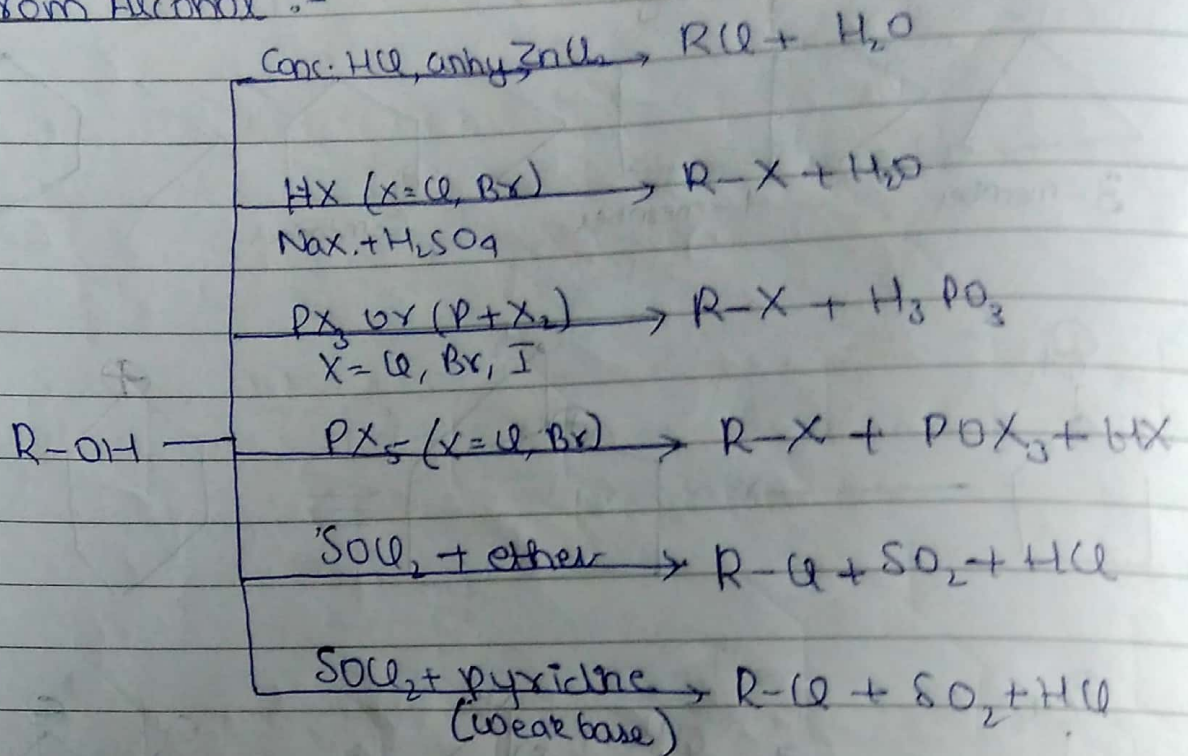


# Preparation of Alkyl Halide

## From Alcohol :-

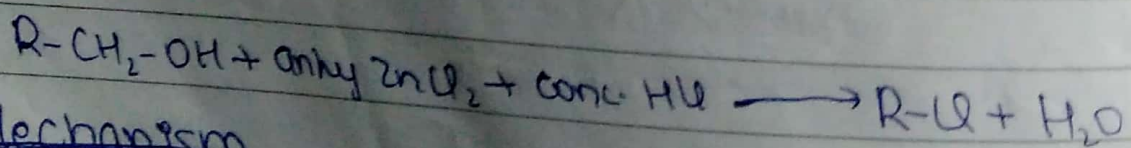


→ Lucas Reagent - (conc. HCl, anhy ZnCl<sub>2</sub>) - It is a mixture of conc. HCl & anhy ZnCl<sub>2</sub>.

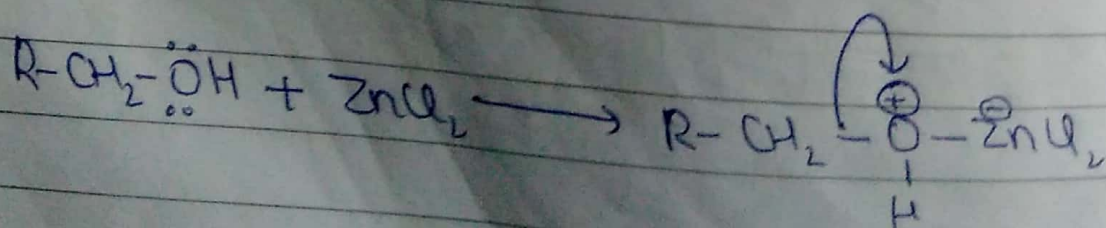
Lucas Test - It is method to distinguish 1°, 2° or 3° alcohol. According to this

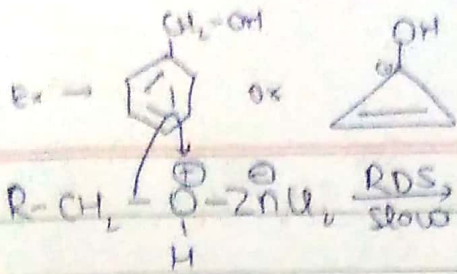
- 3° alcohol → white cloud or white ppt immediately
- 2° alcohol → " " " or " " " in 5 to 10 minutes
- 1° alcohol → do not give white ppt or white cloud or it gives white ppt after hours

→ From Lucas Reagent - S<sub>N</sub>1



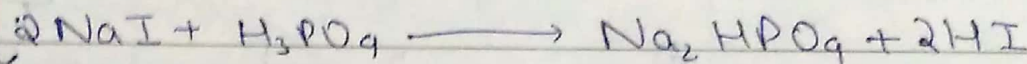
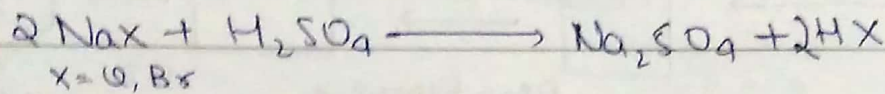
### Mechanism



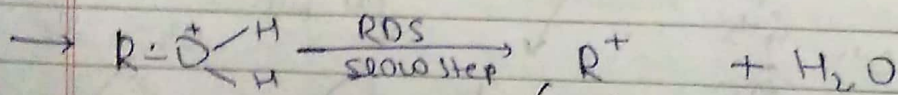
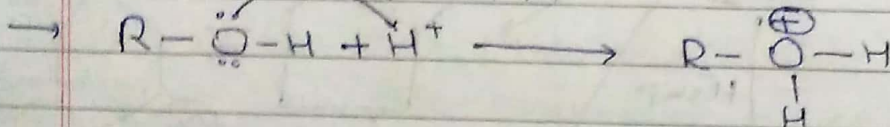
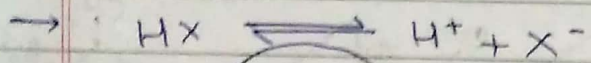


Any compound which in which carbocation stabilises itself will give Lucas Test (react with Lucas Test).

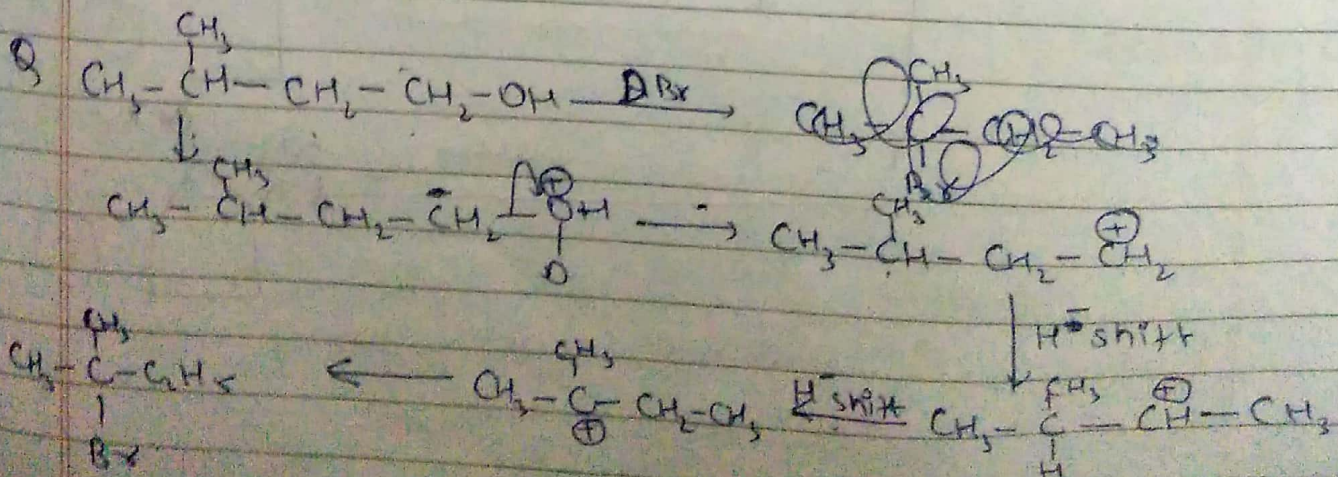
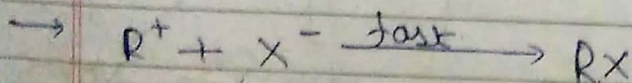
→ Rxn with HX ( $\text{NaX} + \text{H}_2\text{SO}_4$ ;  $\text{X} = \text{Cl}, \text{Br}$ ) →  $\text{S}_{\text{N}}1$

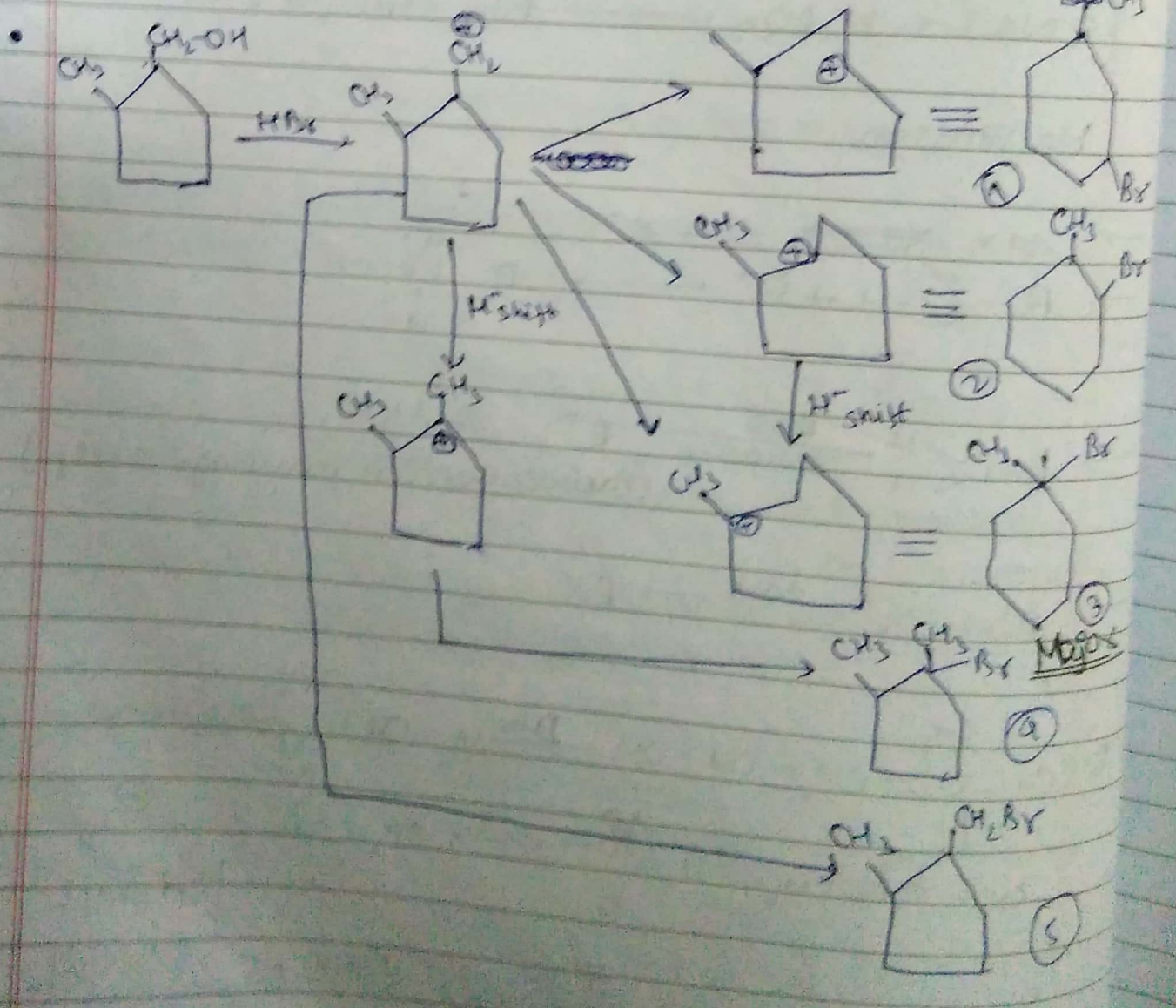
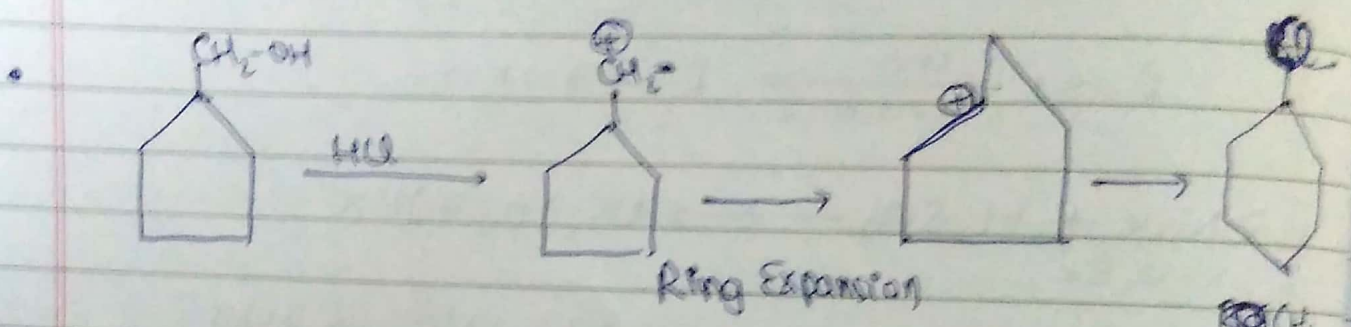
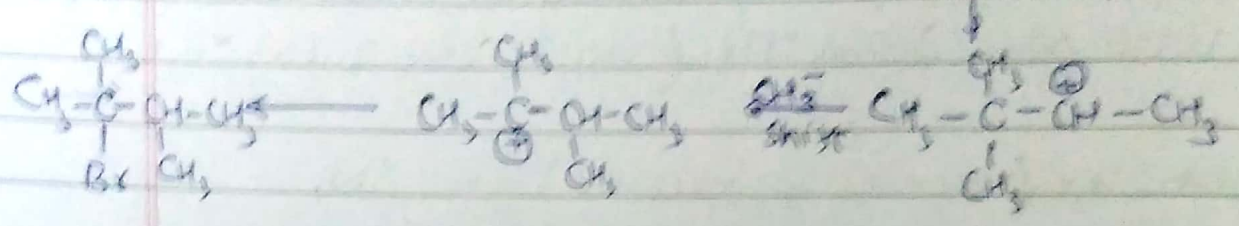
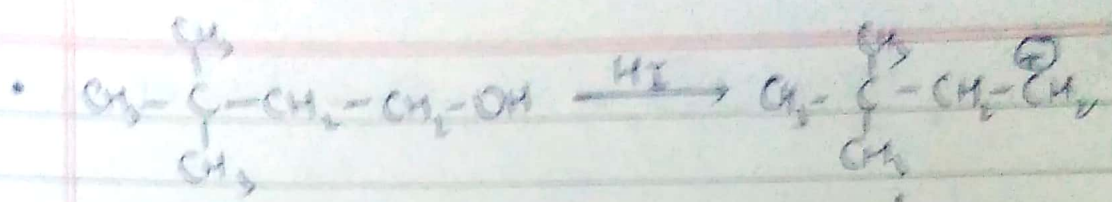


Mechanism

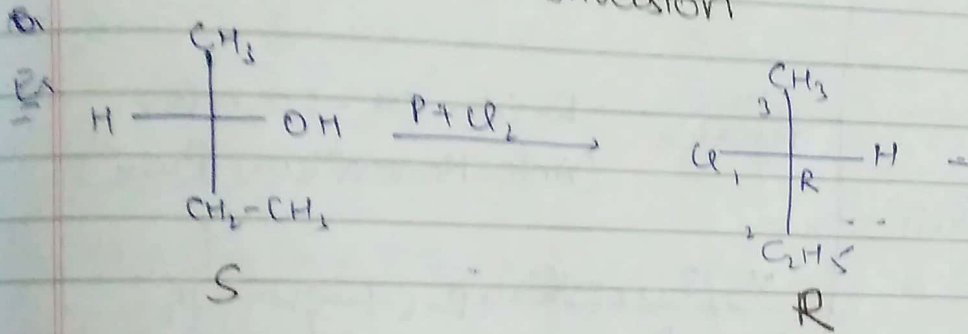
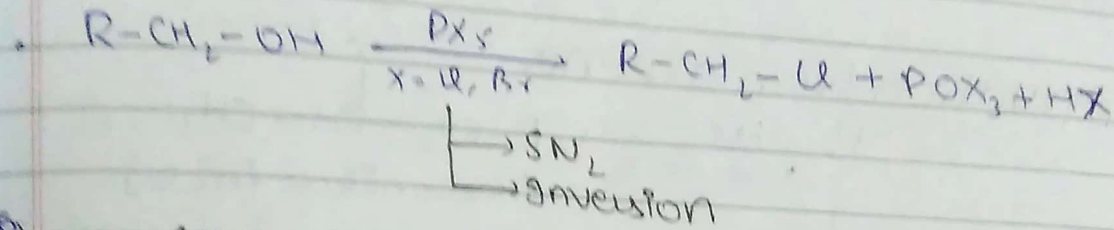
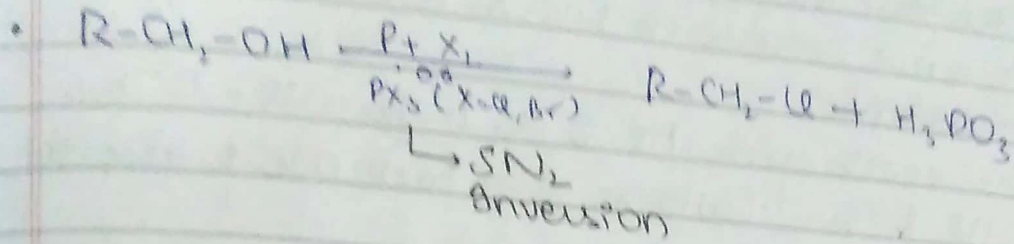


(Carbocation can rearrange itself)

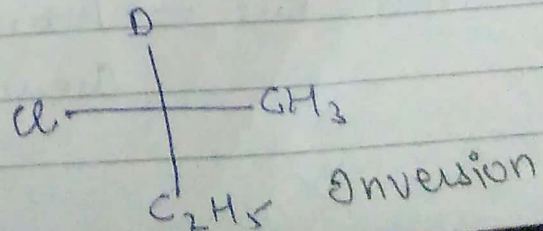
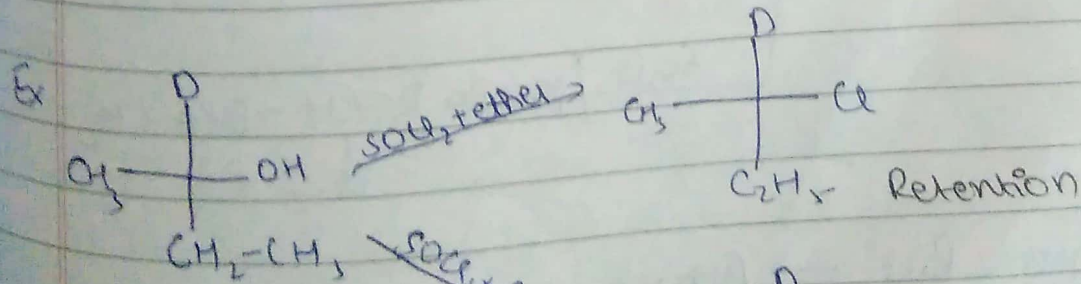
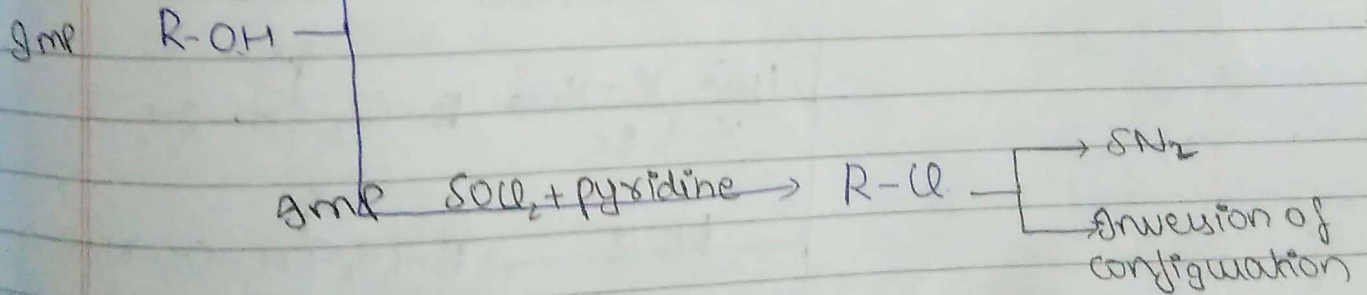
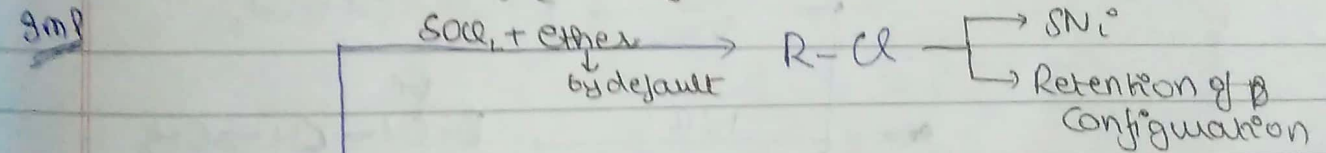




→ Rxn with  $PX_3$  ( $P+X_2$ ) →

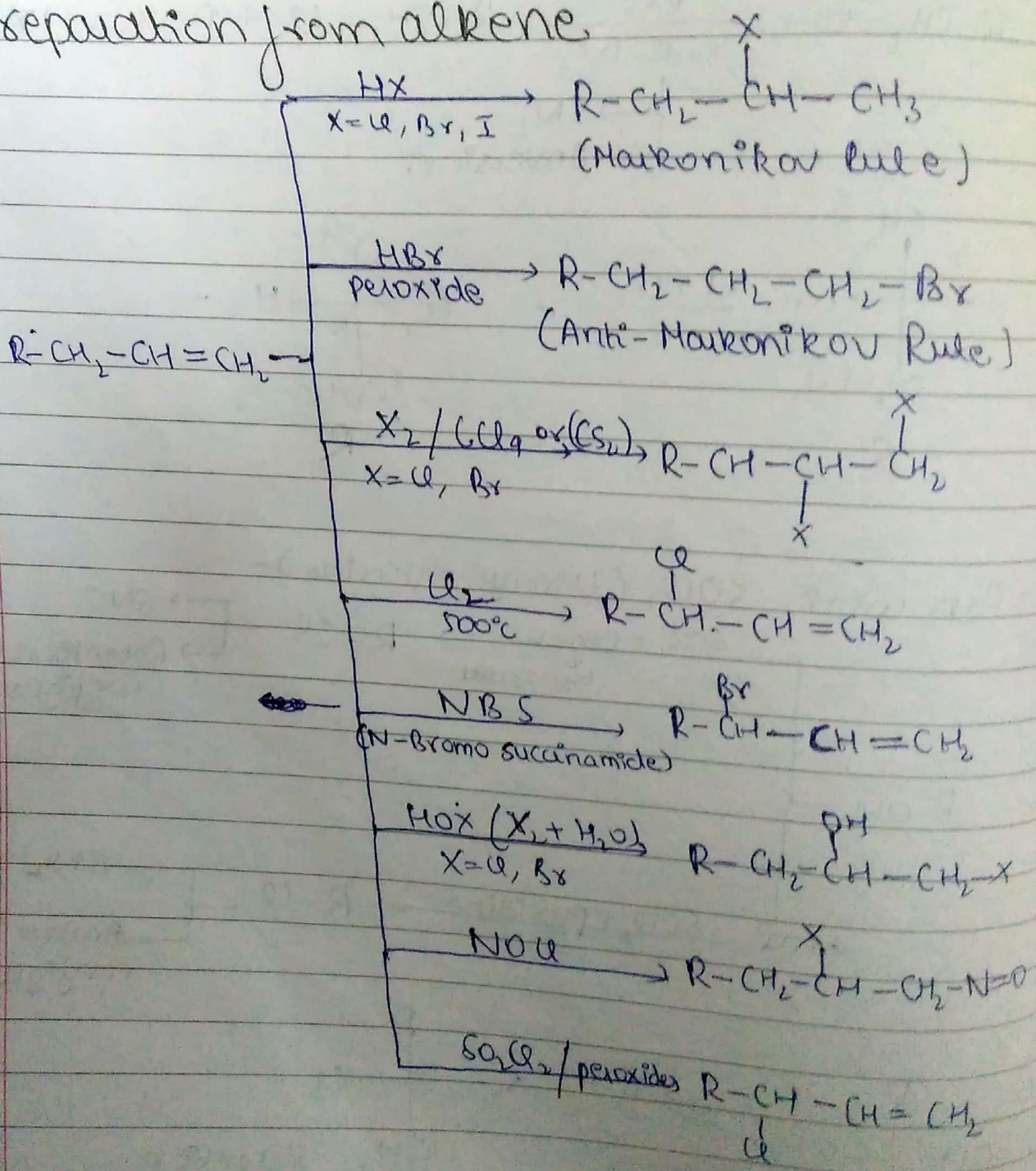


→ Rxn with  $SOCl_2$  (thionyl chloride) -




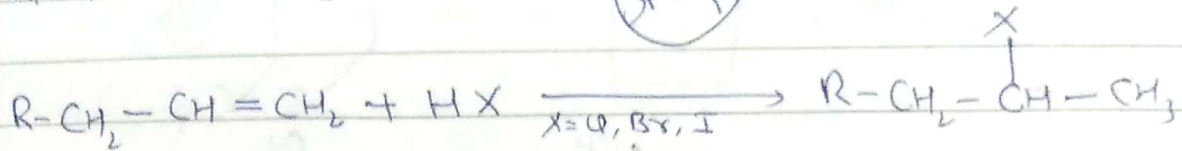
- \* HCl is the rxn intermediate
- \* ether does not react with HCl so it creates  $\text{Cl}^-$  from within molecule.
- \* Pyridine reacts with HCl & so it fixes the  $\text{Cl}^-$  ion from HCl & so it attacks from back side to give  $\text{SN}_2$

## Preparation from alkene

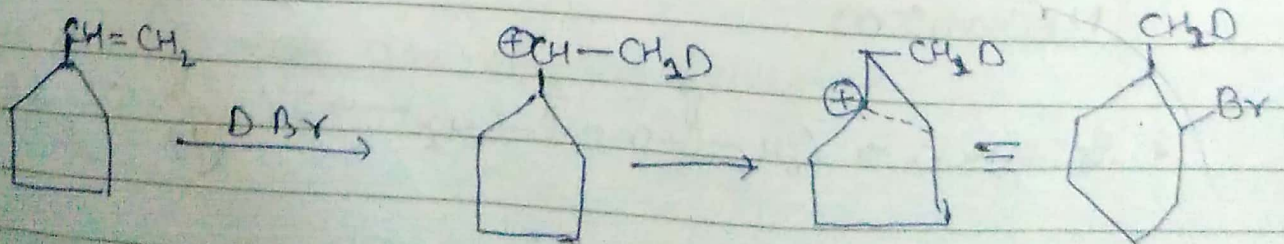
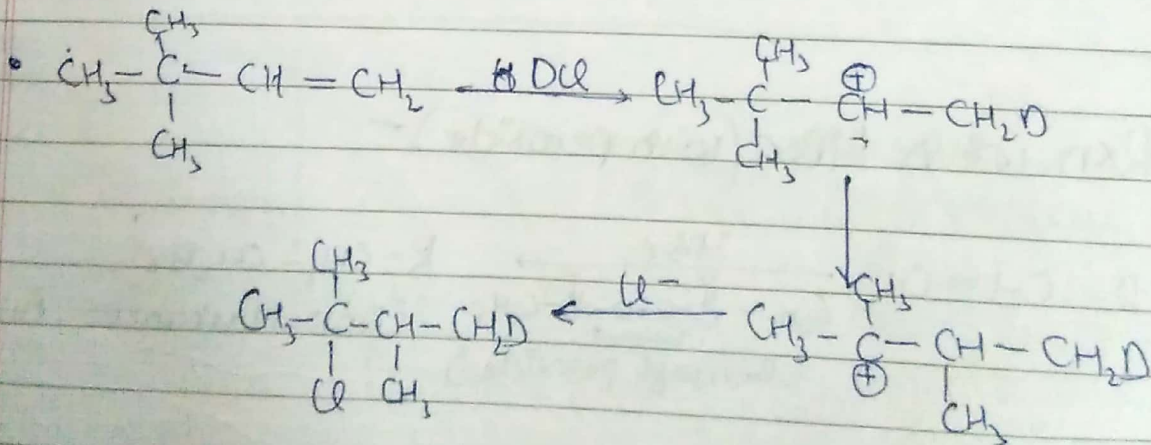
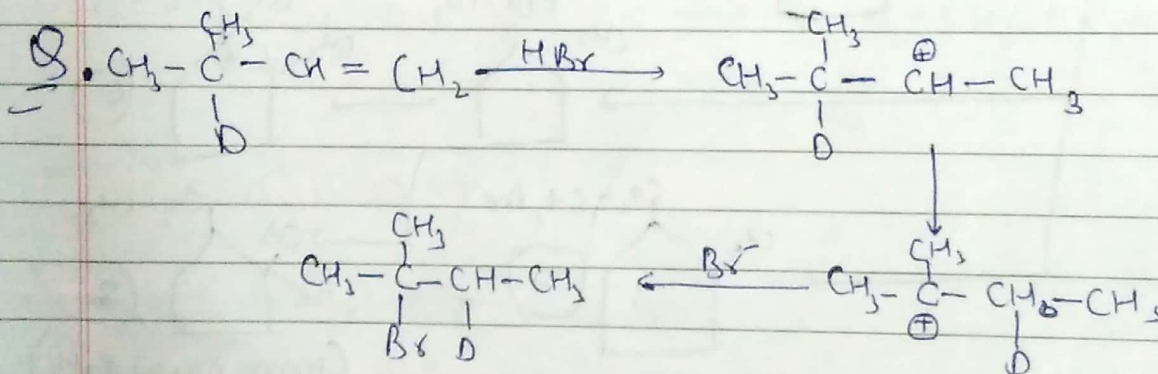
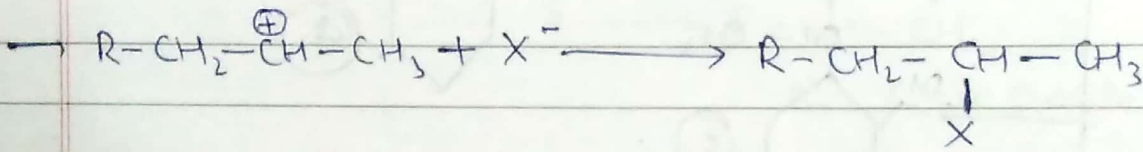
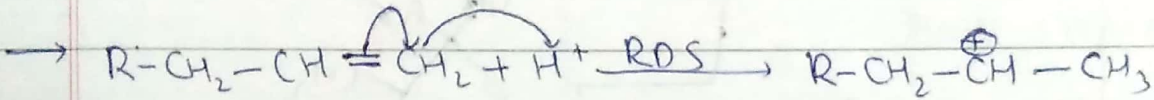


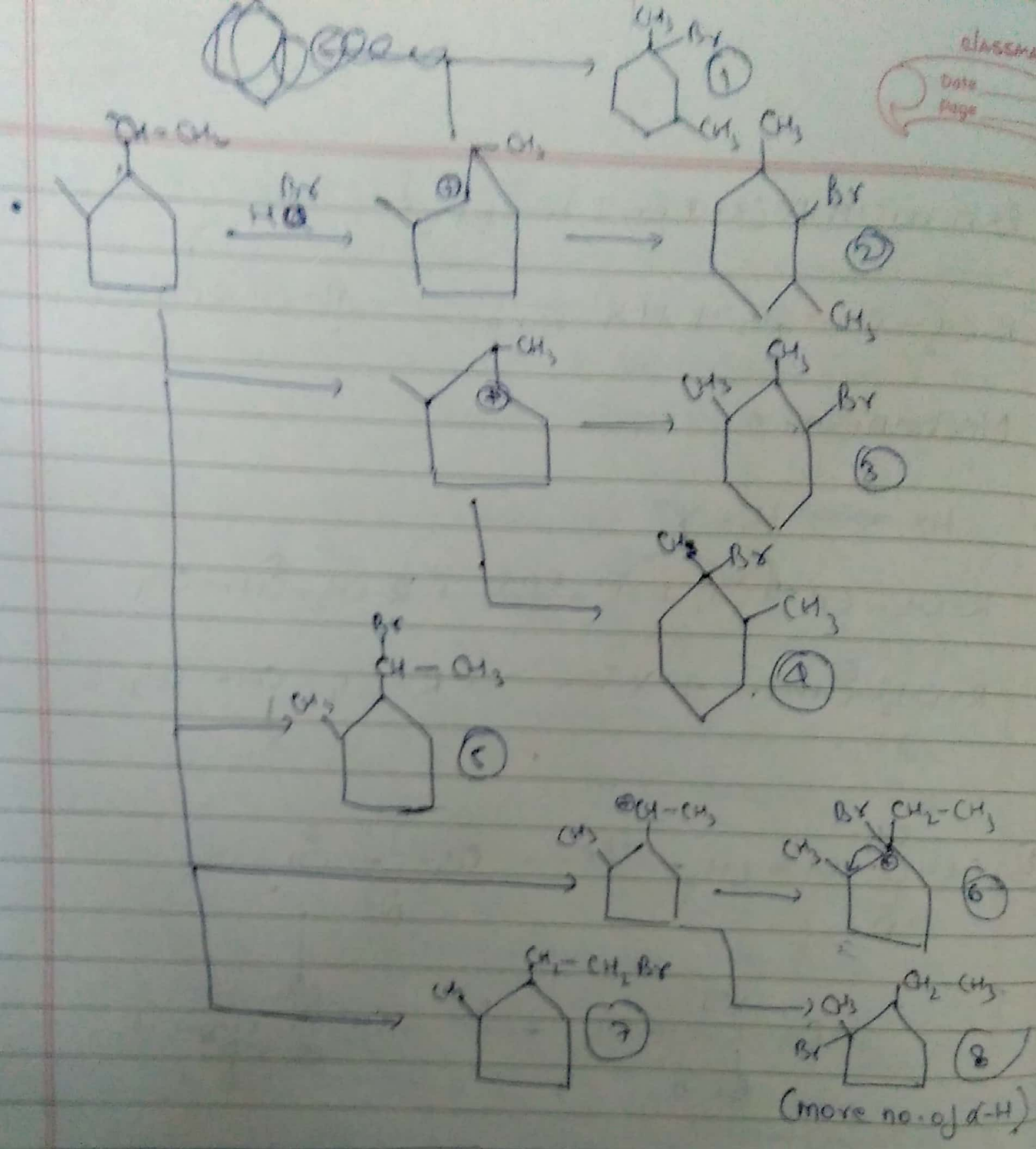
Markonikov Rule  $\rightarrow$  Attack where less no. of hydrogens are present

→ Rxn w/ HX (X=Cl, Br, I). 

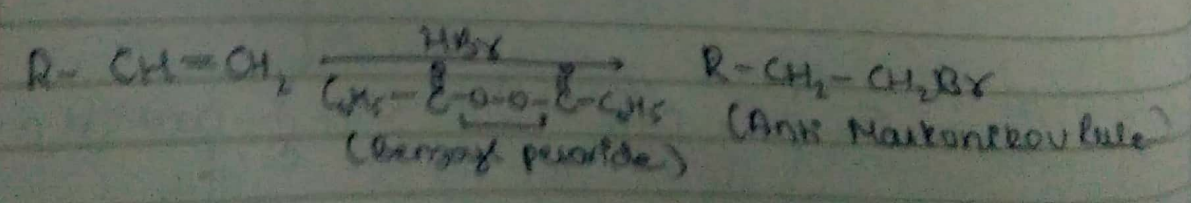


Mechanism ⇒

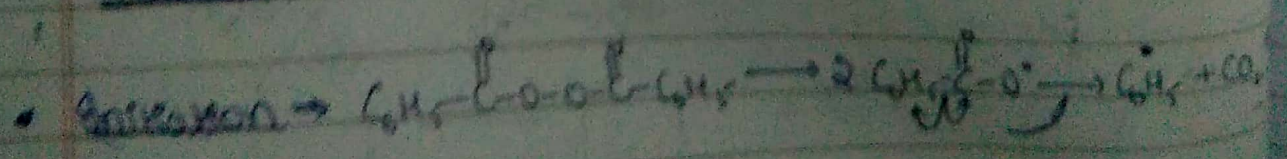




Imp → Rxn with HBr (with peroxide) -

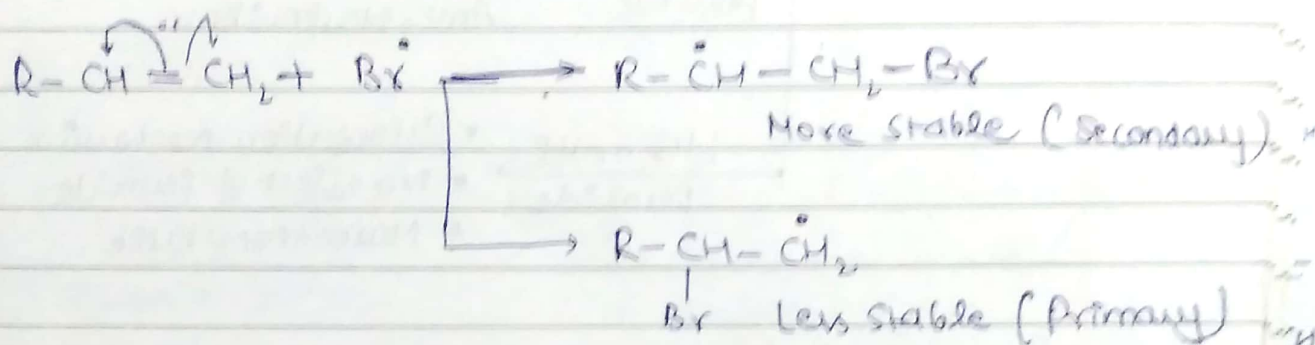


Mechanism

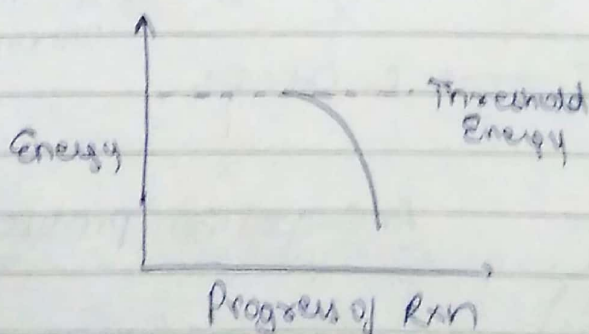


- \* Peroxide generate free radical
- \* Heat will generate free radical (Thermolysis) classmate
- \* Photolysis will " " "
- \*  $O_2$  is free radical inhibitor

• Propagation  $\Rightarrow$



• Termination  $\Rightarrow$



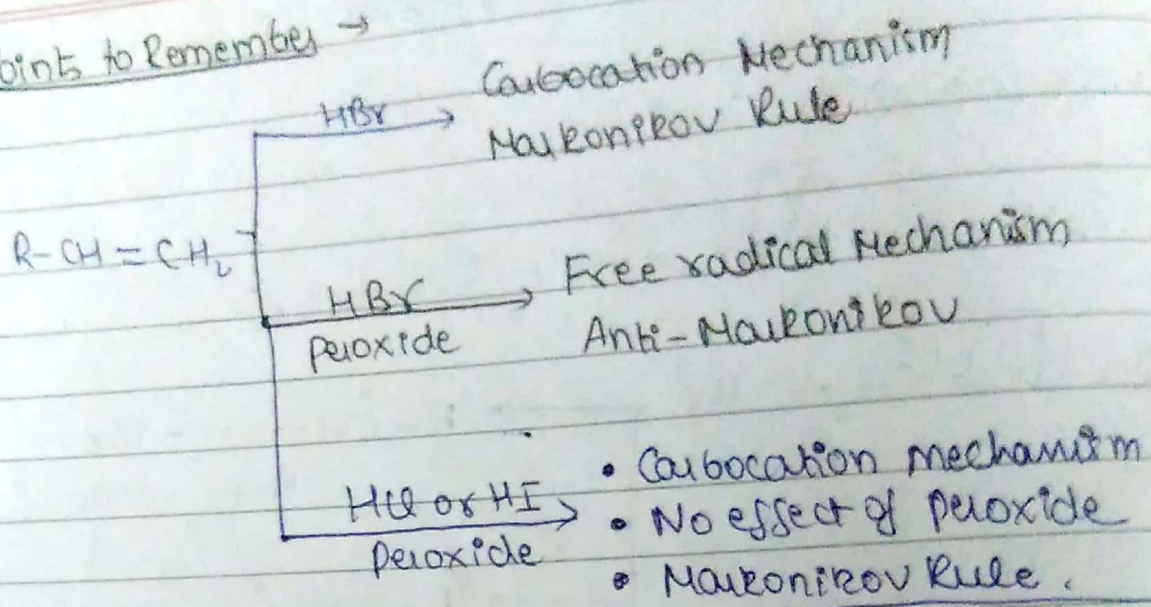
\* Activation energy of free radical rxn is 0.

\* Rate of reactivity is infinite.

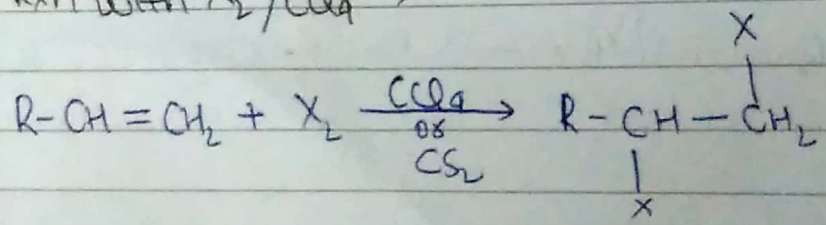
\* Free radical ~~are~~ are highly reactive.



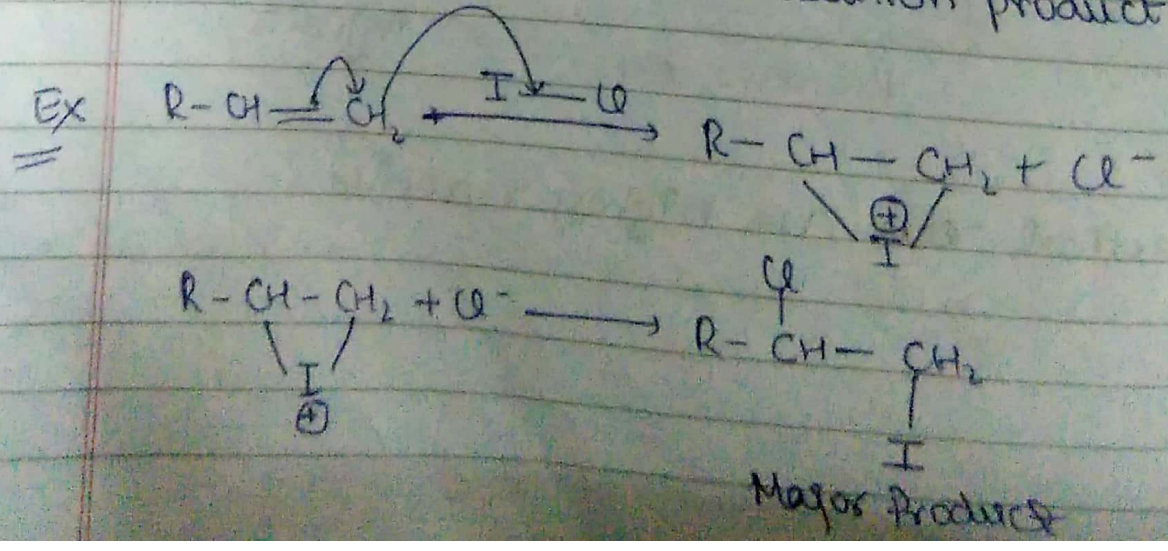
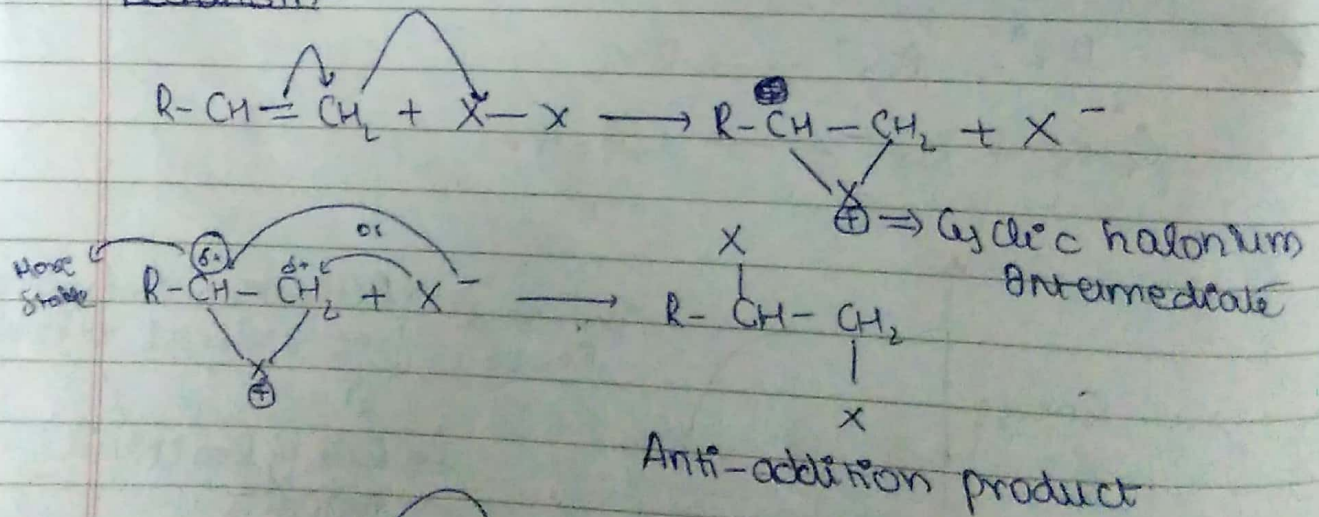
Imp Points to Remember →



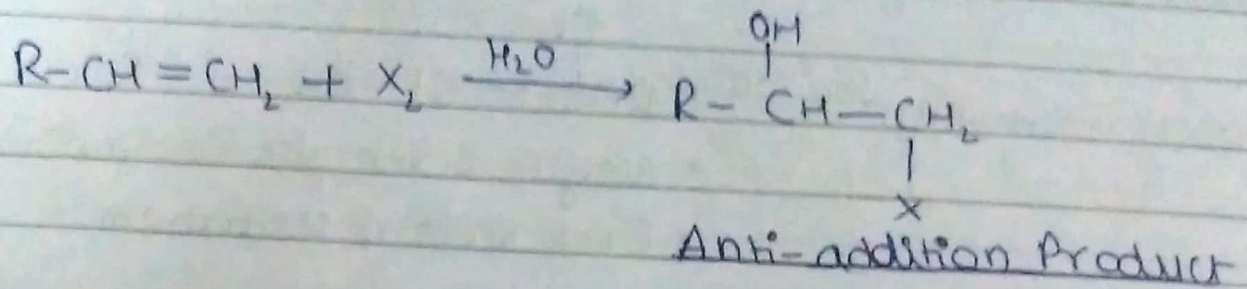
→ Rxn with  $X_2/CCl_4$  →



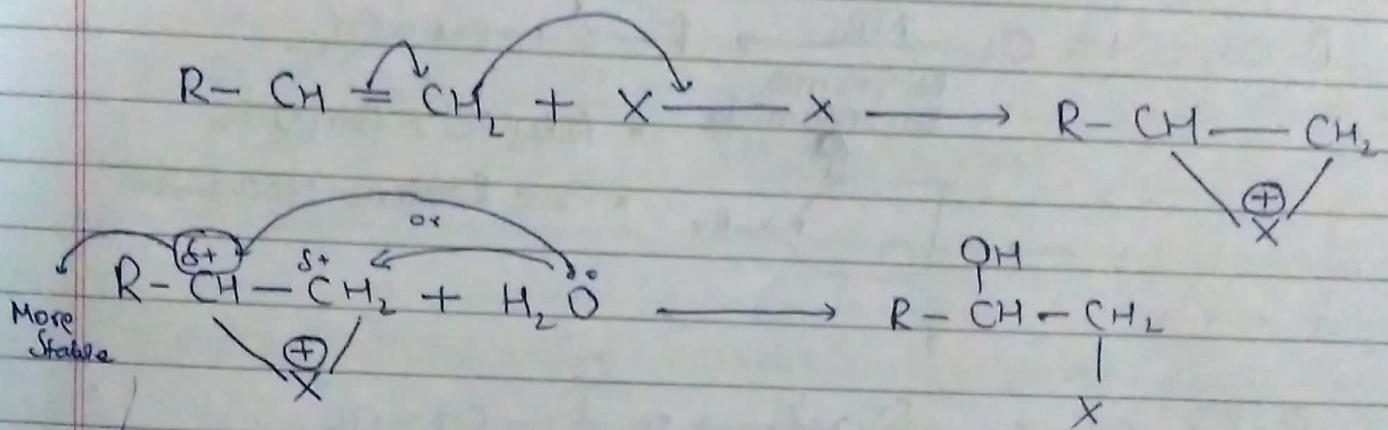
Mechanism-



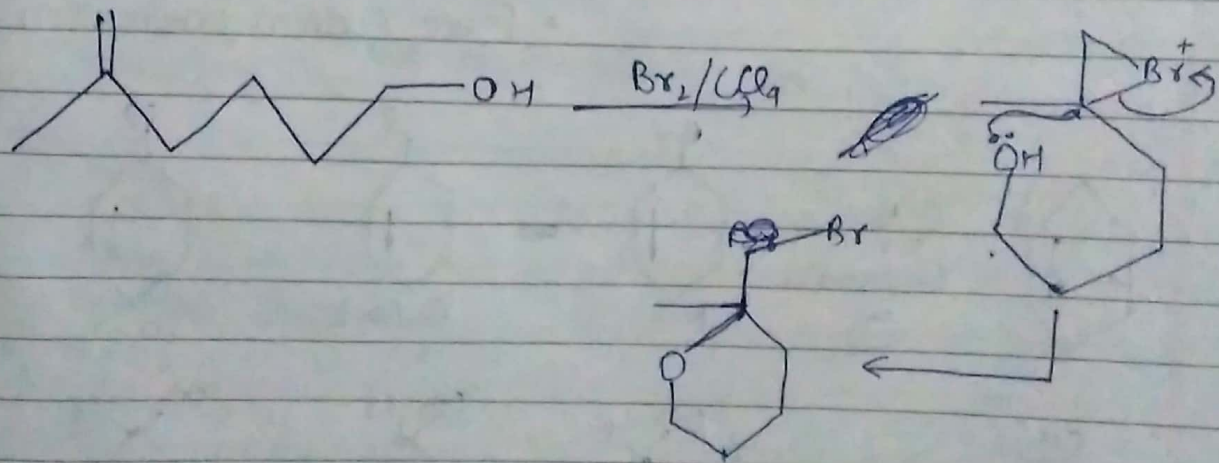
→ Rxn with  $X_2/H_2O$  (HOX) -



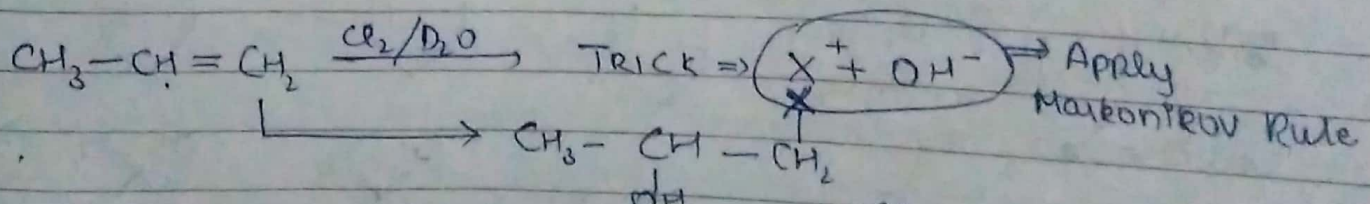
Mechanism -



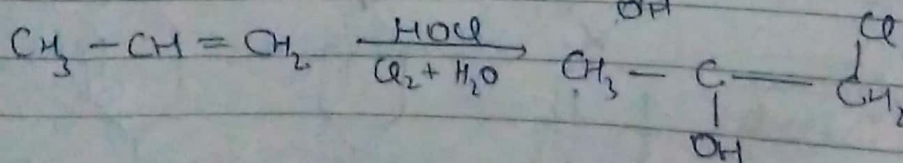
Ex



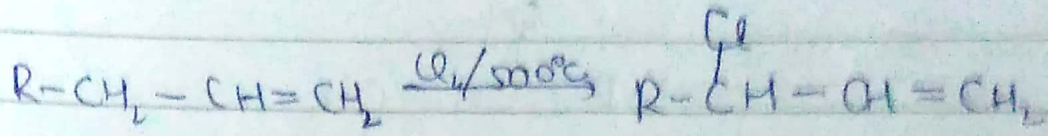
Ex



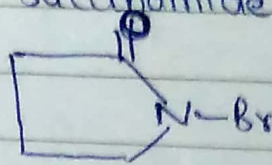
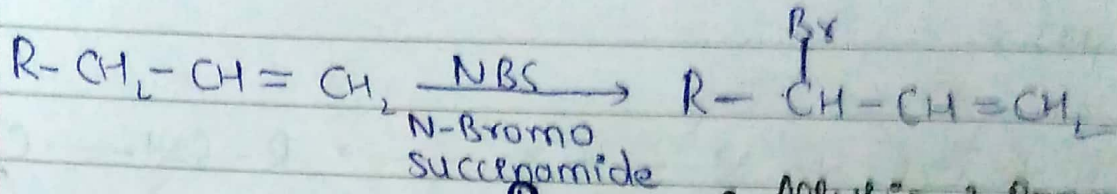
Ex



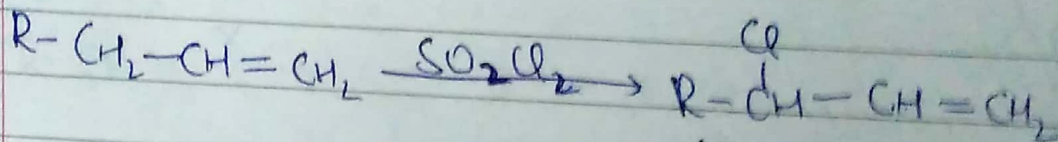
→ Rxn with  $Cl_2 / 500^\circ C$  -



- Allylic & Benzylic Substitution
- Free Radical Mechanism

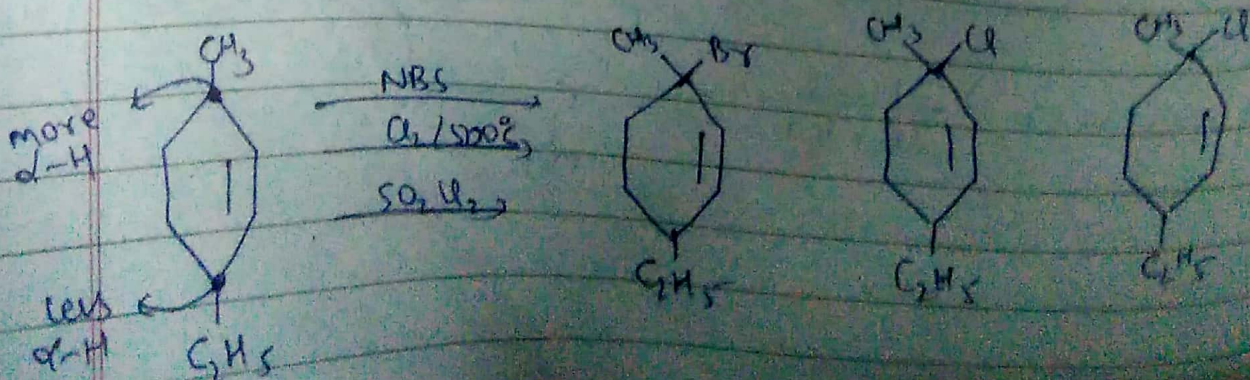
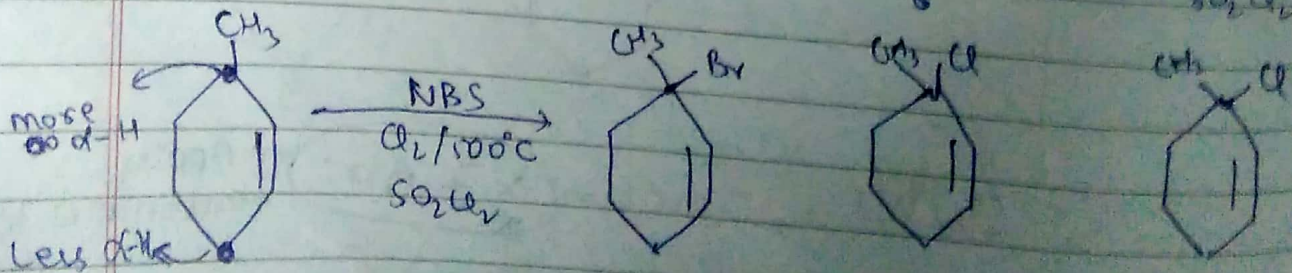
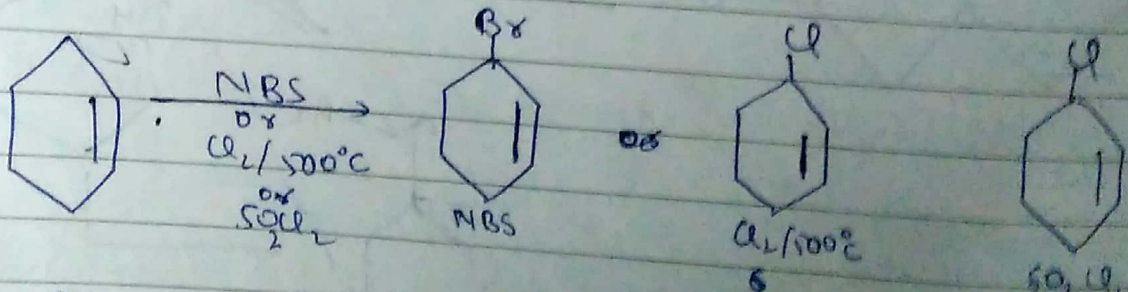


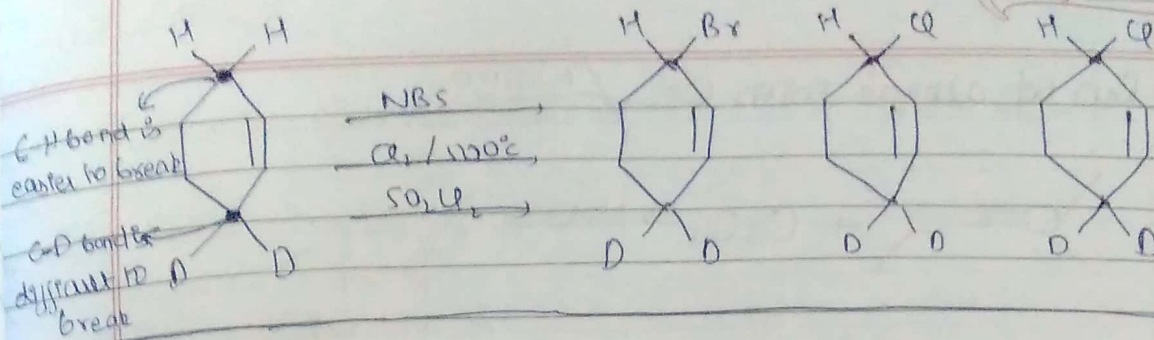
- Allylic & Benzylic
- Free Radical Mechanism



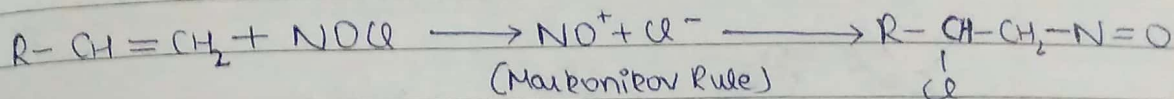
- Allylic & Benzylic Substitution
- Free radical mechanism

Q



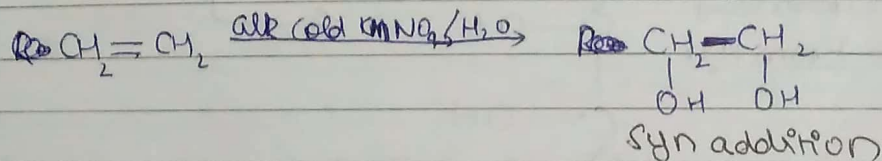


→ Rxn with NOCl

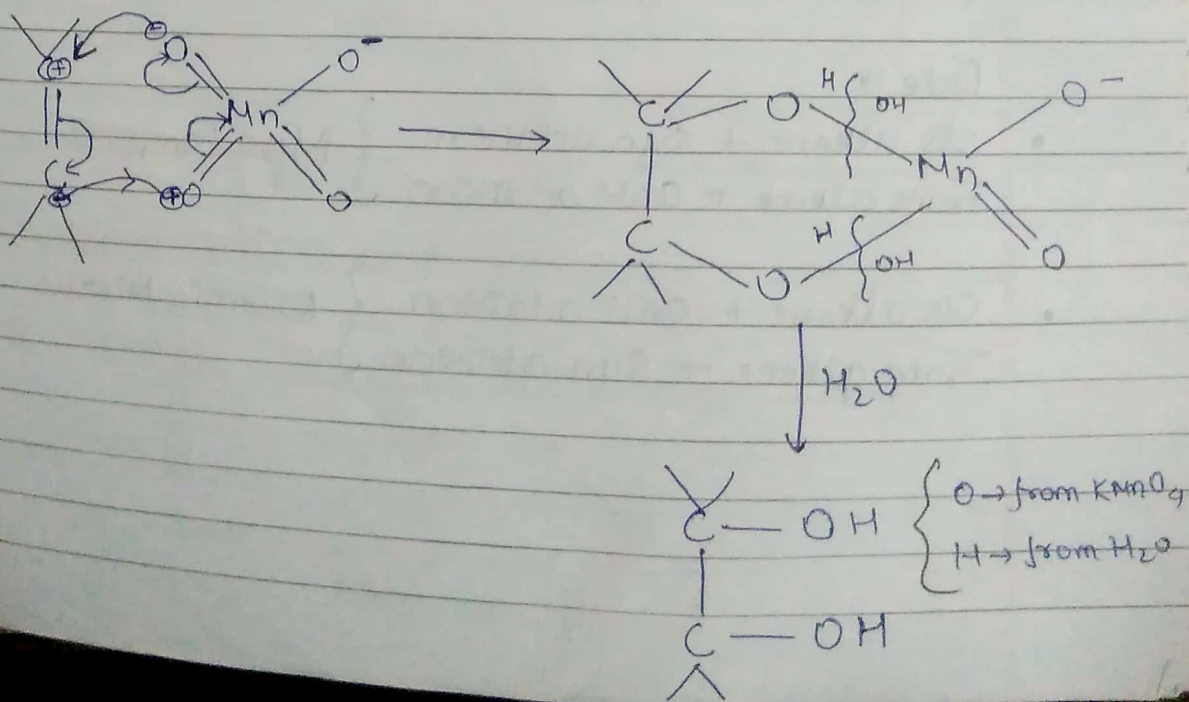


→ Rxn of alkene with Bayer's Reagent

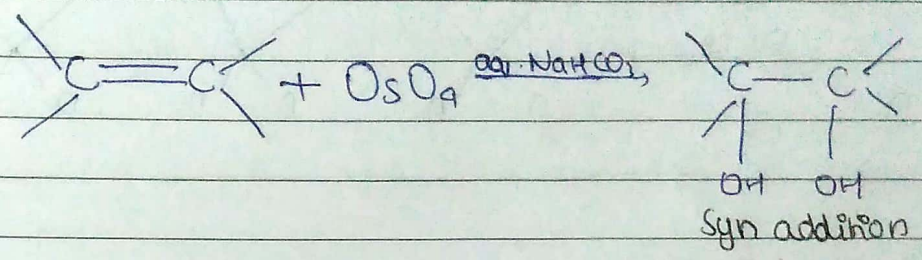
Bayer's Reagent → cold aqueous alkaline  $\text{KMnO}_4$



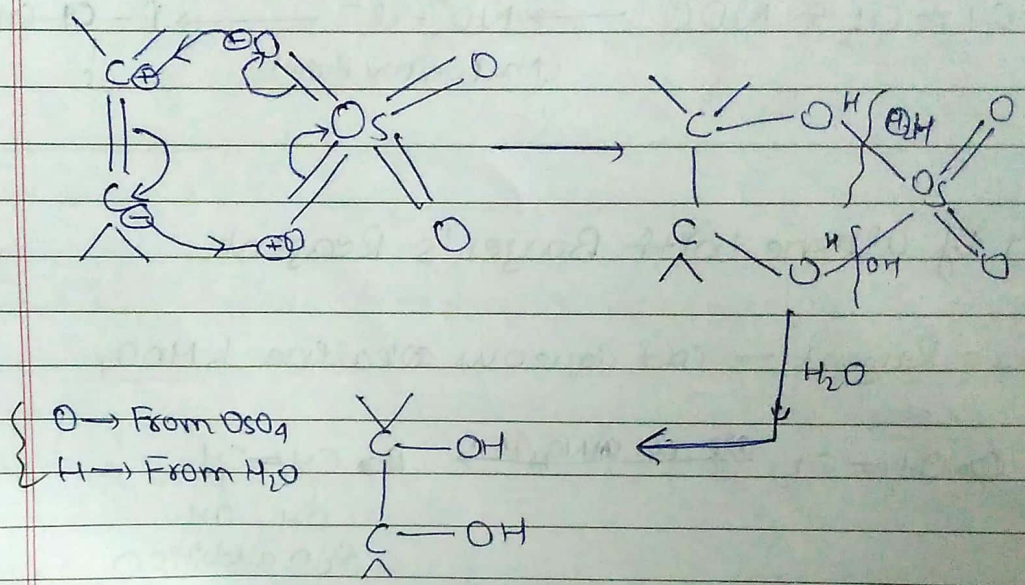
Mechanism



→ Rxn of alkene with  $OsO_4 / NaHCO_3$



Mechanism -



Stereochemistry of Addition Rxn ⇒

Rule →

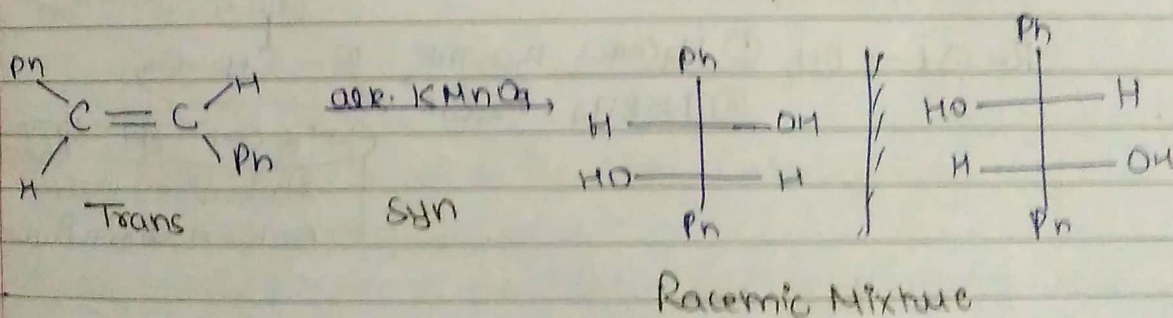
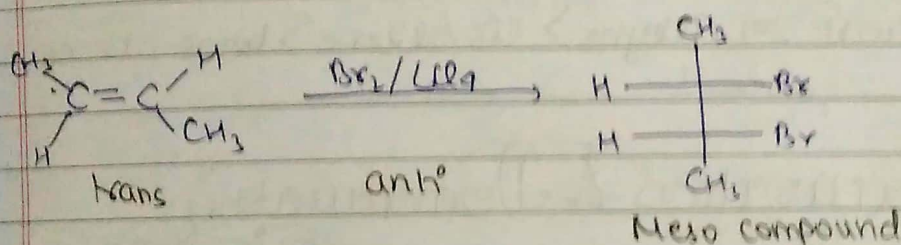
- cis alkene + syn addition } Meso Compound
- Trans alkene + anti addition }
  
- cis alkene + anti addition } Racemic Mixture
- Trans alkene + syn addition }

## Example of Syn Addition -

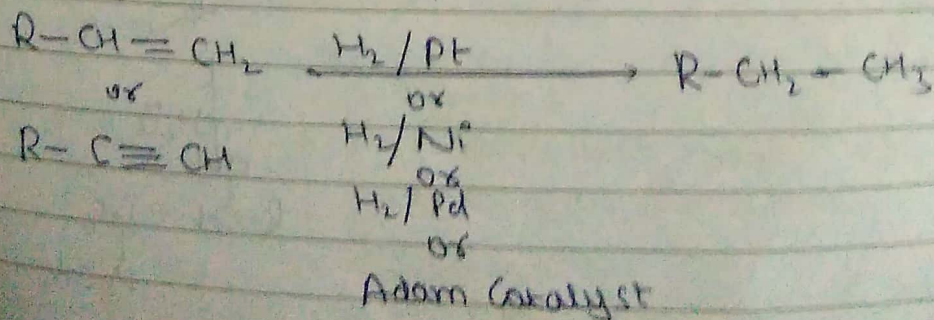
- Hydrogenation of alkene.
- Bayer's Reagent
- Rxn of Alkene with  $\text{OsO}_4$  &  $\text{NaHSO}_3$
- Hydroboration and oxidation

## Example of Anti Addition -

- Addition of  $\text{X}_2$  in  $\text{CCl}_4$
- Addition of  $\text{HOCl}$  &  $\text{NOCl}$
- Oxymercuration & Demercuration

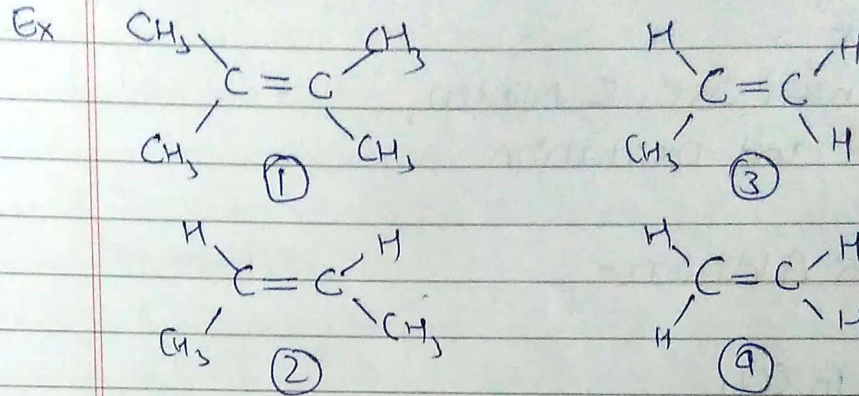


## → Hydrogenation of Alkene -



Ans • Stability of Alkene = No. of  $\alpha$ -Hydrogen

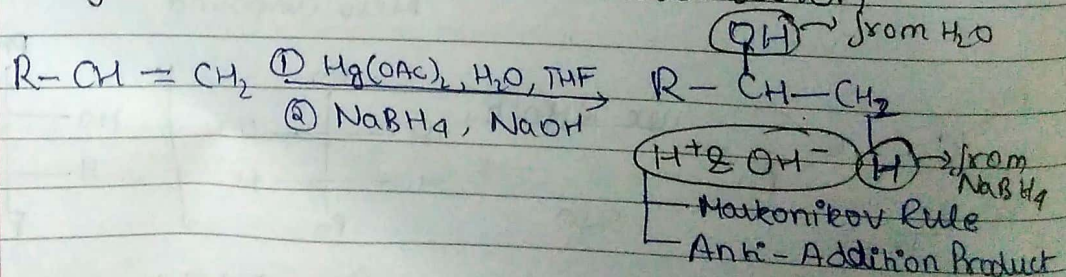
\* Stability of alkene  $\propto$   $\frac{1}{\text{Heat of hydrogenation}}$



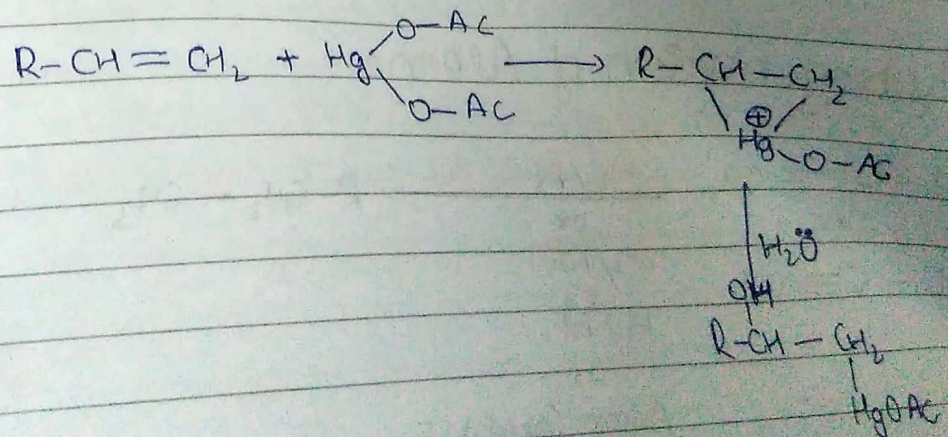
Order of H.O.H  $\Rightarrow$  4 > 3 > 2 > 1

\* Order of H.O.H  $\Rightarrow$  alkyne > cis alkene > trans-alkene

### → Oxymercuration & Demercuration

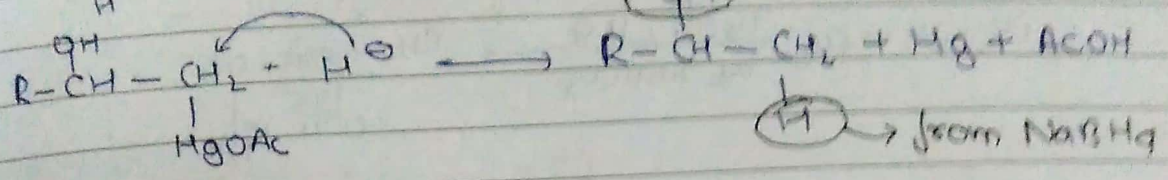
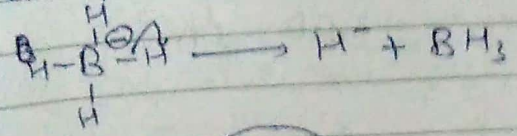
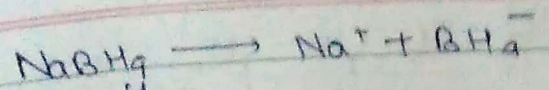


#### Mechanism -

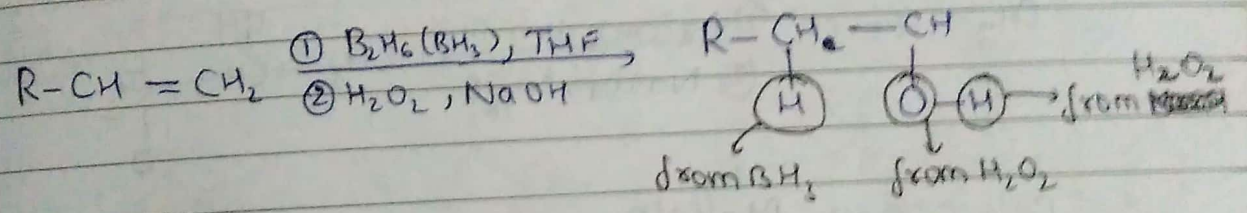




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$\rightarrow$  Hydroboration & Oxidation  $\rightarrow$

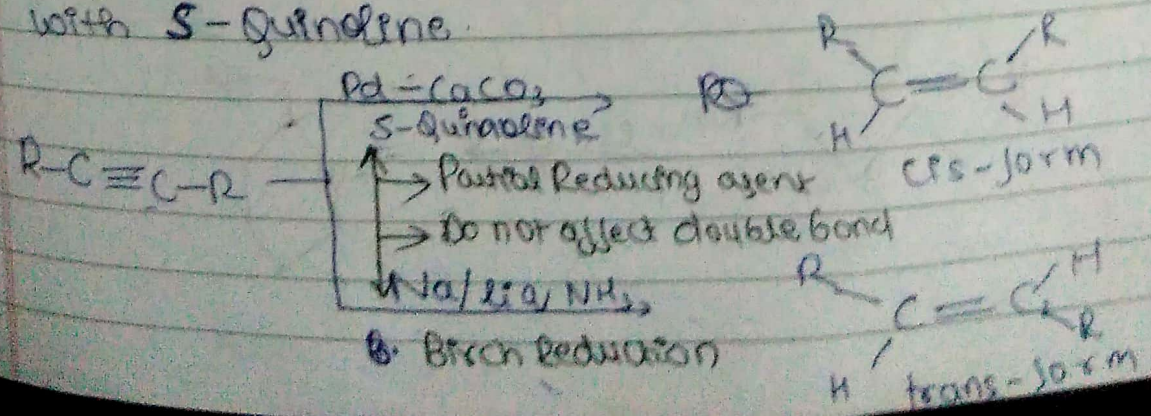


$\text{H}^+ + \text{OH}^- \rightarrow$    
 $\rightarrow$  Anti Markovnikov Rule   
 $\rightarrow$  Syn addition

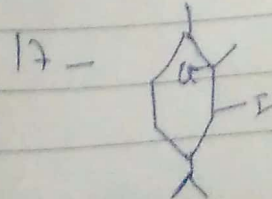
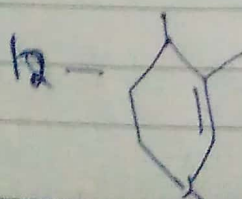
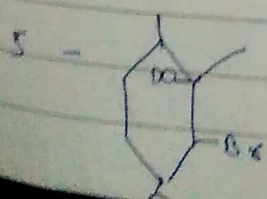
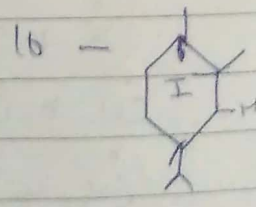
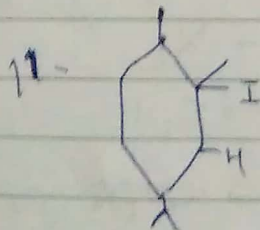
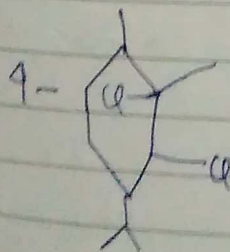
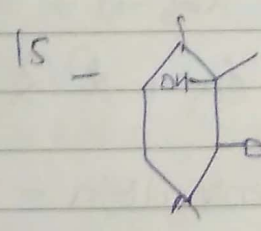
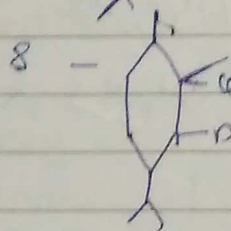
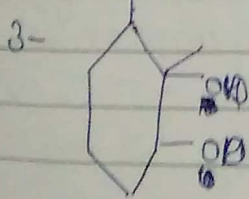
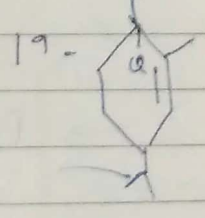
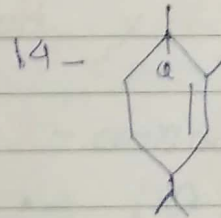
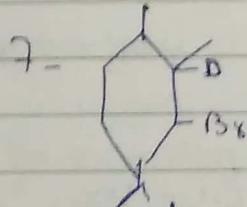
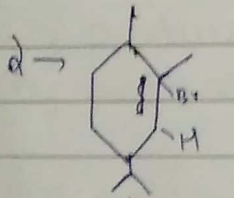
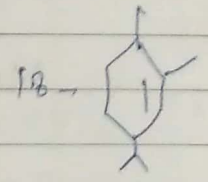
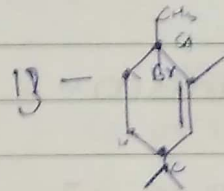
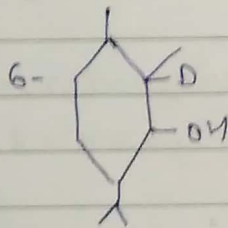
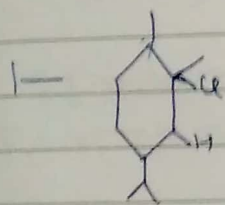
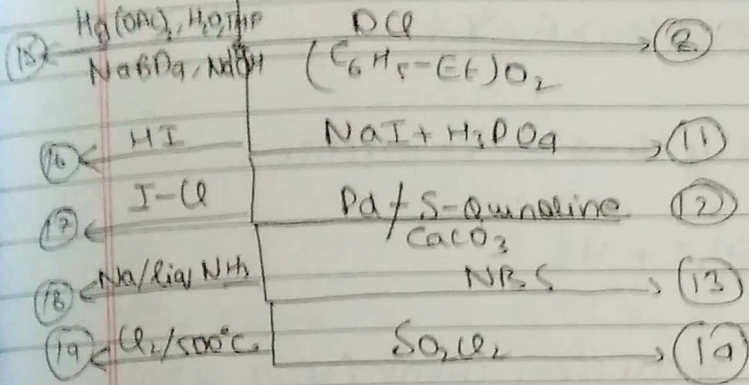
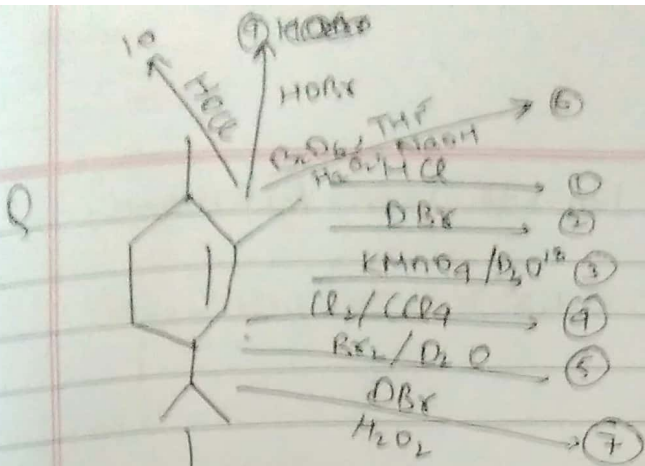
$\rightarrow$  Rxn of alkene with Lindlar Catalyst -

$\rightarrow$  Partial Reduction   
 Lindlar Catalyst - It is palladised  $\text{CaCO}_3$ , poisoned with lead acetate.

Modified Lindlar Catalyst - It is palladised  $\text{CaCO}_3$  & poisoned with S-Quinoline.

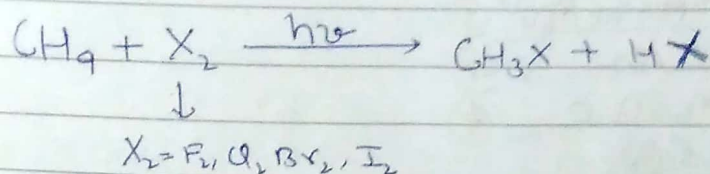






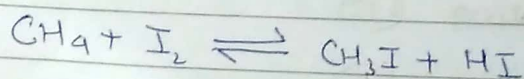
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- Preparation of Alkyl Halide from Alkane-



Rate of Reactivity  $\Rightarrow \text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

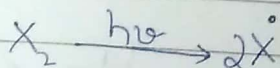
\* Fluorination is very slow & reversible.



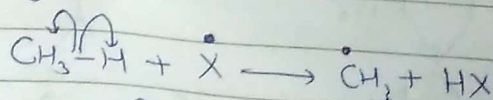
\* HI is consumed by reducing agent ( $\text{HNO}_3, \text{HIO}_4$ )

Mechanism -

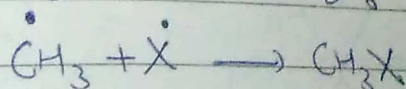
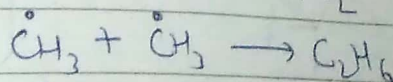
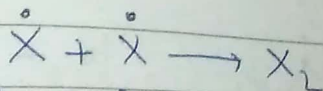
→ Initiation -



→ Propagation -



→ Termination -



Reactivity  $\Rightarrow \text{Cl}_2 > \text{Br}_2$

Selectivity  $\Rightarrow \text{Br}_2 > \text{Cl}_2$

For  $\text{Cl}_2 \rightarrow$

$$r_p : r_s : r_t = 1 : 3.8 : 5$$

$r_p$  = rate of rxn for primary

$r_s$  = rate of rxn for secondary

$r_t$  = rate of rxn for tertiary

For  $\text{Br}_2 \rightarrow r_p : r_s : r_t = 1 : 82 : 1600$

% of product on monohalogenation by removal of primary H  $\Rightarrow \frac{r_p n_p}{r_p n_p + r_s n_s + r_t n_t} \times 100$

% of product on monohalogenation by removal of secondary H  $\Rightarrow \frac{r_s n_s}{r_p n_p + r_s n_s + r_t n_t} \times 100$

% of product on monohalogenation by removal of tertiary H  $\Rightarrow \frac{r_t n_t}{r_p n_p + r_s n_s + r_t n_t} \times 100$

$n_p \Rightarrow$  no. of primary H

$n_s \Rightarrow$  no. of secondary H

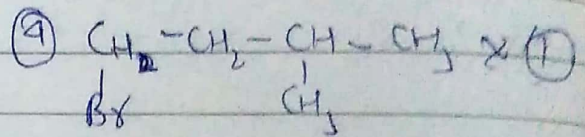
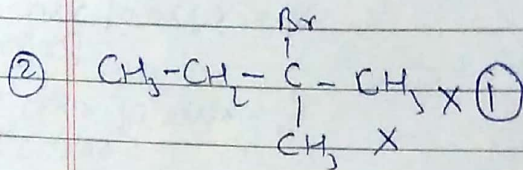
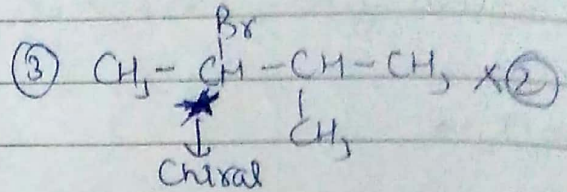
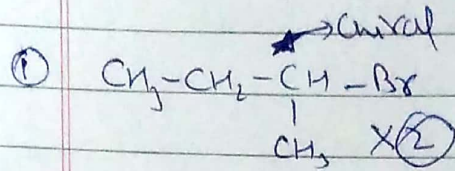
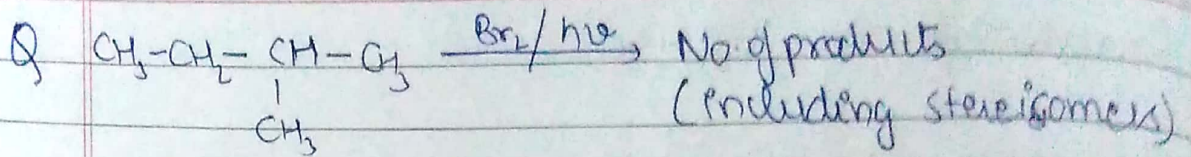
$n_t \Rightarrow$  no. of tertiary H

$r_p$  = rate of reactivity of p-H

$r_s$  = " " " " s-H

$r_t$  = " " " " t-H

$$\delta_p : \delta_s : \delta_t = 1 : 82 : 1600$$



Total Products = 6

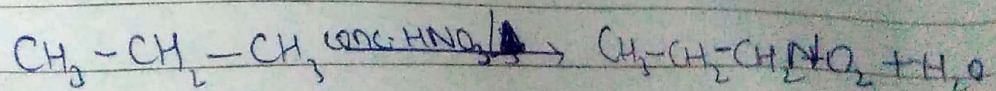
For ①  $\Rightarrow \frac{1 \times 6}{1 \times 9 + 2 \times 82 + 1 \times 1600} \times 100$    
 (No. of P.H for ① product)   
 (Total no. of P-Hydrogen)

For ②  $\Rightarrow \frac{1 \times 1600}{1 \times 9 + 2 \times 82 + 1 \times 1600} \times 100$

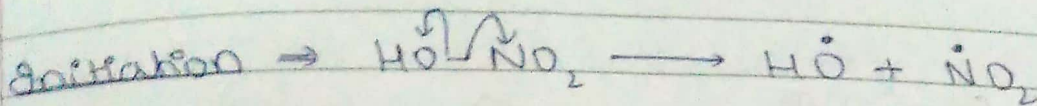
For ③  $\Rightarrow \frac{2 \times 82}{1 \times 9 + 2 \times 82 + 1 \times 1600} \times 100$

For ④  $\Rightarrow \frac{3 \times 82}{1 \times 9 + 2 \times 82 + 1 \times 1600} \times 100$

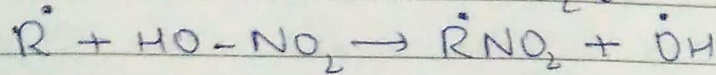
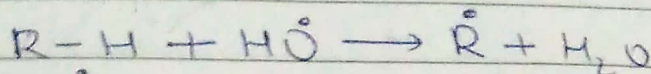
### Nitration of Alkanes $\rightarrow$ (Vapour Phase Nitration)



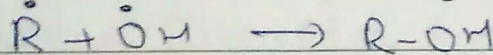
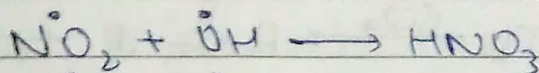
## Mechanism -



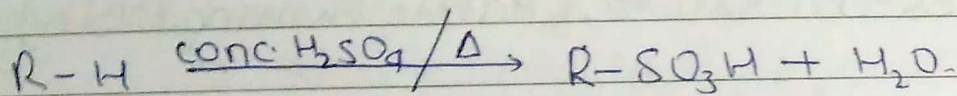
Propagation  $\rightarrow$



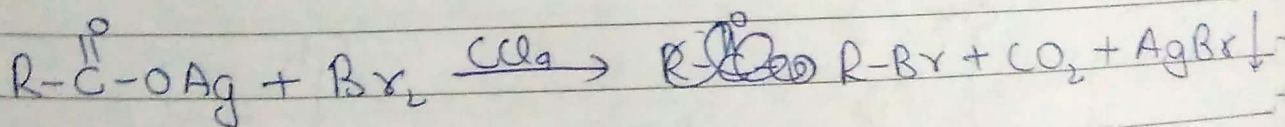
Termination  $\Rightarrow$



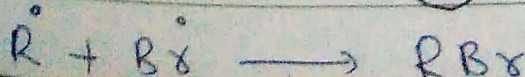
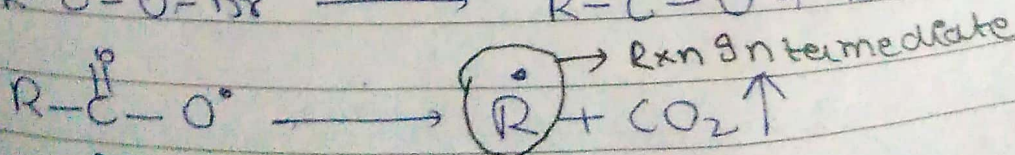
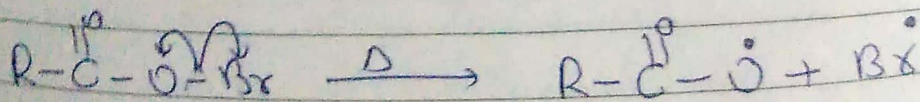
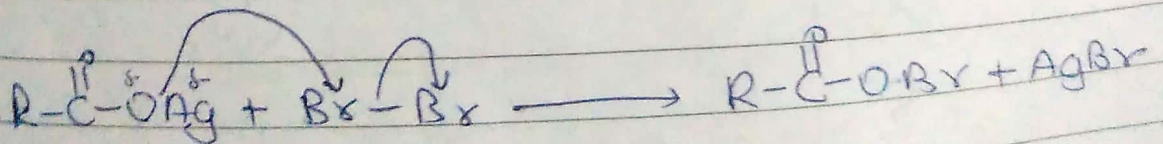
Sulphonation of Alkanes :- (Free Radical Mechanism)

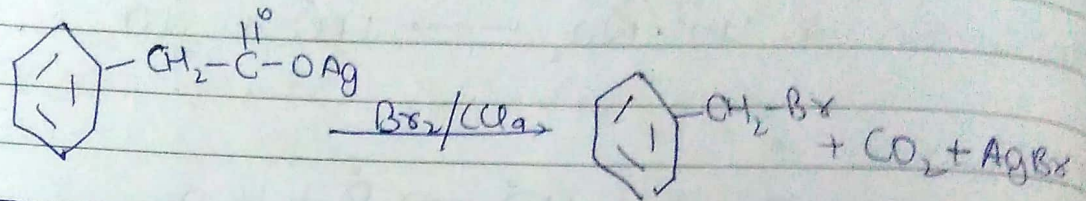
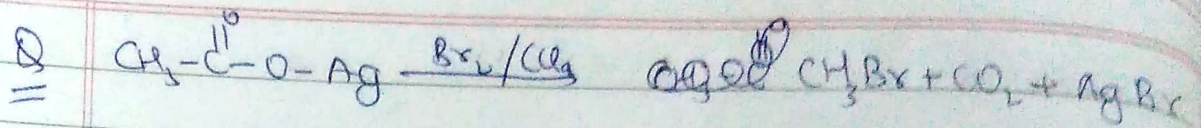


Preparation of Alkyl Halide from Silver Salt of Fatty Acid  $\Rightarrow$  (Hunsdiecker Rxn)

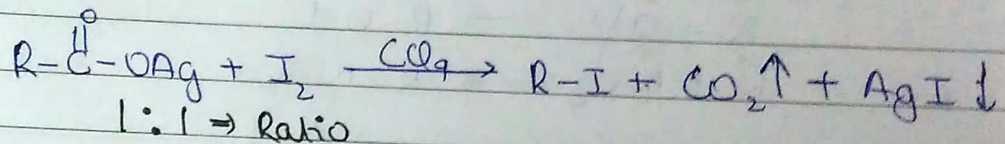
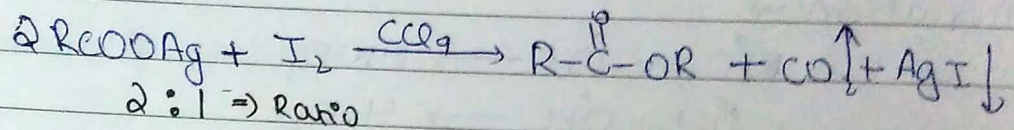


Mechanism  $\Rightarrow$

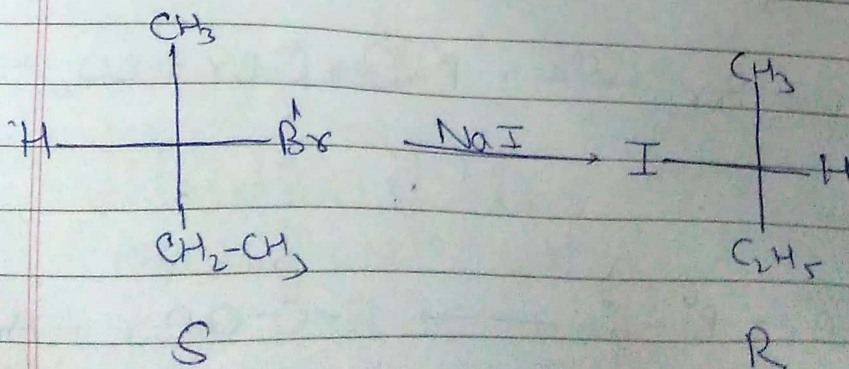
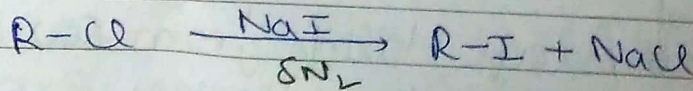
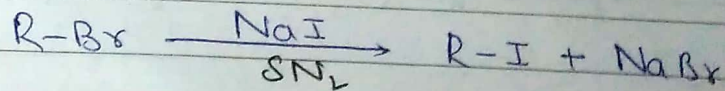




Simonni Rxn  $\Rightarrow$



Finkelstein Rxn  $\Rightarrow$  (Halide Exchange Rxn)



Rxn with alkyl halide  $\xrightarrow{\text{Dry Ag}_2\text{O}}$  form ether

$\xrightarrow{\text{Moist Ag}_2\text{O}}$  form alcohol

alc. NaOH or KOH  $\rightarrow$  SN<sub>1</sub>

alc. NaOH or KOH  $\rightarrow$  Elimination

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## Physical Properties of Alkyl Halide $\Rightarrow$

• Physical State, Colour & Odour  $\Rightarrow$

Alkyl halides are colourless when pure but bromide, & iodides develop colour when exposed to light

• Boiling Point  $\Rightarrow$  From same alkyl group, B.P order

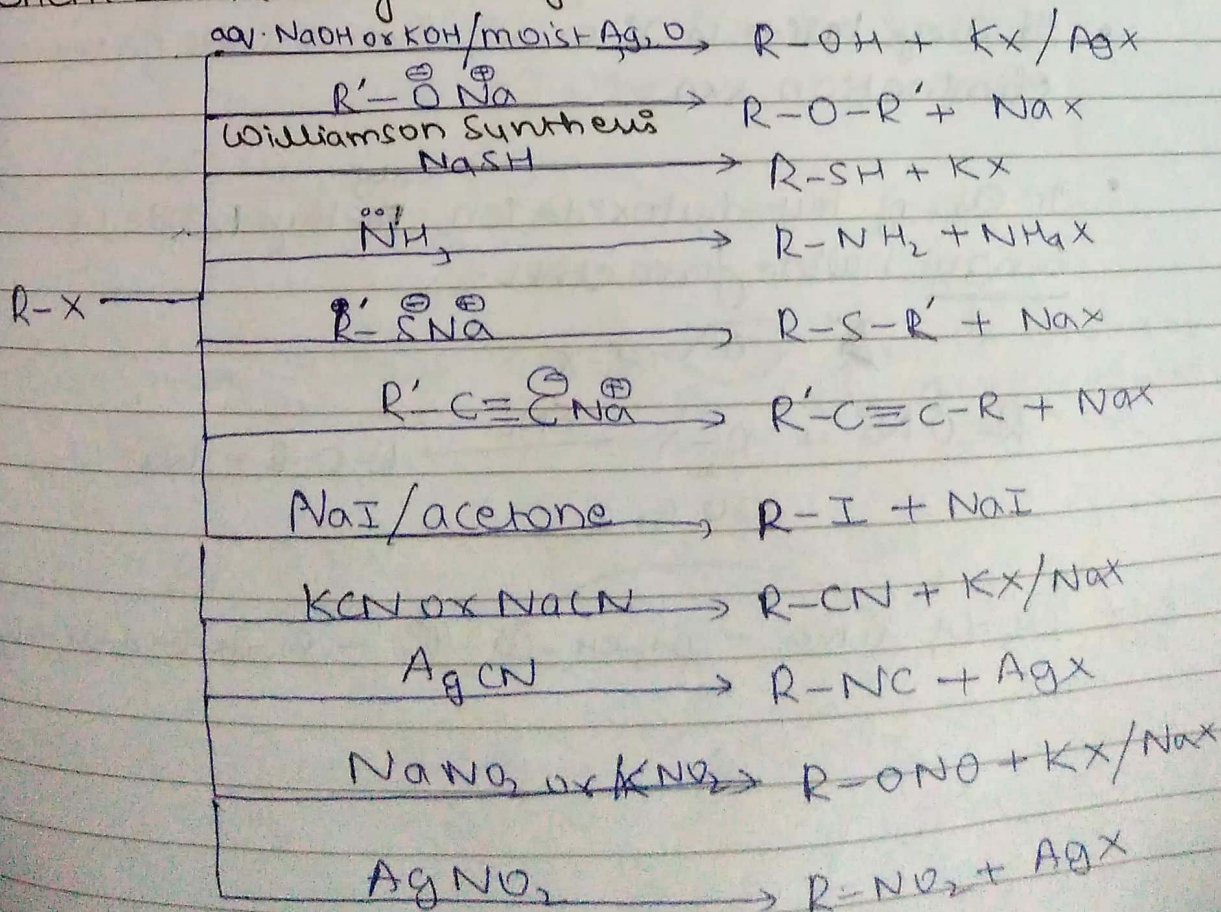


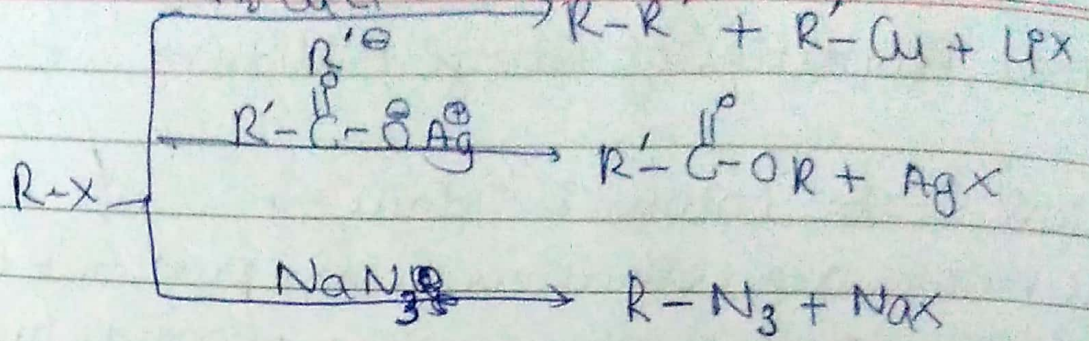
As branching increases, boiling point decreases

2

• Density  $\Rightarrow$  Alkyl fluorides & chlorides are generally lighter than water whereas alkyl bromide & iodide are heavier.

## Chemical Rxn of Alkyl Halide $\Rightarrow$





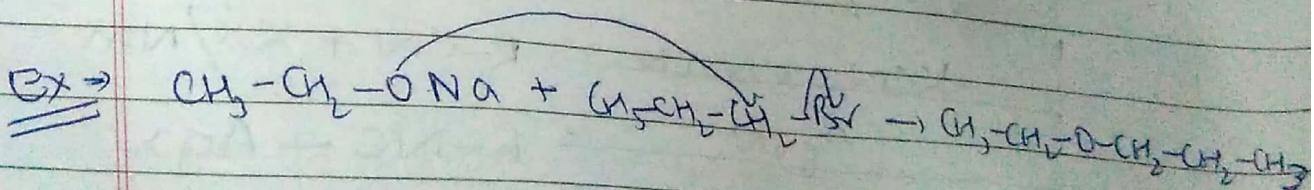
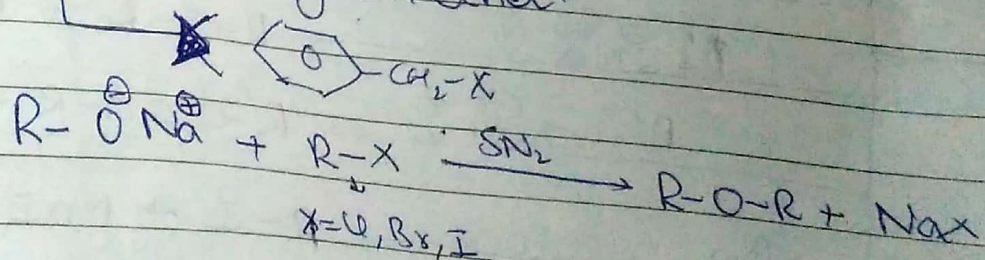
## Imp Williamson Synthesis Rxn $\Rightarrow$ ( $\text{S}_{\text{N}}2$ )

\* Rxn of sodium alkoxide with alkyl halide to form ether.

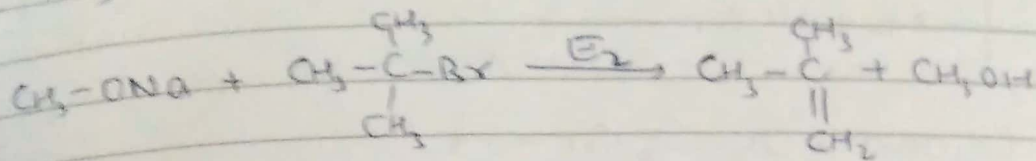
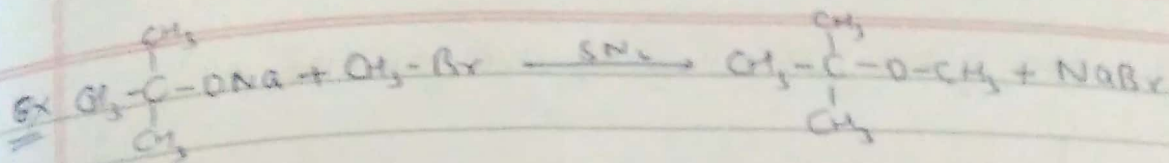
Imp Points to remember -

- Sodium alkoxide may be primary, secondary or tertiary while alkyl halide should only be primary. Then it will give substitution rxn to form ether.
- If alkyl halide is  $2^\circ$  or  $3^\circ$ , then it will give elimination rxn.

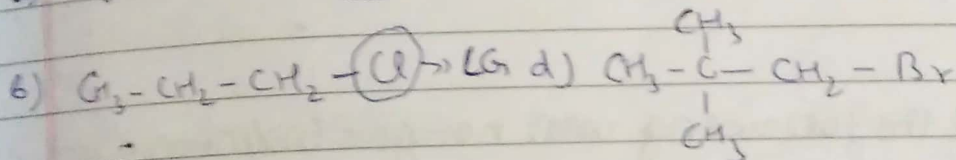
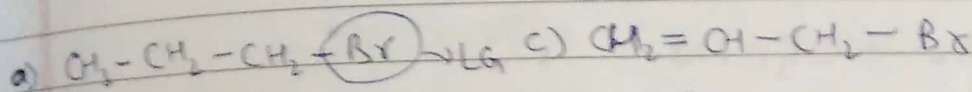
In case of tert-butoxide ion, <sup>only</sup> benzyl halide form ether.





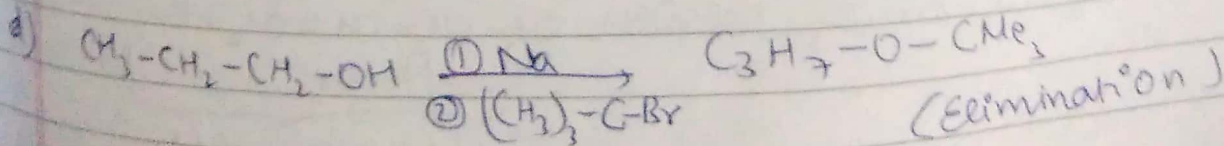
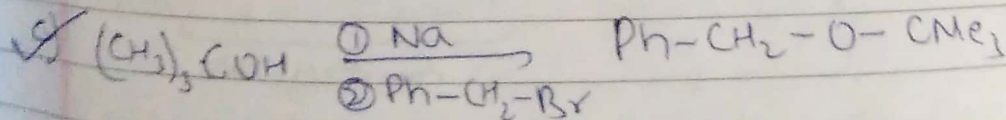
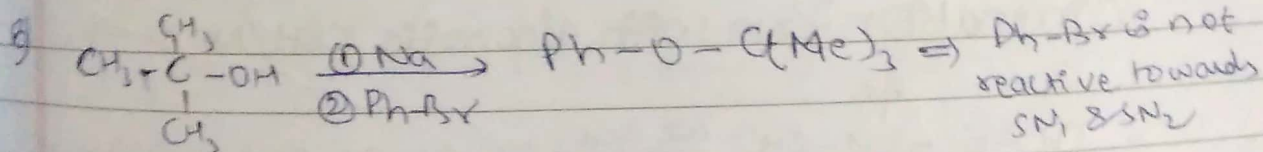
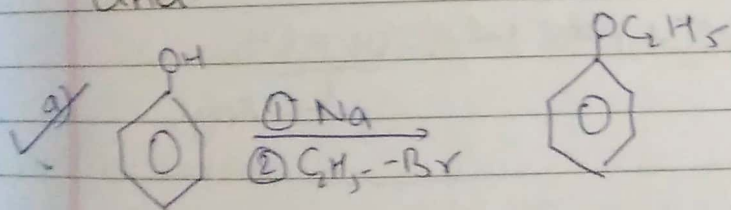


Q Write decreasing order of reactivity for Williamson Synthesis:

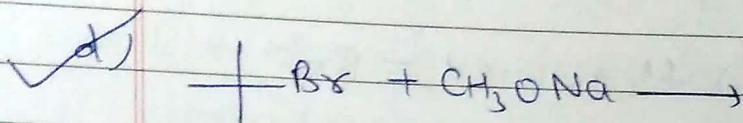
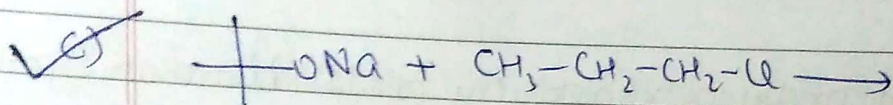
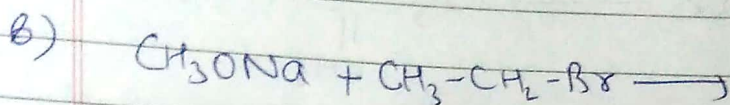
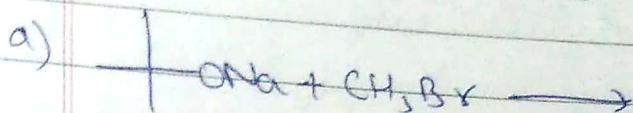


$\boxed{c > a > b > d}$

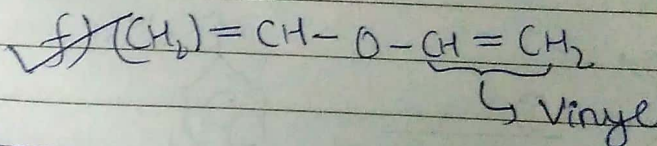
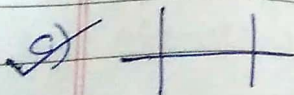
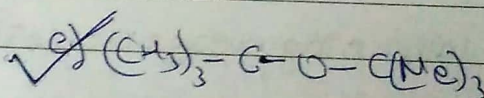
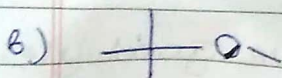
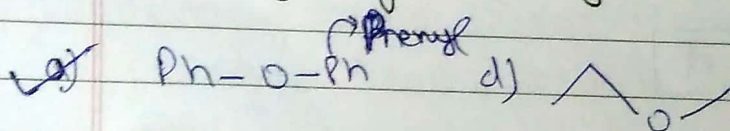
Q Which of the following reagent will give good yield of ether.



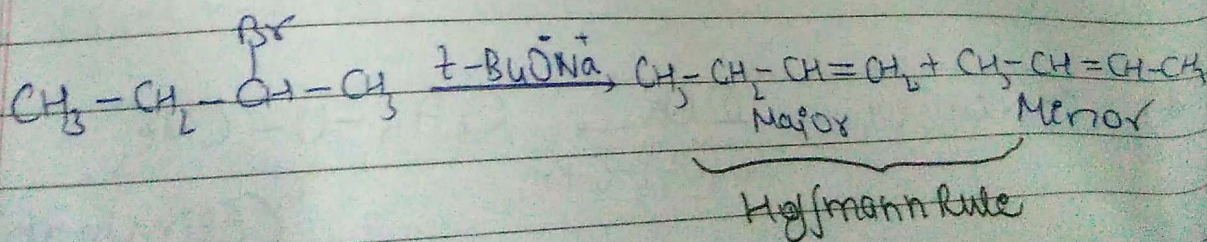
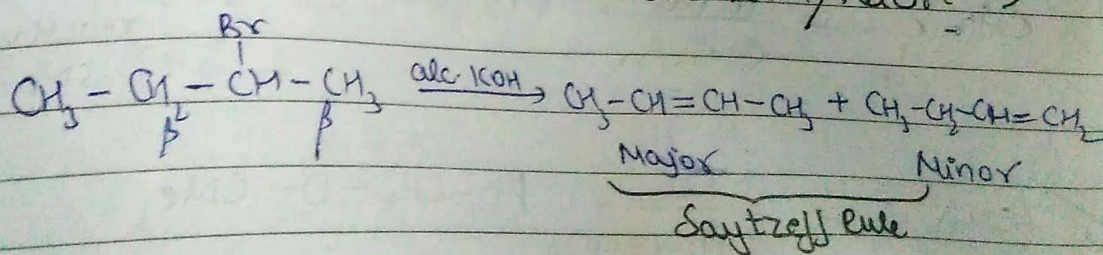
Q Which of the following do not give ether →

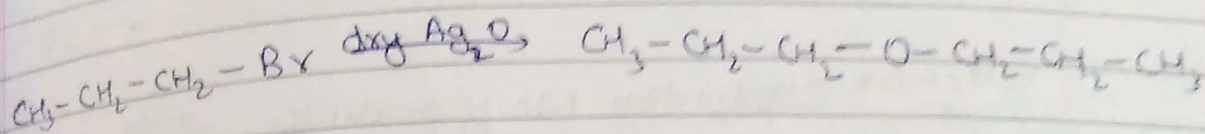
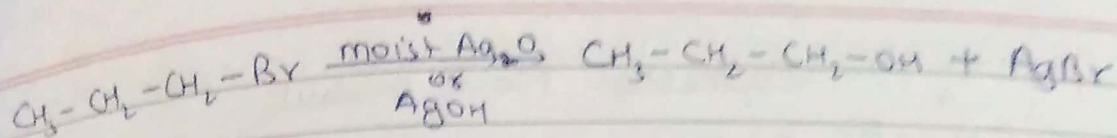


Q Which of the following will not give Williamson rxn

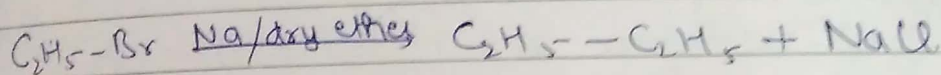
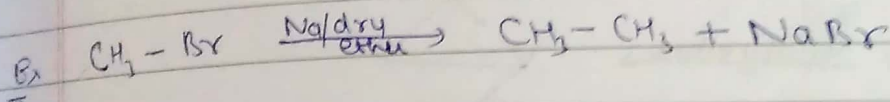
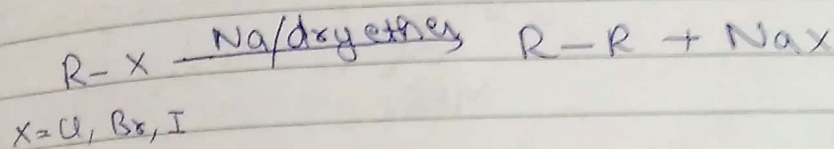


Elimination Rxn with alcoholic KOH/NaOH ⇒

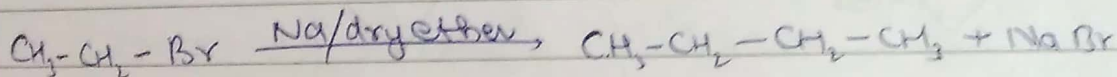




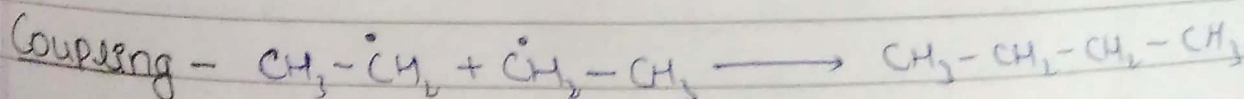
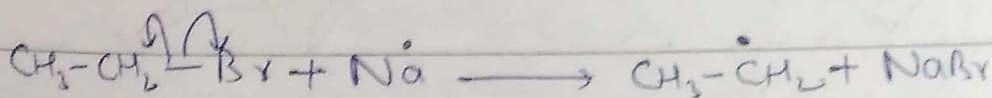
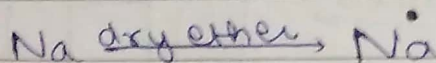
## Wurtz Reaction $\Rightarrow$



## Free Radical Mechanism -

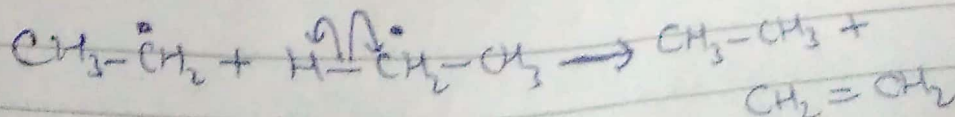


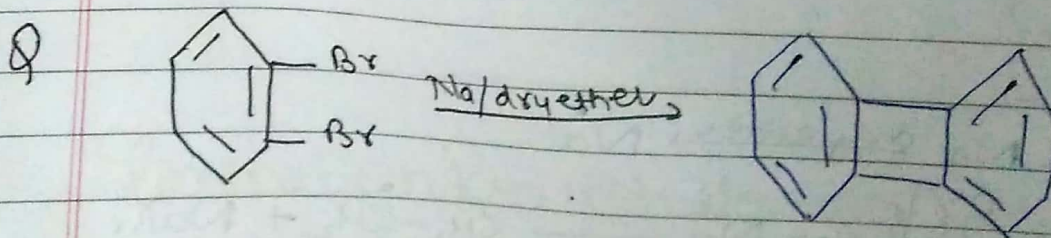
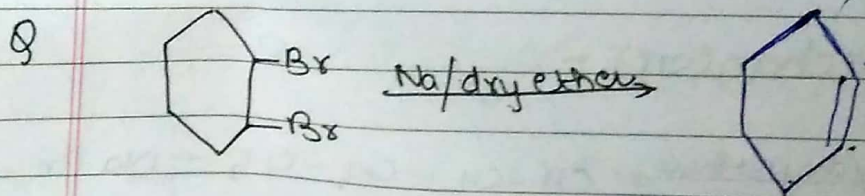
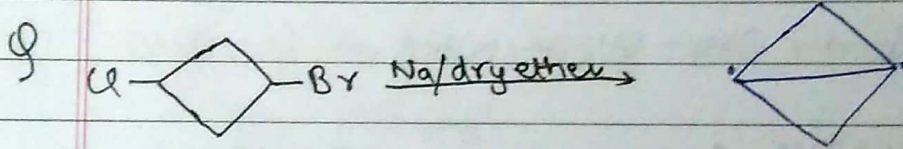
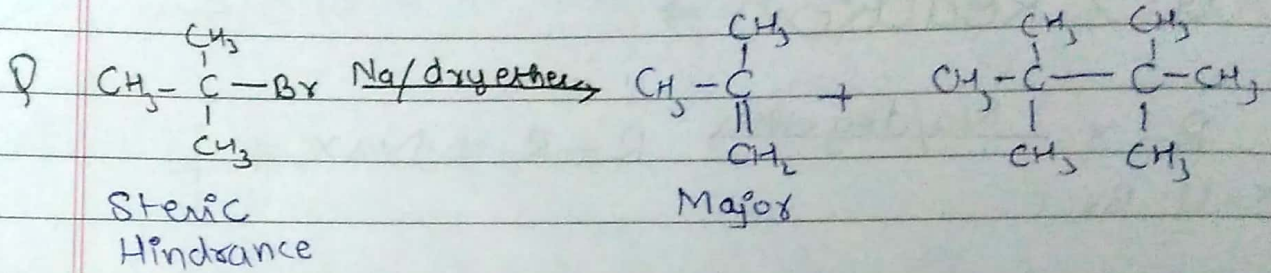
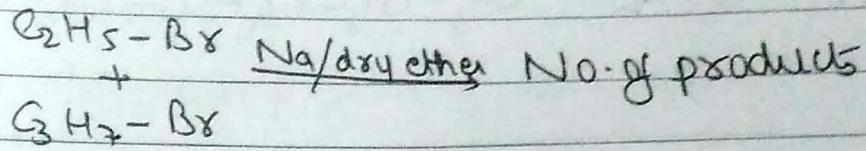
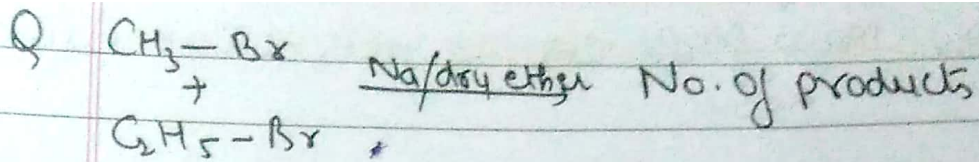
Mechanism -



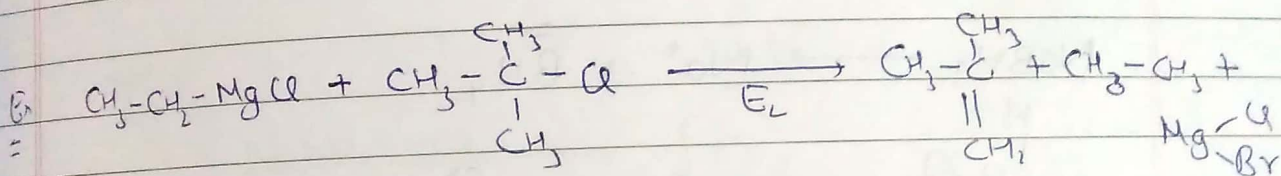
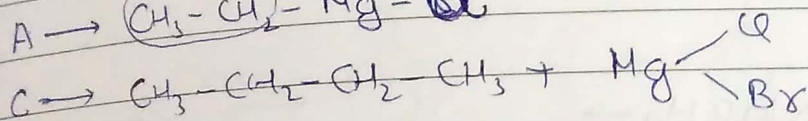
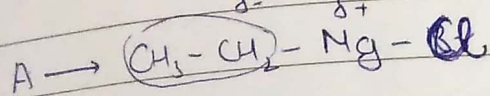
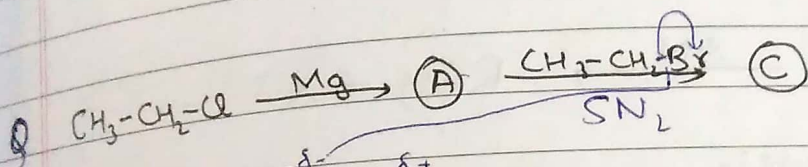
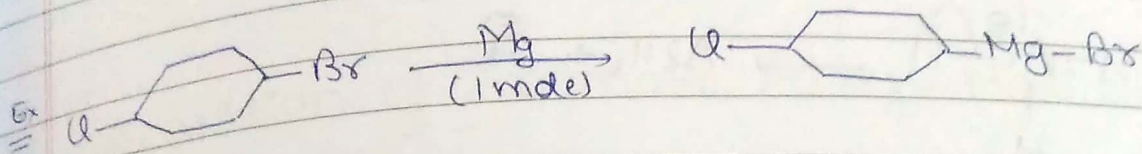
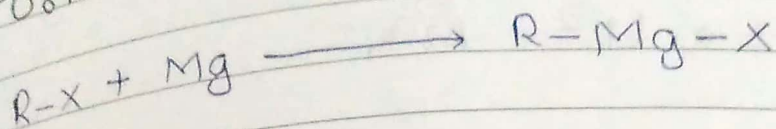
Cross Coupling -  $\times \rightarrow$  does not give  
 Different alkyl group is not present

Self Disproportionation -

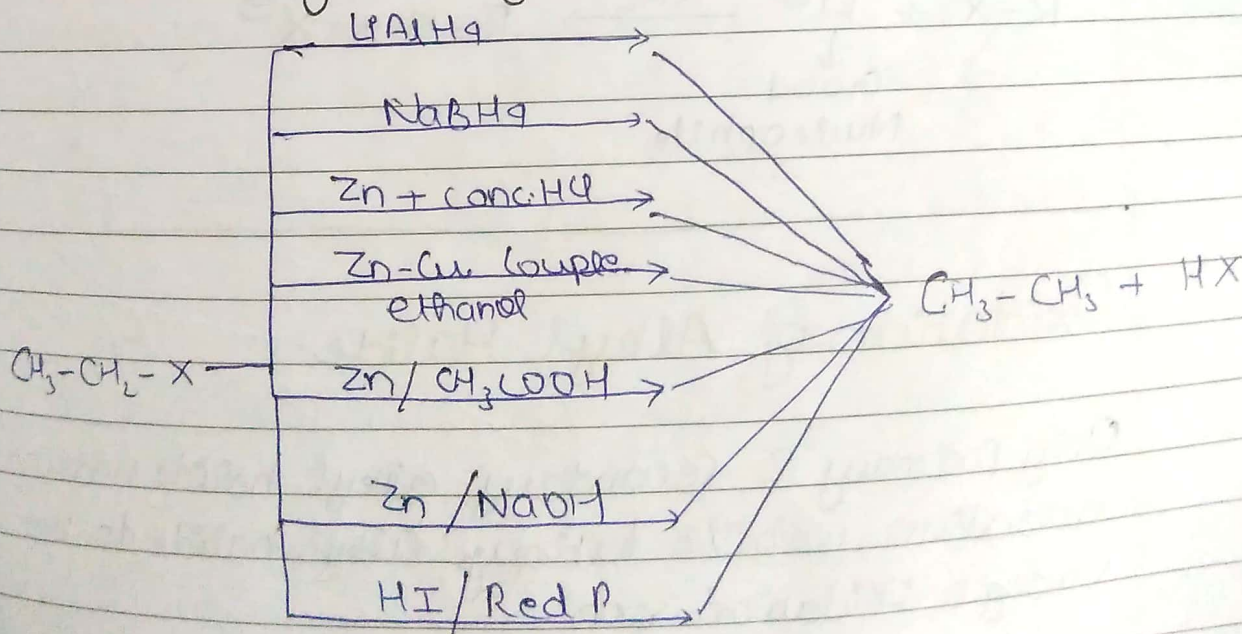




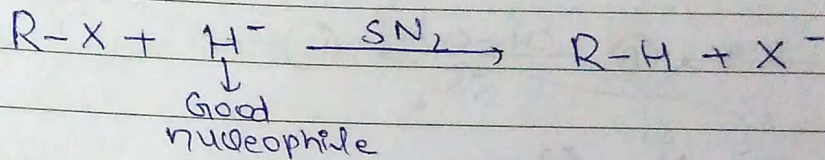
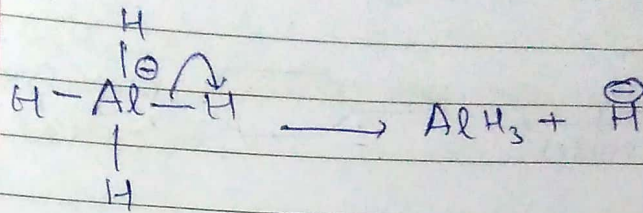
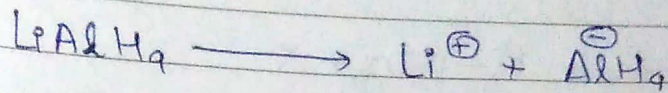
# Formation of Grignard Reagent



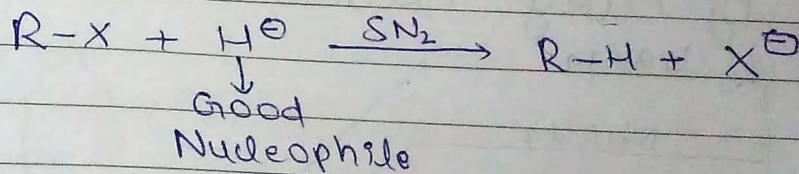
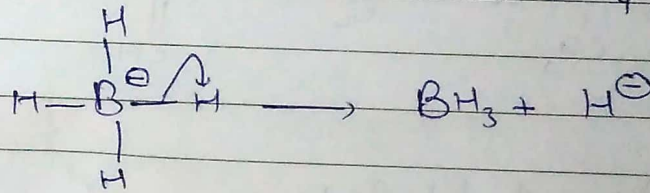
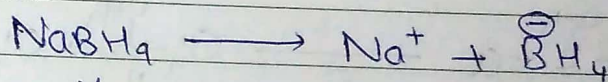
## Reduction of Alkyl Halide $\Rightarrow$



Rxn with  $\text{LiAlH}_4 \rightarrow$

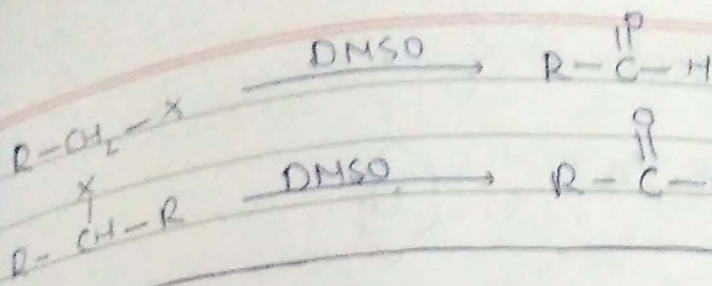


Rxn with  $\text{NaBH}_4 \rightarrow$

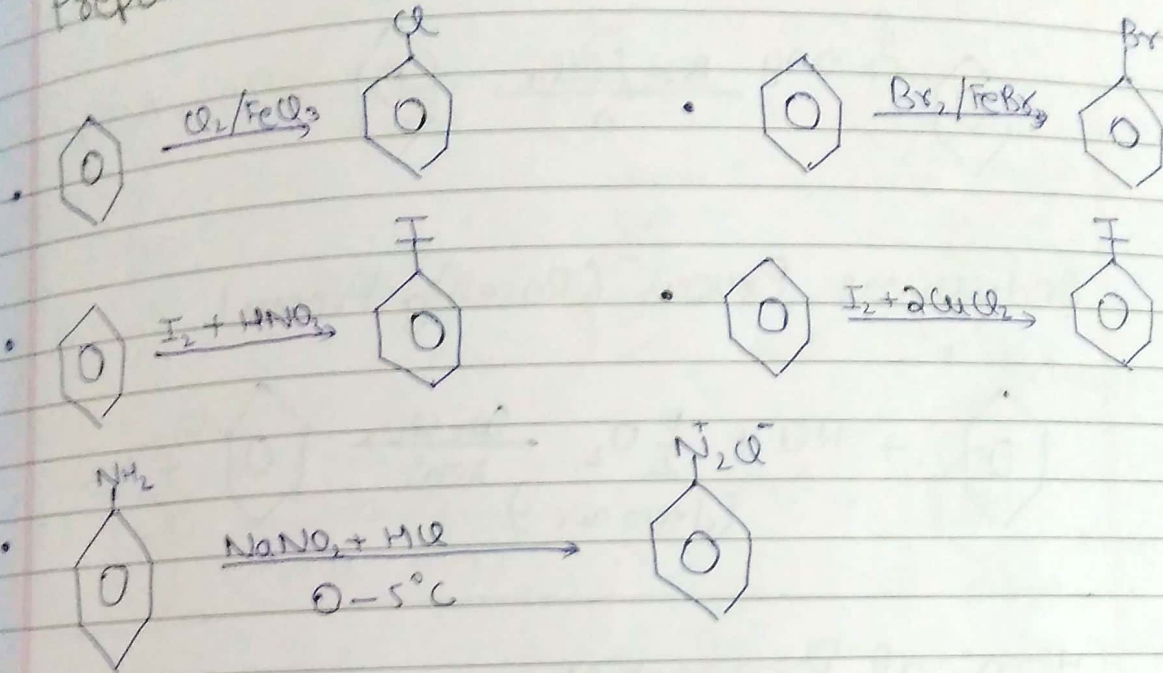


## Oxidation of Alkyl Halide-

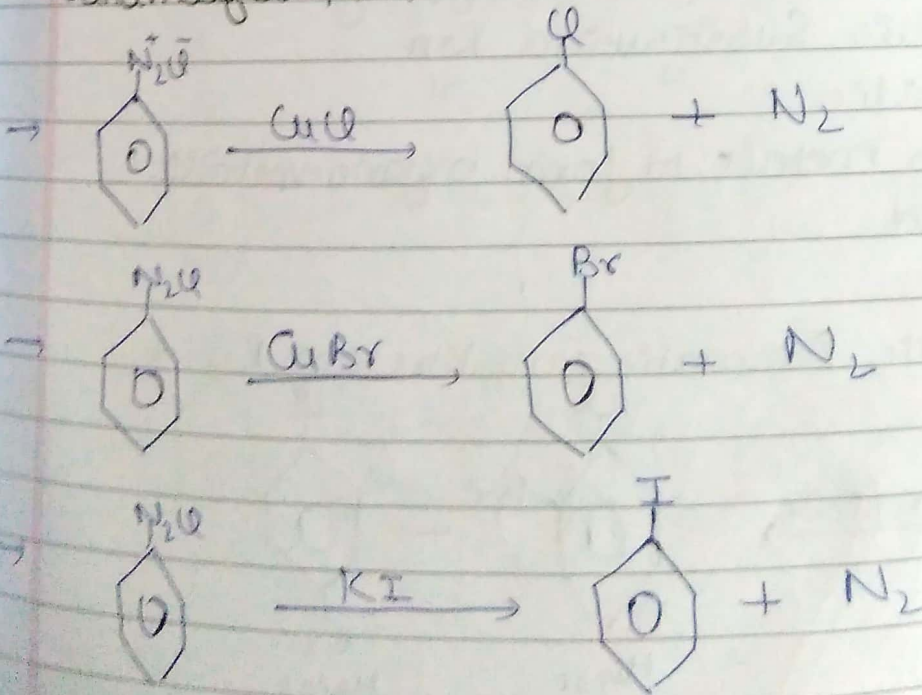
Only primary & secondary alkyl halide undergo oxidation while tertiary alkyl halide do not undergo oxidation rxn.

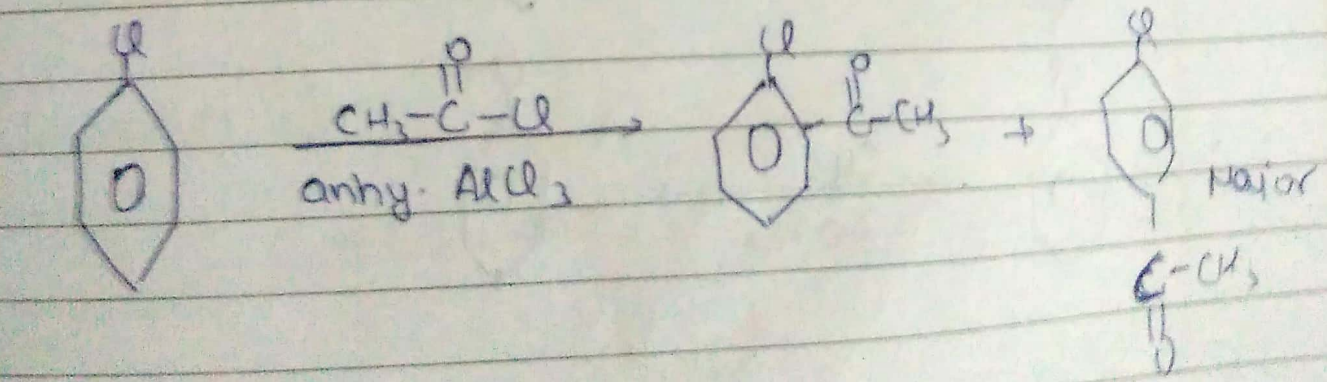
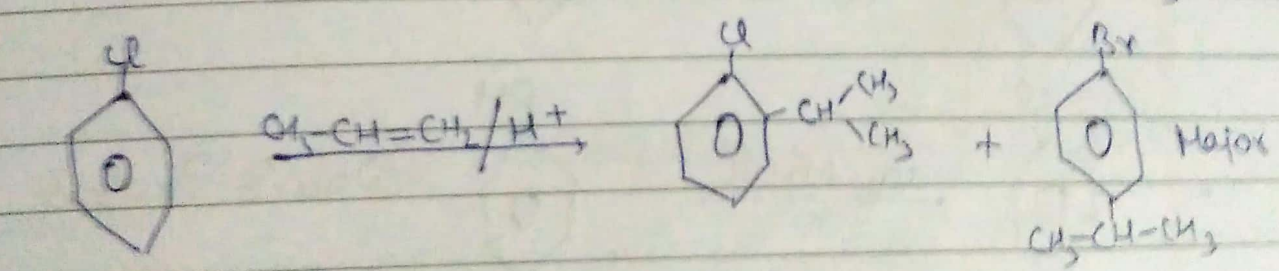
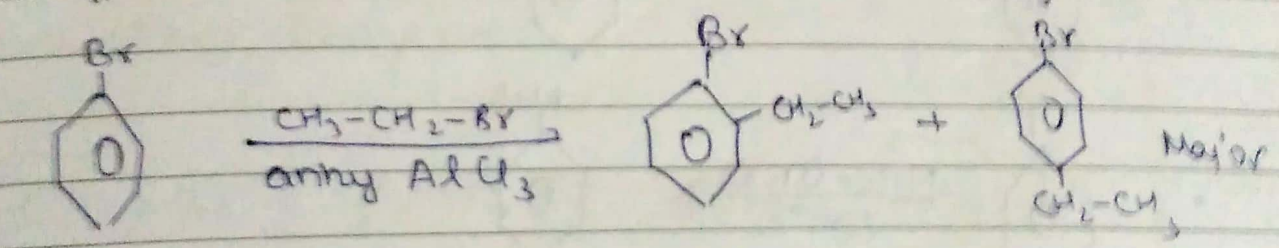
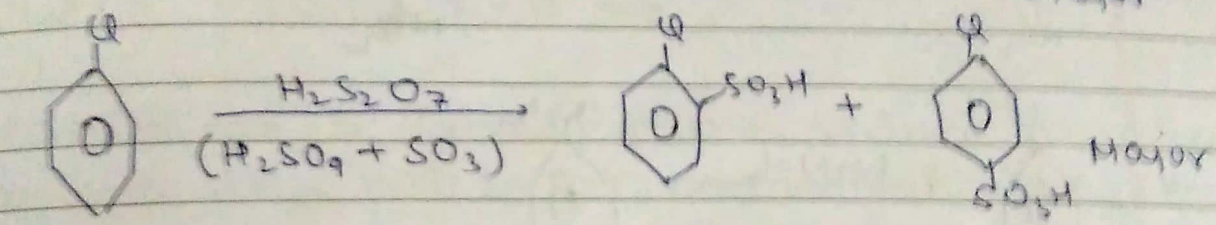
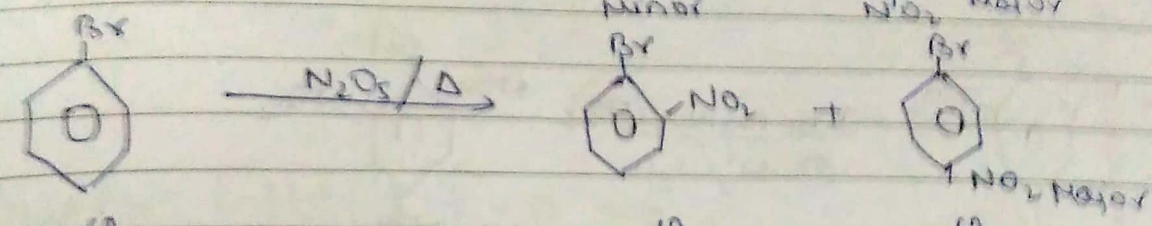
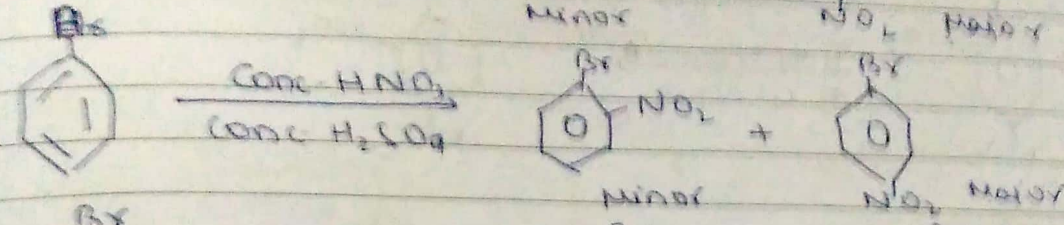
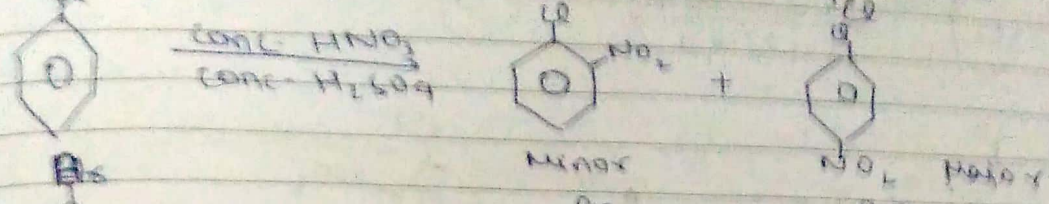
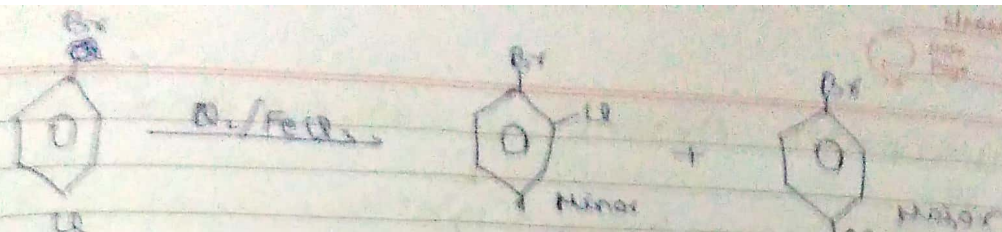


### Preparation of Aromatic Alkyl Halide $\rightarrow$



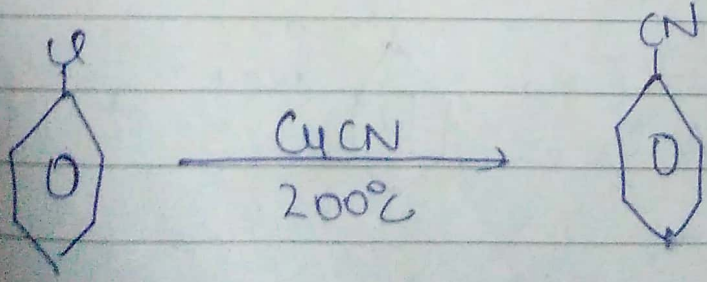
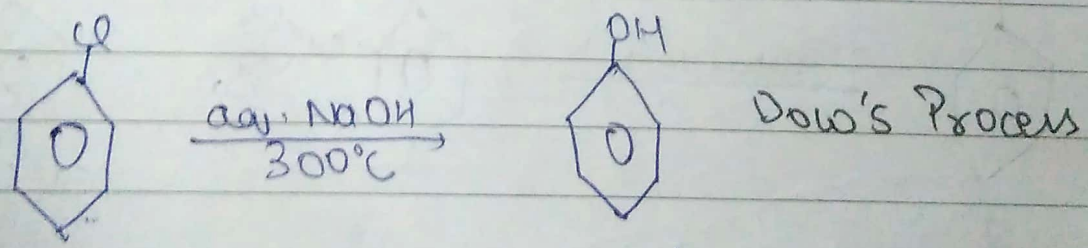
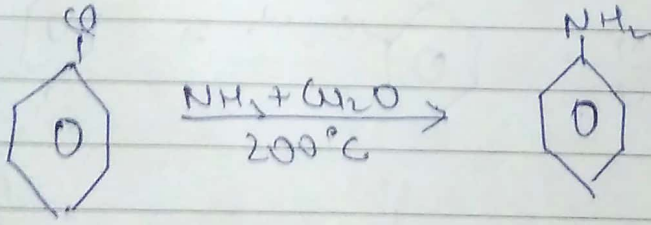
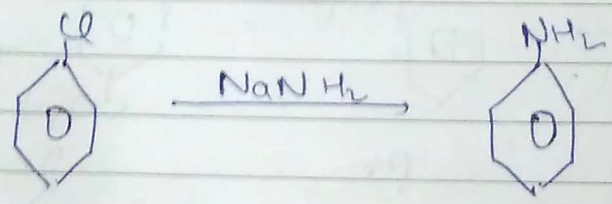
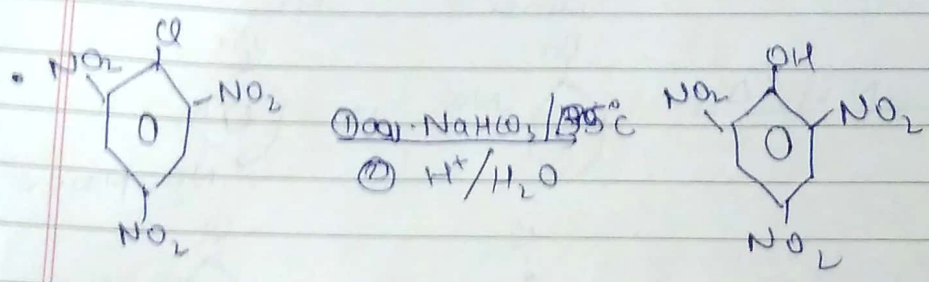
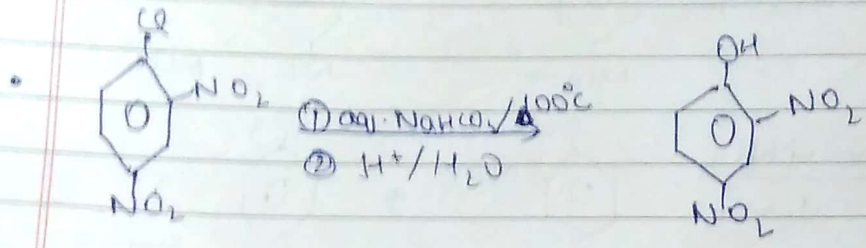
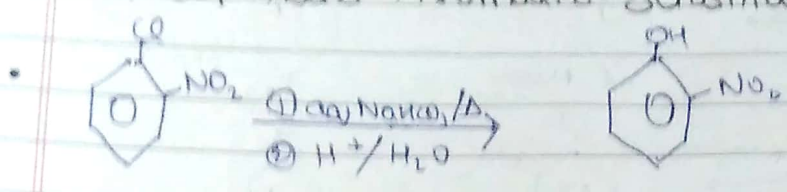
### Sandmeyer Rxn $\Rightarrow$



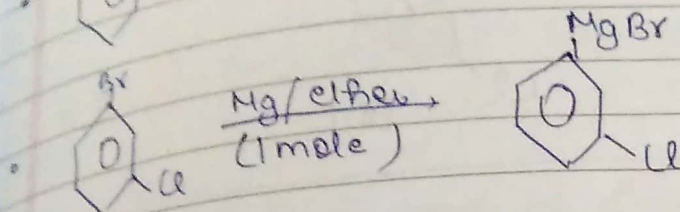
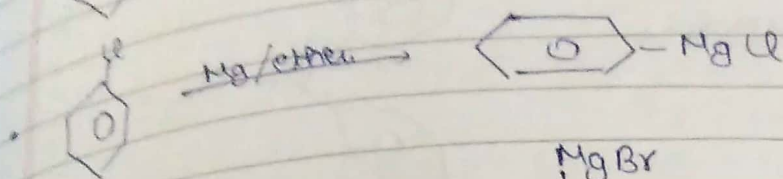
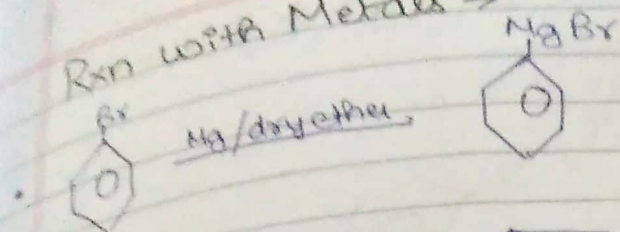




# Nucleophilic Aromatic Substitution Reaction $(A_{\text{R}}\text{SN}_2)$

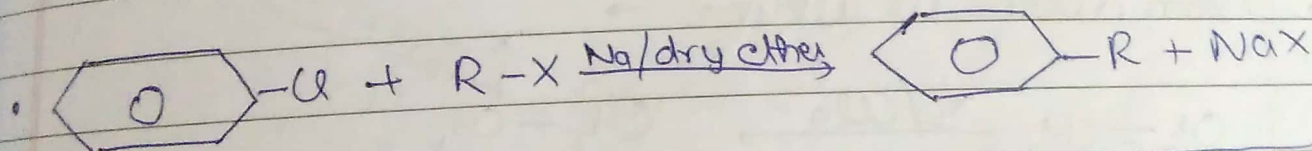
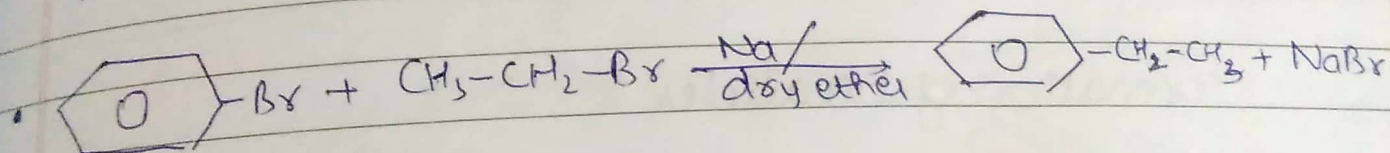


Rxn with Metals  $\rightarrow$

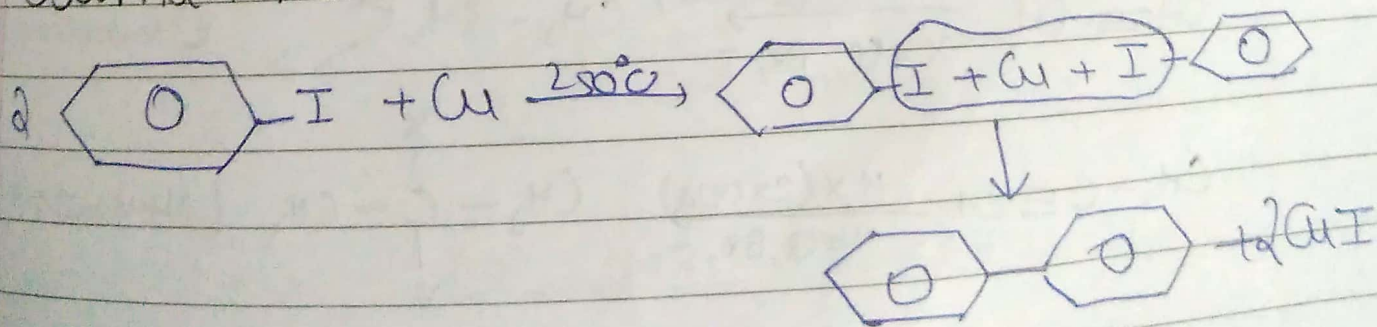


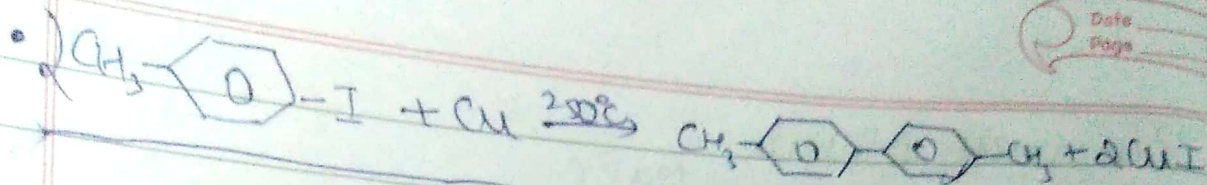
Wurtz Fittig Rxn  $\Rightarrow$

• Chloro Benzene & Bromo Benzene undergo coupling rxn with alkyl halide in presence of Na/dry ether gives alkyl benzene.

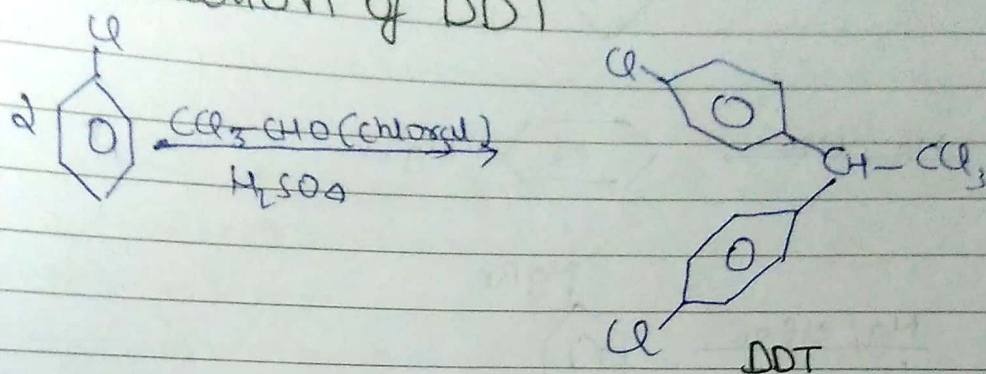


Ullmann Rxn

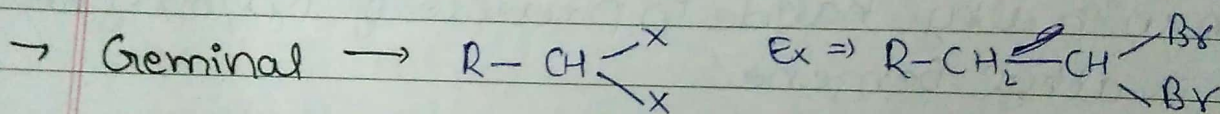
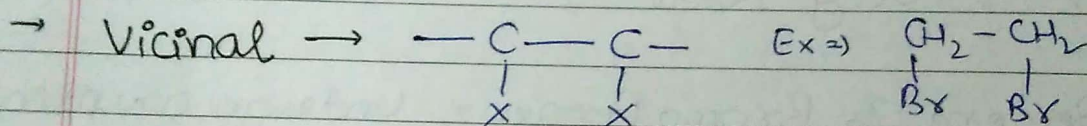




### Formation of DDT

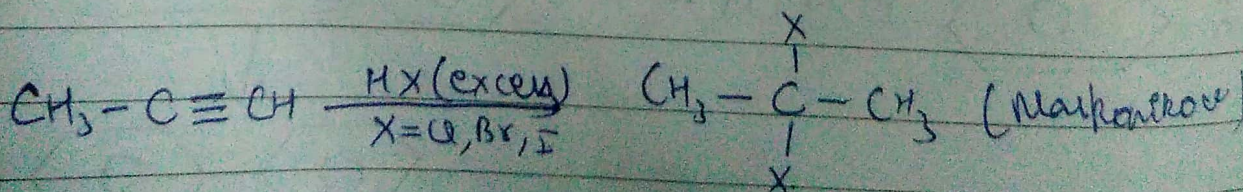
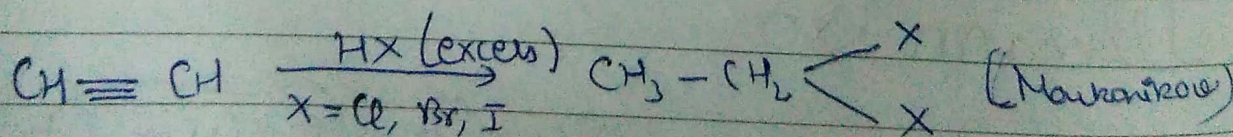
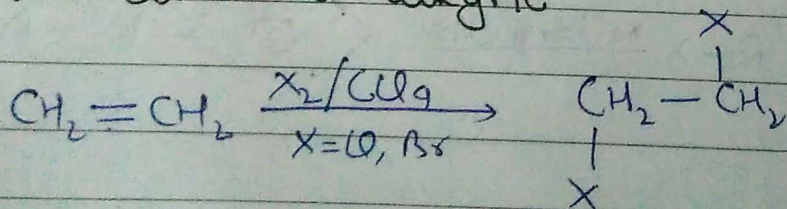


### Polyhalides $\Rightarrow$

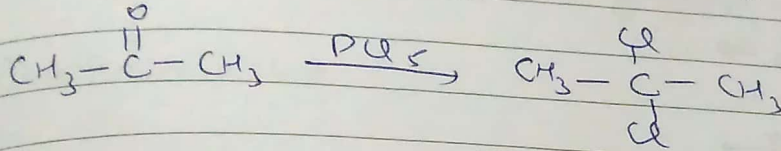
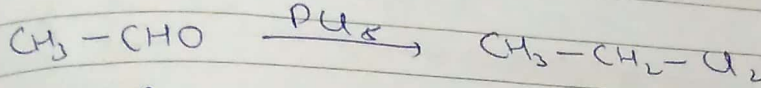
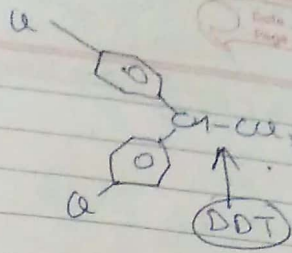
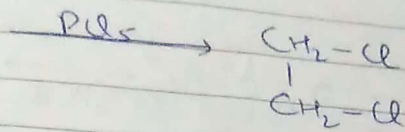
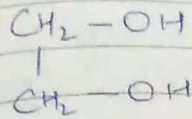


### Formation of Dihalides

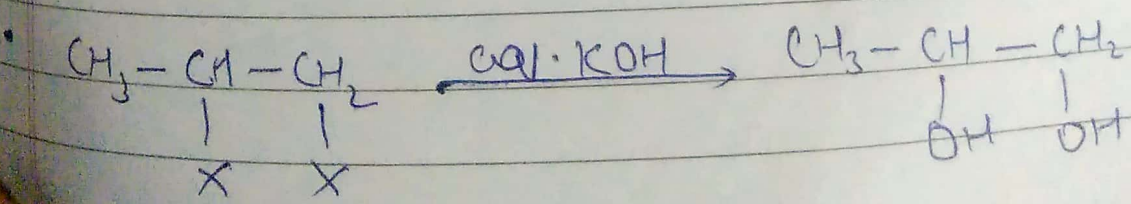
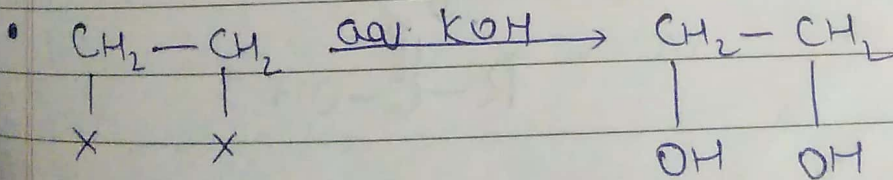
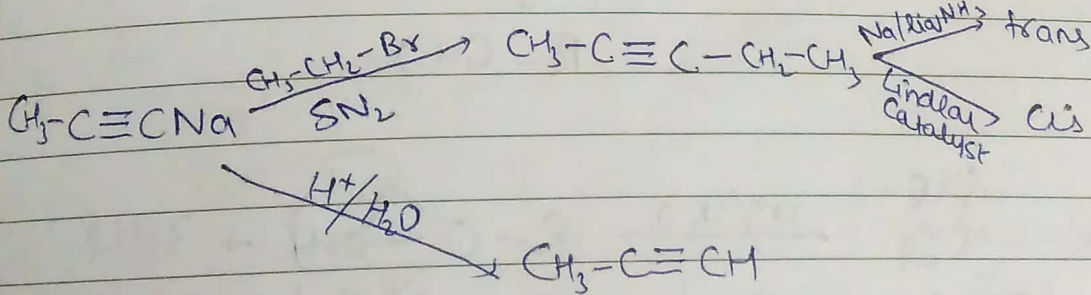
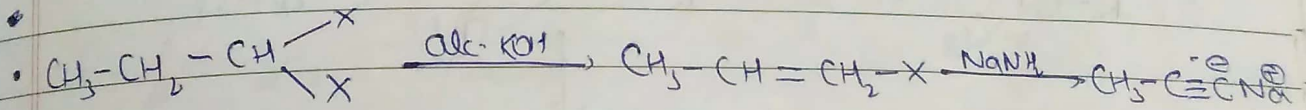
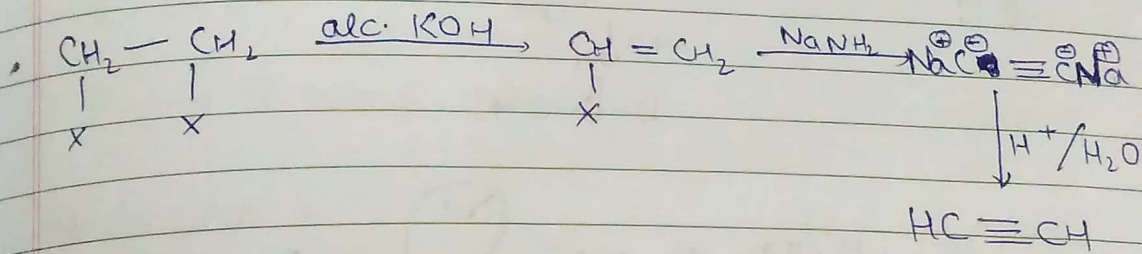
• From alkene or alkyne  $\rightarrow$

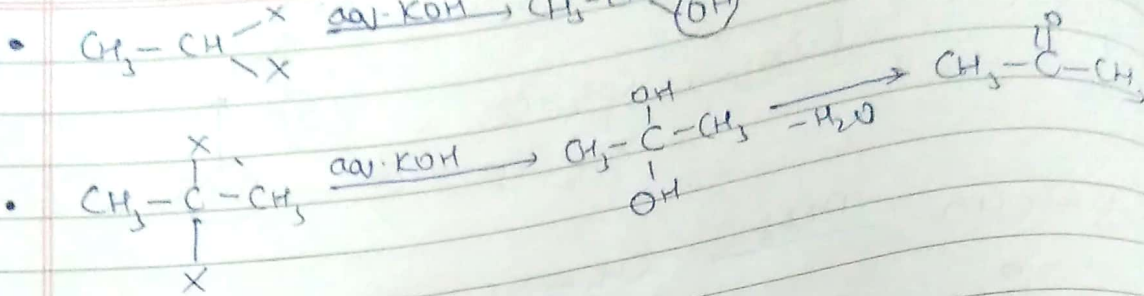
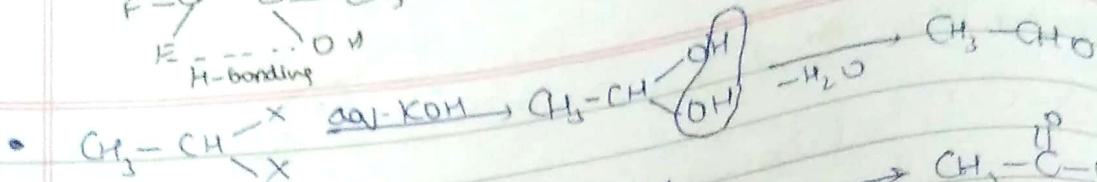
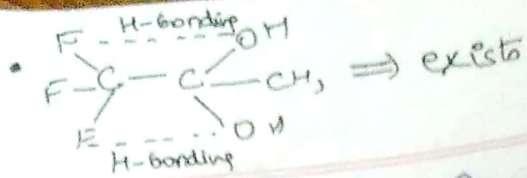


From PCl<sub>5</sub> →

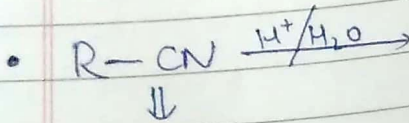


### Chemical Reactions of Dihalides →

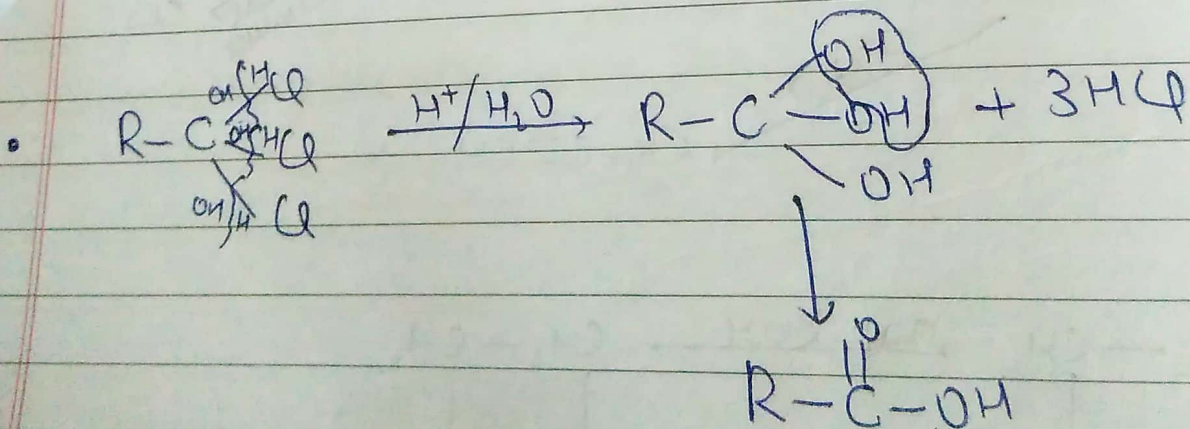
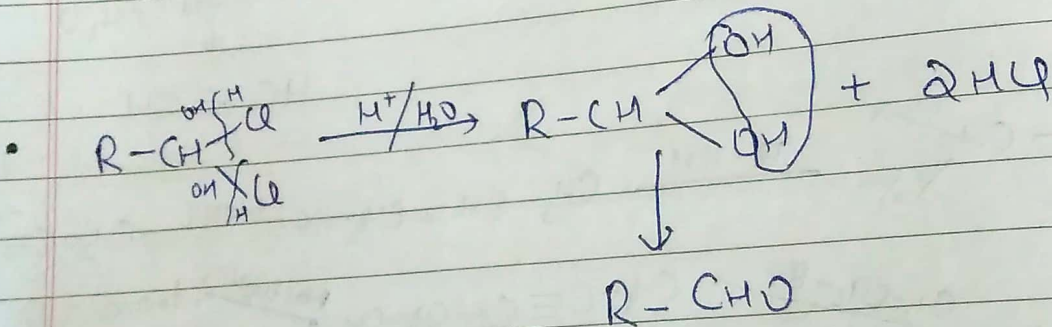
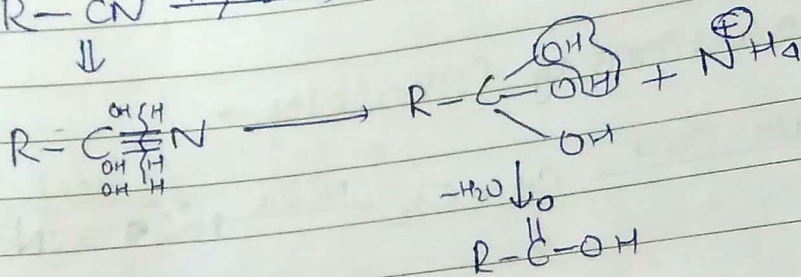




Hydrolysis  $\Rightarrow$



TRICK

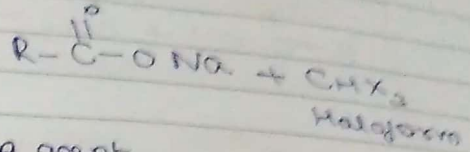
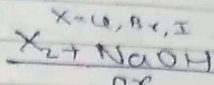
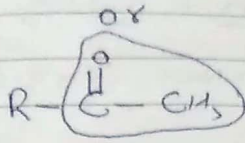
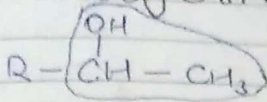


$\text{CHCl}_3$   
Chloroform  
(gas)

$\text{CHBr}_3$   
Bromoform  
(liquid)

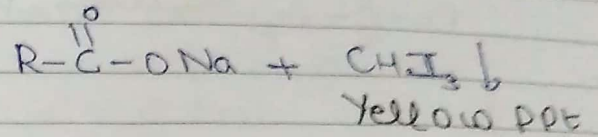
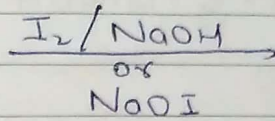
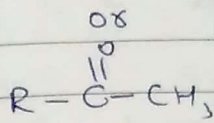
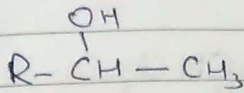
$\text{CHI}_3$   
Iodoform  
(solid)  
(yellow ppt)

## Haloform Reaction $\rightarrow$



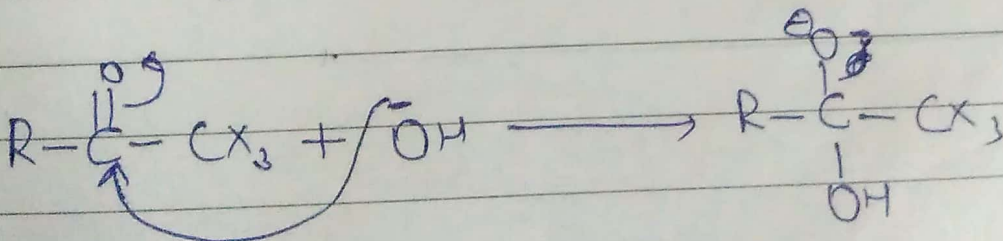
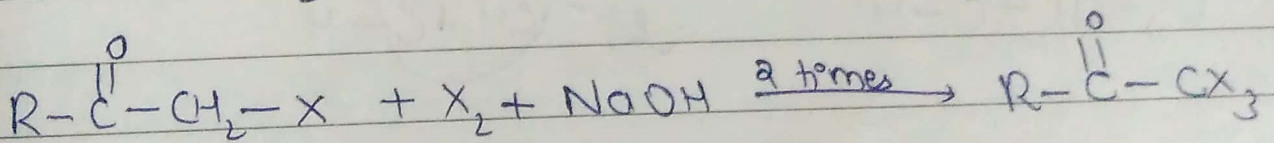
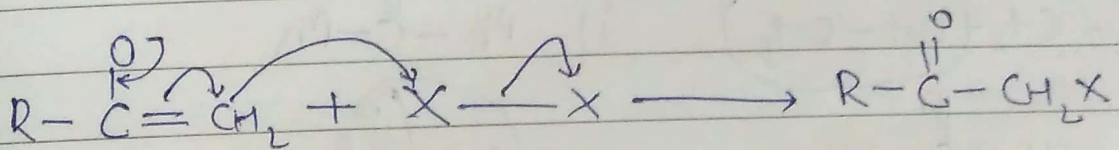
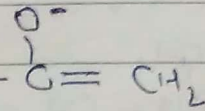
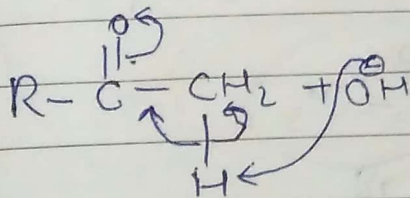
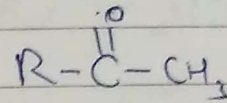
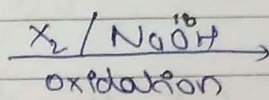
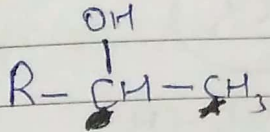
NaOX  
 $\rightarrow$  oxidising agent

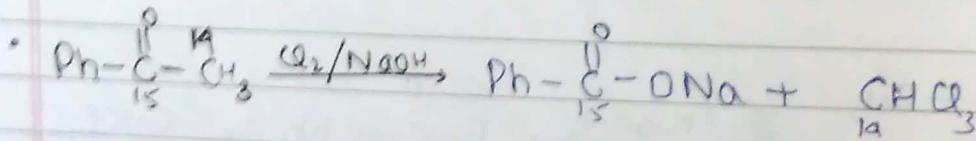
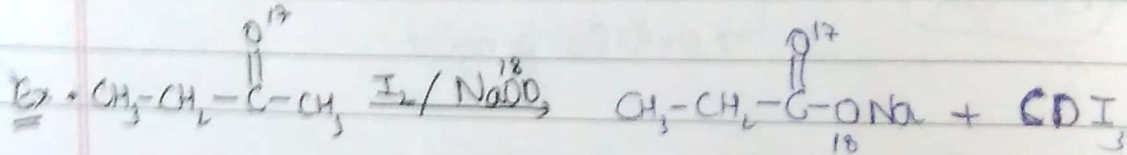
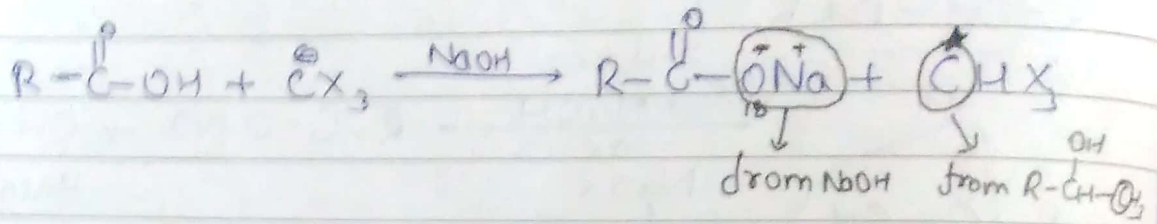
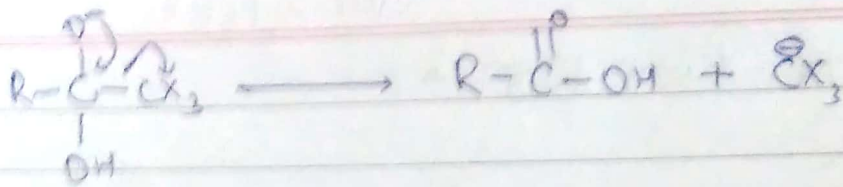
## Haloform Test $\rightarrow$



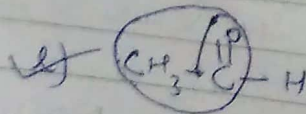
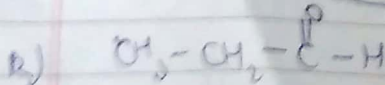
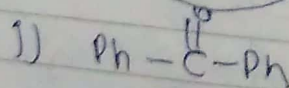
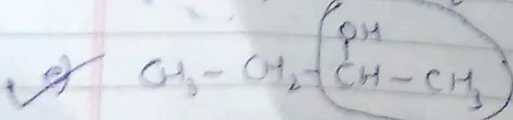
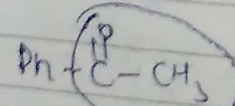
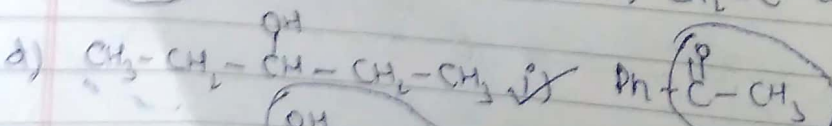
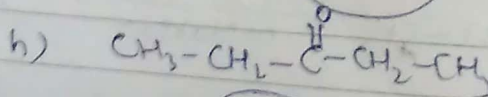
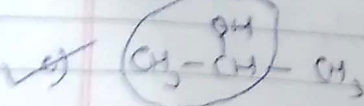
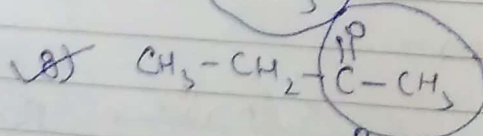
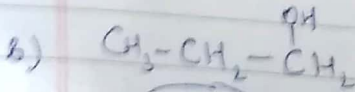
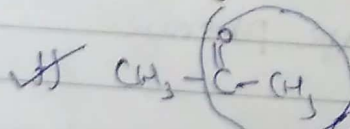
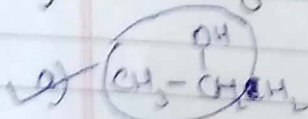
$\text{R} \rightarrow \text{H, alkyl, phenyl.}$

## Mechanism -

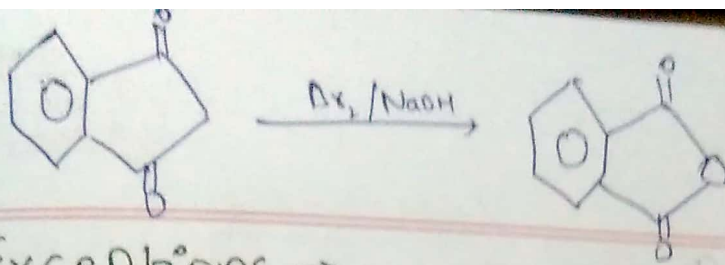




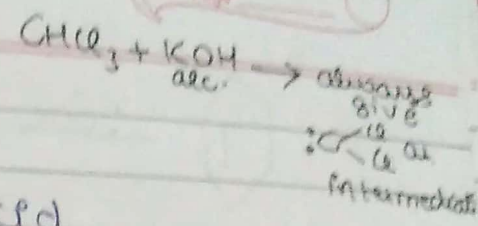
Q Which of the following can give iodoform test?



Q



classmate  
Date \_\_\_\_\_  
Page \_\_\_\_\_

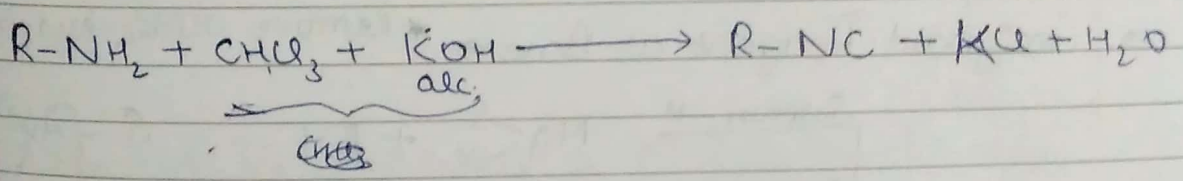


### Exceptions $\Rightarrow$

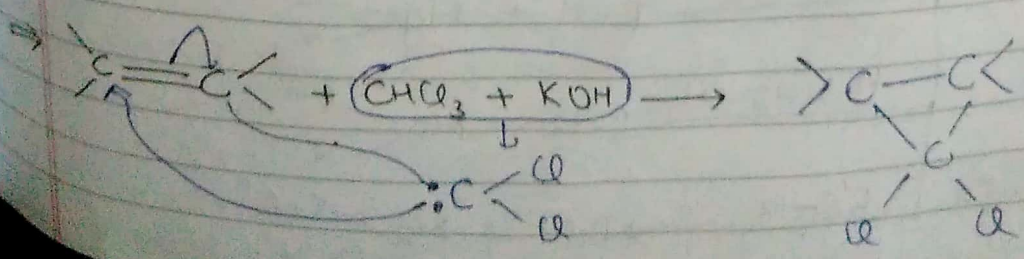
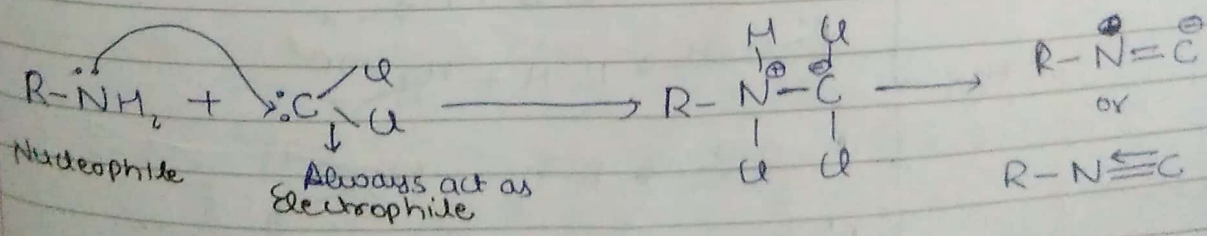
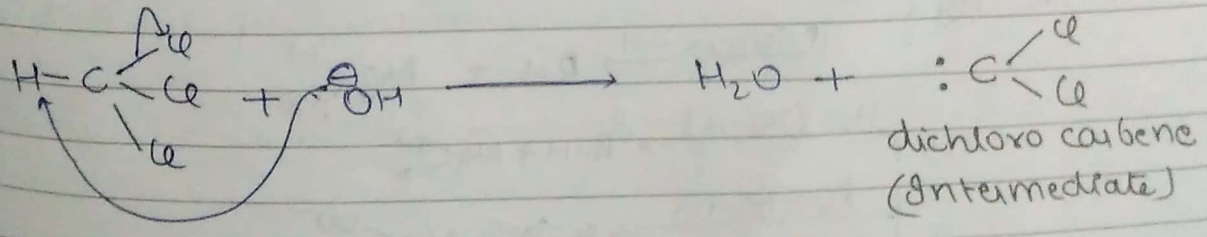
- $\text{CH}_3 - \overset{\text{OH}}{\text{CH}} - \text{COOH} \Rightarrow$  Lactic Acid
- $\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - \text{COOH} \Rightarrow$  Pyruvic Acid

### Carbylamine Test

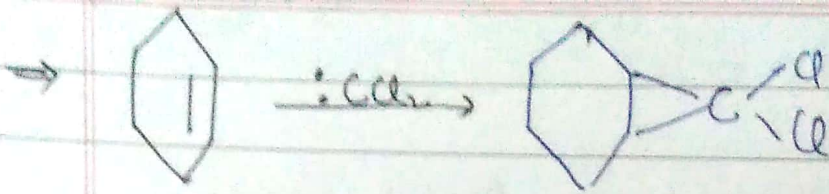
- It is given ~~by~~ only by primary amines.
- This test is also given by aromatic  $1^\circ$  amines
- $2^\circ$  &  $3^\circ$  amines do not give this test.



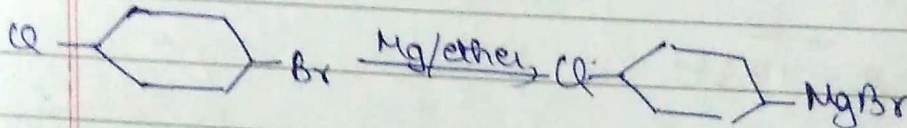
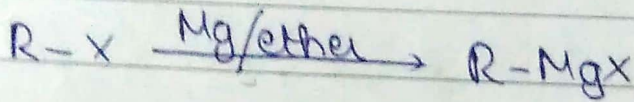
### Mechanism -





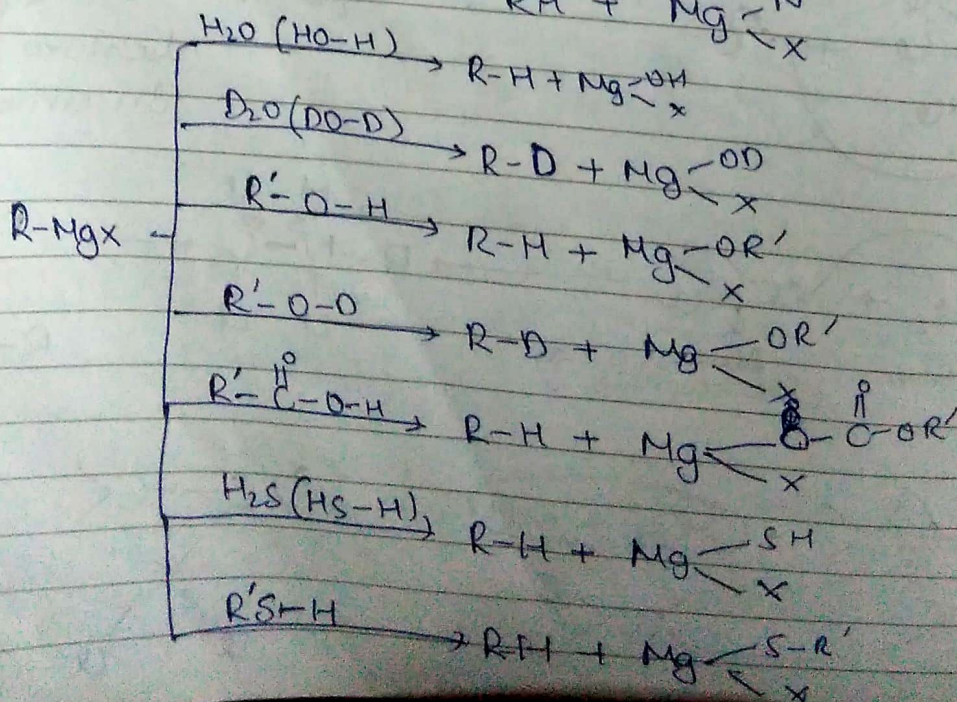
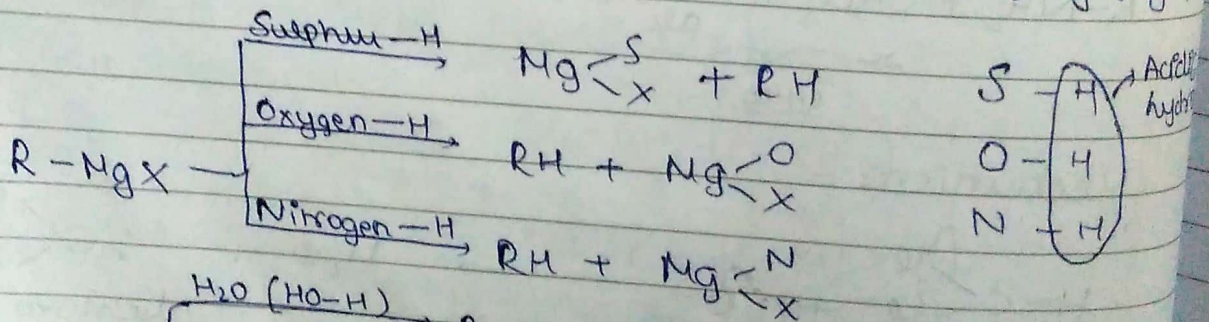


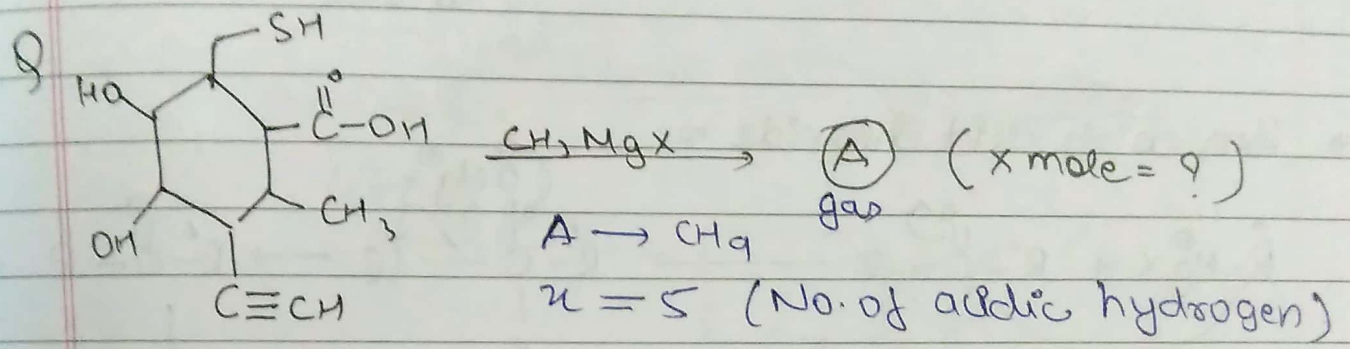
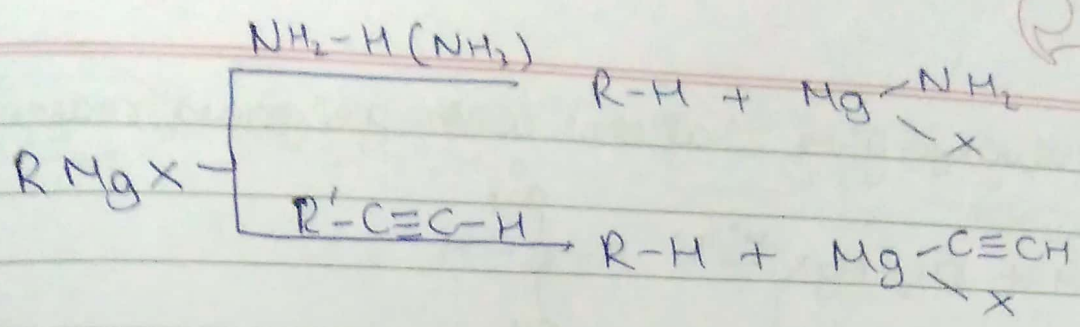
# Grignard Reagent



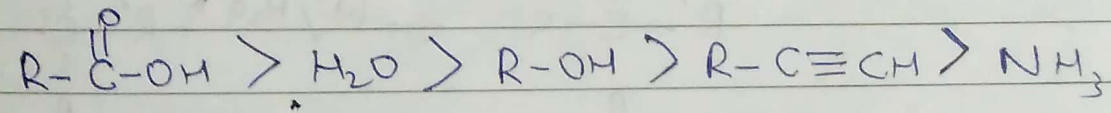
- \* Grignard Reagent can act both as  $\rightarrow$
- $\rightarrow$  Nucleophile
- $\rightarrow$  Base

$\Rightarrow$  Grignard Reagent as Base  $\Rightarrow$  \* Remove acidic hydrogen



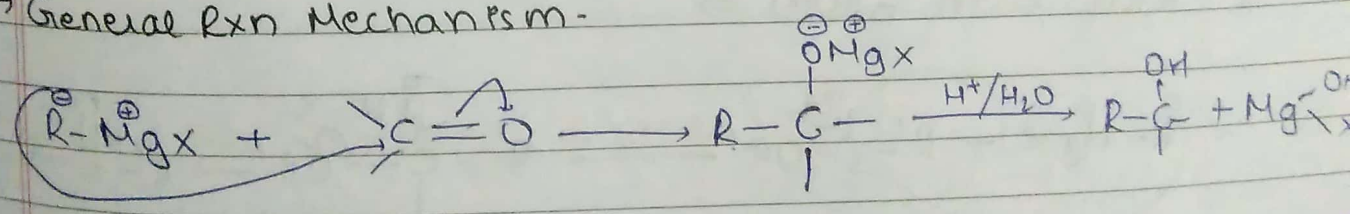


~~Good~~ Reactivity order of grignard reagent as a base  $\Rightarrow$

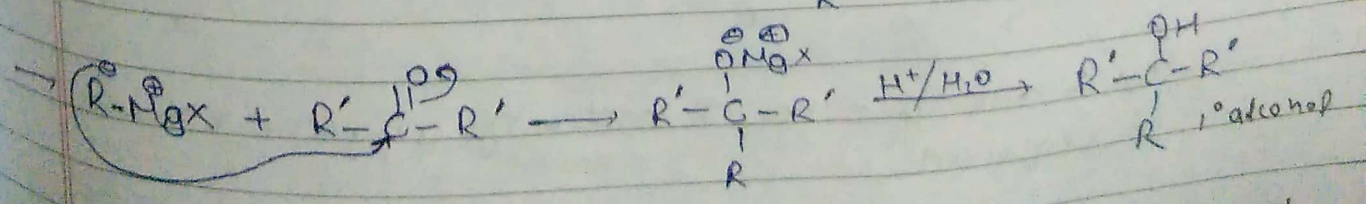
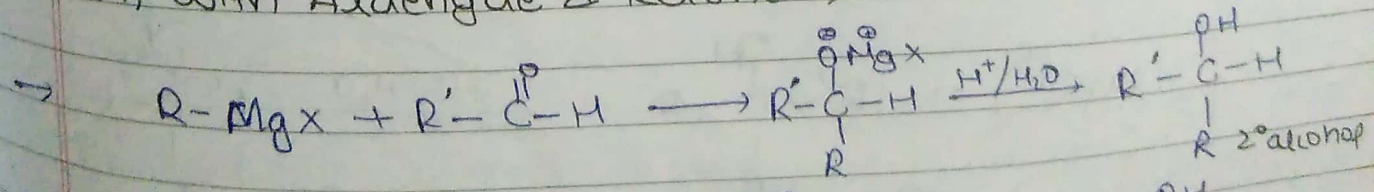


Grignard Reagent as a Nucleophile  $\Rightarrow$

$\rightarrow$  General Rxn Mechanism-

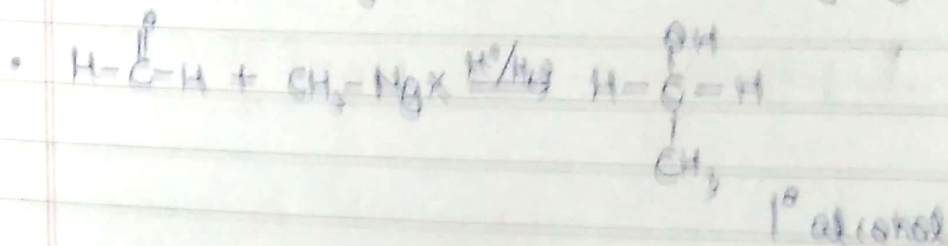


\* Rxn with Aldehyde & Ketone  $\Rightarrow$

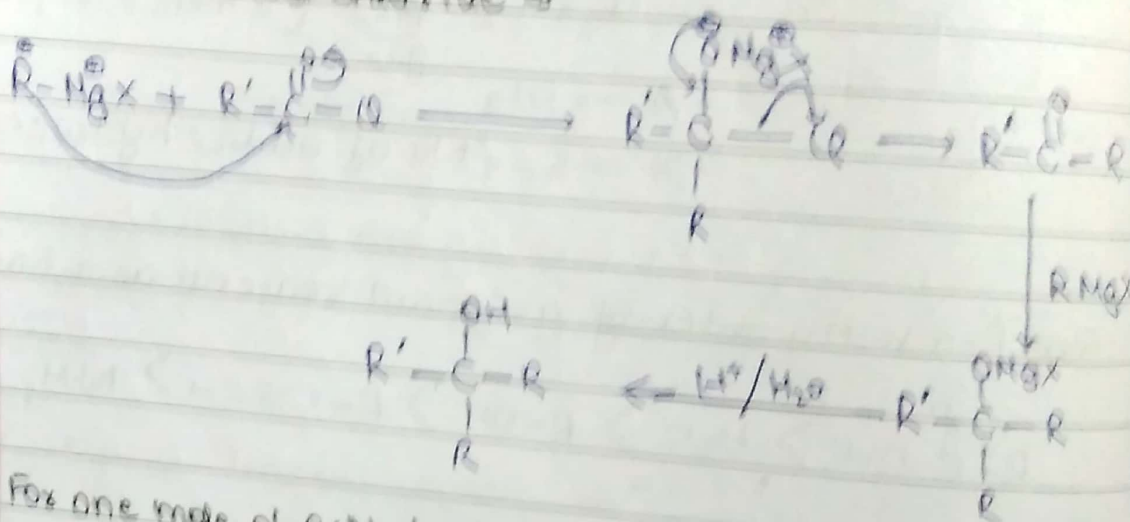


\* Only formaldehyde can give 1° alcohol with grignard

\* Ketone always gives 2° alcohol with Grignard reagent

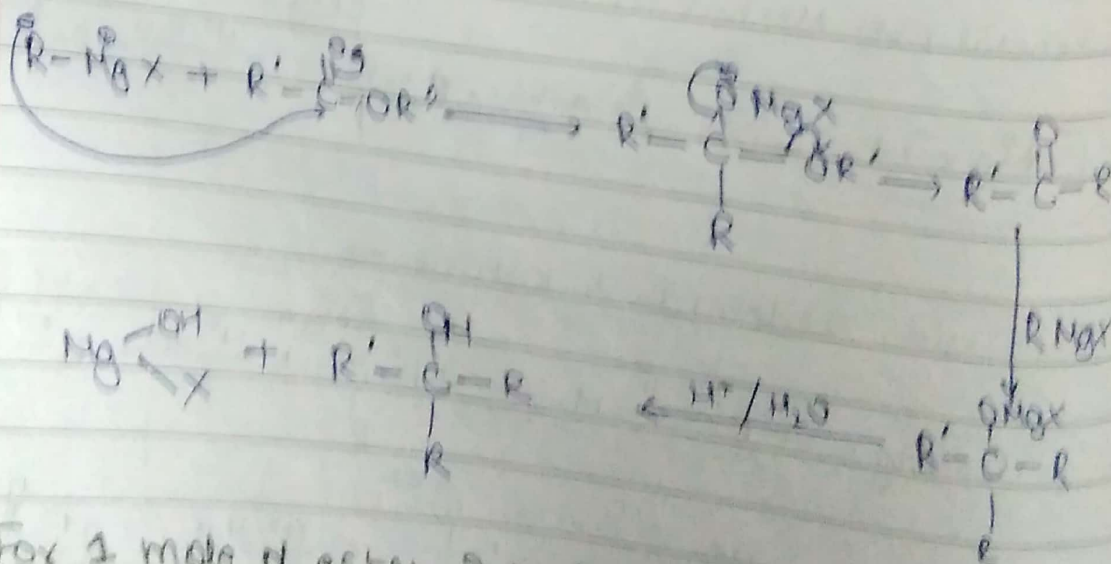


\* Rxn with acid chloride ⇒

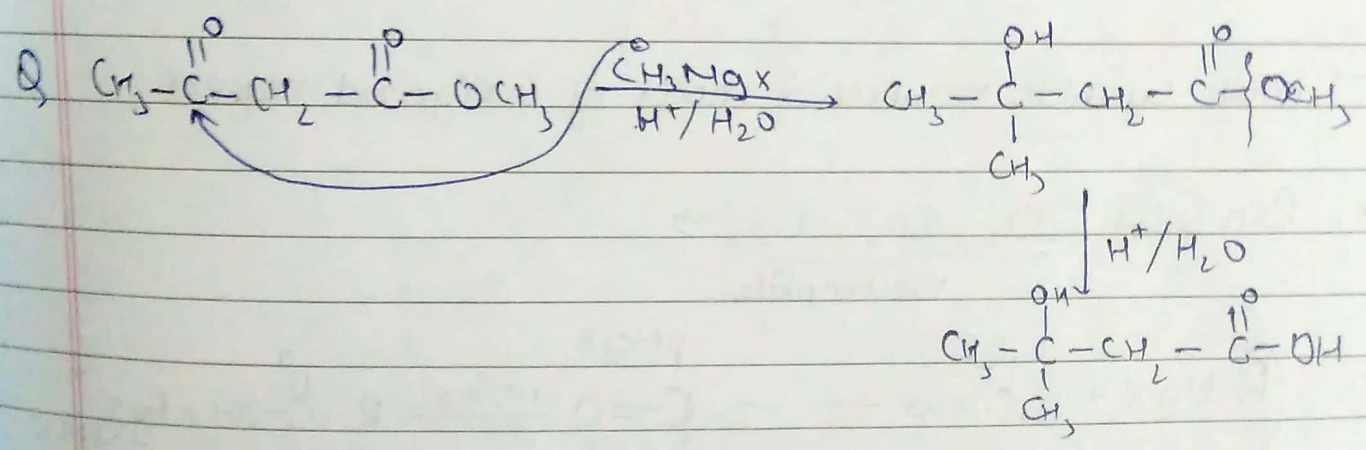
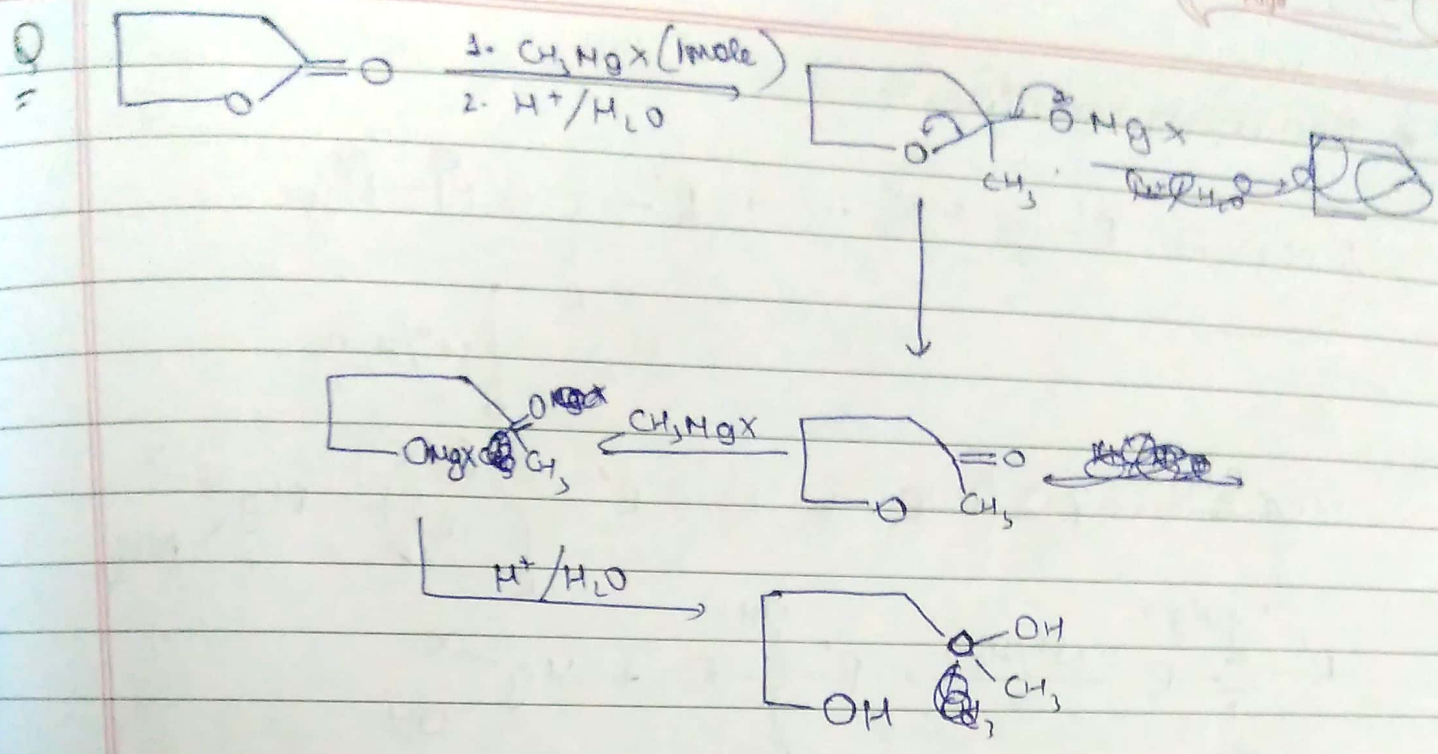


→ For one mole of acid chloride, 2 moles of Grignard reagent is required

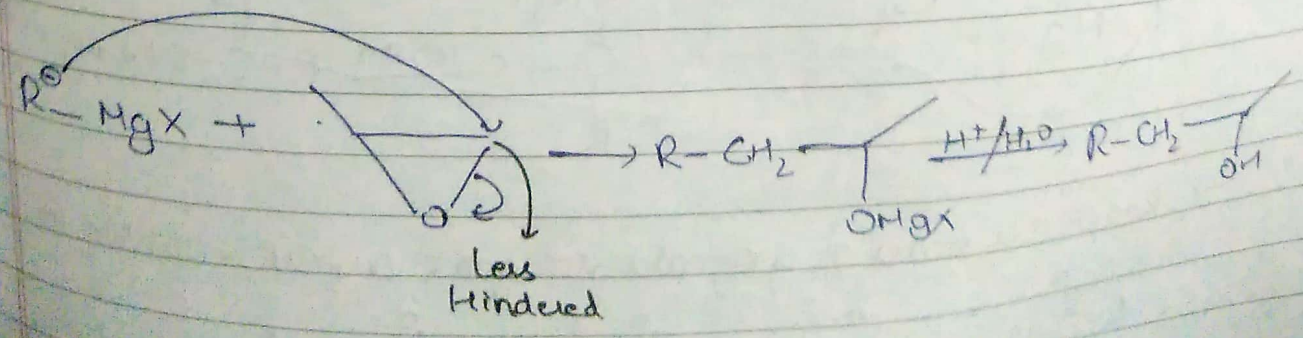
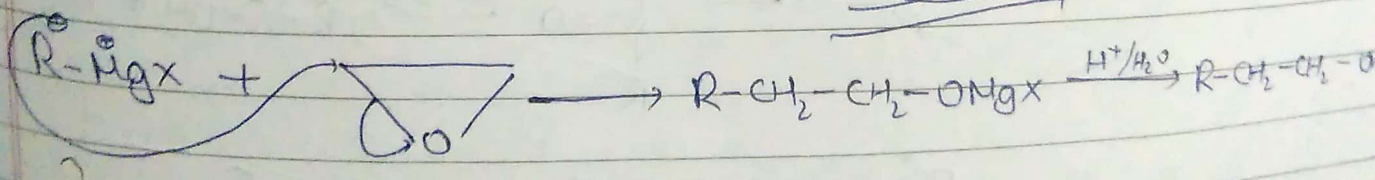
\* Rxn with Ester ⇒



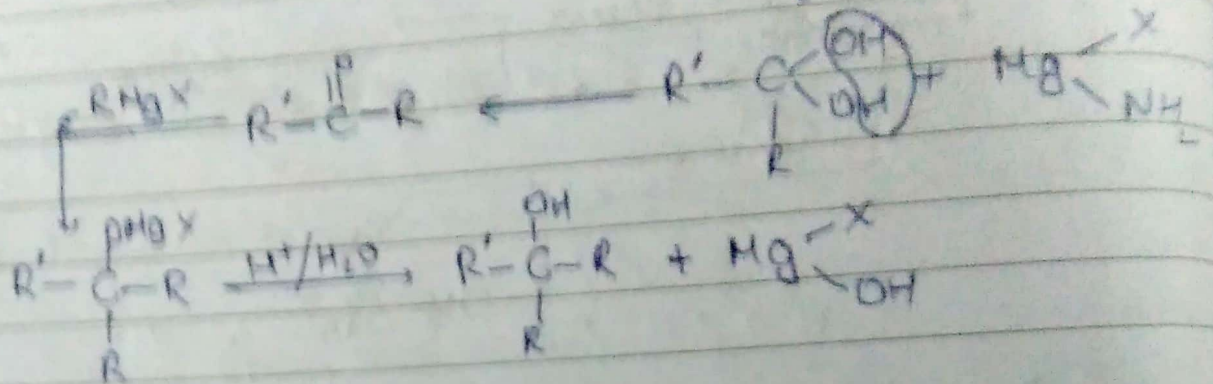
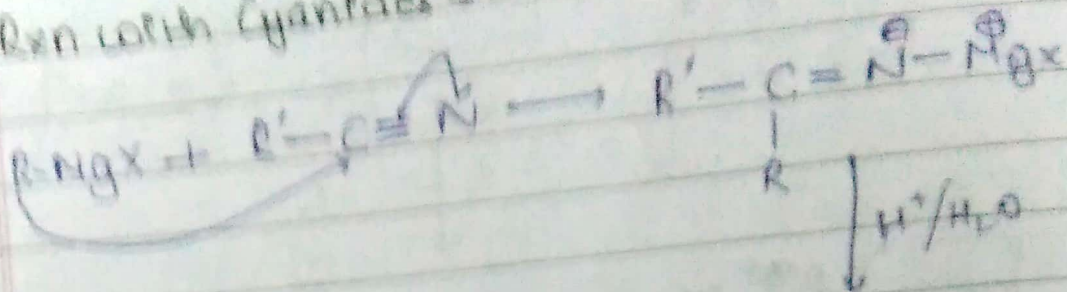
→ For 1 mole of ester, 2 moles of Grignard reagent is required



\* Rxn with Epoxides (Oxiranes)  $\Rightarrow$  SN<sub>2</sub>

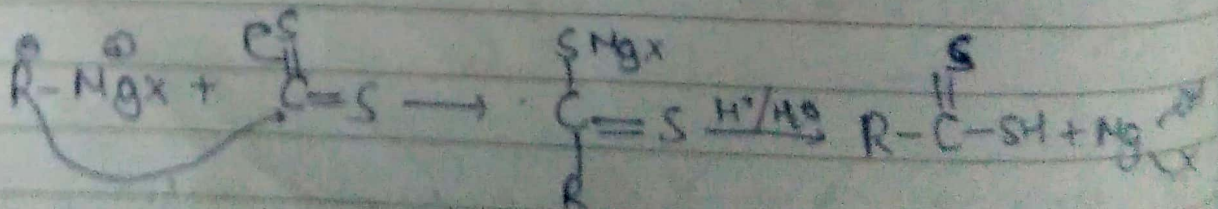
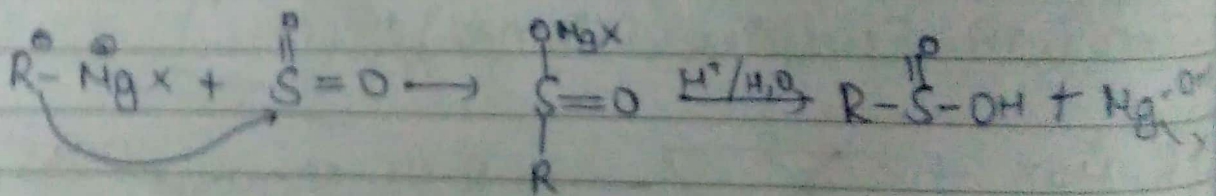
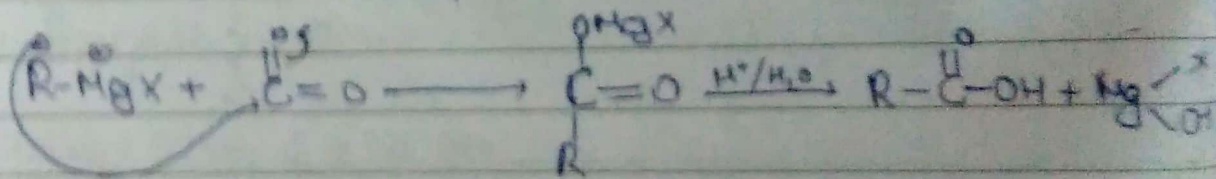


\* Rxn with Cyanides  $\Rightarrow$



$\rightarrow$  Imine cyanide requires 2 moles of Grignard reagent

\* Rxn with  $CO_2, SO_2, CS_2 \Rightarrow$   
electrophile.



$\rightarrow$  Reactivity order of Grignard reagent as nucleophile  $\rightarrow$



