Hydrocarbons

ALKANE

Preparation

1) From Unsaturated H.C. —

This process is also known as
Sabatier Senderson Rxn.

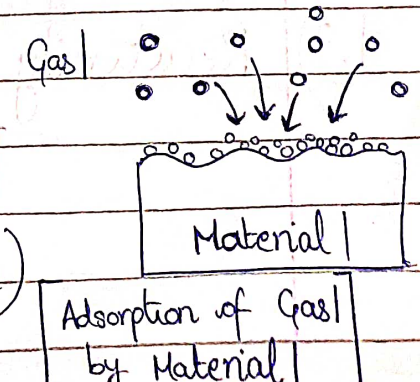
$$CH_2=CH_2 \xrightarrow[Ni/Pt/Pd/Rh/PtO_2]{H_2,\ \Delta} CH_3-CH_3$$

Can also be isotopes of H.

$$HC\equiv CH \xrightarrow[Ni/Pt/Pd/Rh/PtO_2]{2(H_2),\ \Delta} CH_3-CH_3$$

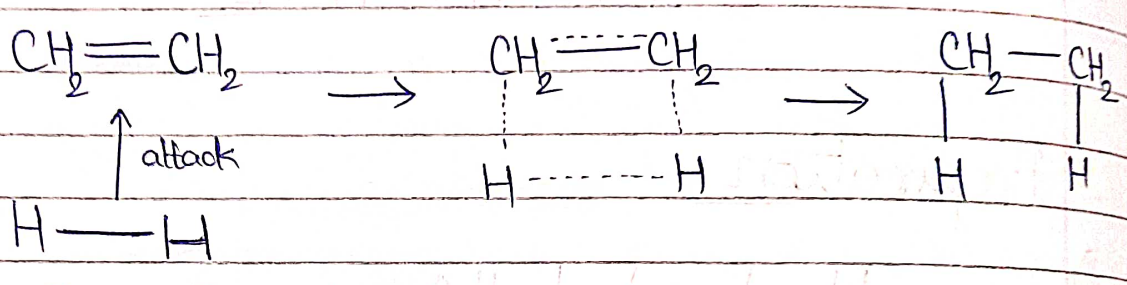
Mechanism : —

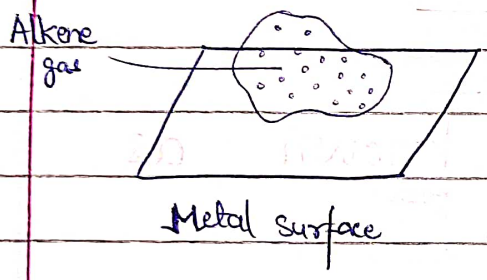
1.1) Happens via Adsorption.
(Molecules ka surface pe chipak jana)



We take a metal surface as catalyst. It has H_2 gas adsorbed.

Alkene is kept over metal surface as gas.





Both H atoms attack from SAME SIDE

$\Rightarrow$ (Syn.) addⁿ.

1.2) Ni / Pd / Pt are used as they —

1.2.1) have good adsorbing power

1.2.2) provide surface area for interaction of gaseous reactant.

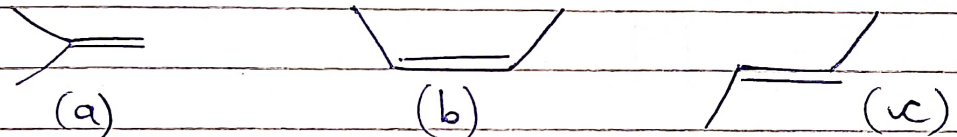
1.3) Reactivity towards Catalytic hydrogenation

Alkyne > Alkane

Reasons : 1.3.1) While add^n of H_2 into alkane, steanic hinderance due to H atoms of alkane is very much.

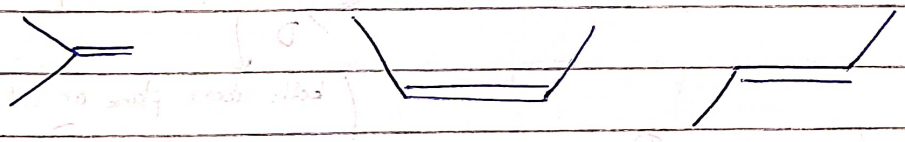
1.3.2) Since size of alkyne molecule is less than alkane molecule, there can be more alkyne molecules per unit surface area of metal surface than alkane molecules.

Q) Predict reactivity order —



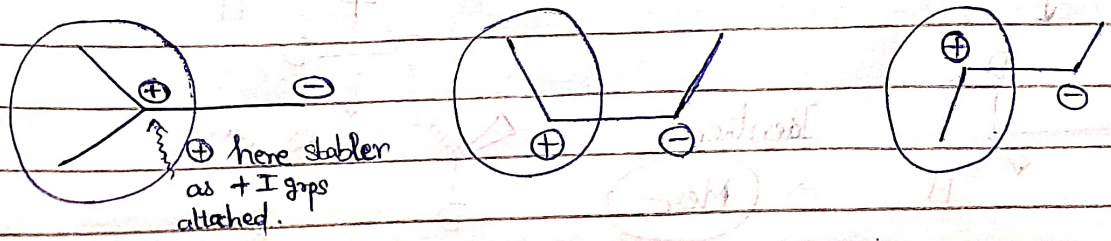
(a) (b) (c)

A) ☆ Compare using stability order!



#α H : 6 6 6

☆ When #α H same, break double bond.



Seeing α H wrt ⊕ : 6 3 3

⇒ (a) more stable than (b) & (c).

Now, (b) → Cis & (c) → Trans.

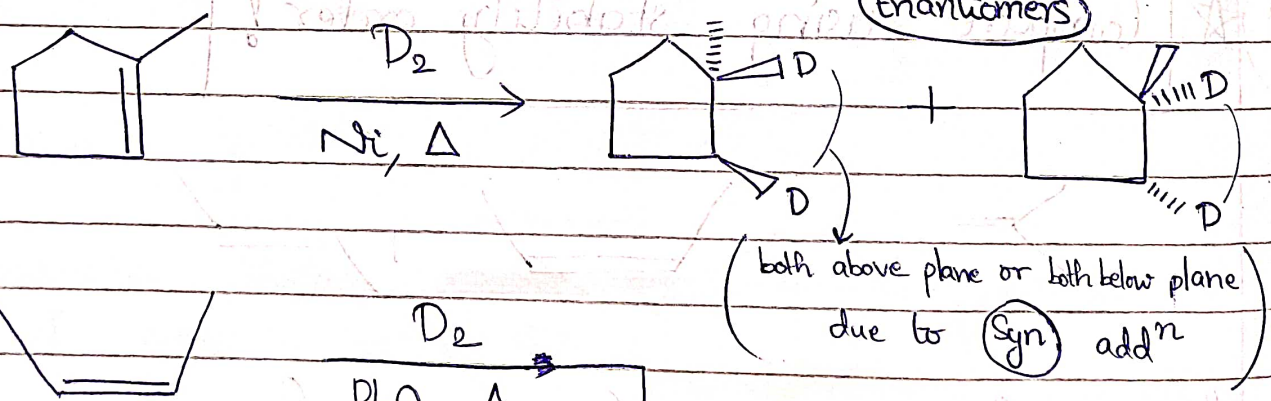
Stability: Trans > Cis.

⇒ Stability: a > c > b

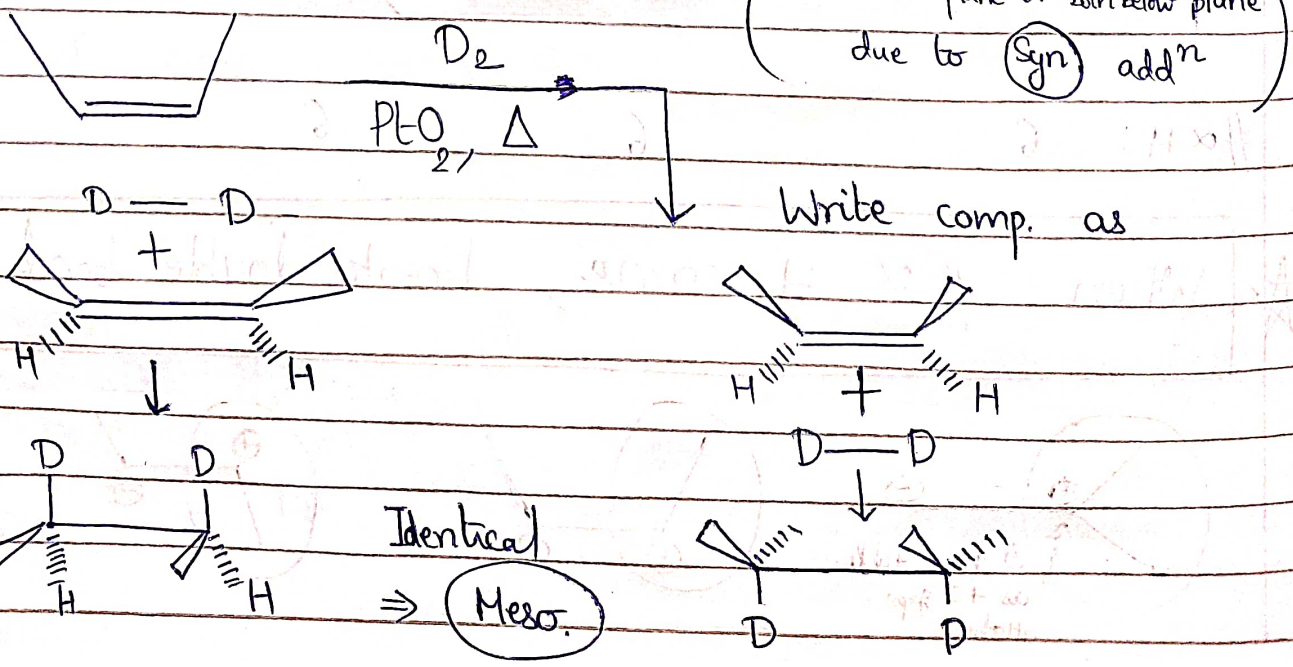
⇒ **Reactivity: b > c > a**

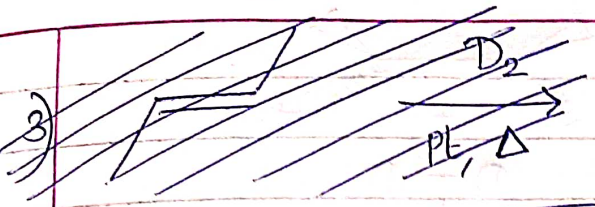
Q) Write product in following rxn —

☆ 1)



☆ 2)



3) 

★ For symmetric molecules,

Cis Anti Racemic.

i.e. anti add^n in cis symmetric comp. gives racemic mix.

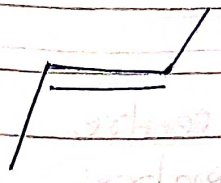
Now, keep any 1 same & change the other 2.

Cis Syn Meso.

i.e. syn add^n in cis symmetric comp. gives meso. comp.

Similarly, Trans Anti Meso.

Trans Syn Racemic.

3) 

Racemic Mix.

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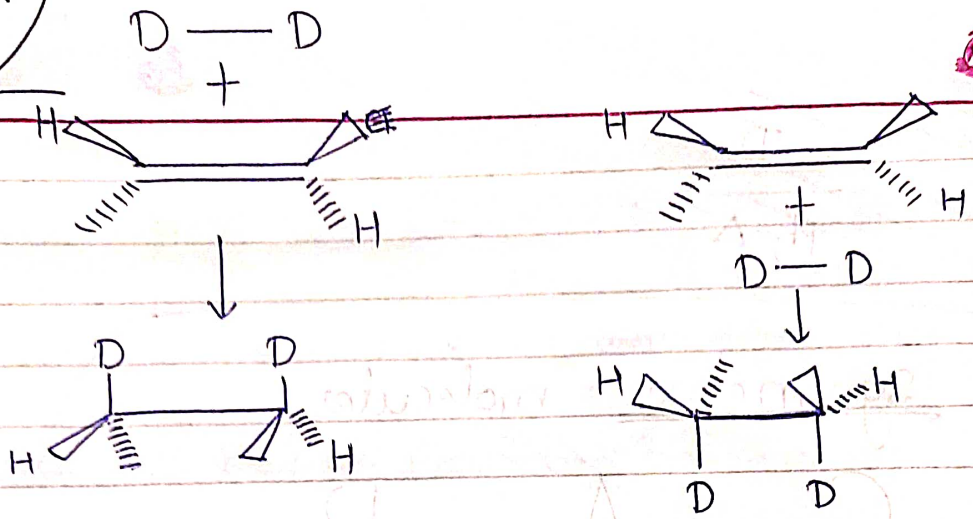
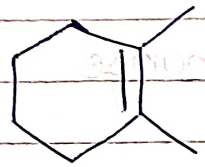
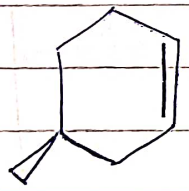
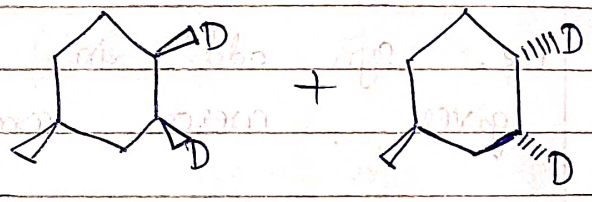


Enantiomers

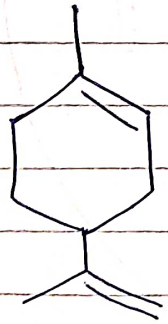
4) 

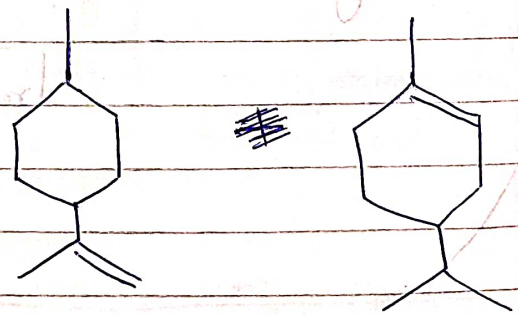
D_2, Ni, Δ → Meso.

5) 

D_2, Ni, Δ → 

Diastereomers

6) 

1 mol H_2, PtO_2 → 

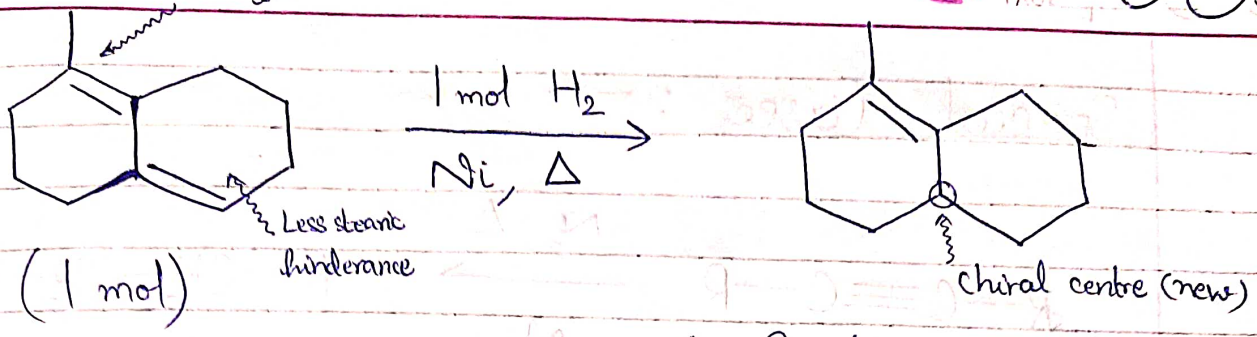
(1 mol)

(As in 5)

(as more steric hinderance in above = bond) ✗ ✓

☆ If comp. already contains a chiral centre & after addⁿ new chiral centres appear ⇒ Diastereomers are formed.

(as 1 chiral ~~centre~~ centre fix ⇒ symmetry won't come in prod.)

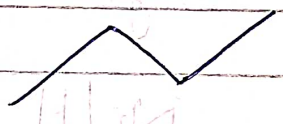
7) 

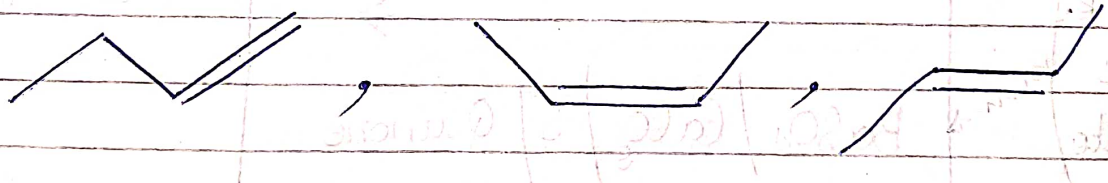
⇒ Enantiomers

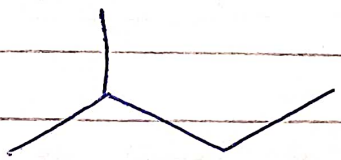
☆ In a region,

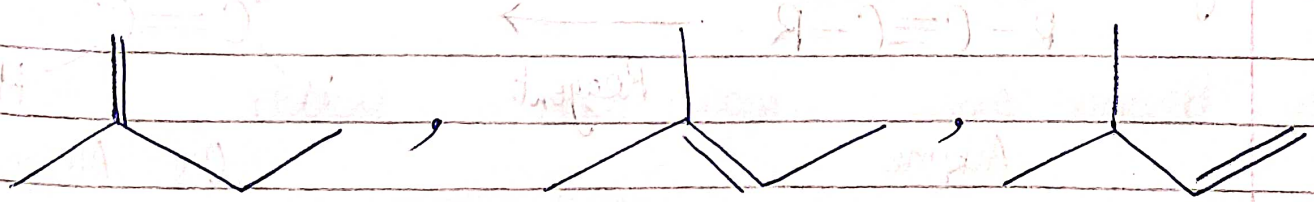
More H atoms ⇒ Less steanic hinderance

↳ Less bulky grps present

8) (# Alkenes) $\xrightarrow[Ni,\ \Delta]{H_2}$ 

A) 

9) (# Alkane) $\xrightarrow[Ni,\ \Delta]{H_2}$ 

A) 

Special Cases :—

$$R-C\equiv C-R \xrightarrow[Ni]{N_2,\ \Delta} R-CH_2-CH_2-R$$

$$\left(\text{dashed} \rightarrow R-CH=CH-R \text{ dashed} \right)$$

We can stop rxn in b/w to get alkenes.

1) Lindlar's Reagent & Rosnmund's Reagent :

(Metal ki surface gher lete hain) ⇝

$Ni/H_2,\ \Delta$ $BaSO_4/CaCO_8/S/$ Quinone	(Cis Alkene)

Eg :

$$R-C\equiv C-R \xrightarrow[\text{Reagent}]{\text{Lindlar's}} \underset{H}{\overset{R}{}}C=C\overset{R}{\underset{H}{}}$$

Alkyne — Cis. Alkene

Eg :

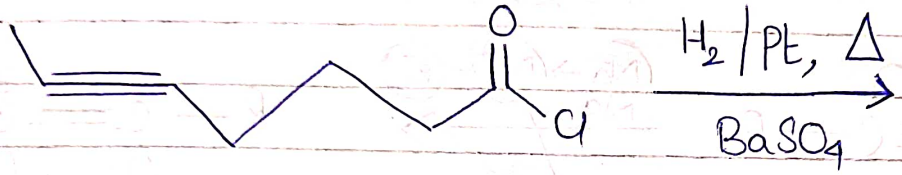
$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{Reagent}]{\text{Rosnmund's}} R-\overset{O}{\overset{\|}{C}}-H + HCl$$

Acid halide — Aldehyde

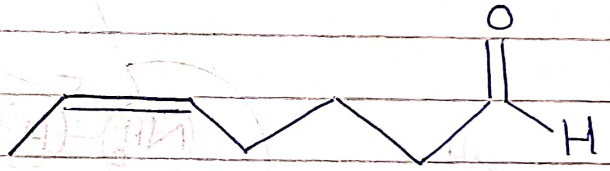
~~Aldehyde (SOH)~~
~~Aldehyde~~

With alkyne, we call it Lindlar's

With acid halide, we call it Rosenmund's

Q) 

A) Cis & ~~Aldehyde~~ $-COH$



2) Birch's Reagent :

$$\xrightarrow[\text{liq. } NH_3]{Na/Li,\ \Delta} \text{(Trans Alkene)}$$

Reduces alkynes into trans alkene

Also, reacts with conj. double bonded system

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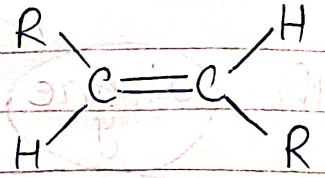
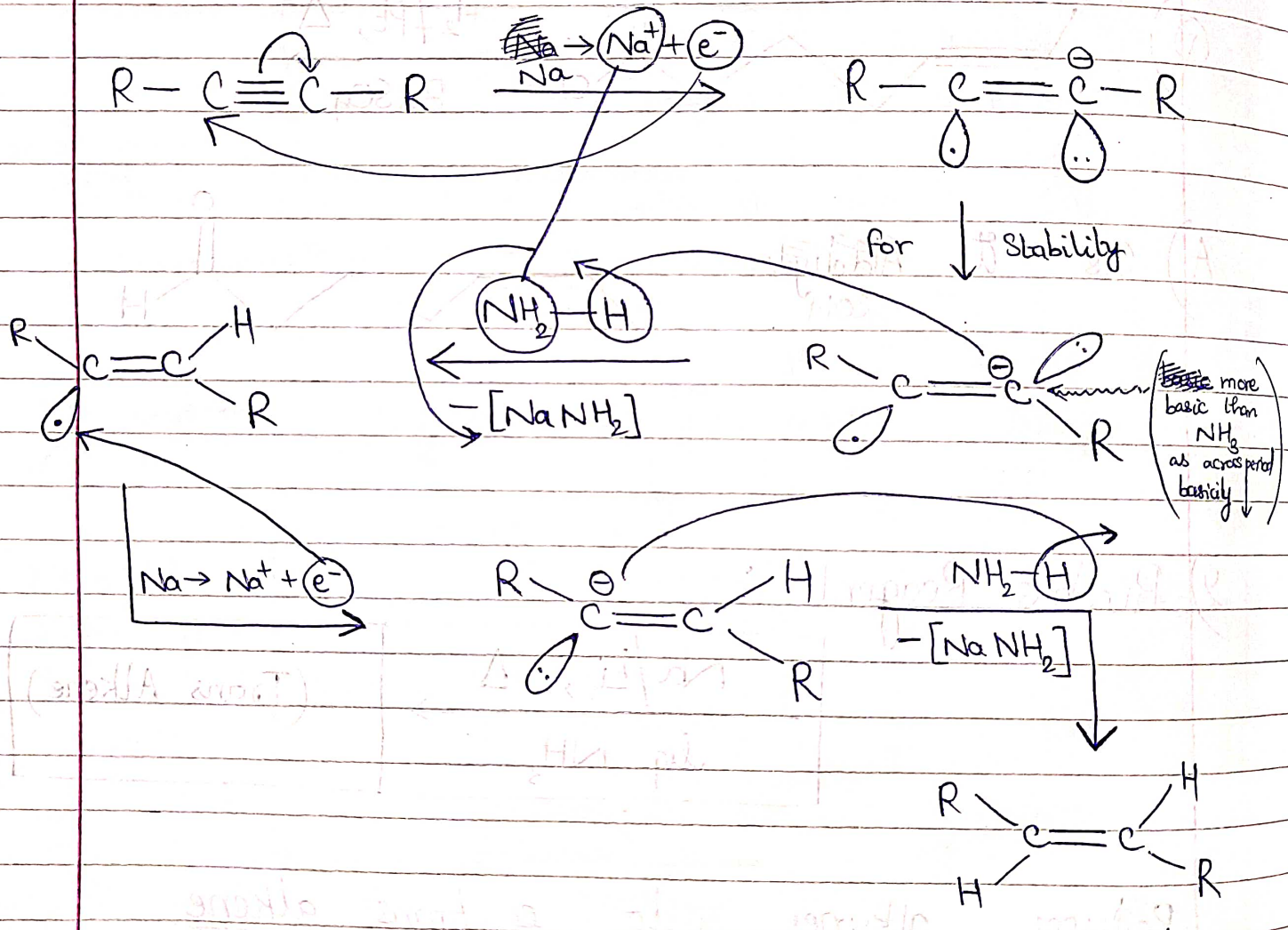
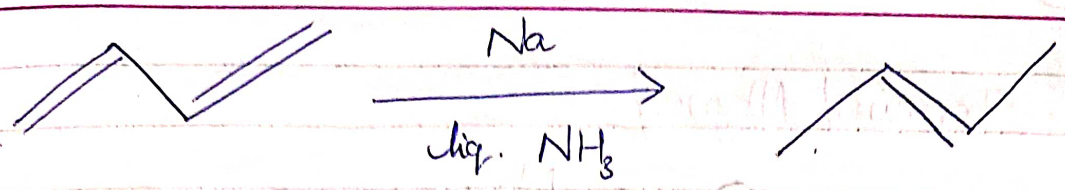
2.) $R-C\equiv C-R \xrightarrow[\text{liq. } NH_3]{Na}$ 

Trans alkene.

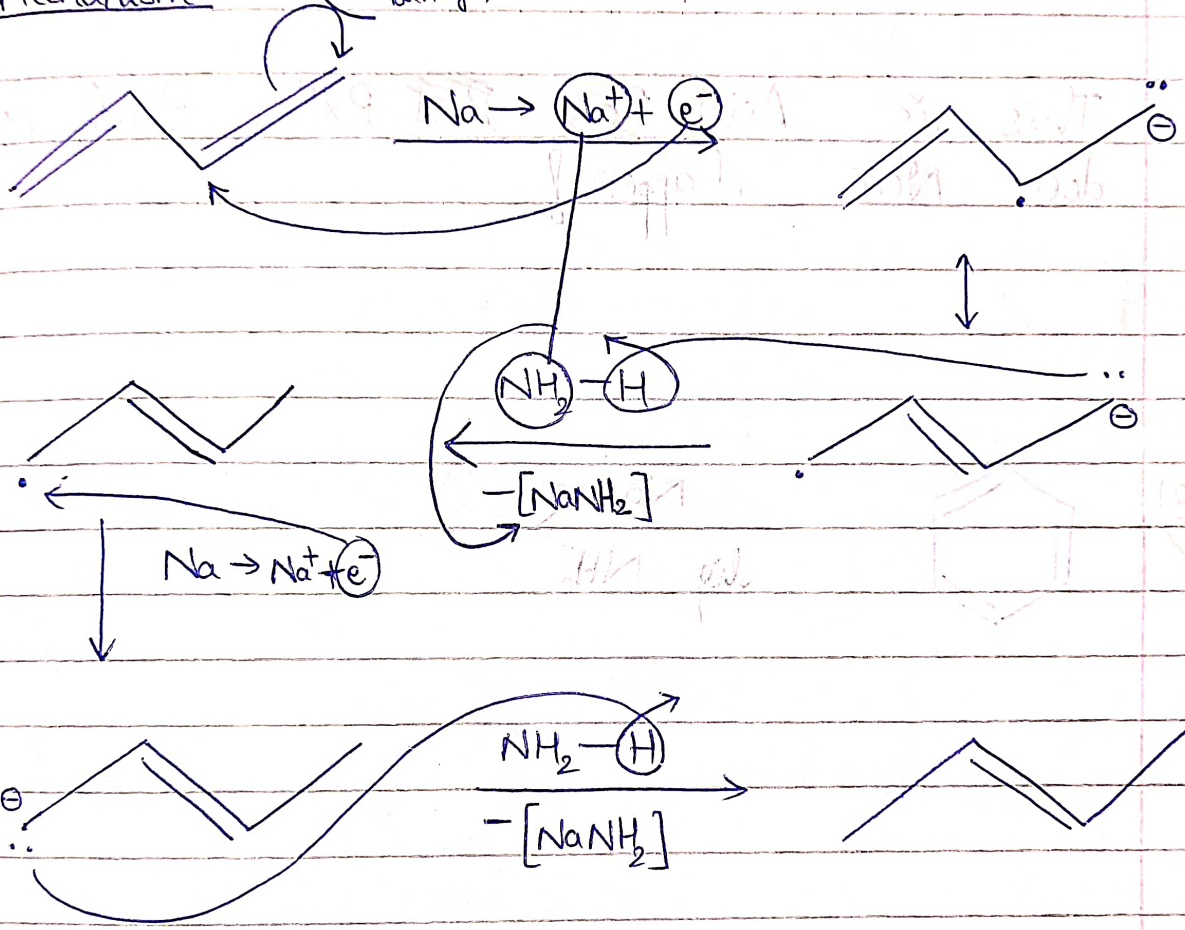
Mechanism -



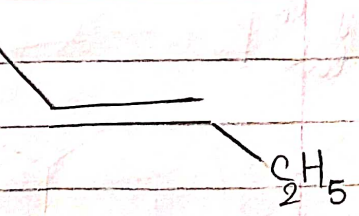
Q.2)



Mechanism — (kisi bhi side tod do, since ek ⊕ aur ek ⊖ banega, same stability in this case)



Q) Write product —

1) $CH_3-C\equiv C-C_2H_5$ —Li, liq. NH_3→ 

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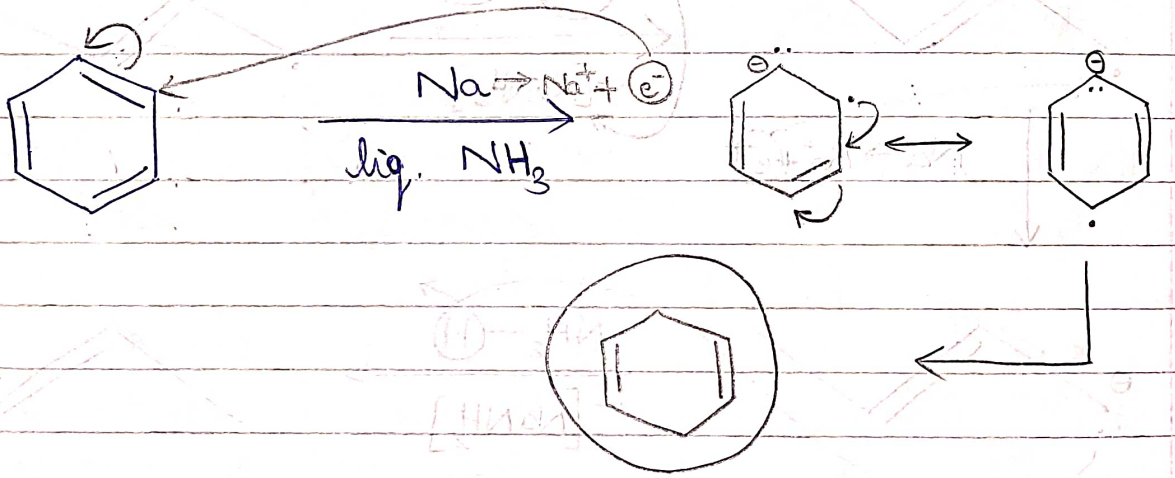
Terminal Alkyne!

★ 2) $CH_3-C\equiv C-H \xrightarrow[\text{liq. } NH_3]{Na} CH_3\equiv C^{\ominus}\ Na^{\oplus} + \frac{1}{2}H_2$

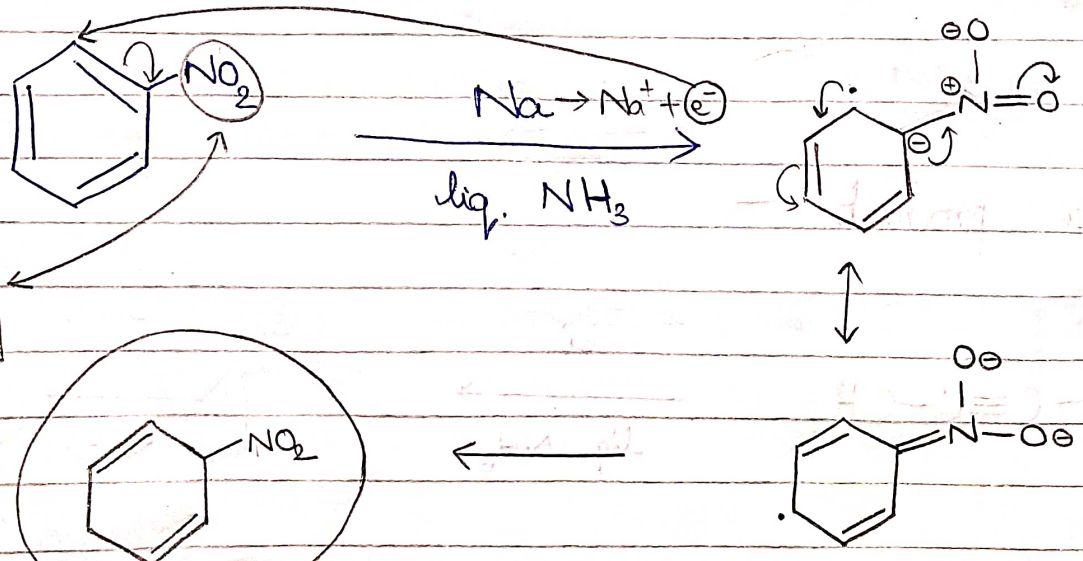
acidic.

This is: Acid Base ~~Red~~ RX^n Birch rx^n
does NOT happen!

3)



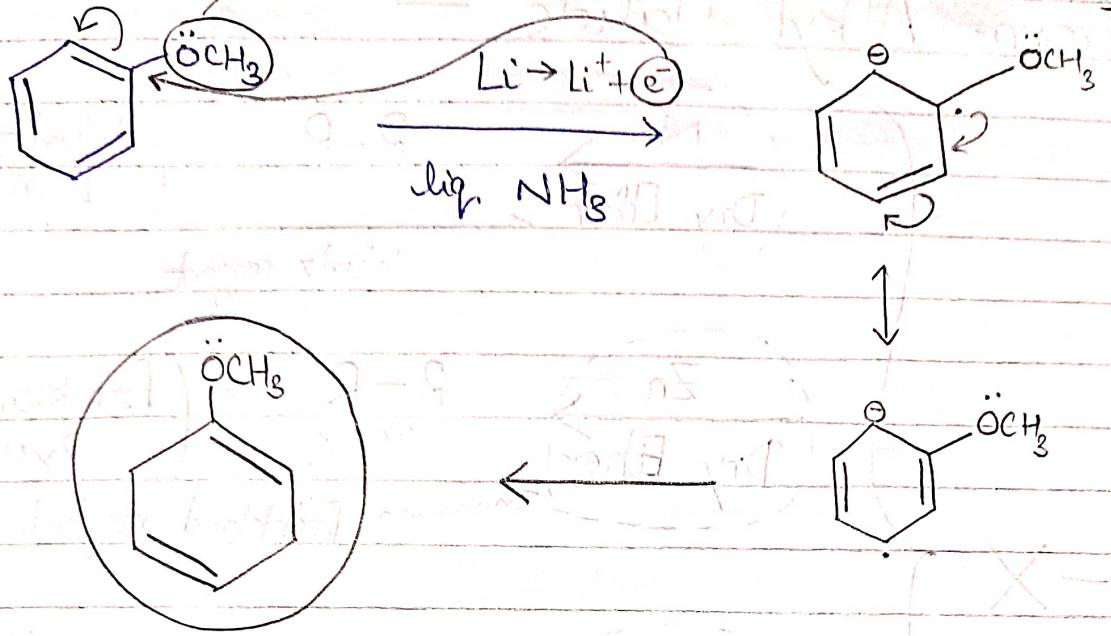
4)



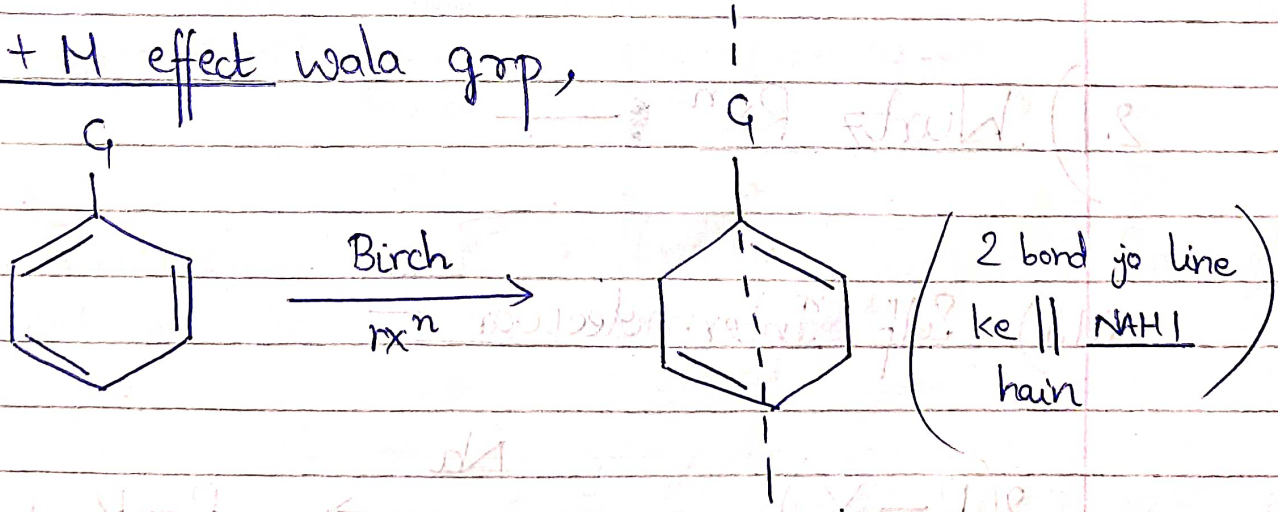
Since strong -M effect, ⊖ charge yaha side todo

[Since strong +M effect, ⊕ charge uski side todo!]

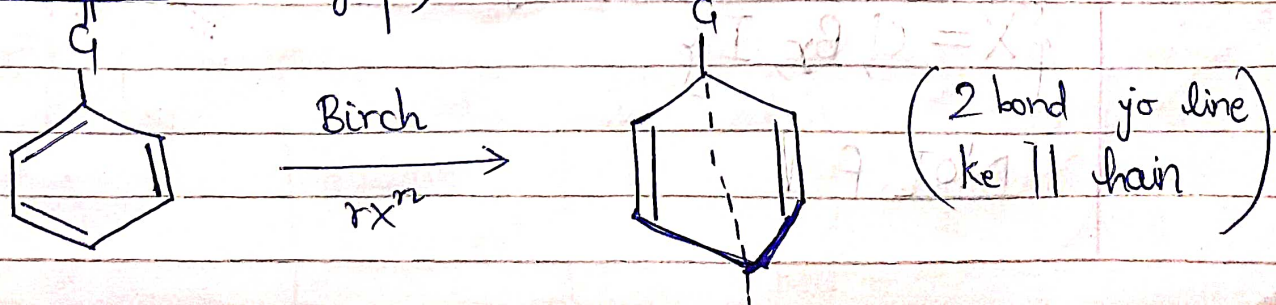
5)



If +M effect wala grp,



If −M effect wala grp,



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2) from Alkyl Halide —

R–X (Alkyl Halide)

- $\xrightarrow[\text{Dry Ether}]{Na}$ R–R (Wurtz Rx^n) ← Wurtz reagent
- $\xrightarrow[\text{Dry Ether}]{Zn}$ R–R (Frankland's Rx^n) ← Frankland reagent
- $\xrightarrow[\text{Dry Ether}]{R'_2CuLi}$ R–R' (Corey House Synthesis) ← Gilmann's reagent
- $\xrightarrow{LiAlH_4}$ R–H

2.1) Wurtz Rx^n —

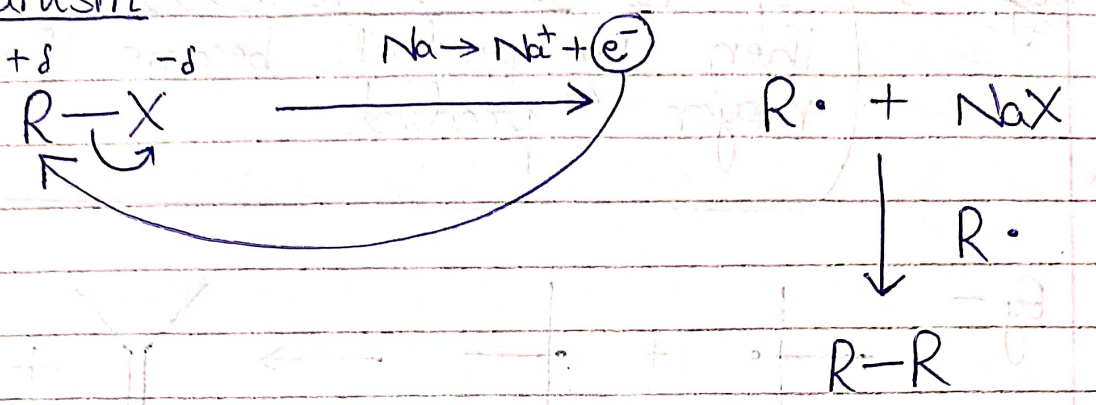
2.1.1) Self Intermolecular —

$$2(R-X) \xrightarrow[\text{Dry Ether}]{Na} R-R + 2NaX$$

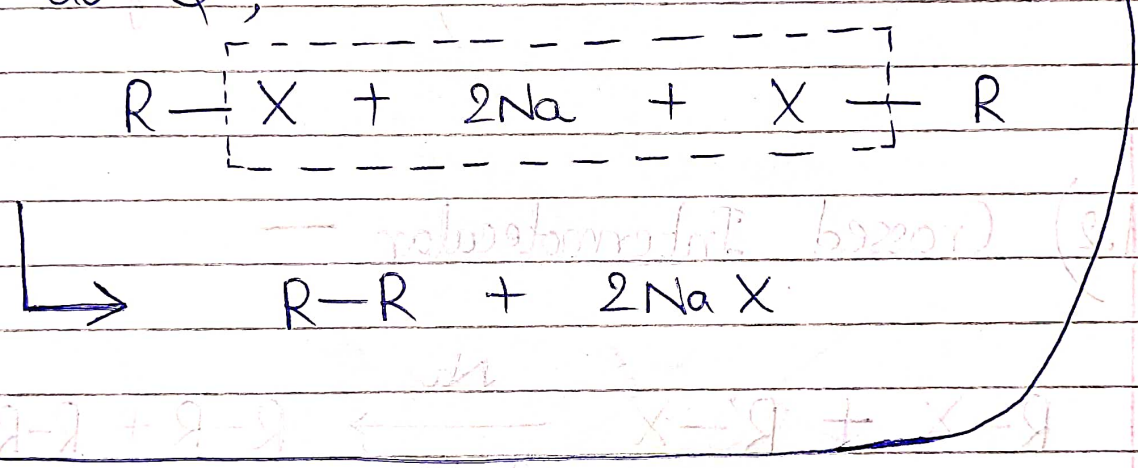
{X = Cl, Br, I}

NOT F !

Mechanism –



☆ To do Q,



Eg – $CH_3-CH_2-Cl \xrightarrow[\text{Dry Ether}]{Na} CH_3-CH_2-CH_2-CH_3$

2.1.1.1) Symmetrical alkane (with even no. of C atoms) will be formed as major product

2.1.1.2) Some side prodcts may be formed.

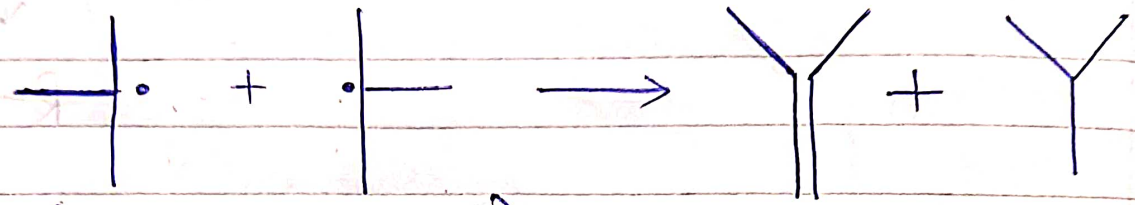
Eg – $CH_3-\dot{C}H_2 + \dot{C}H_2-CH_3 \longrightarrow CH_2=CH_2 + CH_3-CH_3$ (Oxd^n – Red^n)

(may break homolytically)

This is Diprop. Redox Rx^n

Eg ☆ If 3° alkyl halide are given, then by products become the major product

Eg –



(Bulky ⇒ Diff. to join due to Steanic Hinderance)

Major Products

2.1.2) Crossed Intermolecular —

$$R-X + R'-X \xrightarrow[\text{Dry Ether}]{Na} R-R + R-R' + R'-$$

(3 Major Products)

Now,

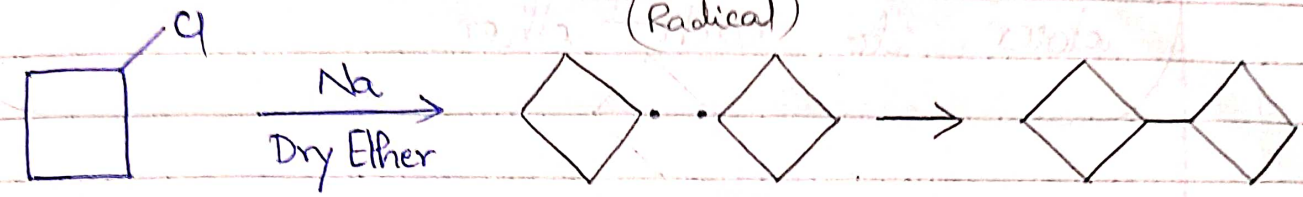
	R	R'
R	R-R	(R-R')
R'	(R-R')	R'-R'

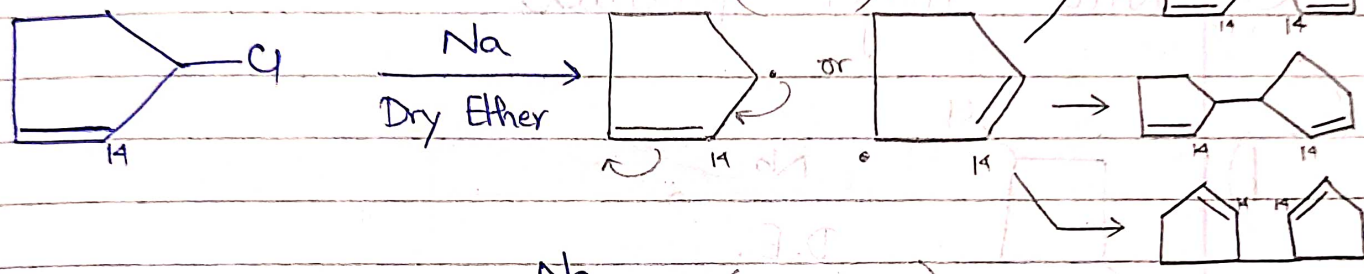
It may be observed that out of major products, R-R' will be formed max.

But ratio may NOT be 1 : 2 : 1 !

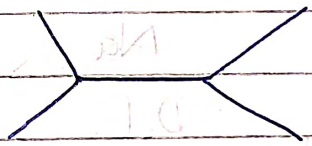
☆ In general, in any crossed intermolecular rxn yield of major products is reduced.

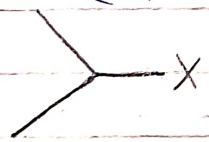
Q) Write major products —

1) 

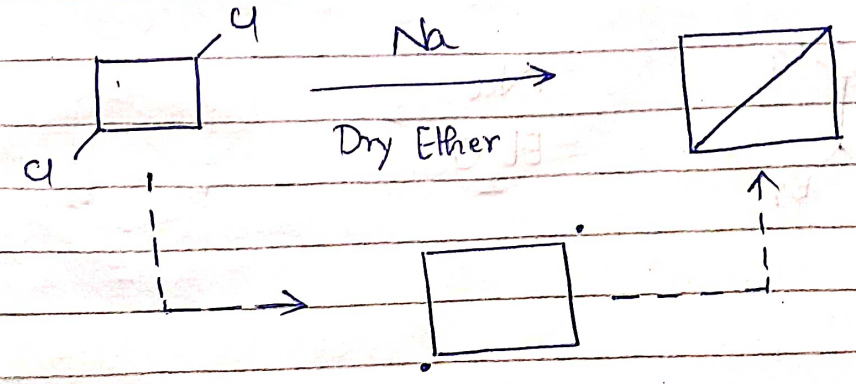
2) 

3) $CH_2=CH-(C_{14})H_2-Cl \xrightarrow[D.E.]{Na}$ (Similar to above)

4) (?) $\xrightarrow[D.E.]{Na}$ 

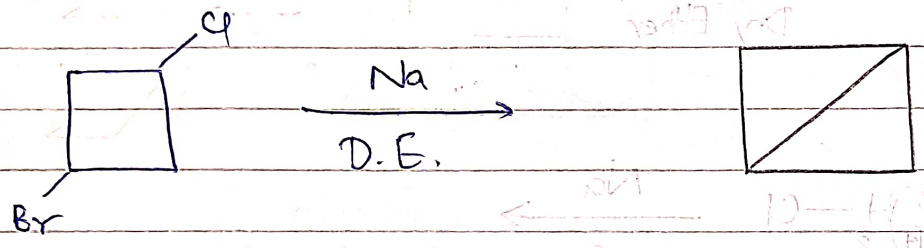


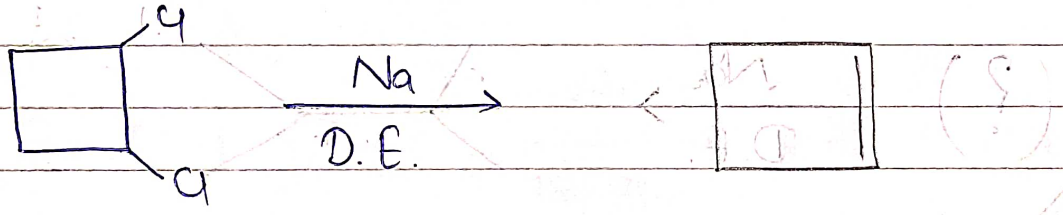
2.1.3) Intramolecular —

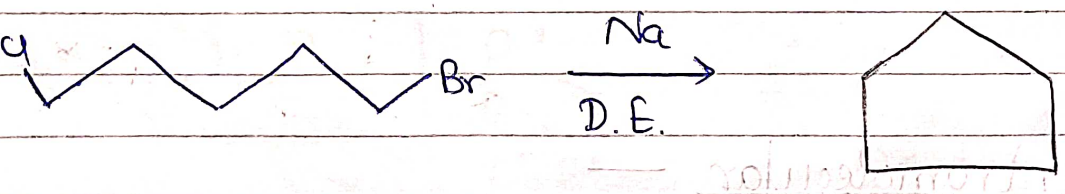
Eg - 

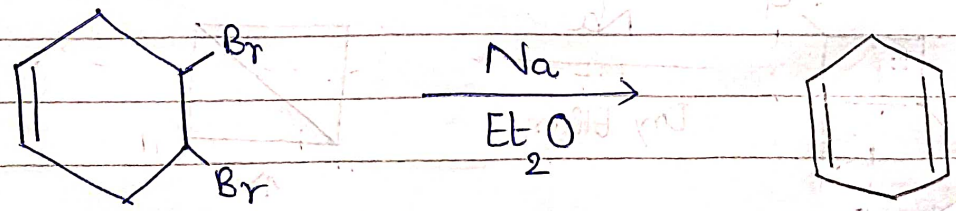
☆ Generally, intramol. rx^n happens faster than intermol. rx^n as radicals are closer to each other.

Q) Write major products —

1) 

2) 

3) 

4) 

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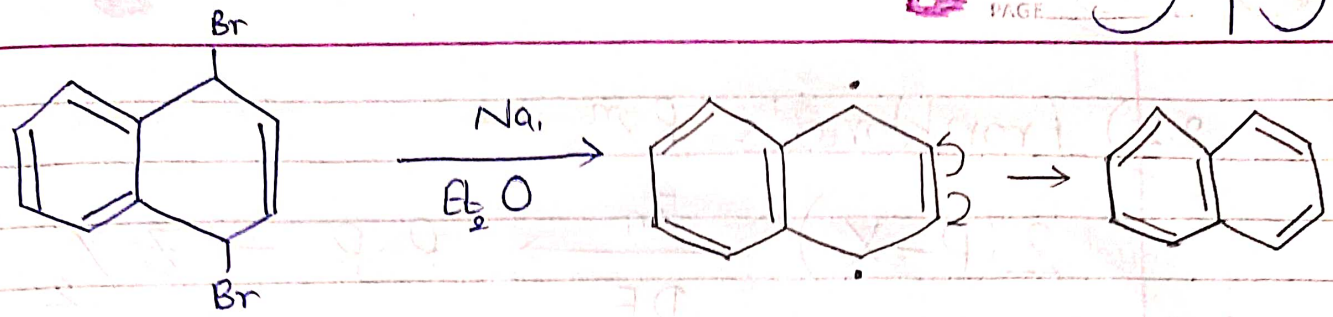
5)



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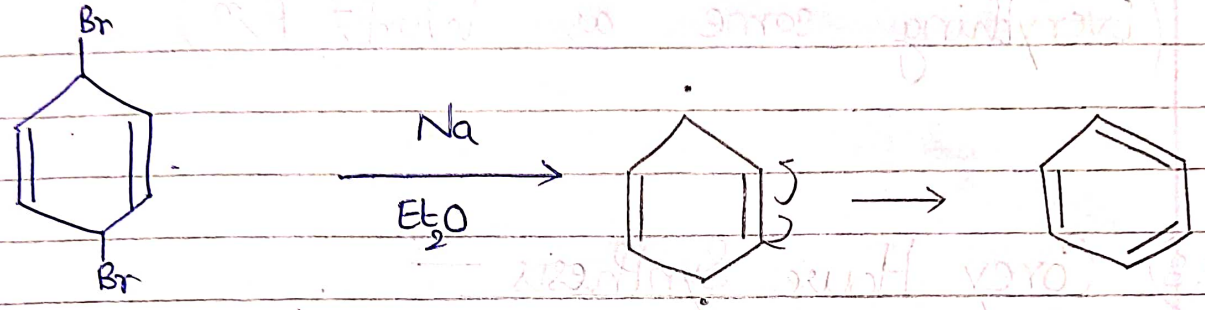
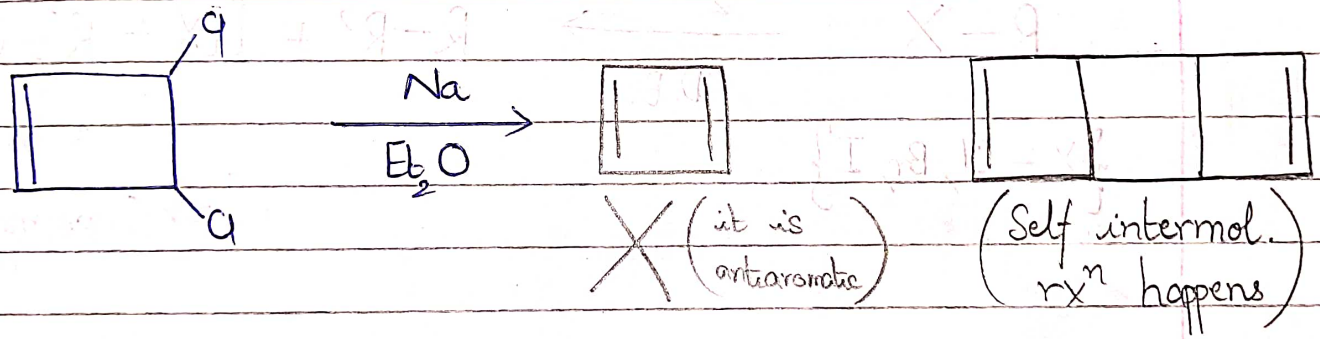
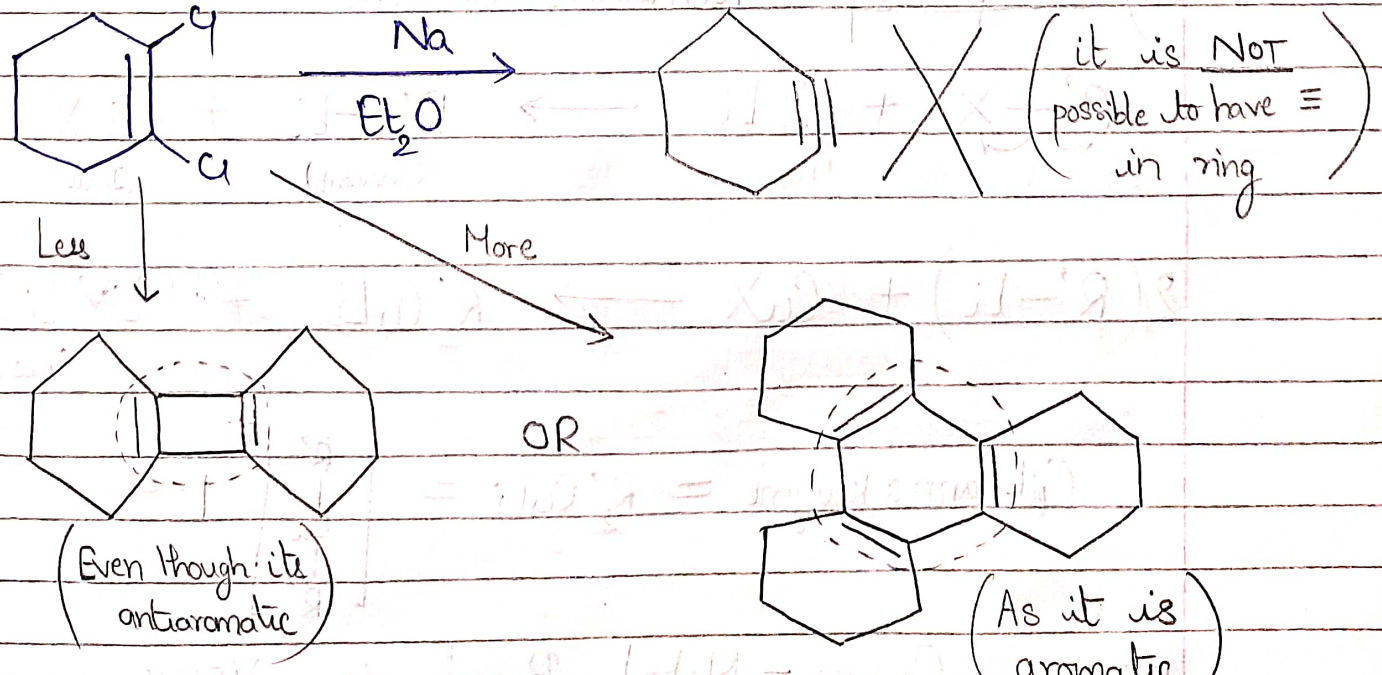


7) ☆



8) ☆



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2.2) Frankland's Rxn —

$$2(R-X) \xrightarrow[D.E.]{Zn} R-R + ZnX_2$$

(Everything same as Wurtz Rxn)

2.3) Corey House Synthesis —

$$R-X \xrightarrow[D.E.]{R'_2CuLi} R-R' + LiX + R'-Cu$$

$\{X = Cl, Br, I\}$

Covalent Bond

⇒ Organometallic comp.

2.3.1) Prepⁿ of Gilmann's Reagent —

$$R'-X + 2Li \longrightarrow \underset{\text{(Covalent)}}{R'-Li} + \underset{\text{(Ionic)}}{LiX}$$

$$2(R'-Li) + CuX \longrightarrow R'_2CuLi + \cancel{LiX}\ \text{(ionic)}$$

Gilmann's Reagent = $R'_2CuLi = \left[\begin{matrix} R' \\ | \\ Cu \\ | \\ R' \end{matrix}\right]^{\ominus} Li^{\oplus}$

Now, Carbon – Metal Bond is VERY weak.

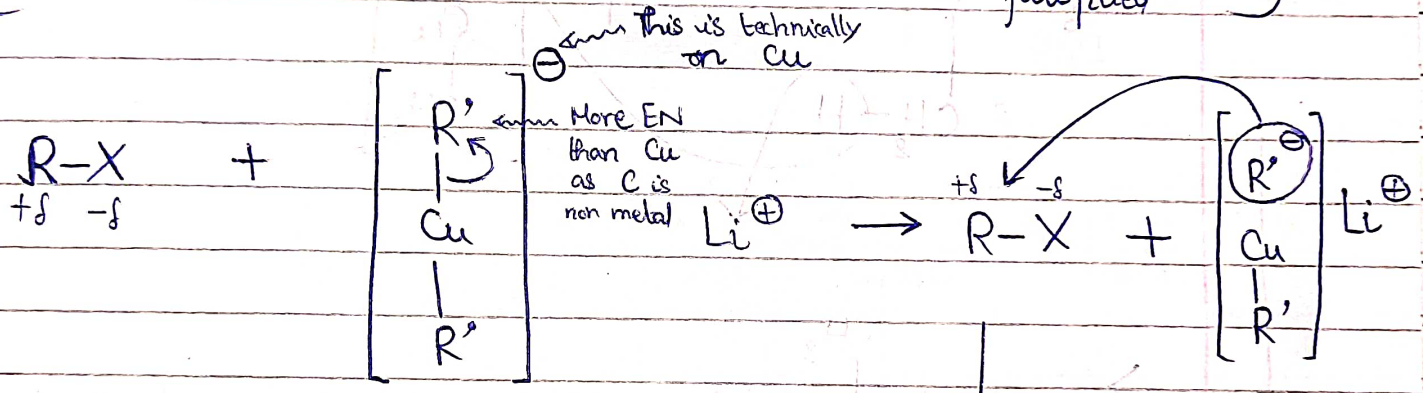
(Unrelated)

2.3.2) Mechanism –

In aq. sol^n, Cu^{2+} ~~is~~ more stable as huge energy released by hydration

In vapour phase, Cu^+ more stable.

$Cu = [Ar]\, 4s^1\, 3d^{10} \Rightarrow Cu^+ = [Ar]\, 3d^{10}$ (full filled)



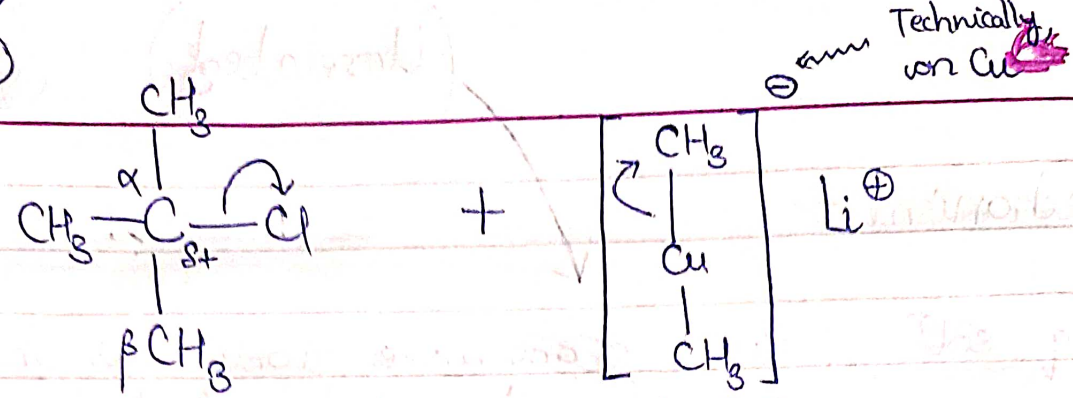
Here, $Nu^{\ominus}$: $R'^{\ominus}$ substitutes

$Nu^{\ominus}$: $X^{\ominus}$ ⇒ Nucleophilic Substitution

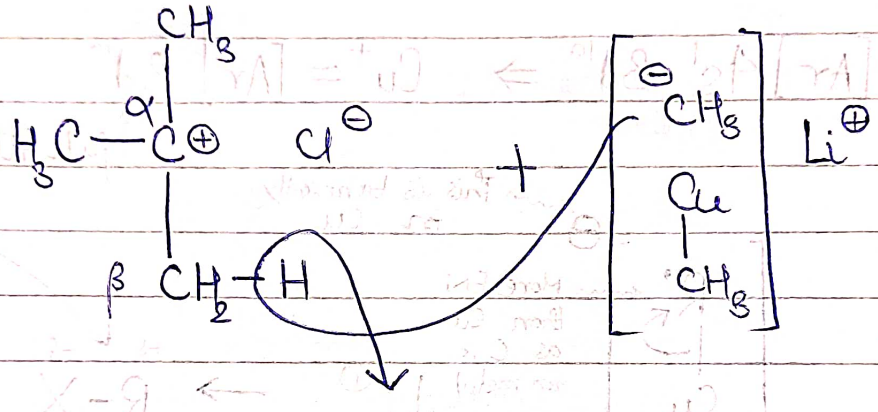
$R–X + R'–Cu \rightarrow R–R' + Cu–R' + LiX$

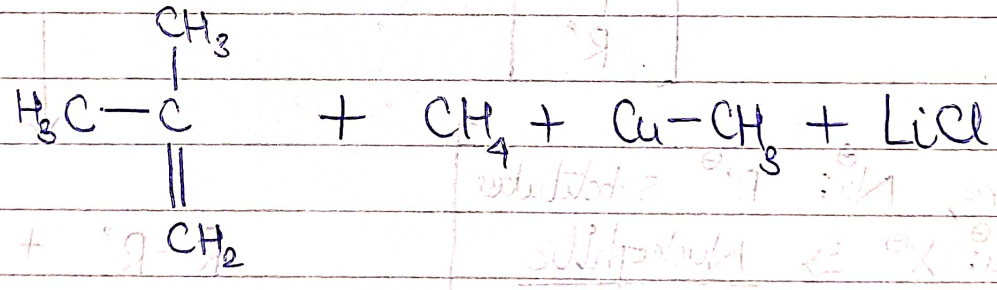
2.3.3) In this rx^n, R–X must be 1° or 2°

2.3.4) In case of 3° R–X, Elimination rx^n will occur. (In any rx^n with strong $Nu^{\ominus}$ not just this rx^n)



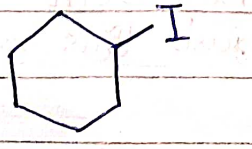
Can't attact α C as very much Stearic Hinderance

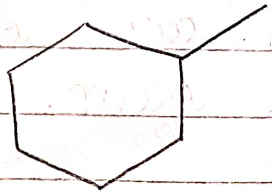




Q) Write major products —

1) $(CH_3)_2CuLi$ $\xrightarrow{Et_2O}$





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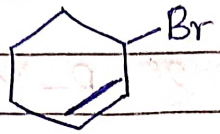
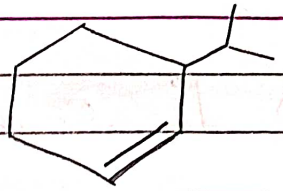
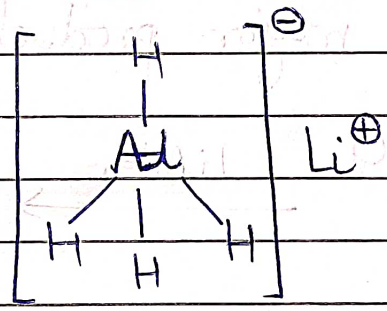
2) $\left(\begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>CH\right)_2CuLi \xrightarrow{Et_2O}$  

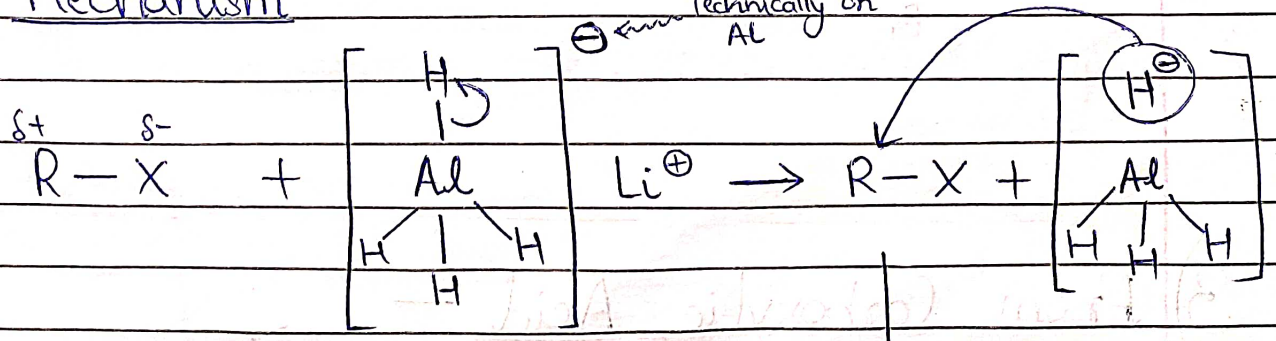
2.4) Rxn with $LiAlH_4$ —

$LiAlH_4$ is a Strong Redn agent

$$R-X \xrightarrow{LiAlH_4} R-H + AlH_3 + LiX$$

$LiAlH_4$ = 

2.4.1) Mechanism —



$$R-H + AlH_3 + LiX$$

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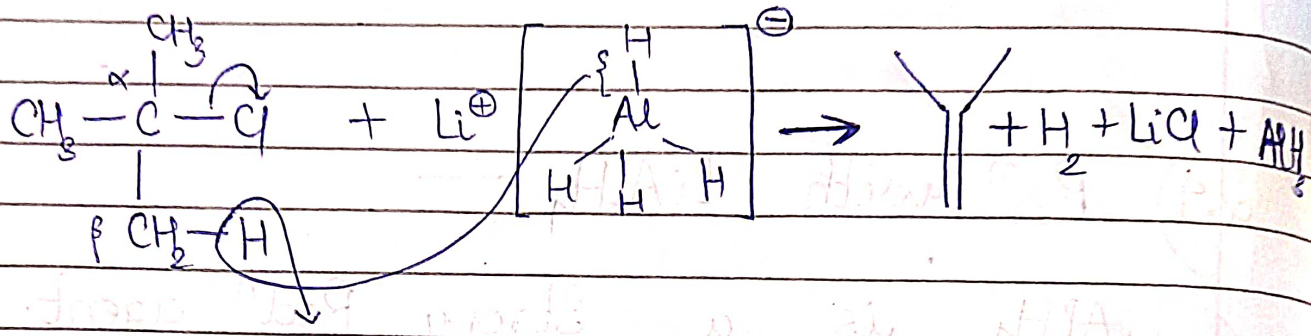
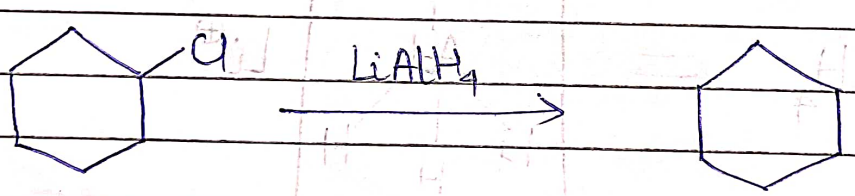
2.4 2) 1° or 2° R–X must be used

2.4 3) In case of 3° R–X, Elimination rxn occurs.

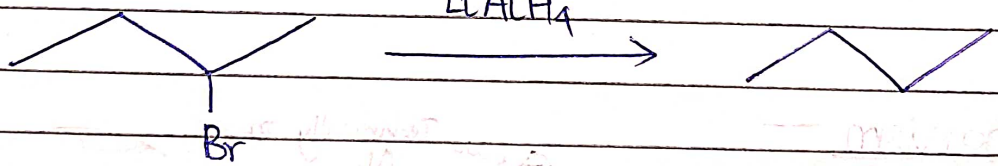


Q) Write major products –

1)



2)

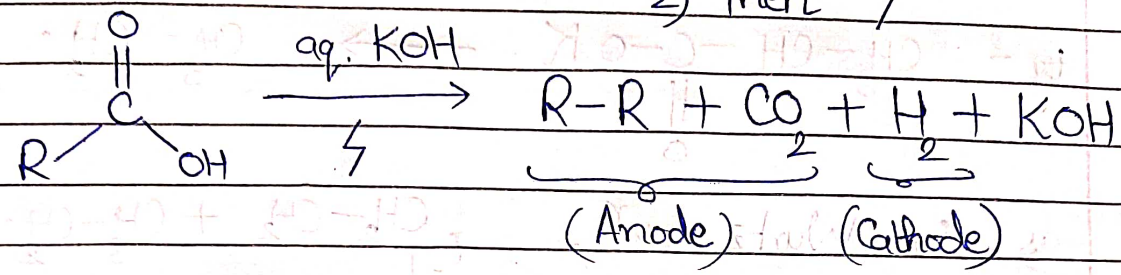


3) From Carboxylic Acid –

(Kolbe's Electrolysis) & (Soda Lime Decarboxylation)

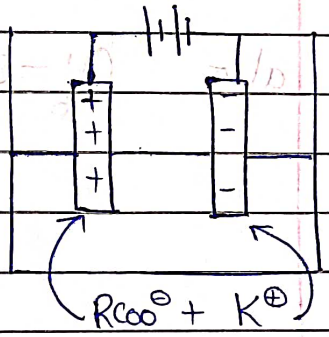
3.1) Kolbe's Electrolysis —

1) first Acid + Base → Salt
2) Then ↯

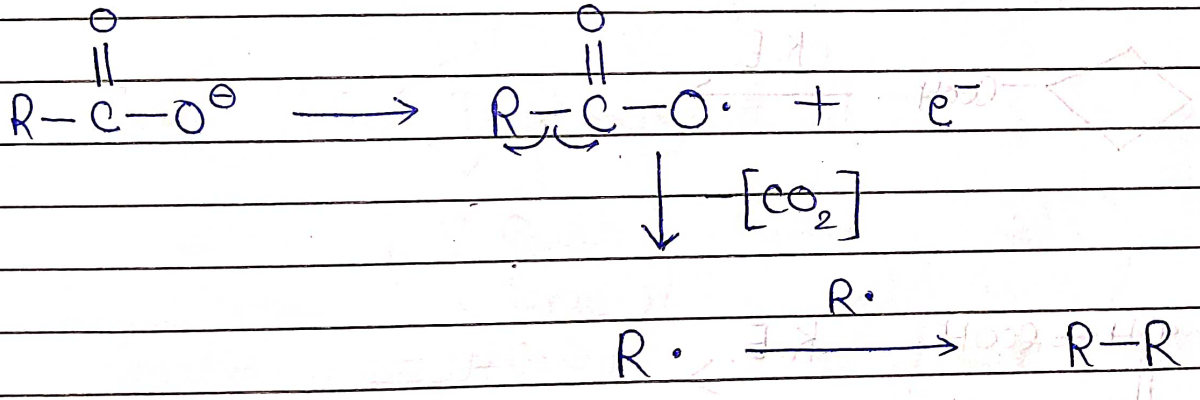


3.1.1) Mechanism —

★ Oxdⁿ at Anode
Redⁿ at Cathode



At Anode



At Cathode

$$K^+(aq.) + e^- \longrightarrow K(s)$$
(deposit on cathode)

$$K(s) + H_2O(l) \longrightarrow KOH(aq.) + \frac{1}{2}H_2(g)$$

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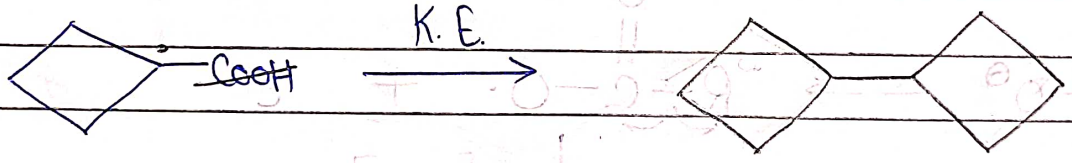
3.1.2) By Products → are also formed. (Alkene, Alkane, Ester)

Eg - $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OK \longrightarrow CH_3-CH_2\cdot$

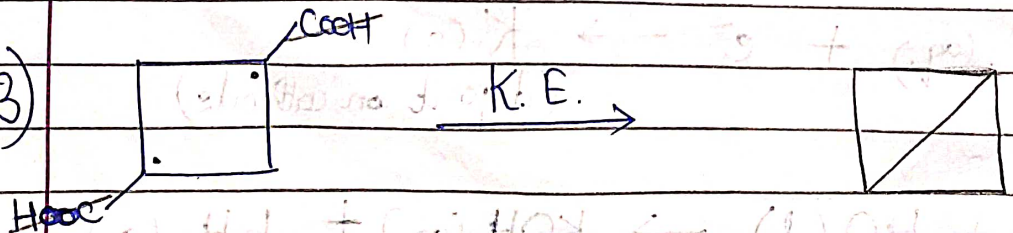
as in Wurtz rxn, $CH_2-CH_2 + CH_3-CH_2\cdot \longrightarrow$ ($CH_2=CH_2$) + (CH_3-CH_3)

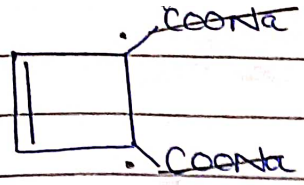
also $CH_3-CH_2\cdot + CH_3-CH_2-\underset{\underset{O}{\|}}{C}-O\cdot \longrightarrow C_2H_5-\underset{\underset{O}{\|}}{C}-OC_2H_5$

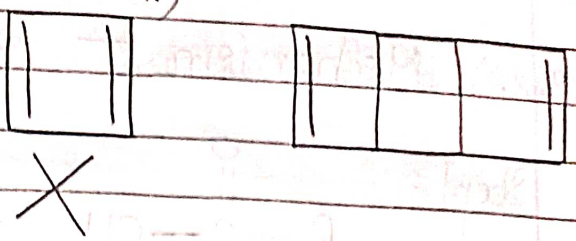
Q) Write major products —

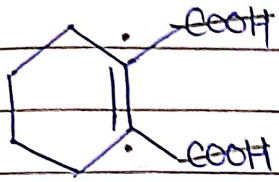
1) 

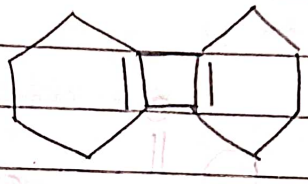
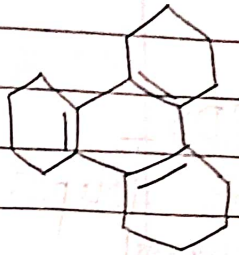
2) $\cdot CH-COOH$ (double bond) $\cdot CH-COOH$ $\xrightarrow{K.E.}$ $HC\equiv CH$

3) 

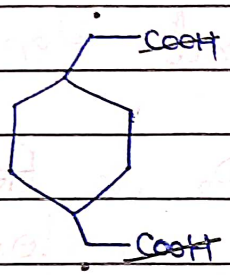
4) 

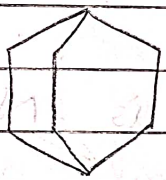
K.E. (as A.A.)


5) 

K.E.

OR


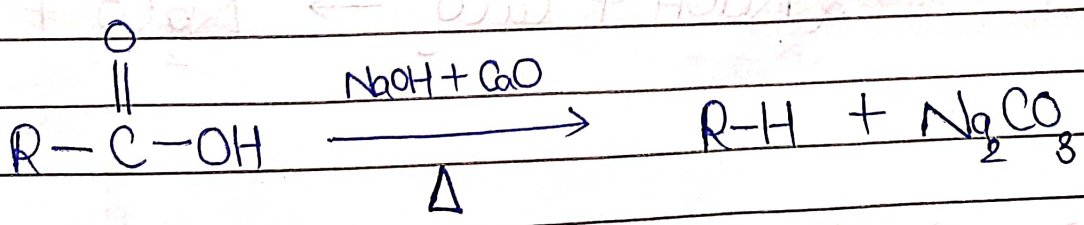
(≡ NOT possible in ring)

6) 

K.E.


3.2) Soda Lime Decarboxylation —

(Caustic Soda (NaOH)) + (Quick Lime (CaO)) → (Soda Lime (NaOH & CaO))



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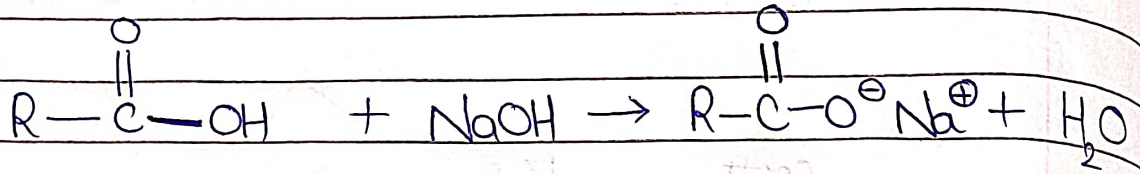
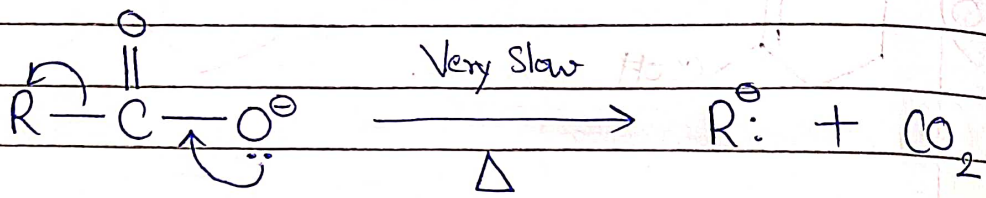
3.2.1) Mechanism —

Step1 :



RDS
Rate Determining Step.

Step2 :

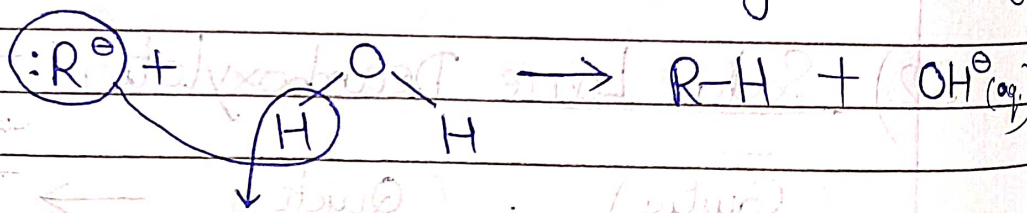


It is diff. to break C–C bond. Hence, RDS

Now, $:R^{\ominus}$ is Nucleophile. CO_2 is Electrophile (Lewis Acid)

To stop their rxn, we have CaO
It reacts with ~~CO~~ CO_2 to give (Strong Base) $CaCO_3$

Step3 :



$$Na^+(aq.) + OH^{\ominus}(aq.) \longrightarrow NaOH$$

Step 4 :

$$2NaOH + CaCO_3 \longrightarrow Na_2CO_3 + Ca(OH)_2$$

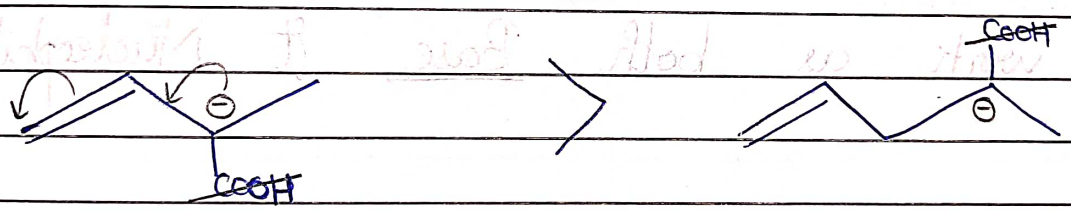
3.2.2) In this rxn, Intermediate is Carboanion ($:R^{\ominus}$)

3.2.3) **Reactivity (RoR) ∝ (Stability of Carbocation)**

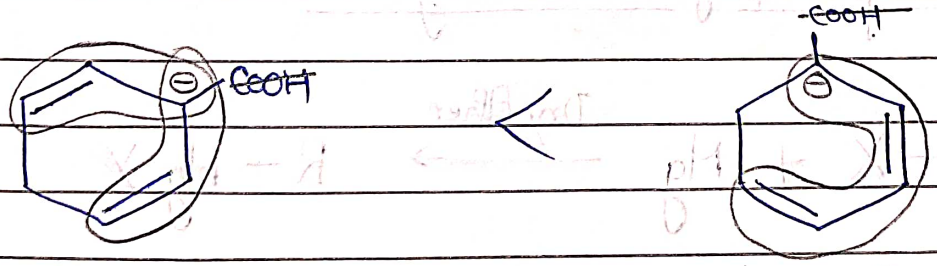
As in RDS, rxn more fwd if carboanion more stable.

3.2.4) This rxn helps to reduce 1 C atom from main chain.

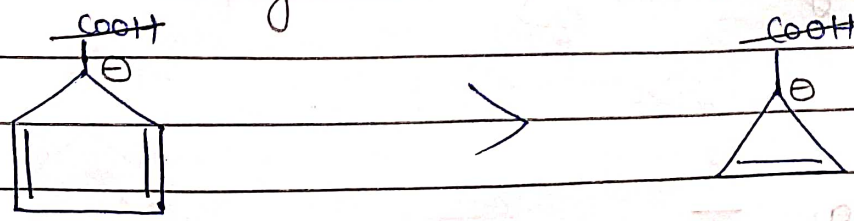
① Compare rate of soda lime decarboxylation

1) 

Res. No res.

2) 

Cross. Conj. Linear Conj.

3) 

A. A.A.

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4) From Organometallic Comps. —

Organometallic Comps — Comps. in which C is covalently bonded with metal atom.

Eg - R_2CuLi, $R-Li$, $R-MgX$, ...

(Grignard reagent)

Grignard Reagent = $R-\underset{\text{Covalent}}{Mg}\ \underset{\text{Ionic}}{X}$

Can work as both Base & Nucleophile.

4.1) Prepⁿ of Grignard's Reagent —

$$R-X + Mg \xrightarrow{\text{Dry Ether}} R-MgX$$

{X = Cl, Br, I}

4.2) As a Base —

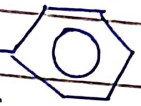
Grignard reagent is destroyed by those species which have protic H.

oxygen
active methylene
H — SON(AM) X ← halogen (can be F also)
Protic Hydrogen
nitrogen
Sulphur

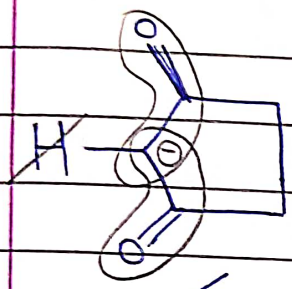
(R-MgX) Can react with —

H — OH ✓

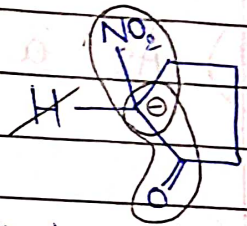
H — SH ✓

H — O —  ✓

 ✓
(as after rxn, aromatic)

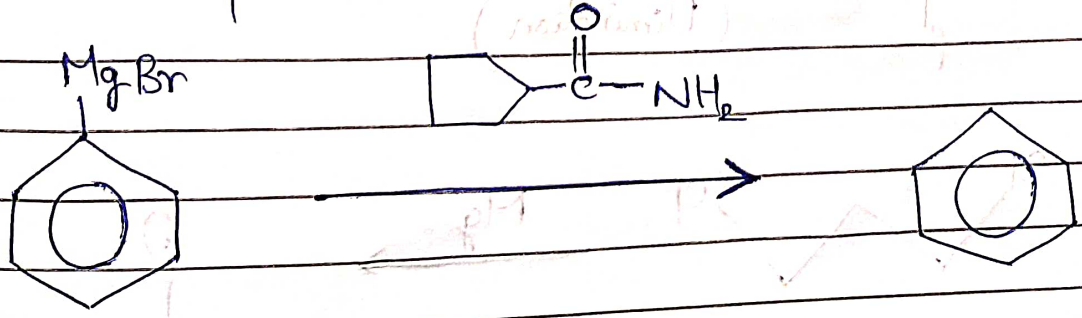
 ✓
(as it is A.M.)

H — C≡C — CH_3 ✓
(as Terminal alkyne)

 ✓
(as strong −M effect π conj.)

$$R - MgX + (\text{Anything from above}) \longrightarrow R - H$$

Q) Write products —

1) 

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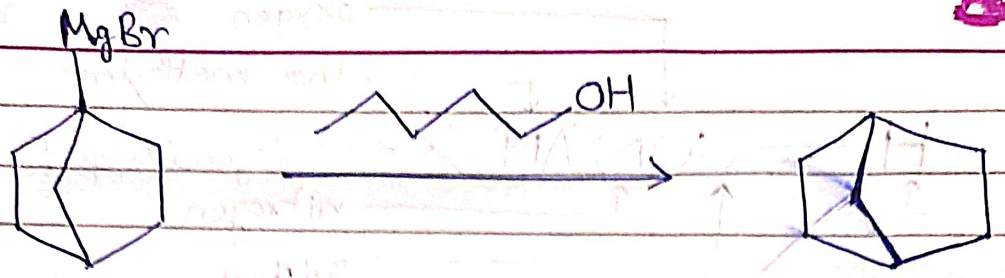
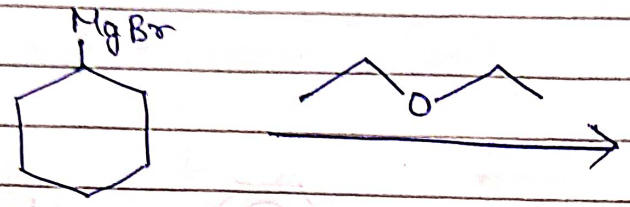
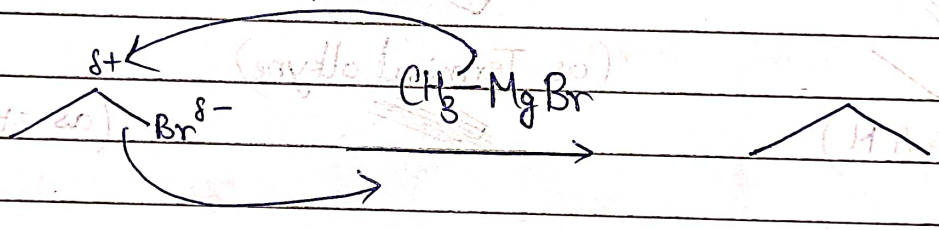
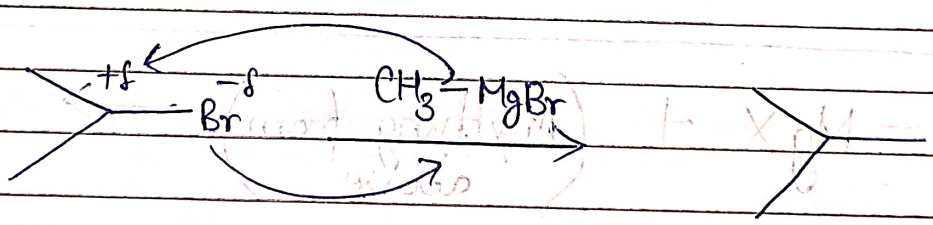
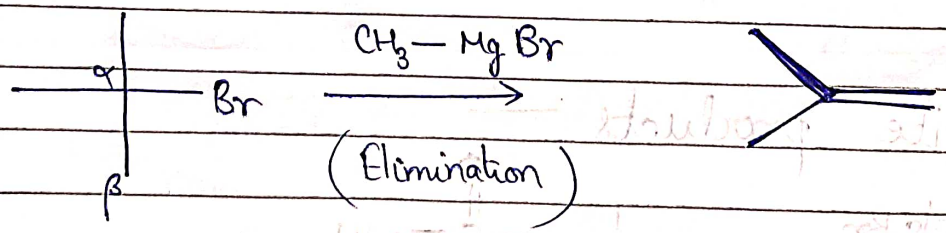
2) 

3) 

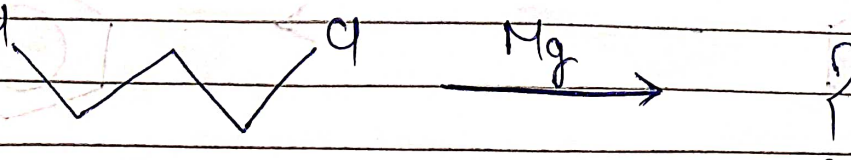
4.3) As a Nucleophile —

Eg - 

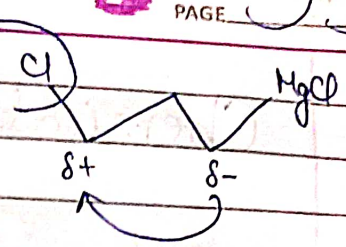
Eg - 

☆ Eg - 

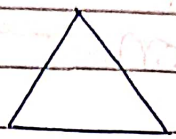
(Tert. Alkyl)

☆ Eg - 

First Grignard reagent form,



Reacts with itself,



Here, 

doesn't form.

If # C ≥ 4, then (m) this forms.

It is called <u>Dignignard Reagent</u>

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Chemical Prop^{t}s

1) Halogenation — (Free radical substitution)

$$CH_3-CH_3 \xrightarrow[\{X = Cl, Br\}]{X_2,\ h\nu} CH_3-CH_2-X + HX$$

1.1) Mechanism — (In general, of free radical substitution)

Step 1 (Chain Initiation) :

$$X-X \longrightarrow 2\,\dot{X}$$

Step 2 (Chain Propogation) :

$$CH_3-CH_2-H + \dot{X} \longrightarrow CH_3-\dot{C}H_2 + HX$$

(H· formed reacts extremely fast)

☆ Here, H· is NOT formed as it is HIGHLY unstable.

$$CH_3-\dot{C}H_2 + X-X \longrightarrow CH_3-CH_2-X + \dot{X}$$

If alkane in excess ⇒ Monosubstituted Alkyl Halide is major product

If halogen in excess ⇒ Fully substituted Alkyl Halide is major product.

Step 3 (Chain Termination):

$$X\cdot + \cdot X \longrightarrow X_2$$

$$CH_3-\dot{C}H_2 + \dot{C}H_2-CH_3 \longrightarrow$$ 

1.2) Reactivity of X_2: $\boxed{F_2 > Cl_2 > Br_2 > I_2}$

Reason – Stability of R–X bond (in vapour phase). If bond easily break, then chain initiation becomes reversible it goes bwrd

1.3) for iodination, strong oxd^n agent such as HIO_3 or HNO_3 is req. as necessary reagent.

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$$CH_3-CH_3 + I_2 \underset{}{\overset{h\nu}{\rightleftharpoons}} CH_3-CH_2-I + HI$$

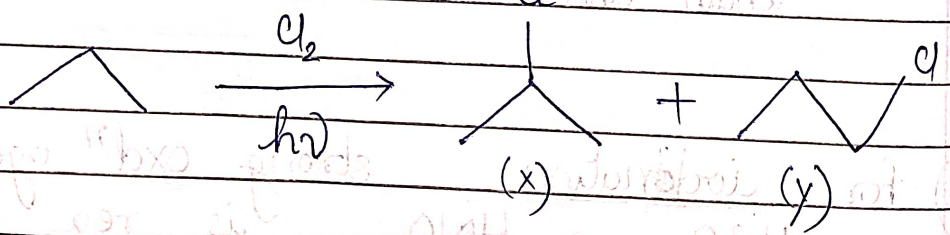
$$HNO_3 + HI \longrightarrow I_2 + NO_2 + H_2O$$

Since HI reacts to form I_2, conc of I_2 inc. & conc. of HI dec.

$\Rightarrow$ Halogenation shifts frwd

1.5) Reactivity —

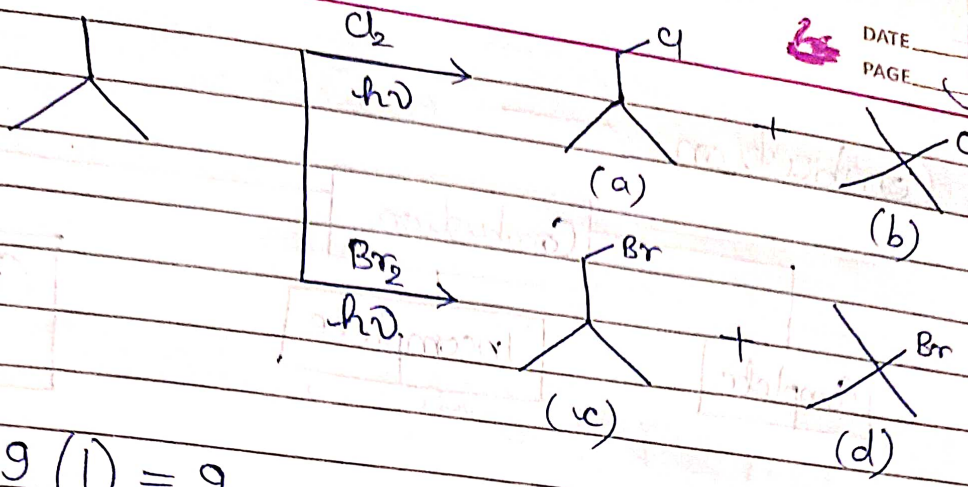
X_2	1° H	2° H	3° H
F_2	1	1	1
Cl_2	1	3.8	5.2
Br_2	1	80	1600

Eg — 

$$\left(\frac{x}{y}\right) = \frac{(\#\ 2°\ H) \times (\text{Reactivity with } 2°H)}{(\#\ 1°\ H) \times (\text{Reactivity with } 1°H)}$$

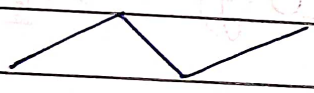
$$= \frac{2(3.8)}{6(1)} = \left(\frac{7.6}{6}\right) > 1 \Rightarrow \boxed{x\% > y\%}$$

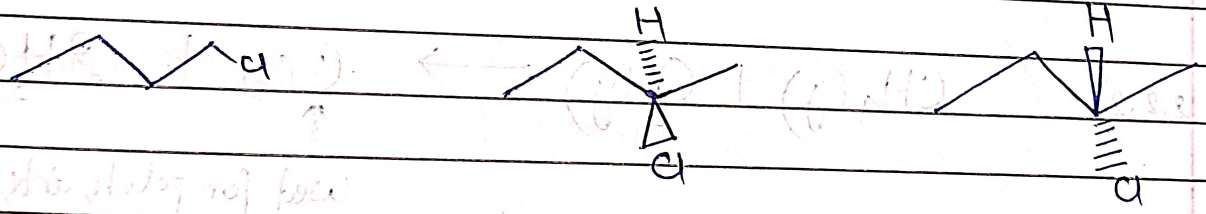
Eg -

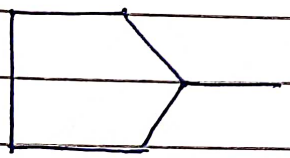


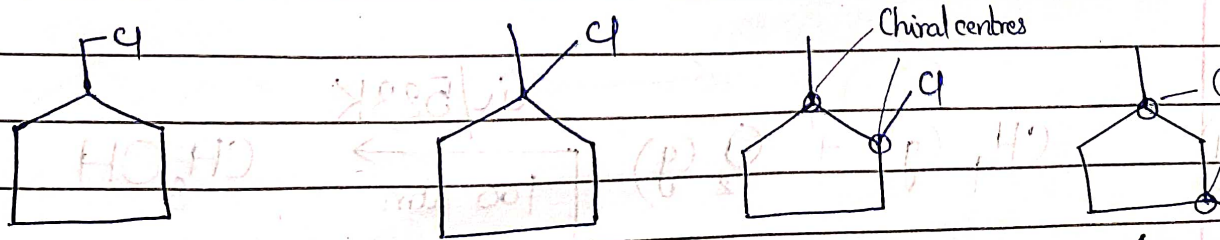
(a) = 9 (1) = 9
(b) = 1 (5.2) = 5.2
(c) = 9 (1) = 9
(d) = 1 (80) = 80

Q) Calc. total no. of monochonination products of —

1)  = (3)

A) 

2)  = (10)

A) 

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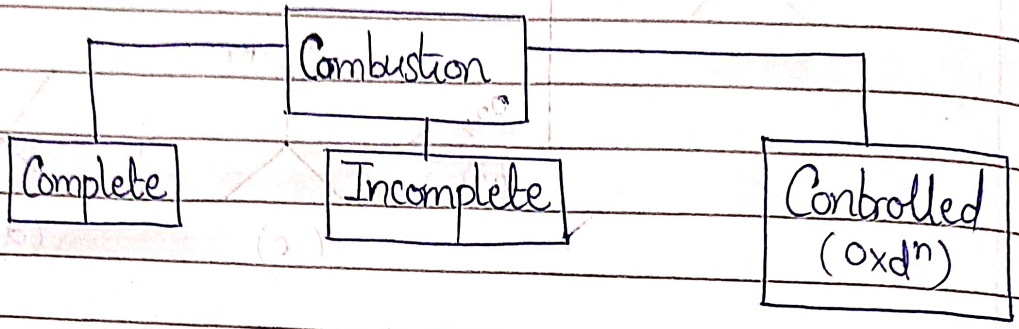
2) Combustion —



2.1) Complete Combustion —

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

2.2) Incomplete Combustion —

2.2.1) $$CH_4(g) + \frac{3}{2}O_2(g) \longrightarrow CO(g) + 2H_2O(l)$$

2.2.2) $$CH_4(g) + O_2(g) \longrightarrow C(s) + 2H_2O(l)$$

used for polish, ink, ...

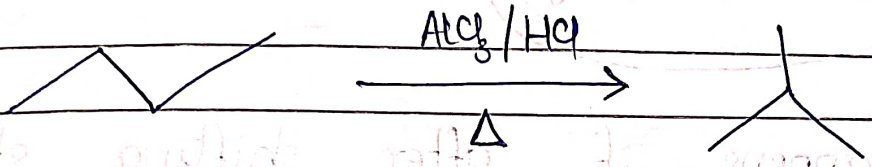
2.3) Controlled Combustion —

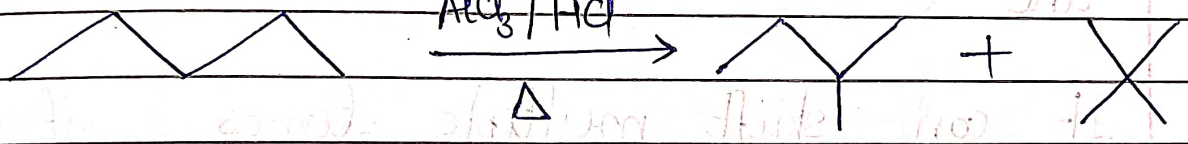
2.3.1) $$CH_4(g) + O_2(g) \xrightarrow[100\ atm]{Cu/523K} CH_3OH$$

2.3.2) $$\xrightarrow[\Delta]{Mo_2O_3} HCHO + H_2O$$

2.3.3) $CH_3-CH_3\,(g) + O_2\,(g) \xrightarrow[\Delta]{(CH_3COO)_2Mn} CH_3COOH + H_2O$

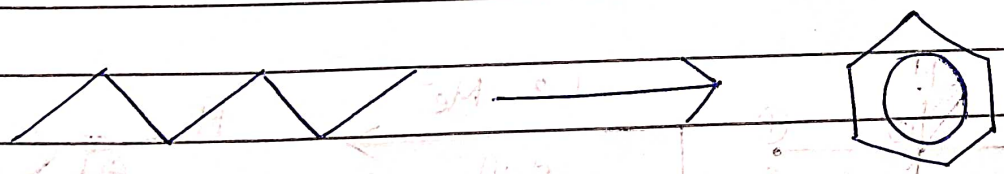
3) Isomerisation ($AlCl_3$ in presence of Acid)

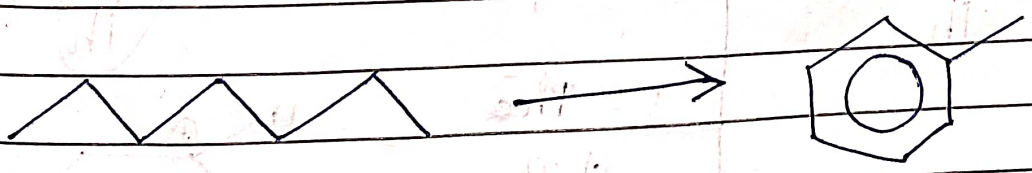
3.1) 

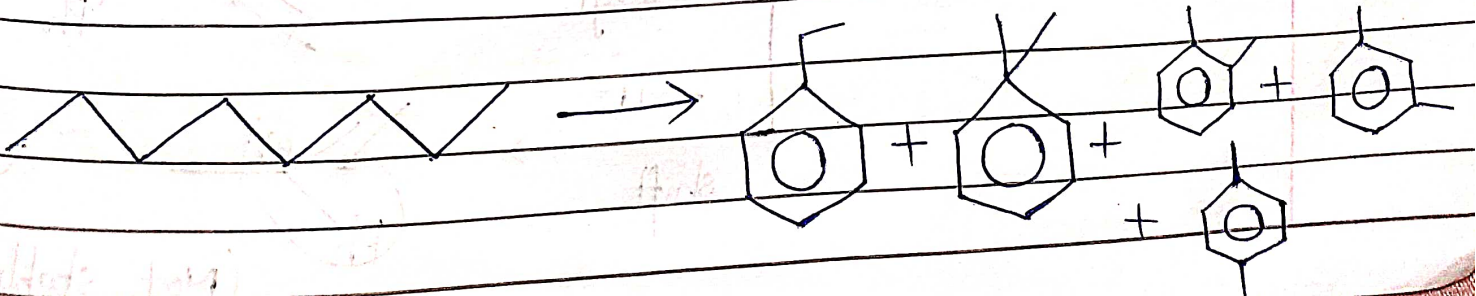
3.2) 

All possible branched isomers are formed.

4) Aromatisation $\left(\frac{Cr_2O_3 / Mo_2O_3 / Al_2O_3}{773\,K,\ 10-20\ atm}\right)$

4.1) 

4.2) 

4.3) 

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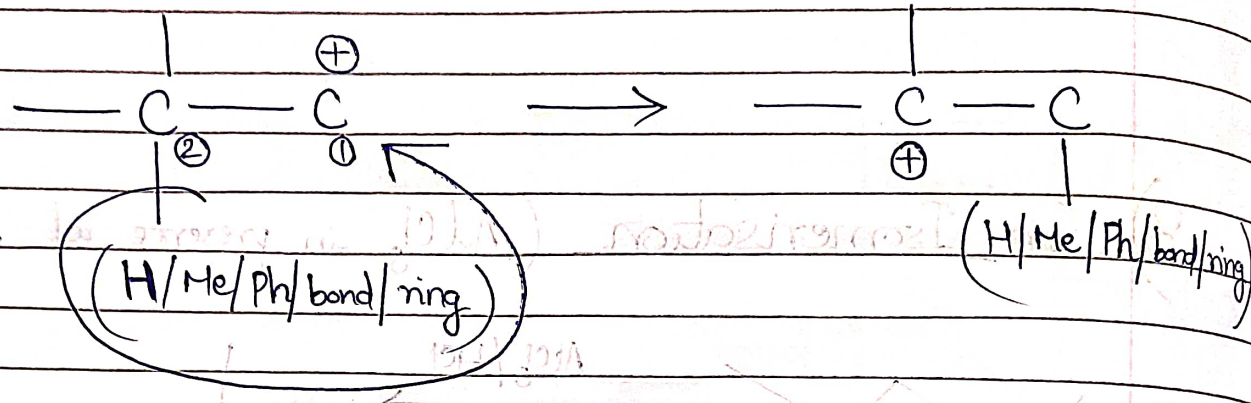
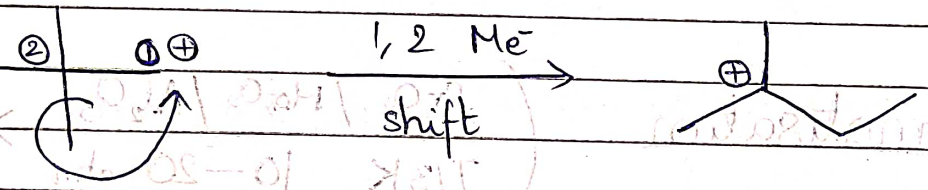
Rearrangement Propt of Carbocation



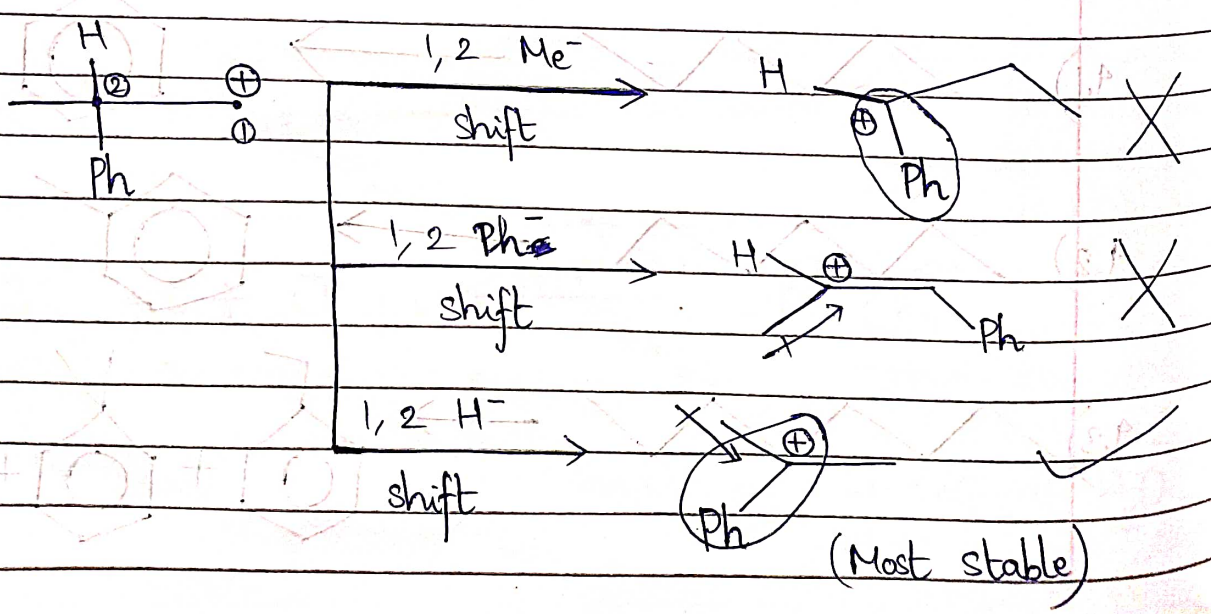
This happens if after shifting stability inc.

It can shift multiple times, if stability (strictly) inc. in EVERY SINGLE SHIFT

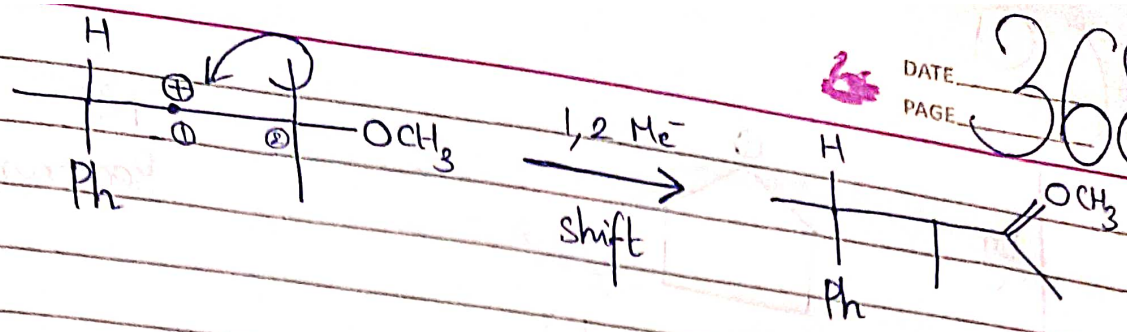
Eg -



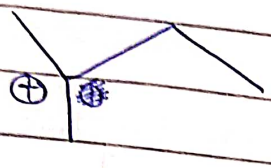
Eg -



Eg –

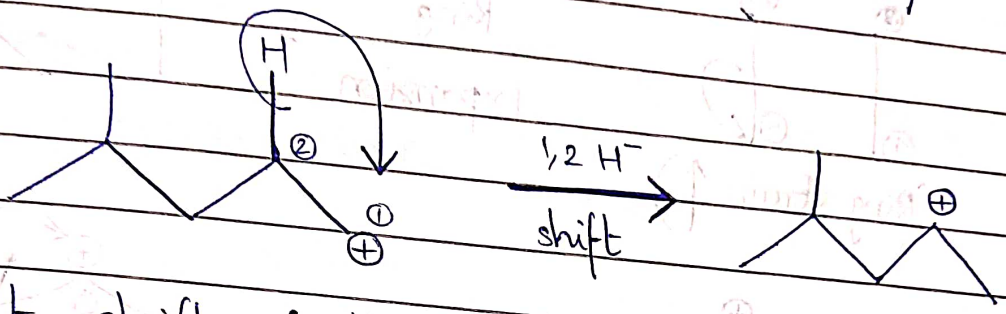


Eg –



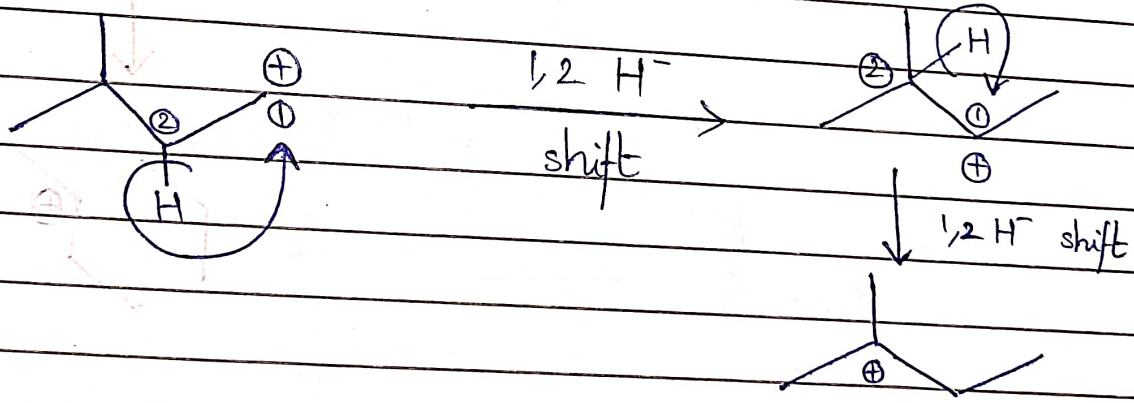
→ No shift

☆ Eg –

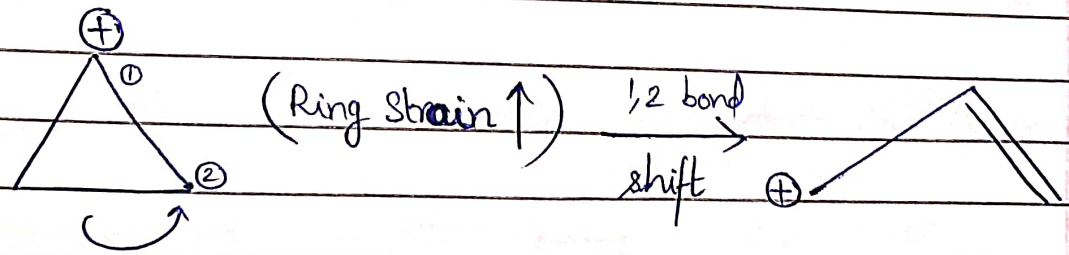


won't shift further as # α H reduces while it remains 2° carbocation

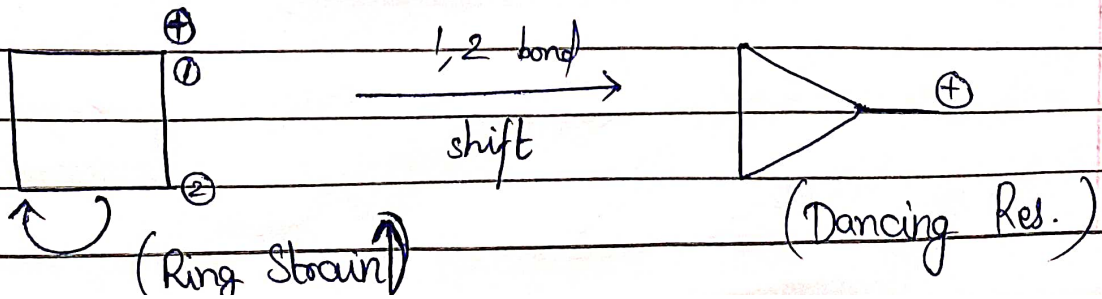
Eg –



☆ Eg –



☆ Eg –



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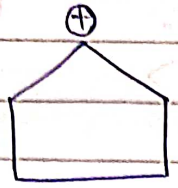
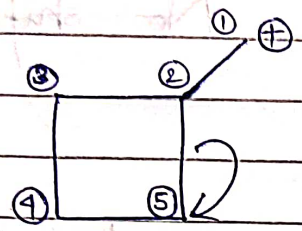
Eg –



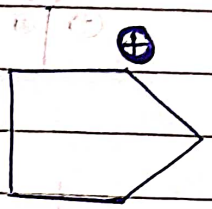
→ (No Rearrangement)

(Ring Strain ↓)

Eg –

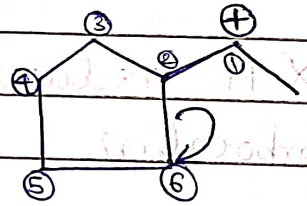


Ring Expansion

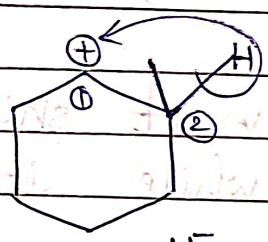


(Ring Strain ↑)

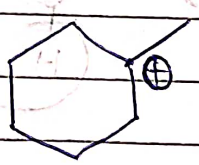
Eg –



Ring Expansion



1,2 ~~Hc~~ shift



ALKENE

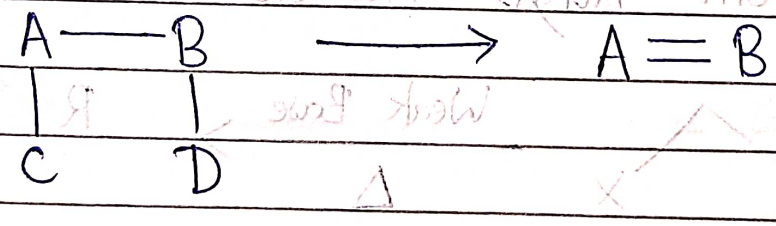
Preparation

1) From Unsaturated H.C. —

{ Done in Special Case of Hydrogenation (Pg 334) }

2) From Alkyl Halide / Alcohol —

2.1) Elimination Rx^n —



Breaking of 2 σ bonds to form 1 π bond

They occur at high temp, i.e. they are endothermic in nature

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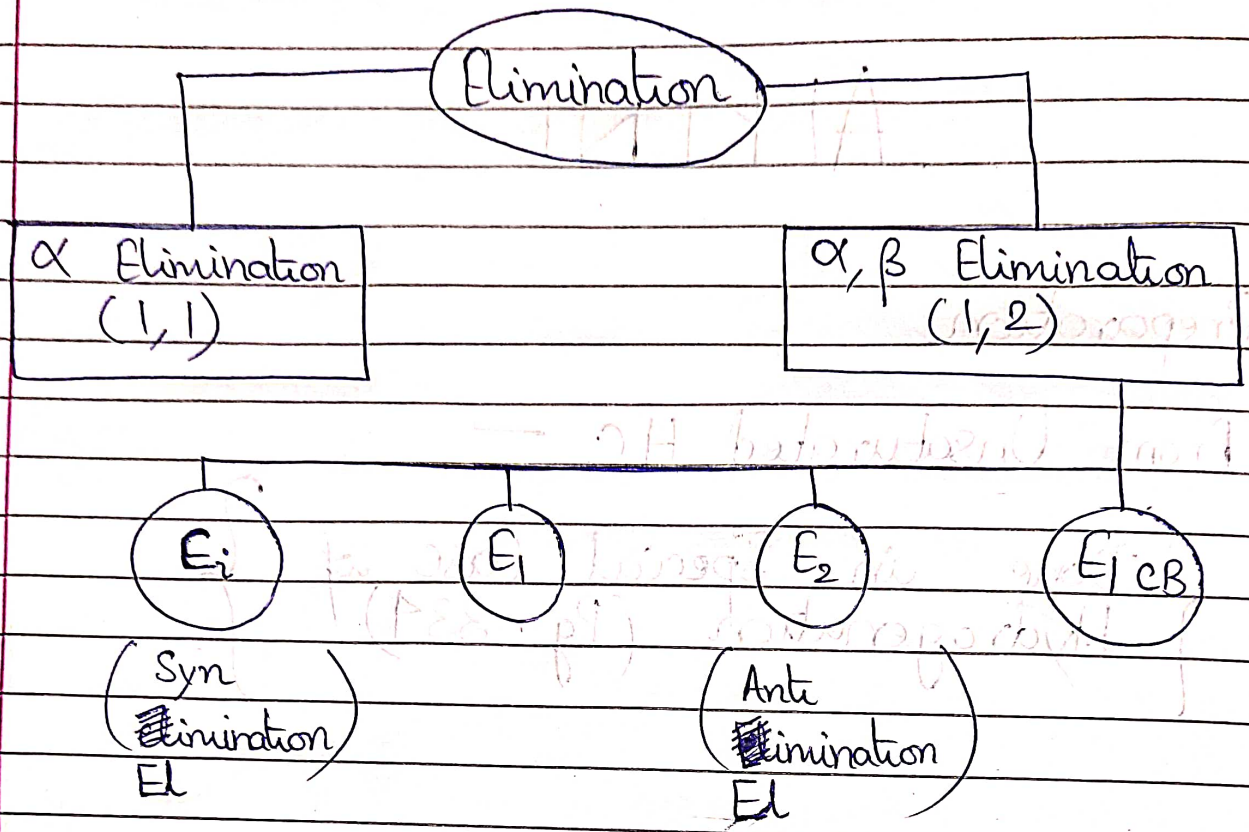
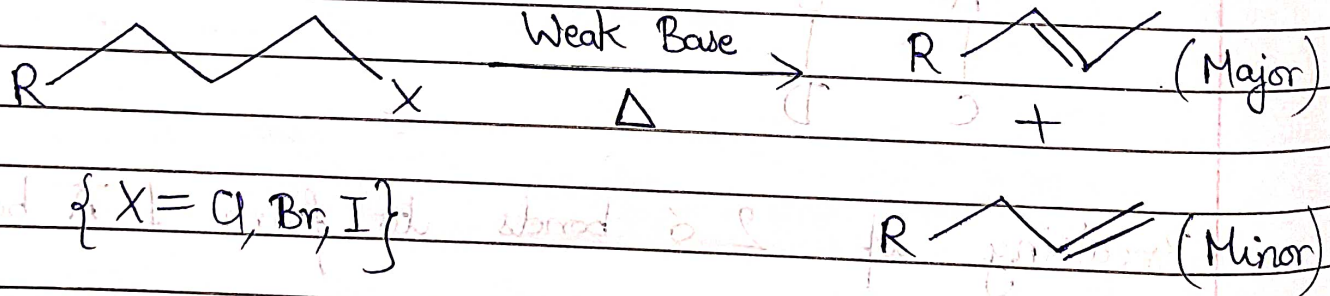


2.2) E_1 ≡ Elimination —

Cl — From Alkyl Halide



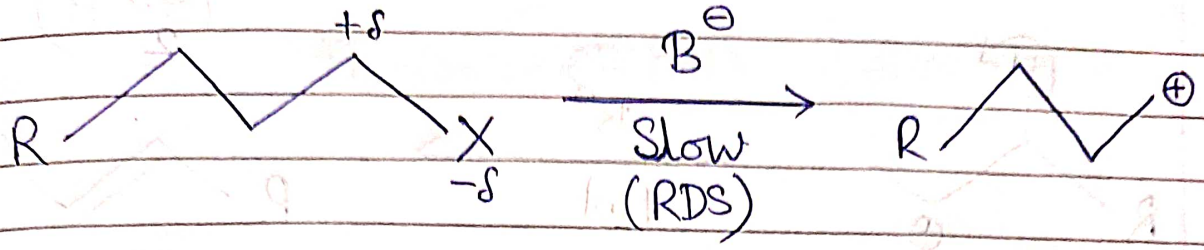
{X = Cl, Br, I}

☆ If an e^- rich species (in general),

Acts like Base ⟺ Elimination

Acts like Nucleophile ⟺ Substitution

Mechanism is —

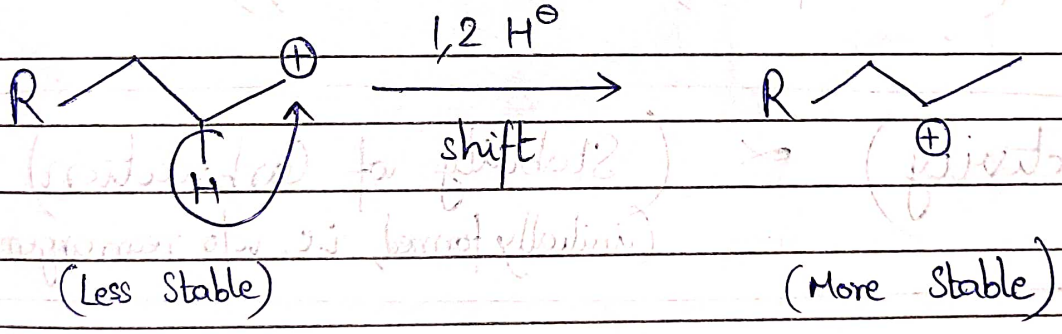


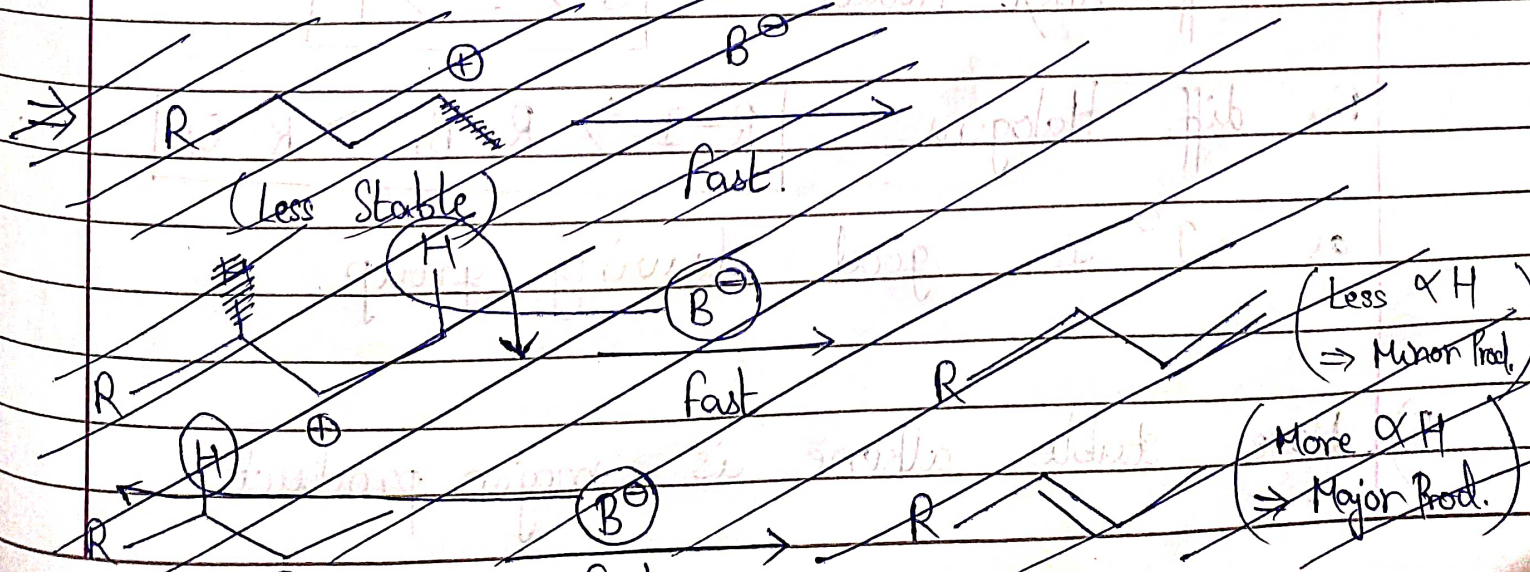
B^- is weak base ⇒ Attracts +δ, but travels slowly.

By that time, X has already left.

Since in this rxn, only 1 molecule (alkyl halide) is there. (B^- is NOT a reactant as it only attracts)

⇒ Unimolecular rxn ⇒ E_1





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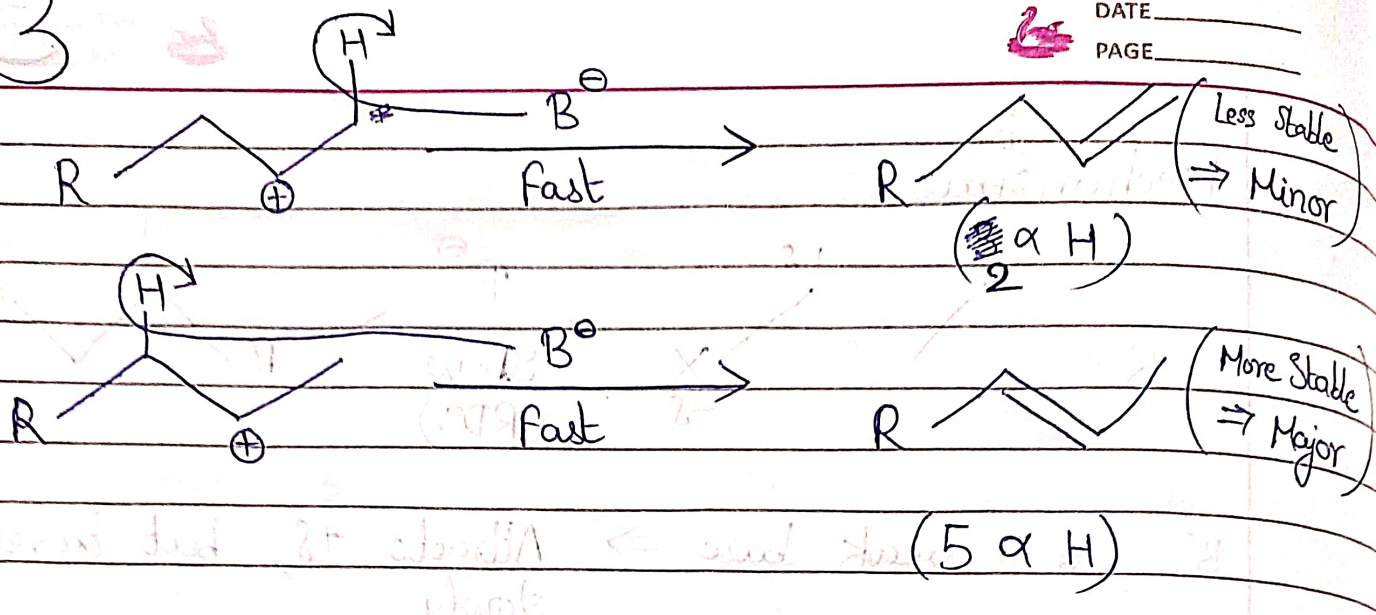


1) In 1st step carbocation is formed, which may rearrange.

2) Kinetically, $\text{Rate} = k\,[R\text{-}X]^1$

$\Rightarrow$ (Order of rxn) = (Molecularity) = 1

3) (Reactivity) $\propto$ (Stability of Carbocation (initially formed, i.e. w/o rearrangement))

4) For diff Alkyl Halide, $3^\circ > 2^\circ > 1^\circ$

For diff. Halogens, $R\text{-}I > R\text{-}Br > R\text{-}Cl$.

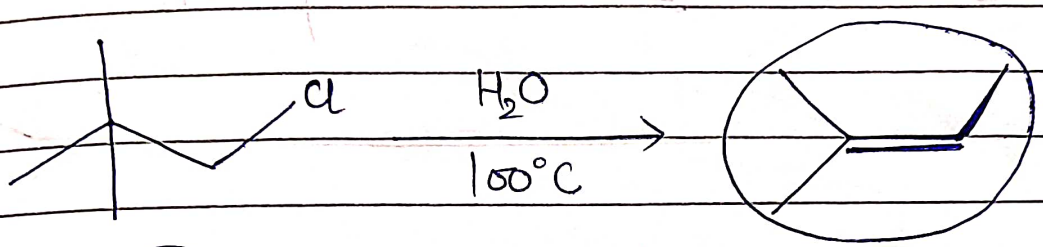
as $I^\ominus$ is good leaving group.

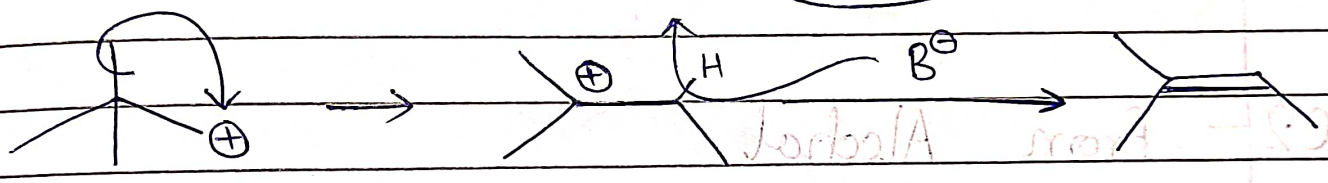
5) More stable alkene is major product.

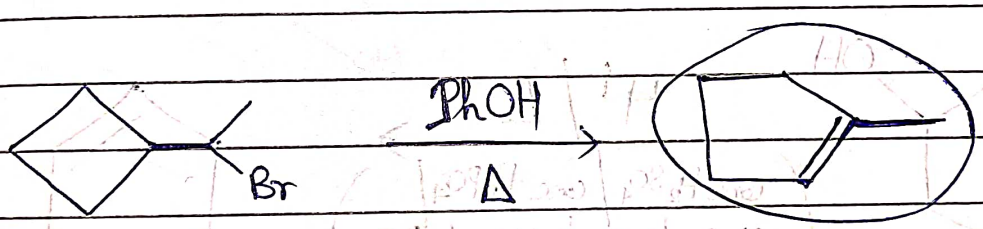
6) Occurs in presence of weak base.

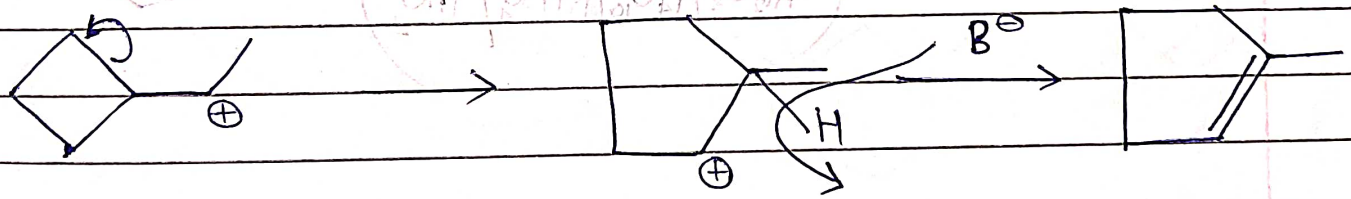
Eg- H_2O, $Ph-OH$, CH_3OH, C_2H_5OH, ...

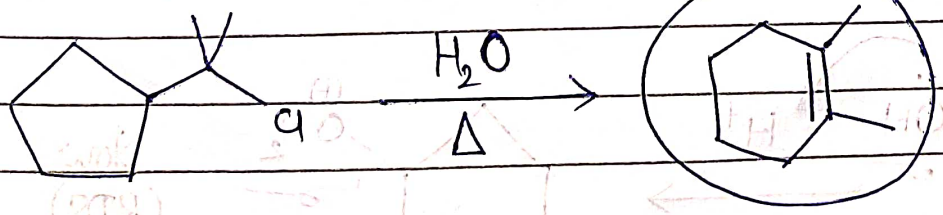
Q) Write major product.

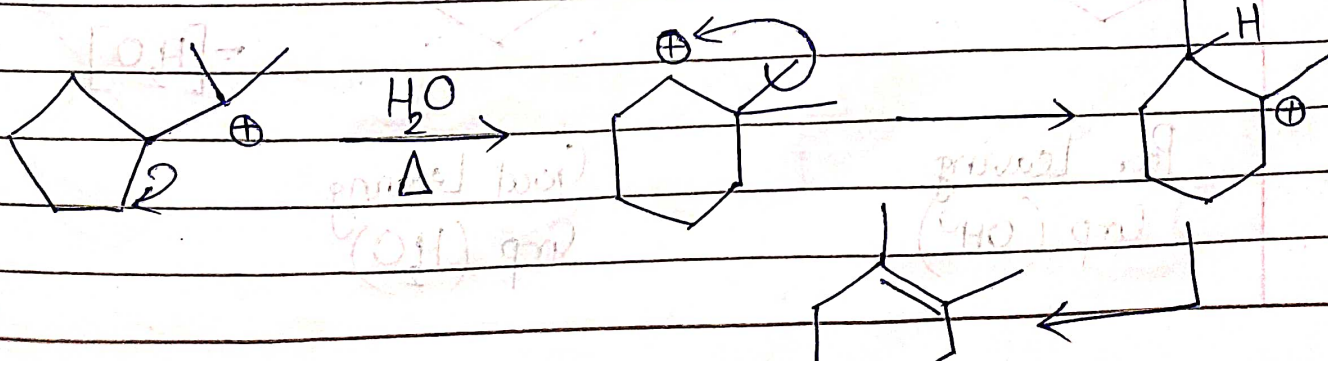
1) 

A) 

2) 

A) 

3) 

A) 

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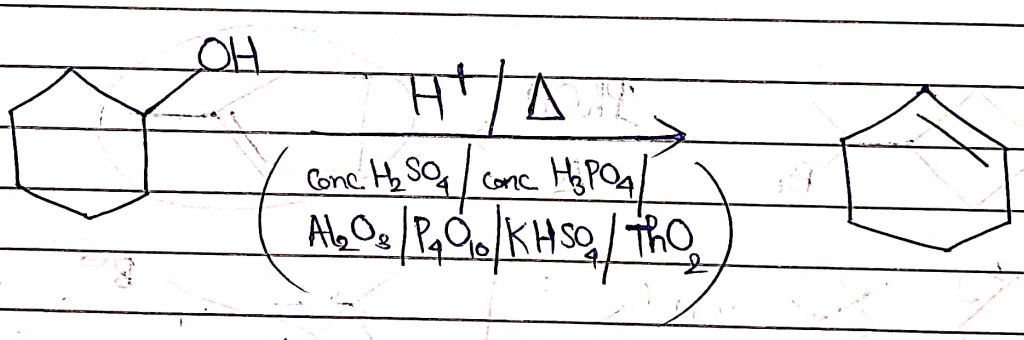
☆

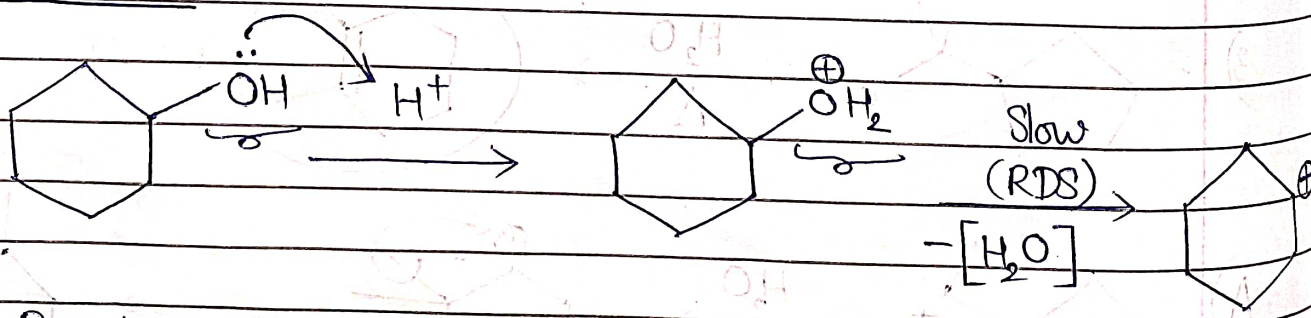
1) In E1 elimination from Alkyl Halide, both (Cis) & (Trans) can form.

2) To find out from where to remove H & make double bond, find α C with LEAST no. of H.

C2- From Alcohol



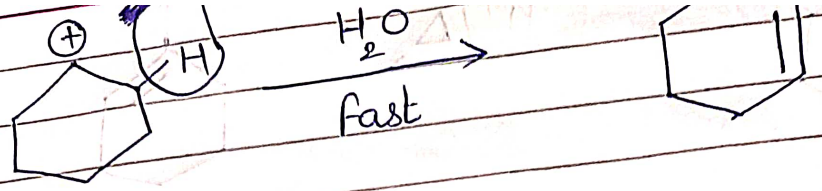
Mechanism -



Poor Leaving Grp ($OH^{\ominus}$)

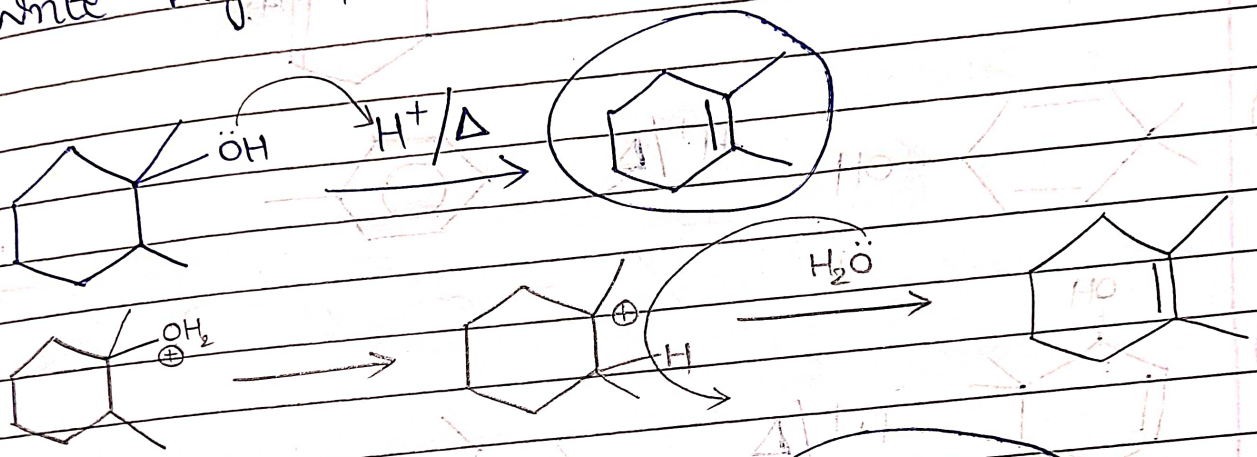
Good Leaving Grp (H_2O)

Now,



Q) Write major product

1)



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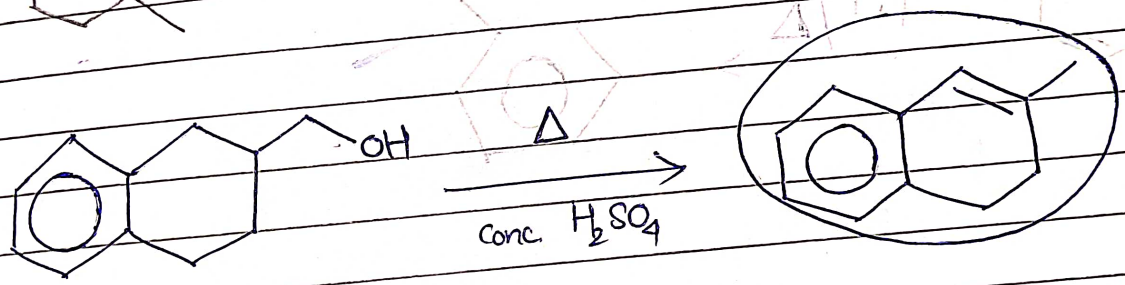

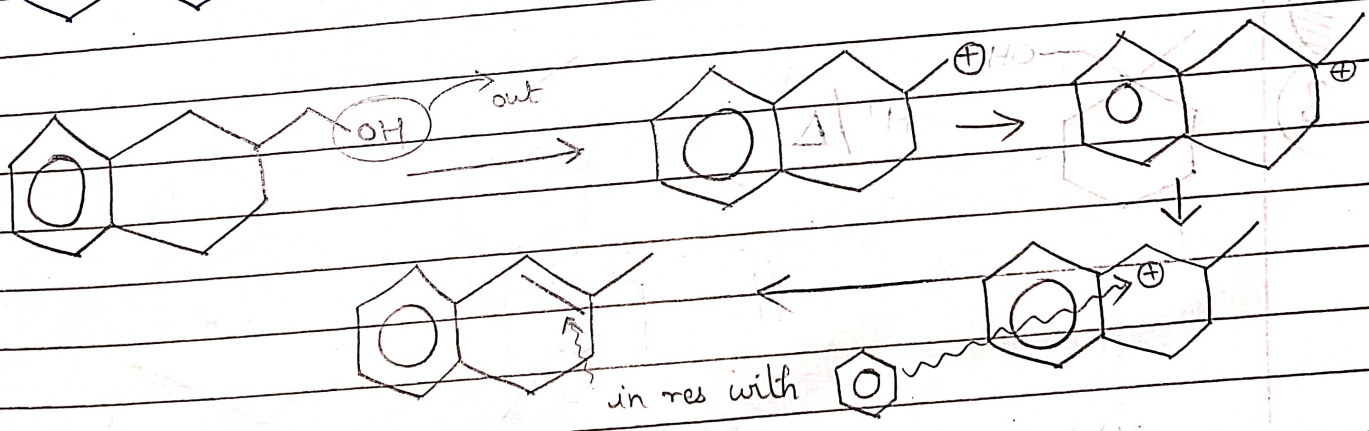

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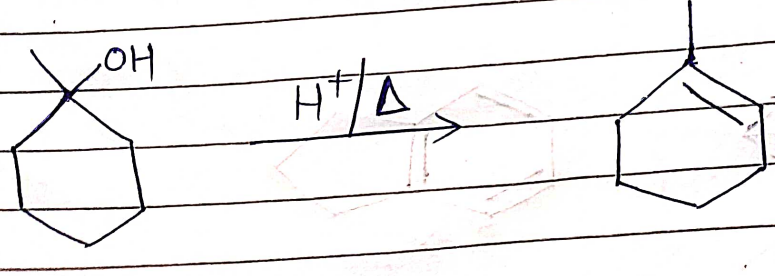

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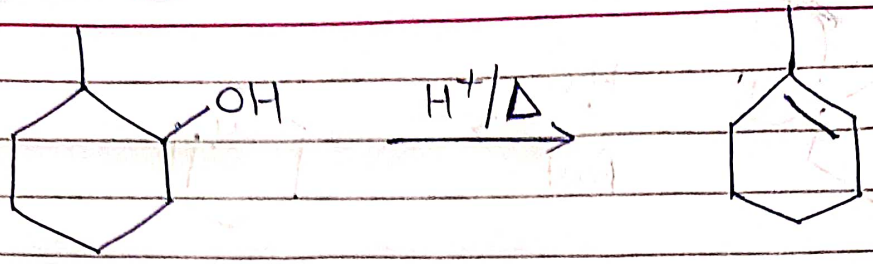
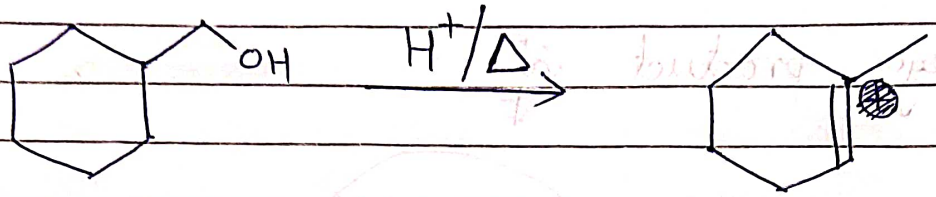
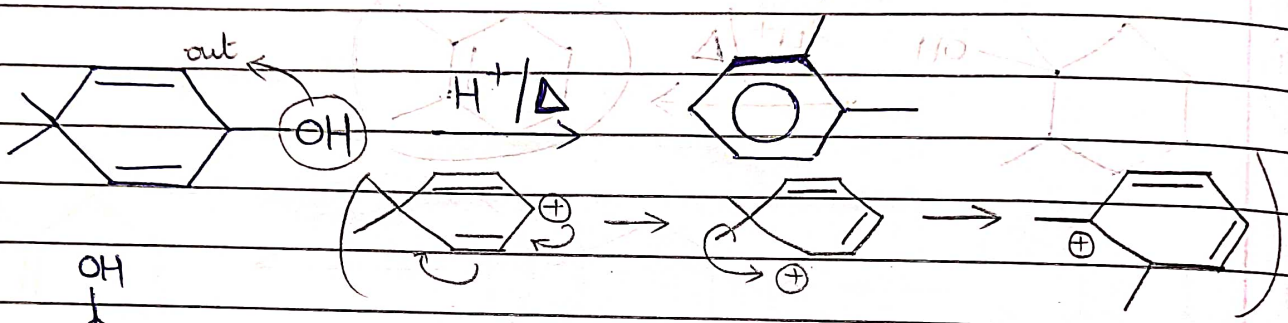
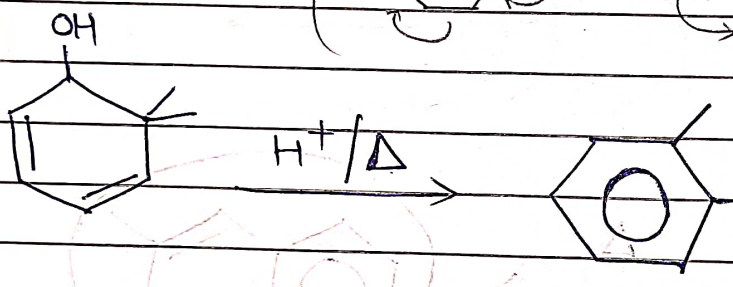
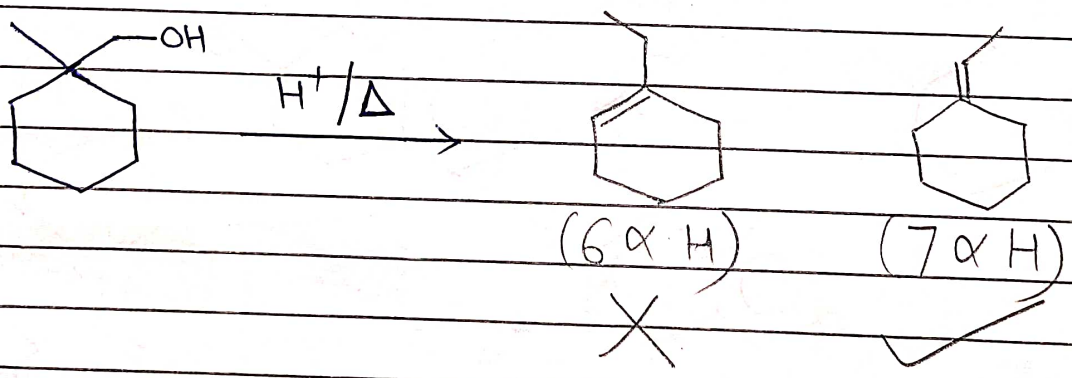
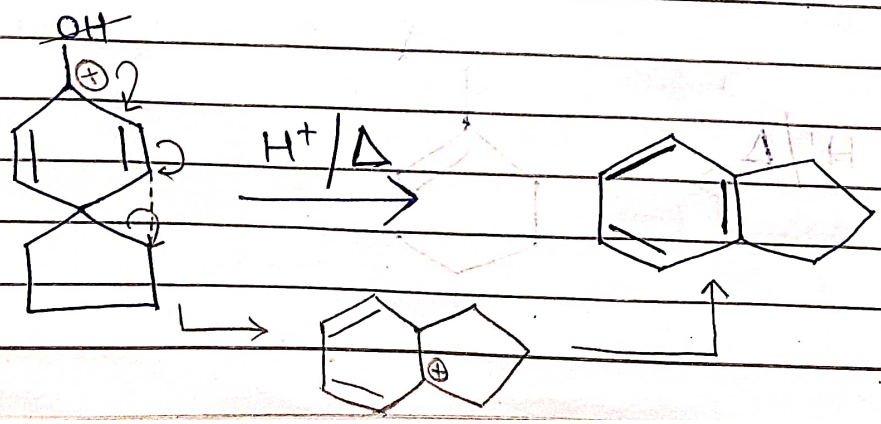
4) 

5) 

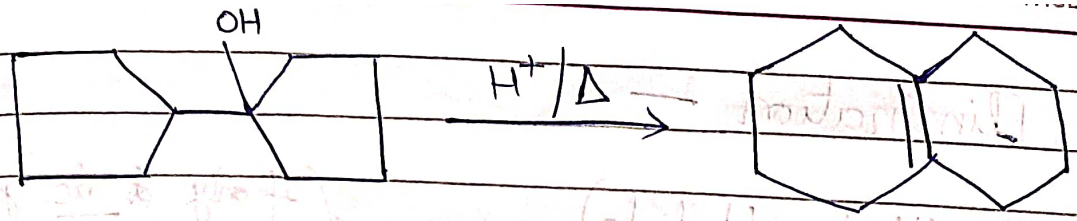
6) 

7) 

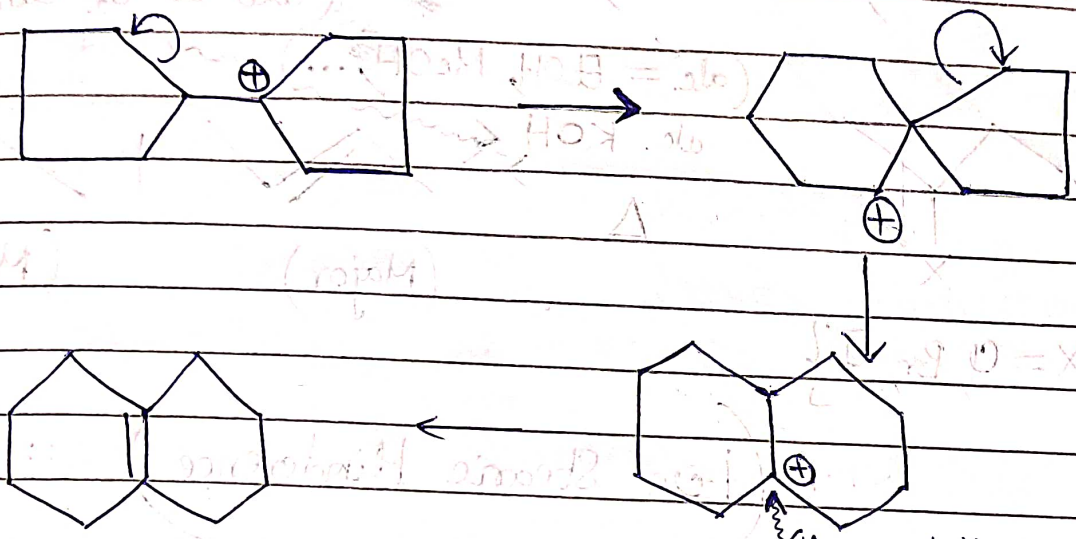
8) 

9) 

★10)

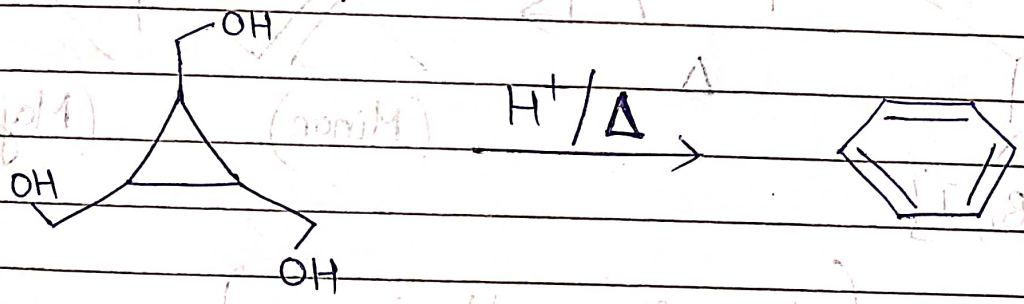


A)

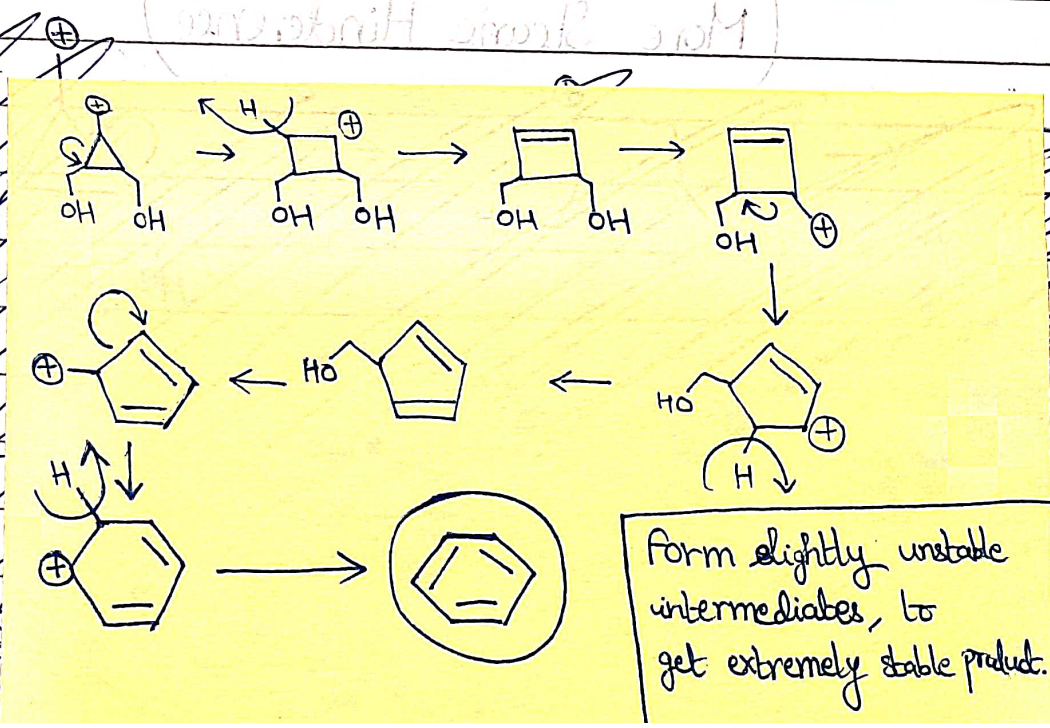


this is stable even though it is bridge head C, as it is planar

★11)



A)



form slightly unstable intermediates, to get extremely stable product.

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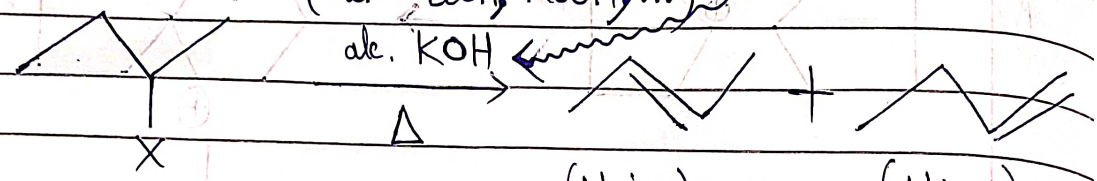
2.3) E_2 Elimination —

(From Alkyl Halide)

(If only alc. given, then also do E_2 elimination)

(alc. = EtOH, MeOH ...)

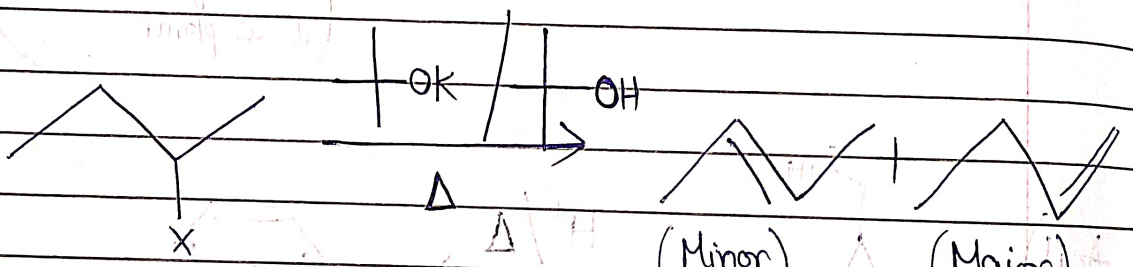
C1:



{X = Cl, Br, I}

(Less Steric Hinderence)

C2:

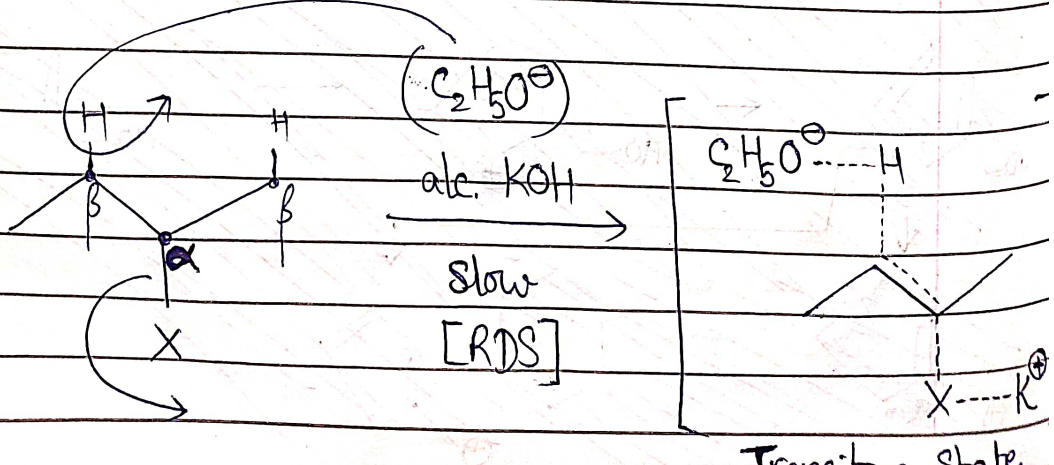


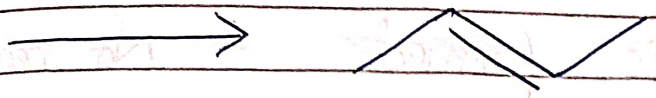
{X = Cl, Br, I}

(More Steric Hinderence)

Mechanism —

C1:




(Major)

☆ H & X should be (Anti) & in same plane.

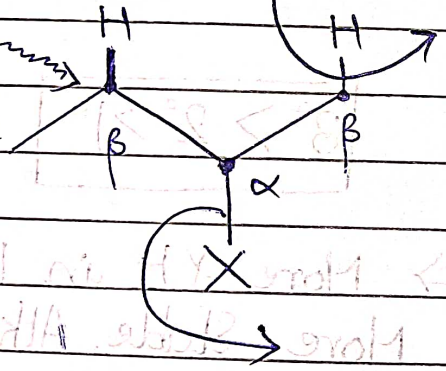
[Saytzeff product]

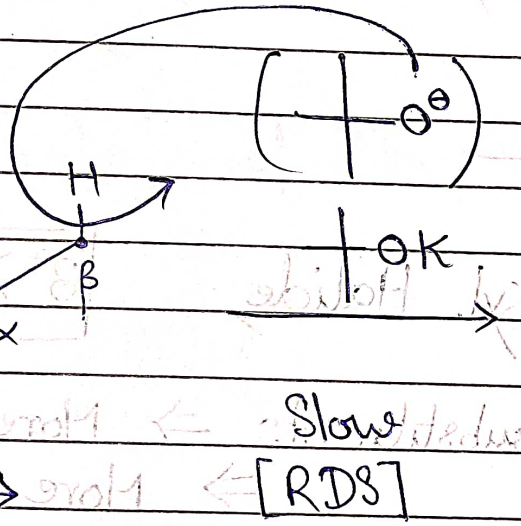
(More substituents present in product)

Here, H & X leave simultaneously as KOH is strong base.

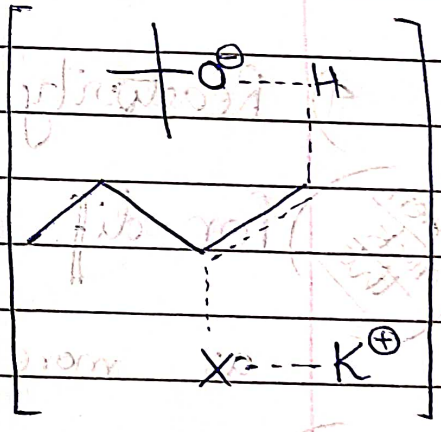
C2:

(More steric hinderance)



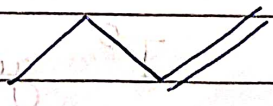


Slow [RDS]



Transition State

☆ H & X should be (Anti) & in same plane.



Less substituents present in product

[Hoffmann Product]

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1) No carbocation is formed. ∴ No rearrangement

2) Rate = $k[R-X][Base]$

Order = 2 Molecularity = 2

⇒ Bimolecular Elimination Rxn.

3) Strong Base is req. $CH_3O^{\ominus}K^{\oplus}/CH_3OH$

Eg - alc. KOH, $NaNH_2$, ~~$CH_3COO^{\ominus}K/CH_3COOH$~~, ~~OK~~

4) Reactivity —

(Then check this) For dif. Alkyl Halide, $3^{\circ} > 2^{\circ} > 1^{\circ}$

as more substituents ⇒ More α H in Hyperconj.
⇒ More Stable Alkene formed

(First check this) for Halogens, (diff.) $R-I > R-Br > R-Cl$

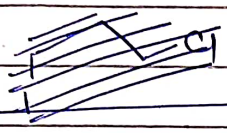
as $I^{\ominus}$ good leaving grp.

5) In general, to compare reactivity —

1) Compare # α H for hyperconj. in product.
2) Compare # β H in reactant.

6) X & H removed should be (Anti). & in same plane.

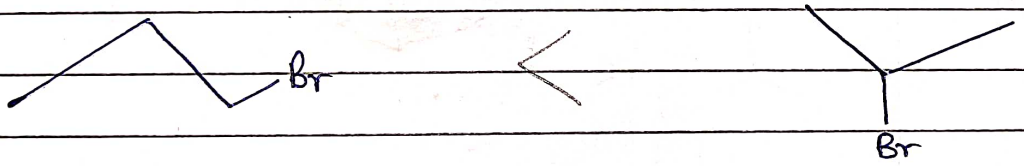
7) Isotopic Effect —

Reactivity :  $CH_3-CH_2-Cl > CH_2D-CH_2-Cl > CH_2T-CH_2-Cl$

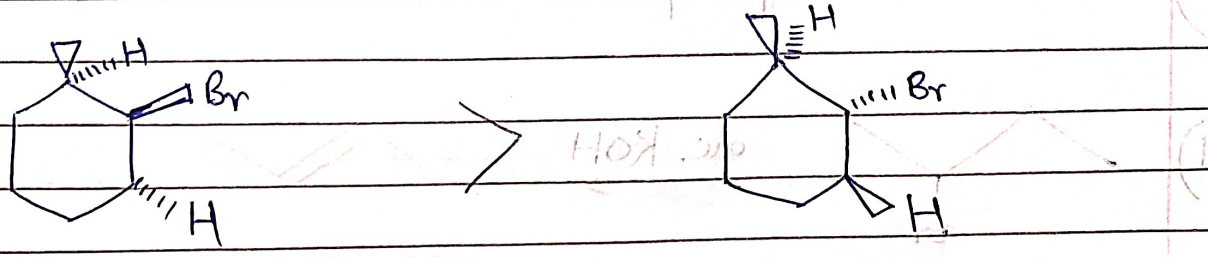
as

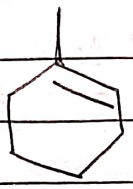
Bond Strength : C–H < C–D < C–T

Q) Compare rate of E_2 —

1) 

1° R–X 2° R–X

2) 



More α H

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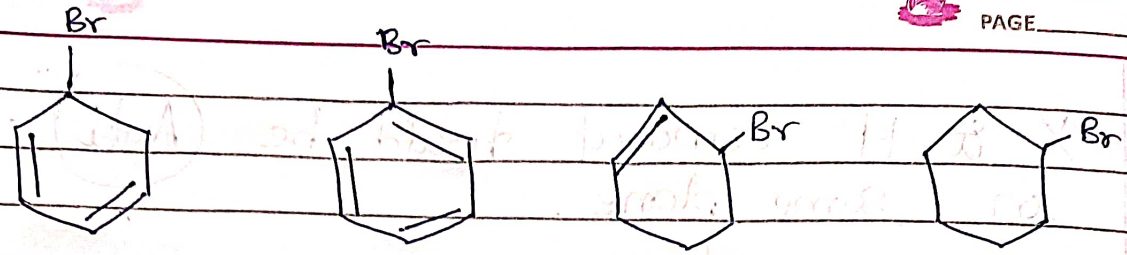
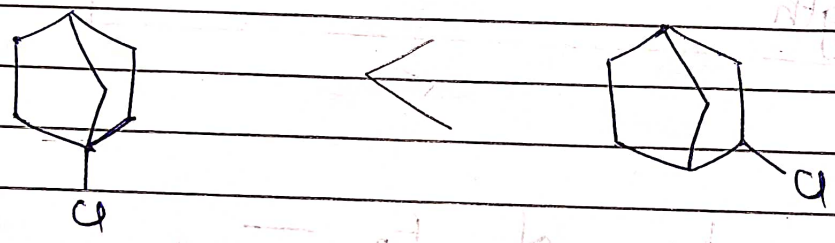
3)

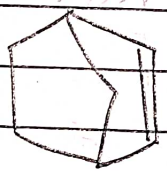


1 > 3 > 4 > 2

4)

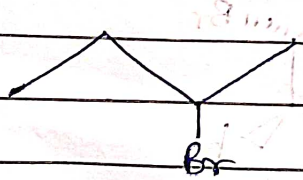


Breadt's Rule



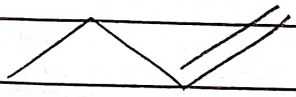
Q) Total no. of product obtained when E_2 —

1)

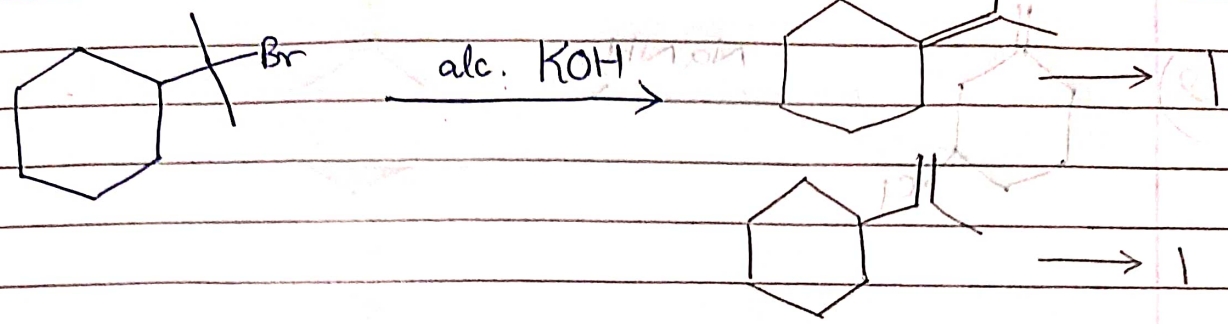


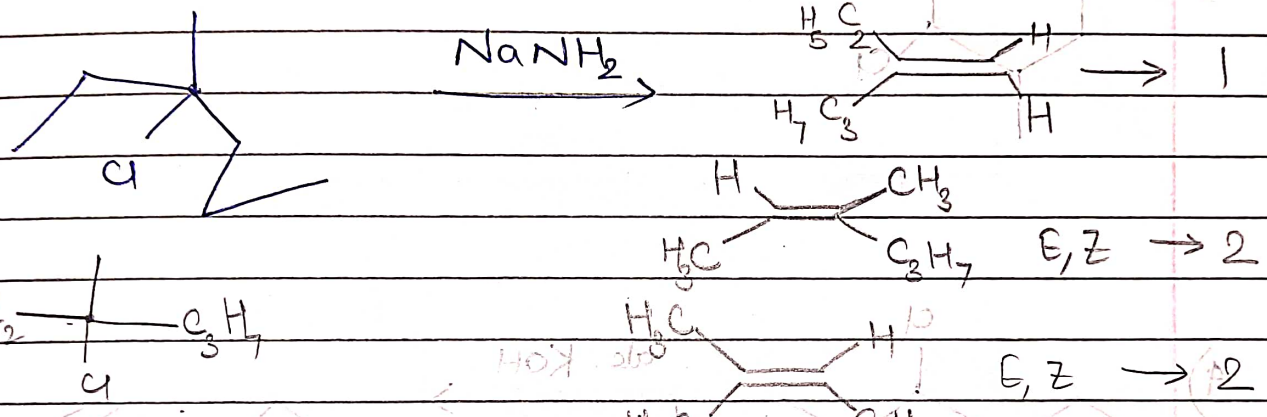
alc. KOH →

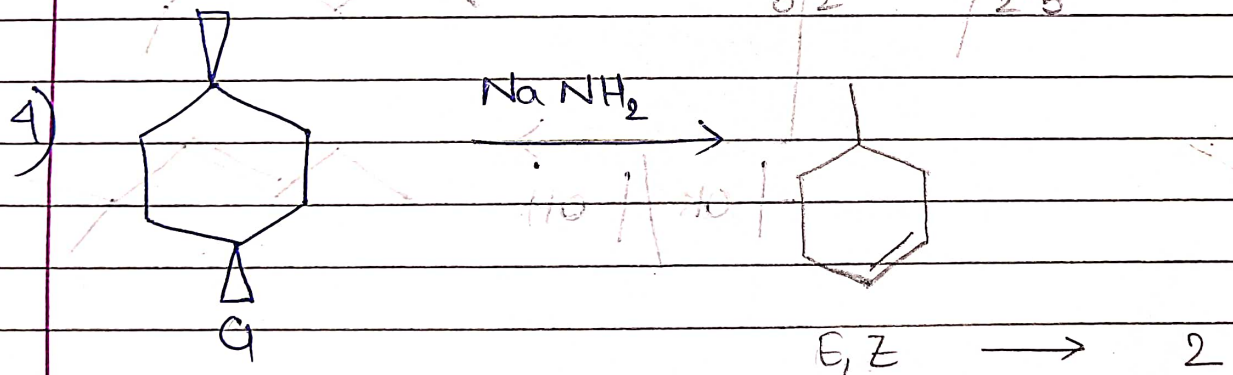
E, Z → 2



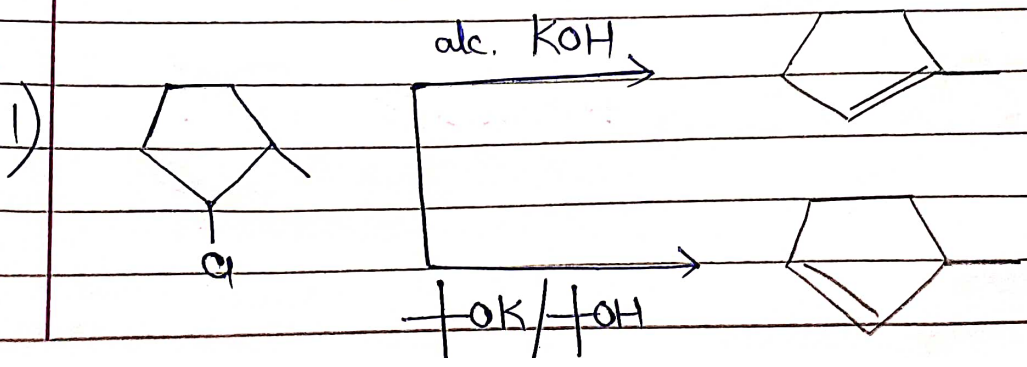
→ 1

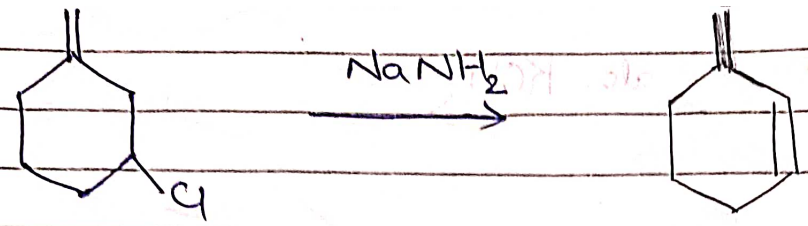
2) 

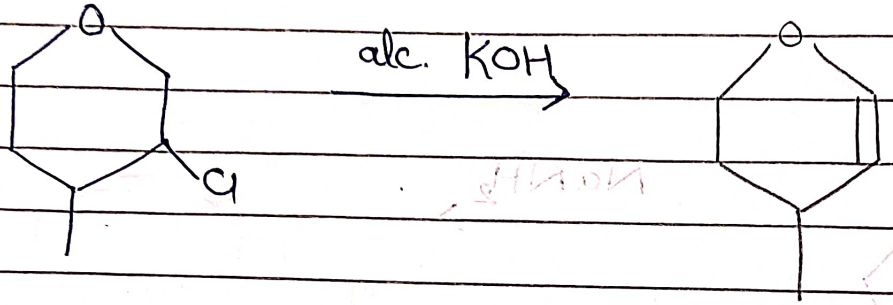
3) 

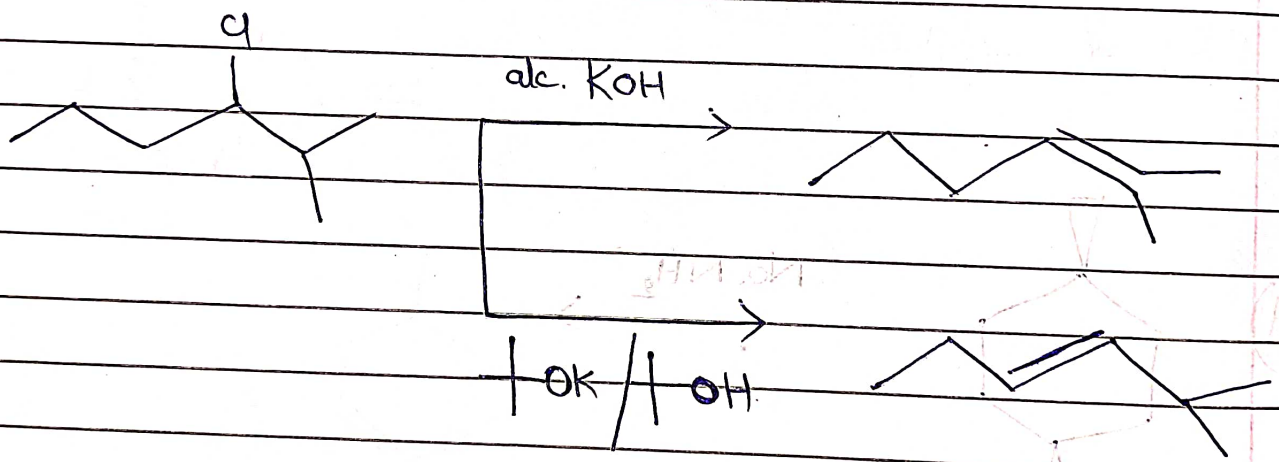
4) 

Q) Write Major Product —

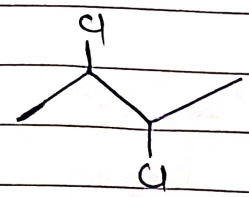
1) 

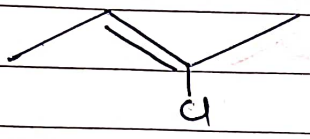
2) 

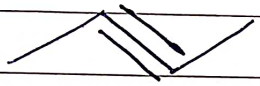
3) 

4) 

Q) Write final product —

☆ 1)  alc. KOH → (A) $NaNH_2$ → (B)

A) A — 

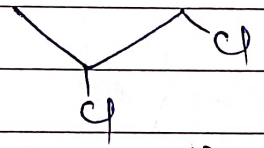
B — 

(Can't remove H from sp^2 C atom)

alc. KOH → No rxn !

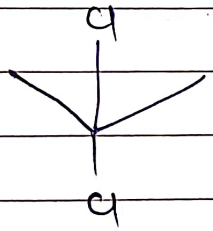
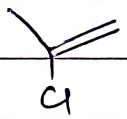
☆ $NaNH_2$ stronger than alc. KOH

Q) Calc. x in following for complete rxn —

☆ 1)  (1 mol) x $NaNH_2$ →  (acidic) + $NaNH_2$ (basic) → Rx^n ✓

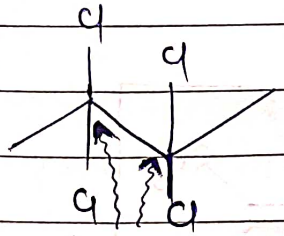
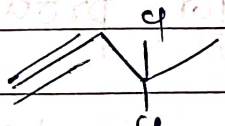
($CH_3-C\equiv C^{\ominus}Na^{\oplus} + NH_3$)

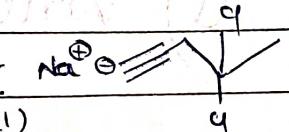
③ $NaNH_2$ req.

2)  x $NaNH_2$ →  (acidic) + $NaNH_2$ (basic) → Rx^n ✓

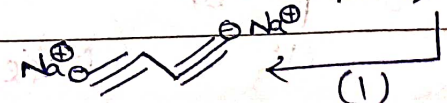
($CH_3-C\equiv C^{\ominus}Na^{\oplus} + NH_3$)

③ $NaNH_2$ req.

3)  x $NaNH_2$ →  (2)

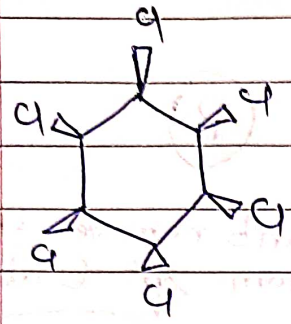
 (1)

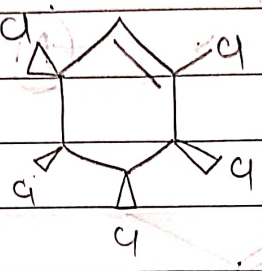
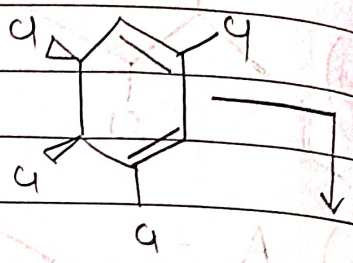
(2) 

 (1)

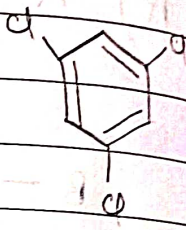
(Na H available !) ⑥ $NaNH_2$ req.

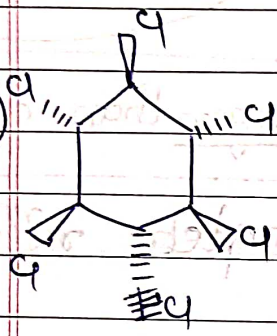
Q) Find # Cl undergoing E_2 rx^n with alc. KOH-

1) 

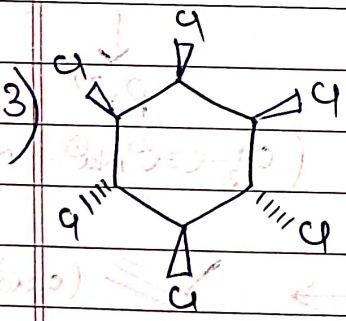
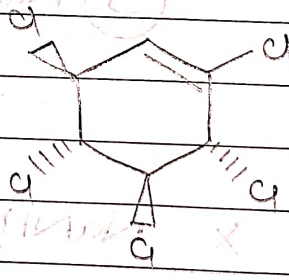
(3) Cl out



2) 

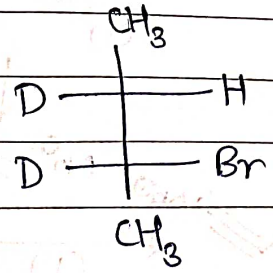
No rx^n.

(0) Cl out

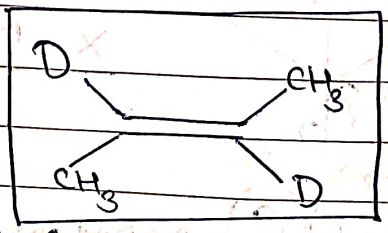
3) 


(1) Cl out

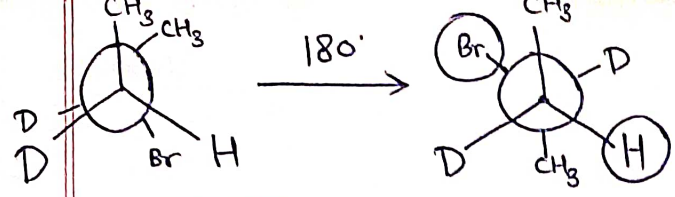
Q) Write major product —

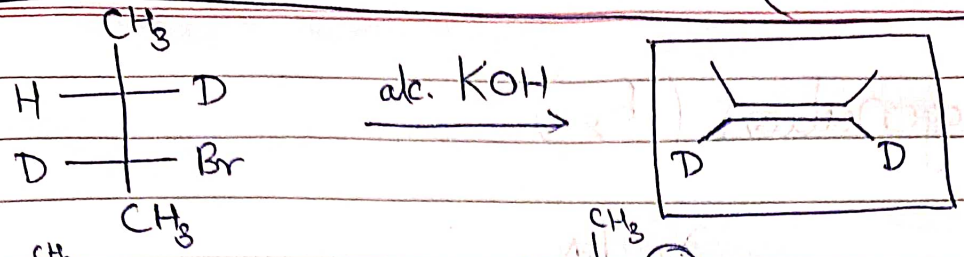
★ 1) 

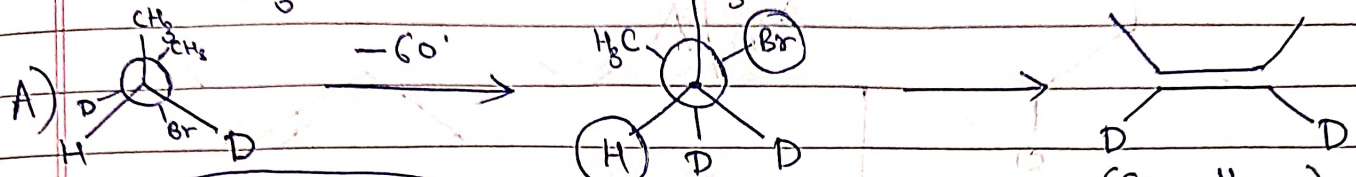
alc. KOH →

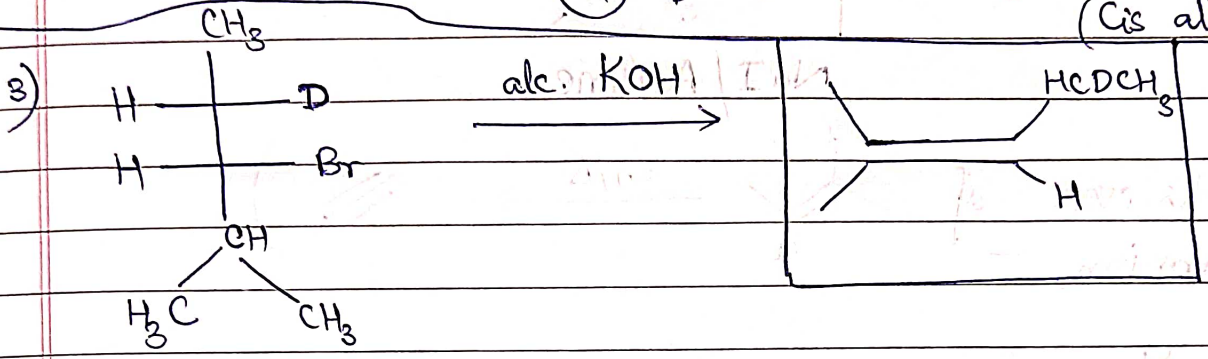


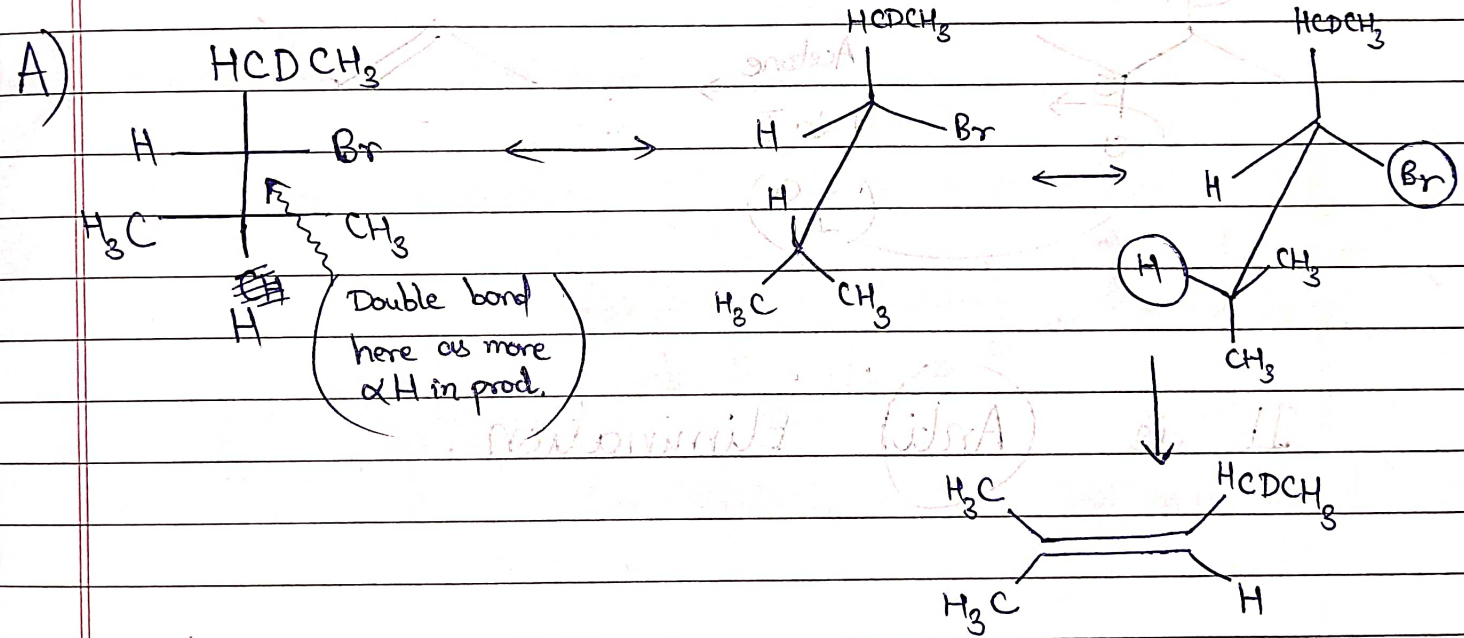
(Make Newmann!) (We can also use Sawhorse!)

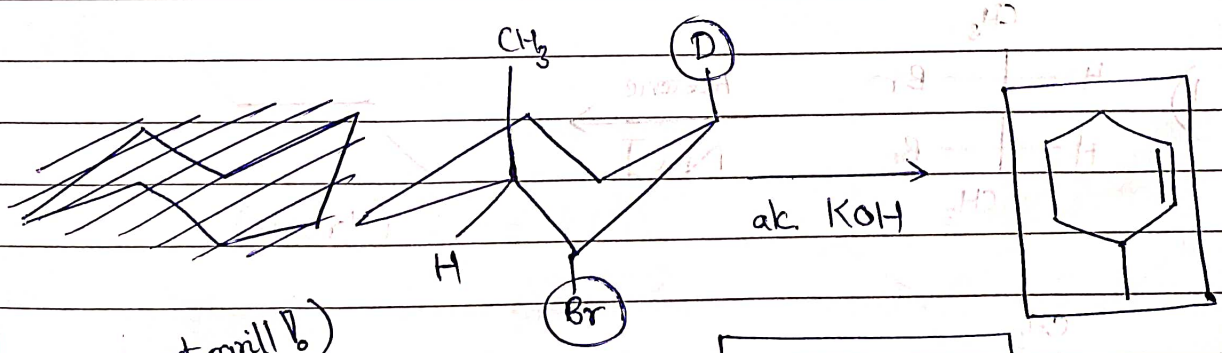
A) 
180°
alc. KOH
Trans alkene

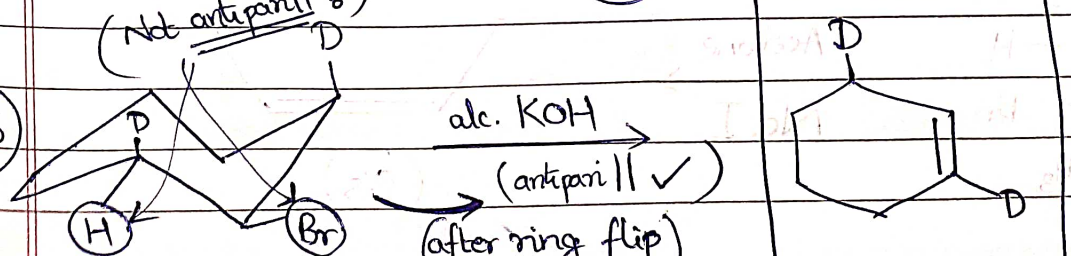
2) 
alc. KOH

A) 
-60°
(Cis alkene)

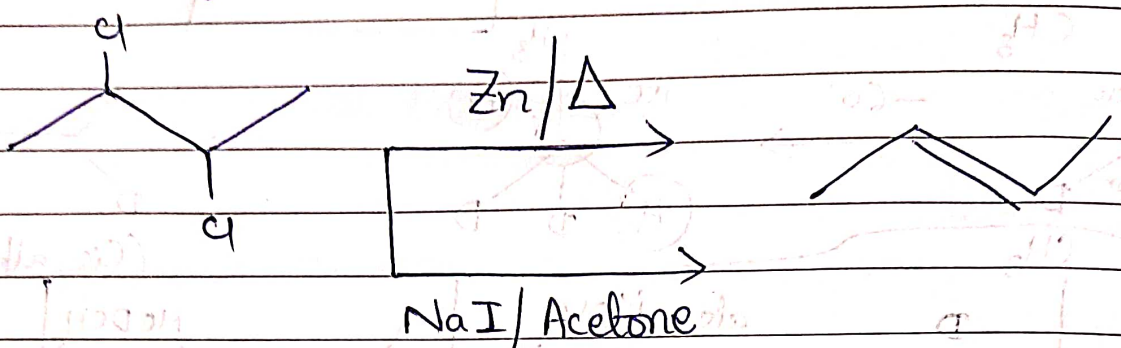
3) 
alc. KOH

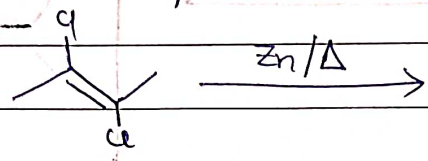
A) 
Double bond here as more αH in prod.

4) 
alc. KOH

☆5) 
(Not antiparll l)
alc. KOH
(antiparll ✓)
(after ring flip)

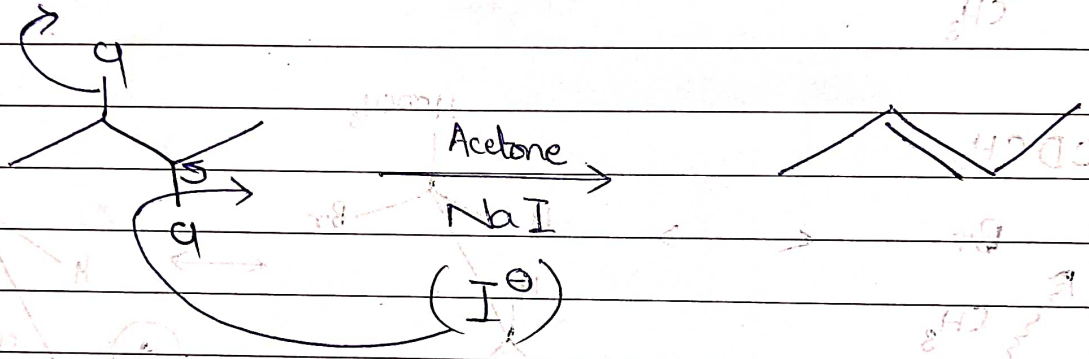
2.3.1) De-Halogenation (E_2) —



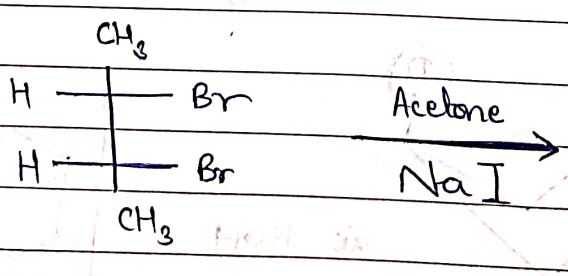
(Works even if 

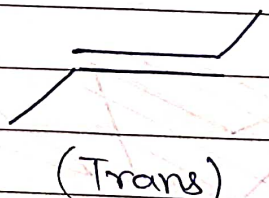
)

Mechanism —

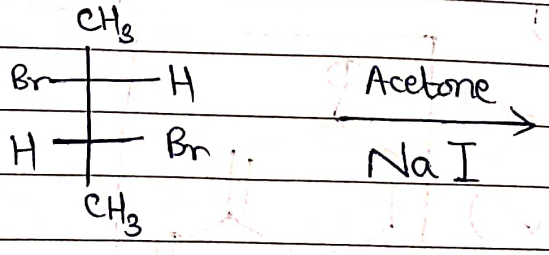


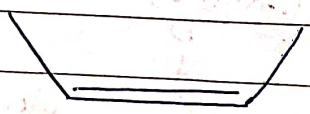
It is (Anti) Elimination.

Q) 1) 

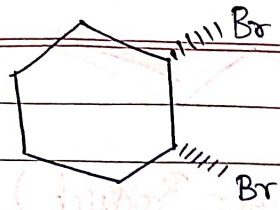


(Trans)

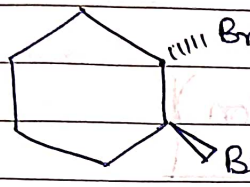
2) 

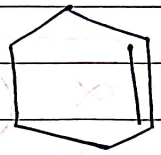


(Cis)

3) 

$\xrightarrow{Zn/\Delta}$ No rxn

4) 

$\xrightarrow{Zn/\Delta}$ 

2.4) $E_{1(cb)}$ Elimination —

If bad leaving grp. (like $-F$, $-\overset{\oplus}{N}R_3$, $-\overset{\oplus}{S}R_2$, ...),

{alc. = EtOH, MeOH, ...}

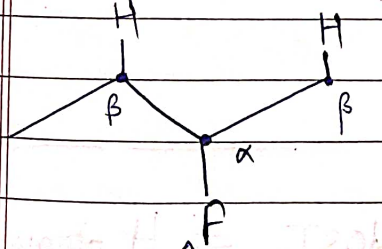
(If only alc. given then also do rxn)

alc. KOH/Δ

OR $NaNH_2$

(Hoffmann product)

Mechanism —

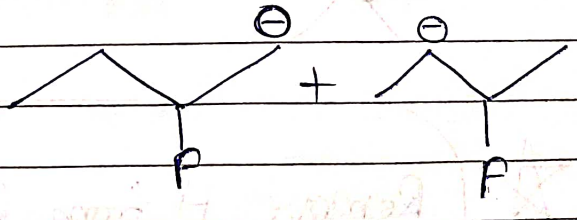


won't leave as bad l.g.

alc. KOH

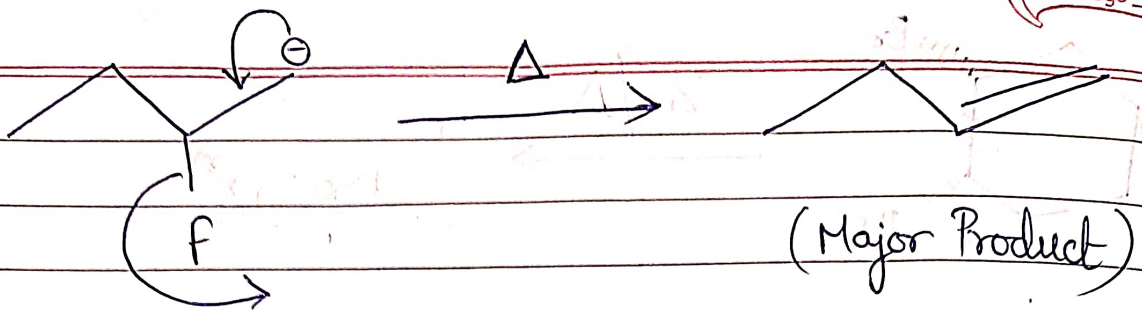
Slow

[RDS]



(More Stable) (Less Stable)

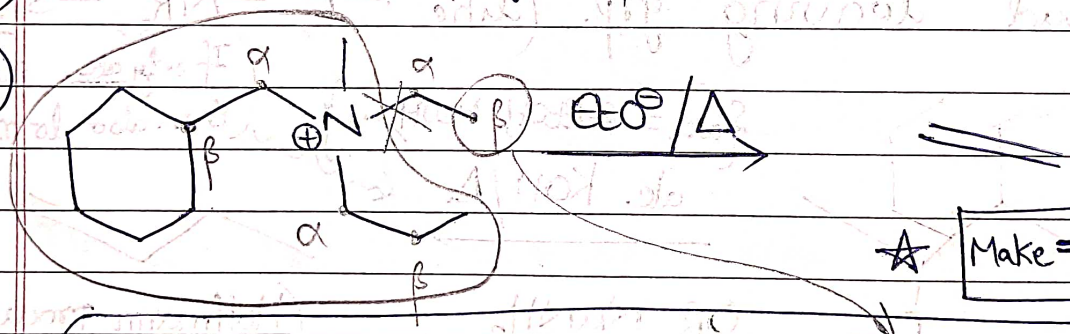
6



1) Reactivity ∝ (Stability of Carbanion).

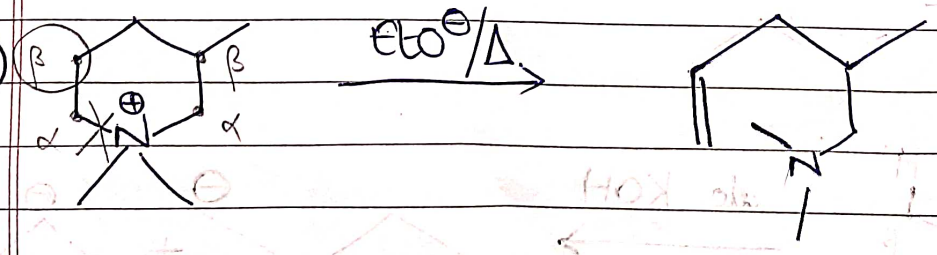
2) Hoffmann product is major product.

Q) Write the major product —

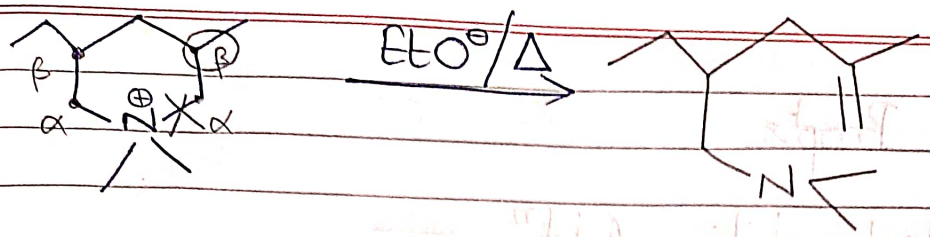
★ 1) 

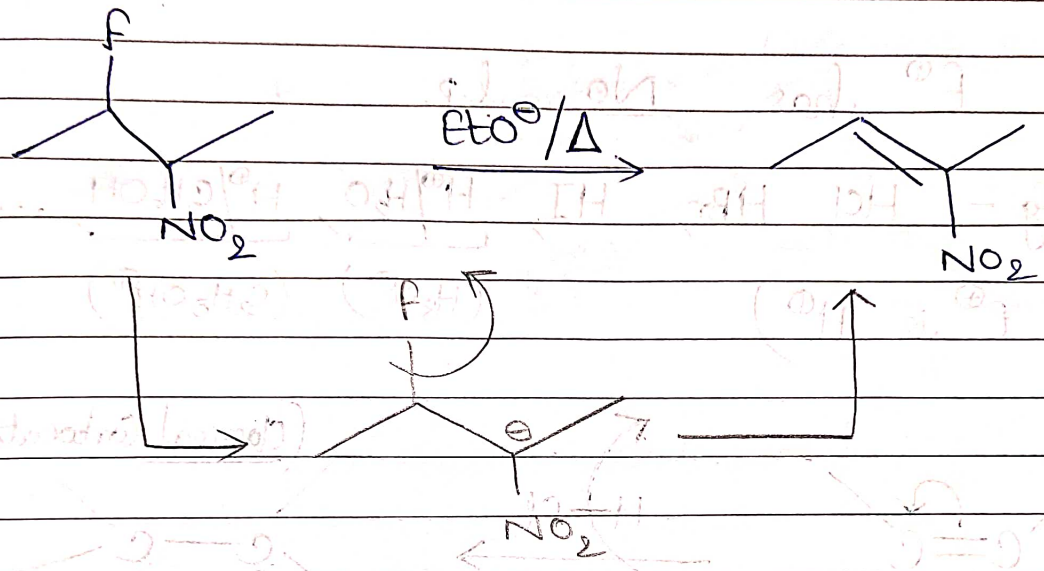
★ Make = b/w α & β

A) ★ Remove H from β C with MOST # H atoms! (In general)

2) 

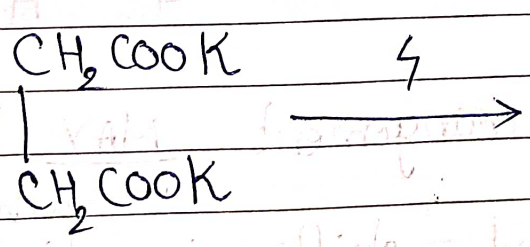
★ Remove H from β C with MOST # H atoms!

3) 

4) 

~~Prep" of Alkene (Contd.)~~

3) ~~Kolbe's~~ Electrolysis —



8

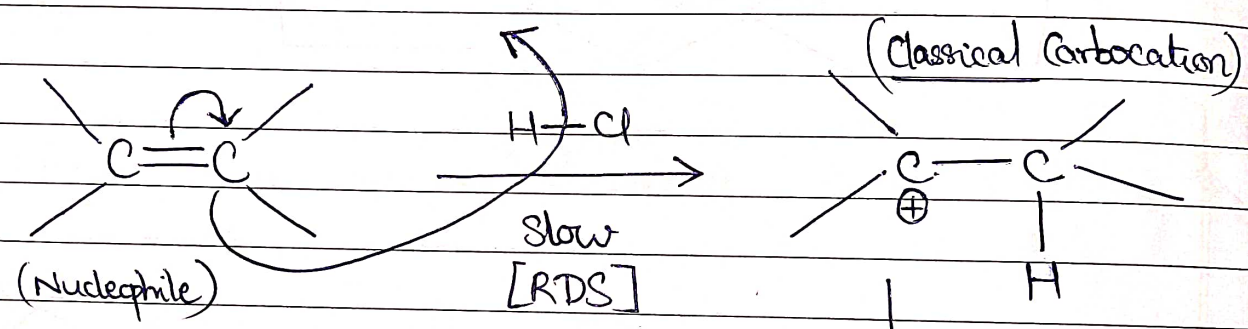
Chem. Props

1) ~~Add~~ Electrophilic Add^{n} —

Cl: $E^{\oplus}$ has No l.p.

Eg - HCl, HBr, HI, $H^{\oplus}/H_2O$ ($H_3O^{\oplus}$), $H^{\oplus}/C_2H_5OH$ ($C_2H_5OH_2^{\oplus}$) ...

(Here, $E^{\oplus}$ is $H^{\oplus}$)



Since, first $E^{\oplus}$ joins.

⇓

It is called $E^{\oplus}$ add^{n}.

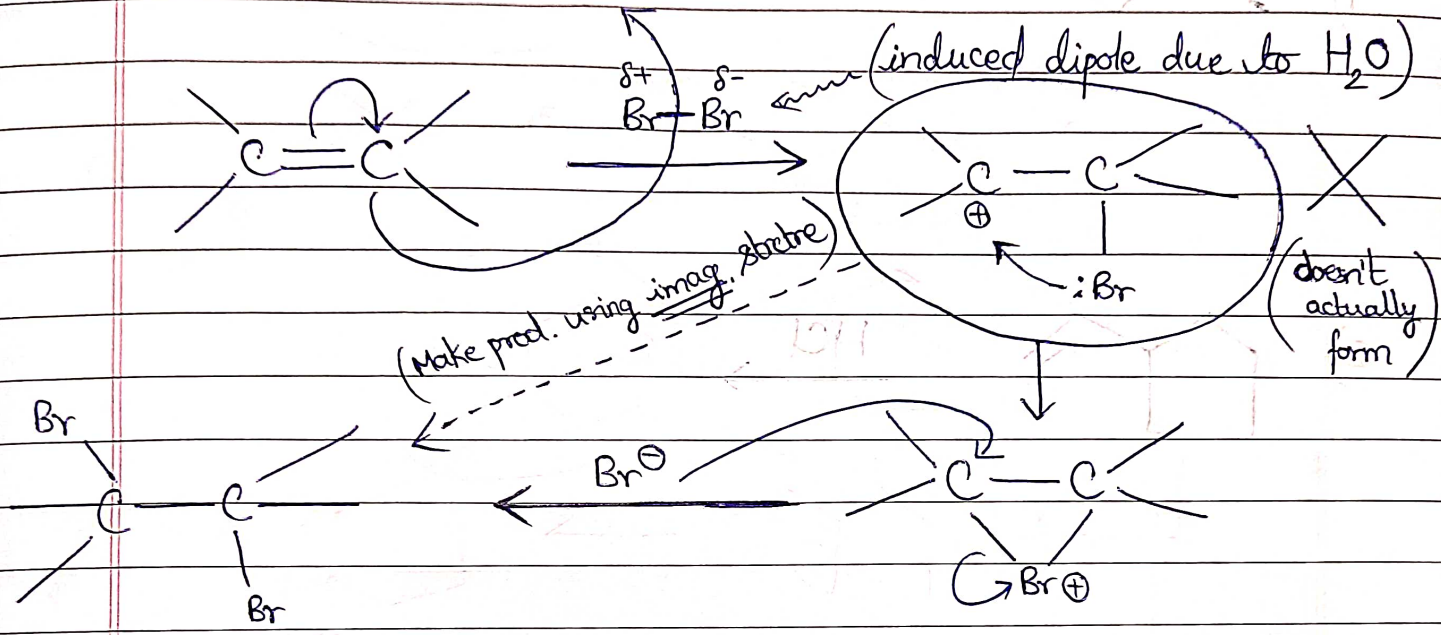
1) In 2nd step, rearrangement MAY happen.

2) In 1st step, bond shifts in such a dirn so as to inc. stability of carbocation formed.

3) (Reactivity) $\propto$ (Stability of Carbocation)

Q: $E^{\oplus}$ HAS l.p.

Eg - Br/H_2O, $X-X'/H_2O$, ... $\{X, X' \neq F\}$



(Anti Add^n)

Cyclic Halonium Ion
(NON classical carbocation)

☆ Peeche se add hoga!
Uss side, yiss side agar carbocation banta to jyada stable hota!

[Rearrangement NOT possible!]

1) No rearrangement is possible as Non Classical carbocation formed.

2) [(Reactivity) $\propto$ (Nucleophilicity of Alkene)]

Eg -

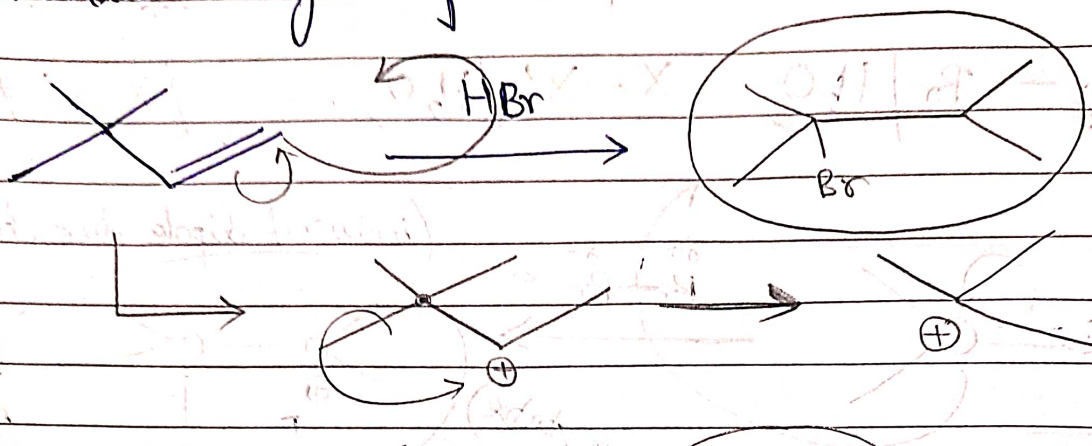
Reactivity: $>C=C<$ (+4I) $>$ $>C=CH_2$ (+2I) $>$ $CH_2=CH_2$

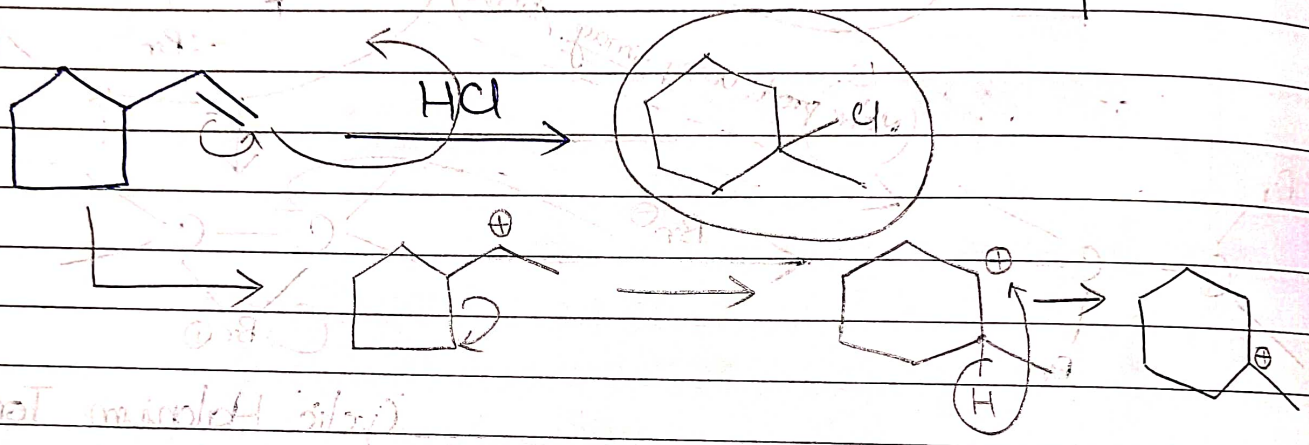
$CH_2=CH-CHO$ (-I)

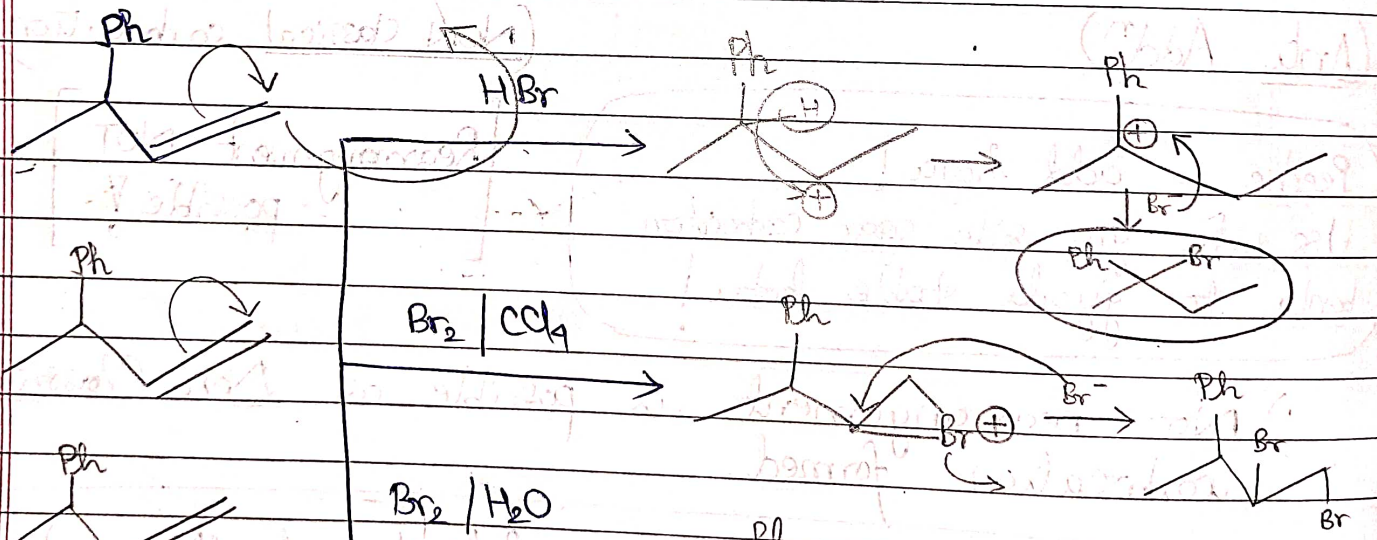
3) Anti Add^n occurs.

10

Q) Write major prod. —

1) 

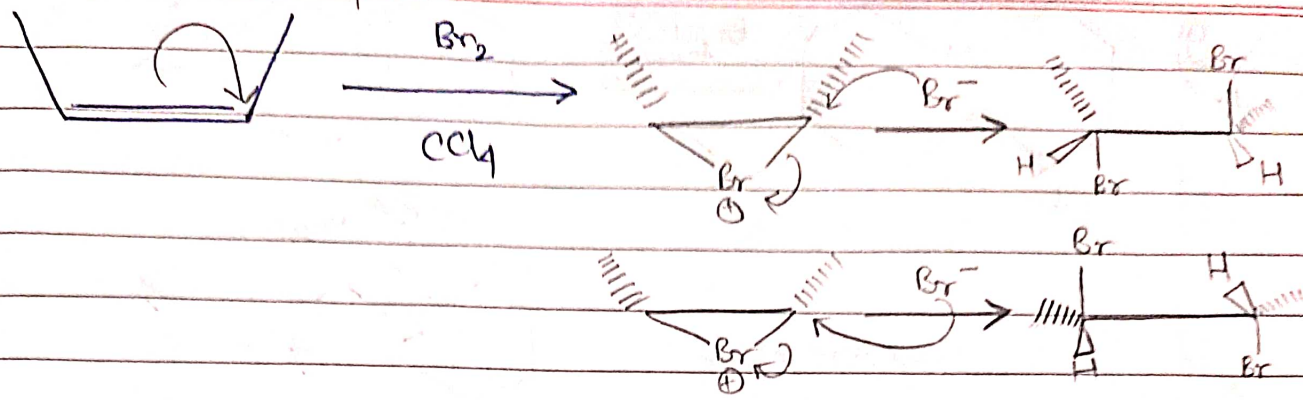
2) 

3) 

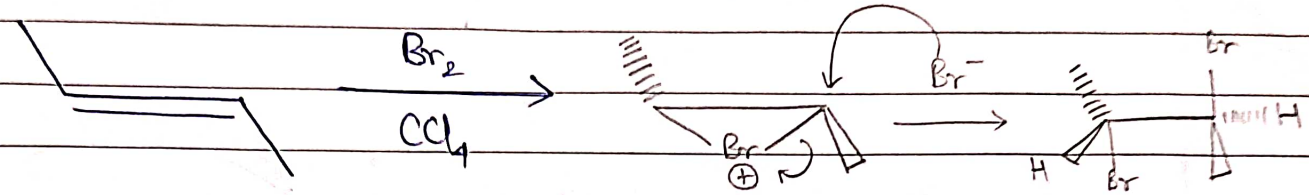
(CAR)

Cis Symmetric Comp + Anti Addⁿ → Enantiomers

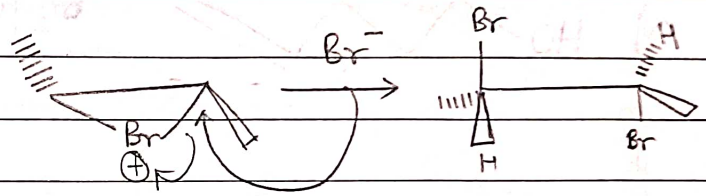
4)



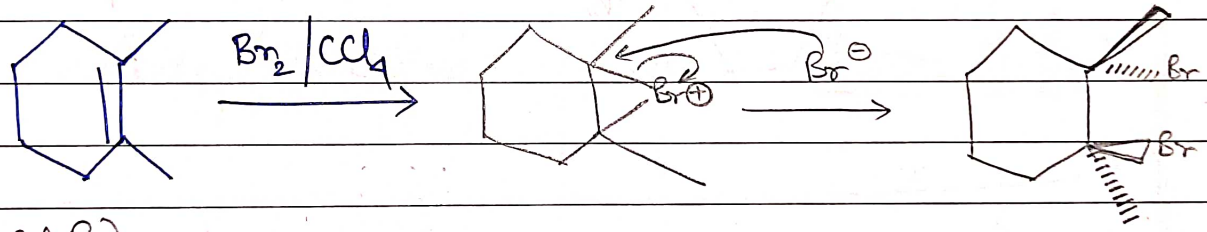
5)



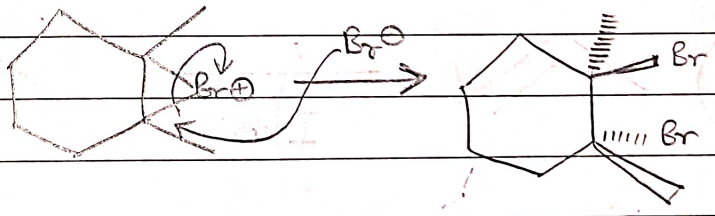
(TAM)



6)



(CAR)



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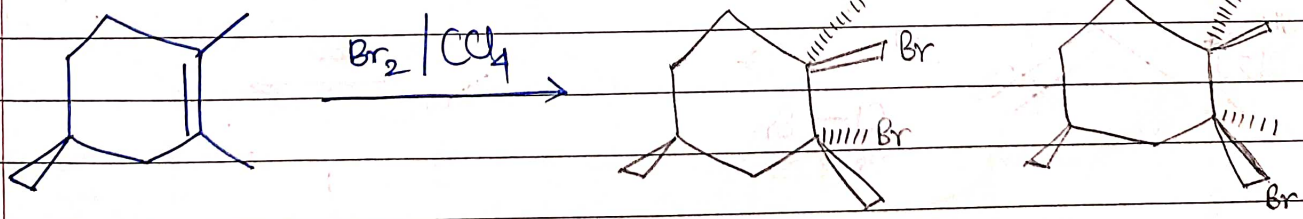
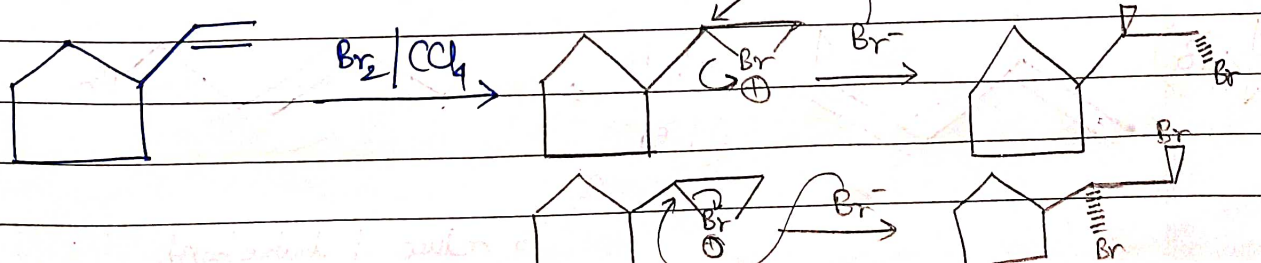


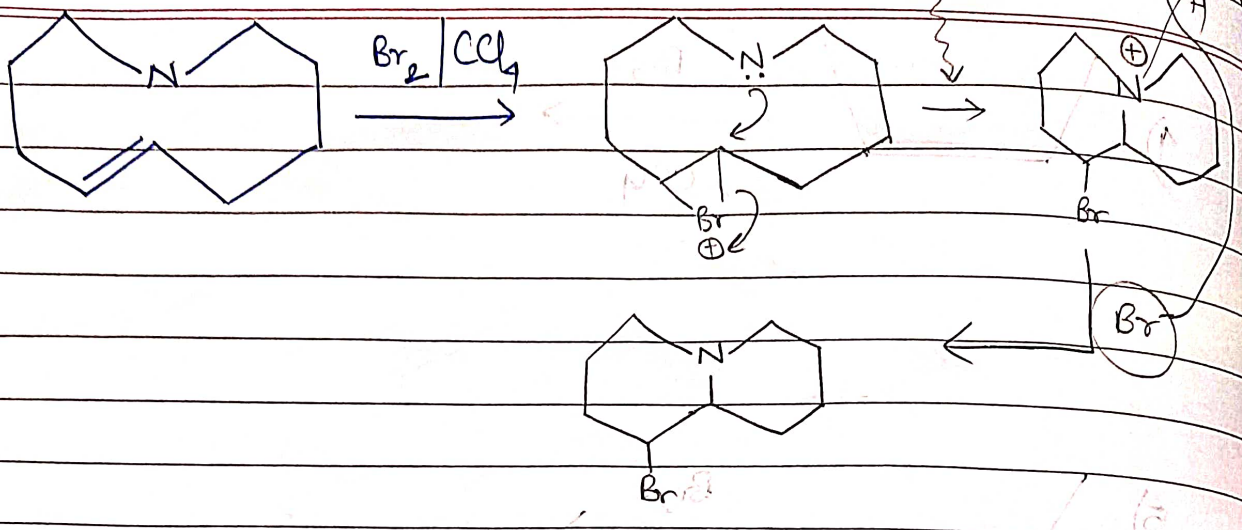
8)



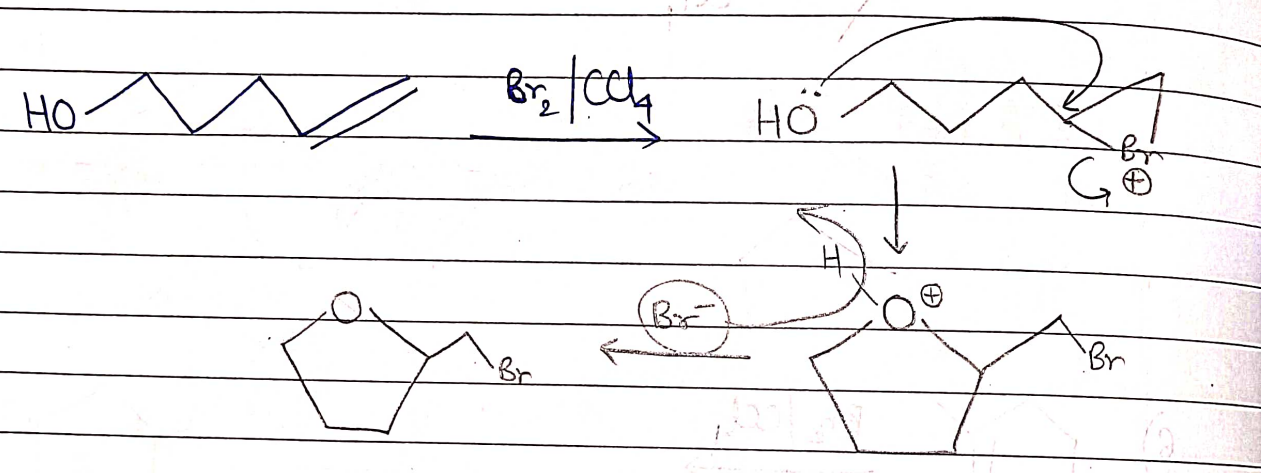
12

Intramolecular classmate
Attack very ... Base Page !

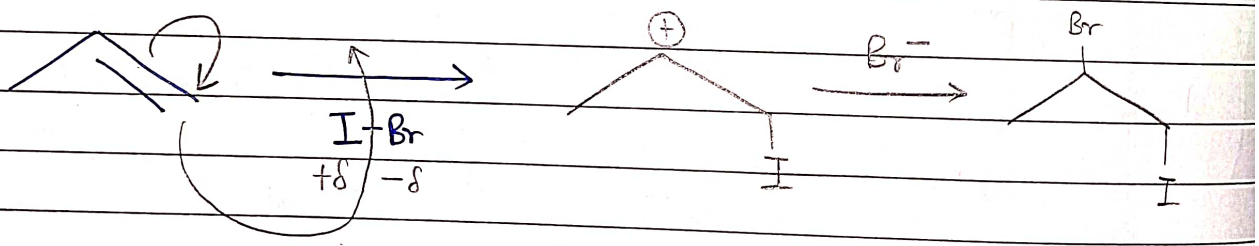
9) ☆



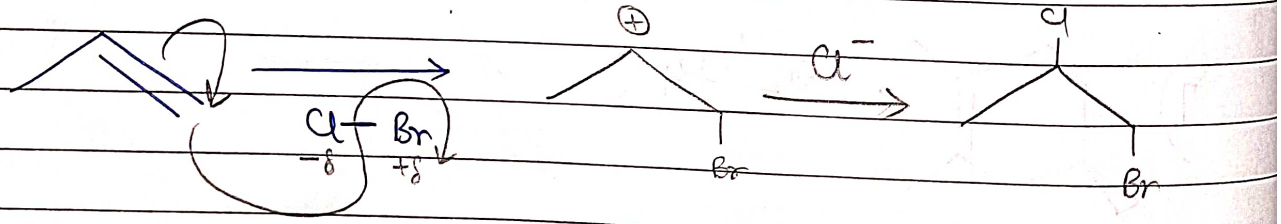
10)



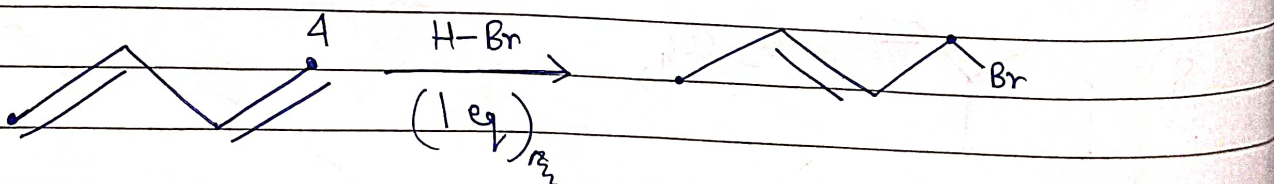
11) ☆



12)



☆ 13)



To reduce 1 double bond.

Rxns are of 2 types —

1) Thermodynamically Controlled — Product Stable

2) Kinetically controlled — Intermediate Stable

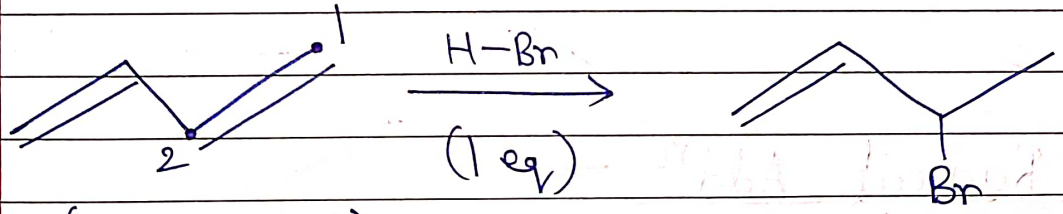
When (2) double bonds in Conjugation,

then Therm. Control ⇒ (1,4) addn

Kin. Control ⇒ (1,2) addn

(If nothing specified, assume Therm Control.)

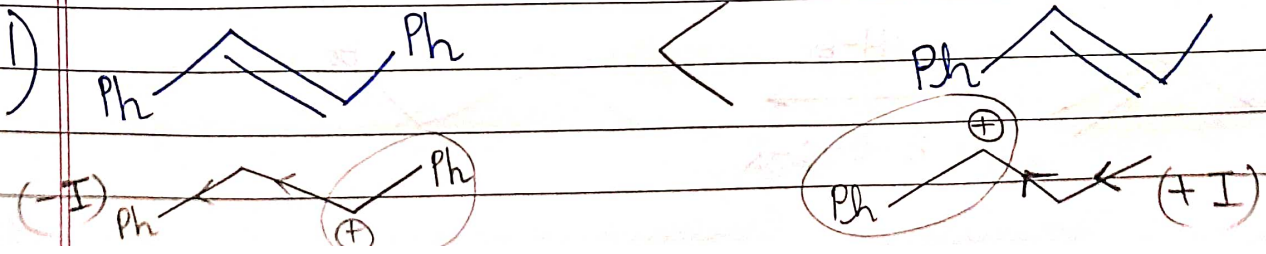
★ 14)



(Kin. Control)

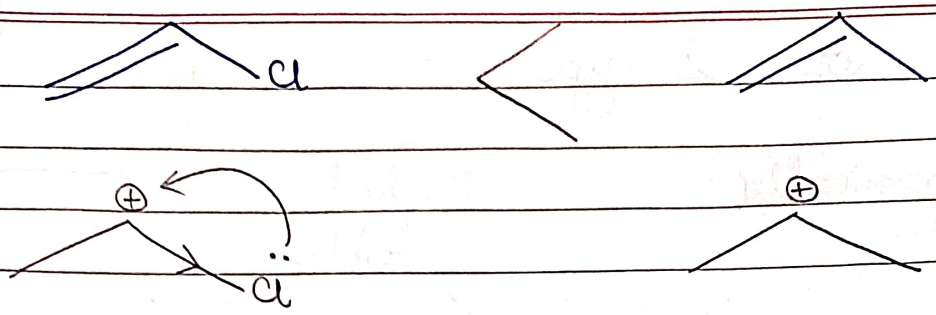
Q) Compare reactivity towards $E^{\oplus}$ addn —

1)



14

2)

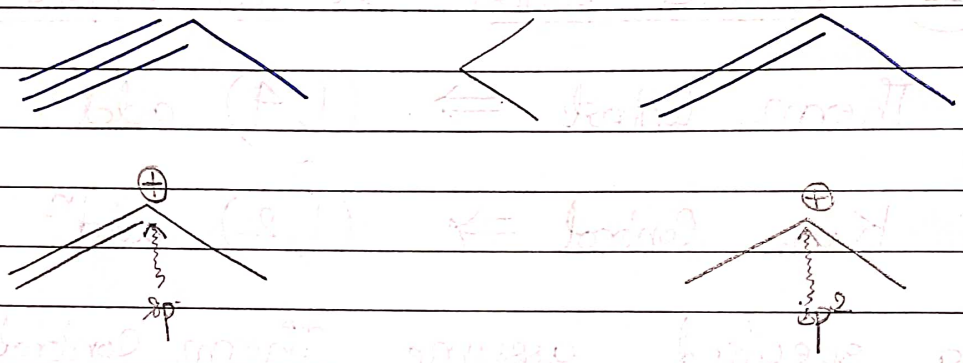


(+M, −I)

for halogens, −I stronger.

$6 \propto H$

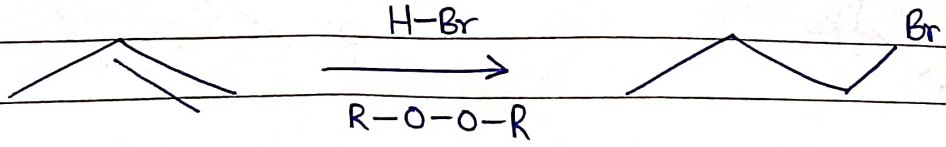
3)



2) Free Radical Addⁿ —

If HBr molecule added to assymmetrical alkene in presence of peroxide (R_2O_2), it generally gives Anti-Markonikov addⁿ of H & Br.

This is called Kharash effect.



Mechanism –

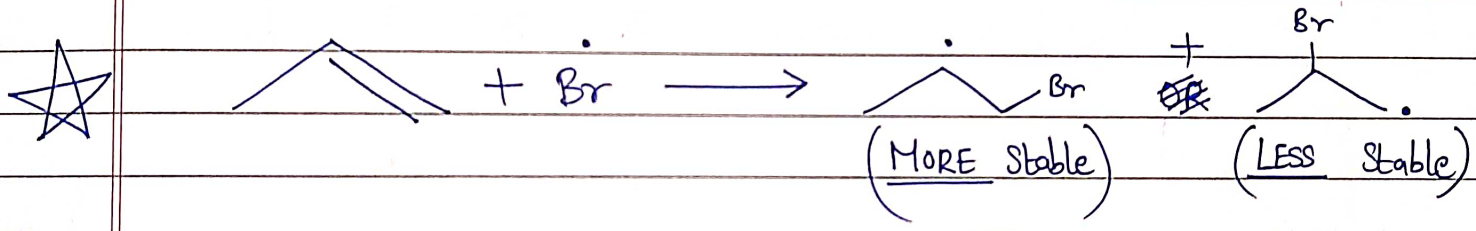
Step 1: Chain Initiation

$$R-\overset{\curvearrowleft}{O}-\overset{\curvearrowright}{O}-R \longrightarrow 2\ R-O\cdot$$

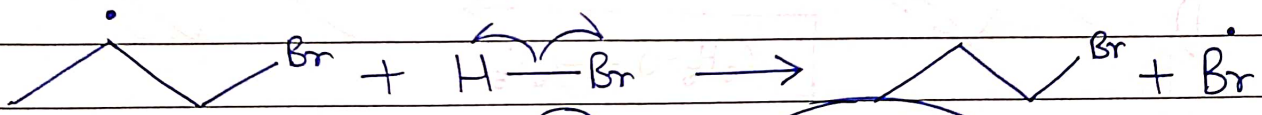
Step 2: Chain Propogation

$$R-O\cdot + H-Br \longrightarrow R-OH + \dot{B}r$$

In this step, ~~for (Br)~~ $\Rightarrow$ $\Delta H = (-ve)$ for all halogens.



In this step, for (Br) $\Rightarrow$ $\Delta H = (-ve)$

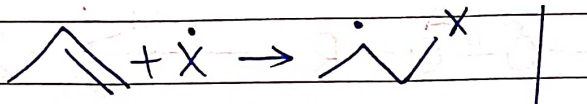
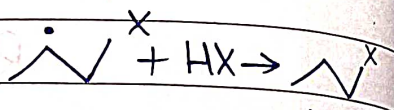


In this step also, for (Br) $\Rightarrow$ $\Delta H = (-ve)$

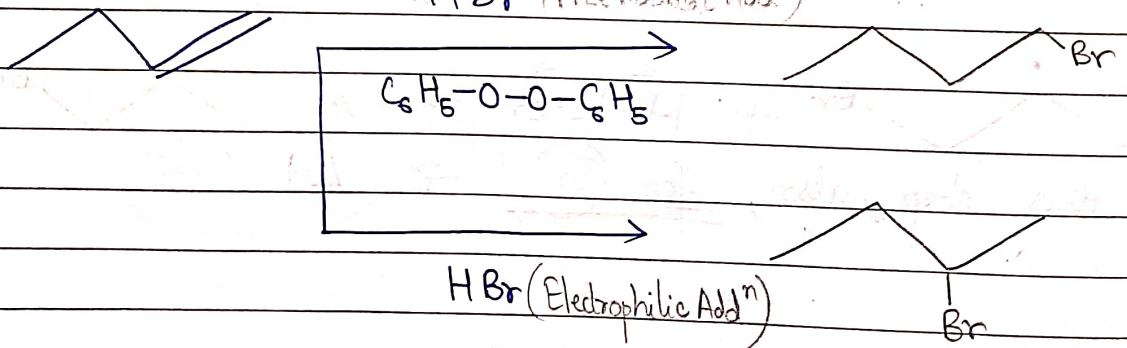
Step 3: Chain Termination

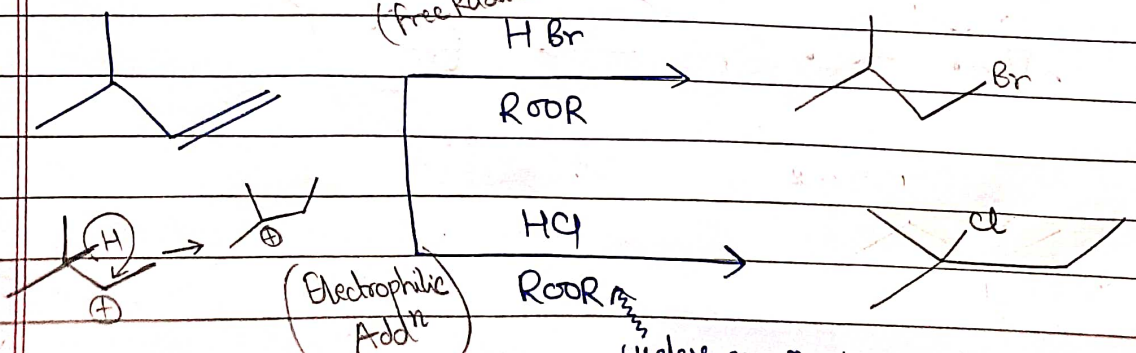
$$Br\cdot + \cdot Br \longrightarrow Br_2$$

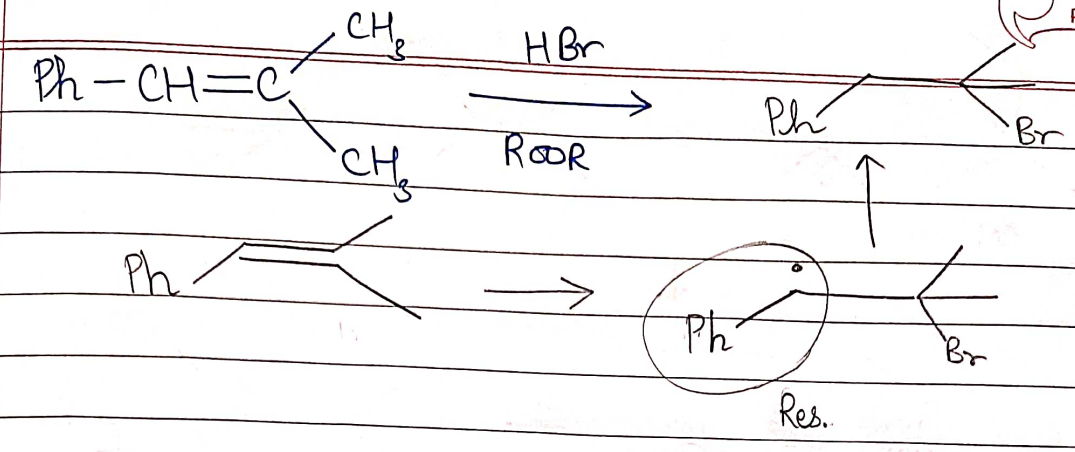
The occurance of this rx^n depends on energy involved in propogation step.

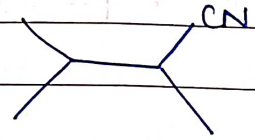
Rx^n	Reagent		
X	HCl	$\Delta H = (-ve)$	$\Delta H = (+ve)$
✓	HBr	$\Delta H = (-ve)$	$\Delta H = (-ve)$
X	HI	$\Delta H = (+ve)$	$\Delta H = (-ve)$

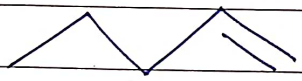
Q) Write major product —

1) 

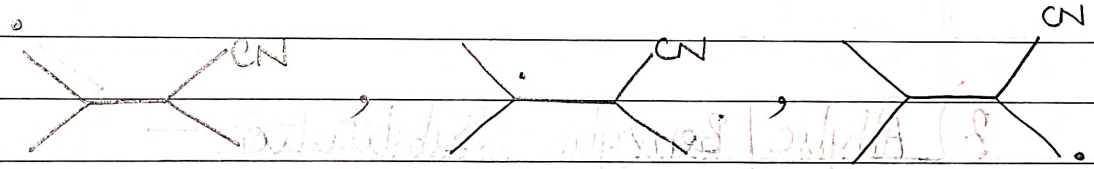
2) 

3) 

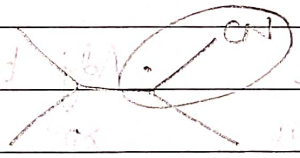
☆ 9) 

A +  → B

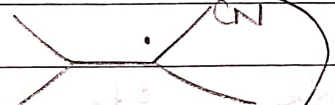
find A & B. (major products)

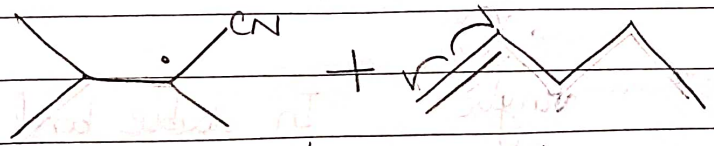
A) A = 

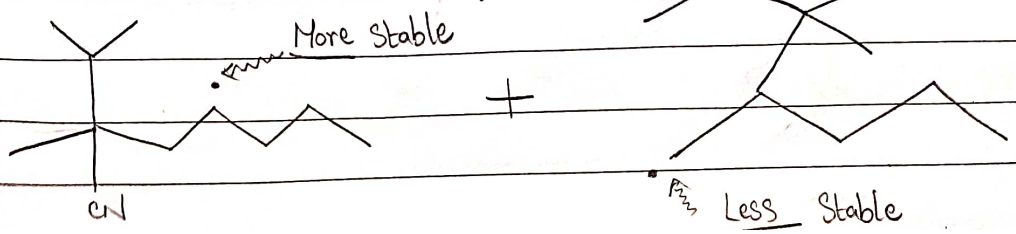
(Peroxide takes H with it.)

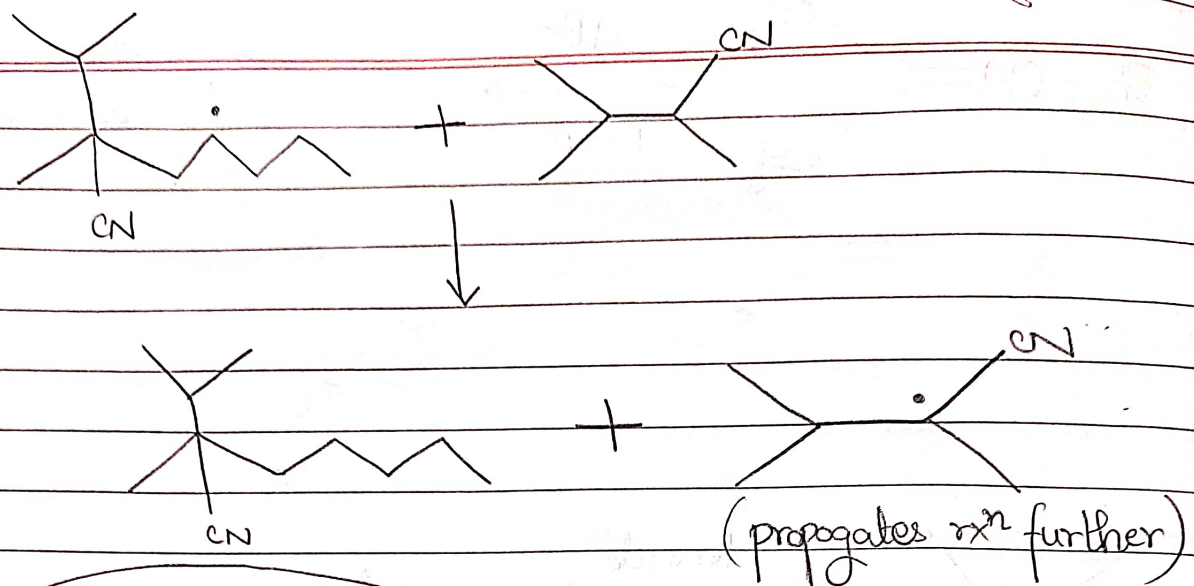
OR 

Res. (Most stable)

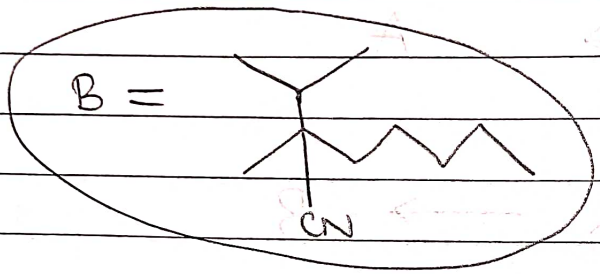
⇒ A = 

Now, 

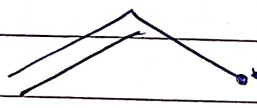




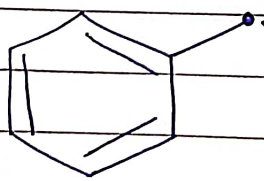
⇒ B =



3) Allylic / Benzylic Substitution —

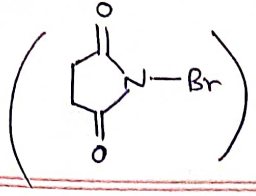


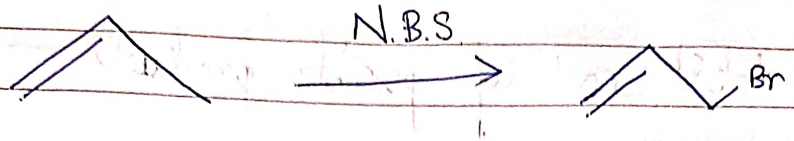
Adj. to double bond,
sp^3 C atom



Adj. to ~~Base~~ benzene,
sp^3 C atom

In double bond,
sp^2 C atom

N-bromosuccinamide 

Eg: 

☆ NBS is best reagent for this substitution, as it produces Low g/y of Br_2.

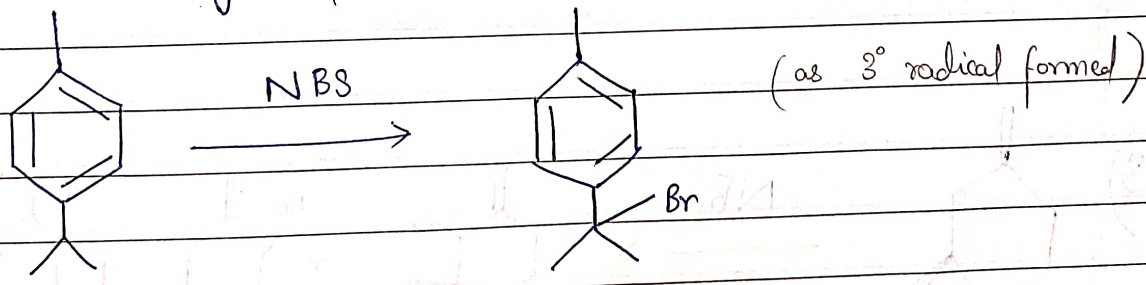
If conc. of Br_2 is High, then E⊖ add^n rx^n happens

With NBS, yield of E⊖ add^n is very low & yield of substitution is very high.

The rx^n follows Free Radical Substitution Mechanism.

Other reagents : $Br_2/h\nu$, SO_2X_2, ...

Q) Write major product –

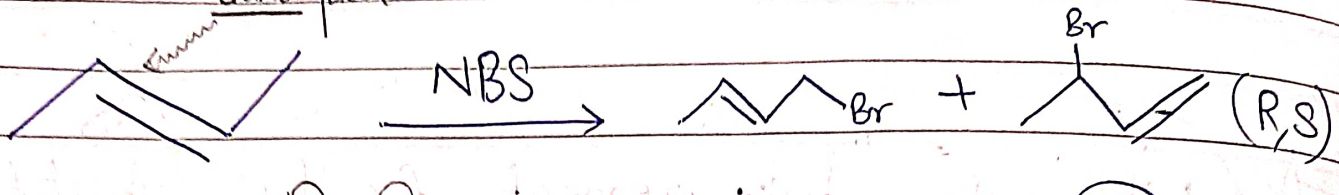
1) 

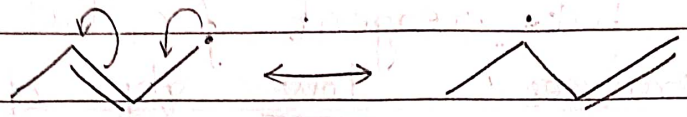
(as 3° radical formed)

☆ When nothing specified, think of monosubstitution. That too at post. where radical is most stable.

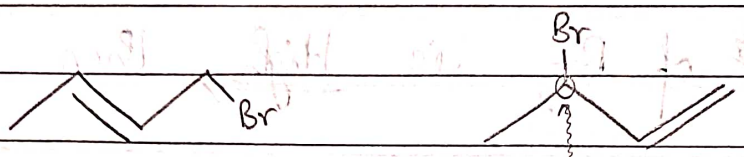
Q) find total no. of possible products —

trans fixed

1) 

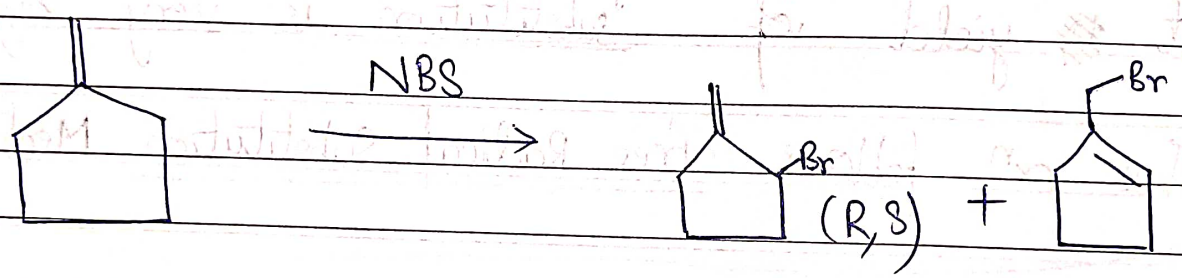
Radical : 

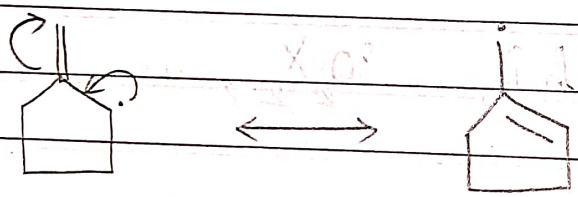
3



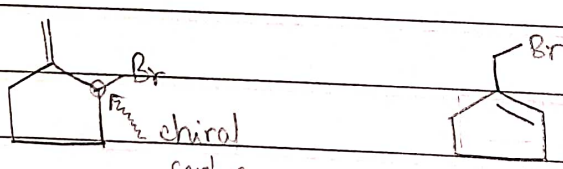
No chiral centre

chiral centre

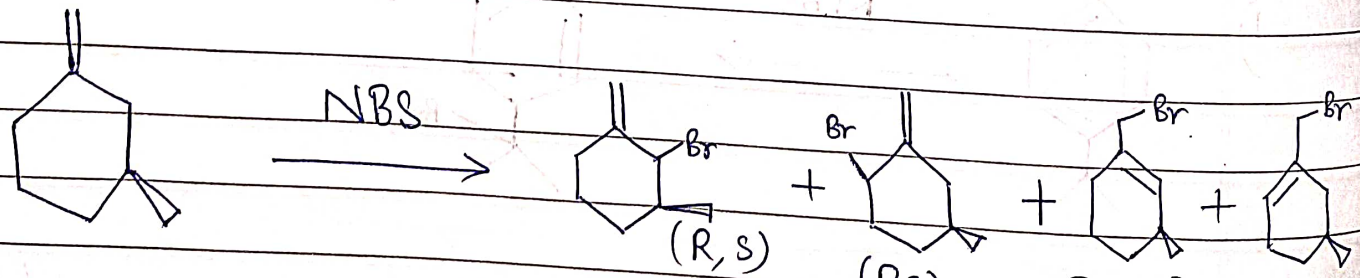
2) 

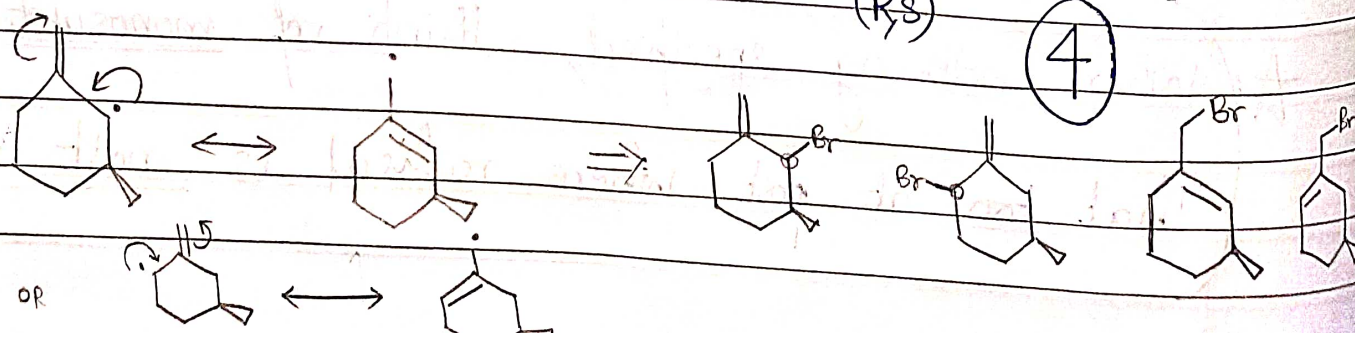


3

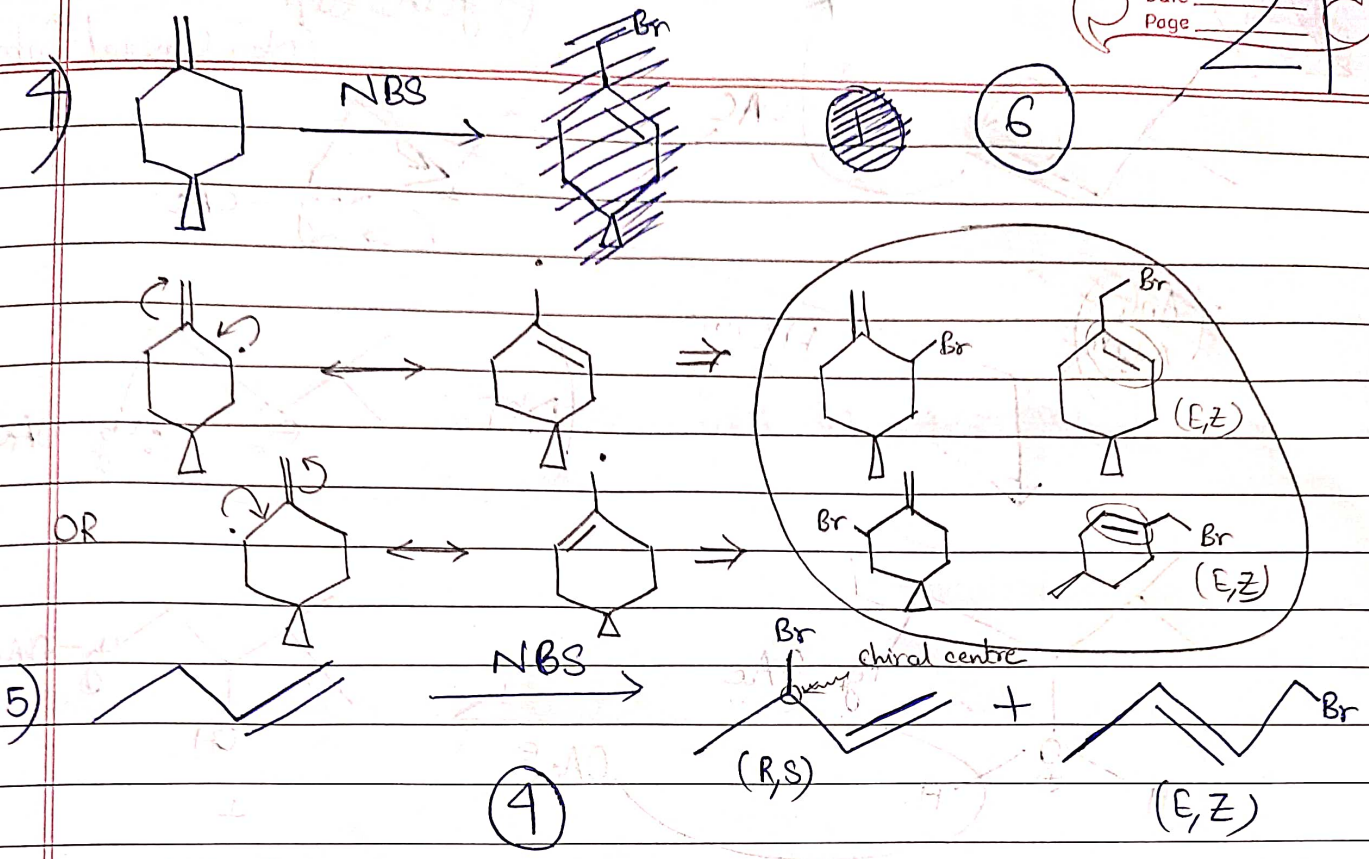


No chiral centre

3) 



4



4) Oxymercuration — Demercuration Rxn —

Oxymercuration

1) $Hg(OAc)_2$, THF, H_2O

To generate Electrophile — Solvent — Nucleophile

Demercuration

2) $NaBH_4$, OH^-

$AcO^- \equiv CH_3-\overset{\overset{O}{\|}}{C}-O^-$

Acetate

THF = Tetrahydrofuran

This is an E⊕ Addn rxn.

Step 1: $Hg(OAc)_2 \xrightarrow{H_2O} [Hg(OAc)]^{\oplus} + OAc^{\ominus}$

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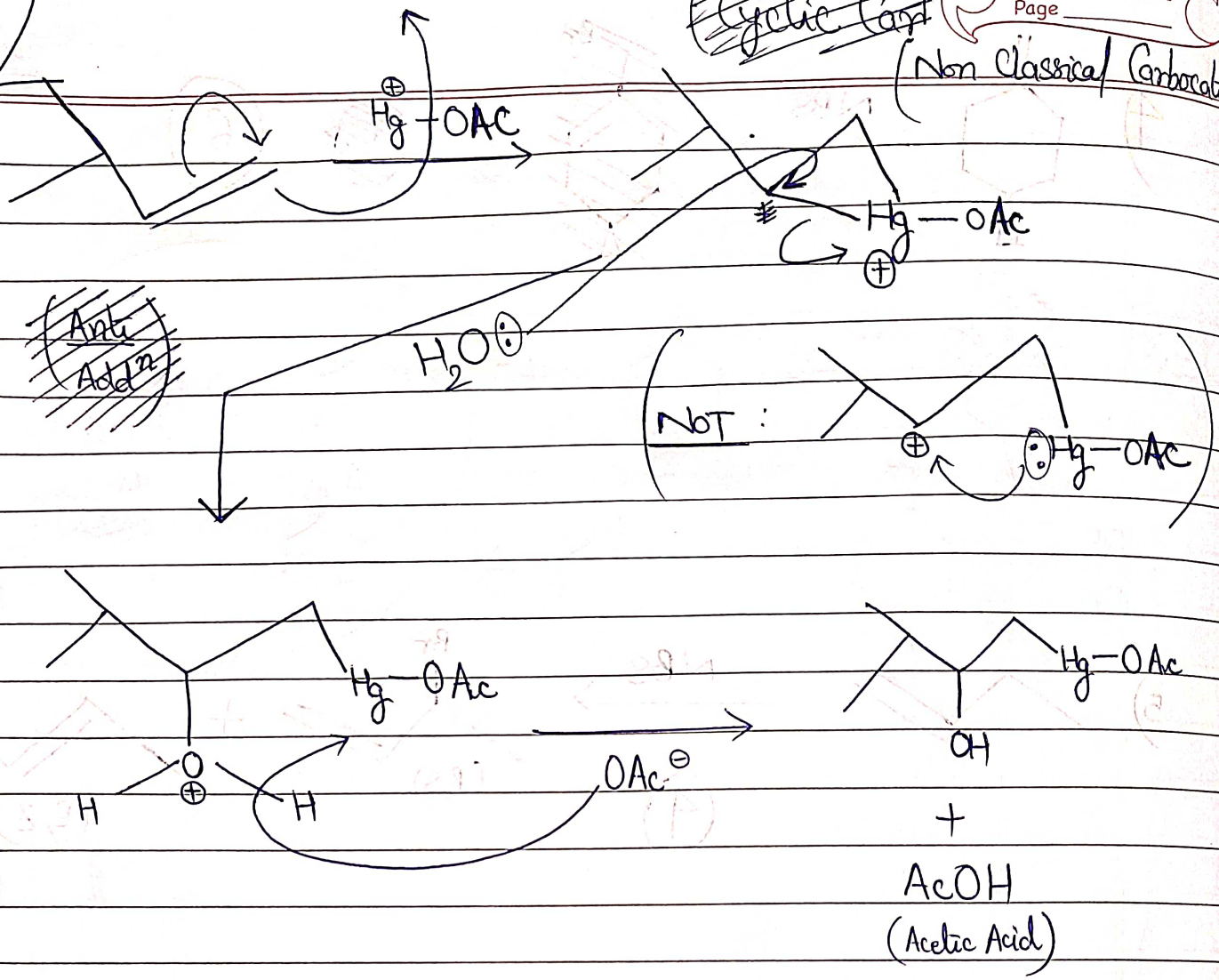
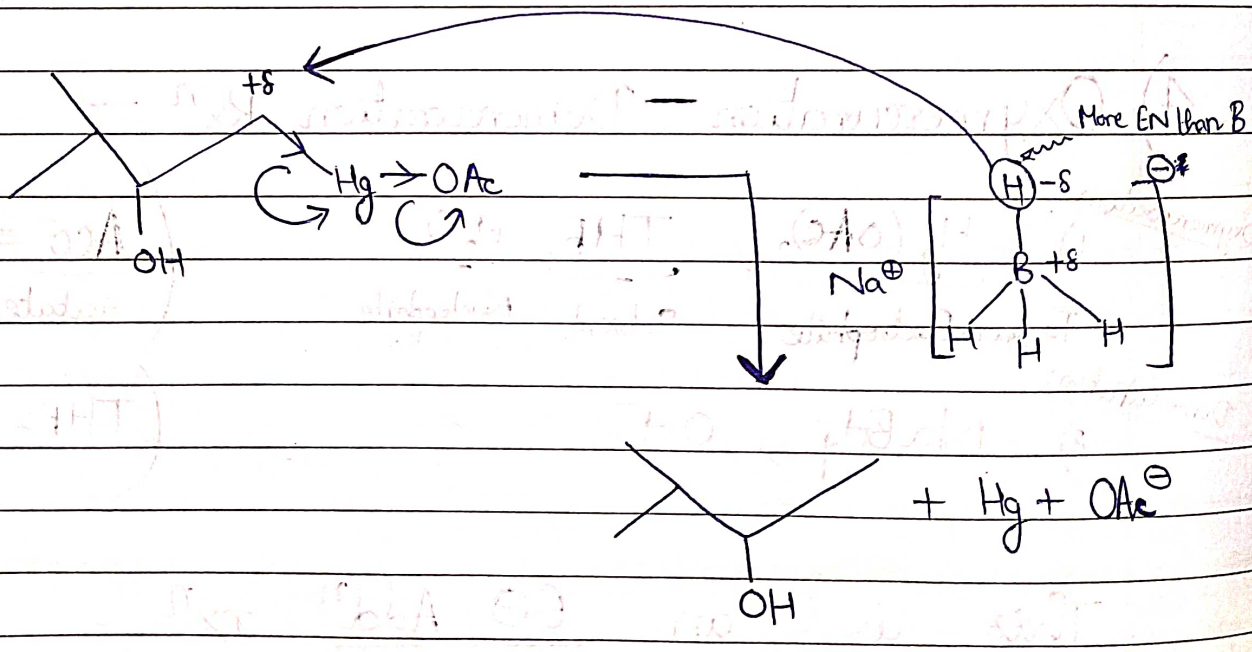
~~Cyclic Cat~~ (Non Classical Carbocation)



Step 2:



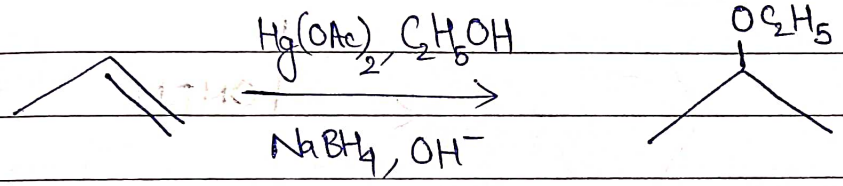
4.1) All this was to ensure Markonikov addn of H_2O across double bond.

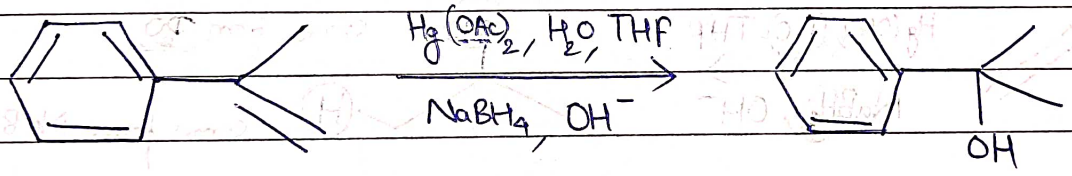
4.2) Here, H_2O is NOT special. We can use ANY electrophile of the form H—(Rest)

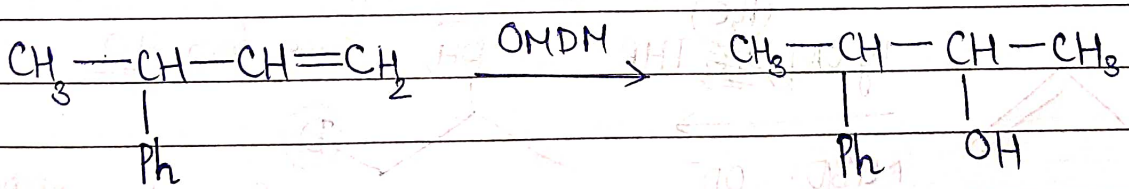
Eg- C_2H_5OH, NH_3, H_2SO_4, ...

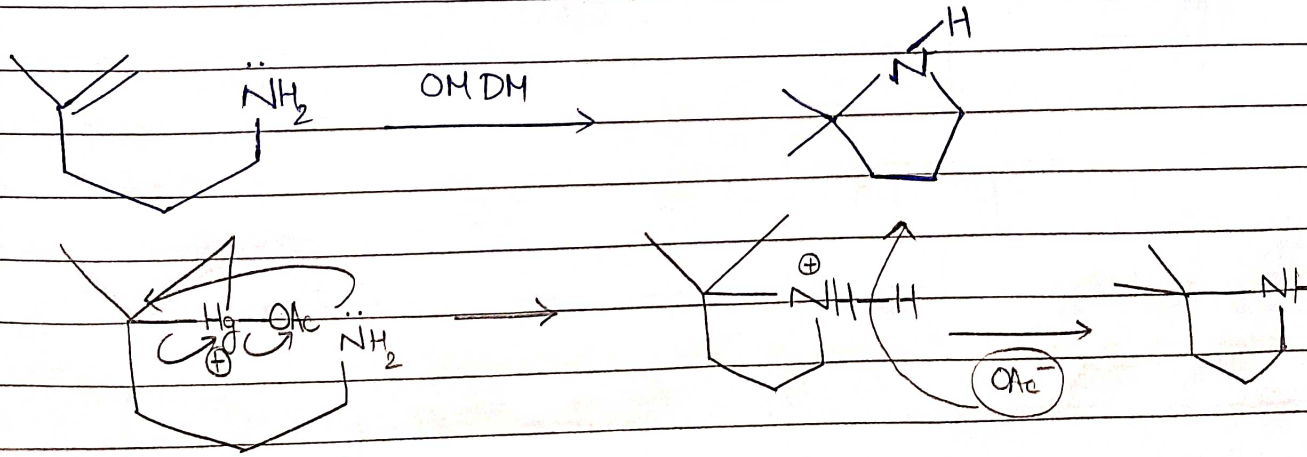
4.3) Just add across double bond in accordance with Markonikov Rule.

Q) Write major product

1) 

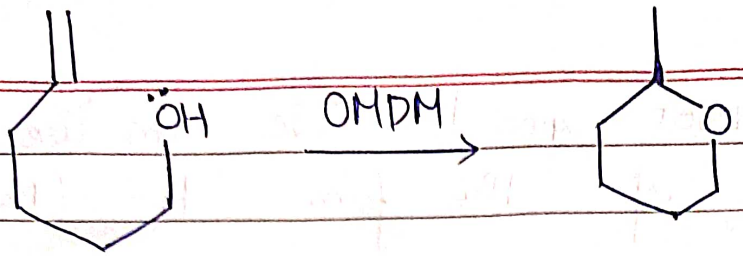
2) 

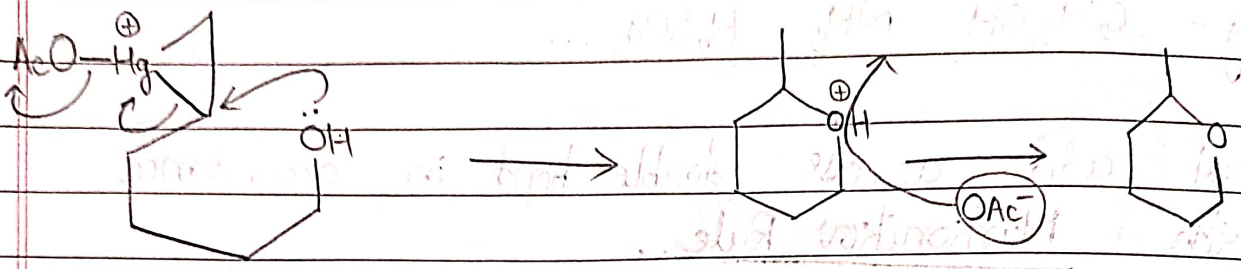
3) 

4) 

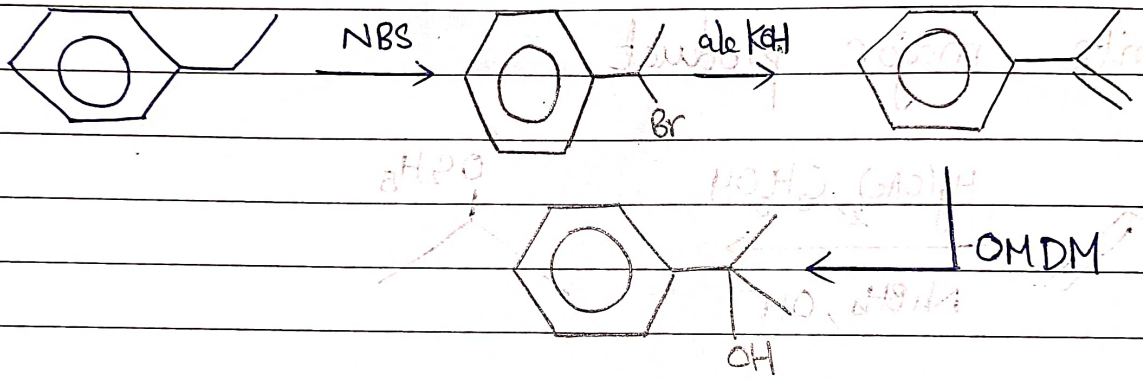
24

5)

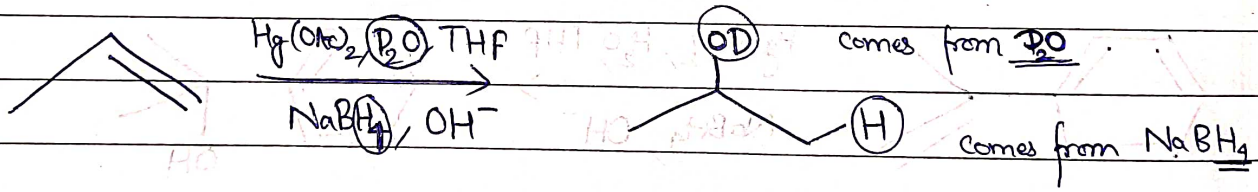




6)



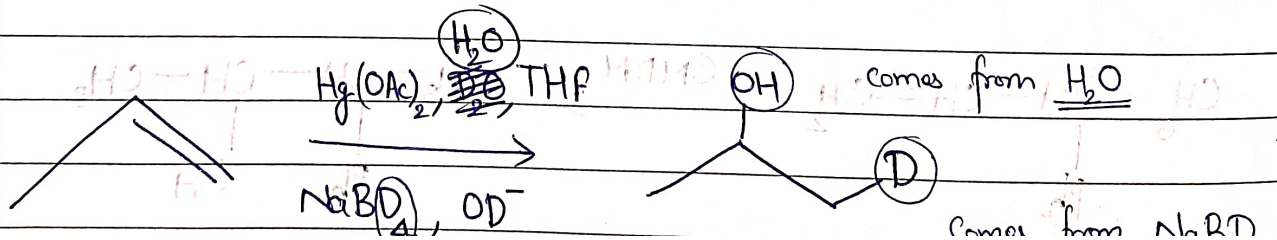
☆ 7)



comes from D_2O

comes from $NaBH_4$

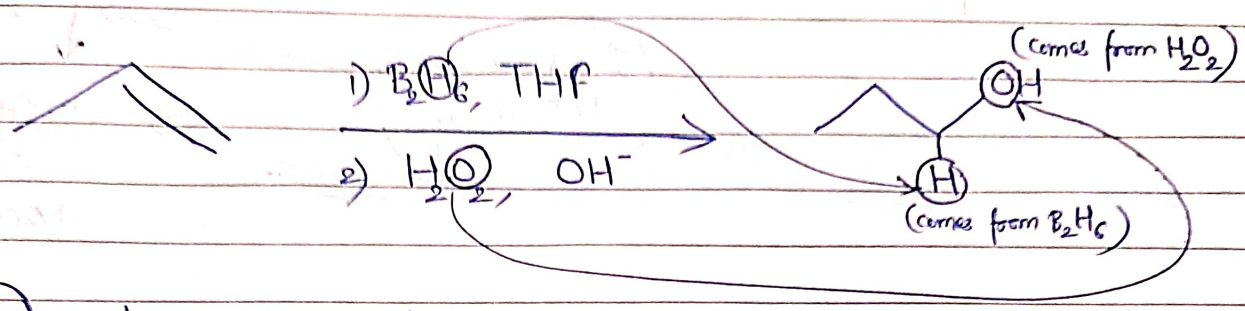
☆ 8)



comes from H_2O

comes from NaBD

5) Hydroboration - Oxidation —



(H) wahan, jahan Steric Hinderance JYADA.

(OH^-) wahan, jahan Steric Hinderance KAM.

Hydroboration

Step I : $CH_3-CH=CH_2$ + $H-BH_2$ ($-\delta$, $+\delta$) → $CH_3-CH\cdots CH_2$ with $H\cdots BH_2$

↓

$\{\phi = CH_3-CH_2-CH_2-\}$ $\phi-BH_2 \equiv$ $CH_3-CH_2-CH_2$ with BH_2

Again, $CH_3-CH=CH_2$ + $H-BH\phi$ ($-\delta$, $+\delta$) → $CH_3-CH\cdots CH_2$ with $H\cdots BH\phi$

↓

$BH(\phi)_2 \equiv$ $CH_3-CH_2-CH_2$ with $BH\phi$

finally, repeating above gives $B(\phi)_3$ ⟵ ~~Tertiary~~ Alkyl Borar
Tri

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Oxidation

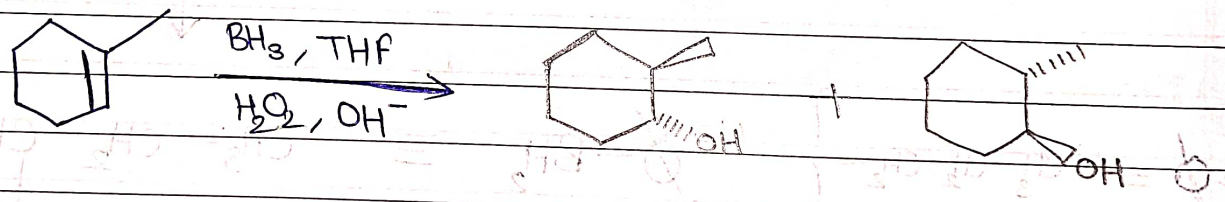
Step 2: $\phi_3B \equiv (CH_3-CH_2-CH_2)_3B$ $\xrightarrow{H_2O_2,\ OH^-}$ $3(CH_3-CH_2-CH_2-OH) + H_3BO_3$

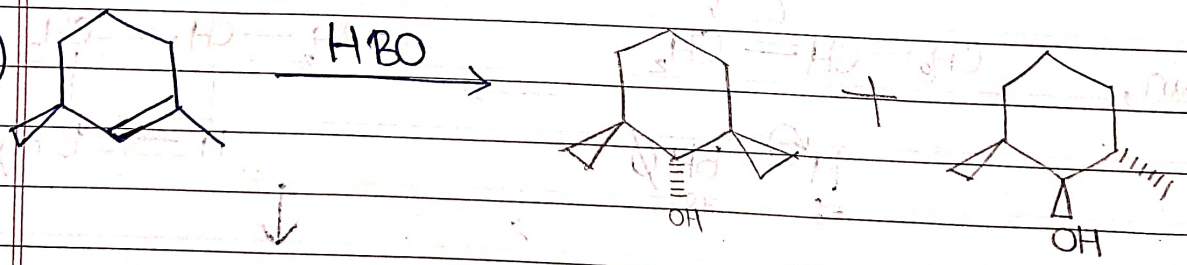
(This happens in a LOT of steps)

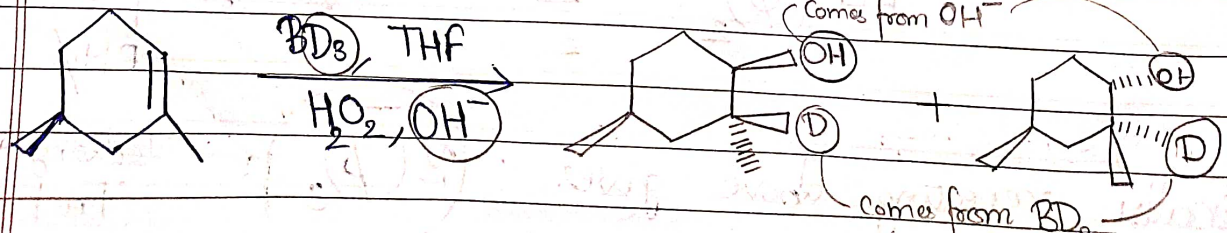
In this whole rxn carbocation is NOT formed ⇒ No rearrangement.

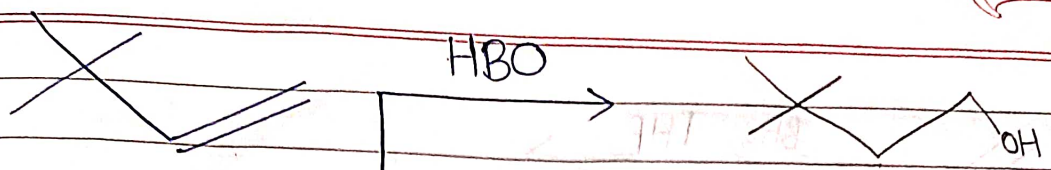
Also, it is (Syn) add^n.

Q) Write major product —

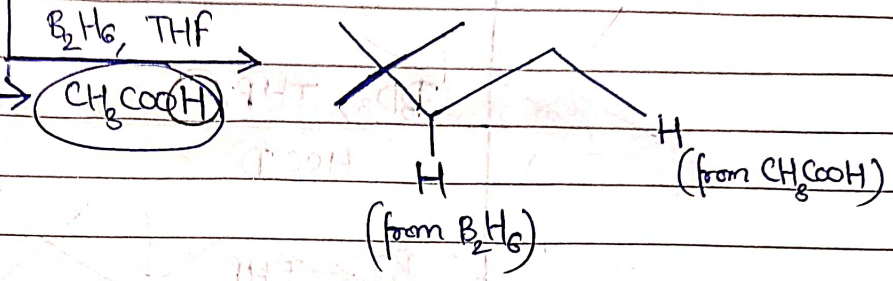
1) 

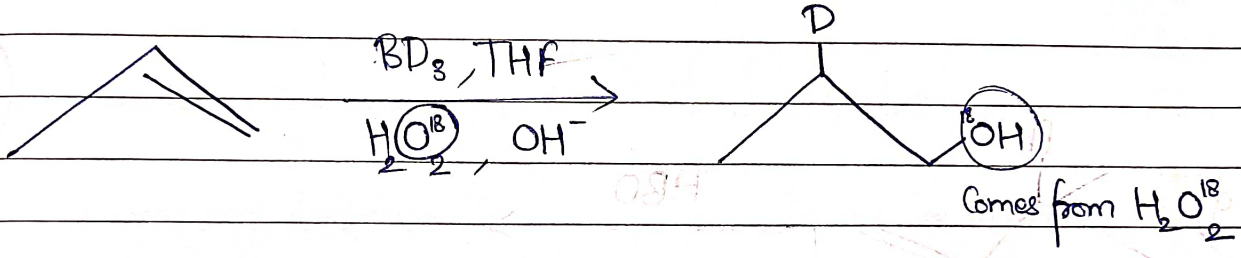
2) 

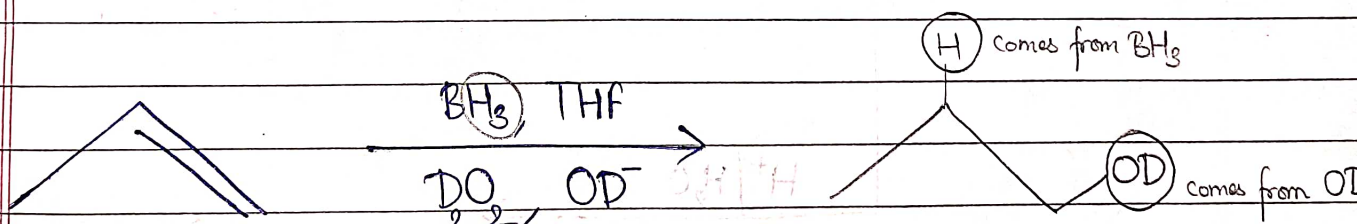
3) 

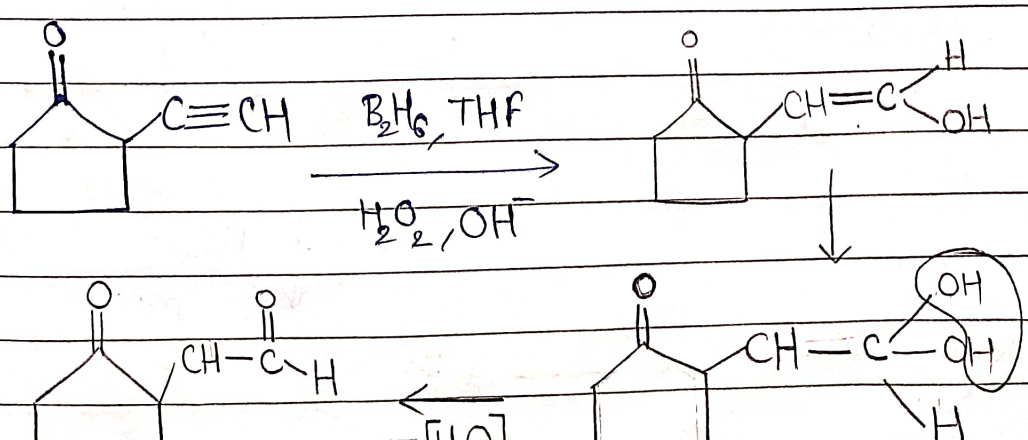
4) 

★ Instead of OH, H will attach as CH_3COOH can liberate H



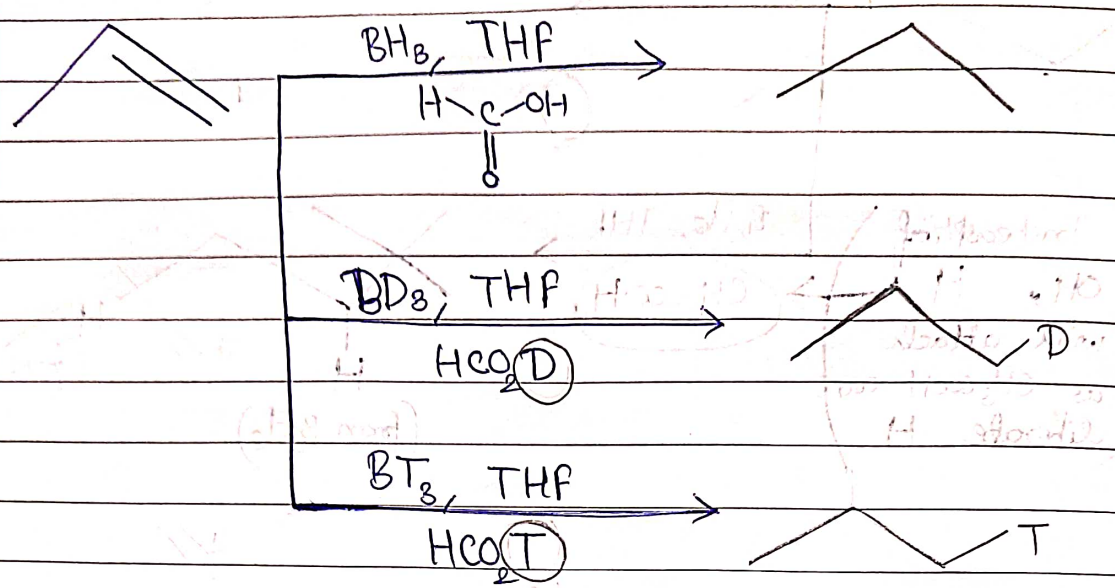
5) 

6) 

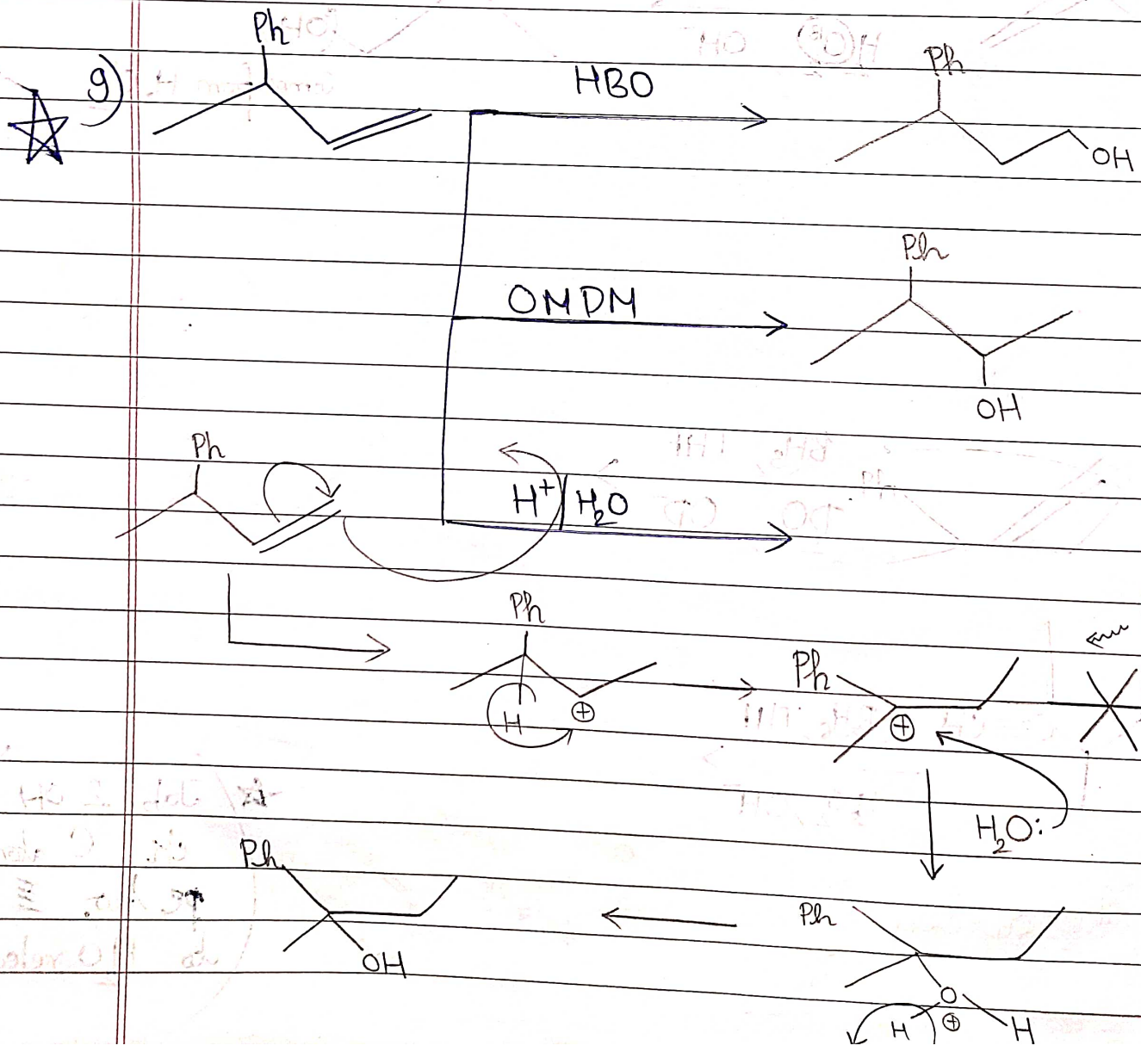
7) 

★ Jab 2 OH ek C ab pe ho, ≡ to H_2O relea

8)


BH3, THF
H-C(=O)-OH
BD3, THF
HCO2D
BT3, THF
HCO2T
D
T

9)


Ph
HBO
OH
OMDM
OH
H+ / H2O
OH⁻ is bad leaving grp.
H2O:
OH

6) Ozonolysis —

Ozonolysis

Reductive

O_3, H_2O

Zn or $(CH_3)_2S$

Possible Products :

Aldehyde, Ketone, CO_2

Oxidative

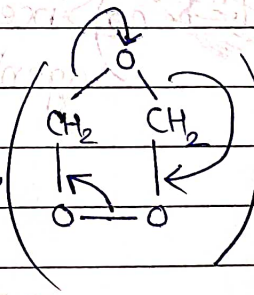
O_3, H_2O

(Nothing) or Ag_2S

Possible Products :

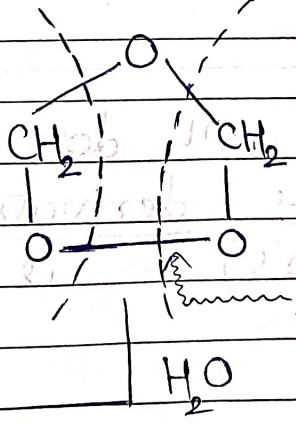
Ketone, Carboxylic Acid, CO_2

$CH_2 = CH_2 \xrightarrow[Zn]{O_3,\ H_2O} 2\ HCHO$



Mechanism :

$CH_2 = CH_2 \xrightarrow{O_3}$

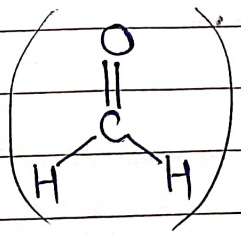


(Ozonide)

bhari repulsion

H_2O

H_2O_2 + 2



Oxd^n Agent

6.1) If Aldehydes are present, they will oxidise to Carboxylic Acid, unless Zn or $(CH_3)_2S$ is present.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

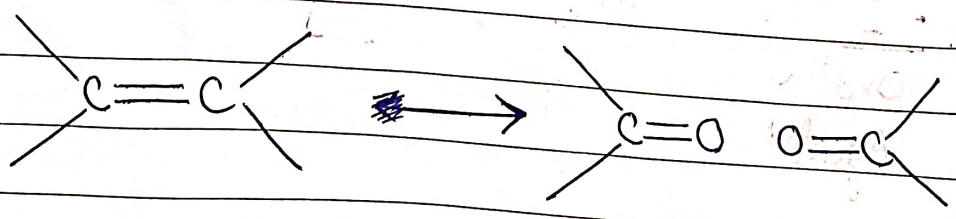
$$2H_2O_2 + 2e^- \longrightarrow 2H_2O + 2OH^-$$

$$Zn + 2H_2O_2 \longrightarrow Zn(OH)_2 + 2H_2O$$

6.2) Since H_2O_2 formed was mild oxd^n agent, Ketones are NOT oxidised!

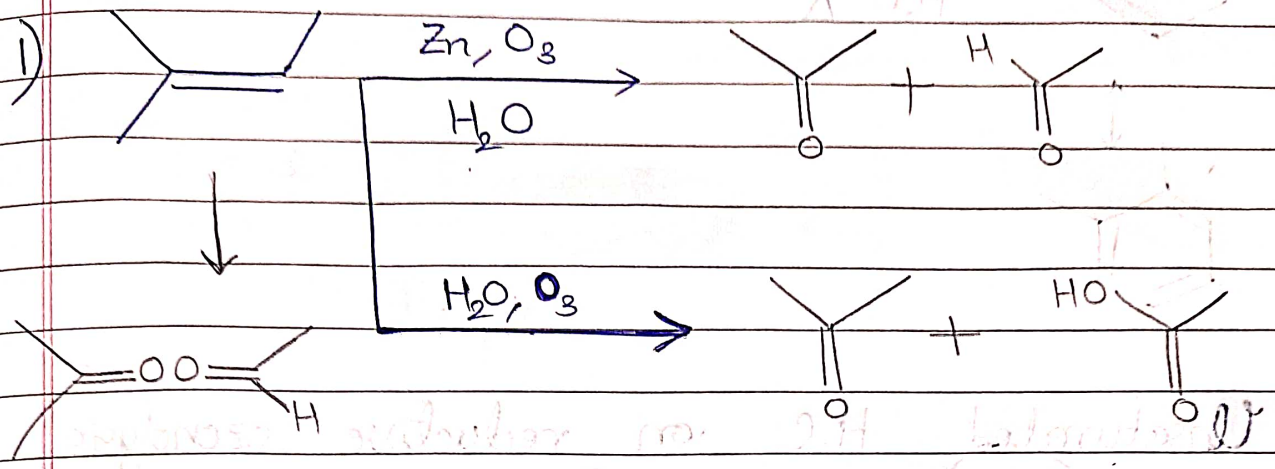
★ If rx^n done with Benzene or its derivatives, then high temp. (> 50°C) is req.

★ Trick:

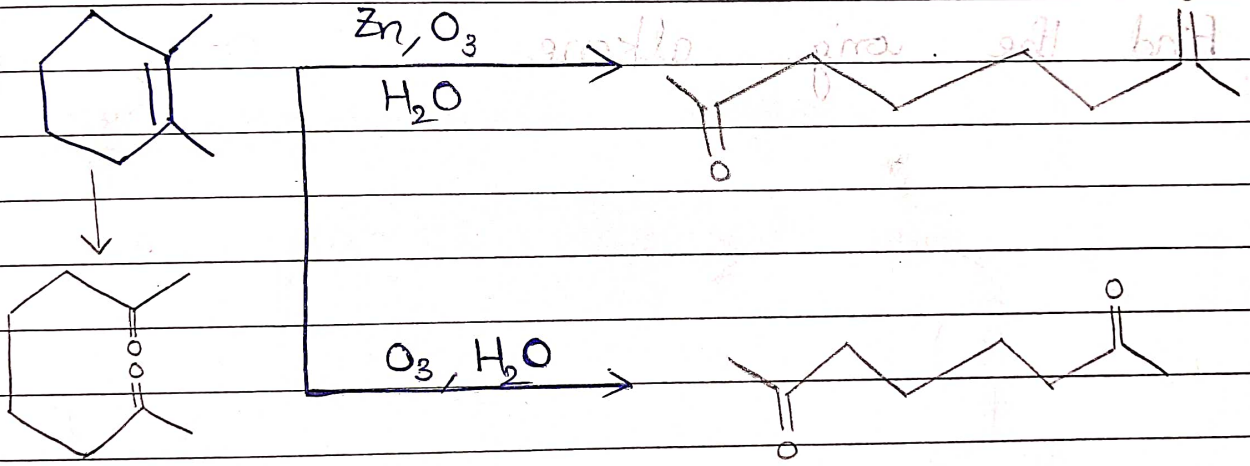


Q) Write major products —

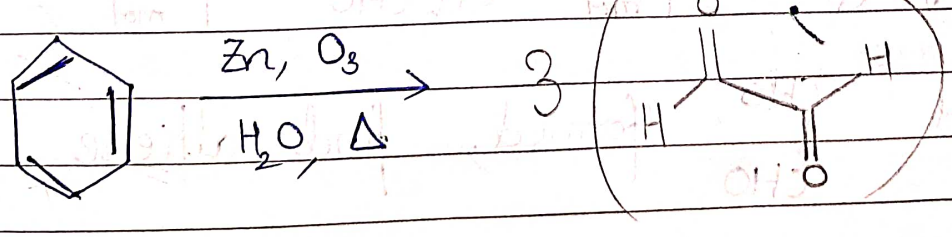
1)

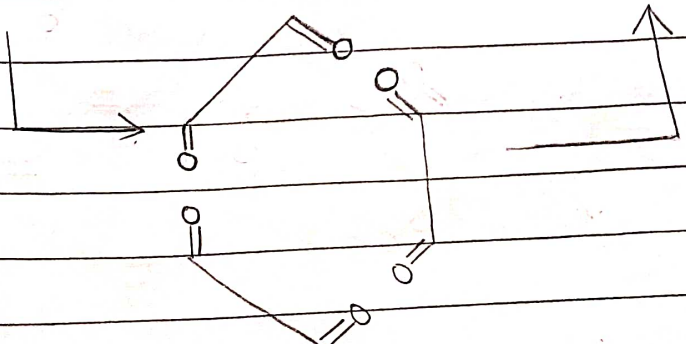


2)

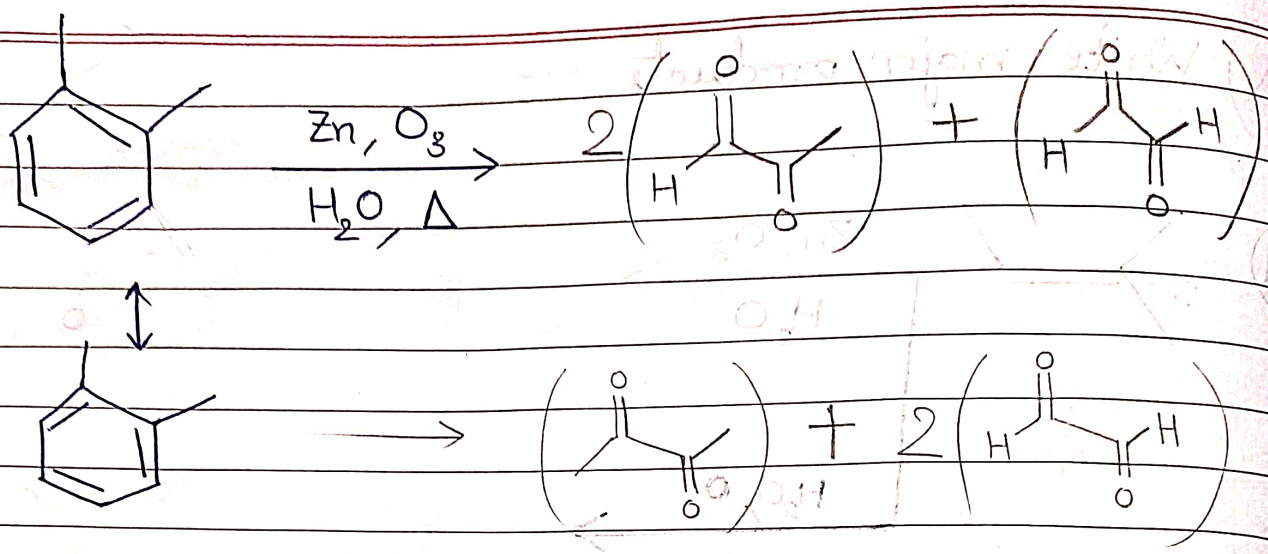


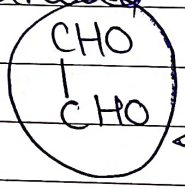
3)





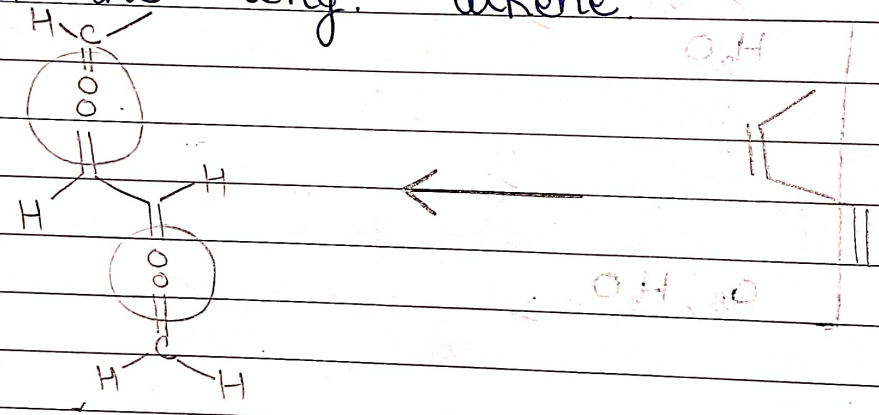
32

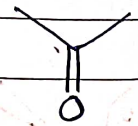
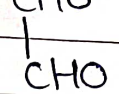
★ 4) 

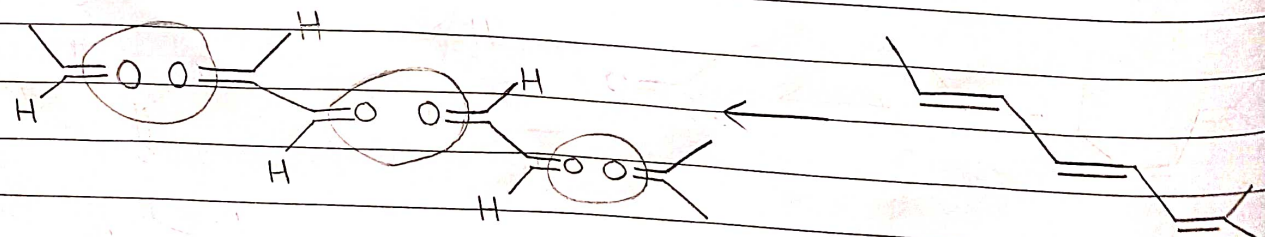
Q) Unsaturated H.C on reductive ozonolysis gives  , HCHO & CH_3CHO.

Glyoxyl

Find the orig. alkene.

A) 

Q) If in prev. Q, 1 mol CH_3CHO, 1 mol  & 2 mol  formed, find alkene...

A) 

7) Rxn with $KMnO_4$ —

7.1) Dil. Cold $KMnO_4$ (Baeyer's Reagent) — (≈ 1% conc., alkaline)

Color = Purple

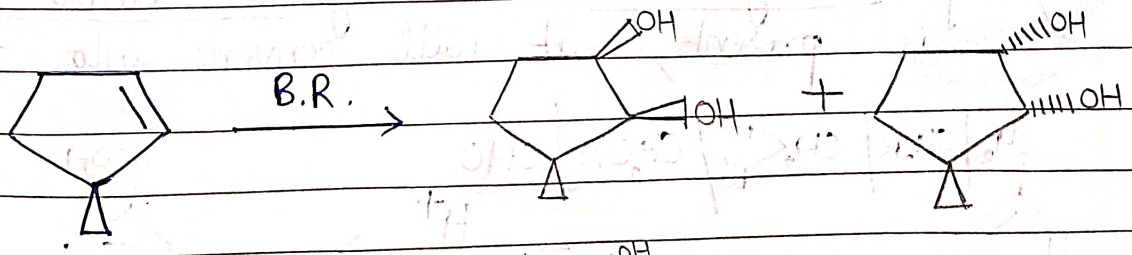
$$CH_2=CH_2 \xrightarrow{B.R.} \underset{\substack{| \\ OH}}{\overset{\substack{| \\ OH}}{CH_2-CH_2}} + MnO_2$$

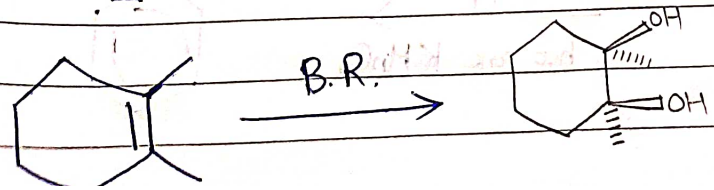
7.1.1) Syn Hydroxylation happens.
(Same side OH lag jata hai)

7.1.2) It is a Redox rxn.

7.1.3) OsO_4 in alkaline sol^n can also be used.

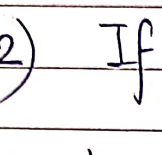
7.1.4) Test for Unsaturated H.C. (Purple → Colorless)

Q) 1) 

2) 

7.2) ~~CO~~ Hot Conc. $KMnO_4$ —

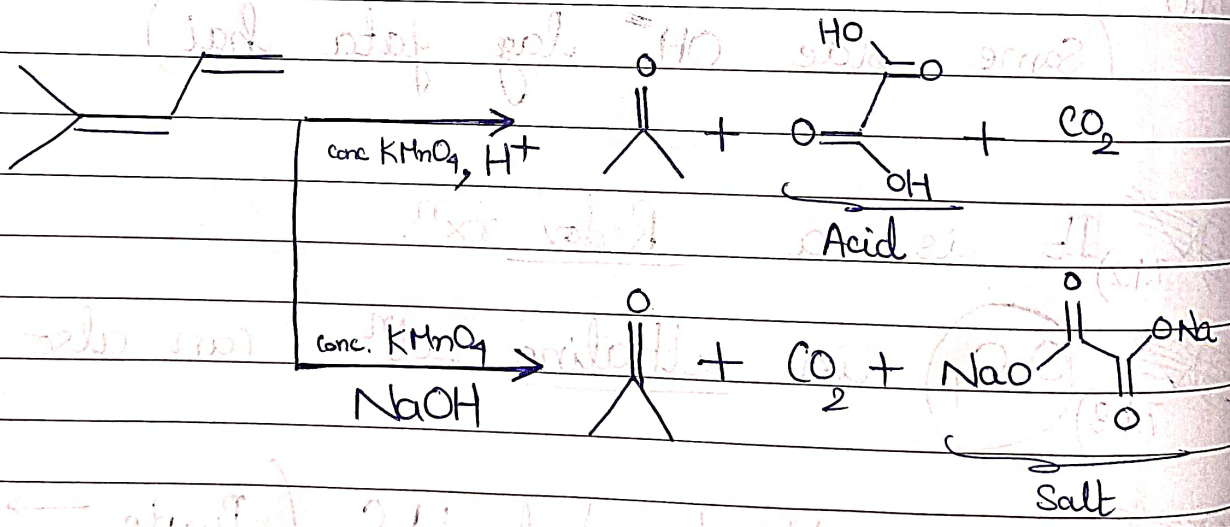
7.2.1) Products similar to Oxidative ozonolysis.

7.2.2) If  (formic acid) is formed, it will further oxidise to CO_2.

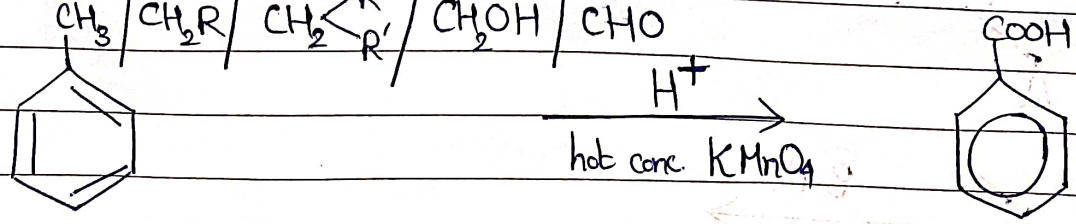
7.2.3) Benzene remains unaffected (and its derivatives)

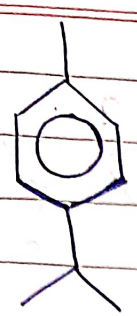
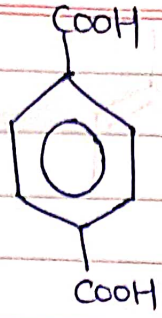
7.2.4) In basic medium, if carboxylic acid produced, it will react to give salt.

Eg:

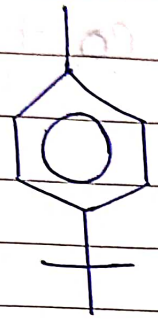
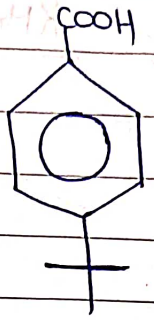


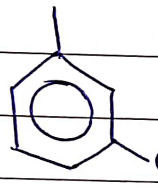
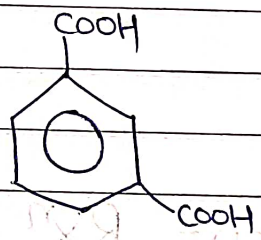
7.2.5) If benzylic C containing at least 1 H is present, it will convert into —COOH.

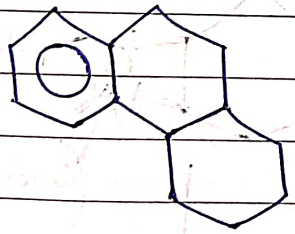
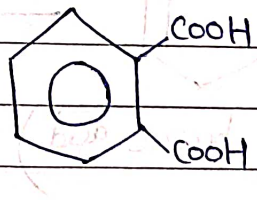


Q: 1)  $\xrightarrow[\Delta]{KMnO_4,\ H^+}$ 

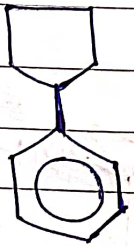
(Terephthalic Acid)

2)  $\xrightarrow[\Delta]{KMnO_4,\ H^+}$ 

3)  $\xrightarrow[\Delta]{KMnO_4,\ H^+}$ 

4)  $\xrightarrow[\Delta]{KMnO_4,\ H^+}$ 

(Phthalic Acid)

5)  $\xrightarrow[\Delta]{KMnO_4,\ H^+}$ 

(Benzoic Acid)

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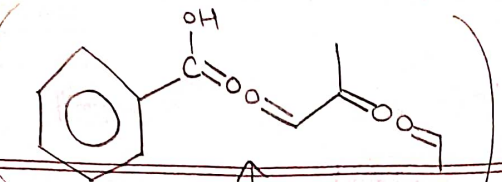
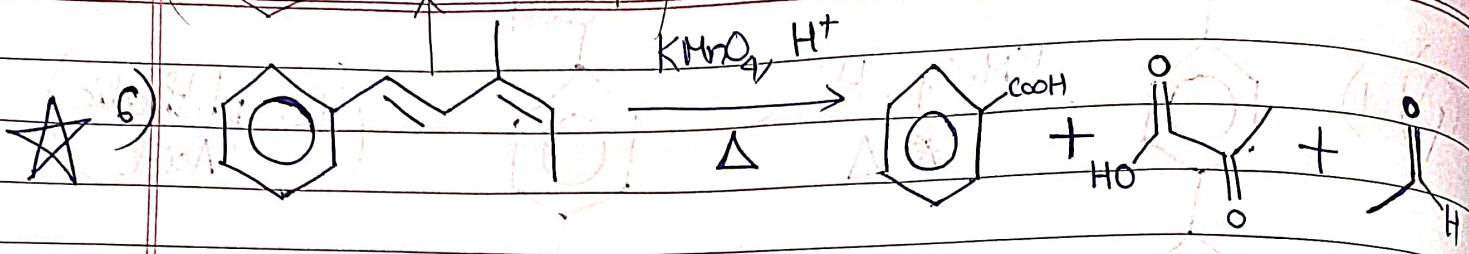
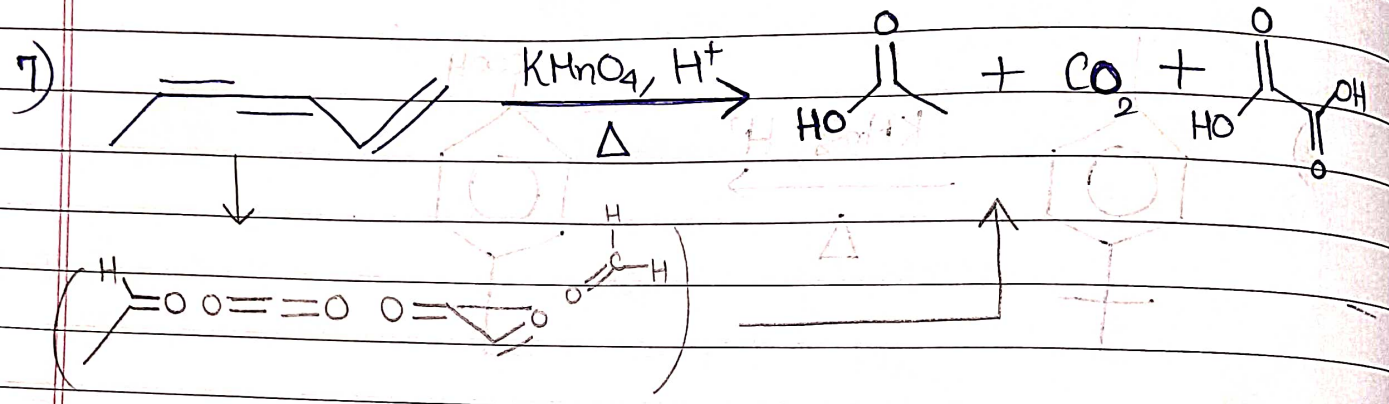
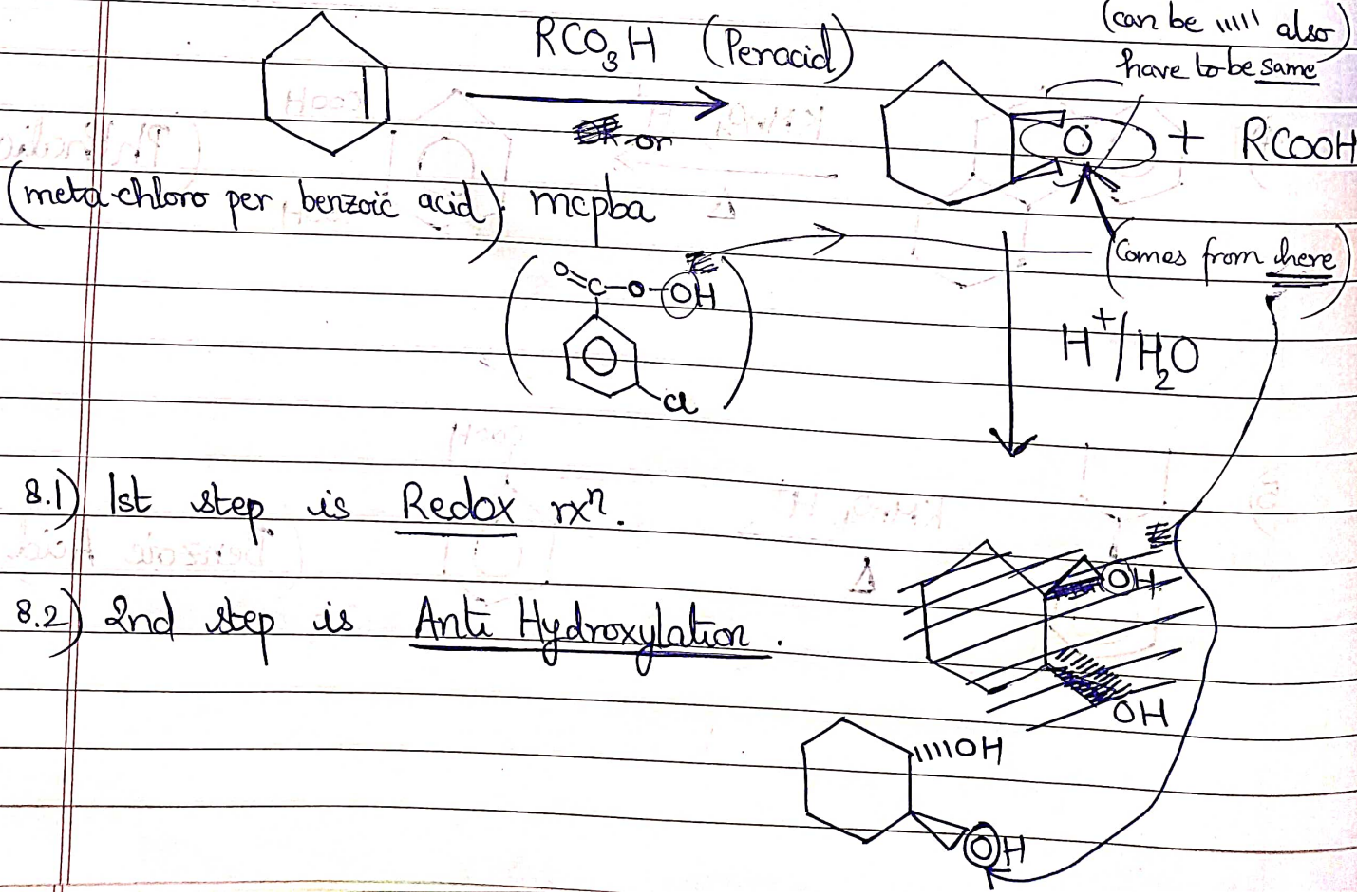






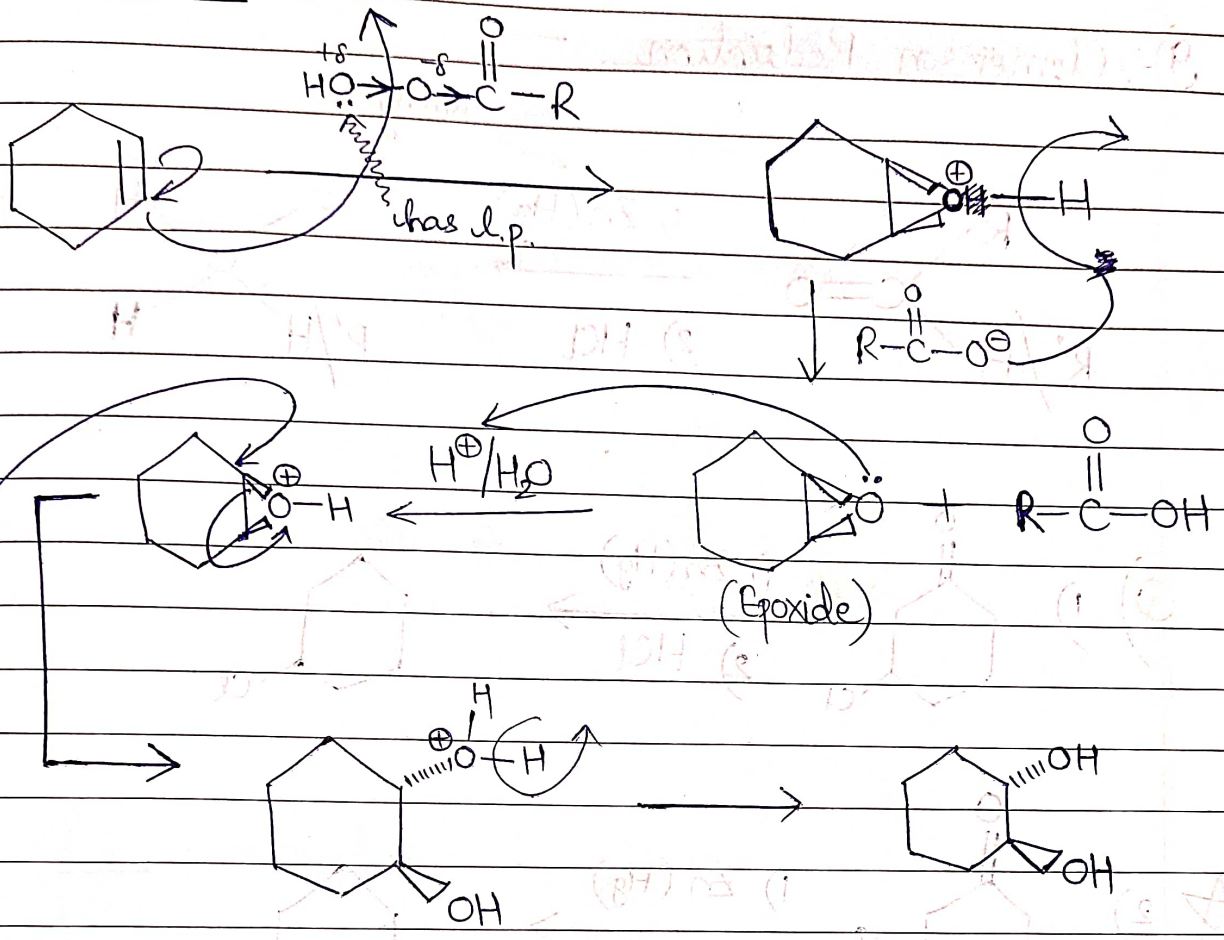
8) Prilischeiv Rxn —

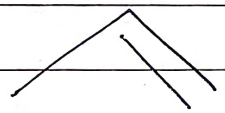


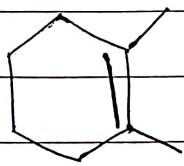
8.1) 1st step is Redox rxn.

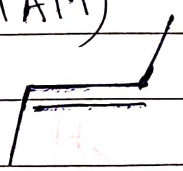
8.2) 2nd step is Anti Hydroxylation.

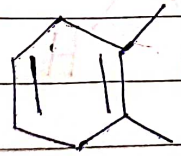
Mechanism —



1) ≡ 
mcpba
H^+/H_2O
Diasteromer

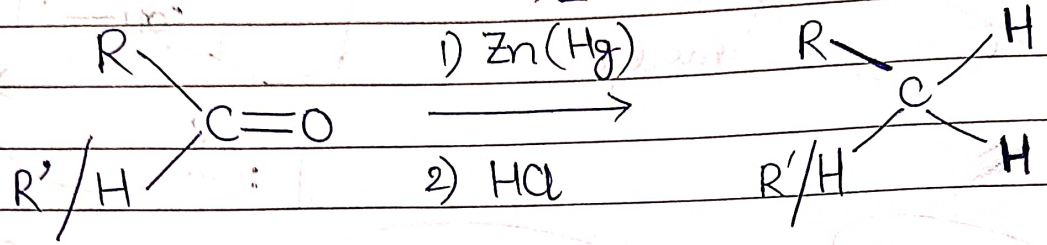
2) 
mcpba
H^+/H_2O
Racemic Mix.

3) (TAM) 
mcpba
H^+/H_2O
Meso.

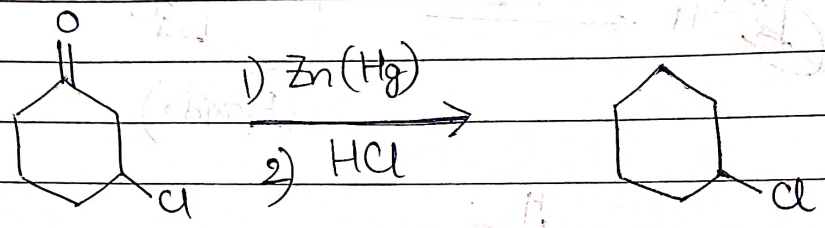
4) 
mcpba; H^+/H_2O
(1 eq.)

(as right side // is MORE nucleophilic. as more $\bar{e}$ density due to hyperconj. due to $-CH_3$

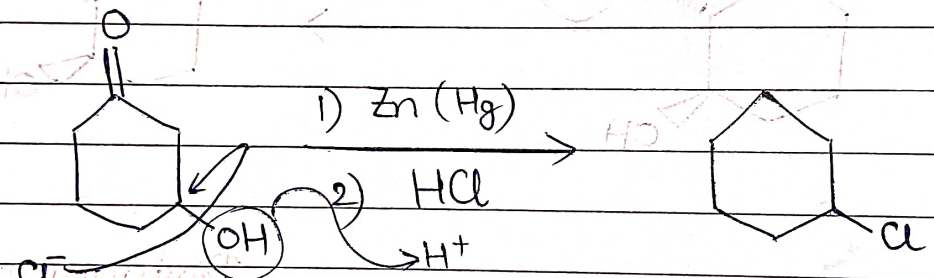
9) Clemenson Reduction —



Q) 1)

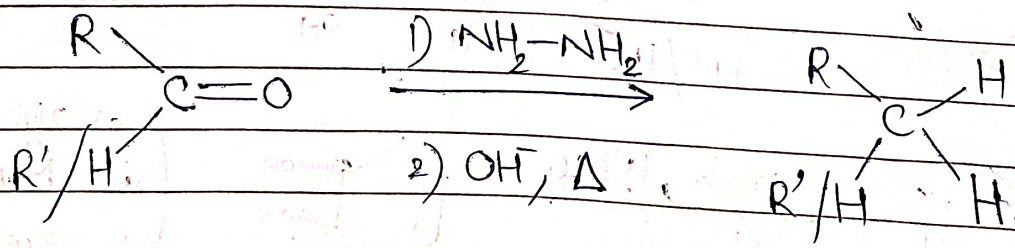


★ 2)

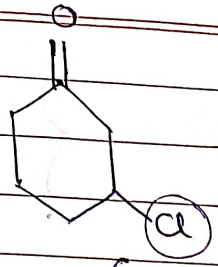


(Since good leaving grp., react with HCl)

10) Wolf-Kishner Reduction —

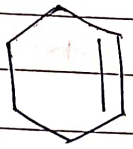


Q) 1)



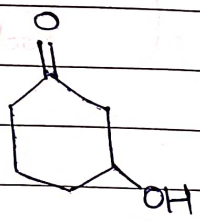
1) NH_2-NH_2

2) OH^-, Δ



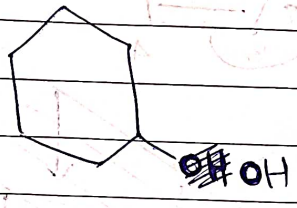
(E_2 elimination (as in alkyl halide) happens)

2)



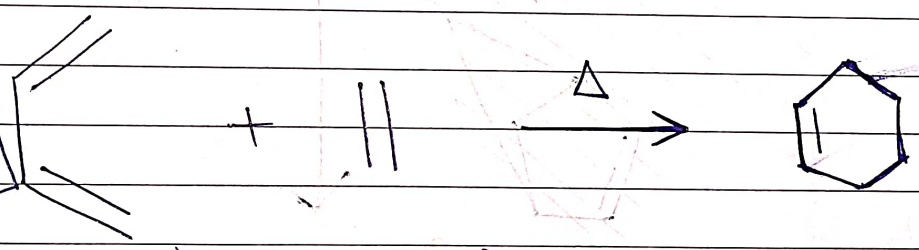
1) NH_2-NH_2

2) ~~OH^-~~, Δ



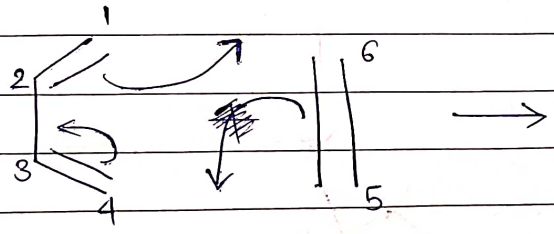
II) Diel's Alder Rxn —

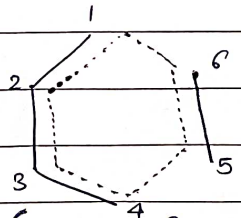
☆ ~~Aromatic~~ H.C. do NOT show this rxn!



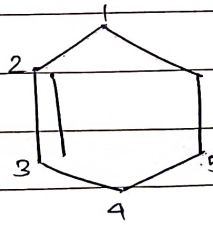
(conj. diene of cisoid form) (alkene)

Mechanism —

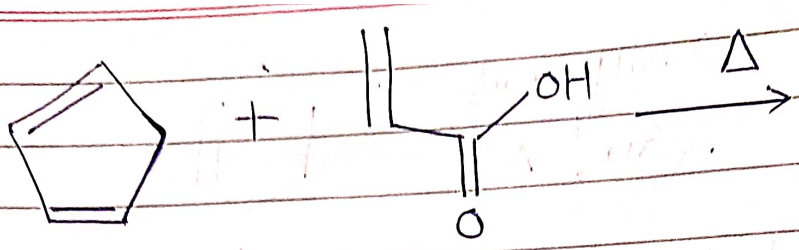




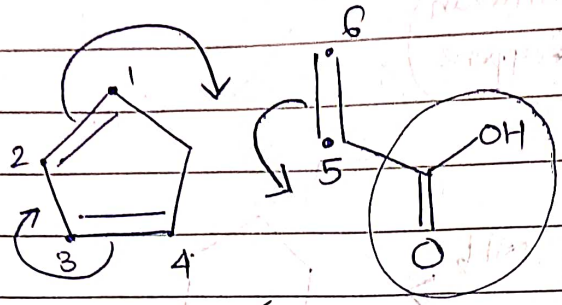
(Stable 6 membered cyclic transition state)



Q)

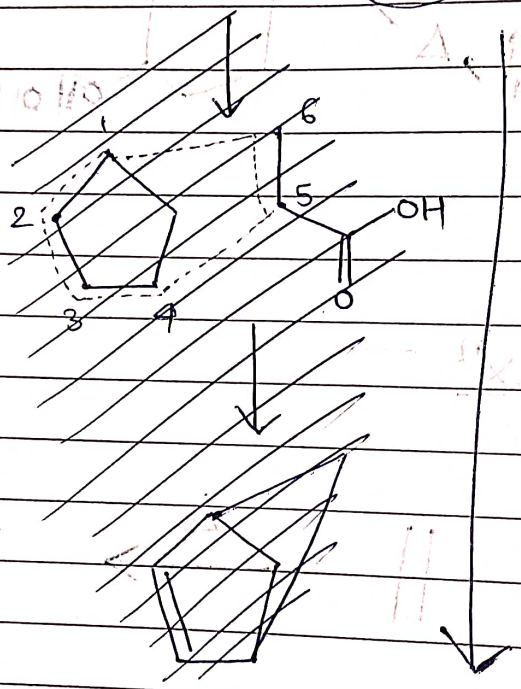


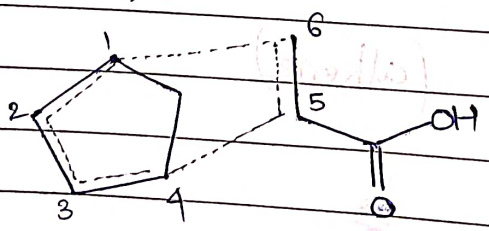
A)

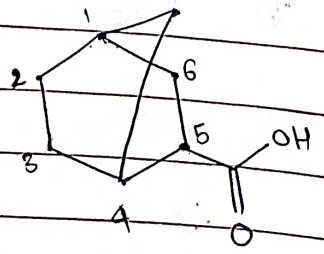


(-M) effect

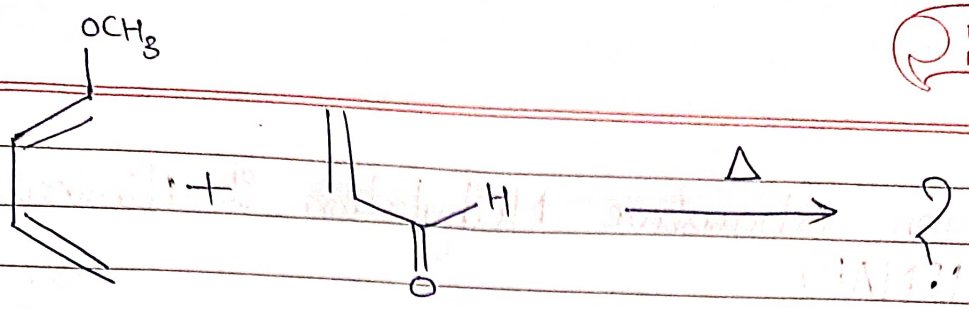
(To bond isk baaf tootega!)



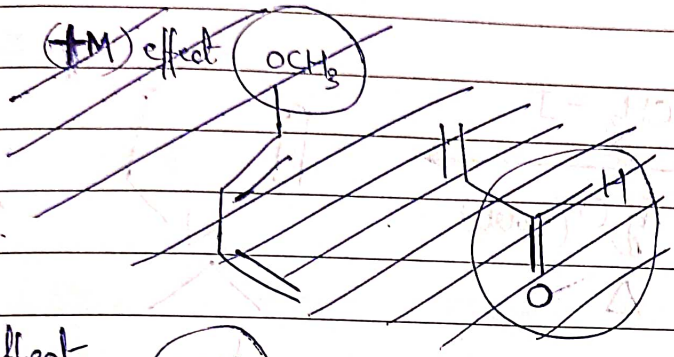




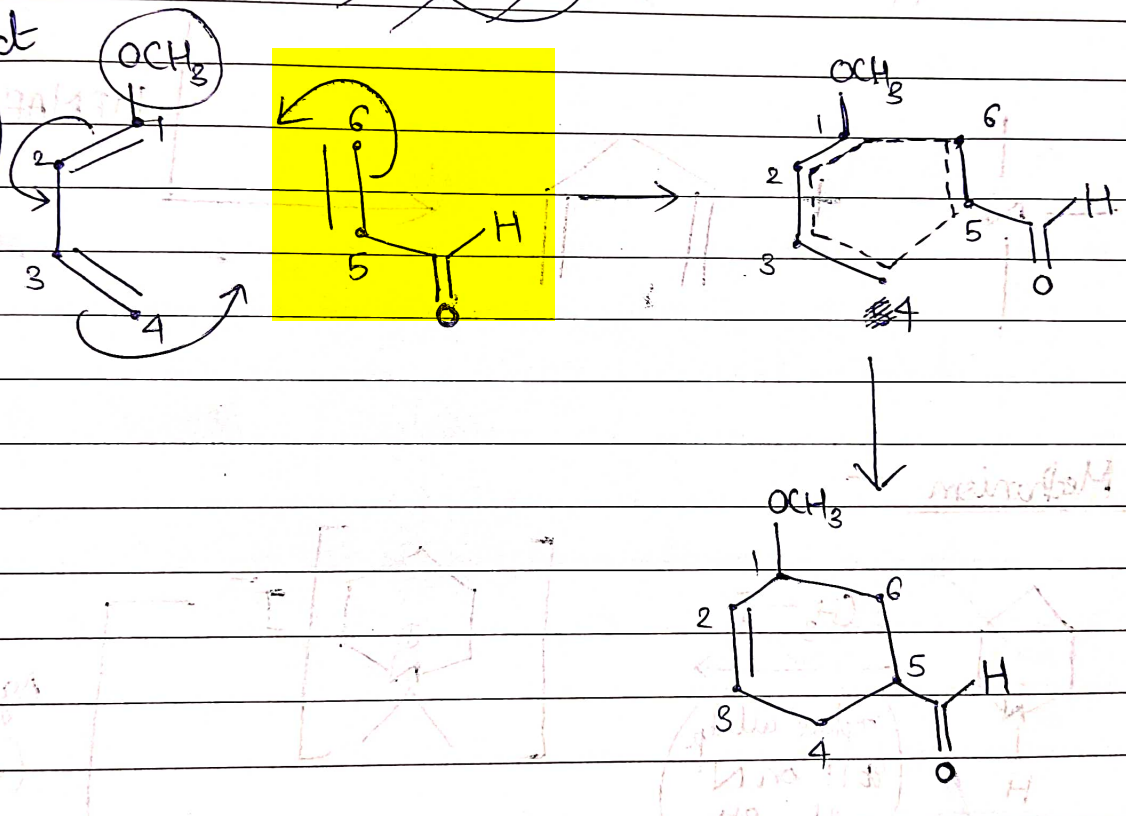
Q)



A)



(+M) effect
(π_σ bond uss taraf jaatega!)



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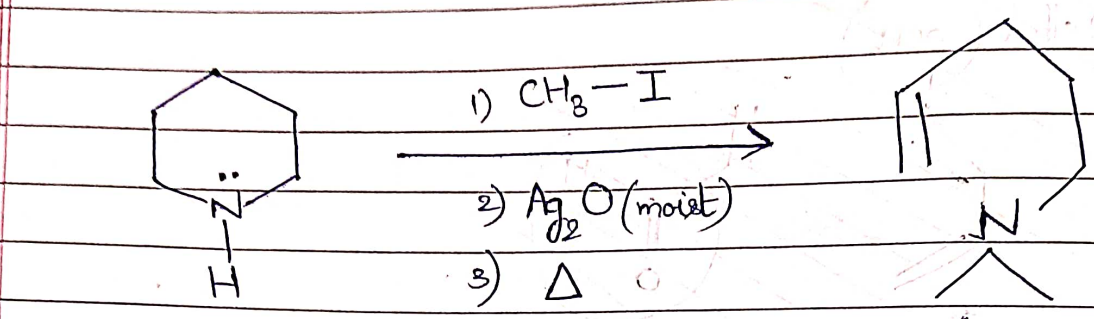
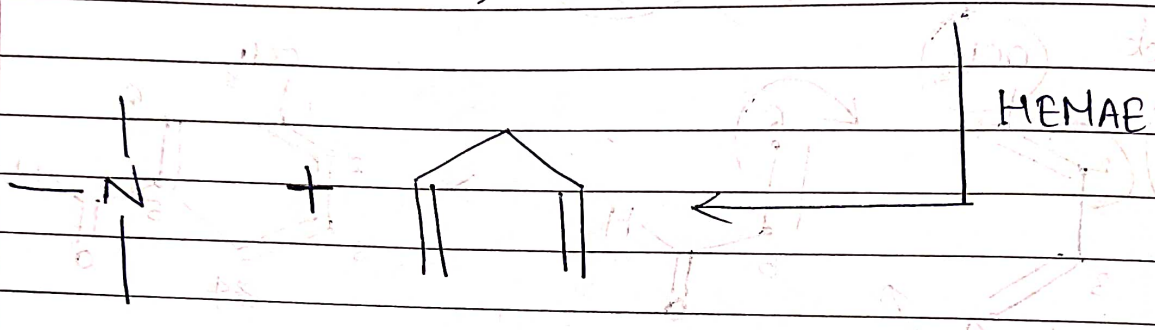
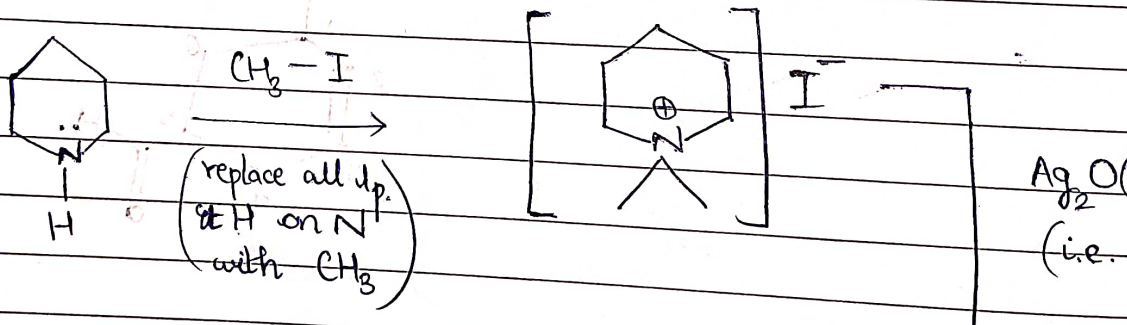
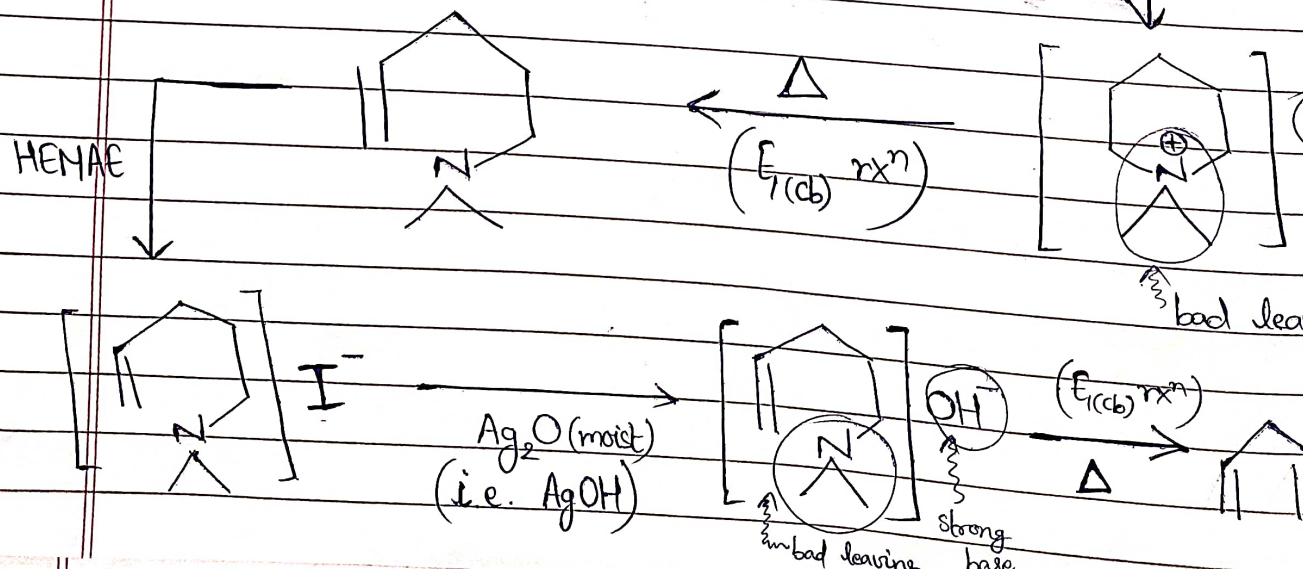
Hoffmann Exhaustive Methylation & Elimination (HEMAE)





Mechanism —



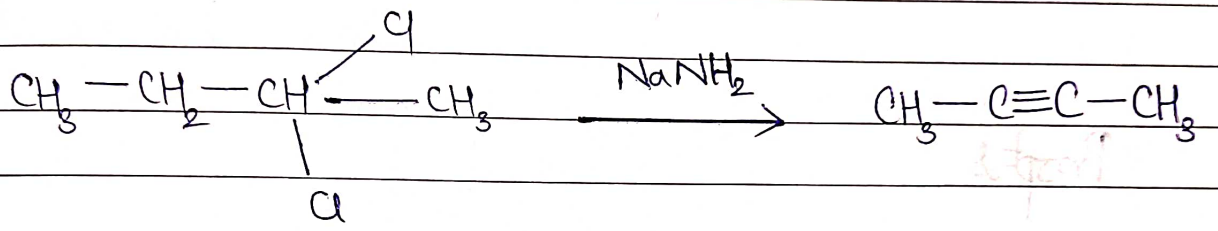


ALKYNE

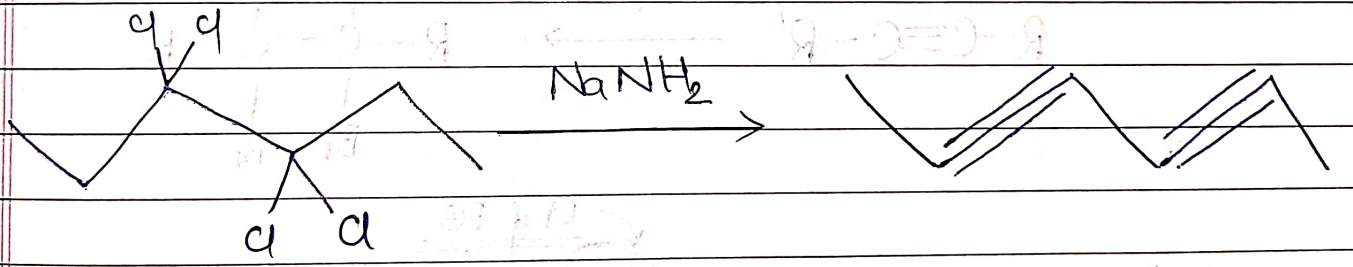
Prepⁿ

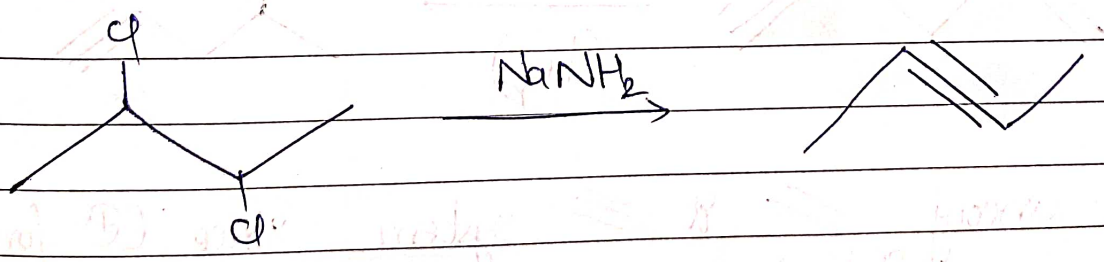
1) from Alkyl Halide —

1.1) from Geminal dihalides —

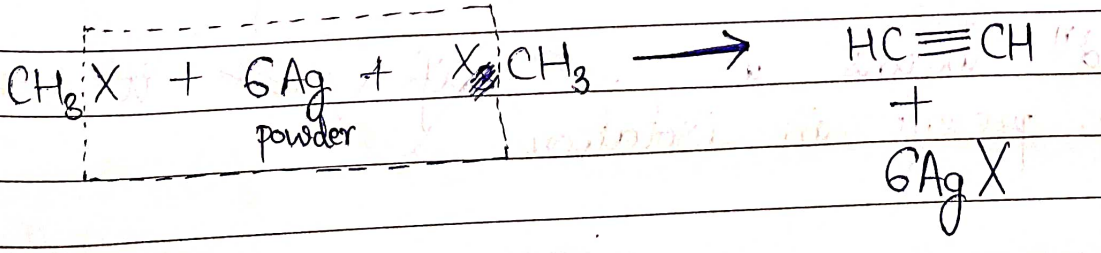


1.2) from Vicinal dihalides —





1.3) from Geminal trihalides —



2) From Calcium Carbide —

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + HC\equiv CH$$

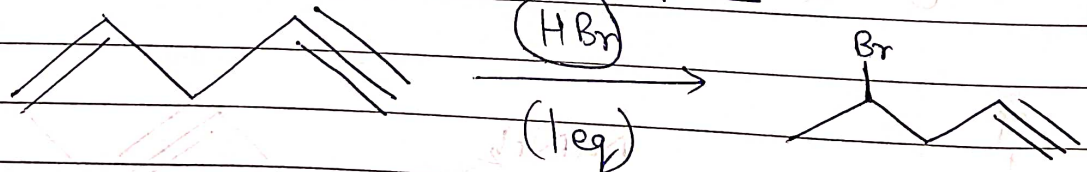
$$CaC_2 = Ca^{2+}\left[\ominus C \equiv C \ominus\right]$$

Propts

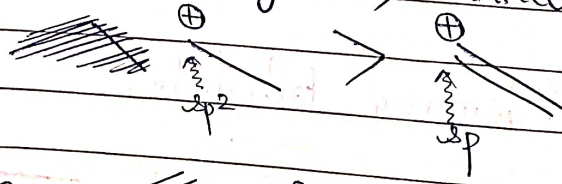
D) Electrophilic Add^n —

$$R-C\equiv C-R' \xrightarrow{Br_2 / CCl_4} R-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-R'$$

★ 1.1)

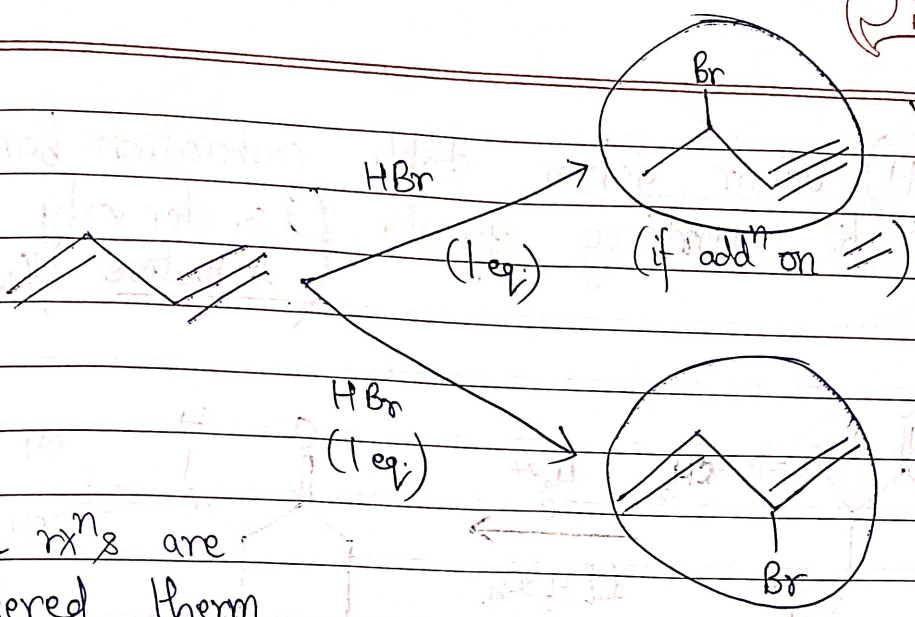


In unconj. $=$ & $\equiv$ system, since C⊕ formed is Stable:



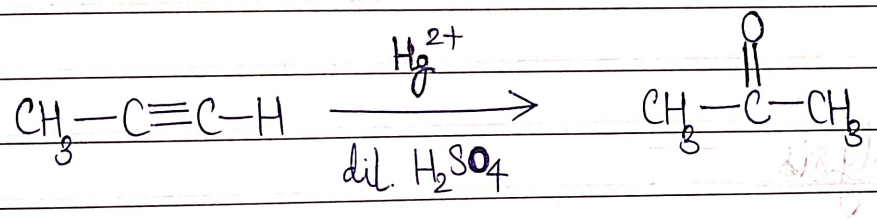
, hence add^n occurs on $=$, if $=$ & $\equiv$ are present in isolation.

★ (1,2)

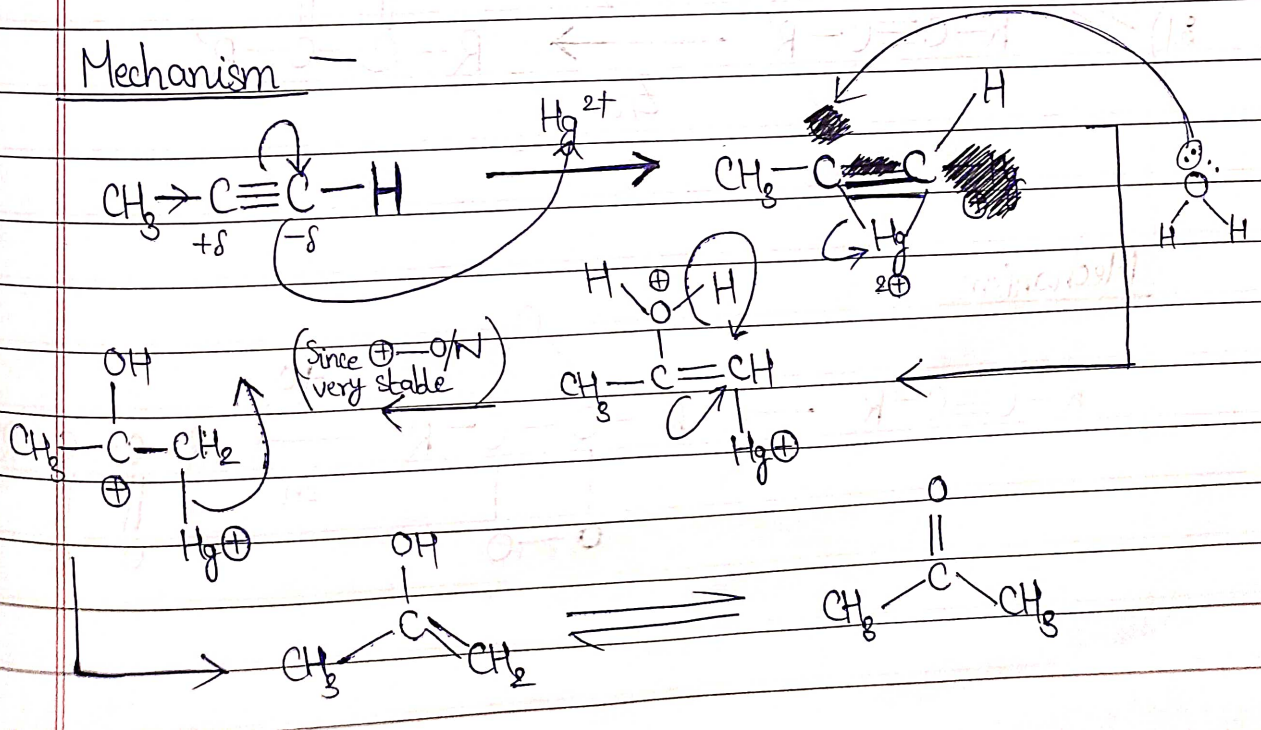


Since rxⁿs are considered therm. controlled, more stable product formed.

2) Hydration of Alkynes (Kucherov Rxⁿ) —



Mechanism —



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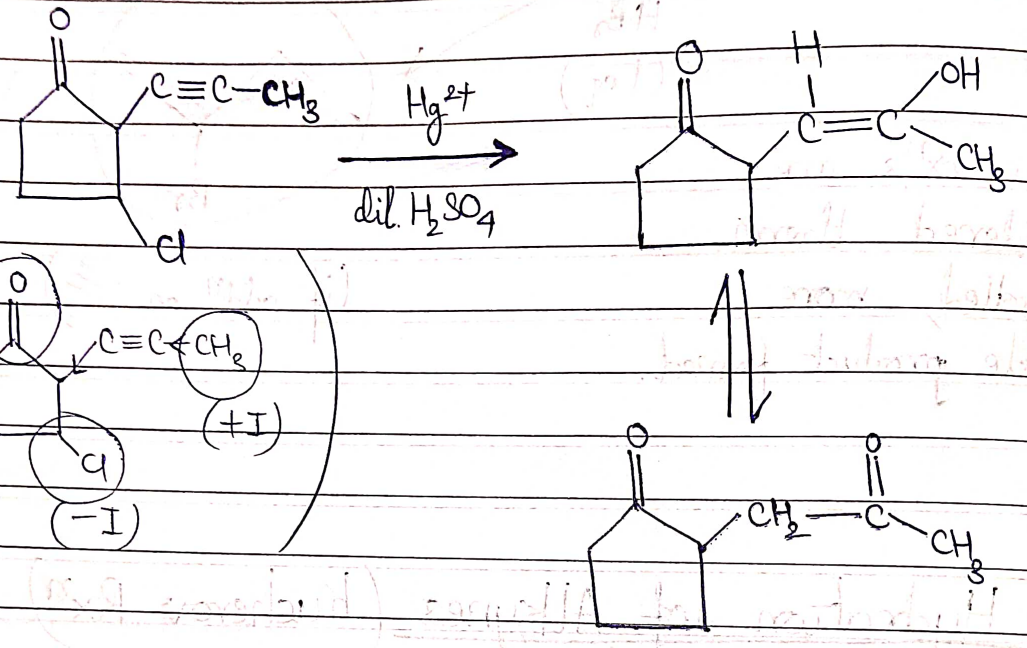
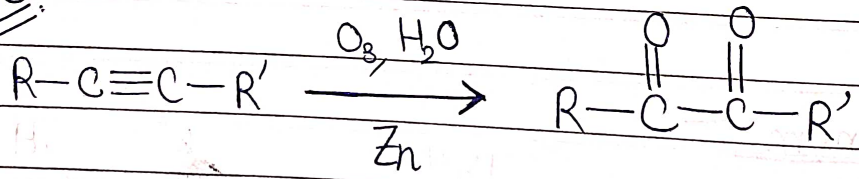
2.) (OH) udhar jahan stable carbocation banne ki tendency jyada. (consider only Inductive effect!)

★ Q)

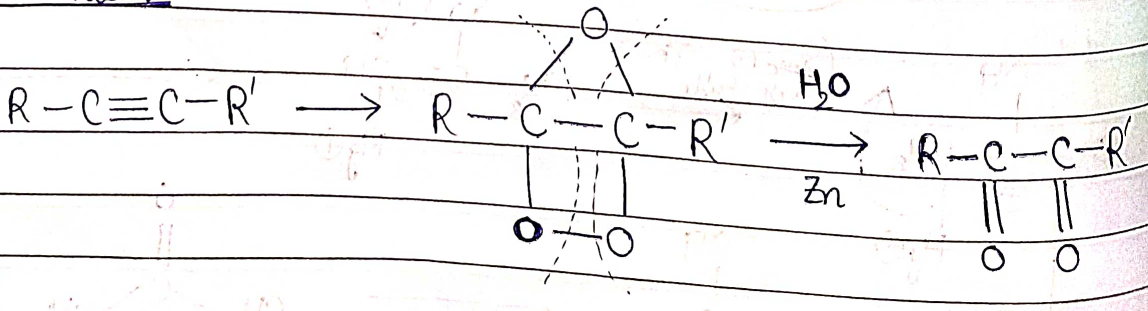


3) Ozonolysis —

3.1) Reductive:



Mechanism —



3.2) Oxidative