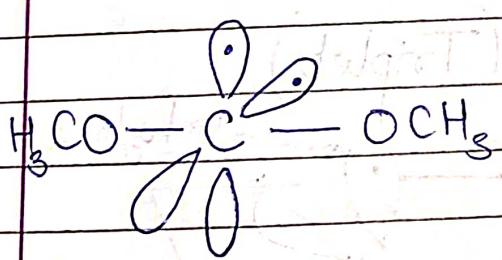
⇒ Spin multiplicity = 3 (as  $S=1$ )

★ Generally, Stability: (Triplet Carbene)  $>$  (Singlet Carbene)

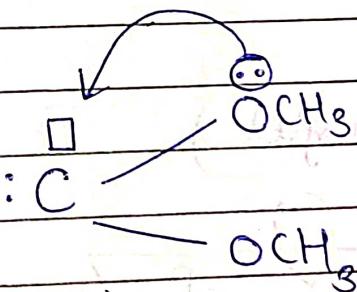
as in ~~the~~ triplet carbene, there is less b.p. - b.p. repulsion.

Except: In case bonded to atom with (l.p.), then in singlet carbene MORE stable.

Reason: Back bond.

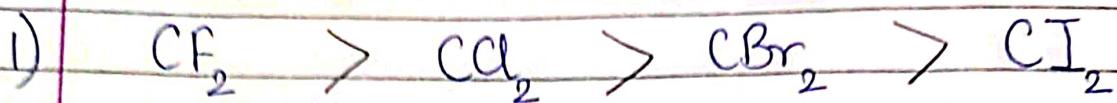


Back Bond X  
(no vacant orbital)



Back Bond ✓  
(vacant orbital)

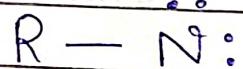
Q) Compare stability.



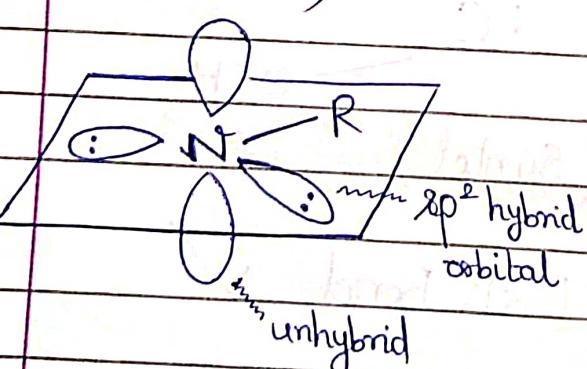
Overlap:  $2p-2p < 2p-3p < 2p-4p < 2p-5p$

### Nitrene

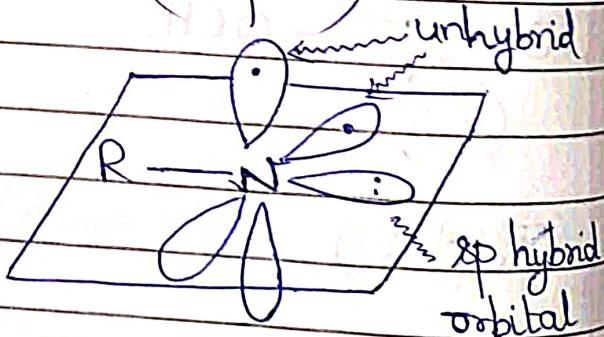
Nitrene is Nitrogen analogue of Carbene



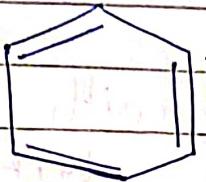
(Singlet)



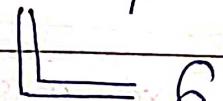
(Triplet)



## Benzyne

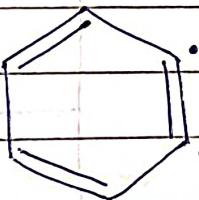


No. of  $sp^2$  C atoms  $\neq 4$



6

Actually  $\equiv$  does NOT exist.



In reality,