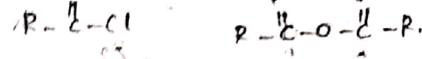


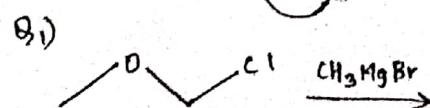
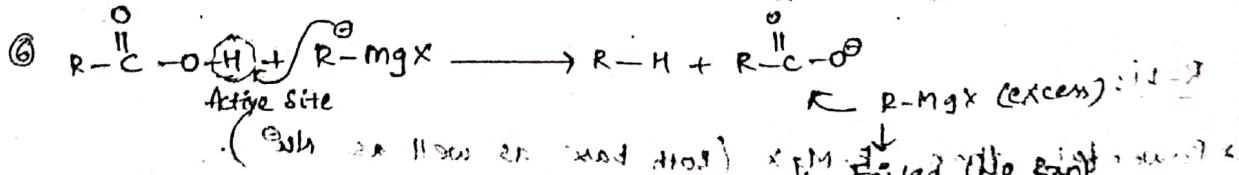
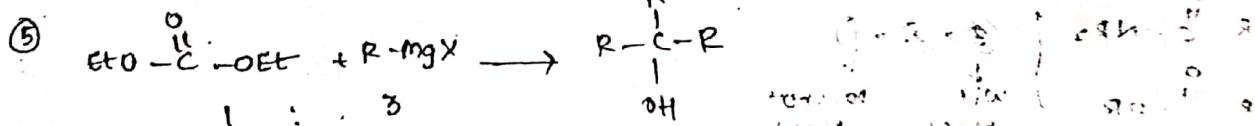
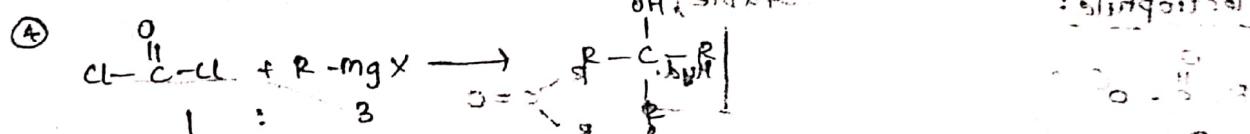
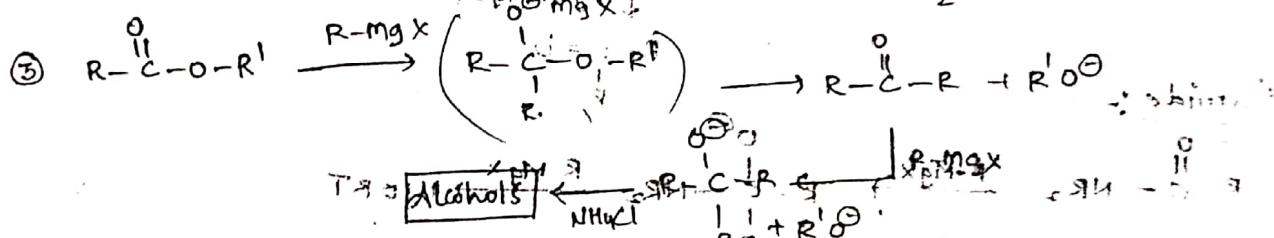
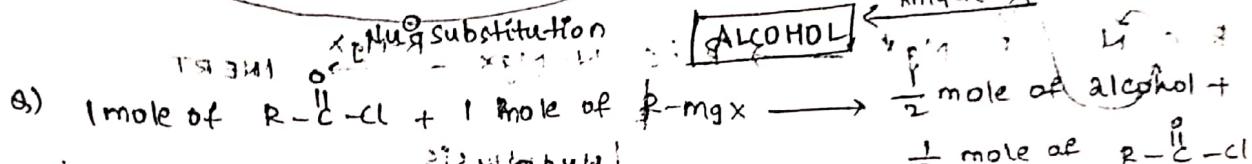
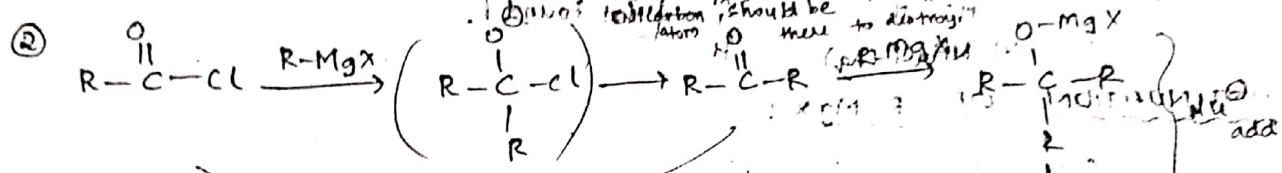
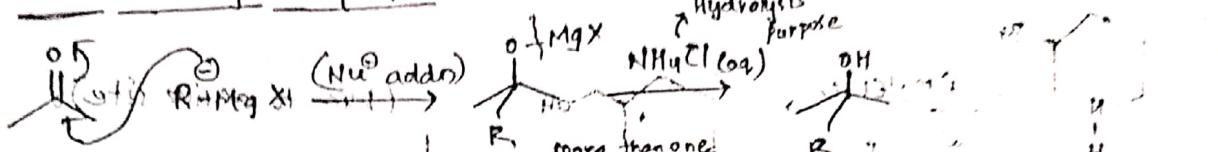
# GRIGNARD REAGENT:

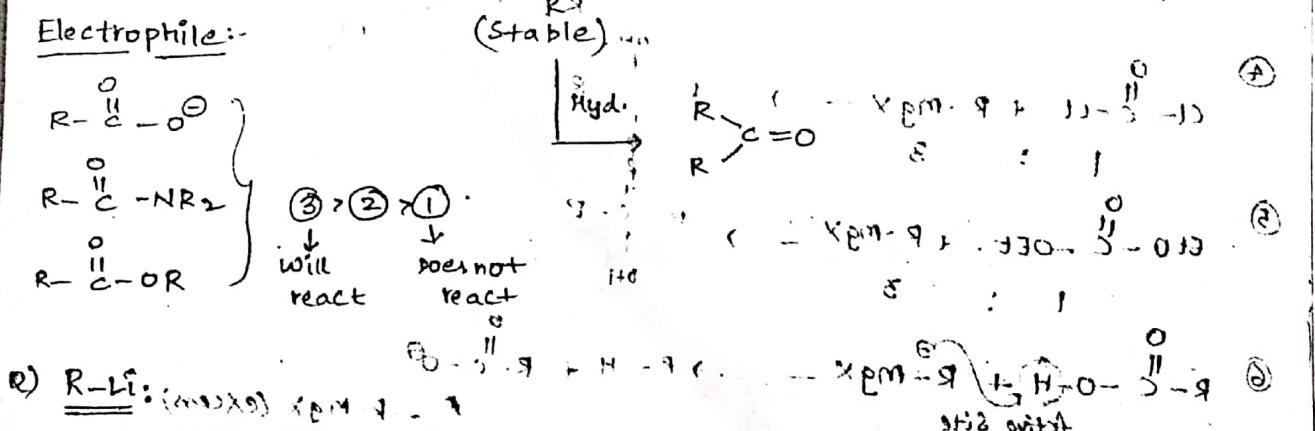
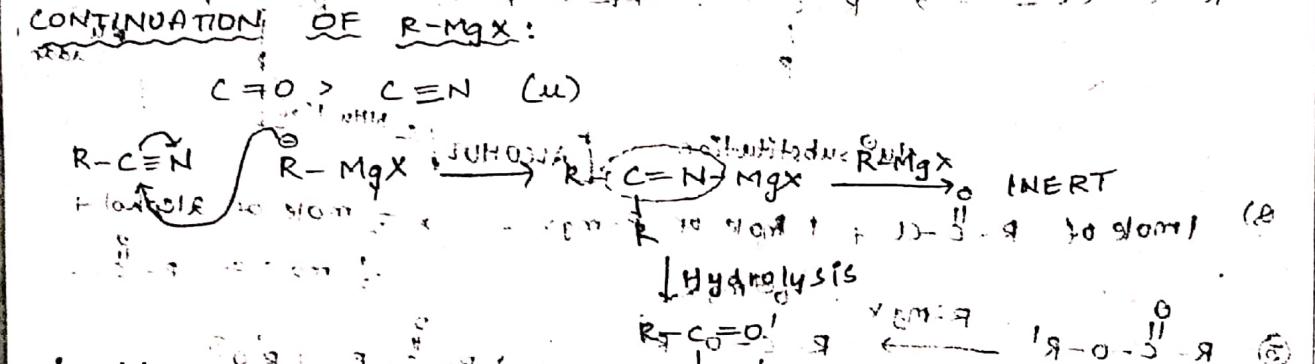
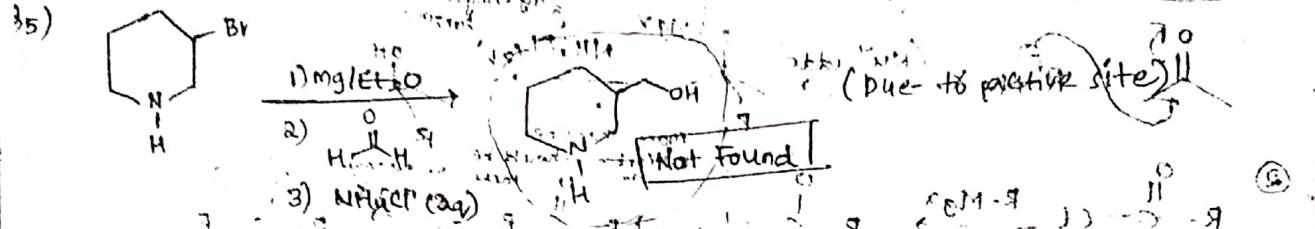
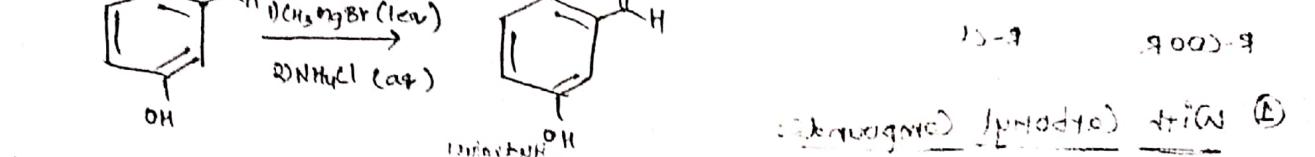
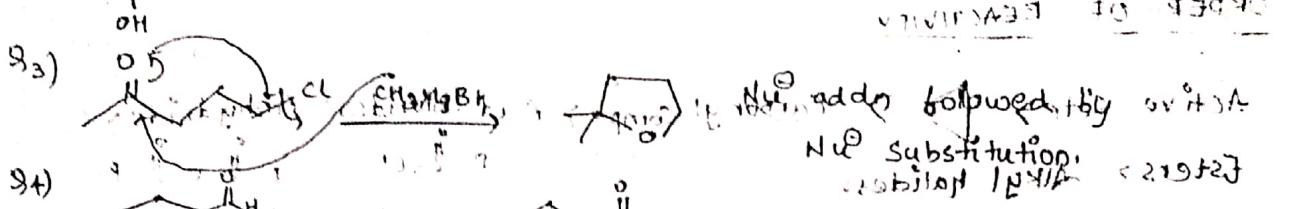
## ORDER OF REACTIVITY:

Active sites  $\rightarrow$  Carbonyl Comp.  $\rightarrow$  Acid chlorides, Anhydrides  
 Esters  $\rightarrow$  Alkyl halides.



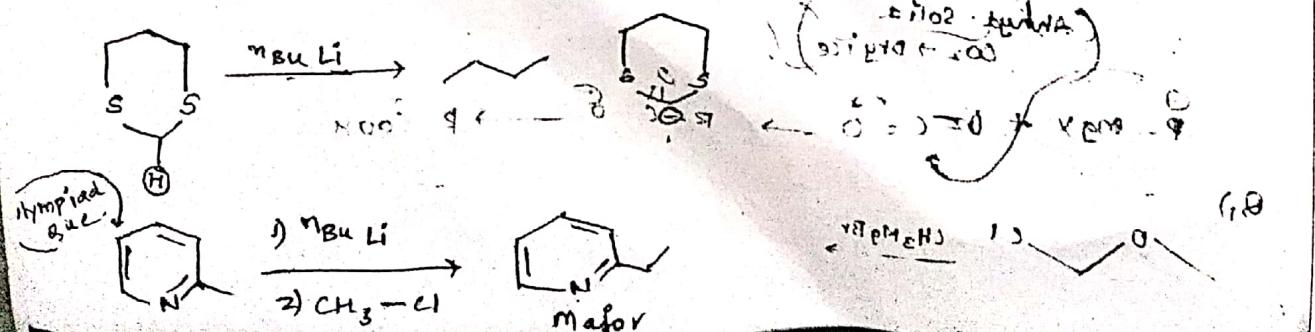
## ① With Carbonyl Compounds:





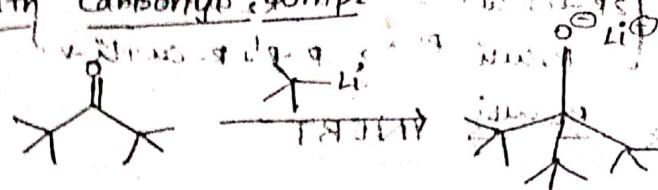
→ Powerful than  $\text{R-MgX}$  (both base as well as  $\text{N}^{\oplus}$ ).

1) Eq for Base:

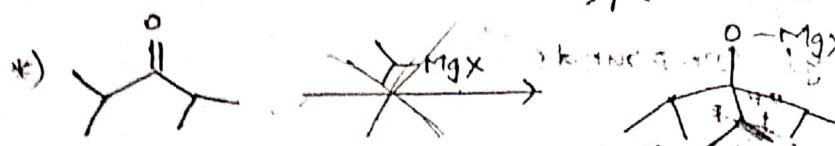


Nucleophilicity examples

→ with CARBONYLS, ROMPs

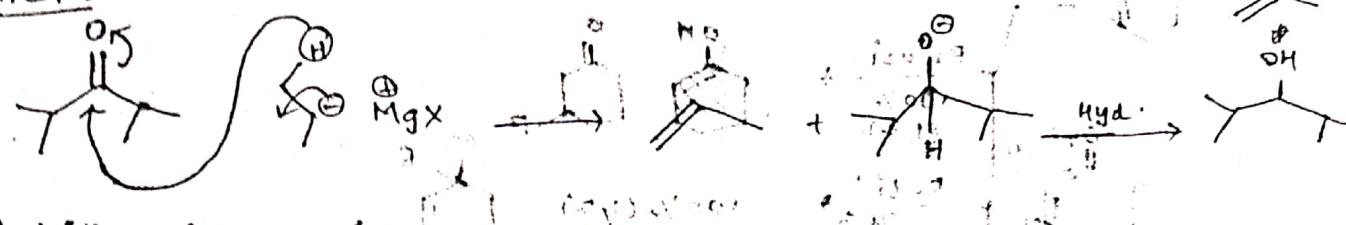


(100% Forward Rxn  
without equilibrium.)

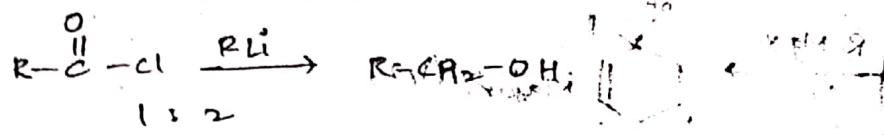


(Does not take place)

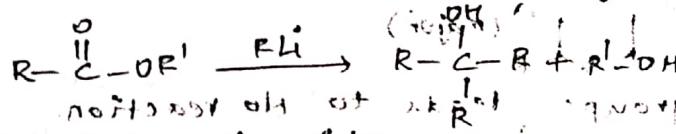
FACT:



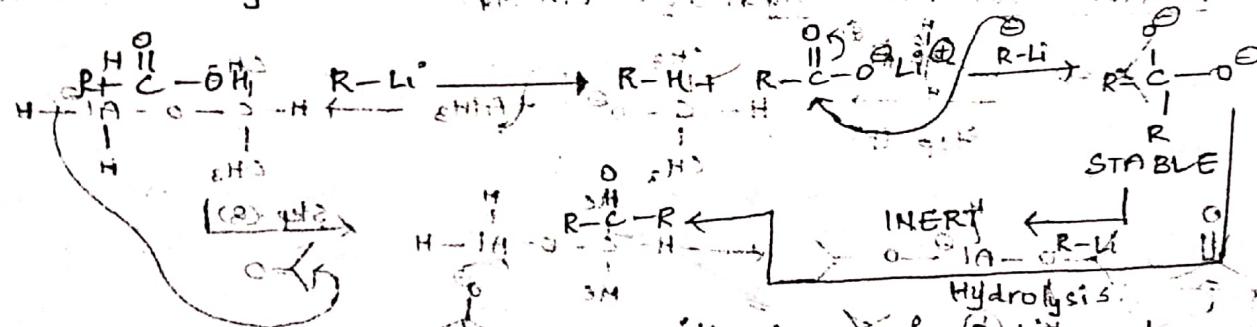
→ With acid chloride:



→ with Ester:

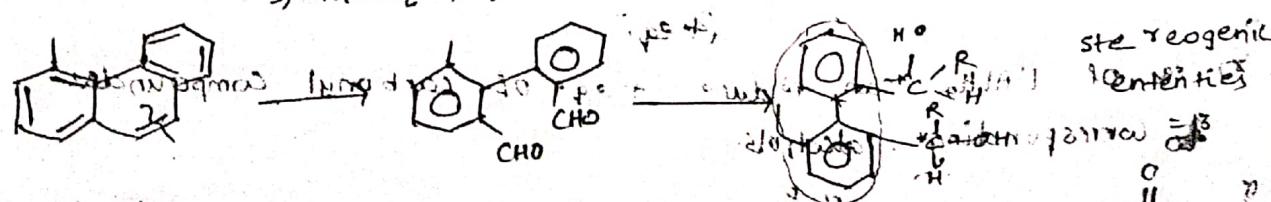
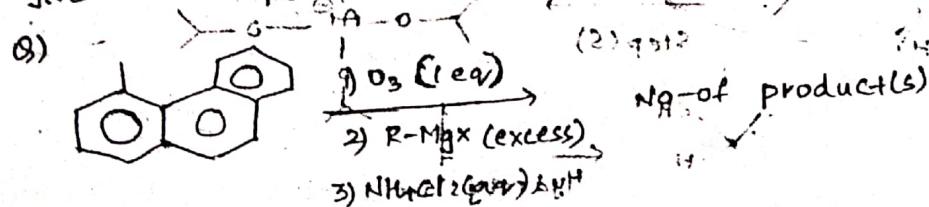


→ with Carboxylic acids:

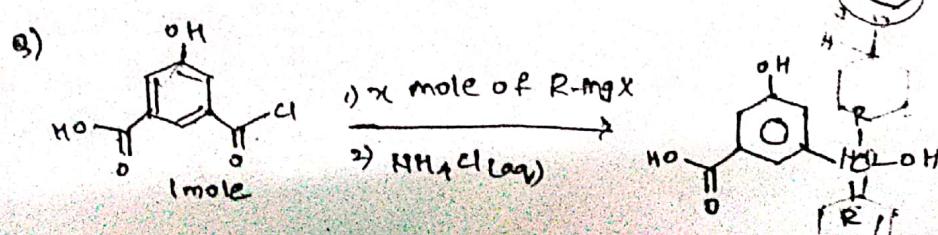


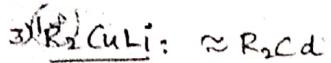
→ 1 eq. of Carboxylate ion reacts with 1 eq. of R-Li and

gives Corresponding 1 eq. of Ketone

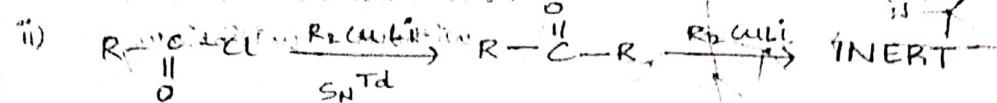


ste reogenic  
contenies

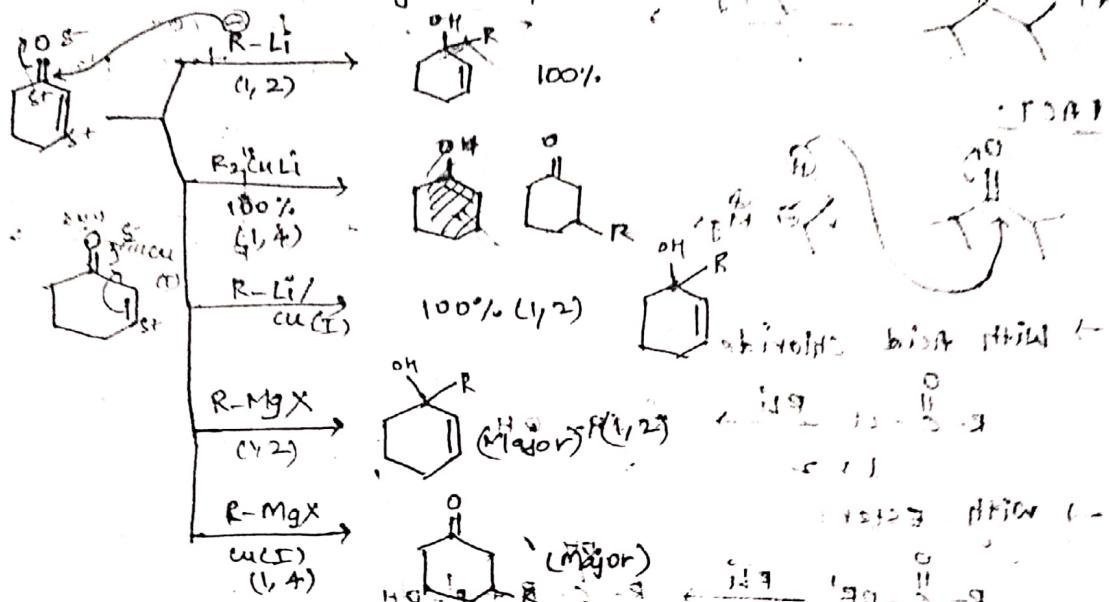




i) Revised Corey-House Synthesis.

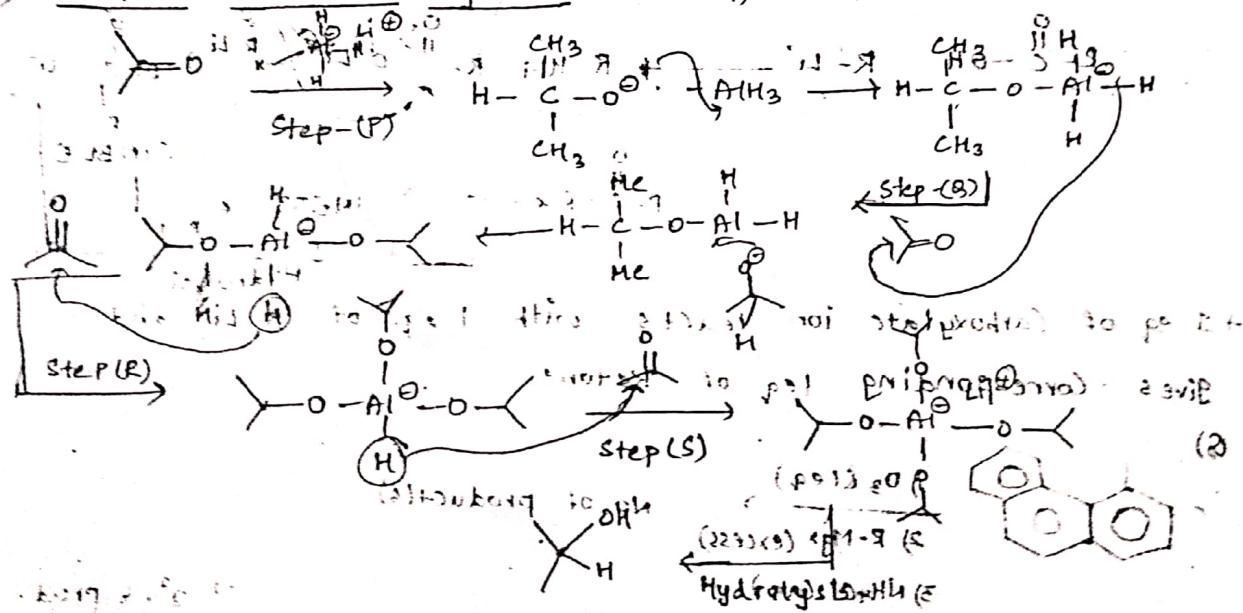


iii)  $\alpha,\beta\text{-unsaturated carbonyl compounds}$

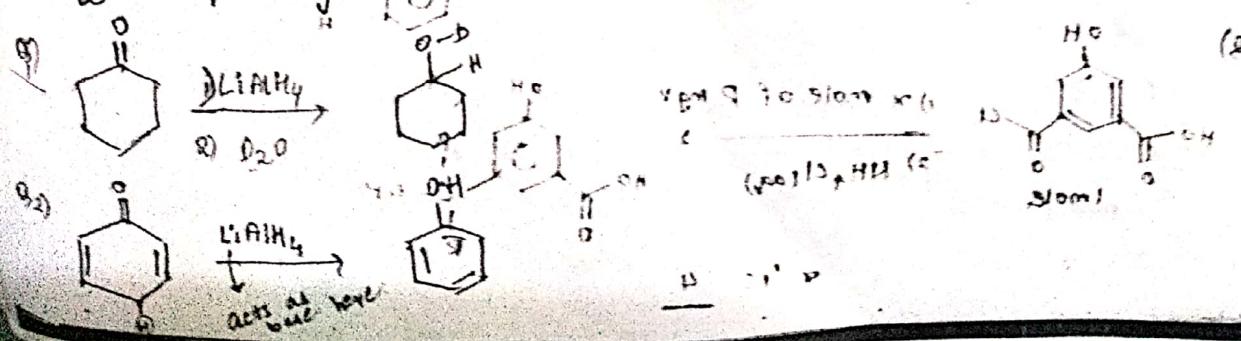


→ other all functional groups leads to No reaction.

4) Lithium Aluminium Hydride: - ( $LiAlH_4$ )



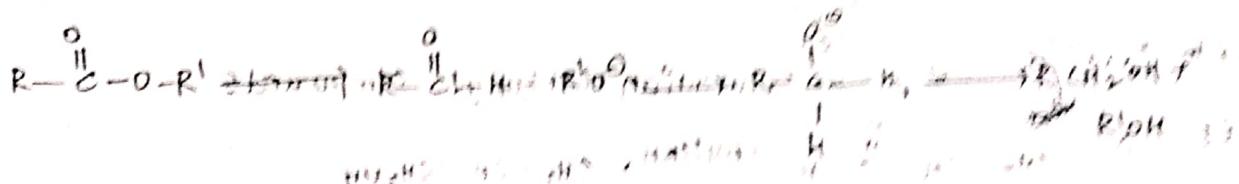
→ 1 form of  $LiAlH_4$  can reduce + eq. of carbonyl compounds  
→ Corresponding lactols.



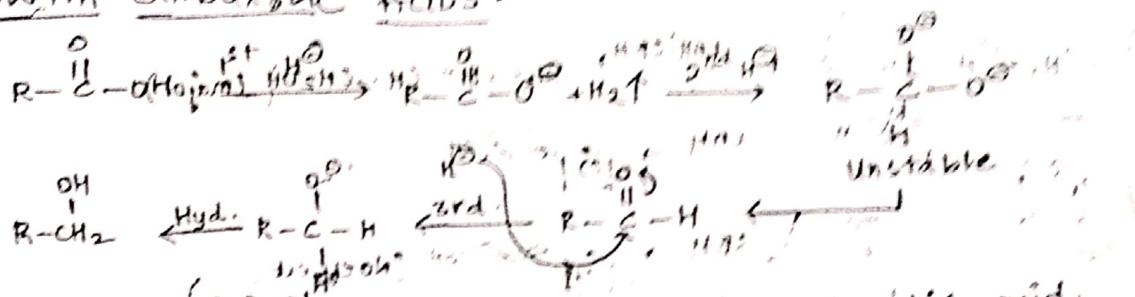
→ Eq. of LiAlH<sub>4</sub> can reduce 2 eq. of acid chloride to corresponding alcohol.



→ Eq. of LiAlH<sub>4</sub> can reduce 2 eq. of ester to corresponding alcohol.

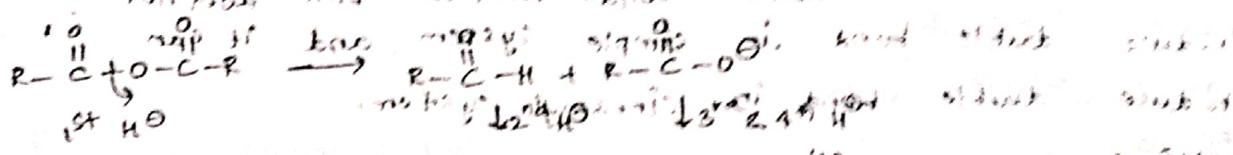


### WITH CARBOXYLIC ACIDS



→ Eq. of LiAlH<sub>4</sub> can reduce 4 eq. of carboxylic acid to corresponding alcohol.

→ Eq. of LiAlH<sub>4</sub> can reduce 2 eq. of carboxylic acid anhydride to corresponding alcohol.



→ It is a powerful reducing agent) reduces Nitro group

- Nitro group

- cyano group

- amides etc.

### 5) SBH: (Sodium Boro Hydride)

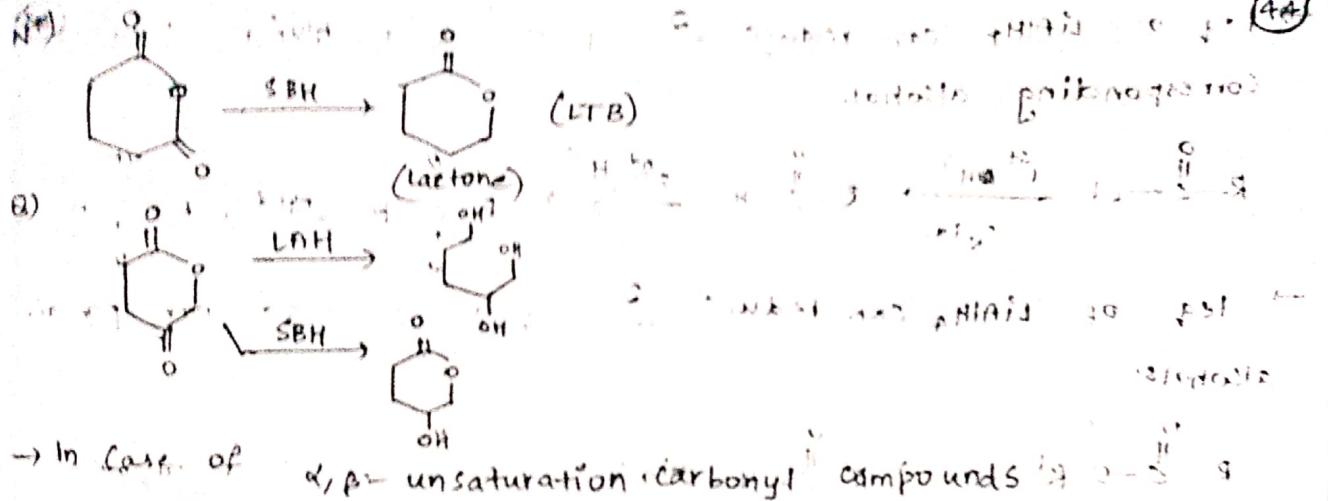
→ less mild reducing agent than LAH.

→ Reduce

i) Carbonyl compounds to alcohols.

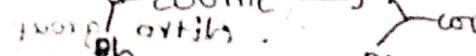
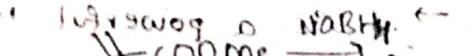
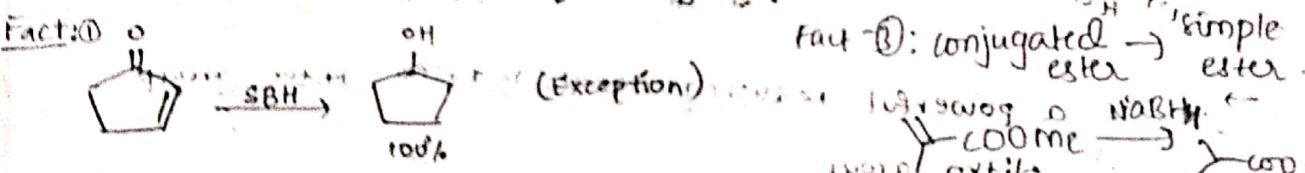
ii) Acid chloride to alcohols.

iii) All other functional groups are inert except cyclic anhydrides.



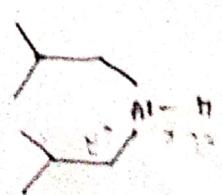
- Ex:
- $\text{CH}_2=\text{CH}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{H} \xrightarrow{\text{LAH/SBH}}$ ,  $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$  (Major) as well as  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{OH}$
  - $\text{CH}_3-\text{CH}=\text{CH}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{H} \xrightarrow{\text{LAH/SBH}}$ ,  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$  (Major) as well as  $\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$
  - $\xrightarrow{LAH}$   $\xrightarrow{SBH}$  (No effect for D.B.)
  - $\xrightarrow{LAH}$   $\xrightarrow{SBH}$  (Effect on triketone)

→ SBH never effect double bond, whereas LAH does not reduce double bond in simple system, and it can reduce double bond in cinnamyl system.



• HgI<sub>2</sub> work on primary amine

### 6) DIBAL-H / DIBAL:



Function: Carboxylic acid  $\text{R}-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{OH}$

• Alotable ester (ketone/aldehyde)

• Alotable alcohols (ketone/aldehyde)

• Alotable amides (ketone/aldehyde)

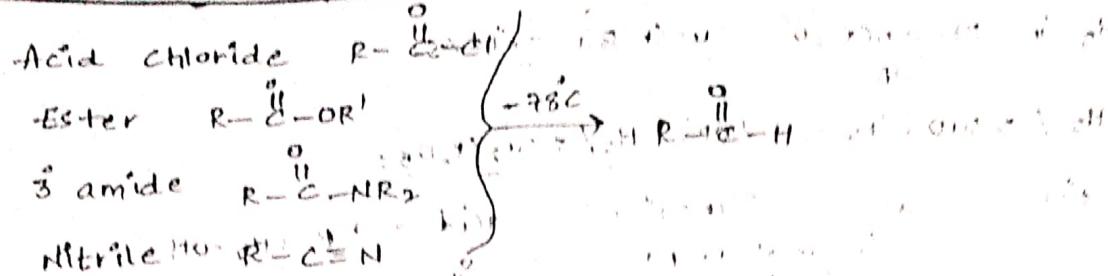
• Alotable acids

\*)

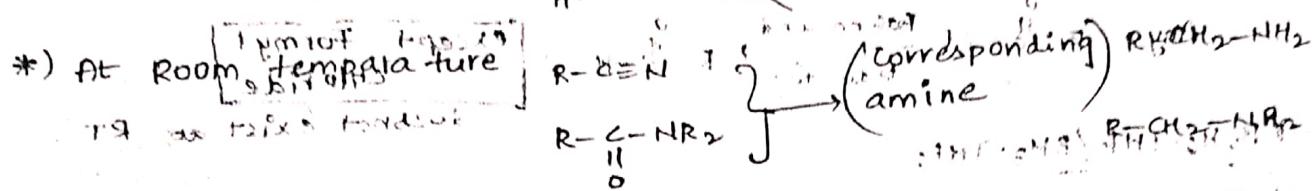
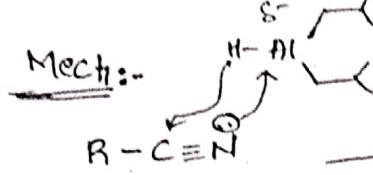
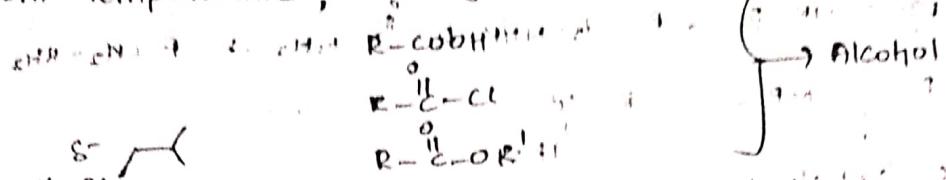
R-

R-

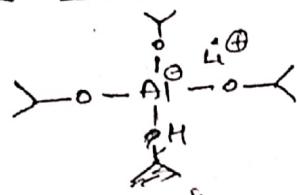
O



→ At room temperature, carbonyl compounds



### 7) Trialkoxy Lithium Aluminium Hydride



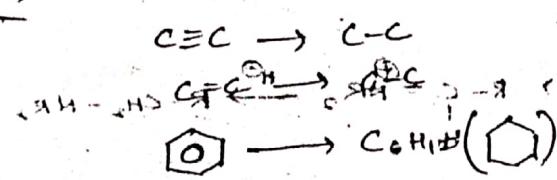
Hint:

Rate for Sodium Borohydride:  $\textcircled{S} > \textcircled{R} > \textcircled{Q} > \textcircled{P}$

Rate for LiAlH<sub>4</sub>:  $\textcircled{P} > \textcircled{Q} > \textcircled{R} > \textcircled{S}$  [the reaction may be -I]

Function: Same as DIBAL-H

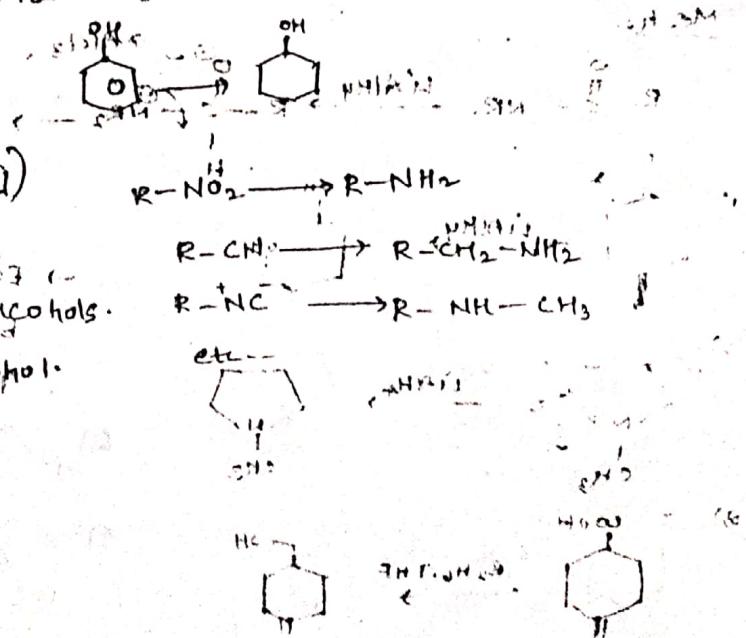
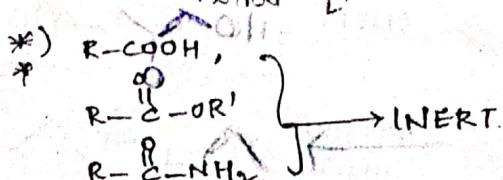
### B) H<sub>2</sub> in presence of Ni/Pt/AlCl<sub>3</sub>



Carbonyl → Alcohols

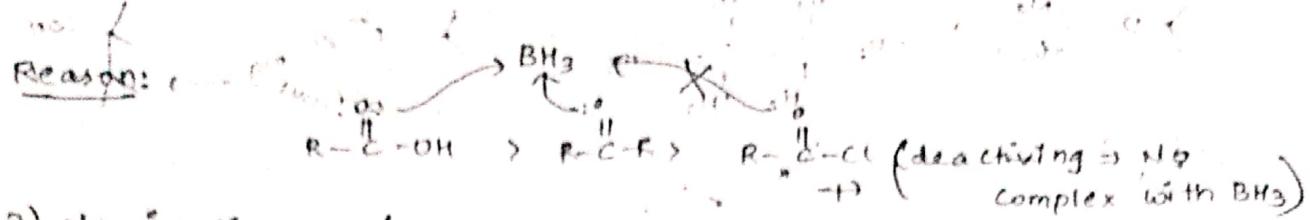
Formic acid → Alcohol  
 Acetic acid → Alcohol

Anhydride → Alcohol

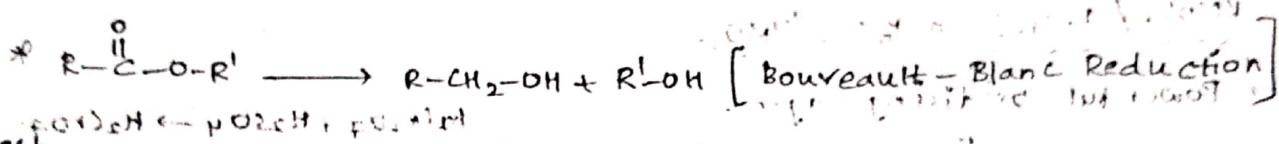
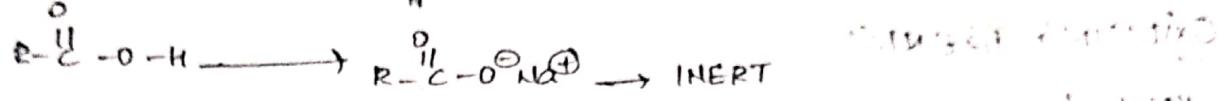
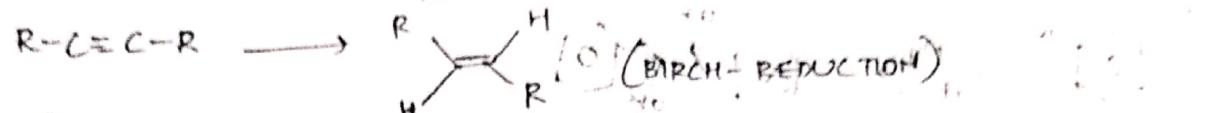
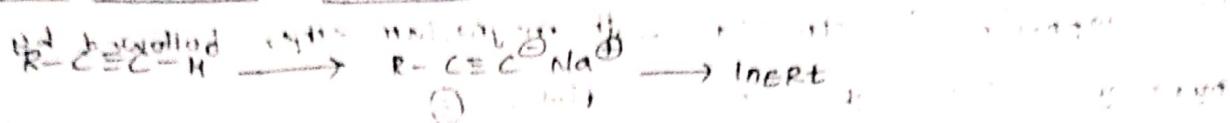




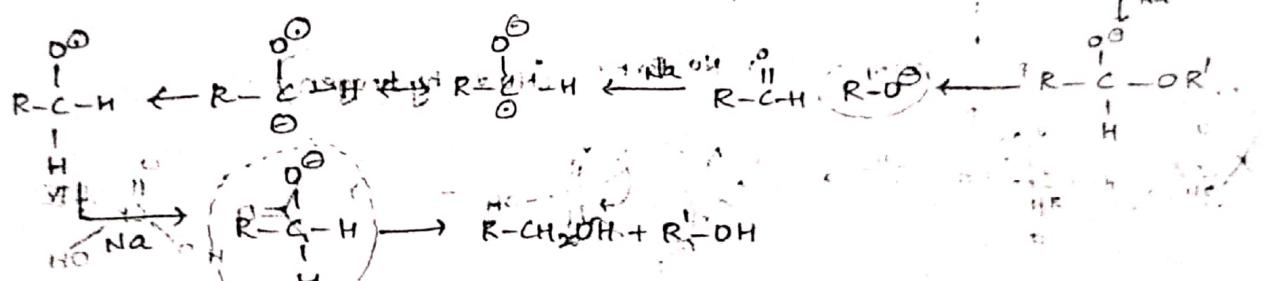
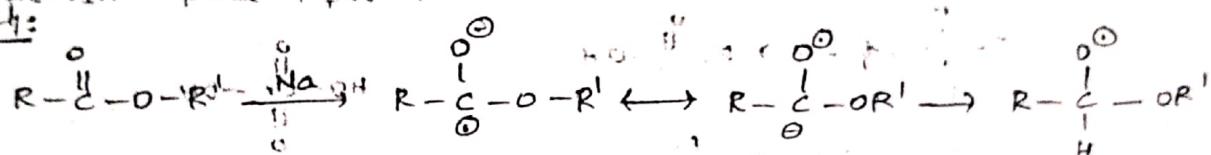
$\text{BH}_3$  readily reduces acids and carbonyl compounds but not acid chlorides.



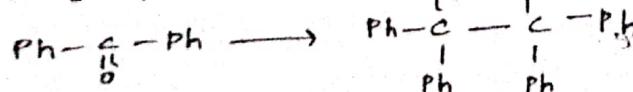
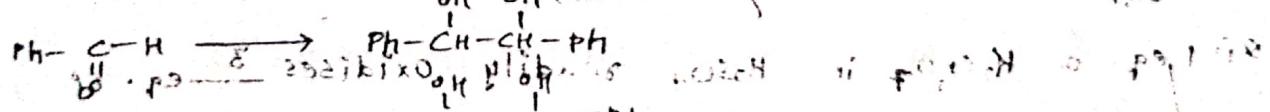
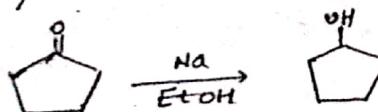
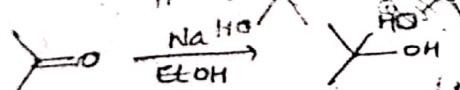
(2) Na in liq. NH<sub>3</sub> / Na-Stopper



mech.



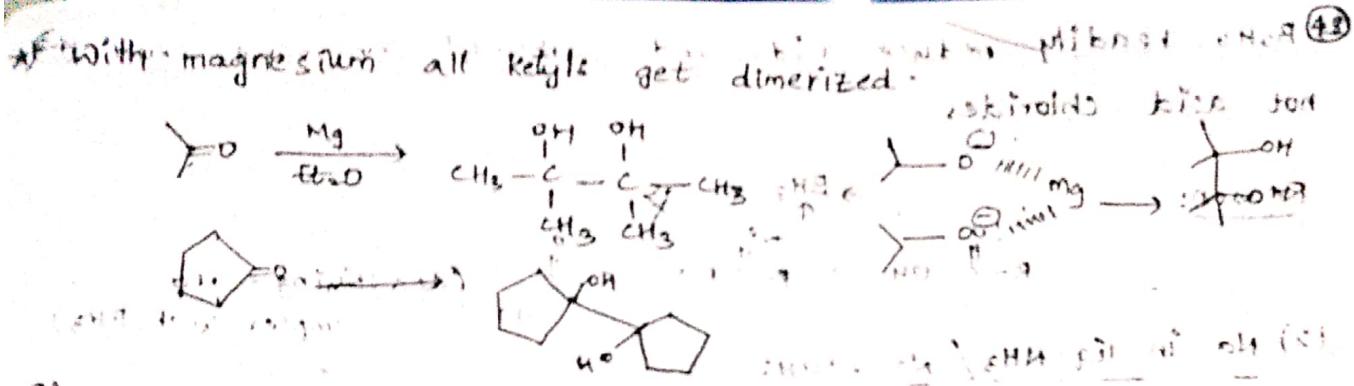
## ELECTRONS:- (page no: 217 & 218 - Peter Seykes)



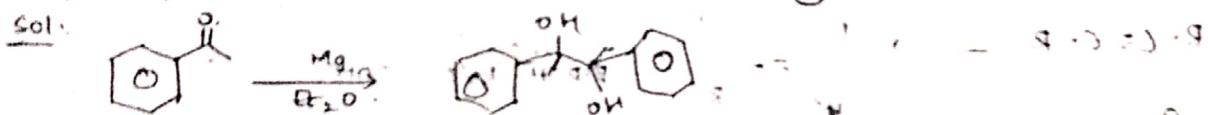
→ Since, stable Ketyl  $\left[ \text{Ph}-\overset{\underset{\text{H}}{\text{C}}}{\overset{\text{O}}{\text{O}}} \text{Na} \right] \rightarrow \text{Ph}-\overset{\text{O}}{\underset{\text{O}_\text{H}}{\text{C}}} \text{O}^-$  it undergoes

dimerisation. Unstable Ketyl's undergo forward rxn. (a)



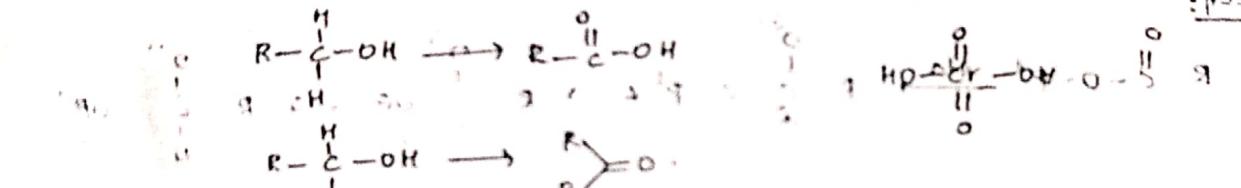


B) Acetophenone is treated with magnesium ether followed by hydrolysis. Find the No. of diols. ③

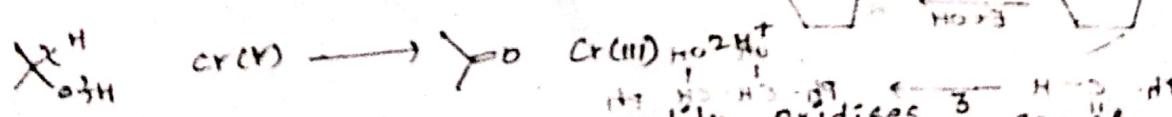
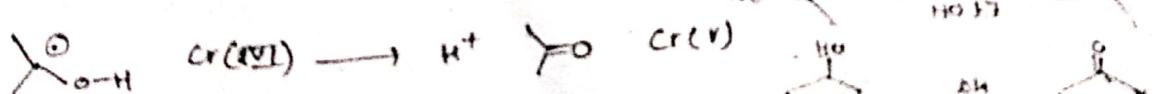
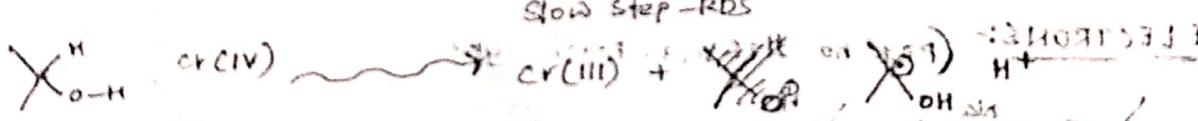
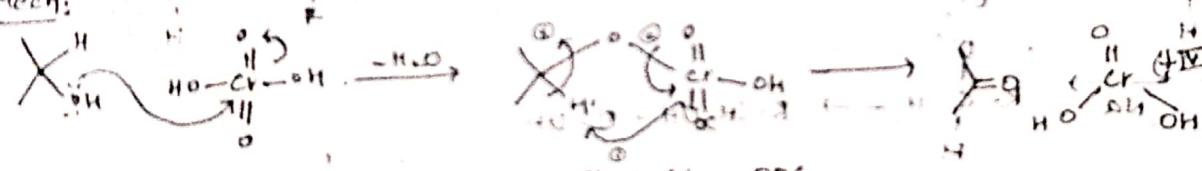


### OXIDISING AGENTS:

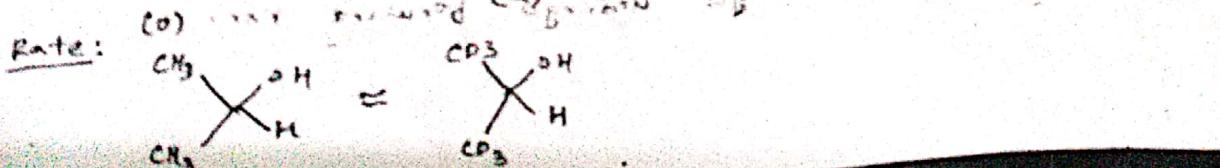
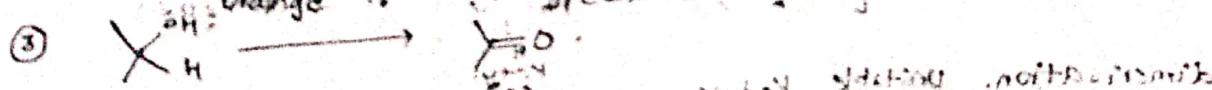
Q)  $\text{KMnO}_4 / \text{K}_2\text{Cr}_2\text{O}_7$  in  $\text{H}_2\text{SO}_4 / \text{HNO}_3$ :  
 → Powerful oxidising agent.

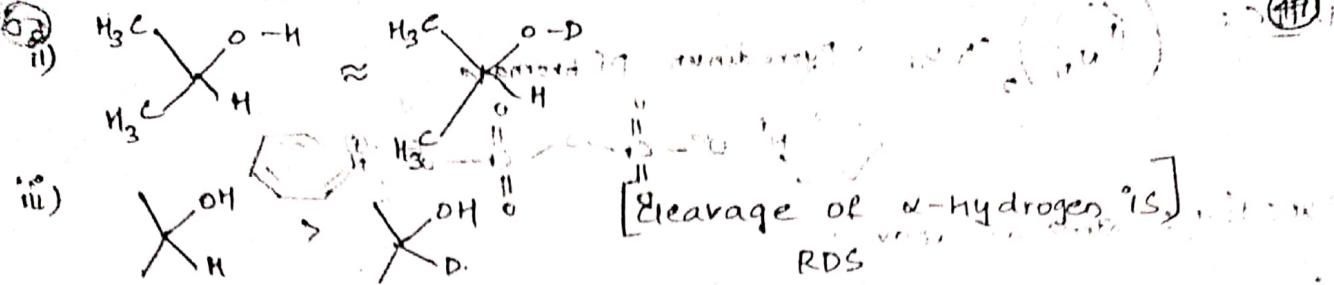


Mech:  $\text{R}-\overset{\text{H}}{\underset{\text{R}}{\text{C}}}-\text{OH} \xrightarrow{\text{Oxidation}} \text{R}-\overset{\text{O}}{\underset{\text{R}}{\text{C}}}-\text{OH}$  (No R-H (No ex. hydrogen))

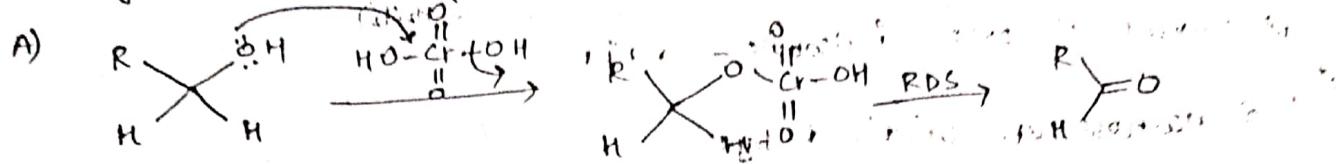


B) 1 eq. of  $\text{K}_2\text{Cr}_2\text{O}_7$  in  $\text{H}_2\text{SO}_4$  readily oxidises 3 eq. of isopropyl alcohol to acetone.

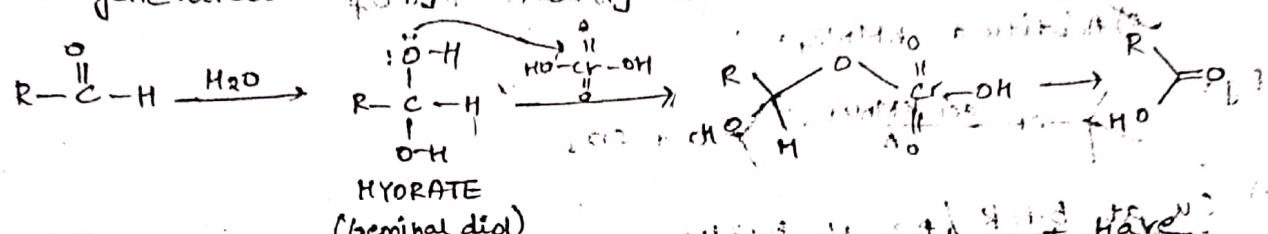




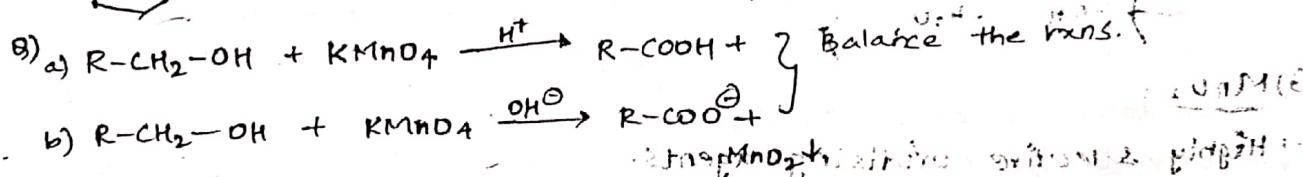
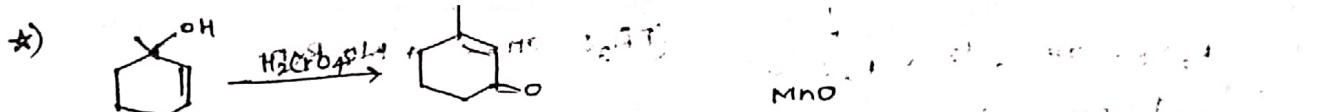
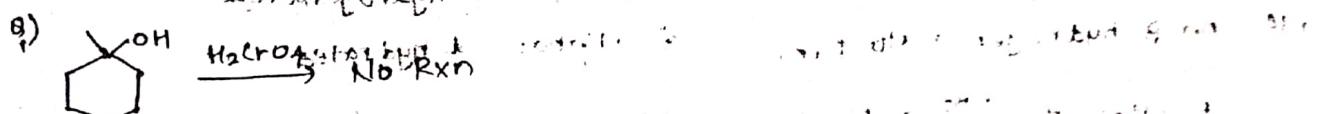
→ Why  $\alpha$ -alcohols become acids?



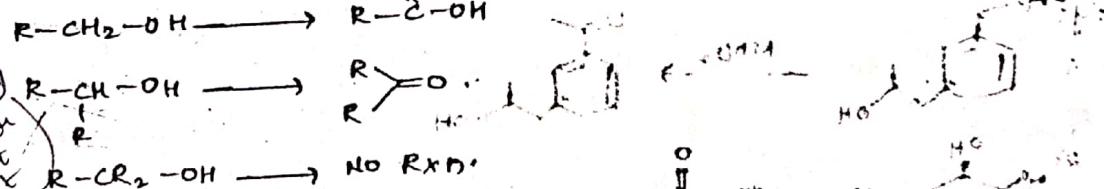
→ The generated aldehyde is hydrated.



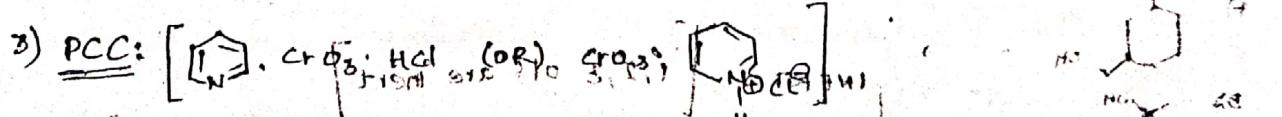
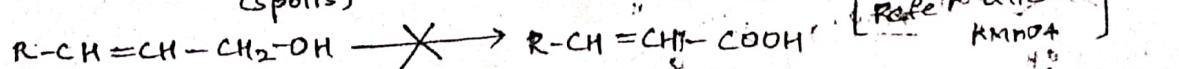
→ Even ketone gets hydrated but the hydrate does not have  $\alpha$ -hydrogen because it remains as a ketone.



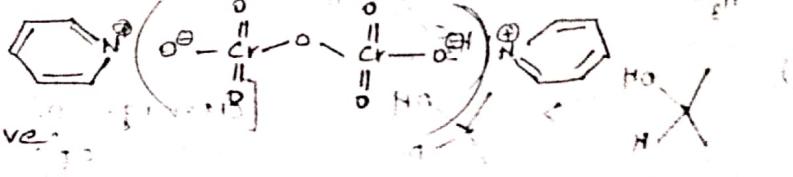
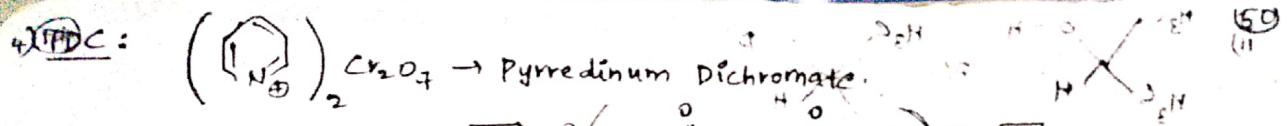
② JONES REAGENT:  $(CrO_3 + aq. H_2SO_4 + \text{acetone}) \rightarrow$  Jones reagent



anhydrous  $CrO_3$  doesn't affect unsaturation since no water is present in it. Both ① & ② effects unsaturation. It must be weaker than  $CrO_3$ .



Function: Without destroying unsaturation,  $\alpha$ -alcohols  $\rightarrow$  aldehydes;  $\beta$ -alcohols  $\rightarrow$  ketones;  $\gamma$ -alcohols  $\rightarrow$  No Rxn.



Function: Same as above.

7) PDC

$\xrightarrow{\text{R}_2\text{O}}$

8) Lumic

9) Prevo

10) Woo

①

O

ESTE

case - C

\* R-1

Mech:

O

O

O

O

O

O

Eg:

O

1)  $\text{CH}_3\text{OH} \xrightarrow[\Delta]{\text{acid. KMnO}_4}$   $\text{CH}_3\text{CO}_2 + \text{CO}_2$

2)  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CO}_2$

3)  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CO}_2$

4)  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CO}_2$

5)  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CO}_2$

6)  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CO}_2$

7)  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CO}_2$

8)  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CO}_2$

9)  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CO}_2$

10)  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CO}_2$

→ Ester

case - C

R-1

→ Ester

case - C

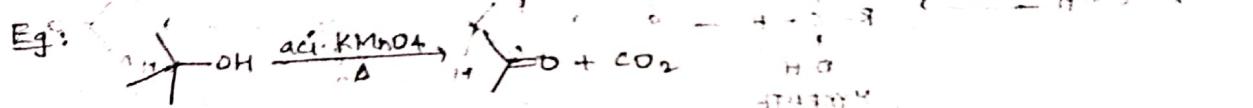
N\* → PCC and PDC reactions are conducted in DCM solvents.

If solvent is DMF, i alcohols → acids.

N\* → 3 alcohols are oxidised by:

a) Neutral  $\text{KMnO}_4$       b) Basic  $\text{KMnO}_4$       c) Acidified  $\text{KMnO}_4$

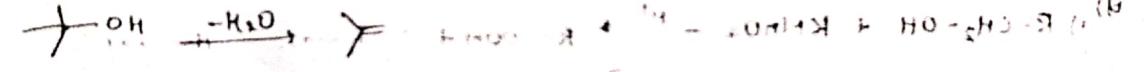
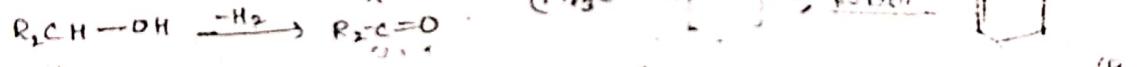
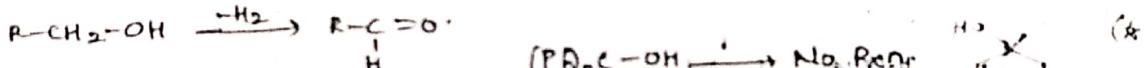
Acidified  $\text{KMnO}_4$ :



5) Cu, pt, 573K / Ag at 573K:

→ without spoiling unsaturation i alcohol dehydrogenated  
i alcohol dehydrogenated

→ If no β-hydrogen ⇒ No Rxn.

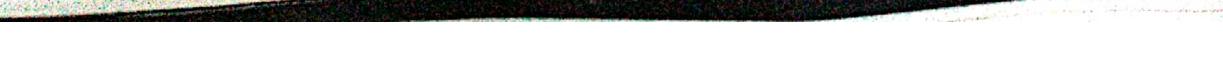
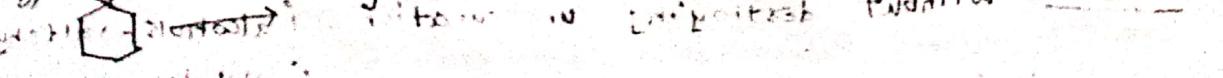
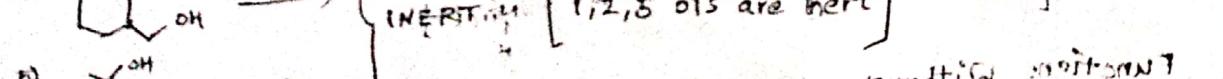
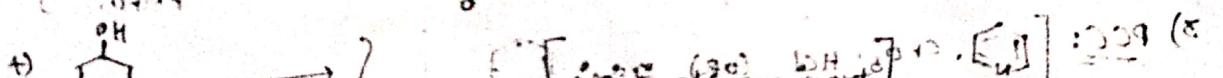
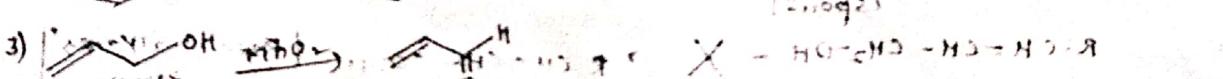
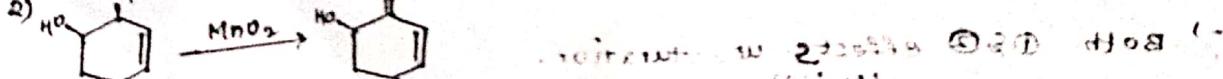
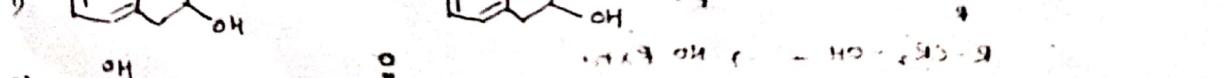
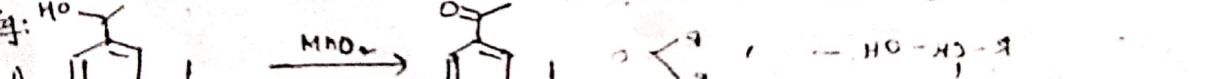


6)  $\text{MnO}_2$ :

→ Highly selective oxidising agents.

→ Selectively oxidises:  $\text{Benzyllic alcohol} \rightarrow \text{Allylic Alcohol}$

Eg:  $\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH} \xrightarrow{\text{MnO}_2} \text{HO}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OH}$



## 50) $\text{SeO}_2$ : (selenium dioxide)

→ Revise alkenes  
Allyl to allyl alcohol

Carbonyl to Dicarbonyl

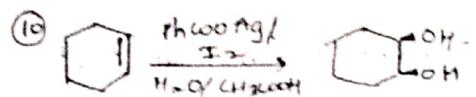
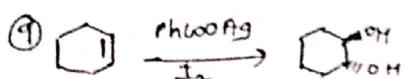
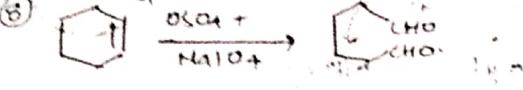
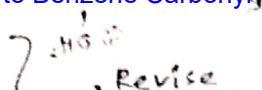
Benzyl to Benzene Carbonyl

8) Lumex-Johnson

9) Preost-oxidation

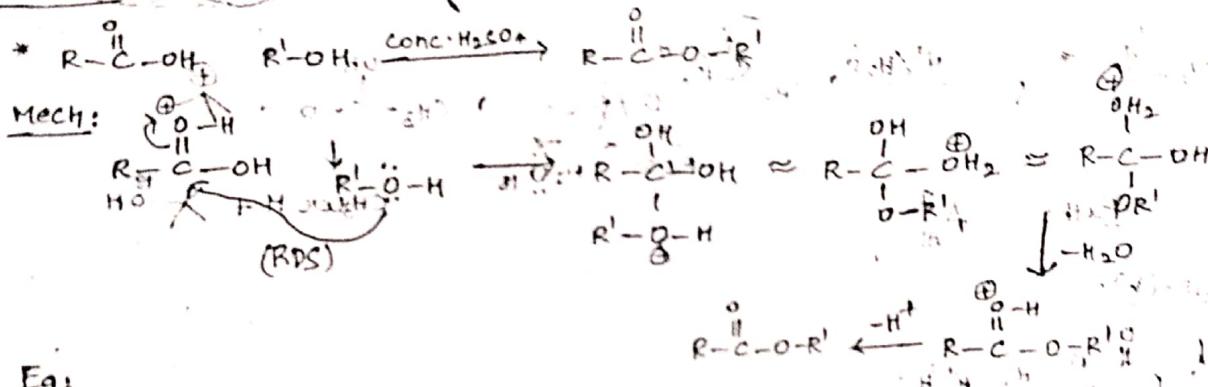
10) Wood Ward-Oxidation

OsO<sub>4</sub> doesn't react with alkynes

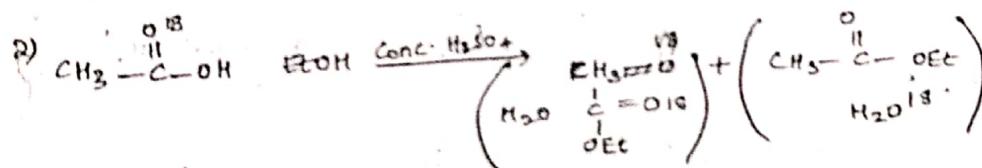
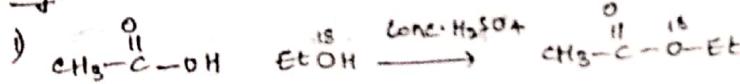


## ESTERIFICATION & HYDROLYSIS OF ESTERS:

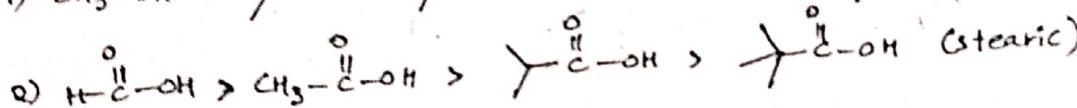
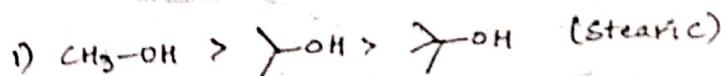
case-(i): Acidic medium (Esterification / Fischer-Esterification)



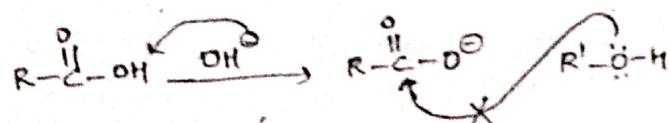
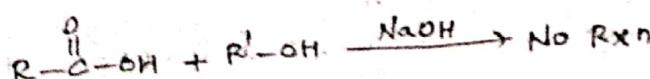
Eg:



### → RATE OF ESTERIFICATION:

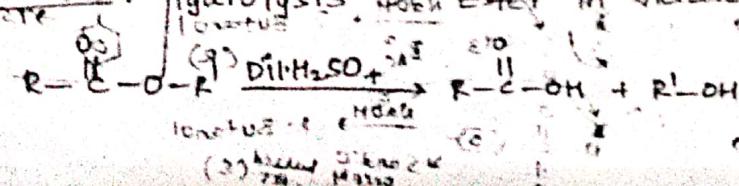


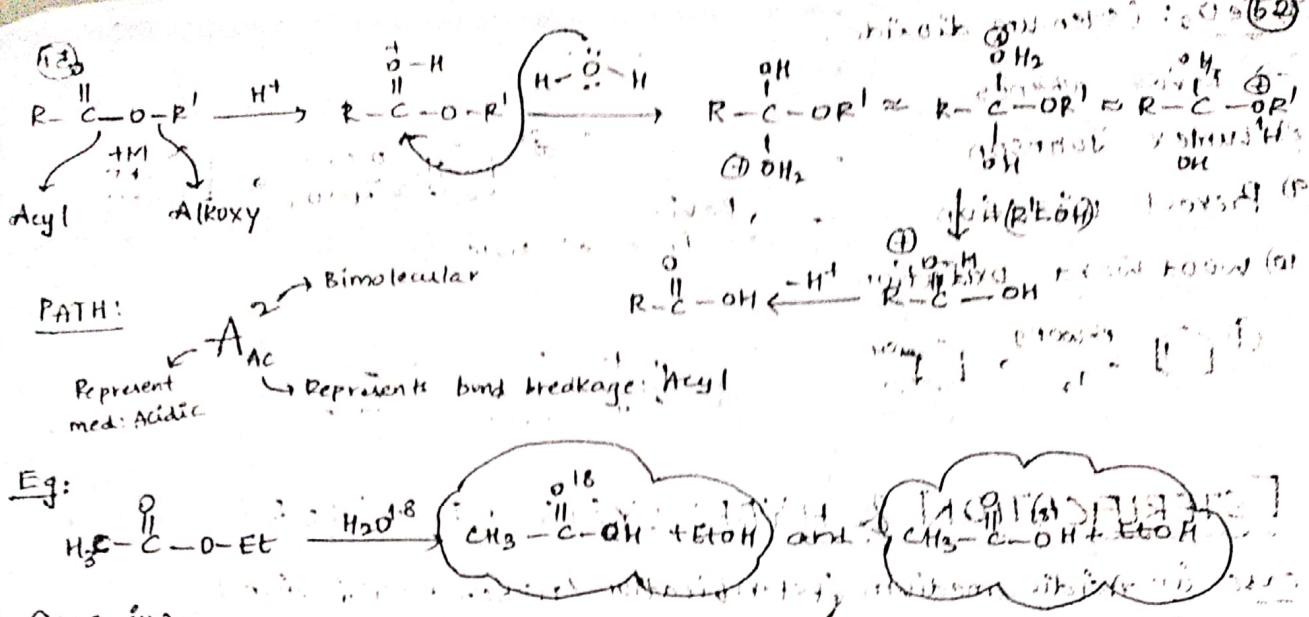
case-(ii): Esterification in Basic Medium.



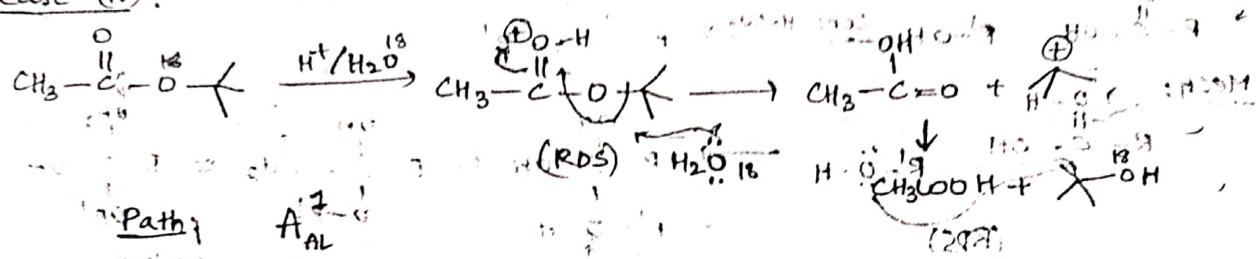
→ Esterification never takes place in basic medium.

case-(iii): Hydrolysis of Ester in acidic medium:

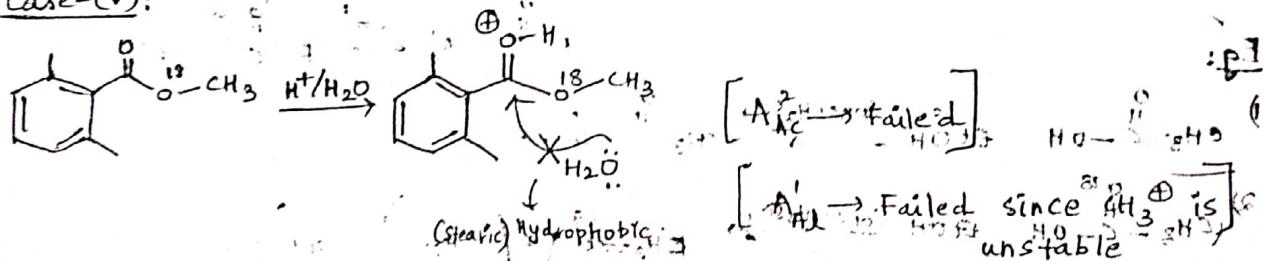




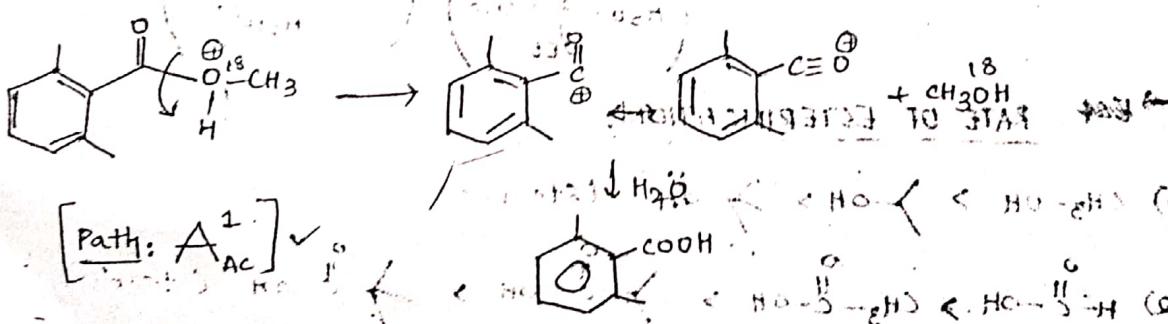
Case-(iv) :



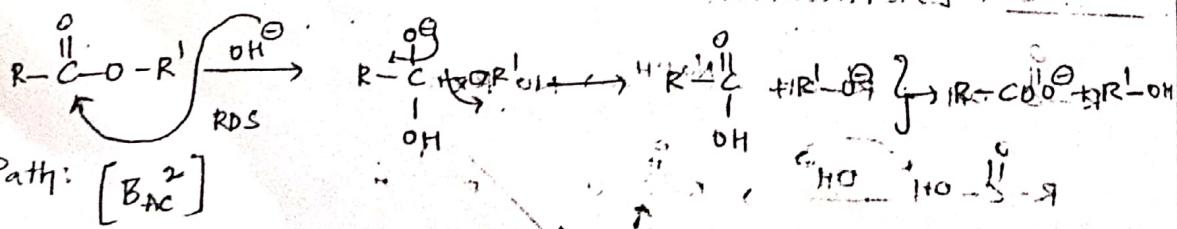
Case-(v):



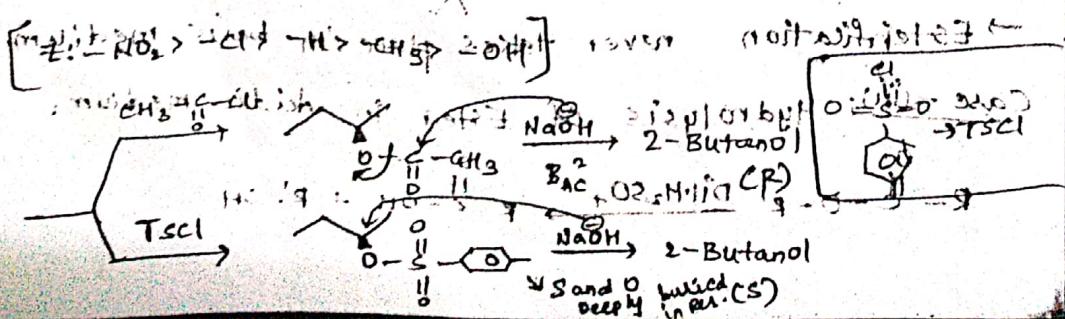
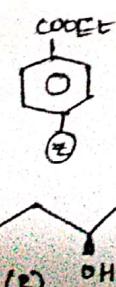
Mech.



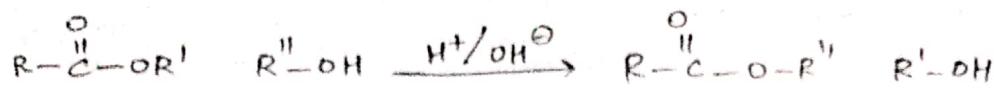
case-(vi): Hydrolysis of ester in basic medium. (SAPONIFICATION)



Rate:



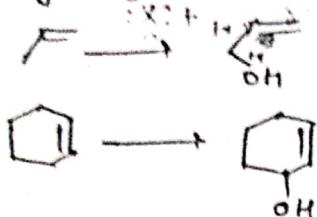
## Case - (ii): TRANS-ESTERIFICATION



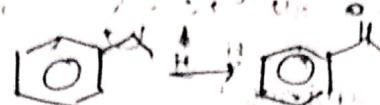
→ Exchanging of alkoxy groups is trans-esterification.

Selenium dioxide in prg v pages:-

1. Allylic  $\xrightarrow{\text{SeO}_2}$  Alcohol



2. Benzylic  $\xrightarrow{\text{SeO}_2}$  Carbonyl



3. Carbonyl  $\rightarrow$  1,2-dicarbonyl

