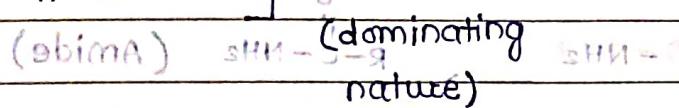
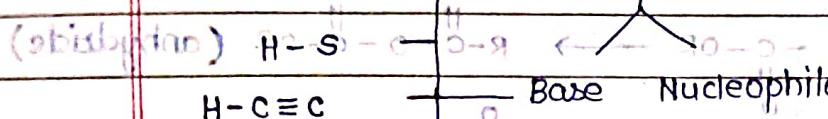
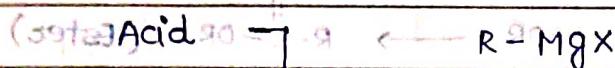
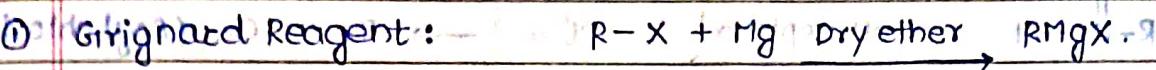
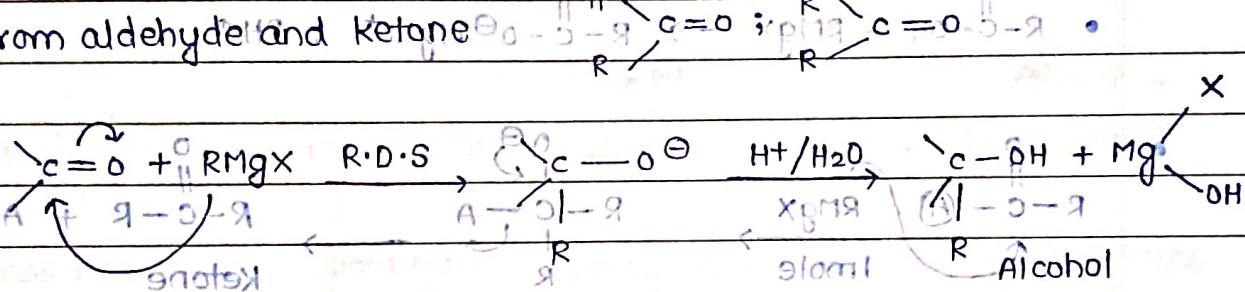


## Alcohol Phenol Ether

### - Method of preparation:



### - From aldehydes and ketones

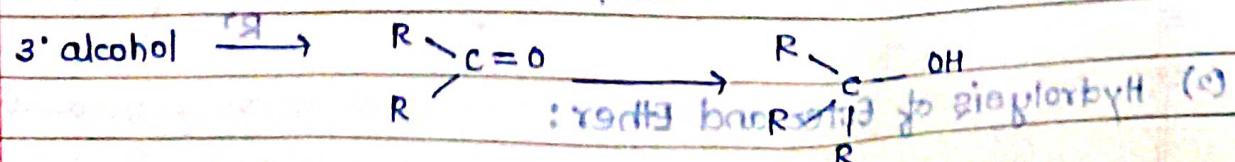
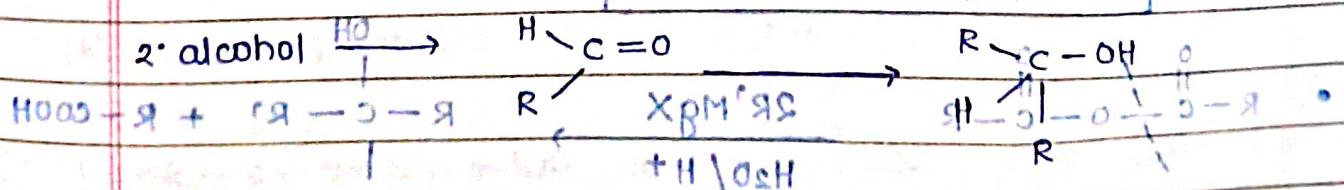
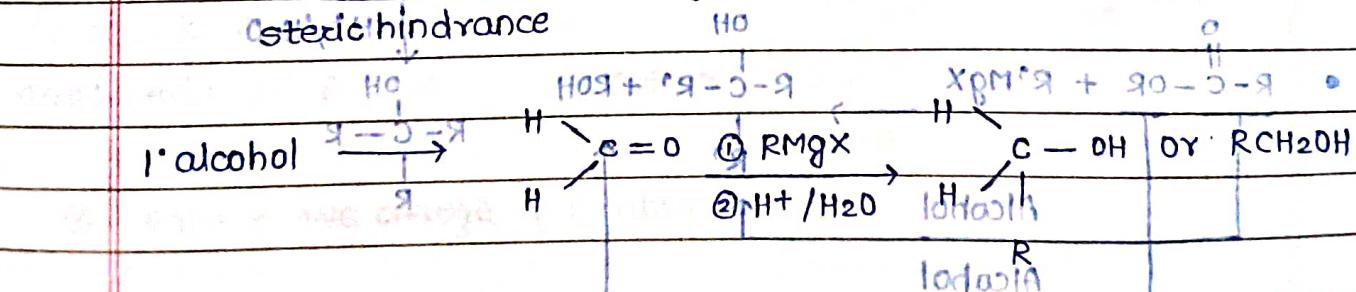


### ① Rate $\propto$ relative charge on C-atom of aldehyde and

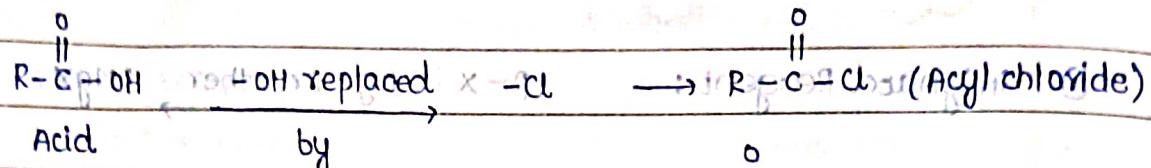
ketone. Variable:  $O-, S-, Cl- = A < O < S < Cl$

① - I effect group.

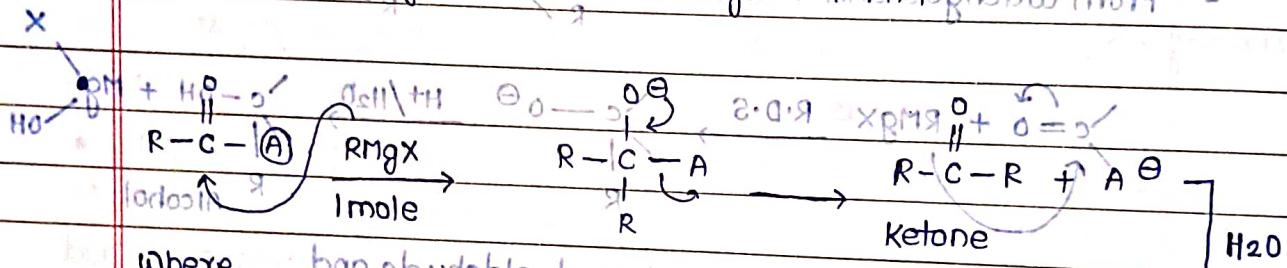
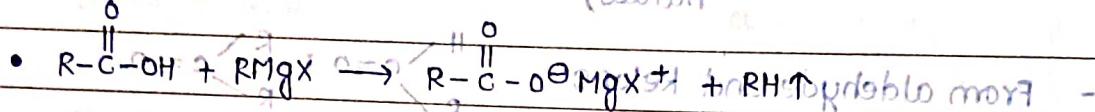
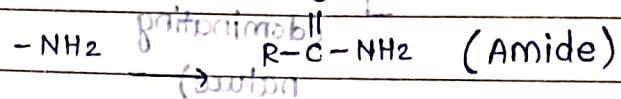
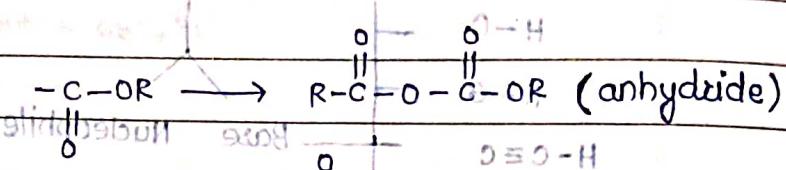
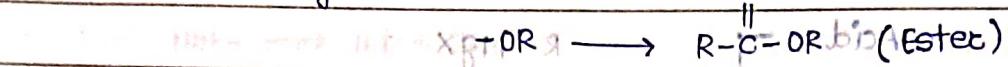
### ② Rate $\propto$ 1/k (only alkyl group attached).



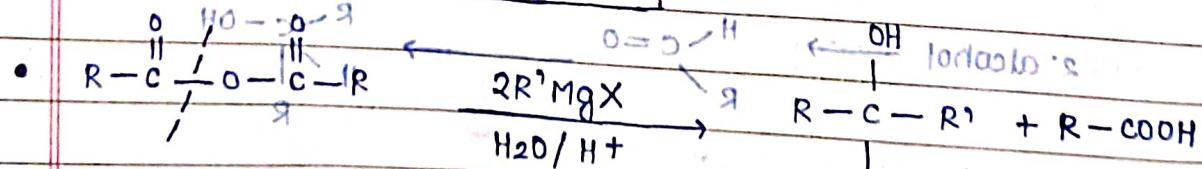
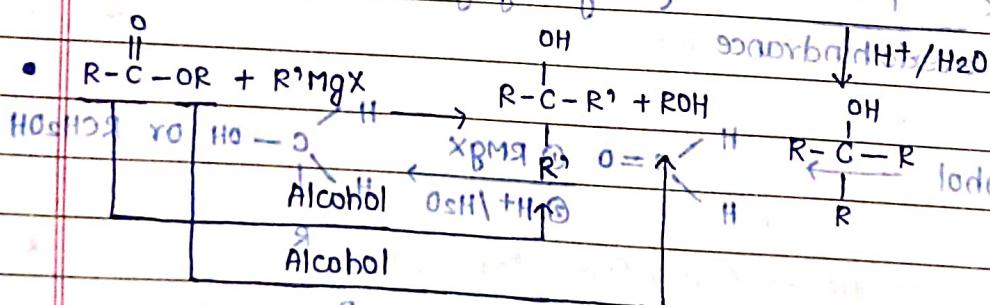
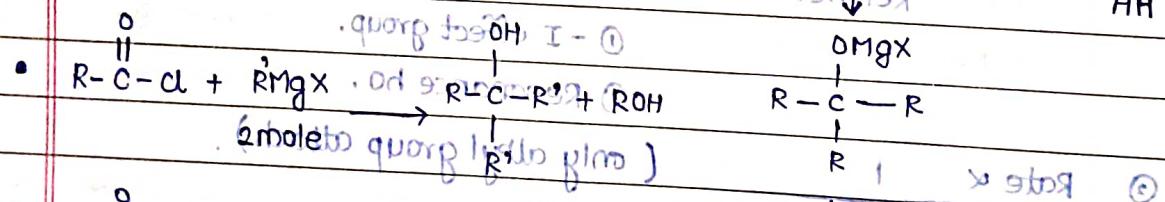
- From Acid and Acid Derivative:



Acid by

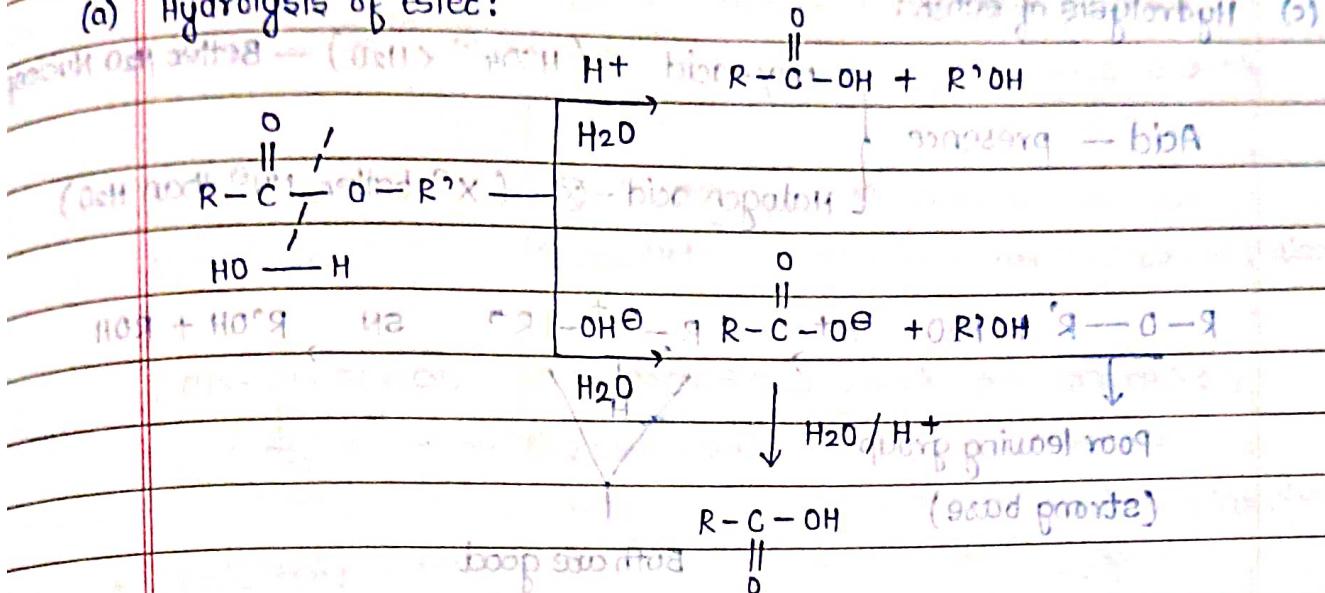


Where,  $\text{R}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{A}$  is a substituent and  $\text{RMgX}$  is a reagent.

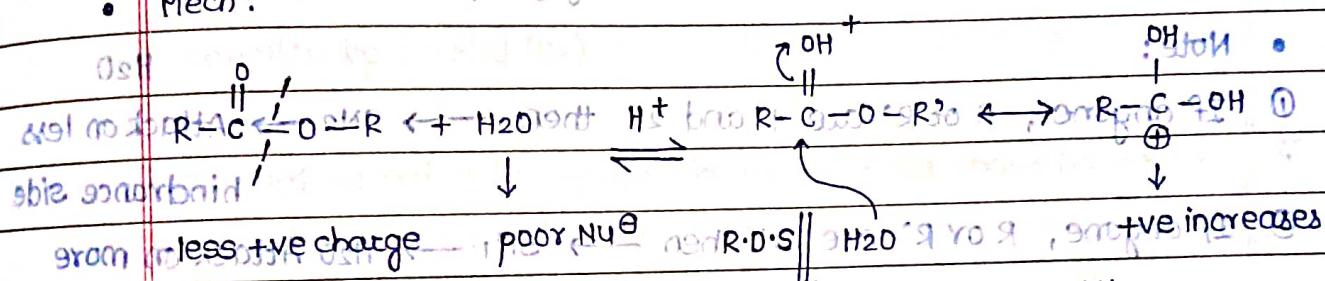


(2) Hydrolysis of Ester and Ether:

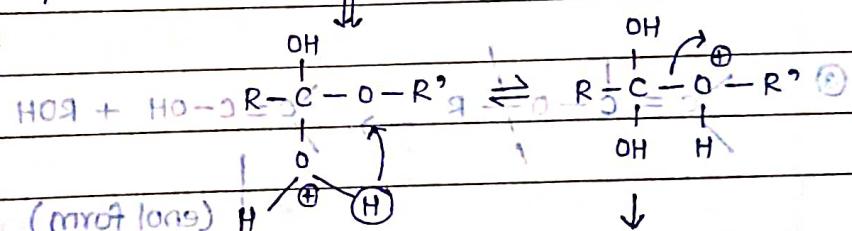
### (a) Hydrolysis of Esters:



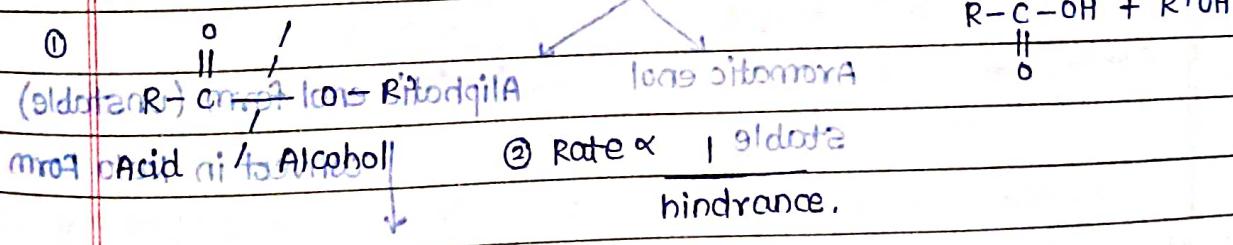
- ## • || Mech:



- .~~due to Resonance~~

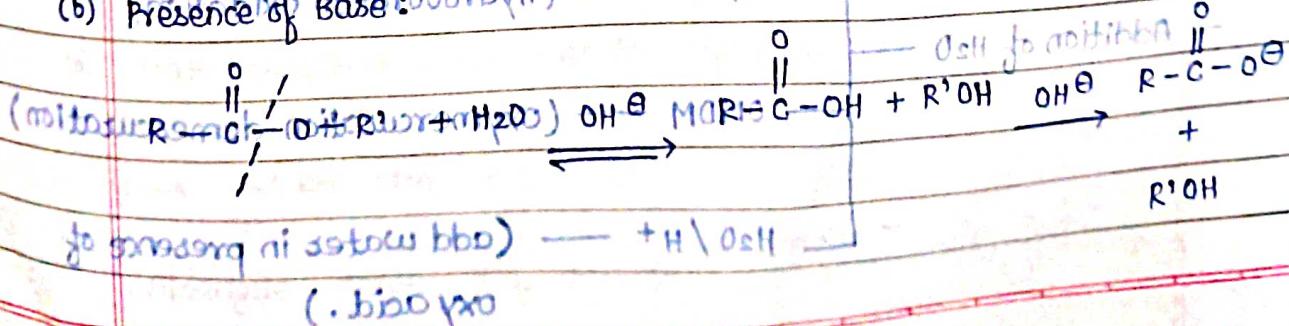


- || Note:



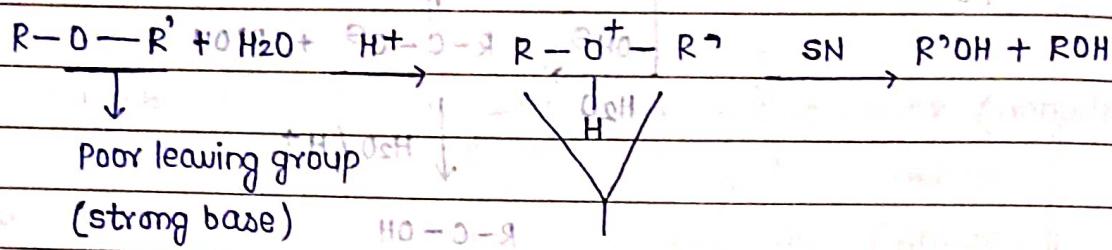
③ Rate  $\propto$  +ve charge of c-atom.

(b) Presence of Base:  $\text{H}_2\text{O} + \text{NH}_3 \rightarrow \text{H}_3\text{O}^+ + \text{NH}_4^+$



### (c) Hydrolysis of ester:

Acid - presence  $\left\{ \begin{array}{l} \text{-oxy-acid } (\text{HSO}_4^- < \text{H}_2\text{O}) \rightarrow \text{Better H}_2\text{O Nucleophile} \\ \text{Halogen acid - } \ominus (\text{X}^- \text{ better Nu}^- \text{ than H}_2\text{O}) \end{array} \right.$



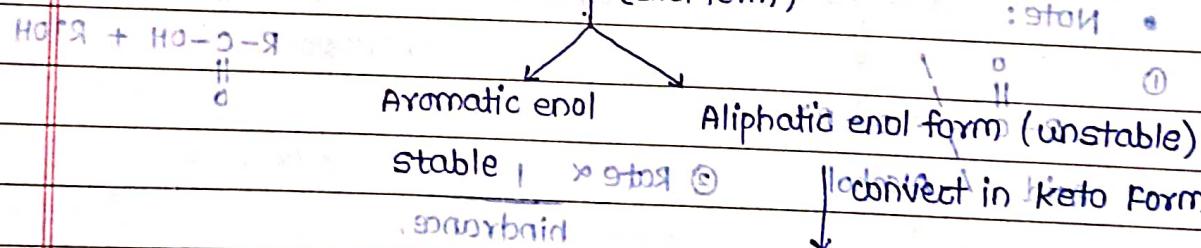
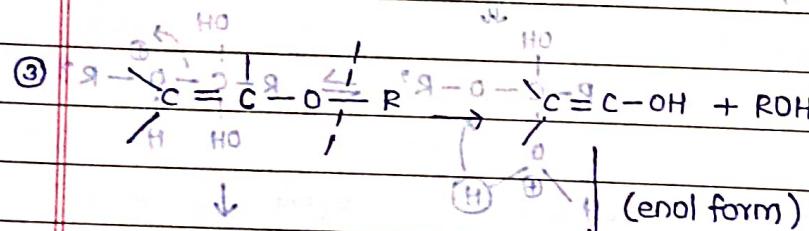
Both are good

leaving group.

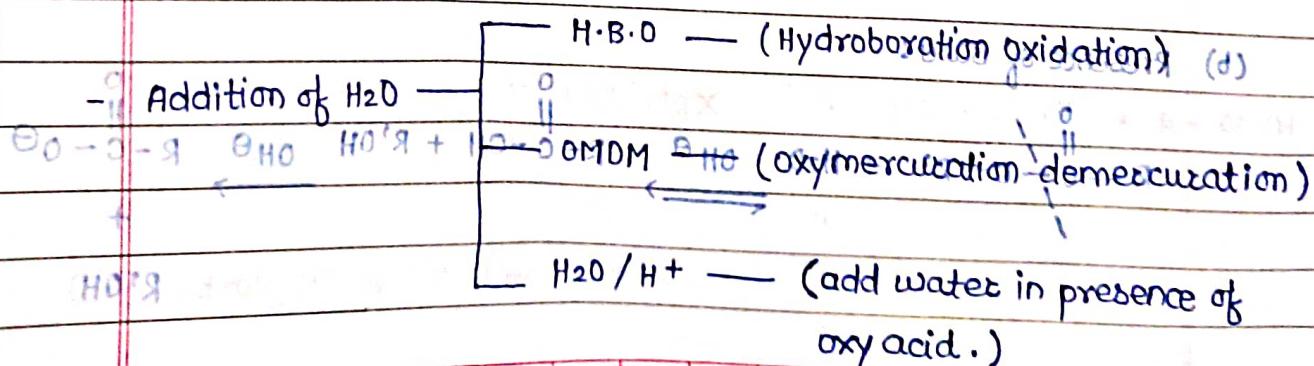
#### • Note:

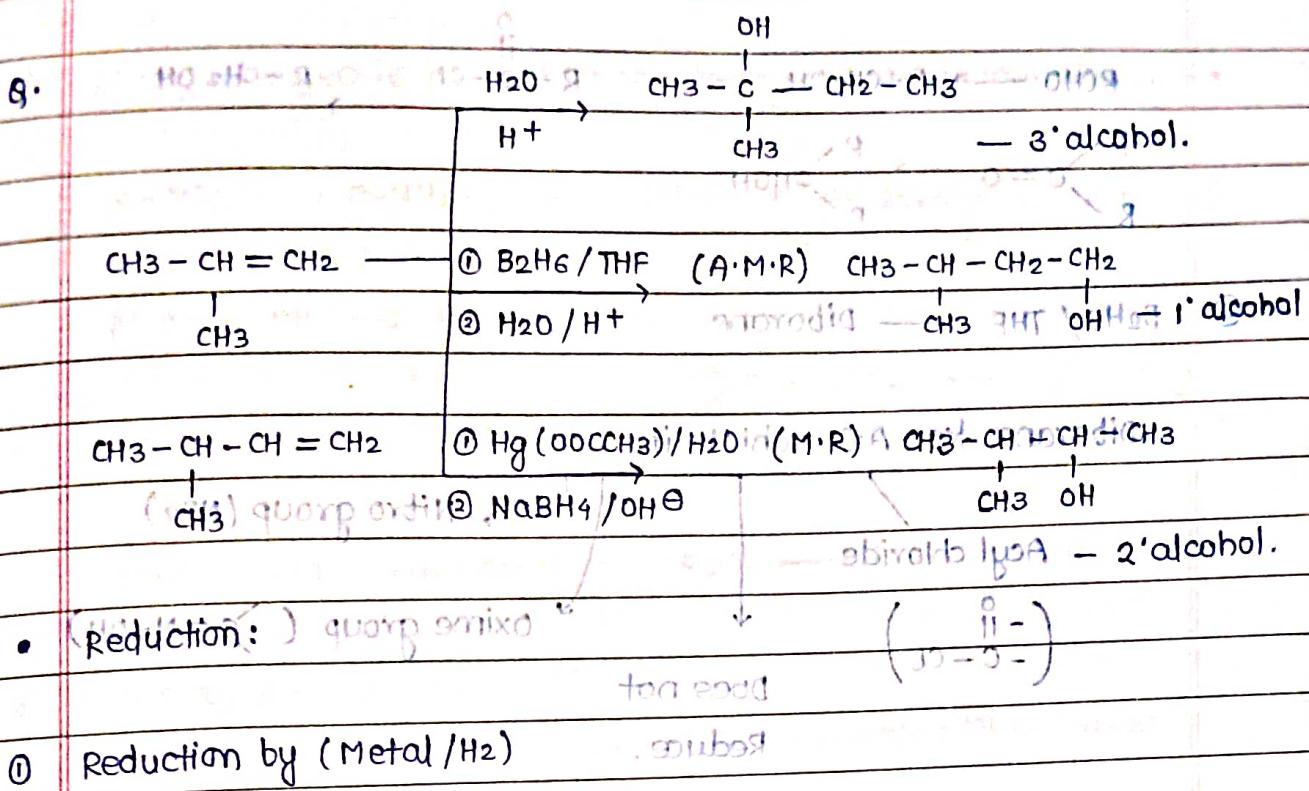
① If anyone,  $\text{R}$  or  $\text{R}'$  are  $1^\circ$  and  $2^\circ$  then  $\rightarrow \text{S}_{\text{N}}2 \rightarrow$  Attack on less hindrance side

② If anyone,  $\text{R}$  or  $\text{R}'$  are  $3^\circ$  then  $\rightarrow \text{S}_{\text{N}}1 \rightarrow$   $\text{H}_2\text{O}$  Attack on more hindrance side.

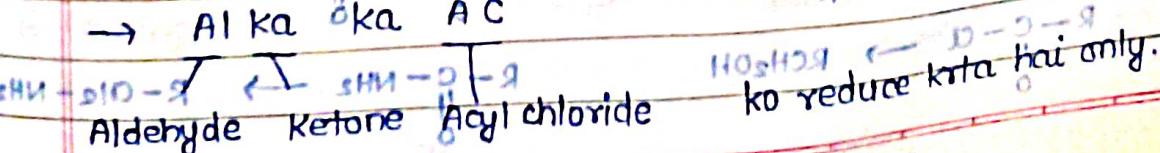
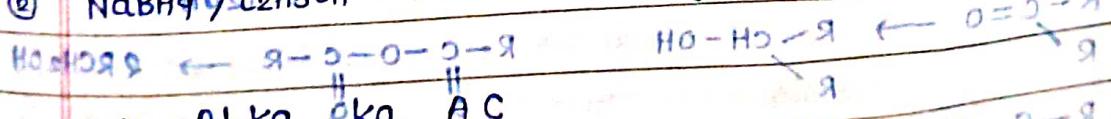
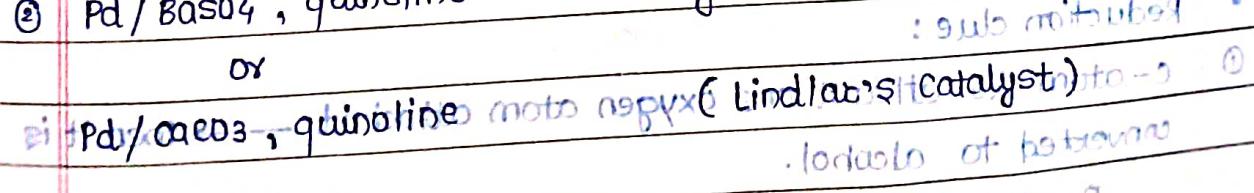
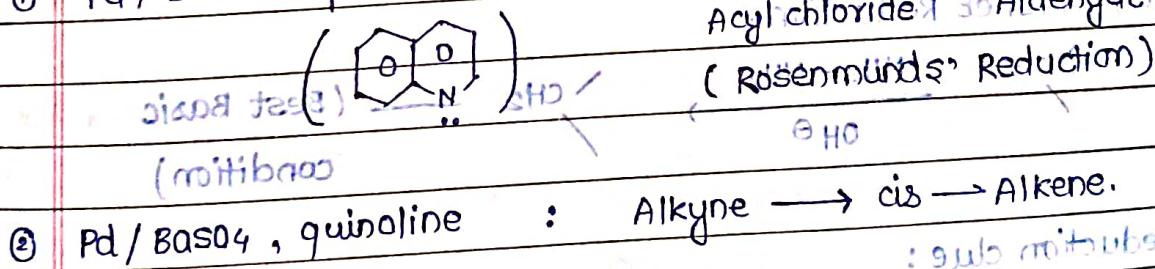
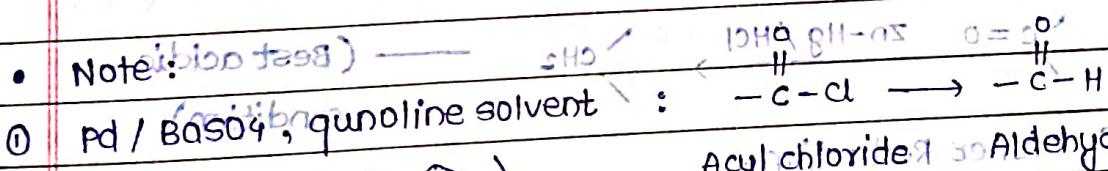


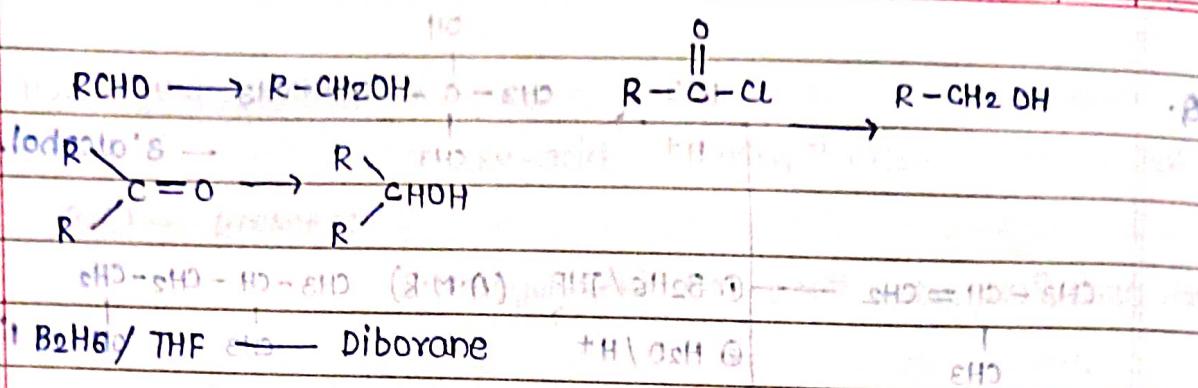
### (3) By alkene.





"Metals ko haisabhi pyrate, Pr-Pd-hai kuch khaas humare, gi Ru-C buti cu Bdc-acboxiden hi krite hain acid (-COOH) ko alcohol mein convert pyaare."





Diborane - kan A.C. nahi hai  $\text{H}_2\text{ON}(\text{NO}_2)_2$   $\xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{O} + \text{H}_2\text{O}$

Iodo's  $\xrightarrow{\text{HO}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}} \text{Cl}}$  Acyl chloride  $\xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{O} + \text{H}_2\text{O}$

$(-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{Cl})$   $\xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{O} + \text{H}_2\text{O}$

Does not

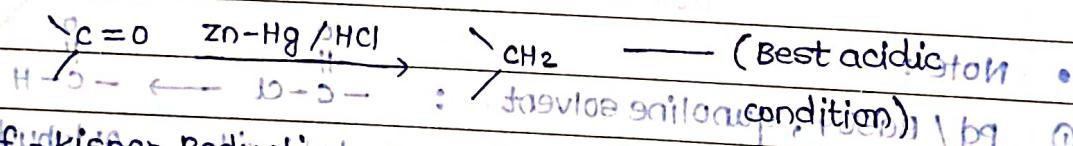
Reduce.

Oxime group ( $\text{C}\equiv\text{N}-\text{OH}$ )

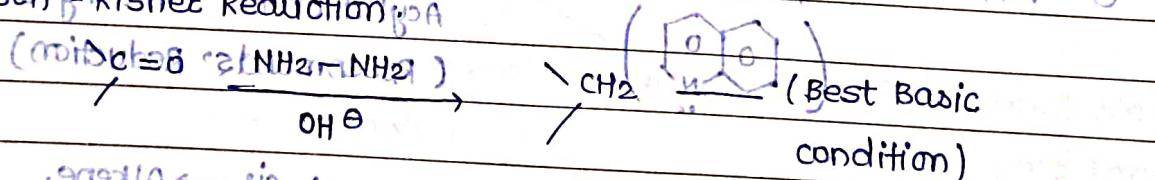
Nitro group ( $\text{NO}_2$ )

④  $\text{LiAlD}_4 / \text{ether}$   $\xrightarrow{\text{H}_2\text{O}}$  all functional groups are reduced by  $\text{LiAlD}_4$  except iodine.

### Clemmensen Reduction

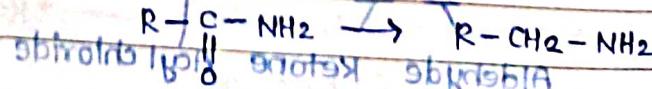
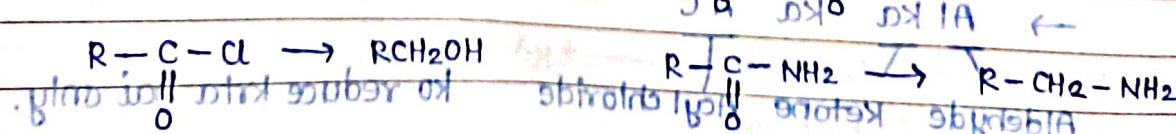
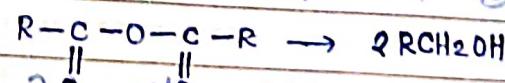
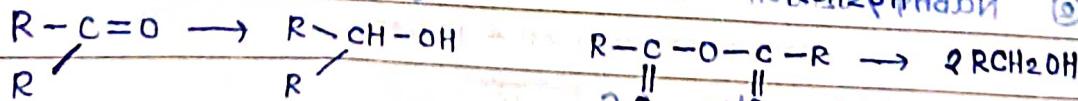
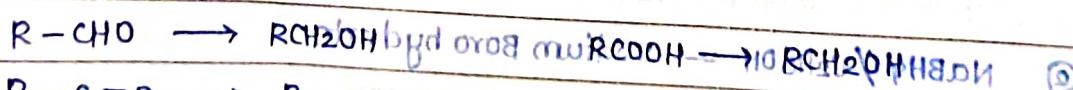


### Wolff Kishner Reduction

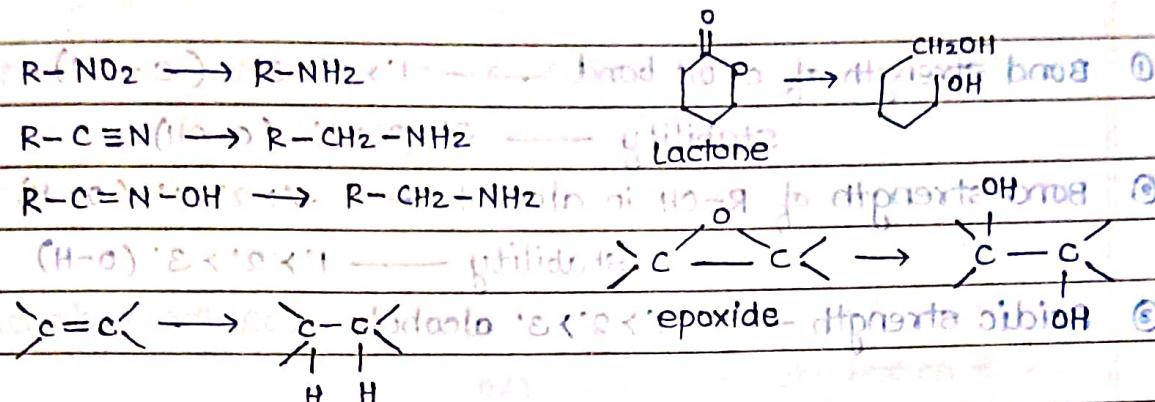


### Reduction due:

① C-atoms ko at least one oxygen atom attached hain, therefore it is converted to alcohol.

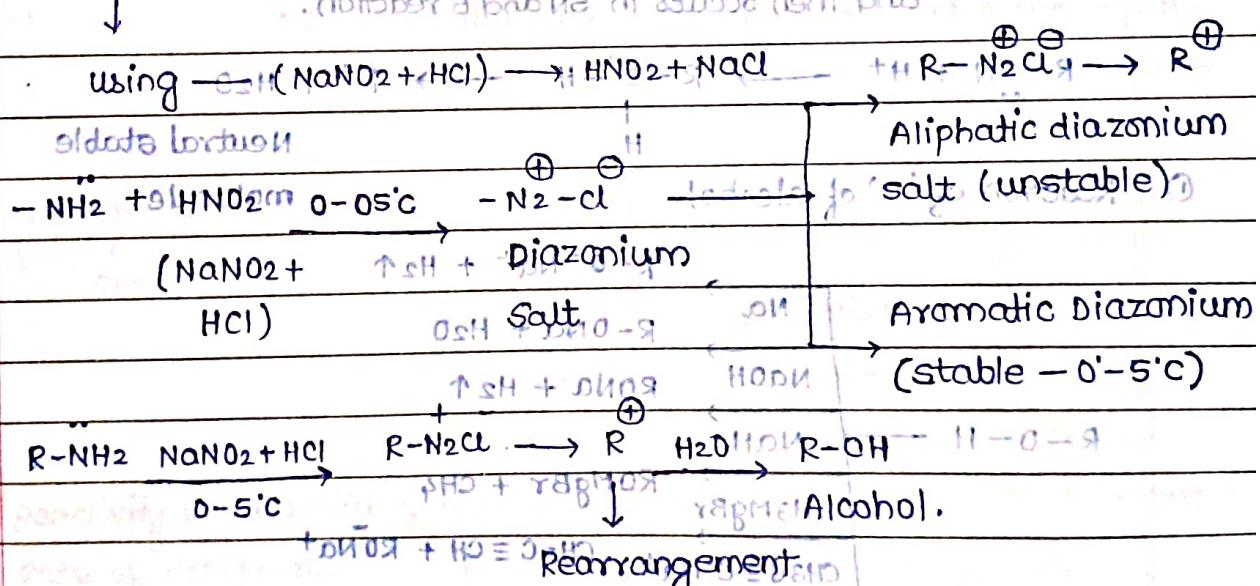


② If any nitrogen is present then directly convert it into  $\text{NH}_2$ .



M.O.P By Nitrous acid:

$\text{HNO}_2$  — nitrous acid  $\rightarrow$  unstable bop of behaviour



### • Physical properties:

- ① 1 - 4 number alcohol — highly soluble in water — Due to hydrogen bonding.
  - ② Boiling point  $\propto$  No. of  $-OH$  group.  $\text{HO}-\text{R} + \text{H}-\text{O}-$  bonding.
  - ③ Boiling point  $\propto \frac{1}{M}$  (M.wt  $\rightarrow$  constant)
  - Branch - R : No. of  $-OH$  group + same)  $\text{R}-\text{O}-\text{R}$

• Chemical properties: alcohols with both drawing at aspiration gno 91

① Bond strength of C-OH bond —  $1 > 2 > 3 \quad \text{e}(-\text{C}-\text{OH})-\text{R}$   
 stability —  $3 > 2 > 1 \quad \text{e}(\text{C}-\text{OH})-\text{R}$

② Bond strength of R-OH in alcohol.  $3 > 2 > 1 \quad \text{e}(\text{O}-\text{H})$   
 $\text{R}-\text{O}-\text{H} \quad \longleftrightarrow \quad \text{H}-\text{O}-\text{R}$  stability —  $1 > 2 > 3 \quad (\text{O}-\text{H})$

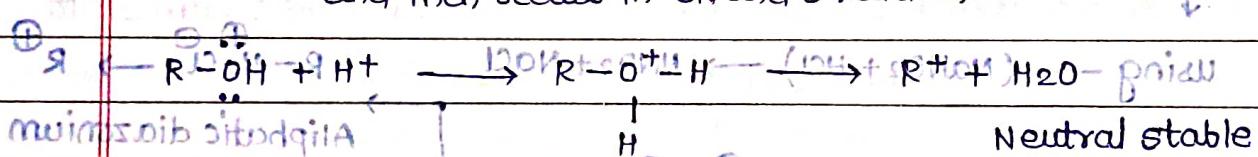
③ Acidic strength  $1 > 2 > 3$  alcohol  $\text{H}-\text{O}-\text{R} \quad \longleftrightarrow \quad \text{H}-\text{O}-\text{R}$

• Concept:  $\text{H}-\text{R} \quad \text{R}-\text{O}-\text{H} \quad \text{Active Hydrogen} \quad \text{①} \quad \text{Basic condns}$   
 mein acid-

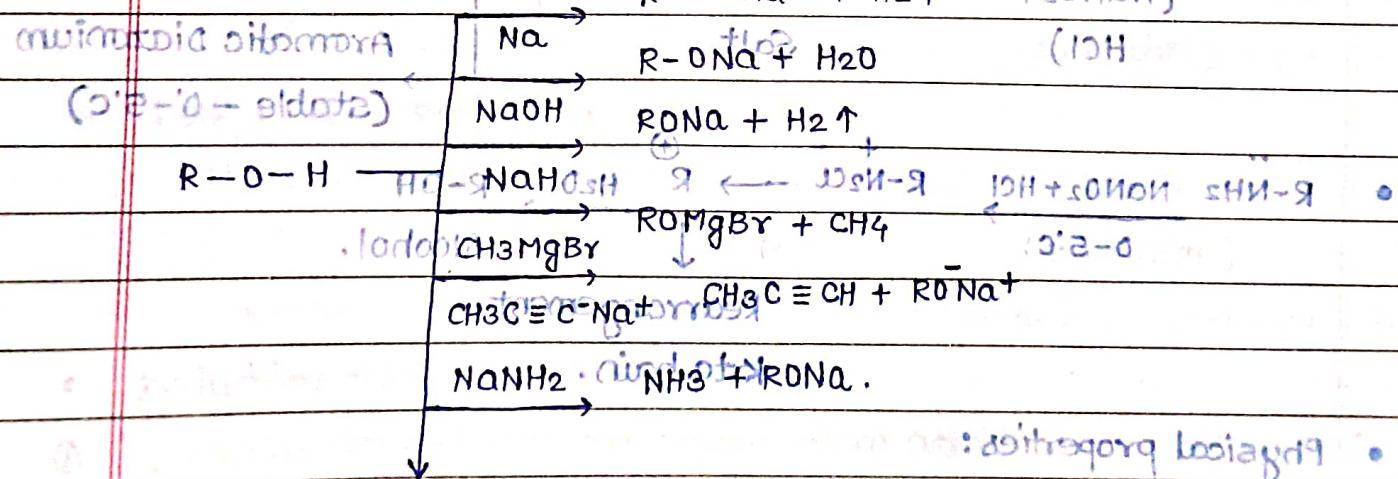
② Poor L.G.  $\quad \text{③ Nucleophile nature}$  base rxn kya hain

H<sup>+</sup> or Lewis acid get

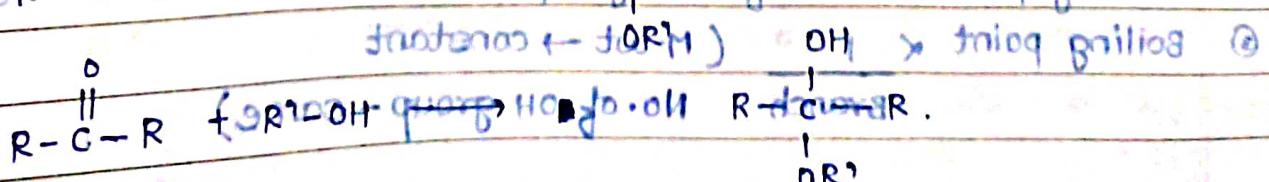
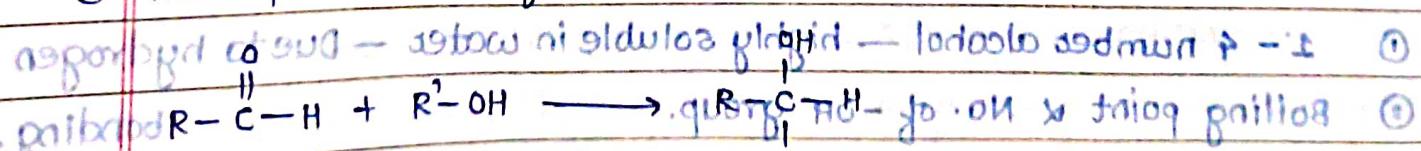
converted to good L.G.  $\leftarrow$  base anion  $\rightarrow$  some  
 and then occurs in S<sub>N</sub> and E reaction.

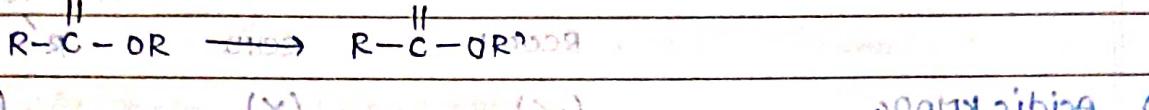
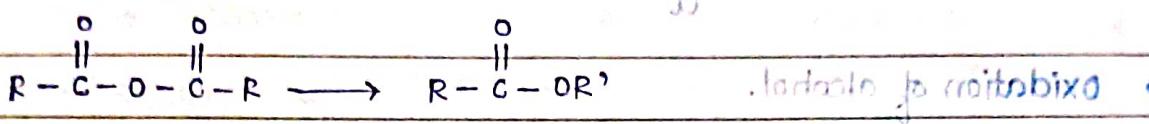
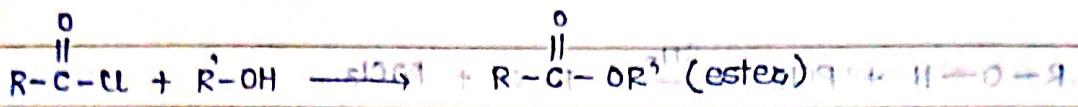


⑤ Reaction of H<sup>+</sup> of alcohol.  $\text{R}-\text{O}-\text{H} + \text{H}^+ \rightarrow \text{R}-\text{O}-\text{H}_2^+$  molecule  $\leftarrow \text{H}_2^+$



⑥ Nucleophilic nature of alcohol (R-OH)

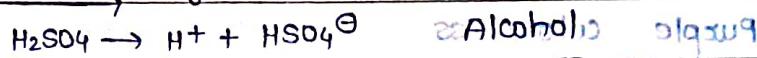




(v)  $\text{R}-\text{C}(=\text{O})-\text{OR}'$  (x)  $\text{R}-\text{C}(=\text{O})-\text{OR}'$  (v) Acidic nature ①

### ③ Reaction with Acid (A-O property)

oxg-acid  $\rightarrow$  dehydration of alkene



Alcohol  $\rightarrow$  Behaves as a Bulky Base.



$\text{HSO}_4^-$  Behaves as a Bulky Base.

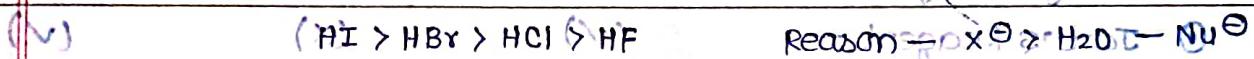
Iodoalcohol : starch

ester of benzene part

Halogen acid  $\rightarrow$  substitution  $\xrightarrow{\text{HX}}$  alkyl

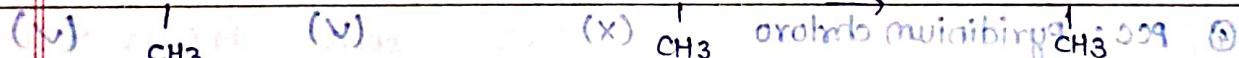
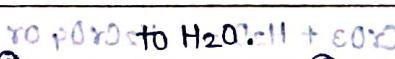


Reaction with halide



Reason:  $X^- \approx \text{H}_2\text{O} \approx \text{Nu}^-$

More basic  $\text{Nu}^-$  in compare



$\text{CH}_3-\text{C}-\text{CH}_3$   $\xrightarrow{\text{X}^- (\text{Nu}^-)}$  more basic

$\text{CH}_3-\text{C}-\text{CH}_3$   $\leftarrow$  subs. Rxn with  $\text{H}_2\text{SO}_4^-$

$\text{CH}_3-\text{C}-\text{CH}_3$   $\leftarrow$  (base)

• Reactivity & stability of carbocation: Elimination

Rate of dehydration }  $\propto$  stability of carbocation  $\text{CH}_3-\text{C}-\text{CH}_3$

Reactivity order with HBr }  $\propto$  stability of carbocation  $\text{CH}_3-\text{C}-\text{CH}_3$

• Note:  $\text{C}=\text{C}-\text{OH} \rightarrow$  Never do dehydration or substitution rxn.

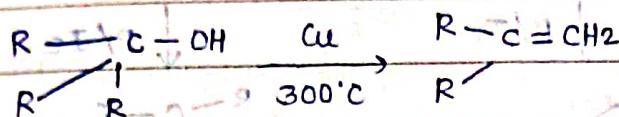
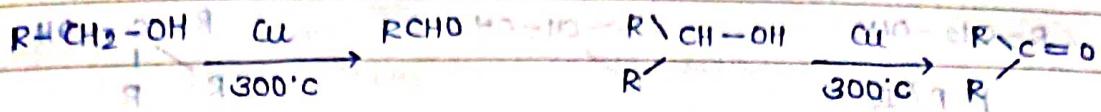
Due to partial double bond character.



Iodoalcohol: Reaction with  $\text{PCl}_3$  or  $\text{Red P}/\text{Cl}_2$ ,  $\text{PCl}_5$  or  $\text{SOCl}_2$  etc. go to test

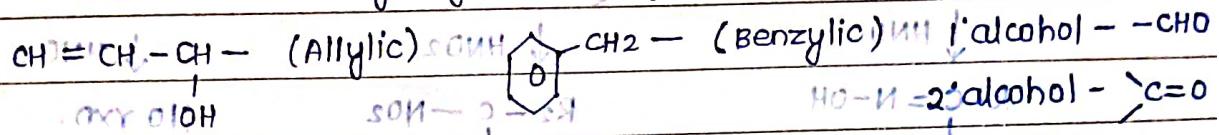
Alkyl halide ke MOP me bataya hain. (Iodoalcohol)





Note:  $MnO_2$  — oxidising agent

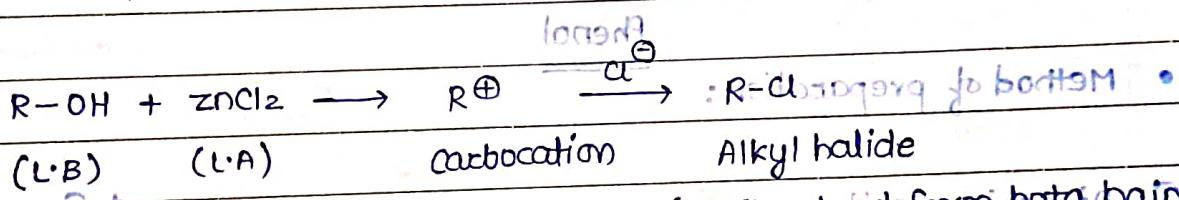
$MnO_2$  — selective oxidising agent for Allylic and Benzylic position.



- Test of Alcohol:

- Lucas Reagent

$ZnCl_2 / \text{conc. HCl}$  solution  $\rightarrow L.R.$



1'-Alcohol  $\xrightarrow[ZnCl_2]{HCl}$  No rxn at room temperature

(Does not form white cloud)

2'-Alcohol  $\xrightarrow[ZnCl_2]{HCl}$  in high temp  $\rightarrow$  white cloud form.

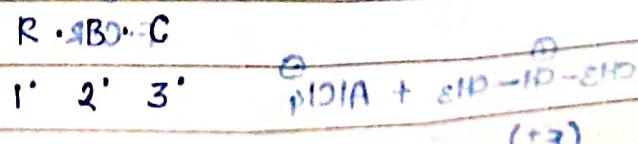
3'-Alcohol  $\xrightarrow[ZnCl_2]{HCl}$  white cloud form after 3-5 minutes.

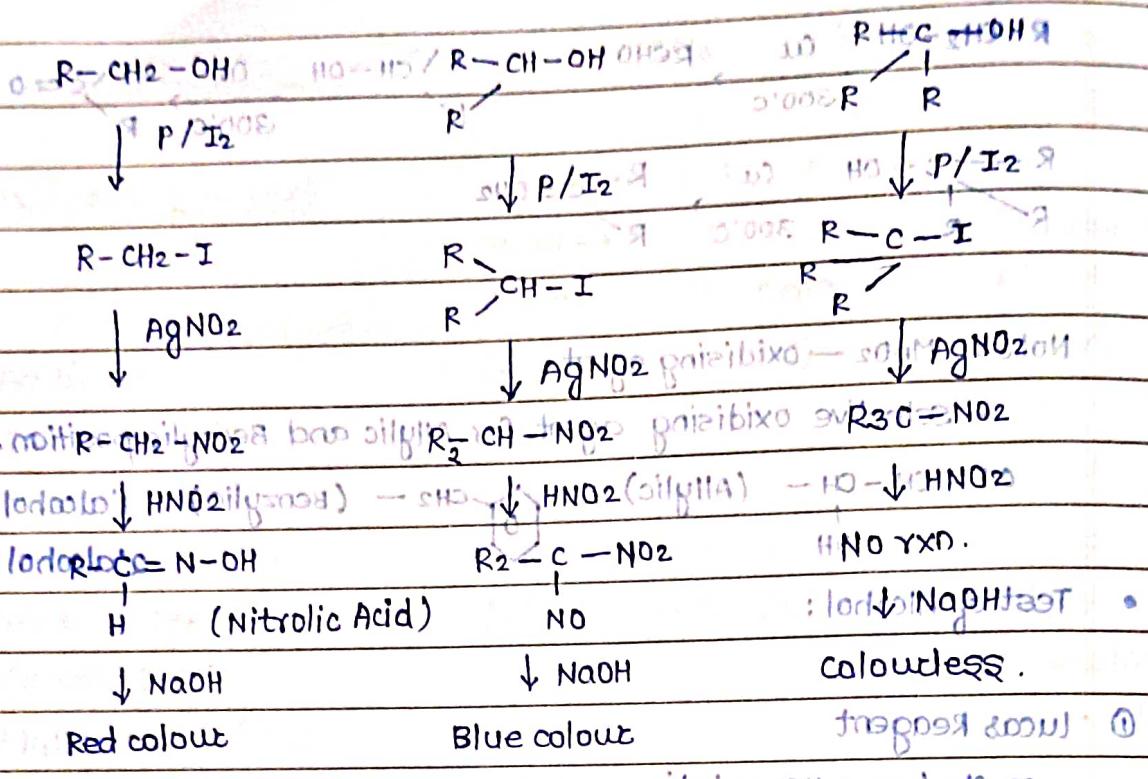
White cloud form within 1-2 minutes.

- Reactivity of L.R. with alcohol  $\propto$  stability of carbocation.

(Note:  $\begin{array}{c} C=C-OH \\ | \\ O \end{array} \rightleftharpoons L.R^{\oplus} \rightleftharpoons \text{NO rxn} \quad \begin{array}{c} O \\ | \\ O \end{array}$ )

- Victor-Mayer test:





## Phenol

- Method of preparation:  $\text{Ar} \leftarrow \text{ArOCl} + \text{HO}-\text{R}$

stabilized (A.R)      (A.R)      (R.B)

(① Diazonium salts of nitro)

$\text{R-N}_2\text{Cl}$  - Unstable.

successive nitration to give OH  
 $\text{-NH}_2 + \text{HNO}_2 \rightarrow \text{Ar-O-N}_2\text{Cl}$        $\xrightarrow{\text{NaOH}}$        $\text{Ar-O-N}_2^+$

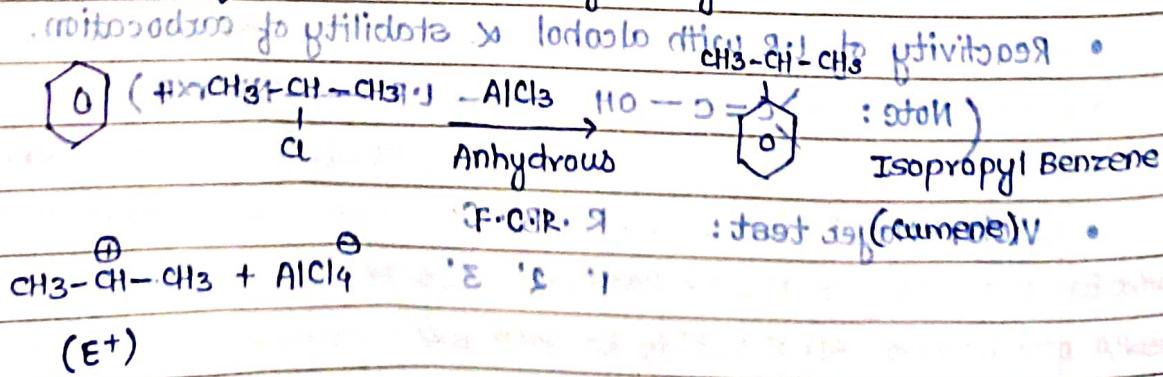
metabolism by  $\text{N}_2\text{O}_4$  - gives  $\text{Ar-N}_2\text{Cl}$  - stable

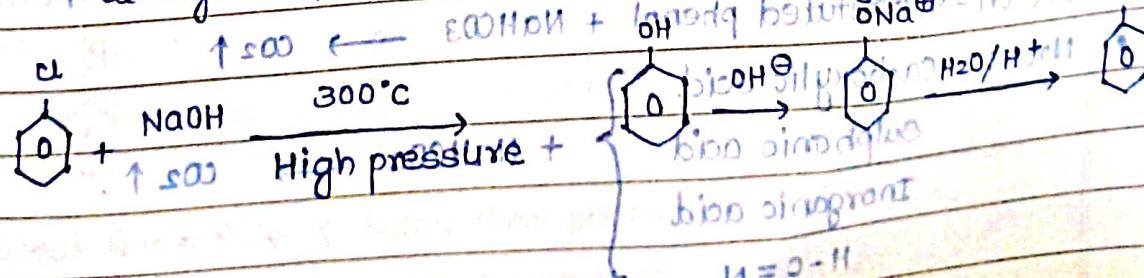
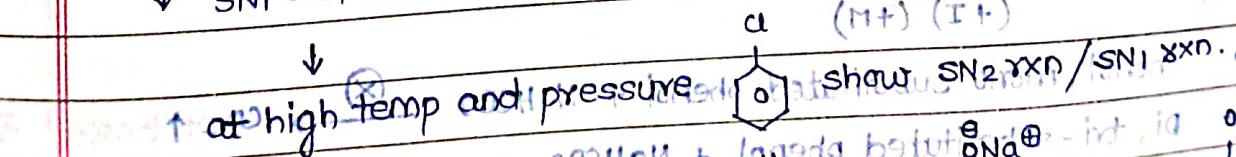
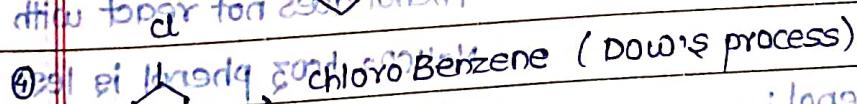
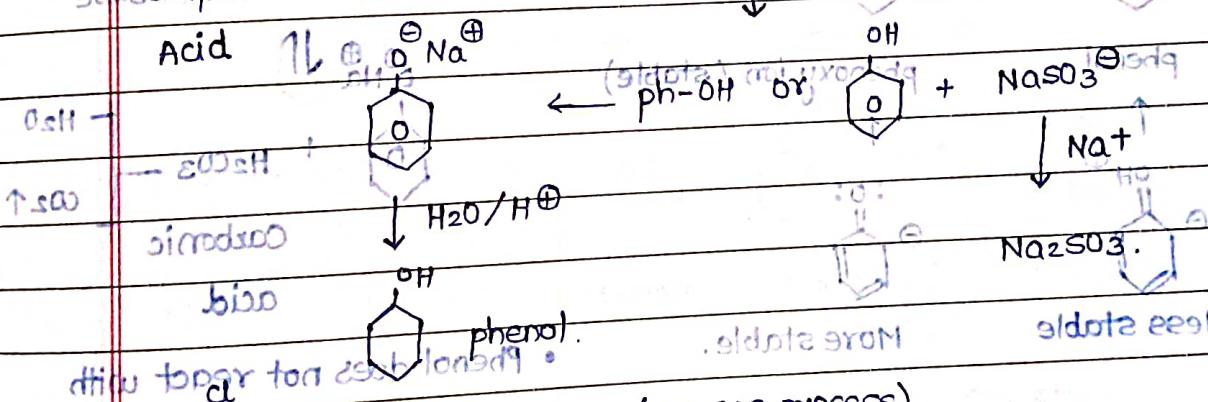
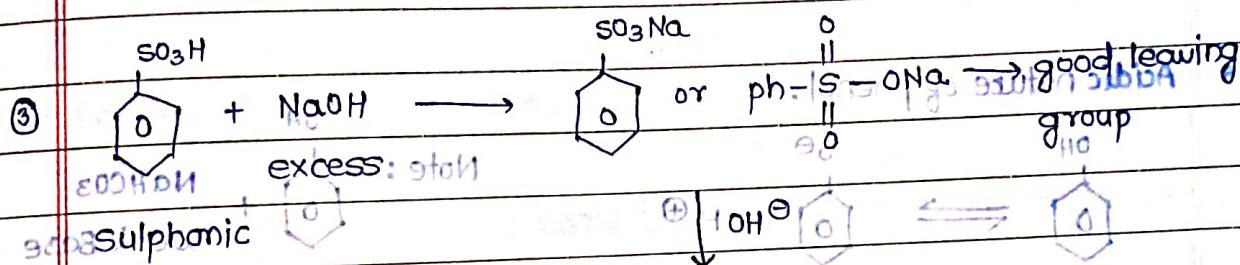
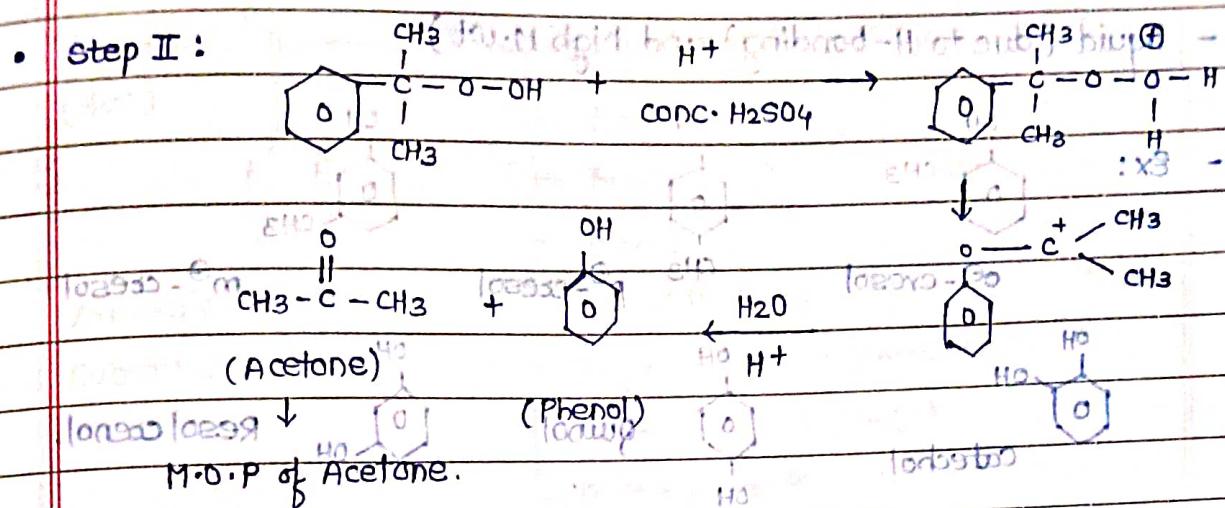
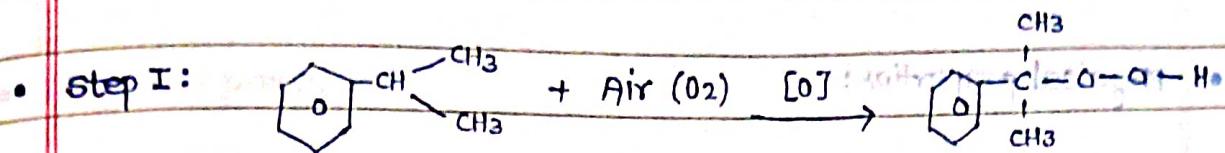
$\text{Ar-N}_2\text{Cl}$  -  $5^\circ\text{C}$

$\text{Ar-O-N}_2^+ \xrightarrow{\text{NaOH}}$   $\text{Ar-OH}$        $\xrightarrow{\text{HCl}}$   $\text{Ar-N}_2\text{Cl}$

2. Air oxidation of cumene further catalysed by Acid.

② Air oxidation of cumene further catalysed by Acid.

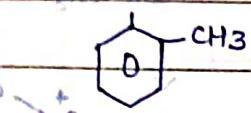




Physical properties: [O] (CO) via + : I gets •

- liquid (due to H-bonding) and high M.wt) : II gets •

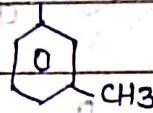
- Ex:



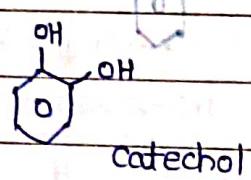
$\text{EtOH} \rightarrow$  o-cresol



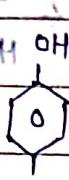
$\text{EtOH} \rightarrow$  m-cresol



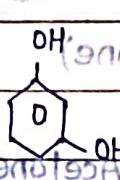
p-cresol



catechol

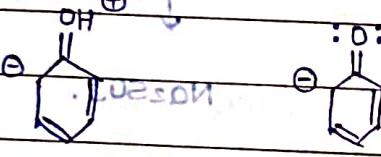
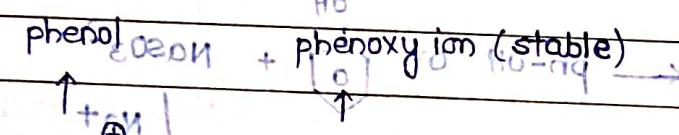
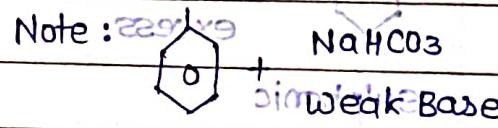


quinol

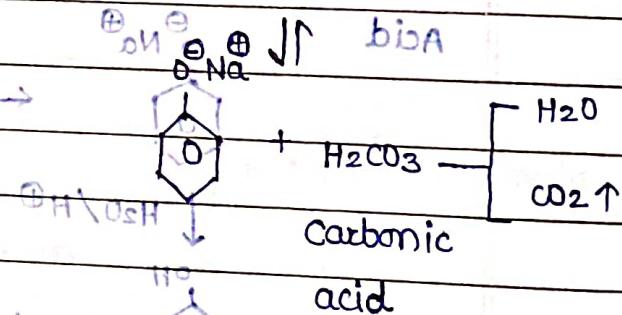


Resol crenol.

Acidic nature of phenol:  $\text{HO}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+$



More stable.



• Phenol does not react with

Acidic strength of phenol:

acidic than  $\text{H}_2\text{CO}_3$ .

$A.S \propto (-I) (-M)$   $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$   $\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$

(+I) (+M)

• Phenol, mono-substituted phenol +  $\text{NaHCO}_3 \rightarrow \text{CO}_2 \uparrow$

Di, tri-substituted phenol +  $\text{NaHCO}_3 \rightarrow \text{CO}_2 \uparrow$

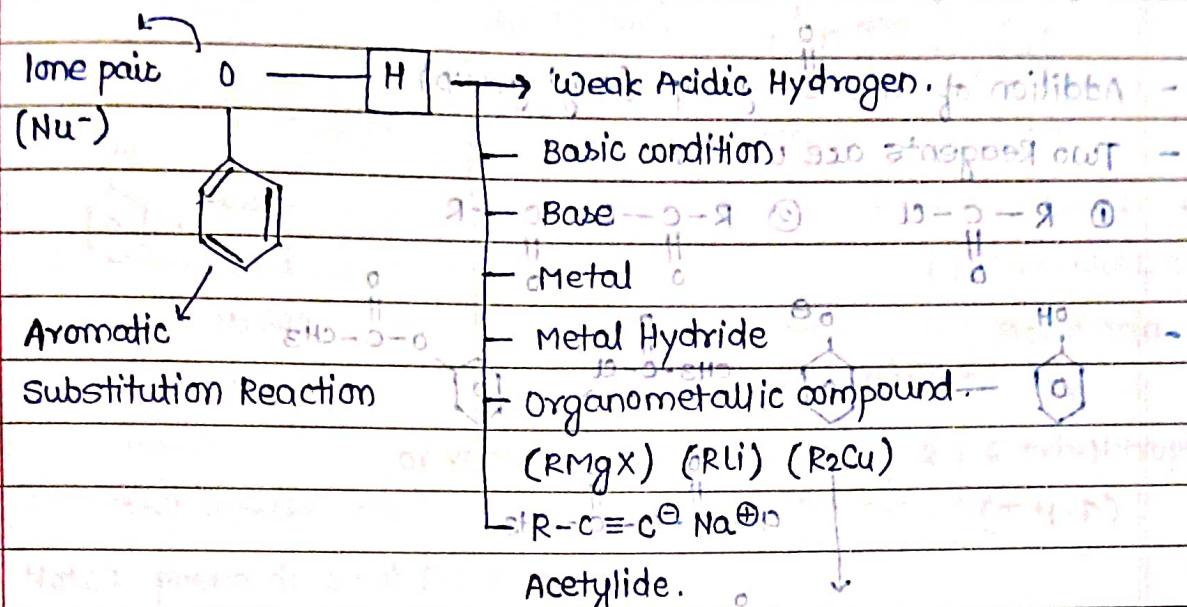
Note: Carboxylic acid

Sulphonic acid

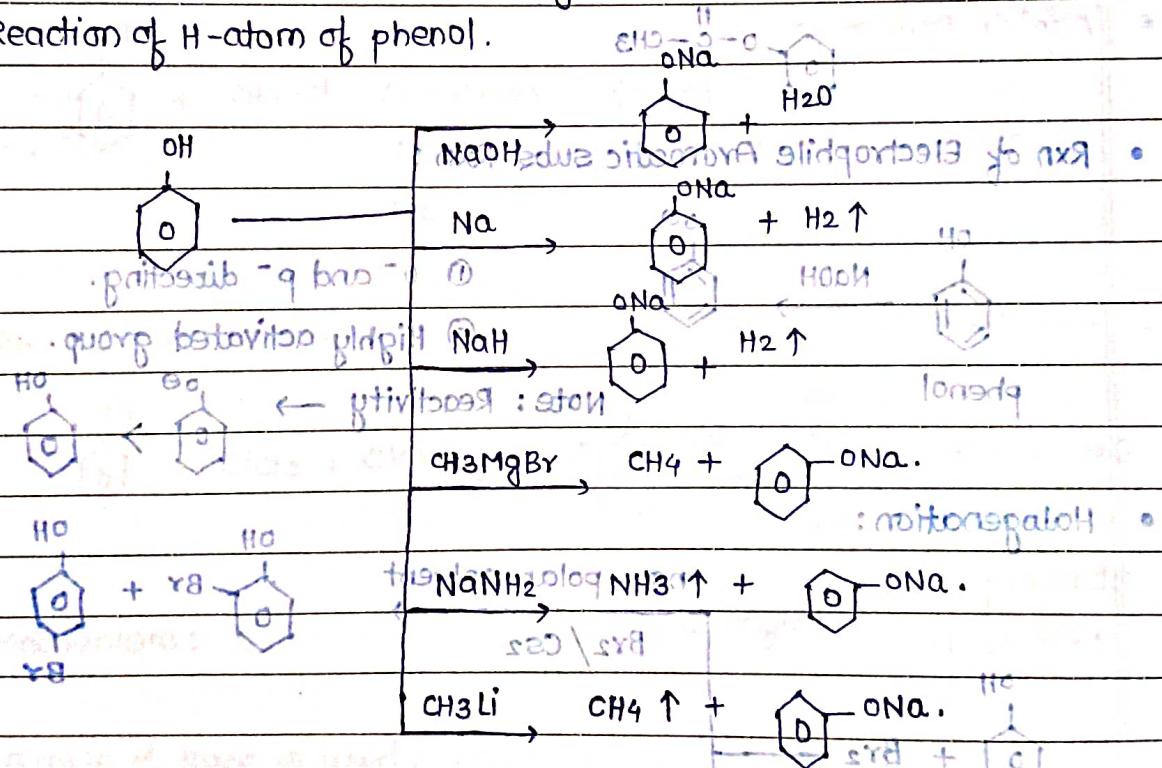
Inorganic acid

$\text{H}-\text{C}\equiv\text{N}$

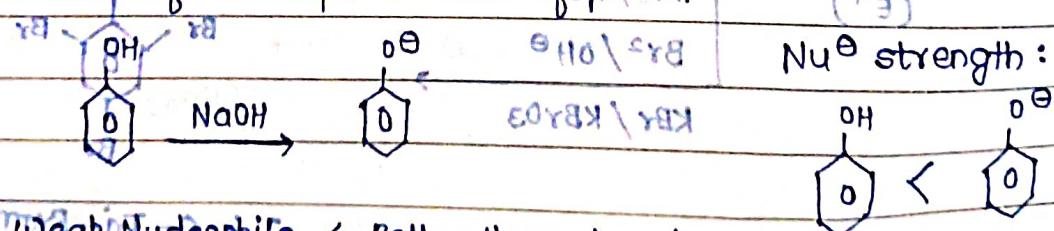
## • Chemical properties:



### ① Reaction of H-atom of phenol.



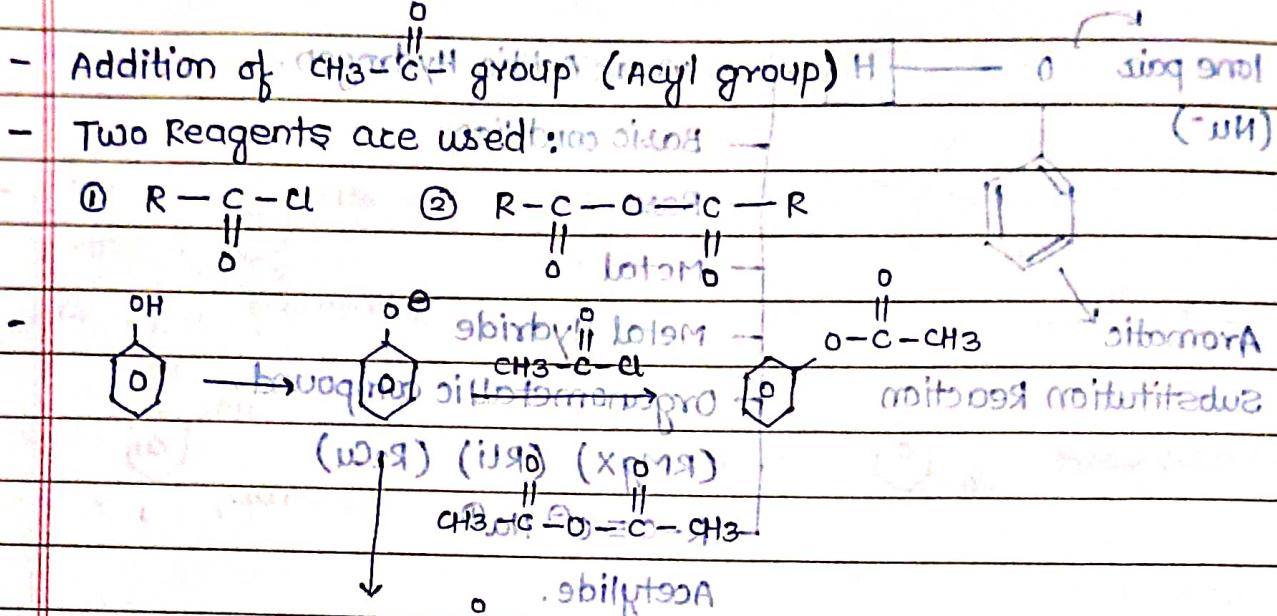
### ② Reaction of Nucleophilic nature of phenol



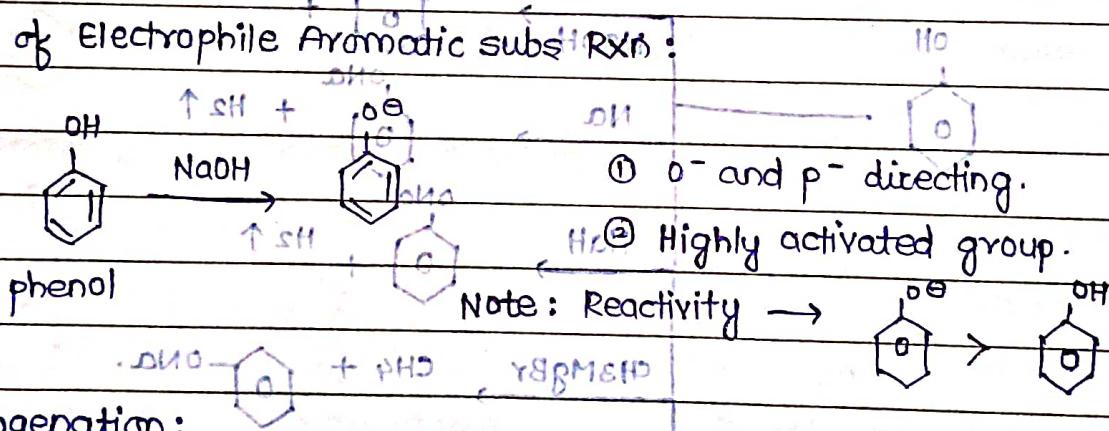
Weak Nucleophile  $<$  Better than phenol  
 - Resonance (W)  
 - -ve charge hain.  
 - Bulky

## • Acylation of phenol:

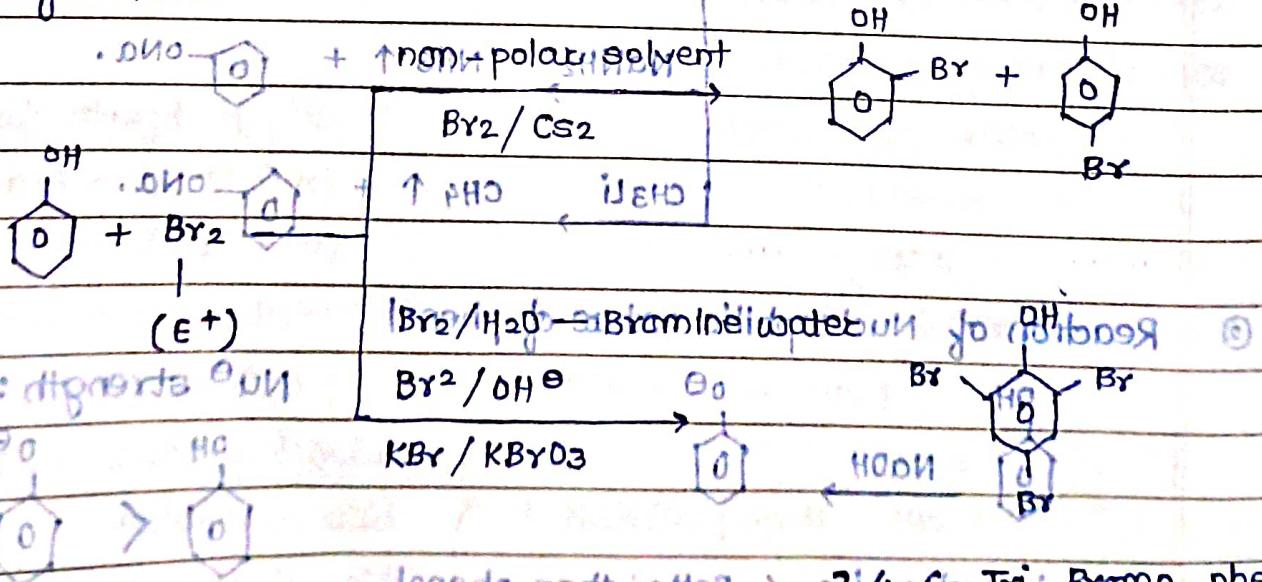
: ditrigonal bipyramidal



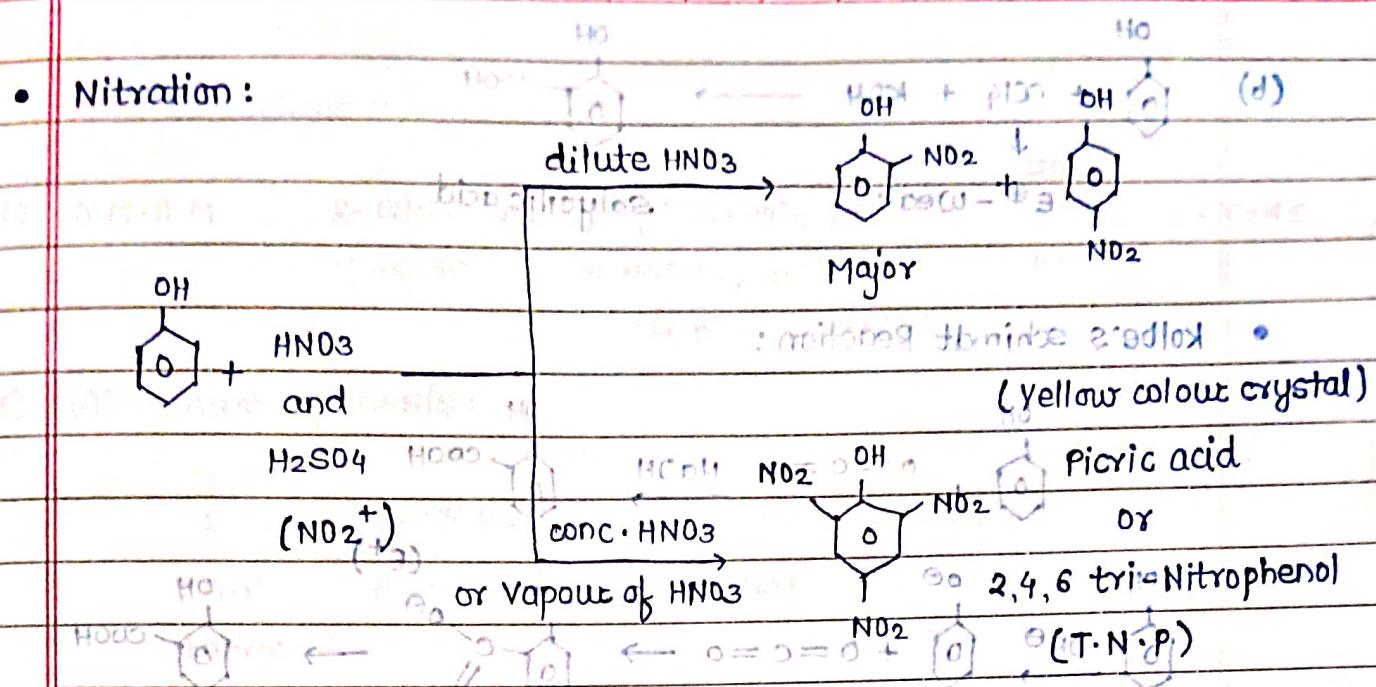
## • Rxn of Electrophile Aromatic subs RXN:



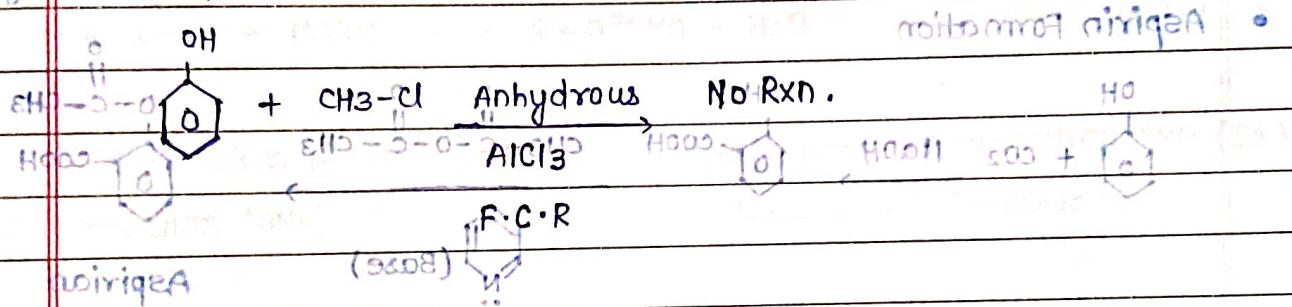
## • Halogenation:



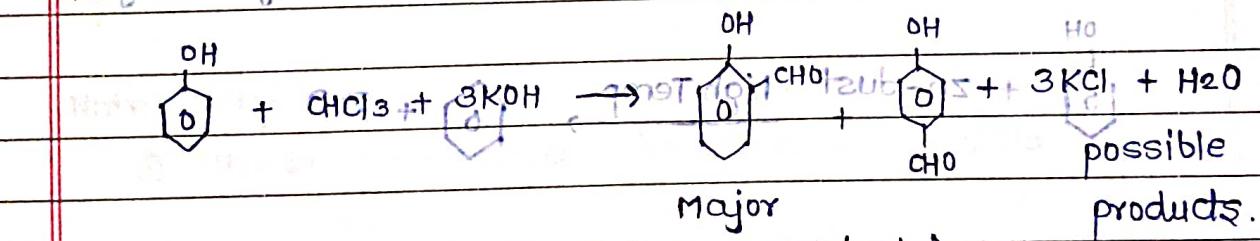
- Nitration:



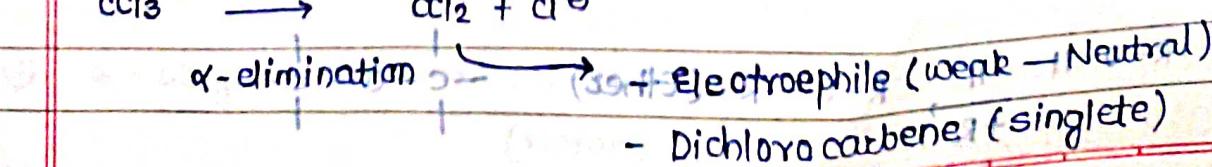
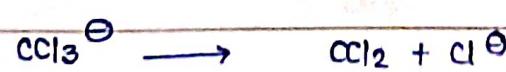
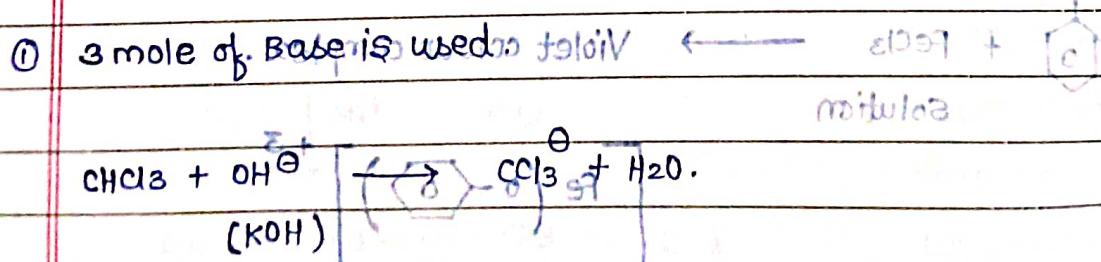
Note: phenol does not F.C.R

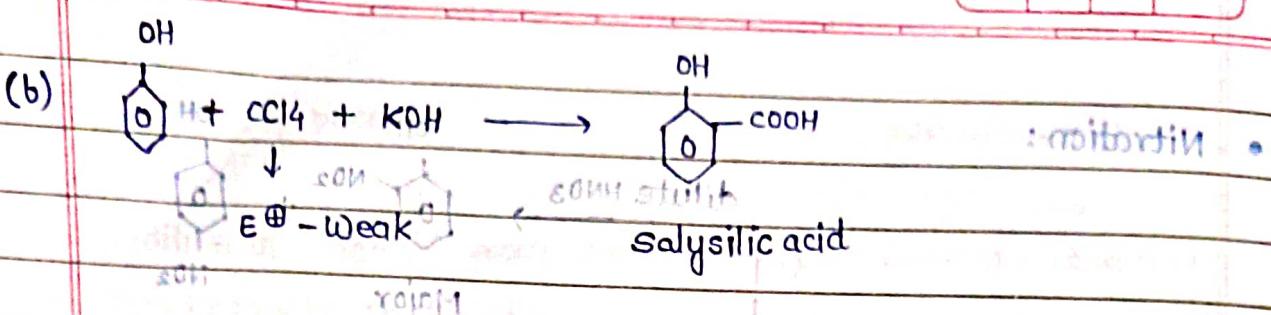


- Riemer-Tiemann Reaction:

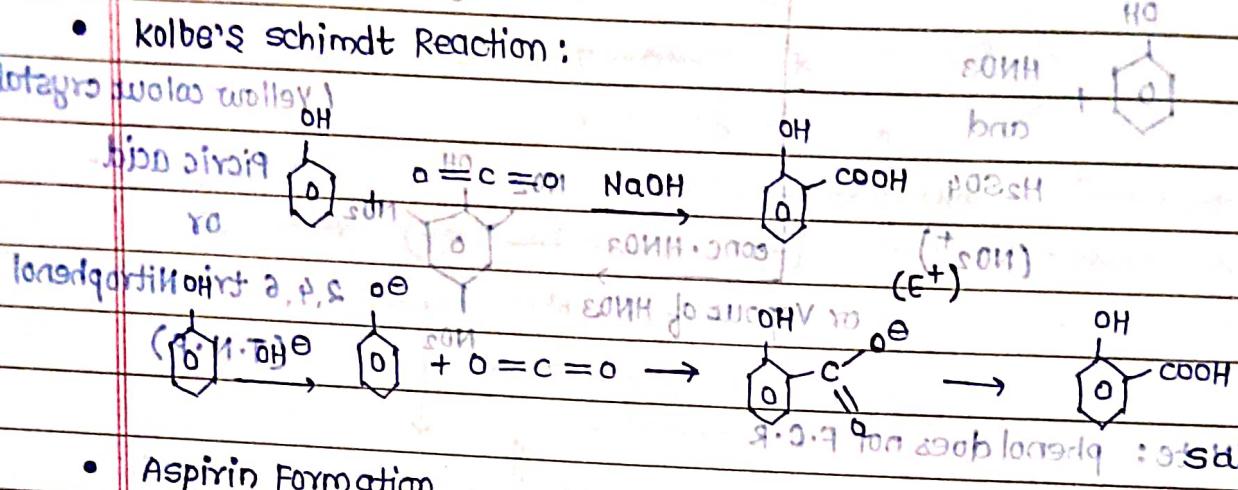


- Mechanism:

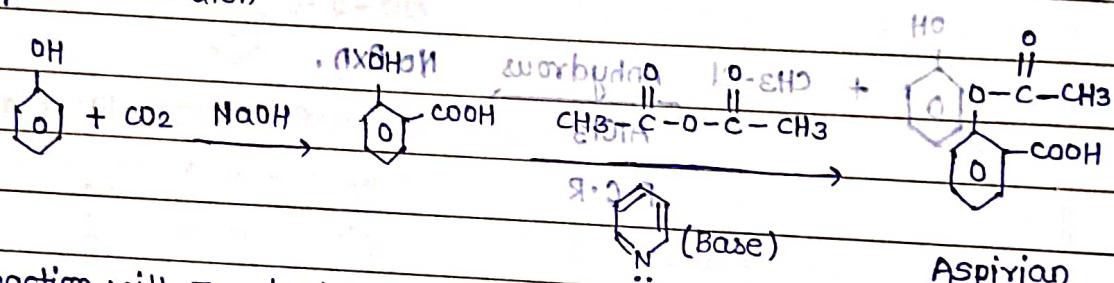




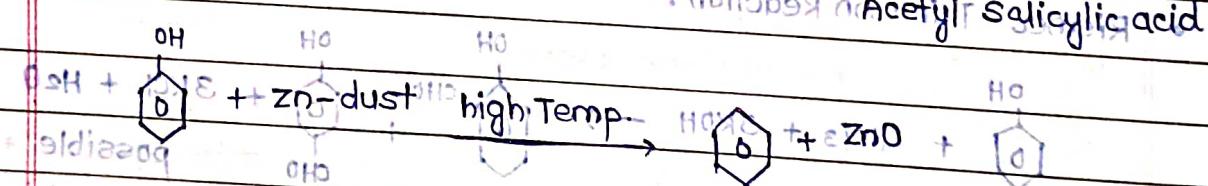
- Kolbe's Schmidt Reaction:



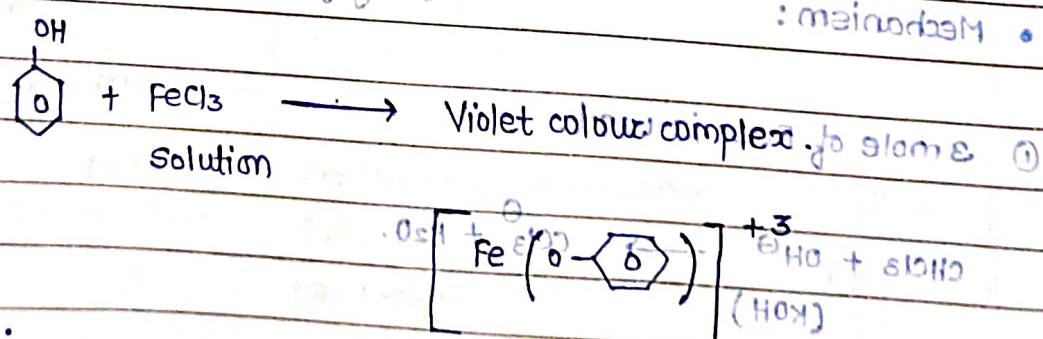
- ## • Aspirin Formation



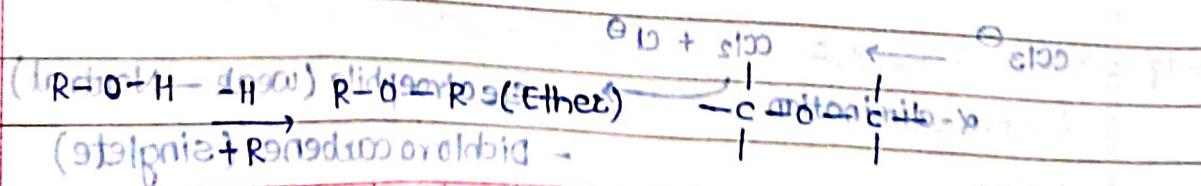
- ## • Reaction with Zn-dust:



- Test of phenol! (abysablestigfifloz)



- ## • || Ether:

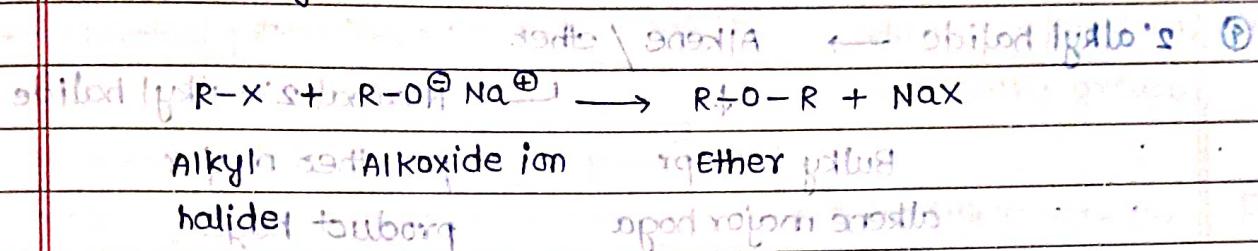


- M·O·P:  $\text{R}-\text{CH}_2-\text{CH}_2-\text{CO}-\text{O}-\text{R}'$

$$\text{R}-\text{CH}_2-\text{CH}_2-\text{CO}-\text{O}-\text{R}' + \text{Hg}(\text{OOCCH}_3)_2 / \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{minn}} \text{R}-\text{CH}_2-\text{CH}_2-\text{CH}(\text{OOCCH}_3)-\text{O}-\text{R}'$$

$$\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}(\text{OOCCH}_3)-\text{O}-\text{R}' + \text{NaBH}_4 / \text{OH}^- \xrightarrow{\text{minn}} \text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{R}'$$

## ② Williamson synthesis:



(stabilized lysine- $\beta$ -is) acidic thaborate reagent

Substitution  $\leftarrow$  Strong Nu $^\ominus$       strong Base - Elimination Rxn (E<sub>2</sub>)

Reaction ( $\text{S}_{\text{N}}2$ )  $\leftarrow$   $\xrightarrow{\text{H}-\text{I}}$  steric hindrance  $\leftarrow$

### (a) Ether Formation:

Note: Alkyl halides -  $\text{CH}_3\text{-CH}_2\text{-IldBr} \longrightarrow \text{CH}_3\text{-CH}_2\text{-IldBr}$

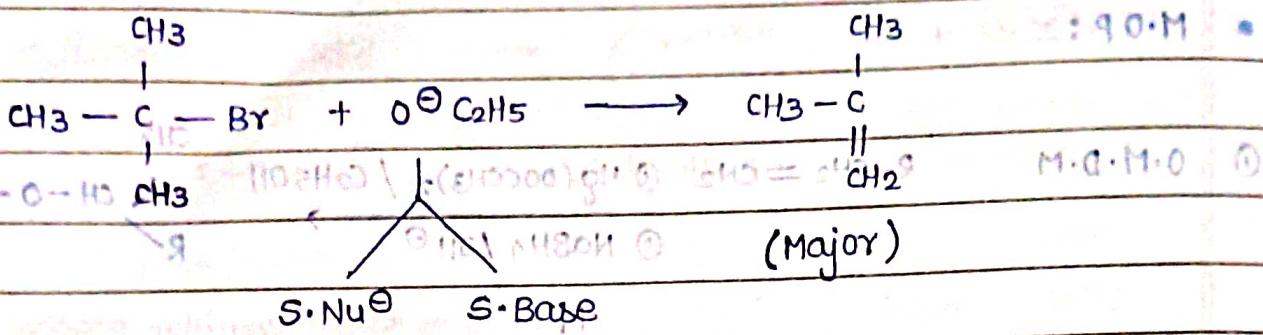
② 1° alkyl halide → ether (Major)

$$R-O-CH_3 + NaBr \quad (E)$$

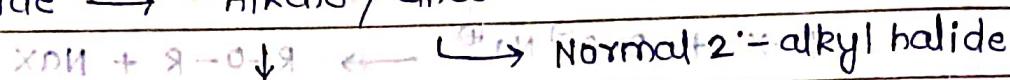
$\text{CH}_3\text{CH}_2\text{Br} + \text{NaOCH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{OCH}_3 + \text{NaBr}$  (100%)

- No Byproduct  
 - Best method for formation of Ether by Williamson synthesis

③ 3°-alkyl halide → Alkene  
(Major)



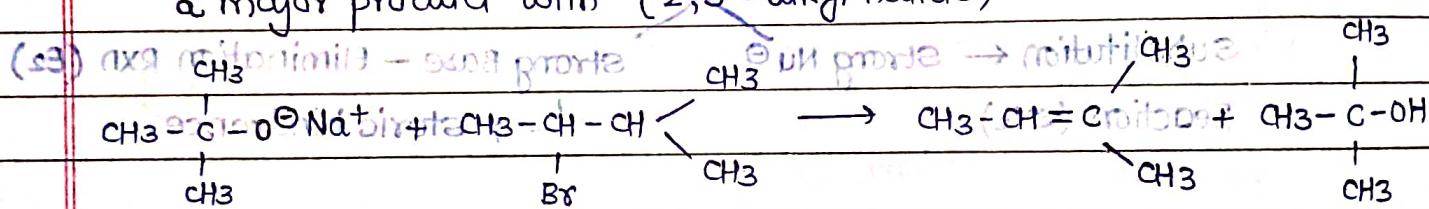
④ 2' alkyl halide  $\rightarrow$  Alkene / ether



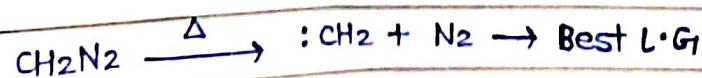
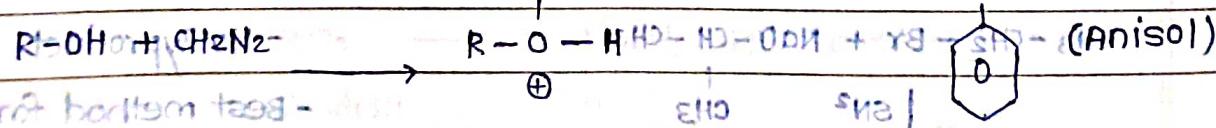
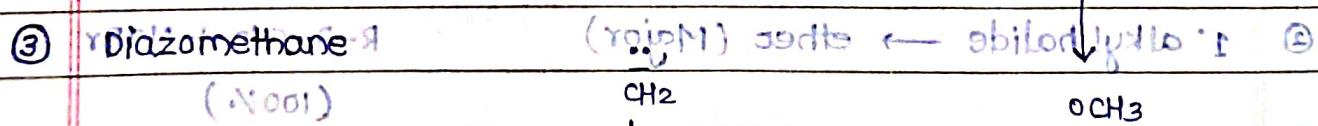
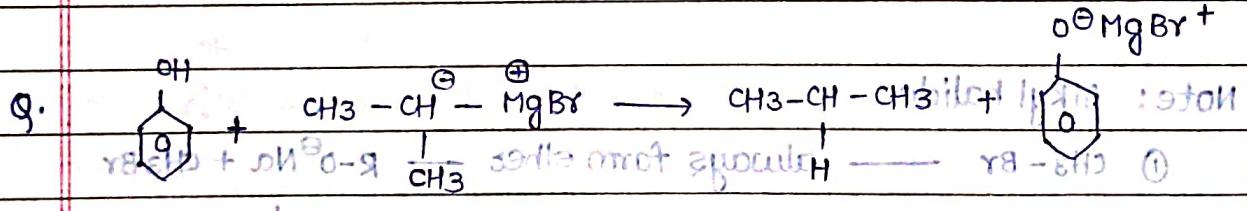
Bulky hui pr  
alkene major hogा

ether major  
product hogा!

- Note: In case of Bulky Alkoxyde (3-carbon), Alkene forms as a major product with (2,3'-alkyl halide)



(Base) :  $\text{NH}_2^\ominus \text{O}^\ominus \text{R}^-$  (D)

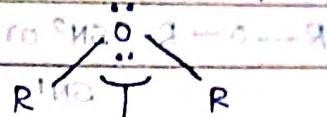


Diazomethane. Carbene  $\longleftrightarrow$  Alkene  $\longleftrightarrow$  Carbonyl (rojir M)

- Physical properties:

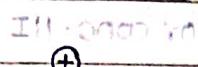
$R-O-R \rightarrow$  absence of H-bonding  $\rightarrow sp^3 (109.5^\circ)$

B.p =  $R-OH > R-O-R$

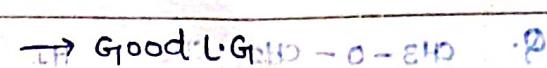
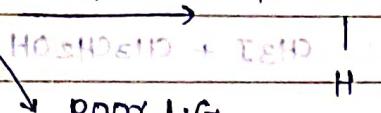
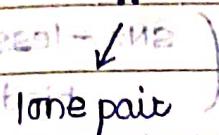
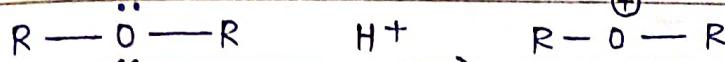


$110^\circ$  — Due to

Chemical properties:  $H-O-H$   $\rightarrow$   $III-H-O-H$  electronic Repulsion b/w

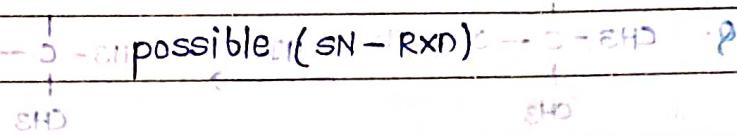
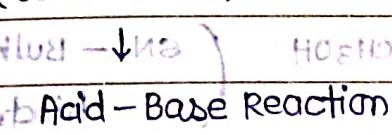


two bulky groups.



(Lewis Base)

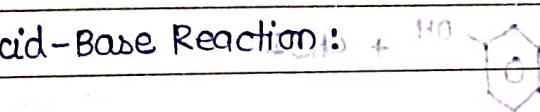
\* Substitution Reaction



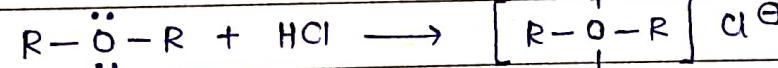
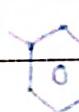
Acid-Base Reaction

SN

- Acid-Base Reaction:



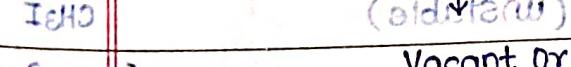
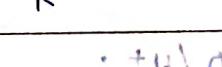
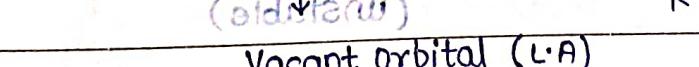
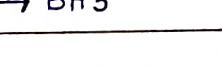
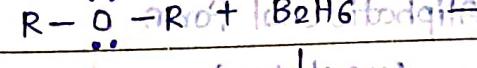
III



H-O-H

Cl-

H



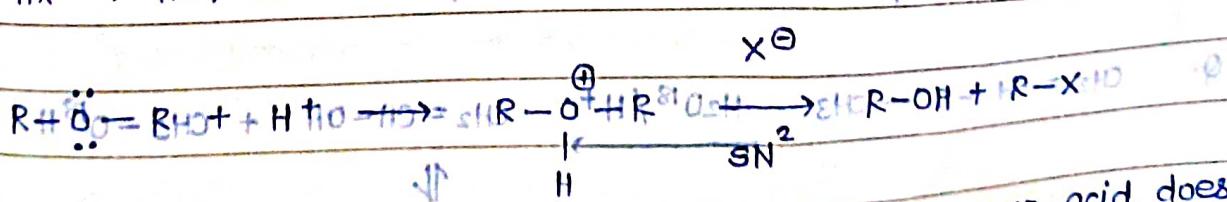
(old term)

Vacant orbital (L.A)

: + H) diff. due to molar

- Reaction with HX (Halogen acids)  $\rightarrow R-OH + HX \rightleftharpoons R-OH + H + X^-$

$HX \rightarrow HI > HBr > HCl > HF$  (same as the order of the acids)

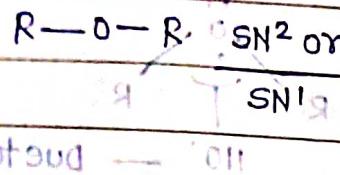


$Nu^- \rightarrow I^- > Br^- > Cl^- > F^-$

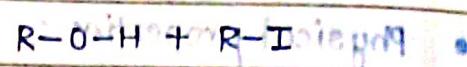
A.S.  $\rightarrow HI > HBr > HCl > HF$

Note: oxo-acid does not give this type of rxn.

(a.eo1) Eqa e

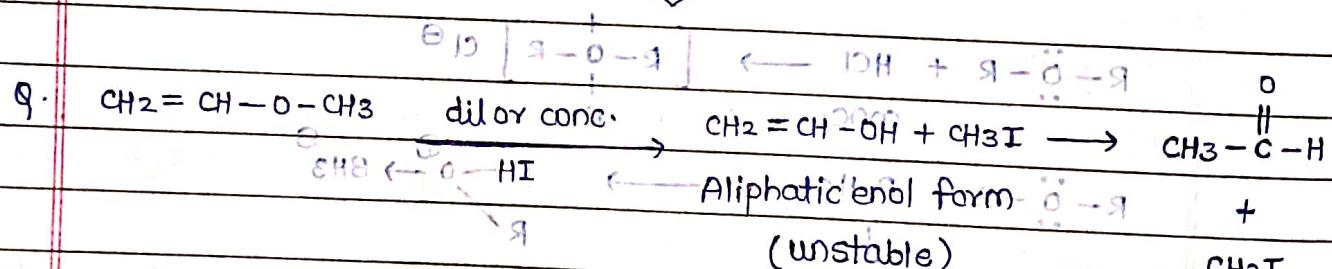
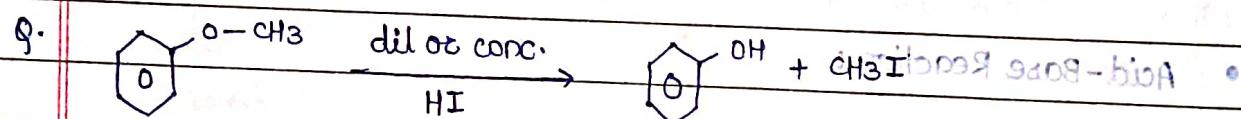
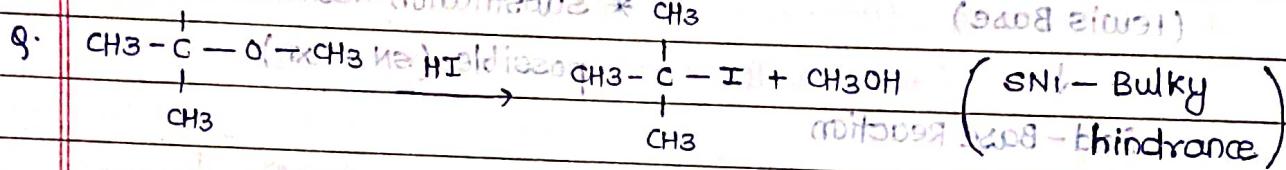
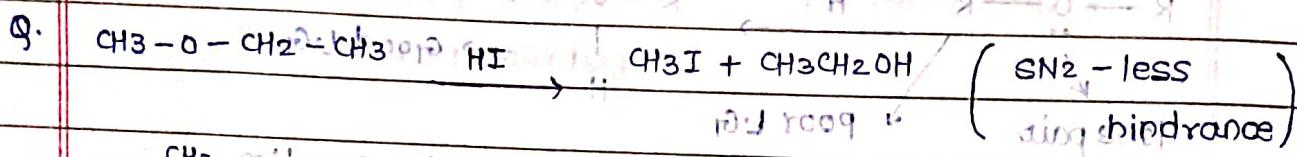
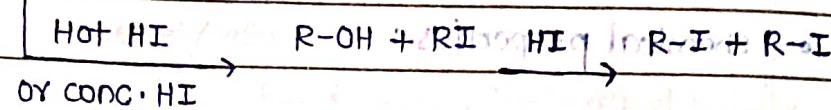


Cold HI

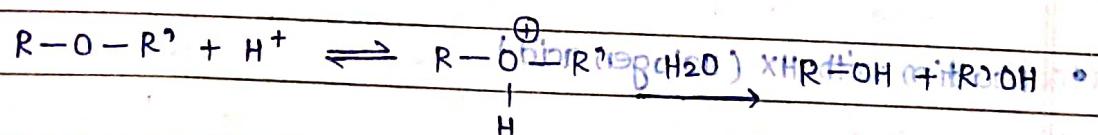


or dilute HI

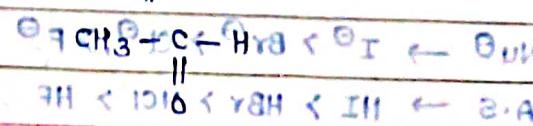
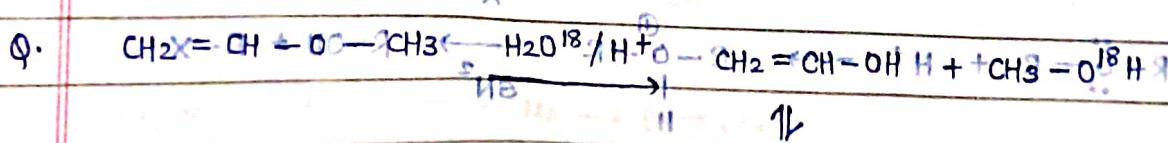
solvolysis Reactions  
with Bulky Groups



• Reaction with H<sub>2</sub>O / H<sup>+</sup> : (A.R.) (Acidic reagent)



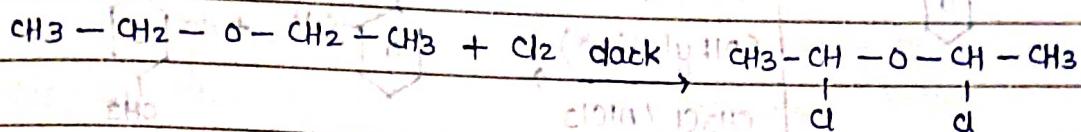
Note: All concept are same (HI > HCl > HBr > H<sub>2</sub>S > H<sub>2</sub>O > H<sub>2</sub>)



Note: Oxo-acid, strong acid  
mix of eqt. with eqt.

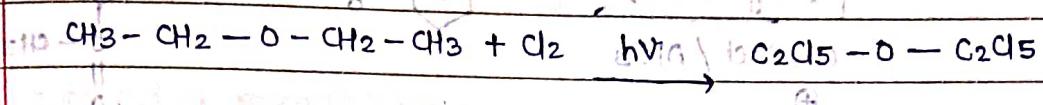
- Halogenation:

(a) In Dark (absence of sunlight or  $h\nu$  energy)

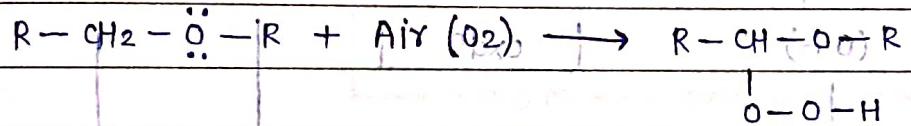


Mono-halogenation.

(b) In presence of sunlight:



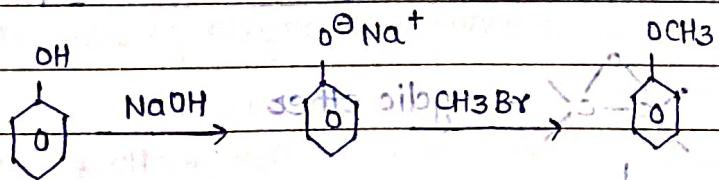
- Oxidation: Ether oxidise by air in very slow rate and form peroxide ether.



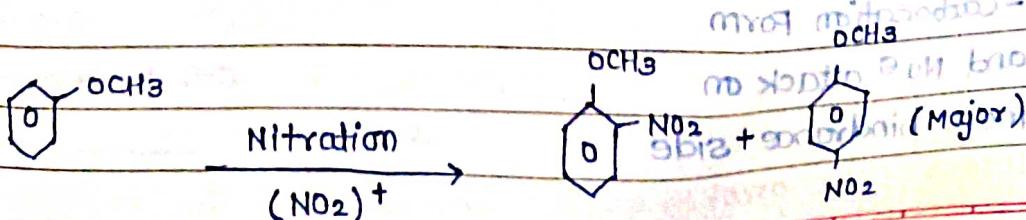
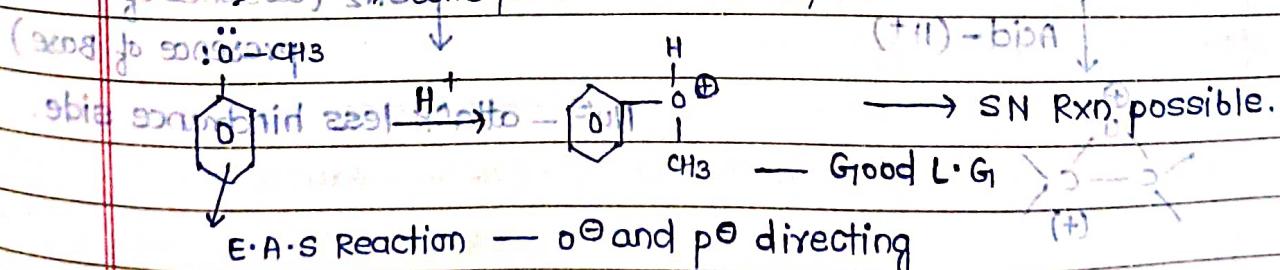
Ether

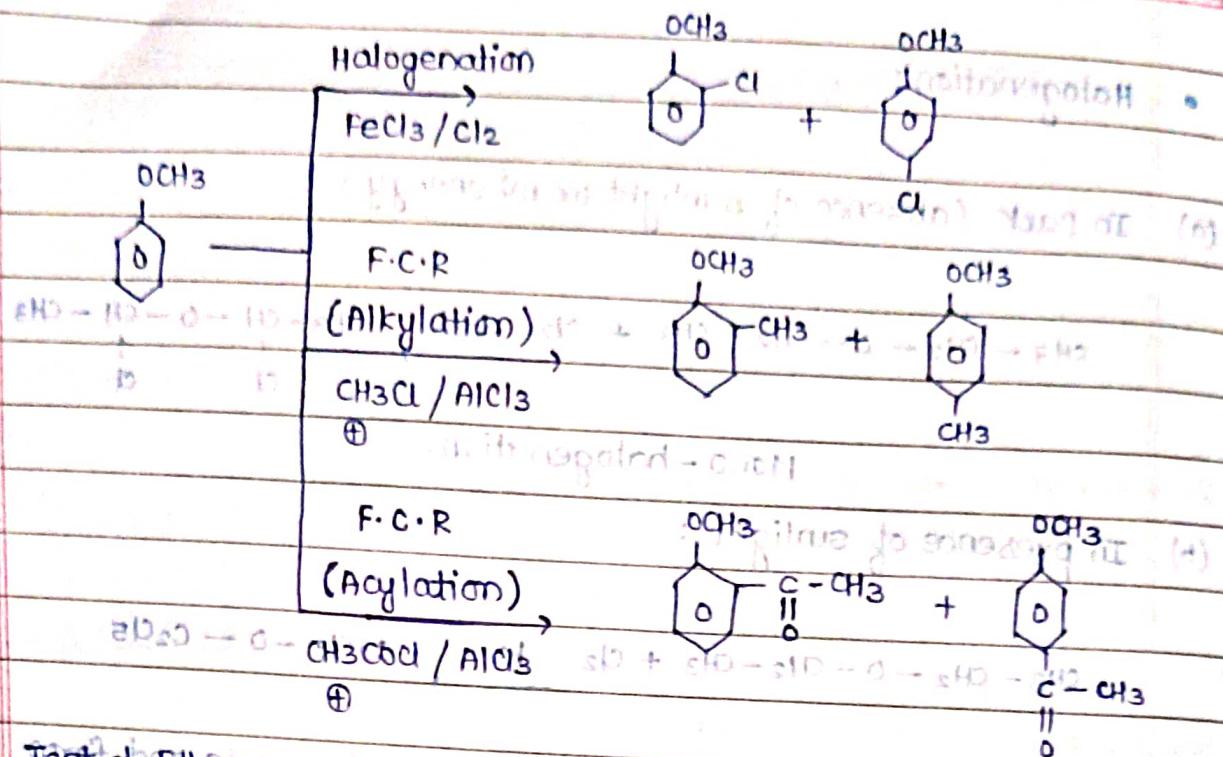
peroxide ether.

- Aromatic ether:

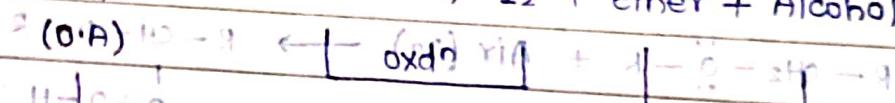
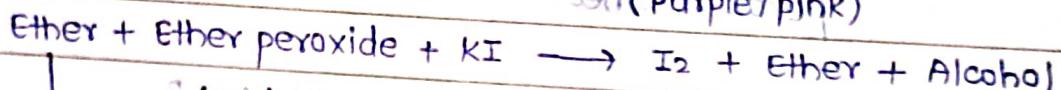


~~base~~  $\text{O}^\ominus$   $\text{Na}^+$   $\text{O}^\ominus$   $\text{Na}^+$   $\text{O}^\ominus$   $\text{Na}^+$





- Test of Ether: *nitroso* (purple/pink)

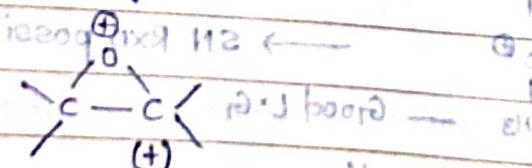
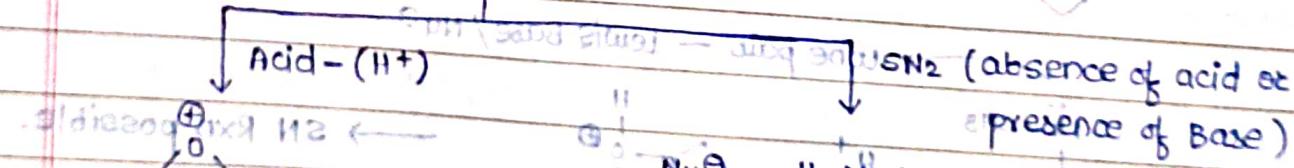
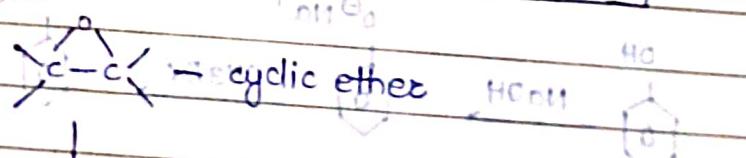


*ether*

Redn

*nitroso isomer*

- Epoxide Ring:

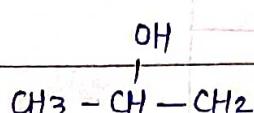
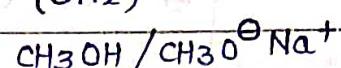
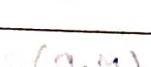
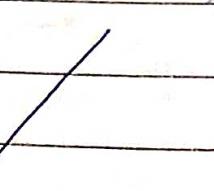
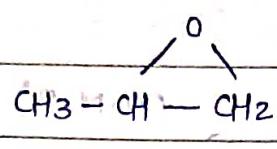


- Carbocation Form

and  $\text{Nu}^{\ominus}$  attack on

*more hindrance side*

$=\text{OH}$



Reaction mechanism: