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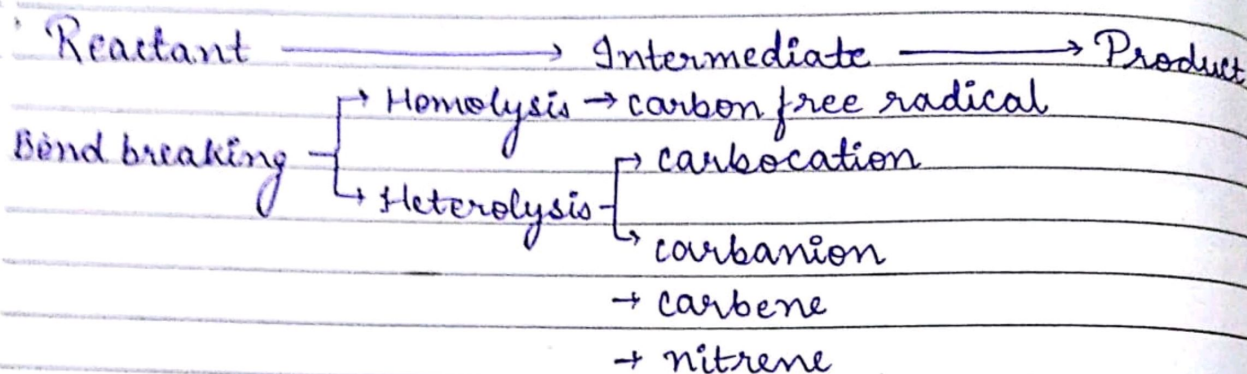
Notes, Papers, Syllabus

Practice Paper, Sample Paper

Reaction Mechanism - I

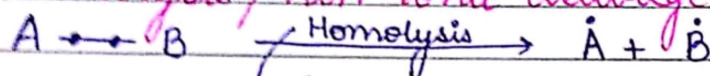
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G.O.C.



Covalent cleavage

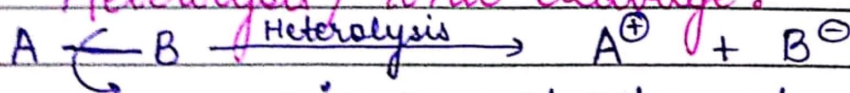
Homolysis / non-ionic cleavage :-



$\rightarrow$ in +ve non-polar solvent like CCl_4 , benzene, CS_2 etc.

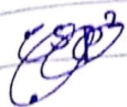
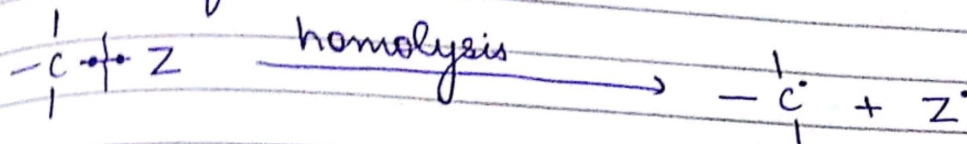
- in +ve of sunlight ($h\nu$)
- High Temp.
- Vapour Phase reacⁿ
- in +ve of peroxide
- when attacking reagent is free radical

Heterolysis / ionic cleavage :-



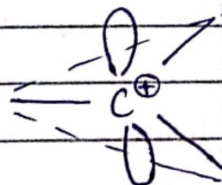
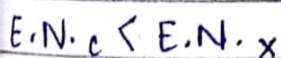
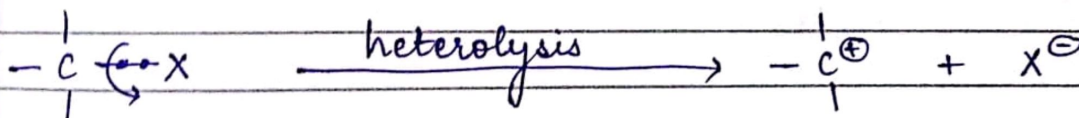
- in +ve of polar solvent like H_2O , R-OH
- Low Temp.
- when attacking reagent is ions
- Acid / Base

1. Carbon free Radical :-



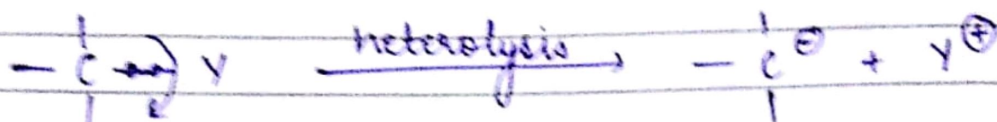
- sp^2
- trigonal Planar
- incomplete octet
- highly unstable
- more reactive
- behave as electrophile

2. Carbocation :-



- sp^2
- trigonal Planar
- incomplete octet
- highly unstable
- more reactive
- behave as electrophile.

Carboanion :



$E.N._C > E.N._Y$

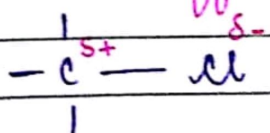


- sp^3
- Pyramidal
- complete octet
- highly unstable
- more reactive
- behave as nucleophile

Factors affecting stability of Intermediate :-

1. Inductive Effect
2. Resonance
3. Hyperconjugation
4. Electromeric Effect

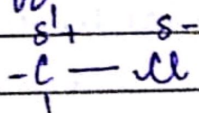
1. Inductive Effect :



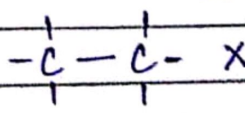
- induction due to E.N. diff.
- inductive effect.

• Inductive Effect arise due to E.N. difference of 2 atoms

gp.

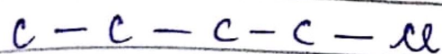


✓



• Partial shifting of σ bonded e^- towards more E.N. atom is k/n as inductive effect.

- inductive is a permanent effect
- Inductive is distance dependent & after 3 or 4 atoms ind. effect not considered.



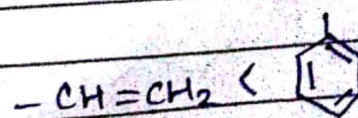
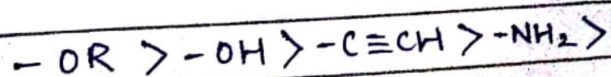
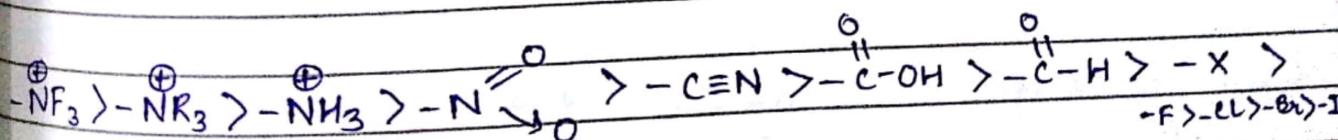
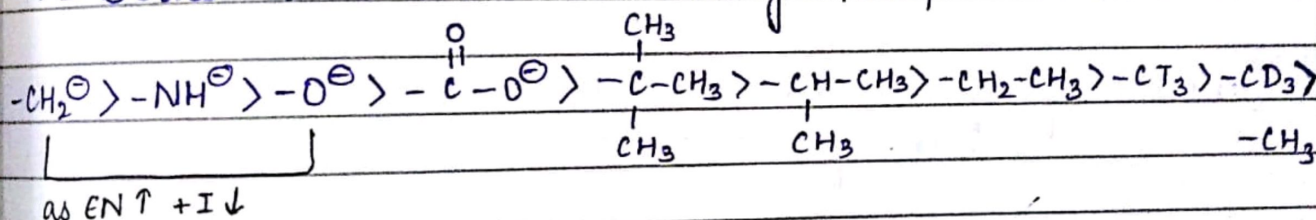
$$I \propto \frac{1}{\text{distance}}$$

std $\rightarrow$ ind. effect of $H = 0$

Two type

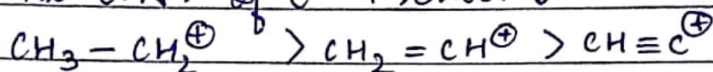
1. $+I$
2. $-I$

$+I$ Series :- Electron Donating Group

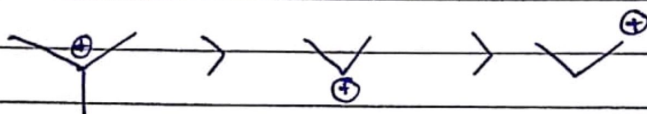


Stability of C^+

Rule (1) As E.N. of C^+ $\uparrow$ stab. $\downarrow$



Rule (2) If E.N. is same then
stab. $3^\circ > 2^\circ > 1^\circ$



Rule (3) If Rule (1) & Rule (2) fail
Stab. of $C^+ \propto \frac{+I}{-I}$

Priority

Order for I effect

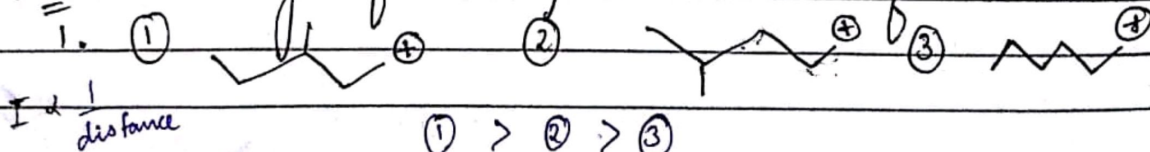
$D > N > P$

$D \rightarrow$ Distance

$N \rightarrow$ no. of α^{IGP} attached

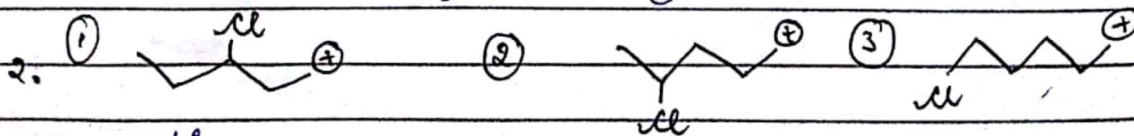
$P \rightarrow$ Power

Ques Arrange following in $\uparrow$ order of stab.



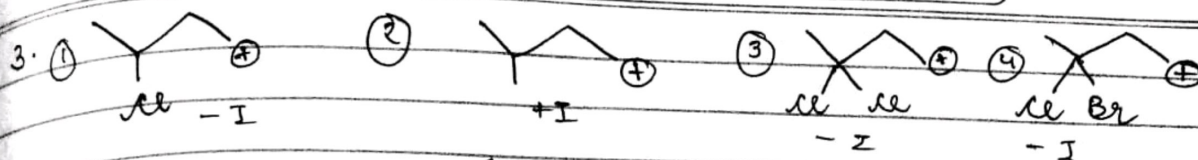
$I \propto \frac{1}{\text{distance}}$

$1 > 2 > 3$



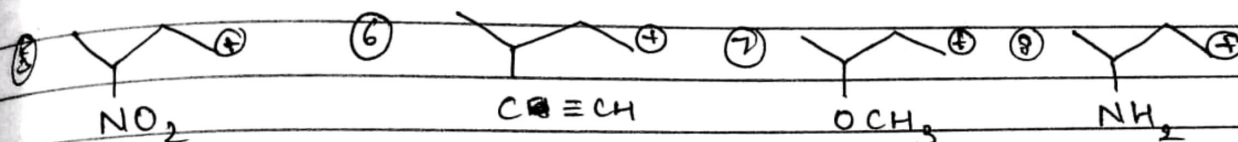
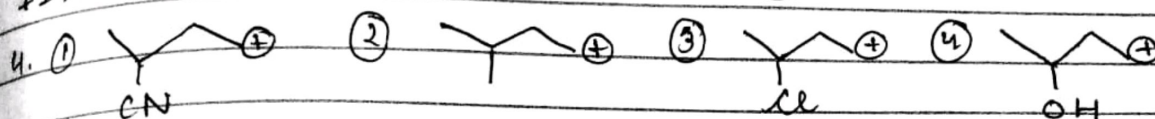
$-I \propto \text{dist.}$

$1 < 2 < 3$

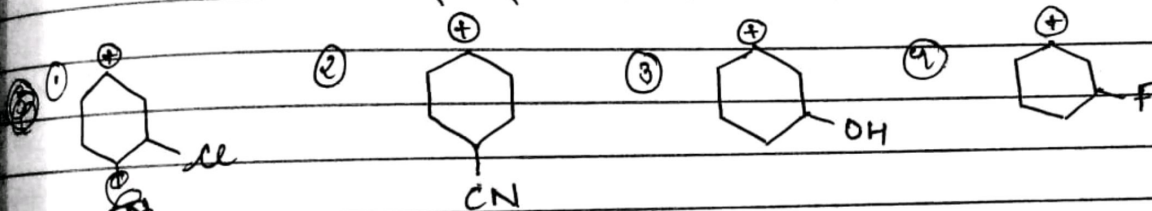


+I > -I

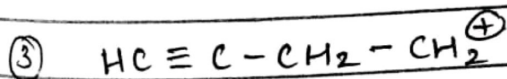
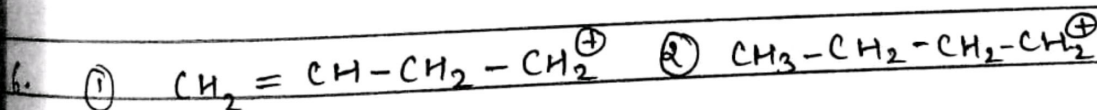
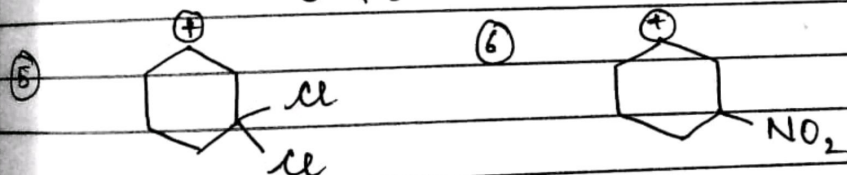
③ < ④ < ① < ②



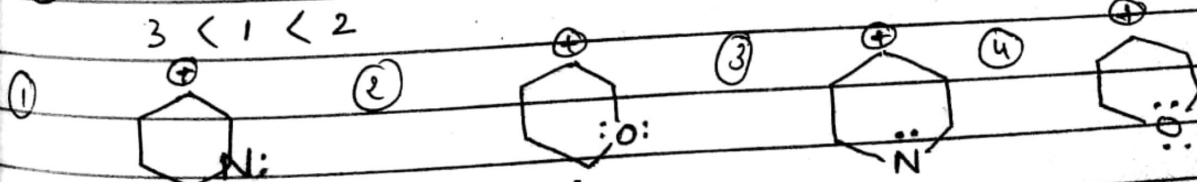
5 < 1 < 3 < 7 < 4 < 6 < 8 < 2



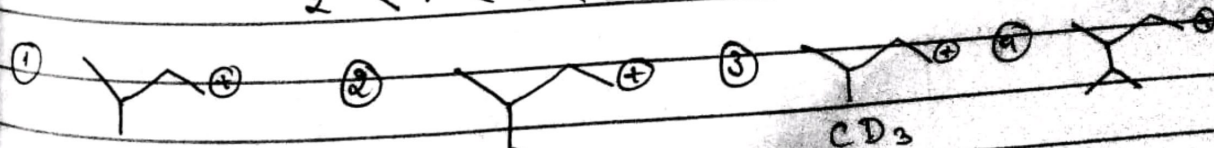
5 < 6 < 4 < 1 < 3 < 2



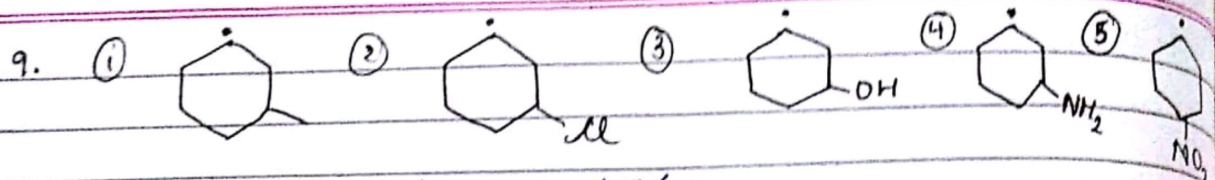
3 < 1 < 2



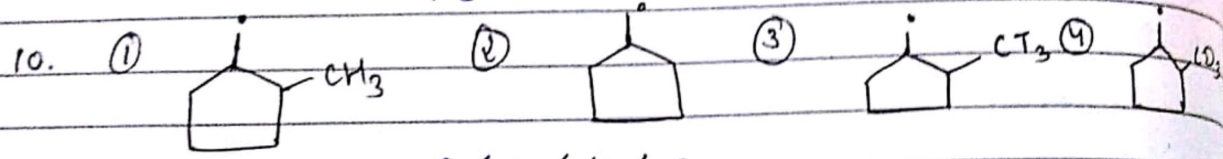
2 < 1 < 4 < 3



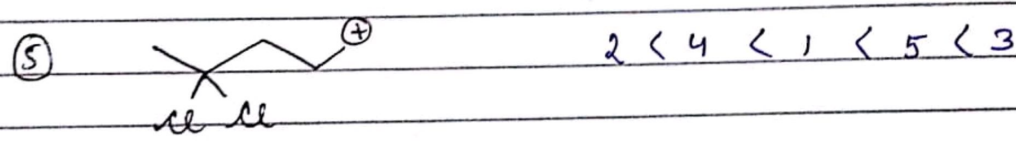
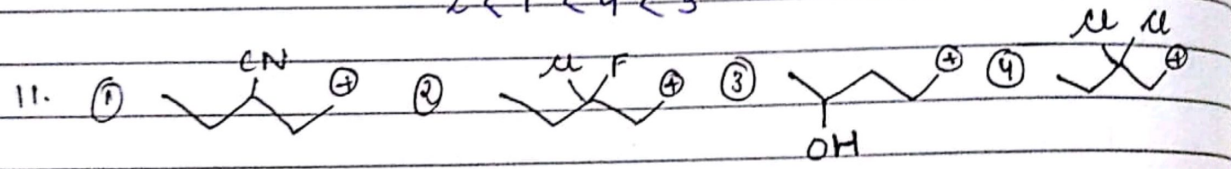
1 < 2 < 2 < 4



$2 < 3 < 4 < 5 < 1$

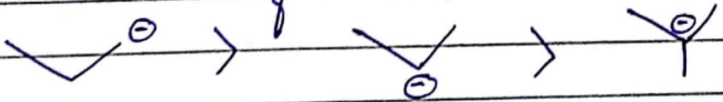


$2 < 1 < 4 < 3$



Stability of Anion :-

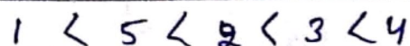
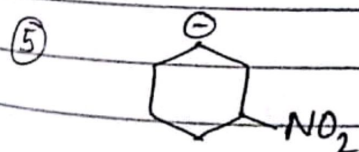
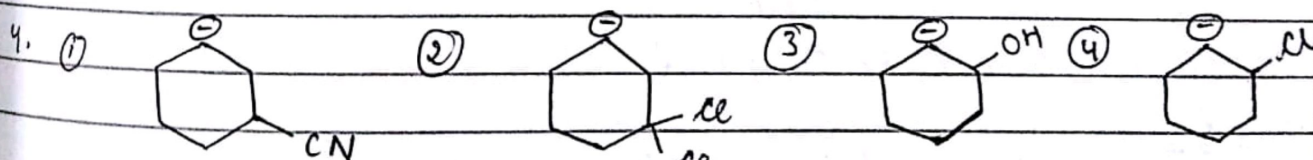
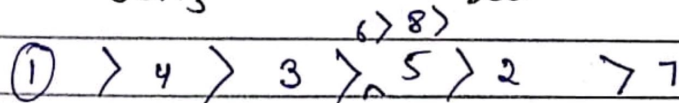
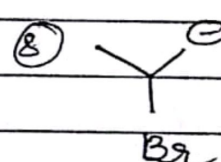
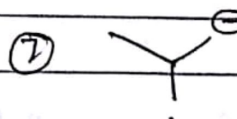
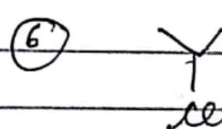
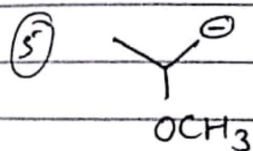
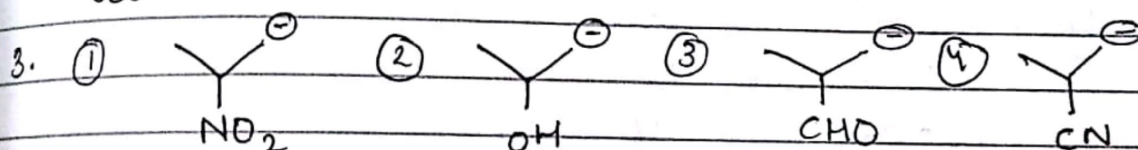
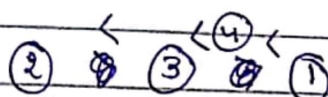
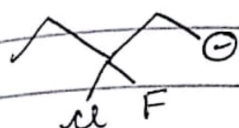
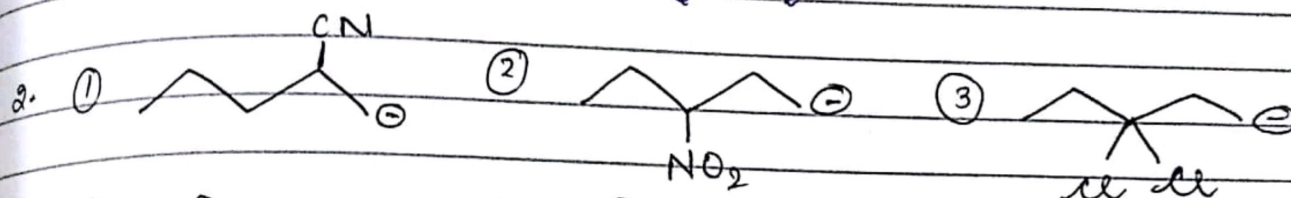
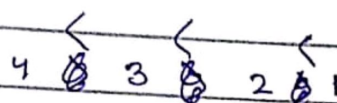
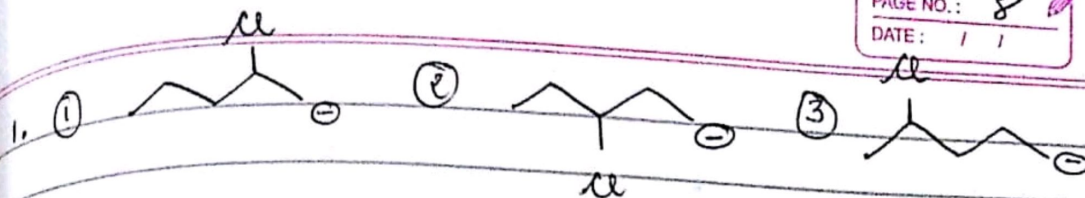
Rule (1) as $E.N. \uparrow$ stab. of anion $\uparrow$
 $CH_3-CH_2^- < CH_2=CH^- < CH \equiv C^-$

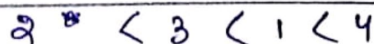
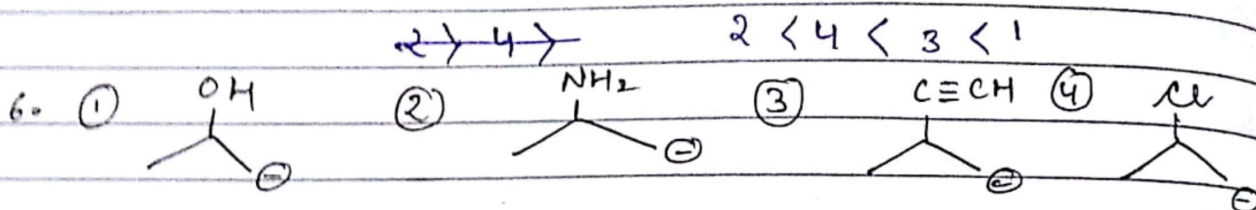
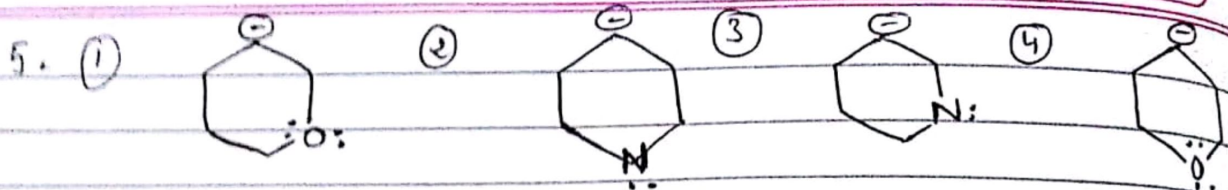
Rule (2) if $E.N.$ same
 stab. of anion $1^\circ > 2^\circ > 3^\circ$


Rule (3) If Rule (1) & (2) fail
 Stab. of anion $\propto \frac{-I}{+I}$

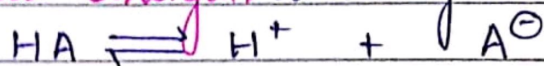
$D > N > P$ Priority order for I effect

Ques Arrange following in $\uparrow$ order of stab.





Acidic Strength: which gives H^+ ion.



- as stab. of anion $\uparrow$
- ~~eqm~~ eqm shift forward
- $[H^+] \uparrow$
- A.S. $\uparrow$

A.S. $\propto$ stab. of Anion $\propto \frac{-I}{+I}$

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

$[H^+] \uparrow$ A.S. $\uparrow$ $K_a \uparrow$ $pK_a \downarrow$

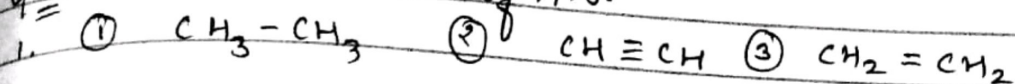
A.S.

(1) In a pd period :- L $\rightarrow$ R as E.N. $\uparrow$ A.S. $\uparrow$
 $CH_4 < NH_3 < H_2O < HF$

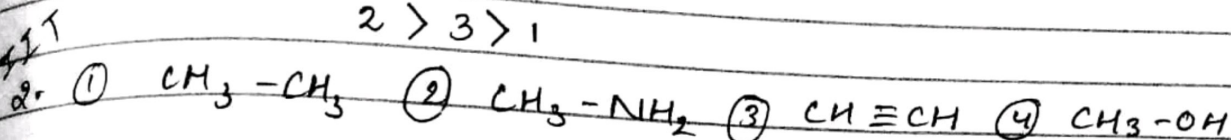
(2) In a gp: down the gp as size of anion $\uparrow$ A.S. $\uparrow$
 $HF < HCl < HBr < HI$ A.S.



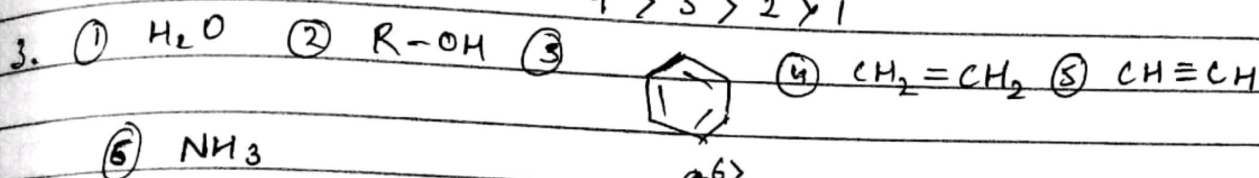
Ques write ↑ order of A.S.



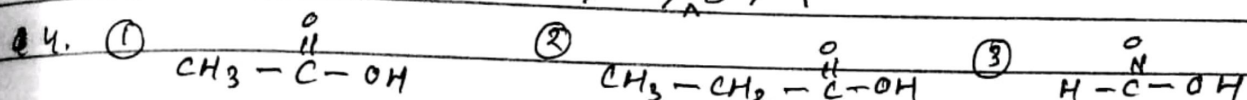
2 > 3 > 1



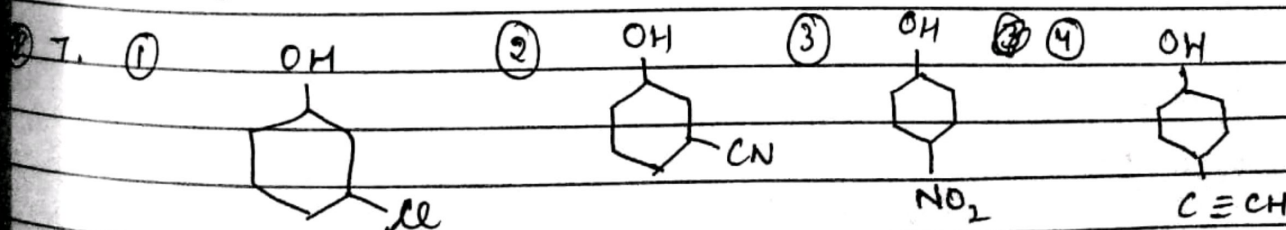
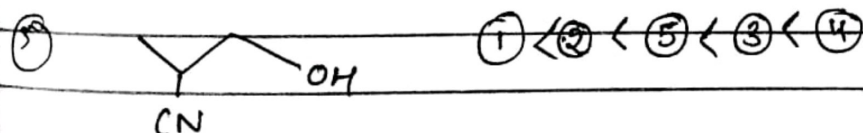
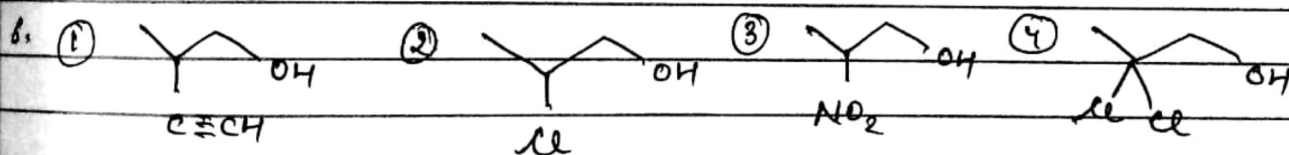
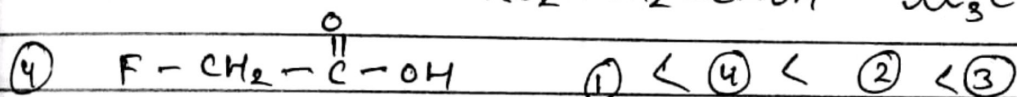
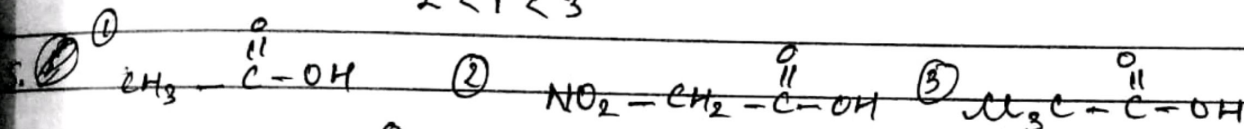
4 > 3 > 2 > 1



1 > 2 > 5 > 3 > 4

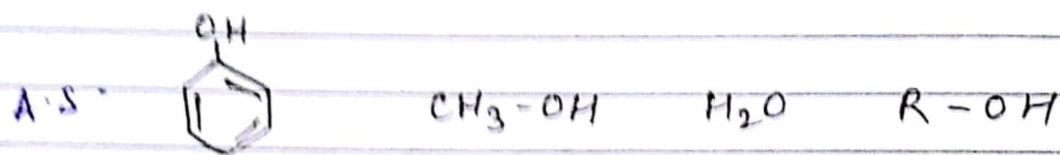


2 < 1 < 3



① Oxalic acid ② Malonic Acid ③ Succinic Acid

④ adipic acid.



$\text{pK}_a \rightarrow$ 9.3 15.54 15.74 ~ 16

Basic Strength:- (B.S.)

Base :- Species which donate lp to H^+ c/a Base.

B.S. $\propto$ E.D.G.

(Electron Donating Grp.)

$\propto +I$
 $-I$

Ques Arrange following in order of B.S.

1. ① $\text{CH}_3\text{CH}_2\text{-CH}_2^\ominus$ ② $\text{CH}_2=\text{CH}^\ominus$ ③ $\text{CH}\equiv\text{C}^\ominus$

1 > 2 > 3

2. ① $\text{CH}_3\text{-CH}_2\text{-}\ddot{\text{N}}\text{H}_2$ ② $\text{CH}_3\text{-CH}=\ddot{\text{N}}\text{H}$ ③ $\text{CH}_3\text{-C}\equiv\ddot{\text{N}}$

1 > 2 > 3

3. ① NH_3 ② $\text{CH}_3\text{-NH}_2$ ③ $\text{CH}_3\text{-CH}_2\text{-}\ddot{\text{N}}\text{H}_2$ ④ $\text{CH}_2\text{-}\ddot{\text{N}}\text{H}_2$

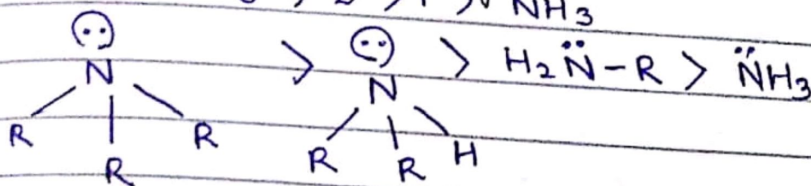
$\text{H}-\ddot{\text{N}}\text{H}_2$ $+I$ $+I$ $\text{NH}_2 -I$

4 < 1 < 2 < 3

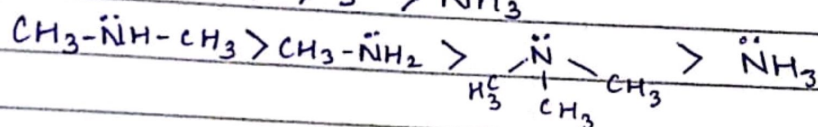
4. ① $\text{CH}_3\text{-NH}_2$ ② $\text{CH}_3\text{-}\ddot{\text{O}}\text{H}$ ③ $\text{CH}_3\text{-}\ddot{\text{F}}:$

B.S. of Amines :-

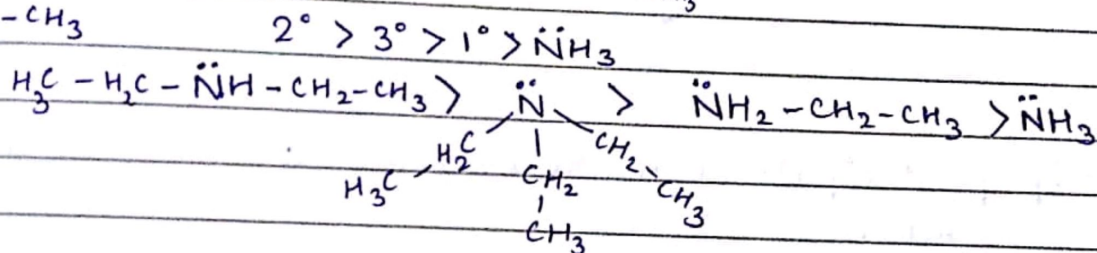
1. B.S. of amines in gaseous medium :-
 $3^\circ > 2^\circ > 1^\circ > \text{NH}_3$



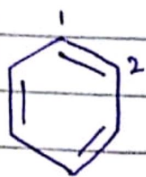
2. B.S. of amines in aq. medium :-
 $\text{R} = -\text{CH}_3$
 $2^\circ > 1^\circ > 3^\circ > \text{NH}_3$



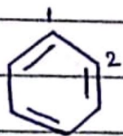
$\text{R} = -\text{CH}_2-\text{CH}_3$



Resonance :-



or



≡



C_1-C_2 B.L. $\rightarrow 1.34 \text{ \AA}$

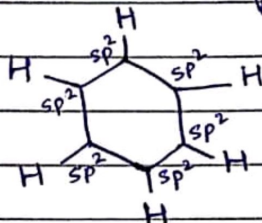
C_1-C_2 B.L. $\rightarrow 1.54 \text{ \AA}$

B.L. $\rightarrow 1.39 \text{ \AA}$

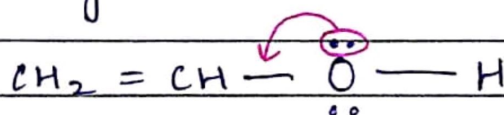
Resonating str.
or
canonical str.
or
contributing str.

- Resonance hybrid
- min^m. energy str.
- most stable form
- explain all phy. & chem. properties

- Resonance is a hypothetical phenomena.
- It is an intramolecular phenomena.
- It is a stabilizing phenomena
- Permanent effect
- Atoms remain in same posⁿ only.
- Delocalisation of πe^- , +ve charge, -ve charge, free radical takes.
- molecule should be planar.



- lp participating in resonance are not considered in hyb.



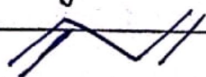
$$2bp + 1lp = 3 \rightarrow sp^2$$

All Average structure of all resonating str. is c/a Resonance hybrid.

$$\text{Resonance Energy (R.E.)} = \text{Energy of R.H.} - \text{Energy of most stable Canonical str.}$$

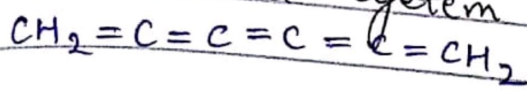
Type of System :

1. Conjugated System :



Reso. ✓

2. Conjugated System



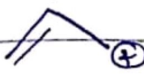
Reso X

3. Isolated System

Reso X



Condⁿ for Resonance :-



vacant orbital Reso.



Migration of $2e^-$

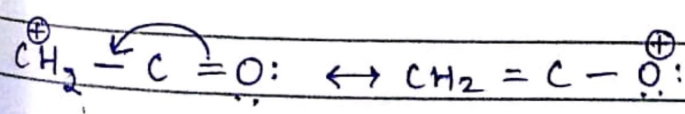
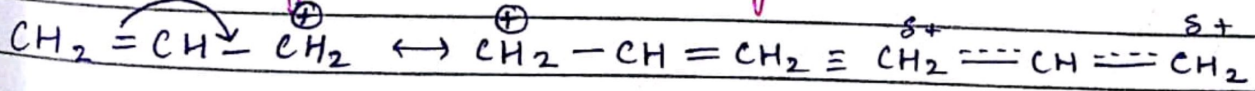


migration of $1e^-$

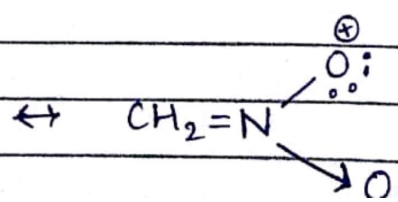
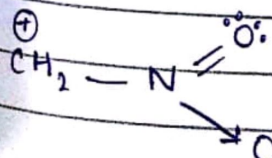


Hypothetical concept

① = conjugated with $\oplus$ charge

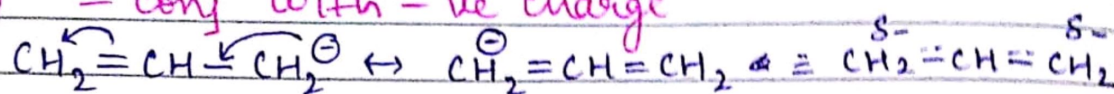


R.H.

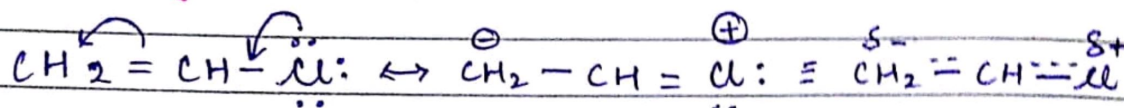


no Reso
more E.N. or incomplete
octet not given
example

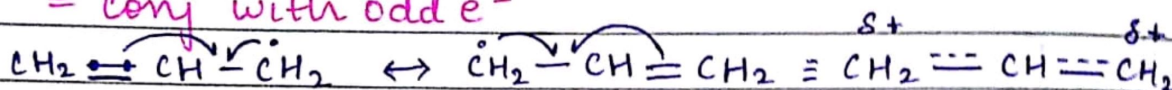
(2) = conj with -ve charge



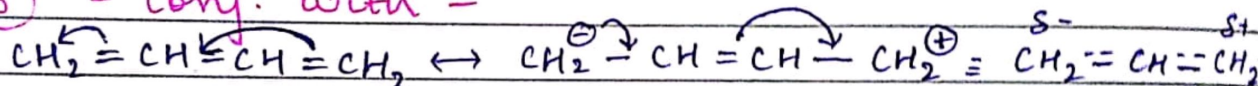
(3) = conj. with lp



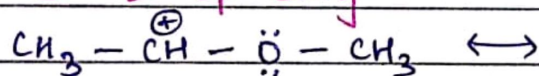
(4) = conj with odd e⁻



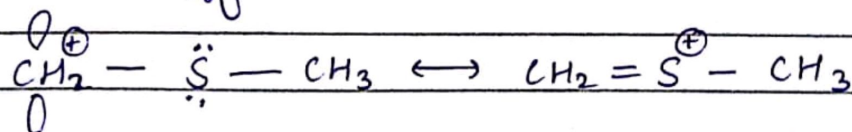
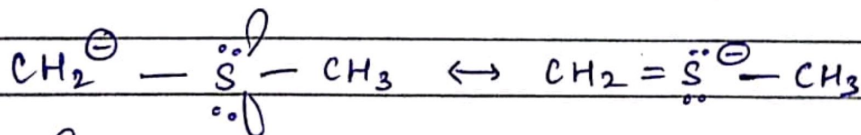
(5) = conj. with =



(6) ⁺ & lp conj.



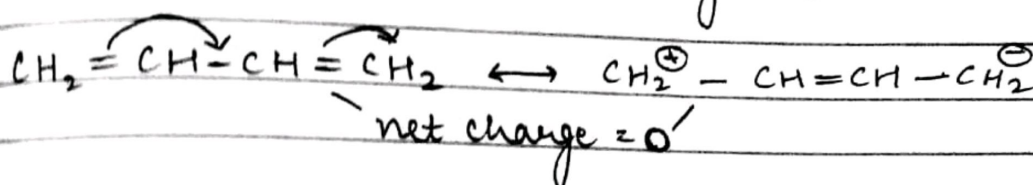
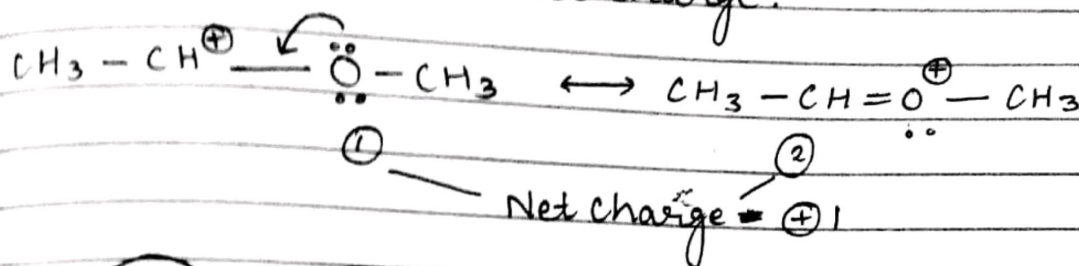
(7) vacant orbital Resonance



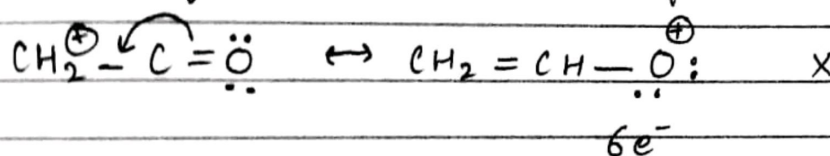
CH

Rules for Resonance :-

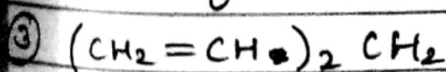
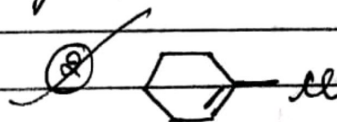
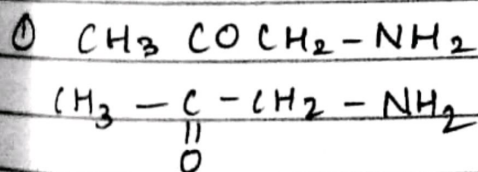
- All atoms remains at their posⁿ only delocalisation πe^- , lp, -ve charge, $\oplus$ charge or odd e^- takes place.
- All R.S. have same net charge.



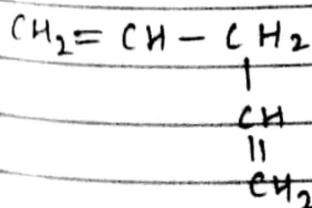
- All R.S. have same no. of πe^- & lp.
- All R.S. follow Lewis Octet Rule



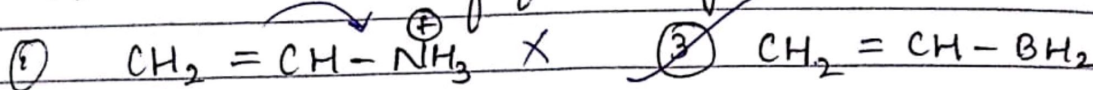
Ques In which of following Resonance is possible



④ all

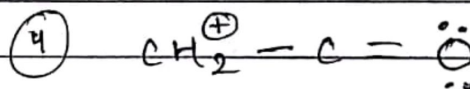
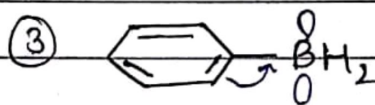
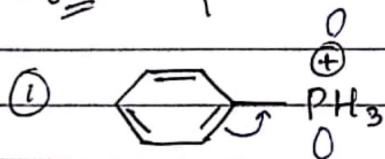


Ques In which of following Resonance is possible:



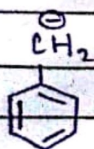
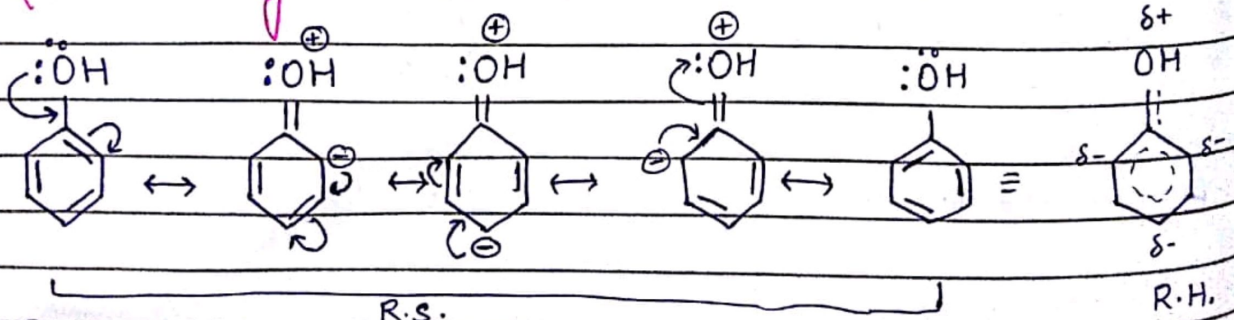
(4) None

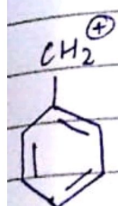
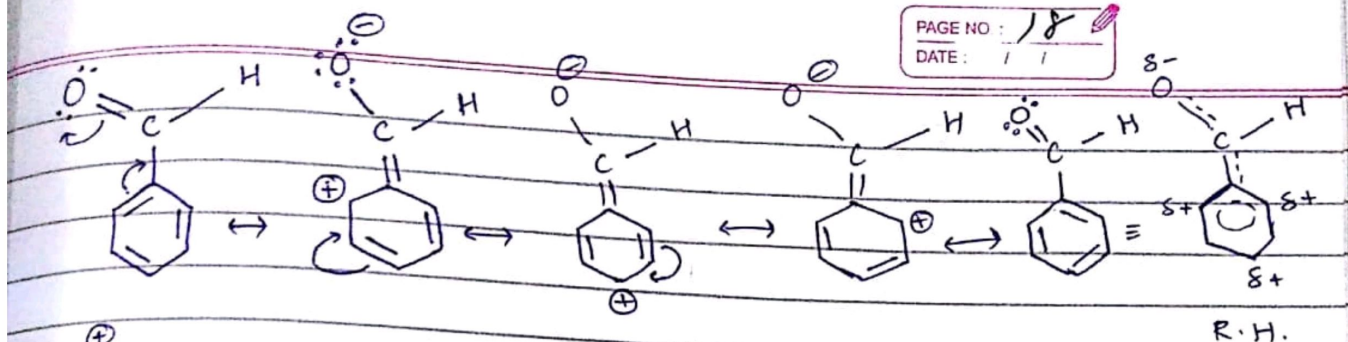
Ques Resonance is not possible in -



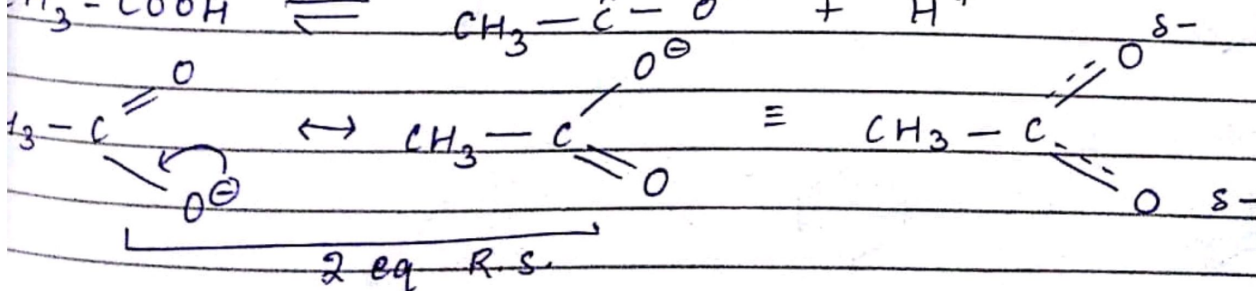
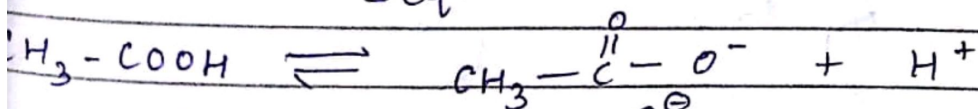
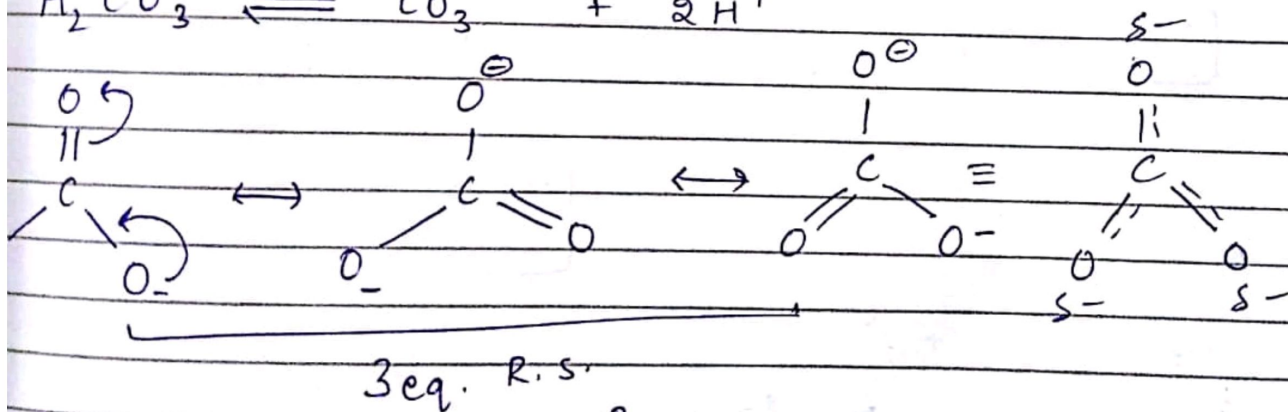
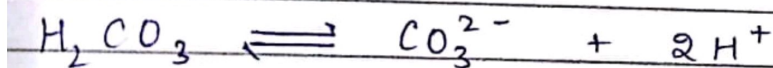
E.N. atom पर incomplete octet ~~होना~~ wala
R.S. नहीं बनायेगा

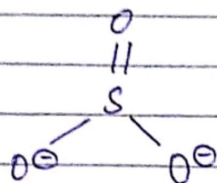
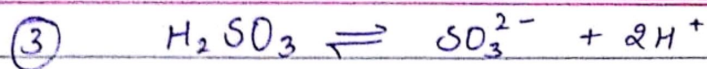
Resonating Structure :-





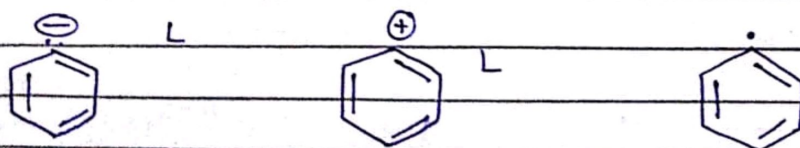
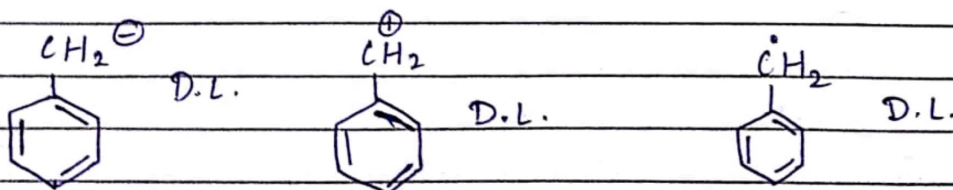
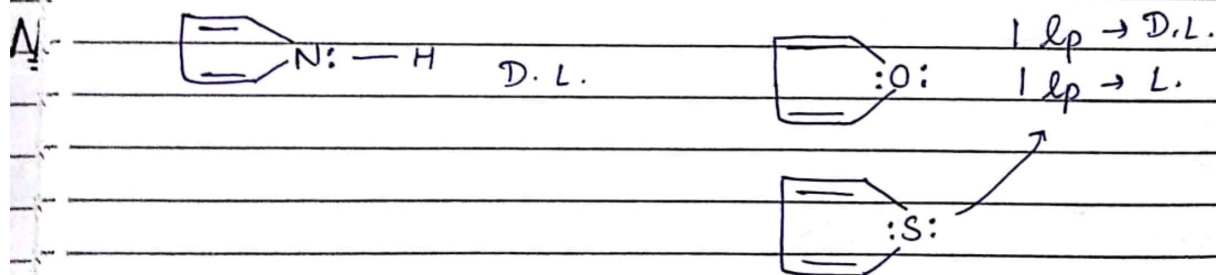
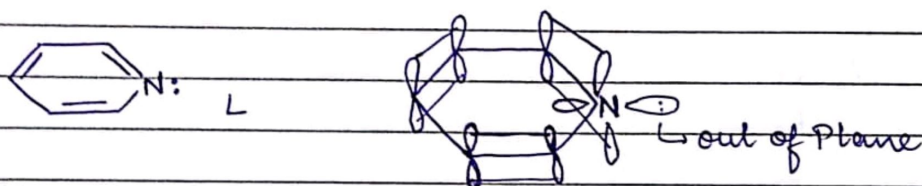
In benzene Mesomeric Effect / Reso is observed at ortho & para posⁿ only





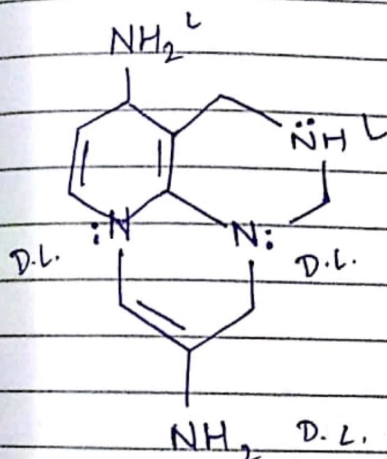
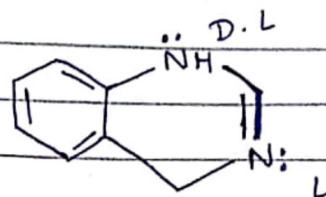
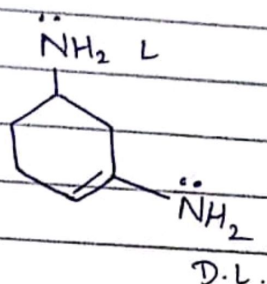
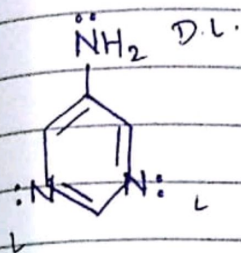
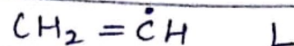
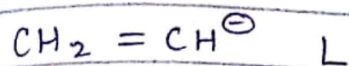
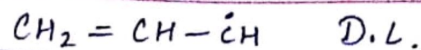
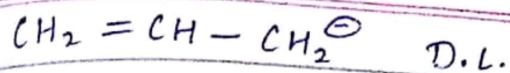
Note: Equivalent reso. is always more effective than normal reso

Localised & Delocalised e^-



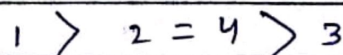
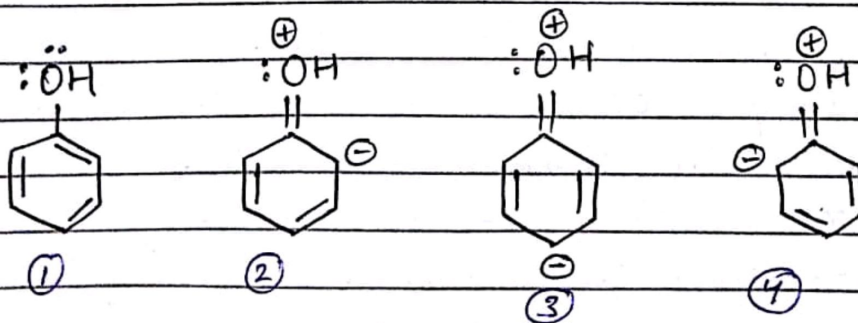
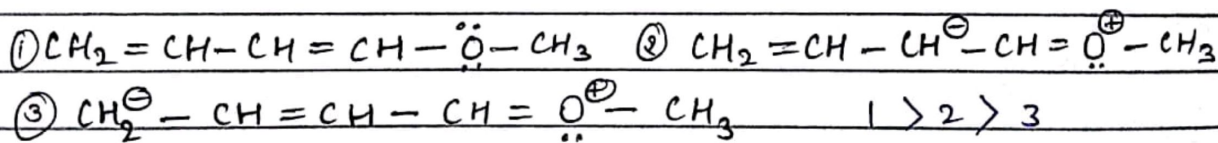
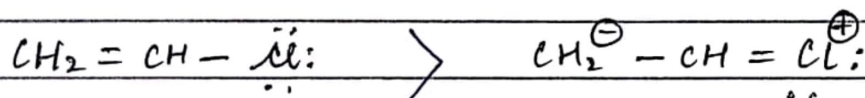
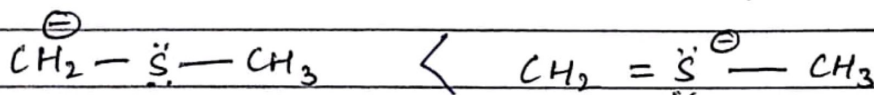
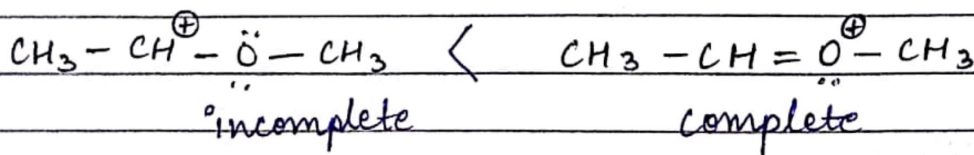
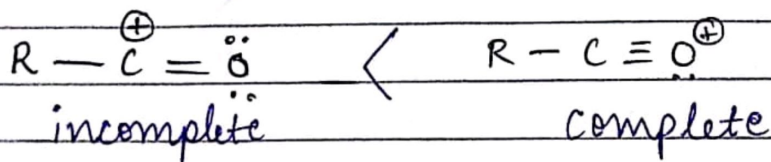
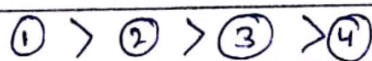
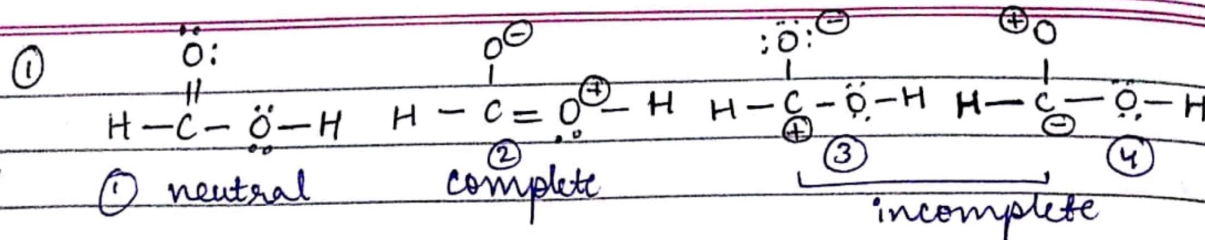
PAGE NO. : 28

DATE : / /



Stability of R.S. :-

- ① non Polar R.S. (neutral) > Polar R.S. (charged)
- ② Polar R.S. with complete octet > Polar R.S. with incomplete octet
- ③ -ve charge on more E.N. is more stable R.S.
- ④ +ve charge on more E.N. is less stable R.S.
- ⑤ as charge separation b/w opp. charge ↓ stab ↑
as charge separation b/w same charge ↓ stab ↓
- ⑥ $\oplus$ & $\ominus$ distance ↓ stab ↑
- ⑦ $\oplus$ & $\ominus$ d ↑ stab ↓
- ⑧ $\oplus$ & $\oplus$ } d ↑ stab ↑
- ⑨ $\ominus$ & $\ominus$ } d ↓ stab ↓

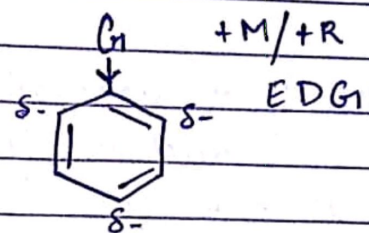


Type of RESONANCE / MESOMERIC Effect :-

1. $+R/+M \rightarrow \text{EDG}$
2. $-R/-M \rightarrow \text{EWG}$

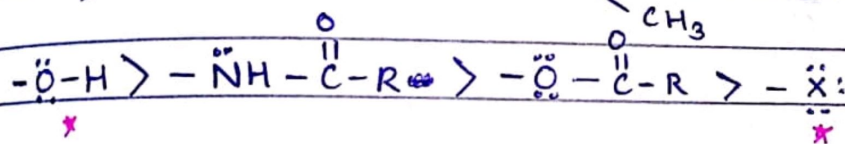
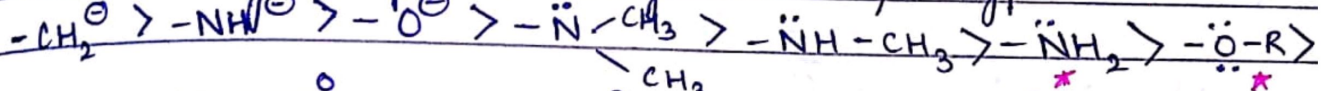
1. $+R/+M$

- e⁻ density on Ring $\uparrow$
- activate Ring



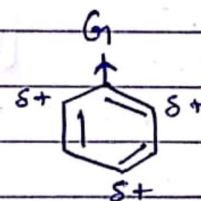
- $+M/+R \rightarrow \text{O/P directing gp}$

- -ve charge & lp containing are $+M/+R$ gp



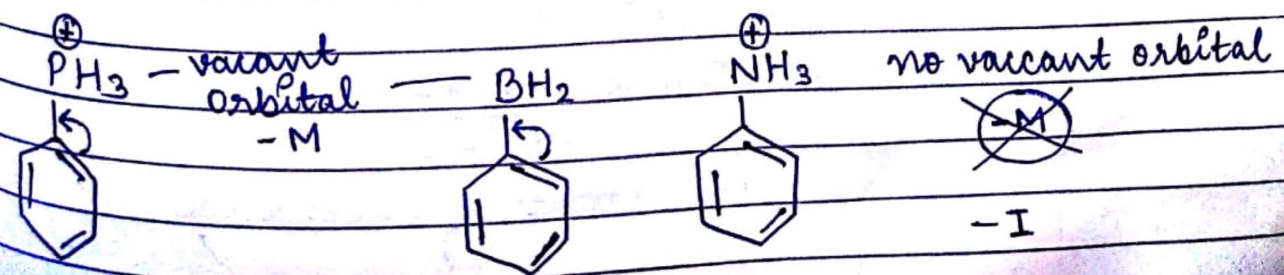
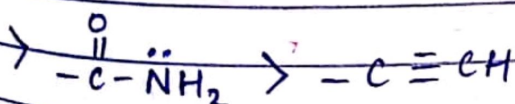
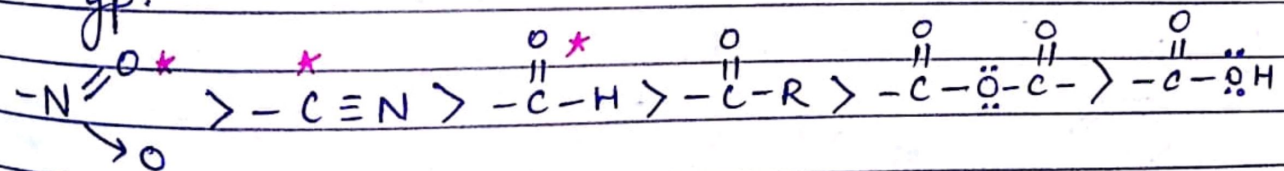
2. $-R/-M$

- e⁻ density of ring $\downarrow$
- deactivate ring



- $-M/-R \rightarrow \text{meta directing}$

- polar π bond & vacant orbital containing gp are $-M/-R$ gp.

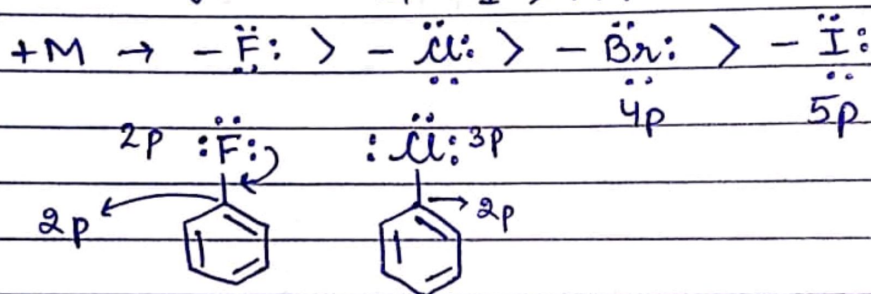


gp. which works as +M as well as -M.
 $-\ddot{\text{S}}\text{H}$, $-\ddot{\text{P}}\text{H}_2$, , $-\text{CH}=\text{CH}_2$, $-\ddot{\text{N}}=\text{O}$

Note: # Generally mesomeric effect is more effect than inductive effect but in following 2 case ind. effect is more dominant.

① Halogen -X

$\hookrightarrow -I > +M$



$-I \propto \text{E.N.} \neq -\ddot{\text{F}}: > -\ddot{\text{Cl}}: > -\ddot{\text{Br}}: > -\ddot{\text{I}}:$

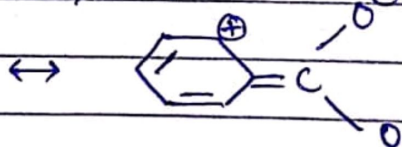
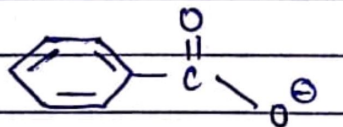
When halogens in resonance

Overall Halogens works as EWG

$-\text{F} < -\text{Cl} < -\text{Br} < -\text{I}$

② $-\text{C}(=\text{O})-\text{O}^-$

+I $>$ -M



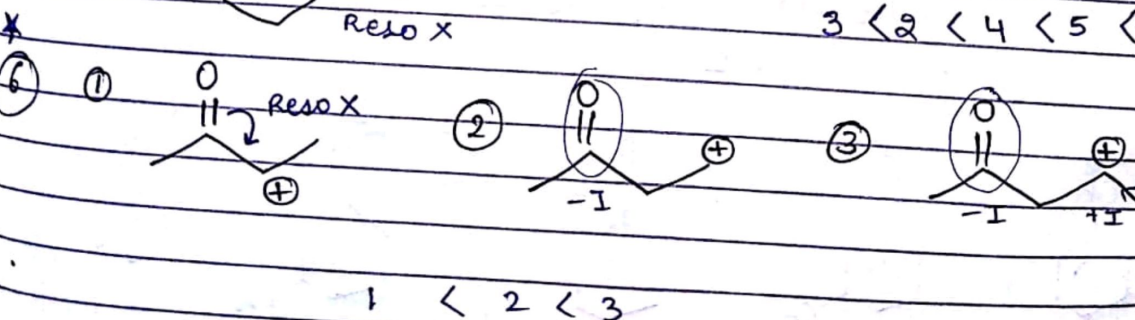
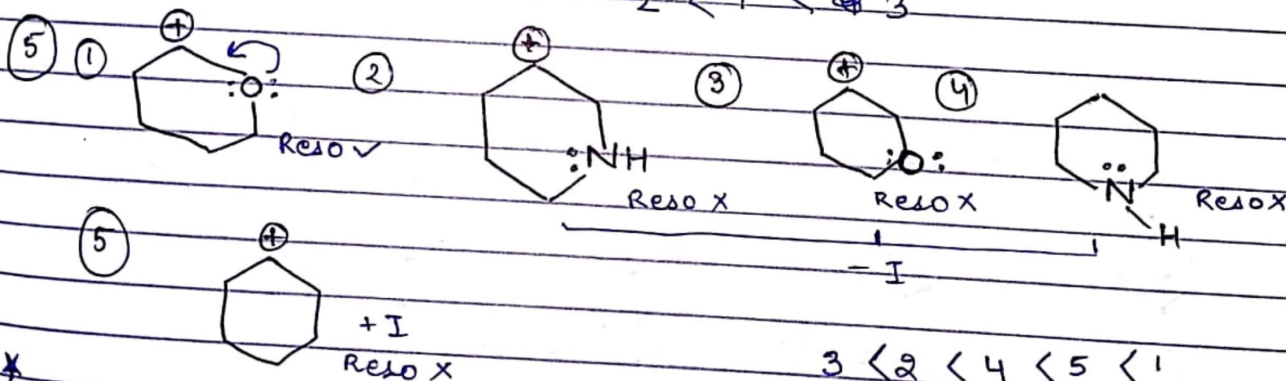
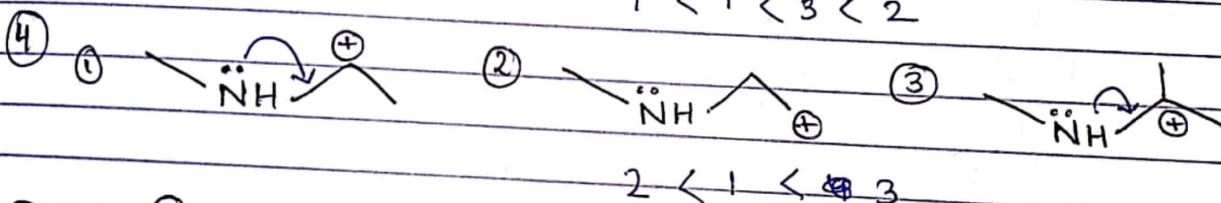
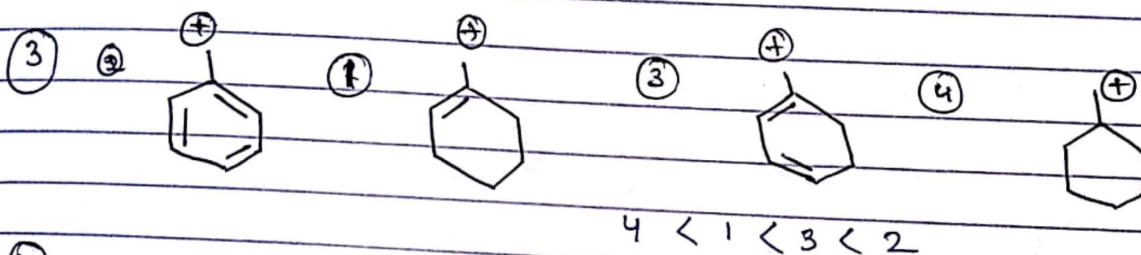
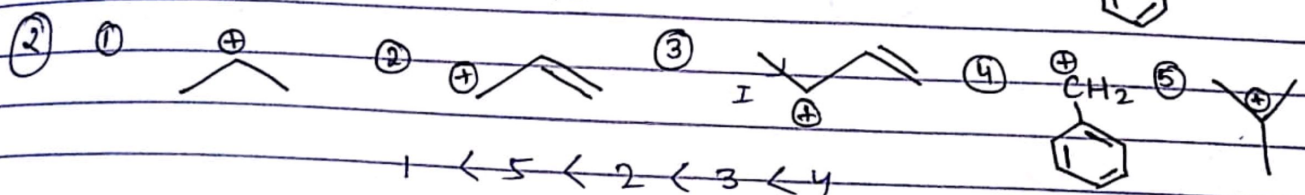
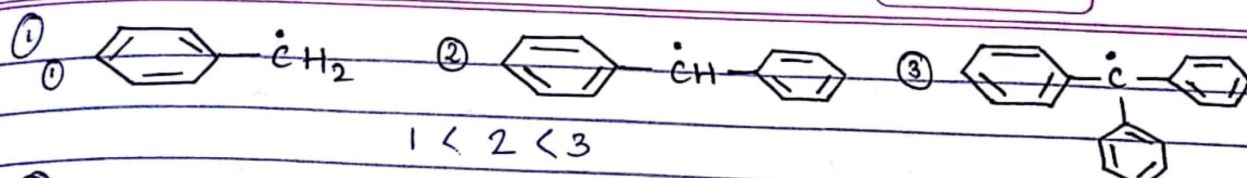
repulsion
unstable
Reso X

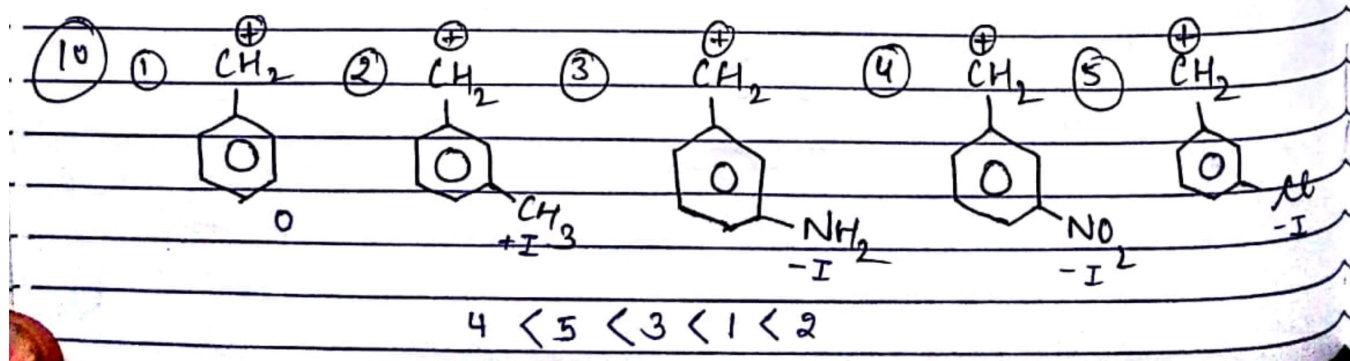
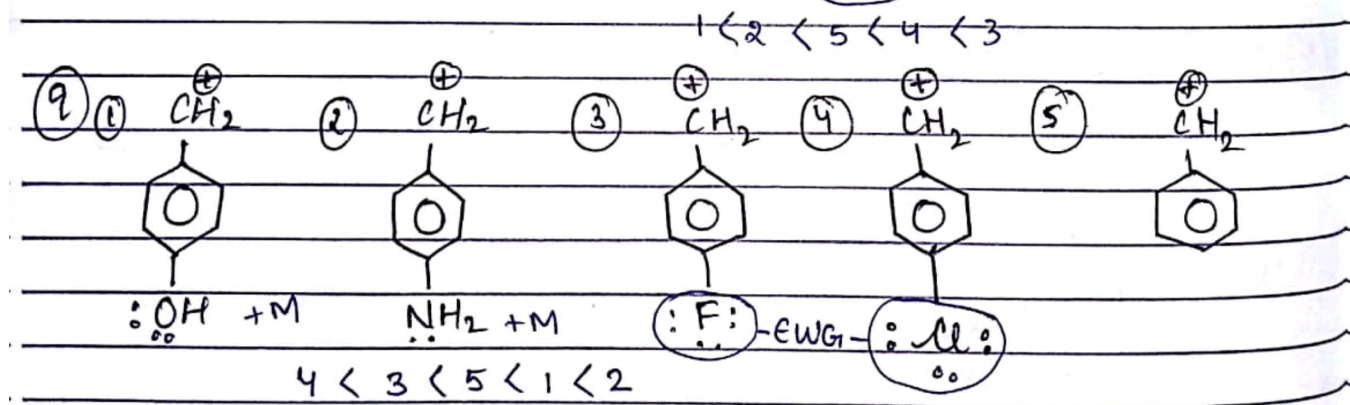
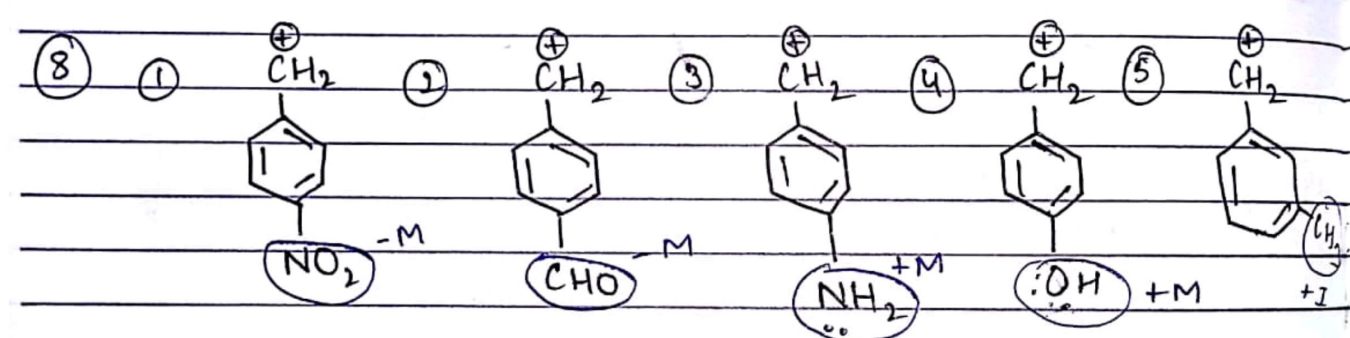
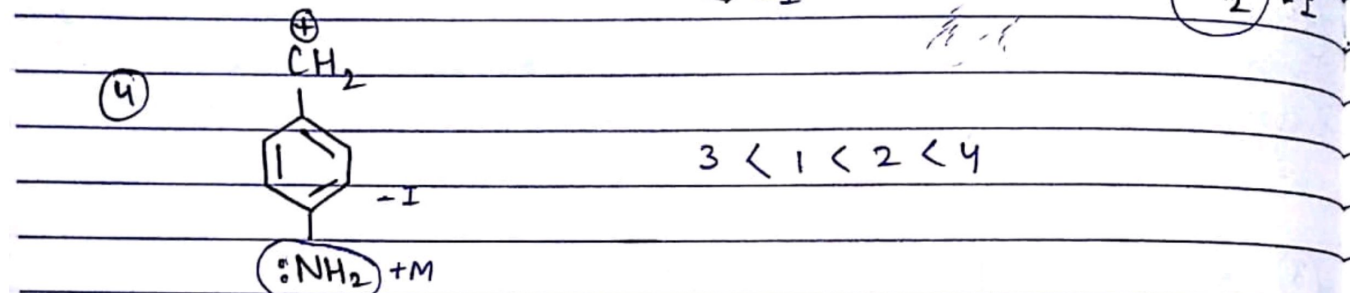
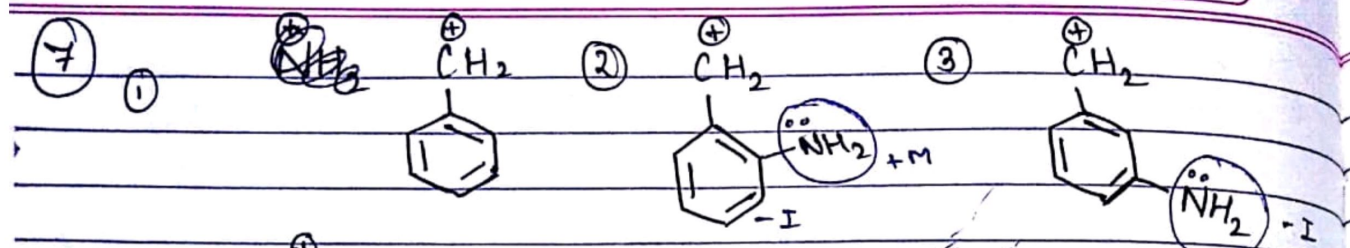
Applications of Resonance / Mesomeric Effect.

1. Stability of C^+ & C^-

Stab. of $\text{C}^+/\text{C}^- \propto \text{EDG} \propto \frac{+M/+I}{-M/-I}$

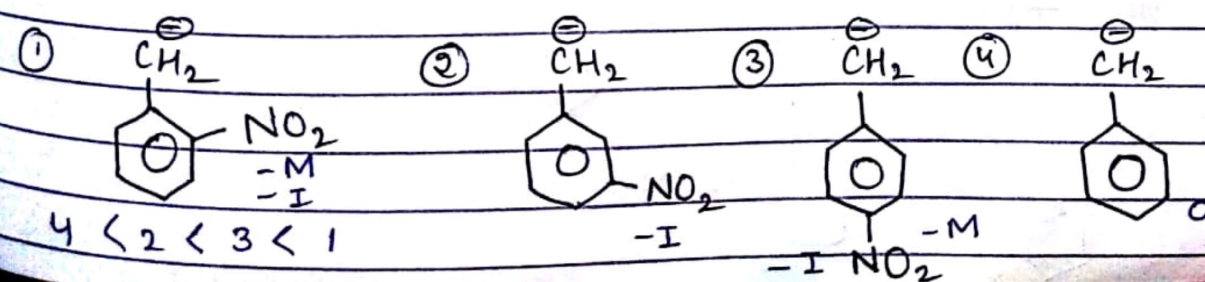
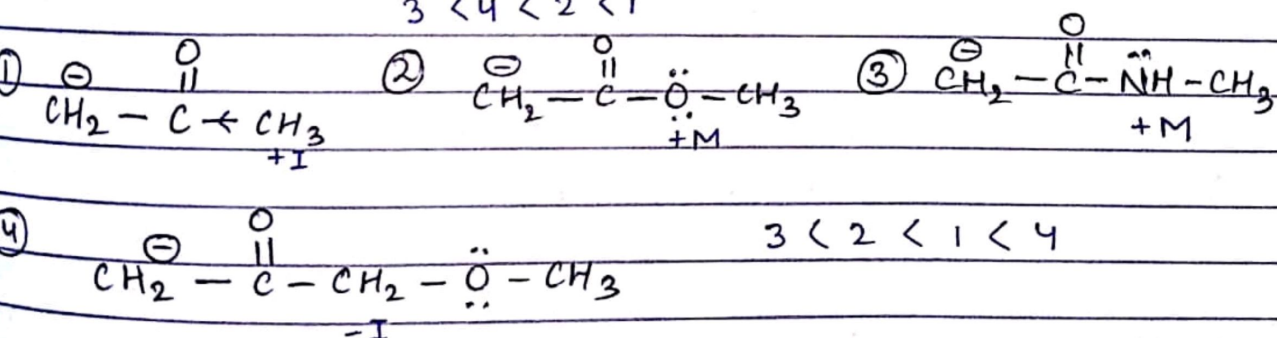
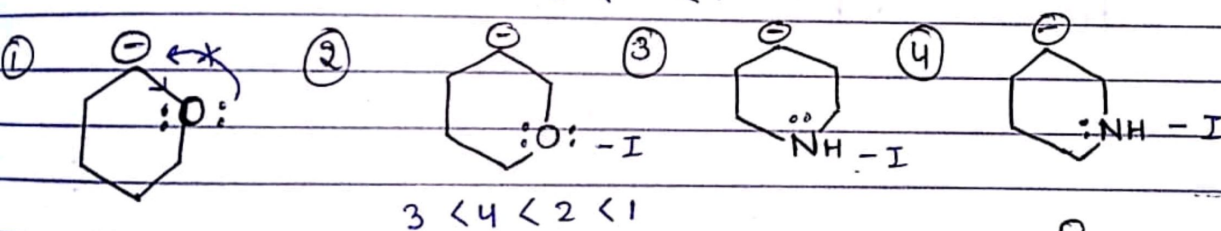
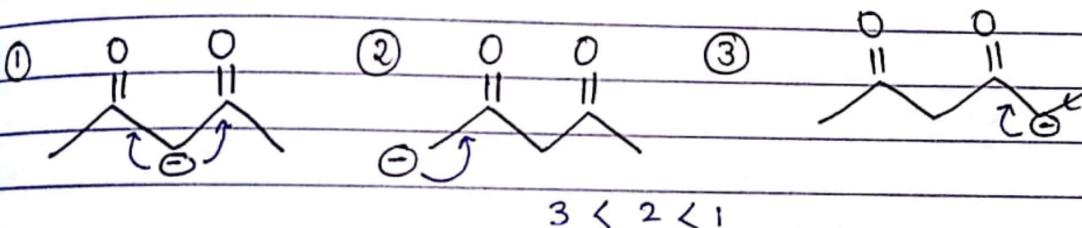
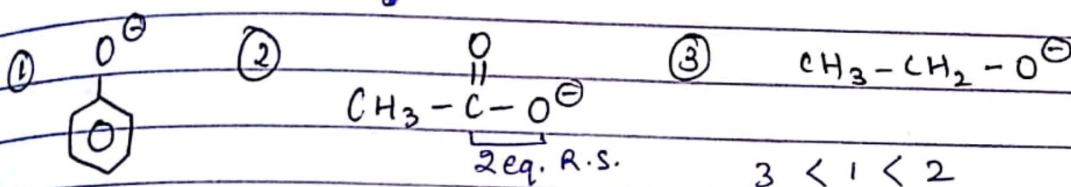
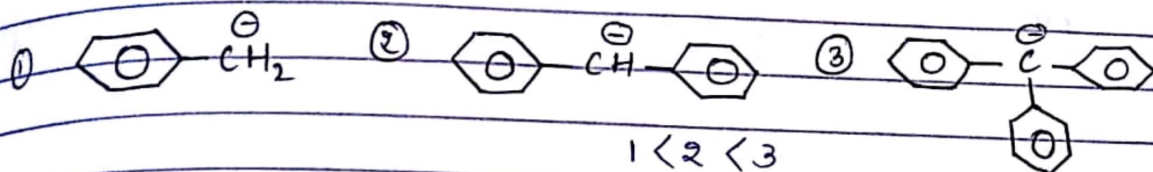
$\propto$ extent of resonance

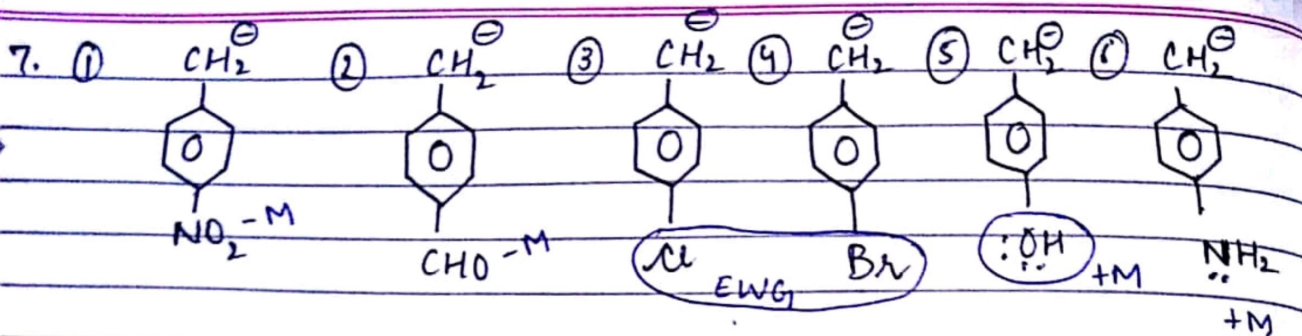




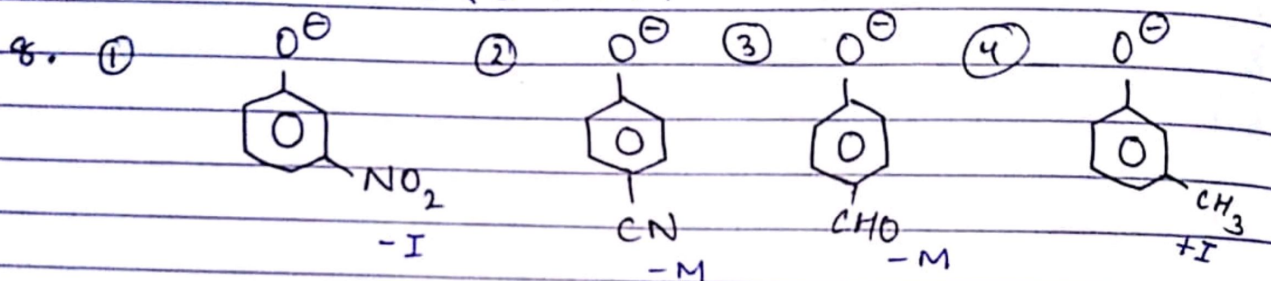
2. Stability of anion :-

Stab. of anion $\propto$ EWG $\propto \frac{-M/-I}{+M/+I} \propto$ extent of Resonance





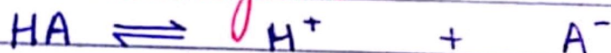
$6 < 5 < 3 < 4 < 2 < 1$



$4 < 1 < 3 < 2$

V.V.IMP NEET I Que

Acidic Strength :-



anion stability $\uparrow$

$\text{eq}^m \rightarrow$

$[\text{H}^+] \uparrow$

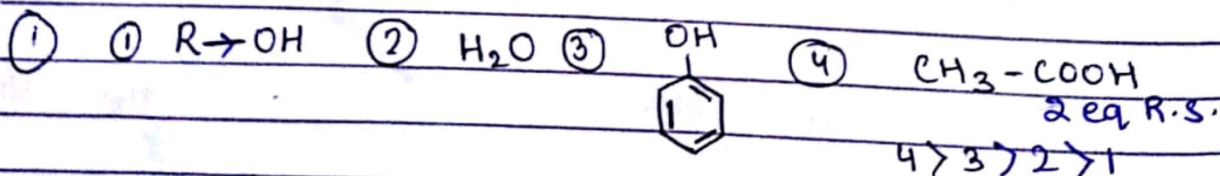
A.S. $\uparrow$

$K_a \uparrow$

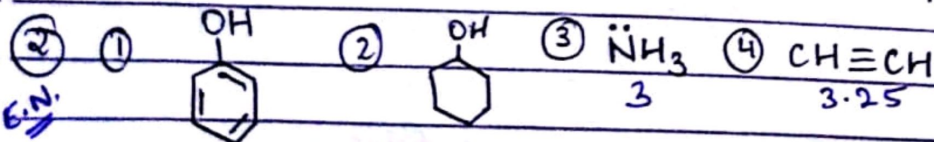
$\text{p}K_a \downarrow$

A.S. $\propto$ stability of anion $\propto$ EWG $\propto -M/-I \propto 1$

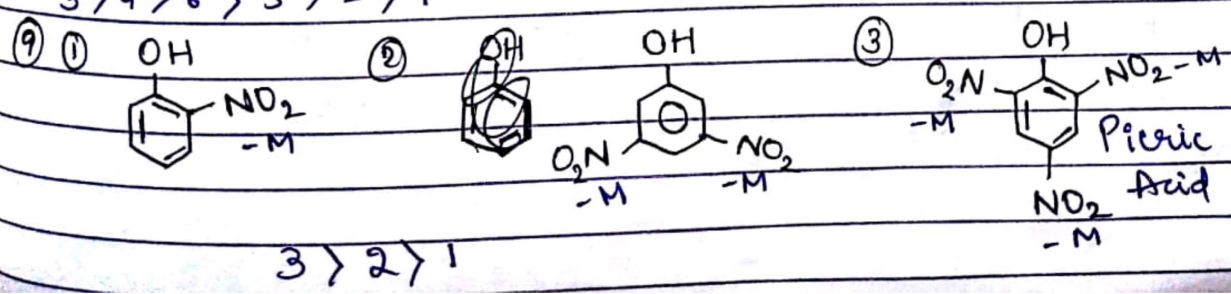
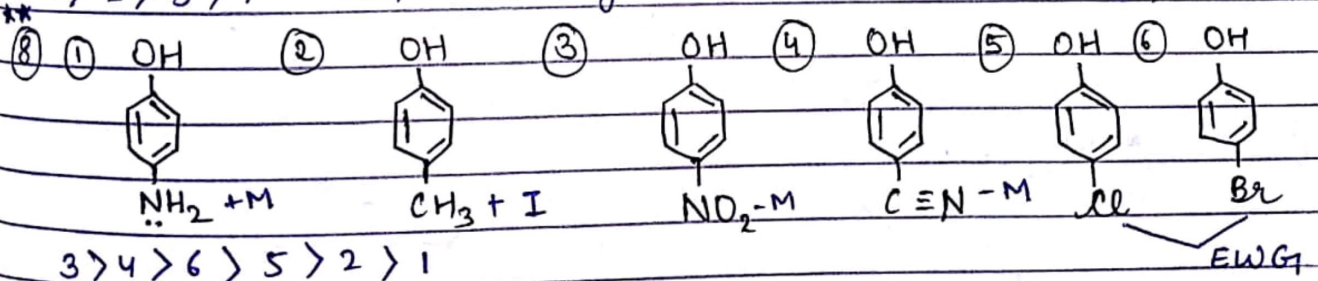
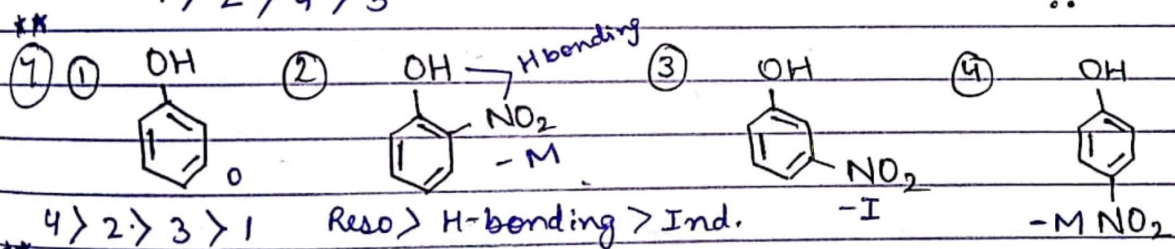
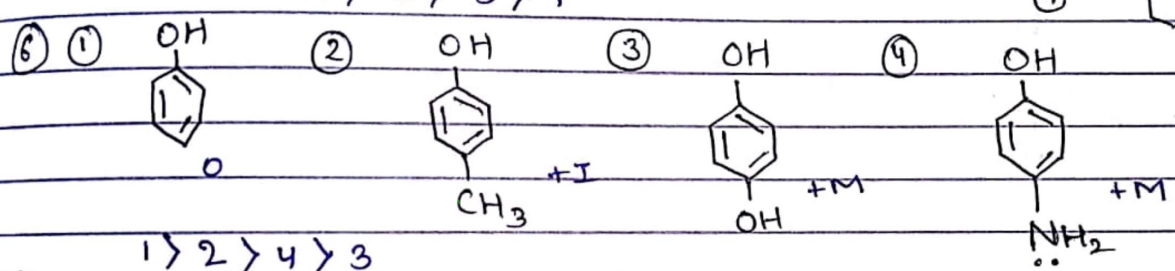
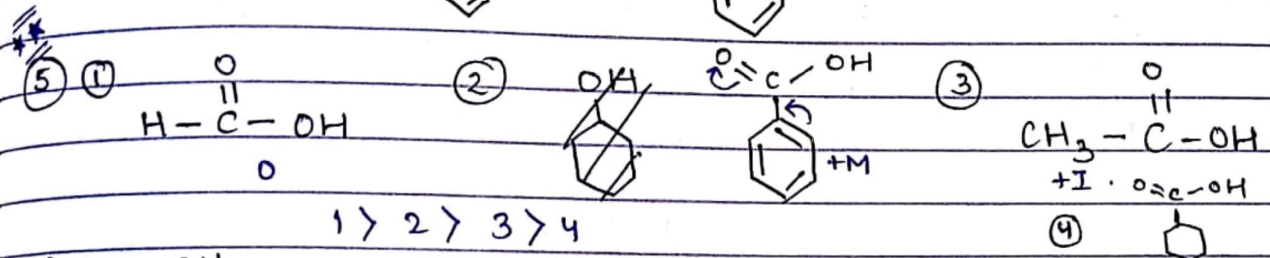
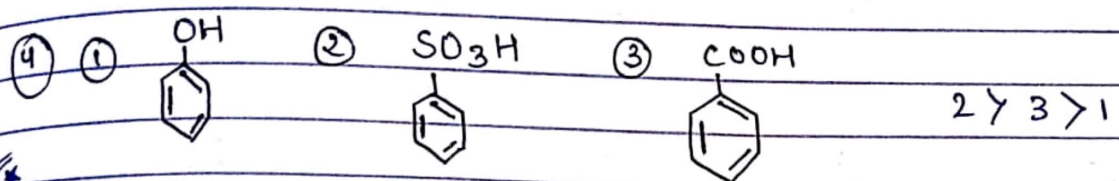
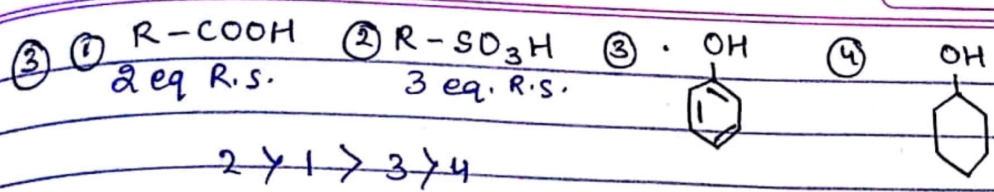
$+M/+I$

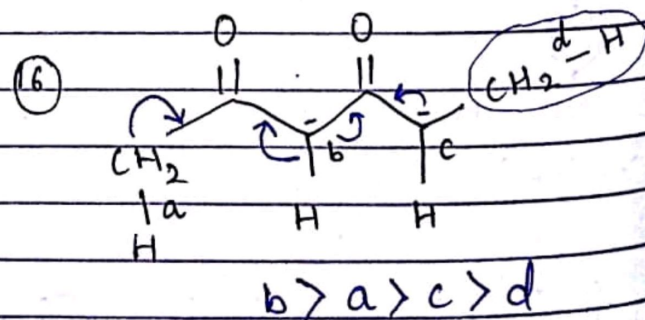
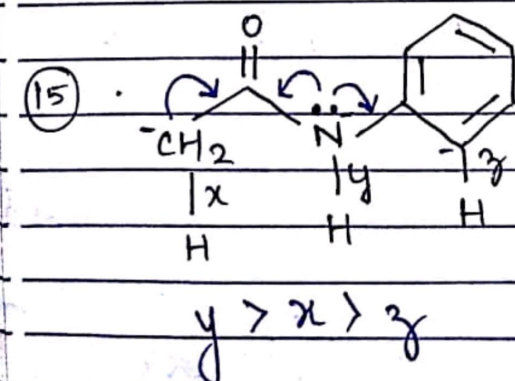
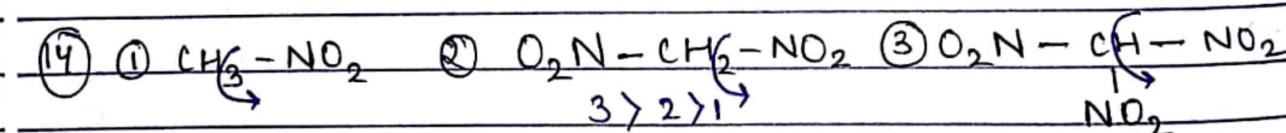
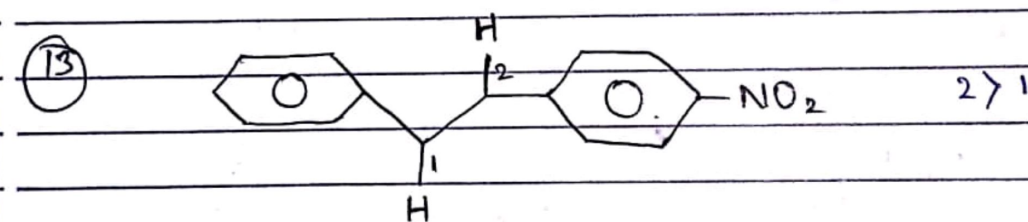
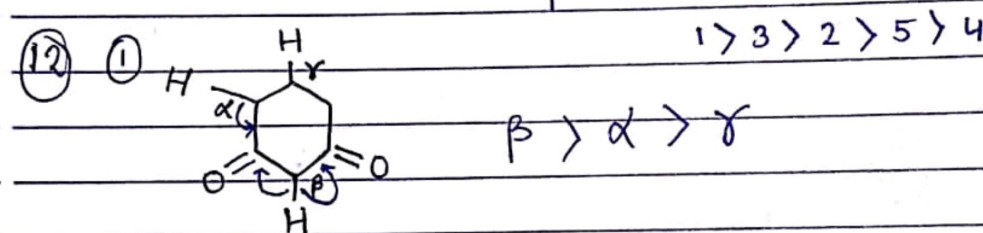
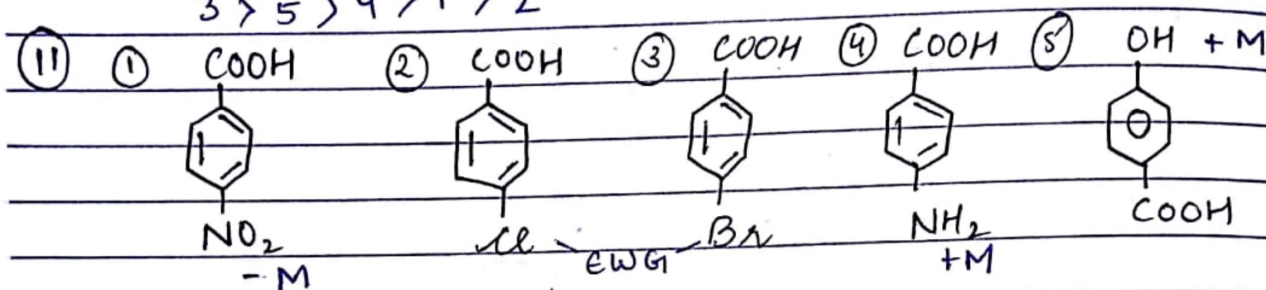
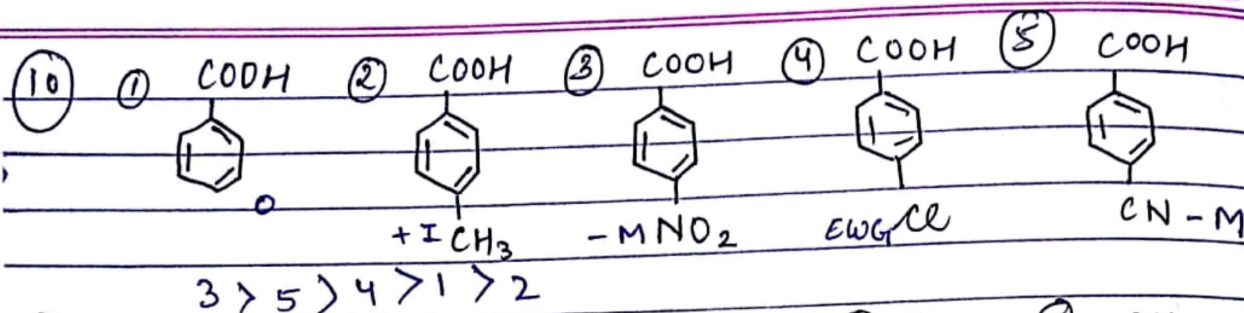


$4 > 3 > 2 > 1$



$1 > 2 > 4 > 3$

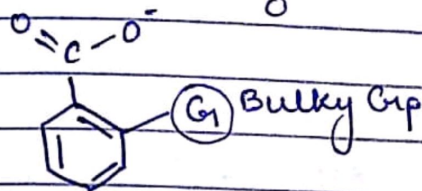




Ortho Effect :- Only for aromatic carboxylic acid

When bulky bulky gp is substituted at benzoic acid then ortho substituted benzoic acid is more acidic than meta & Para isomers.

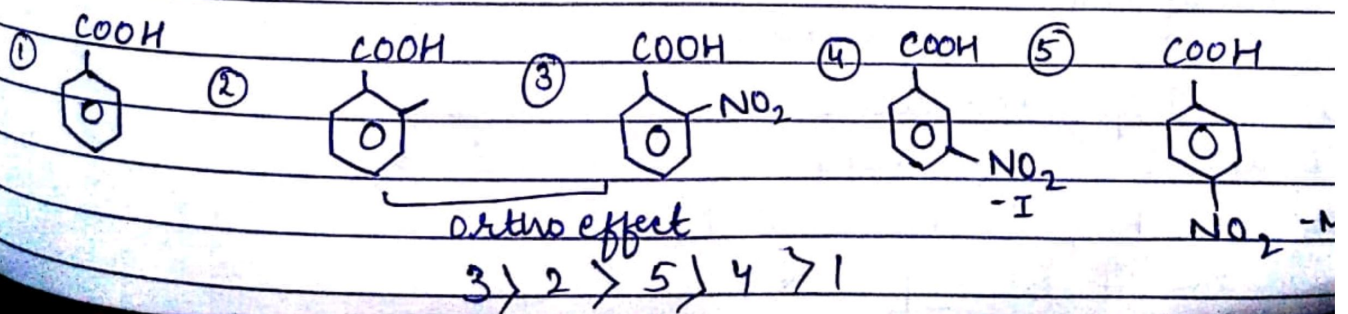
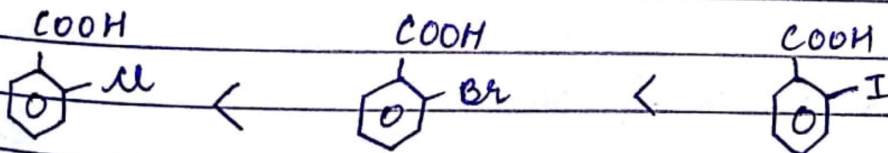
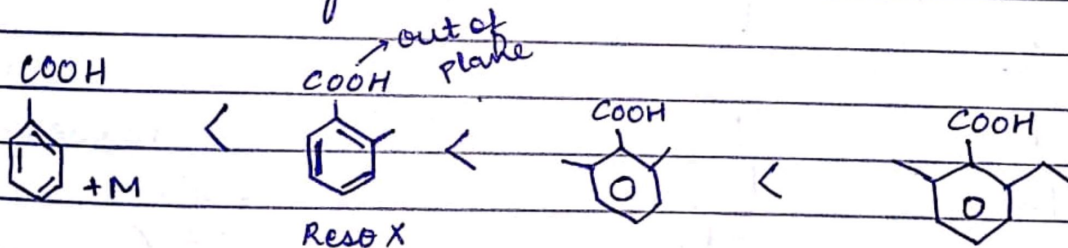
- There is steric hindrance b/w $\text{C}-\text{O}^\ominus$ & bulky gp which rotate $-\text{C}-\text{O}^\ominus$ & it comes out of plane

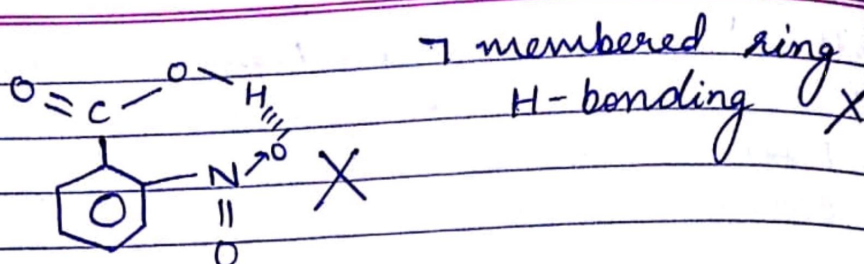


- R
- NO_2
- Cl / Br / I

- So now there is no resonance b/w benzene (+M) & $-\text{C}(=\text{O})\text{O}^\ominus$.

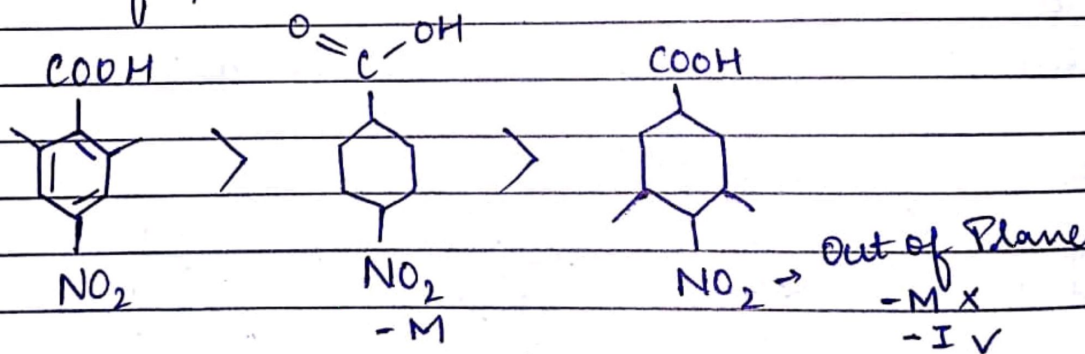
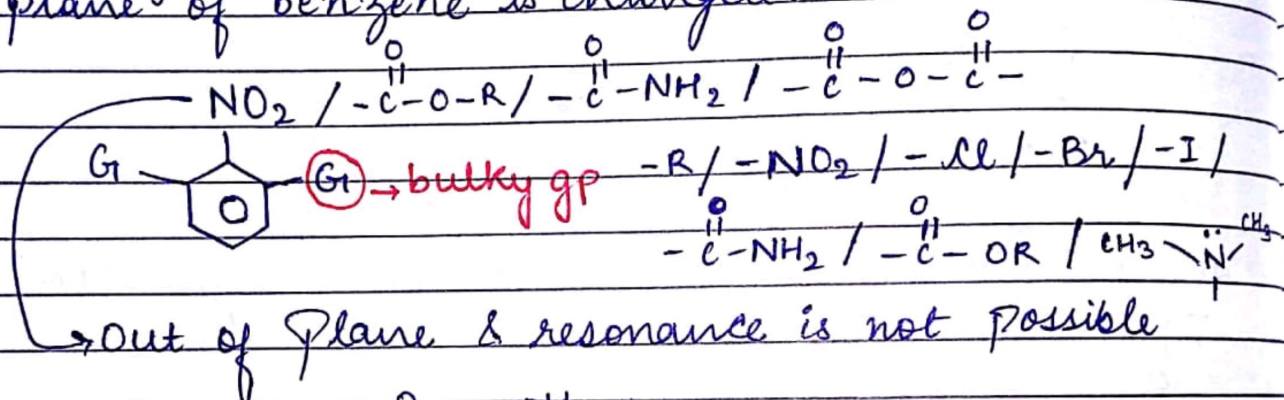
- hence stab. of anion $\uparrow$ hence the A.S. $\uparrow$





Steric inhibition in Resonance (SIR Effect)

When bulky gp are attached on ortho position of triangular gp then due to steric hindrance plane of benzene is changed.



Basic Strength :-

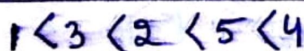
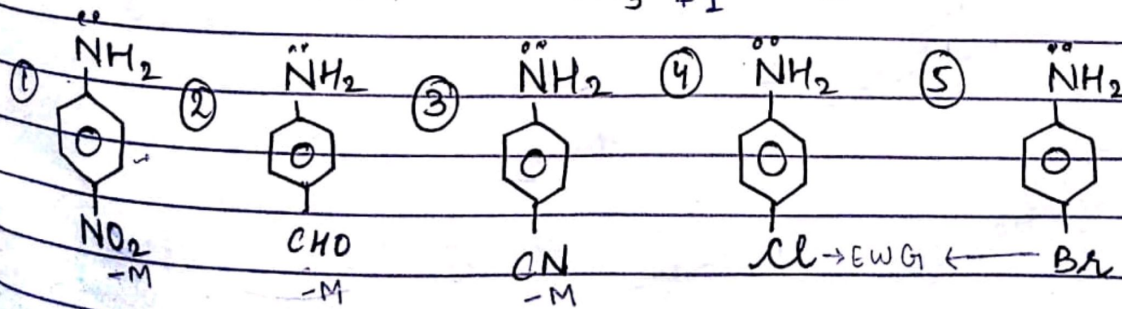
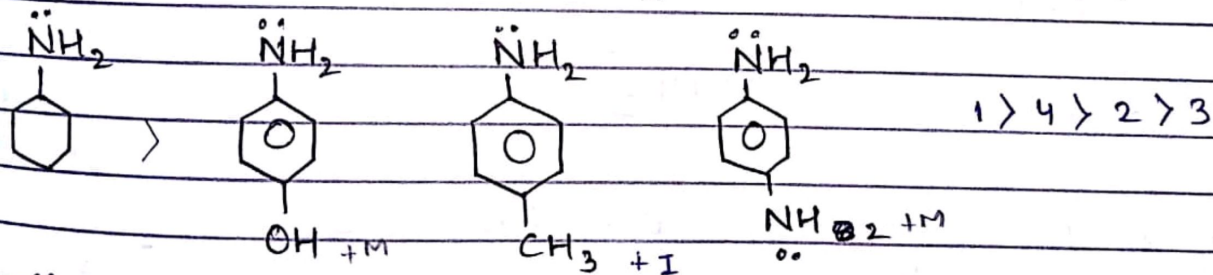
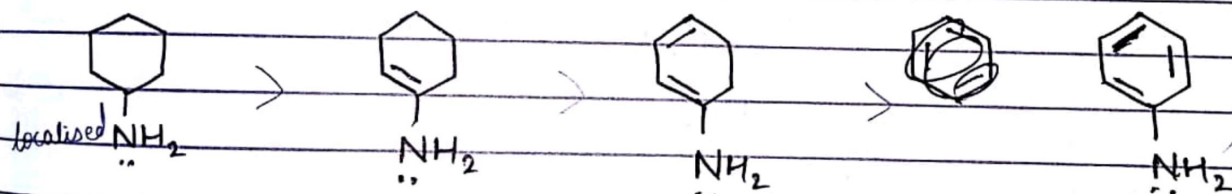
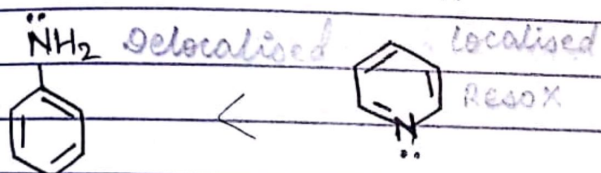
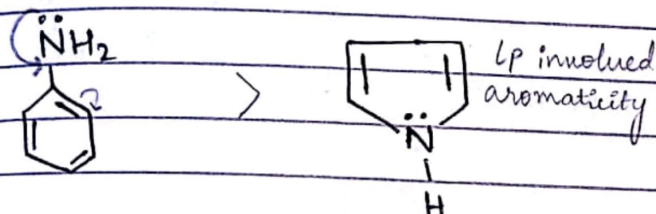
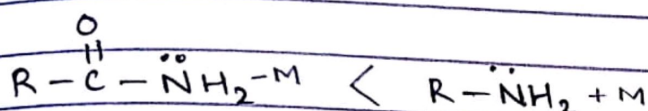
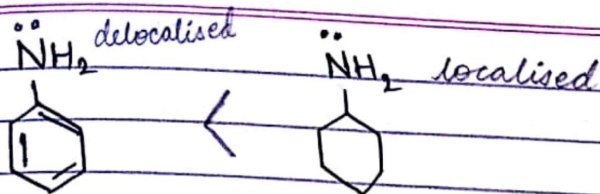
Base : which donate lp to H⁺

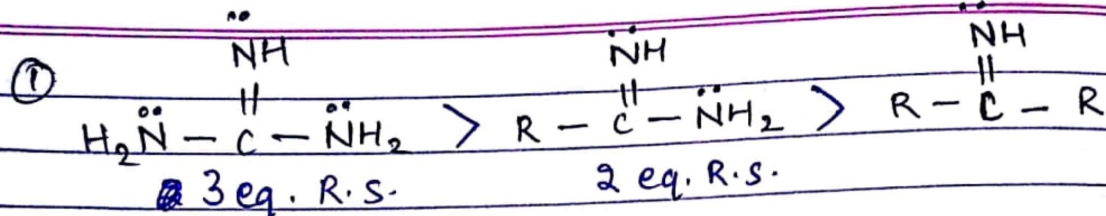
B.S. of amines < $\frac{1}{\text{Resonance}}$ < +I < -I

localised lp of amine > delocalised lp of amine > lp involved in aromaticity

$\ddot{N}sp^3 > \ddot{N}sp^2 > \ddot{N}sp$

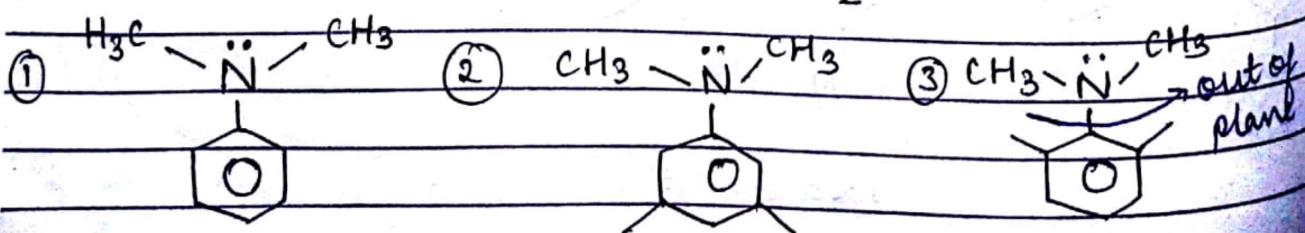
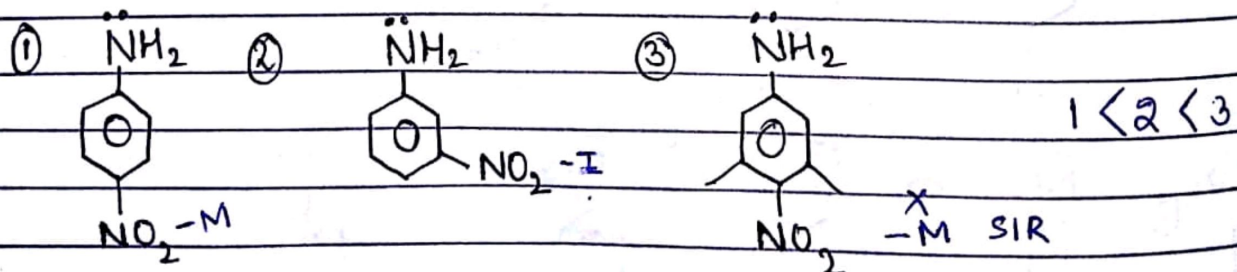
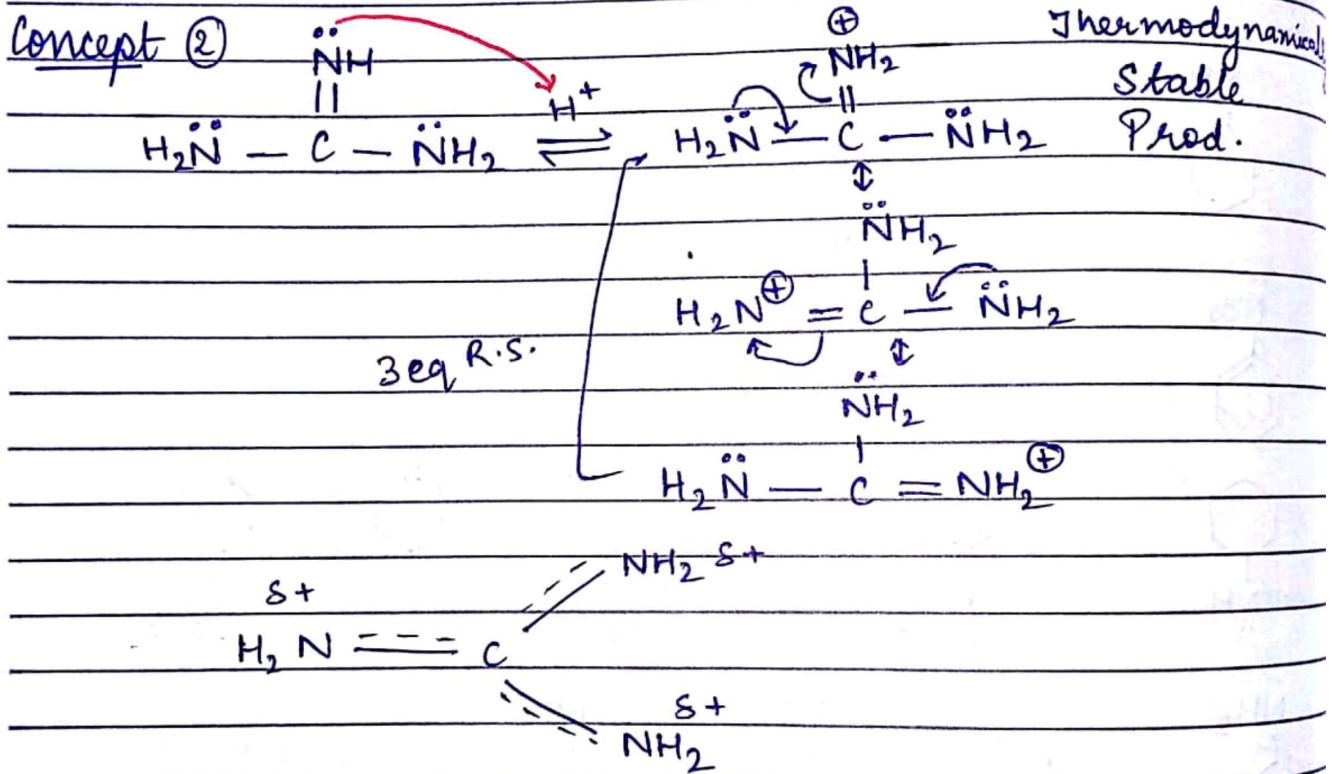
B.S. ↑ K_b ↑ pK_b ↓

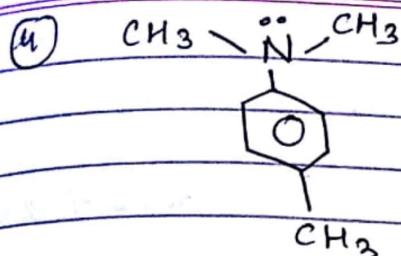




Guanidine

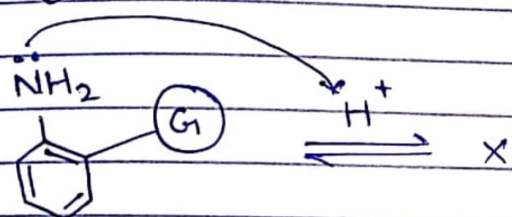
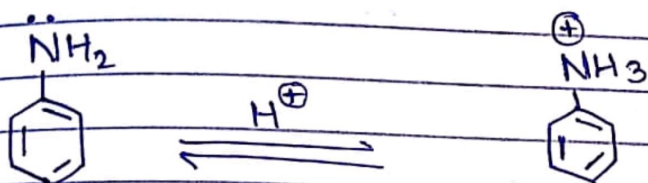
$\ddot{\text{N}}\text{H}_3 + \text{M}$ e⁻ density
B.S. ↑



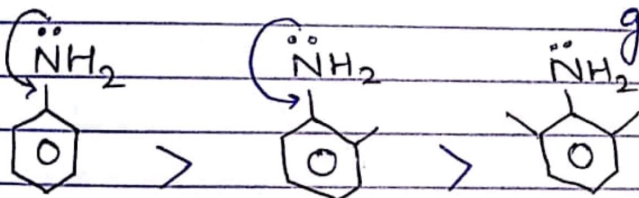


1 < 4 < 2 < 3

Steric inhibition in Protonation :- (SIP Effect)



Effective collision b/w lp & H^+ is not possible due to steric hindrance of bulky gp at ortho posⁿ.



Aromaticity :- Huckle Rule

- ① Aromatic (A)
- ② Non-Aromatic (N.A.)
- ③ Anti-Aromatic (A.A.)

Aromatic

① Compd. must be cyclic

② Compd must be planar

Non-Aromatic

If any of the 4 given condⁿ is not followed then comp. is N.A.

Anti-Aromatic

1. Compd. must be cyclic

2. Compd. must be planar.

Aromatic

③ Compd must have
reso. over entire
cycle

④ Comp. must follow
Huckle rule

$$4n + 2 = \pi e^- \text{ in conj.}$$

$$n = 0, 1, 2, 3, \dots$$

Anti-Aromatic

③ Compd. must have
reso. over entire
cycle.

④ Compd must follow
Huckle rule

$$4n = \pi e^- \text{ in conj.}$$

$$n = 1, 2, 3, 4, \dots$$

Stability $A > N.A. > A.A.$



Cyclic ✓
Planar X
N.A.



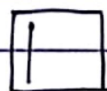
Cyclic ✓
Planar X
N.A.



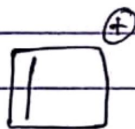
Cyclic ✓
Planar ✓
reso ✓
 $4n + 2 = 2$
 $n = 0$ (A)



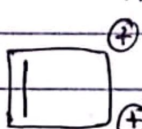
Cyclic ✓
Planar ✓
reso ✓
 $4n = 4$
 $n = 1$
AA



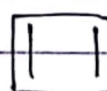
Planar X
NA



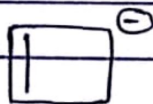
Planar X
NA



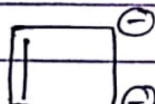
$4n + 2 = 2$
 $n = 0$ (A)



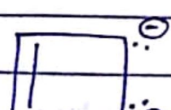
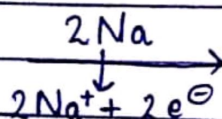
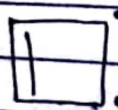
Cyclic ✓
Planar ✓
reso ✓
 $4n = 4$
 $n = 1$
(AA)



Planar X
N.A.



$4n + 2 = 6$
 $n = 1$
A

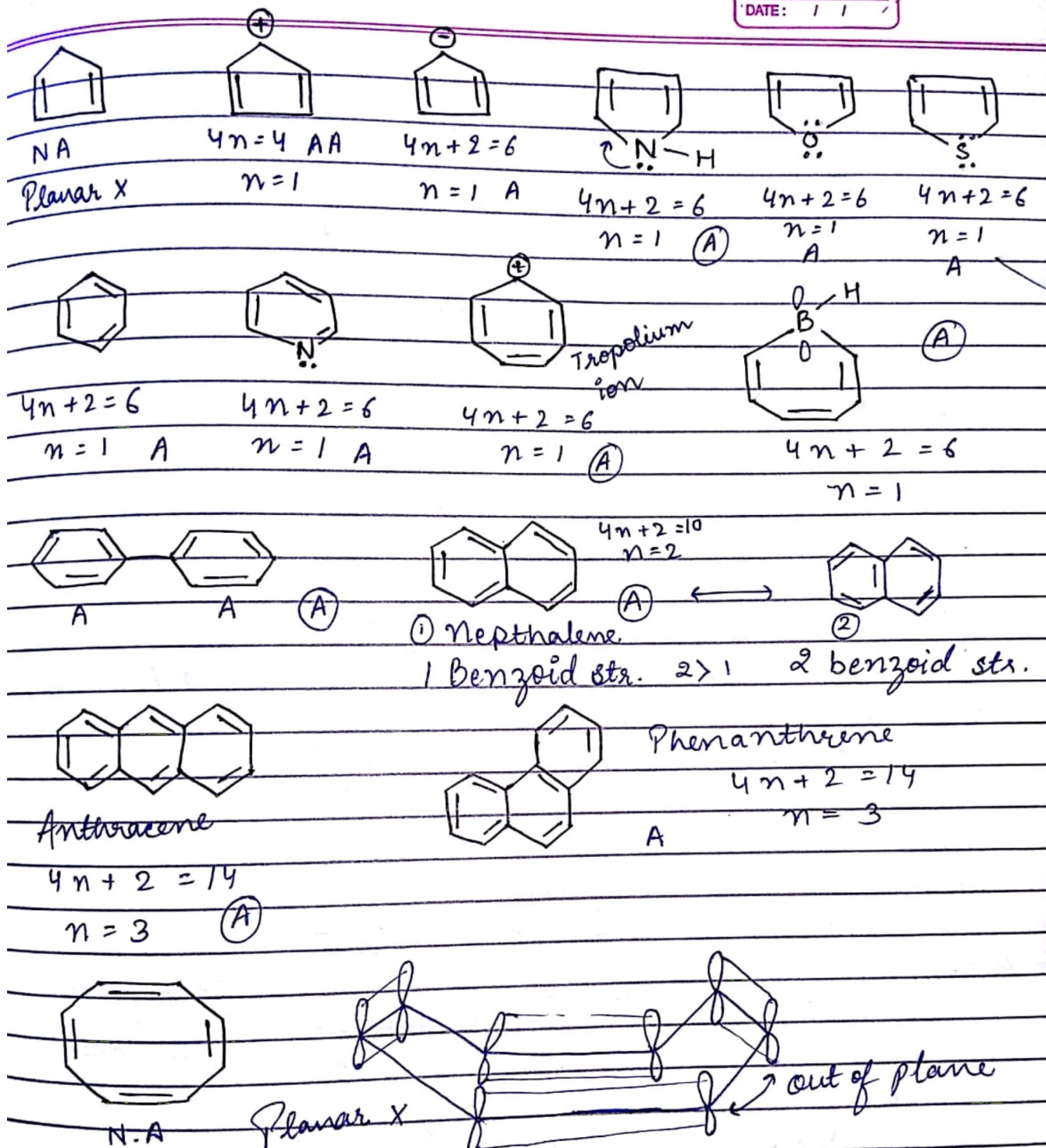


A

or

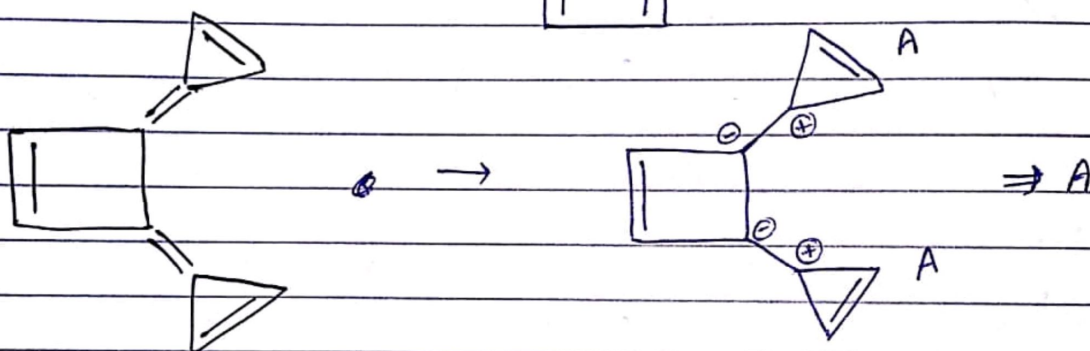
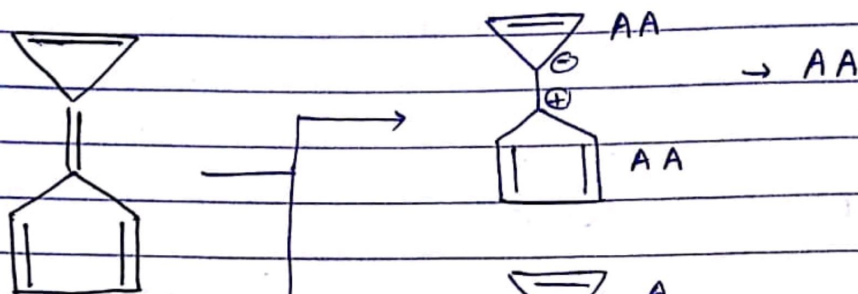
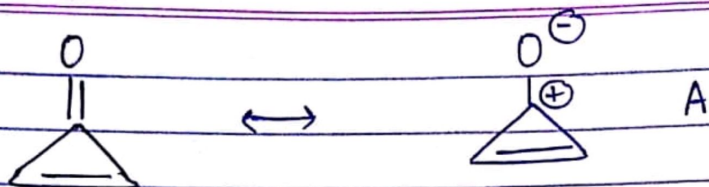


A

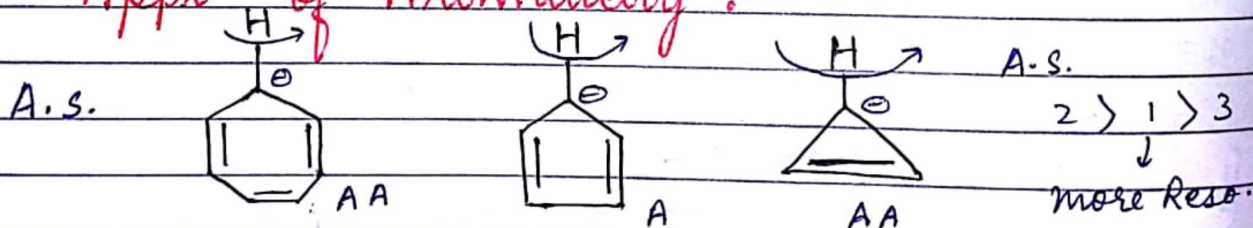


More than 7C containing cyclic compd. are non planar

NA



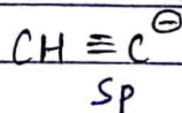
Applⁿ of Aromaticity :-



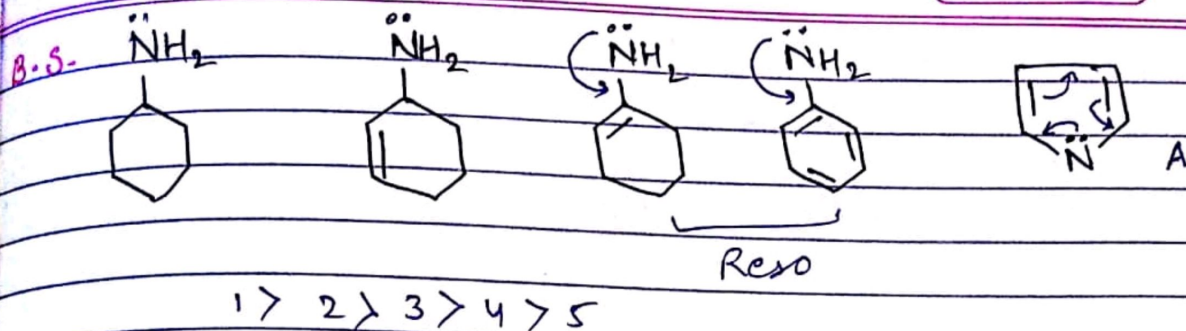
Stability of Anion

Priority Order

Aro. > E.N. > Reso. > Hyper. > Ind.



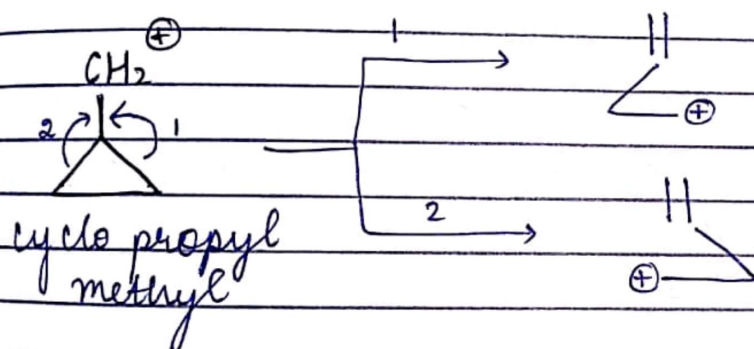
1 > 2 > 3



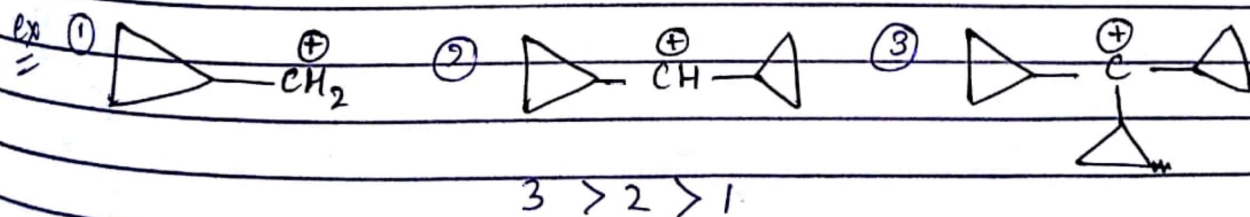
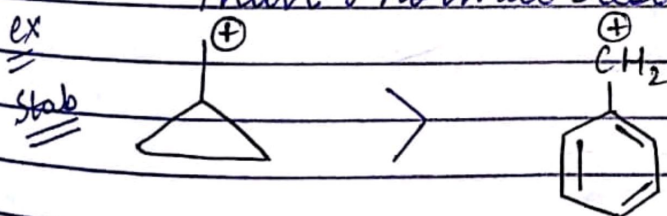
Dancing Resonance



σ bond of cyclo propane behave as π bond due to high angular strain.



Note: Dancing Resonance is always more effective than normal reso.



Resonance Effect on Bond Length & Bond Strength

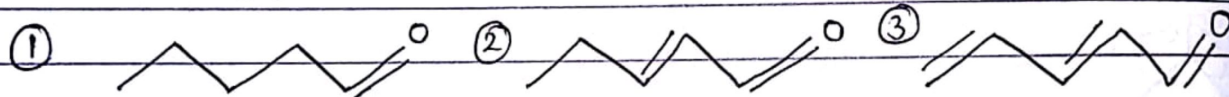
— to =
db CH^{r} $\uparrow$ due to Reso. B.L. $\downarrow$ B.S. $\uparrow$

= to —
db CH^{r} $\downarrow$ due to Reso B.L. $\uparrow$ B.S. $\downarrow$

① CH_3-CH_3 ② $\text{CH}_2=\text{CH}_2$ ③ $\text{CH}\equiv\text{CH}$ ④ 
Pure db Pure tb

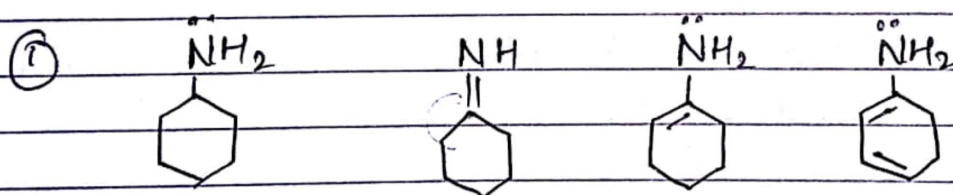
B.L. $1 > 4 > 2 > 3$

B.S. $1 < 4 < 2 < 3$



C-O B.L. $1 < 2 < 3$

B.S. $1 > 2 > 3$

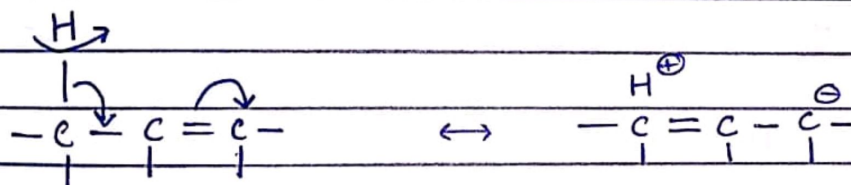
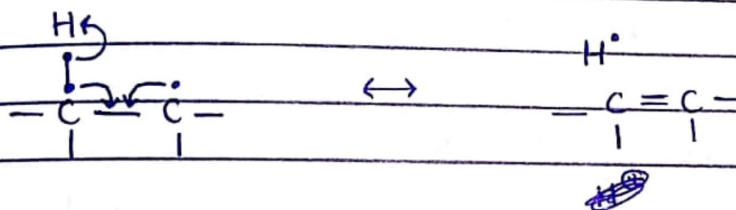
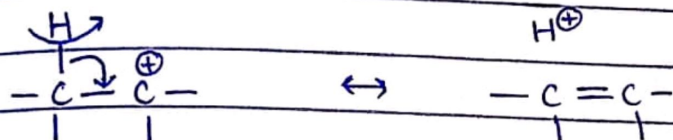
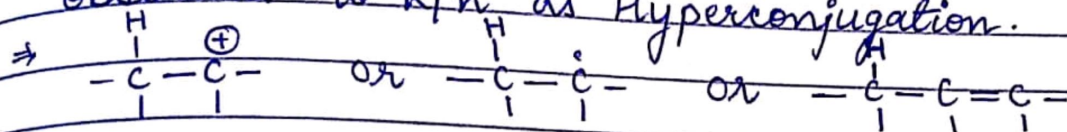


B.L. $1 > 4 > 3 > 2$

B.S. $1 < 4 < 3 < 2$

Hyperconjugation :-

When atleast one C-H σ bond is +nt at alternate posⁿ of $\oplus$ charge / carbon free radical / π bond then delocalisation of σ bond takes place & the effect observed is k/n as Hyperconjugation.

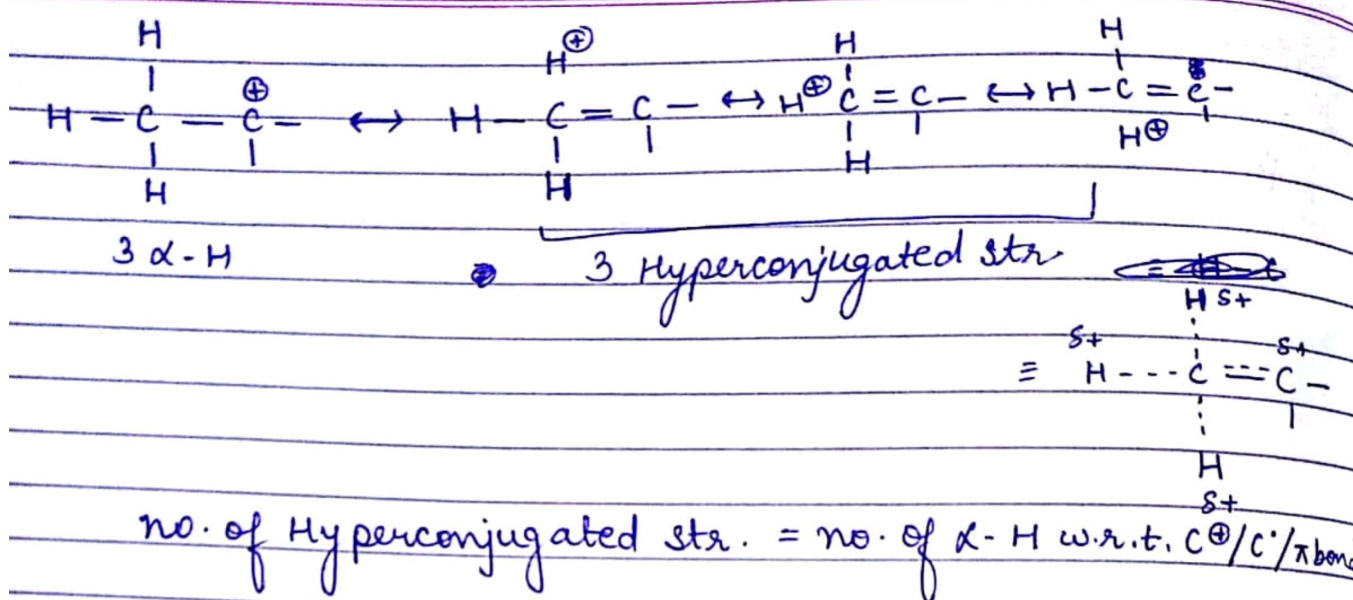


In Hyperconjugation $\text{H}^+/\text{H}^{\cdot}$ exist without any bond so it is also k/n as no-bond resonance.

- σ - π conjugation
- Nathan Baker effect

Note : Hyperconjugation only takes place when atleast one α -H is +nt in conjugation with $\text{C}^+/\text{C}^{\cdot}/\pi$ bond but not in case of anion. alkene alkynes

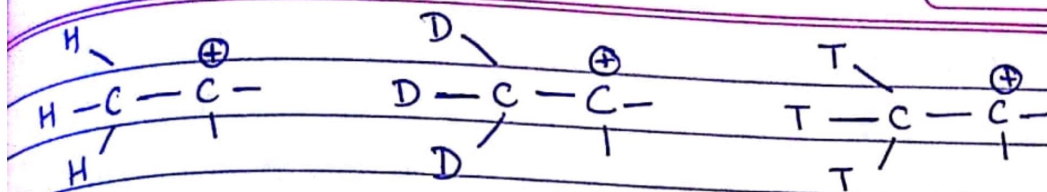
** like resonance as no. of Hyperconjugated str. $\uparrow$ stab. of molecule $\uparrow$



Stab. of molecule $\propto$ no. of Hyper. str. $\propto$ no. of $\alpha\text{-H}$

Ques which of the following do not show Hyperconjugation

- ① $\text{CH}_3 - \text{CH}_2 - \text{CH}_2^{\oplus}$ ✓ ⑧ $\text{CH}_2 = \text{CH} - \text{CH}_3$ ✓ $3 \alpha\text{-H}$
- ② $\text{CH}_2 = \text{CH} - \text{CH}^{\oplus} - \text{CH}_3$ X ⑨ $\text{CH}_2 = \text{CH} - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \text{CH}_3$ X
- ③ $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2^{\oplus}$ ✓
- ④ $\text{CH}_3 - \text{CH}_2 - \text{CH}_2^{\ominus}$ X
- ⑤ $\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \text{CH}^{\oplus} - \text{CH}_3$ ✓ $3 \alpha\text{-H}$
- ⑥ $\text{CH}_3 - \dot{\text{C}}\text{H}_2$ ✓
- ⑦ $\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \dot{\text{C}}\text{H}_2$ X



C-H bond
→ weak bond
→ break easily
→ more Hyperconjugation

C-T
→ strong bond
→ doesn't break easily
→ less Hyperconjugation

+H Effect $-\text{CH}_3 > -\text{CD}_3 > -\text{CT}_3$

+T Effect $-\text{CH}_3 < -\text{CD}_3 < -\text{CT}_3$

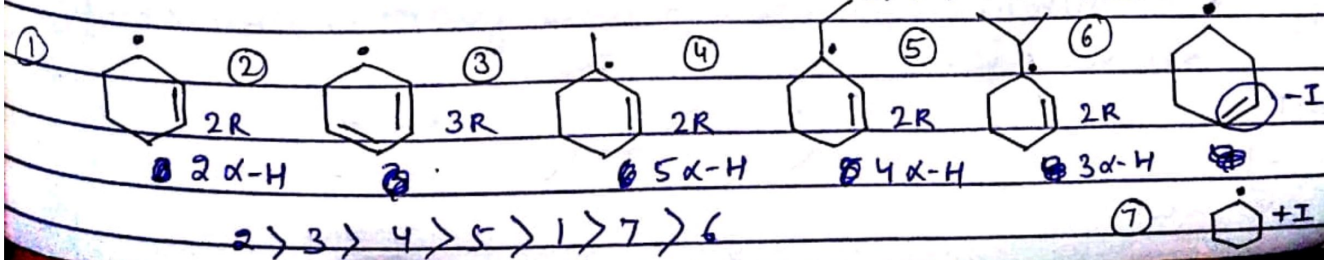
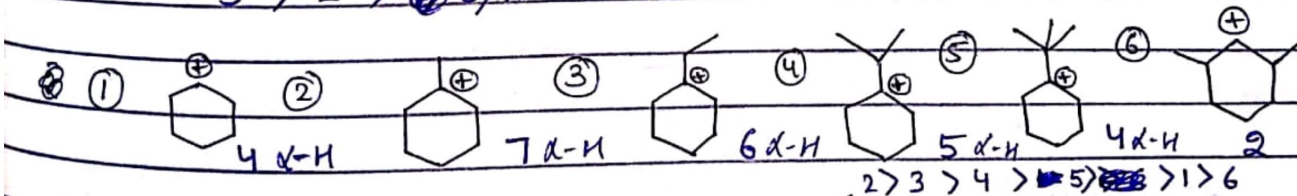
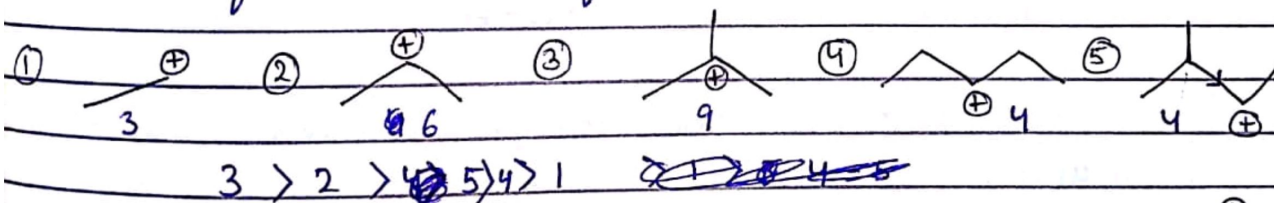
Order of effectiveness:

Aromaticity > E.N. > Reso. > Hyper. > Inductive

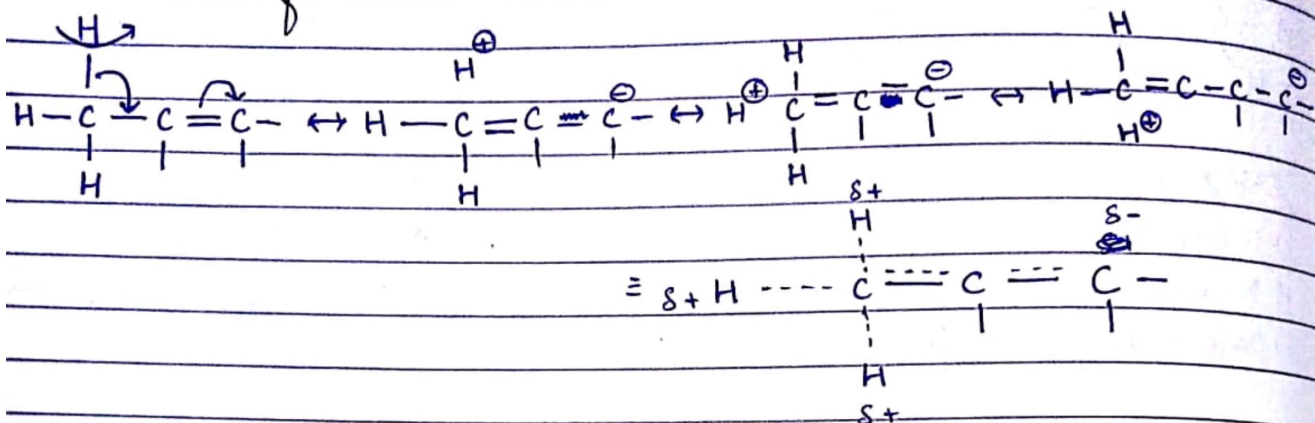
Applⁿ of Hyperconjugation :-

① Stab. of C^+ / $\text{C}^\bullet$:-

stab. of C^+ / $\text{C}^\bullet \propto$ no. of α -H

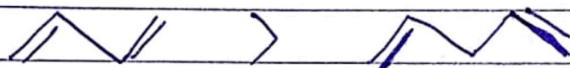


2. Stab. of Alkene :-

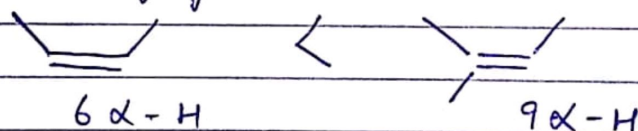


Stab. of Alkene :-

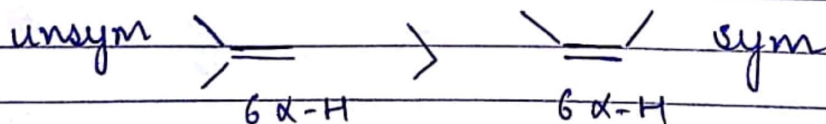
① Conj. Alkene > non-conj. alkene



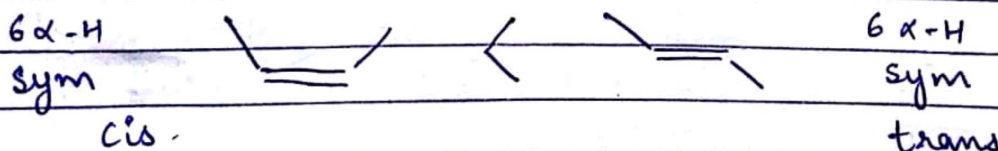
② In non-conjugated alkene, stab. of alkene $\propto$ no. of α -H

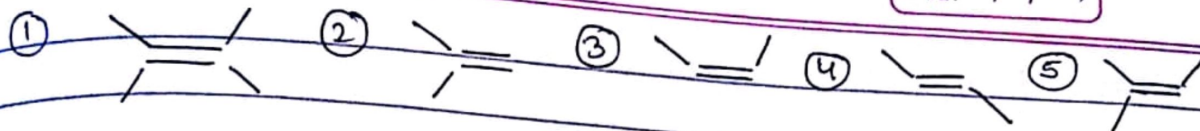


③ If no. of α -H same, then unsymm. alkene is more stable.

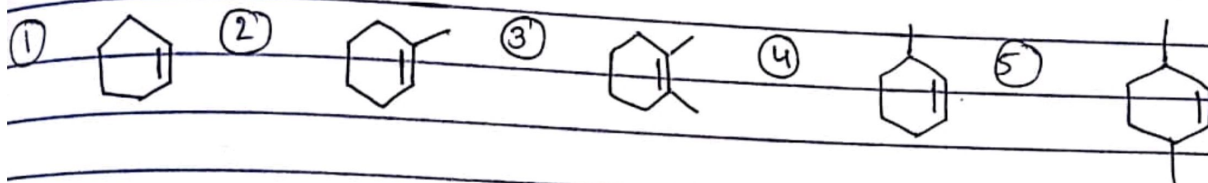


④ In symm. alkenes, trans form is more stable than cis.





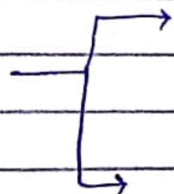
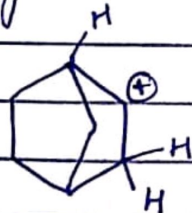
1 > 5 > 2 > 4 > 3 > 6 > 7



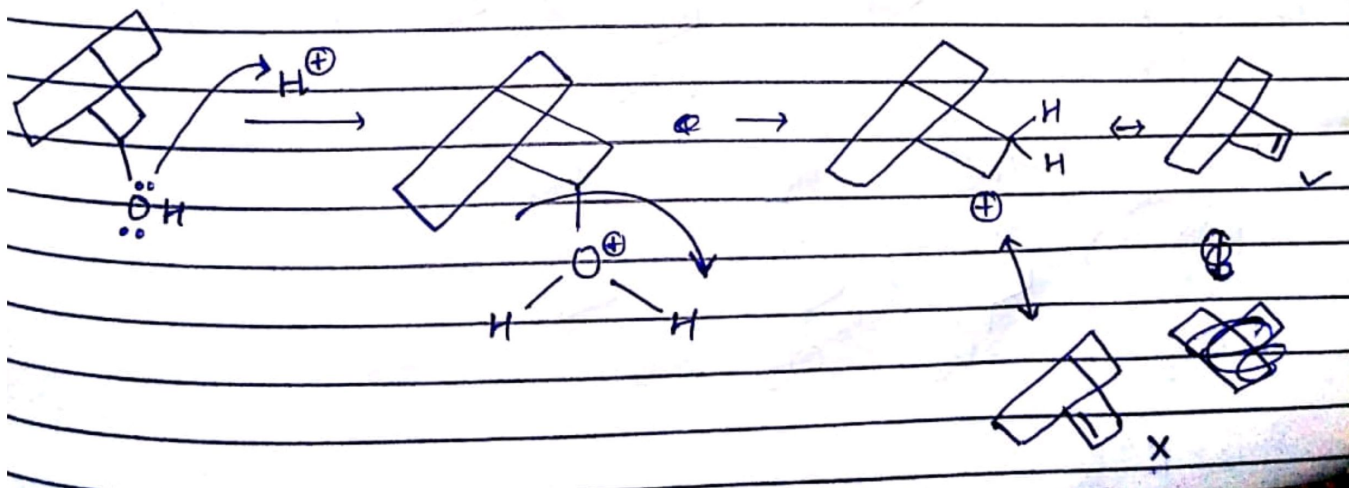
3 > 2 > 1 > 4 > 5

Bredt Rule :-

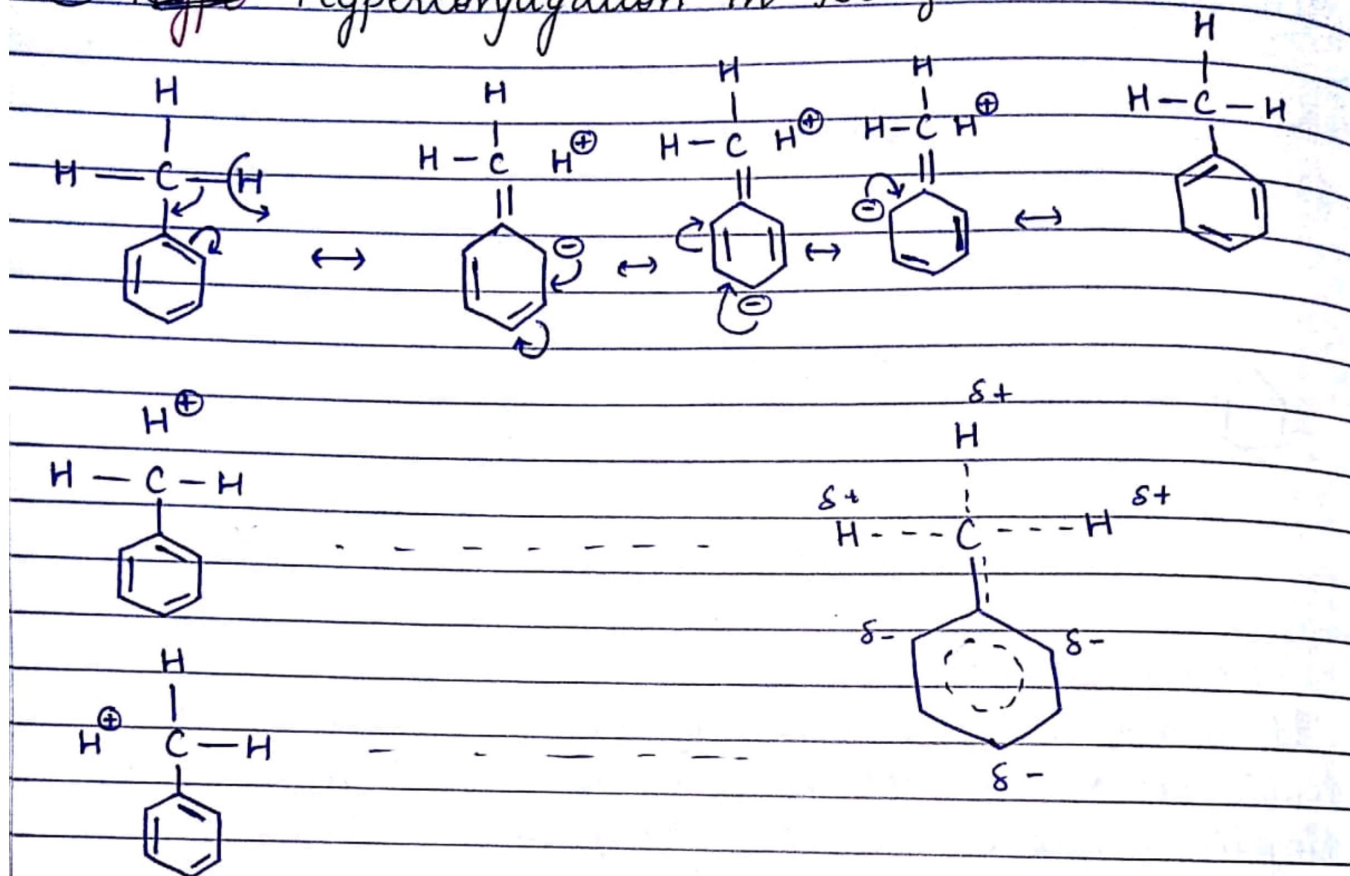
It states that in case of bicyclic compounds double bond cannot be formed at bridge head of bicyclic rings unless the ring is large enough.



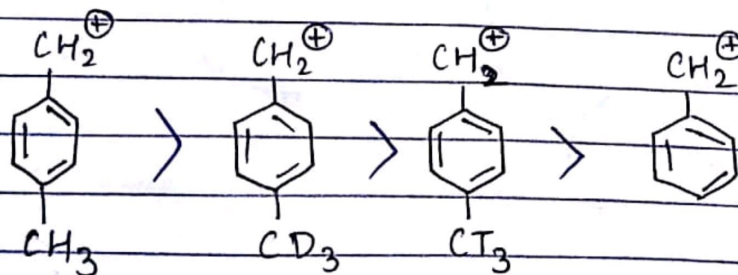
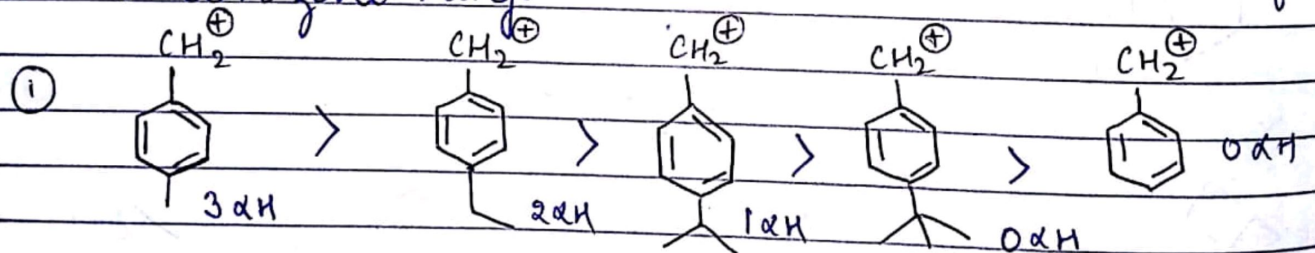
Bredt Rule Violated

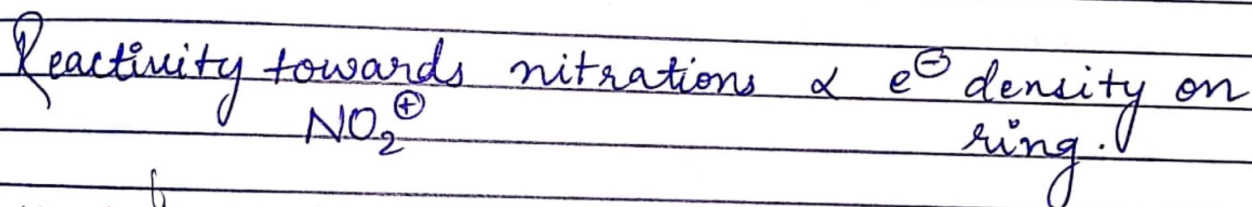
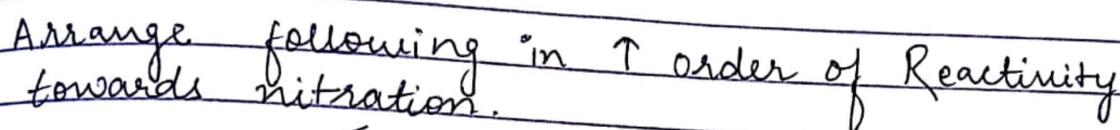


③ ~~Hyper~~ Hyperconjugation in Benzene :-

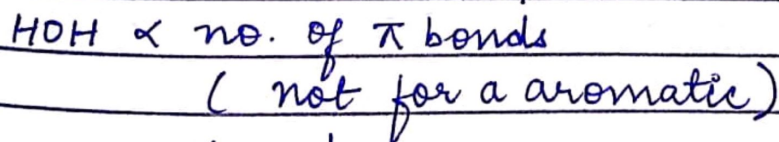


Hyperconjugation takes place at ortho & para posⁿ of benzene ring.

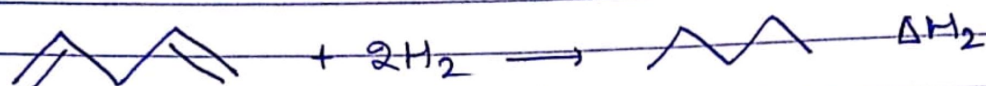
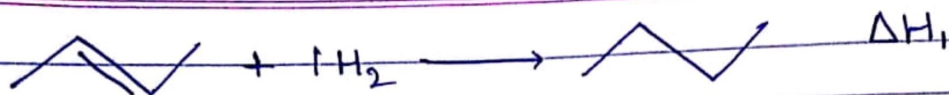




Amt. of heat liberated when hydrogenation of an unsaturated compound takes place.



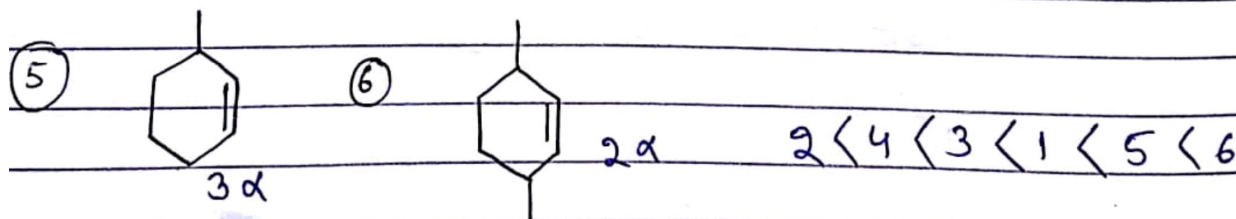
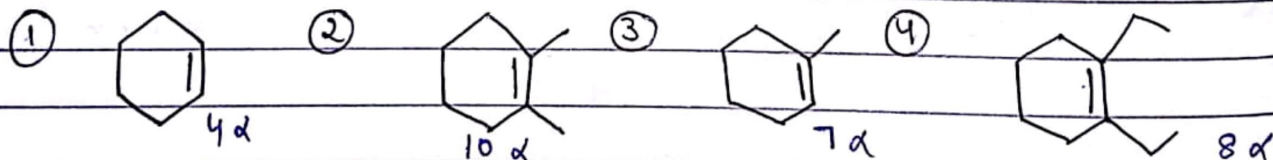
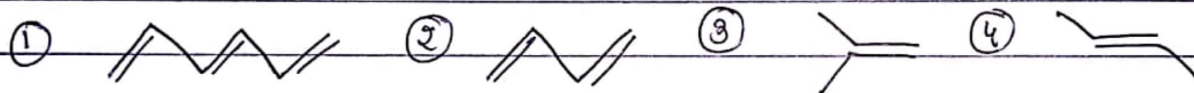
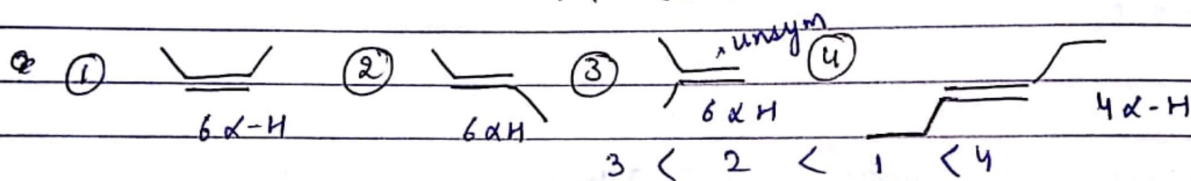
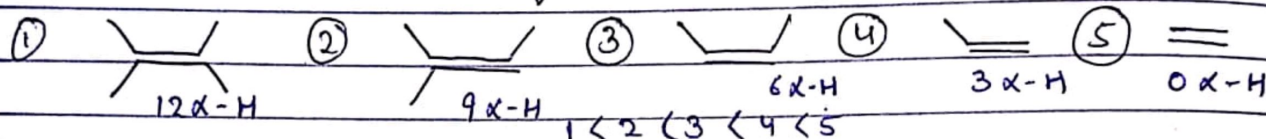
Stab. of alkene
(when no. of π bond same)



$$\Delta H_2 > \Delta H_1$$



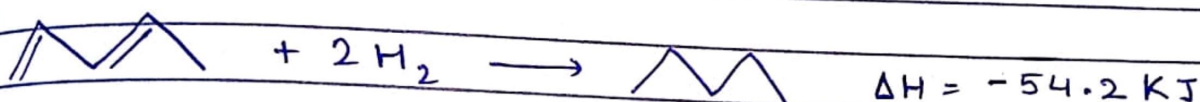
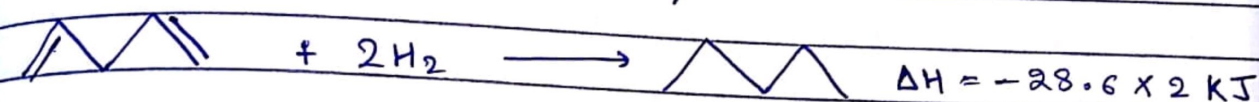
Ques Write following in ↑ order of H_{OH} :-



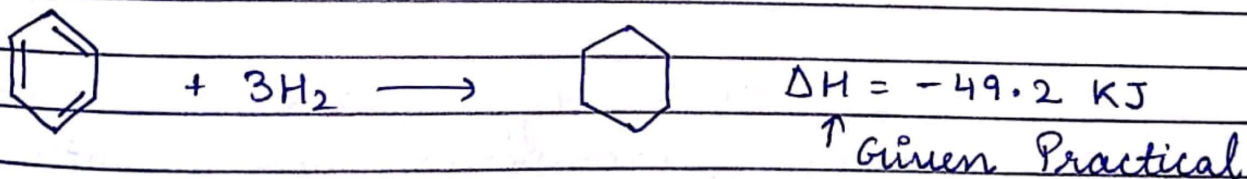
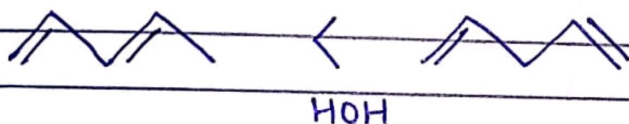
Resonance Energy R.E. Based on H.O.H. :-

$$\text{R.E.} = \text{Theoretical HOH} - \text{Practical HOH}$$

1 π bond $\rightarrow -28.6 \text{ KJ/mol}$



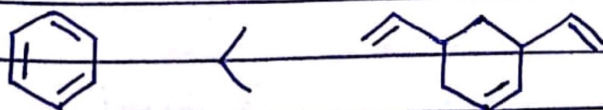
$$\text{R.E.} = 57.2 - 54.2$$
$$= 3 \text{ KJ}$$



$$1 \pi \text{ bond} \rightarrow -28.6 \text{ KJ}$$

$$3 \pi \text{ bond} \rightarrow -28.6 \times 3 = -85.8 \text{ KJ} \rightarrow \text{Theoretical}$$

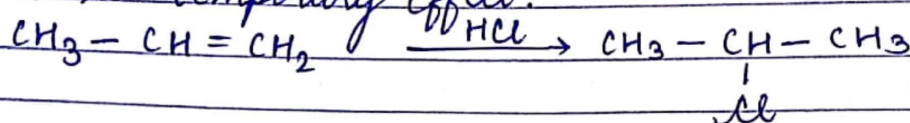
$$\text{R.E.} = 85.8 - 49.2 = 36.4 \text{ KJ}$$



Electromeric Effect :-

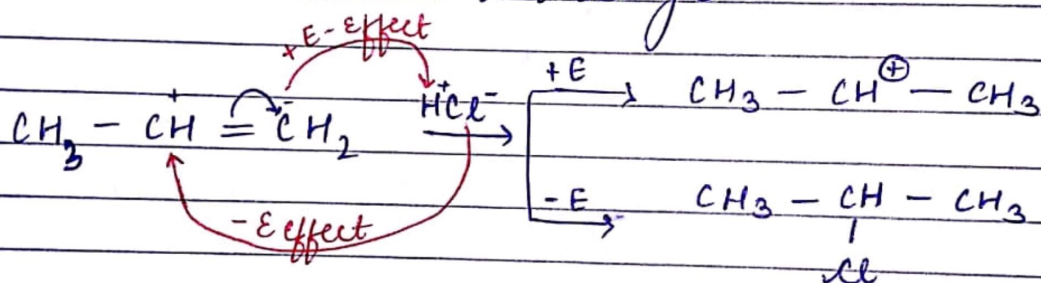
When complete delocalisation of πe^- takes place in +ve of attacking reagent the effect observed is called Electromeric Effect.

→ it is temporary effect.

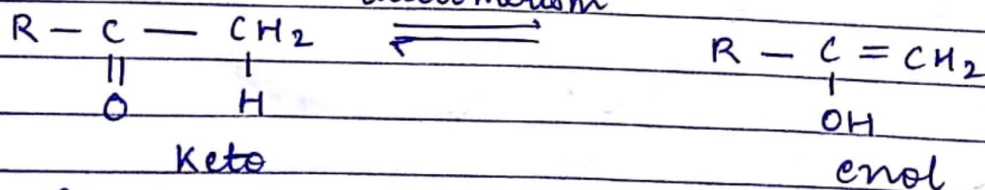


+E - Effect : When attacking reagent attack on atom which is gaining e^- .

-E Effect : When attacking reagent attack on atom which is losing e^- .



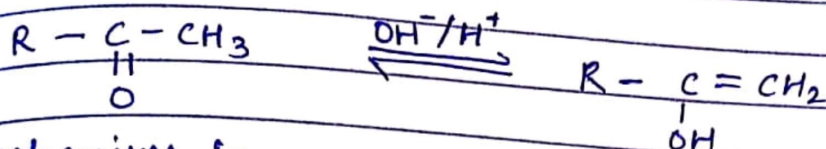
Tautomerism :- It is a type of structural isomerism when interconversion b/w 2 functional groups takes place due to oscillation of hydrogen ion (H^+) phenomenon observed is k/n as Tautomerism



• It also shows functional isomerism but priority is given to Tautomerism

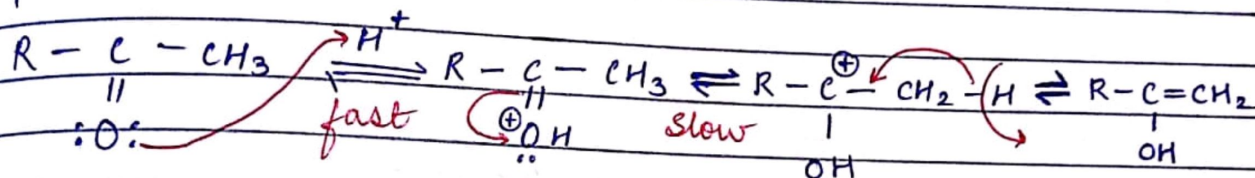
Priority Order : $\text{RCI} > \text{tauto} > \text{F} > \text{Meta.} > \text{C} > \text{P}$

• Tautomerism takes place in neutral/acidic/basic medium.

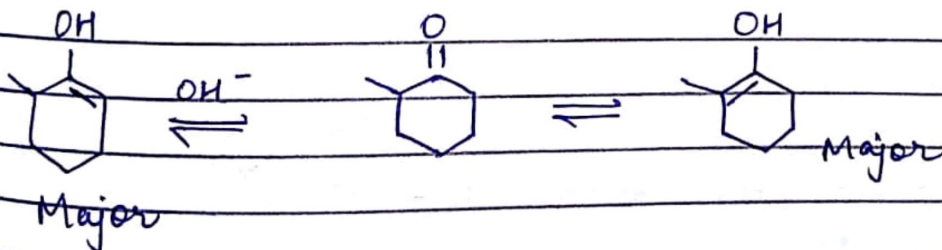
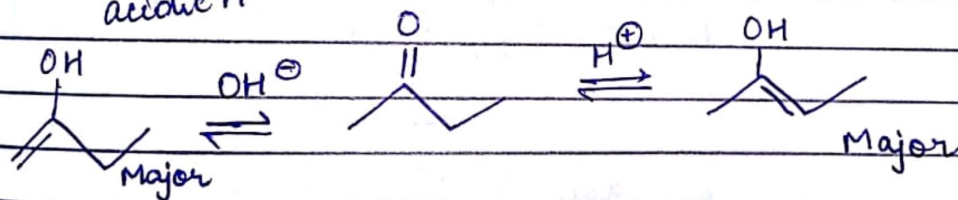
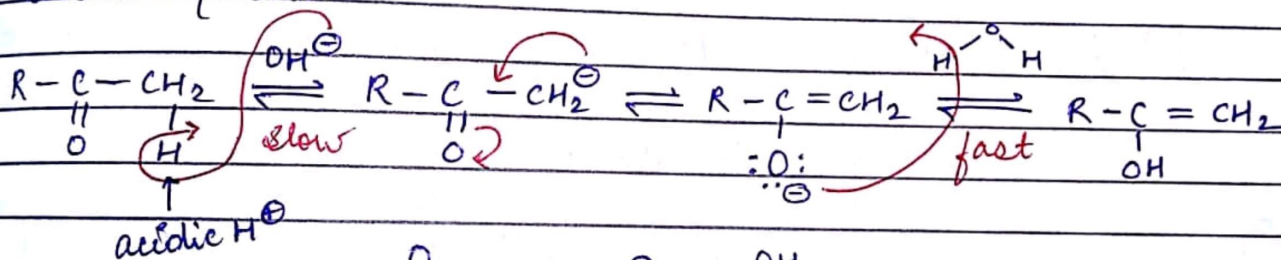


Mechanism :-

Acidic Medium :



Basic Medium

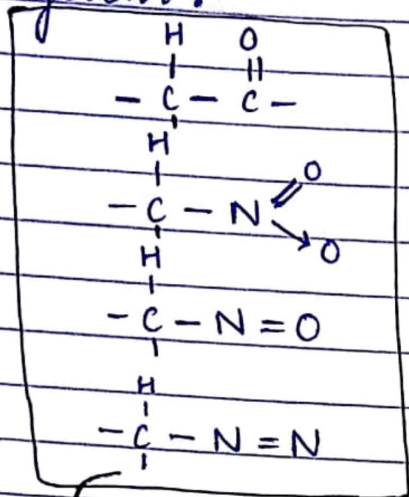


→ In tautomerism, dynamic eq^m takes place so it is also k/n as desmotropism.

desmo → bond

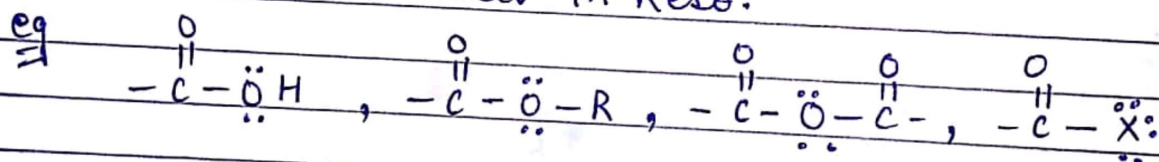
tropism → turning

System :-



$\alpha\text{-C} \rightarrow sp^3$ must have at least one $\alpha\text{-H}$

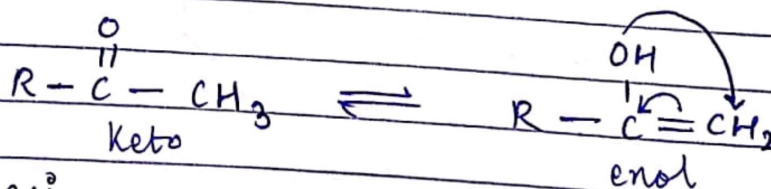
$-\text{C}(=\text{O})-\text{Z}$ do not show tautomerism becoz $-\text{C}(=\text{O})-\text{H}$ π -bond is involved in Reso.



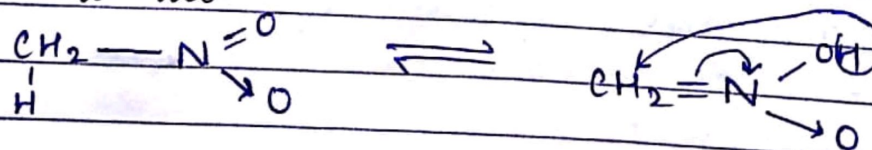
Tautomerism X

Exception : $-\text{C}(=\text{O})-\ddot{\text{N}}\text{H}_2$ के case में करेगा।

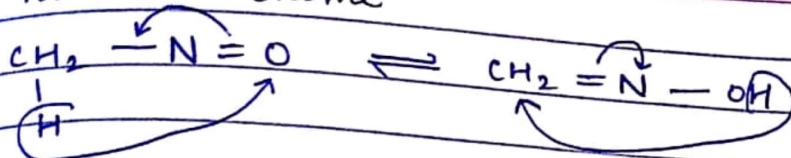
(1) Keto - enol



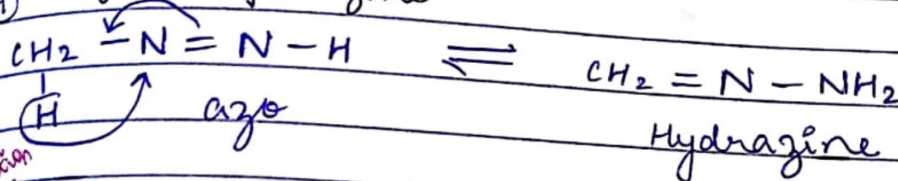
(2) Nitro - aci



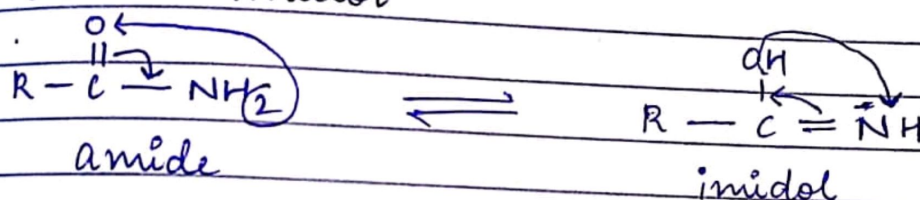
③ nitroso - oxime



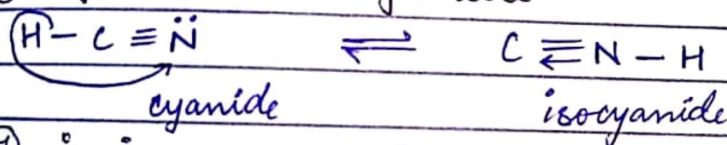
④ azo - hydrazine



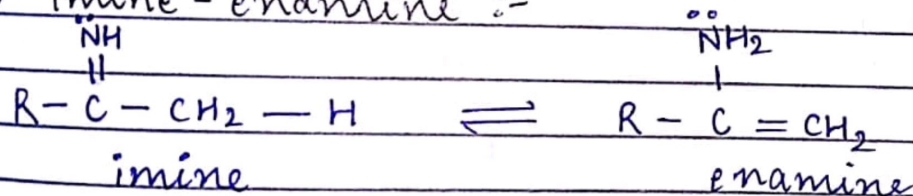
⑤ amide - imidol



⑥ cyanide - isocyanide

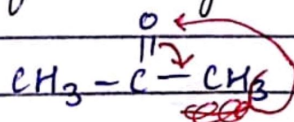


⑦ imine - enamine :-



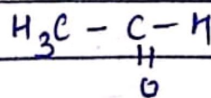
Ques which of the following will show tautomerism?

1. Acetone



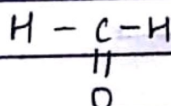
✓

2. Acetaldehyde



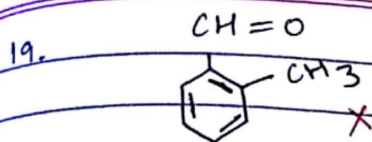
✓

3. Formaldehyde

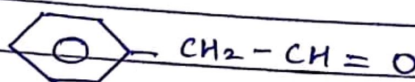
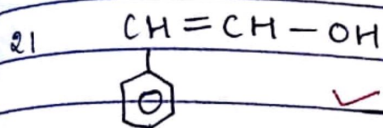
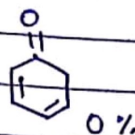
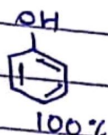


X

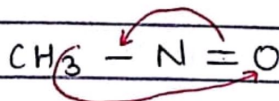
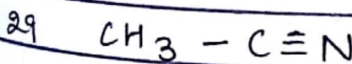
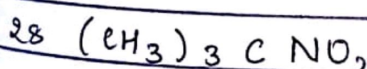
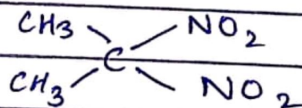
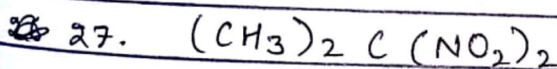
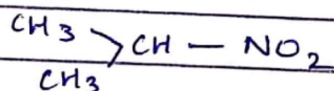
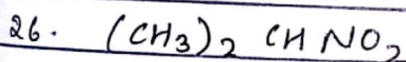
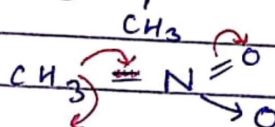
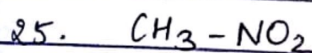
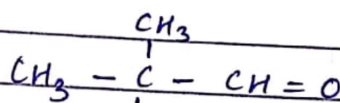
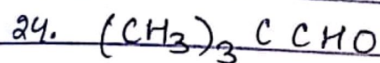
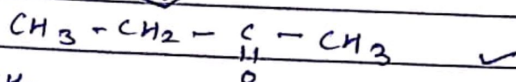
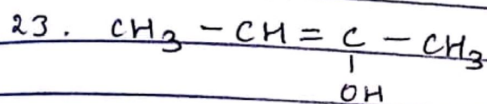
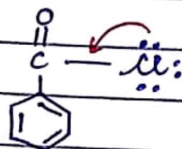
4. Formic Acid $\text{H}-\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{C}-\ddot{\text{O}}\text{H}$ X
5. Acetic Acid CH_3-COOH $\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\ddot{\text{O}}\text{H}$ X
6. methyl propanoate $\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\ddot{\text{O}}-\text{CH}_2\text{CH}_2\text{CH}_3$ X
7. acetic anhydride $\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\ddot{\text{O}}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_3$ X
8. ethanamide $\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\ddot{\text{N}}\text{H}_2$ ✓
9. Propanal $\text{C}-\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{H}$ ✓
10. acryl aldehyde / acrolein $\text{CH}_2=\text{CH}-\text{CHO}$ X
11. Crotonic acid $\text{C}-\text{C}=\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$ X
12. Crotonaldehyde $\text{CH}_3-\text{CH}=\text{CH}-\overset{\text{O}}{\parallel}\text{C}-\text{H}$ ✓
 $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{OH}$
13. 2-Pentanone $\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{C}-\text{C}-\text{C}$ ✓
14. Ethenol ✓ $\text{HO}-\overset{\text{O}}{\parallel}\text{C}=\text{CH}_2 \rightarrow \text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{H}$
15. Benzaldehyde $\text{CH}=\text{O}$ $\alpha-\text{H}$ X
16. Benzoic acid $\text{O}=\text{C}-\text{OH}$ X
17. acetophenone $\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_3$ ✓
18. $\text{Ph}-\overset{\text{O}}{\parallel}\text{C}-\text{Ph}$ X



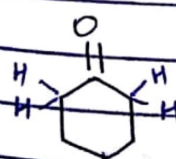
20. Phenol



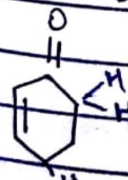
22. Benzene carbonyl chloride

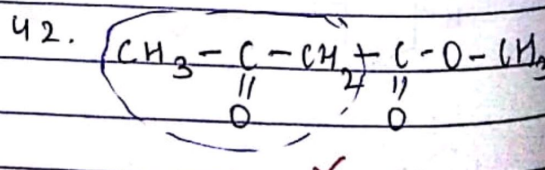
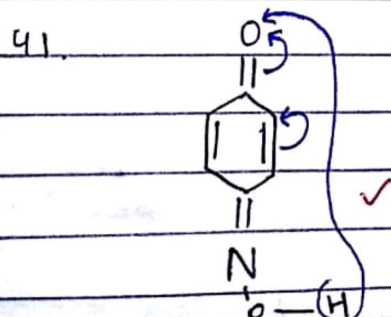
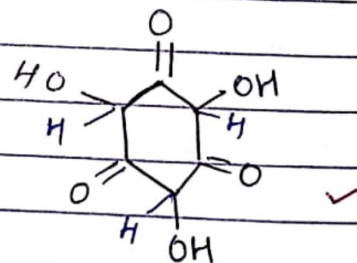
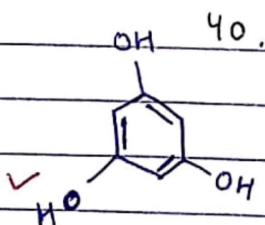
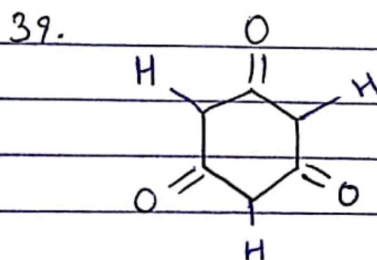
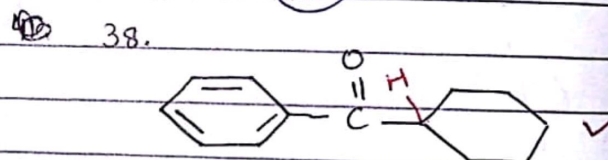
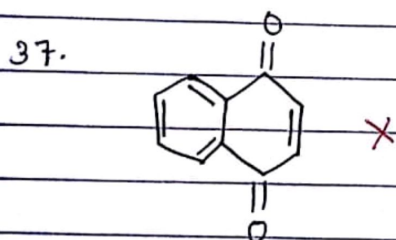
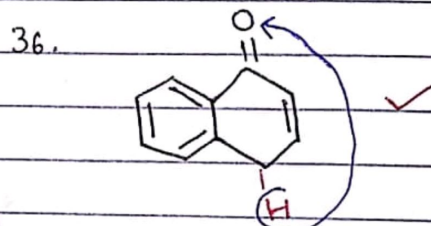
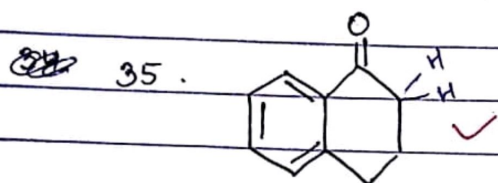
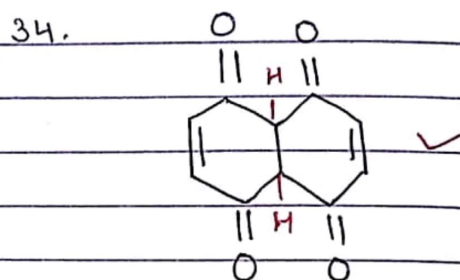
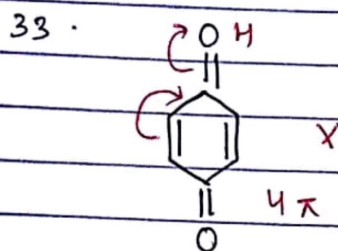
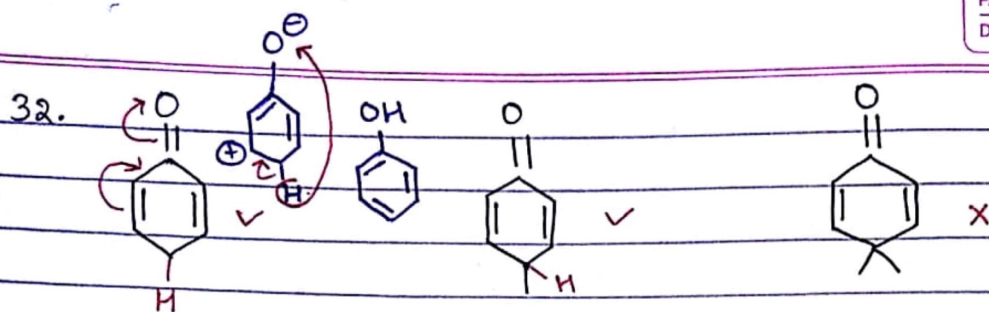


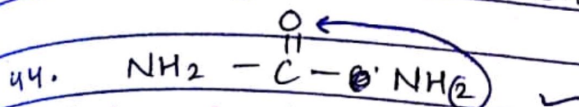
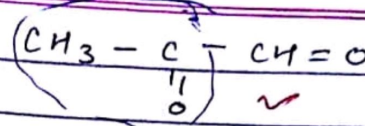
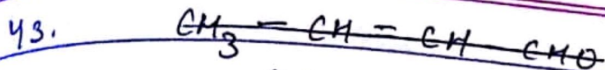
30.



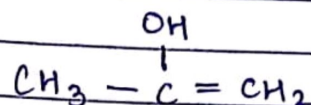
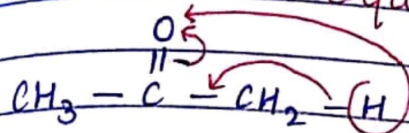
31.







Keto - Enol Equilibrium :-



Keto (99%)

enol (1%)

- Generally, Keto form is more stable becoz
- ① $\text{C}=\text{O}$ bond is thermodynamically more stable & reactⁿ are controlled by thermodynamics.
 - ② $\text{C}=\text{O}$ is polar bond & more stable.

→ Enol form may also be more stable if enol form have :-

1. Aromaticity
2. Resonance

3. H-Bonding

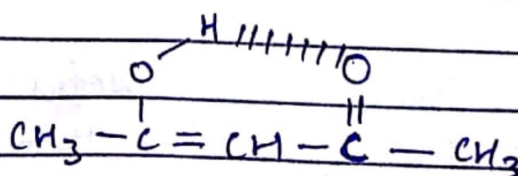
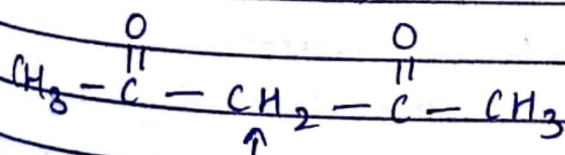
4. no. of $\text{C}=\text{O}$ bond $\rightarrow \text{A.S.} \uparrow$

5. no. of $\alpha\text{-H}$ $\uparrow$



enol (100%)

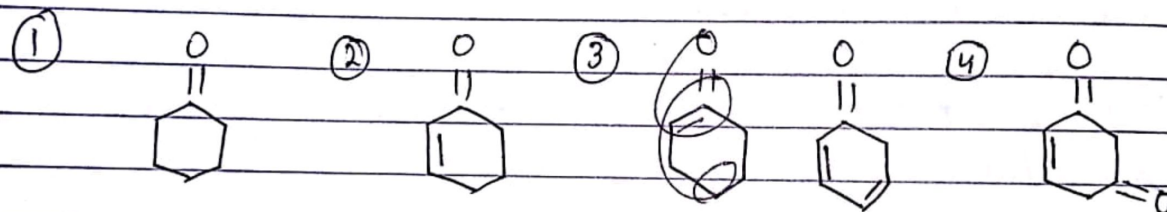
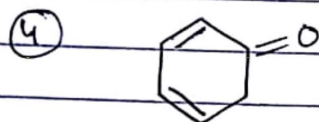
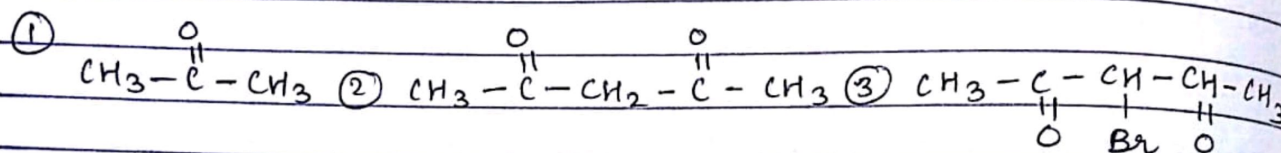
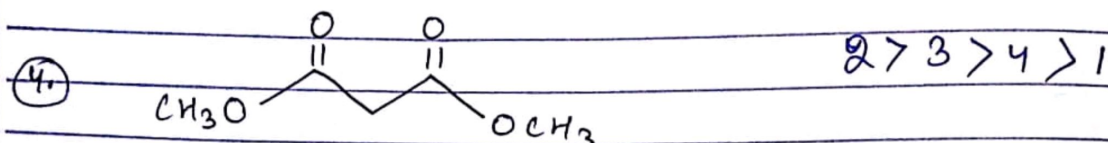
Keto (0%)



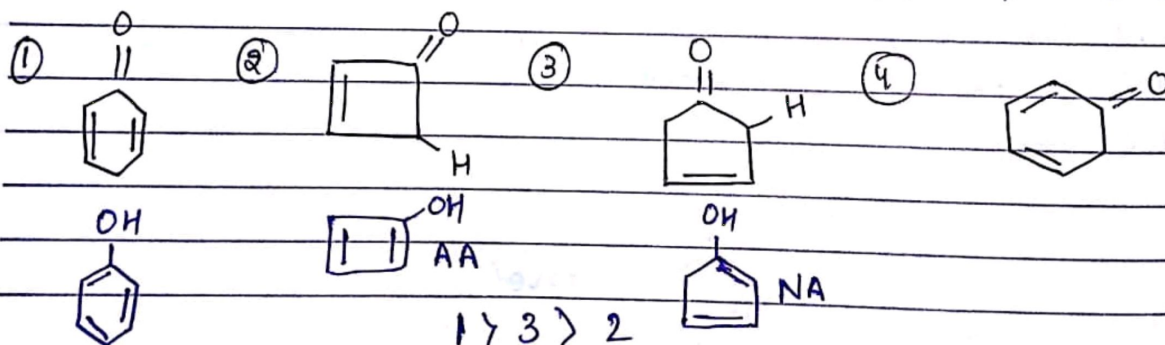
more acidic $\alpha\text{-H}$
Keto (24%)

enol (76%)

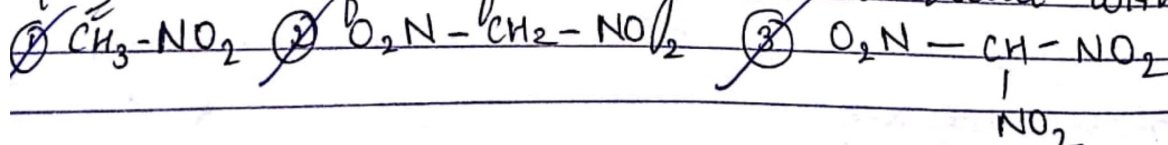
Ques which of the following have highest enol content?



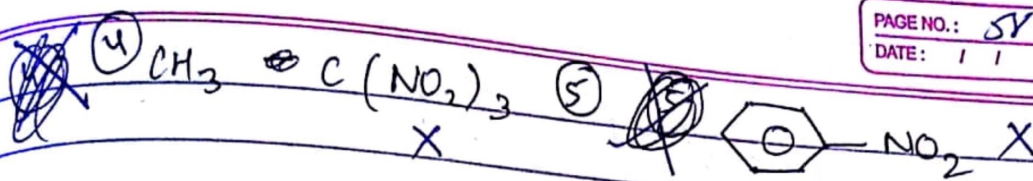
$4 > 3 > 2 > 1$



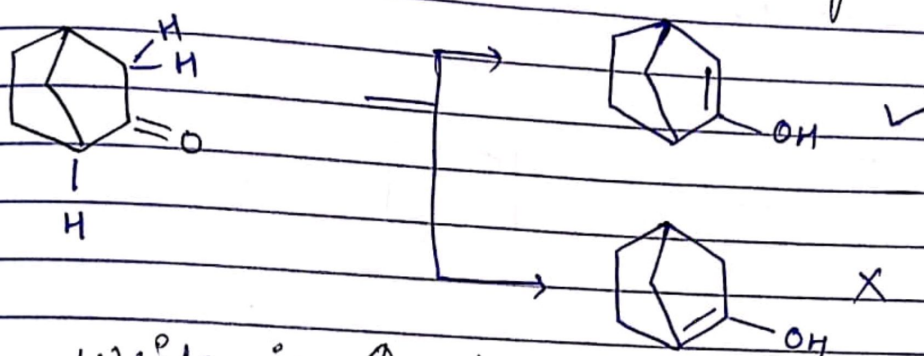
Ques which of the following will not react with NaOH ?



Base $\rightarrow$ acid

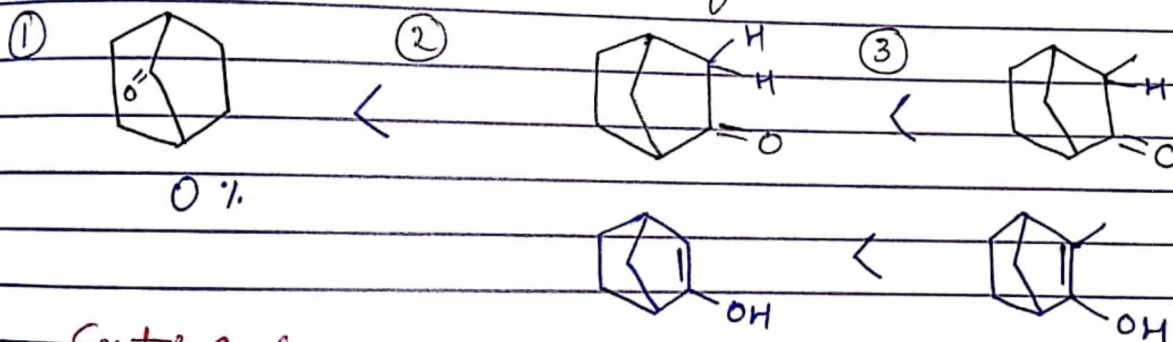


Ques Which product is obtained by reaction with NaOH

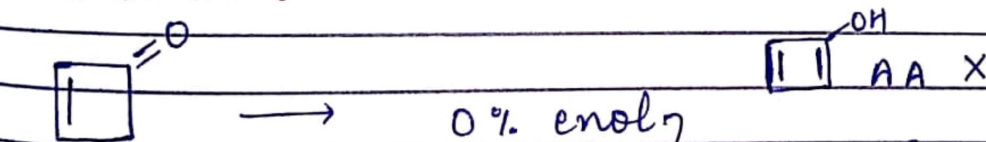


Bredt's Rule Violated

Ques Write in order of enol content

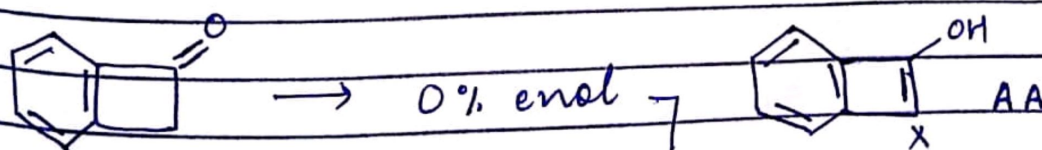


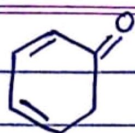
Extra :-



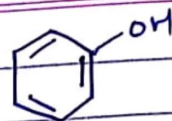
$$4n+2=2$$

$$n=0$$

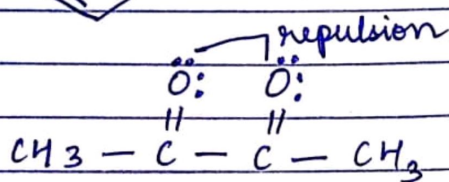




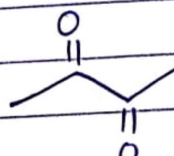
→ 100% enol



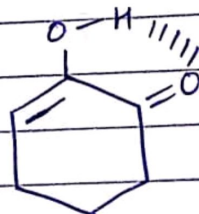
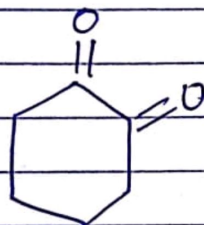
A



rotate



Ketone



100%

enol