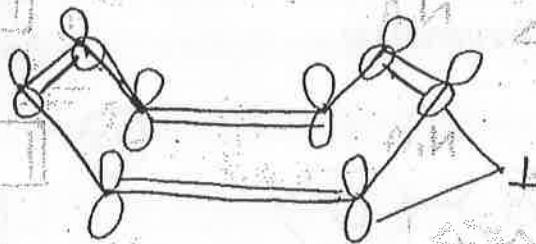
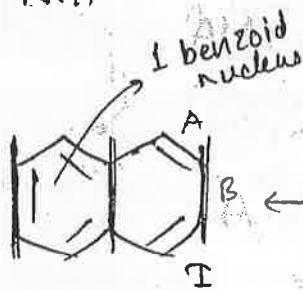




COT
N.A



Non-planes

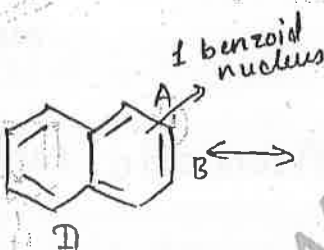


Napthalene

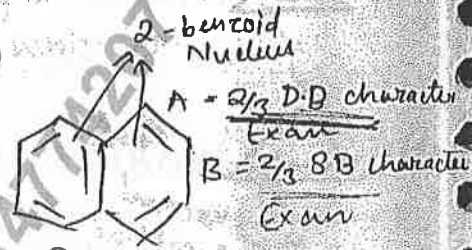
3 R.S

poly cyclic ring

Huckel's rule valid here.



II



DI

$A = \frac{2}{3}$ D.B character
Exam
 $B = \frac{2}{3}$ S.B character
Exam

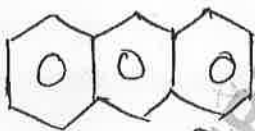
B.L $\Rightarrow A \neq B$

B.L $\Rightarrow B > A$

Fries Rule \Rightarrow No. of Benzoid $\uparrow \Rightarrow$ Stability \uparrow
Nucleus

Stab \Rightarrow DI $>$ I = II

22



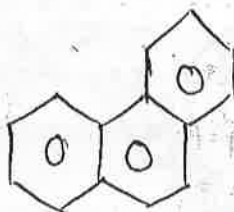
4 R.S.

\rightarrow Aromatic

\rightarrow Anthracene

\rightarrow R.E $\Rightarrow -84$ Kcal/T

23



II

5 R.S

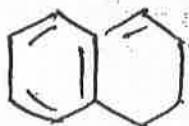
\rightarrow Aromatic

\rightarrow phenanthrene

\rightarrow R.E $\rightarrow -92$ Kcal/Toule

Stab \Rightarrow II $>$ I

24



Aromatic

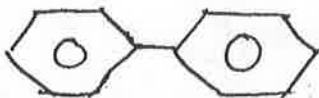
25



Aromatic

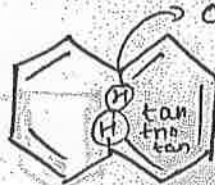


26



Aromatic

27

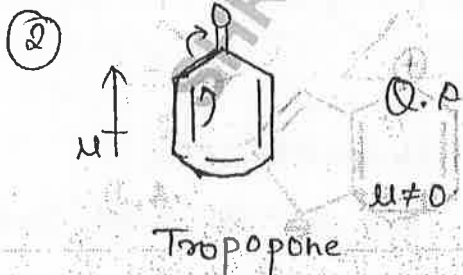
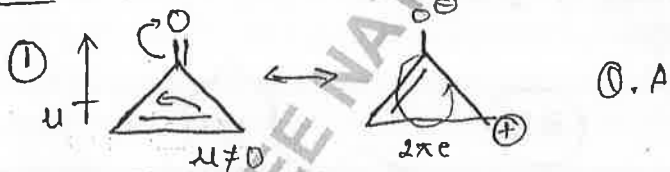


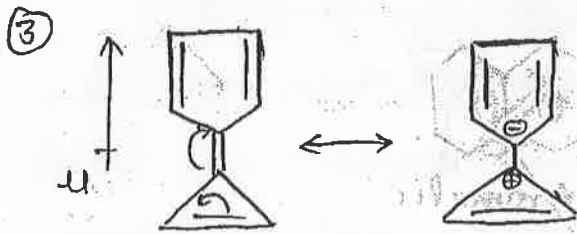
Non Aromatic

Quasi. Aromatic comp:-

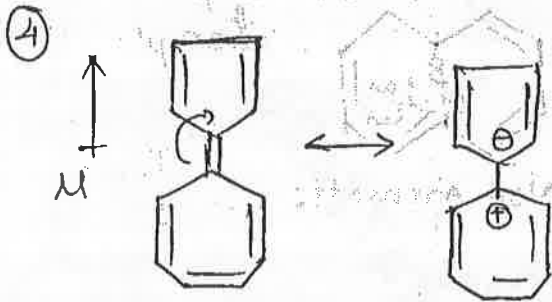
- Ionised aromatic comp. is known as Quasi aromatic compound.
- Quasi Aromatic comp. have always non-zero dipole moment
- Quasi Aromatic comp. soluble in polar solvent.

Ex.

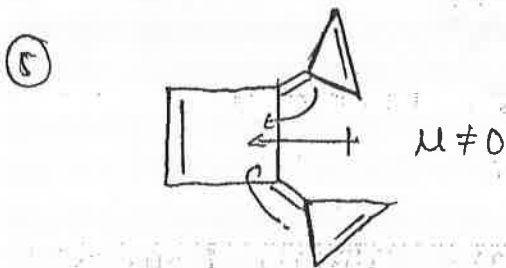




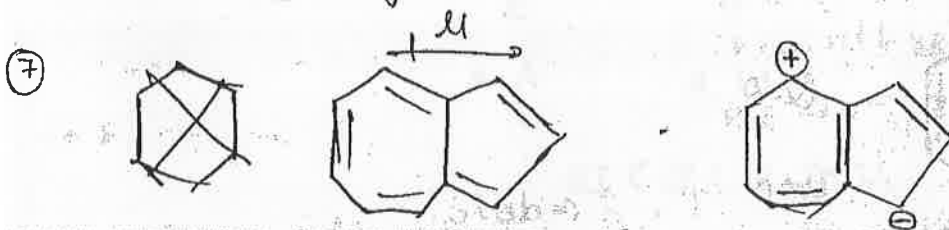
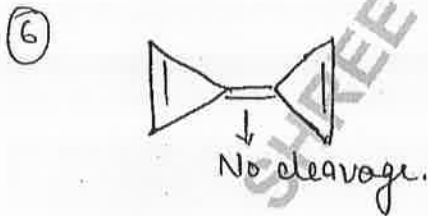
Q.A.



Q.A.



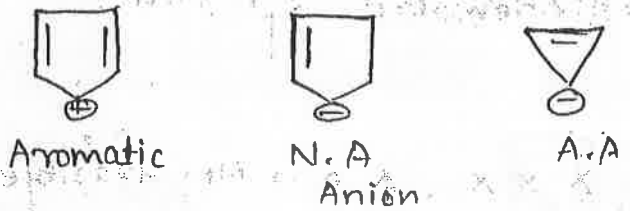
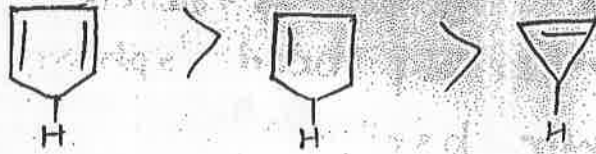
Benzyl anion, Benzyl free radical, aniline
 benzyl cation
 & phenol, all are Aromatic compound.



Q.A. {Azulene}
 → 5-6 Ring
 → $\mu \neq 0$
 → Soluble in H_2O .

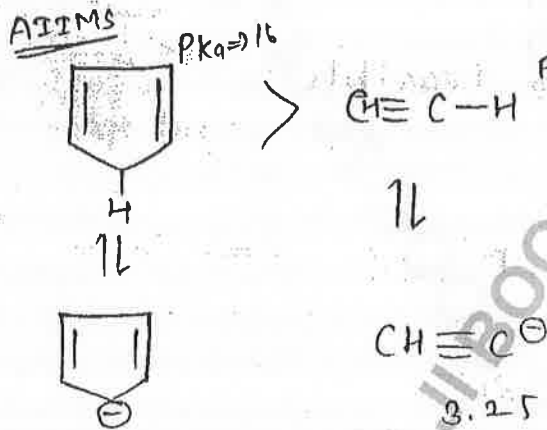
Application of Aromaticity :-

①



⇒ max stable

②



⇒ Aromatic Anion
 ⇒ more stable "

Dipole moment :-



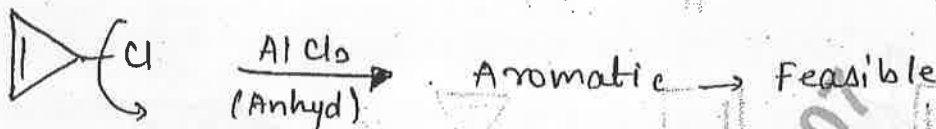
$\mu \Rightarrow I > II > III$

Q Which of the following rxn is feasible.

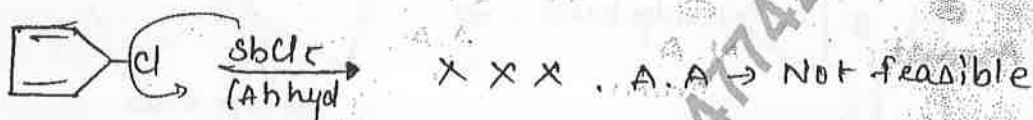
I



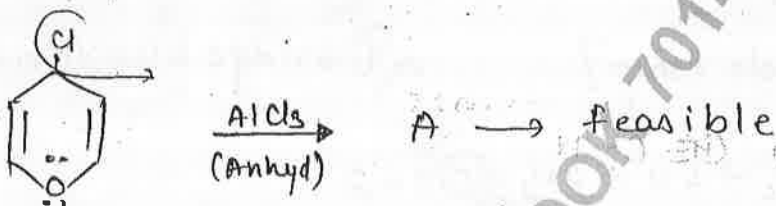
II



III

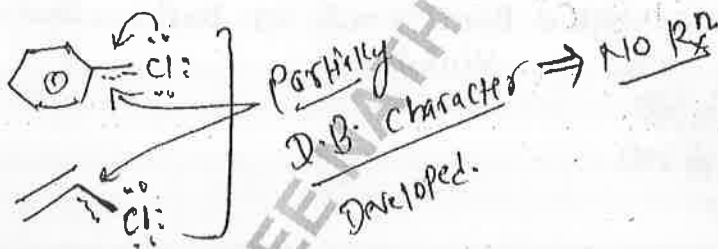


IV



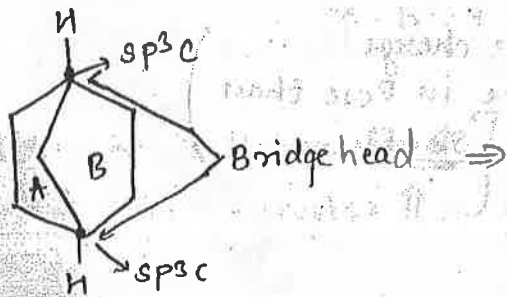
Ans \Rightarrow I, II, IV

V

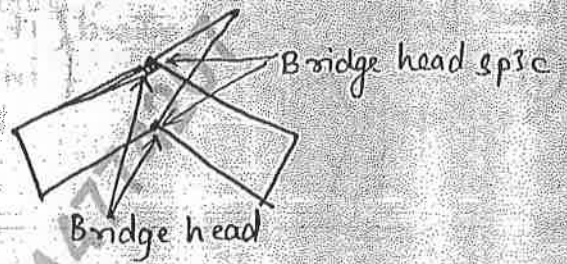


Bredt's Rule ⇒

Acc. to Bredt's ^{case of} in _n bridge bicyclo compound at bridge head planarity can not achieved before 8 Membered ring [Bridge head की hybridisatⁿ कभी-भी sp^2 नहीं हो सकता].



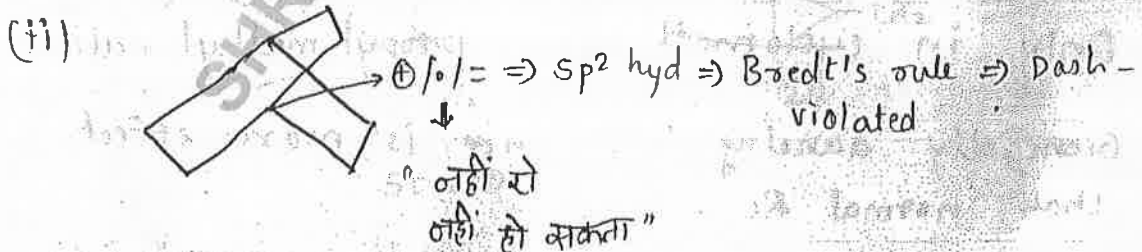
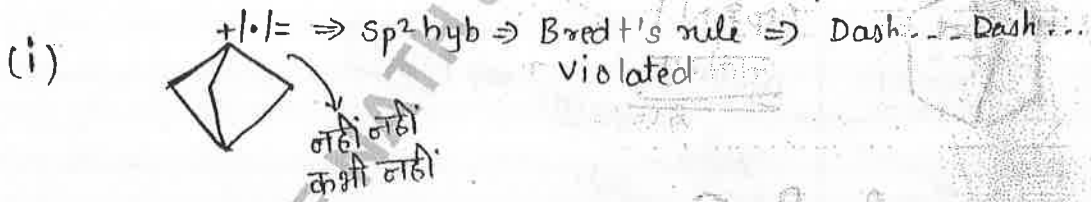
[Bridge bicyclo comp.]



[Bridge bicyclo comp.]

$$C_7H_{12} \Rightarrow C_7H_{16} \Rightarrow 4H \Rightarrow 2H_2 \Rightarrow D.O = 2$$

Concept

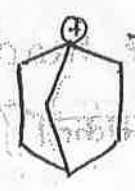


①



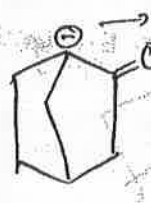
→ Bredt's Rule violate

②



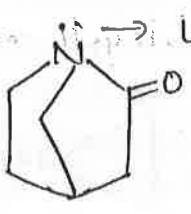
→ xxx → B. R. Rule violate

③



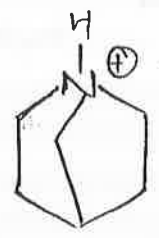
→ Localised (if -ve charge involve in Reso than B. R. Saaf)

④



→ Localised.

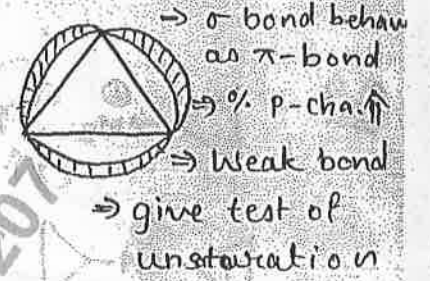
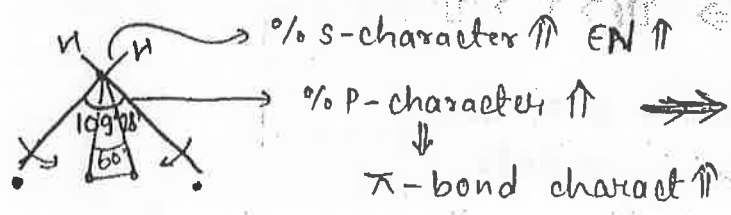
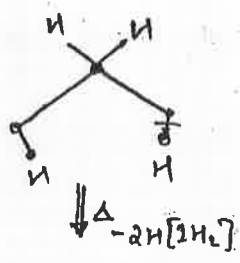
⑤



→ possible (sp³ N) चलैमा

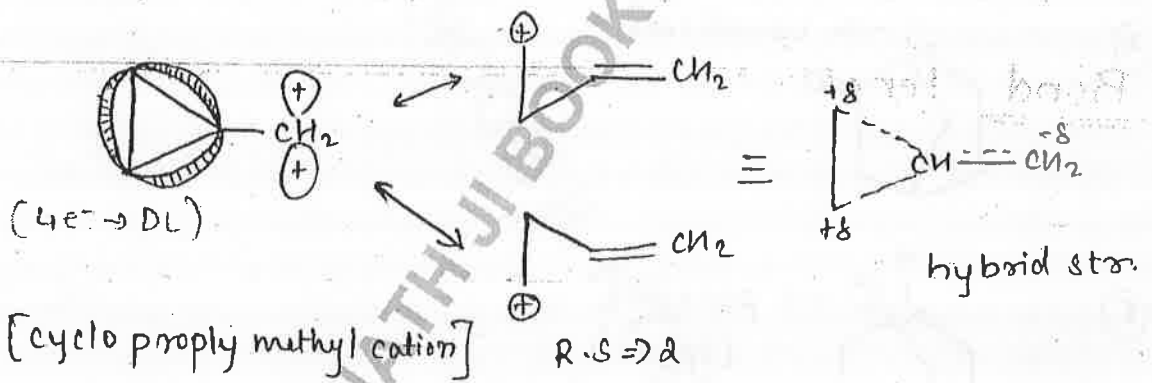
Dancing Resonance :-

- Only in cyclopropyl methyl cation.
- Generally dancing Resonance is more effect than normal Resonance.

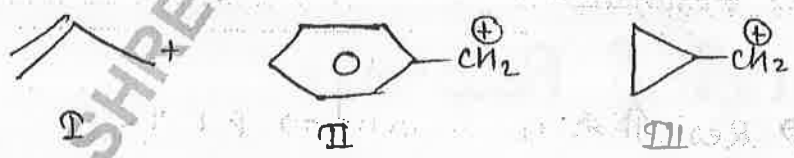


[B.A \downarrow \Rightarrow % P character \uparrow]
 [B.A \uparrow \Rightarrow % S character \uparrow]

Concept \rightarrow

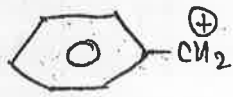


Q. 1



stab \Rightarrow III > II > I

Q.2



I



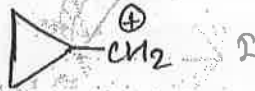
II



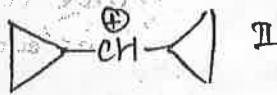
III

stab \Rightarrow III > I > II

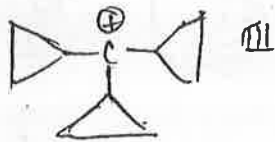
Q.3



I



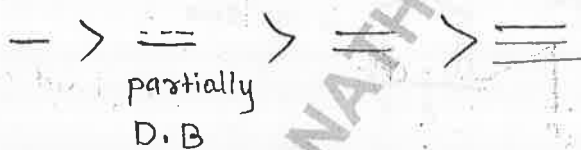
II



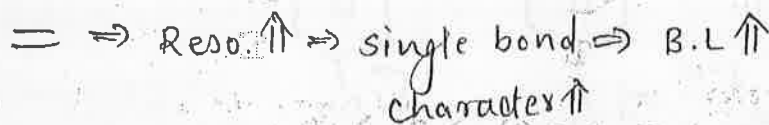
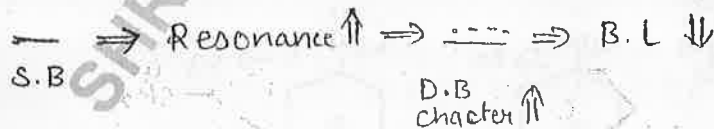
III

stab \Rightarrow III > II > I

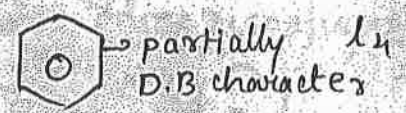
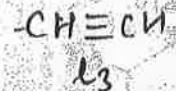
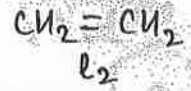
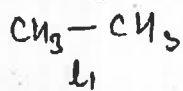
Bond length :-



Concept :-

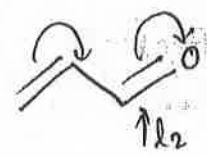
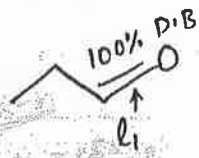


Q.1



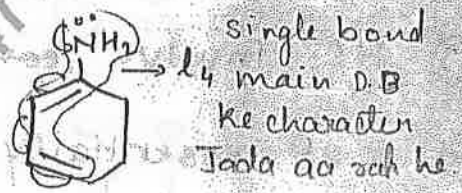
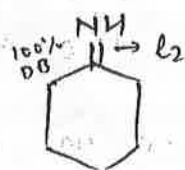
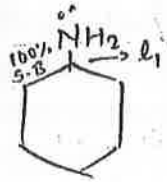
B.I ⇒ l₁ < l₂ < l₃ < l₄

Q.2



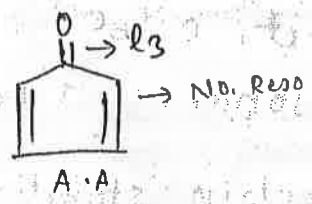
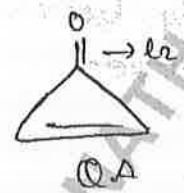
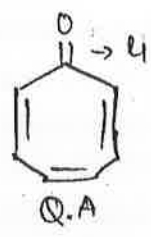
B.I ⇒ l₃ > l₂ > l₁

Q.3



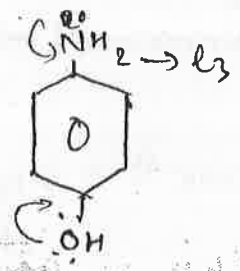
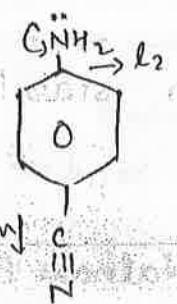
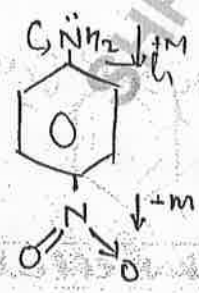
B.I ⇒ l₁ > l₃ > l₄ > l₂

Q.4



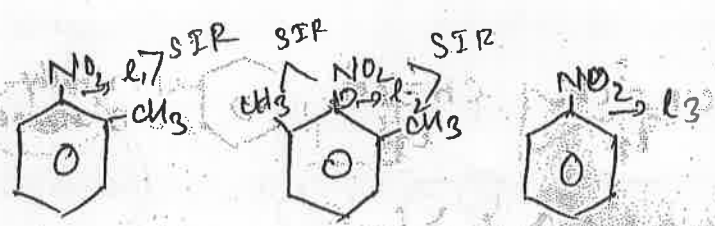
B.I ⇒ l₁ > l₂ > l₃

Q.5)



B.I ⇒ l₃ > l₂ > l₁

Q.6

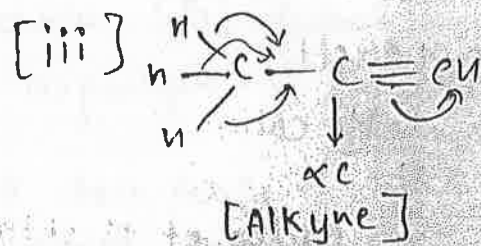
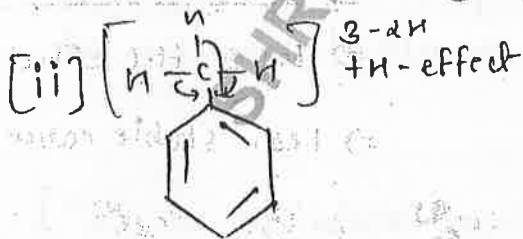
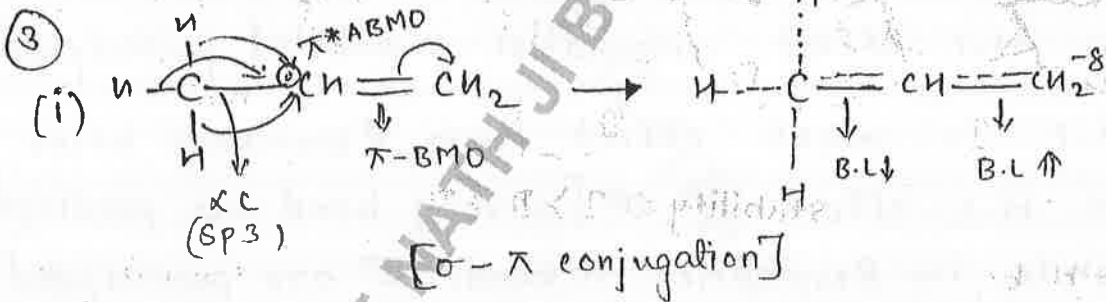
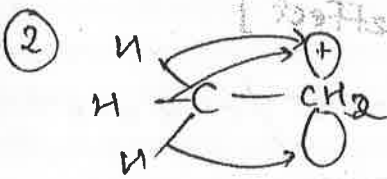
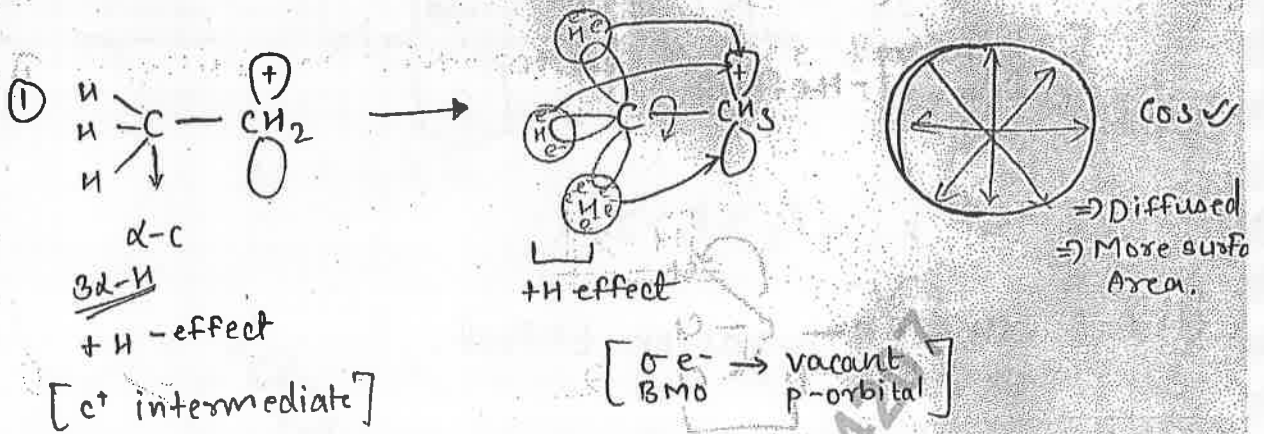


B.L \Rightarrow $l_2 > l_1 > l_3$

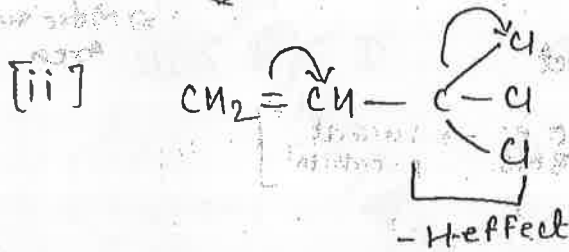
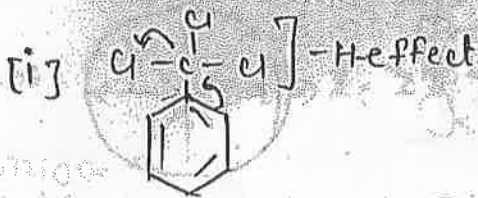
Hyper-Conjugation Effect.

- ① Permanent effect
- ② Hypothetical concept.
- ③ HC involve carbon-hydrogen $C-H \sigma - e^- / C-X \sigma - e^-$
- ④ σe^- essentially participated in H.C effect
- ⑤ In H.C effect unparallel p-orbital participate
- ⑥ H.C is weak effect than Resonance becoz in H.C effect σe^- [strong bond are participated while in Resonance π bonds e^- are participated]
- ⑦ H.C effect explain stability of carbo cation $[C^+]$, free Radicle $[C^\cdot]$, alkene & alkyl having at least 1 α -Hydrogen.
- ⑧ H.C effect can not explain stability of $[C^-]$ due to repulsion factor
- ⑨ H.C effect also known as Nathan Bekov effect / No bond Reso / $\sigma \rightarrow \pi$ conjugation

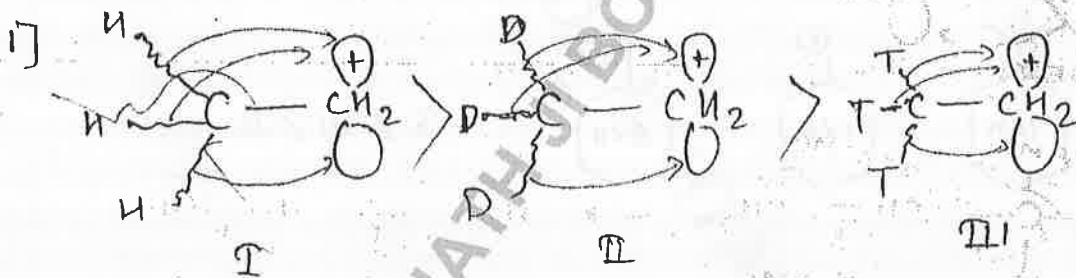
⑩ following conjugator system give hyper conjugatⁿ effect.



(4) -H effect \Rightarrow



K.I.E in [Hyperconjugation effect]

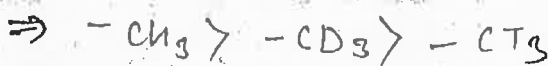


stability \Rightarrow I > II > III

- \rightarrow C-H bond
- \rightarrow Weak bond
- \Rightarrow More break
- \Rightarrow More H.C-effect
- \Rightarrow Max. stable cation

- \Rightarrow C-T bond
- \Rightarrow Strong bond
- \Rightarrow less break
- \Rightarrow less H.C-effect
- \Rightarrow less stable cation

order of +H effect



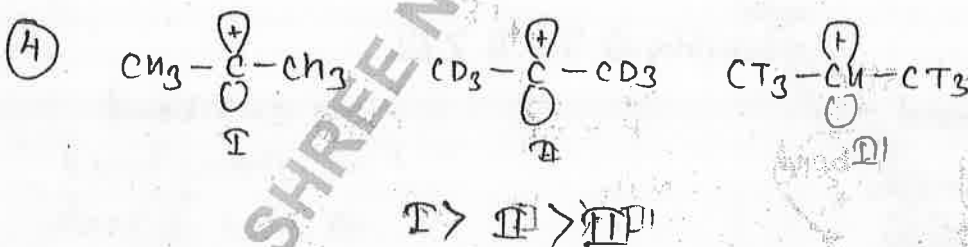
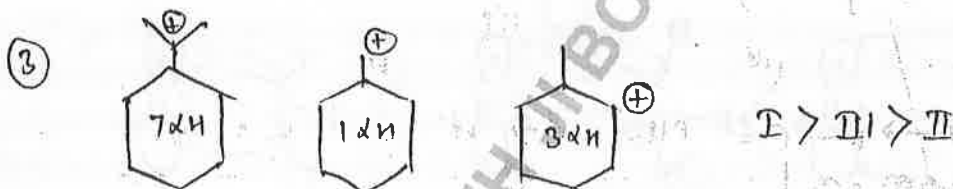
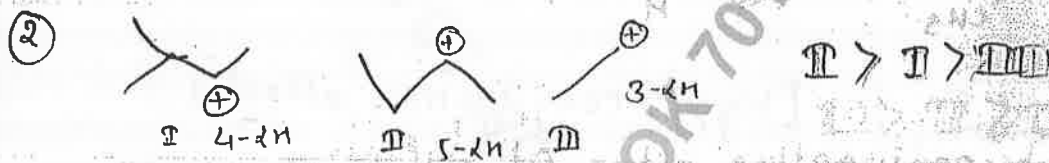
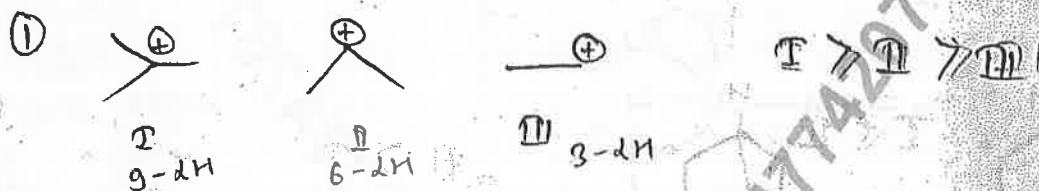
Application of +H effect :-



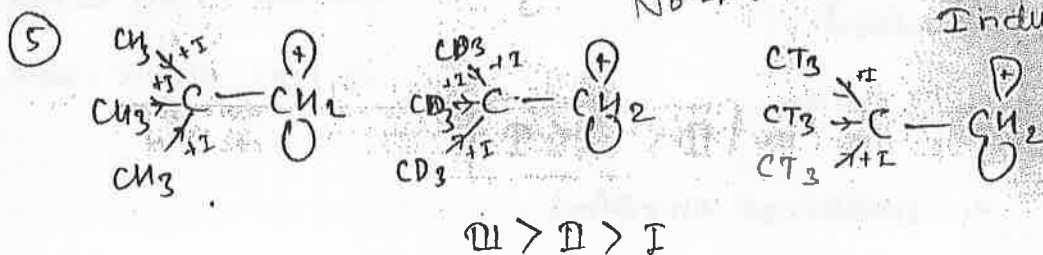
① Stability of carbocation & free radical [C]

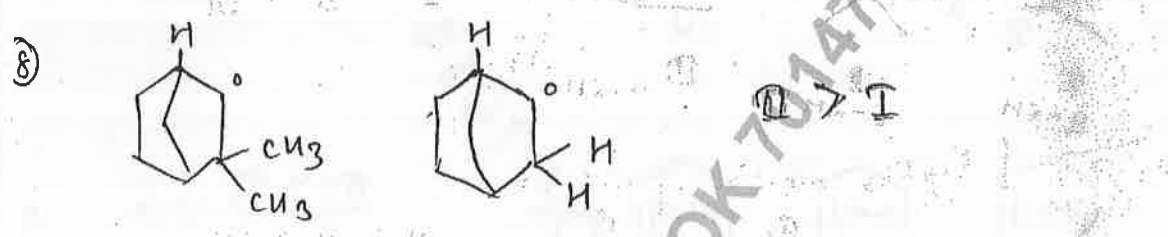
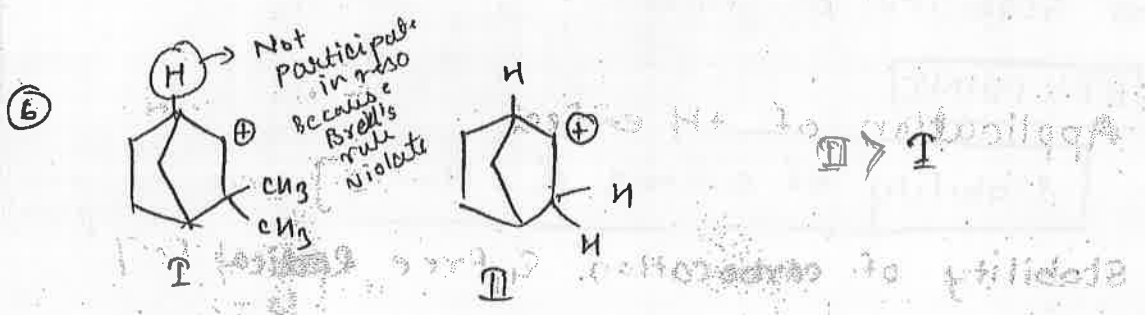
KEY POINT

stability C^+ & $C^\cdot \propto \alpha\text{-H}$

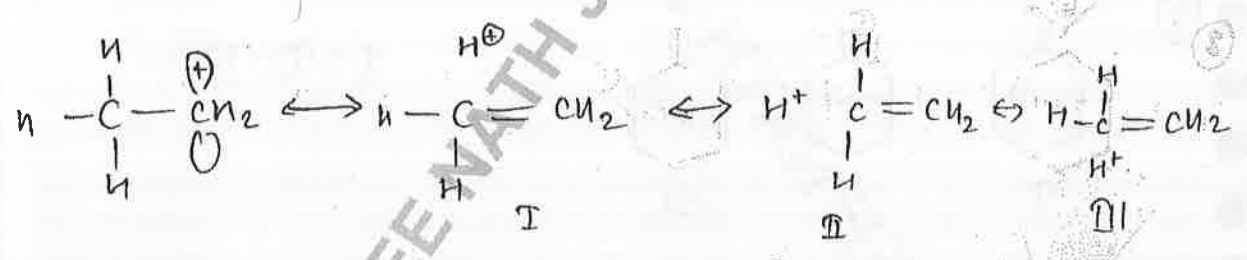


No $\alpha\text{-H}$ then we will see Inductive effect

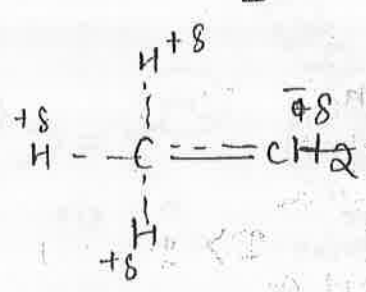




Hyper conjugating str. of cation



No. of H.C Str. involving C-H bond

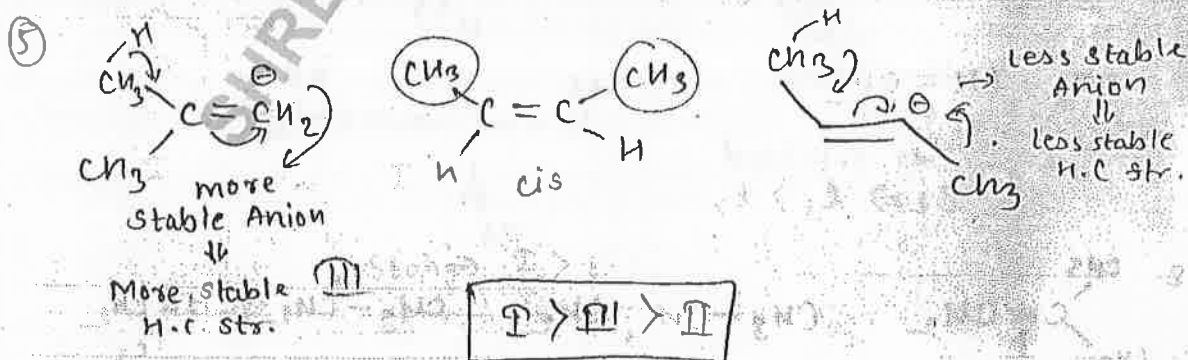
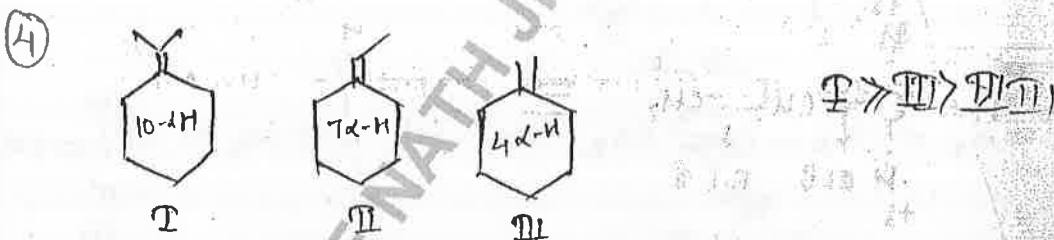
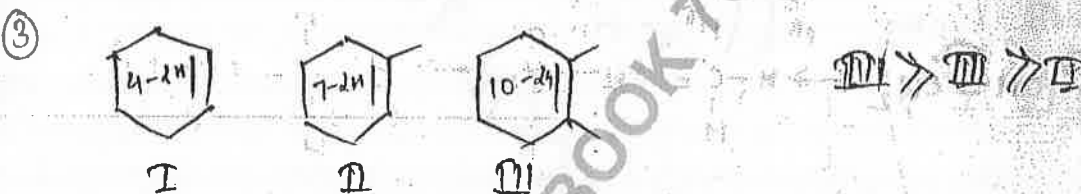


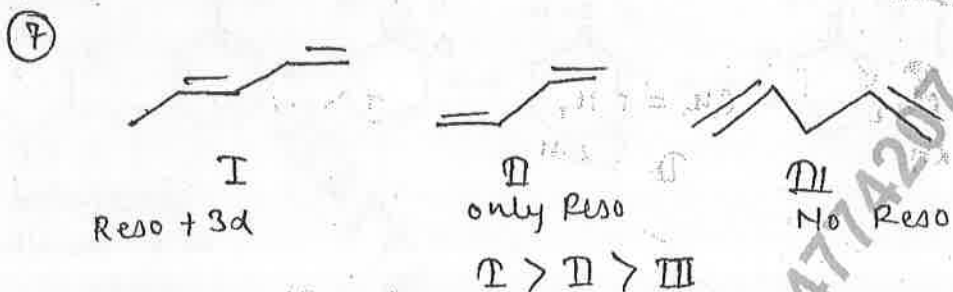
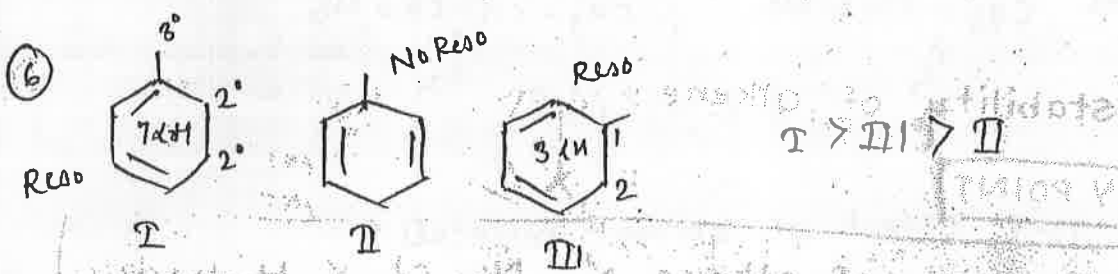
③

stability of alkene:-

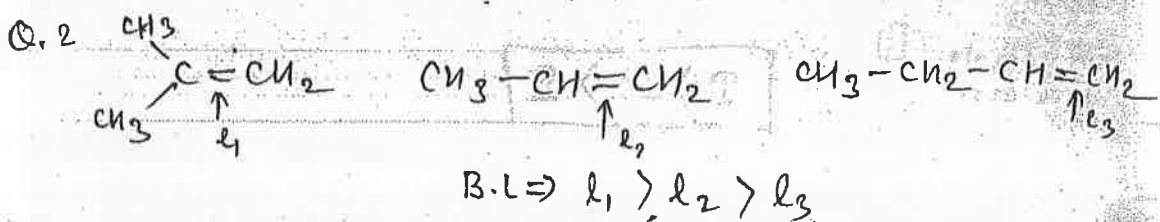
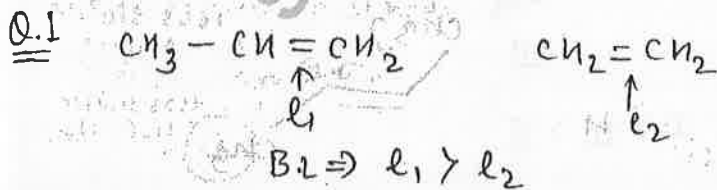
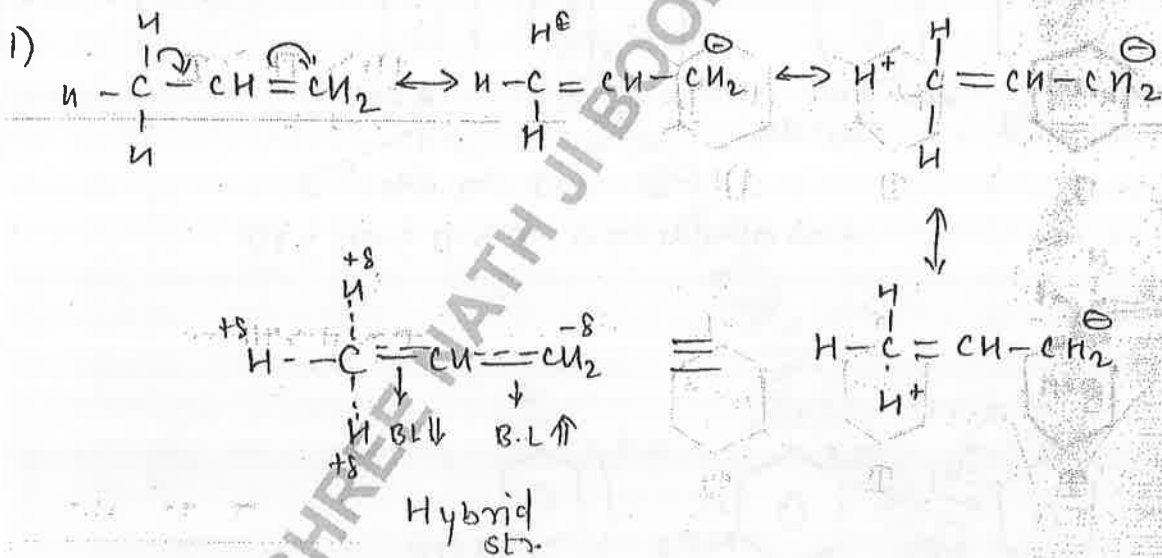
KEY POINT

Stability of alkene \propto No. of α -Hydrogen

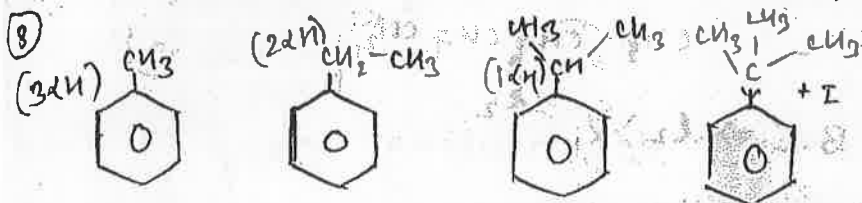




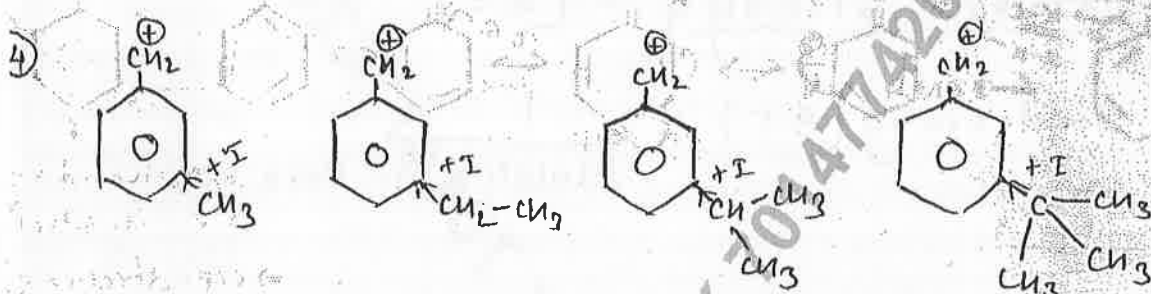
Hyper conjugating str.



Order of e⁻ density in following comp:-

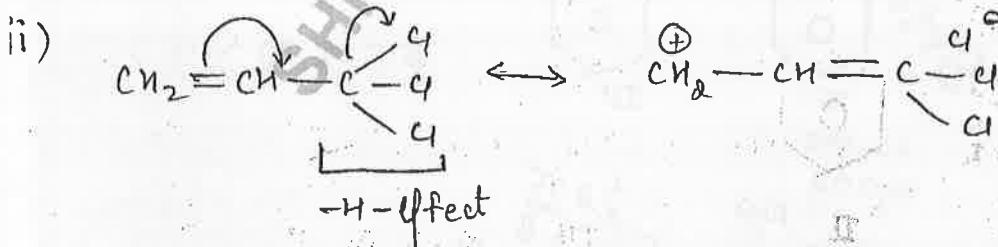
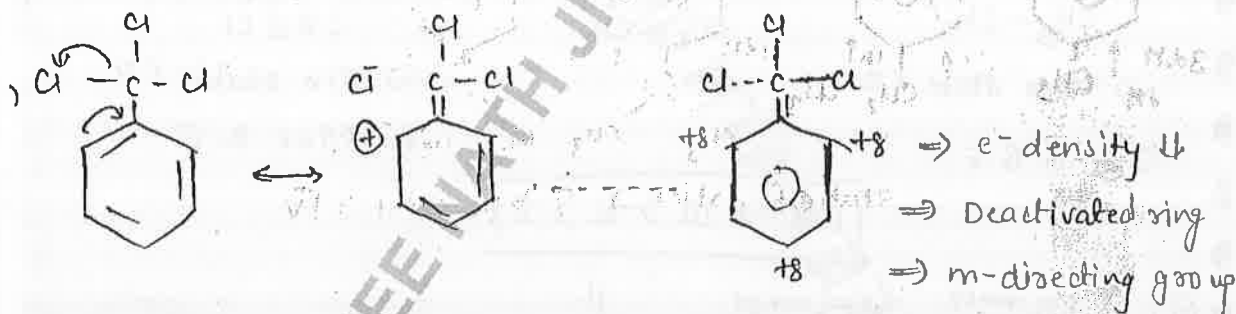


Stab \Rightarrow I > II > III > IV



Stability of c⁺ \Rightarrow IV > III > II > I

-H - Effect / Reverse hyper conjugation:-



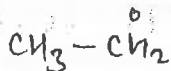
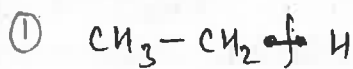
\rightarrow Hyperconjugatⁿ effect observed at ortho & para position of benzene molecules.

→ If any alkyl group having at least 1-H then it given ortho/para directing effect at benzene molecule.

→ $-CCl_3$ is strong deactivating group & this is meta directing group.

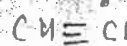
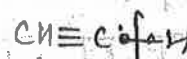
Bond Energy :- [B.E]

Bond Energy (B.E) \propto Stability of Free radical.



⇒ Max stable FR

⇒ Min B.E



⇒ Min stable FR

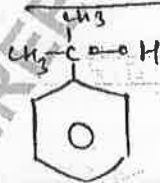
⇒ Max B.E

B.E ⇒ III > II > I

②



I

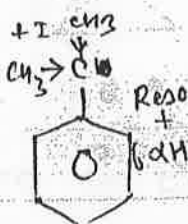


II



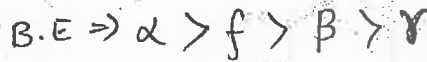
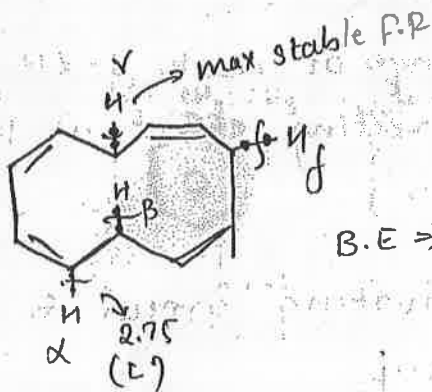
III

B.E ⇒ III > I > II



highly unstable

Q.3



Heat of Combustion:-

Amount of heat released when a substance undergoes complete combustion with oxygen under standard condⁿ.

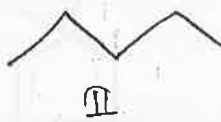
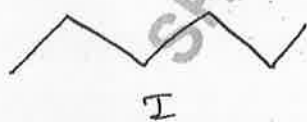
KEY POINT:-

1) H.O.C \propto No. of carbon atoms

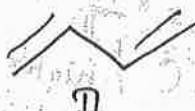
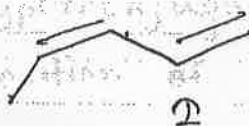
2) IF carbon atoms are equal than H.O.C \propto

H.O.C \propto Stability of comp.

①



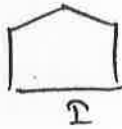
②



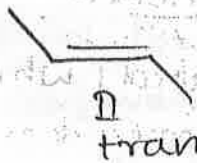
3



4

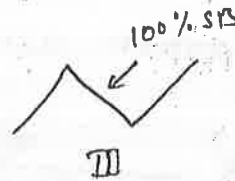
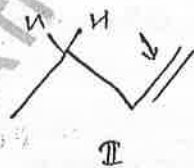


5

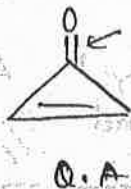


Rotational Energy Barrier Energy

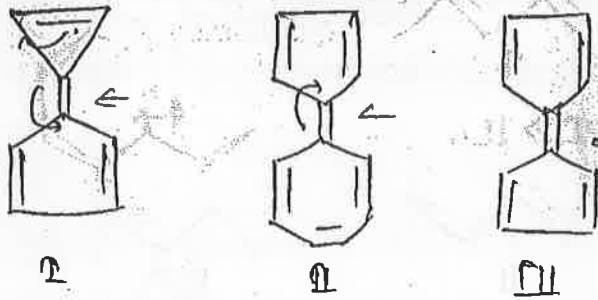
1



2



③

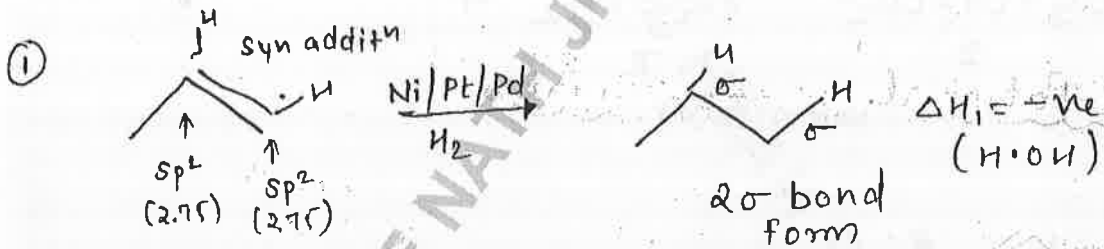


R.B.E \Rightarrow III > I > II

RBE & single Bond character

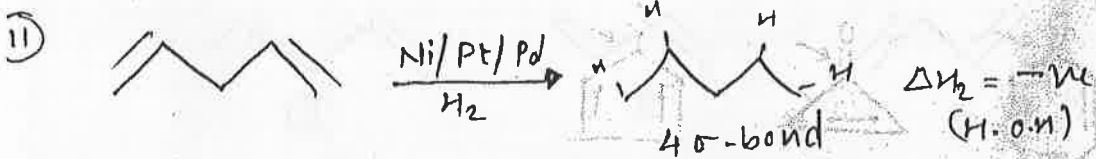
HEAT OF HYDROGENATION

Amount of heat released when 1 mole of unsaturated hydrocarbon completely hydrogenated into saturated compound.



\Rightarrow D.U \Rightarrow 1
 \Rightarrow 1- π bond
 \Rightarrow Weak bond

\Rightarrow 2 σ bond form
 \Rightarrow Strong bond.



H.O.U \Rightarrow $\Delta H_2 > \Delta H_1$

6



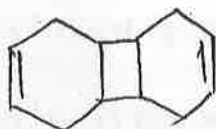
H.O.H \Rightarrow II > I

7

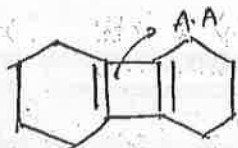


H.O.H \Rightarrow I > II > III

8



I



II

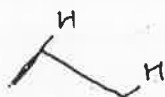
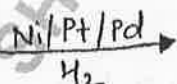
H.O.H \Rightarrow II > I

calculation of Resonance energy on the basis of H.O.H

Resonance \rightarrow Energy difference b/w most stable Energy resonance stru. & resonance hybrid.

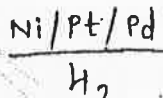
$$RE = \text{Theoretical HOH} - \text{Partically HOH}$$

1

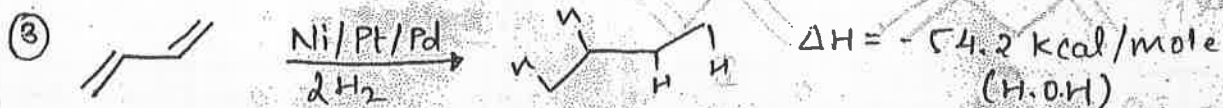


$\Delta H = -28.6 \text{ Kcal/mole}$
(H.O.H)

2



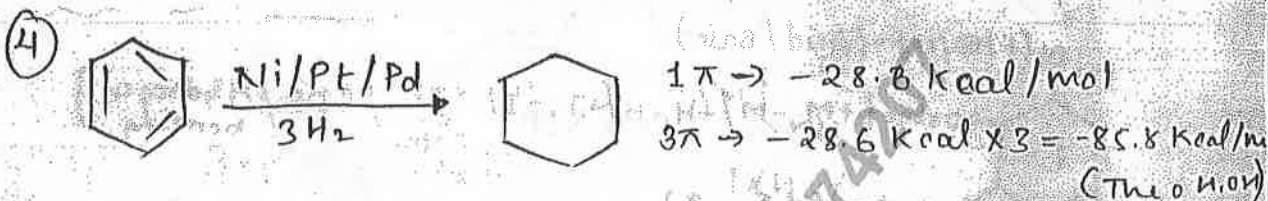
$\Delta H = -57.2 \text{ Kcal/mole}$
(H.O.H)



1-3. Butadiene

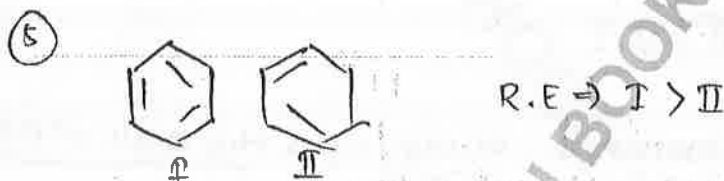
R.E \Rightarrow Theoretical H.O.H - Practical H.O.H

$\Rightarrow 57.2 - 54.2 \Rightarrow 3 \text{ Kcal/mole}$



practically $\Rightarrow -49.8 \text{ kcal/mole}$

RE $\Rightarrow 85.8 - 49.8 \Rightarrow 36 \text{ kcal/mole}$

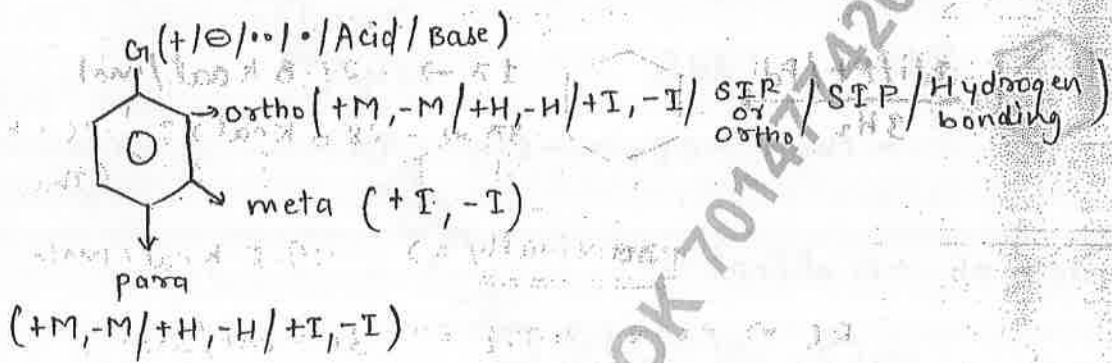


Q.

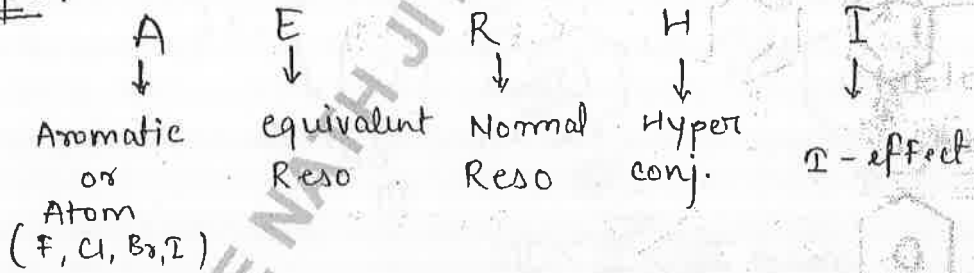


Per π -bond no H / Per mole $H_2 \Rightarrow I > II$

Various effect at ortho & para position:-

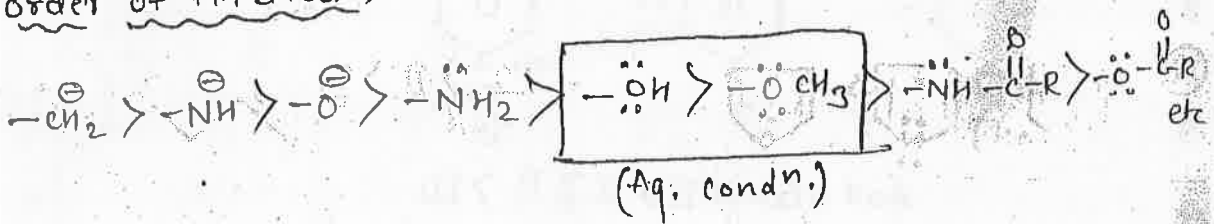


Concept:-

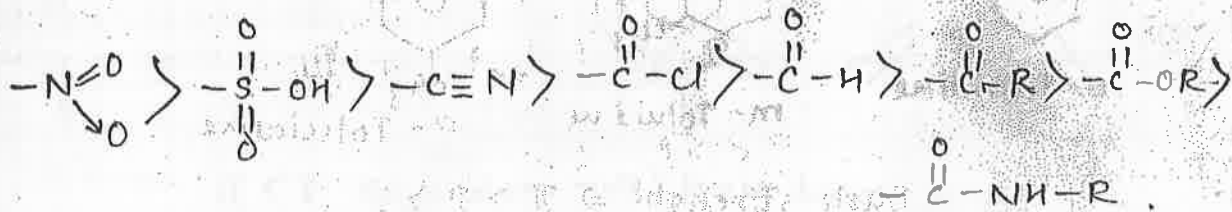


Order of effect \Rightarrow Reso $>$ Hyperconjugation $>$ I-effect.

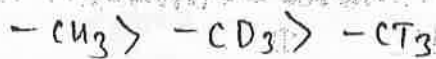
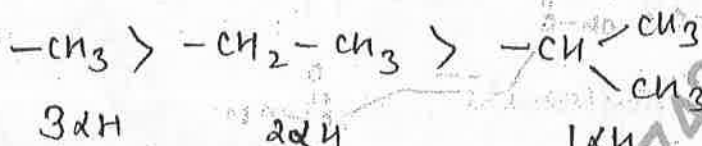
Order of +M effect \Rightarrow



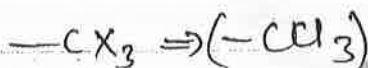
order of -M effect :-



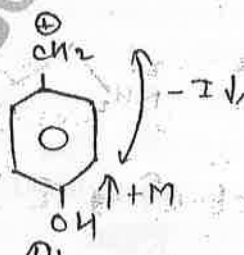
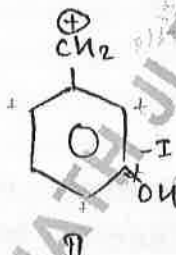
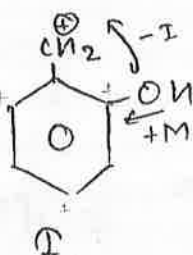
order of +H-effect ⇒



order of -H effect ⇒

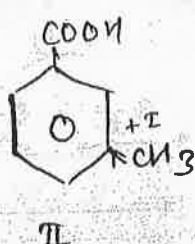
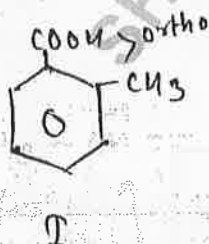


Q.



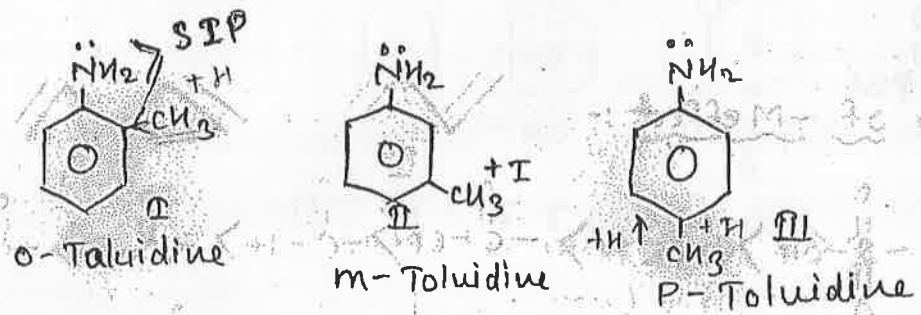
Stab ⇒ III > II > I

Q.2



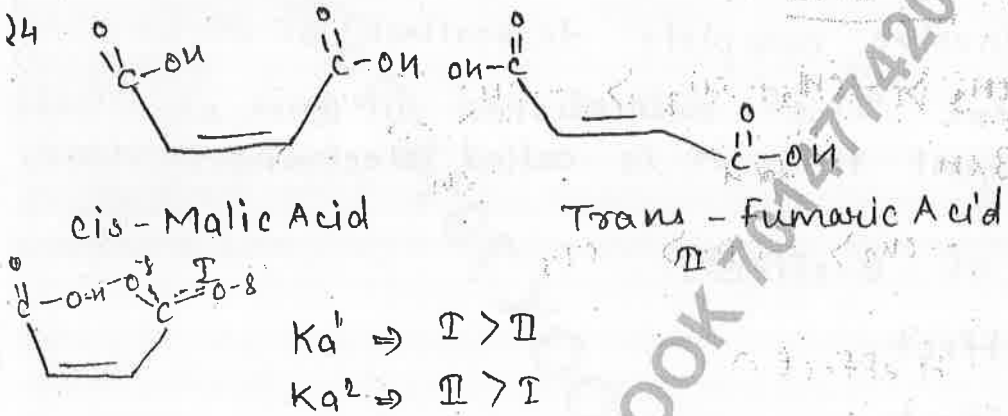
Acid strength ⇒ I > II > III

Q.3

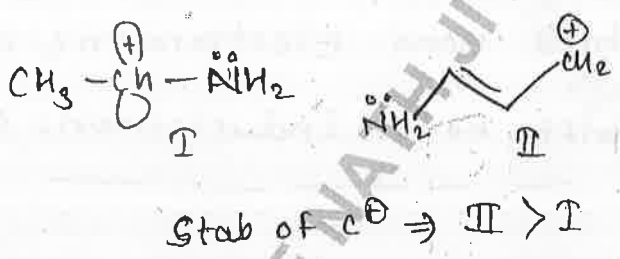


Basic strength \Rightarrow III > II > I

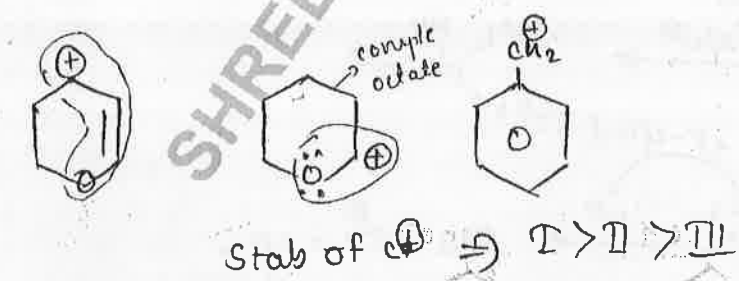
Q.4



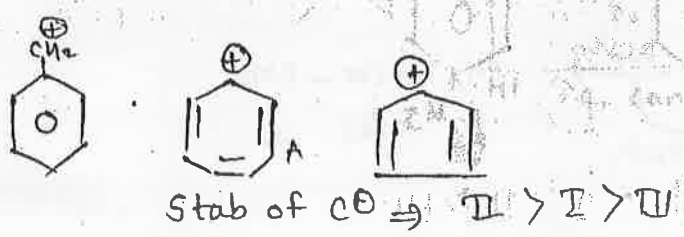
Q.5

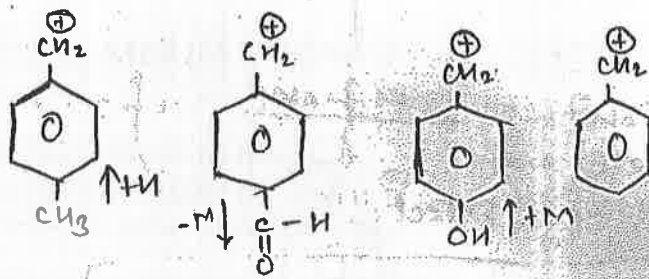


Q.6



Q.7





Stab \Rightarrow III > I > IV > II

Electromeric Effect :- [E effect]

- Temporary effect
- It involve complete delocalisation of e^- .

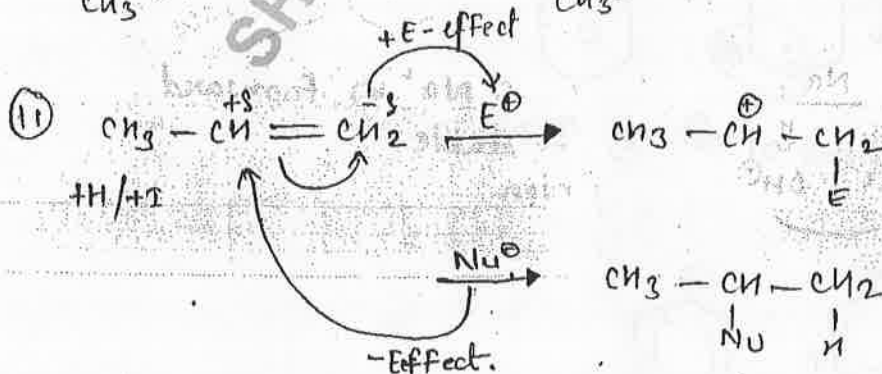
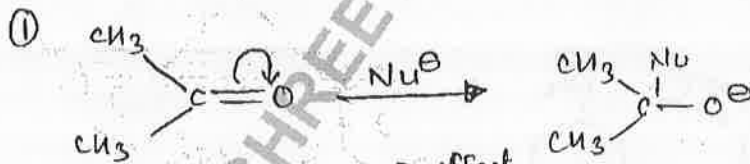
Whenever $\pi - e^-$ delocalised in presence of attacking reagent then it is called electromeric effect.

Type of E-effect :-

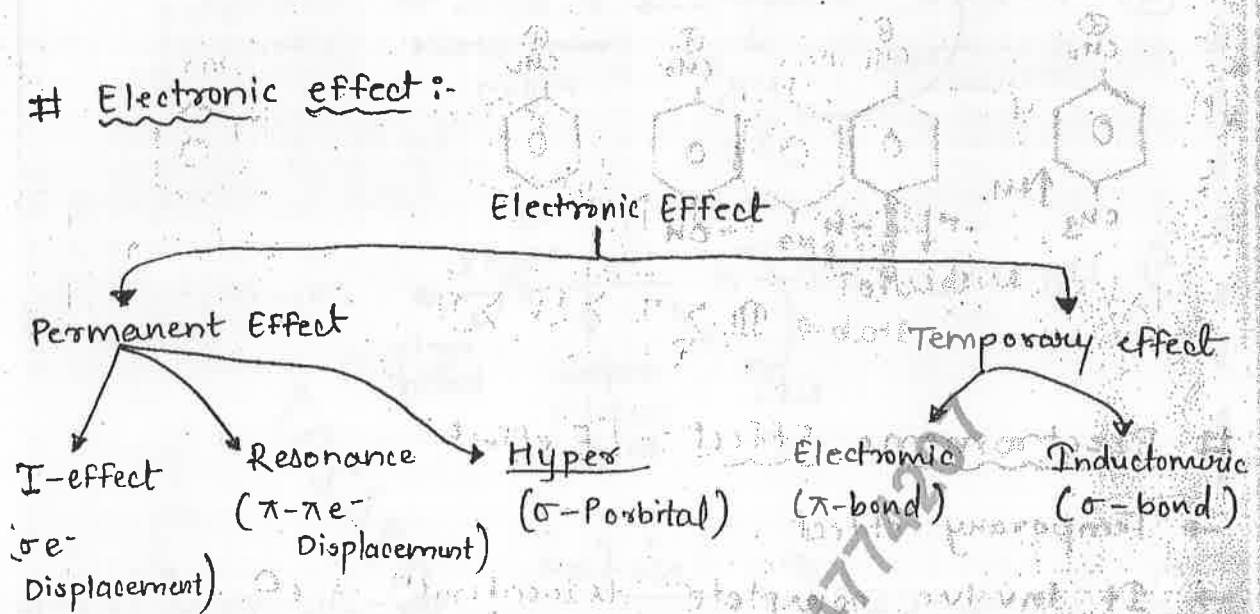
① +E effect:

② -E effect:

π -bond ka shift hona Electromeric effect
 σ -bond ka shift hona Inductomeric effect



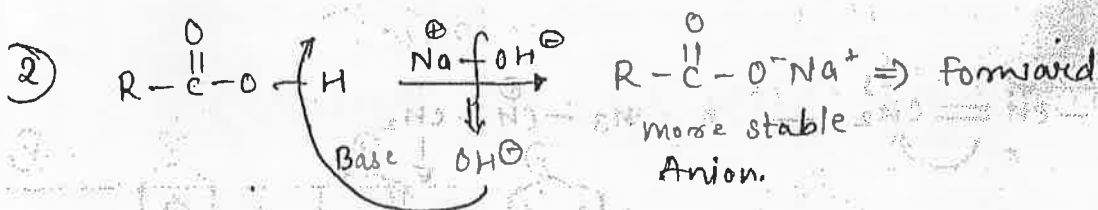
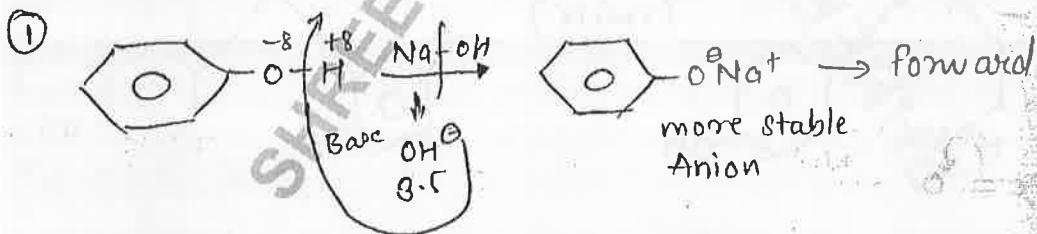
Electronic effect :-

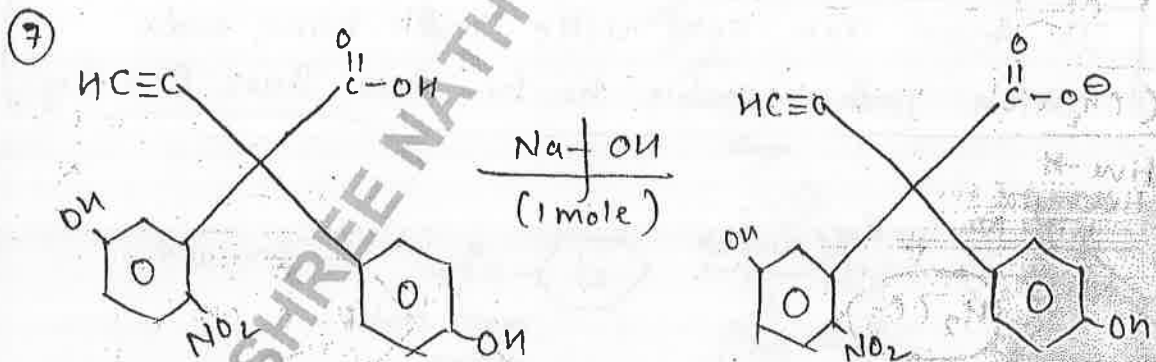
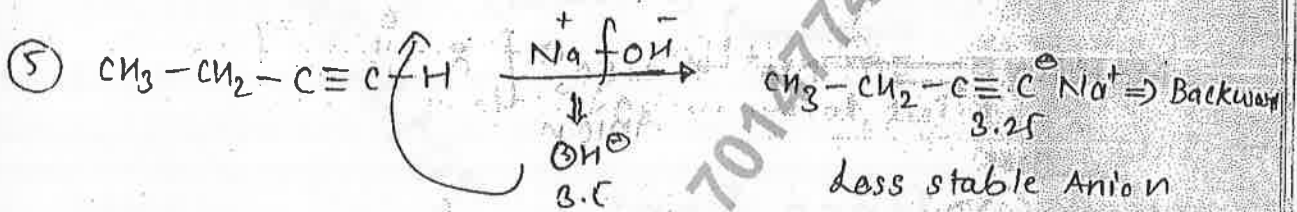
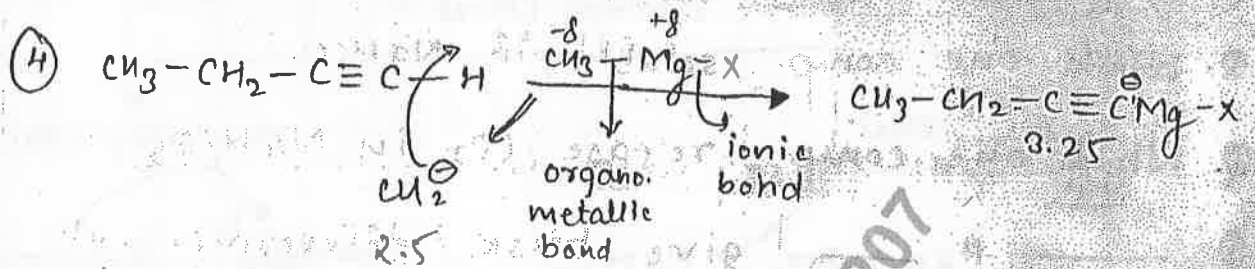
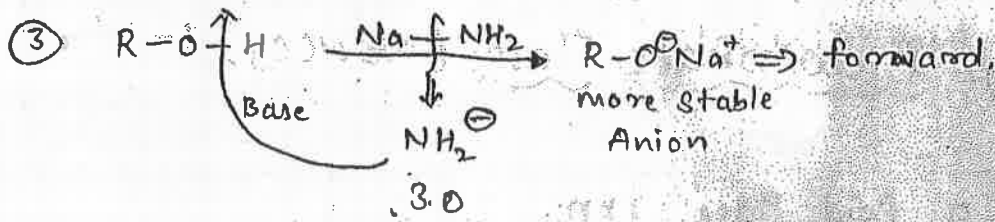


Acid Base Rxn :-

Acid base rxn always goes to weaker components

To Anion rxn kare uske badh bane wala anion jadha stable ho tu Acid Base Rxn hogi





→ ortho nitro phenol is steam volatile mixture of ortho & para nitro phenol → By steam distillation.

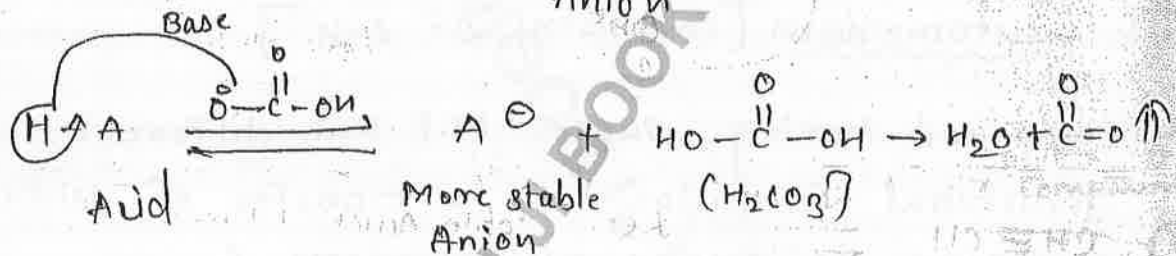
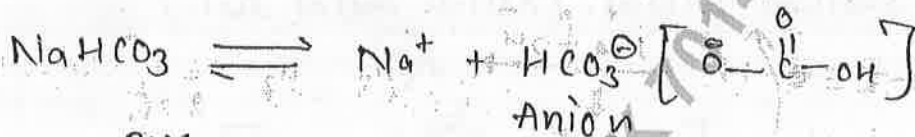
Sodium Bicarbonate Test (NaHCO_3) :-

→ It is a Acid Base rxn.

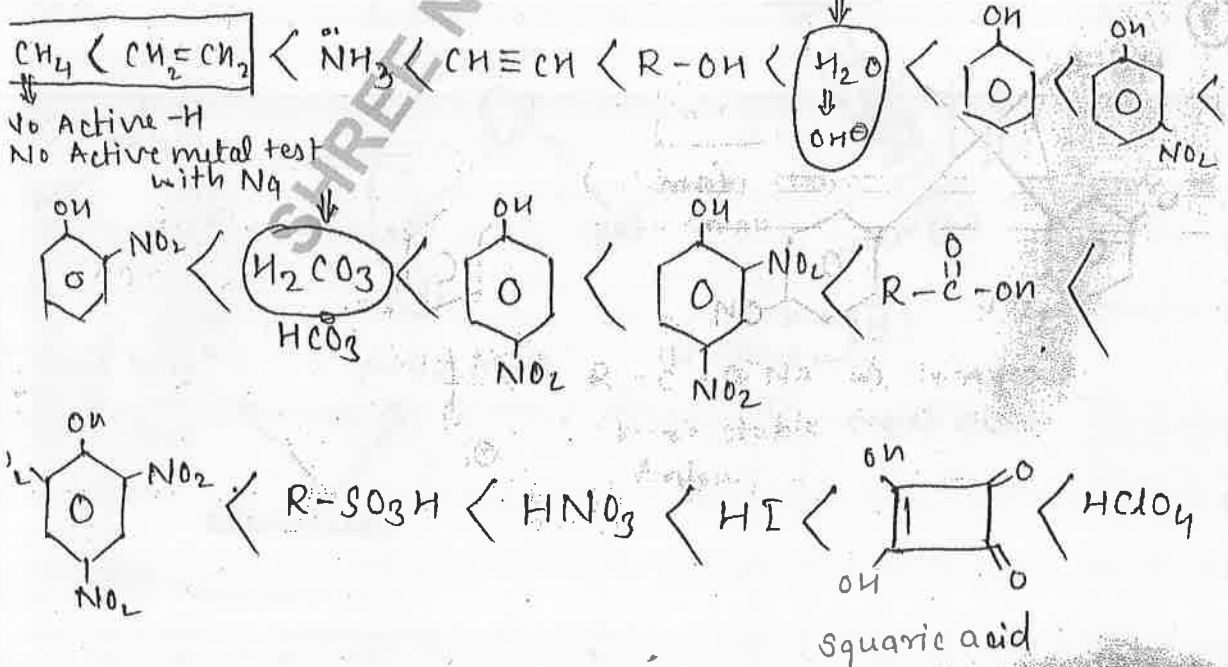
Q. Which one comp. soluble in NaHCO_3

Q. Which one comp. release CO_2 in NaHCO_3

Q. _____ || _____ give brisk efferevnces with NaHCO_3 .



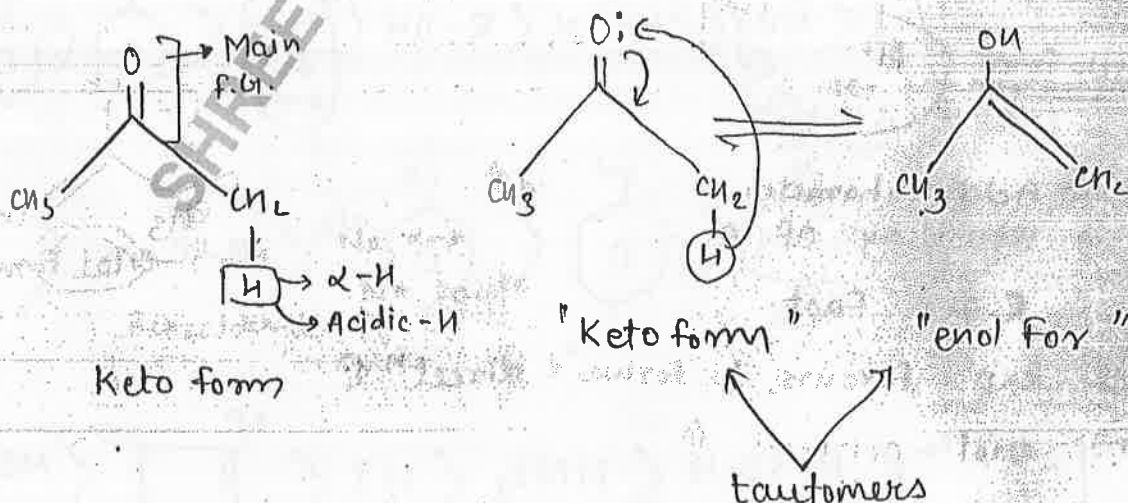
Order of A.S ⇒



- 1) All carboxylic acid & sulphonic acid gives CO_2 with NaHCO_3 .
- 2) Comp's which are more acidic than H_2CO_3 gives CO_2 with NaHCO_3 .
- 3) Comp's which are more acidic than H_2O soluble in NaOH . E,
- 4) Except CH_4 & $\text{CH}=\text{CH}$ all comp. gives H_2 with sodium metal. (Active metal test.)

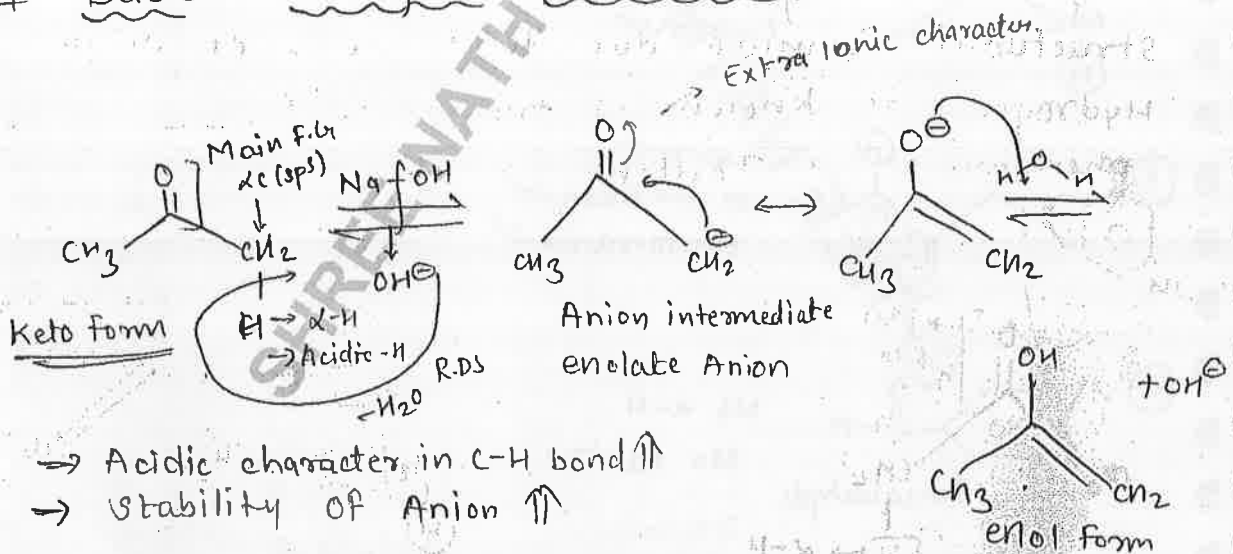
Tautomerism [chemistry of $\alpha\text{-H}$]

Compound having same M.F but different structural formula due to transfer of acidic Hydrogen is known as tautomers & phenomenon is Tautomerism.



- Two tautomers have dynamic eqm that's why tautomerism also known as Desmotropism.
- Due to rapid shifting of H^+ ion tautomerism also known as cationotropy / prototropy.
- All tautomers also have f.g.i but priority given to tautomerism.
- Two tautomeric str. are real in nature while two resonating str. are hypothetical.
- Due to rapid shifting of H^+ ions b/w two atoms of same molecule due to Acid/Base rxn is known as tautomerism.

Base Catalysed Mechanisms:-



- Acidic character in C-H bond \uparrow
- Stability of Anion \uparrow
- ⇒ R.D.S Fast
- ⇒ Rxn favours to forward directⁿ \uparrow
- ⇒ enol content \uparrow

KEY POINT

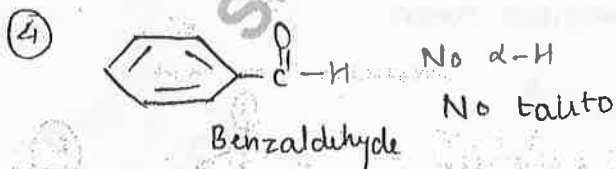
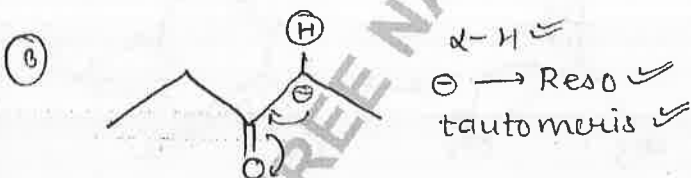
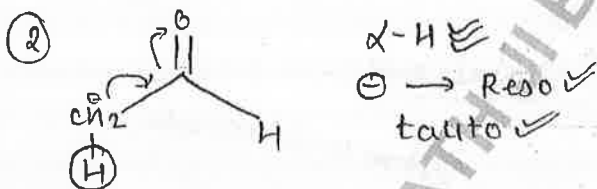
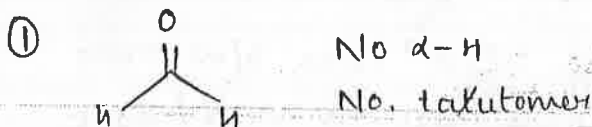
Enol content \propto stability of anion.

\propto Acidic character in C-H bond.

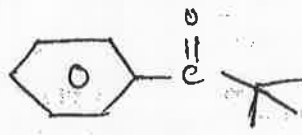
Q. Which one of the following compounds give tautomerism.

KEY POINT

- ① 1st check α -H in given compound.
- ② After trapping H^+ by a base if $-ve$ charge involve in resonance with $C=O$ then all comp. give tautomerism.

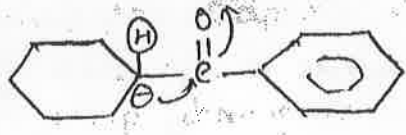


5



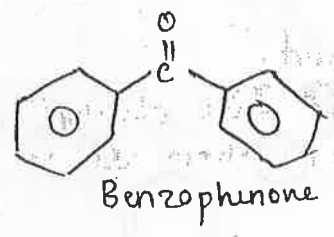
No α -H
No tauto

6



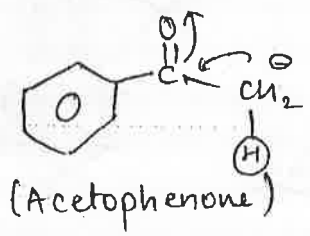
α -H \equiv
 $\ominus \rightarrow$ Reso
 \rightarrow give tautomeris \equiv

7



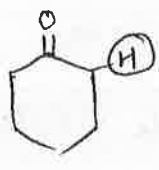
No tauto $\times \times \times$

8



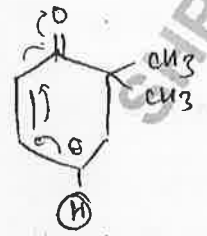
α -H \equiv
 $\ominus \rightarrow$ Reso
give tauto $\checkmark \checkmark$

9



α -H \checkmark
 $\ominus \rightarrow$ Reso \checkmark
give tauto $\checkmark \checkmark$

10



$\ominus \rightarrow$ Reso
 \rightarrow give tauto \checkmark

11



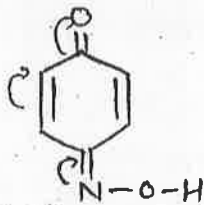
$\ominus \rightarrow$ Reso
give tauto \checkmark
P-tautomerism
pentaid system
space tautomerism

12



No tauto x x

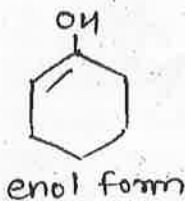
13



⊖ → Reso
give tauto

All Active H → Acidic H⁺

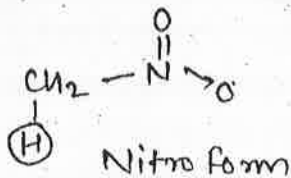
14



enol form

give tauto ✓

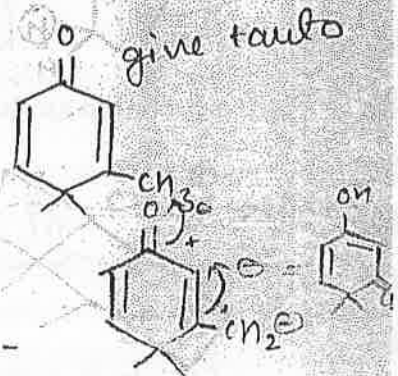
15



Nitro form

give tauto

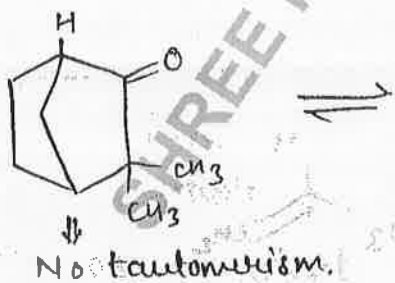
16



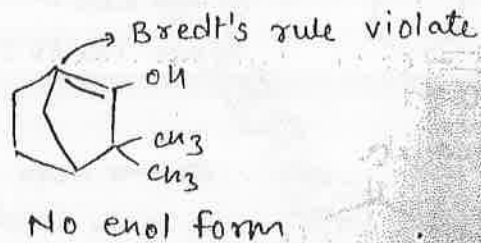
give tauto

|| Bredt's Rule in tautomerism:-

IF Bredt's rule violated in enol form then compound does not exist tautomerism.

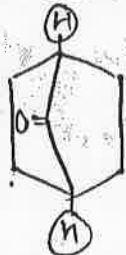


No tautomerism.



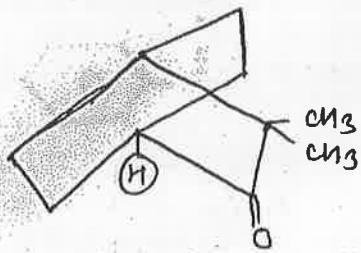
No enol form

2



→ No tauto
→ B.R. violated.

3



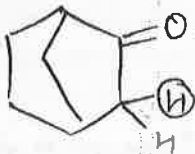
No. tauto

4



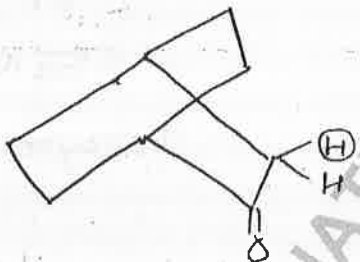
No. tauto

5



give tauto

6

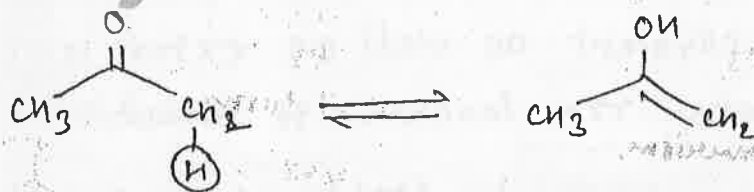


give tauto.

Type of tautomerism :-

① Keto - enol tautomerism.

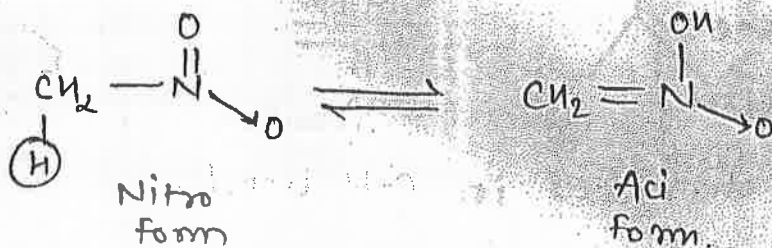
①



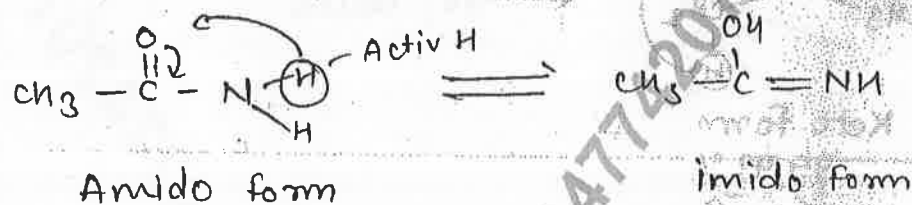
Keto form
triad system

⇒ 6 Deuterium exchange.

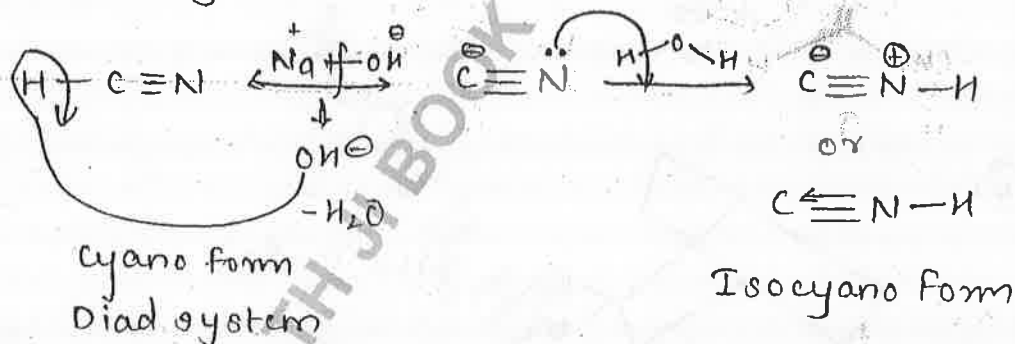
② Nitro - Aci form \rightarrow



③ Amido - imido form tauto \rightarrow



④ Cyano - isocyano tauto \rightarrow



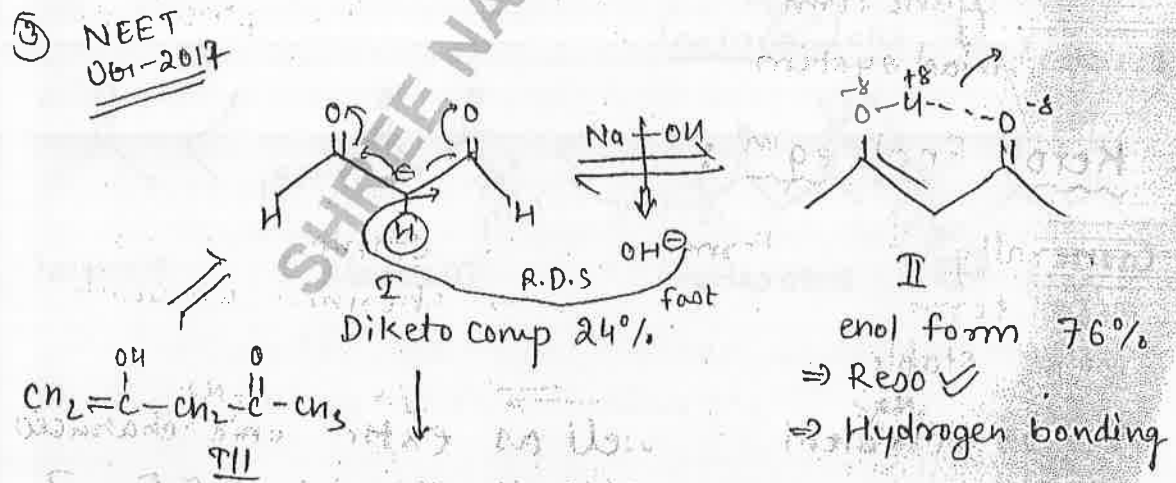
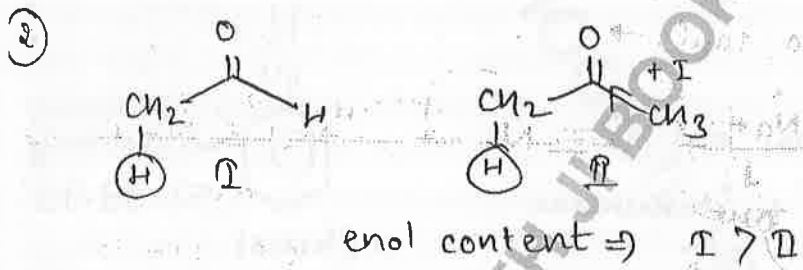
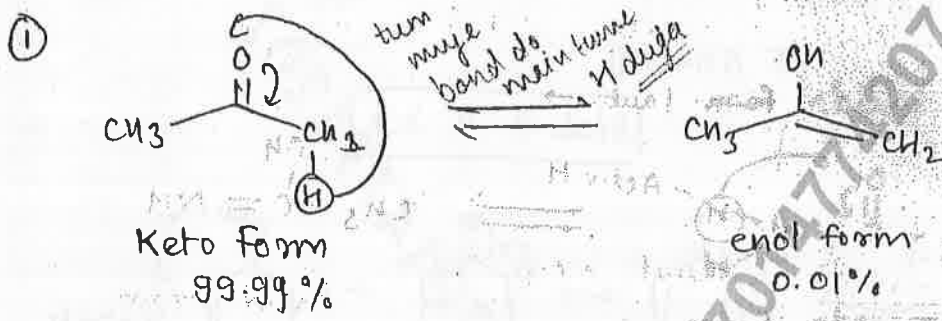
Keto - Enol eqm :-

① Generally keto form is more stable than its enol form because $[\text{C}=\text{O}]$ is thermodynamically more stable bond.

It is as covalent as well as extra ionic character. that's why rxn favours to direction of $[\text{C}=\text{O}]$.

② Enol form may be stable than its keto form if following factors are present in enol form,

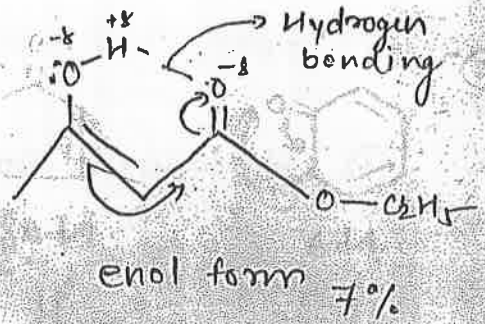
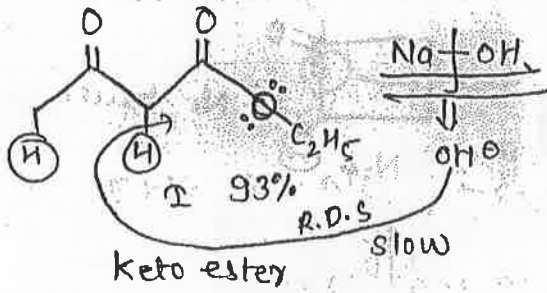
- ① Hydrogen bonding
- ② Resonance
- ③ Aromaticity
- ④ Acidic characters in C-H bond.



\Rightarrow Acidic character in C-H bond \uparrow
 \Rightarrow R.D.S fast
 \Rightarrow enol content

stab = II > I > III

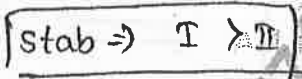
(4)



Aceto Acetic Ester

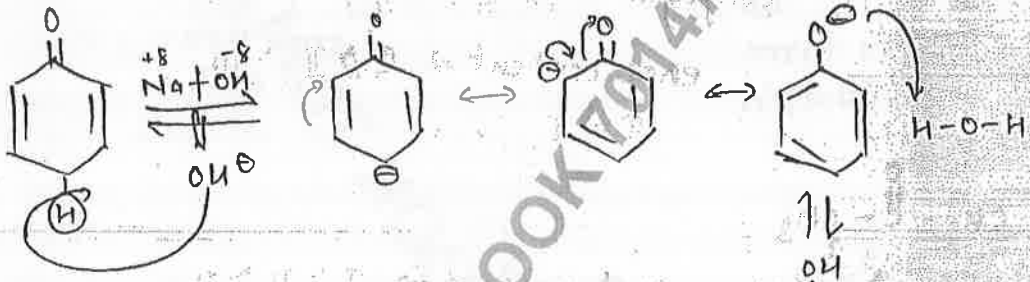
(AAE)

Stability of Anion ↓



⇒ Reso ✓
⇒ Hydrogen bonding

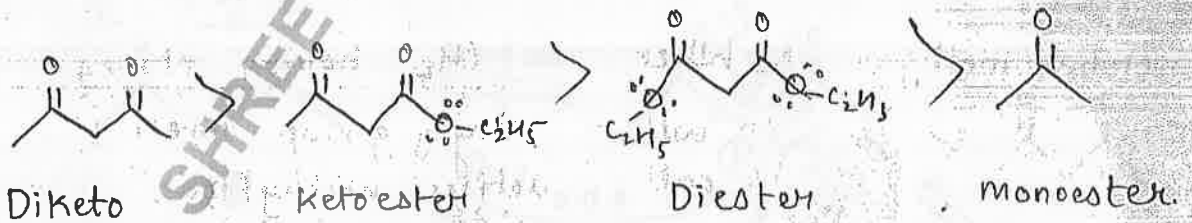
(5)

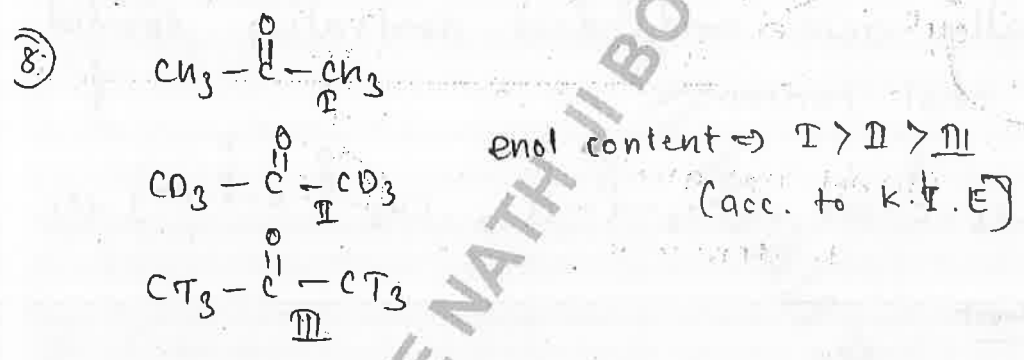
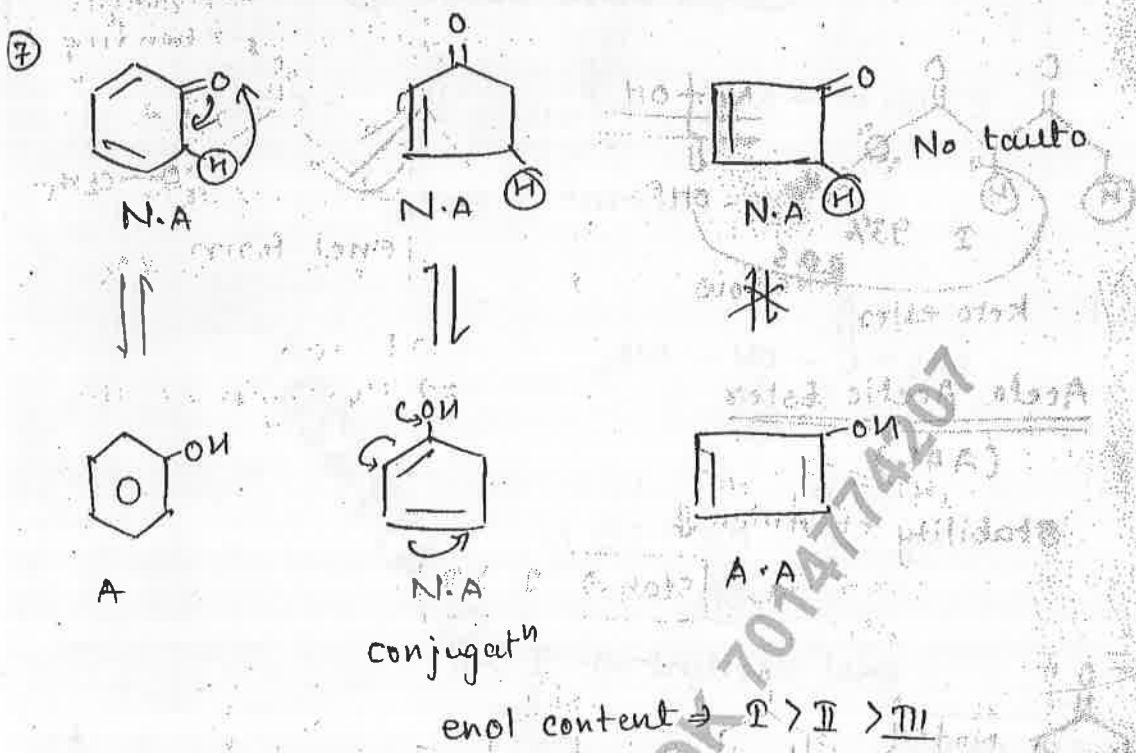


Phenol not give tautomerism.

→ Aromatic
→ 99.99%
→ Phenol
→ enol form

(6) Order of enol content -

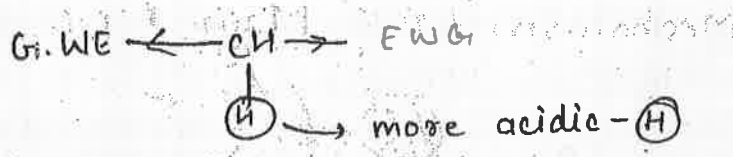




KEY POINT

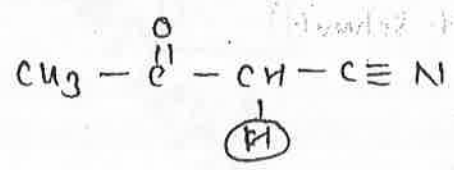
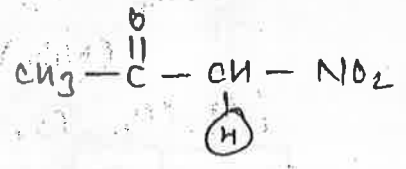
Active methylene \rightarrow Whenever CH₂ having strong e⁻ withdrawing group then it is called active methylene.

In case of Active methylene enol content form always more than 50%.



enol content $> 50\%$

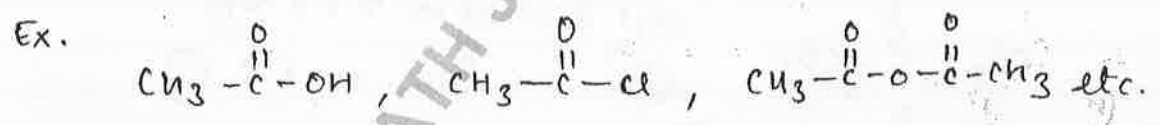
Q.1



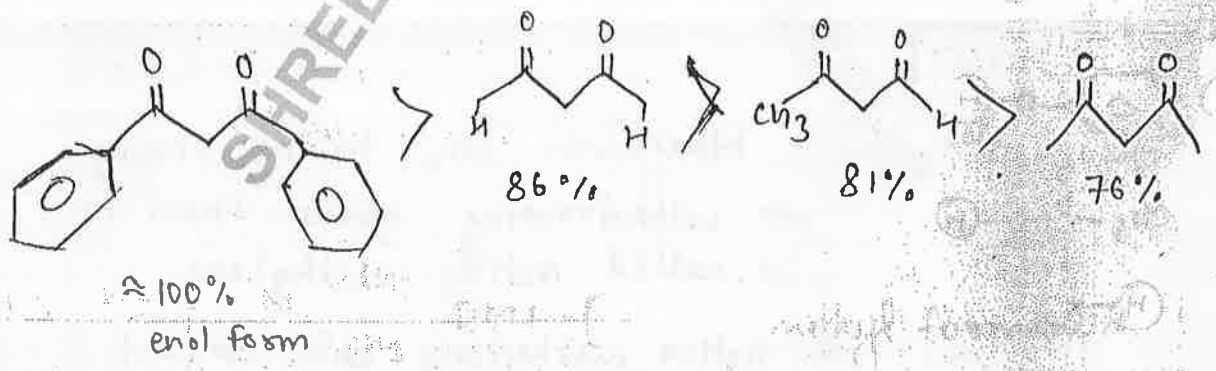
enol content $\Rightarrow \text{I} > \text{II}$

KEY POINT

Generally acid and acid derivatives formed less enol content.



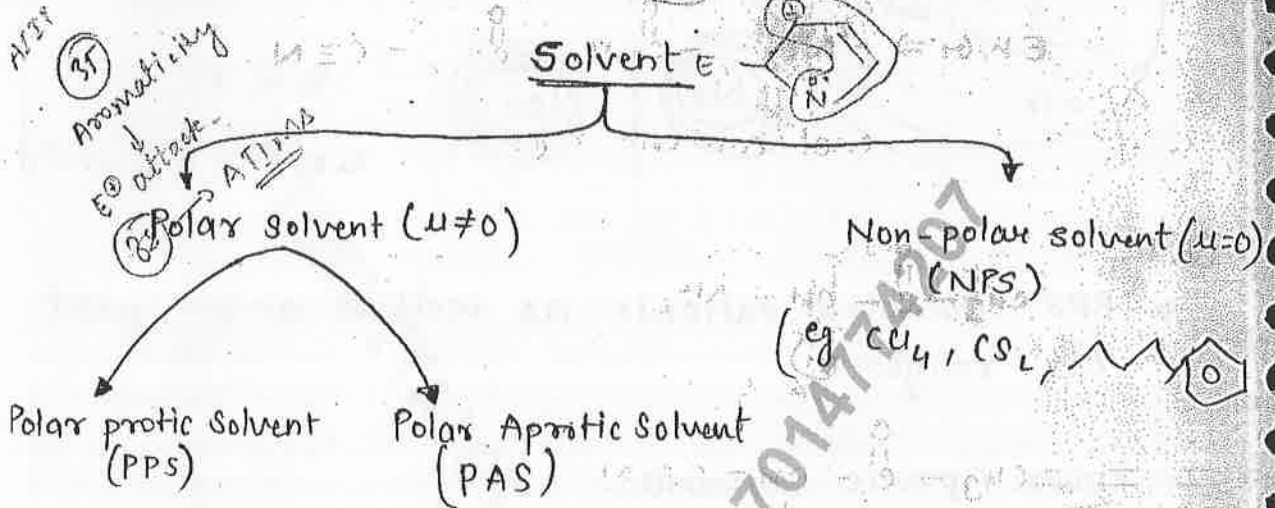
Enol content



Reaction Mechanism - 1

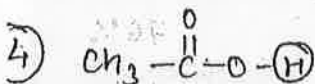
Main Topic

① Solvent:



② Polar protic solvent :- (PPS)

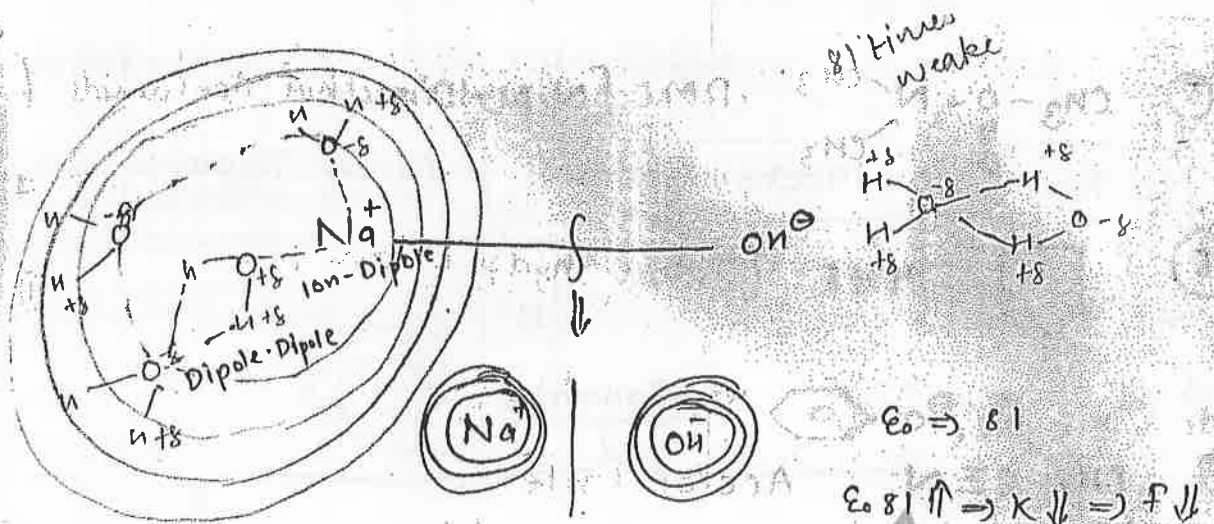
Solvents which are polar in nature & have Active H⁺.



⑥ $NH_3, R-NH_2$ etc.

Polar + Active-H

↓
PPS.

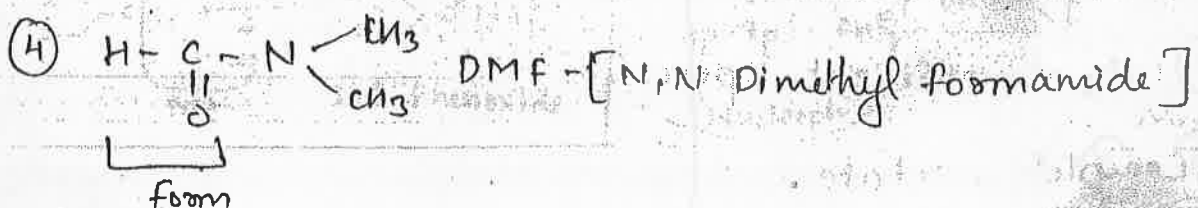
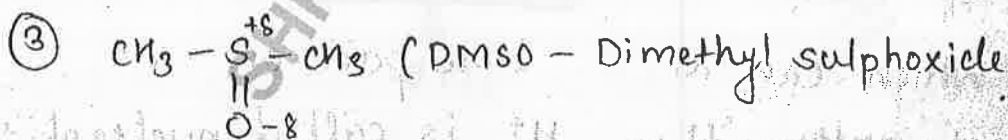
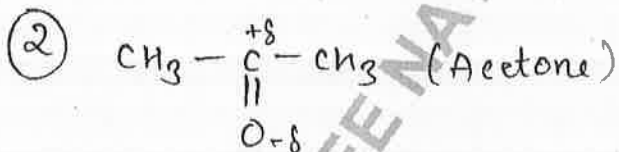


↳ PPs solvated cationic as well as anion part of reagent.

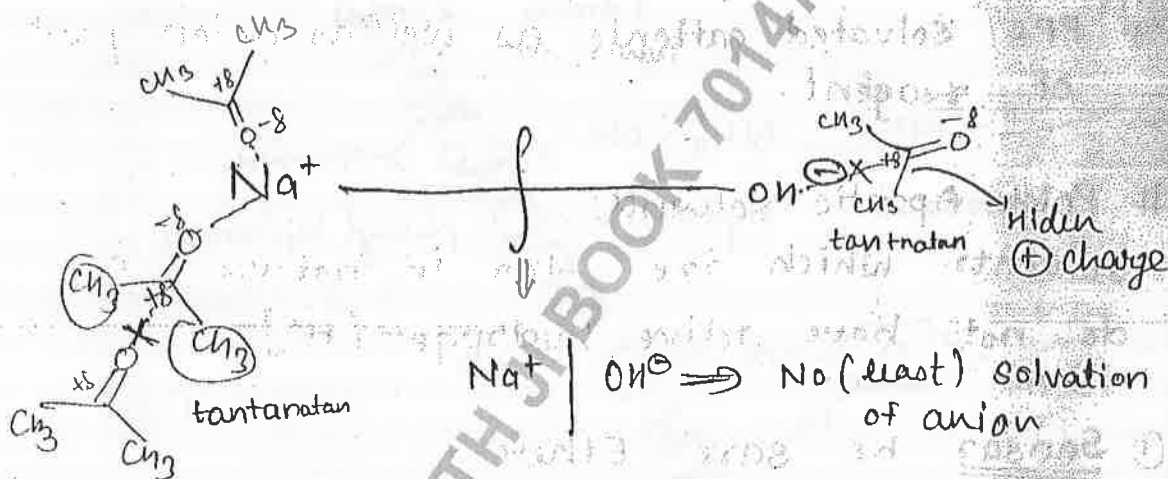
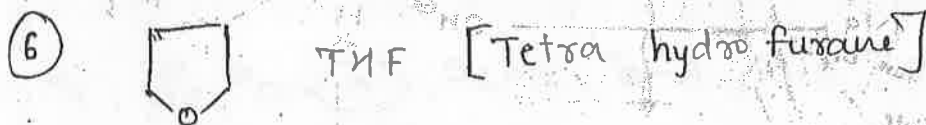
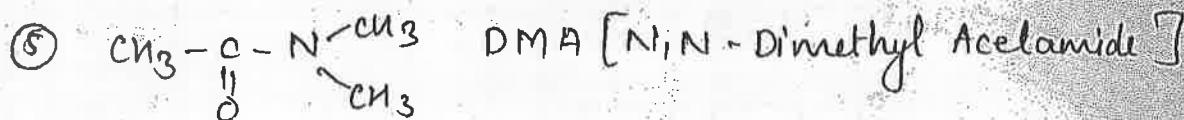
Polar Aprotic Solvents:-

solvents which are polar in nature but do not have active hydrogen $[H^+]$.

① Sansar ke sare Ether



shree nath ji book depot kota



→ Polar aprotic solvent solvate only cation part of reagent.

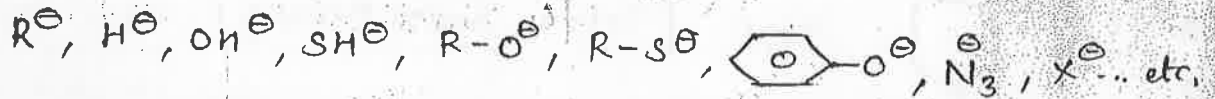
Nucleophile $[\text{Nu}^-]$:-

- Species which can donate lone pair on $-ve$ charge to other than H^+ is called nucleophile
- Electron efficient species.
- Complete octate.

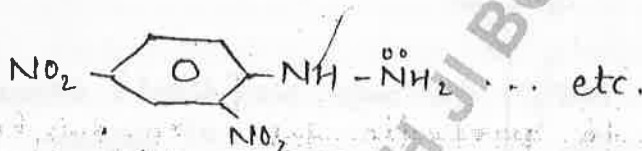
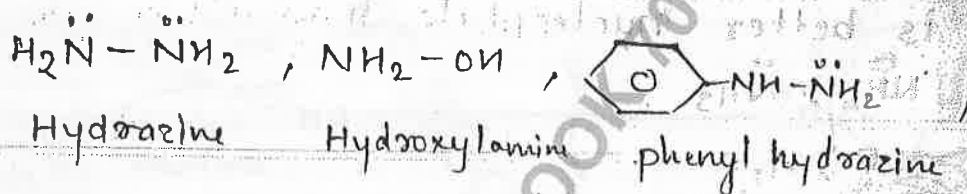
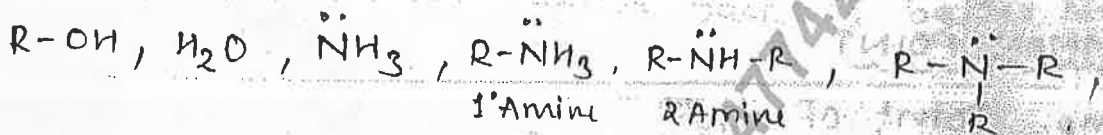
↳ Behave as a Lewis base.

Type of Nu[⊖]

① Anionic Nucleophile.



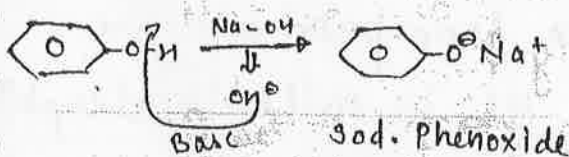
② Neutral Nucleophile:-



Base

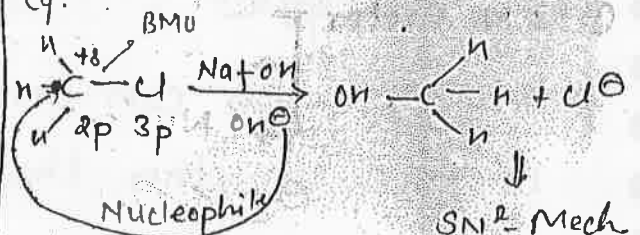
↳ Species which can donate lone pair on -ve charge to H⁺

Eg.



Species which can donate lone pair on -ve charge other than H⁺

Eg.



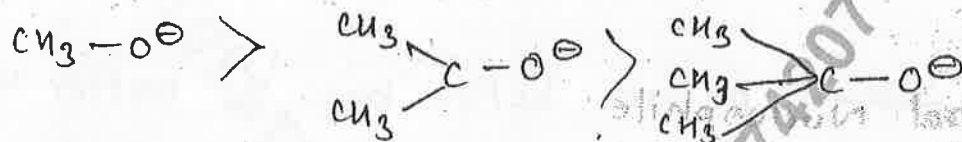
There is no significance of steric hindrance

Thermodynamically controlled process

There is imp. role of steric hindrance.

Nucleophilicity $\propto \frac{1}{\text{steric hindrance}}$

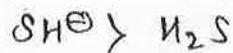
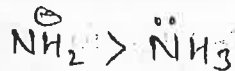
Kinetically controlled process



COMMON POINT

Imp. point of nu^\ominus

① Anion is better nucleophile than its conjugate



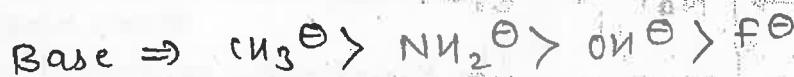
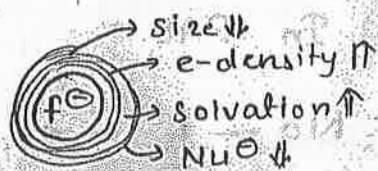
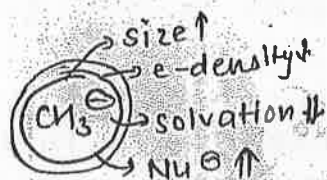
② Nucleophilicity acc. to periodic table co-relation

① Nucleophilicity in period:



① EN factor $\begin{cases} \rightarrow \text{EN} \uparrow \\ \rightarrow \text{stability of Anion} \uparrow \\ \rightarrow \text{Nucleophilicity} \downarrow \end{cases}$

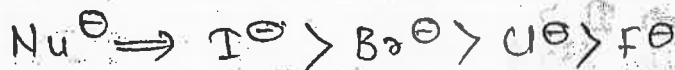
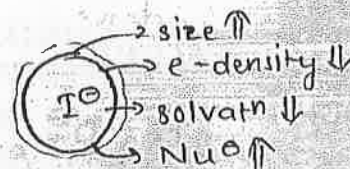
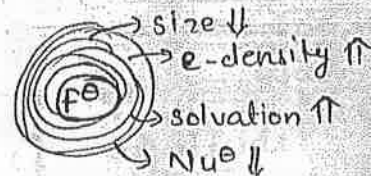
② Solvation \Rightarrow
factor



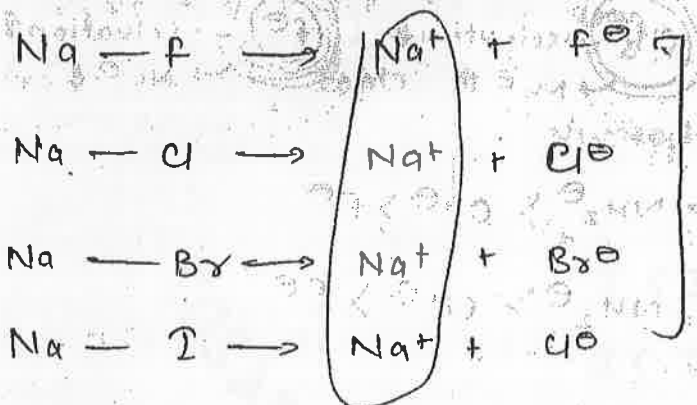
In ~~period~~ period better base is better Nu $^{\ominus}$.

① Nucleophilicity in a group

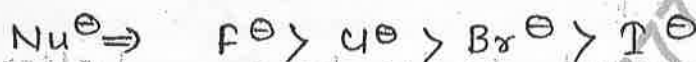
(A) In PPS \rightarrow



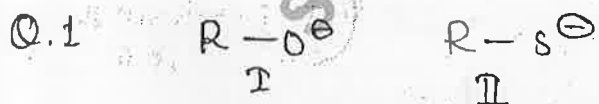
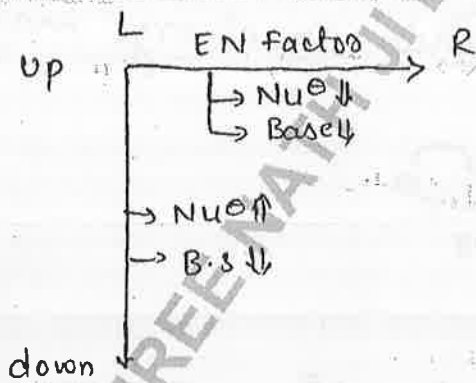
② In PAS →



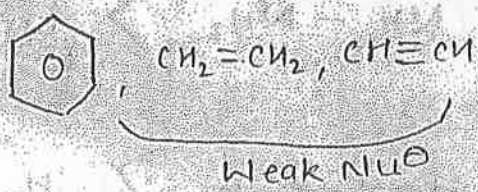
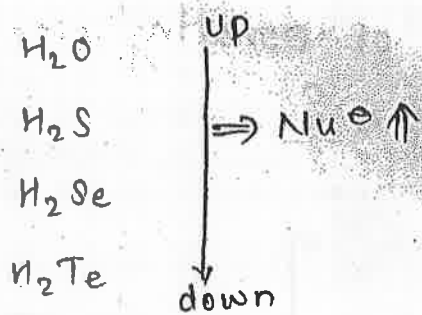
No solvath
of anion



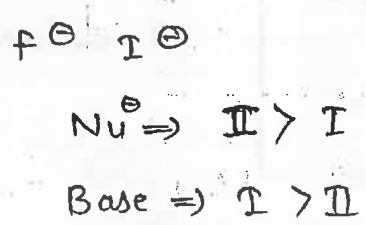
KEY POINT →



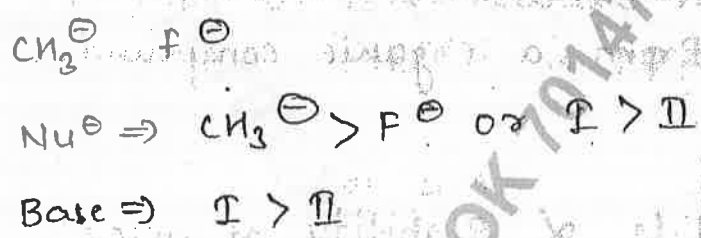
Q.2



Q.3

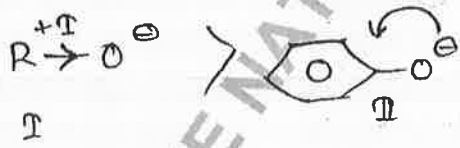


Q.4

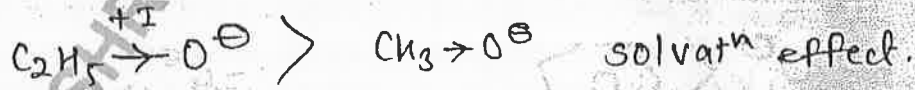


③ Nucleophile depends on charge magnitude:

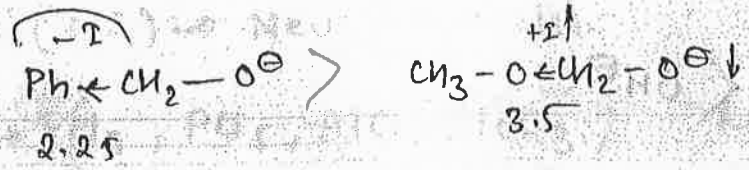
Q.1



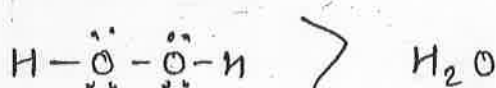
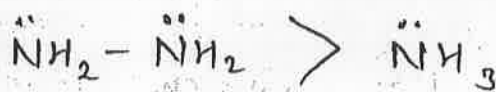
Q.2



Q.3



④ Nucleophilicity \propto No. of Donating site.



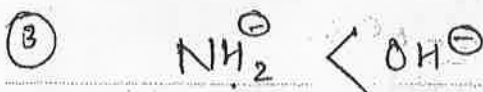
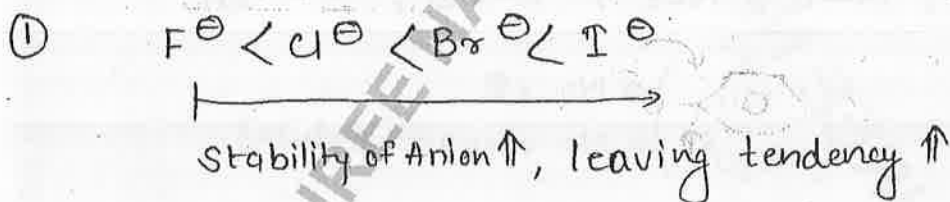
LEAVING GROUP :- (L.G)

Species which can eliminate in the form of $-ve$ charge from a organic compound or substrate

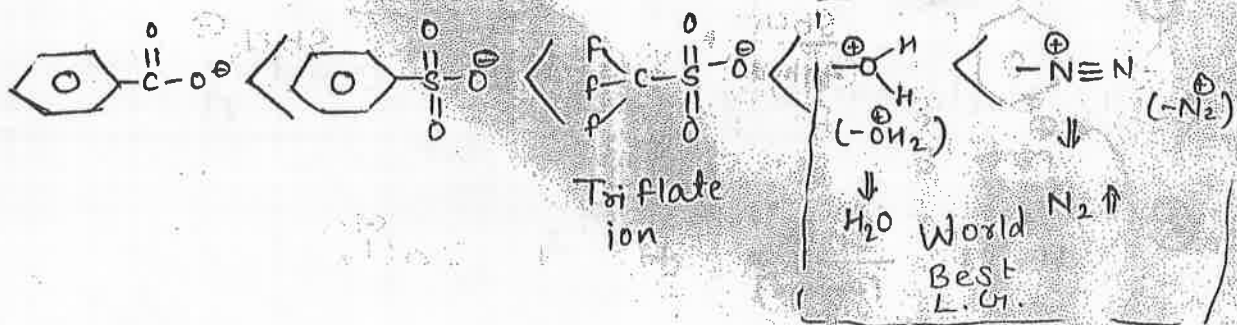
KEY POINT

Ability of L.G \propto Stability of anion

Weaker base are better L.G



OTS, OBS \Rightarrow Leaving group.

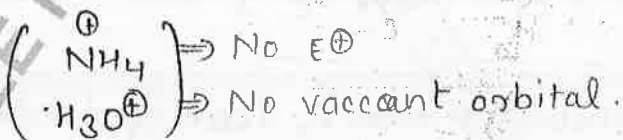
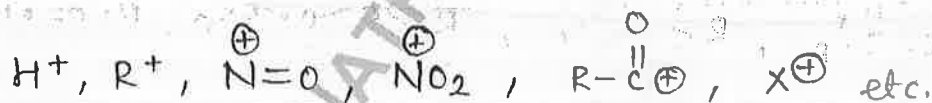


ELECTROPHILE :-

- \hookrightarrow Organic comp. or intermediate having low energy vacant orbital is known Electrophile
- \hookrightarrow Electron deficient species.

Type of electrophile.

(1) Cationic electrophile:-

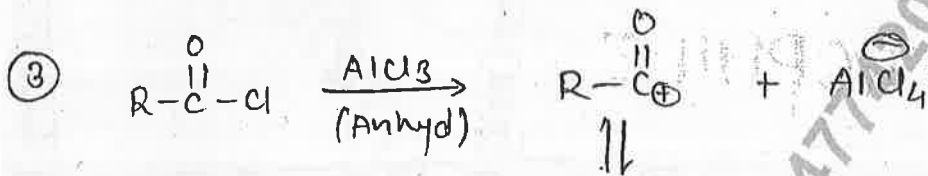
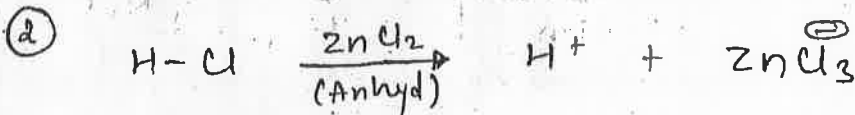
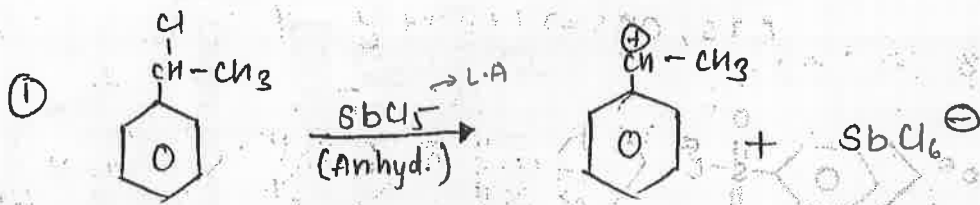


(2) Neutral Electrophile:-

$\hookrightarrow R^0 (f.R) \Rightarrow$ Neutral species.

eg. \hookrightarrow PCl_3 , PCl_5 , $AlCl_3$, $FeCl_3$, Lewis Acid.

\hookrightarrow $GaCl_3$, $SbCl_3$, $SnCl_4$, $ZnCl_2$... etc.

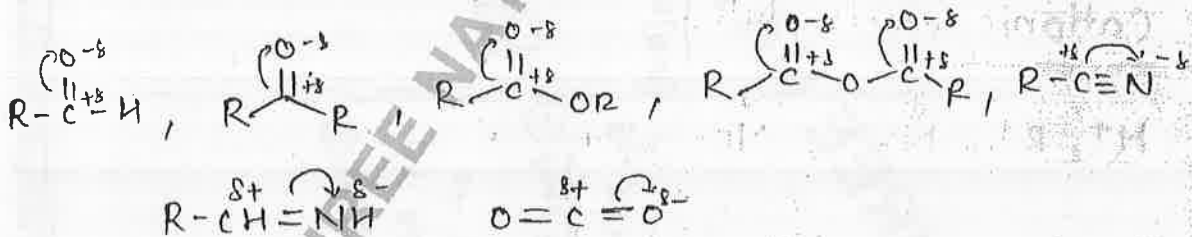


NOTE :-

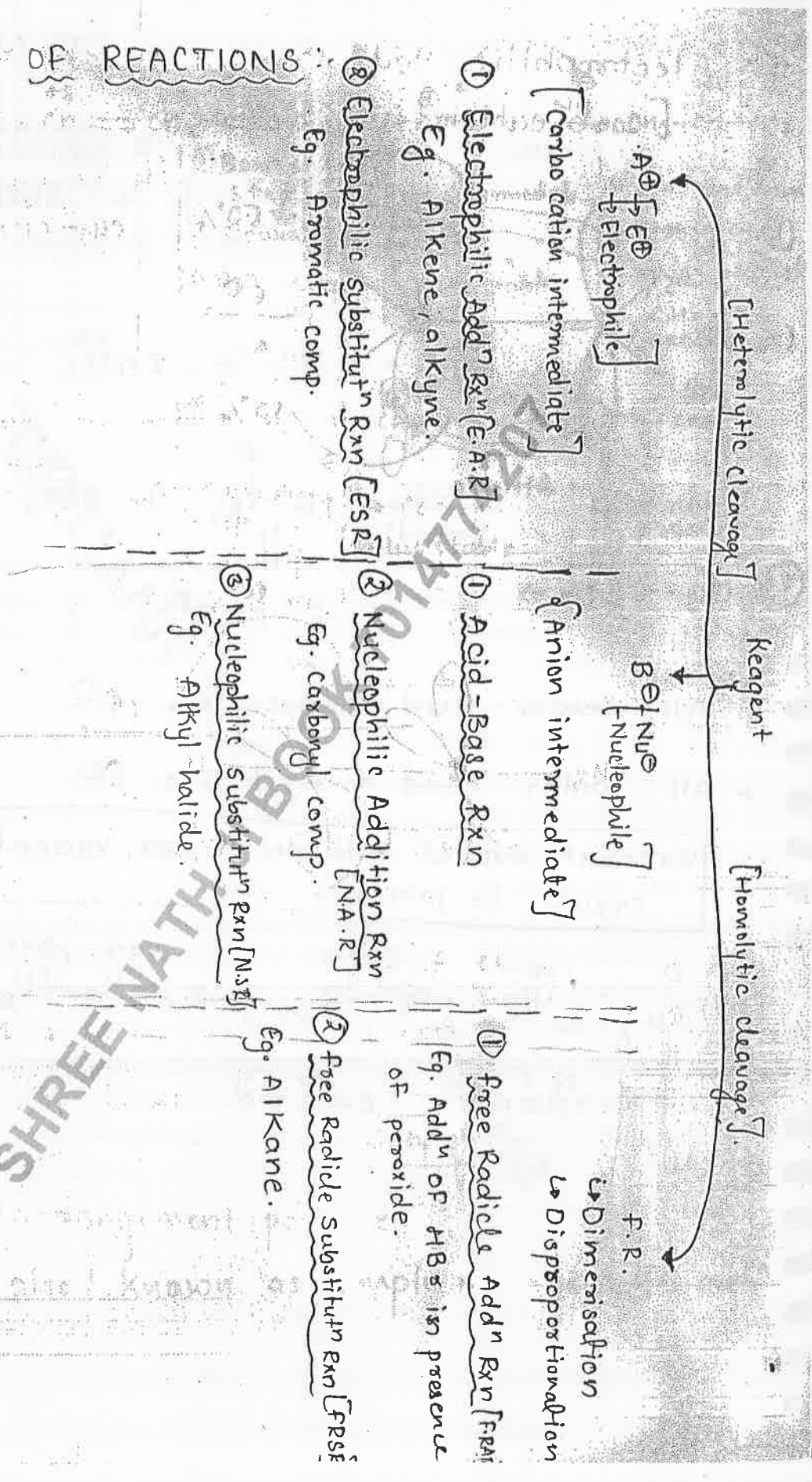
→ All Lewis Acid behave as E^+

→ All polar bond π bond are E^+

Vacant orbital hota nhi h par vacant orbital create ho jata h.



TYPE OF REACTIONS :



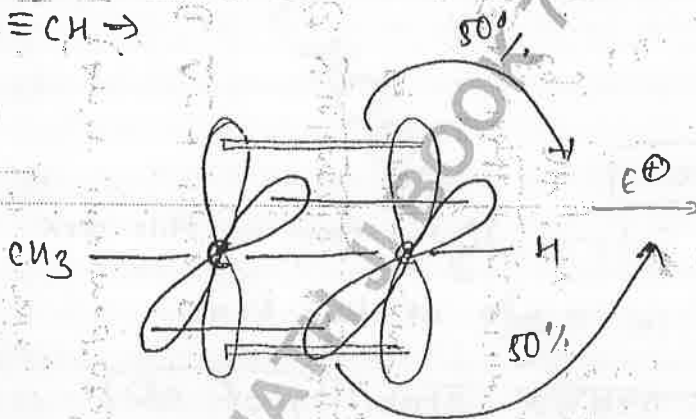
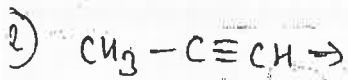
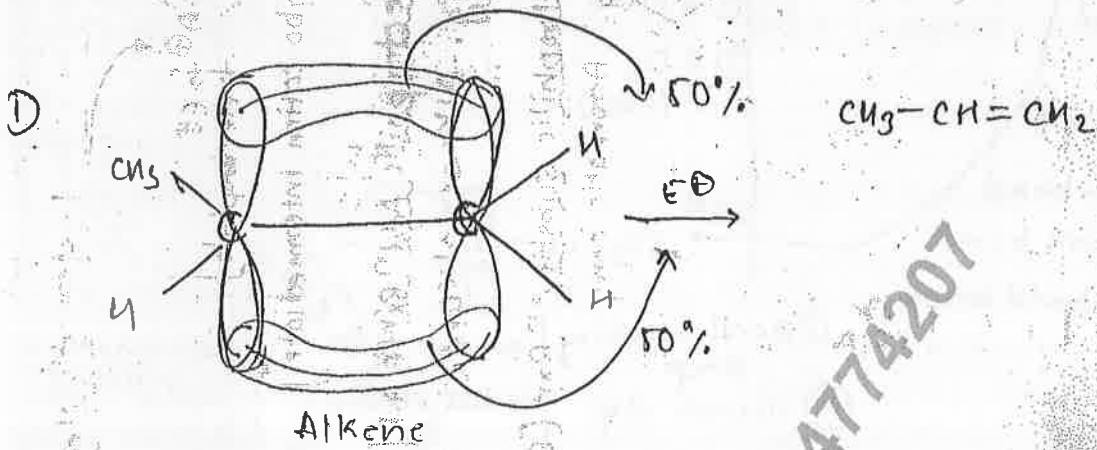
- ① Electrophilic Addn Rxn [E.A.R]
Eg. Alkene, alkyne.
- ② Electrophilic substitun Rxn [E.S.R]
Eg. Aromatic comp.

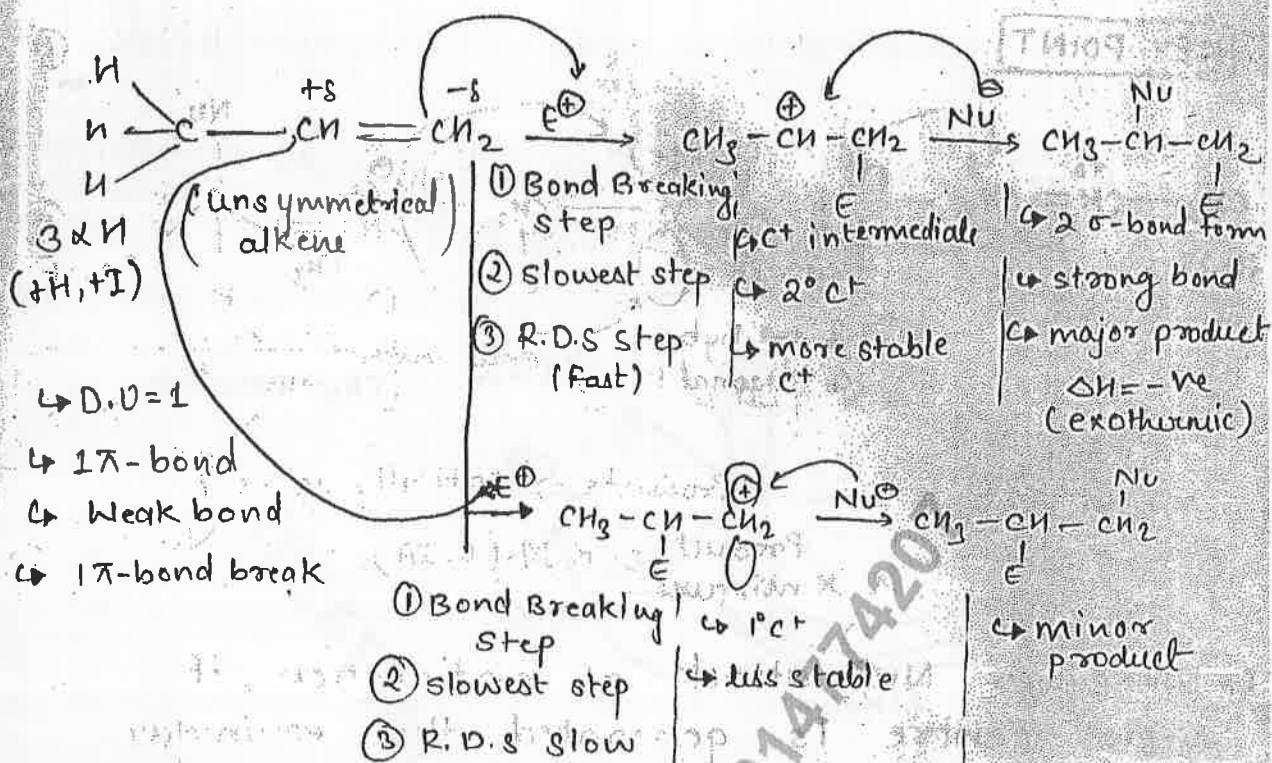
- ① Acid-Base Rxn
- ② Nucleophilic Addition Rxn [N.A.R]
Eg. Carbonyl comp.
- ③ Nucleophilic substitun Rxn [N.S.R]
Eg. Alkyl halide.

- ① Free Radicle Addn Rxn [F.R.A]
Eg. Addn of HB's in presence of peroxide.
- ② Free Radicle Substitun Rxn [F.R.S]
Eg. Alkane.

SHREE NATH

Electrophilic Addⁿ Rxn of Alkene & Alkyne :- [carbocation intermediate]





Important point

↳ Carbo cation intermediate form in this rxn.

↳ formⁿ of C^\oplus in R.D.S of this Rxn.

↳ Reactivity of rxn \propto stability of C^\oplus

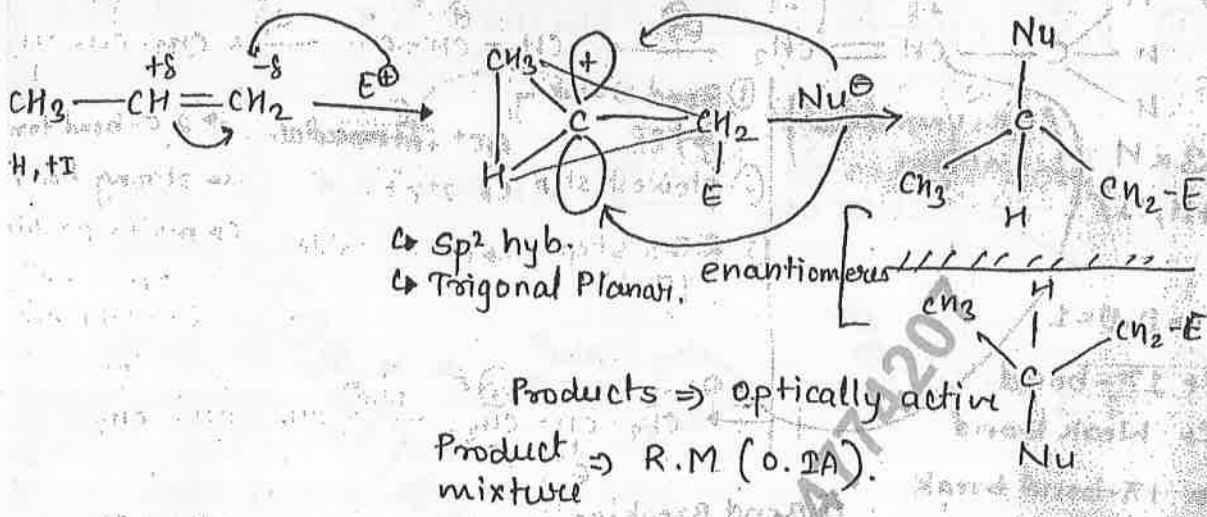
↳ If C^\oplus formed same type then rxn

reactivity of $\text{E}^\oplus_{\text{AR}} \propto \frac{1}{\text{Stability of alkene}}$

↳ C^\oplus rearrangement possible

↳ rxn also known as simple markovnikoff's addⁿ rxn.

KEY POINT

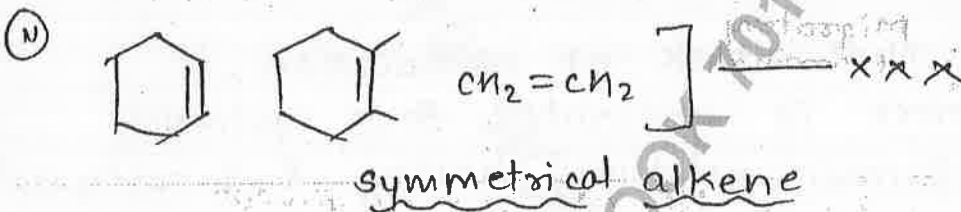
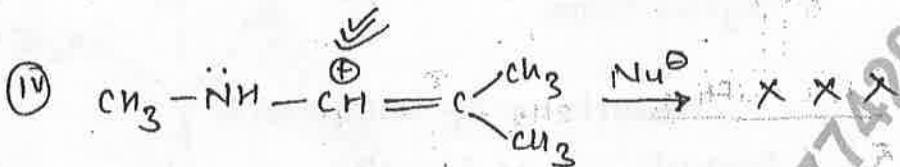
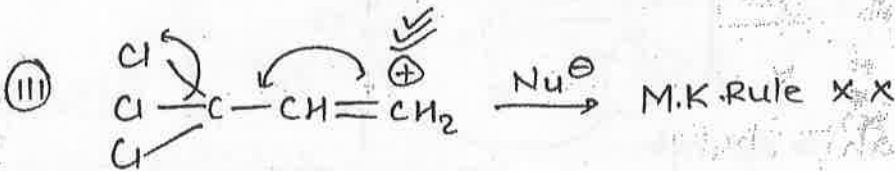
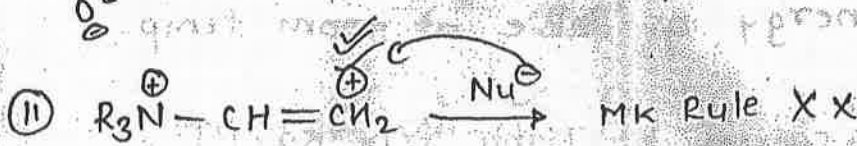


\rightarrow Whenever Nu^\ominus attack at carbocation, if chiral centre is generated then equimolar mixture (Racemic mixture) having R, S configurations with their respective chiral centre obtained as a product.

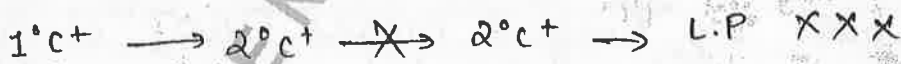
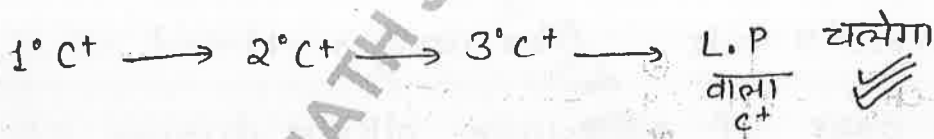
Markovoff's rule (for unsymmetrical alkene)

\hookrightarrow In case of unsymm. alkene during EAR -ve part of reagent means $[\text{Nu}^\ominus]$ always goes to that unsaturated carbon having least no. of hydrogen atom. XXXX. \downarrow
 Not followed always

During EAR -ve part of a reagent means $[\text{Nu}^\ominus]$ always goes to that carbon atom where form max. stable cation.

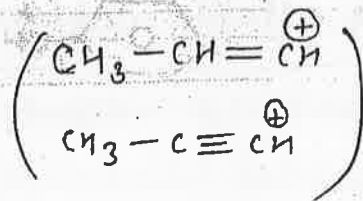


Carbocation Rearrangement



↳ Before product formation C^+ has general tendency to rearrange itself.

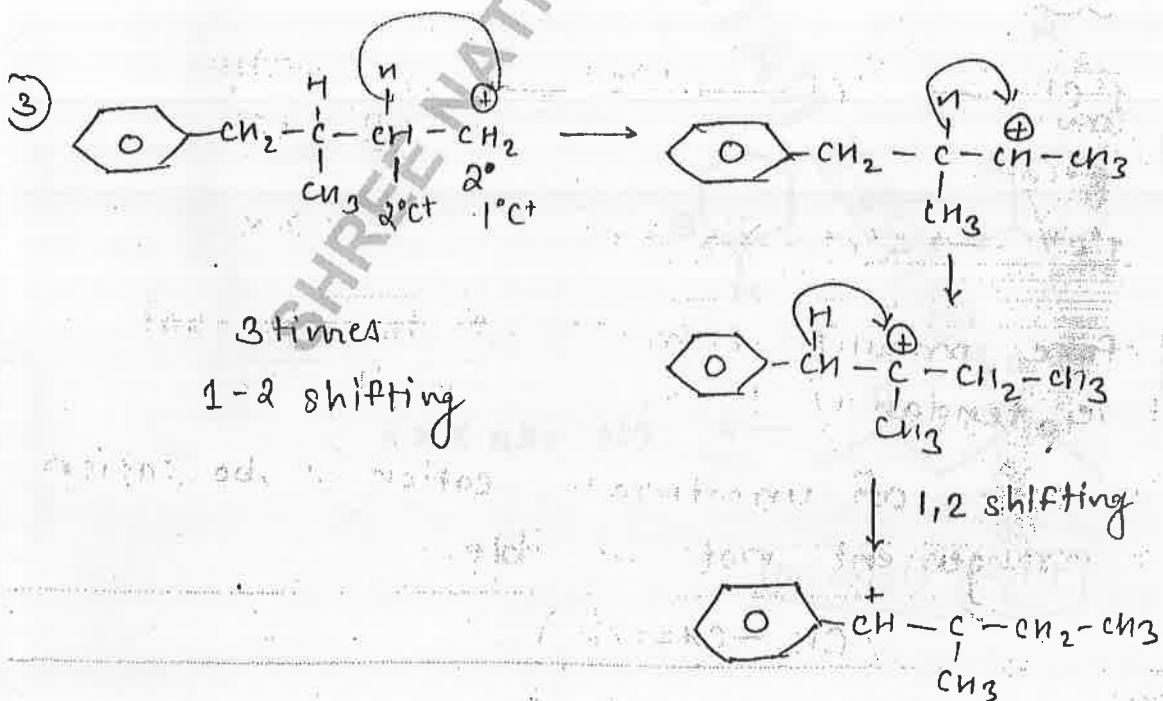
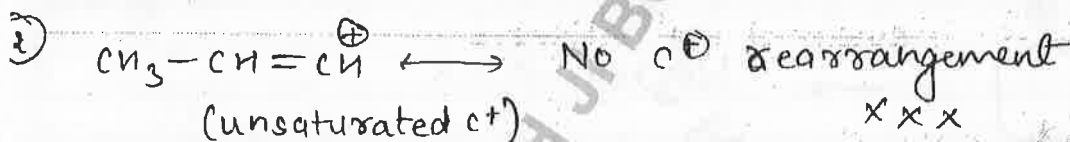
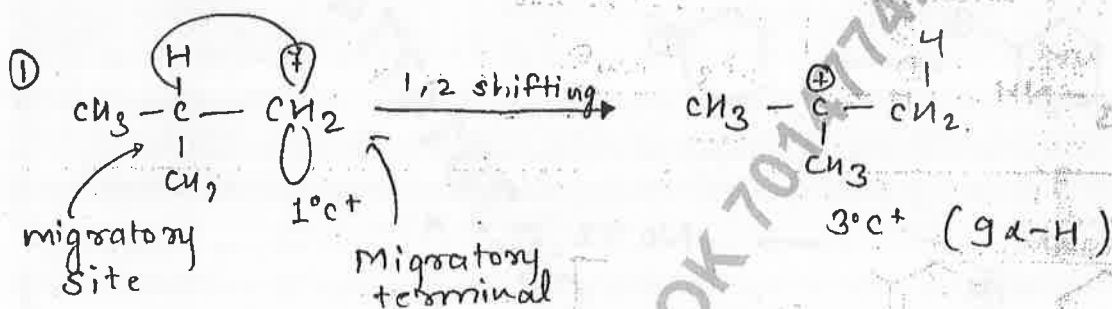
↳ In case of unsaturated cation carbocation rearrangement not possible.

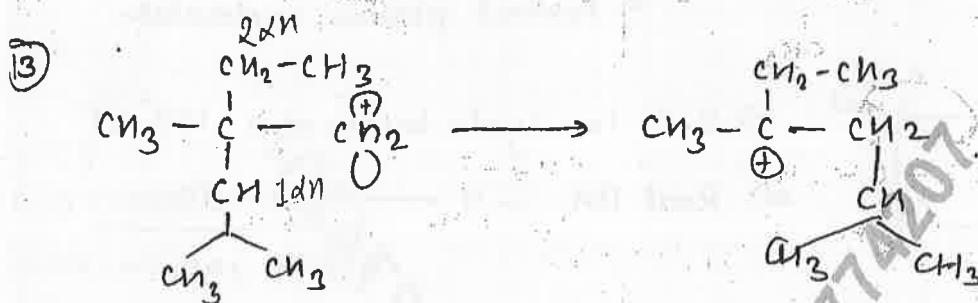
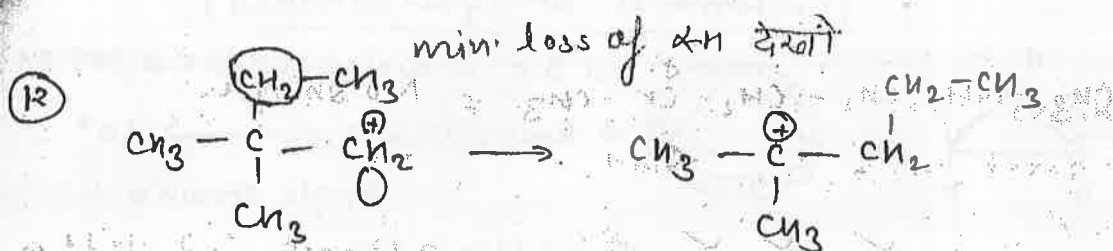


↳ Carbo cation rearrangement is extho exothermic process & energy available at room temp.

① Just carbo cation ka bana rxn ka RDS step

Carbo cation ka rearrangement hona RDS step nahi hota

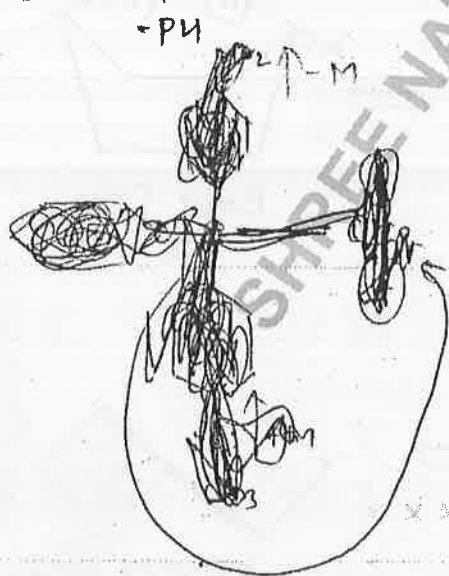




Migratory aptitude

↳ tendency to shift different unit during carbo cation rearrangement.

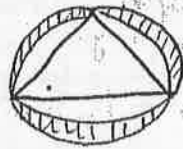
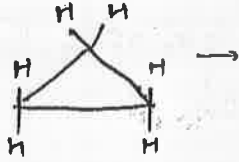
$\text{H}^\oplus > 3^\circ \text{ Alkyl group} > 2^\circ \text{ Alkyl group} > 1^\circ \text{ Alkyl group} > \text{CH}_3$



Ring Expansion :-

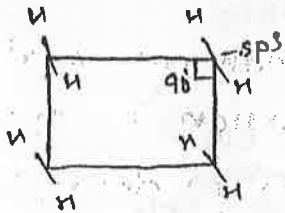
Conformers of cycloalkanes

①



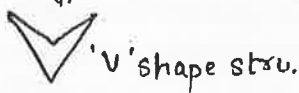
- ⇒ B.A in cyclopropane ⇒ $109^{\circ}28'$
- ⇒ Real B.A —||— ⇒ 60°
- Angle strain ⇒ $49^{\circ}28'$
- ⇒ No flexibility
- ⇒ Perfect planar molecular

②



- ⇒ B.A in cyclobutane ⇒ $109^{\circ}28'$
- ⇒ Real B.A —||— = 90
- A.S ⇒ 19°

Cyclobutane.



- ⇒ More flexible
- ⇒ Non planar.

③

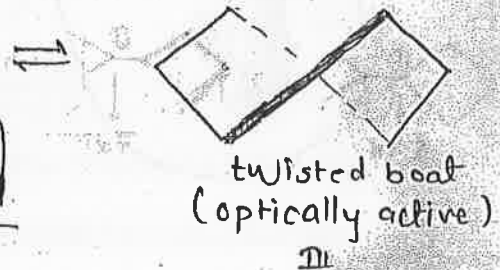
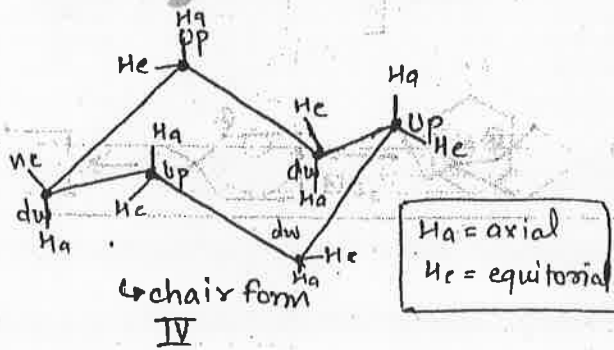
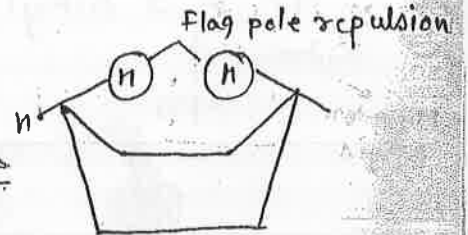
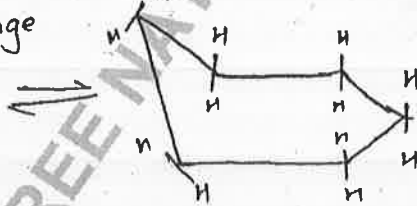
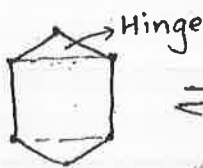


A.S ⇒ 1°

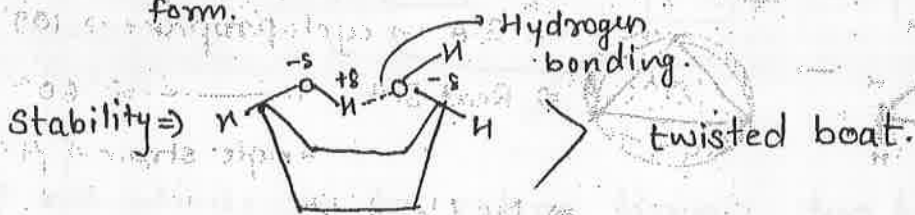


'envelop like str.'

④



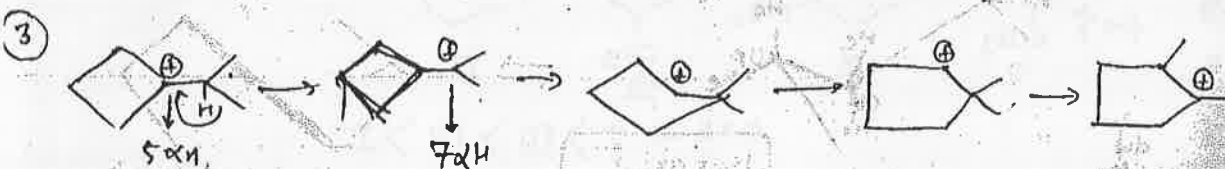
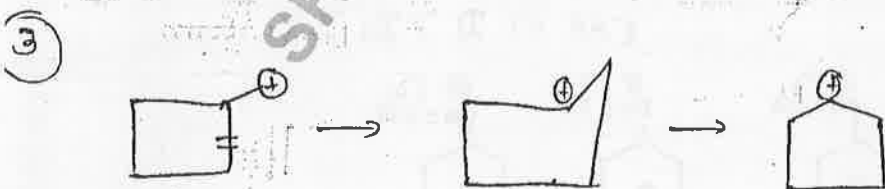
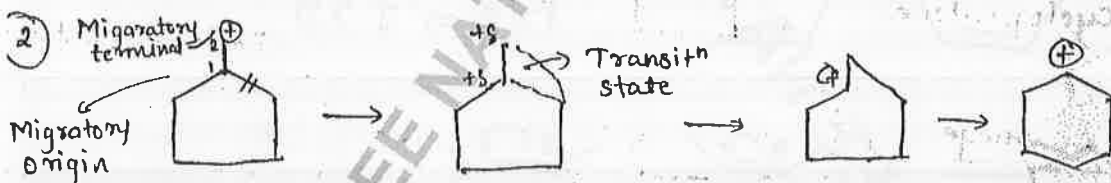
Stability \Rightarrow IV $>$ III $>$ II $>$ I
of Diff. form.



Ring Expansion :-

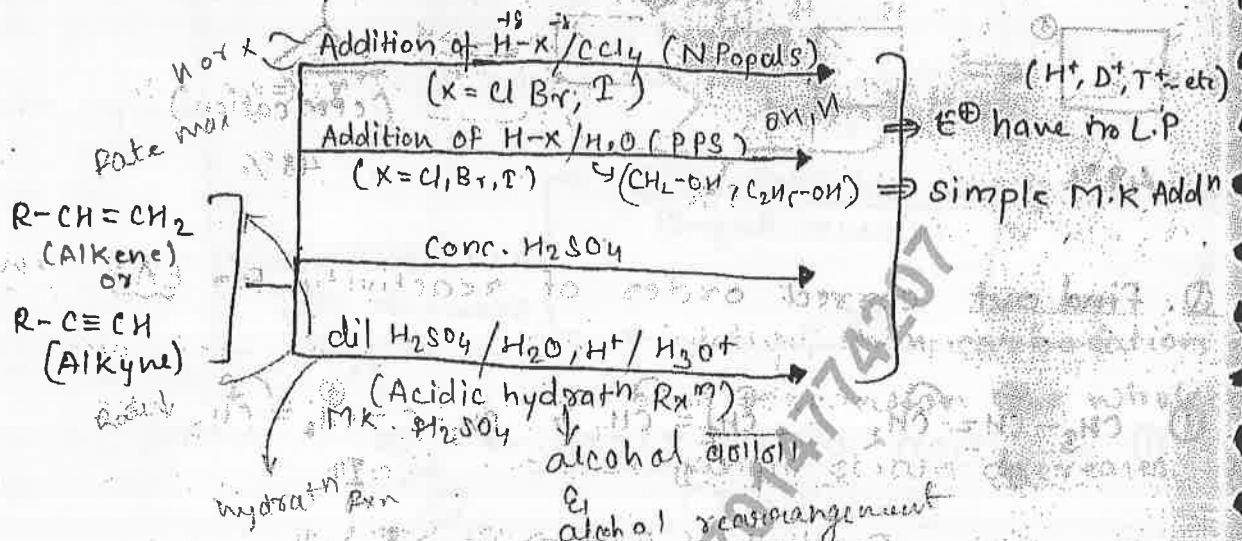
↳ Ring Expansion is more effective than carbocation rearrangement. During ring expansion the whole molecule stable because angle strain decreases.

↳ Ring Expansion is an exothermic process & energy available at room temp.

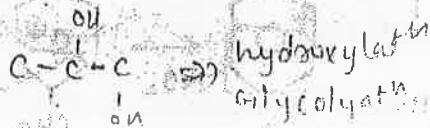
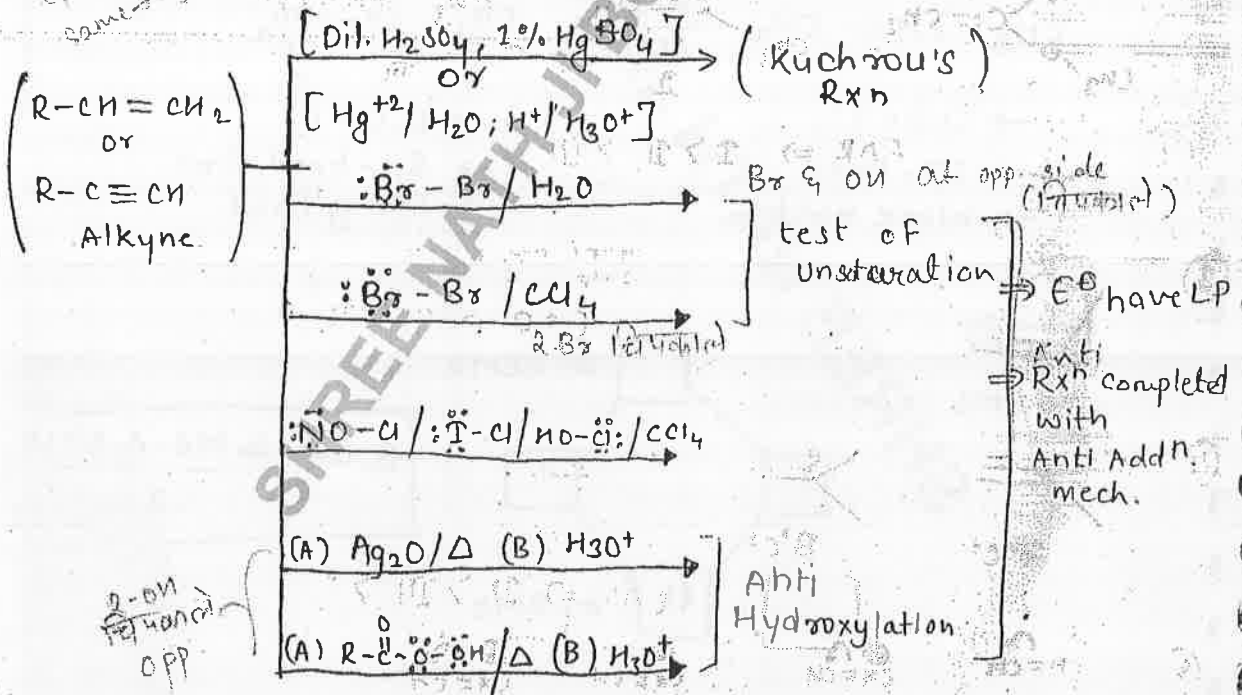


PPS → attack

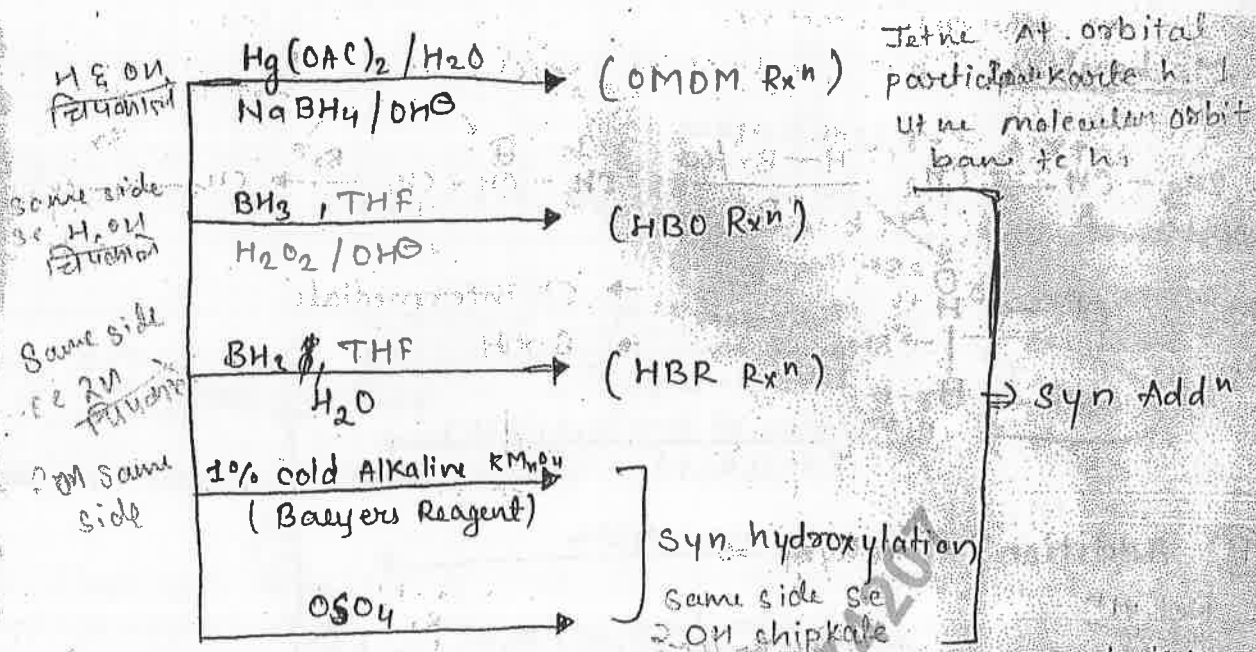
No. L.P. H⁺ → simple M.K. addition



E⁺ & Nu⁻ → anti - L.P. same → syn

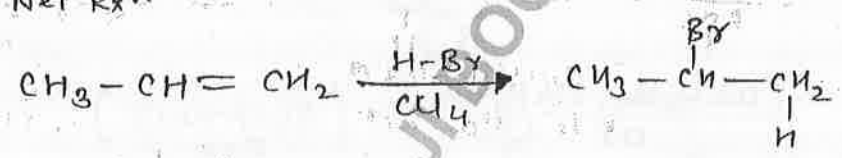


U < V < III < E < SA 3

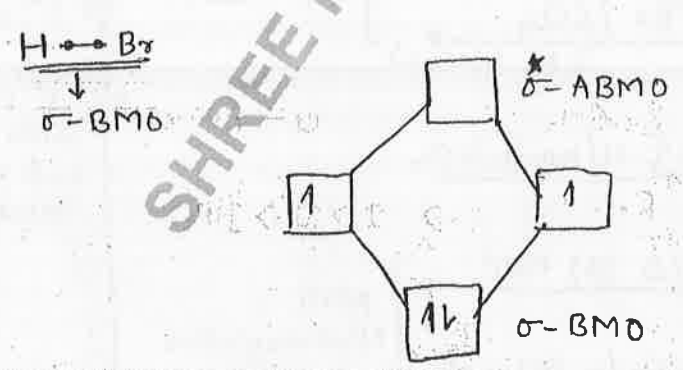


① Addition of H-X/CCl₄ →
 (x = Cl, Br, I)

Ⓐ Addition At Alkene →
 Net Rxn

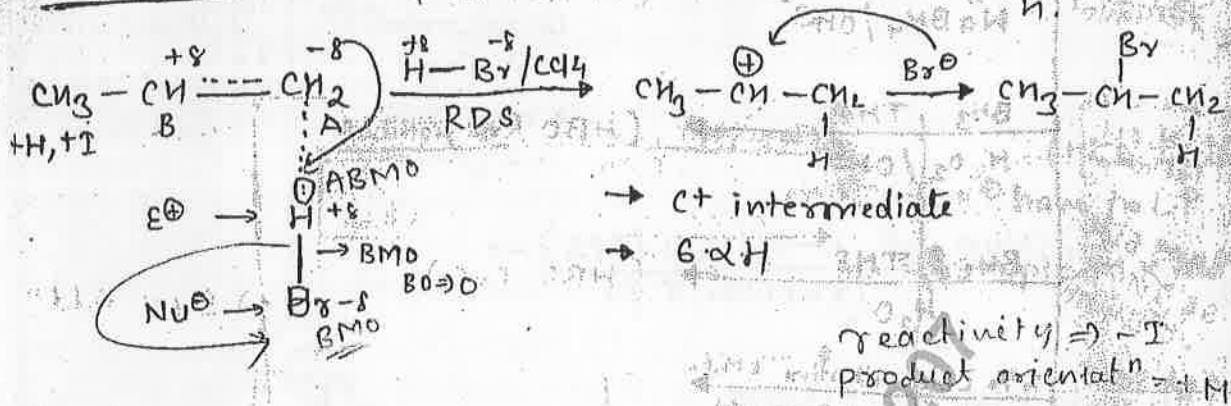


- D.O = 1
- 1π-Bond
- Weak bond
- D.O = 0
- 2σ-bond form
- Strong bond.

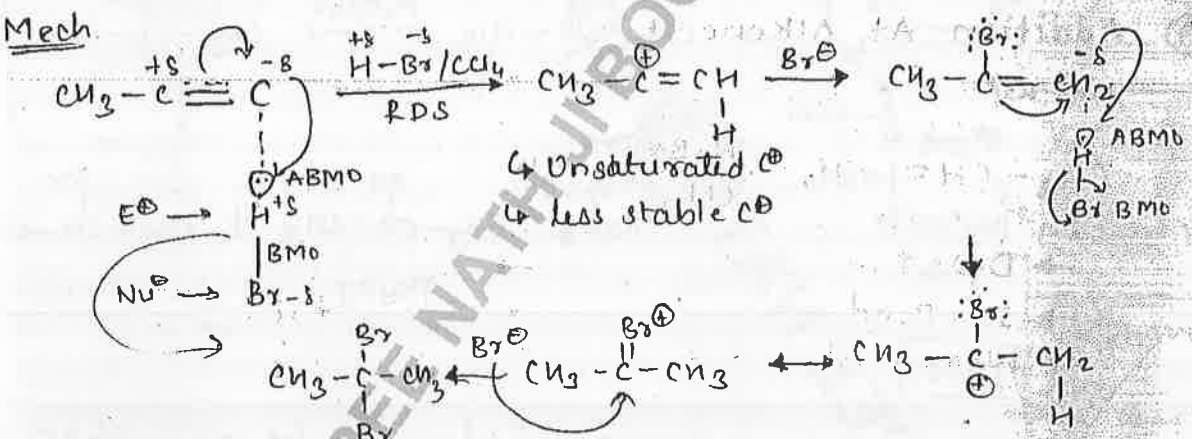
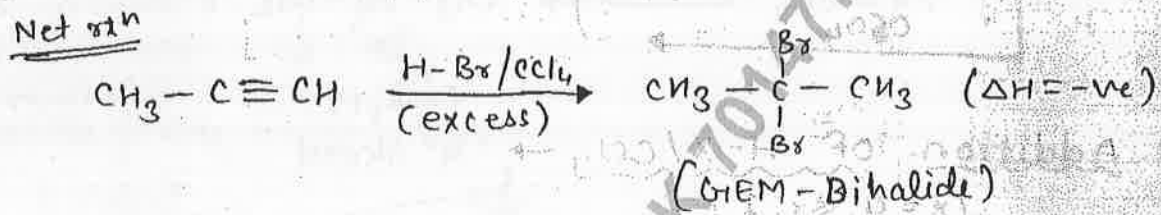


$$\text{B.O} \Rightarrow \frac{\text{B.MO} - \text{A.BMO}}{2}$$

Halogen reactivity - I se control karta hai
Mechanism but product ki orientation ko H⁺ decide karta hai.



B) Addition At Alkyne \Rightarrow



Q. $\text{CH}_3-\text{CH}=\text{CH}_2$ $\text{CH}_2=\text{CH}_2$ $\text{Cl}-\text{CH}=\text{CH}_2$

Reactivity \Rightarrow I > II > III

KEY POINT

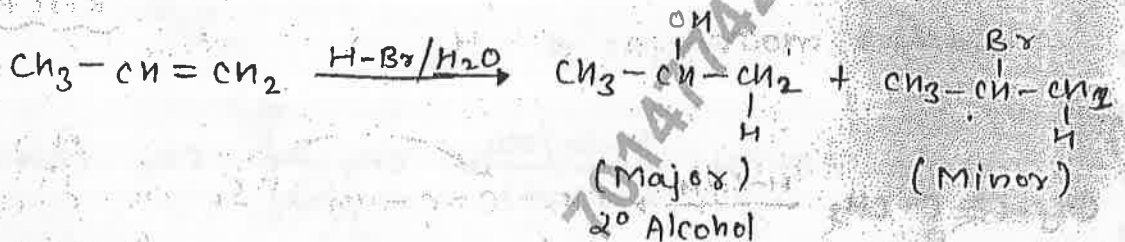
Addⁿ & eliminatⁿ rxn opp. rxn

Generally Reactivity of EAR \Rightarrow Alkene $>$ Alkyne

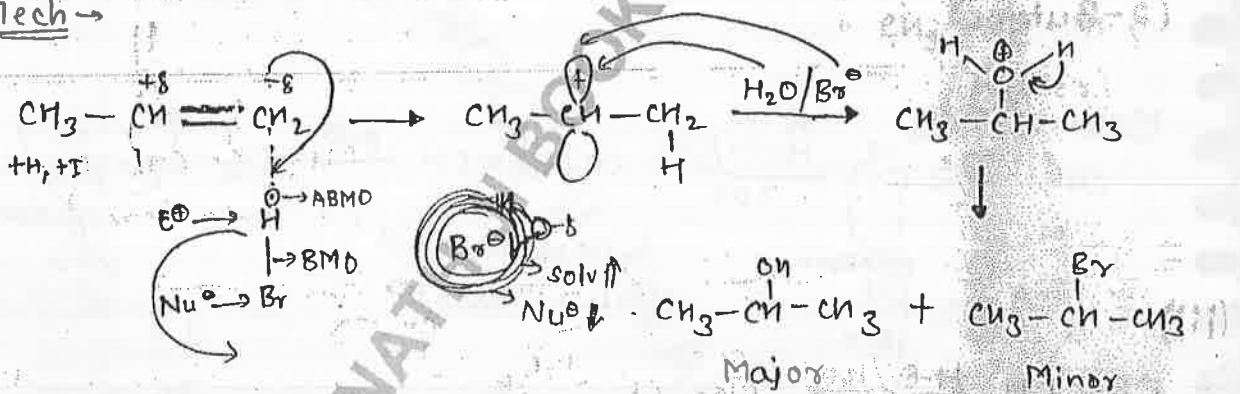
\hookrightarrow saturated c⁺ form \hookrightarrow more stable c⁺ form
 \hookrightarrow Unsaturated c⁺ form \hookrightarrow less stable c⁺ form.

② Addition of H-X/H₂O (PPS) \rightarrow
(X = Cl, Br, I)

① Addition at Alkene



Mech \rightarrow

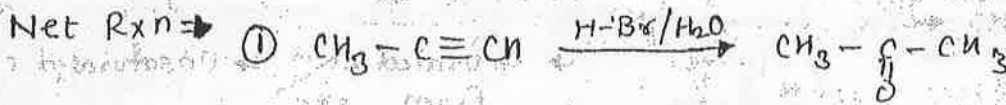


KEY POINT

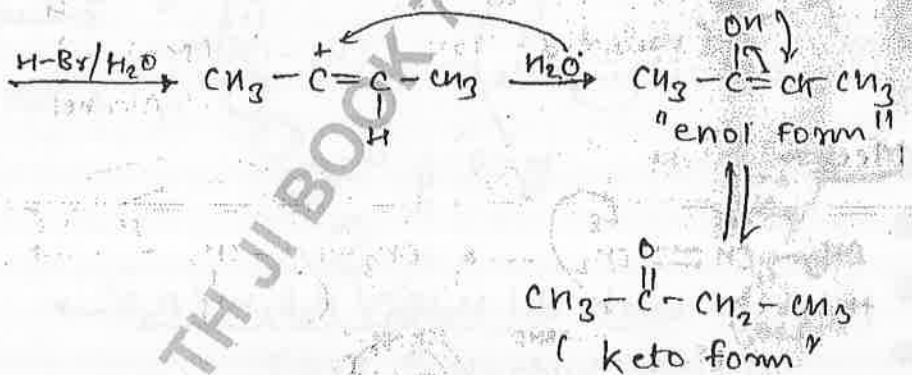
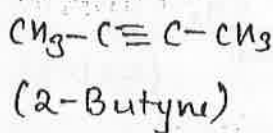
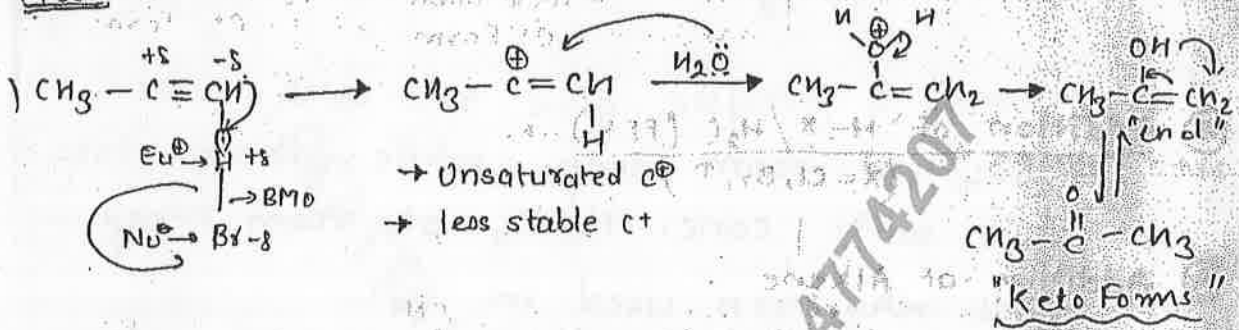
Whenever rxn is carried out in pps then due to solvation of anion its nucleophilicity decreases i.e. solvation solvent addn takes place.

संज्ञा दो

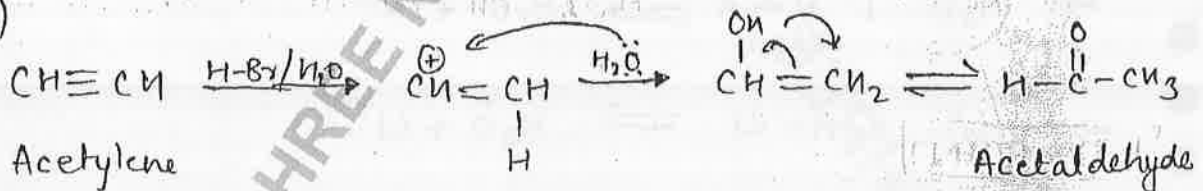
(B) Addition of Alkyne:-



Mech



ii)

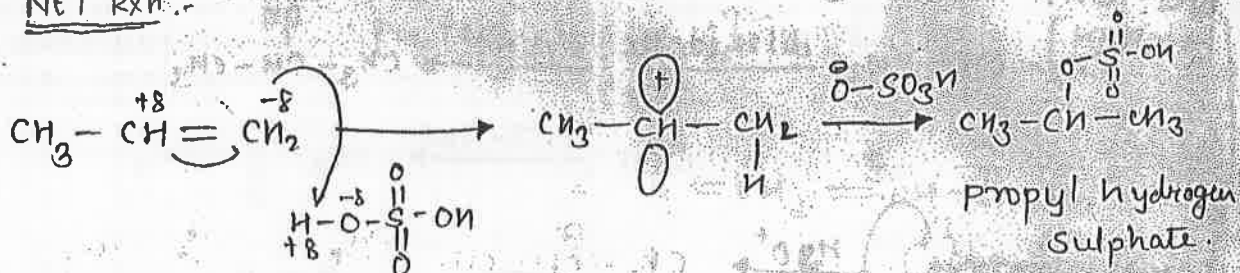


KEY POINT

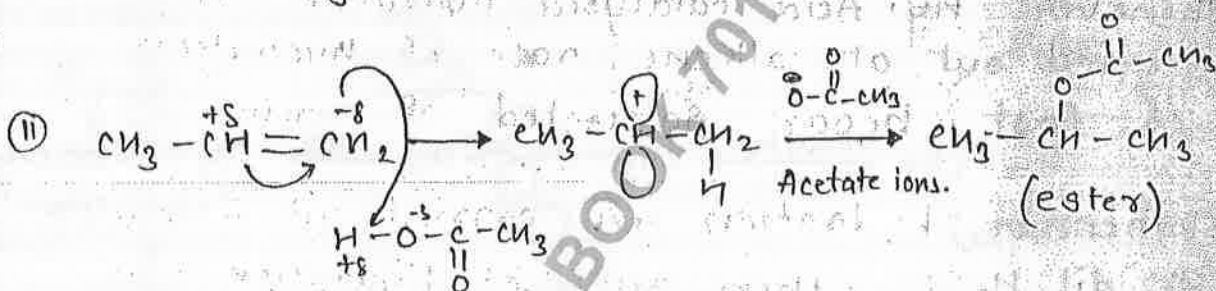
Whenever EAR rxn carried out in alkyne in presence of $\text{H-X}/\text{H}_2\text{O}$, then all alkyne give ketone while acetylene gives aldehyde product.

ⓑ Addition of conc. H_2SO_4 : $\left[\begin{matrix} NaCl \\ KCl \end{matrix} \right] \rightarrow$ No rxn inter configuratⁿ

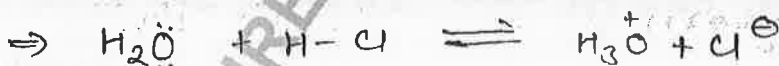
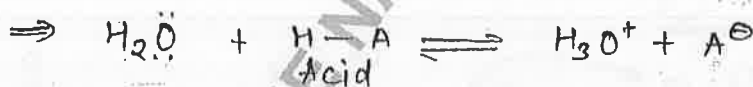
NET Rxn:-



* Alkene & Alkyne give rxn with conc. H_2SO_4 at room temp., while alkane does not react with conc. H_2SO_4 at room temp. That's why rxn used in POC.

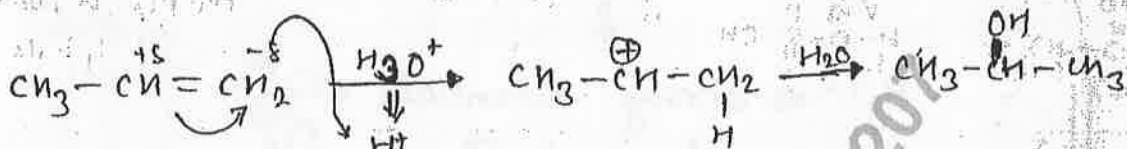
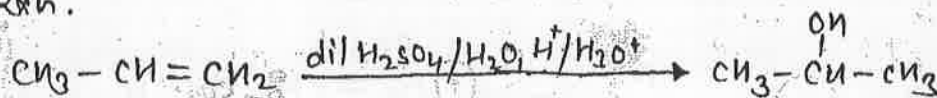


④ Rxn with dil $H_2SO_4 / H_2O, H^+ / H_3O^+$
(Acidic hydration Rxn)



① Addition of Alkene →

Net Rxn.



⇒ C^+ intermediate

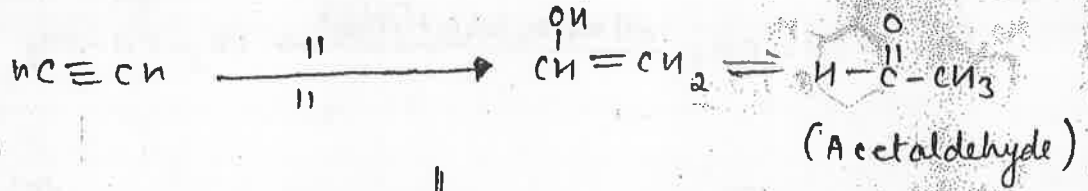
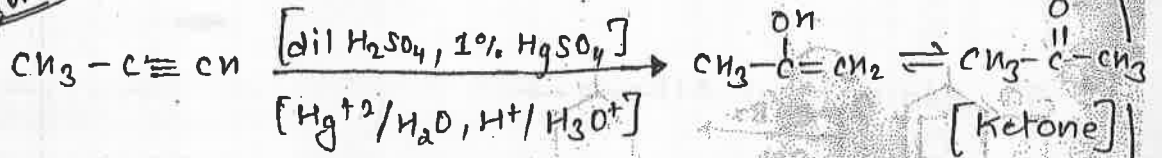
⇒ $\delta \alpha - \text{H}$

Whenever by Acid catalysed hydration rxn carried out at alkene rate of hydration is fast becoz saturated C^+ form.

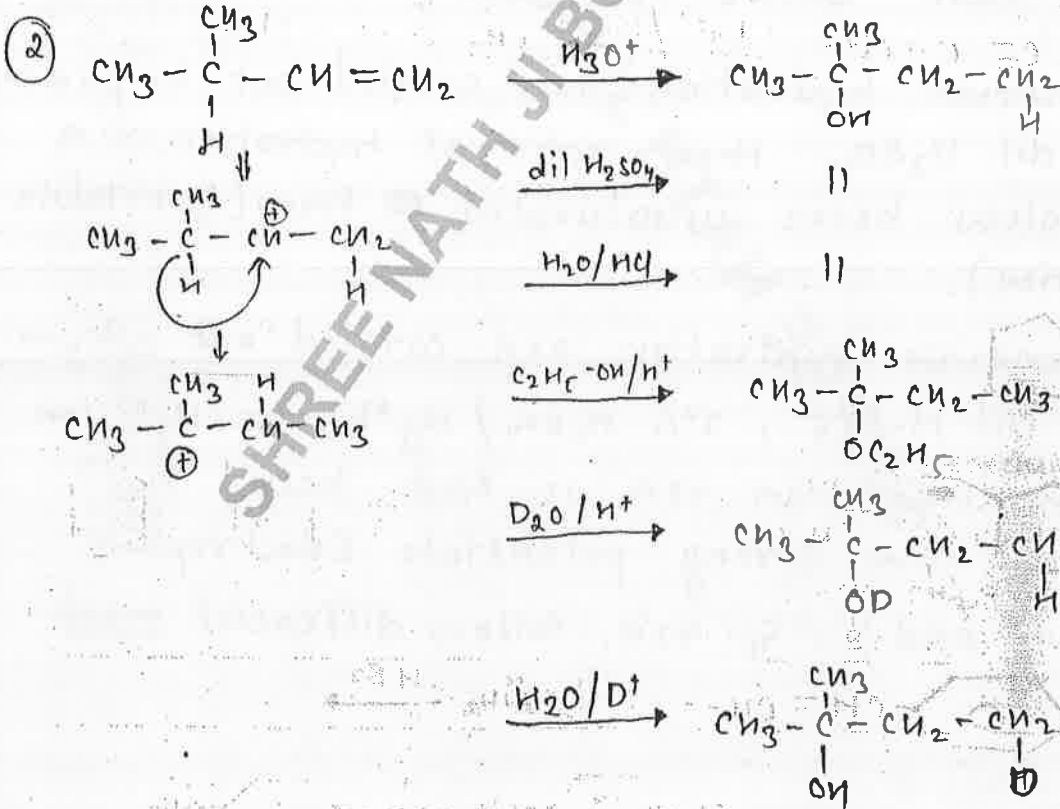
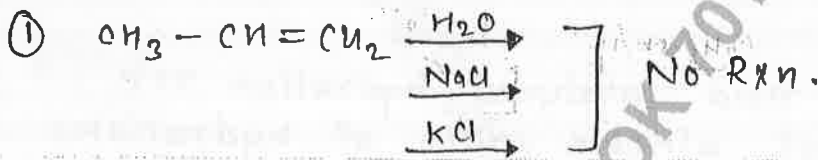
F Whenever hydration rxn carried out in presence of dil H_2SO_4 then rate of hydration rxn is slow becoz unsaturated C^+ form (less stable cation).

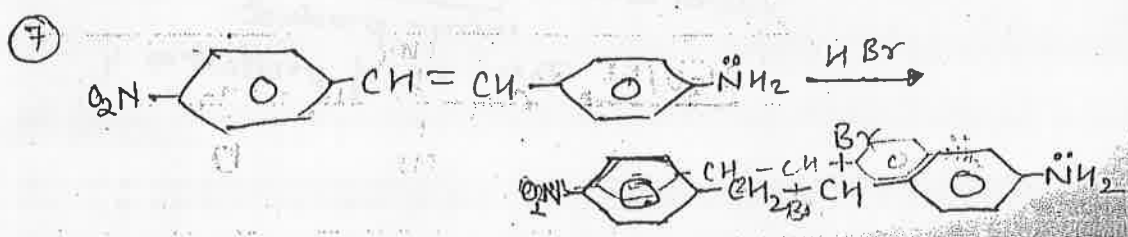
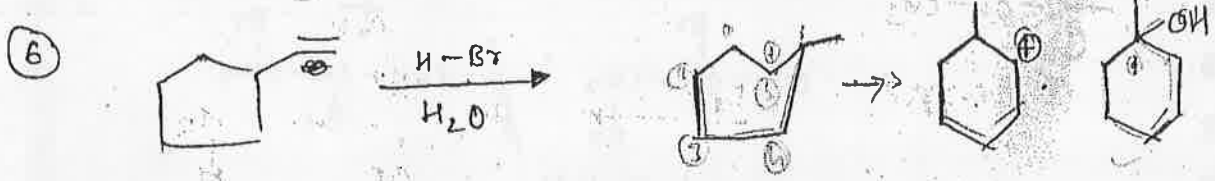
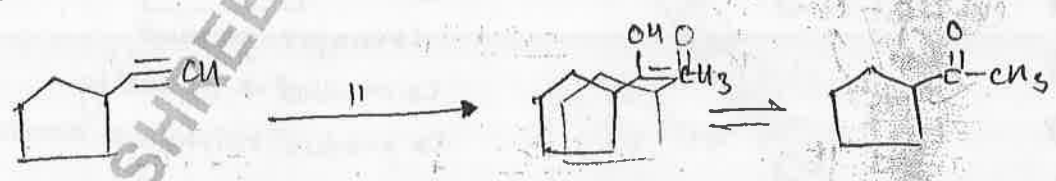
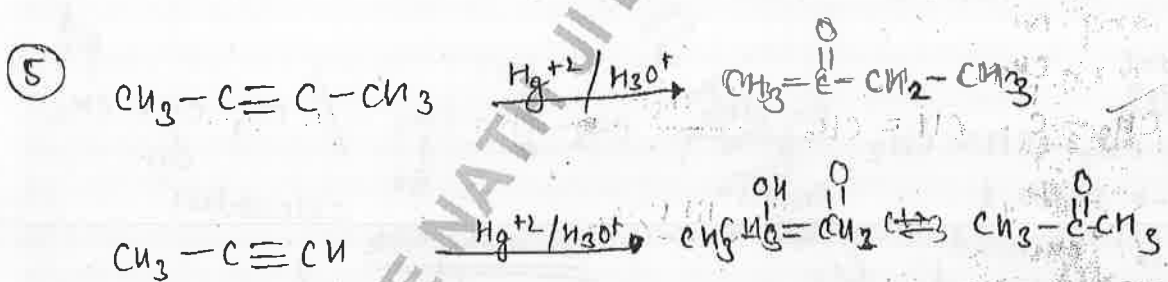
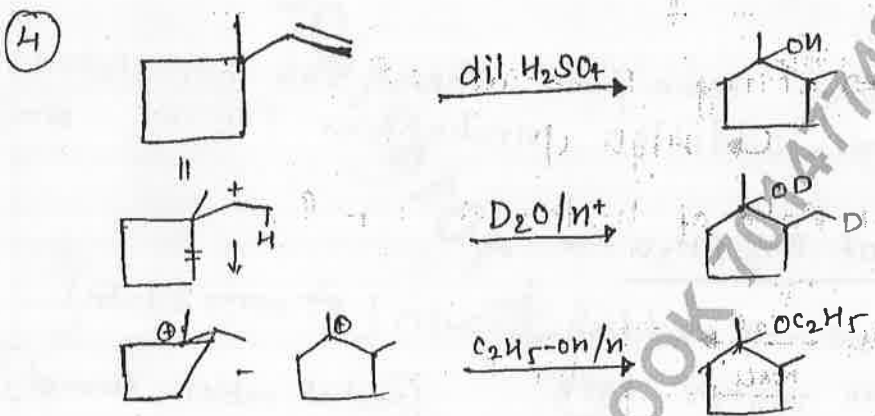
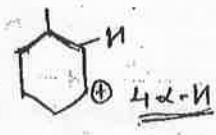
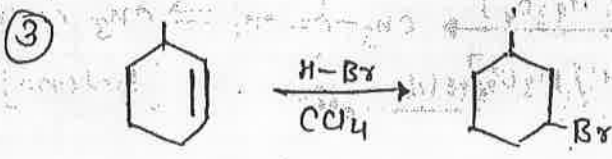
* Whenever hydration rxn carried out alkyne in dil H_2SO_4 , 1% $\text{H}_2\text{SO}_4/\text{Hg}^{+2}$, or Hg^{+2} ion then ^{rate} hydration rxn is fast becoz Hg^{+2} ion have strong potentiate Electrophile (Lewis acid) & rxn follow different mech.

Kucherov's
rxn

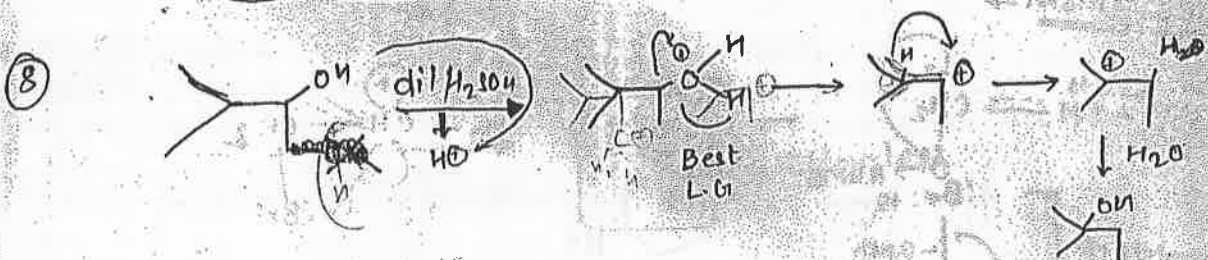


$\text{Hg}^{+2} \Rightarrow$ strong Potentiate E^{\oplus}
 \hookrightarrow High Φ
 \hookrightarrow Rate of hydration Rxn \uparrow .





Addition of $X_2 \rightarrow$ halogenation rxn
 $H-X \rightarrow$ Hydrohalogenation rxn.



Anti-Addition :-

Markonoff's ka Anti se koi relation nahi h.

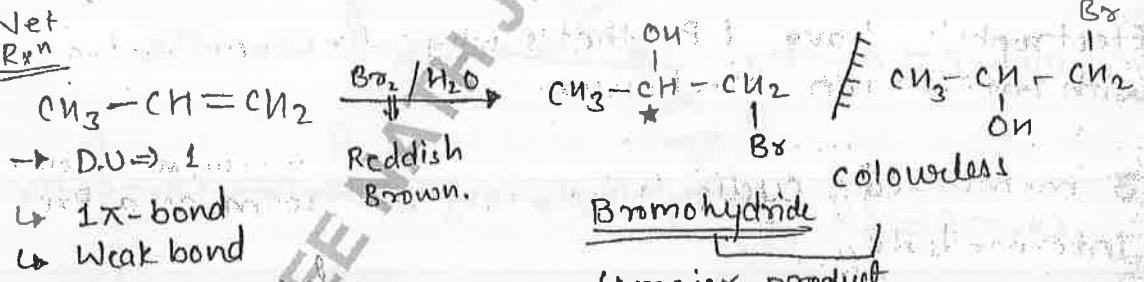
KEY POINT :-

IF E^\oplus have lone pair then rxn completed with anti-addition mechanism. [Cl_2, Br_2, \dots etc.]

① Addition of $Br_2 / H_2O \rightarrow$

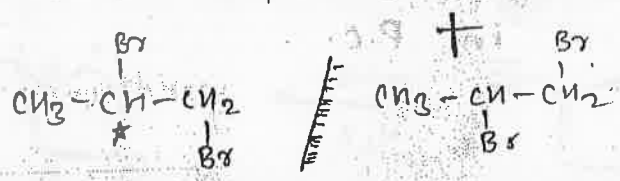
- $\hookrightarrow Br_2 / H_2O \rightarrow$ Reddish Brown (दूरे भाग रंगी हो)
- \hookrightarrow Bromine water test [partial cation formed]
- \hookrightarrow Test of unsaturation.

Net Rxn



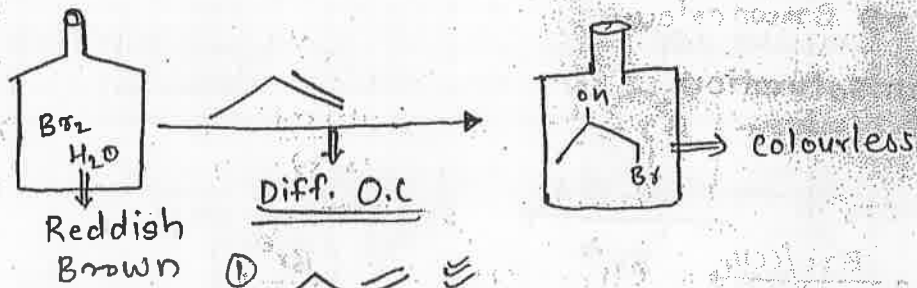
Non-classical
 reaction
 synergistic bonding

Bromohydrin
 \hookrightarrow major product
 \hookrightarrow product \Rightarrow optically
 \hookrightarrow product mixture \Rightarrow racemic mixture



vicinal dihalide minor product
 Total no. of product \Rightarrow 4

POC →



- ① CH3CH=CH2
- ② CH3CH=CHCH3
- ③ C1=CCCC1
- ④ CH3C#CH
- ⑤ CH2=CHCH=CH2
- ⑥ CH3C#CC#CH

⑦ C1CC1 } → give test of unsaturation
Cyclopropane } → Becoz σ-bond behave as π-bond.

⑧ C1=CC=CC=C1 } → Does not give test of unsaturation
Benzene } → Becoz Aromaticity Break.

⑨ C1=CC=C2C=CC=CC2=C1 } → give test of unsaturation
&
Phenanthrene }

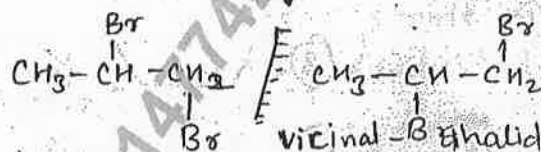
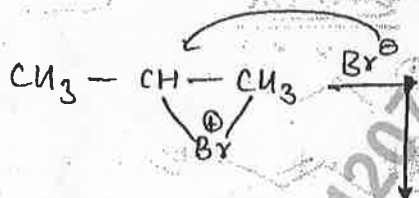
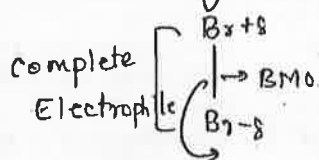
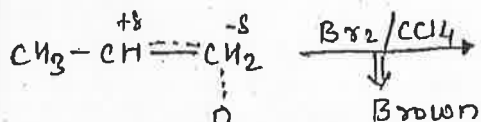
② Addition of $\text{Br}_2/\text{CCl}_4 \rightarrow$

280-287

① $\text{Br}_2/\text{CCl}_4 \Rightarrow$ Brown colour

② Test of unsaturation

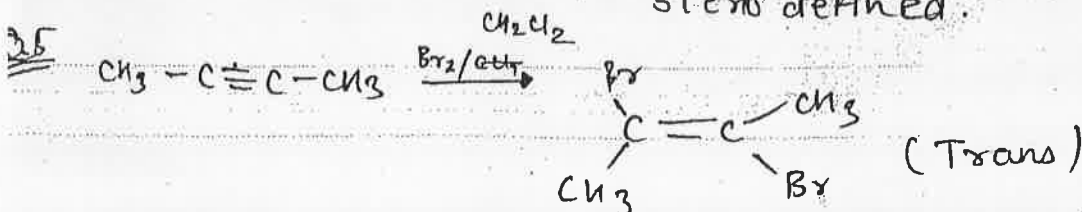
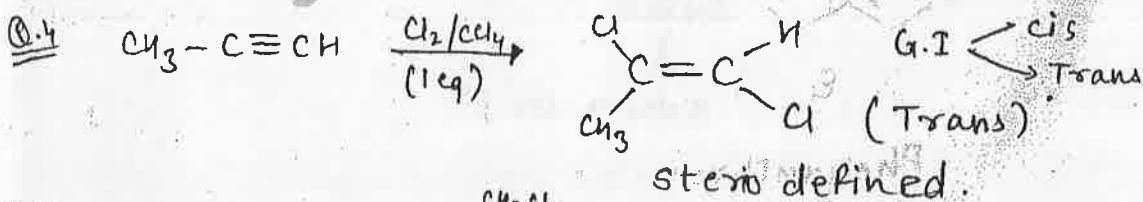
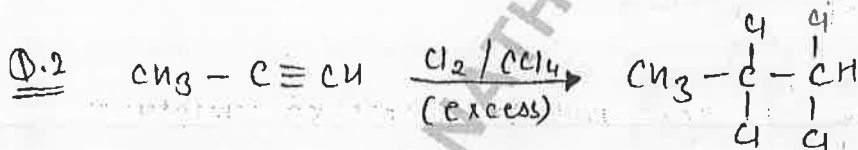
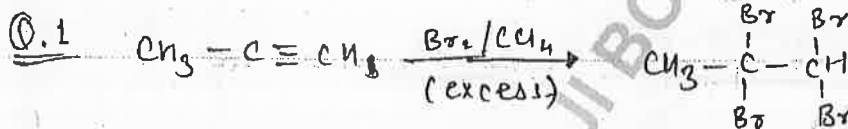
Net Rxn:-



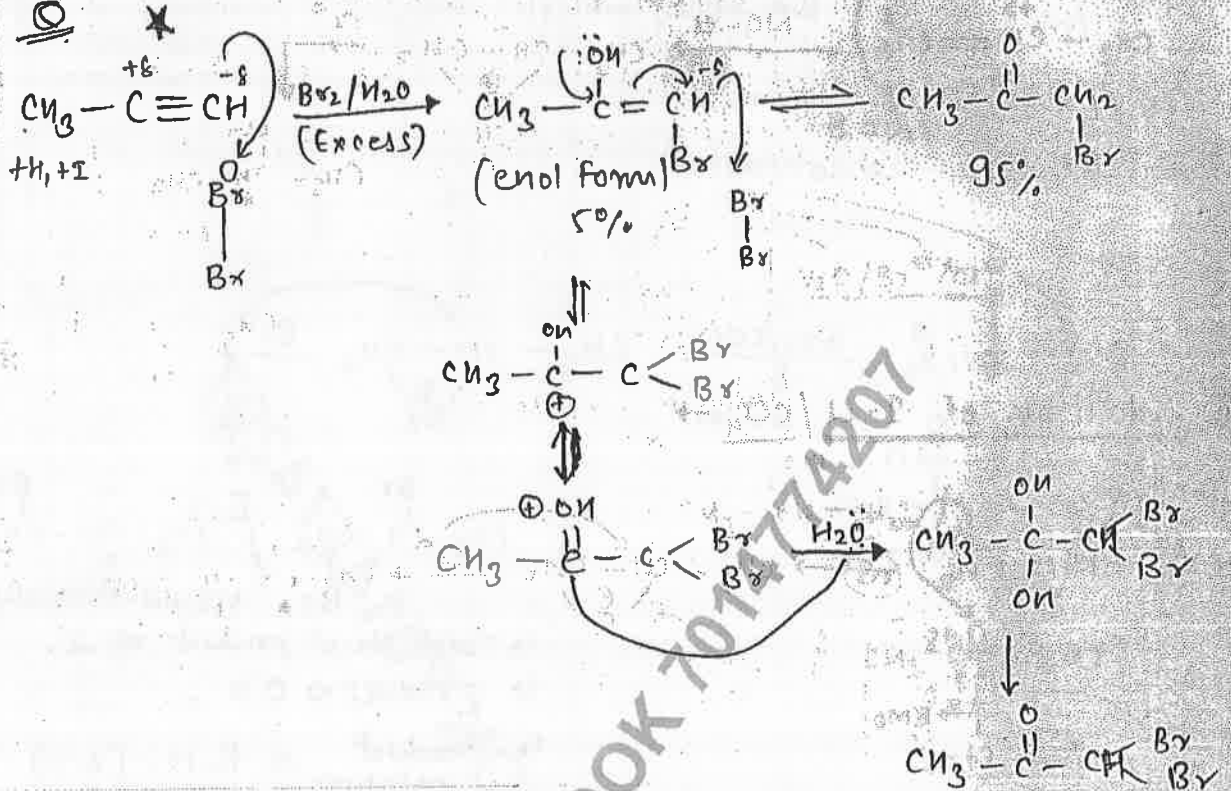
↳ Total No. of product $\Rightarrow 2$

↳ product \Rightarrow O.A

↳ Product mixture \Rightarrow R.M. (O.T)

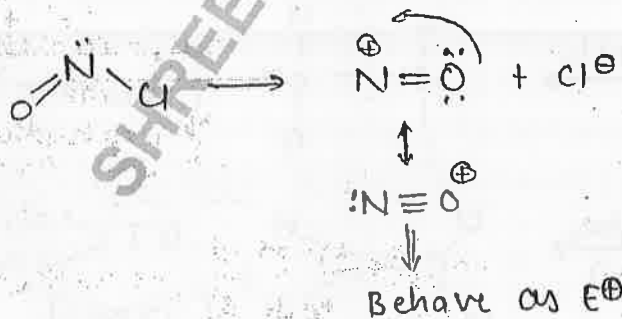
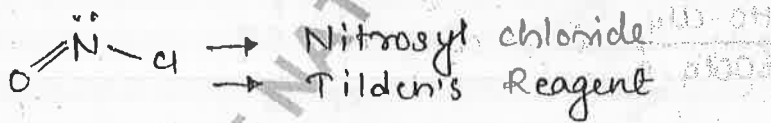


DIT Mains



Addition of NOCl / I-Cl / HO-Cl / CCl₄

(A) Addition of NOCl / CCl₄ →

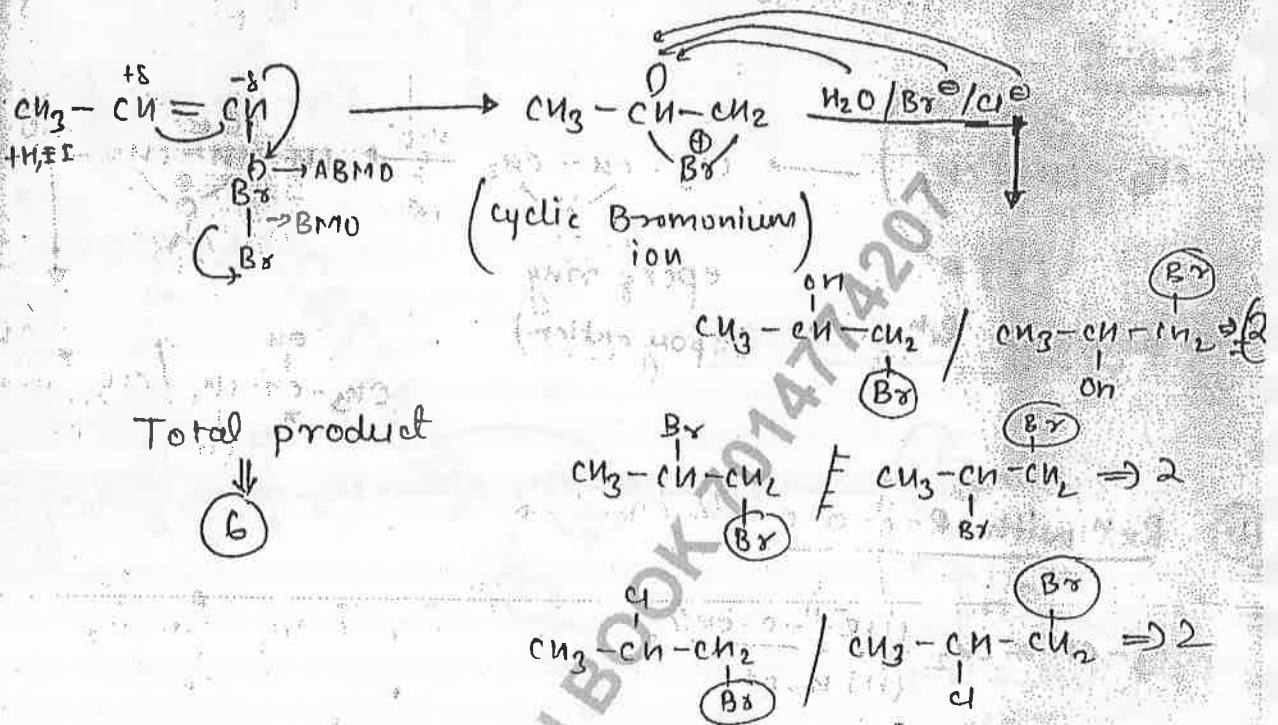


③ Addition of $\text{Br}_2/\text{H}_2\text{O}$ in Brine Solⁿ →

Brine Solⁿ ⇒ Conc. solⁿ of NaCl.

No. of E⁺ ⇒ Br_2 (only one E⁺)

No. of Nu⁻ ⇒ $\text{H}_2\text{O}, \text{Br}^-, \text{Cl}^-$



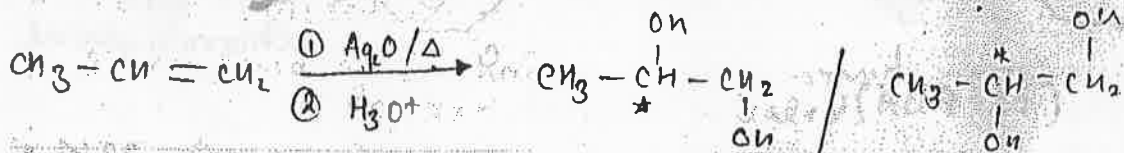
④ Anti hydroxylation Rxn :-

① (A) $\text{Ag}_2\text{O}/\Delta$ (B) H_3O^+

② (A) $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\text{H}/\Delta$ (B) H_3O^+
(Percy acid)

} ⇒ Anti hydroxylation

① Rxn with $\text{Ag}_2\text{O}/\Delta / \text{H}_3\text{O}^+ \rightarrow$

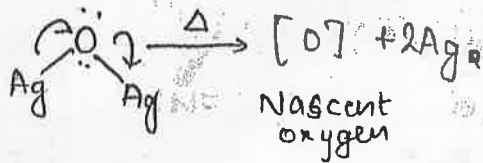


⇒ Vic-Diol

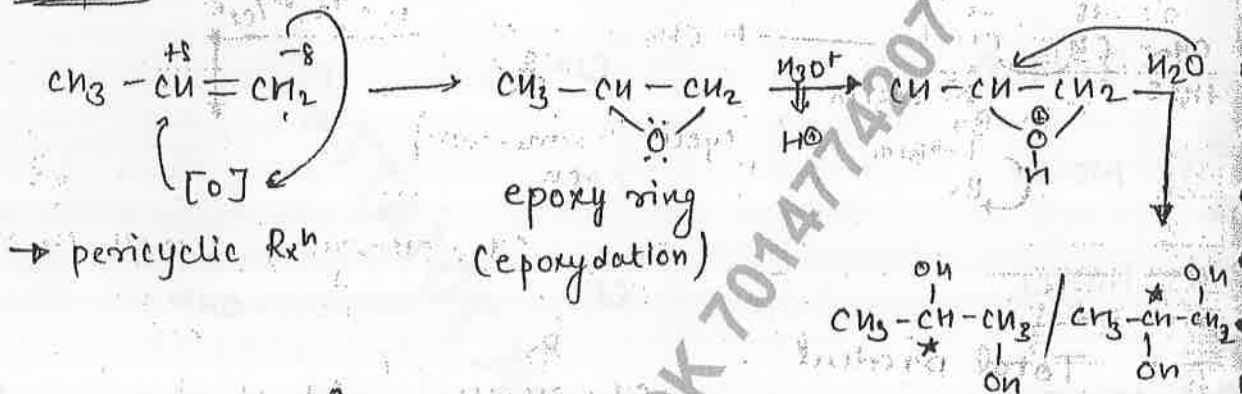
⇒ Anti glycolisation obs.

Mech

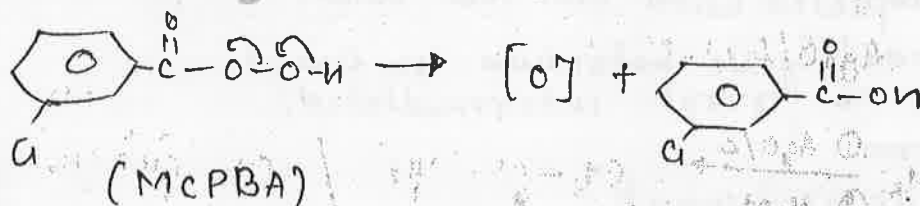
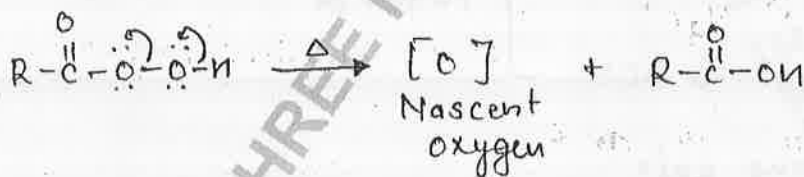
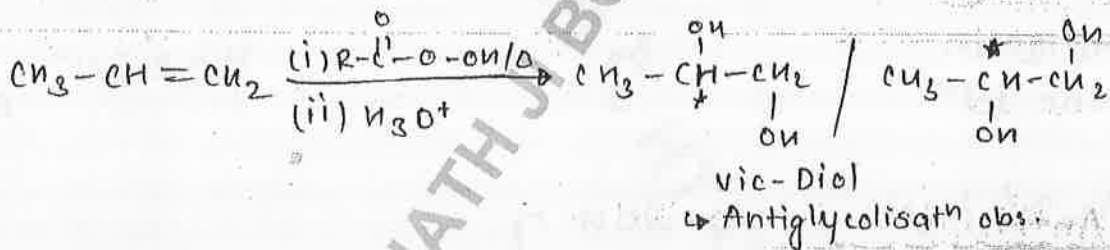
Step-I



Step-II



ii) Rxn with $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\text{H} / \Delta / \text{H}_3\text{O}^+ \rightarrow$



KEY POINT [Trick] ↪

Reagent	E^{\oplus}	Nu^{\ominus}
① Br_2/CCl_4	$[Br_2] Br^{\oplus}$	Br^{\ominus}
② Cl_2/CCl_4	Cl^+	Cl^{\ominus}
③ Br_2/H_2O	Br^+	OH^-
④ Cl_2/H_2O	Cl^+	OH^-
⑤ $NO-Cl$	Cl^+	OH^{\oplus}
⑥ $HO-Cl$	Cl^+	OH^{\ominus}
⑦ $HO-Br$	Br^+	OH^{\ominus}
⑧ Br_2/H_2O in Brine sol ⁿ	Br^+	H_2O, Br^-, Cl^-
⑨ $Ag_2O/\Delta/H_3O^+$	$\Rightarrow 2OH^-$	चिपका लें
⑩ $R-COOH/\Delta/H_3O^+$	$\Rightarrow 2OH^-$	

- ↪ E^{\oplus} have lone pair
- ↪ Rxⁿ completed with Anti Addⁿ mech.
- ↪ 3-membered cyclic halonium ion formed as a rxⁿ intermediate.
- ↪ NCC form
- ↪ No c^{\ominus} rearrangement

Key point-2 \Rightarrow

Reactivity of H-X (Hydrogenation Rxn)

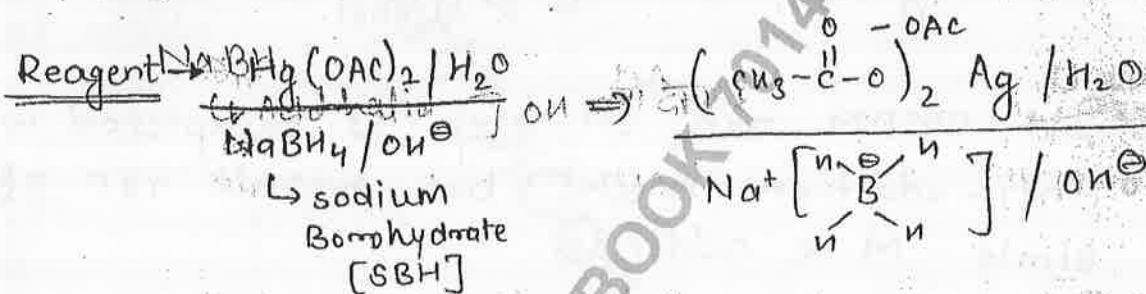


Key point \Rightarrow 3

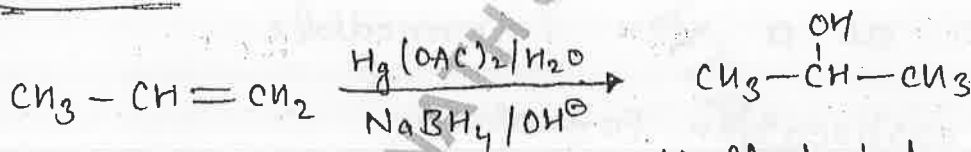
Reactivity of X_2 (halogenation Rxn)



Q1 Oxy-Mercuration - Demercuration Rxn :- (OMPM)



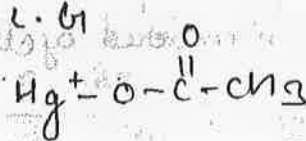
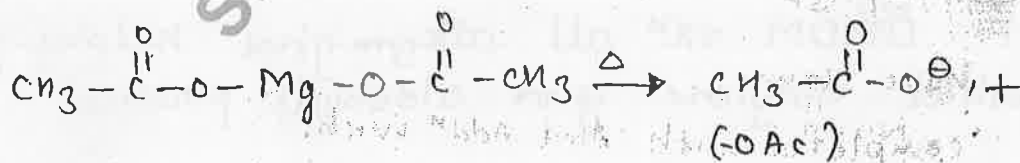
Net Rxn :-



\hookrightarrow 2° alcohol

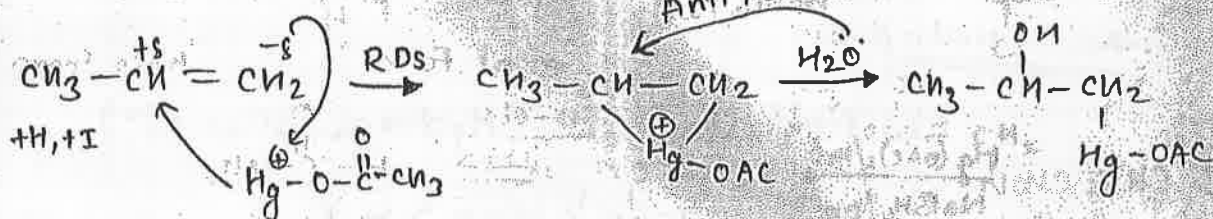
\hookrightarrow simple M.K product.

Mech

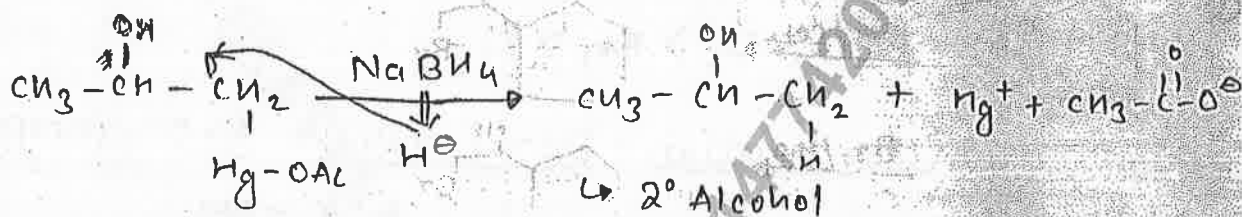


Behave as E^\oplus

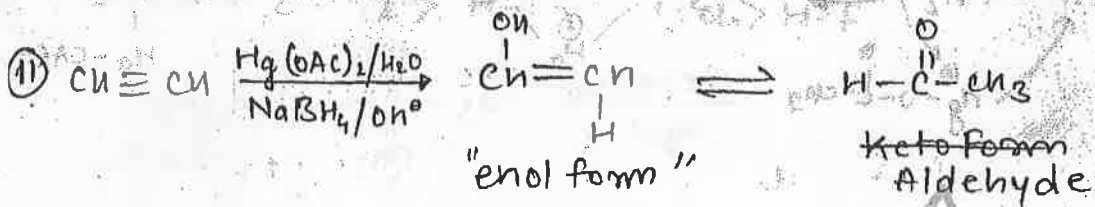
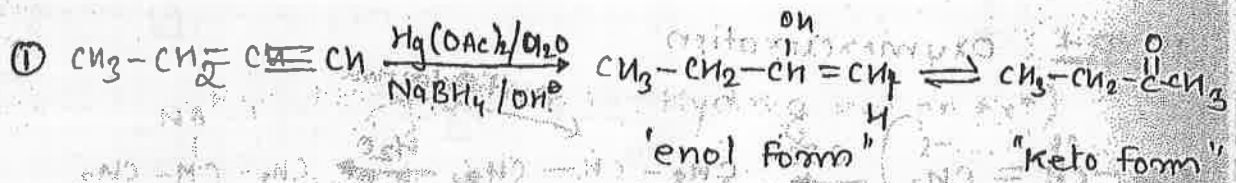
Step-1 Oxymercuration



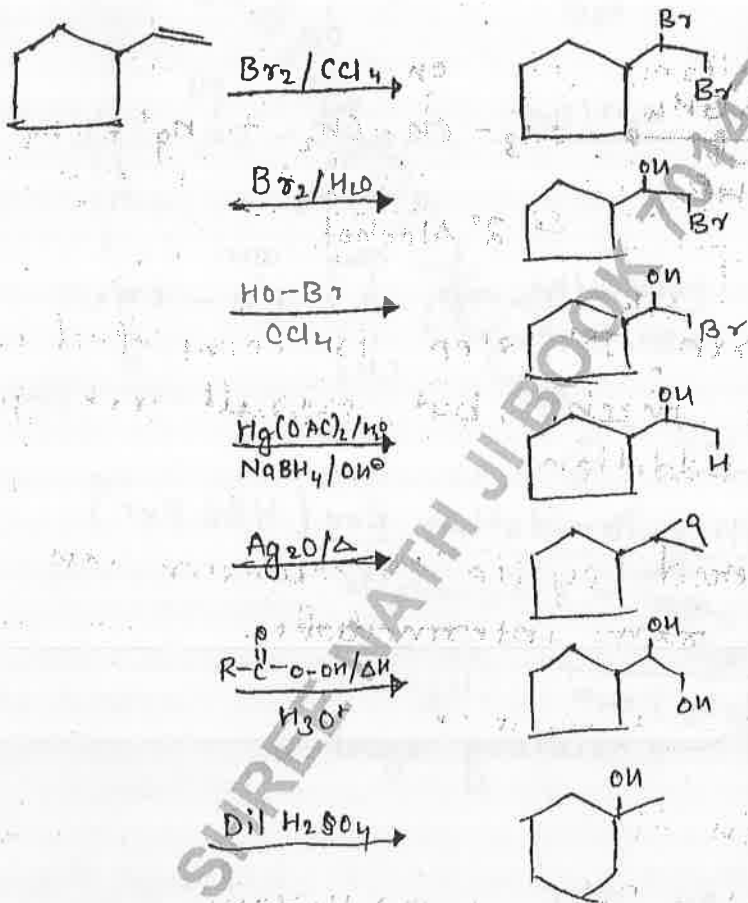
Step-2 Demercuration



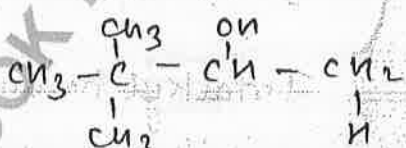
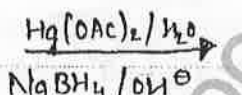
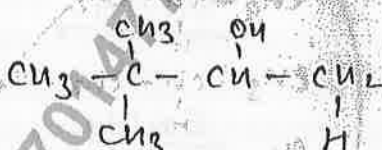
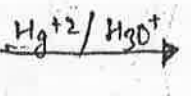
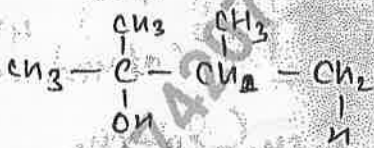
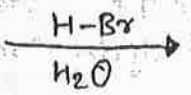
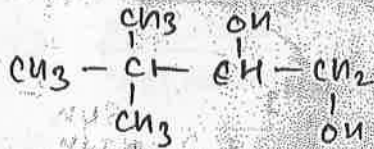
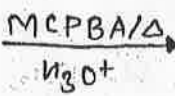
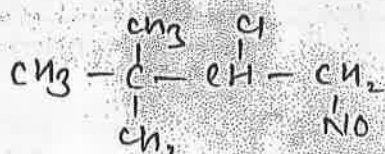
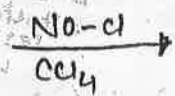
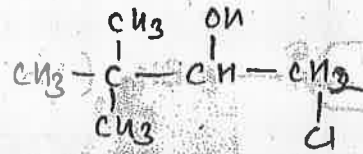
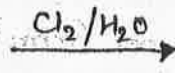
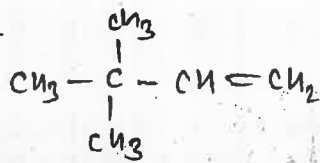
- ① In OMDM rxn ^{only} 1st step is completed with Anti-addition mechⁿ, but overall rxn give simple M. K addition.
- ② Three membered cyclic Mercurium ion form as a rxn intermediate.
- ④ No carbocation formation
- ⑤ NCC form in these rxn
- ⑥ No carbocation [C[⊕]] rearrangement
- ⑦ In OMDM rxn all alkyne give ketone product while acetylene give aldehyde product



D.1

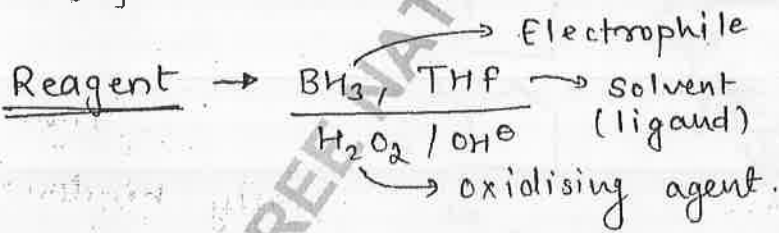


Q.2

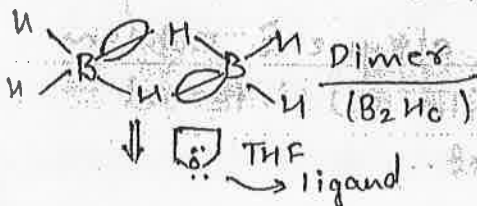
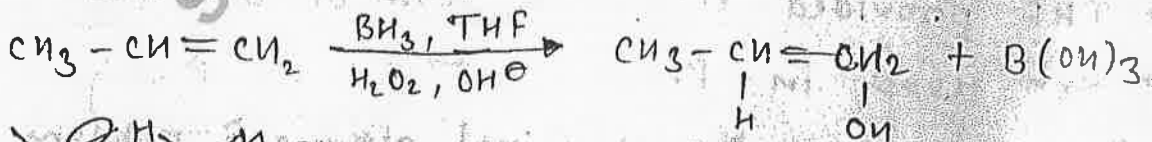


Syn Addition

1. Hydro-boration oxidation Rxn (HBO Rxn)

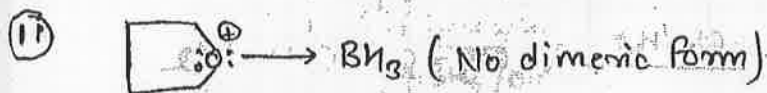


NET RXN

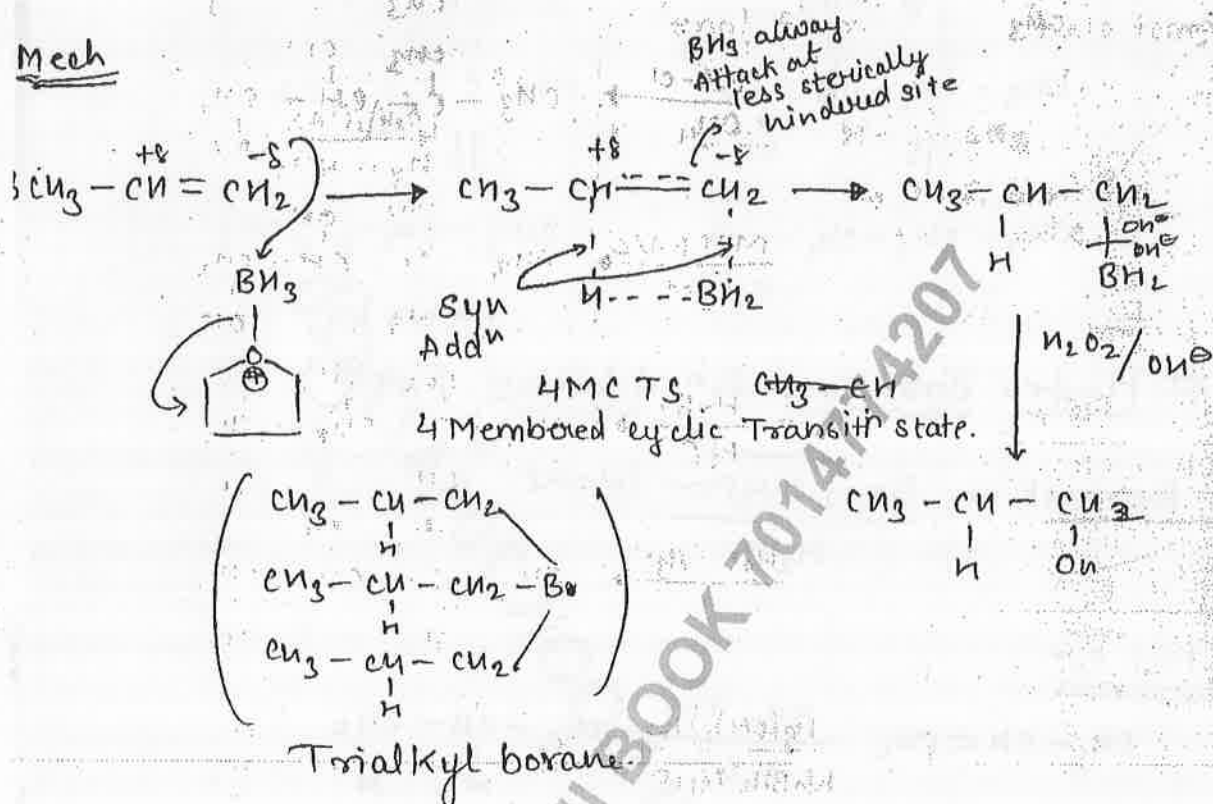


- \hookrightarrow 1° Alcohol
- \hookrightarrow Anti M.K product
- \hookrightarrow Syn Addith.

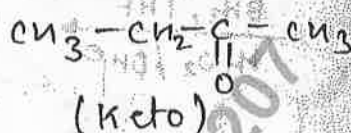
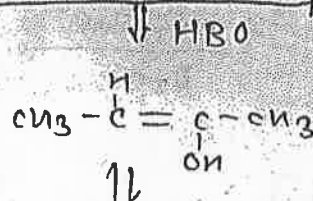
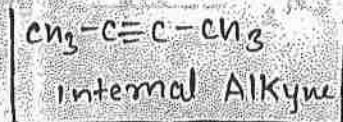
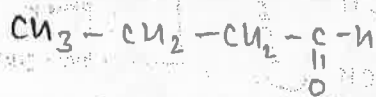
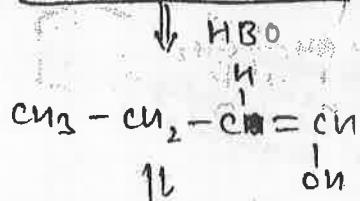
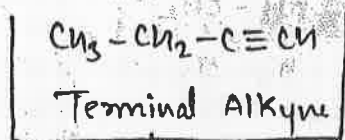
2 BH_3 (Monomeric form)



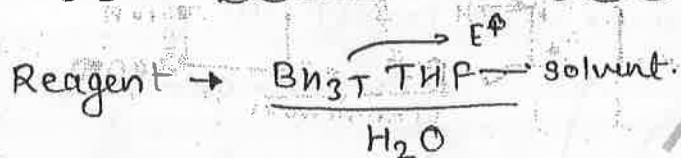
Mech



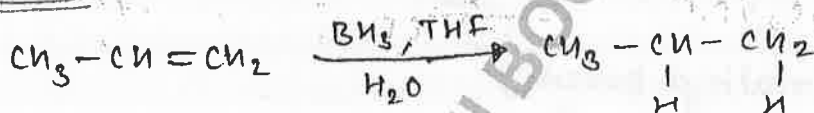
- ↳ HBO rxn completed with syn Addition Mechⁿ
- ↳ In HBO rxn Anti M.K product obtained.
- ↳ 4 MCTS form in these rxn.
- ↳ No carbocation [C⁺] formation
- ↳ No carbocation rearrangement & ring expansion
- ↳ Boron always attack at less sterically hindered site
- ↳ THF provided monomeric form of DiBorane.
- ↳ Rxn used in P.O.C
- ↳ In HBO rxn alko terminal alkyne & acetyne give aldehyde product while all internal alkyne give keton product.



Hydro Boration Rxⁿ Addition (HBR)

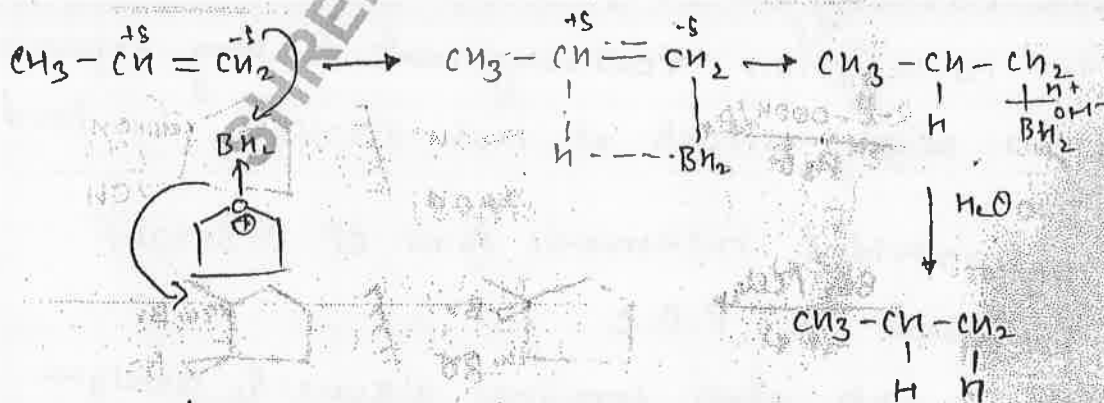


Net Rxⁿ

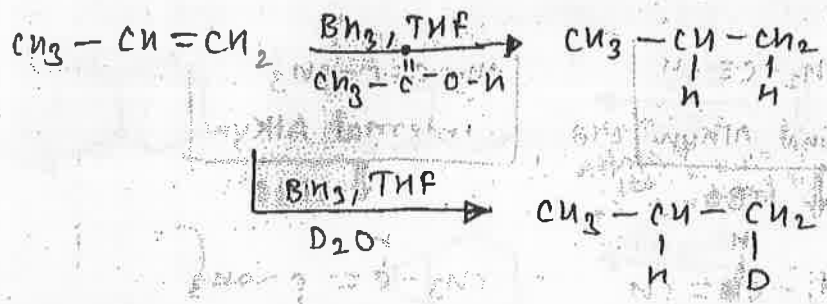


\hookrightarrow syn Addition
 \hookrightarrow Alkane.

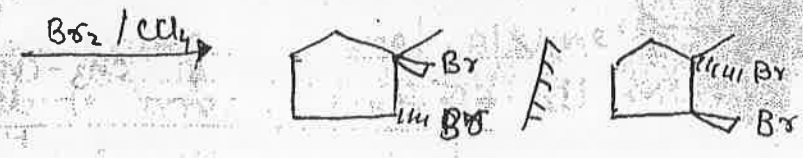
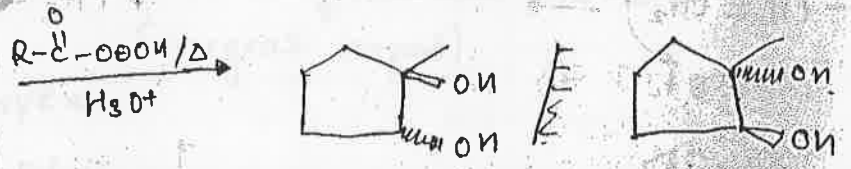
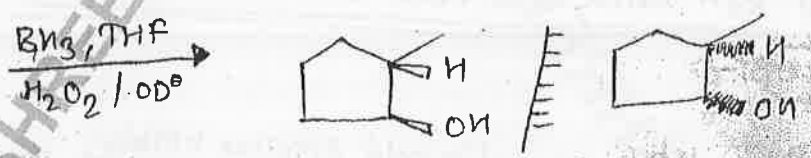
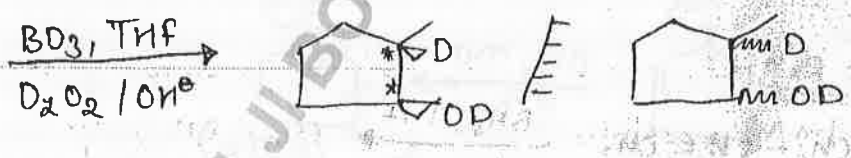
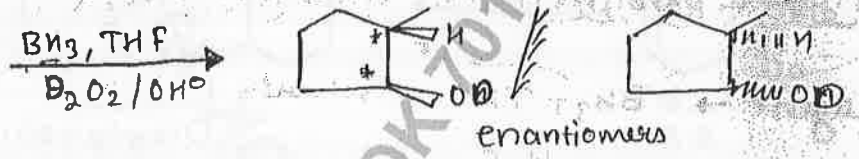
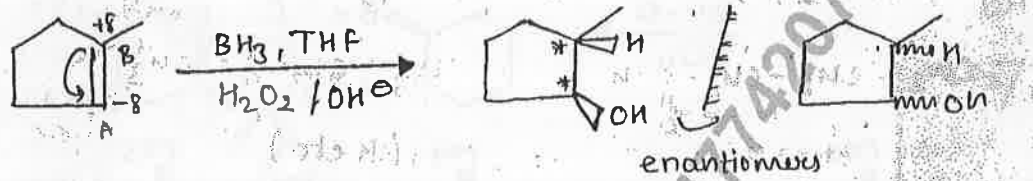
Mech

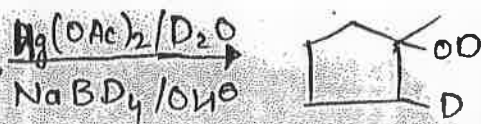


Q.1

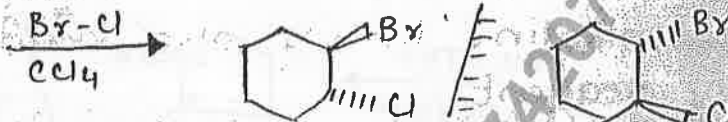
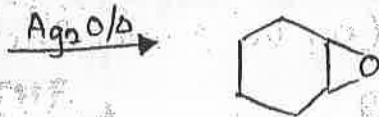


Q.1

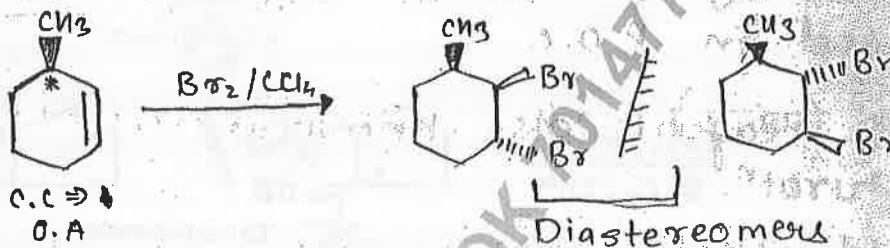




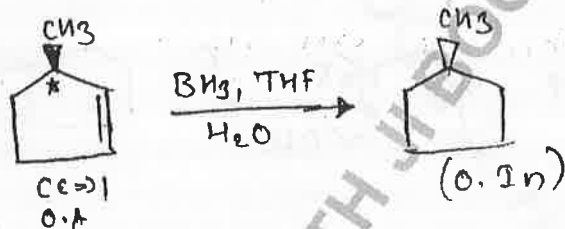
Q.2



Q.3



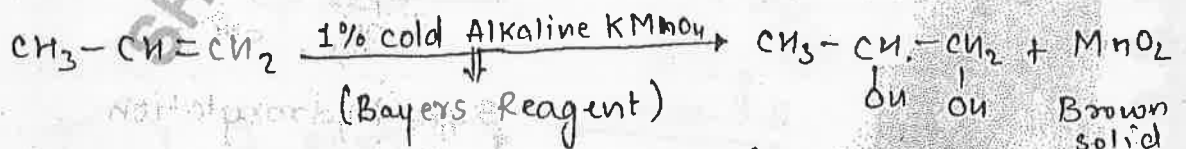
Q.4



Syn-hydroxylation Rxⁿ :-

(A) Rxⁿ with 1% cold alkaline KMnO₄ →

Net Rxⁿ

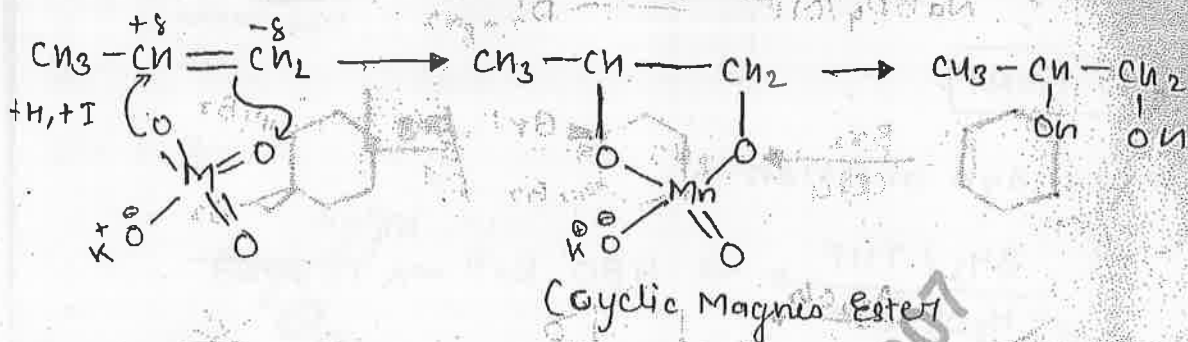


↳ Syn hydroxylation

↳ 1,2-Diol product

↳ Vic-Diol

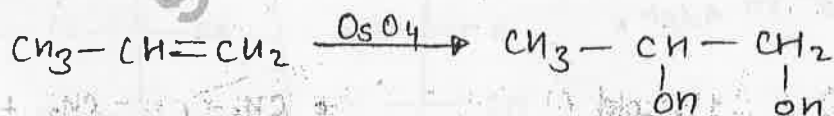
Mech



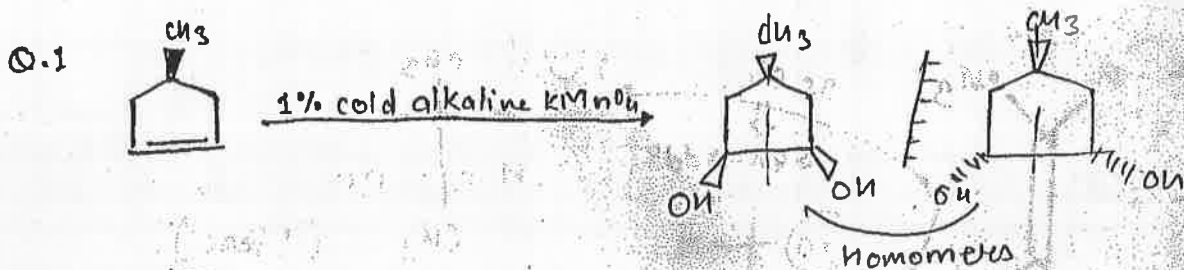
- ▶ 1% cold alkaline KMnO_4 also known as Bayer's reagent.
- ▶ Rxn used in P.O.C
- ▶ Bayer's reagent also known as test of unsaturatⁿ
- ▶ 1% cold alkaline KMnO_4 is a pink colour solⁿ after completion of rxn its change to brown solid.
- ▶ Cyclic Magnesium Ester.

Ⓐ Rxn with OsO_4 →

Net Rxn



- ↳ Syn-hydroxylation
- ↳ 1,2 Diol product
- ↳ Vic-Diol

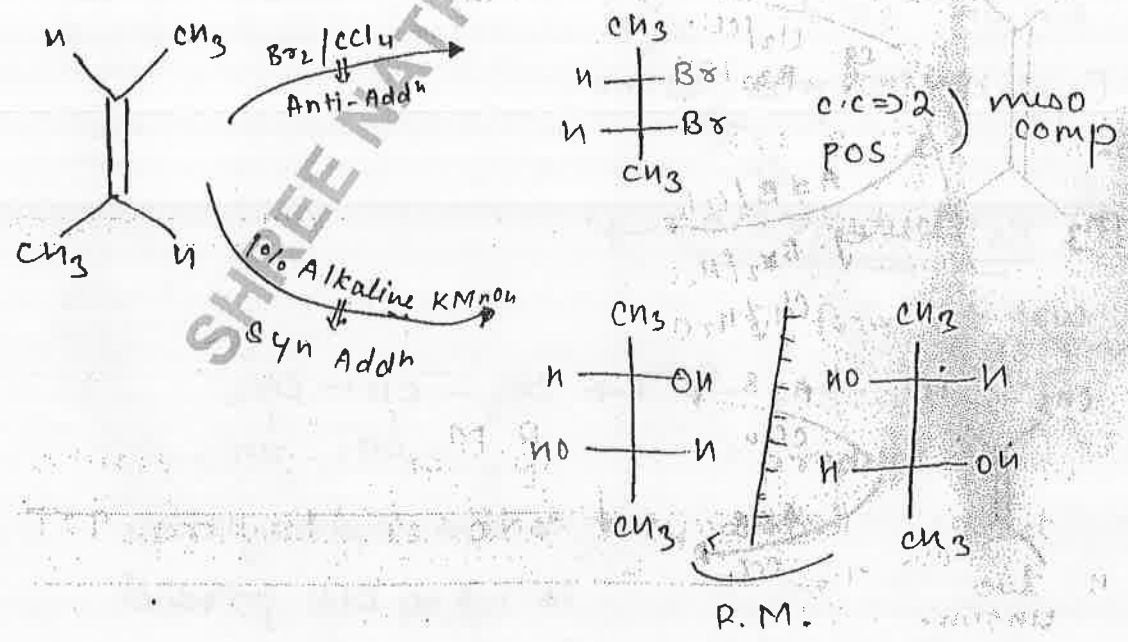


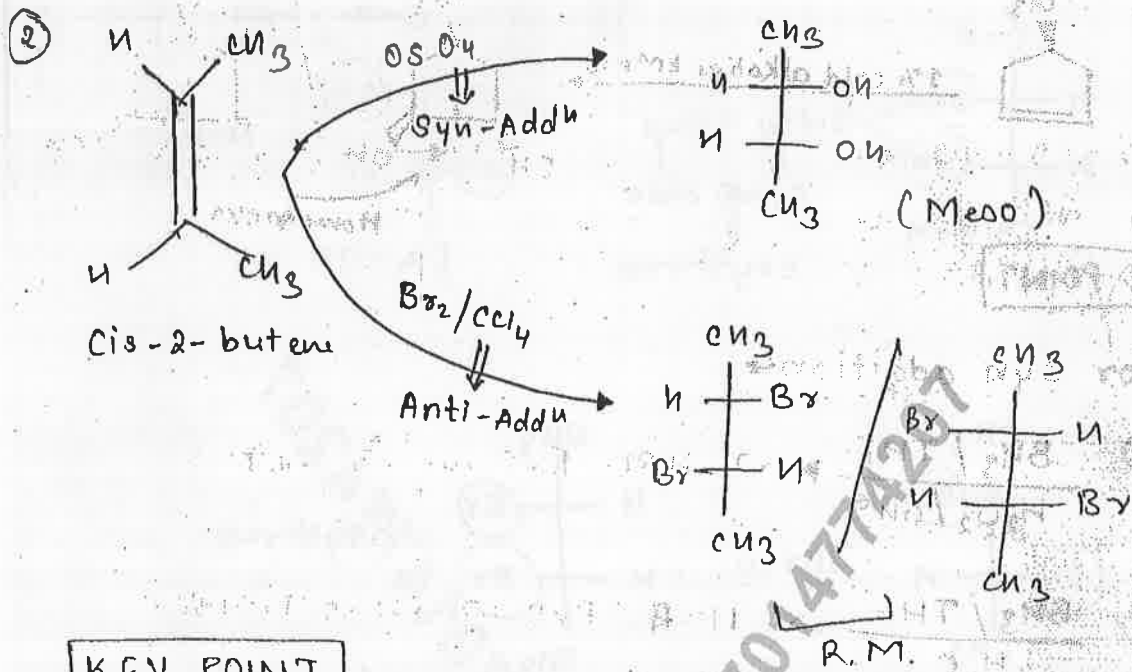
KEY POINT

For syn addition \rightarrow

- ① $\frac{BH_3/THF}{H_2O_2/OH^-} \Rightarrow HBO \text{ Rx}^n \Rightarrow \Delta \text{ चिपकाले}$
- ② $\frac{BH_3/THF}{H_2O} \Rightarrow HBA \text{ Rx}^n \Rightarrow \Delta H \Rightarrow \text{चिपकाले}$
- ③ $1\% \text{ cold alkaline } KMnO_4 \Rightarrow 2 OH \text{ चिपकाले}$
- ④ $OsO_4 \Rightarrow 2 OH \text{ चिपकाले}$
- ⑤ $Ni/Pt/Pd/H_2 \Rightarrow 2H \text{ चिपकाले}$

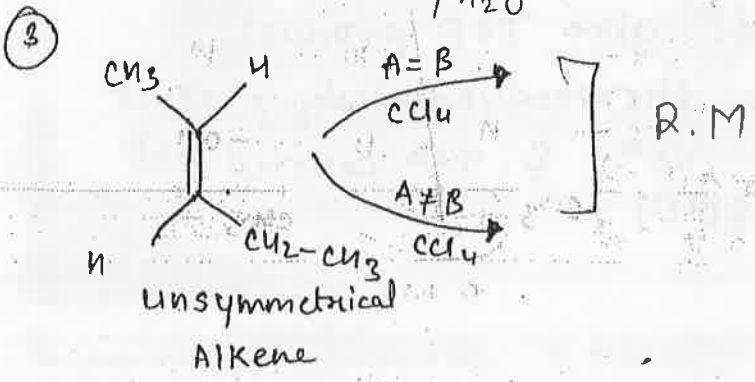
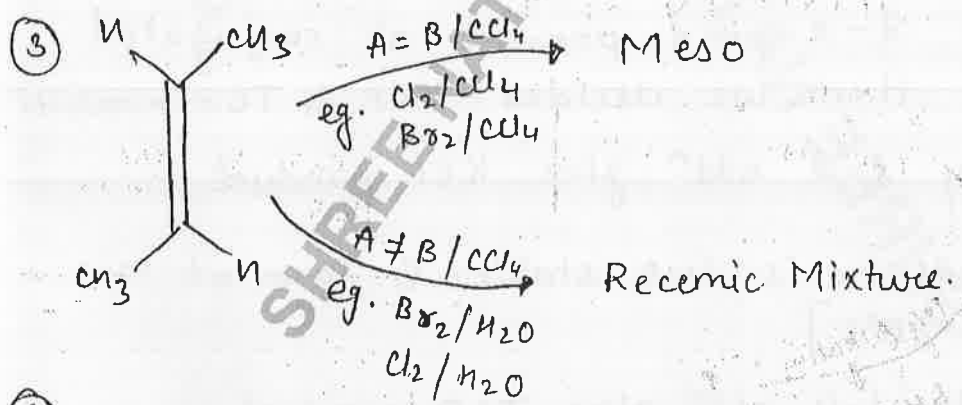
STEREOCHEMISTRY OF EAP :



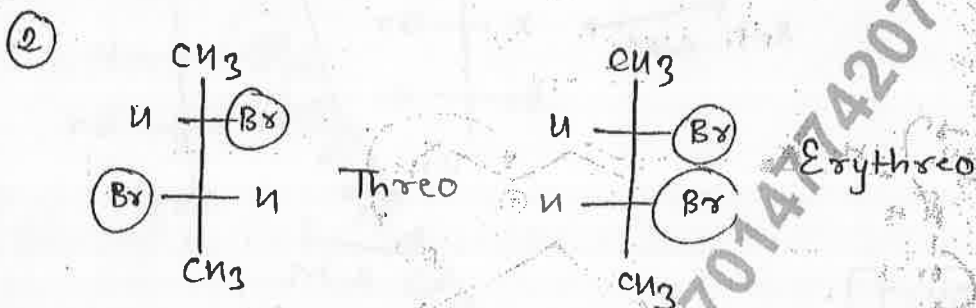
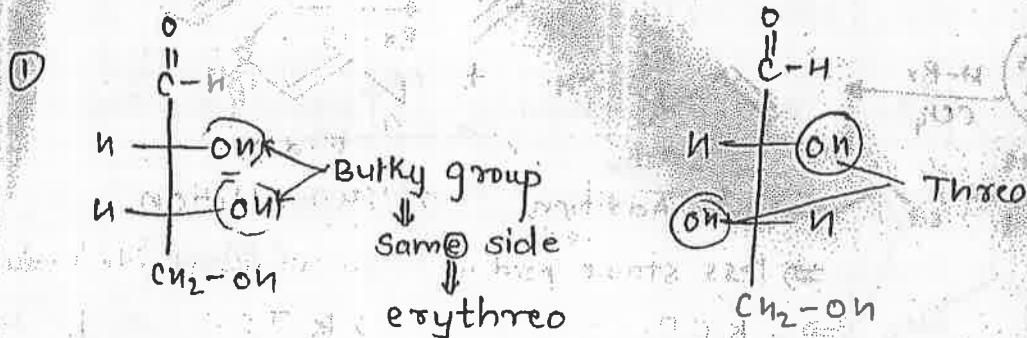


KEY POINT

T	A	→	M
T	S	→	R
C	S	→	M
C	A	→	R



Threo & Erythro Compounds :



KCP & TCP Product :

1 KCP - kinetically controlled product

TCP - Thermodynamically " " "

* Whenever $2-\pi$ bond present at conjugated position then we decided KCP & TCP product.

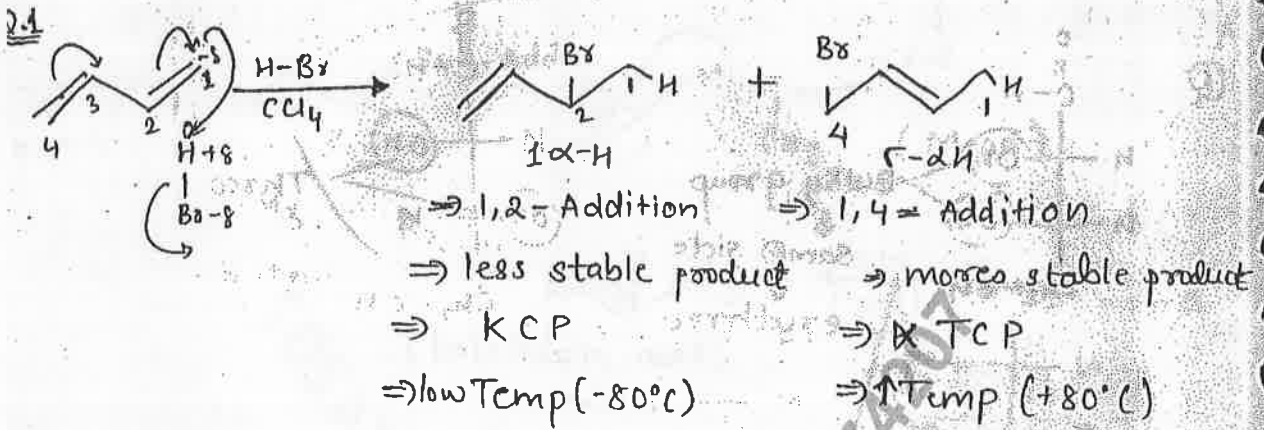
* Generally 1-2 addⁿ give KCP product

* KCP product is less stable & form at low temp. $[-80^{\circ}\text{C}]$

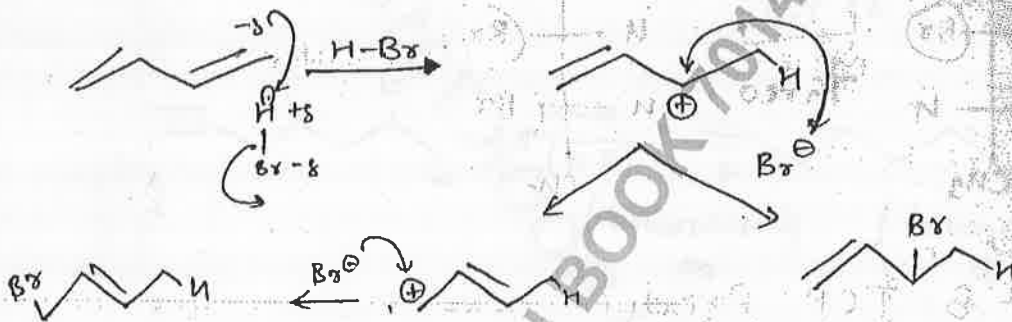
* Generally 1-4 addⁿ give TCP product.

TCP product is thermodynamically product & reversible rxⁿ, & rxⁿ carried out higher temp $[+80^{\circ}\text{C}]$

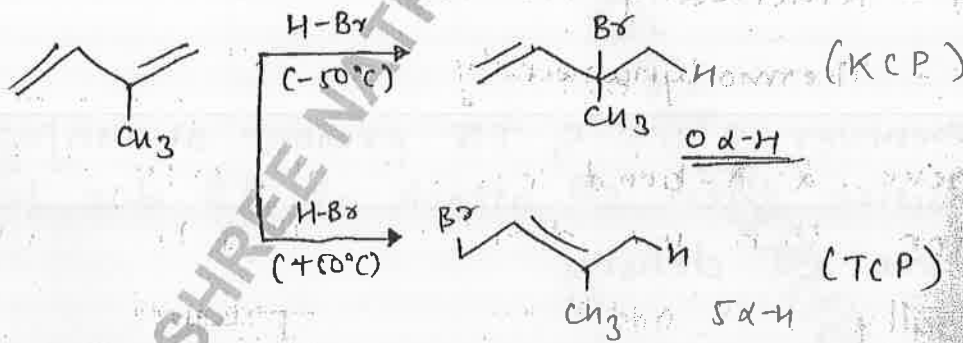
When alkyne & alkene are conjugated then π electrons are attached at IB - electron



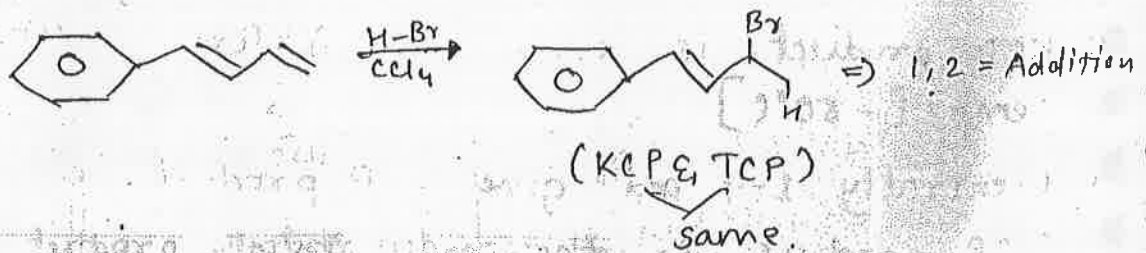
Mech

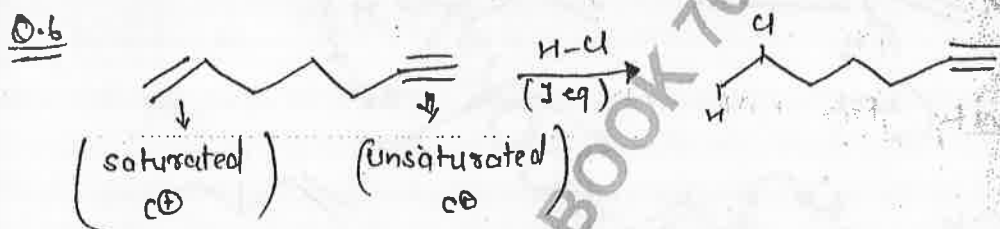
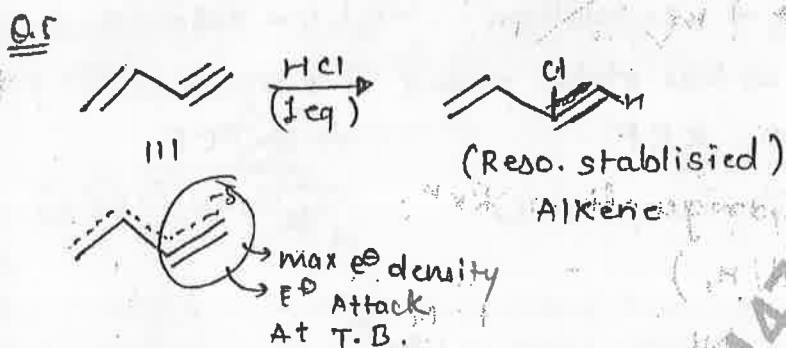
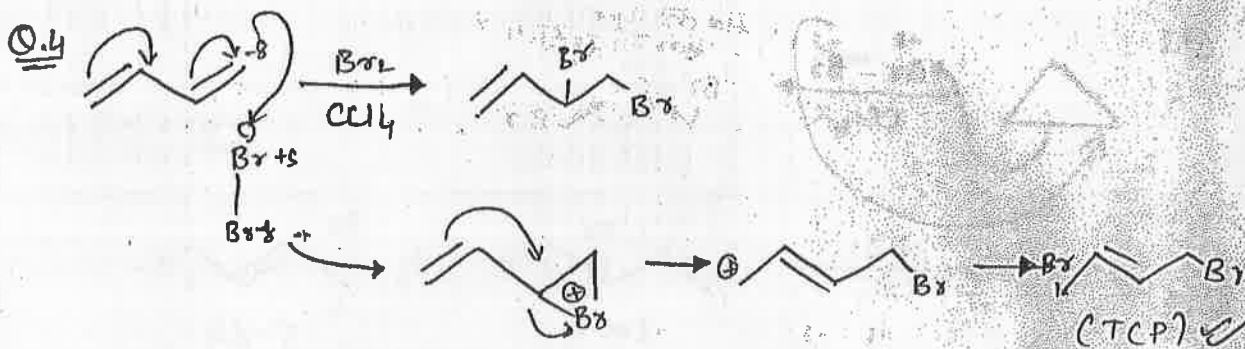


Q.2



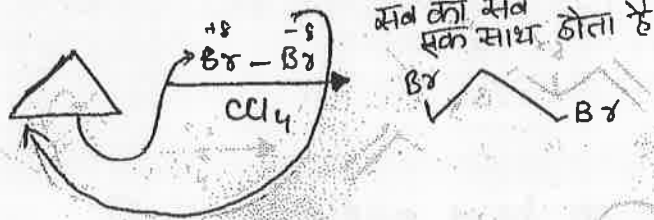
Q.3



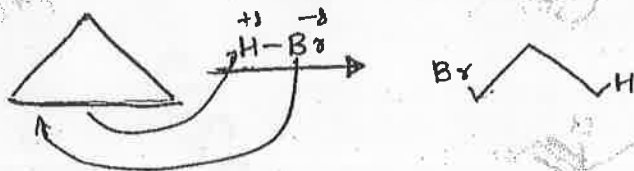


* Whenever 1 DB & TB present at conjugated position then E^+ attack at TB due to more e^- density.

Q.1

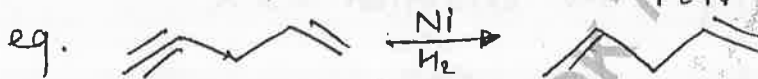


Q.2



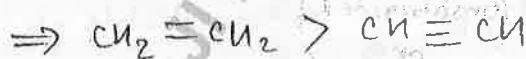
Q.3

Reactivity for hydrogenation Rxn .

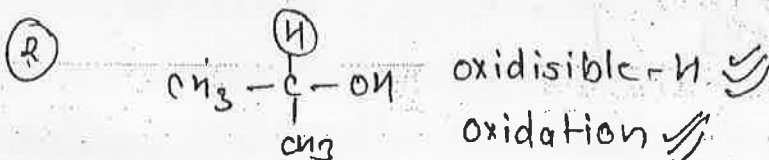
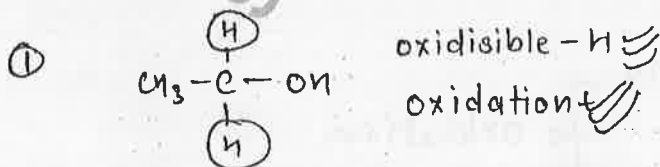


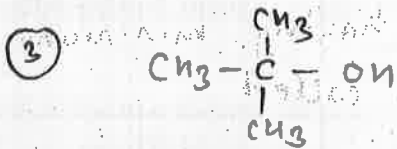
Q.4

Reactivity for EAR rxn .



General Oxidation of OH (organic chemistry)

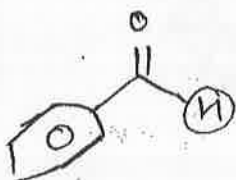
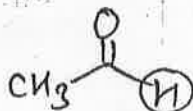
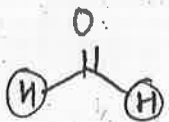




No oxidisable -H XXX

No oxidation -XXX

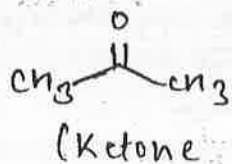
④



All have oxidisable -H

All oxidation

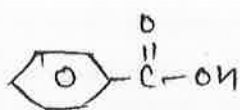
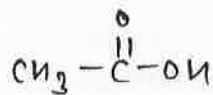
⑤



No oxidisable -H XXX

No oxidation XXX

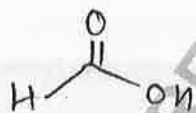
⑥



No oxidisable -H XXX

No oxidation XXX

⑦

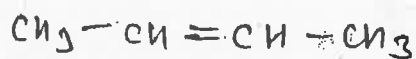


(Formic Acid)

oxidisable -H

oxidation

⑧



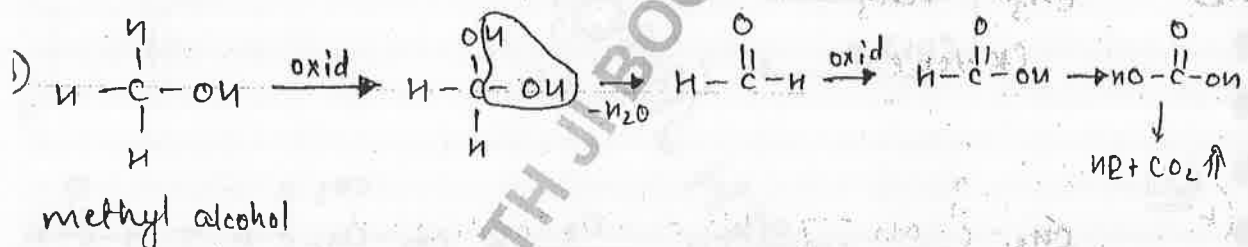
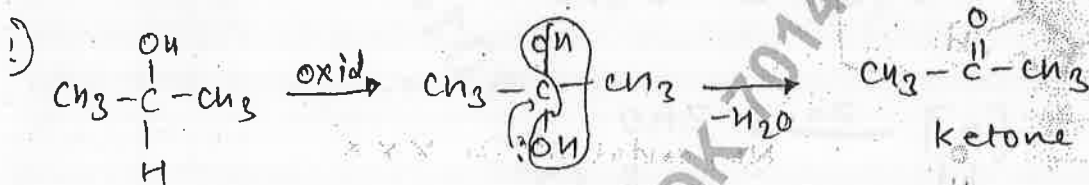
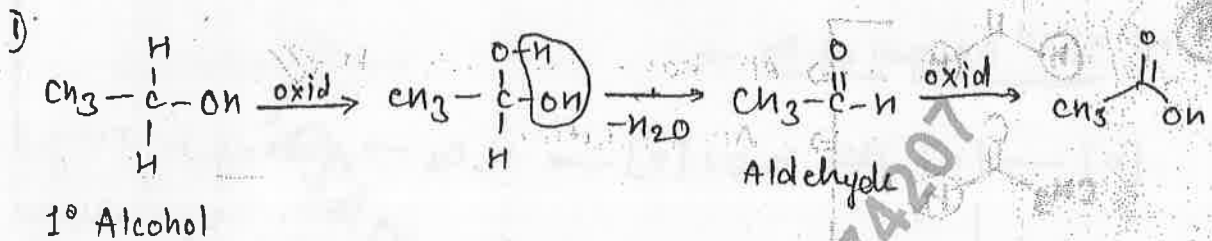
Alkene



Alkyne

oxidation

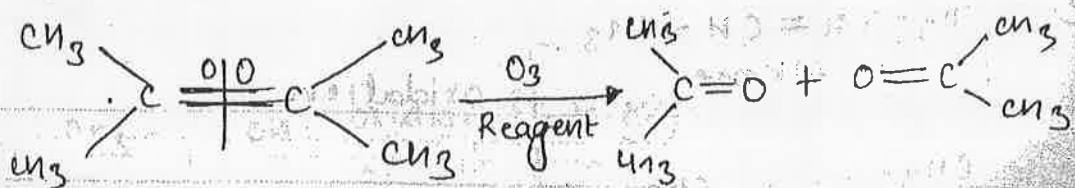
* Hydrogen attached to carbon having minimum one oxygen atom then the 'H' is called oxidisable H⁺.



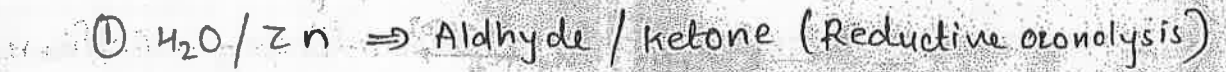
Ozonolysis Rxn (Oxidative cleavage)

- It is a electrophilic addition rxn.
- O₃ behave as a E⁺ in these rxn

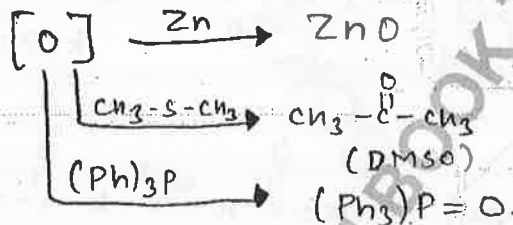
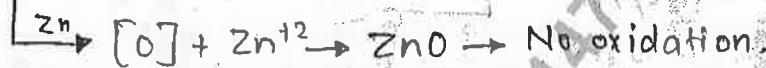
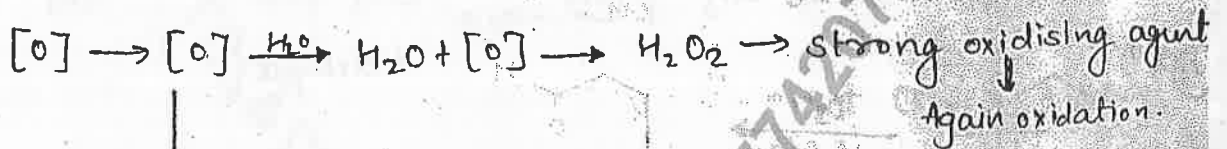
Net rxn



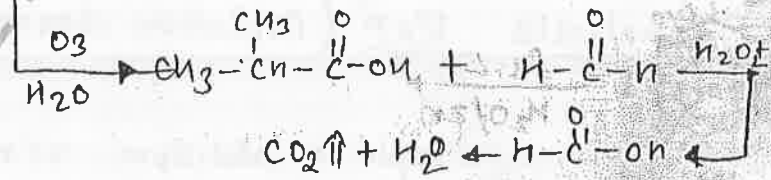
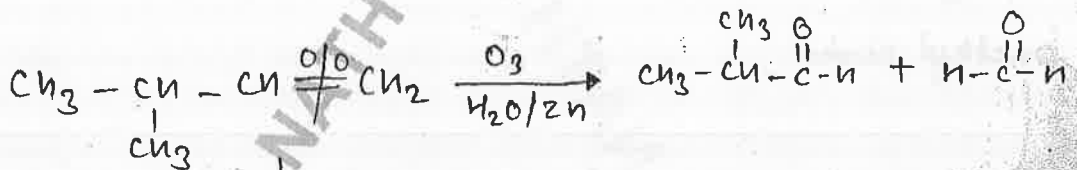
Reagent \Rightarrow



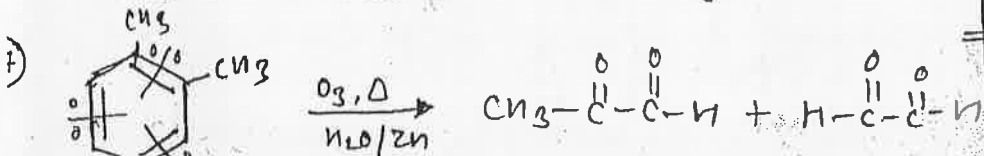
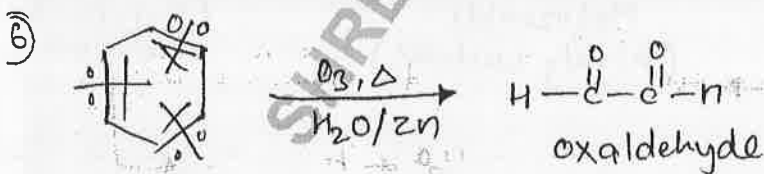
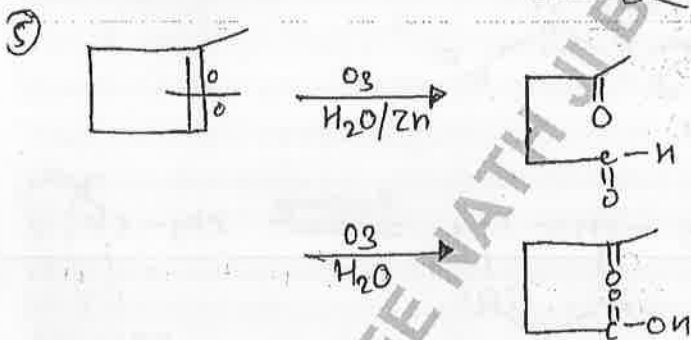
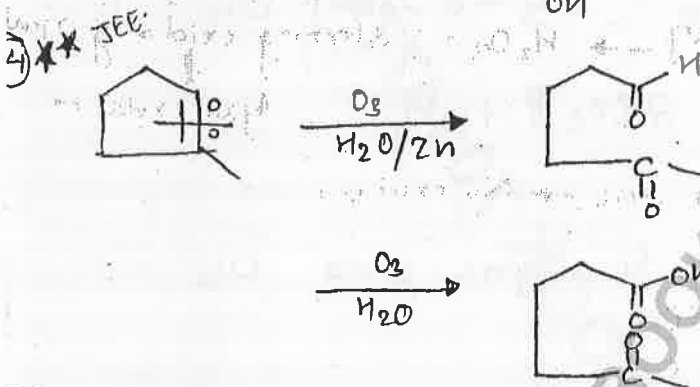
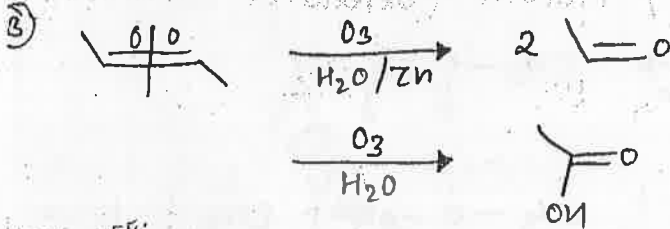
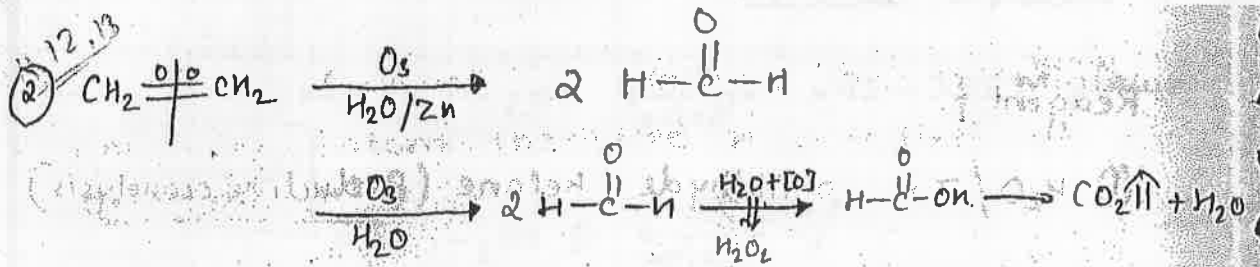
\Rightarrow IIIrd oxygen of $\text{O}_3 \rightarrow$



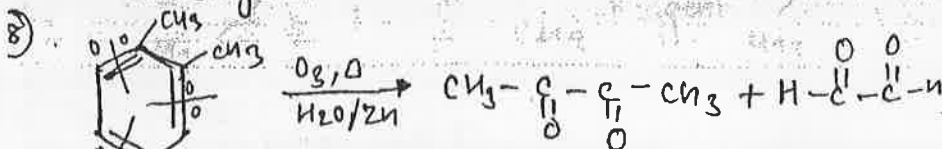
Q.1



Q.2



1,2-Dimethyl benzene



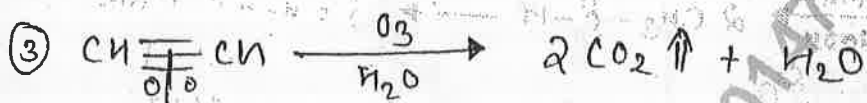
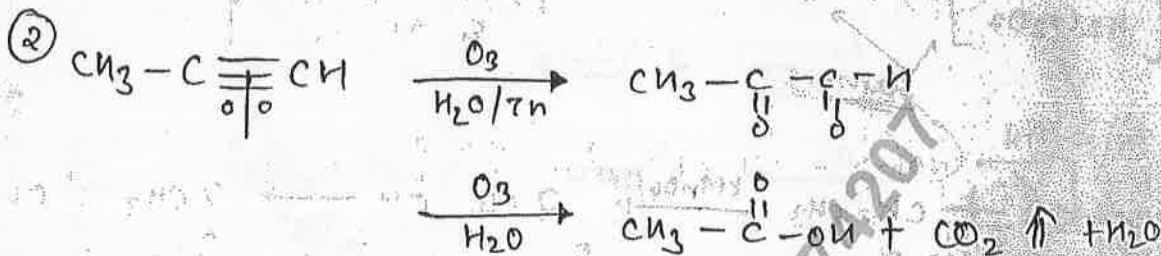
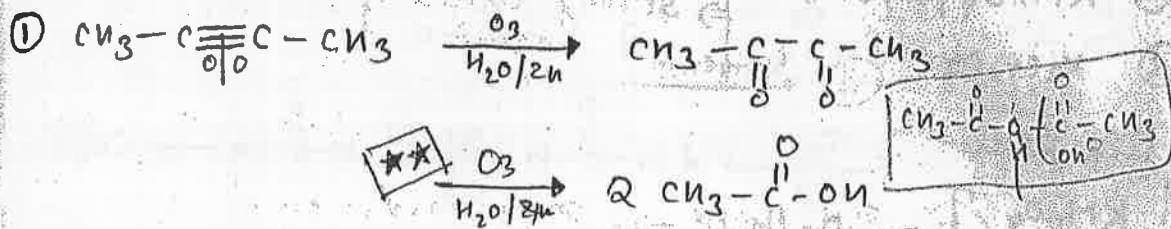
1,2-Dimethyl benzene

⇒ 1,2-Dimethyl ben.
(o-xylene)

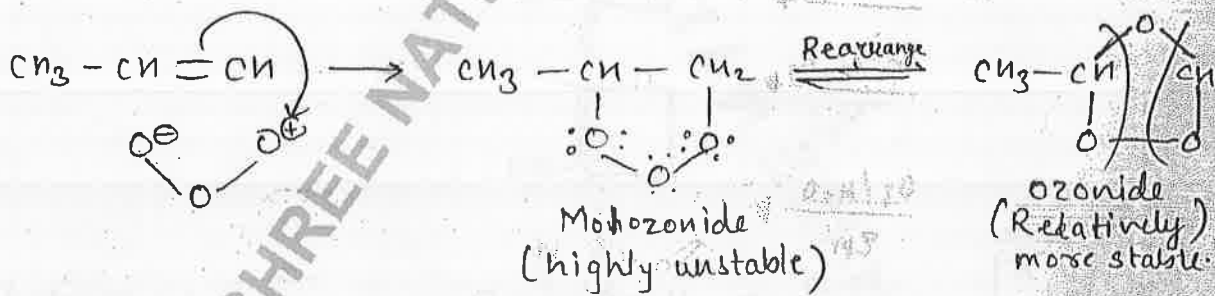
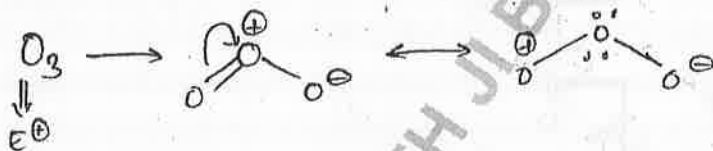
⇒ evidence of
Reso.

⇒ π - e^- cloud
not fixed

Ozonolysis of alkyne :-



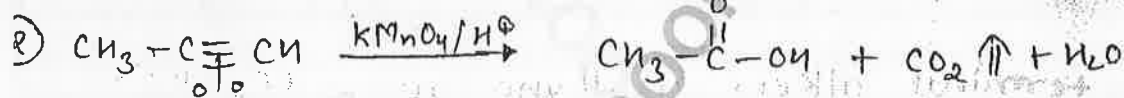
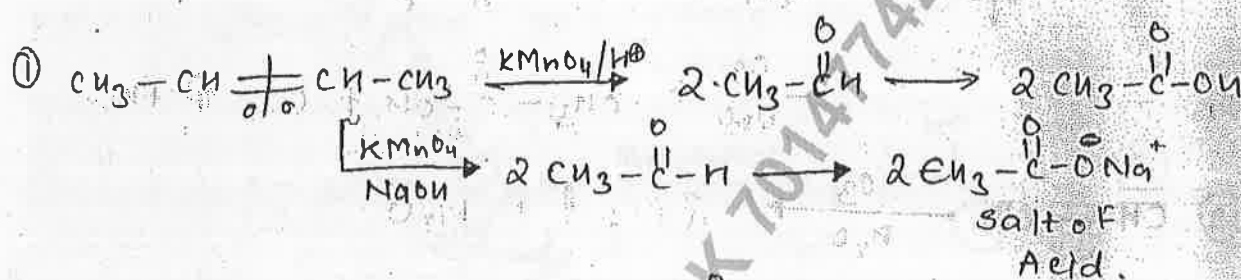
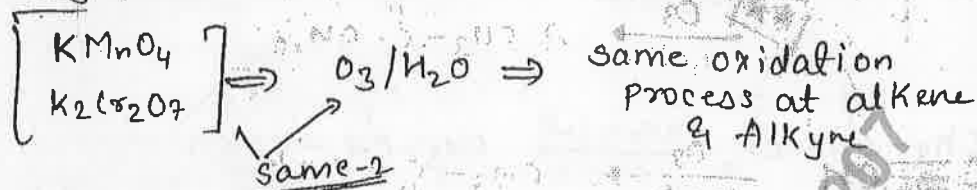
* All terminal alkene & alkyne give CO_2 with $\text{O}_3/\text{H}_2\text{O}$



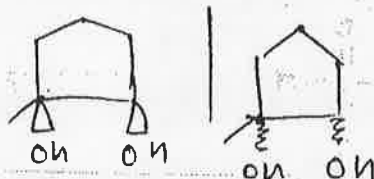
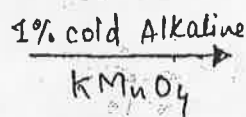
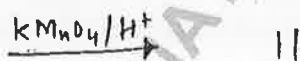
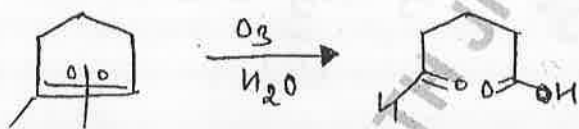
strong oxidising agent →

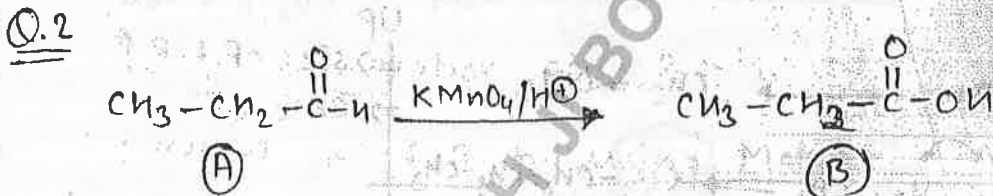
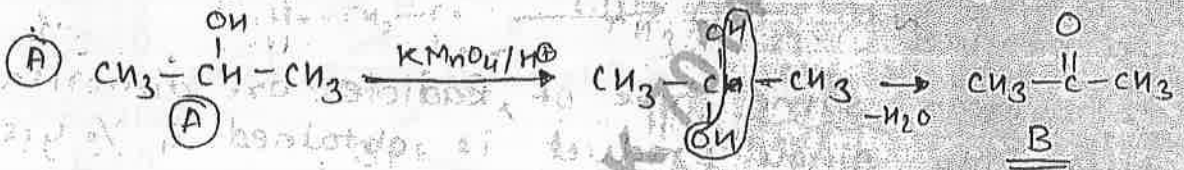
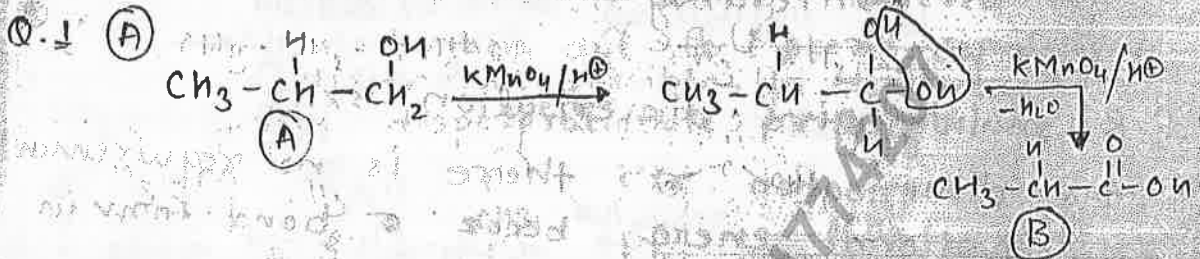
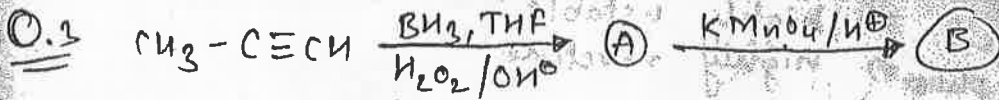
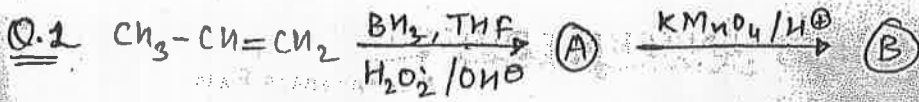
- ① $\text{KMnO}_4 / \text{H}^+ / \text{OH}^- / \Delta$
 ② $\text{K}_2\text{Cr}_2\text{O}_7$ } strong oxidising agent

key point: -



Q.1

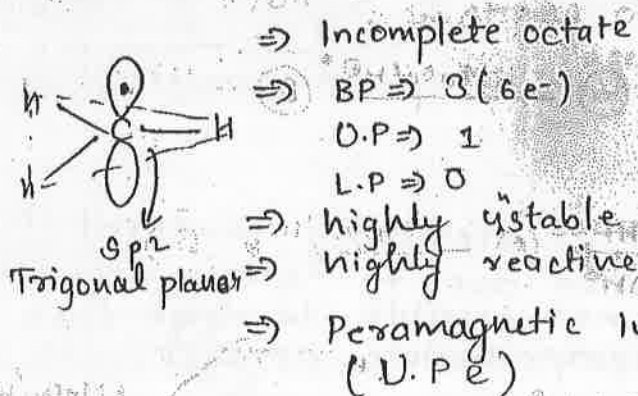




SHREE NATH J BOOK

FREE RADICAL INTERMEDIATE:

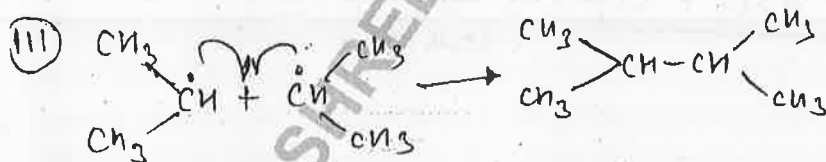
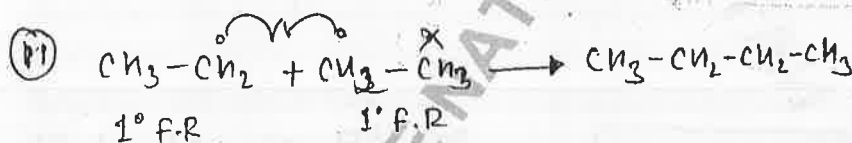
Exothermic Rxn



* F.R mainly give dimerisation rxn.

* During dimerisation rxn there is no requirement of activation energy becoz σ bond form in a product.

* Whenever ² same type of ^{free} Radicle are dimerised then only single product is obtained & % yield of product increase.



UP

\Rightarrow size of F.R \uparrow

\Rightarrow Rate of Dimerisation \uparrow

\Rightarrow Rate of Disproportionation \uparrow

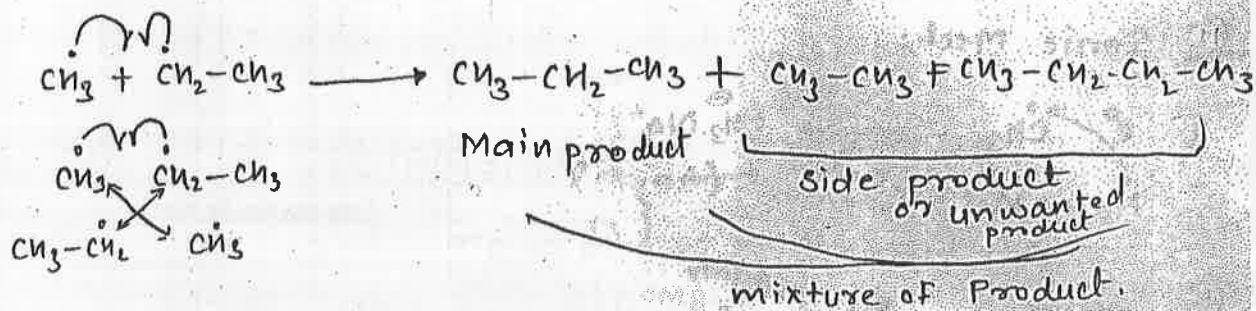
\Rightarrow % yield of main product \downarrow

down

Key point

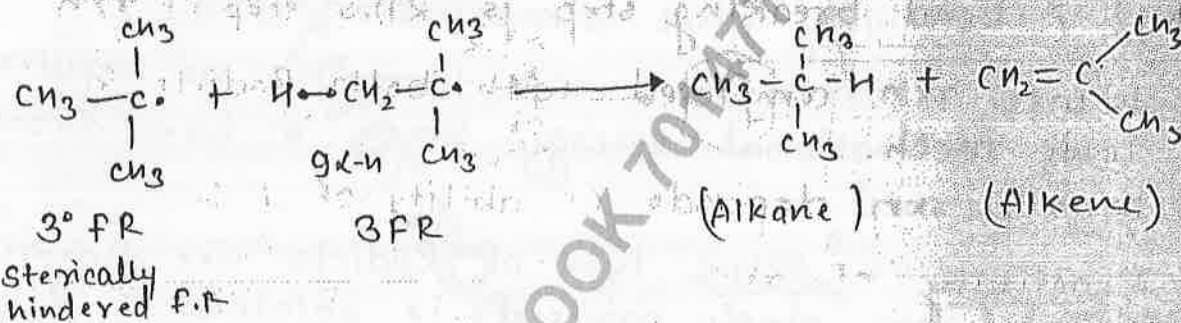
* Rate of dimerisation $\propto \frac{1}{\text{Size of F.R}}$

* Whenever 2 different types of F.R are dimerised then mixture of product obtained & % yield of main product \downarrow , this rxn is known as combination rxn.



* Disproportionation Rxn.

* Whenever 3° F.R or sterically hindered F.R are dimerised then due to steric repulsion effective collision not possible, in these case rxn mainly give disproportionate product.

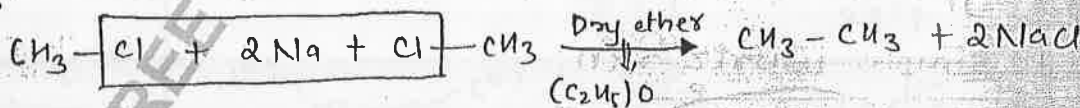


Different Generation of F.R :-

A) Formation of F.R by using Metal :-

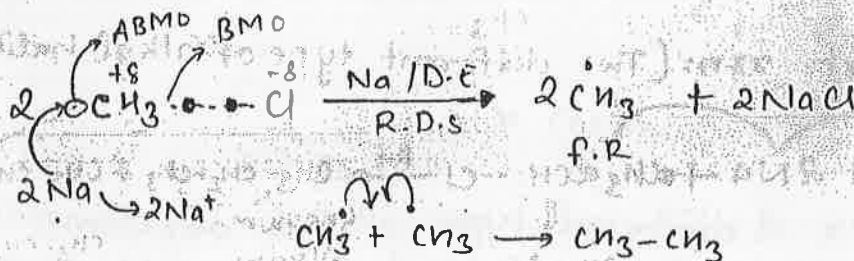
① Wurtz Rxn :-

Net Rxn

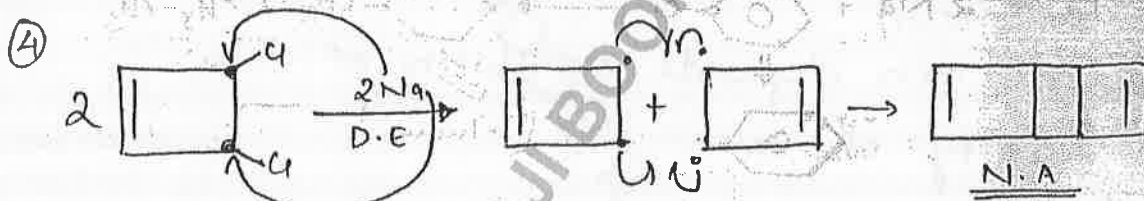
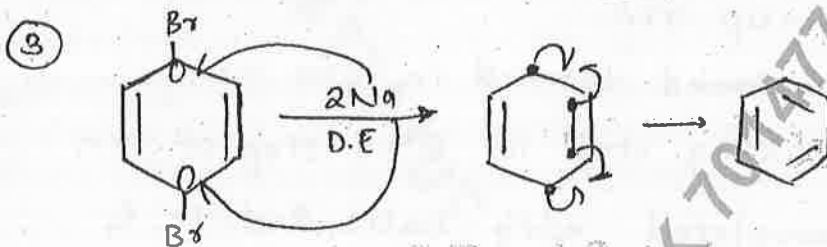
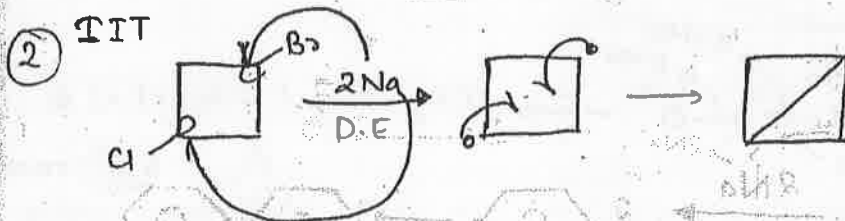
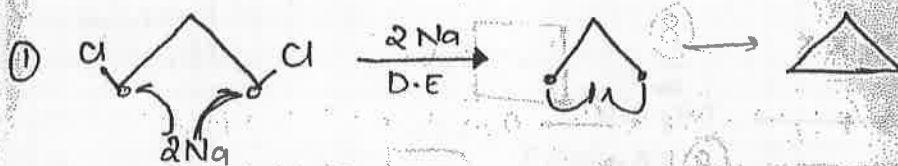


Mech

① F.R Mech ⇒



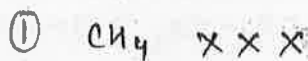
(3) Intra molecular Wurtz:

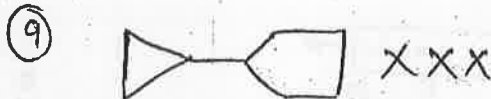
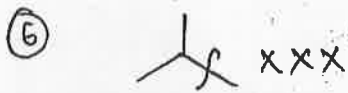
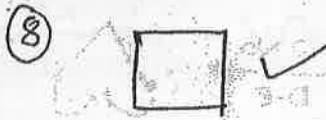
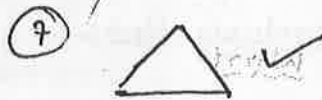


* Odd no. carbon containing alkane (unsymmetrical alkane) does not form by wurtz rxn (not suitable), becuz mixture of product obtained.

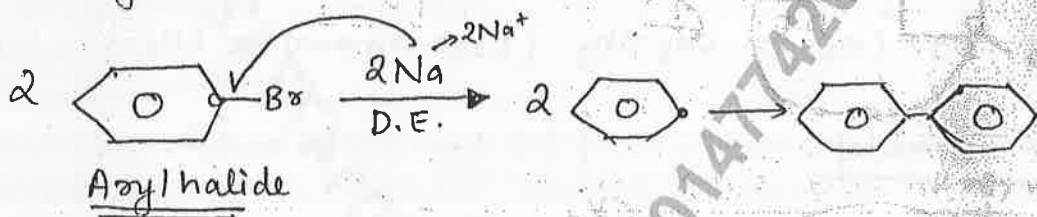
* CH_4 can not form by this rxn.

Q. Which of the following alkane can't form by wurtz rxn with better yield.

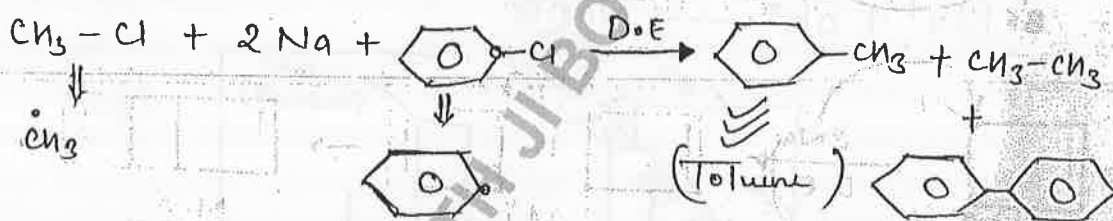




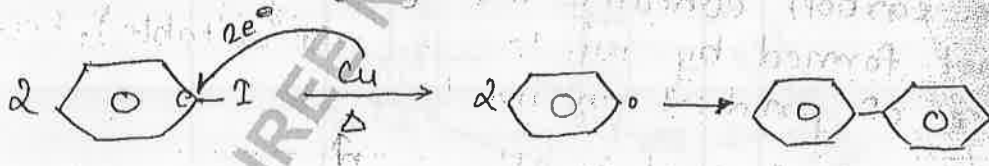
② Fittig Rxn :- [Aromatic]



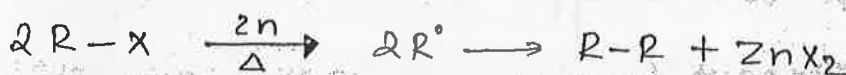
③ Wurtz-Fittig Rxn. :- (चार Party)



④ Wulman's Rxn → [Aromatic]



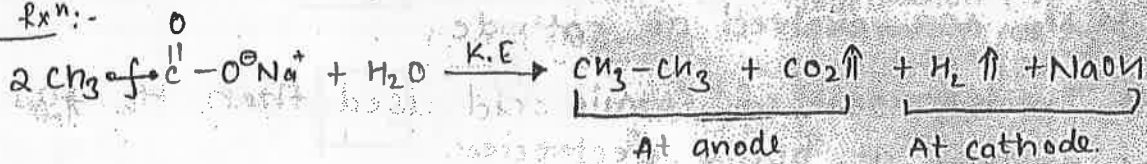
⑤ Franklin Rxn :-



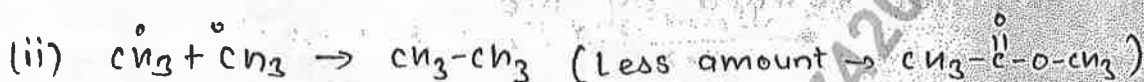
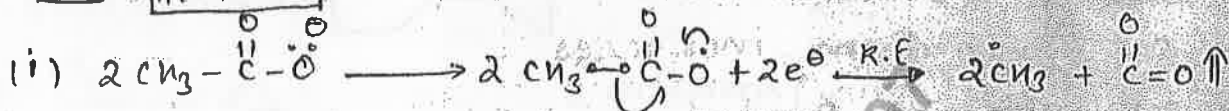
(B) Formation of f.R by using current:-

(1) Kolbe's Electrolysis Rxn:-

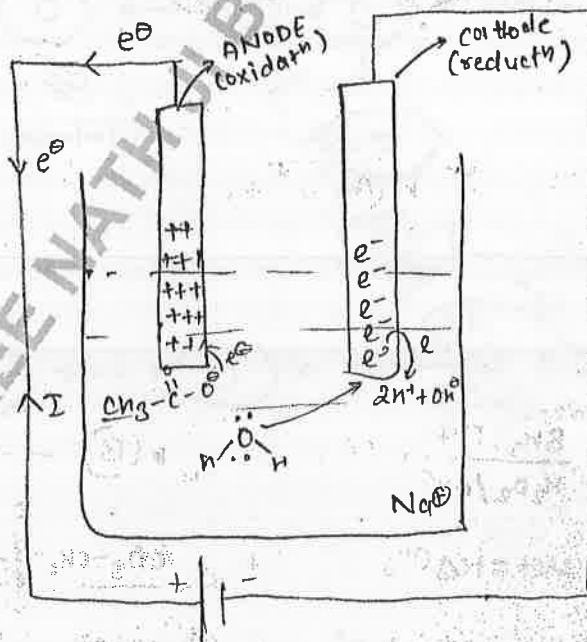
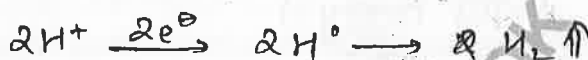
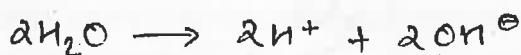
Net rxn:-



Mech. At. Anode →

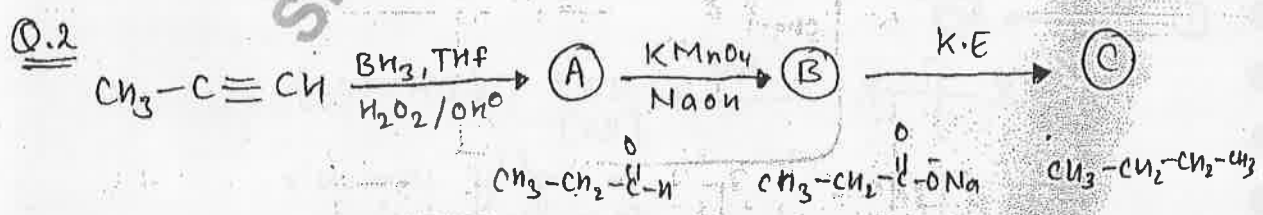
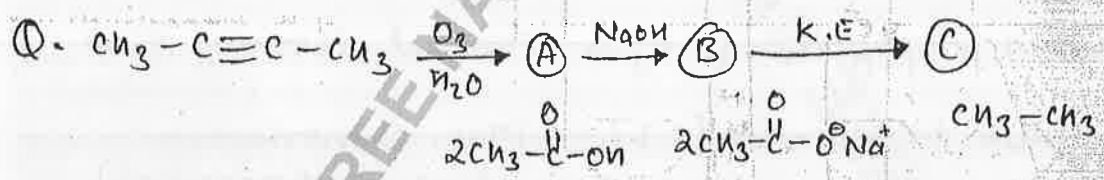
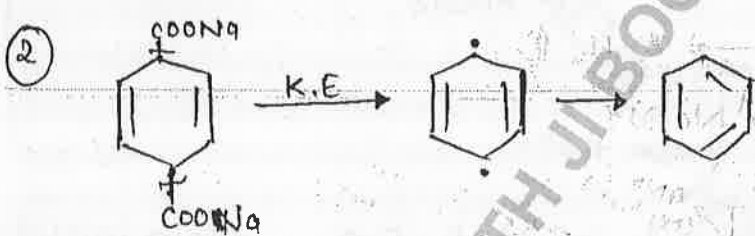
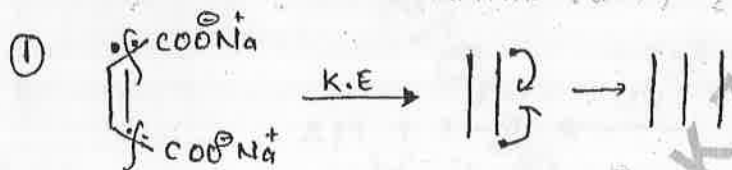


At cathode



Imp points

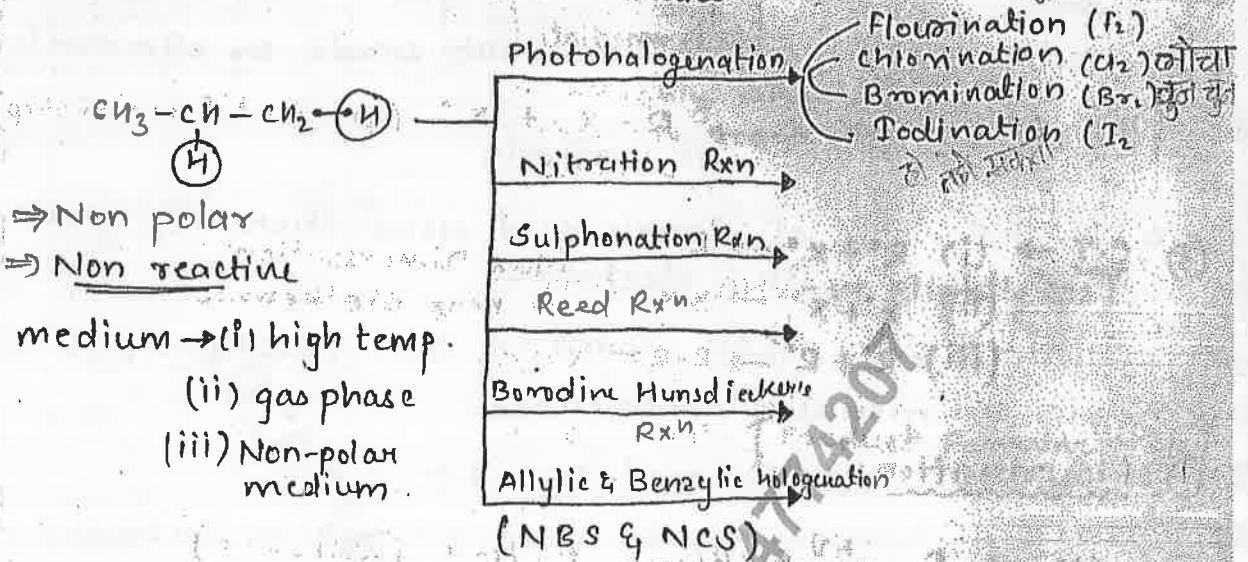
- * In K.E ethane gas evolved at anode by elimination of $\text{CO}_2 \uparrow$ (g).
- * H_2 gas evolved at cathode
- * In K.E salt of formic acid used then H_2 gas evolved at both electrodes.
- * During K.E NaOH form in rxn medium, so PH of medium increases.
- * CH_4 can not formed by K.E



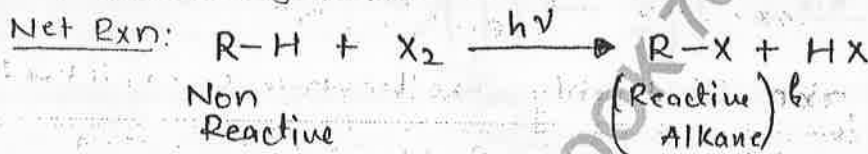
© formation of f.R by using photon:-

Ex. f.R. substitution rxn [FRSP]

AIM: formation of reactive alkane.



Photohalogenation Rxn :-



⇒ General Mech of FRSP ⇒

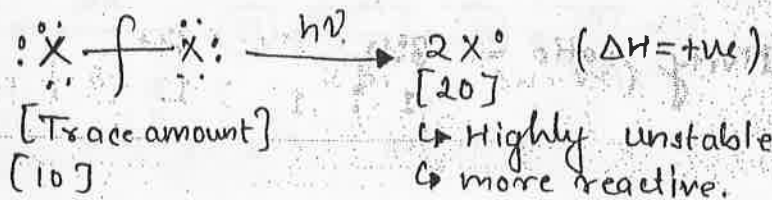
→ f.R chain follow chain Rxn.

[i] chain initiation [C.I.] → $h\nu, \Delta, \text{R}_2\text{O}_2$... chain initiation

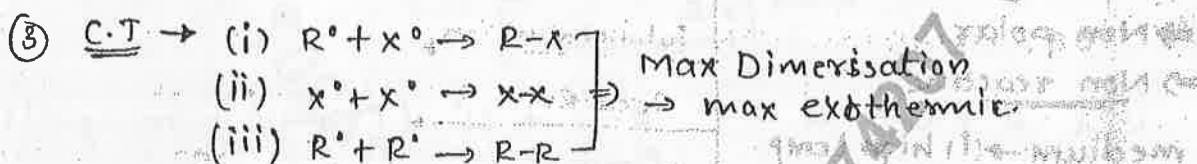
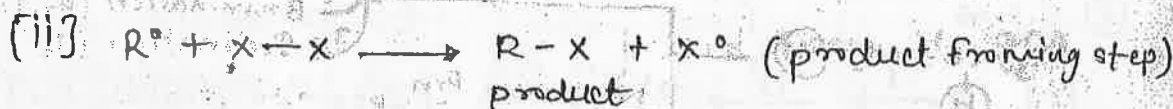
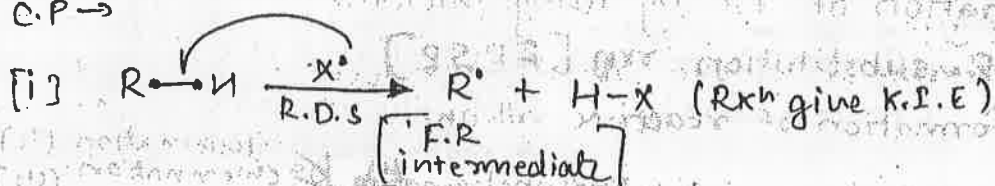
[ii] chain propagation [C.P] → Product forming step.

[iii] chain termination [C.T] → Max. Dimerisation (max. exothermic step)

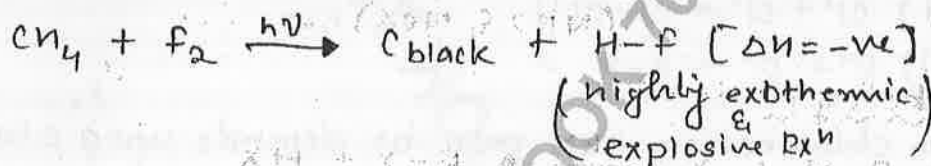
① C.I →



② C.P →

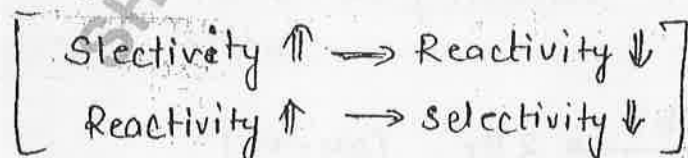


① Flourination:



- * flourination rxn is highly exothermic & explosive Rxn
- * flourination highly reactive & non-selective rxn
- * flourination does not depends upon stability of F.R
- * In flourination rxn carbon black as product.
- * flourination rxn occurs even in dark.

Reactivity / selectivity concept:



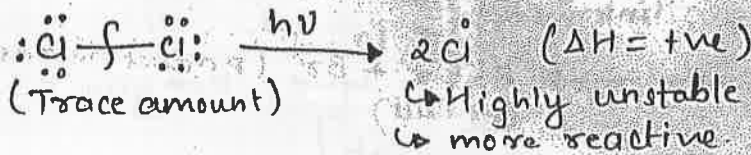
per-H selectivity ratio ⇒ 3°H : 2°H : 1°H

1 : 1 : 1

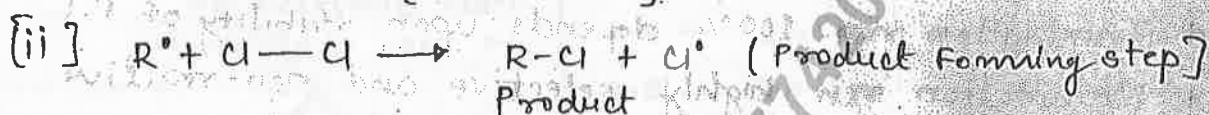
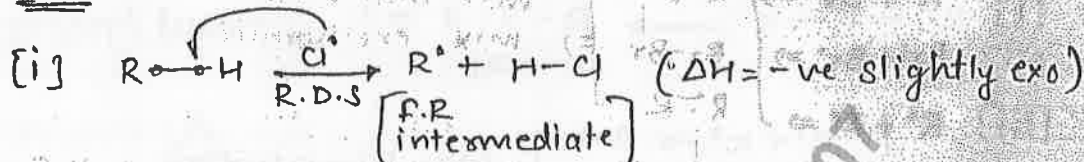
② Chlorination Rxn:



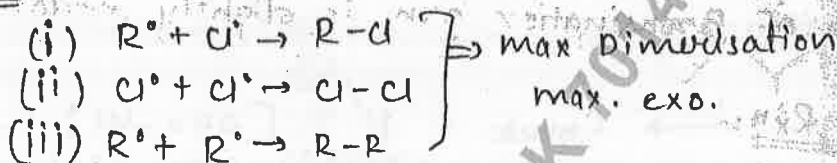
① C.I →



② C.P ⇒



③ C.T →

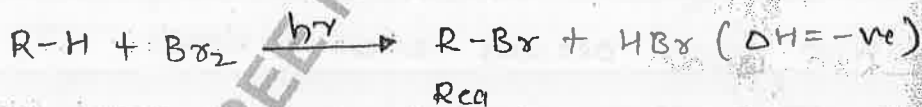


* Chloro chlorination rxn may be depends upon stability of f.r.

* R.D.S step of chlorination rxn is slightly exothermic

Per-H selectivity ratio: ⇒ 3°H : 2°H : 1°H
5 : 3.8 : 1

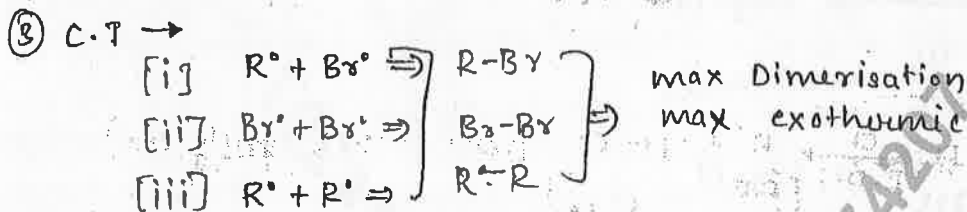
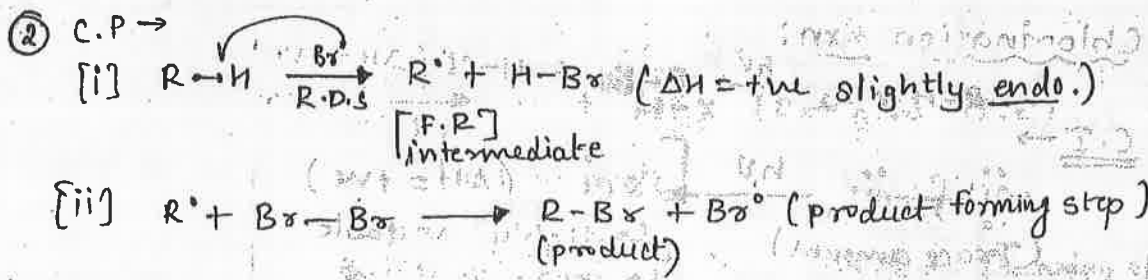
⊛ Bromination Rxn:



Per H - selectivity ratio ⇒ 3°H : 2°H : 1°H
1600 : 82 : 1

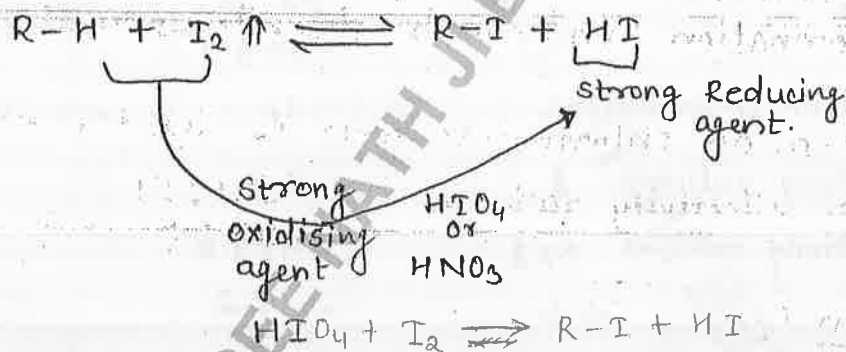
① C.I →



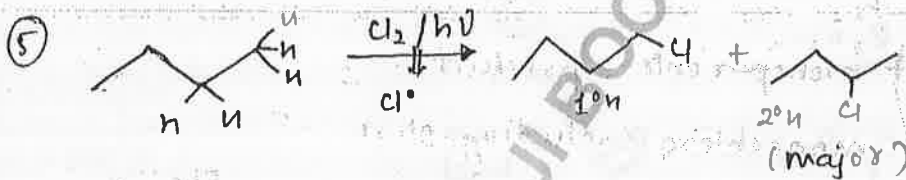
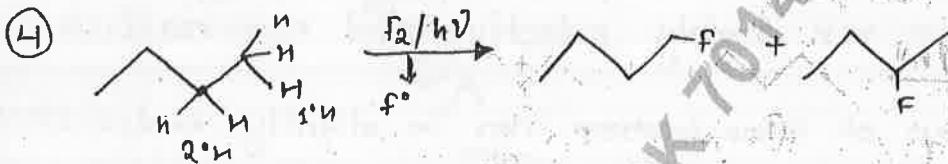
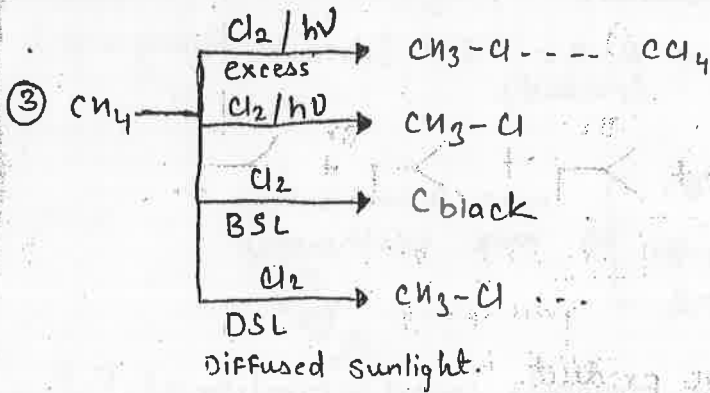
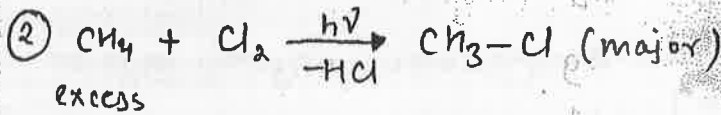
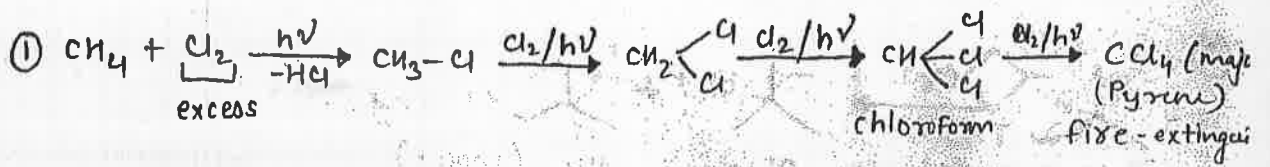


- * Bromination rxn 100% depends upon stability of F.P.
- * Bromination rxn highly selective and non-reactive rxn.
- * R.D.S step of Bromination rxn is slightly endothermic

4) Iodination Rxn:-



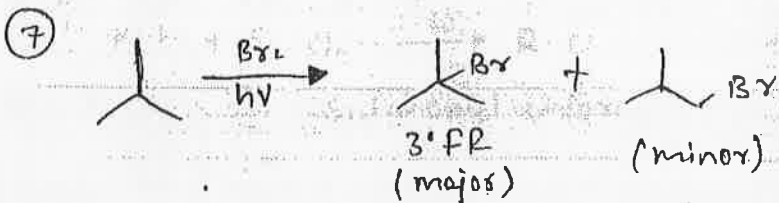
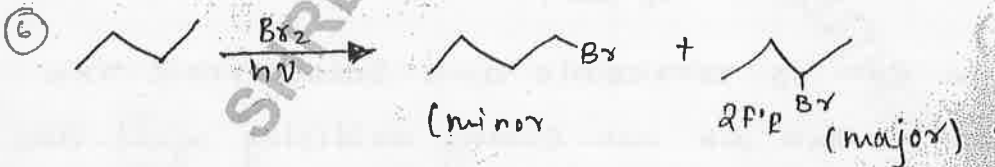
- * Iodination Rxn is reversible and endothermic rxn
- * In Iodination Rxn we use strong oxidising agent like HIO_4 or HNO_3

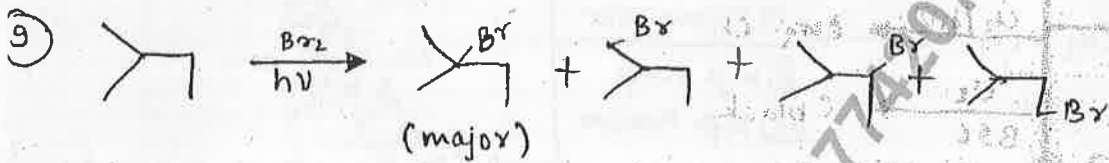
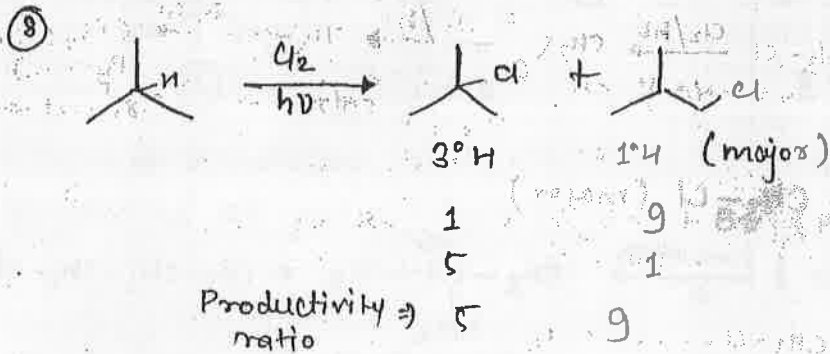


No. of H-Atom ⇒ 6

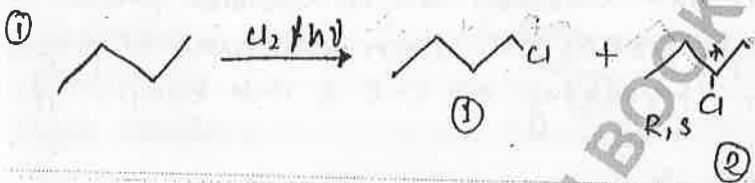
selectivity ratio ⇒ 4 3.8

productivity ratio ⇒ 6×4 4×3.8
 ⇒ 6 ⇒ 15.2





Total no. of monochloro product.

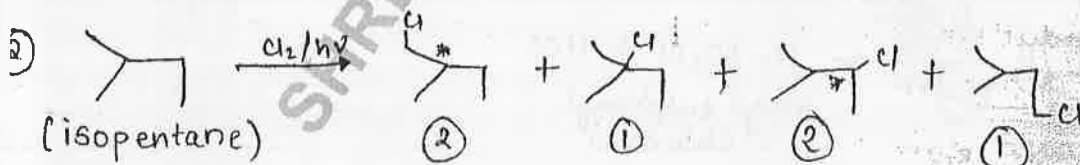


→ Total no. of monochloro product = 3

→ Total no. of monochloro including stereo = 3

→ Total no. of monochloro product excluding stereo product = 2

→ " " " " distilled / fractioned product = 2

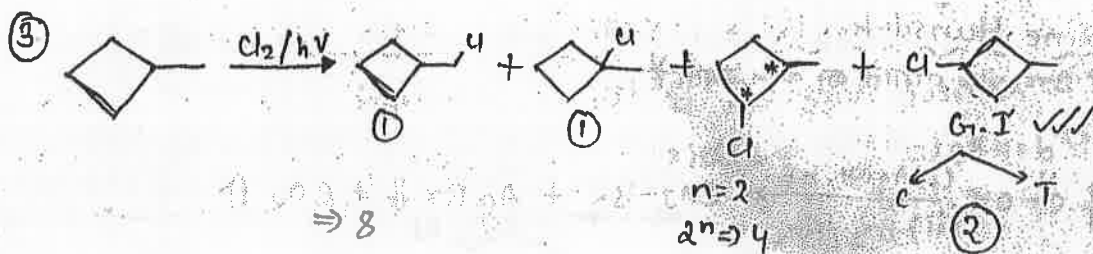


(A) ⇒ 6

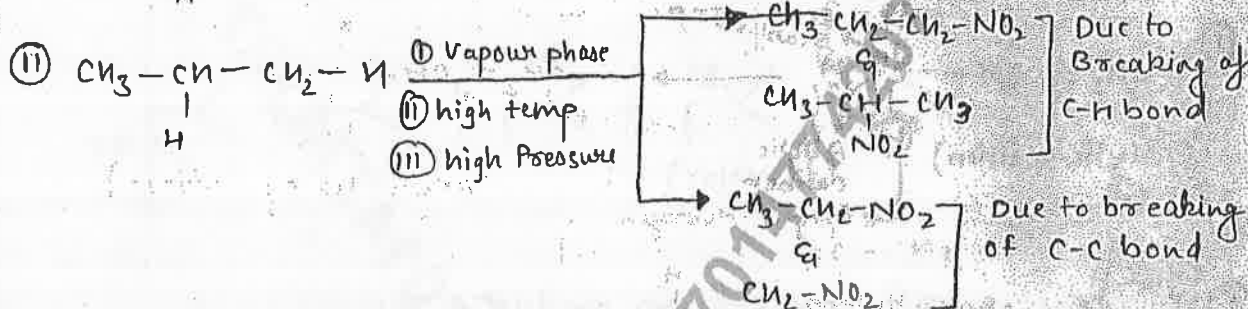
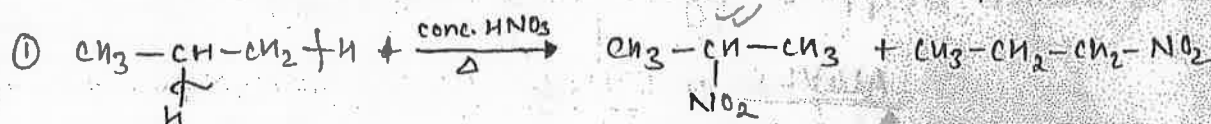
(B) ⇒ 6

(C) ⇒ 4

(D) ⇒ 4

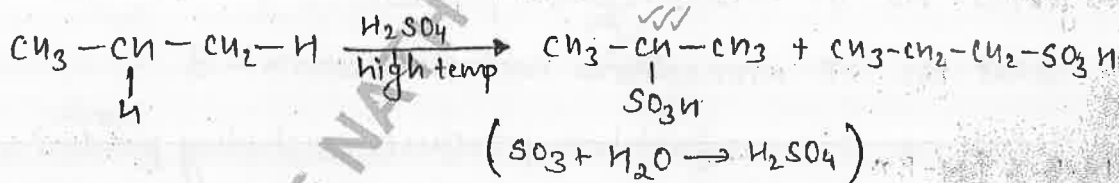


② Nitration Rxn :-

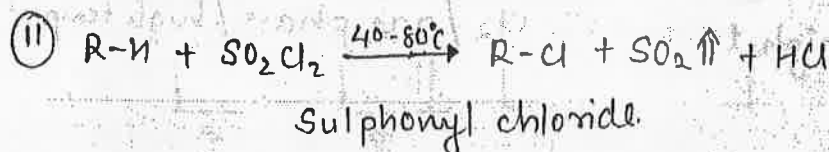
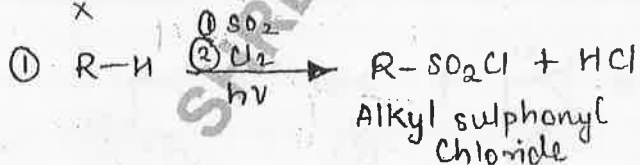


* Whenever nitration rxn carried out in vapour phase, high temp. & high pressure then mixture of product obtained due to breaking of C-C & C-H bond.

③ Sulphonation Rxn \rightarrow

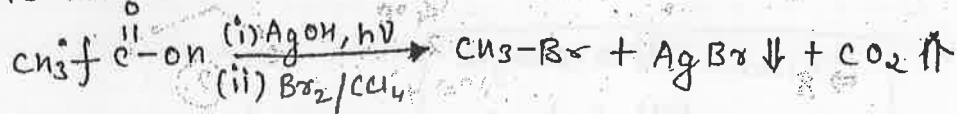


④ Reed Rxn \rightarrow



⑤ Borodine Hunsdiecker Rxn →
 → Bromine लगाने का काम करता है।

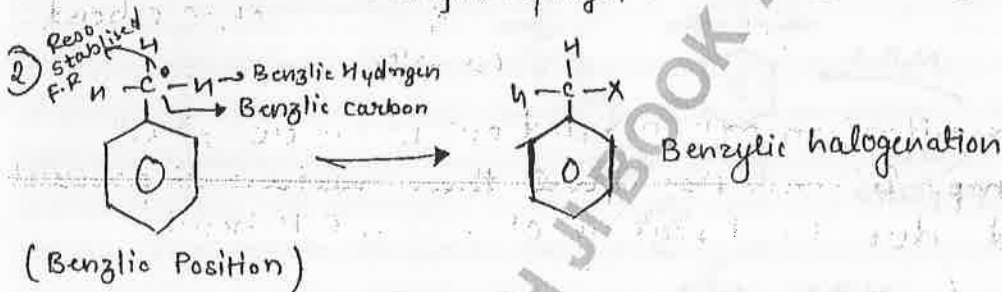
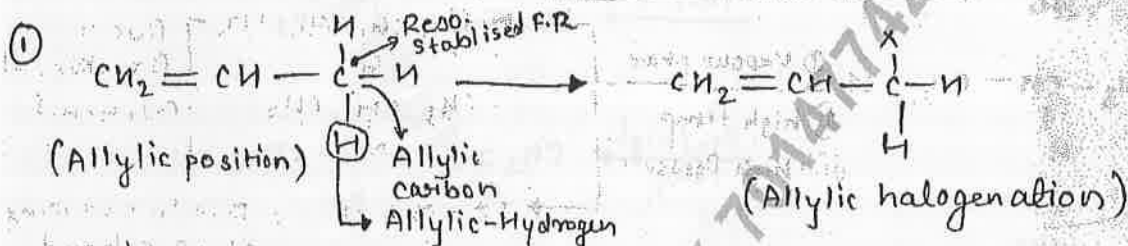
Net Rxn



* It is a stepdown rxn

* formation of ppt of AgBr is driving force of rxn.

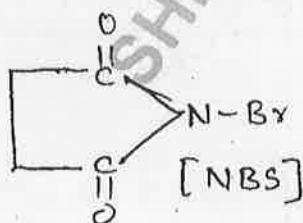
ALLYLIC & BENZYLIC HALOGENATION (selective Halo)



* Reagent used for allylic & Benzlic halogenation:

Bromination

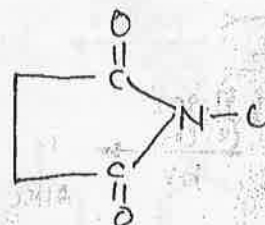
① N.B.S [N-Bromo Succinimide]



② Br₂ / gas phase / high temp, hν

Chlorination

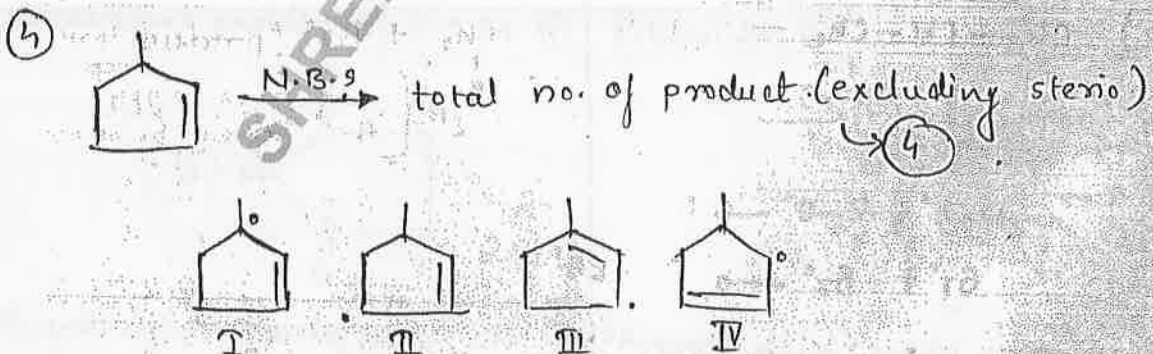
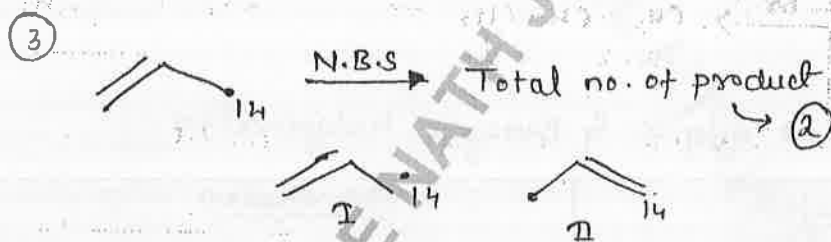
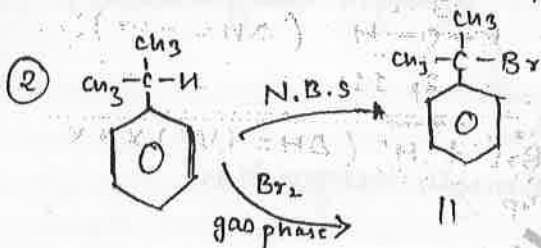
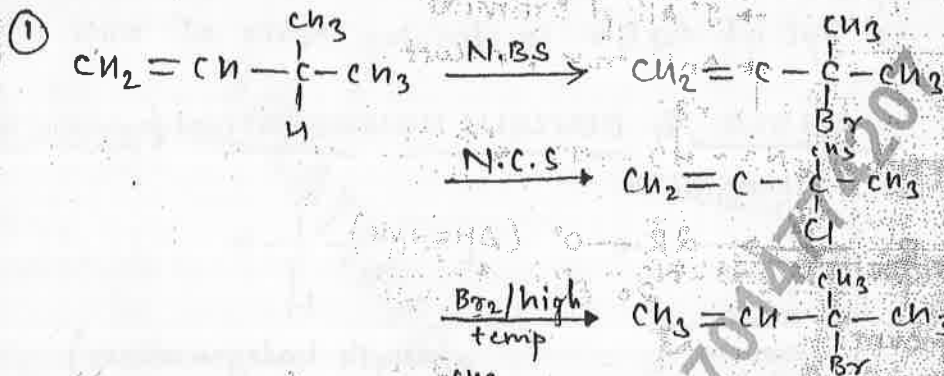
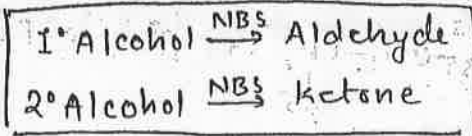
① N.c.s [N-chloro succinimide]



② Cl₂ / gas phase / high temp, hν

N.B.S in ORGANIC CHEMISTRY:

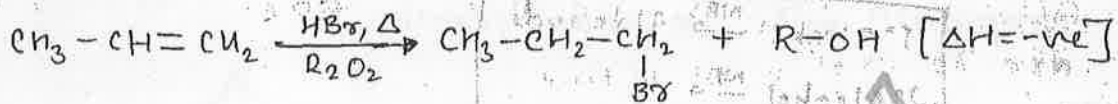
- Allyl Hallogenation at Allylic & Benzylic position
- N.B.S oxidising agent (It oxidised 1° alcohol & 2° alcohol into aldehyde & ketone)
- Mild O.A.



formation of F.R by using heat (Δ). 1 Questⁿ always

1) Free Radical addition Rxn [FRAR]/Peroxide effect / Kharash effect / Anti M.K. rxn.
 polymer

NET Rxn: peroxid $\xrightarrow{\text{always}}$ with HBr (not in molecular form)

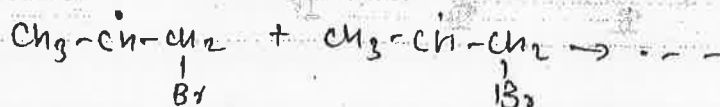
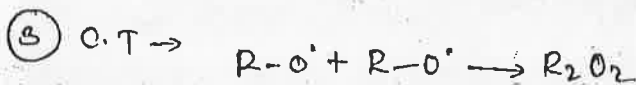
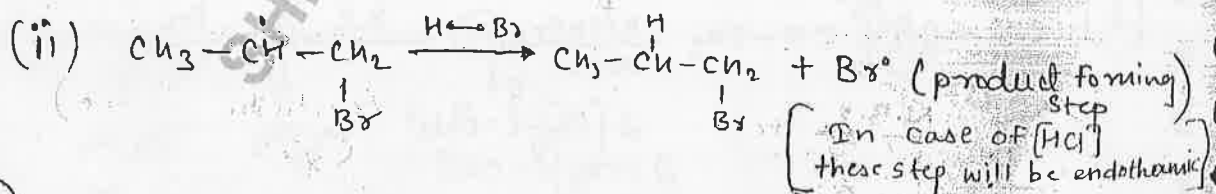
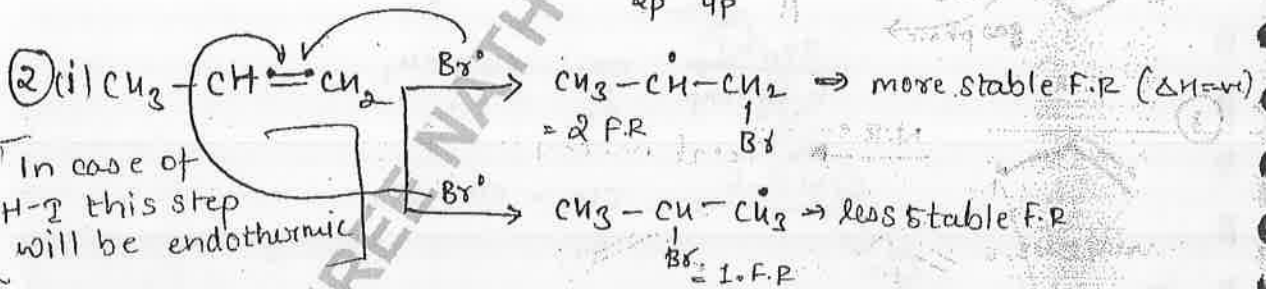
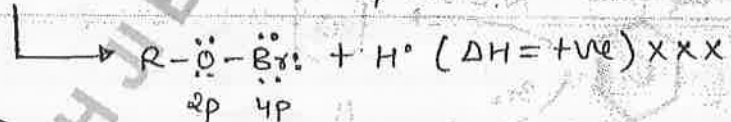
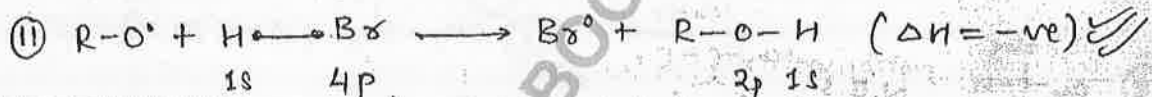
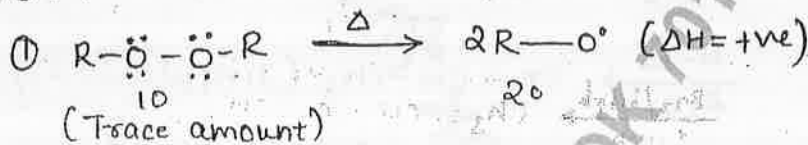


\rightarrow 1° Alkyl Bromide

\rightarrow Anti M.K product.

Mech

① C.T \Rightarrow



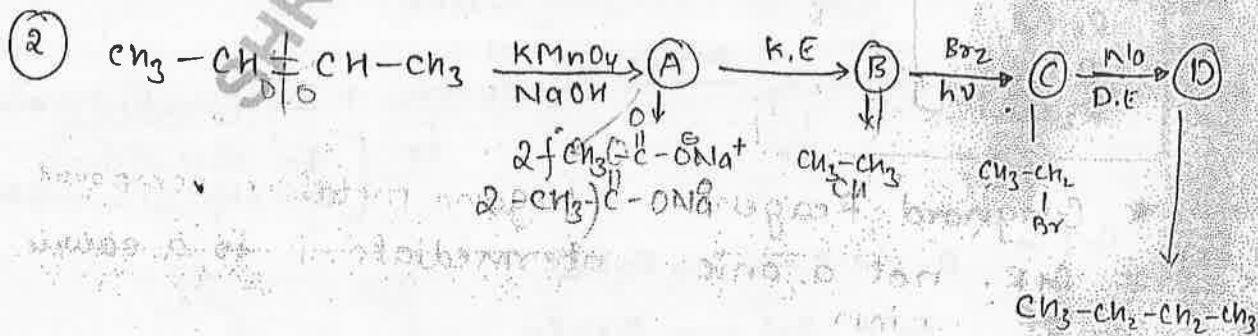
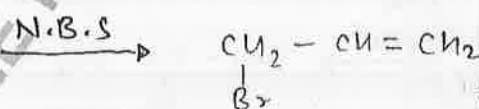
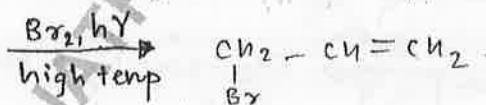
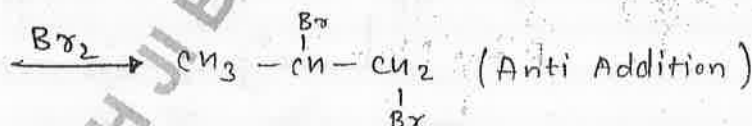
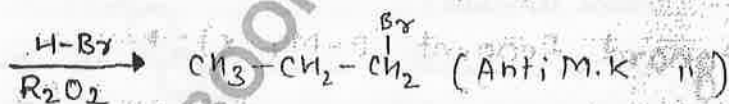
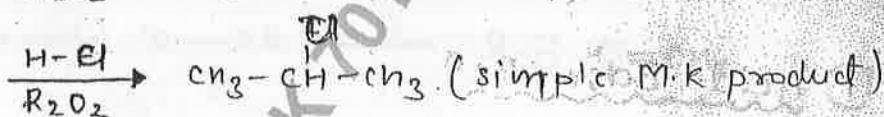
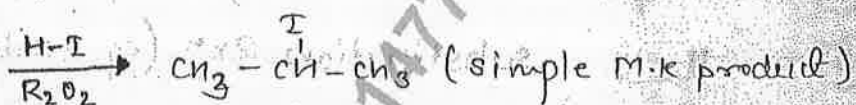
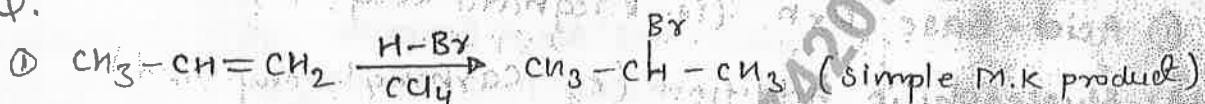
* Rxn completed with RRAR mechanism.

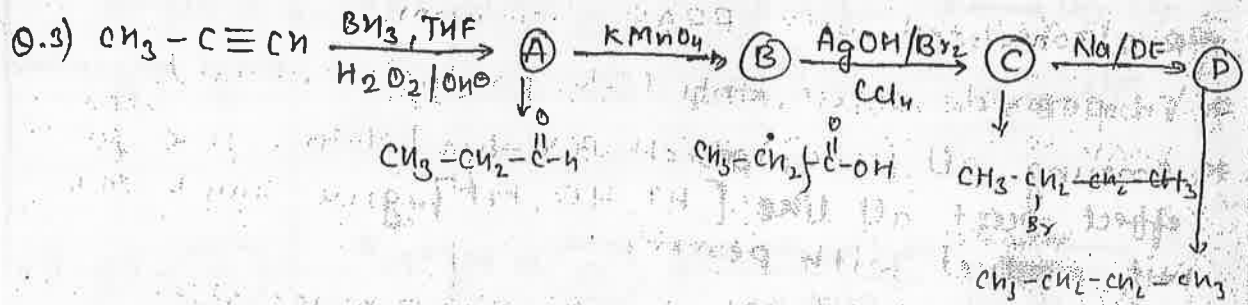
* In peroxide effect Anti M.K. product obtained.

* Among all [H-X] - all H-Br only [H-Br] give peroxid effect rest all like [HI, HCl, HF] give simple M.K. product with peroxide

* In case of [HI] 1st step of chain propagation will be endothermic while in [HCl] 2nd step of chain propagation will be endothermic.

Q.





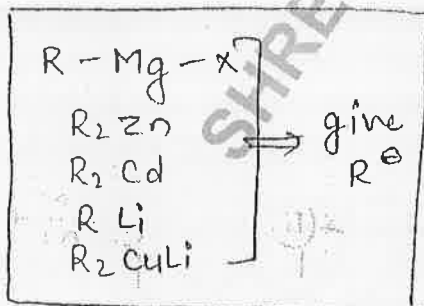
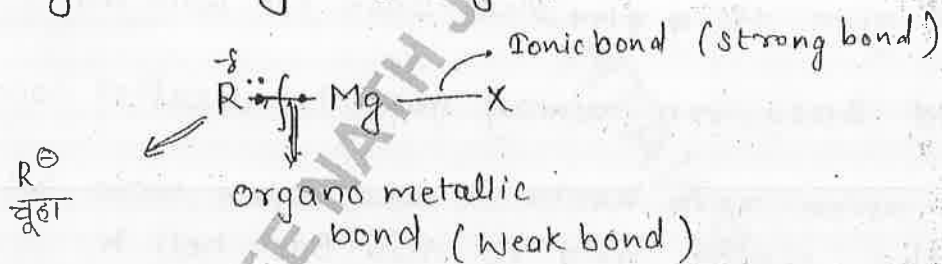
ANION / Nucleophil (nu^-)

* Anion gave mainly three rxn.

- ① Acid-Base Rxn. (eg. Grignard Reagent).
- ② Nucleophilic Addition (eg. carbonyl compound)
- ③ " substitution Rxn (eg. carbonyl halide)

① Acid-Base Rxn.

① Grignard reagent (R-Mg-X) \rightarrow

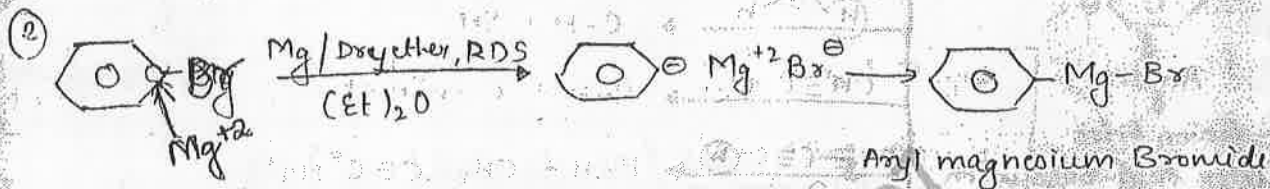
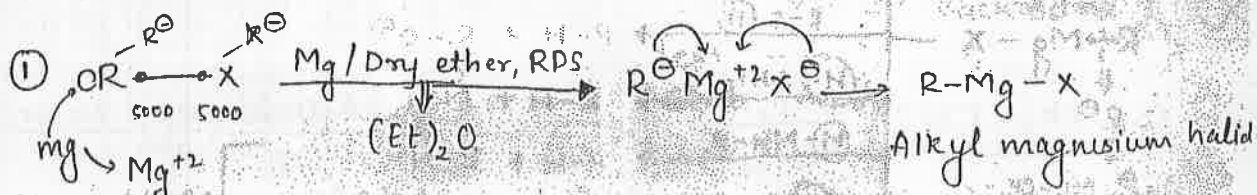


* Grignard reagent is organo metallic compound.

* GR. not a anion intermediate it is a source of anion

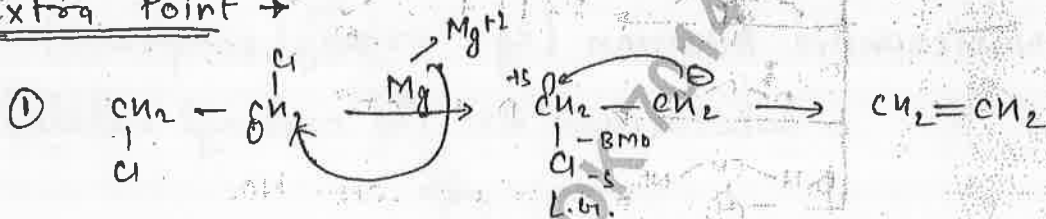
* / /

* Formation of Gr: -



Reactivity of R-X $\Rightarrow \text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$

* Extra Point \rightarrow



Acid-Base Rxn of R-Mg-X

- * Gr. R give 1st of give Acid-base rxn with active-H
- * Acid Base rxn always goes to weaker component.
- * To anion rxn karta h use bane wala anion jadha stable hota to Acid Base hoti h.