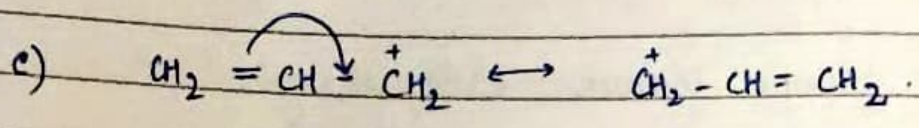
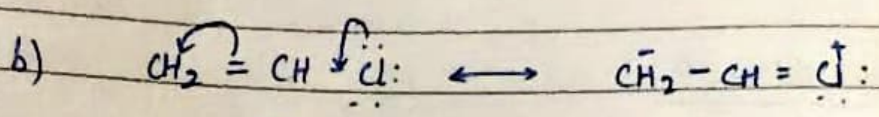
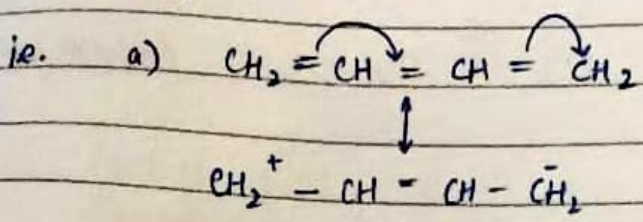


2. Mesomeric Effect:

→ b/w π & σ } Resonance .
 σ & π }
 σ & free radical

→ Conjugation :



→ +M Effect : Electrons moves away from the group.

- O⁻, -NH⁻, -NR₂, -NHR, -NH₂, -OH,
- OR, -SH, -SR, -F, -Cl, -NHCOR, -OCOR.

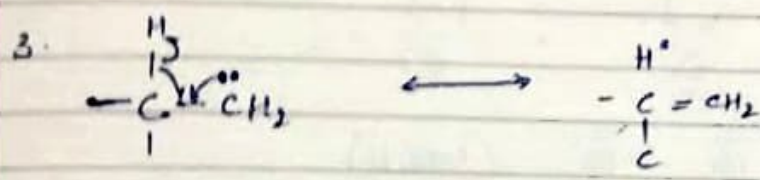
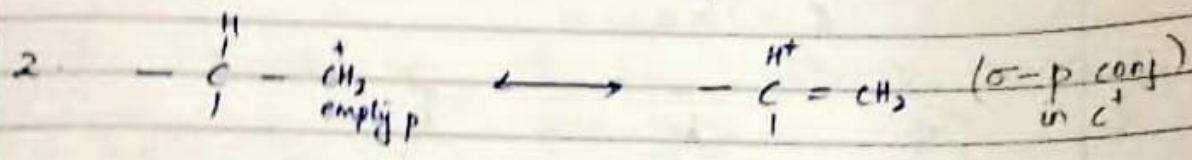
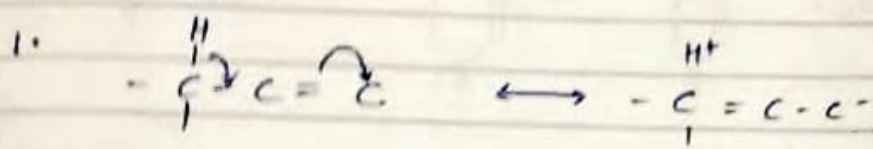
→ -M effect : Electrons moves towards the group.

- NO₂ > -CN > -CHO > -COR > -COOH > -COOR
- * Element next to the one connected to R is more electronegative.
- > -CONH₂

Note: • When -I (EWG), +M (ERG) both → for halogens → consider -I effect → more dominant.

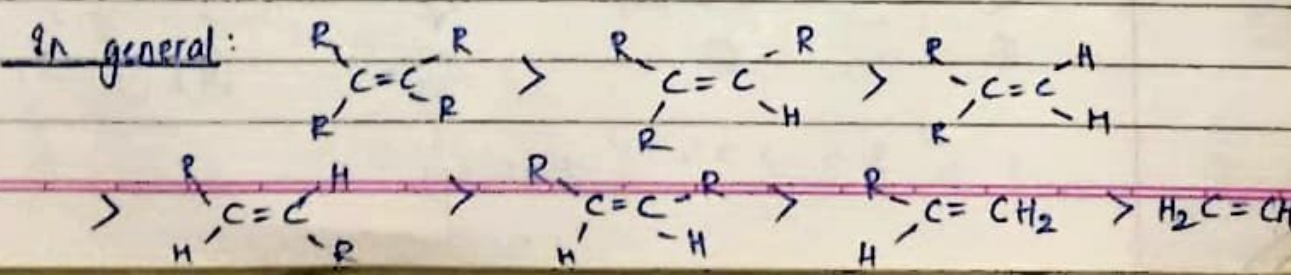
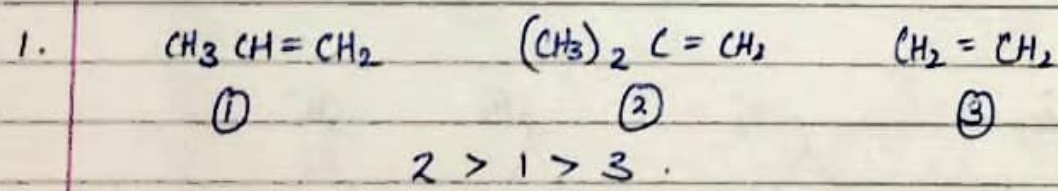
• For -OH, -NH₂, -OR → Both -I & +M, +M is considered. OCCH₃ - +M

3 Hyperconjugation: (No bond resonance) ($\sigma-\pi$ conj)



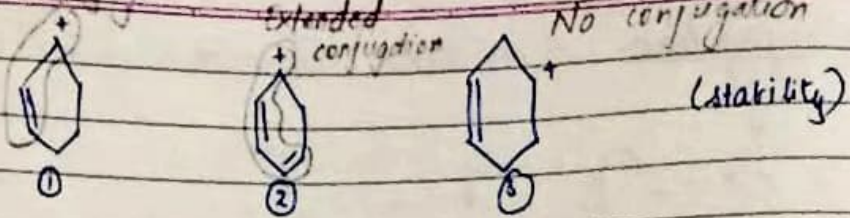
- * No H-effect in carbanions exist.
- Complete transfer of e^- takes place.
- Equally operating, the priority to be given is:
 Resonance > Hyperconjugation > Inductive.
- Mesomeric & Hyperconjugation - distance independent.
- On benzene ring, these effects will operate only in ortho and para position. only π effect in meta.
- The no. of Hyperconjugation ~~resonance~~ structures increases with no. of $\alpha\text{-H}$.
- More no. of $\alpha\text{-Hs}$ \rightarrow more stability.

Examples:



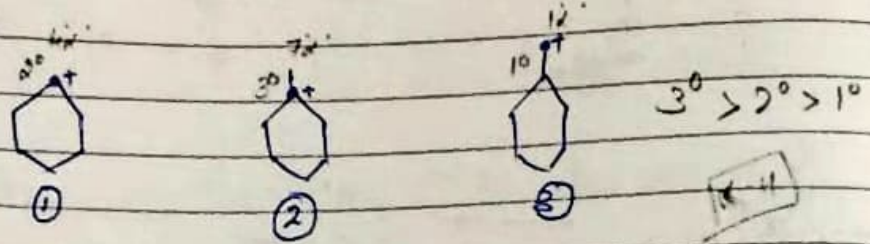
Conjugation

2.



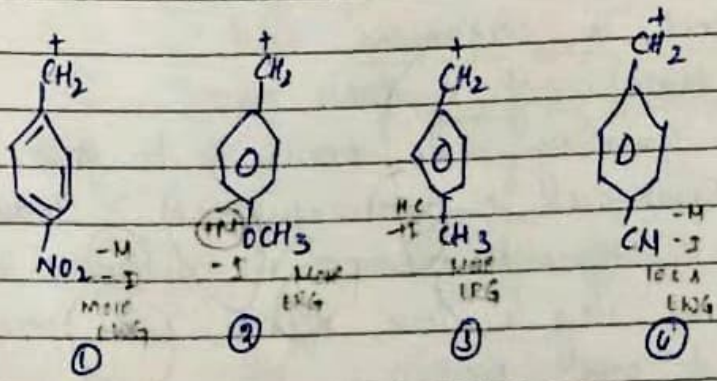
$2 > 1 > 3$

3.



$2 > 1 > 3$ (stability)

4.

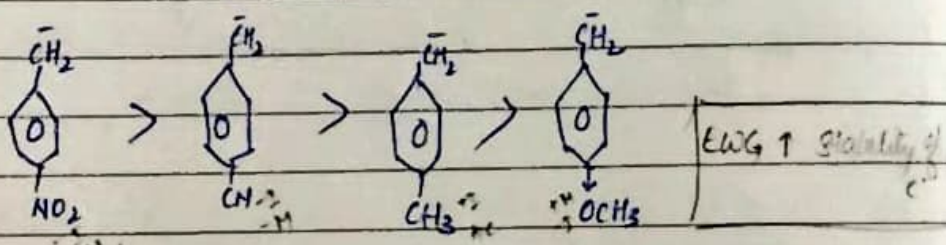


$NO_2 \rightarrow EWG (-D, -M)$
 $OCH_3 \rightarrow ERG (+M)$
 $CH_3 \rightarrow ERG (+I)$
 $CN \rightarrow -I, -M$

ERG ↑ Stability of C^+

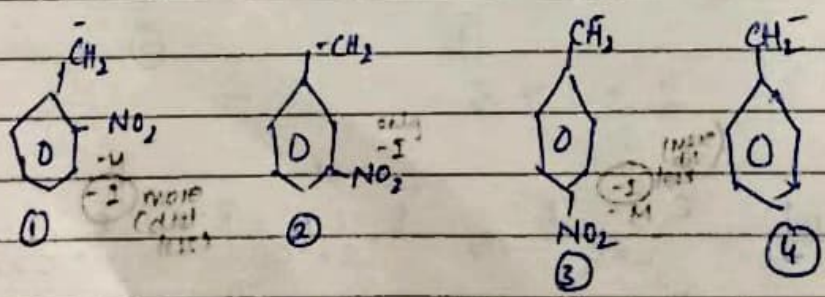
$2 > 3 > 4 > 1$

5.



EWG ↑ Stability of C^+

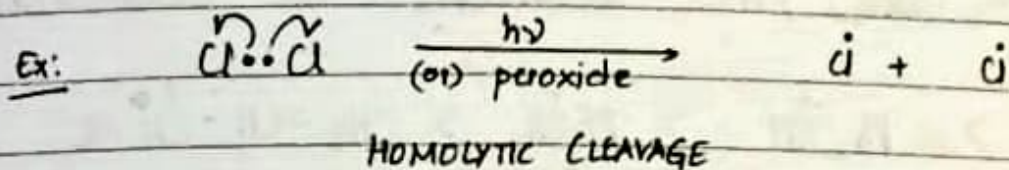
6.



$1 > 3 > 2 > 4$ (stability)

REACTION INTERMEDIATES:

Free radical:



Ex: $\dot{\text{C}}\text{H}_3$ (C: $7e^-$), e^- deficient.

- ↳ Generally, hybridisation - sp^2
- ↳ Generally, no re-arrangement.

• Conditions for generation of free radicals:

→ sunlight

→ peroxides

→ high temperatures (sometimes)

→ oxygen acts as inhibitor for the formation of free radicals

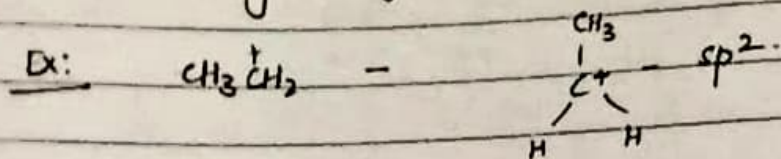
• +I, +M (ERG), H.C increases the stability of free radicals.

• Paramagnetic - unpaired e^-

2) Carbocation:

A carbon-Intermediate having 3 bond pairs and a positive charge on the carbon.

→ Generally hybridisation - sp^2 .

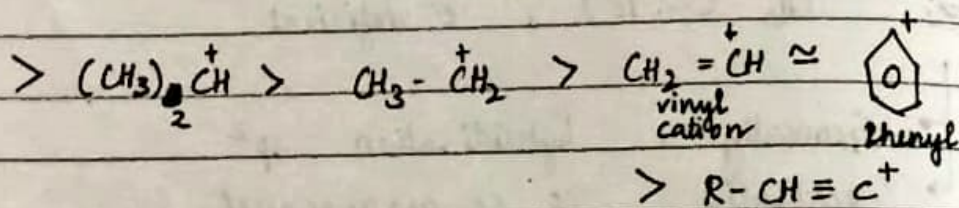
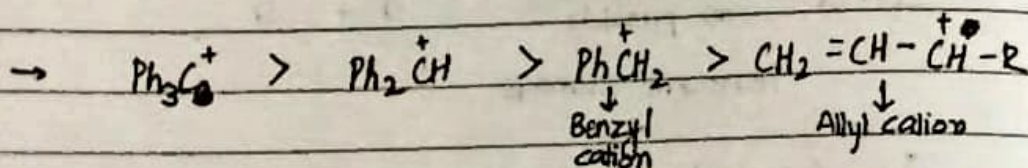


Note: $\overset{\text{vinyl}}{CH_2=CH^+}$ - sp hybridisation.
(~~2~~ 2 σ bonds).

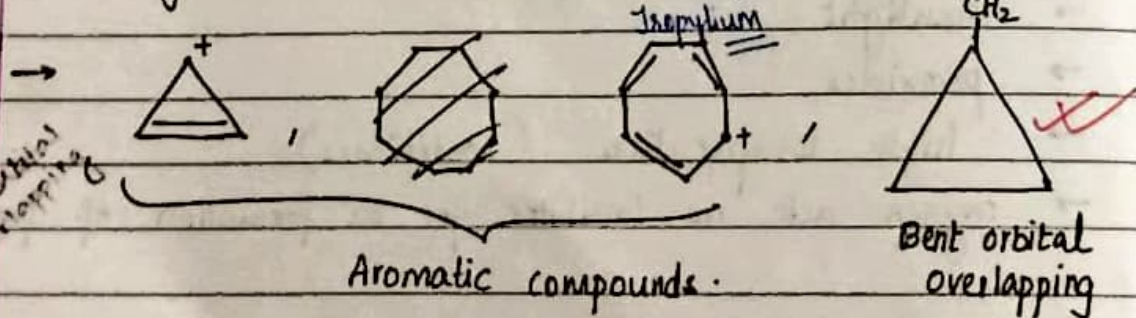
→ Diamagnetic in nature

→ C: 6 valency e^- .

→ +M, +I (ERG), H.C. stabilises the carbocations.



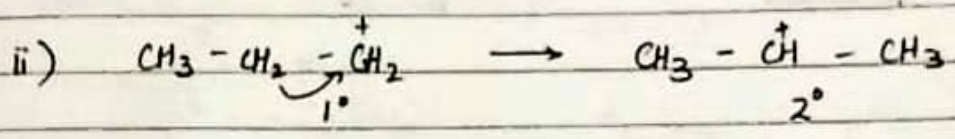
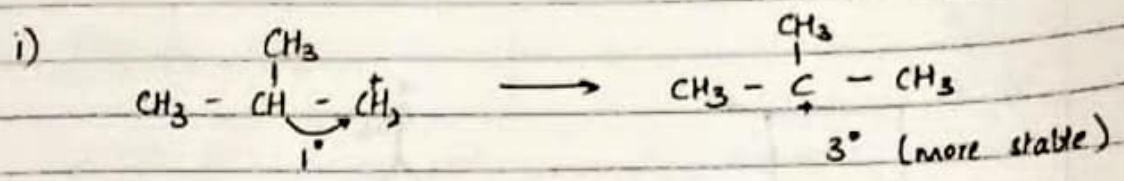
→ Bridgehead cations are least stable (not possible).



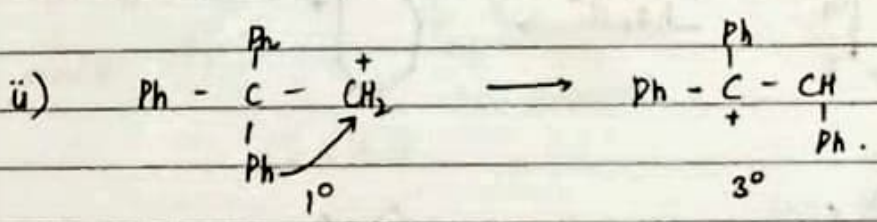
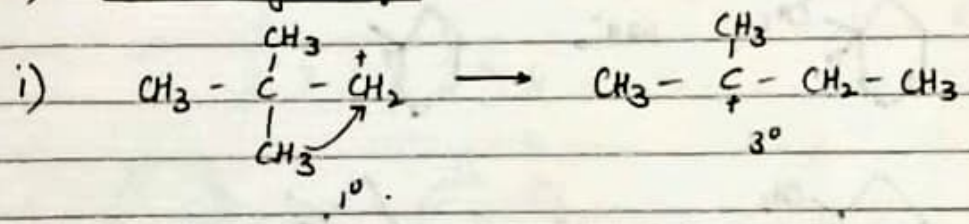
are very stable.

→ Carbocations can undergo re-arrangement whenever it can form more stable carbocation.

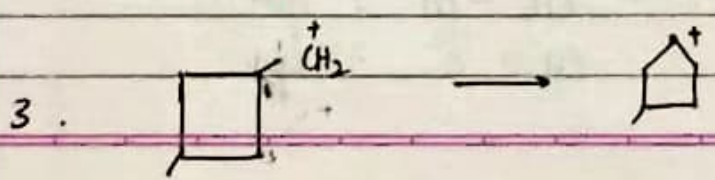
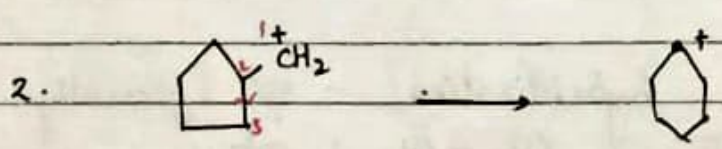
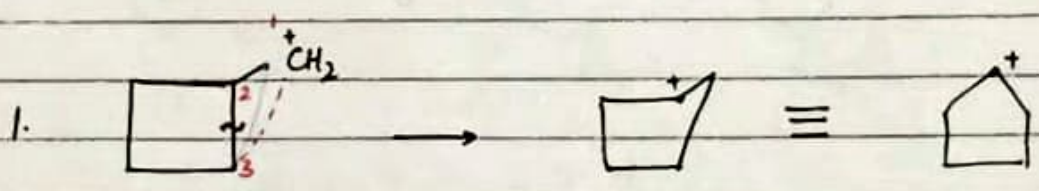
a) 1,2 H⁻ shift :



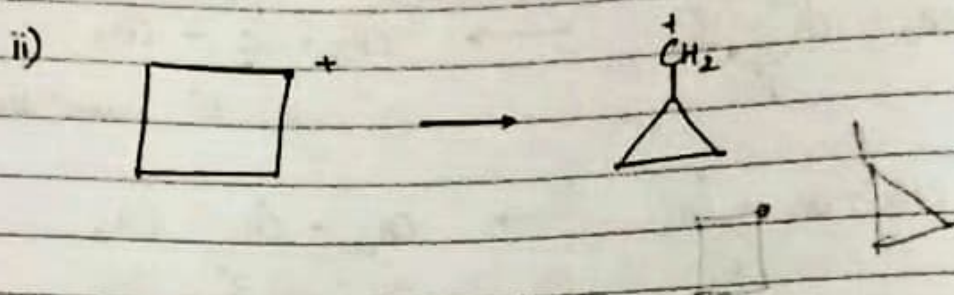
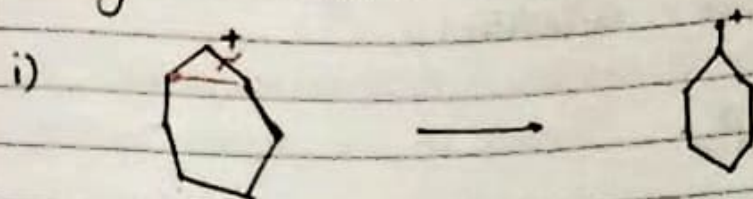
b) 1,2-alkyl shift :



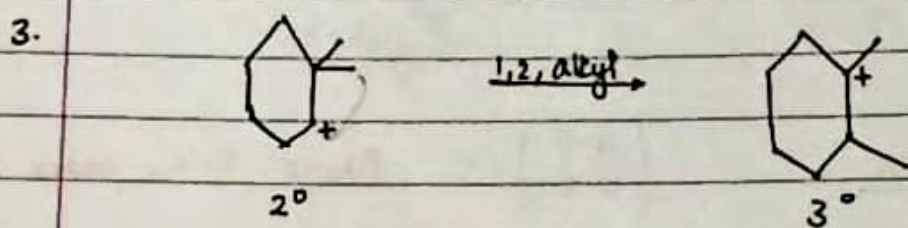
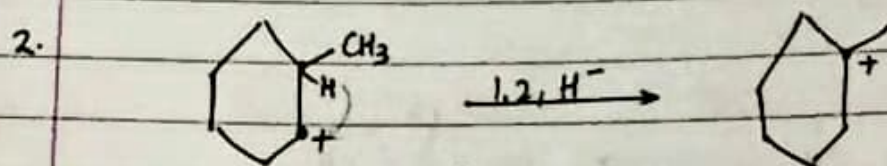
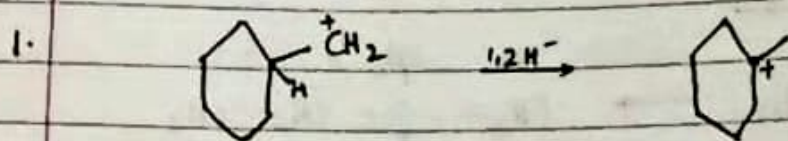
e) Ring expansion : (4-5) (5-6) Break 2-3, make 1-3.



d) Ring contraction:



Ex: Rearrange if possible:

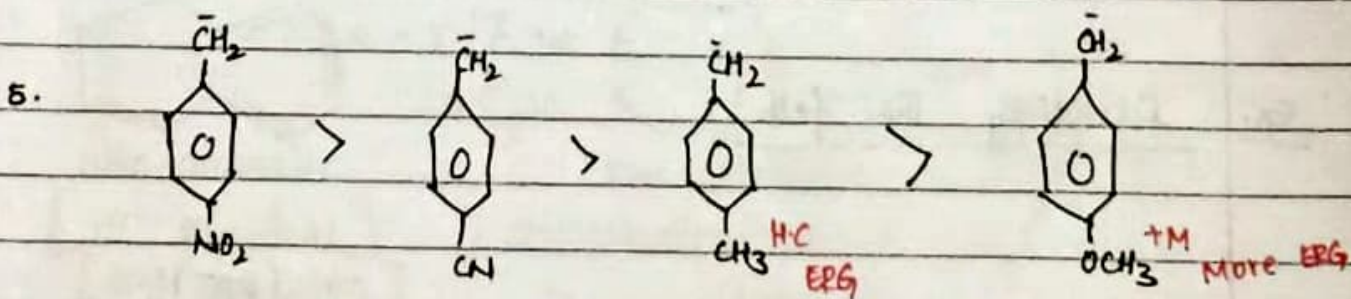
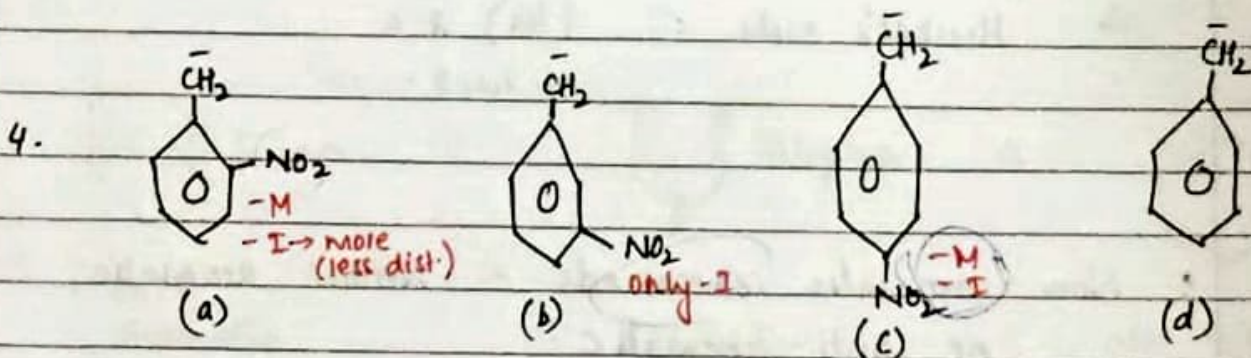
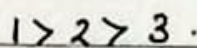
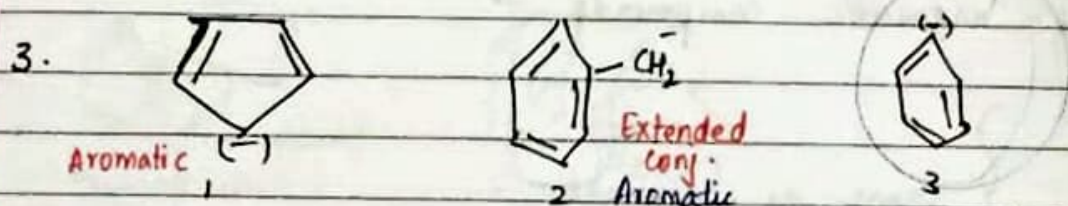
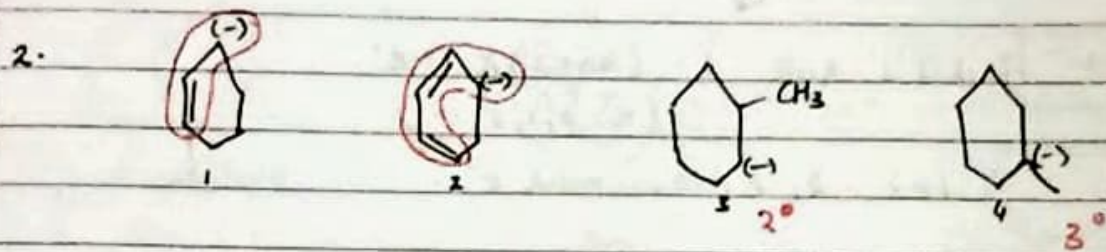
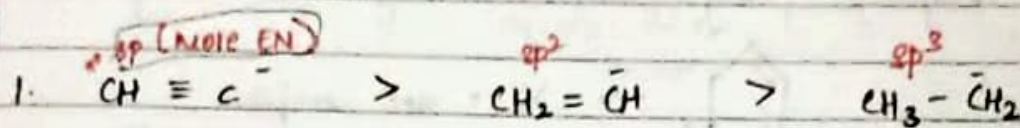


3) Carbanion:

→ Generally - hybridisation - sp^3 (generally)
Note: $\text{CH}_2 = \bar{\text{C}}\text{H} : sp^2$
 $\text{CH} \equiv \text{C}^- : sp$

- 8 valency e⁻
- Diamagnetic in nature
- Stability is increased by -I, -M effects (EWG) and delocalisation.

→ Stability order :



→ Electrophile (Electron Seeking group) : (Lewis acid) (E^+)

Ex: H^+ , Cl^+ , NO_2^+ , BF_3 , $AlCl_3$, SO_3 .

→ Nucleophile : (Lewis bases) (Nu^-)

Ex: Cl^- , NH_2^- , OH^- , $R-OH$

→ Benzene intermediate :



- aromatic
- sp^2
- extra π bond - interaction of sp^2 hybrid orbitals.

→ Carbene intermediate :



- singlet carbene : sp^2
- triplet carbene : sp .