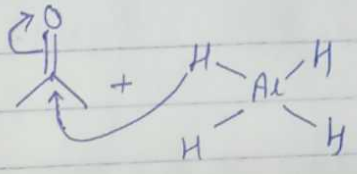
Hydride Donor based reagents (Reduction)

$H^{\ominus}$

Nucleophilic hydride donor

$LiAlH_4$, $NaBH_4$

bcoz in Ist step H^- transfer occurs.

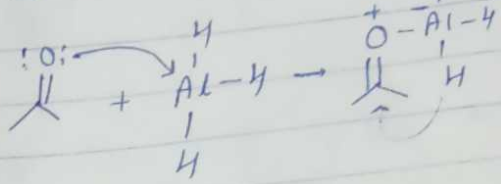


electrophilic hydride donor [Lewis acid]

AlH_3, BH_3

Ist step :- electron accept

IInd " → H^- transfer



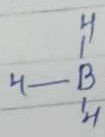
* $LiAlH_4$ V/s $NaBH_4$

$LiAlH_4$

$\rangle Al-H$

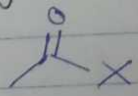
→ High E.N. diff.
→ more ionic Nature
→ H is highly reactive
→ Strong nucleophile
  ↳ can attack at weak electrophilic center also
→ Strong base
  ↳ can abstracts H^+
→ Can't use polar protic solvent due to basic nature
→ use aprotic solvents THF, Et_2O

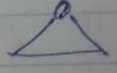
$NaBH_4$



→ less EN diff. bcoz both are non metal
→ more covalent nature
→ Poor nucleophile
→ Poor base
→ polar solvent [EtOH]
→ More Selective in nature

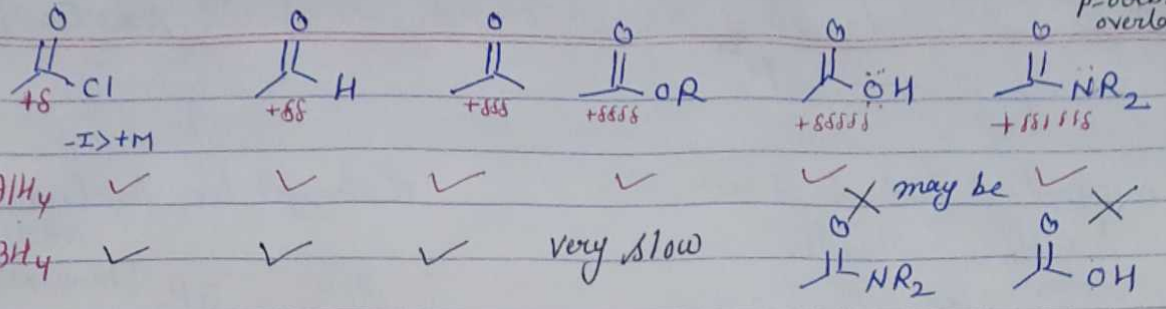
* less selective (more reactive)
* Target molecules → must be polar

 , $R-CN$, $R-NO_2$,] → Reduction

 , $R-OTs/OMs$] → gives substitution rxn.

+m effect

$-OH > -\ddot{O}-CH_3$ – due to steric hindrance p-orbital ↓ overlapping



$LiAlH_4$	✓	✓	✓	✓	✓	✓
$NaBH_4$ (weak)	✓	✓	✓	very slow	✗	✗

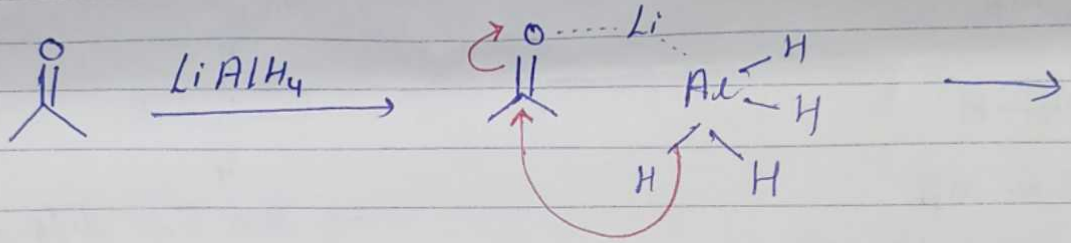
may be

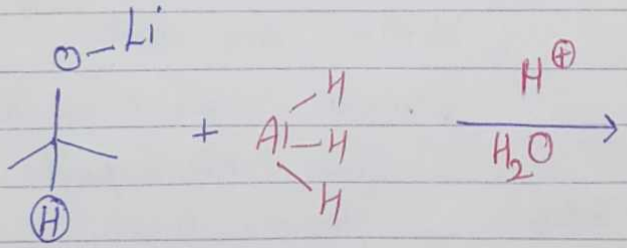
because $LiAlH_4$ is base that abstract H^+ from acid

+M effect of O^- is higher than that of NR_2.

* if we put ester and $NaBH_4$ for a long time, then they may react.

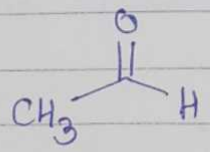
Mechanism :→



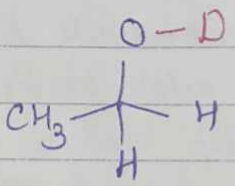


O–H → from solvent

H → this is from AlH_4^-

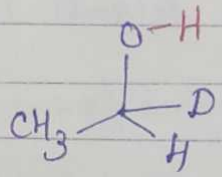
* 

1. $LiAlH_4$
2. D_2O/D^+



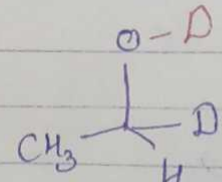
achiral

" 1. $LiAlD_4$
2. H_2O/H^+

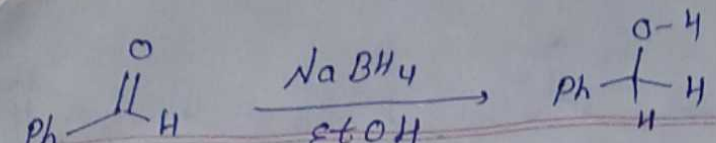


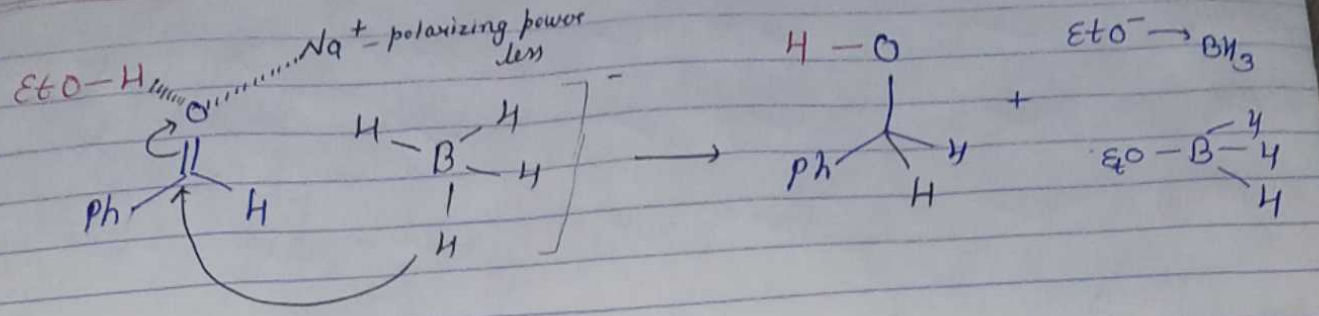
Chiral

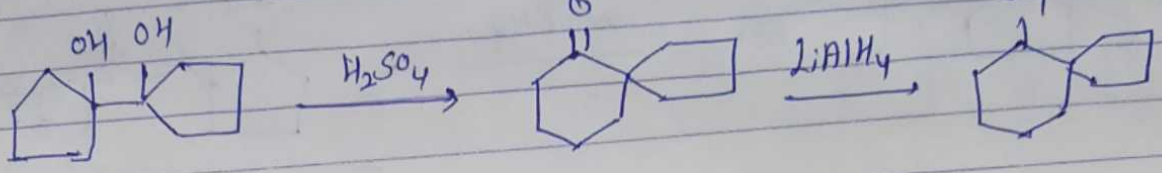
1. $LiAlD_4$
2. D_2O/D^+

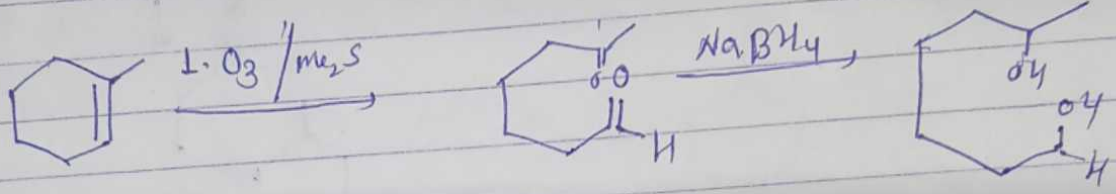


Chiral





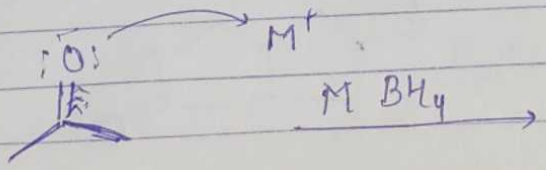
* 

* 

* Role of metal ions with hydride donors:

To enhance the electrophilic nature of carbenyl group.

To create Stereo Selectivity

\# 

↑ if polarizing power of metal is high, it increase the electrophilicity of carbenyl carbon.

$NaBH_4$

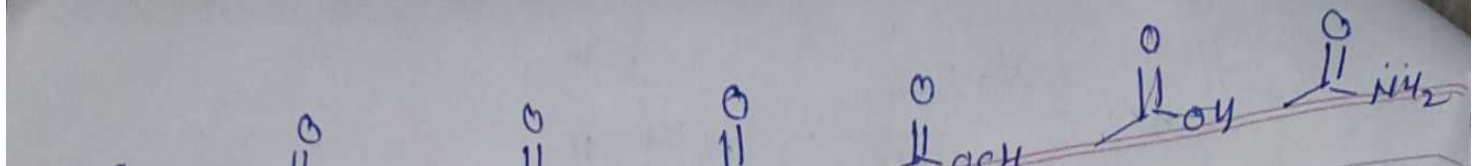
$LiBH_4$

$Zn(BH_4)_2$

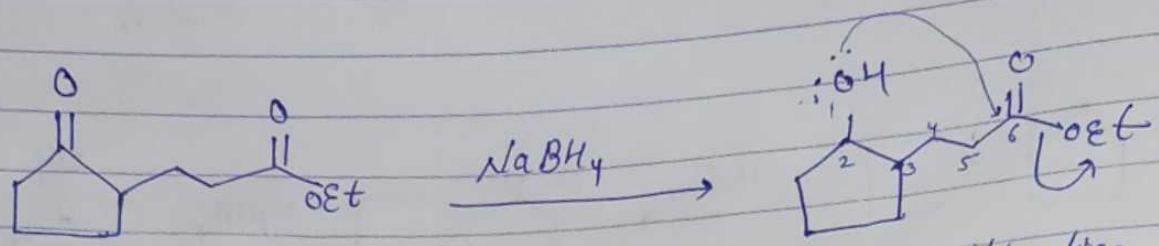
order of polarizing powers

$Zn^{2+} > Li^{+} > Na^{+}$

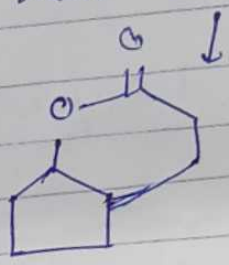
due to small size

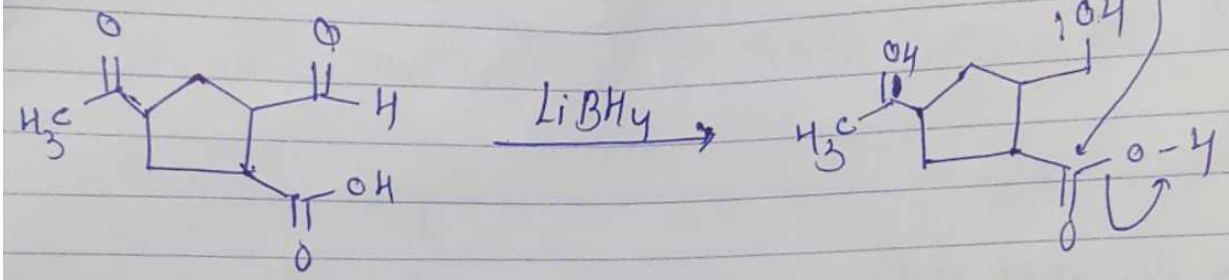


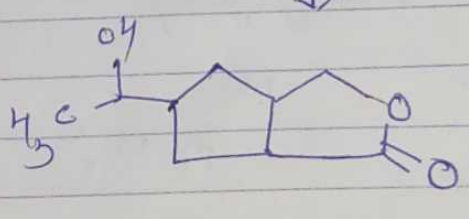
$NaBH_4$	✓	✓	✓	✗	✗	✗
$LiBH_4$	✓	✓	✓	✓	✗	✗
$Zn(BH_4)_2$	✓	✓	✓	✓	✓	✓



Trans - esterification







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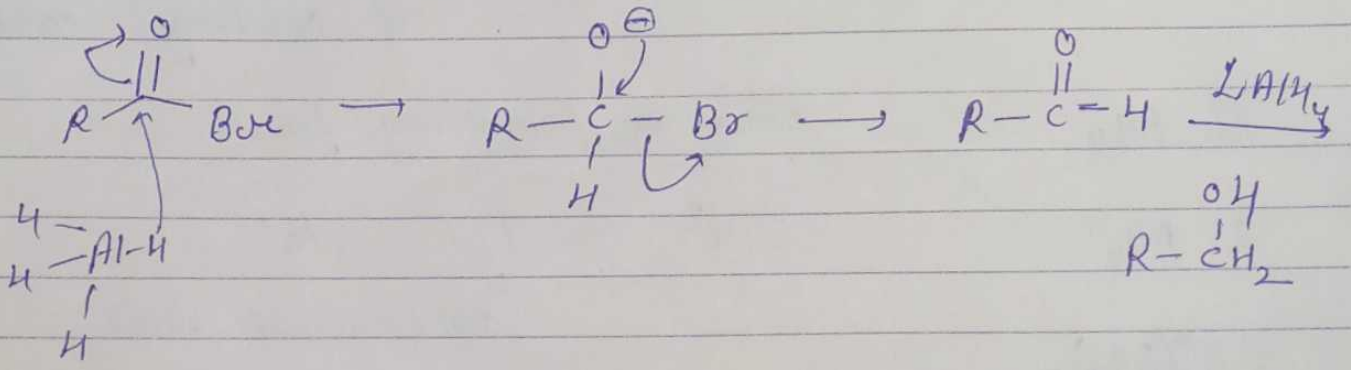
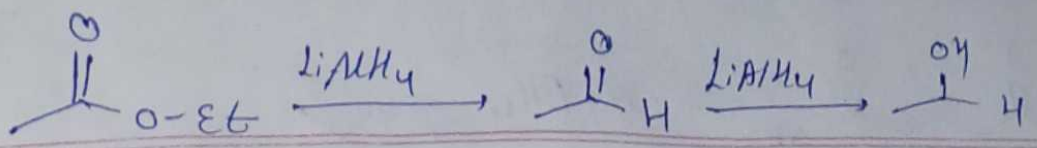
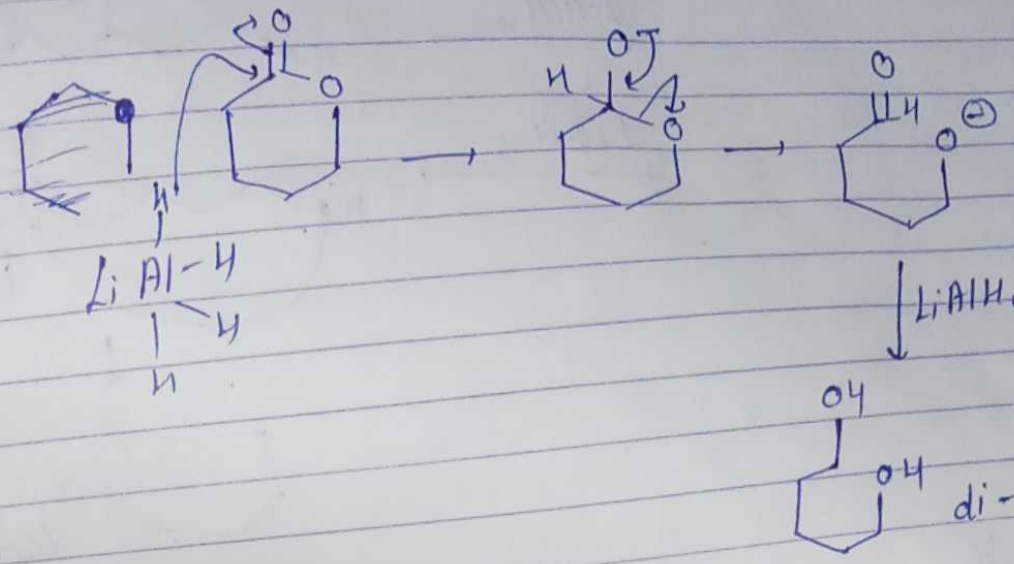
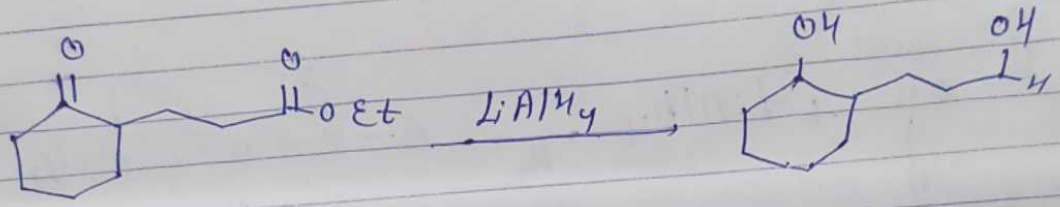
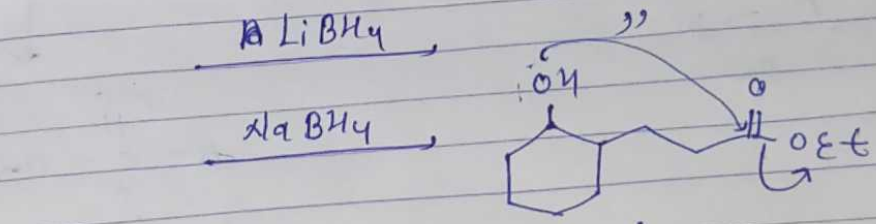
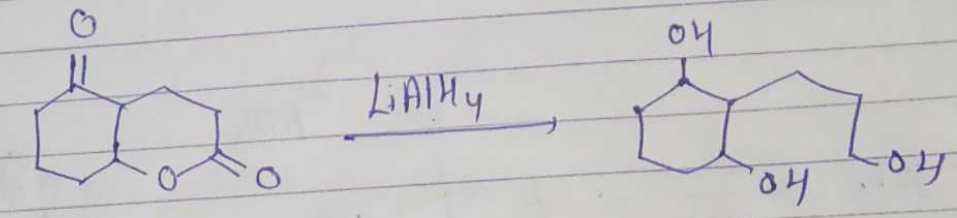


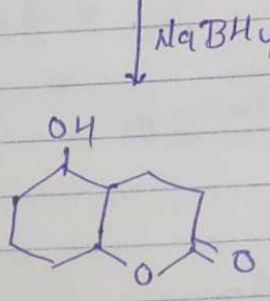

LiAlH4
LiAlH4

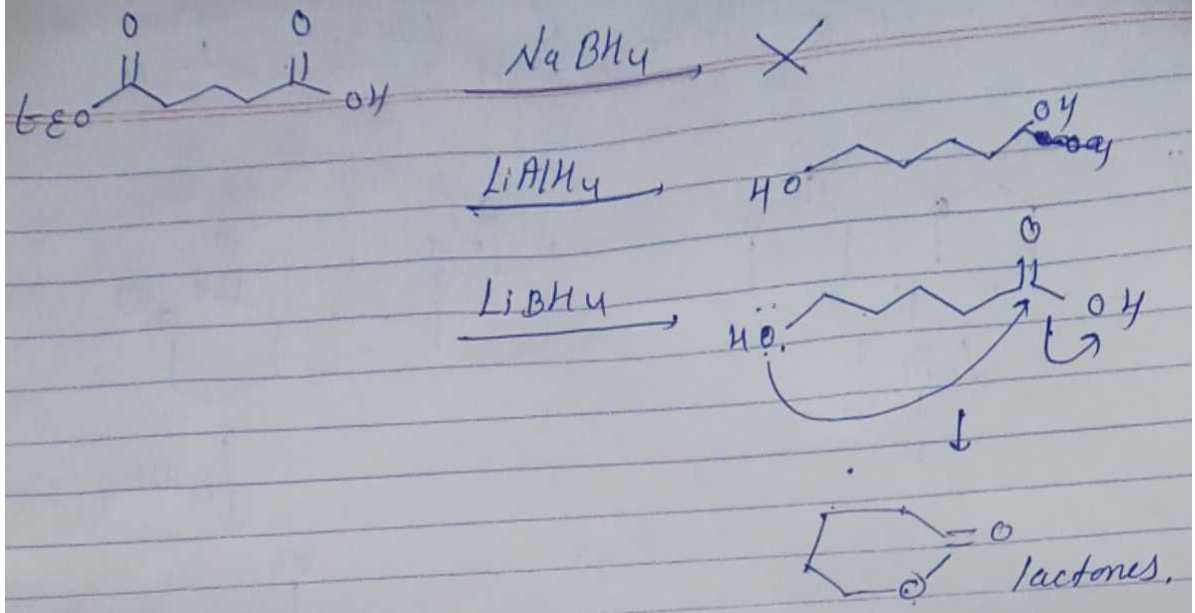

Li Al-H
H
H
LiAlH4
di-ol


LiAlH4

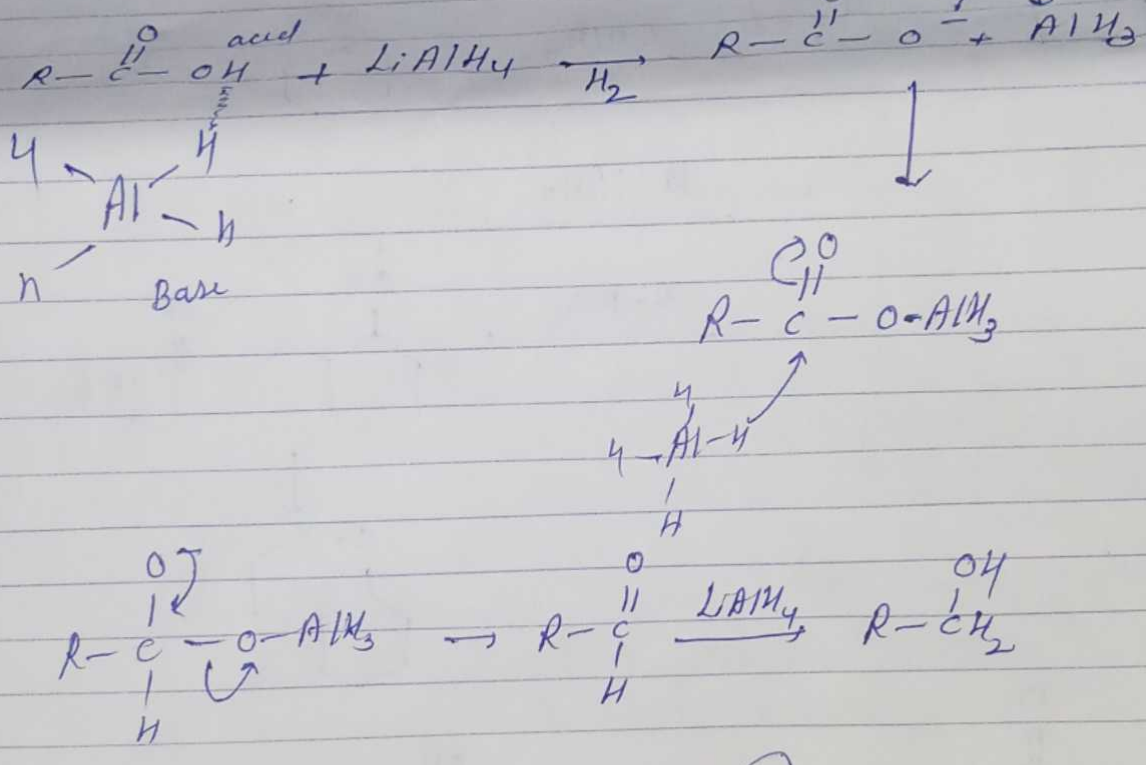

LiBH4
NaBH4


LiAlH4


NaBH4

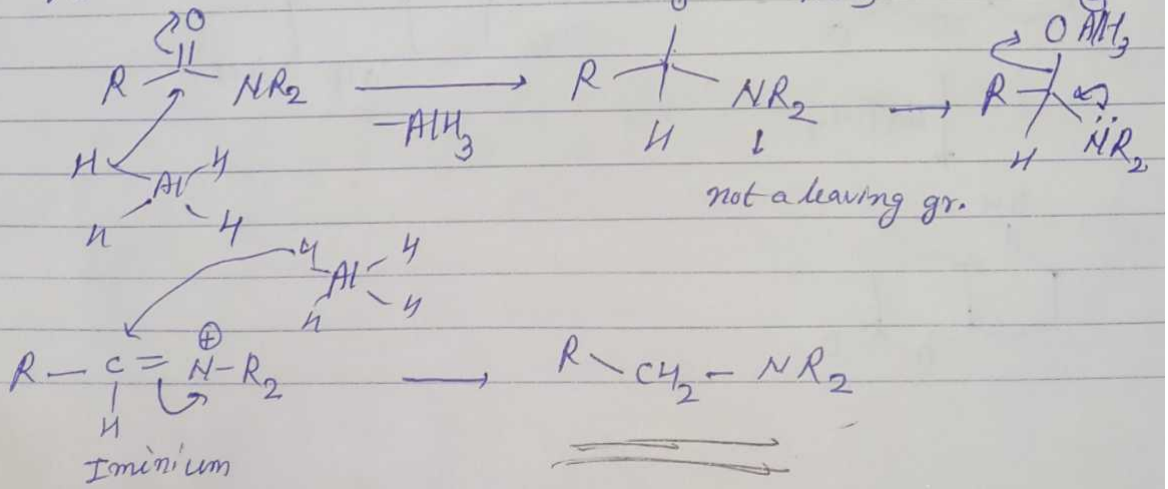

NaBH4
LiAlH4
LiBH4
lactones.

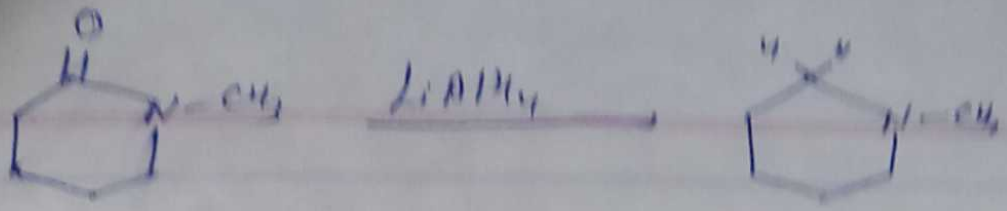
acid

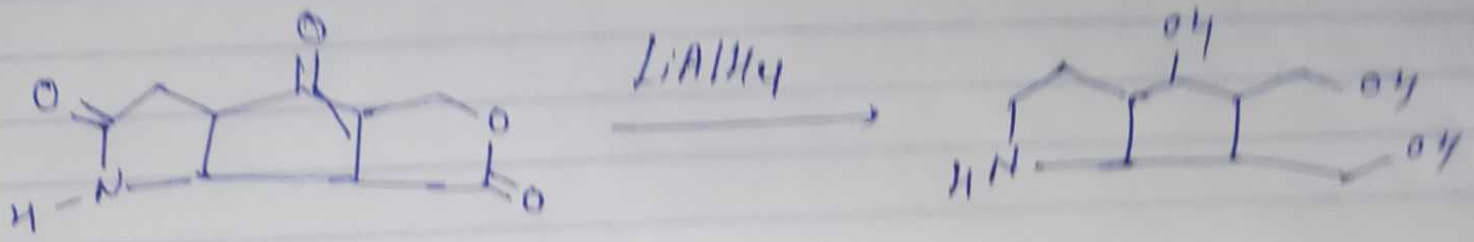

acid
LiAlH4
H2
Base

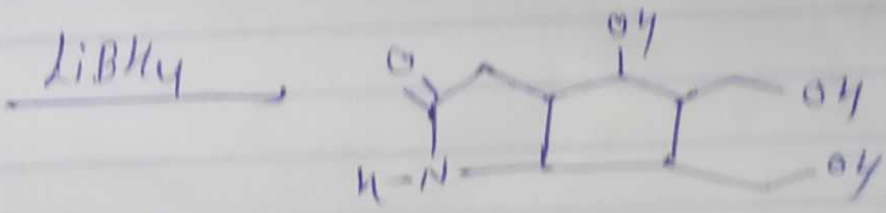
LiAlH4

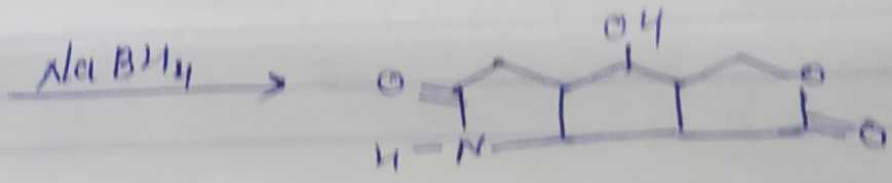
Amide


−AlH3
not a leaving gr.
Iminium


LiAlH4


LiAlH4


LiBH4


NaBH4