

# General Organic Chemistry

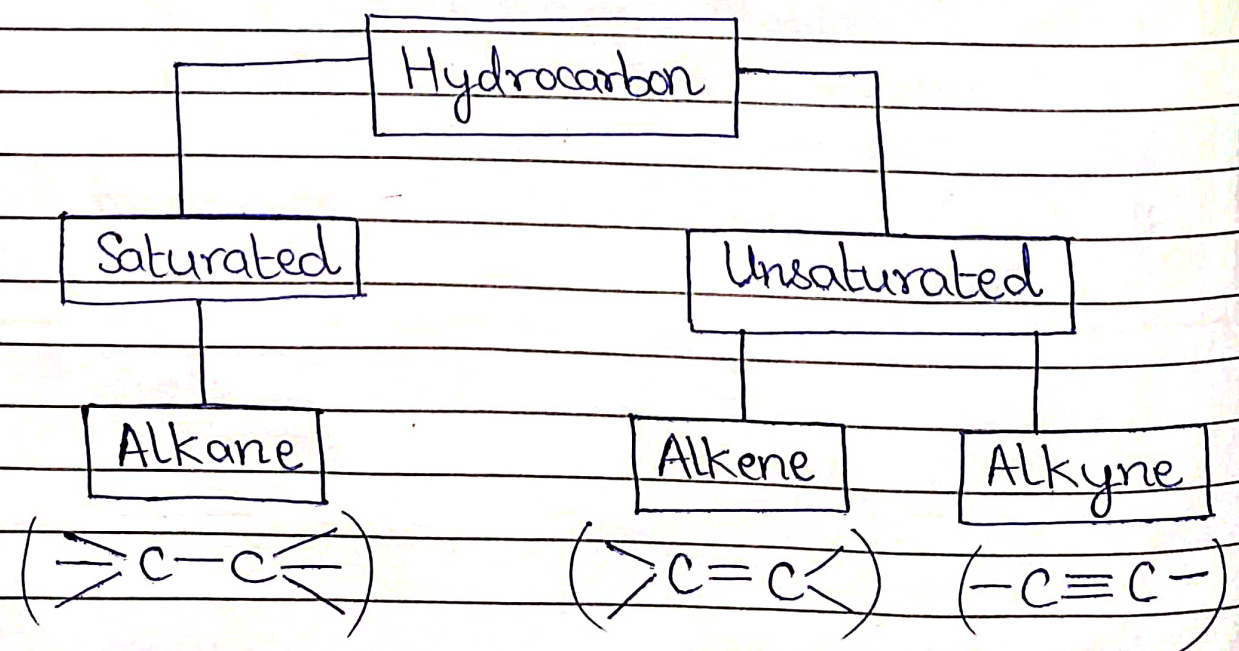
Organic Comps - Hydrocarbons and their derivatives are called organic comps.

Eg:  $CH_4$ ,  $CH_3OH$ ,  $CH_3Cl$ ,  $CH_3CH_3$ , ...

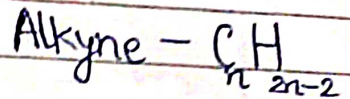
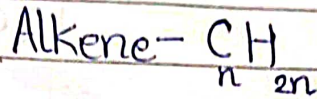


$CCl_4$  is organic

Carbides, carbonates & bicarbonates are inorganic.

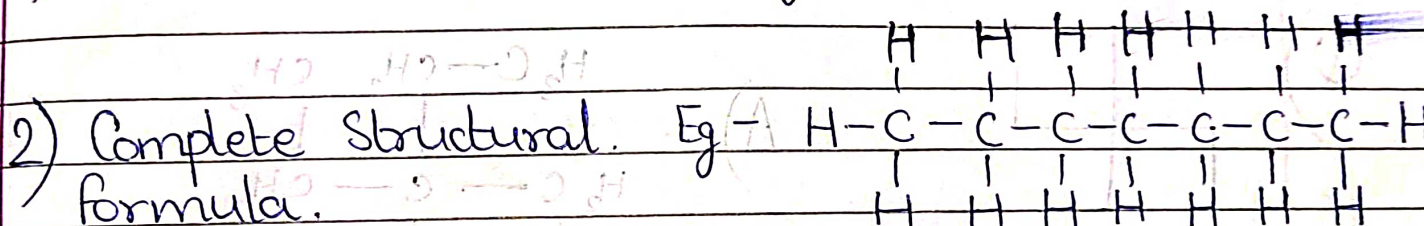


General formula:

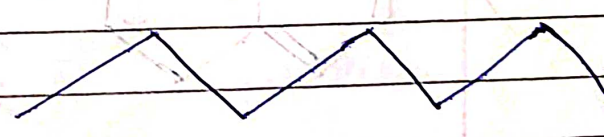


Representation

1) Molecular formula. Eg -  $C_7H_{16}$



3) Condensed Structural formula. Eg -  $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$

4) Bond Line Notation. Eg - 

$(\# \text{ invisible H atoms})$	$=$	$(\text{Valency of Atom})$	$-$	$(\text{No. of Visible bonds})$
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66

Bond Line

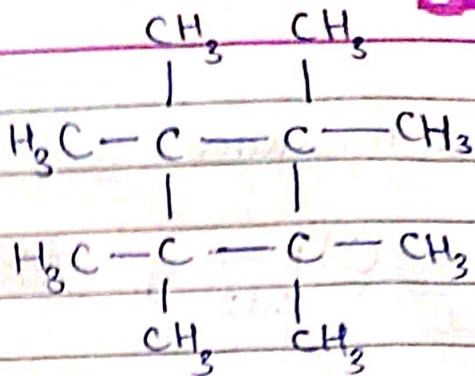
Condensed

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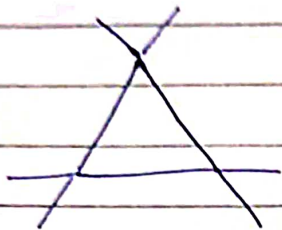
Q)



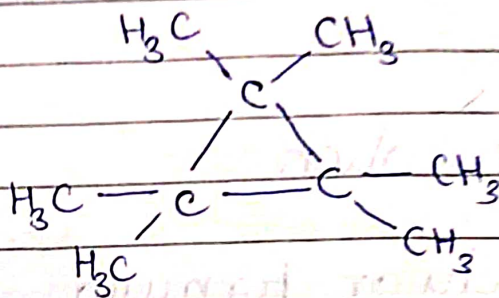
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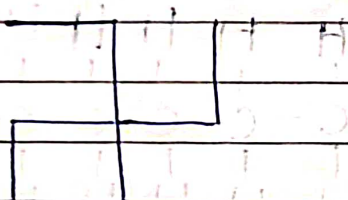
Q)



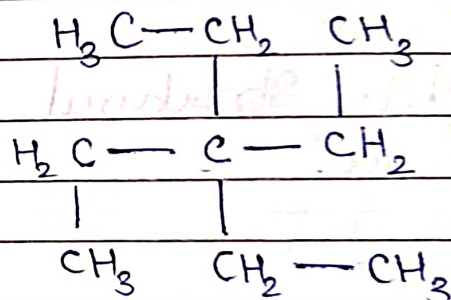
A)



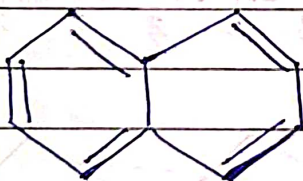
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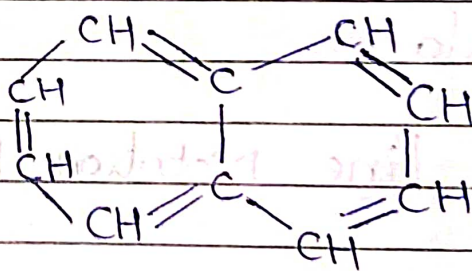
A)



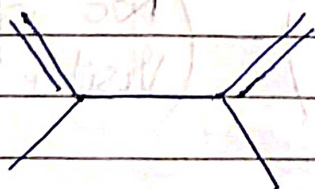
Q)



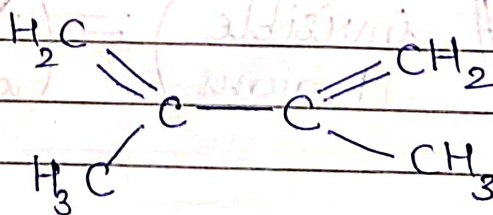
A)



Q)



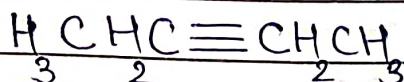
A)



★ Q)



A)

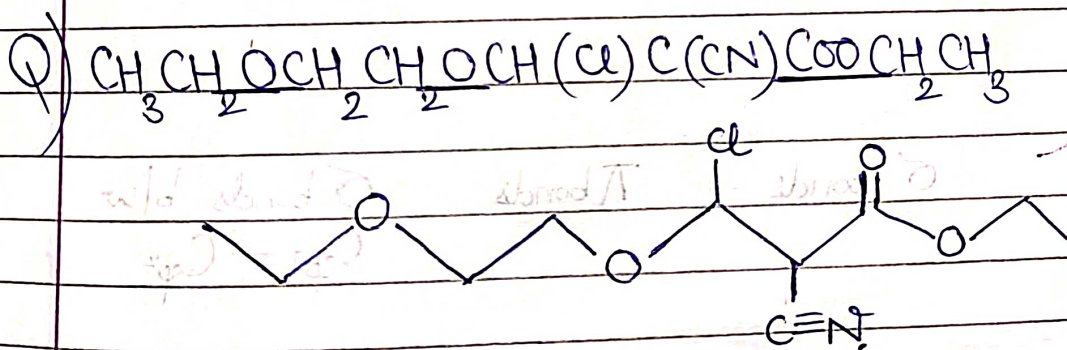
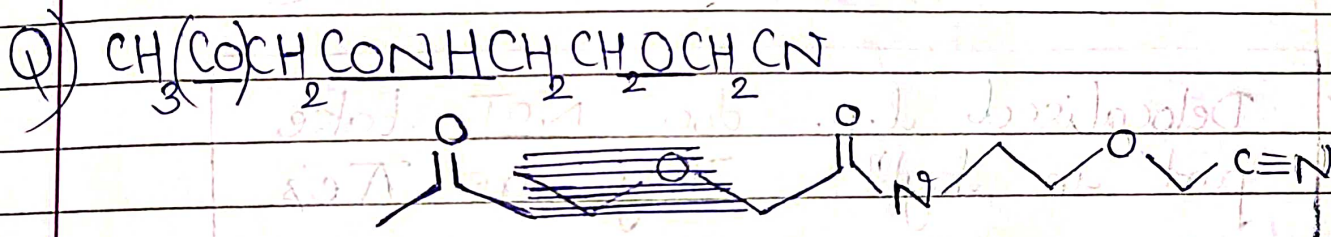
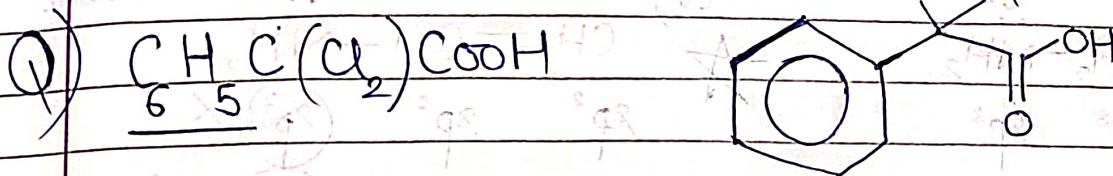
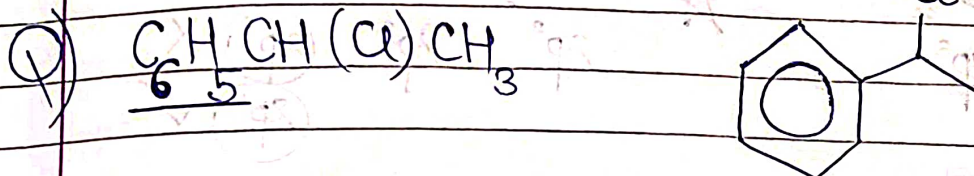
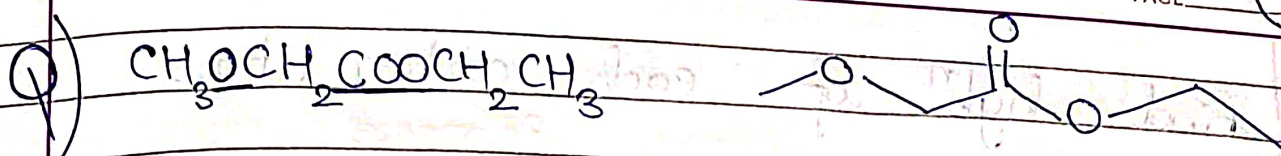


Condensed

Bond Line

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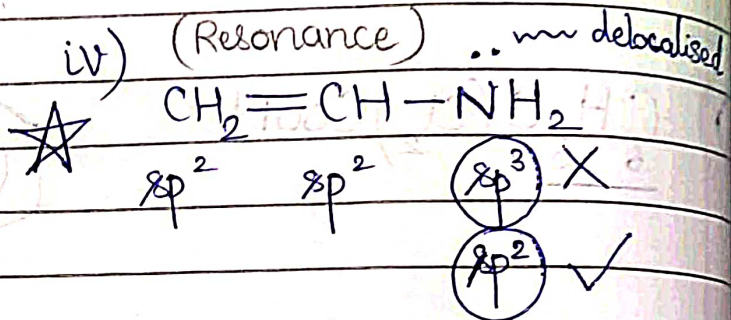
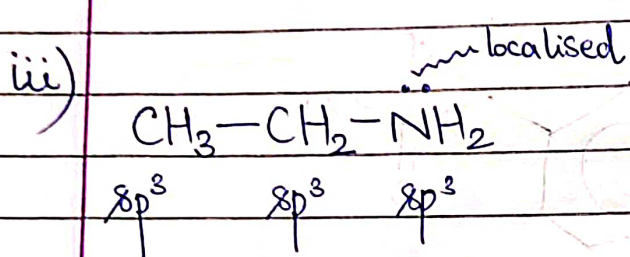
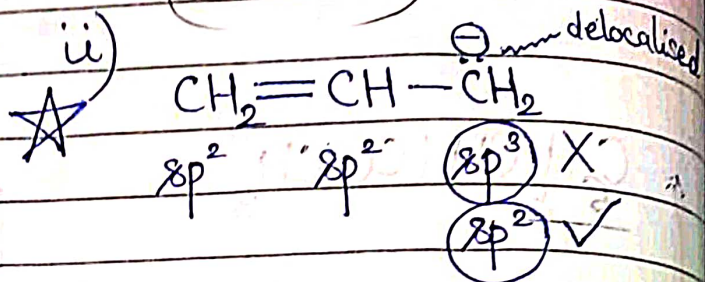
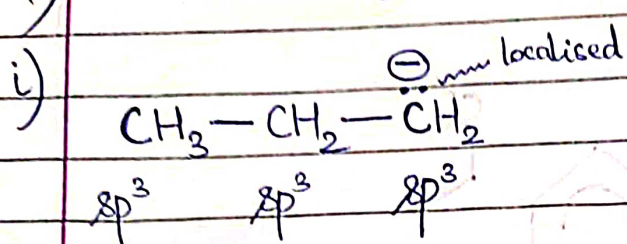
67



★ ( ) ⇒ out of carbon chain



Q) Find  $hyb^n$  of each carbon atom. (Resonance)



Delocalised l.p. does NOT take part in  $hyb^n$ . They are  $\pi e.s$ .

Q)

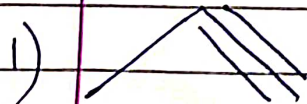
Structure

$\sigma$  bonds

$\pi$  bonds

$\sigma$  bonds b/w

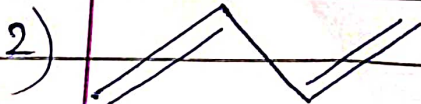
$C_{sp^2} - C_{sp^2}$



6

2

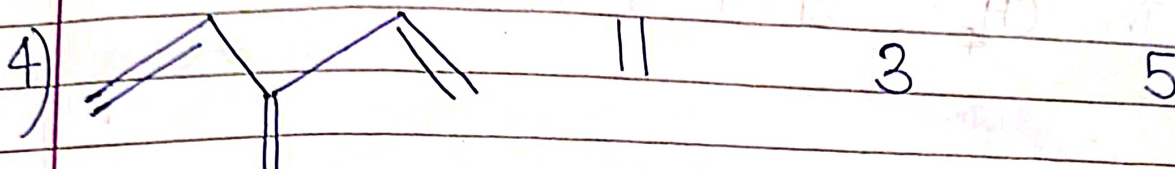
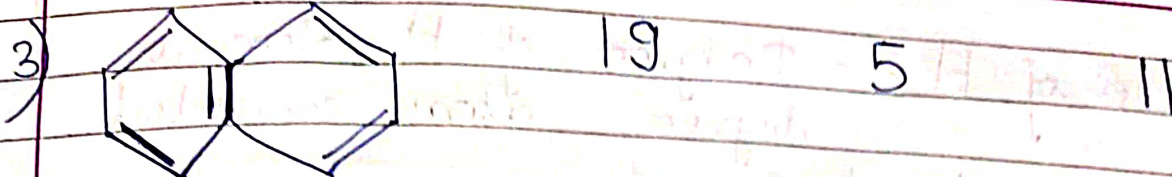
0



9

2

3



## 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

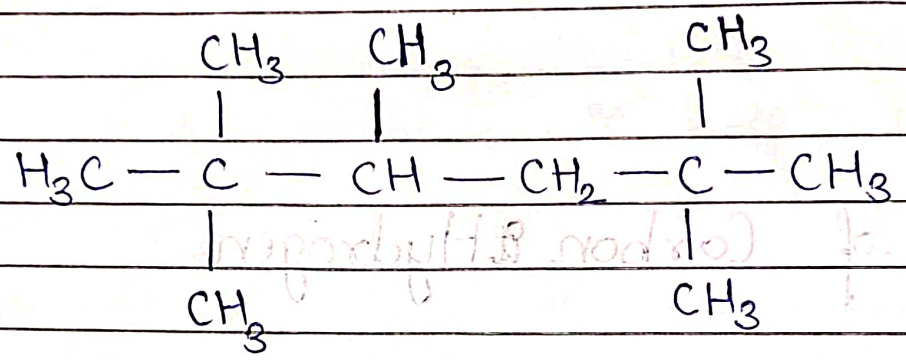
Tertiary C ( $3^\circ$ ) : C connected to 3 other C atoms

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

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

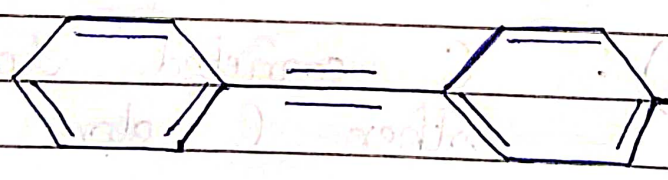
Eg: In  $CH_4$ ,  $\exists$  4  $1^\circ$  H atoms.

Q)



C -	$1^\circ$ :	7	H -	$1^\circ$ :	21
	$2^\circ$ :	1		$2^\circ$ :	2
	$3^\circ$ :	1		$3^\circ$ :	1
	$4^\circ$ :	2			

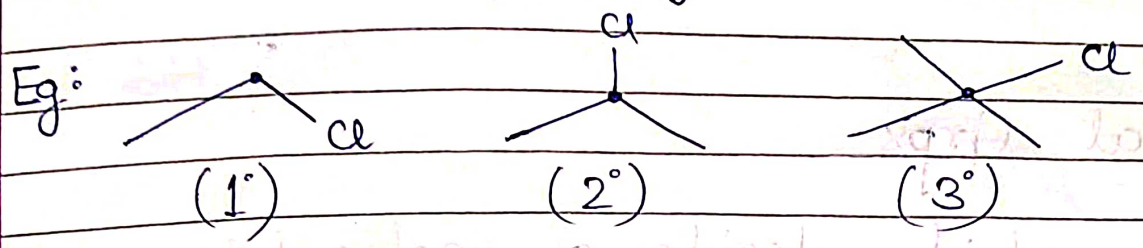
Q)



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

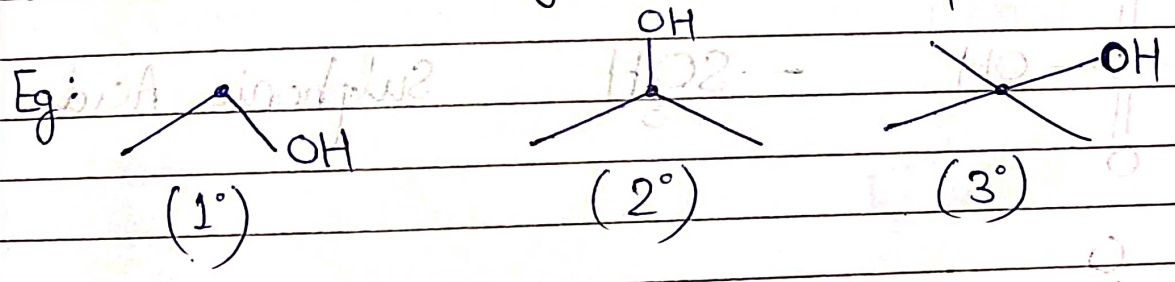
## Degree of Alkyl Halide — R-X

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



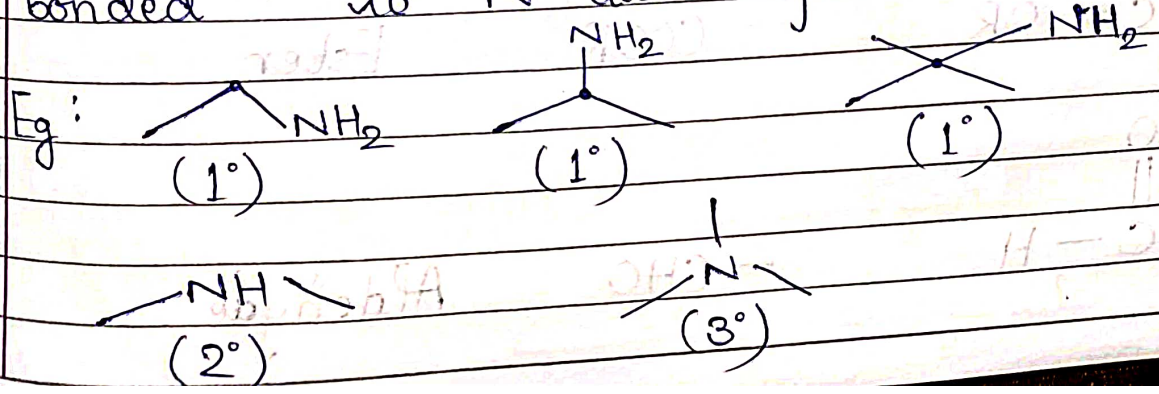
## Degree of Alcohol — R-OH

Degree of Alcohol is degree of C bonded to hydroxyl group.



## Degree of Amines — R-NH<sub>2</sub>

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



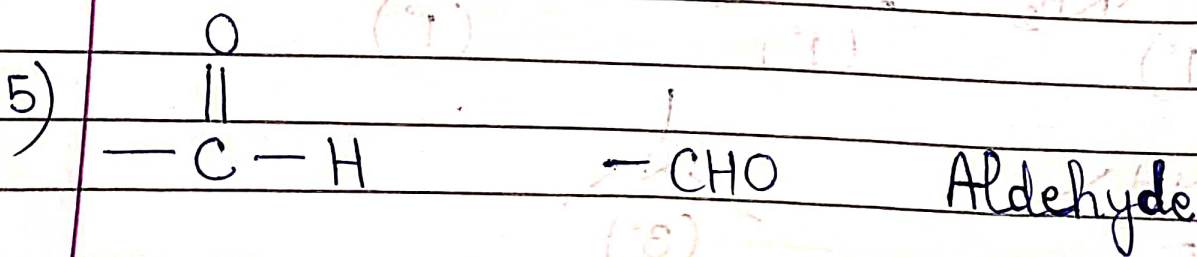
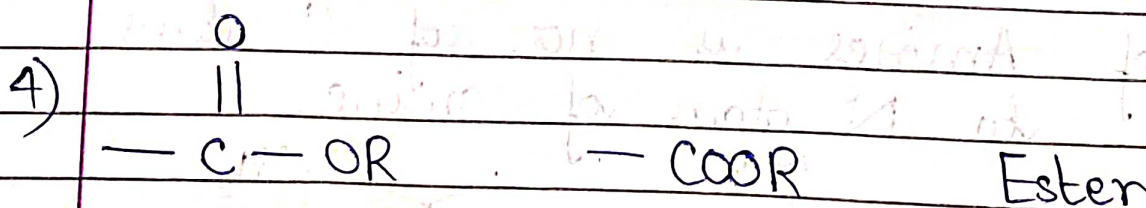
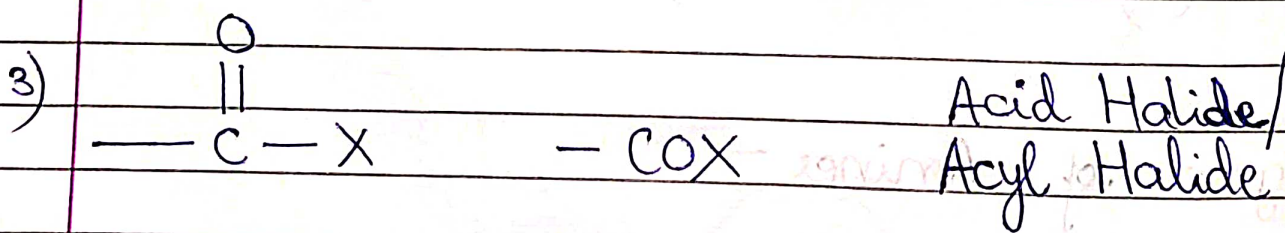
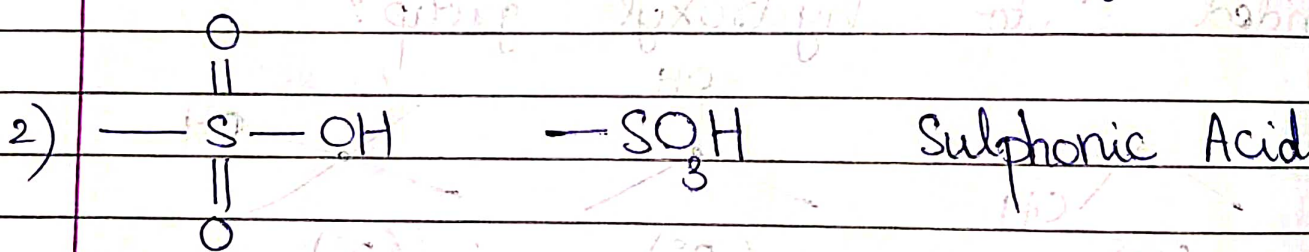
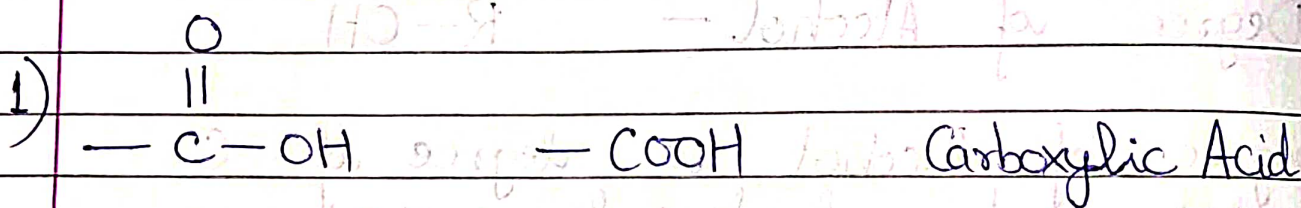


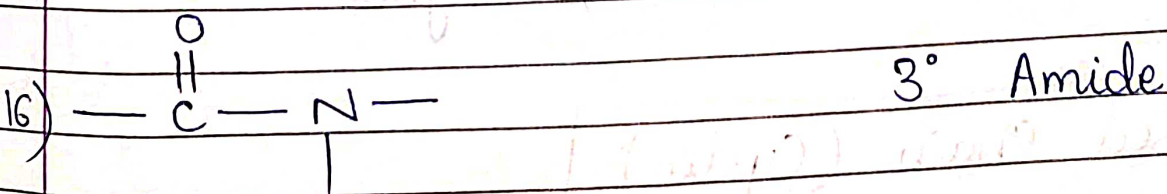
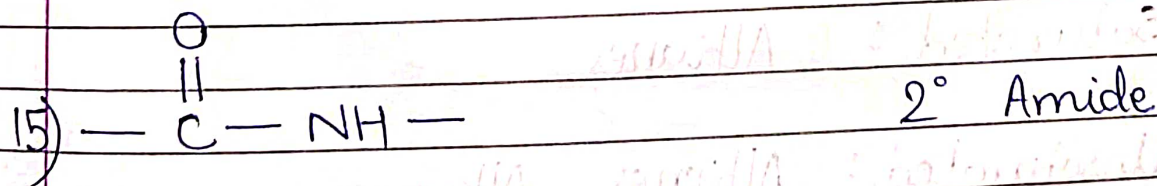
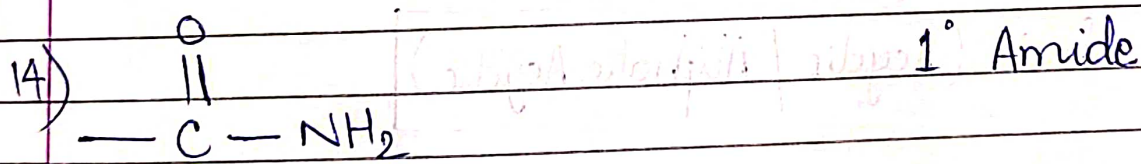
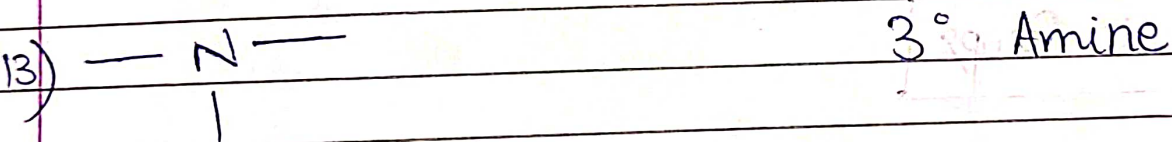
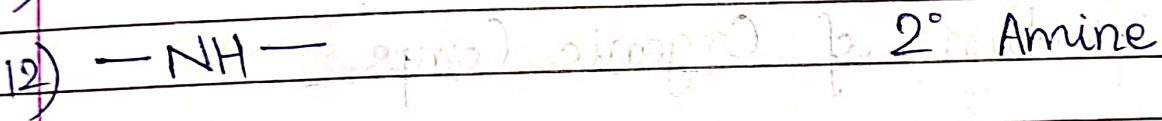
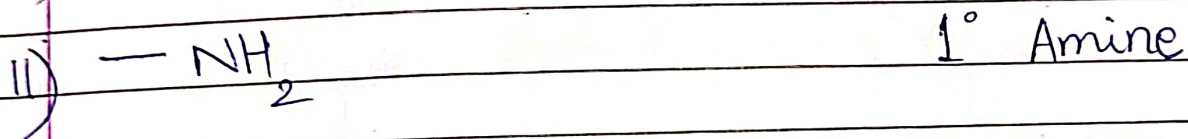
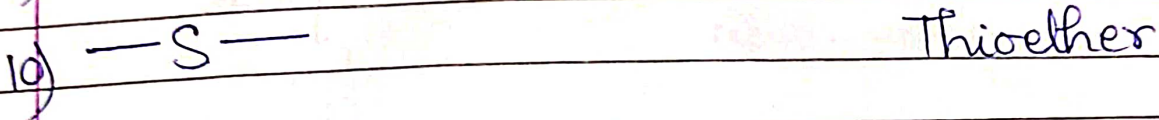
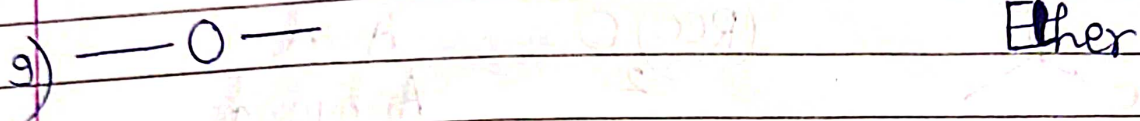
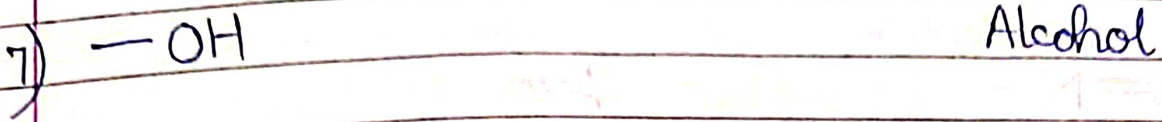
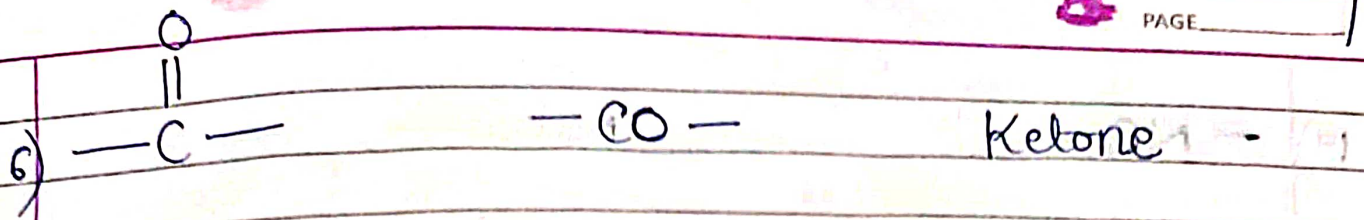


★  $1^\circ$ ,  $2^\circ$ ,  $3^\circ$  amines are separate  
functional groups.

### Functional Groups

Groups which decide a molecule's physical or chem. props.

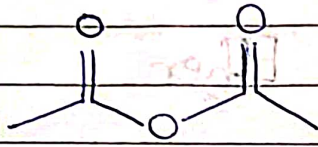




19)  $-\text{NO}_2$  Nitro

20)  $-\text{X}$  Halide

21)  $-\text{N}=\text{N}-$  Azo

22)   $(\text{RCO})_2\text{O}$  Acid Anhydride

## Classification of Organic Comps.

### Organic Comps.

#### Open Chain (Acyclic / Aliphatic Acyclic)

— Saturated: Alkanes

— Unsaturated: Alkenes, Alkynes

#### Closed Chain (Cyclic)

— Homocyclic (Carbocyclic)

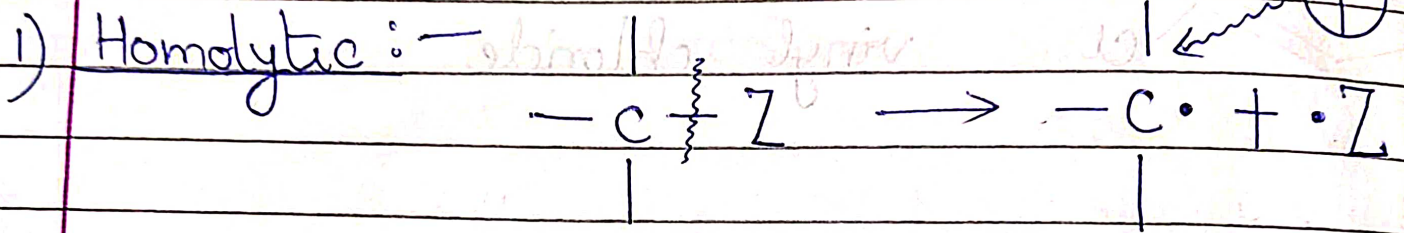


- + Aliphatic Cyclic / Alicyclic
- + Aromatic

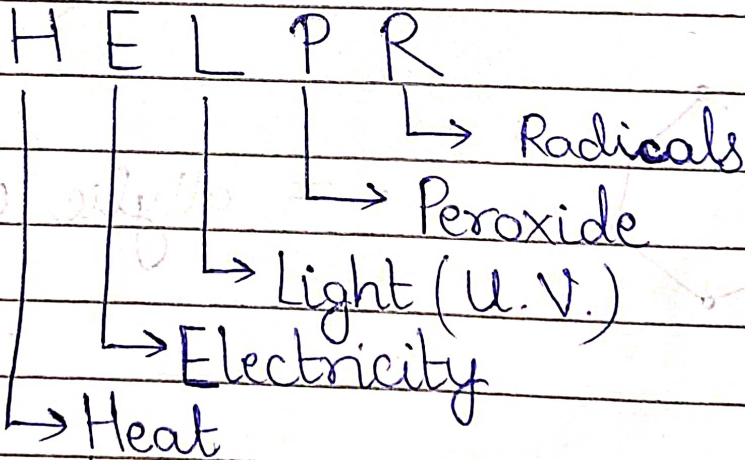
Heterocyclic

- + Aliphatic Cyclic / Alicyclic
- + Aromatic

# Bond Fission



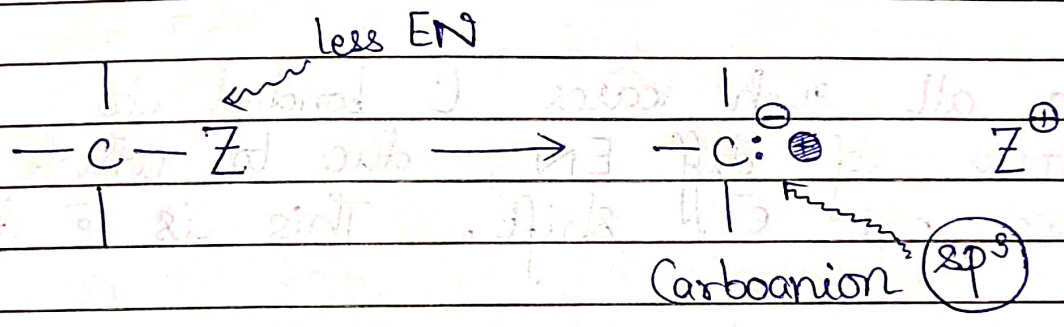
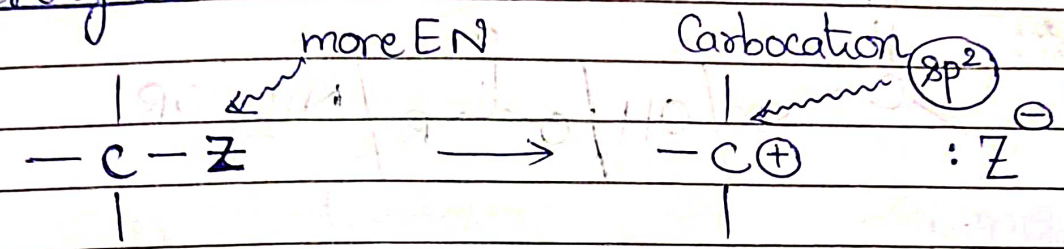
Cond<sup>n</sup>s:





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

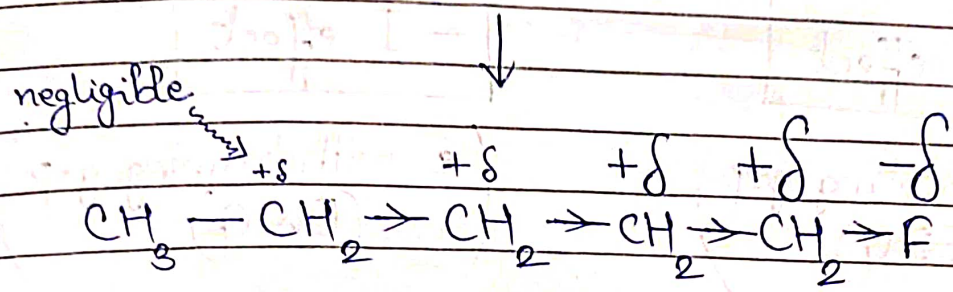
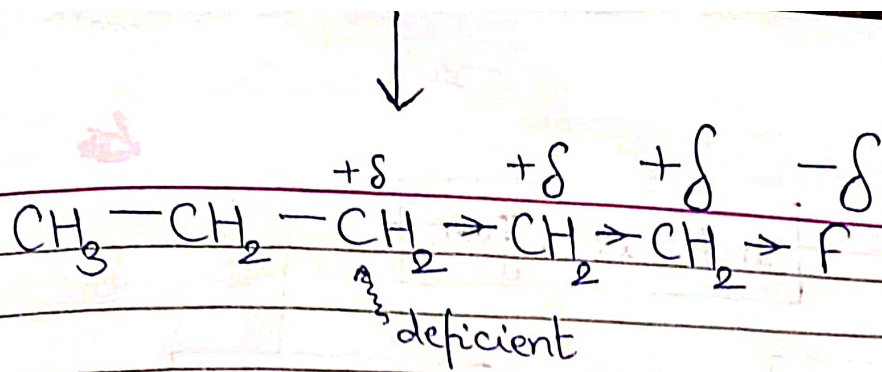
2) Heterolytic :-



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.





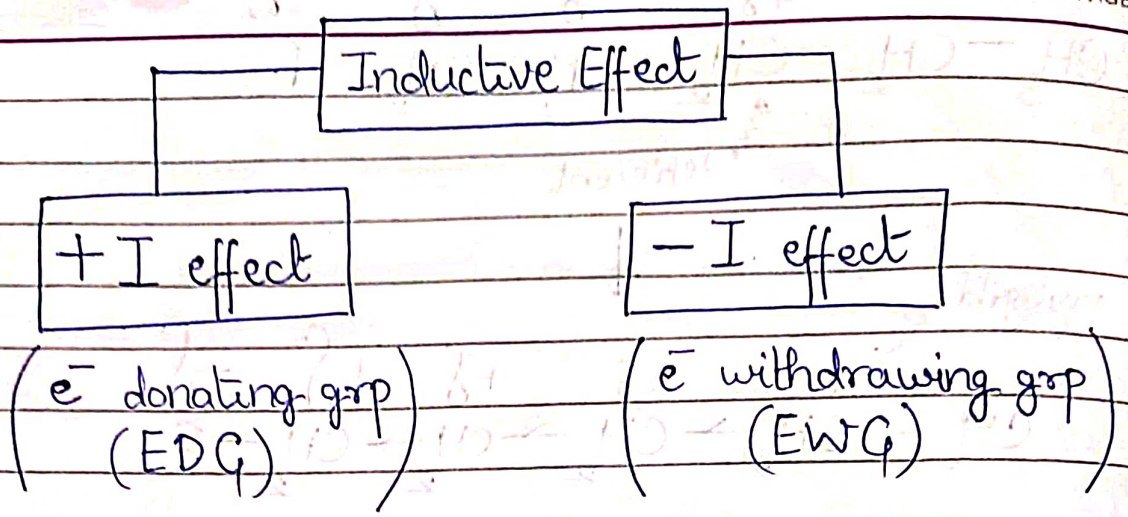
Polarisation of bonds under influence of more EN atom / group of atoms.

OR

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

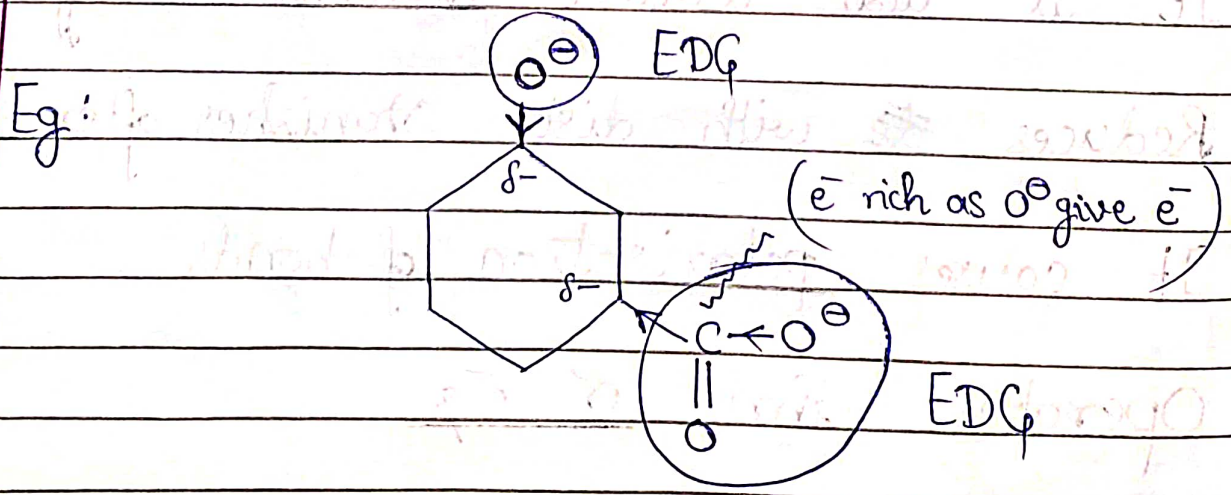
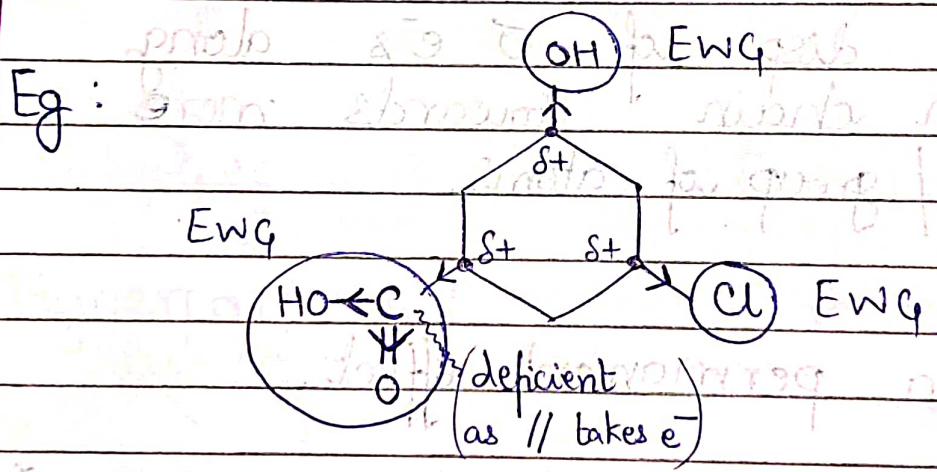
- i) It is a permanent effect.
- ii) It is also called transmission effect.
- iii) Reduces ~~the~~ with dist. Vanishes after 4th C atom
- iv) It causes polarisation of bonds.
- v) Operates thru  $\sigma$  e<sup>-</sup>s.



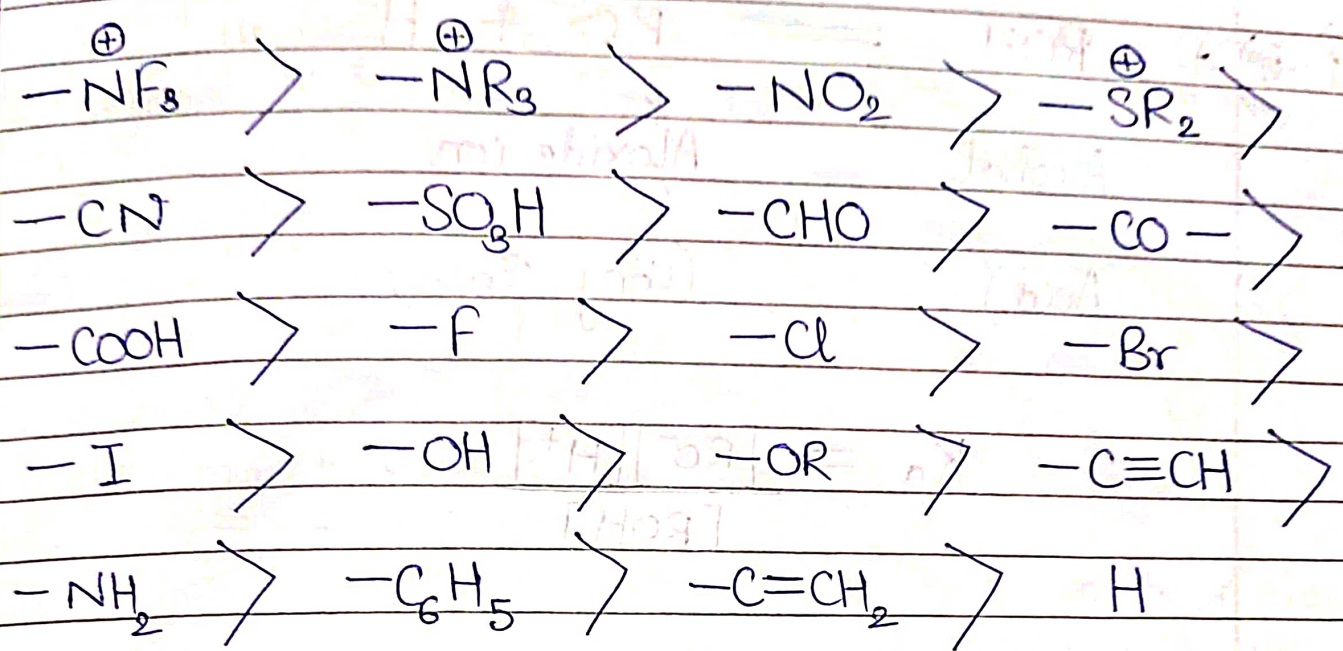


for finding EDG or EWG, we take H atom for reference.

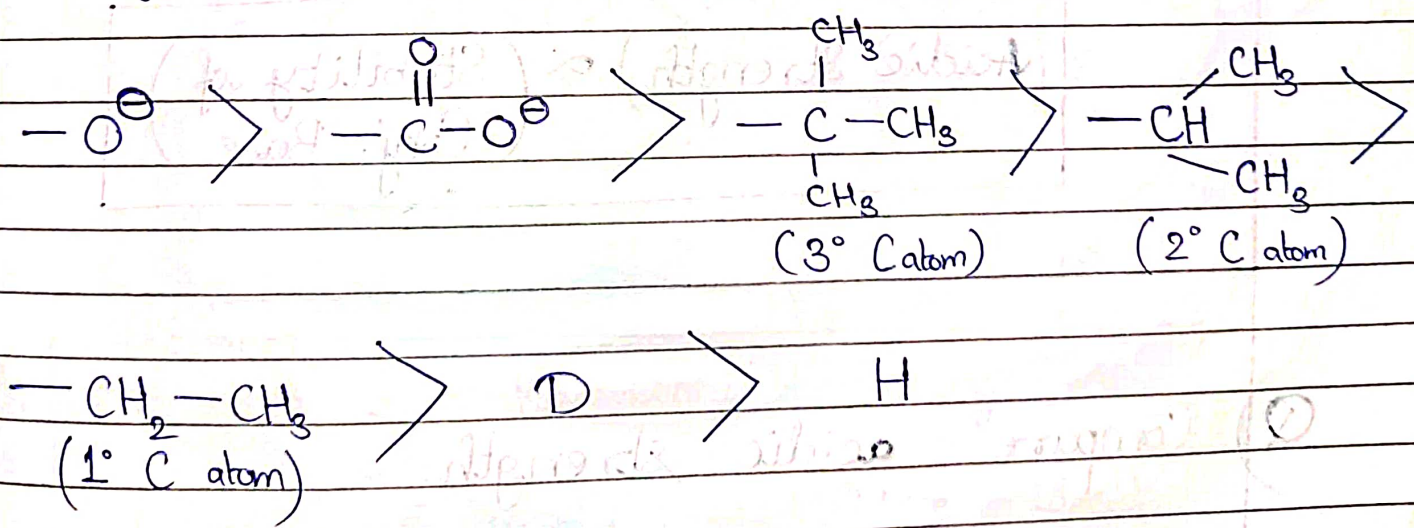
$$EN(EWG) > EN(H) > EN(EDG)$$



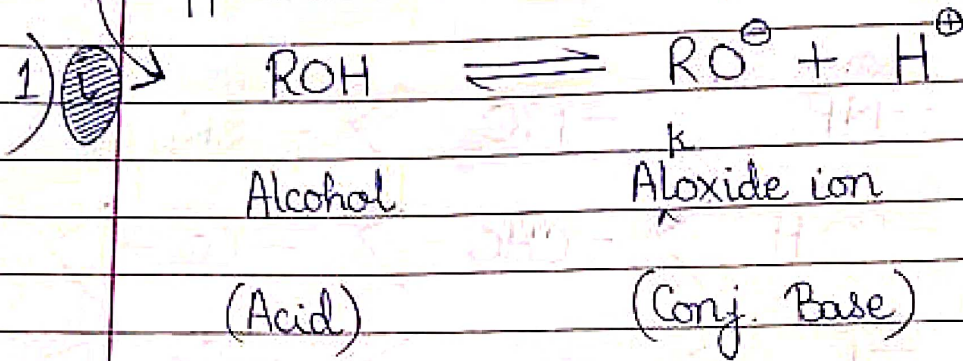
Strength of -I effect :-



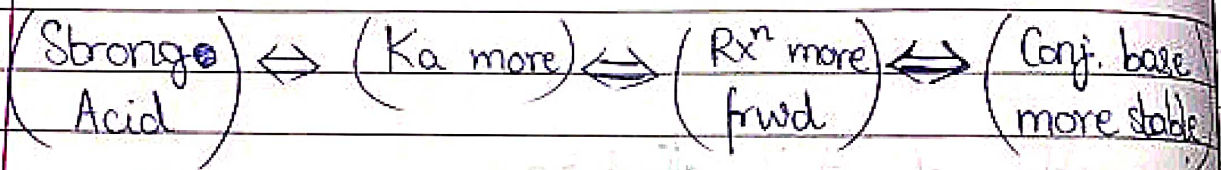
Strength of +I effect :-



Application :-

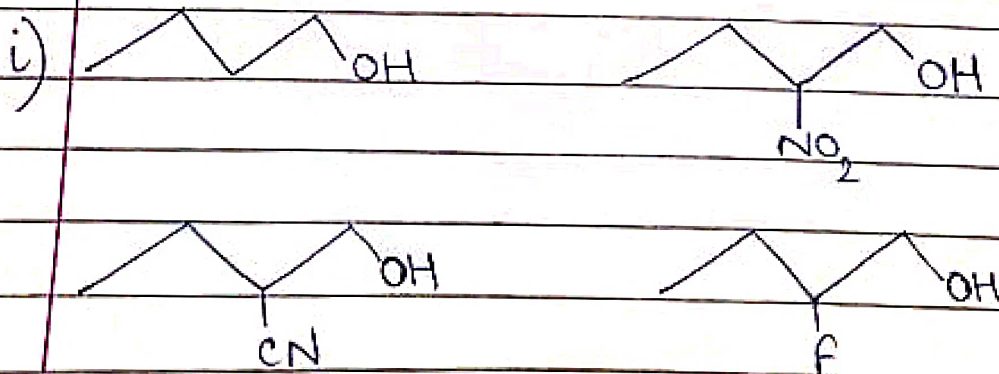


$$K_a = \frac{[\text{RO}^-][\text{H}^+]}{[\text{ROH}]}$$



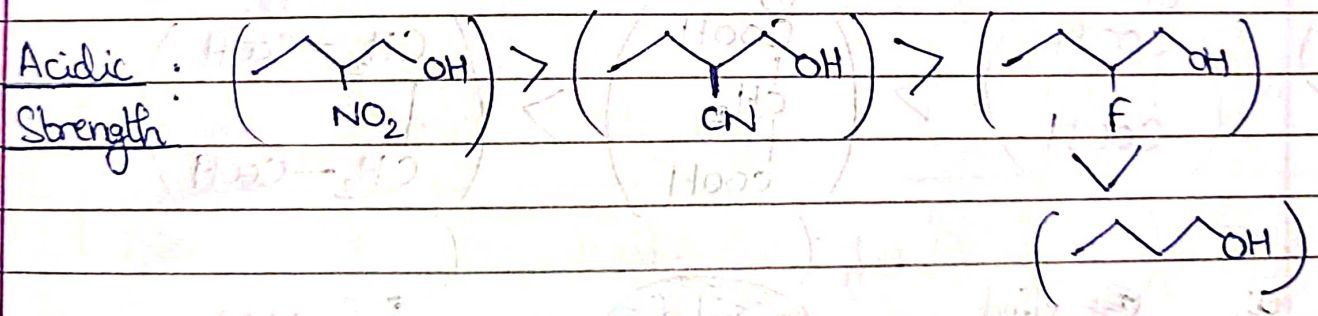
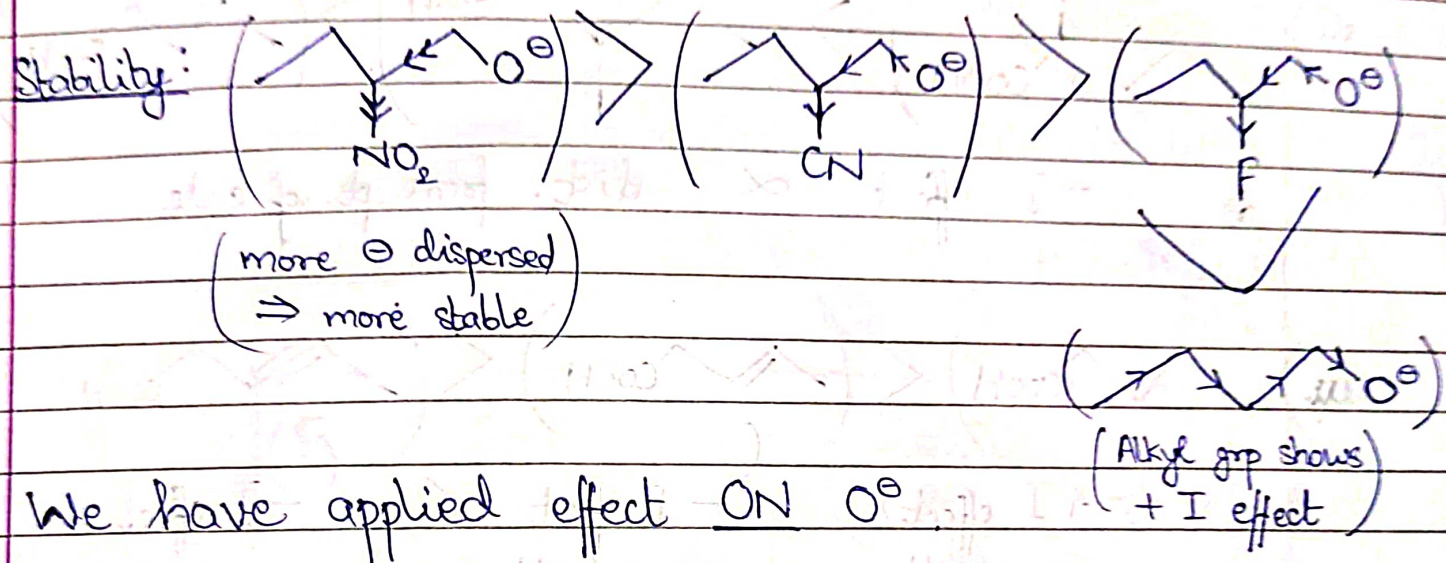
$$\text{(Acidic Strength)} \propto \text{(Stability of Conj. Base)}$$

Q) Compare acidic strength.





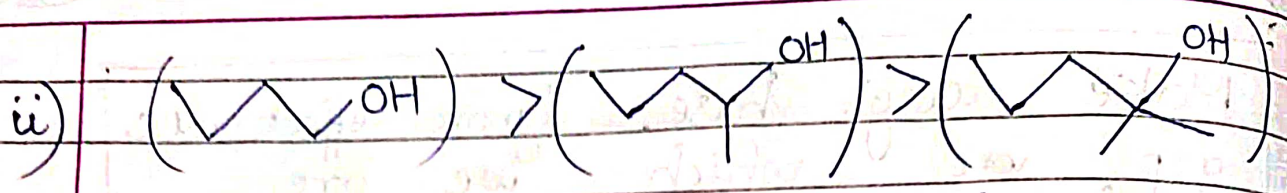
A) Make conj. base. Ignore effect due to grp. on which we are finding effect. In this case ignore +I due to  $O^\ominus$ .



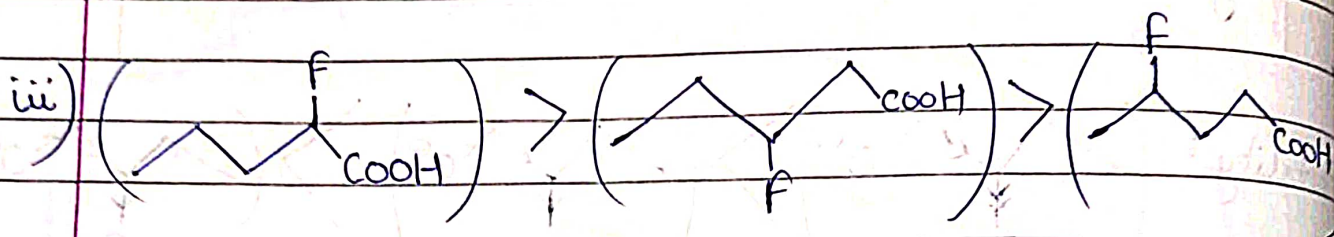
★ No need to make conj. base every time.

(Lesser the  $\bar{e}$  density on  $-\text{OH}, -\text{COOH}, \dots$ )  $\Rightarrow$  (More acidic strength)

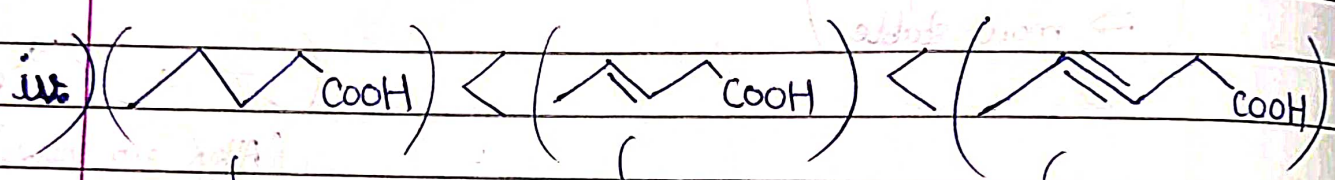
(due to  $-I$  effect)



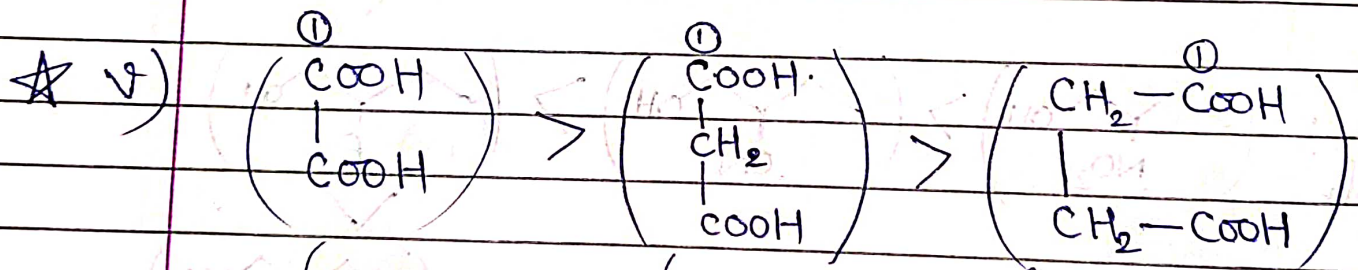
as +I effect of  $3^\circ > 2^\circ > 1^\circ$



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



as +I effect on -COOH  $<$  -I effect on -COOH  $<$  -I effect on -COOH



as effect directed on  $\textcircled{1}\text{COOH}$

only 1C shows +I on  $\textcircled{1}\text{COOH}$

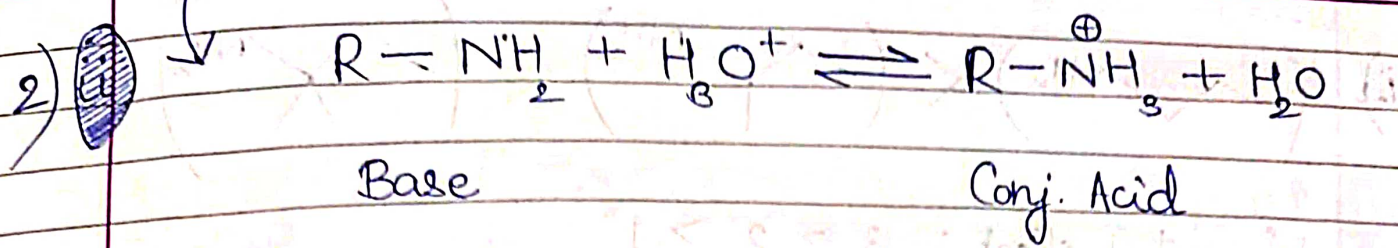
1C b/w  $\textcircled{1}\text{COOH}$  & COOH

2 C atoms show +I on  $\textcircled{1}\text{COOH}$

b/w  $\textcircled{1}\text{COOH}$  & COOH

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

# Basic Strength:



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

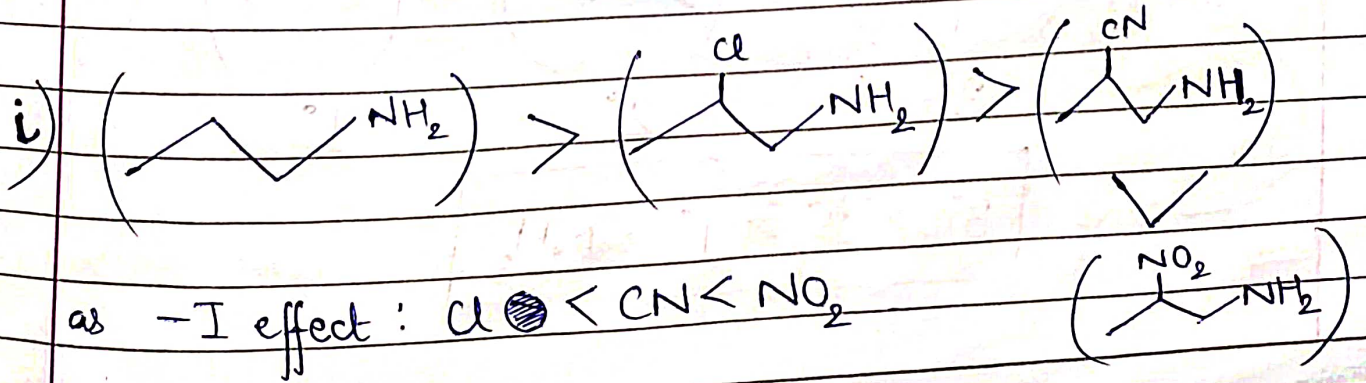
(Strong Base)  $\Leftrightarrow$  ( $K_b$  more)  $\Leftrightarrow$  ( $Rx^n$  more fused)  $\Leftrightarrow$  (Conj. Acid more stable)

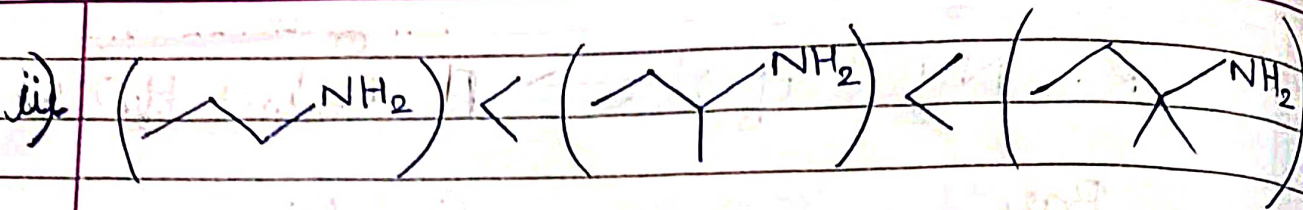
(Basic Strength)  $\propto$  (Stability of Conj. Acid)

1) Compare basic strength.

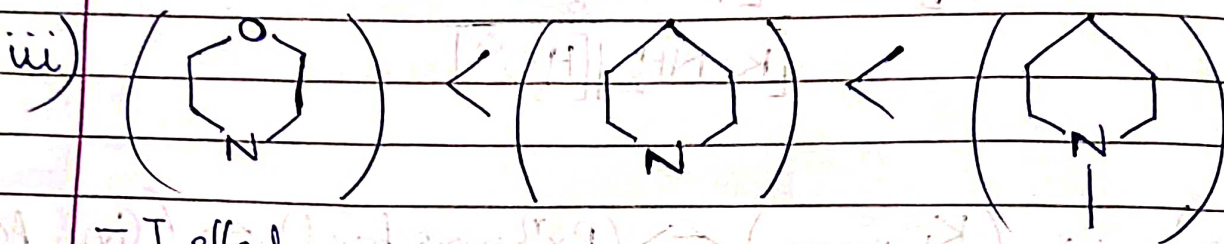
★ No need to make conj. acid every time.

(More the  $\bar{e}$  density on  $-NH_2$ )  $\Rightarrow$  (More basic strength)



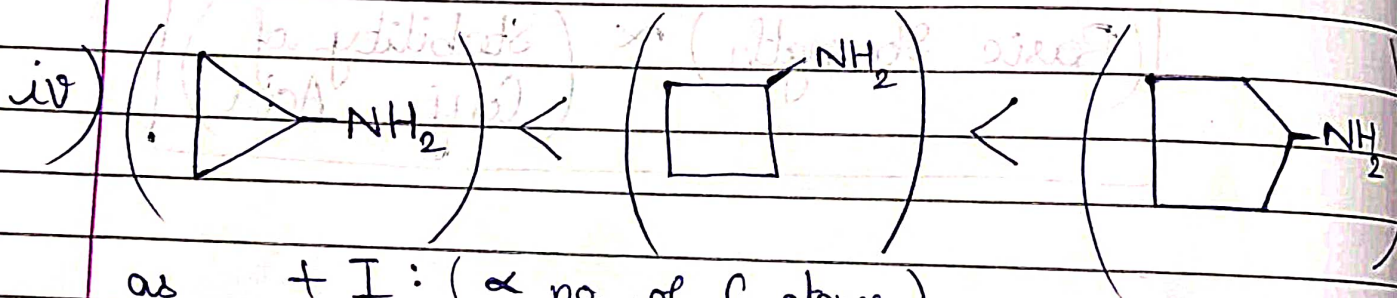


as +I effect:  $3^\circ > 2^\circ > 1^\circ$



-I effect

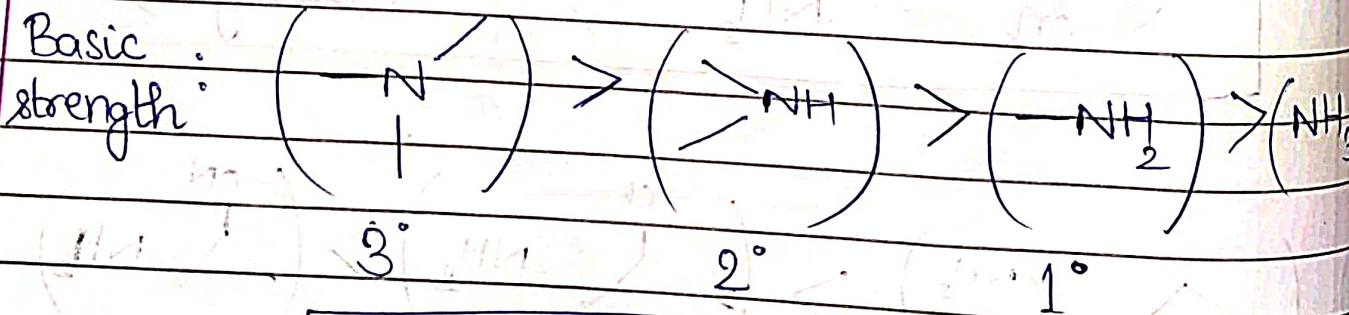
+ I effect: ( $\propto$  more C atoms)



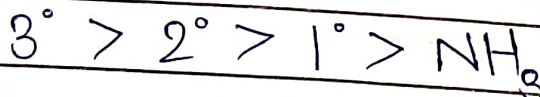
as +I: ( $\propto$  no. of C atoms)  
effect

### Basic Strength of Amines:

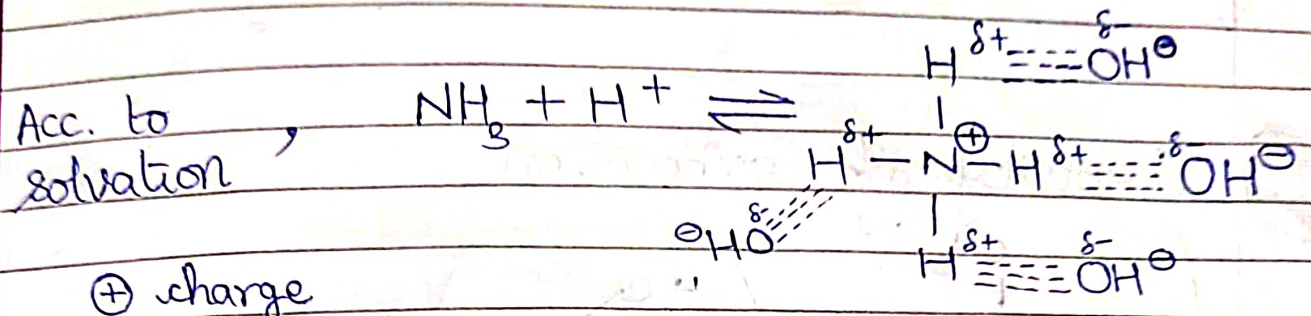
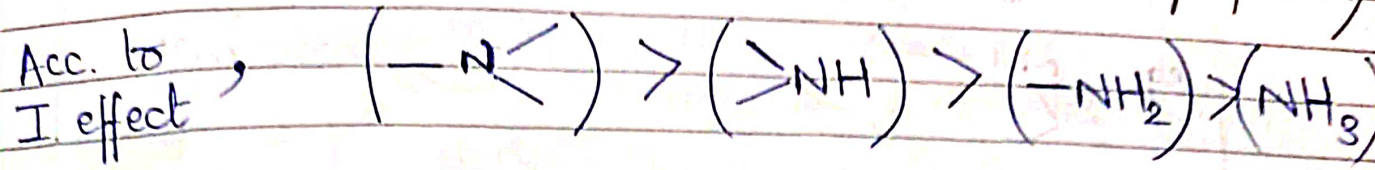
3) C1: - In vapour state,



$\Rightarrow$

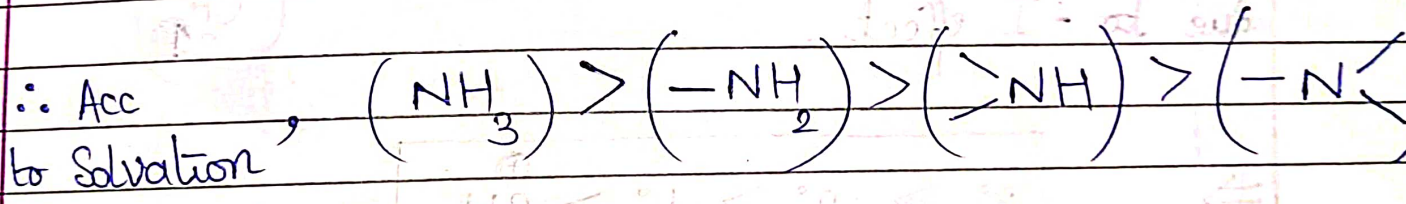


C2 :- In aqueous state, (if nothing specified, assume aq. form)

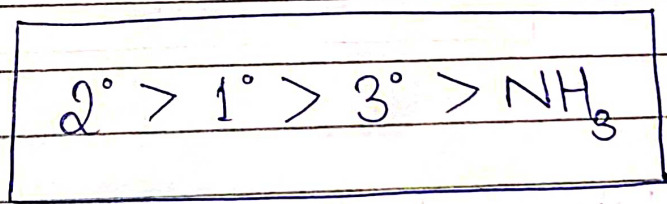


$\oplus$  charge  $\Rightarrow$   $\ominus$  density on N decreases.

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

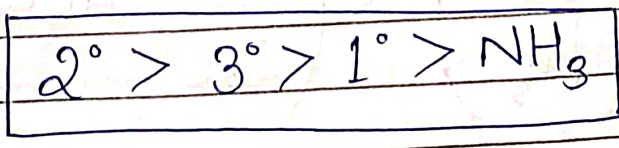


Practically we get,



if alkyl grps  $\ominus$  Methyl.

Practically we get,

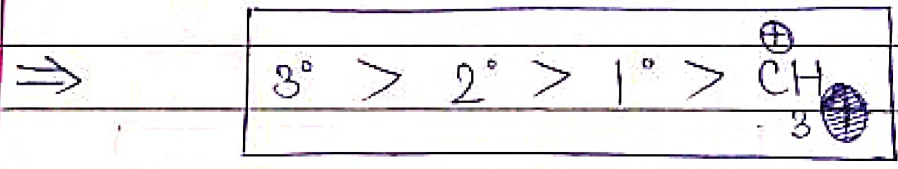
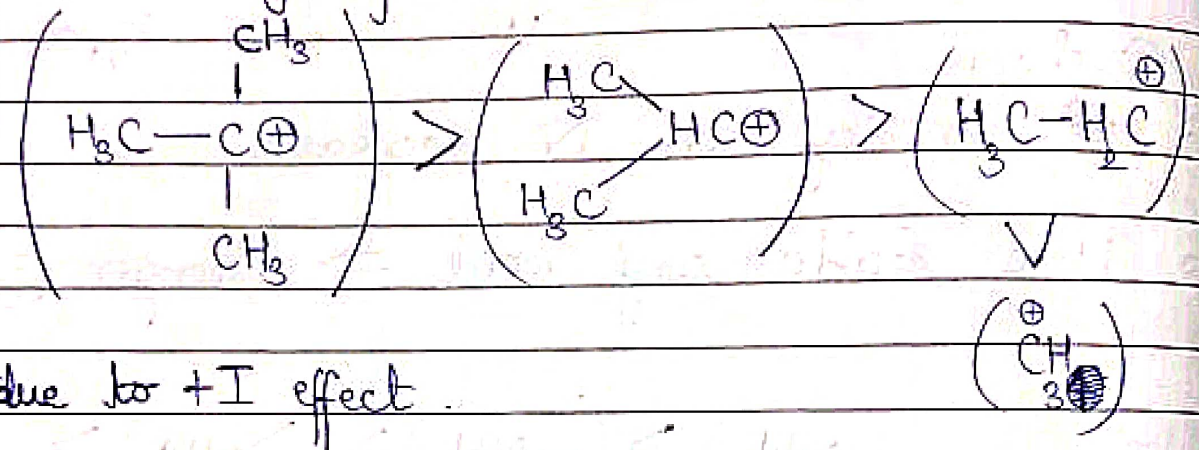


if alkyl grps  $\ominus$  ethyl or higher

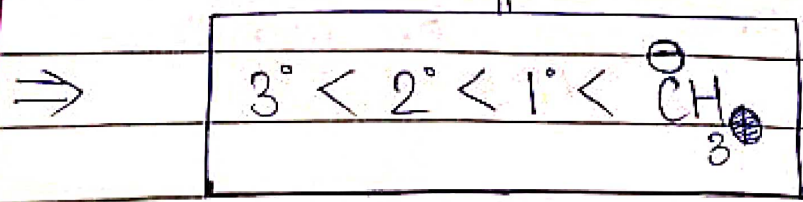
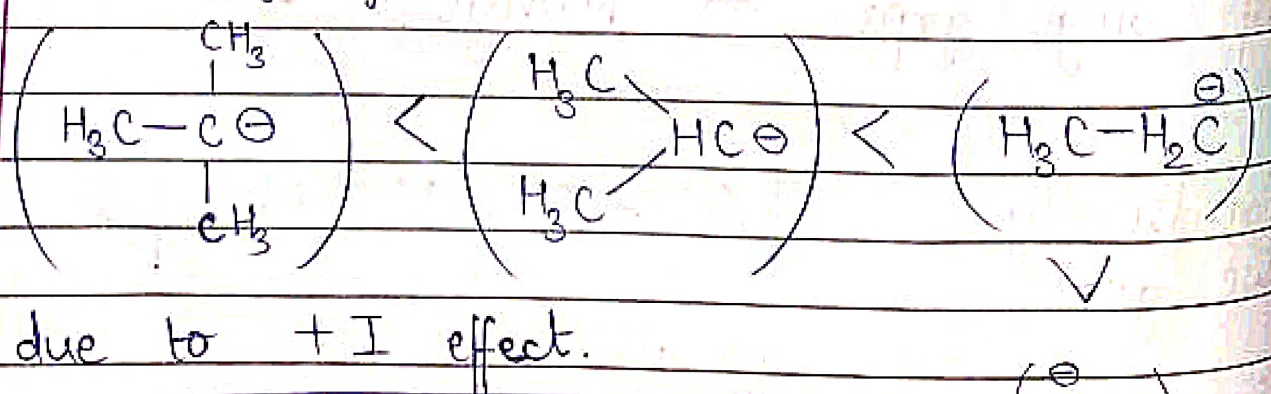


★ If diff. alkyl grps. around N  
(eg  $\begin{matrix} \text{NH} - \\ / \quad \backslash \end{matrix}$ ), then  $2^\circ$  most basic.

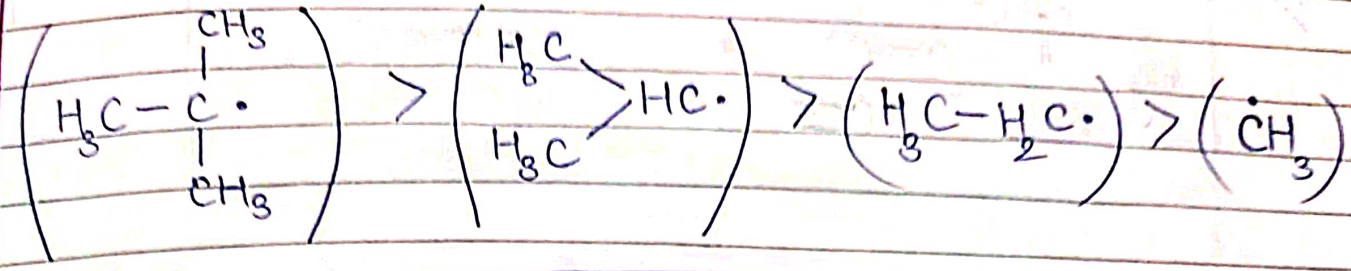
4) Stability of Carbocation:



5) Stability of Carbanion:

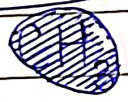


6) Stability of Carbon free radical :



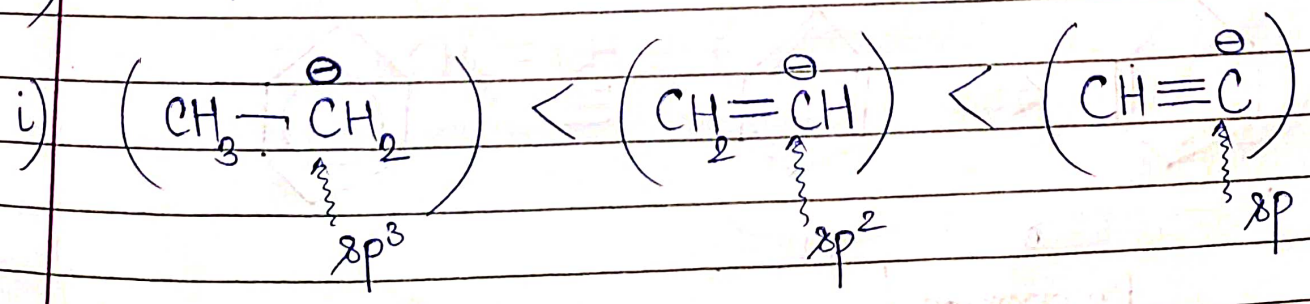
$$\Rightarrow \boxed{3^\circ > 2^\circ > 1^\circ > \dot{\text{C}}\text{H}_3}$$

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

★ Stability:   $\ominus \text{CH}_3 > \oplus \text{CH}_3 > \dot{\text{C}}\text{H}_3$

free radicals are highly energetic.

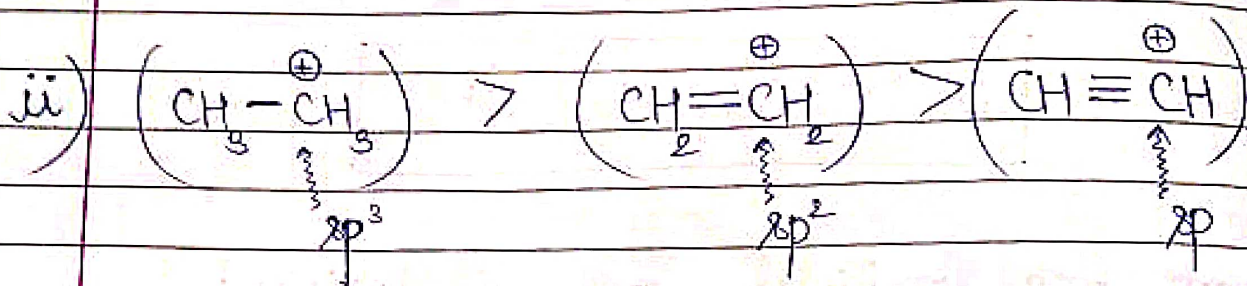
Q) Compare stability of species.



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



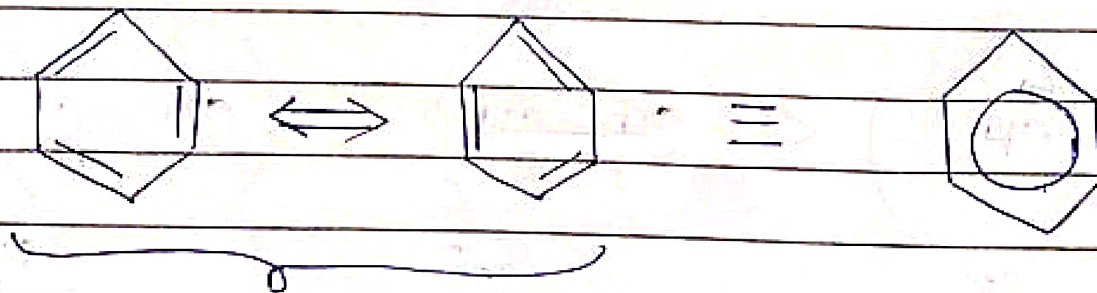
We can't apply I effect becoz I effect is created by  $-C \equiv C-$  or  $>C=C<$ , NOT  $C \equiv$  or  $C=$



EN  $\uparrow$   $\Rightarrow$   $\ominus$  charge Stable  $\Rightarrow$   $\oplus$  charge Unstable

## Resonance (Mesomeric Effect)

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



Resonance/  
Canonical  
Structures

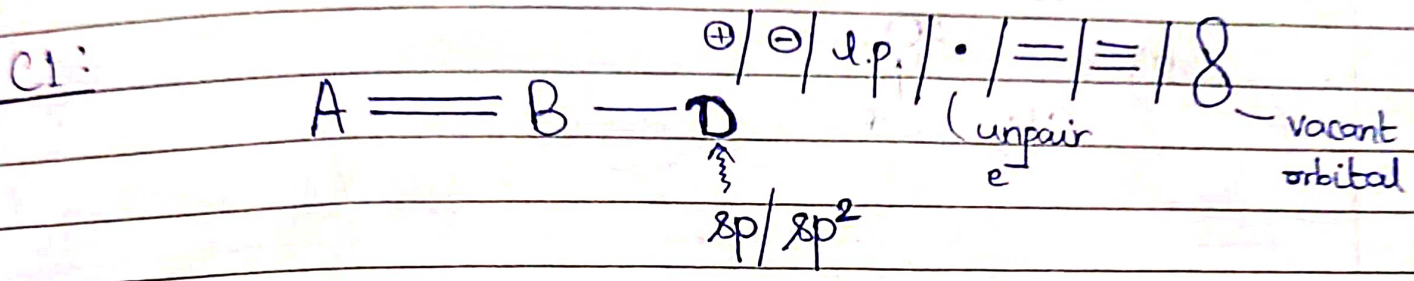
Resonance  
Hybrid

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

Cond<sup>n</sup>s • —

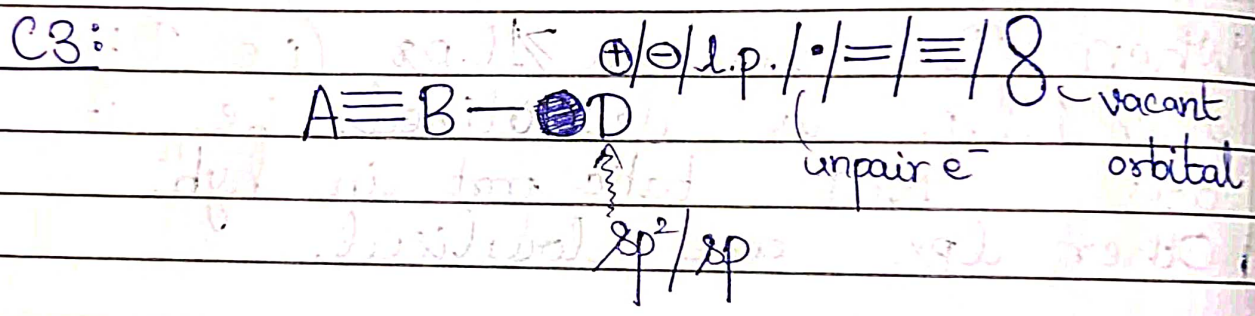
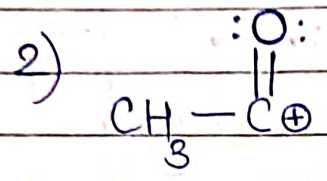
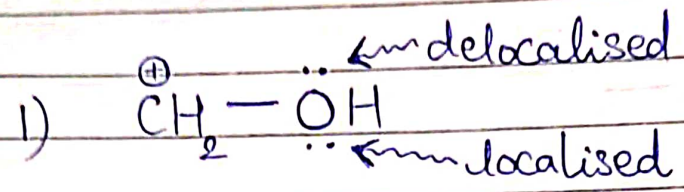
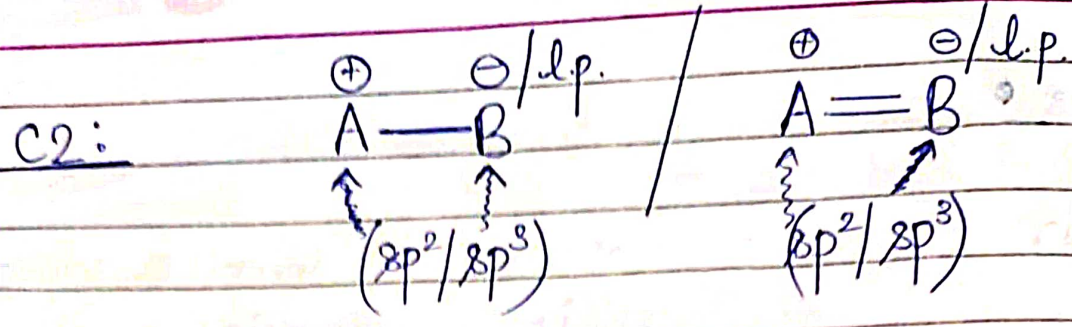
Planar (part of molecule showing resonance should be planar)

Conjugation :-

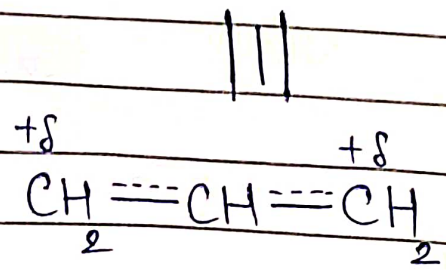
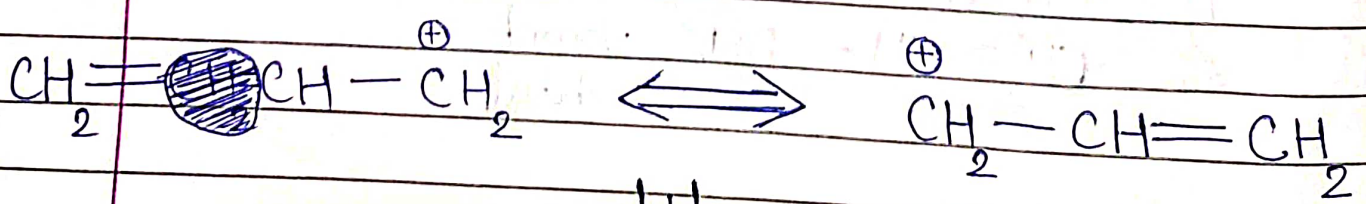
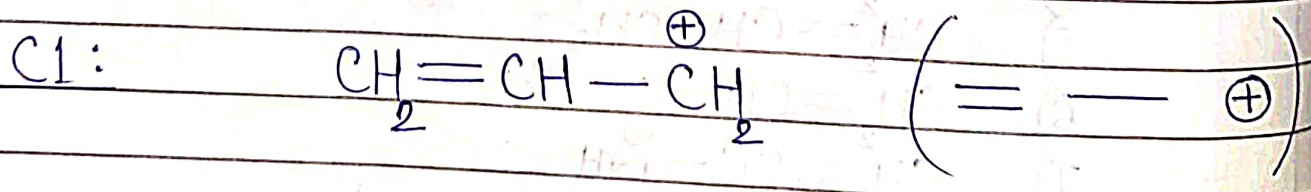


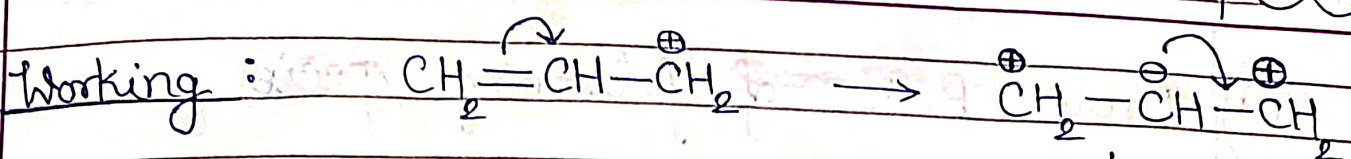
When 'D' has a  $\geq 1$  l.p.s (i.e. D:) then 1 l.p. is delocalised. i.e. it does NOT take part in hyb<sup>n</sup>. Other l.p.s. are localised.

- 1)  $CH_2 = CH - CH = CH_2$
- 2)  $CH_2 = CH - \overset{\oplus}{CH_2}$
- 3)  $CH_2 = CH - \overset{\ominus}{CH_2}$
- 4)  $CH_2 = CH - \overset{\cdot}{N}H_2$
- 5)  $CH_2 = CH - \overset{\cdot}{C}H_2$
- 6)  $CH_2 = CH - C \equiv CH$
- 7)  $CH_2 = CH - \overset{\oplus}{N}H_3$
- 8)  $CH_2 = CH - \overset{\cdot}{B}H_2$  vacant orbital

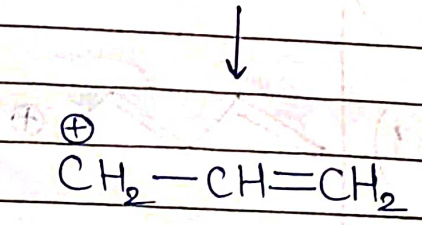


### Resonating Structures





☆  $\oplus$  &  $\ominus$  =  
exchange



Resonance Energy :

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

Lower energy of R.H.



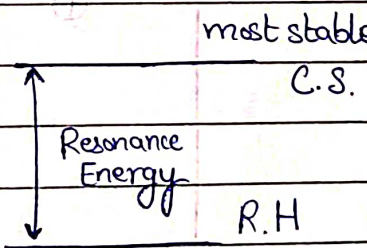
More resonance energy



More stability

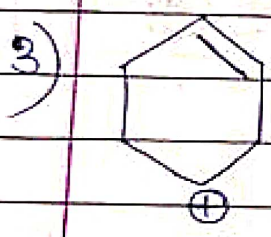
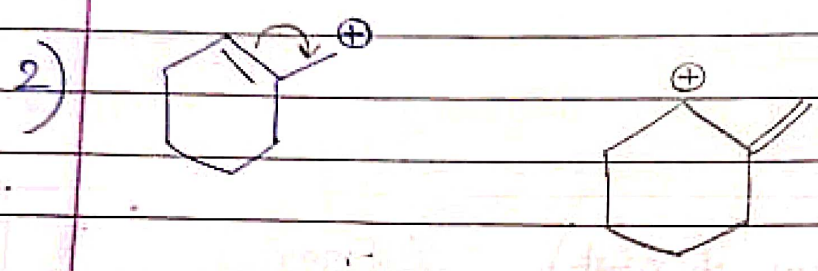
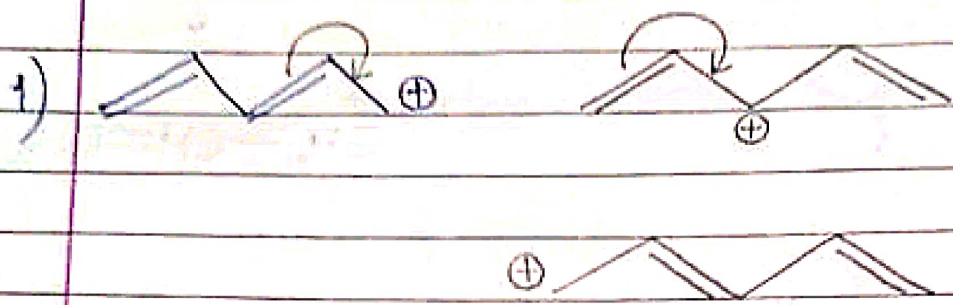


Energy ↑

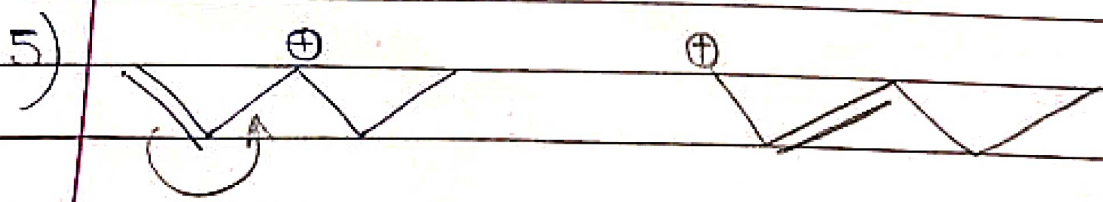
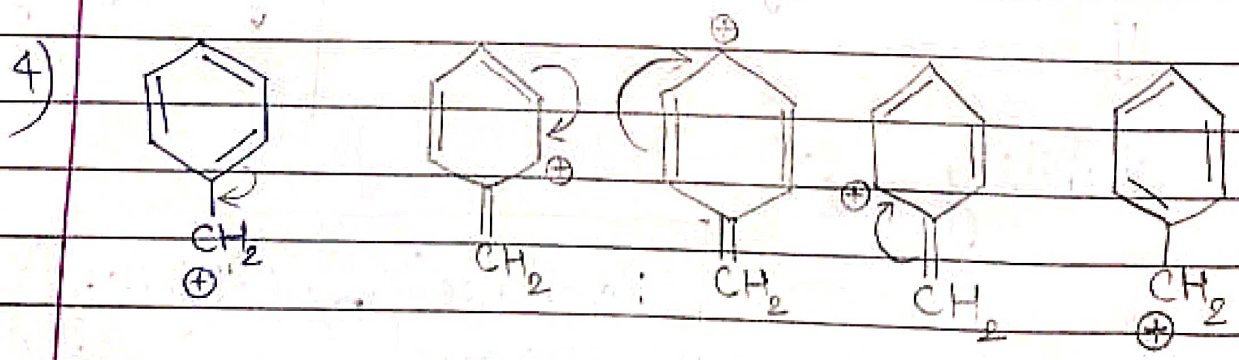


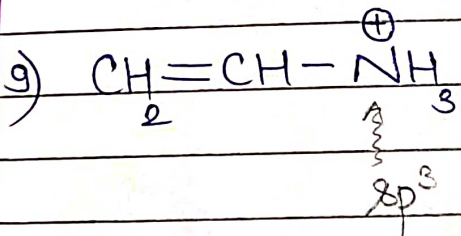
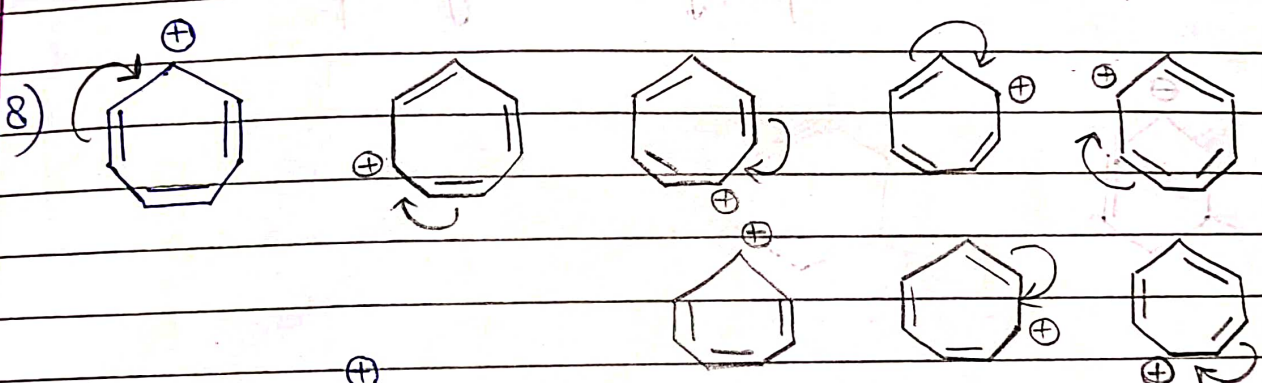
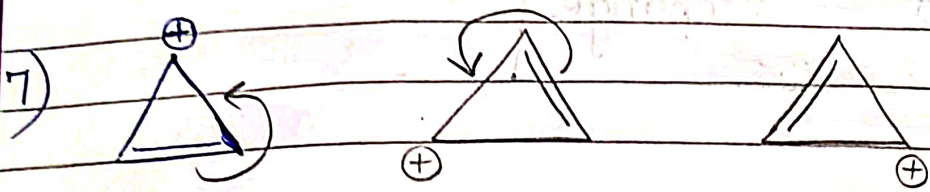
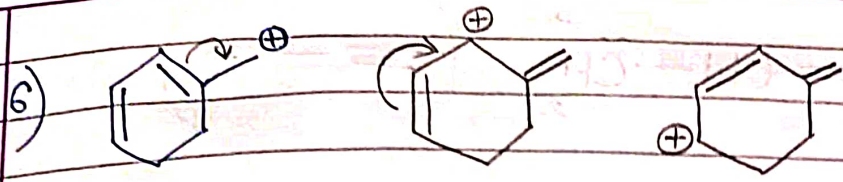
$$\left( \text{Resonance Energy} \right) \propto \left( \text{Stability} \right)$$

Q) Draw R.S. of following species.

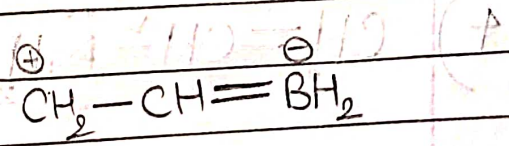
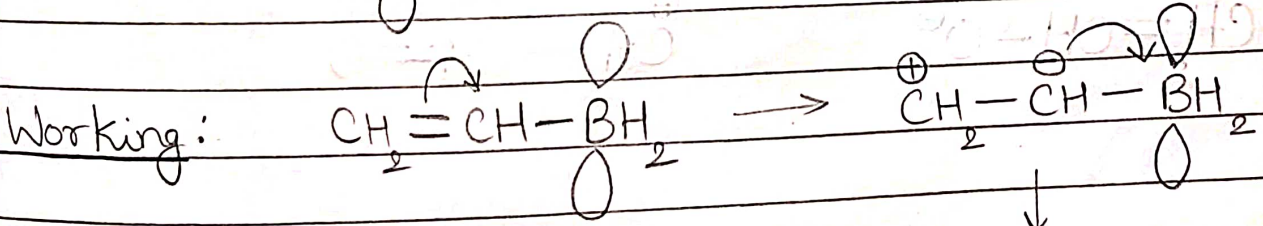
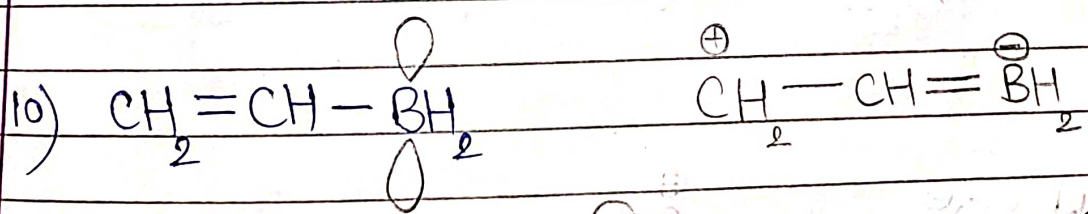


No Resonance

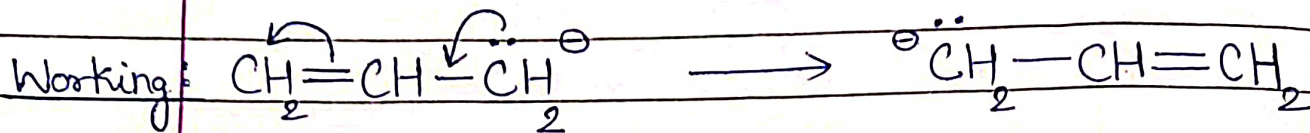
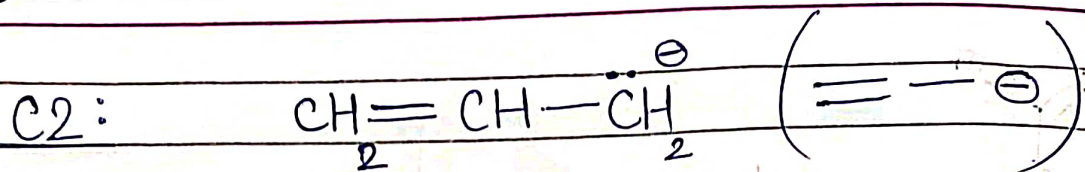




No resonance

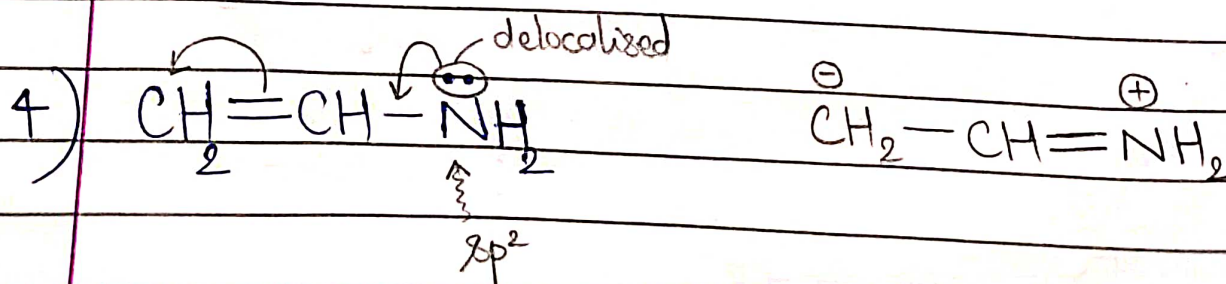
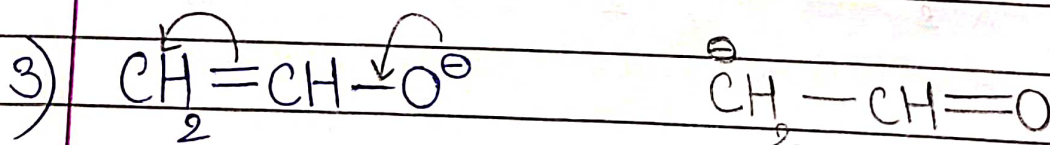
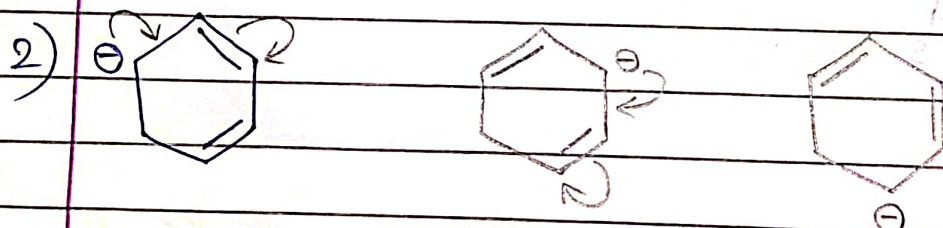
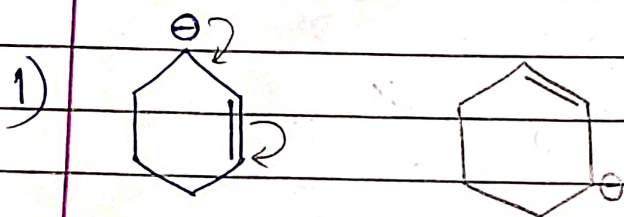


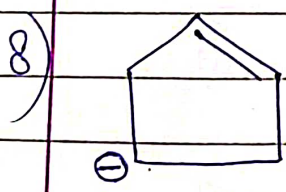
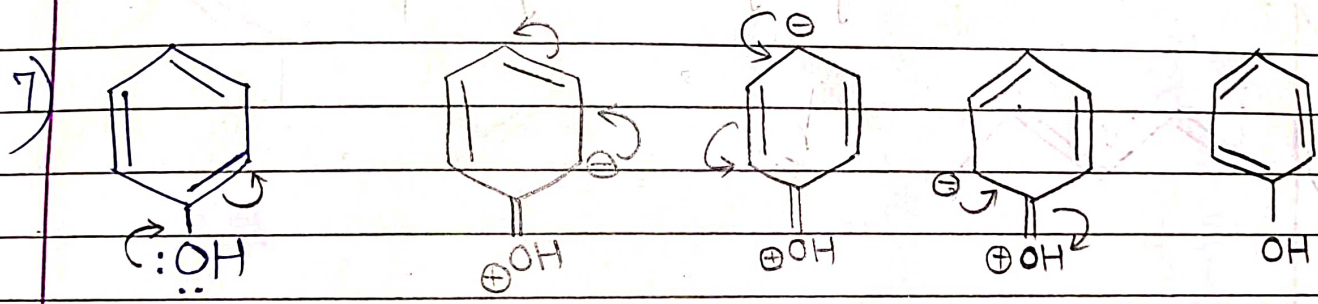
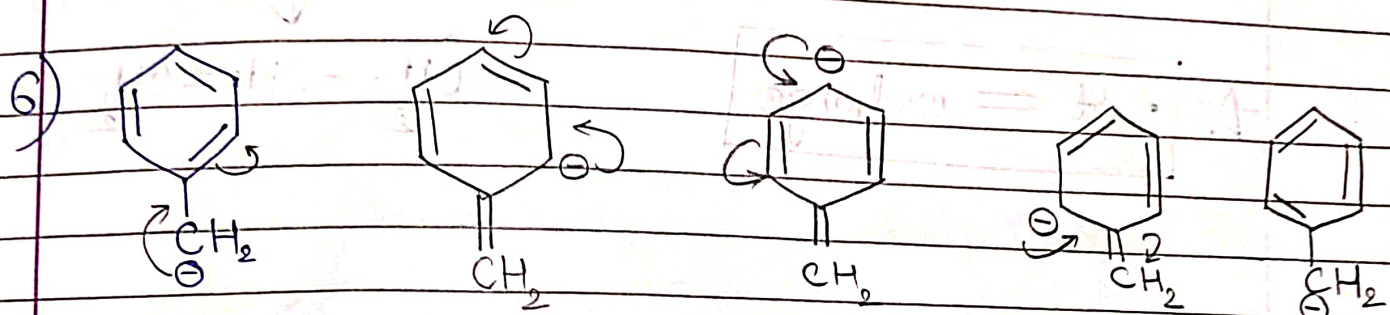
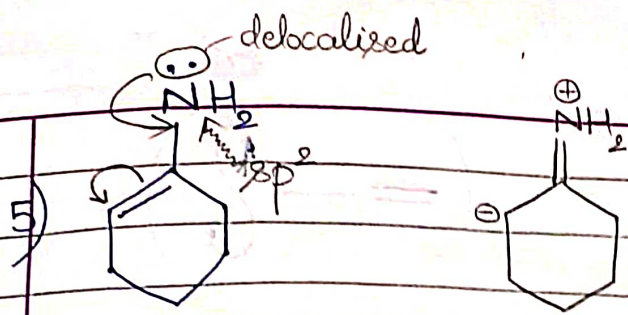


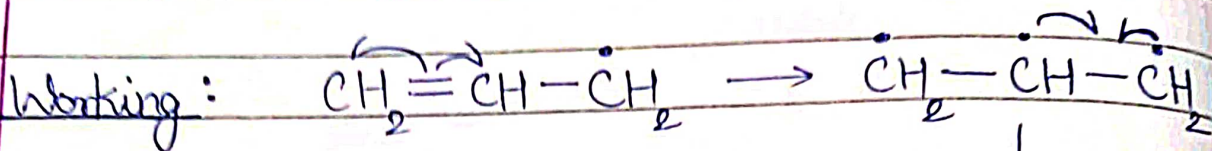
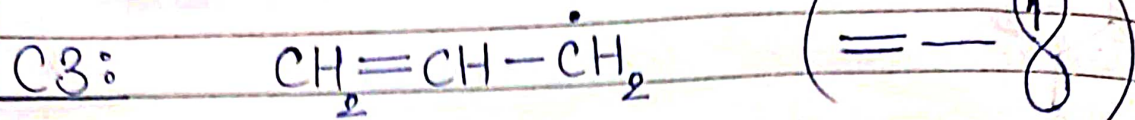


★  $\ominus$  &  $=$  exchange

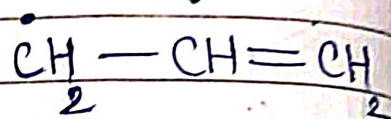
Q) Draw R.S. of following species.



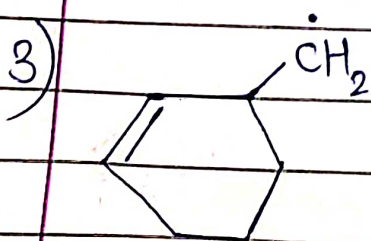
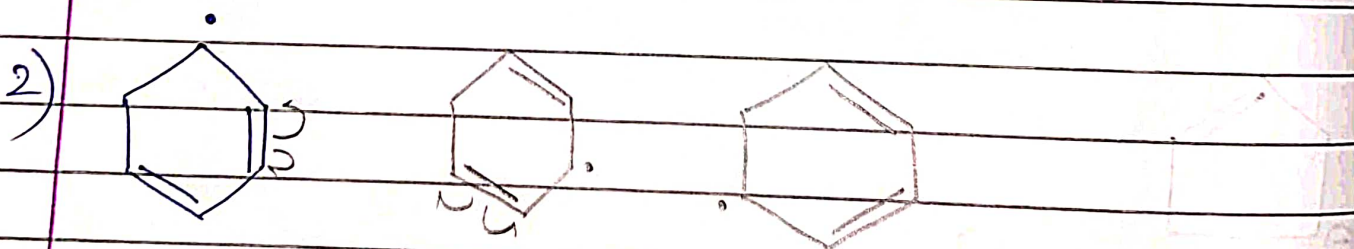
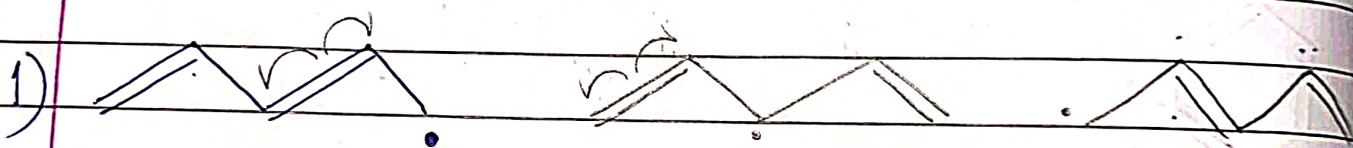




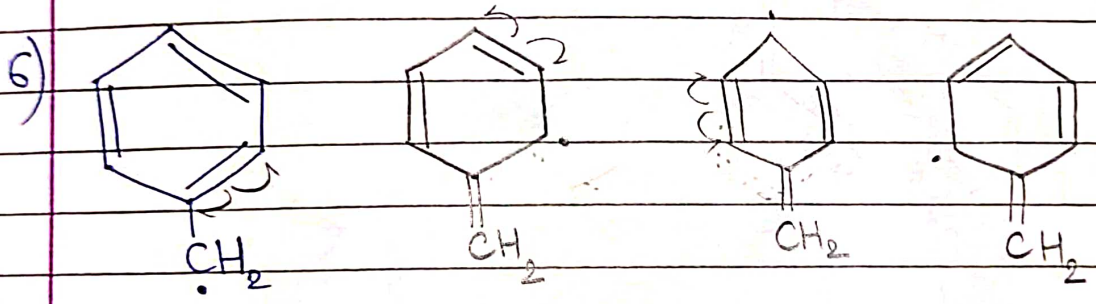
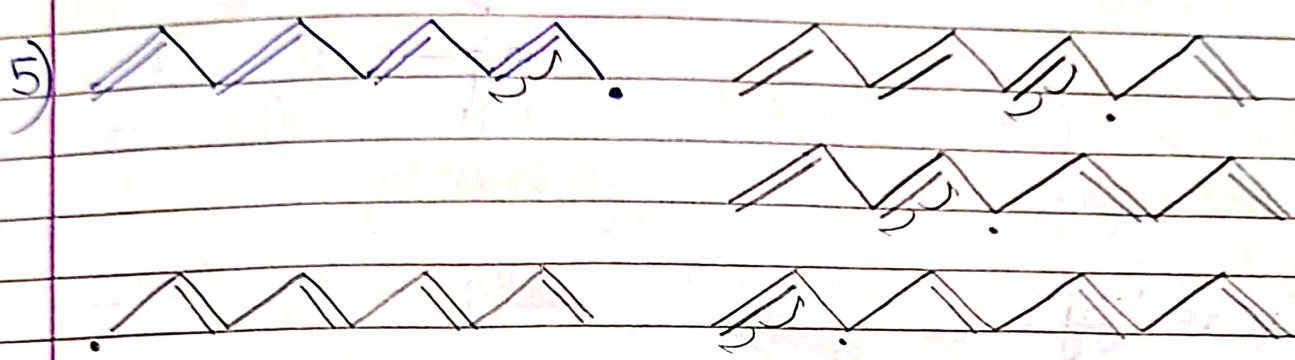
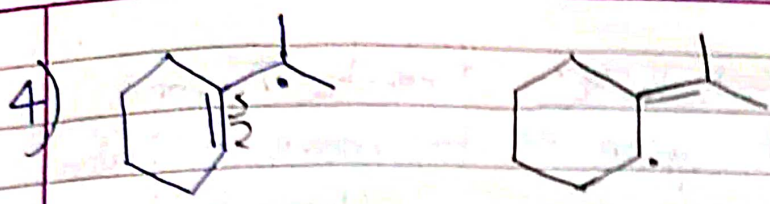
★  $\cdot$  &  $\text{t}$  = exchange



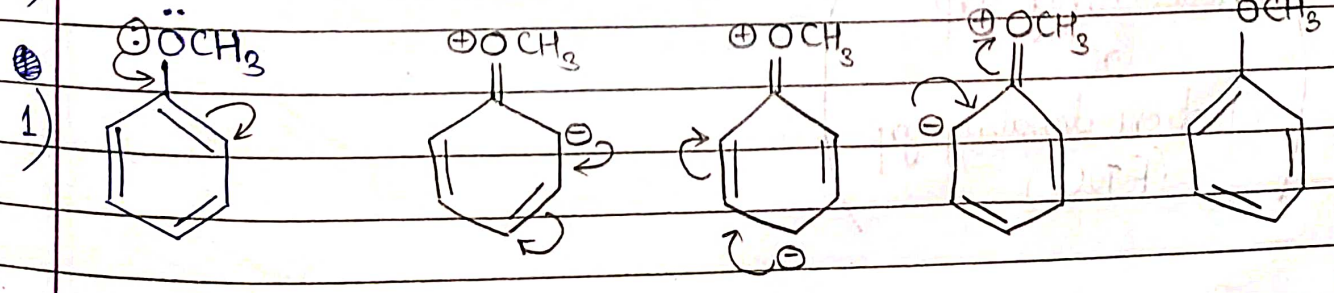
Q) Draw R.S. of following species.



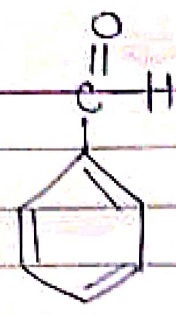
6



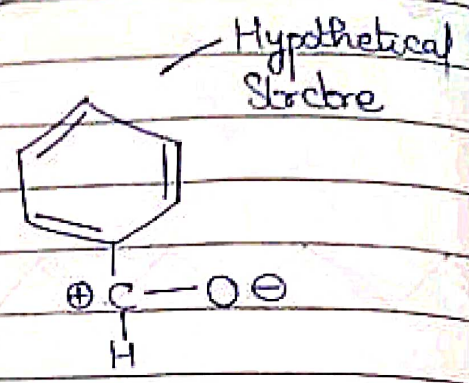
Q) Draw R.S. of following species.



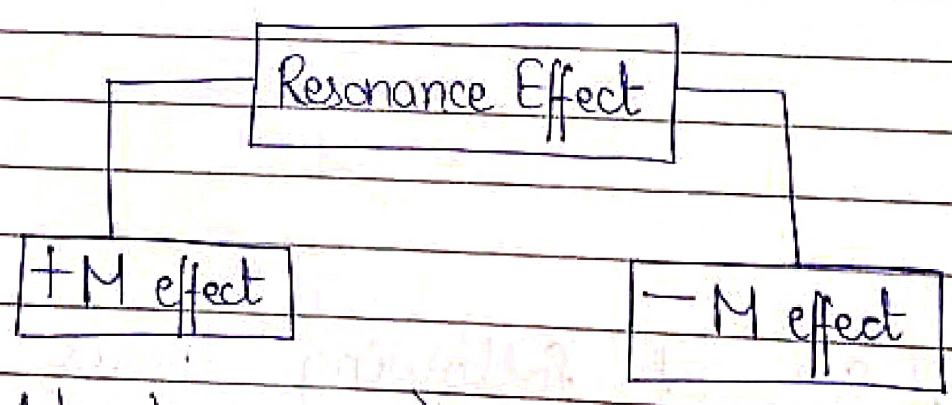
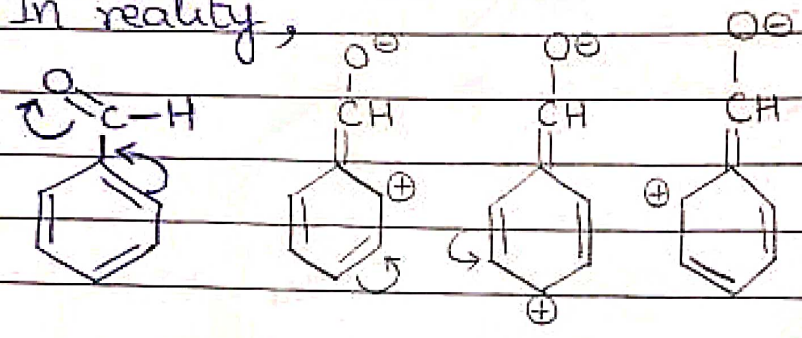
☆2)



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



In reality,

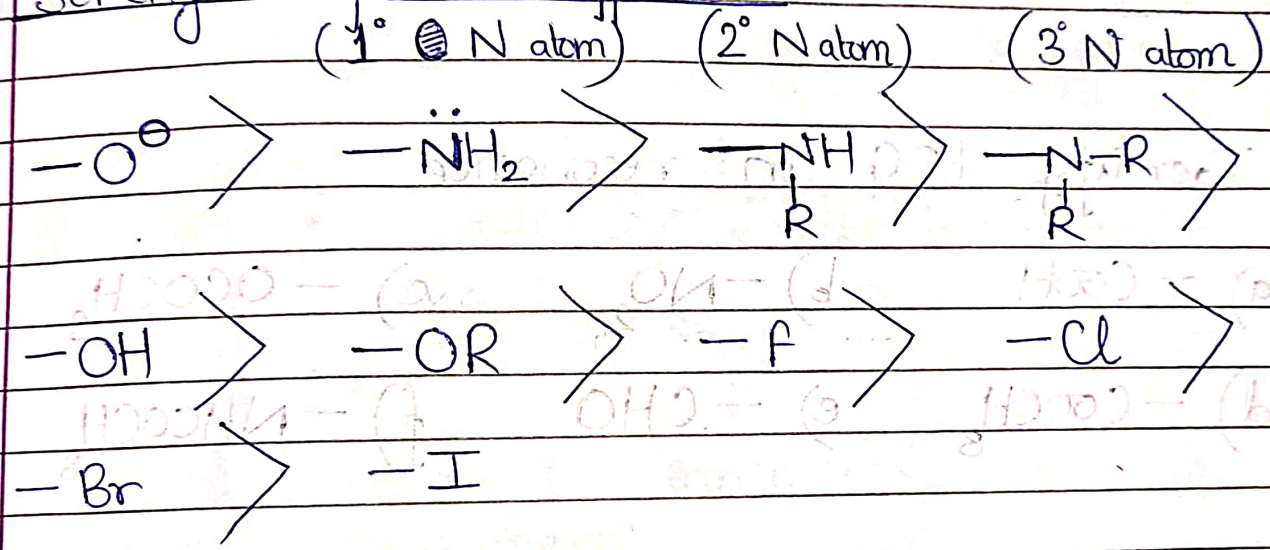


Activating grp  
or  
Electron donating grp  
(EDG)

+M effect :-  $e^-$  donated in ring/chain.

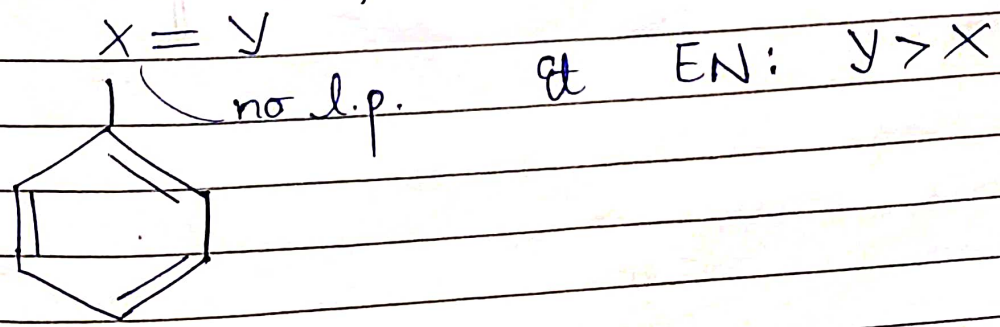
for showing only +M effect, grp. must have at least 1 l.p. without having multiple bond with more EN atom.

Strength of +M effect :-

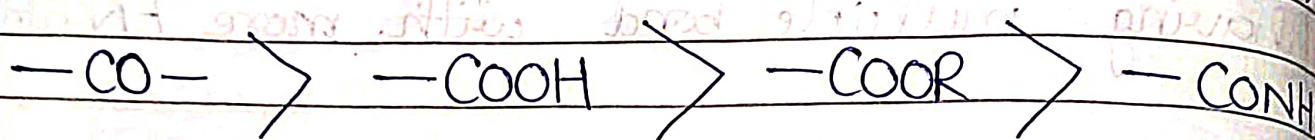
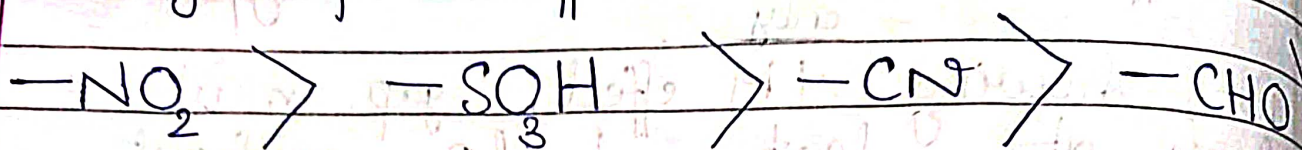


-M effect :-  $e^-$  taken from ring/chain.

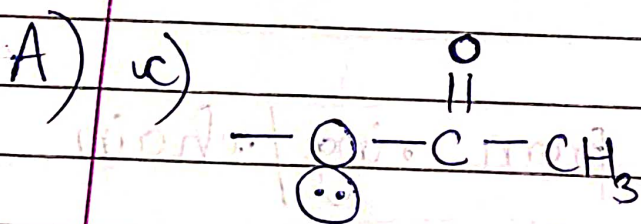
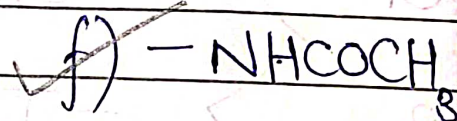
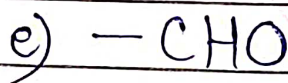
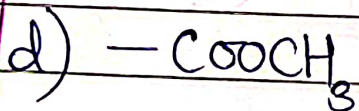
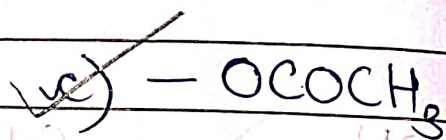
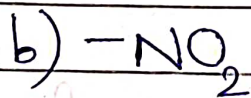
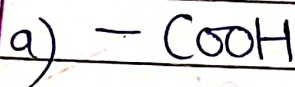
for showing only -M effect, grp. must be multiple bonded to atom with greater EN & not having l.p.



Strength of -M effect: -

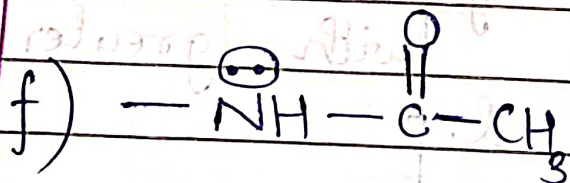


(Q) Identify EDG in resonance -



l.p. It no multiple bond

$\Rightarrow$  +M effect

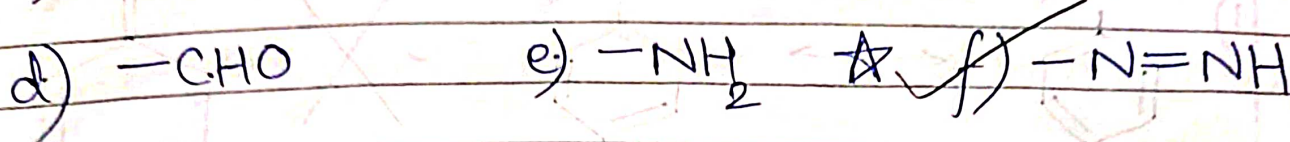
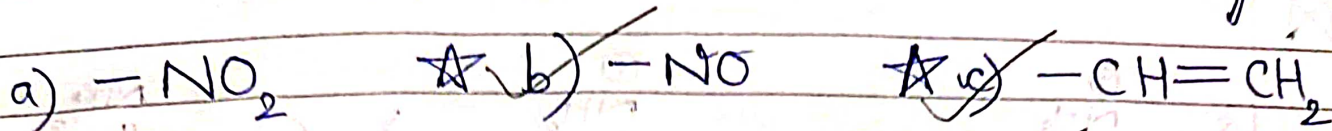


l.p. It no multiple bond

$\Rightarrow$  +M effect

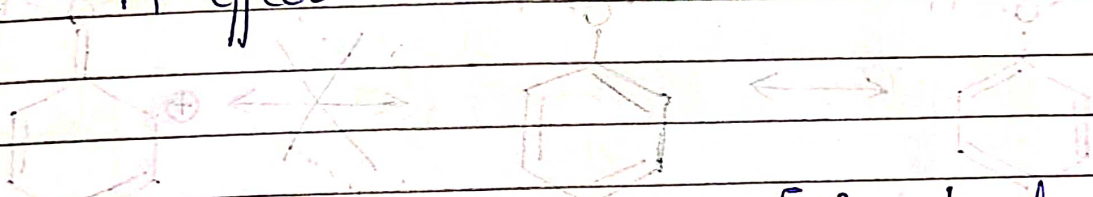


Q) Which can show both +M & -M effect.

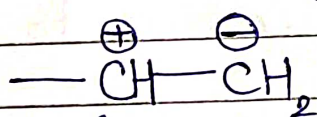


A) b)  $-\text{N}=\text{O}$     Both l.p. & multiple bond with more EN atom

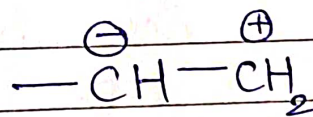
⇒ +M effect due to l.p. &  
-M effect due to double bond.



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



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

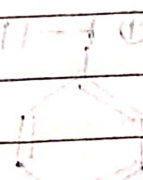


(donate  $\bar{e}$  in chain/ring)

⇒ -M effect



⇒ +M effect



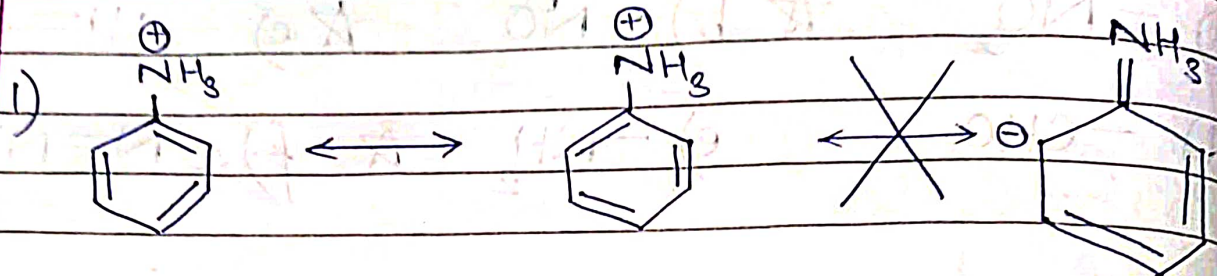
f) same as c).



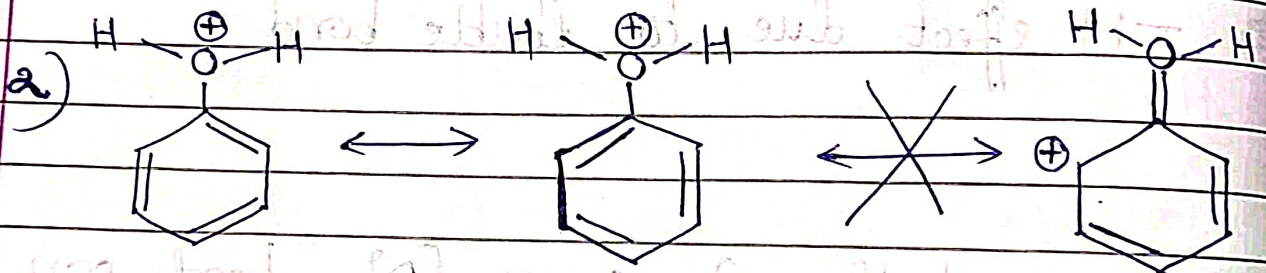
116



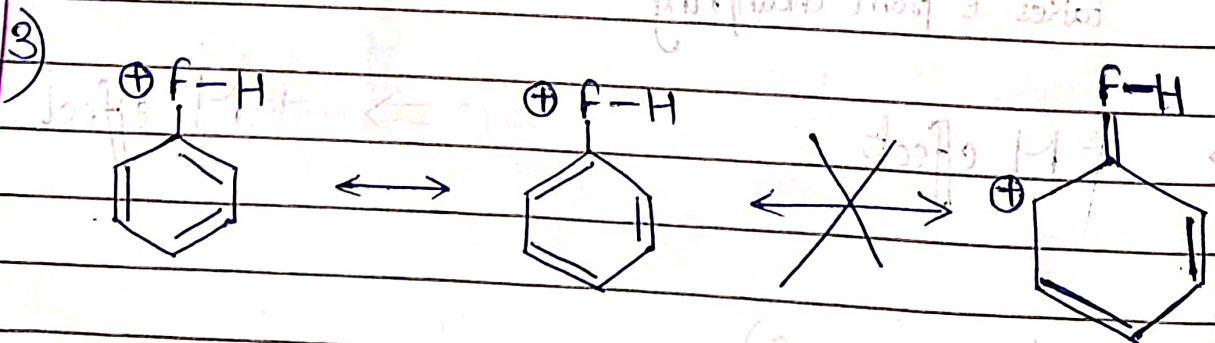
Resonance Structures



as in last strcture 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, Antiaromatic & Non-aromatic

## Aromatic —

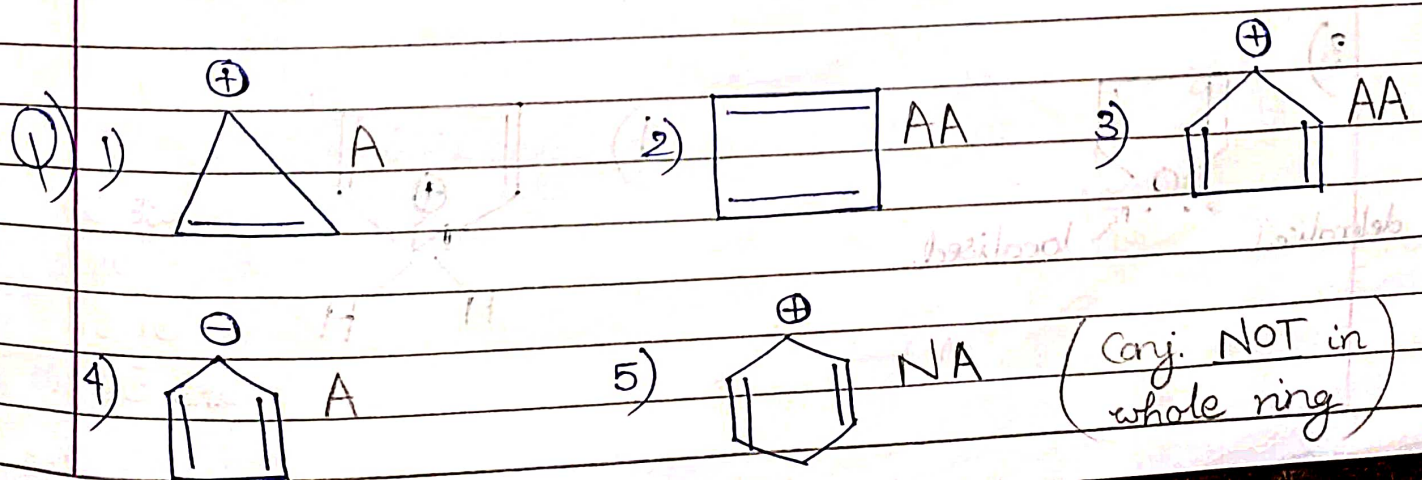
- 1) Cyclic
- 2) Planar
- 3) Every atom  $sp/sp^2$
- 4) Conjugation in whole
- 5) follow Hückel's Rule :  
 $(4n+2) \pi$  delocalised  $e^-$  ( $n \in \mathbb{Z}$ )  
 at Periphery.

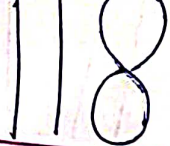
## Antiaromatic —

- 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.

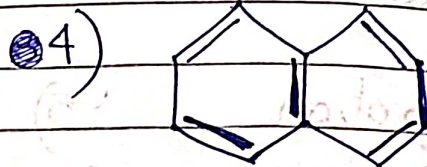
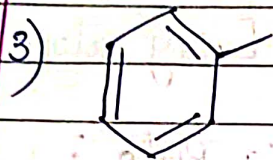
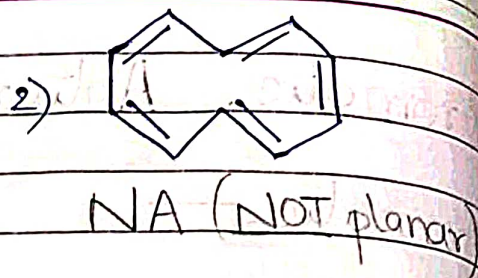
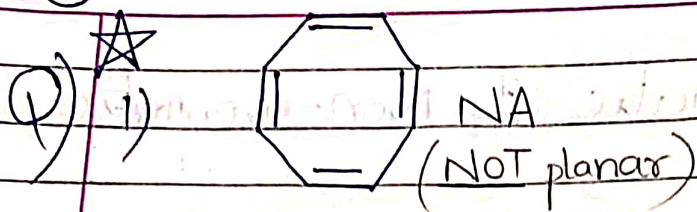
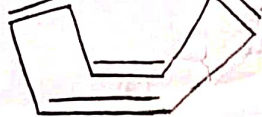
## Non-aromatic —

Neither aromatic nor antiaromatic

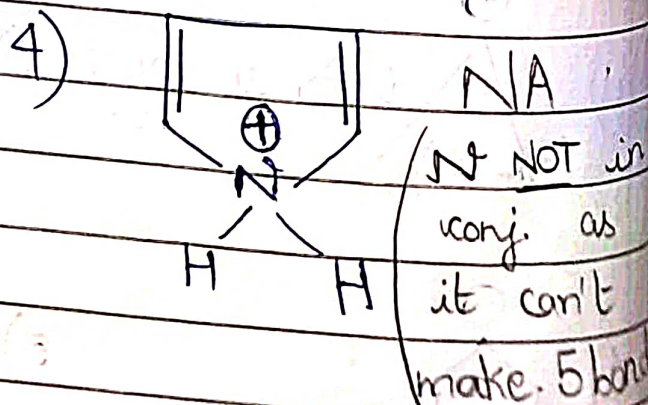
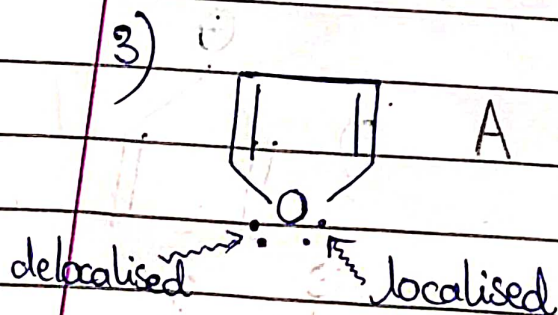
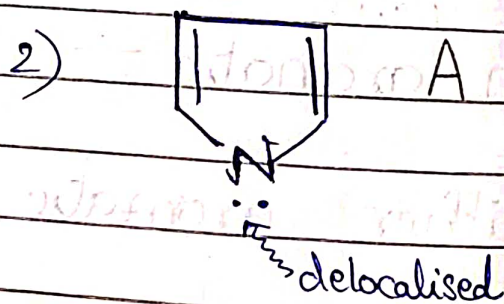
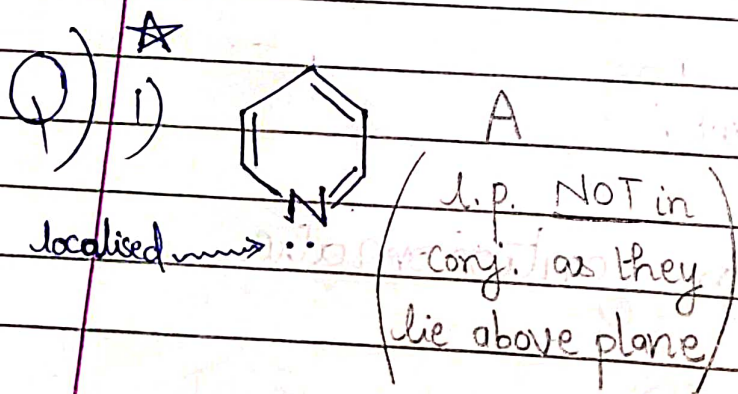




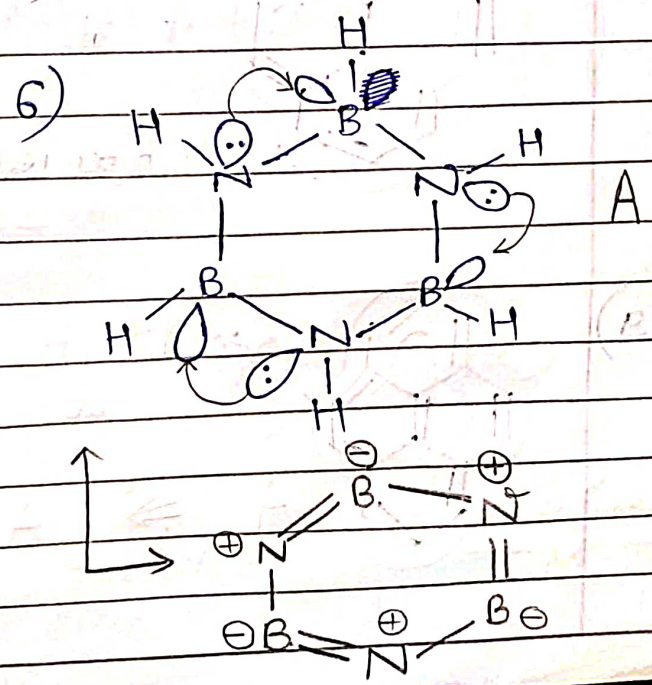
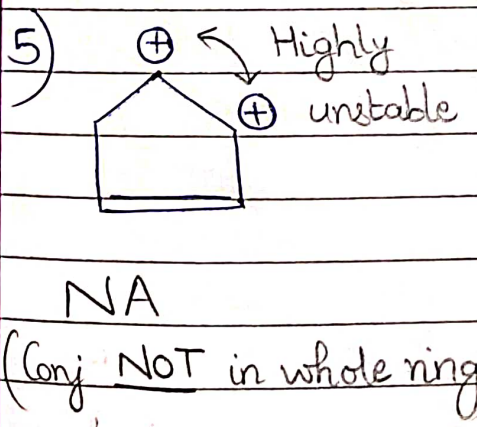
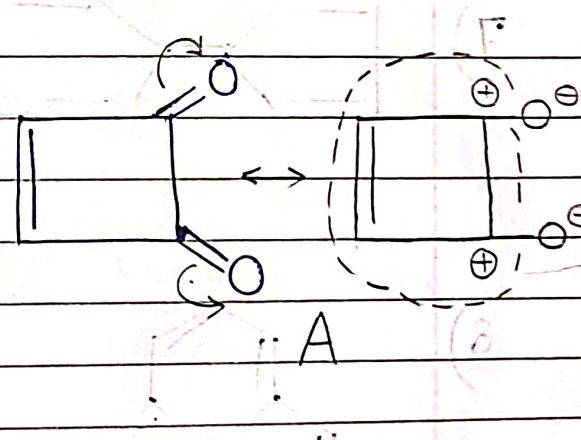
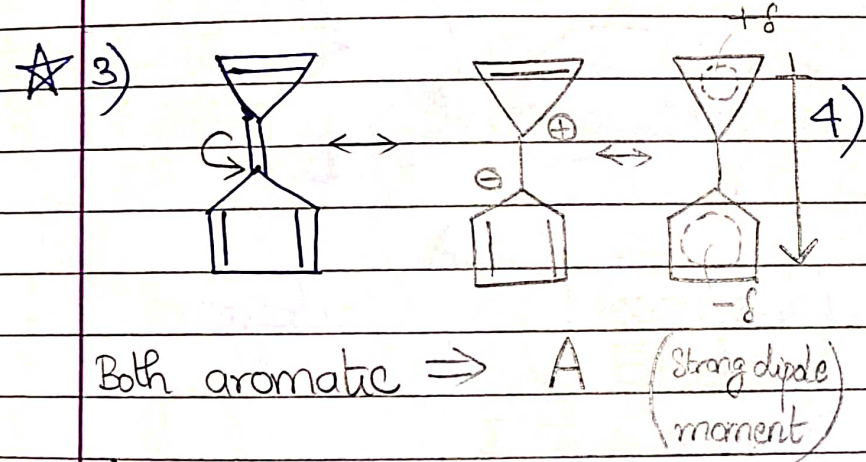
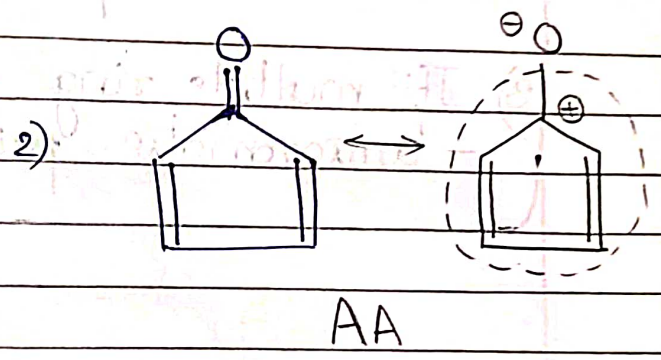
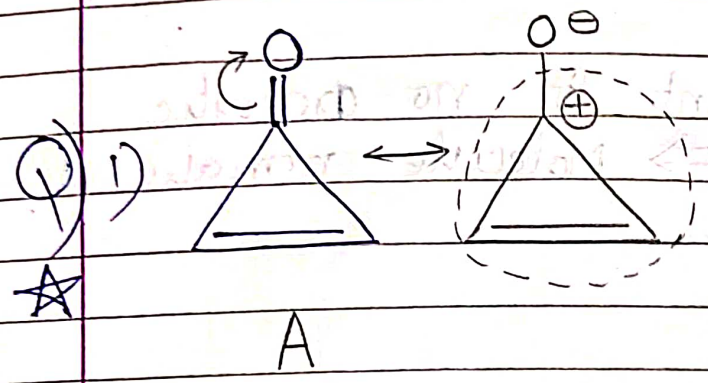
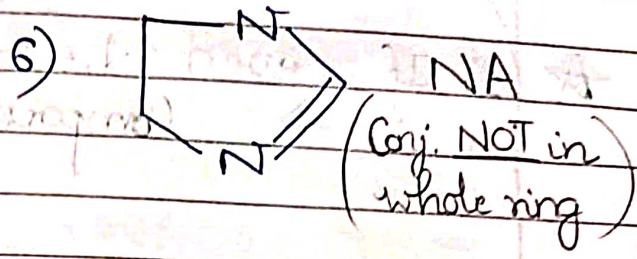
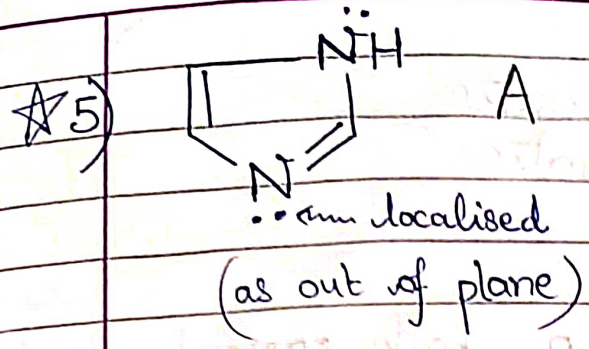
Real Structure:



★ 1) In general,  $\geq 8C \Rightarrow$  Non planar structure.  
 2) If in any molecule, if even 1 ring is aromatic, then whole molecule is aromatic.



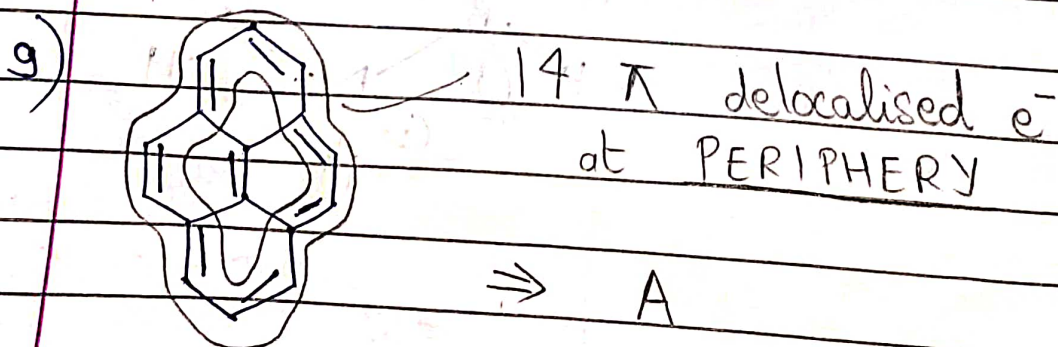
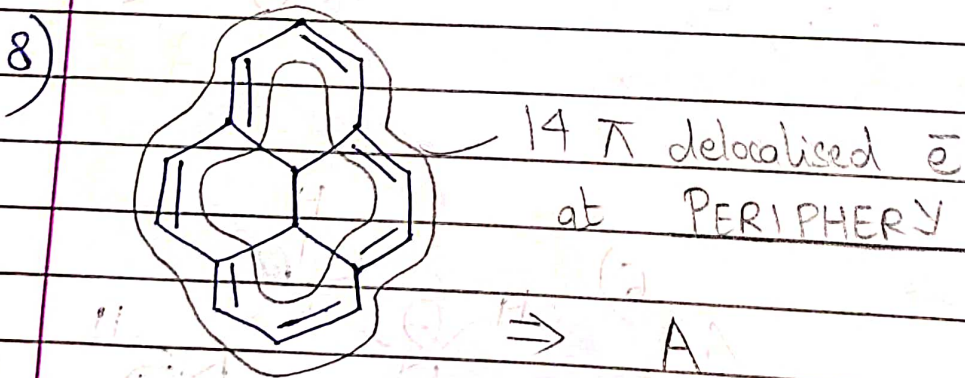
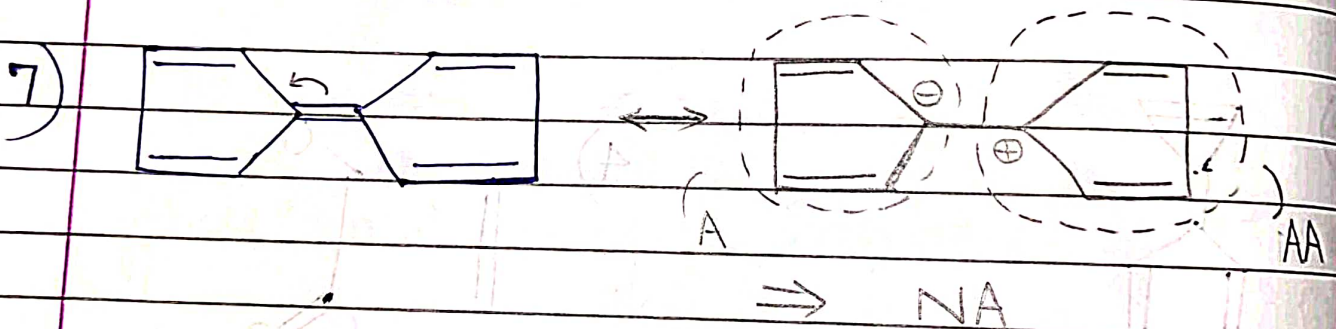
delocalised

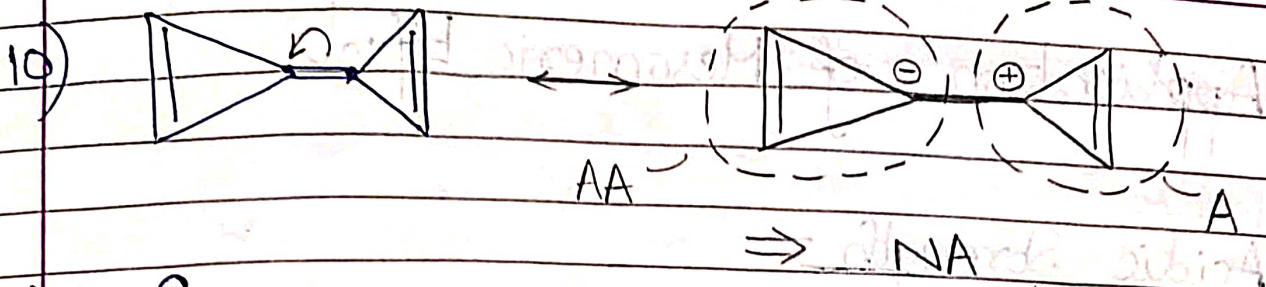


★ 1) If <sup>resonance</sup> even 1 structure aromatic  
 $\Rightarrow$  Compound aromatic.

2) If multiple bond & l.p. both present  
 $\Rightarrow$  l.p. localised

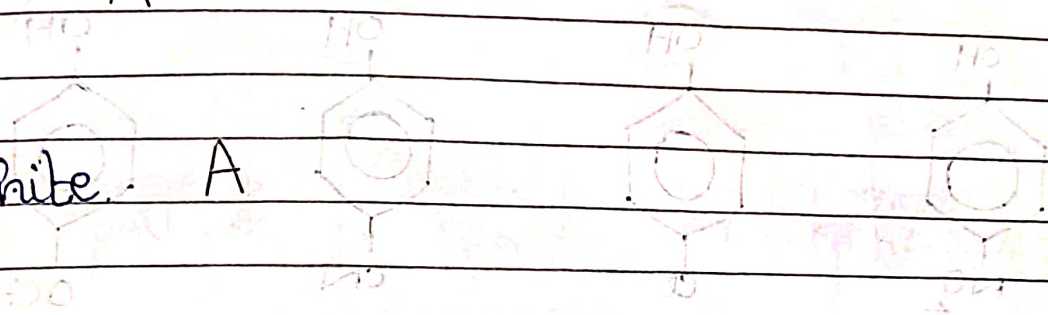
3) If multiple ring present & no aromatic  
 - antiaromatic pair  $\Rightarrow$  Molecule aromatic



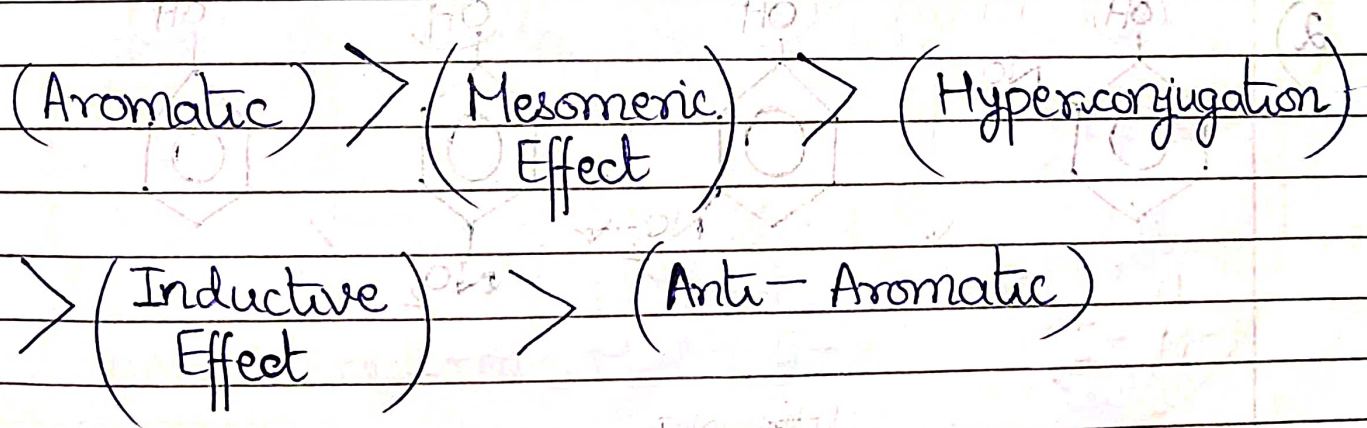


★ 11)  $C_{60}$  A

★ 12) Graphite. A

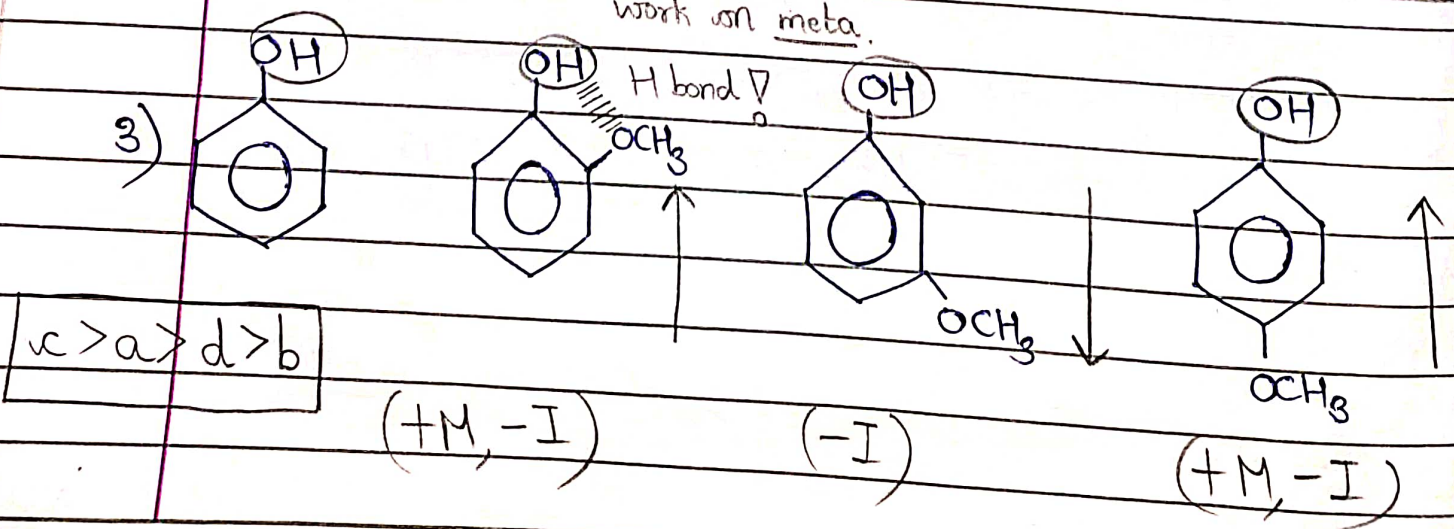
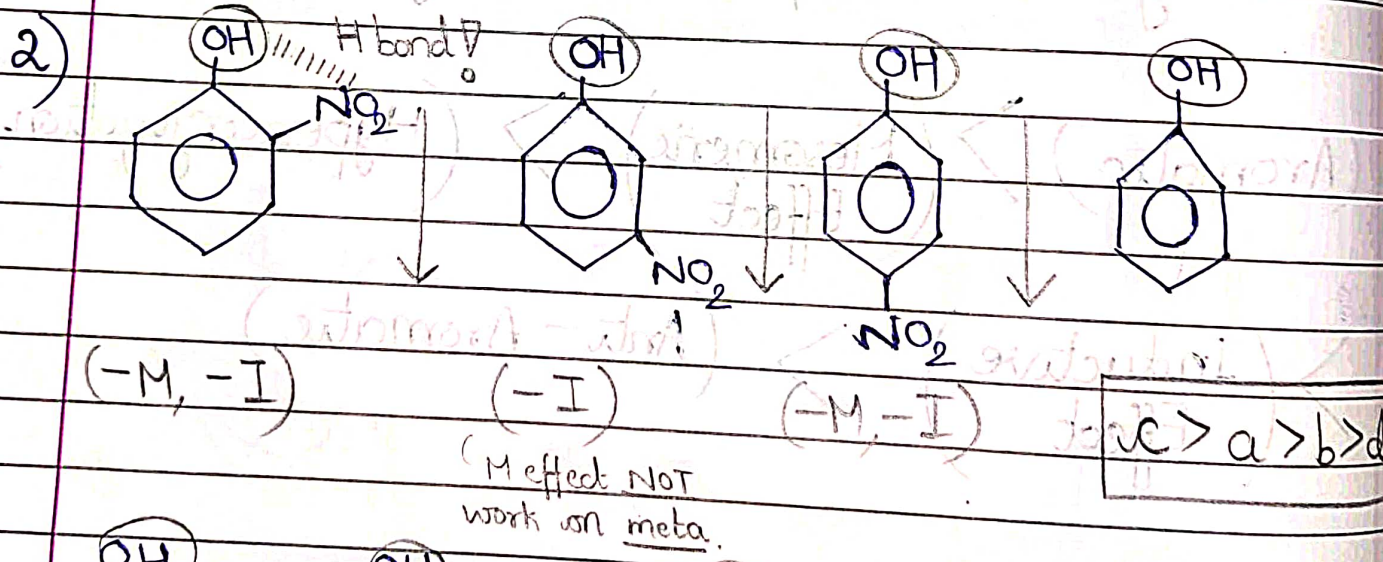
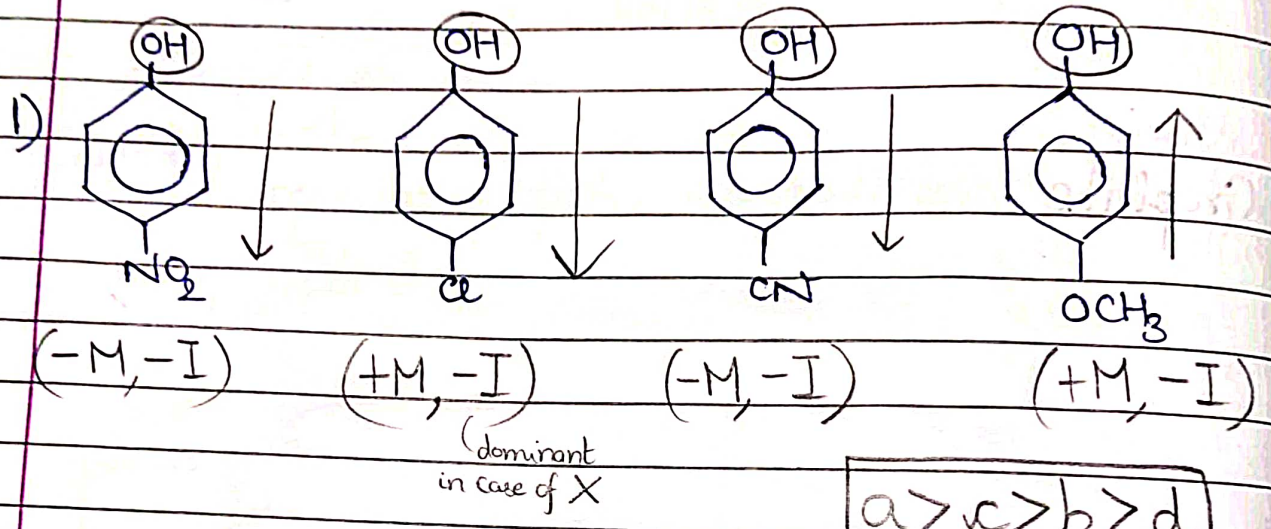


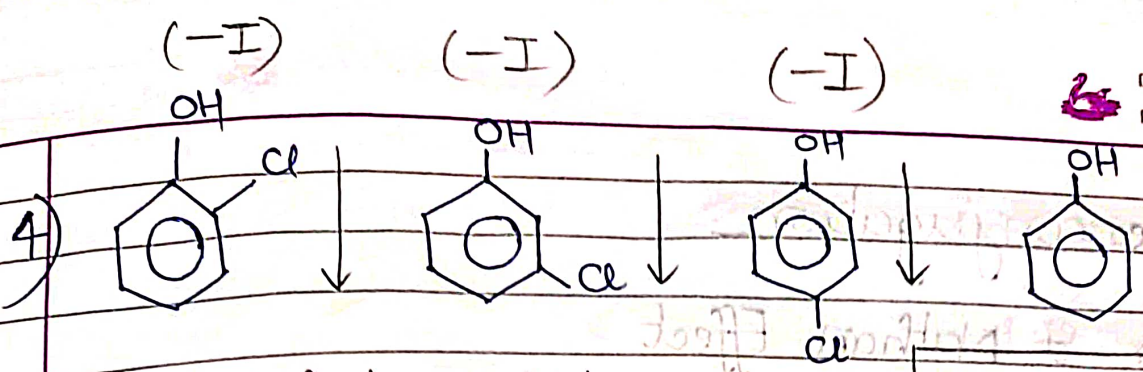
### Priority Order for Q solving



# Application of Mesomeric Effect.

## 1) Acidic Strength -





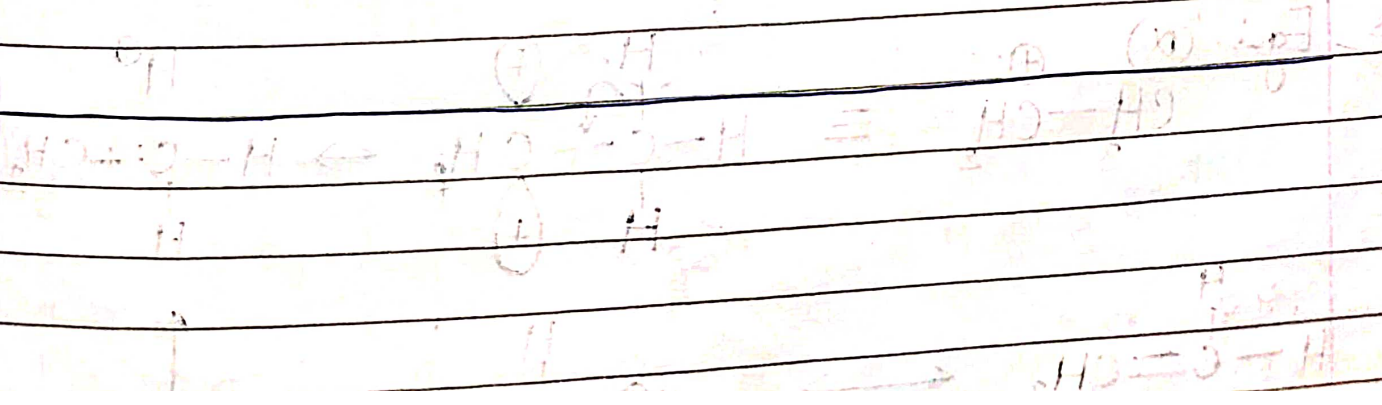
Ignore M effect as Halogen.

a > b > c > d

★ 1) for Halogens, (Inductive Effect) > (Mesomeric Effect)

2) Mesomeric Effect does NOT work on Meta post. as in resonance structures  $\oplus$  or  $\ominus$  charge does NOT appear on meta post.

3) When no. of  $-M$  &  $-I$  effect same, look for H bond. It will reduce H<sub>2</sub> release. in 2 comp.



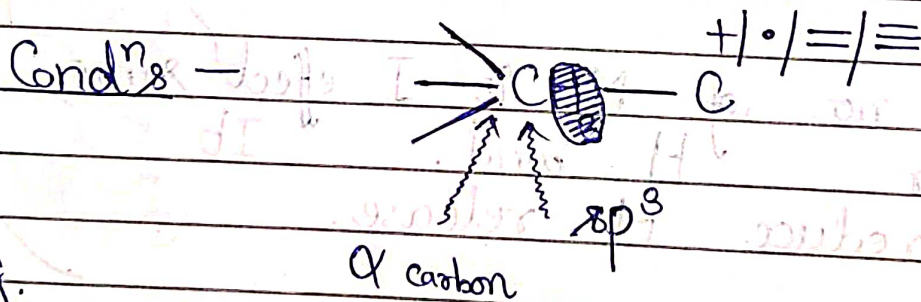


# Hyperconjugation

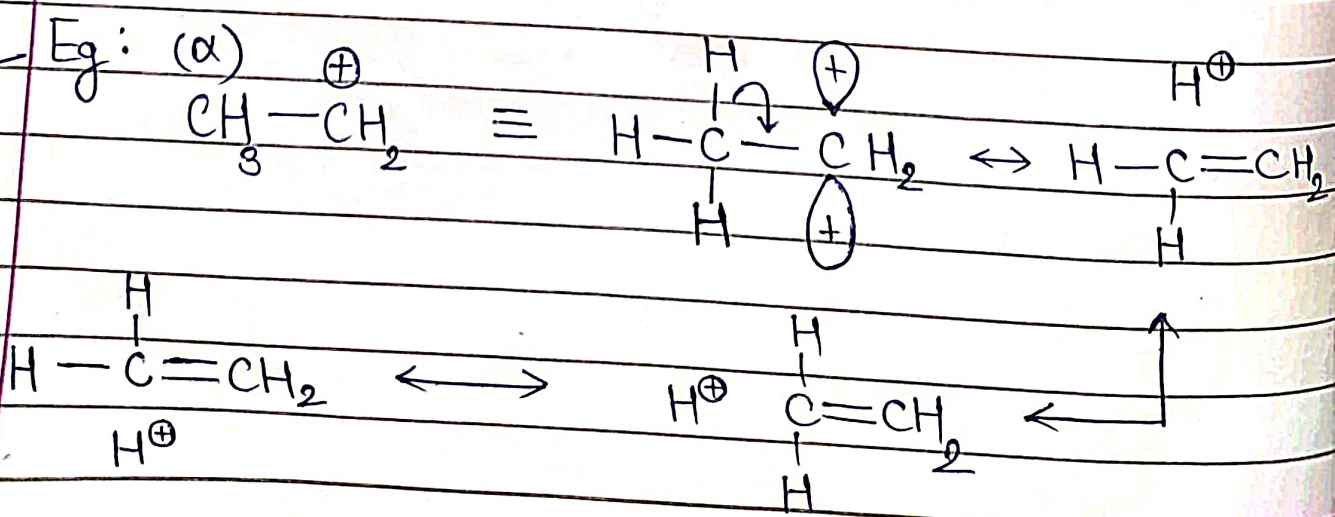
- Baker & Nathan Effect
- No bond resonance
- $\sigma$  bond resonance

It explains the stability of Alkene & Carbon free Radical

It is  $\sigma$  bond conj. with adj. empty or partially filled p orbital, or  $\pi$  bond



Hyperconj.  
Structres

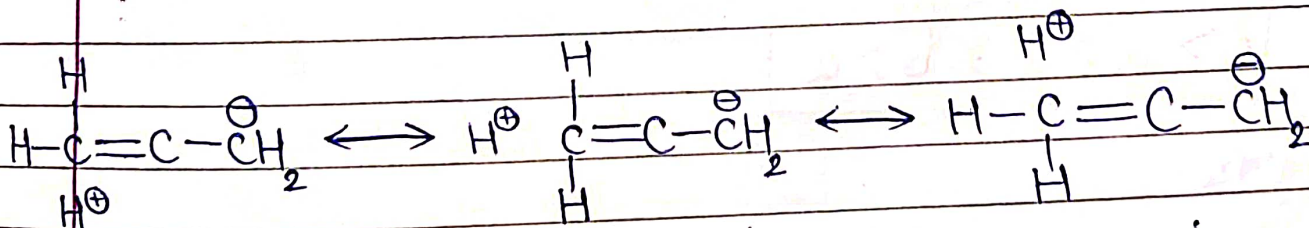
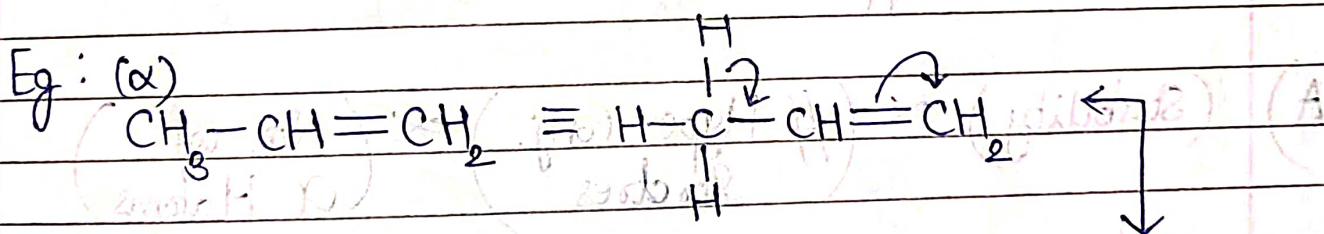
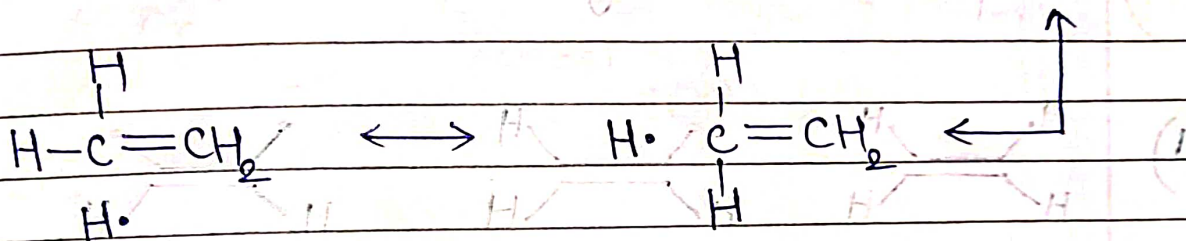
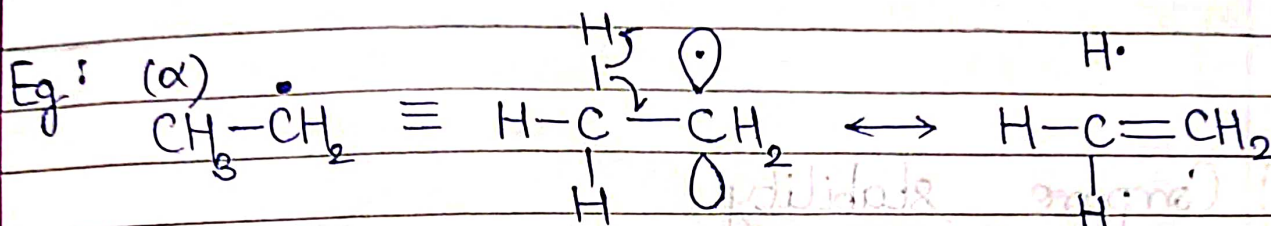


( $\alpha$  H atom) = ~~Atom~~ (H atoms connected to  $\alpha$  C atom)

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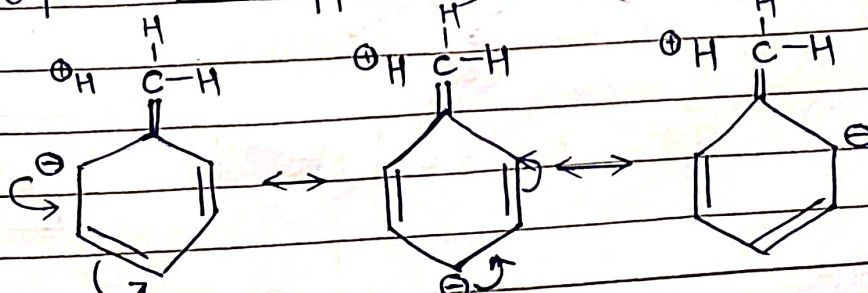
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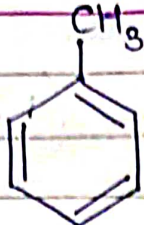
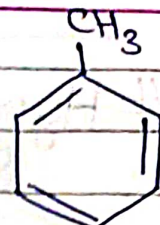
$$\left( \begin{array}{l} \# \text{ Hyperconj.} \\ \text{Structres} \end{array} \right) = \left( \begin{array}{l} \text{No. of } \alpha \text{ H atoms} \\ + \\ 1 \end{array} \right)$$



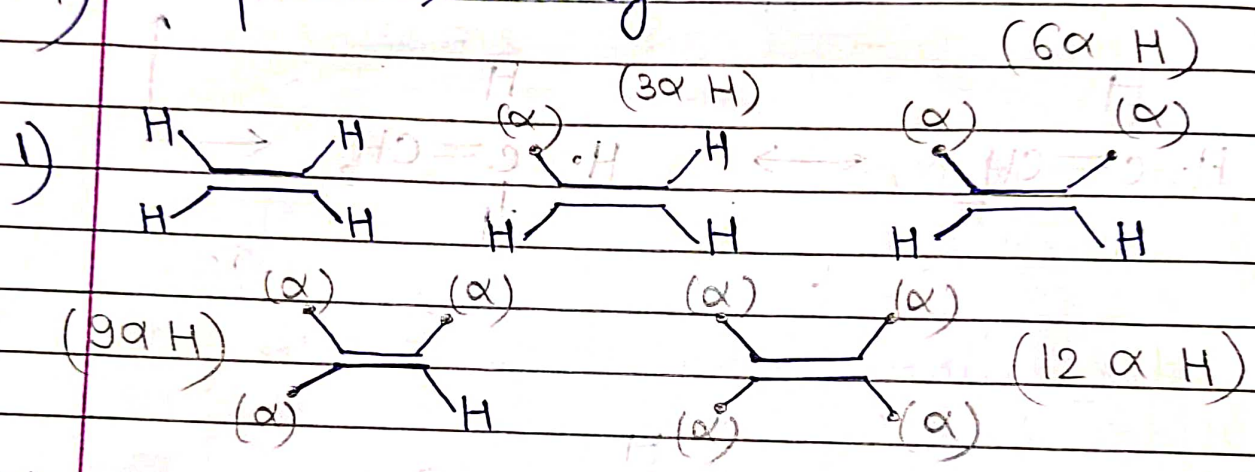
Eg: (Above formula NOT applicable) ! (# Hyperconj: structres) = 10

Due to  
1 H



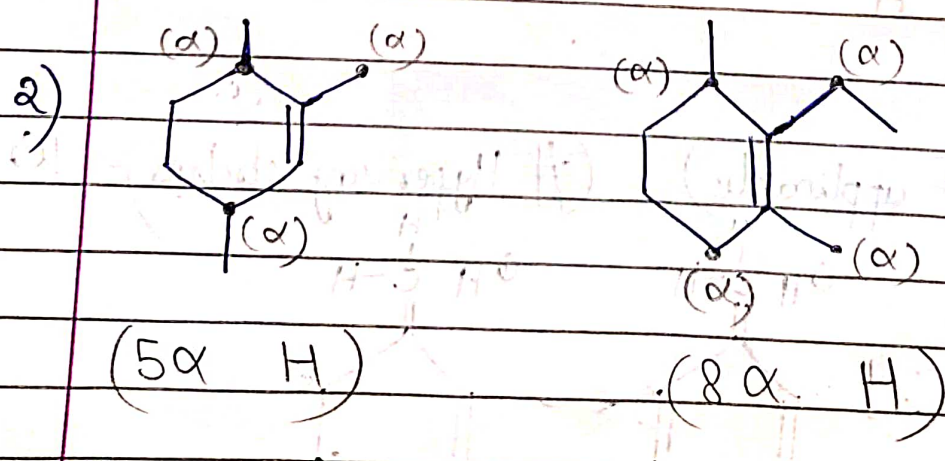
Observe that  and  are Resonance structures, NOT Hyperconj. structures

Q) Compare stability.

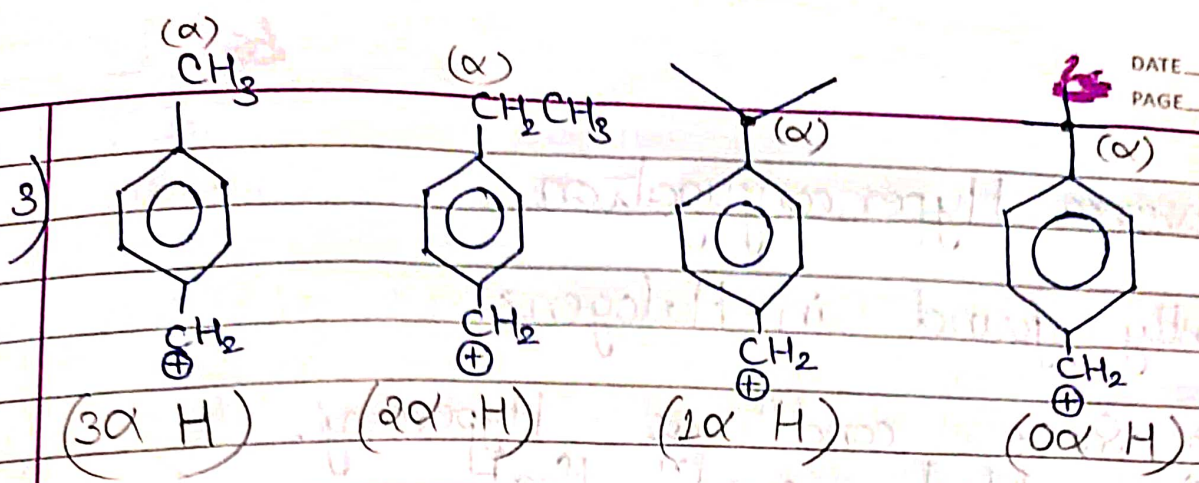


A) (Stability)  $\propto$  (# Hyper Conj. Structures)  $\propto$  (No. of  $\alpha$  H atoms)

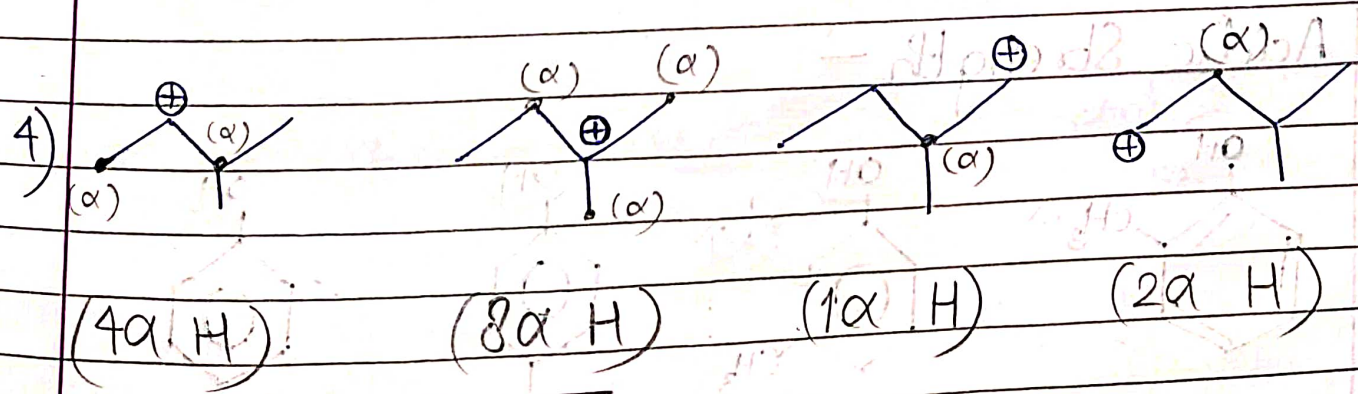
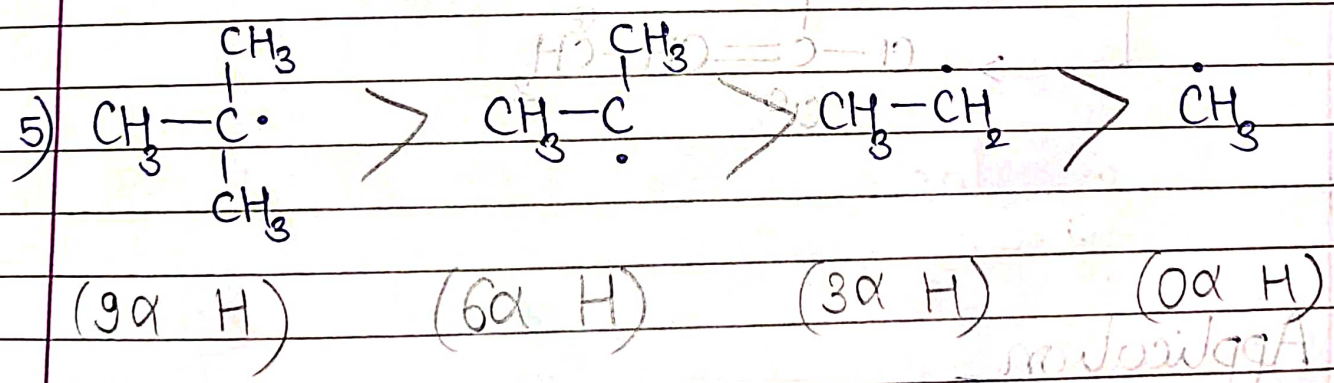
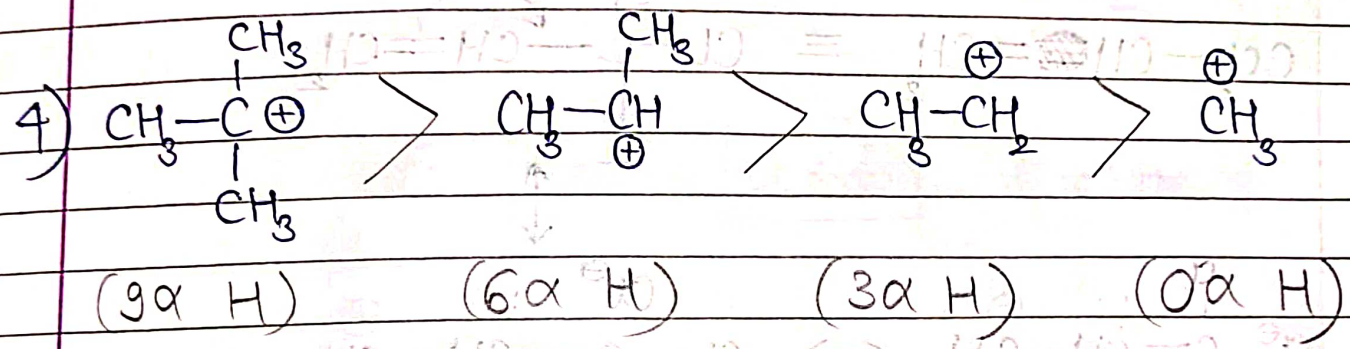
$e > d > c > b > a$



$b > a$



a > b > c > d

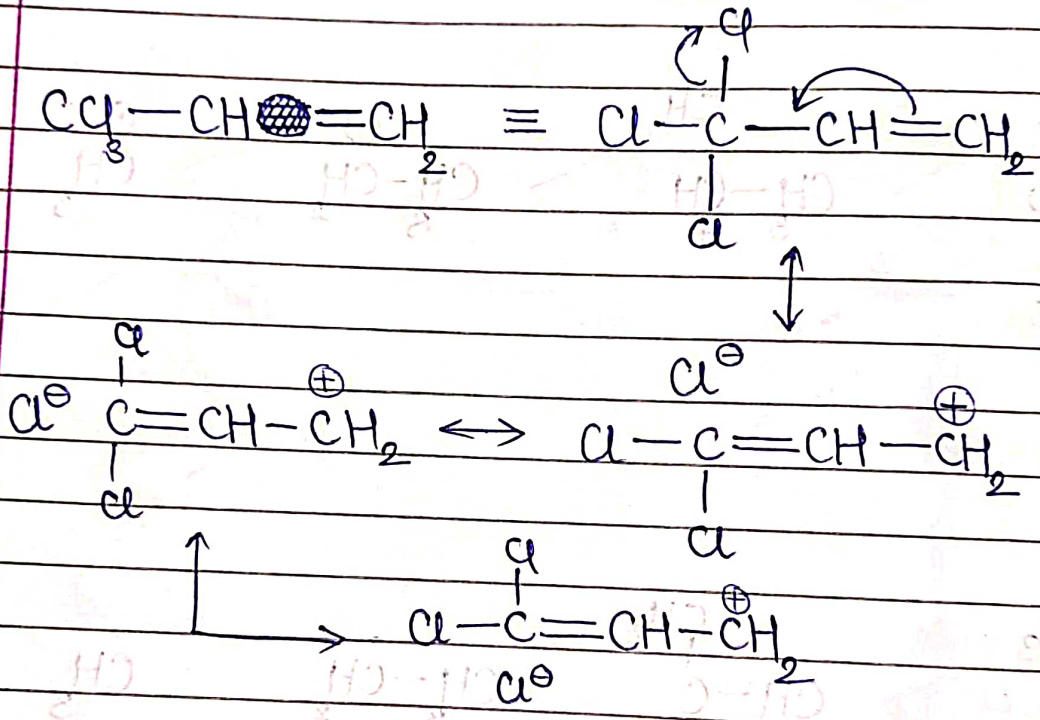


b > a > d > c

## Reverse Hyperconjugation

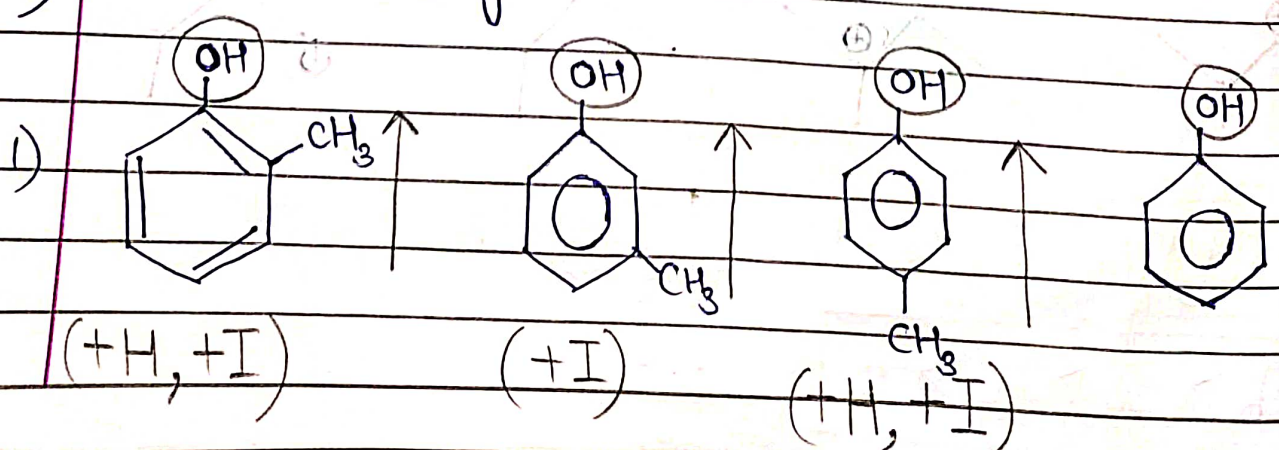
Mostly found in Halogens.

Same cond<sup>n</sup> as Hyperconjug. with added cond<sup>n</sup> that  $\exists$  halogens on  $\alpha$  carbon.

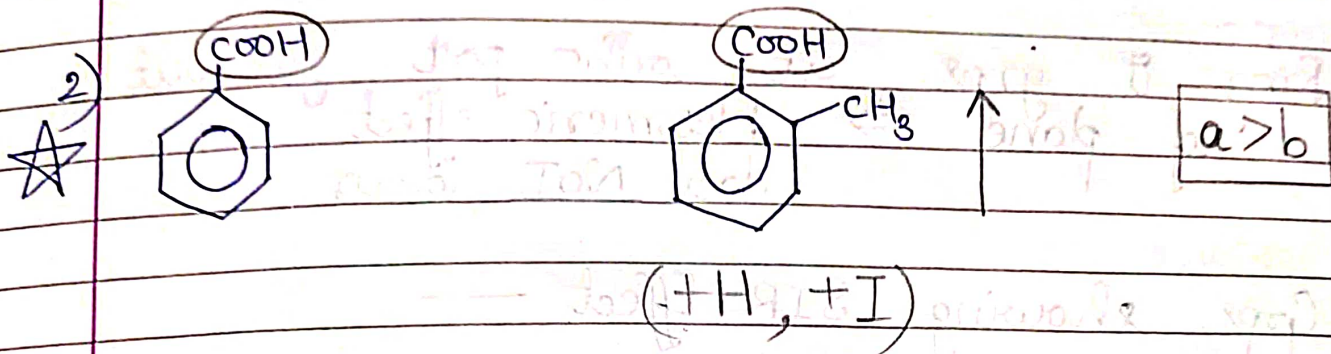


## Application

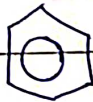
1) Acidic Strength -




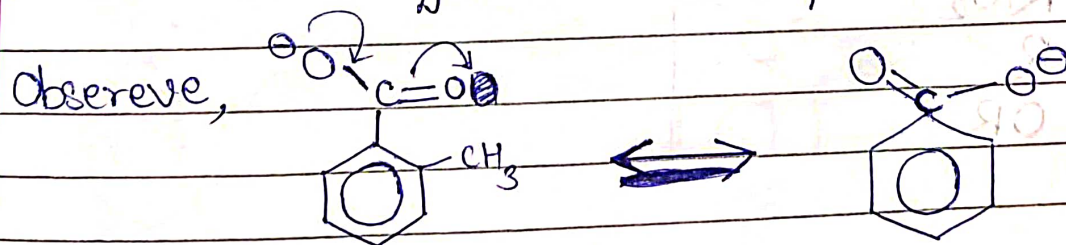
$d > b > c > a$



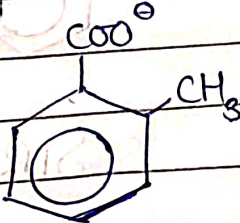
But in this case  $a < b$  due to Ortho Effect.

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

$\Rightarrow$  +  H effect NOT operative.



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 & 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

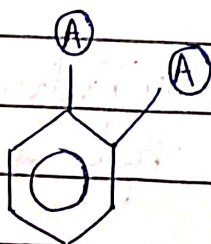
Grp. B

—F

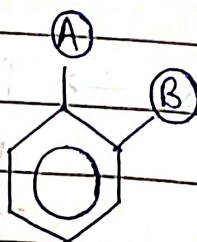
—NH<sub>2</sub>

—CN

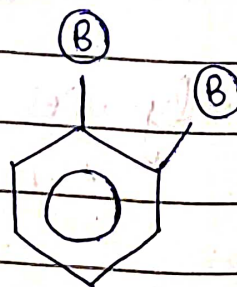
—OH



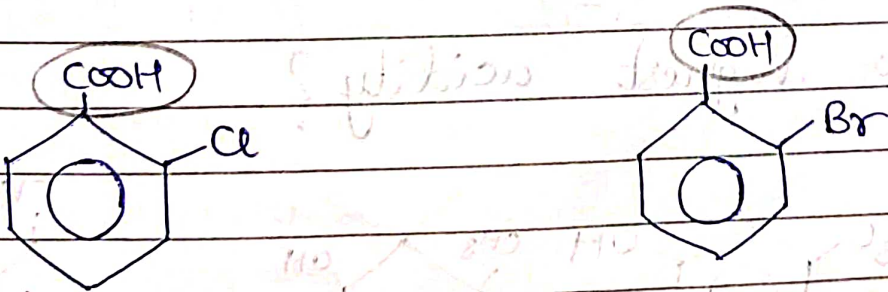
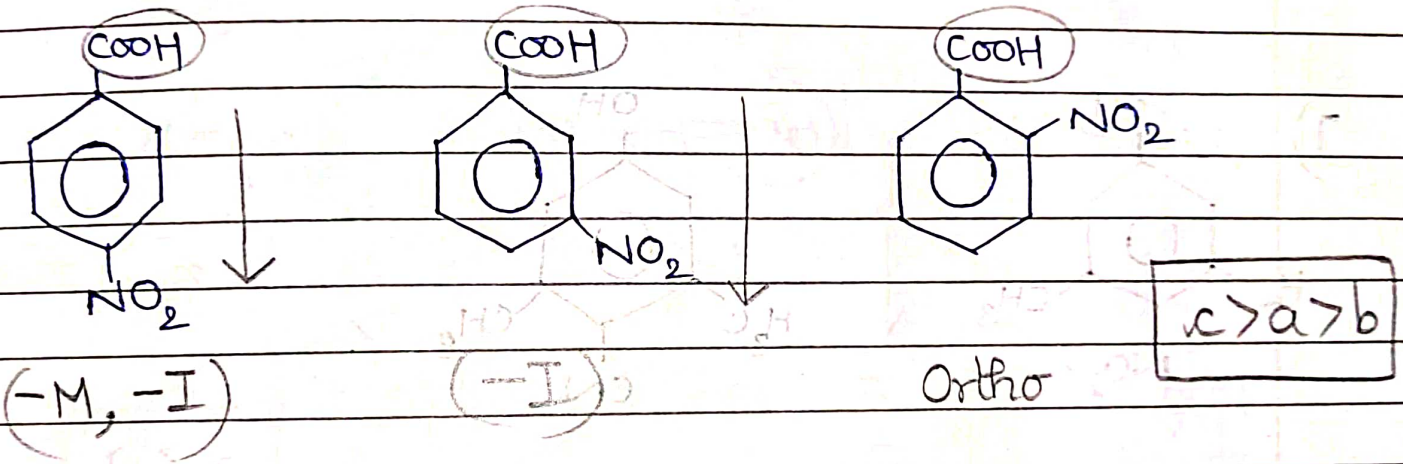
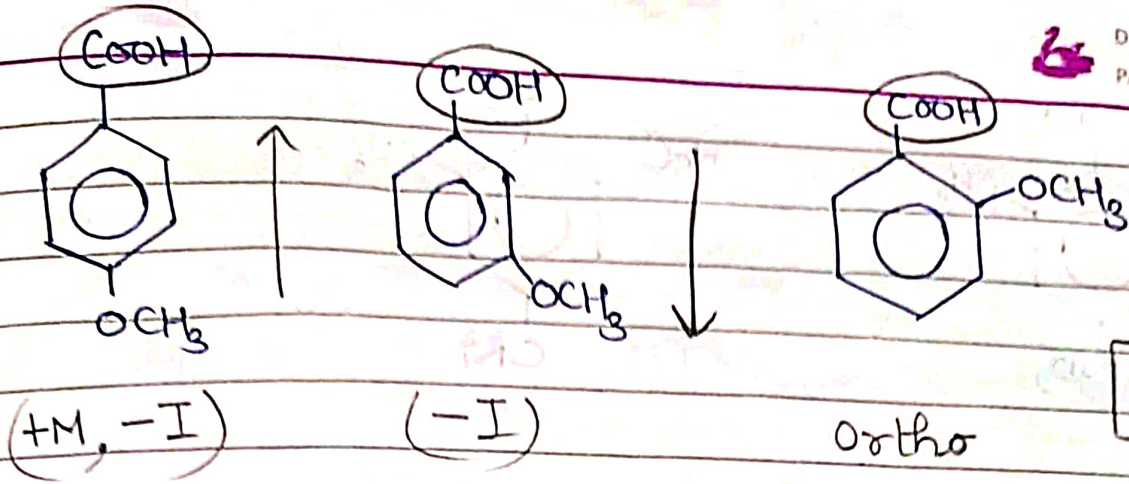
SIR ✓



SIR ✗



SIR ✗



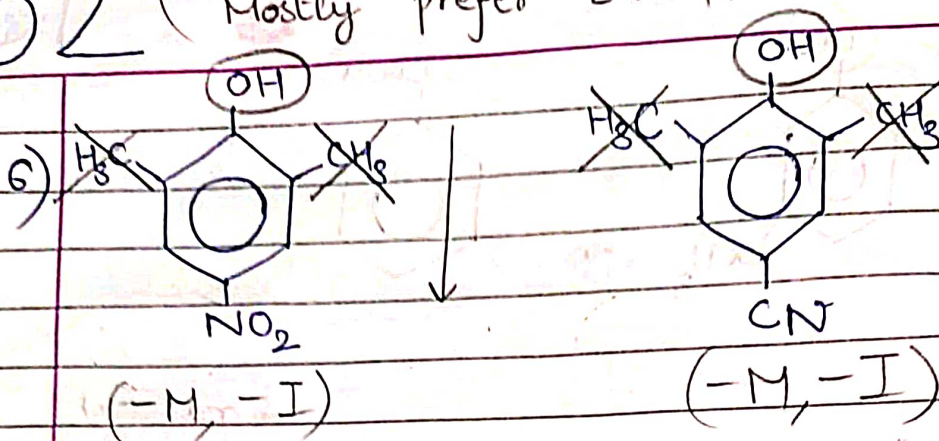
Both show Ortho effect. But Br is more bulky than Cl  $\Rightarrow$  More deviation  $\Rightarrow$  Weaker resonance



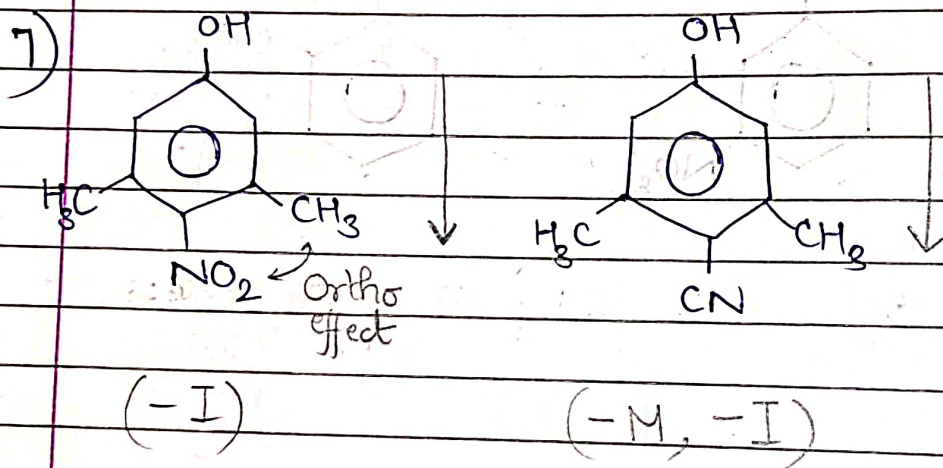
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(Decide acc. to one with higher power. Mostly prefer EWG.)

DATE  
PAGE

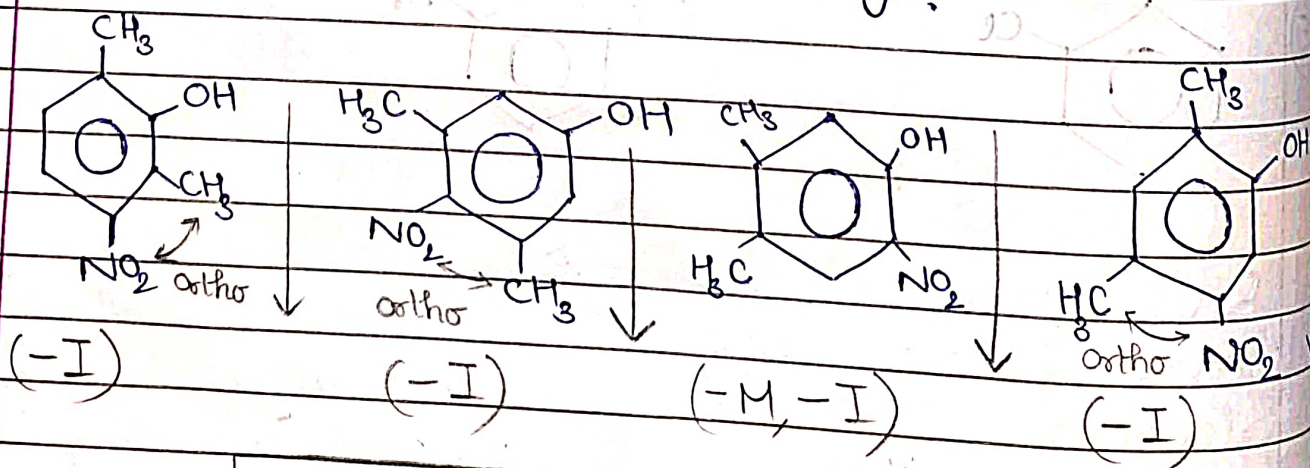


a > b



b > a

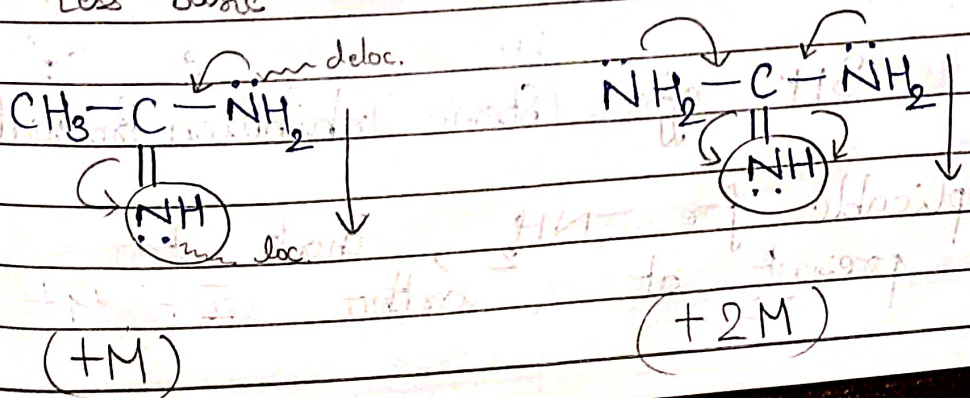
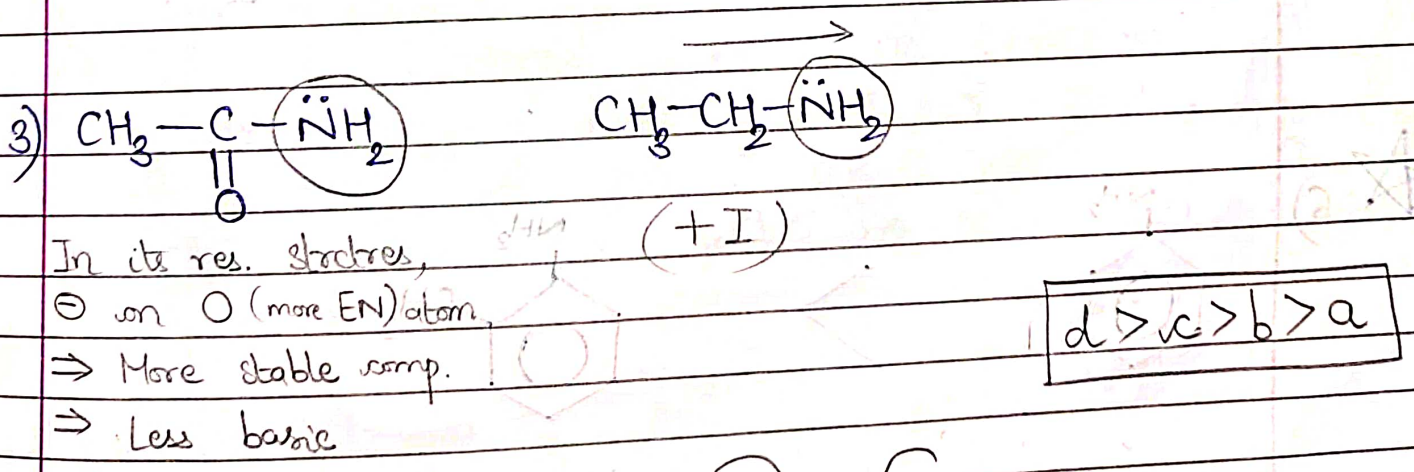
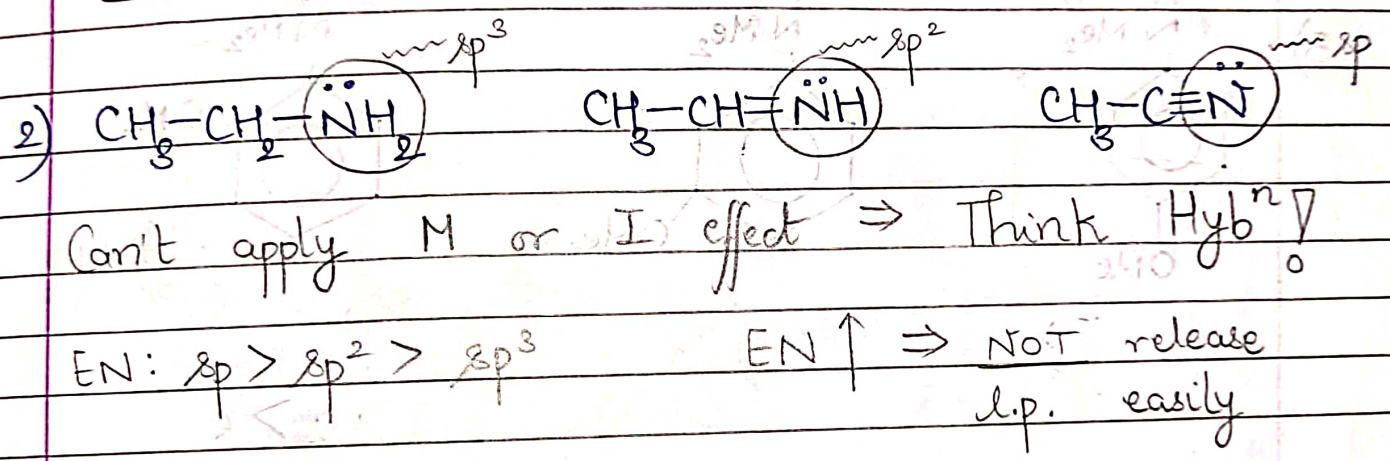
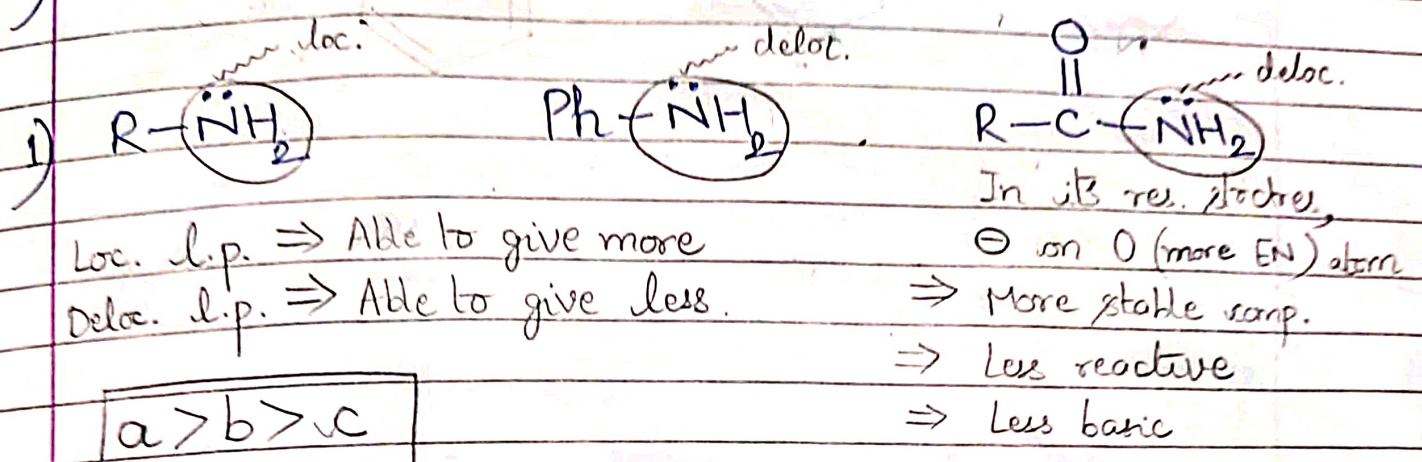
★ 8) Which show highest acidity?



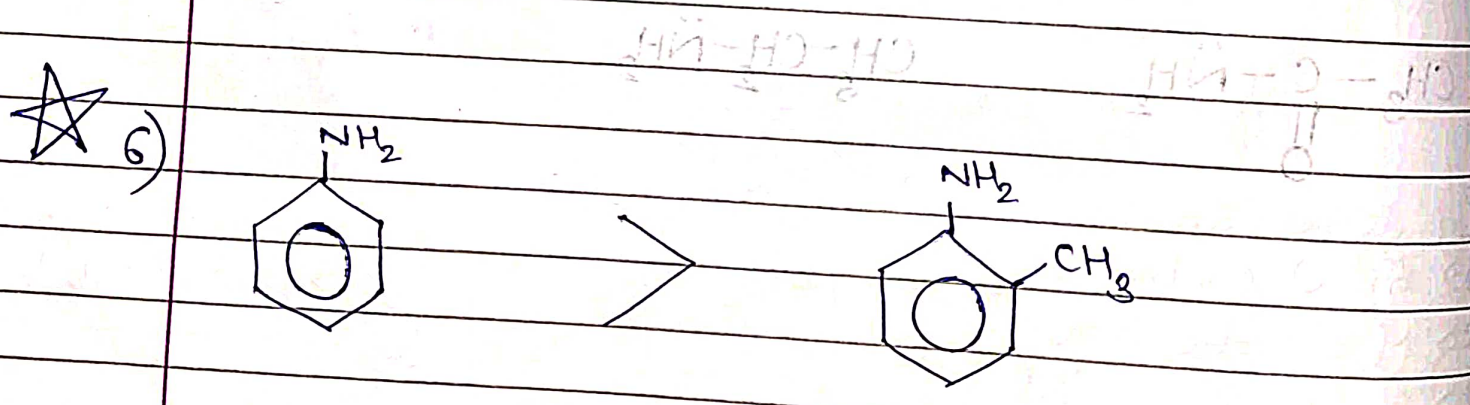
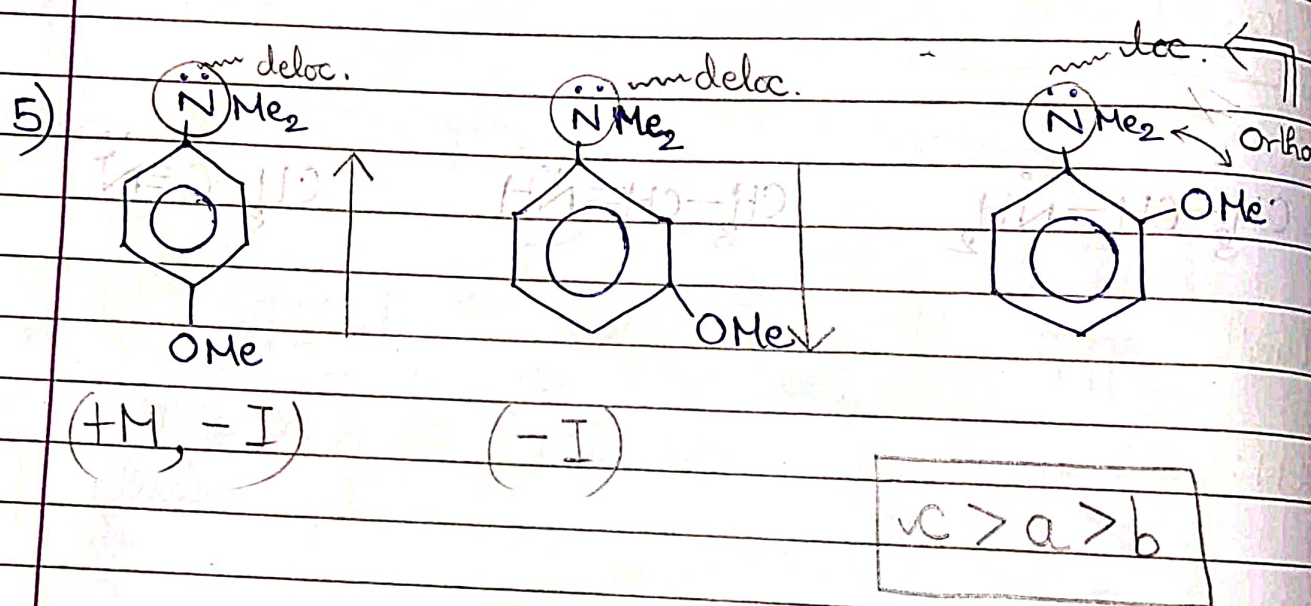
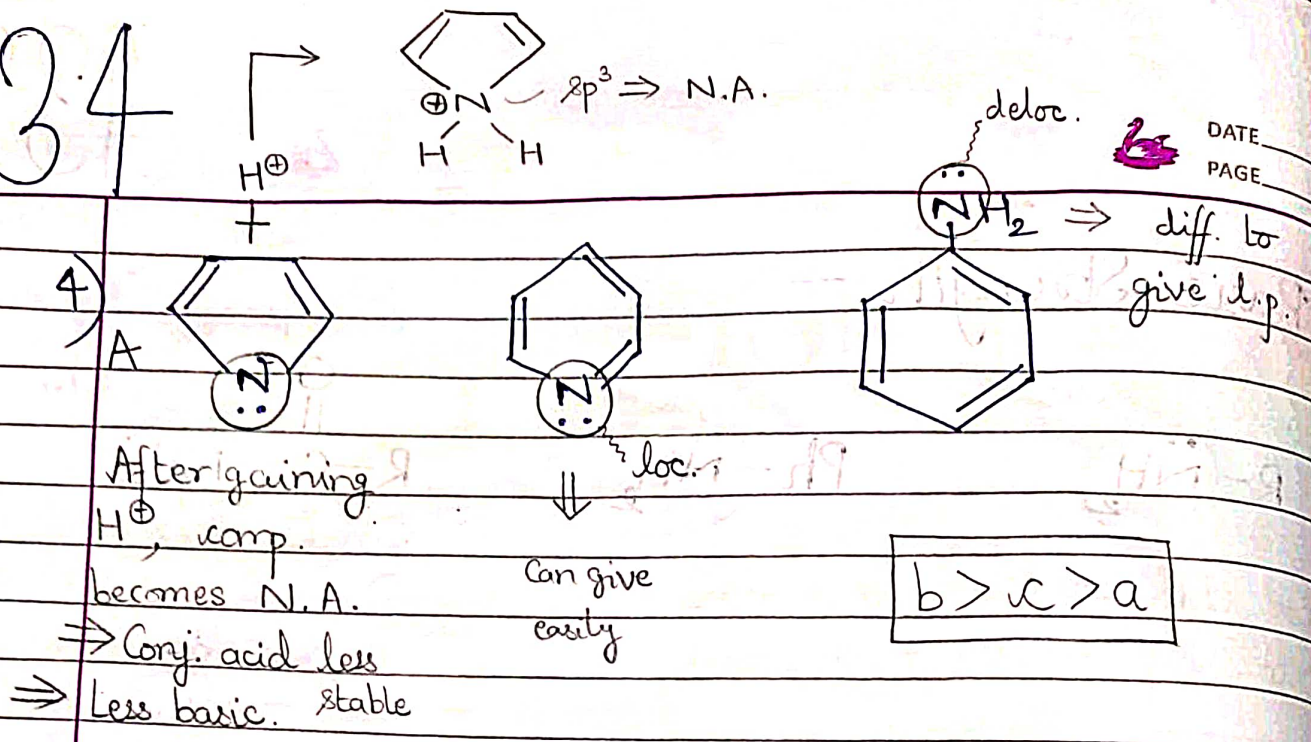
c > d > a > b

(CH<sub>3</sub> jyada power) (NO<sub>2</sub> power)

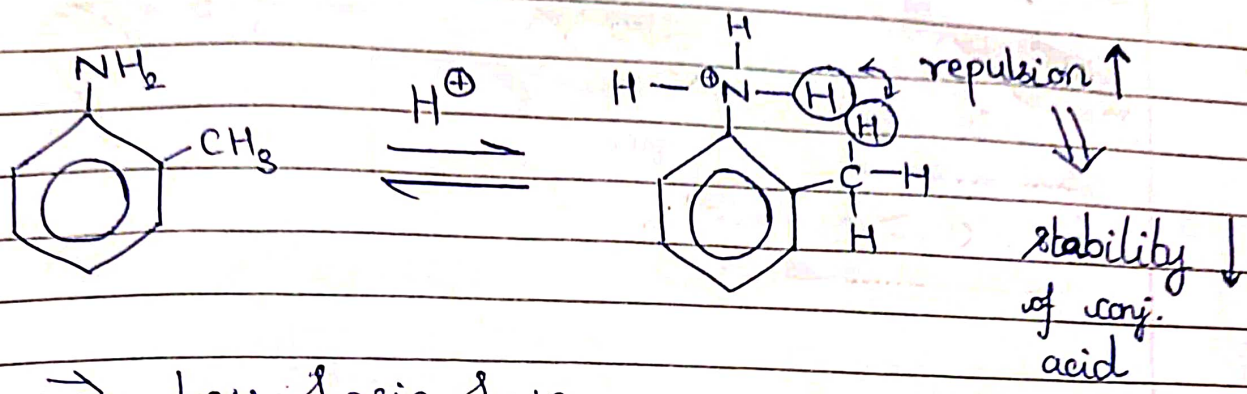
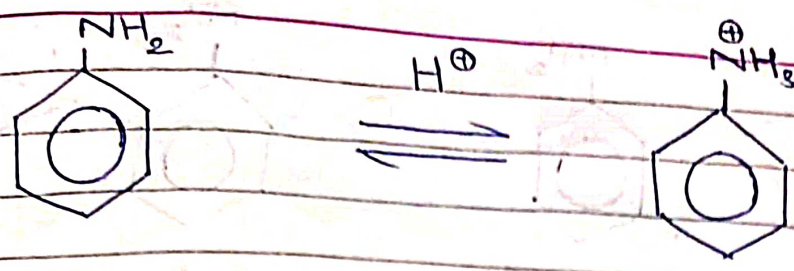
## 2) Basic Strength. -



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Reason: SIP effect (Steric Inhibition Protonation)  
 Only applicable for  $-NH_2$  if gap. present at ortho.



⇒ Less basic base.



1) SIP works when Nc1ccccc1 bulky grp.

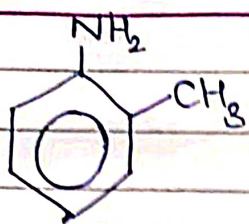
2) If  $\ominus$  charge on more EN atom in ~~any~~ any res. strcture of comp., then no. of res. strcture does NOT matter. It will be more stable.

3) Ring Strain —  $sp^2$  C wants  $120^\circ$ .  
 $\therefore$  6 membered ring more stable

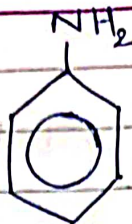
4) In basicity, first check if l.p. localised or delocalised.

136

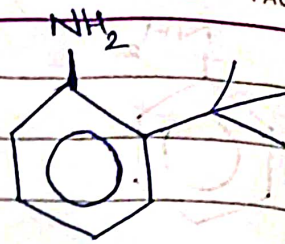
7)



SIP ✓



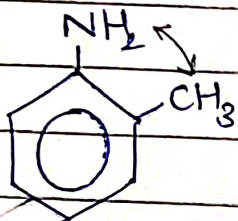
SIP X



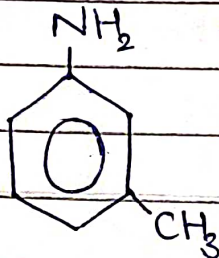
SIP ✓✓

$b > a > c$

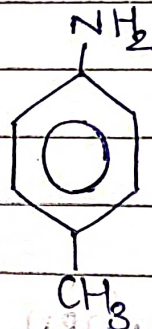
8)



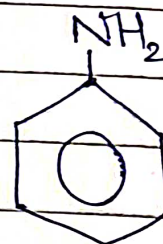
SIP ✓



(+I)

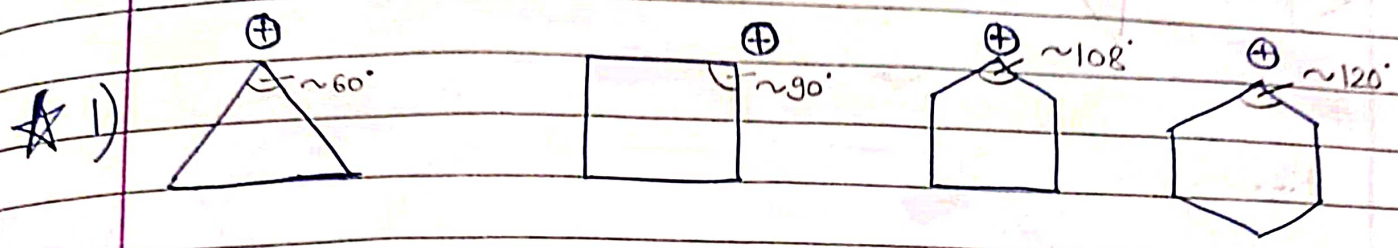


(+M, +I)



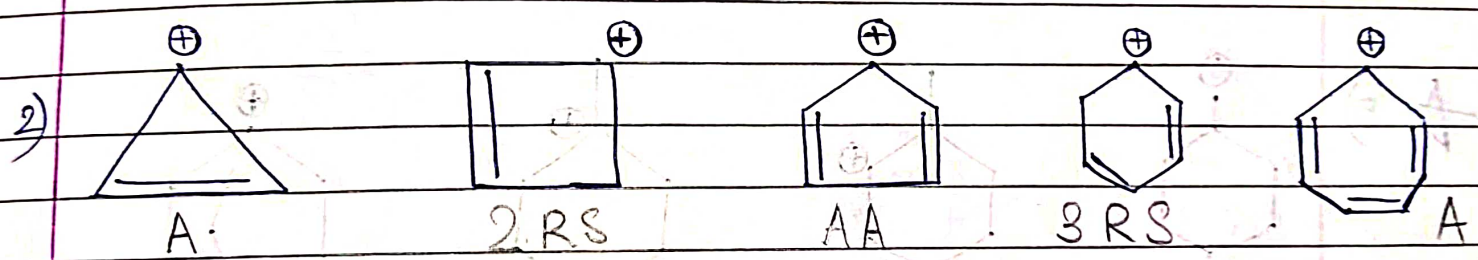
$c > b > d > a$

### 3) Stability of Carbocation —



The  $C^+$  is  $sp^2 \Rightarrow$  It want to have  $120^\circ$

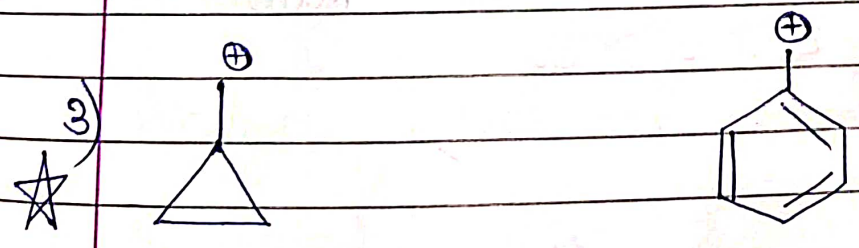
( $\uparrow$  Deviation from  $120^\circ$ )  $\Rightarrow$  ( $\uparrow$  Ring / Angular Strain)  $d > c > b > a$



Less conj.  $\Rightarrow$  Less stable

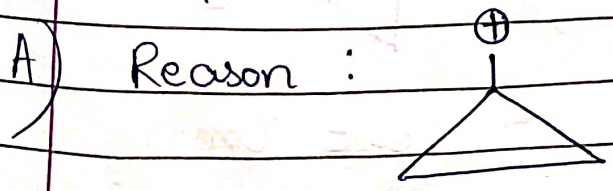
More conj.  $\Rightarrow$  More stable

$e > a > d > b > c$



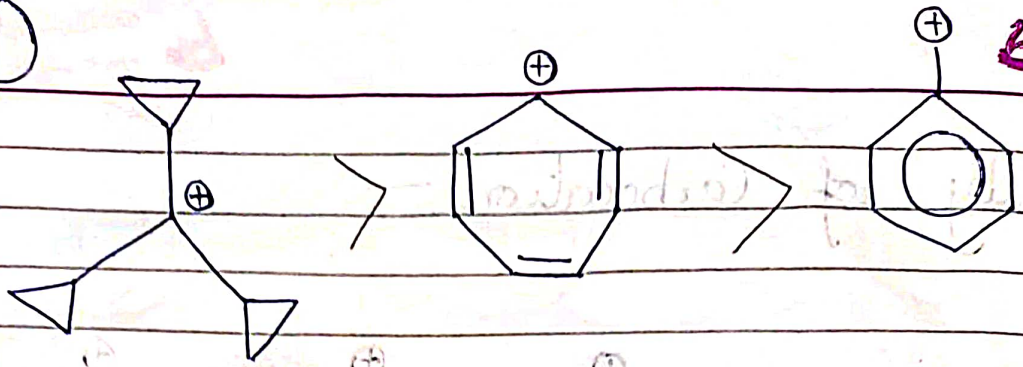
Expected:  $b > a$   
Actual:  $a > b$

Cyclopropyl methyl carbocation



~~It~~ shows Dancing Resonance

4)

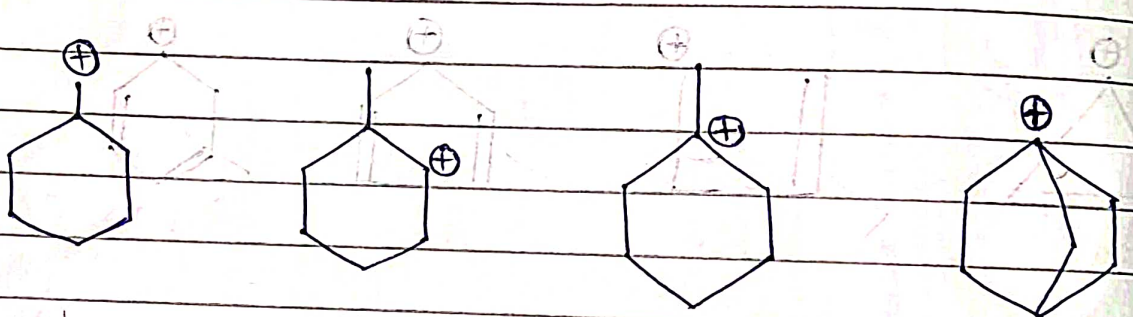


Dancing Res.

More res. structures

Less res. structures

☆ 5)



(α H) atoms

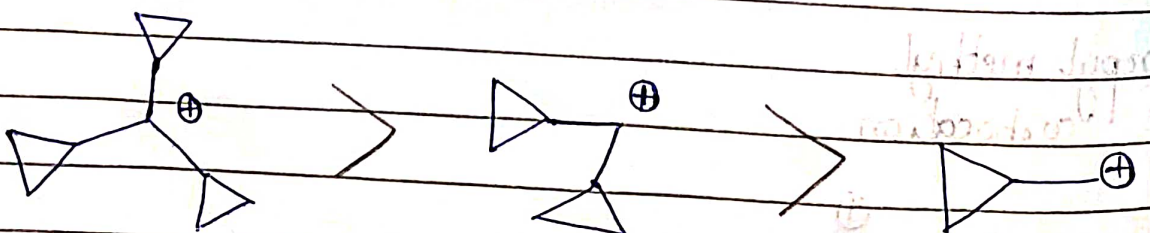
1                      3                      7                      6

Expected -  $c > d > b > a$

Actual -  $c > b > a > d$

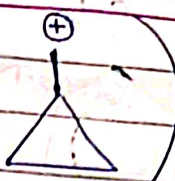
Breadt's Rule

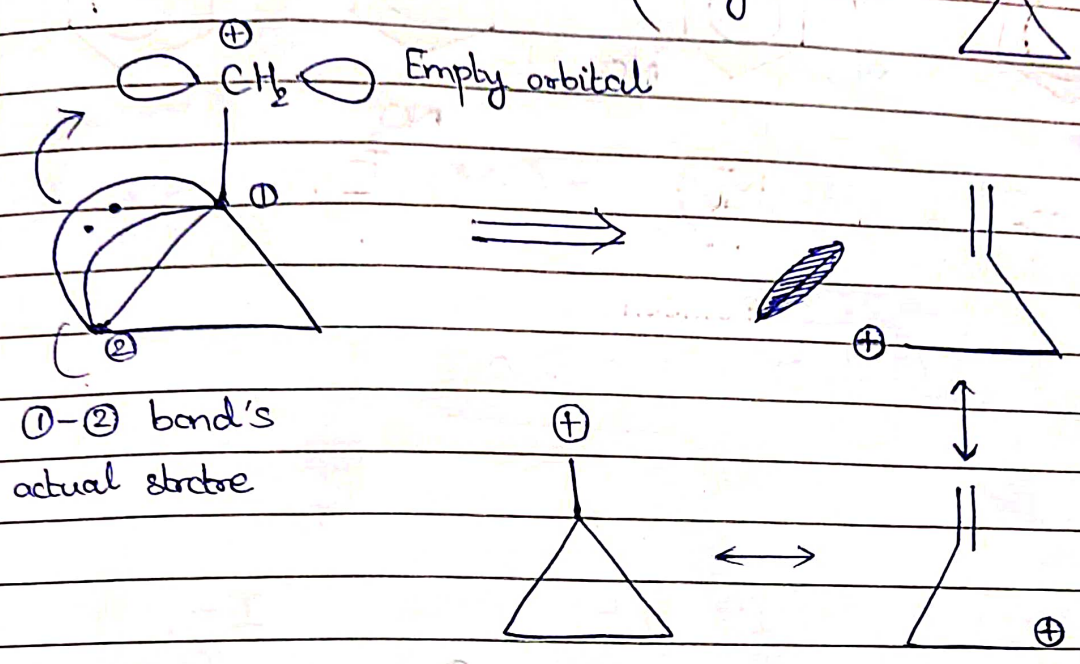
6)



Most Dancing Resonance

Least Dancing Resonance

Dancing Resonance (Only in )



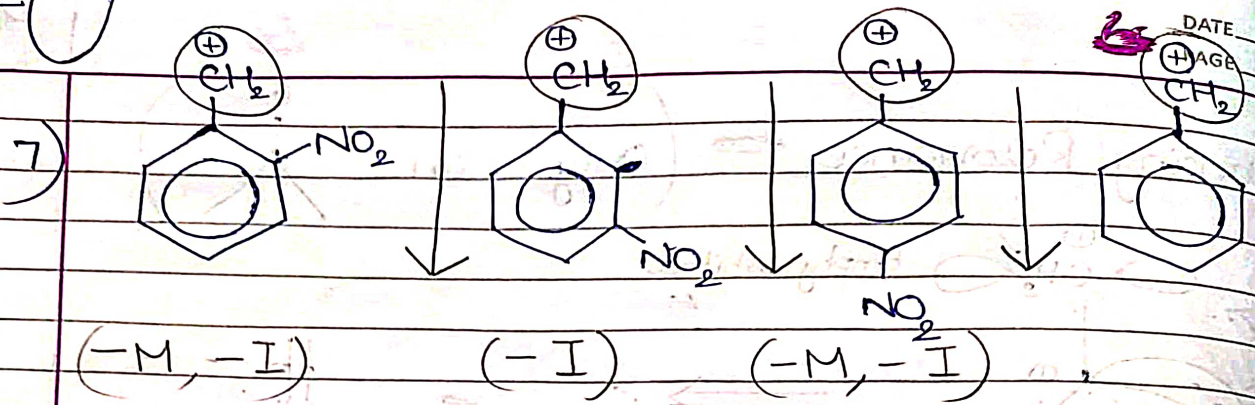
This is HIGHLY stable. (Greater than even Aromatic!)

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

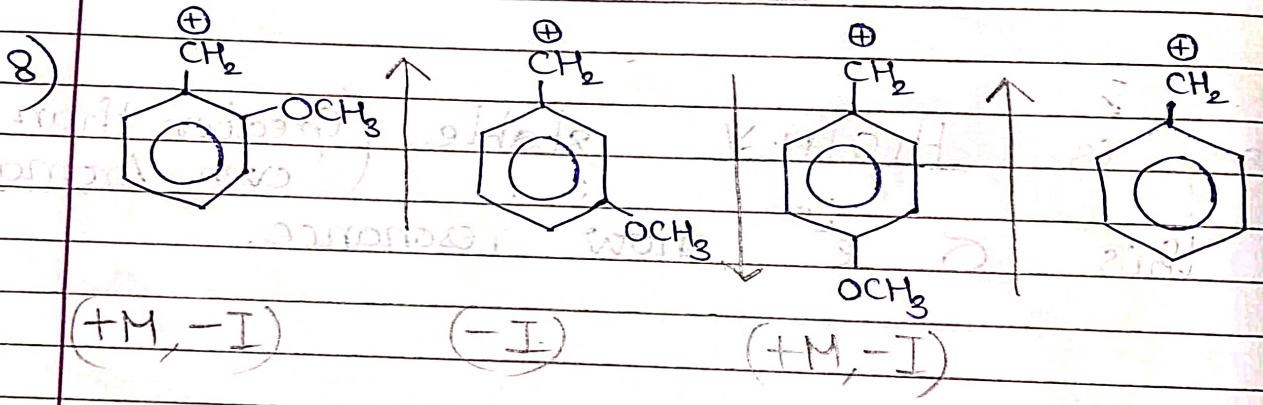
Bredt's Rule

Bridge head C having  $sp^2$  hybrid. is highly unstable, as it loses its planarity.

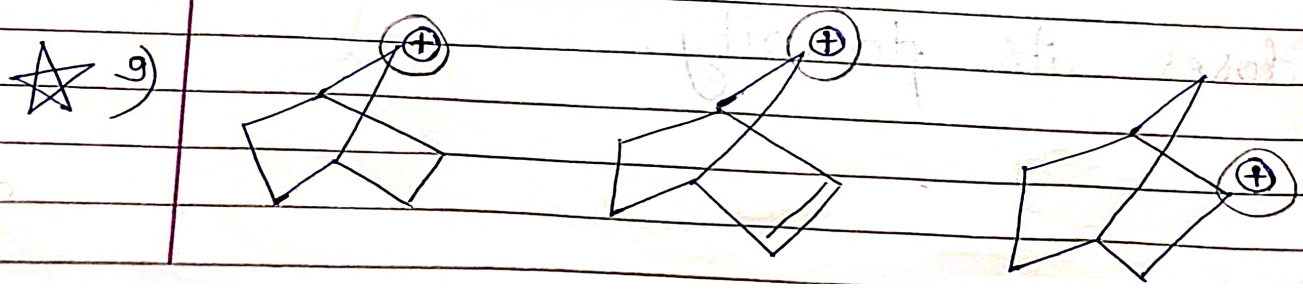




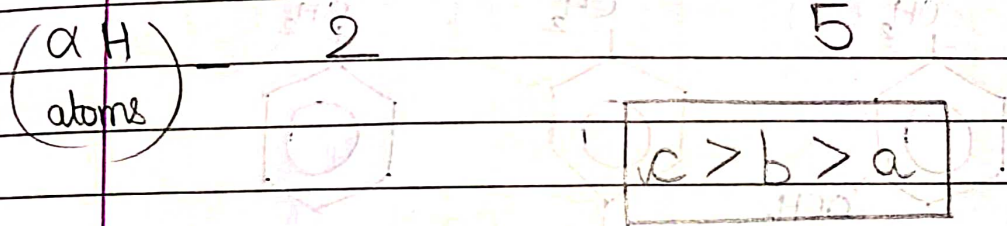
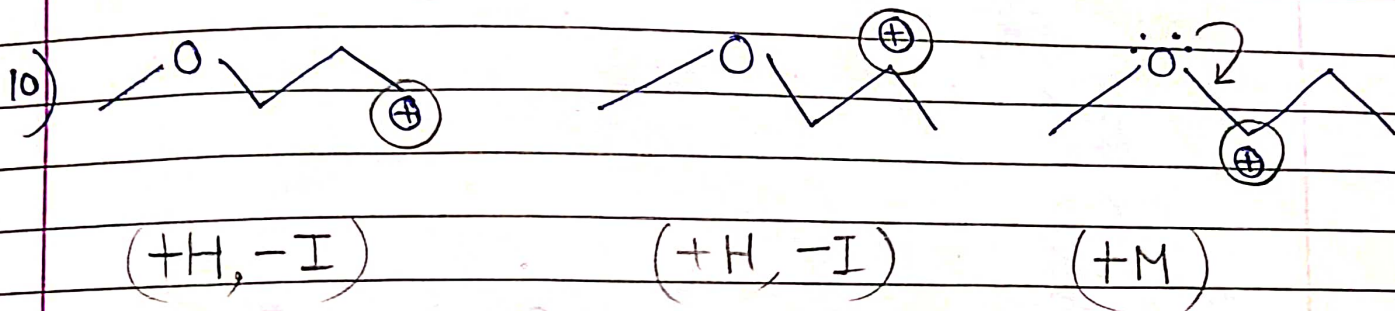
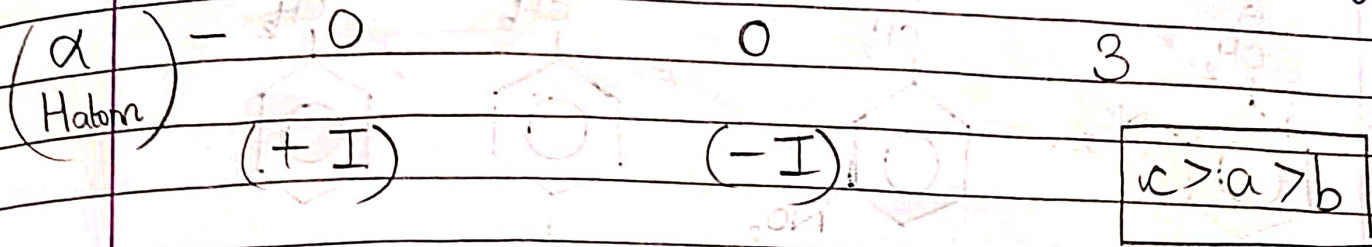
$d > b > c > a$



$c > a > d > b$



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

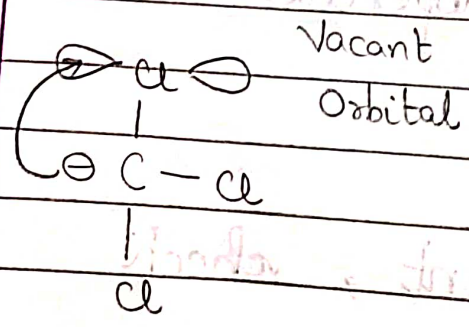
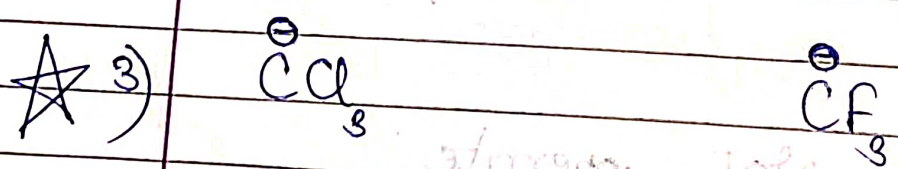
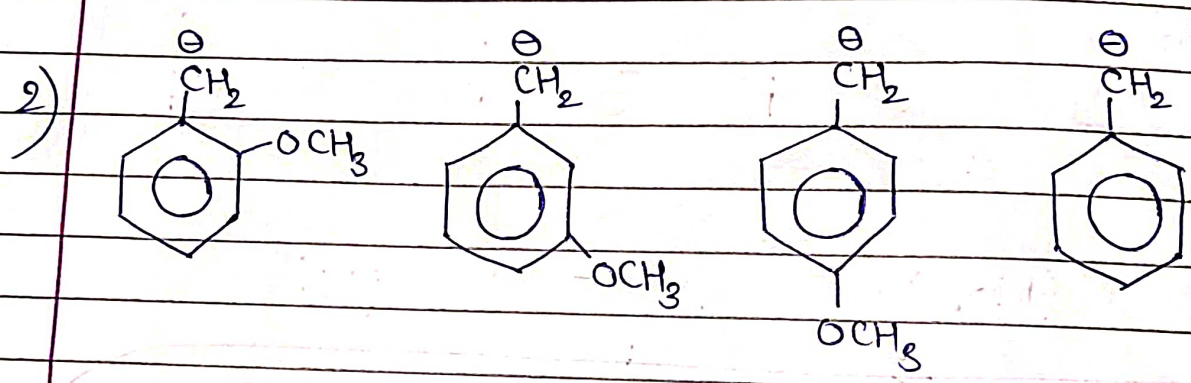
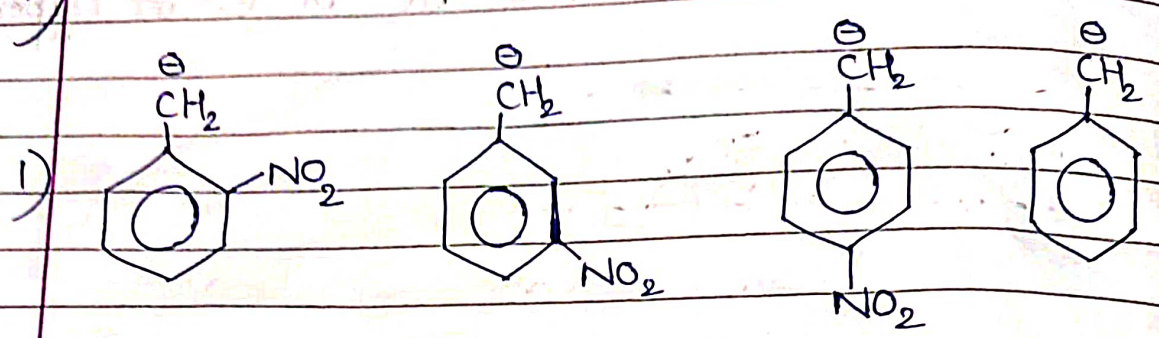


☆ 1) In above Q, we could apply  
 $+H$  effect on  $\oplus CH_2$  as it  
is caused by  $\alpha$  H atoms,  
just presence of  $\oplus C$  is req.

2) Ortho effect NOT operate  
on  $C^{\oplus}$  &  $C^{\ominus}$ .

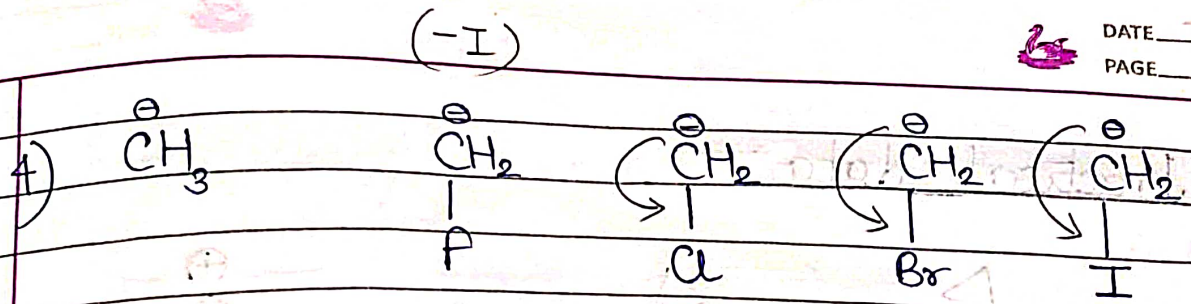
3) When  $\parallel$  or  $\equiv$  present, check  
hyb<sup>n</sup> of atoms.

### 4) Stability of Carboanion



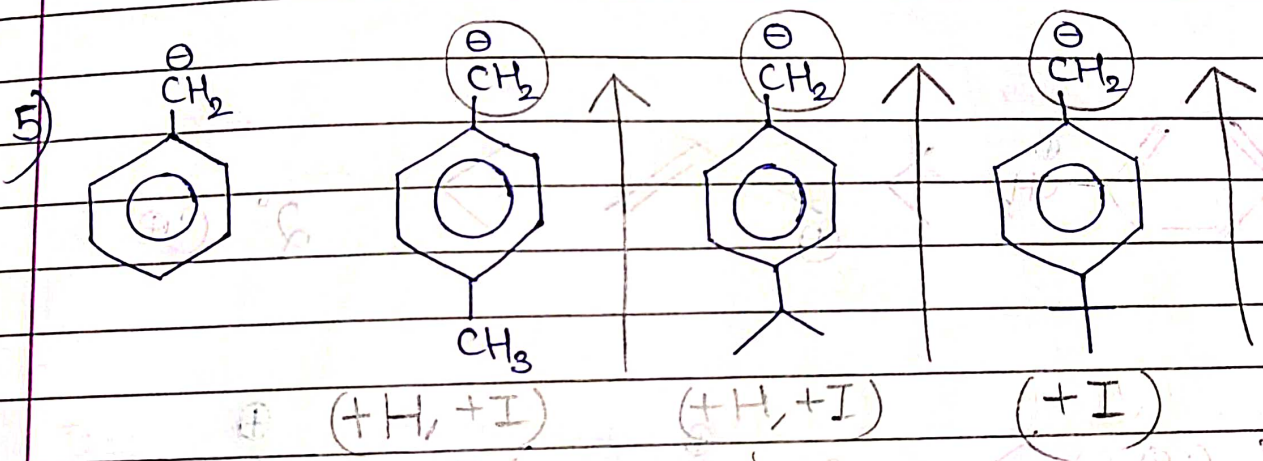
Back Bond reduces  $\ominus$  von C atom

$\Downarrow$   
 $a > b$



$c > d > e > b > a$

very weak back bond

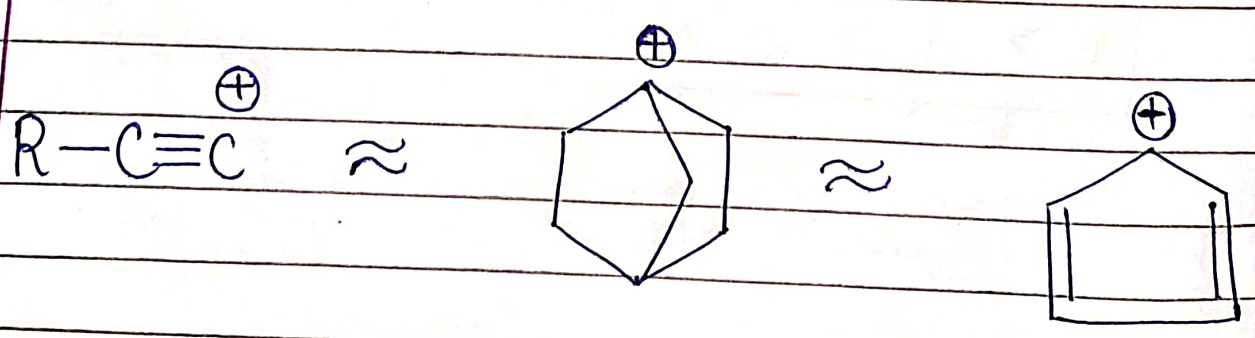
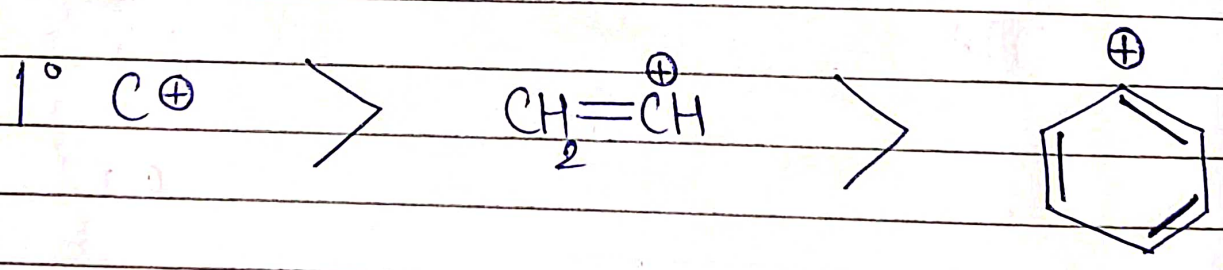
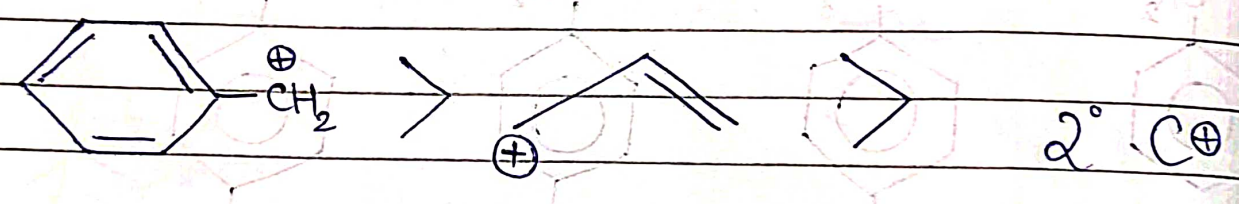
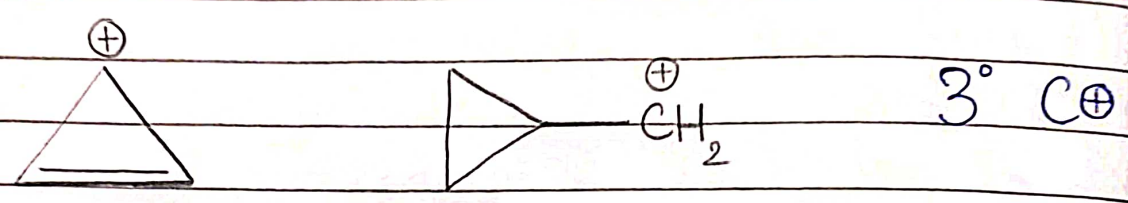
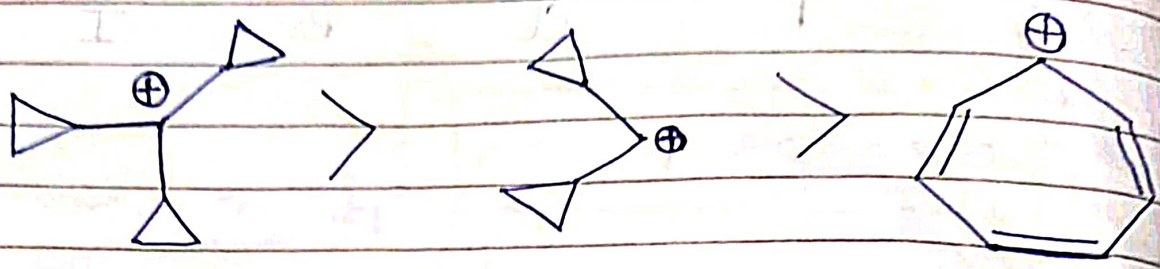


( $\alpha$  H atoms)

$a > d > c > b$



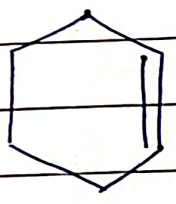
Practical data -



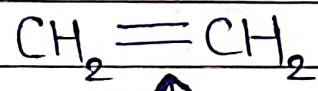
Bond Length, Bond Order & Bond Diss. Energy

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

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



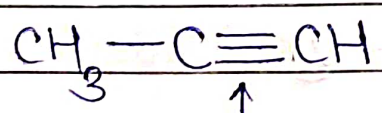
← ①



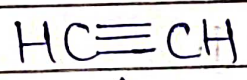
↑  
②

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

⇒ B.O. - ① < ② ⇒ B.E. - ① < ②



↑  
①

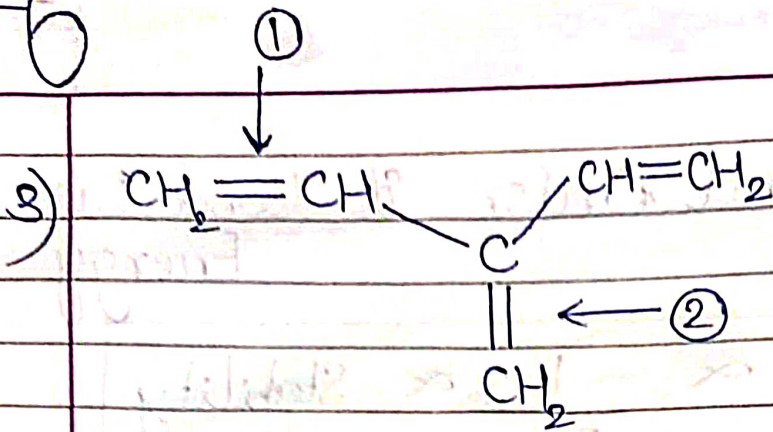


↑  
②

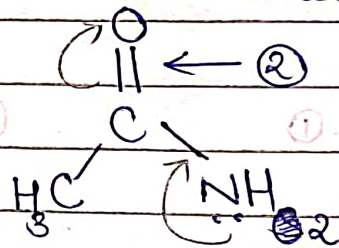
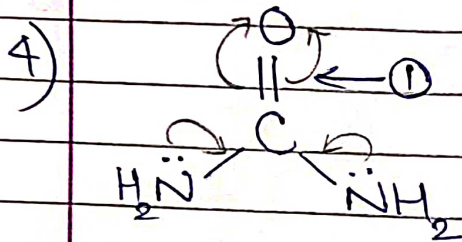
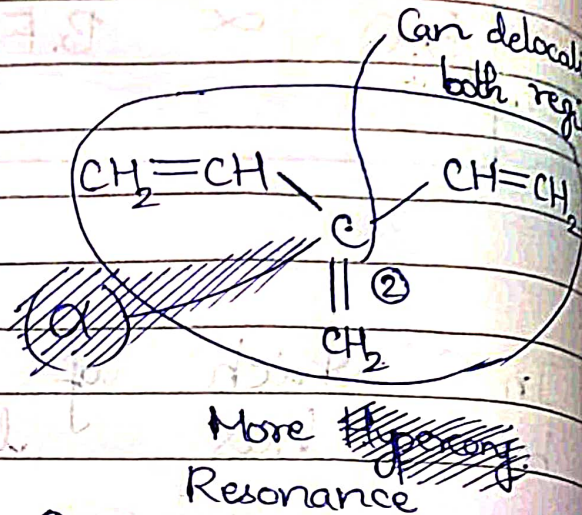
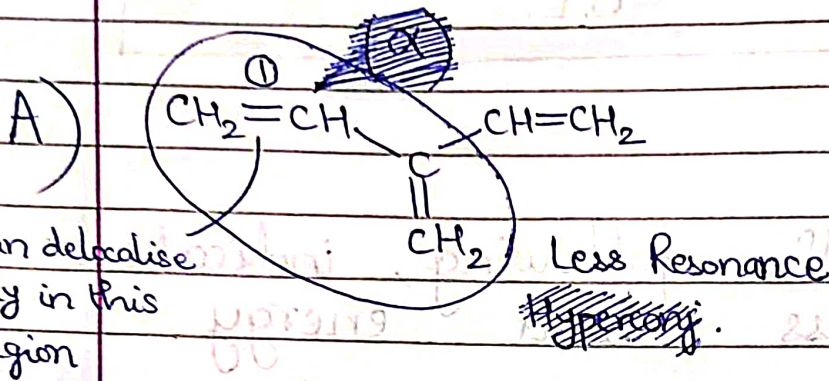
Due to Hyperconj.

B.E. - ① < ②

⇒ B.O. - ① < ②

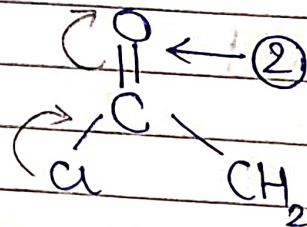
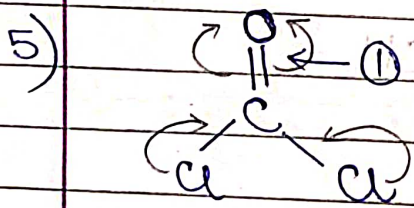


B.O. -  $\textcircled{1} > \textcircled{2}$   
 $\Rightarrow$  B.E. -  $\textcircled{1} > \textcircled{2}$



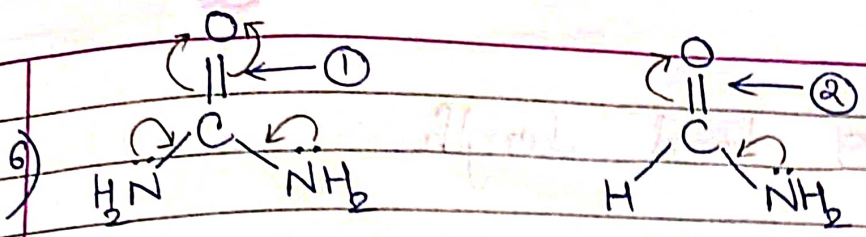
A) B.O. -  $\textcircled{1} < \textcircled{2}$   $\Rightarrow$  B.E. -  $\textcircled{1} < \textcircled{2}$

More res. in  $\textcircled{1}$  than  $\textcircled{2}$



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

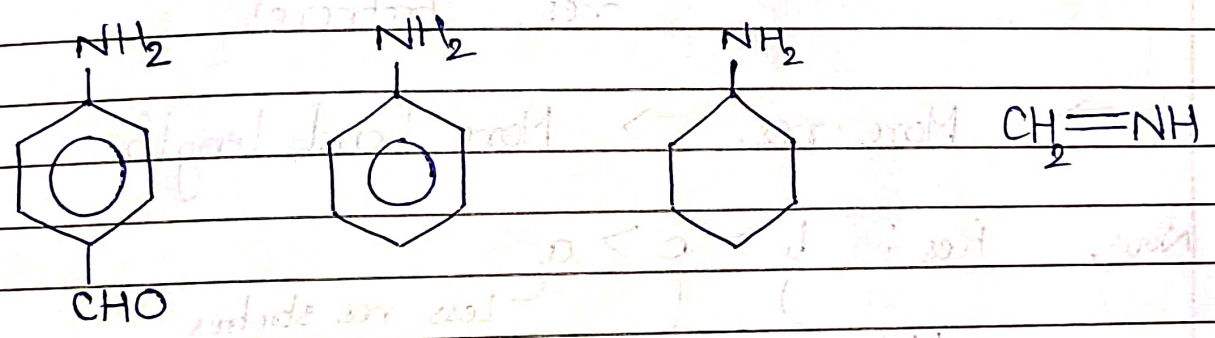
More res. in  $\textcircled{1}$  than  $\textcircled{2}$



A) B.O. - ① < ② ⇒ 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  
CHO

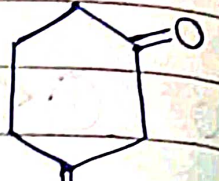
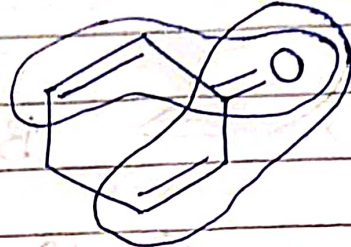
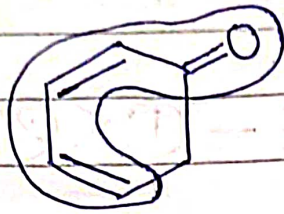
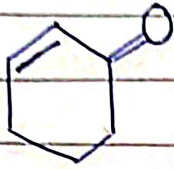
⇒ More res. structures, each with

⇒ (B.O. of C-N) (a) > (b)

⇒ B.L. - c > b > a > d



Q) Compare CO bond length.



Linear  
Conj.

Cross  
Conj.

Pure //

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

$\Rightarrow$  More res.  $\Rightarrow$  More bond length.

Now, Res:  $b > c > a$   
) ( Less res. structures  
 Linear conj. Cross conj.

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



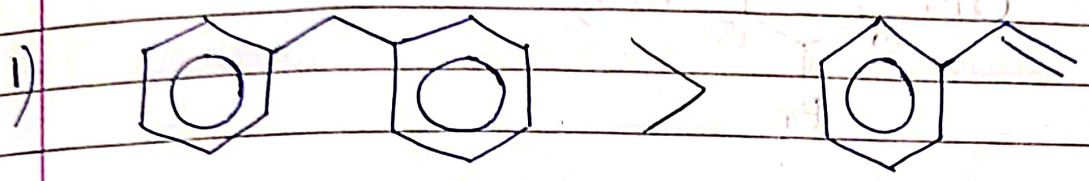
When no. of res. structures same,

Stability -

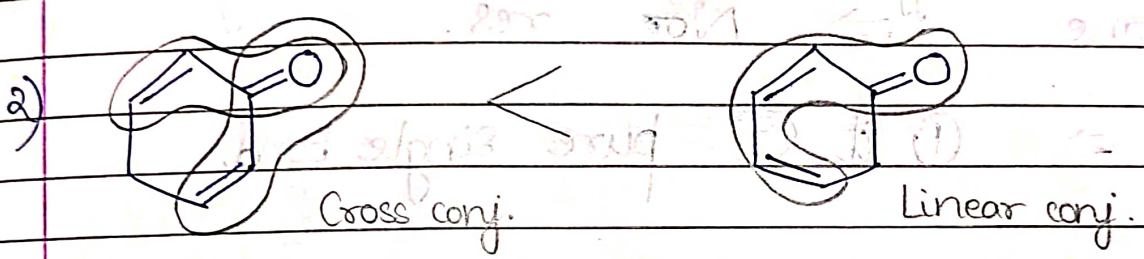
$\left( \begin{array}{c} \text{Linear} \\ \text{Conj.} \end{array} \right) > \left( \begin{array}{c} \text{Cross} \\ \text{Conj.} \end{array} \right)$

Misc. Qs

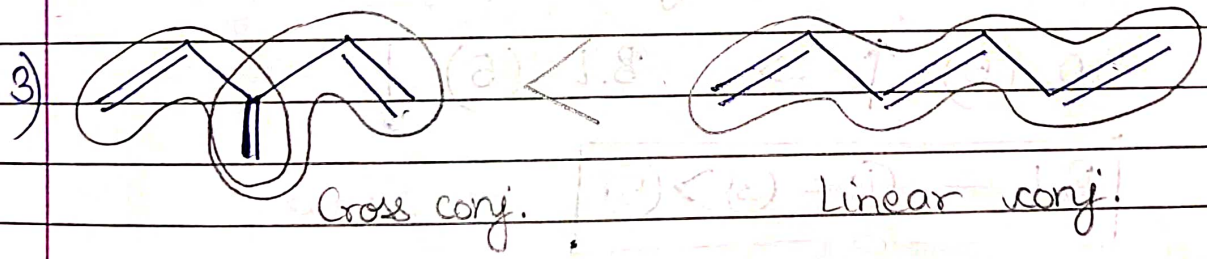
Q) Compare res. energy.  $\propto$  (Stability)



Stability - 1 > 2 as more aromatic rings



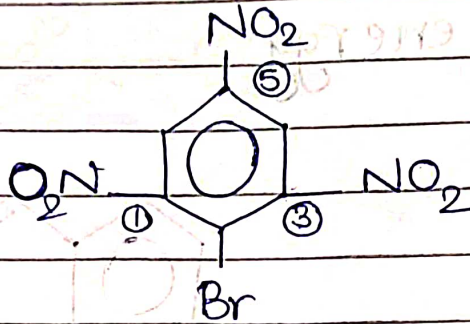
Stability - 1 < 2



Stability - 1 < 2

- ★ 1) If in comparing acidity or basicity, if fx<sup>n</sup>al grp diff, then compare using fx<sup>n</sup>al grp.
- 2) Basicity dec. both along period & down grp.

Q) Compare bond lengths of CN.



A) By Ortho effect, ① & ③ out of plane  $\Rightarrow$  No res.

$\Rightarrow$  ① & ③ pure single bond

However, ⑤ shows res. with res. structures having  $C-N \rightarrow C=N$

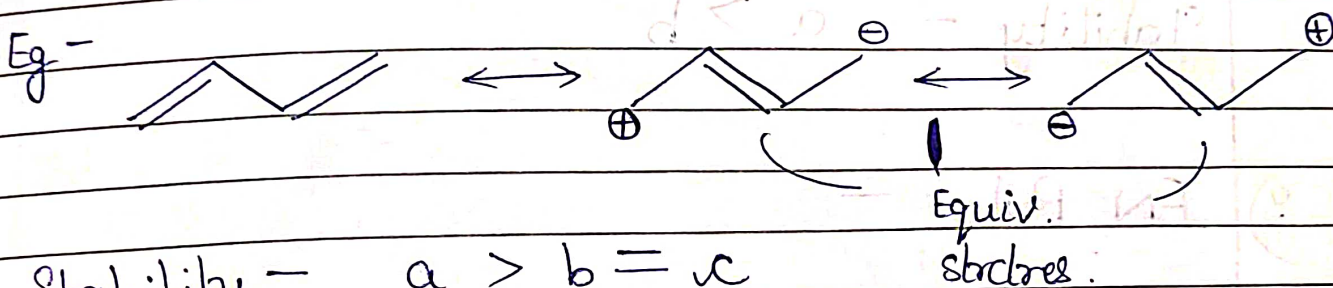
$\Rightarrow$  B.O. (5)  $\uparrow$   $\Rightarrow$  B.L. (5)  $\downarrow$

$\Rightarrow$  B.L. - ① = ③ > ⑤

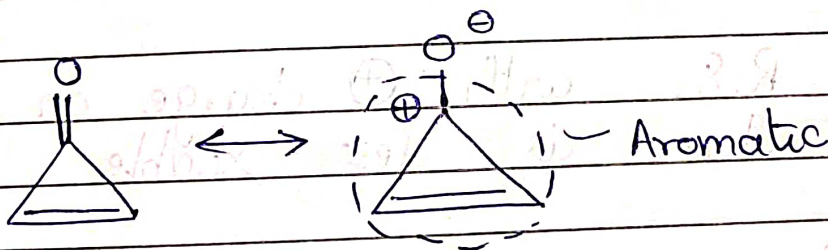
## Stability of Res. Structures

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

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



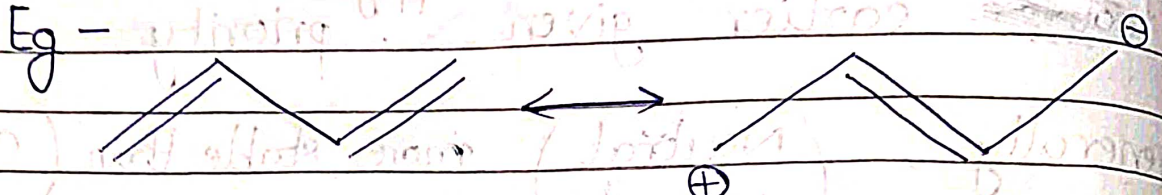
★



⇒ 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.

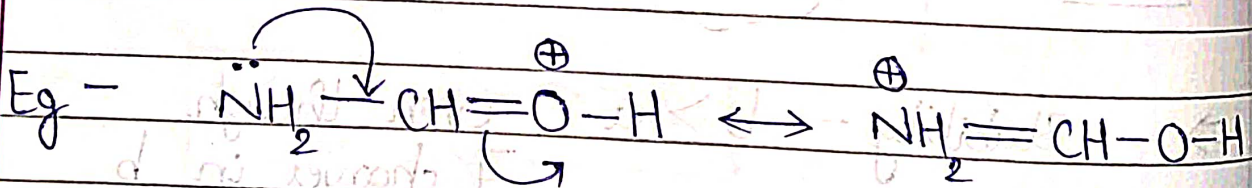


Stability -  $a > b$

3) EN Rule -

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

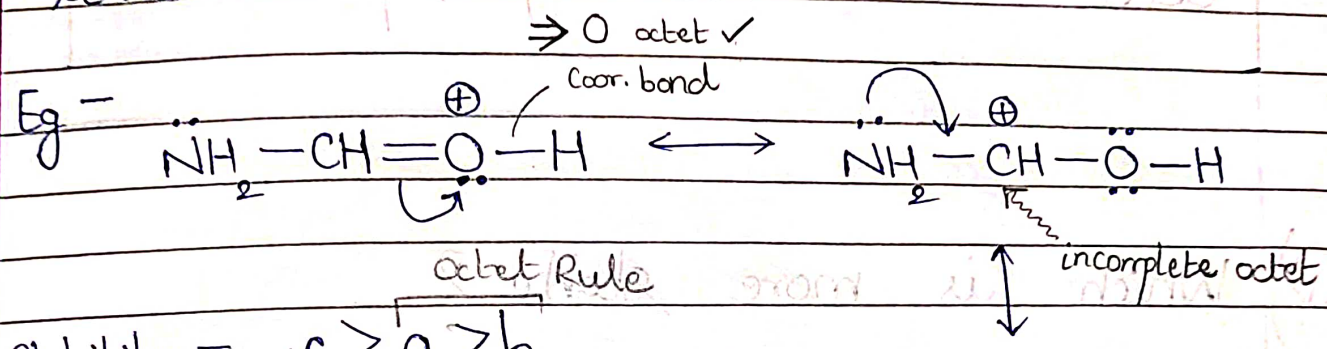
Similarly, R.S. with  $\oplus$  charge on more EN atom is less stable.



Stability -  $b > a$

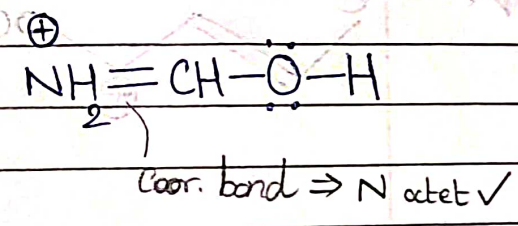
4) Octet Rule -

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

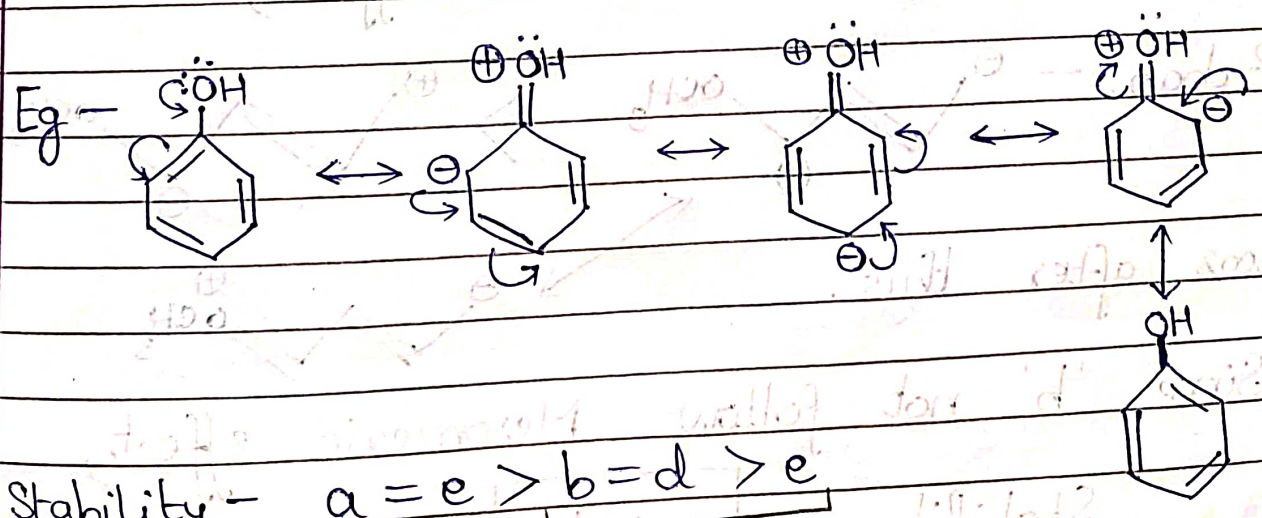


Stability -  $c > a > b$

EN Rule



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



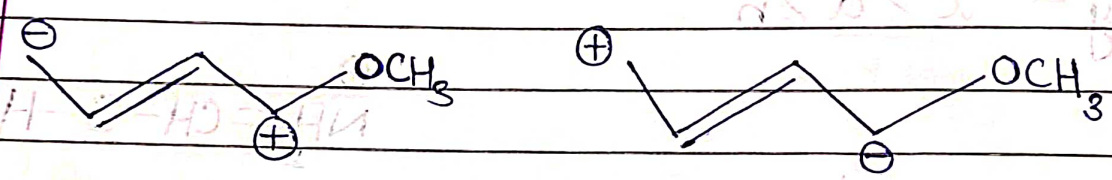
Stability -  $a = e > b = d > c$

Charge sep.

☆ Priority Order —

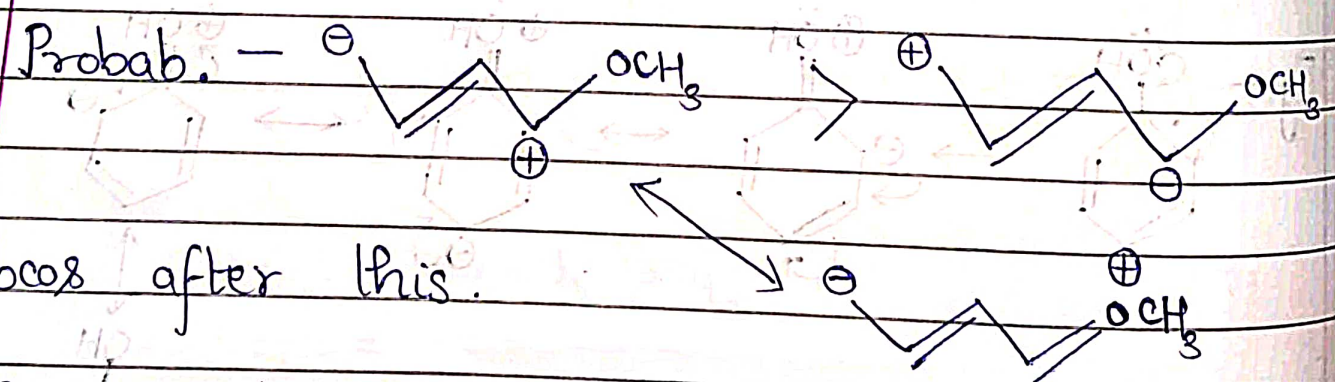
Aromatic > Mesomeric > Neutral {1,2} >  
Octet > EN > Charge sep.

☆ (Q) Which is more stable?



A) Both res. structures of C=CC(=O)OC

Since  $-OCH_3$  show + M effect,

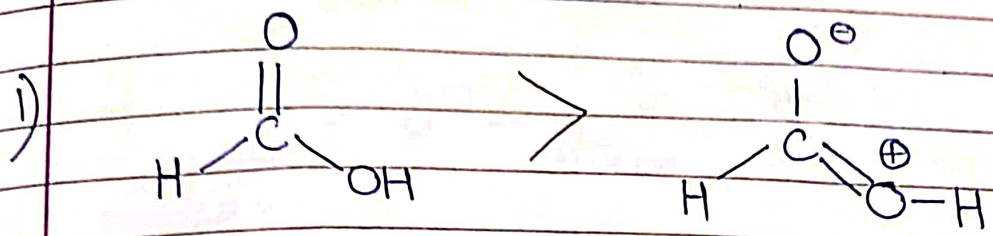


becs after this.

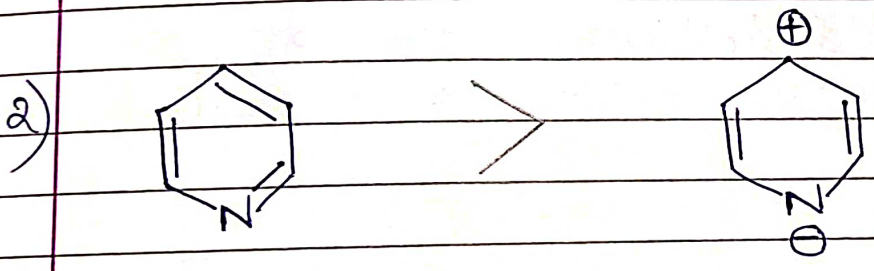
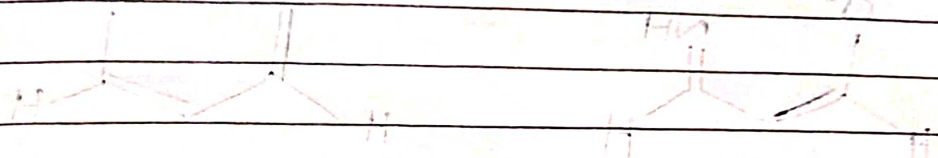
Since 'b' not follow Mesomeric effect,

Stability — a > b

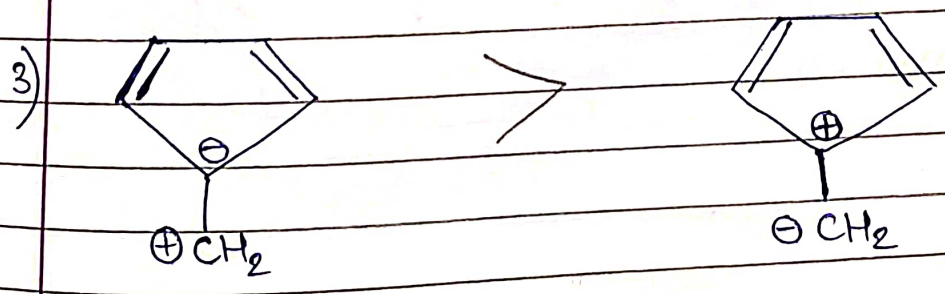
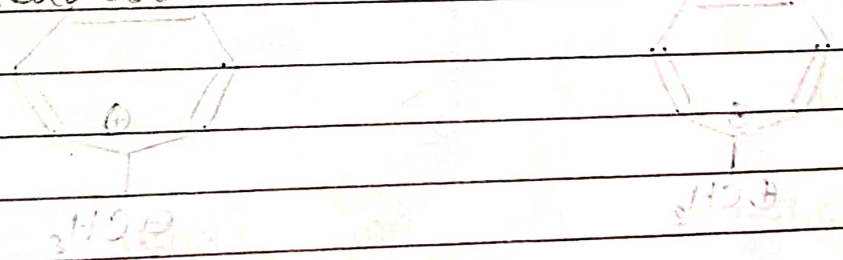
Q) Which is more stable?



Neutral

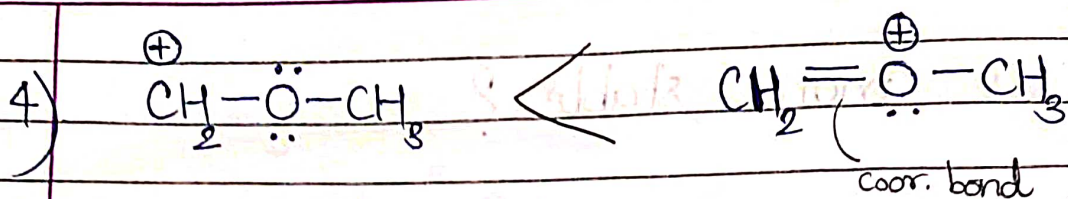


Neutral

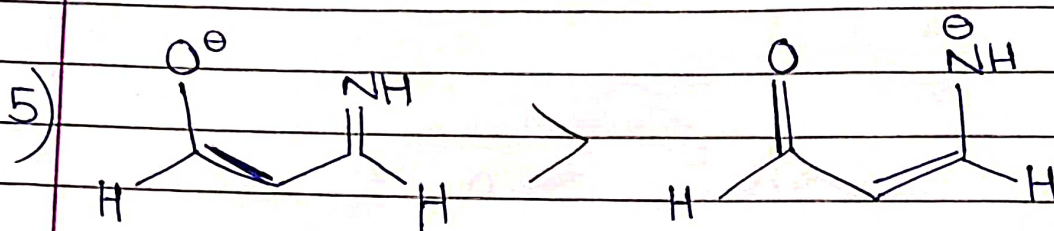


Aromatic

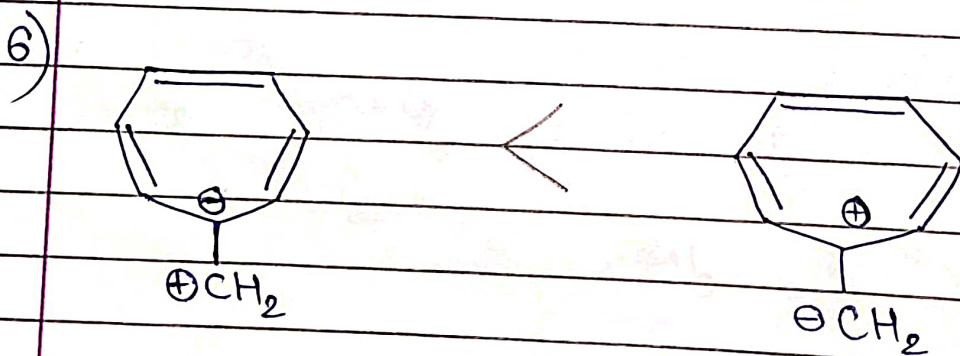




Octet



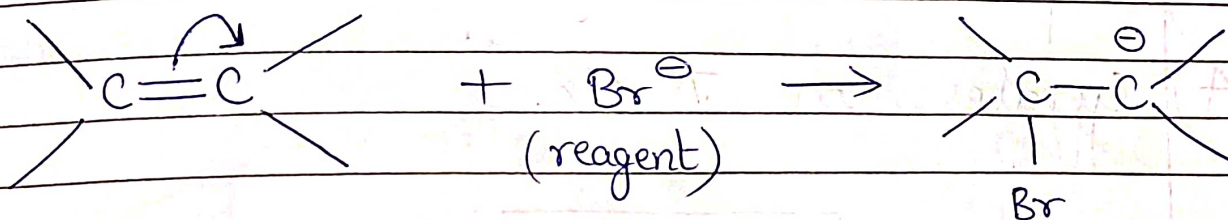
EW Rule



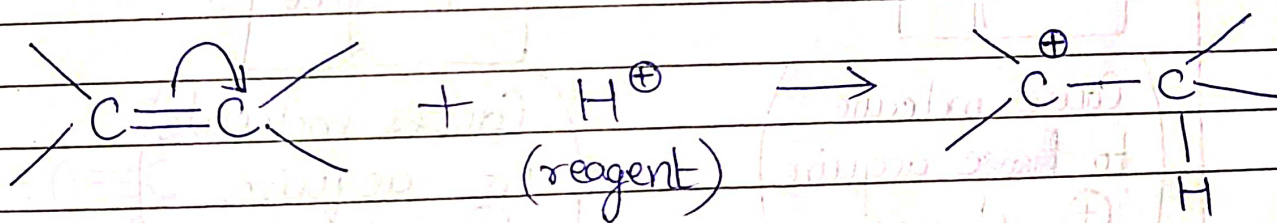
Aromatic

## Electromeric Effect

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



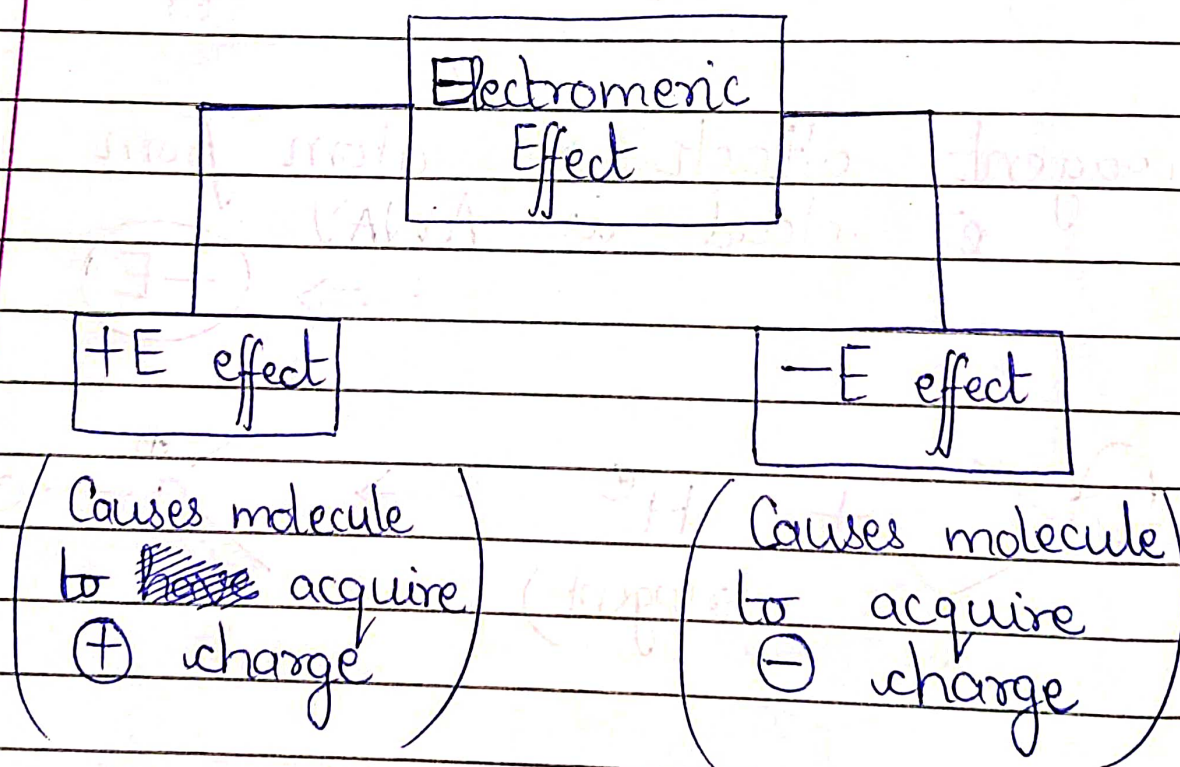
Since, reagent attack on atom from which  $e^-$  cloud is AWAY  $\Rightarrow$   $(-E)$



Since, reagent attack on atom TOWARDS which  $e^-$  cloud shifts  $\Rightarrow$   $(+E)$

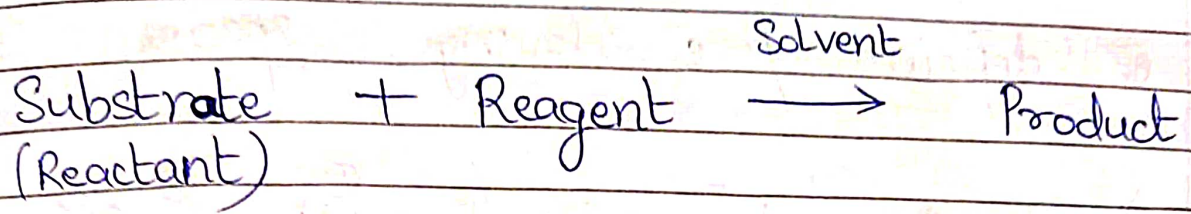
## Characteristics —

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

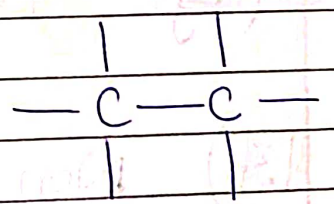
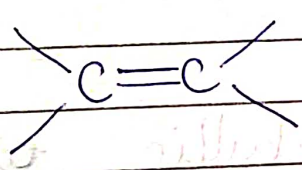
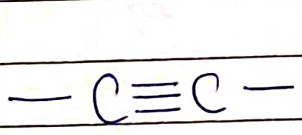
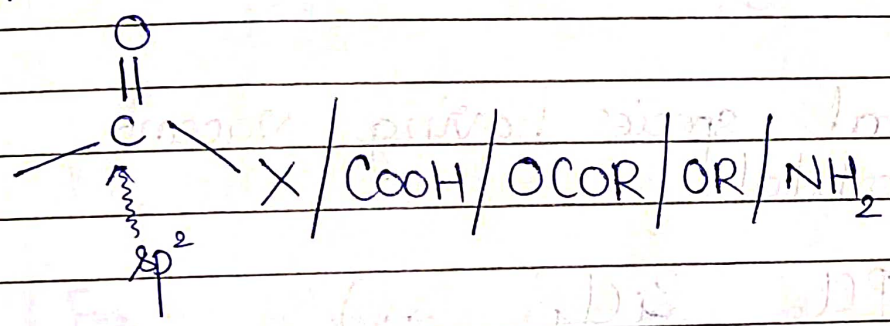
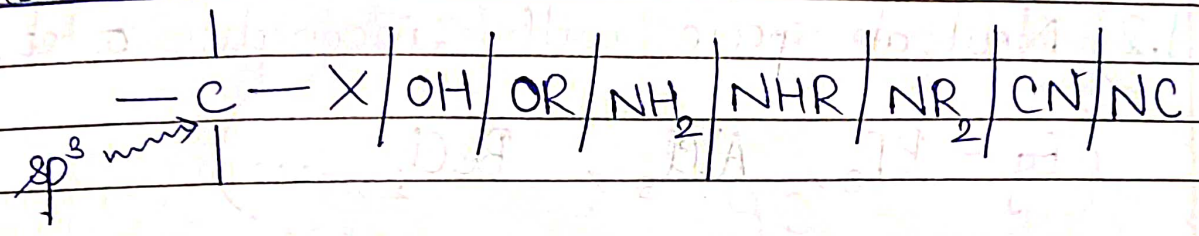




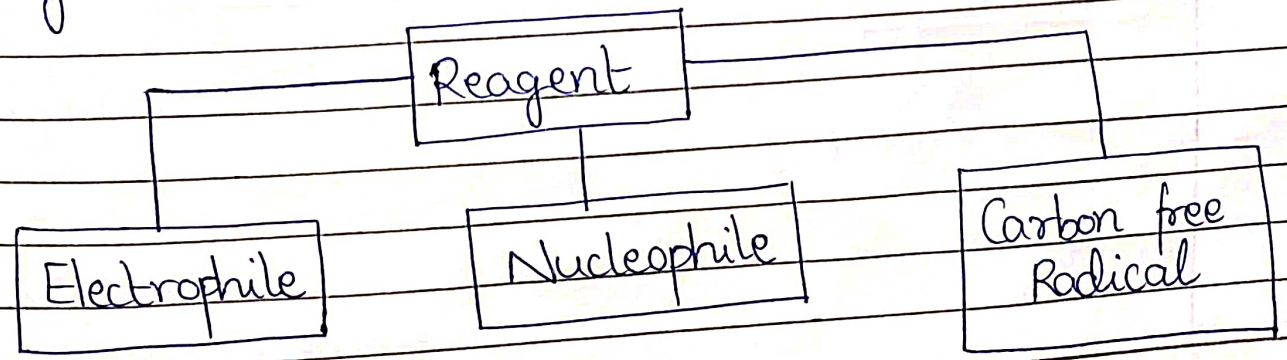
# Reaction Mechanism



## 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 :-

$e^-$  rich / nucleus loving species

2.1)  $\ominus$  charged species. (Eg -  $Cl^-$ ,  $CH_3^-$ , ...)

2.2)  ~~$\oplus$  charged~~ Neutral species having at least 1 l.p.

(Eg -  ~~$PCl_3$~~ ,  $NH_3$ ,  $H_2O$ ,  $NH_2NH_2$ , ...)

2.3) Multiple bonded system.

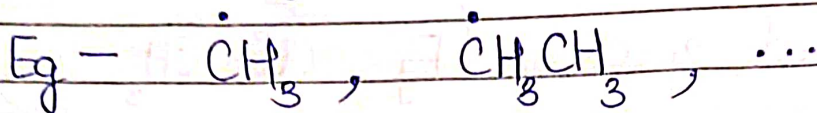
(Eg - Alkene, Alkyne, Benzene derivatives, ...)

Nucleophilicity ~~is~~ ~~discussed~~ ~~in~~ Basicity will be later chapter.

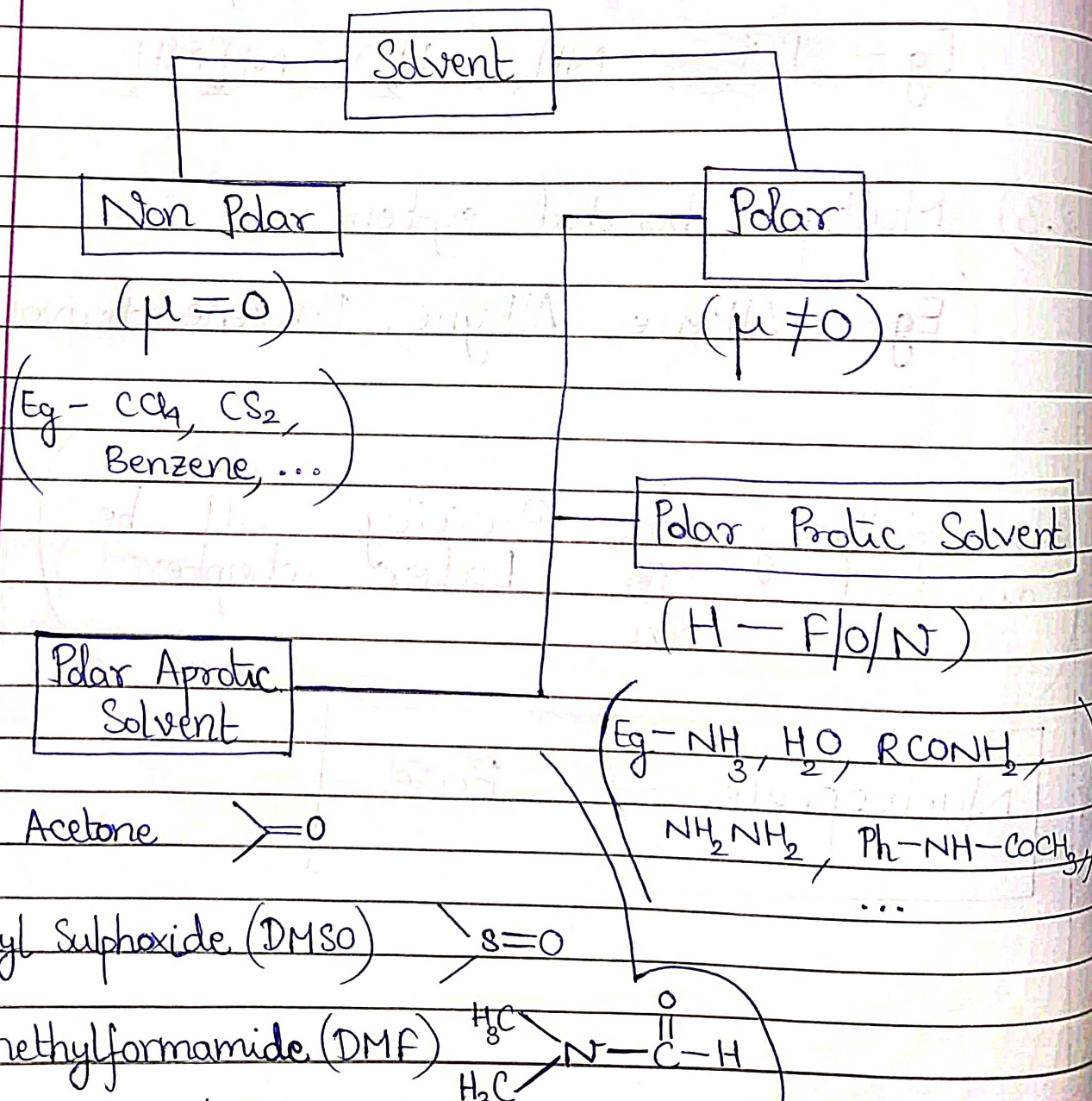
Nucleophile  $\neq$  Base

3) Carbon free radical :-

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



Solvent -





## Reaction Intermediates

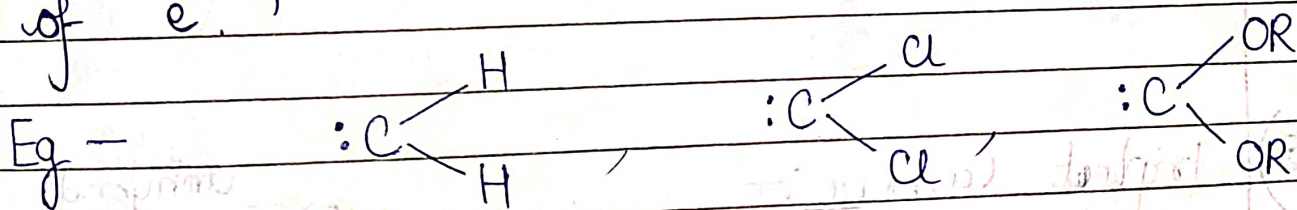
They are formed by breaking of covalent bonds. They are highly unstable & short lived & reactive.

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



### Carbene

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



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

$\Rightarrow$

Electrophiles



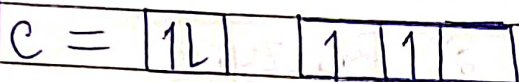
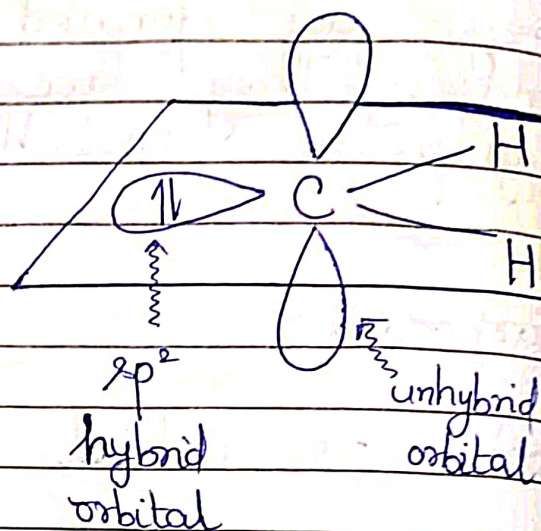
## Types • —

### 1) Singlet Carbene :-

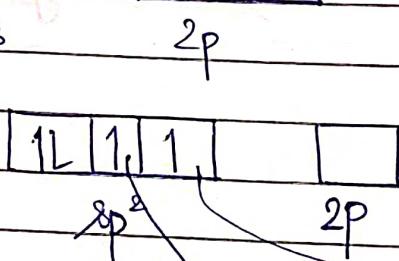
Spin multiplicity

$$= 2|S| + 1$$

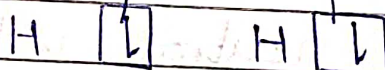
$$= \textcircled{1} \quad (\text{as } S=0)$$



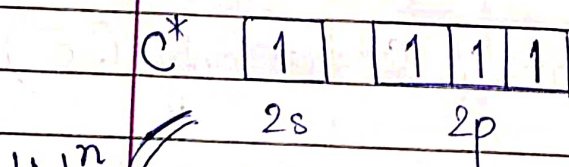
Hyb<sup>n</sup> ↪



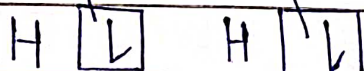
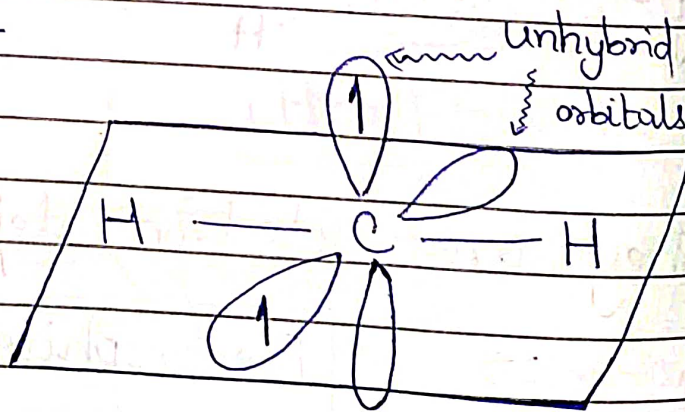
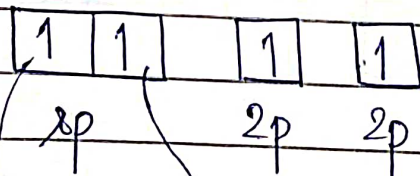
⇒ No unpair e<sup>-</sup>



### 2) Triplet Carbene :-



Hyb<sup>n</sup> ↪



⇒ 2 unpair e<sup>-</sup>



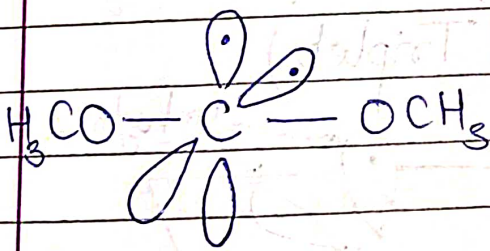
⇒ Spin multiplicity =  $(3)$  (as  $S=1$ )

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

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

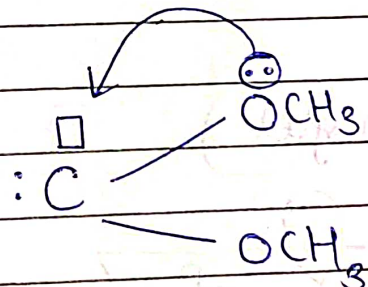
Except: In case C bonded to atom with (l.p.), then in singlet carbene MORE stable.

Reason: Back bond.



(Triplet)

Back Bond X  
(no vacant orbital)

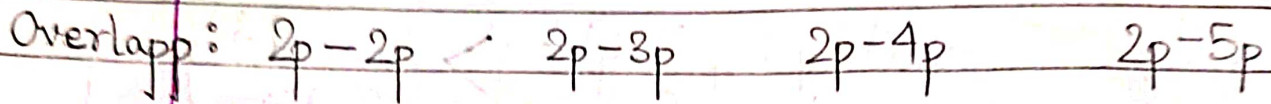
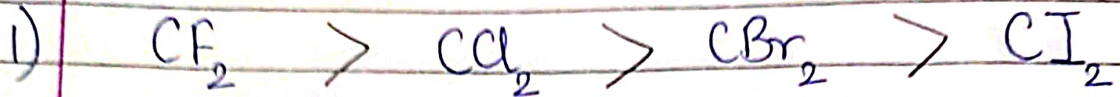


(Singlet)

Back Bond ✓

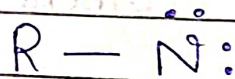
(vacant orbital)

Q) Compare stability.

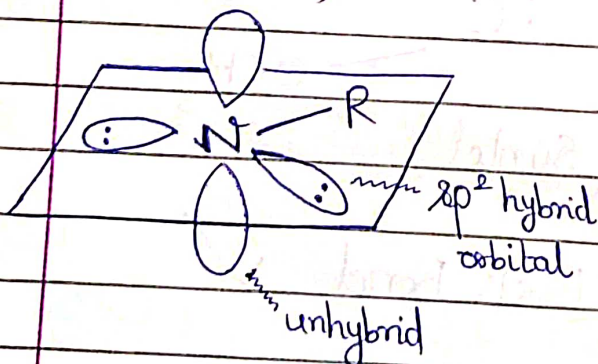


### Nitrene

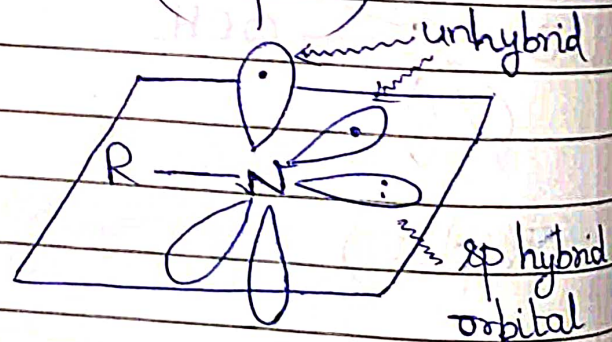
Nitrene is Nitrogen analogue of Carbene



(Singlet)

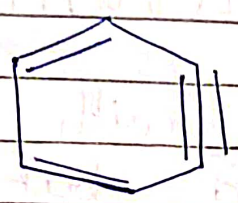


(Triplet)





# Benzyne



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

└ 6

Actually  $\equiv$  does NOT exist.

In reality,

