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CSIR–NET

Chemical Science

Council of Scientific & Industrial Research (CSIR)

Volume - 3

Organic Chemistry - 2

SIERRA INNOVATIONS

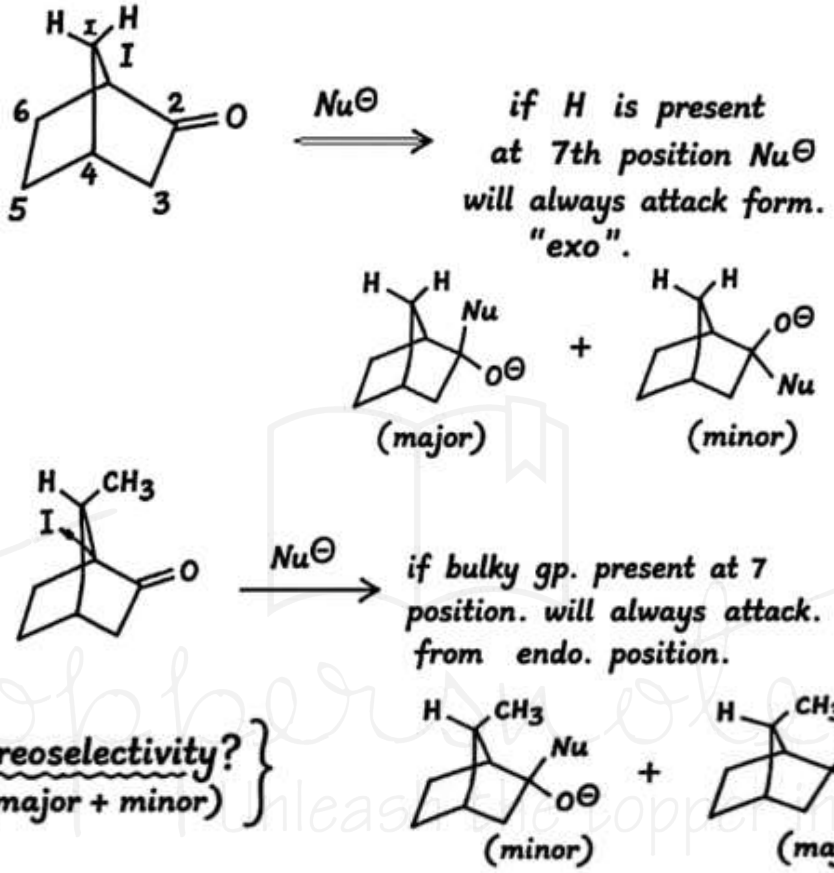
INDEX

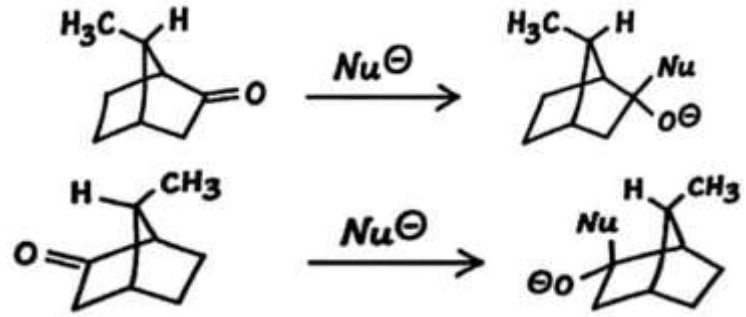
1 CHAPTER

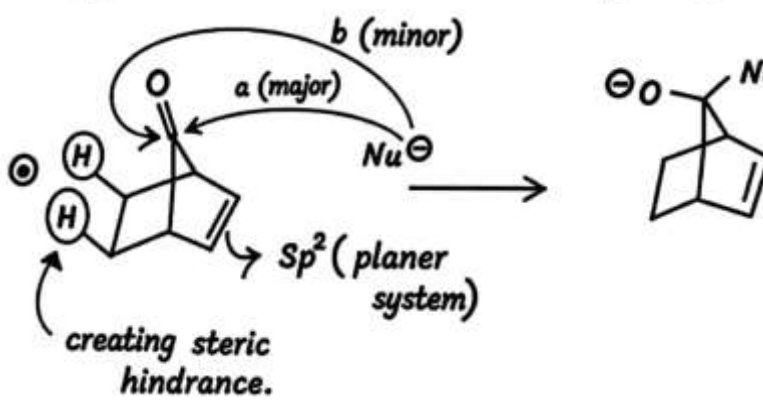
Reagent

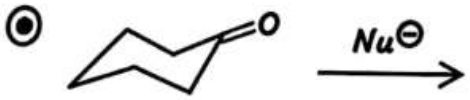
Stereoselectivity:-

- two product (major + minor)

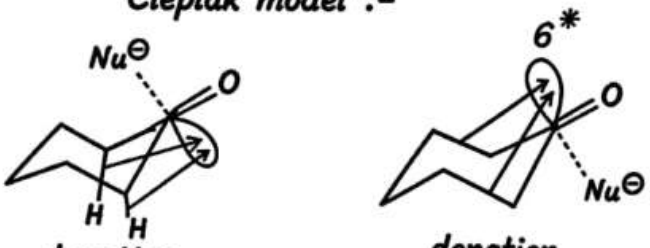








Cieplak model :-

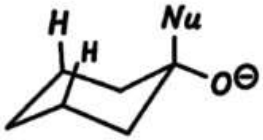


donation by C–H bond.

donation by C–C bond.

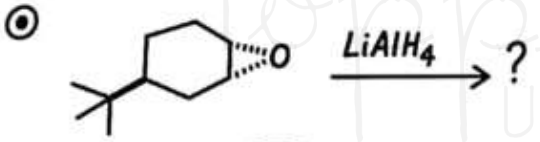
C–H < C–C (strong bond).

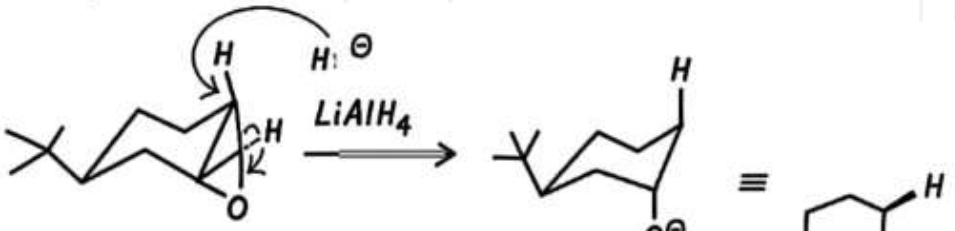
∴ nucleophile attacks from axial position.



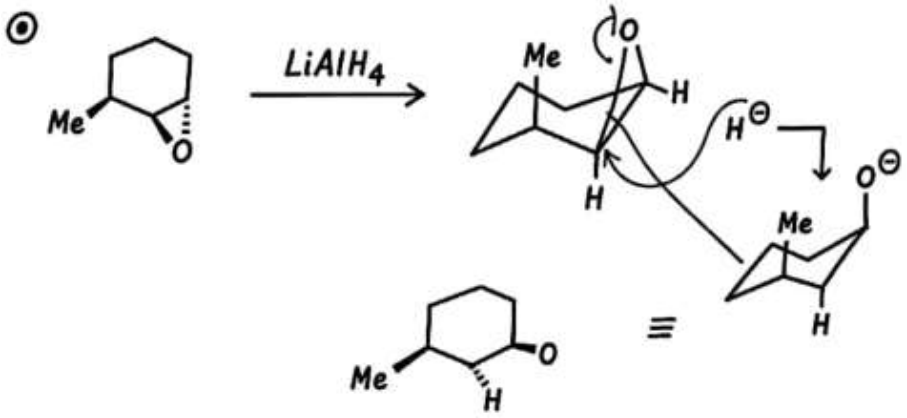
∴ if Nu is bulky, then, 1,3 diaxial NO axial attack.

	Nucleophile.	Axial attack.	Equatorial attack.
	$HC \equiv C^{\ominus}$	88%	12%
	$CH_3{}^{\ominus}$	85%	65%
	$Ph^{\ominus}Li^{\oplus}$	42%	58%
	$CH_3CH_2MgBr.$	29%	71%





Nu will attack. form. axial position.



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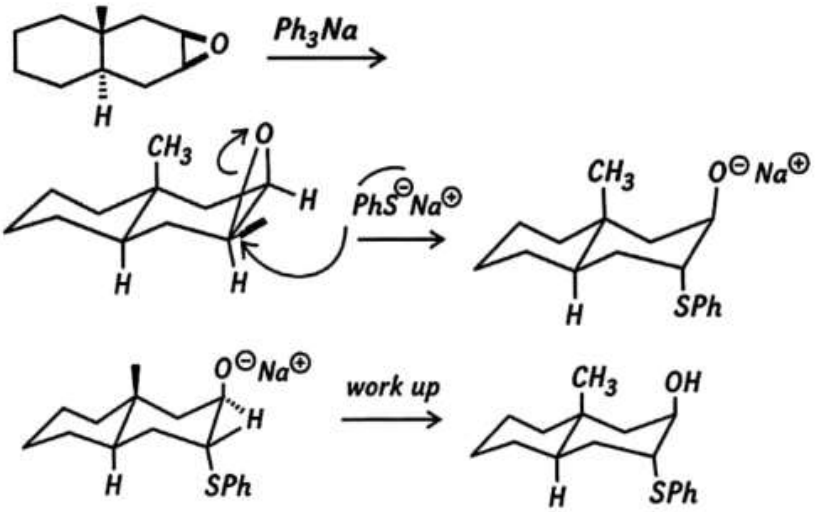

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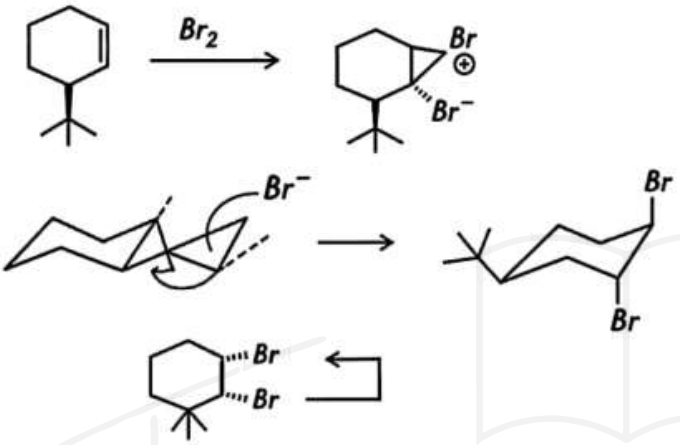

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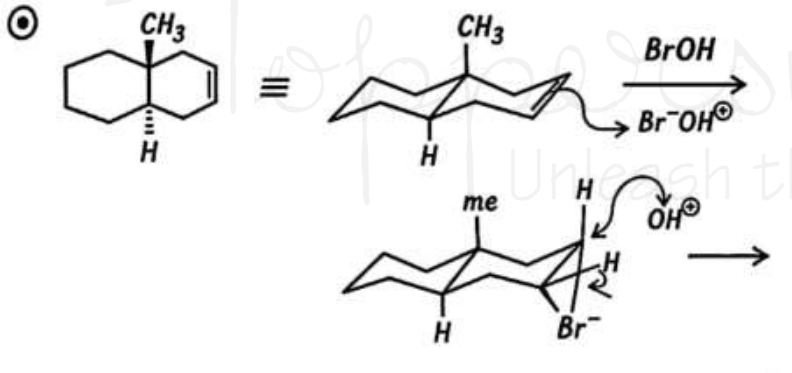
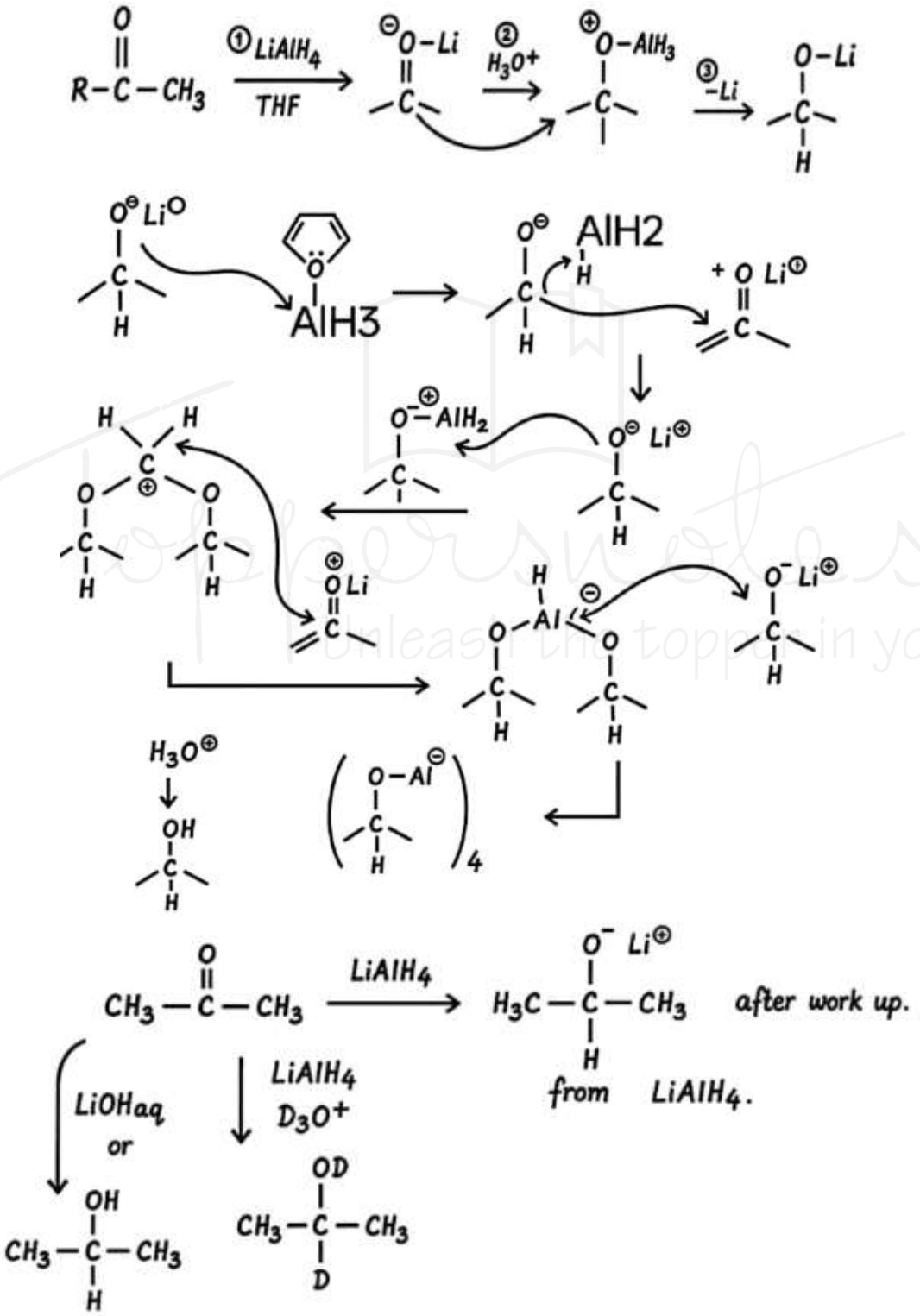
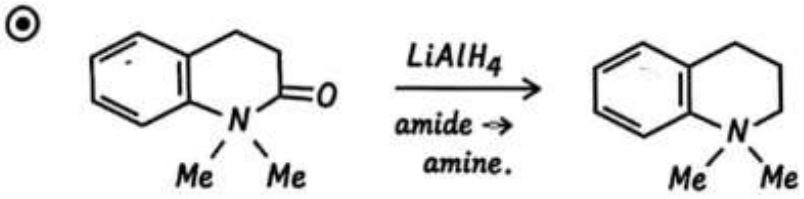


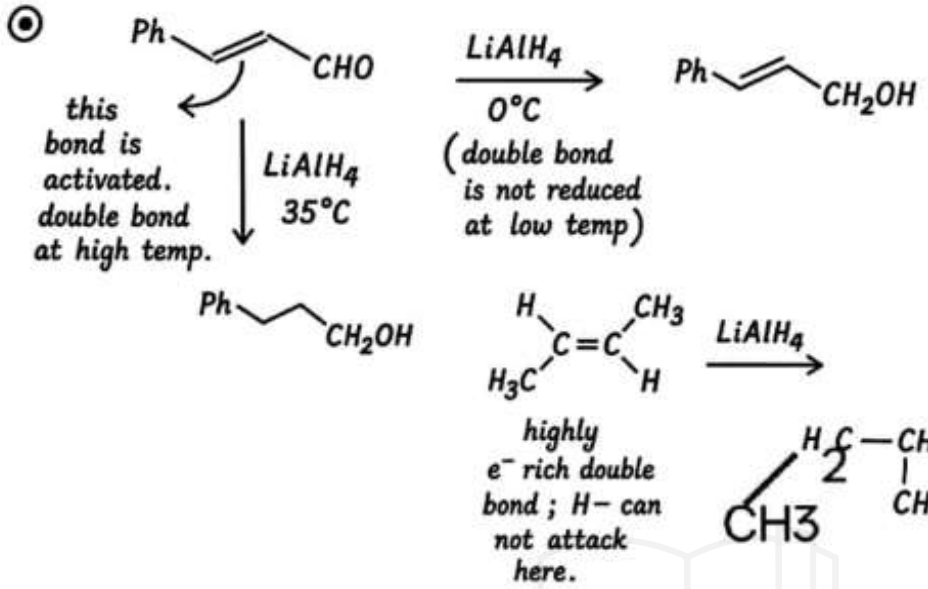
Reducing agents :-

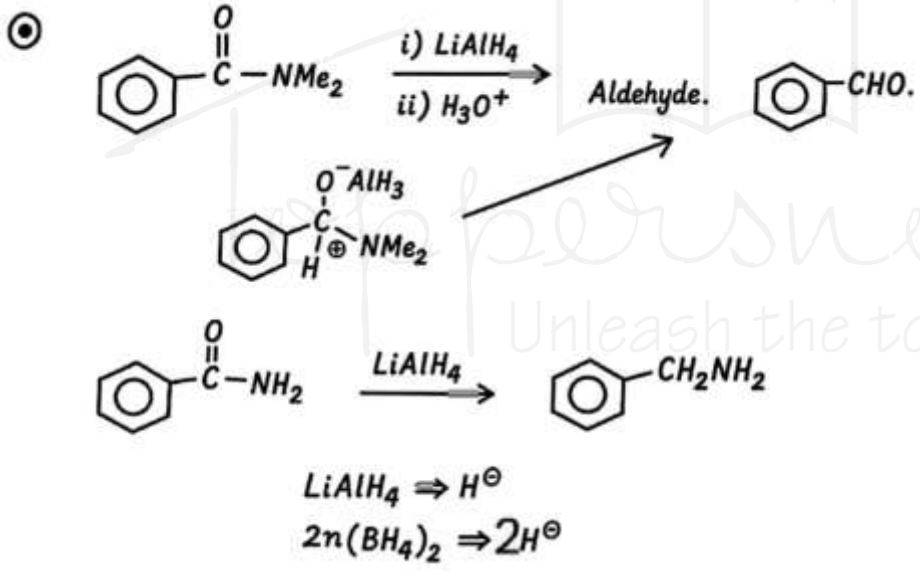
$LiAlH_4$ **:-**

"ldehyde ⟶ alcohol.
Ketone ⟶ alcohol.
Ester ⟶ alcohol.
acid ⟶ alcohol.
amide ⟶ amine.
$RNH_2 \longrightarrow RNH_2$
$R\text{-}CH_2\text{-}$ leaving grp ⟶ alkane ($R\text{-}CH_2\text{-}H$)
$R\text{-}CH_2\text{-}Ots \longrightarrow RCH_3$







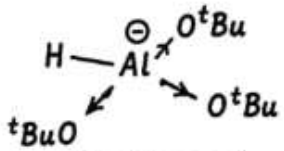


$LiAlH_4 \Rightarrow H^{\ominus}$

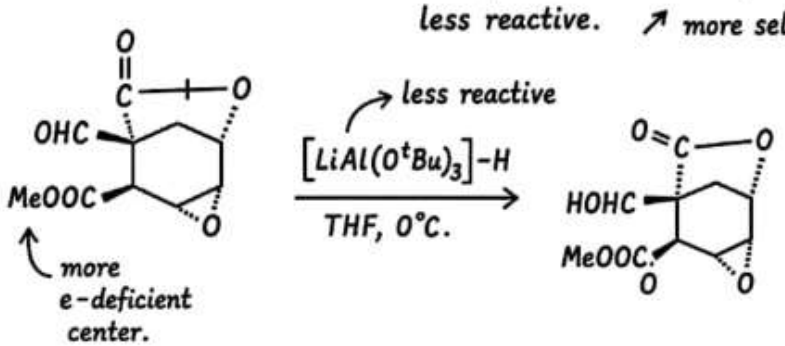
$2n(BH_4)_2 \Rightarrow 2H^{\ominus}$

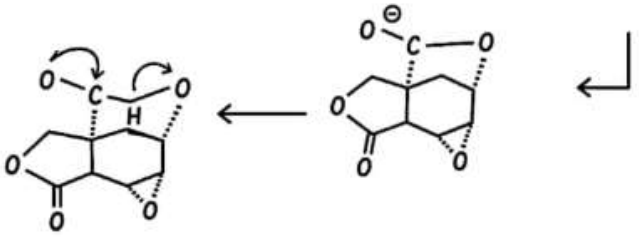
$LiAlH_4$

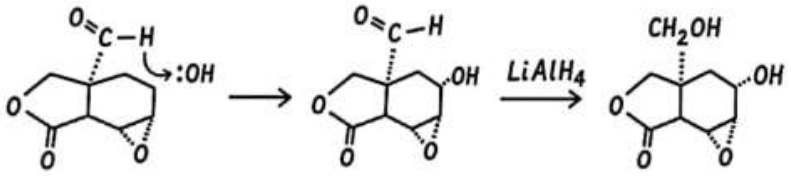
$[LiAl(O\text{-}^tBu)_3H]$

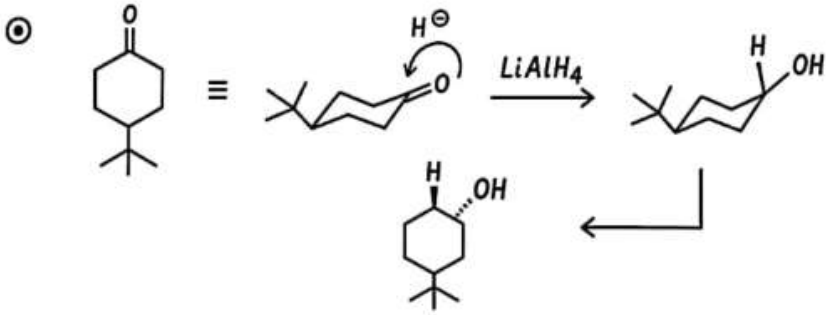


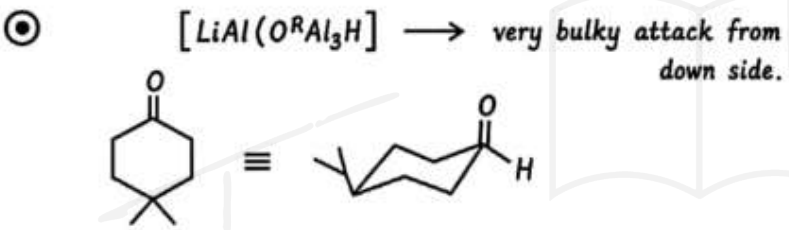
less reactive. therefore ↗ more selective.

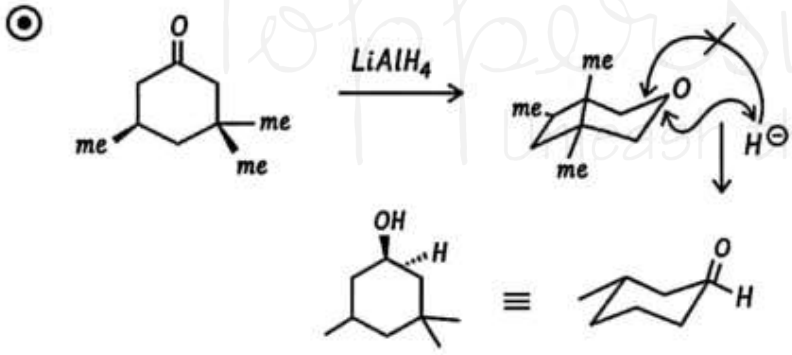


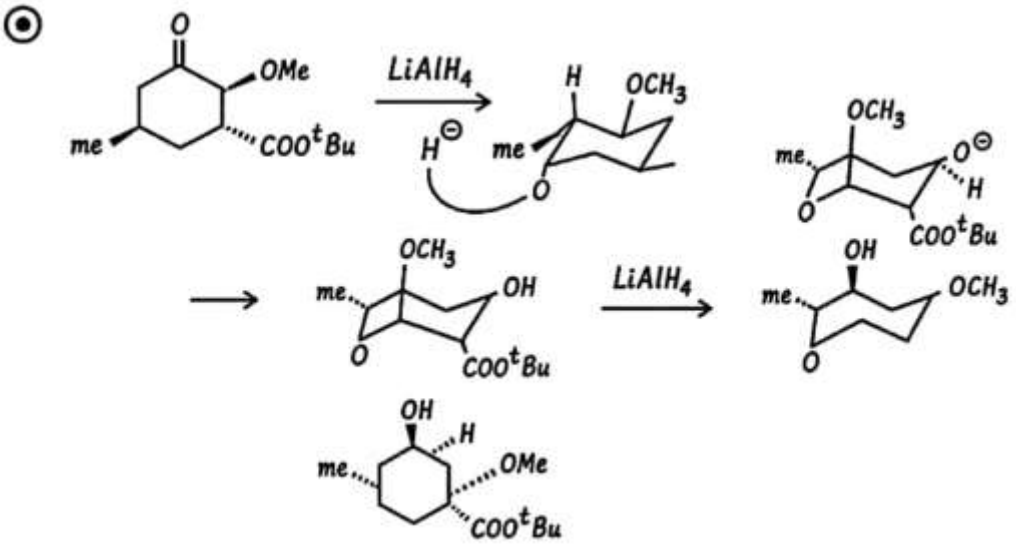


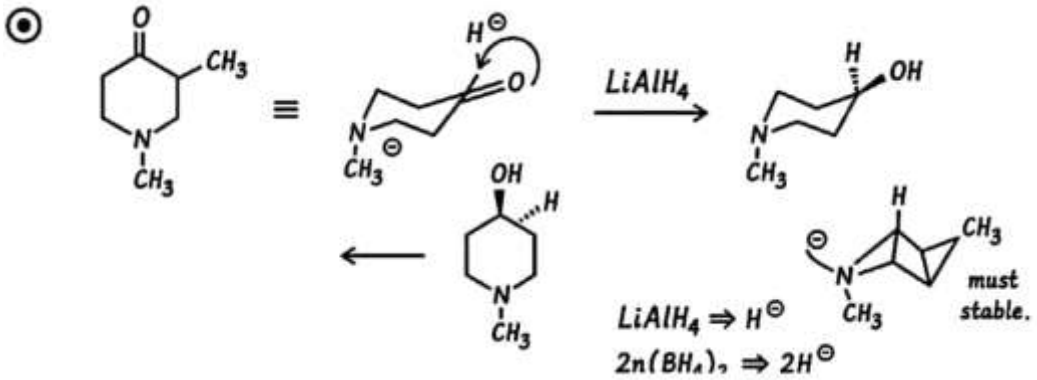


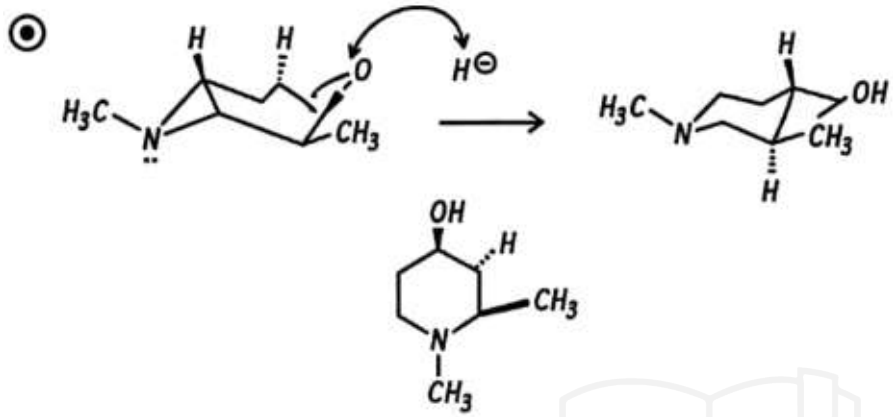


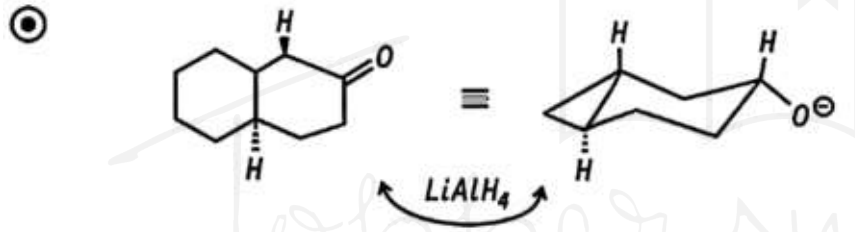


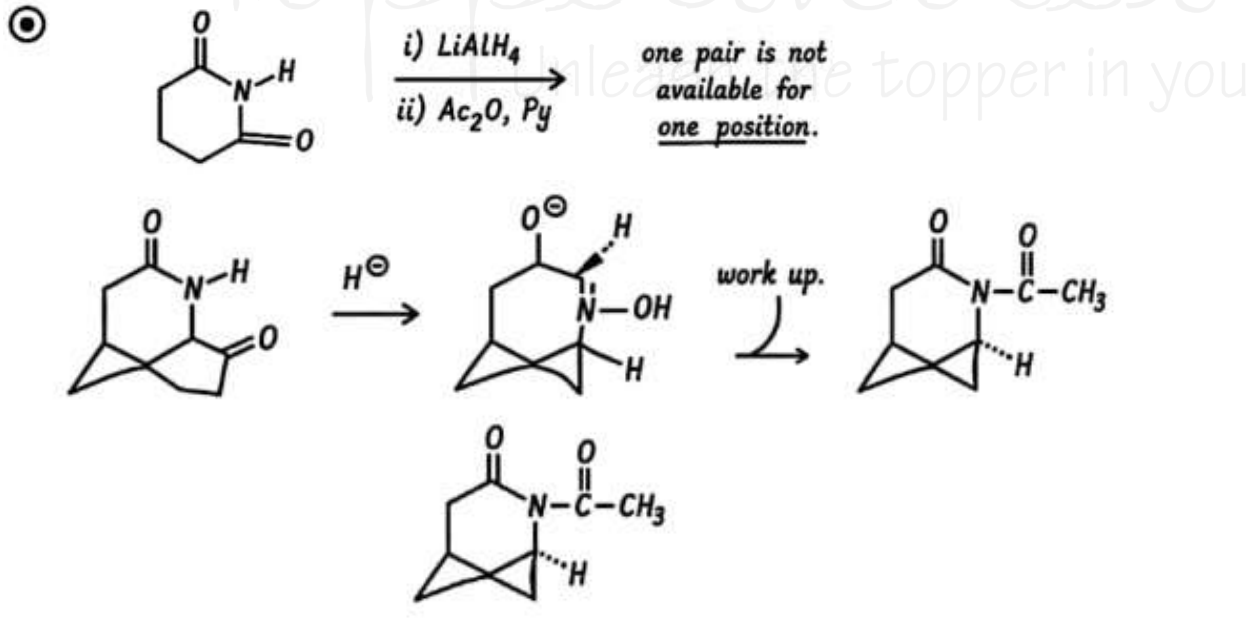


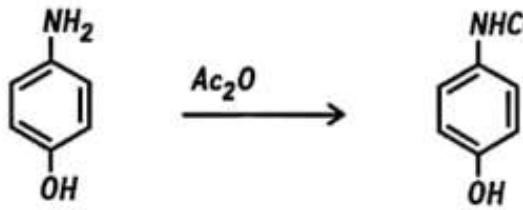






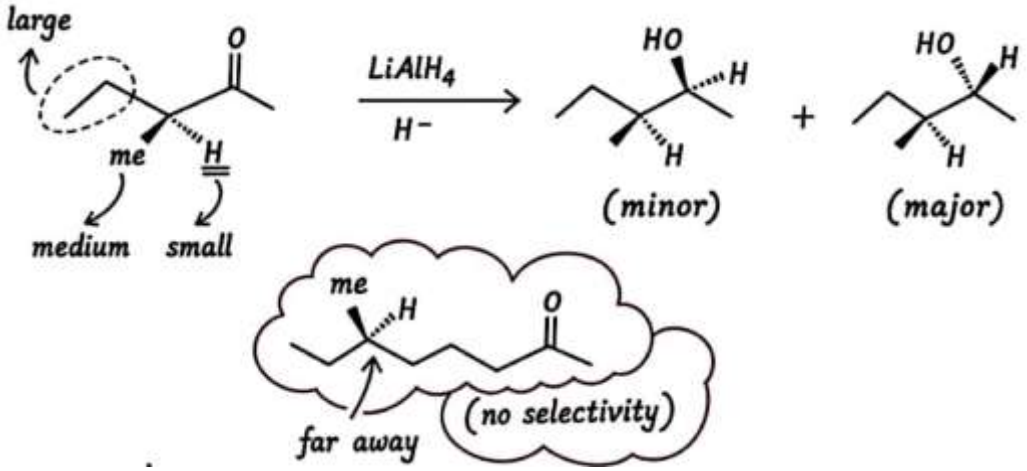






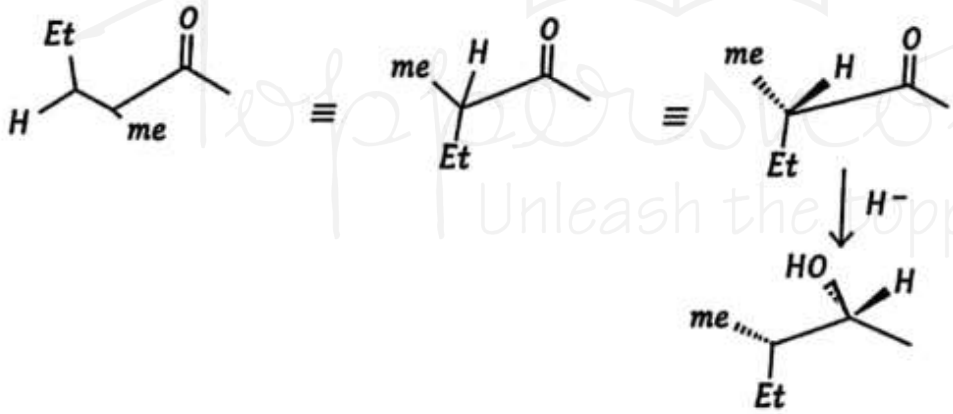
Stereo selectivity in acyclic molecule :-

Cram's Rule :-



Statement of Cram's
⇒ large group must be "anti" to C=O
⇒ attack of $Nu^{\ominus}$ from small group side

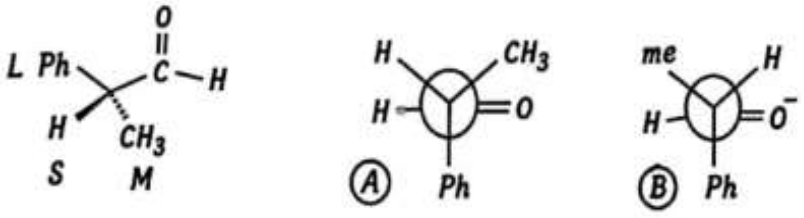
following guideline when R/S.
⇒ large group ⇒ "Syn" to C=O
⇒ attack from medium group side.



Felkin-Anh Model :-

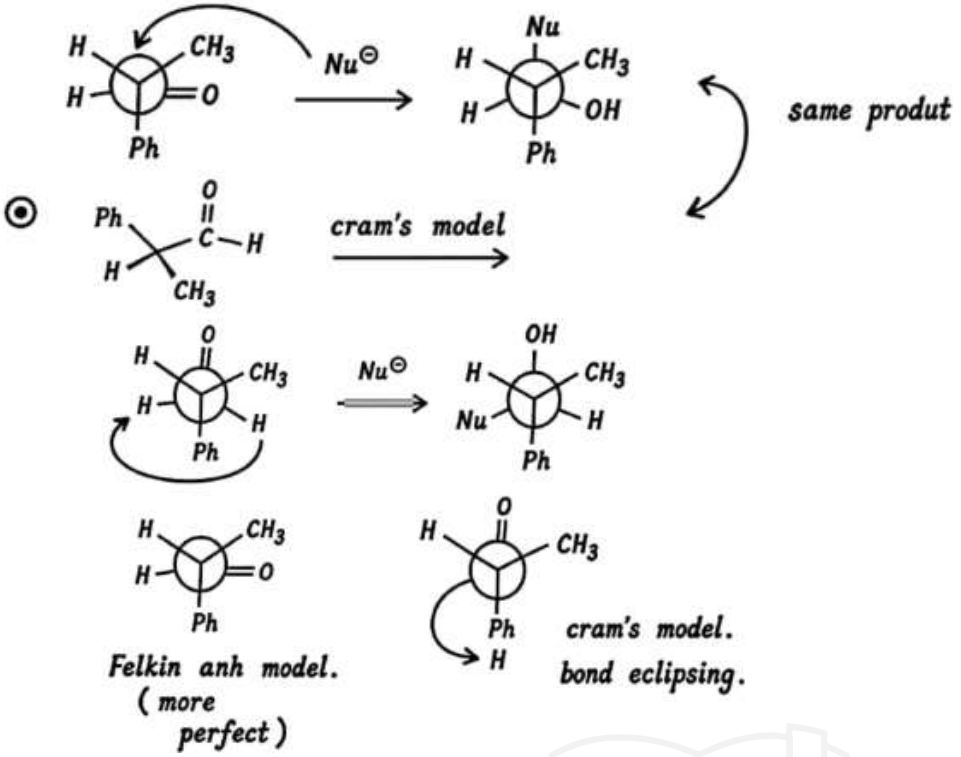
- product is same as Cram's rule.
- this model is more perfect than Cram's model.
- it includes stereo electronic interactions.

1. large gr. should C=O be to carbonyl gr.



2. Medium group should be gauche to group
(A) is more appropiate.

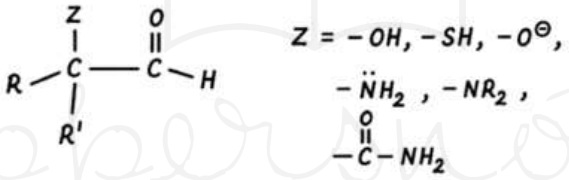
3. Attack will be from small side.



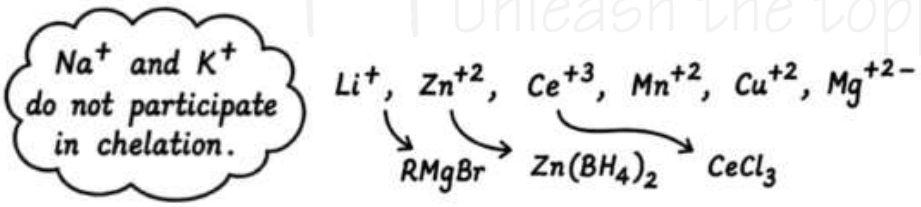
Cram's chelate model (Anti-Cram's Rule)

Condition for chelation :

- must be atleast one gr with unshared lone pair at α position of carbonyl carbon.

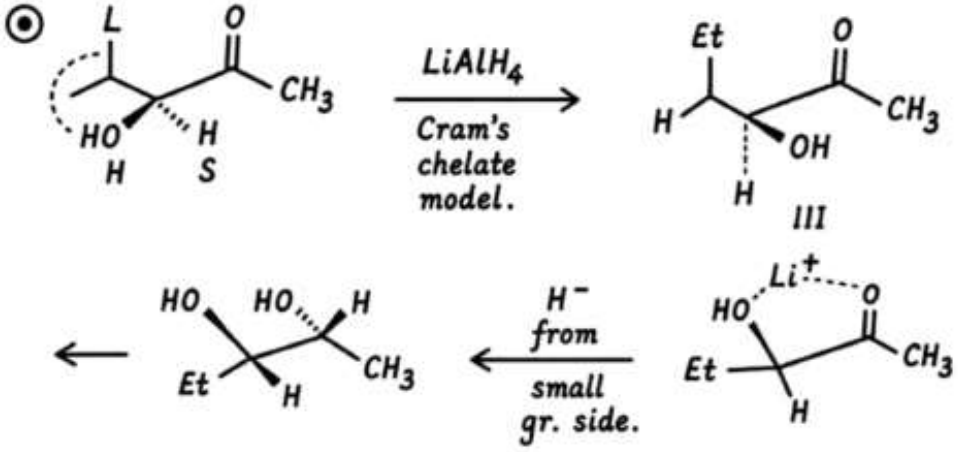


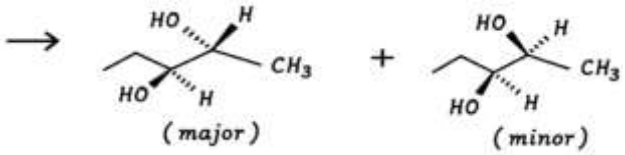
- metal with chelation properties,



Must follow above two condition.

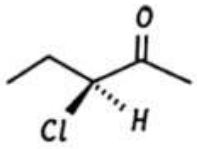
- chelating group should be "Syn" to carbonyl gr.
- attack of $Nu^{\ominus}$ from small group side.

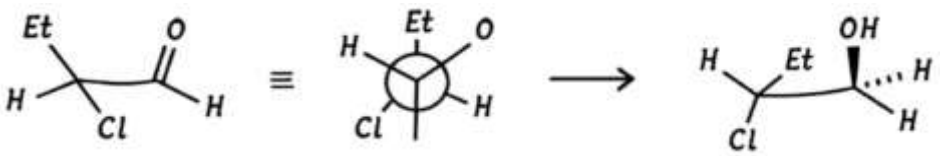




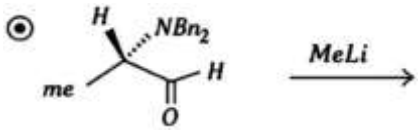
Cornforth Model:-

- If α-halogen is present
- bring halogen anti to carbonyl.
  - attack from Small Side.

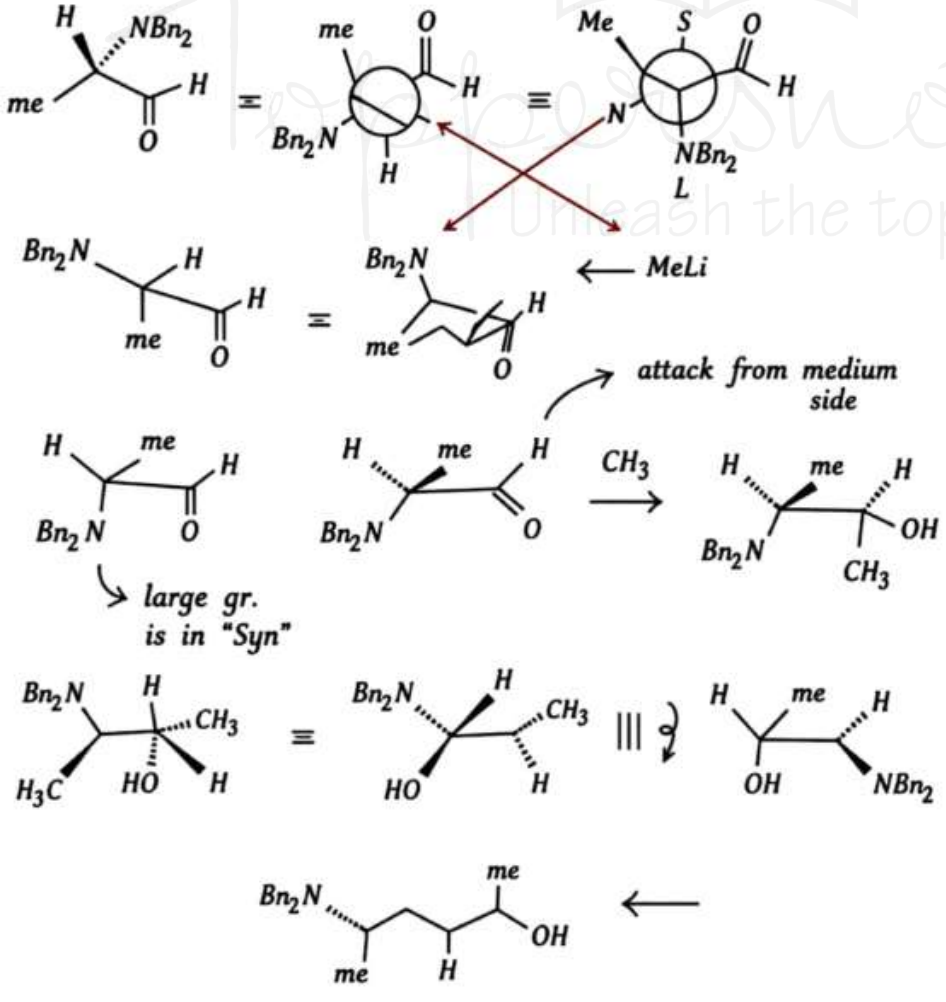


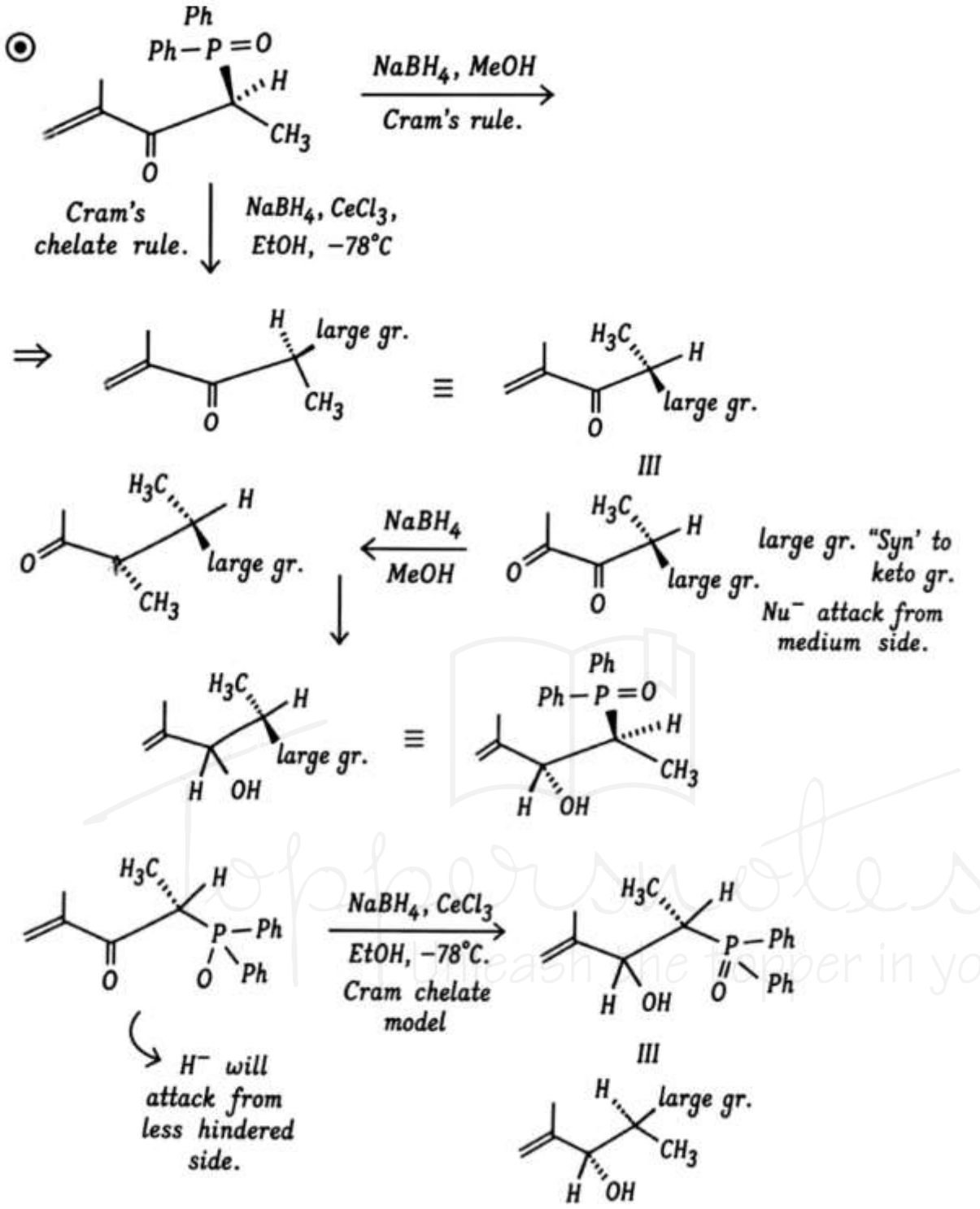


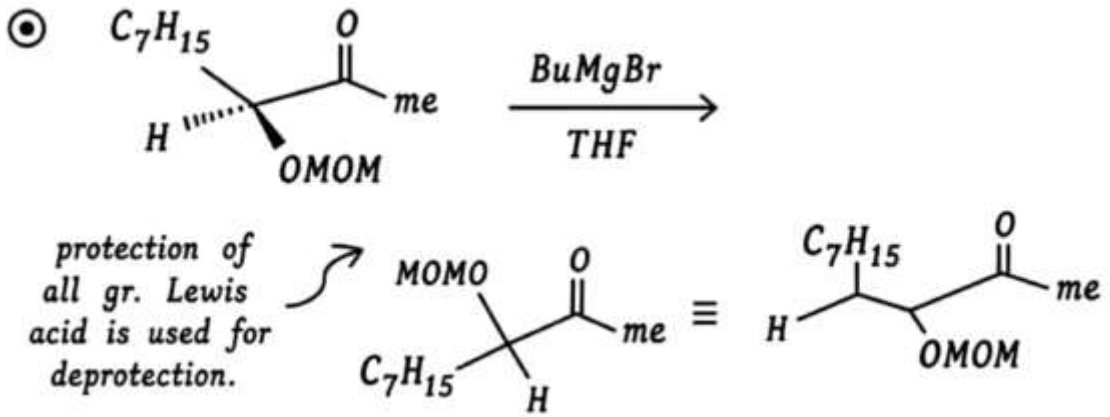
Model.	Adjustment	Attack-from .
1) Cram's Model	i) large → anti ii) large → syn	Small group. medium group.
2) Cram's chelate model.	i) chelating group. → syn.	Small group.
3) Cornforth model.	ii) halogen → anti	Small group.

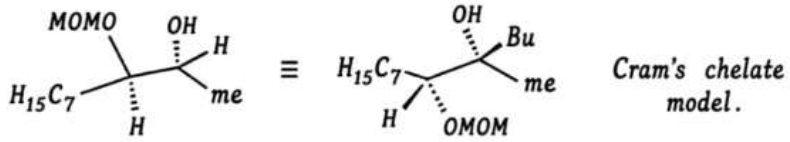


$-\ddot{N}Br_2 \Rightarrow$ lone pair present, due to large. gr. does not participate in chelation i.e. Cram's model is applicable here.



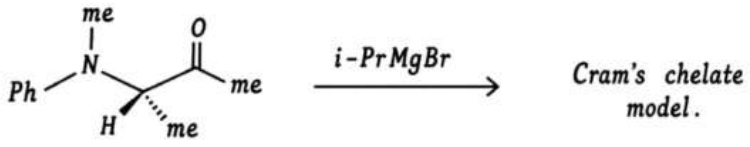

Ph
Ph–P=O
H
CH3
O
NaBH4, MeOH
Cram's rule.
Cram's chelate rule.
NaBH4, CeCl3, EtOH, –78°C
large gr.
H3C
III
NaBH4
MeOH
large gr. "Syn' to keto gr.
Nu⁻ attack from medium side.
OH
H⁻ will attack from less hindered side.
NaBH4, CeCl3
EtOH, –78°C.
Cram chelate model


C7H15
me
OMOM
BuMgBr
THF
protection of all gr. Lewis acid is used for deprotection.
MOMO

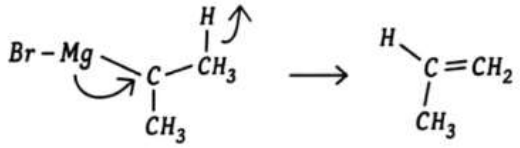


Cram's chelate model.

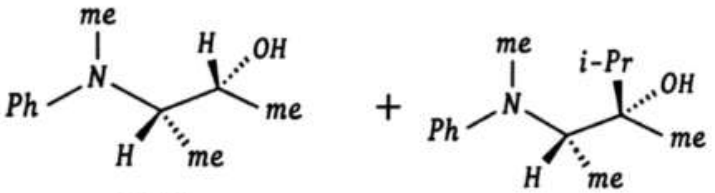
⊙



Cram's chelate model.



H MgBr.



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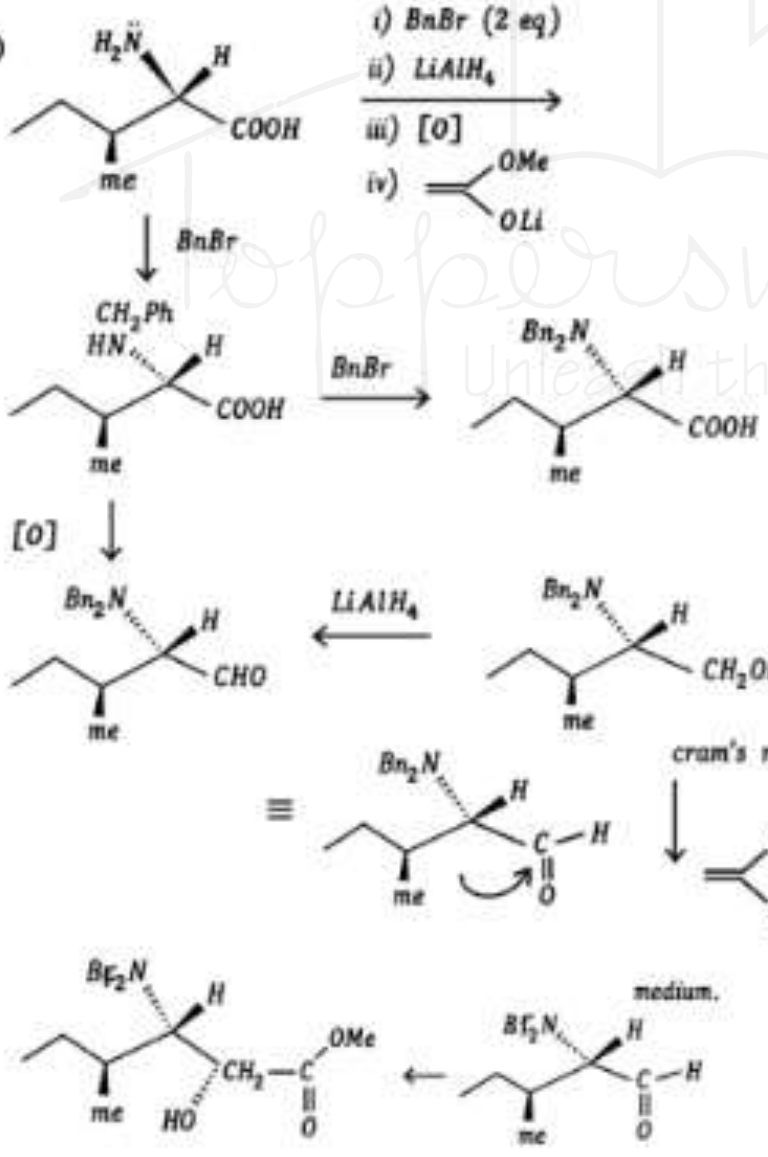

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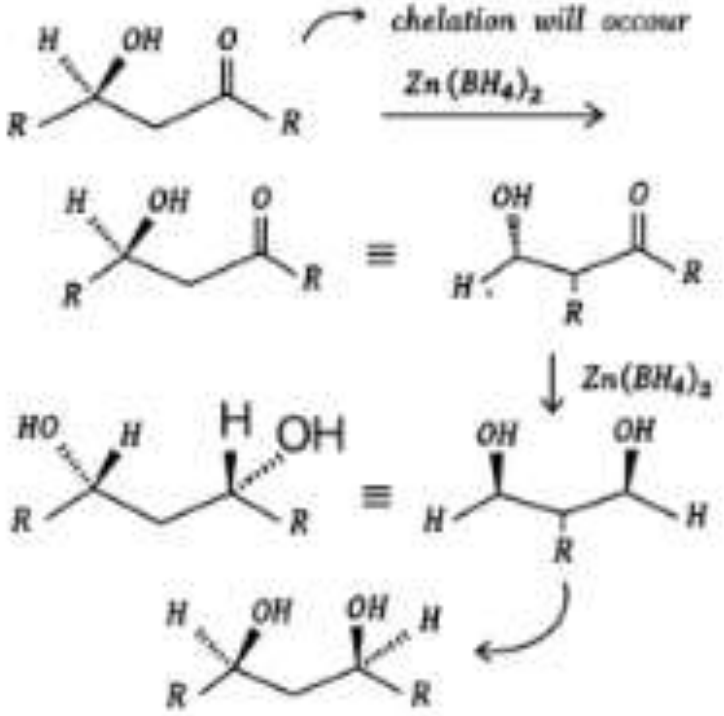

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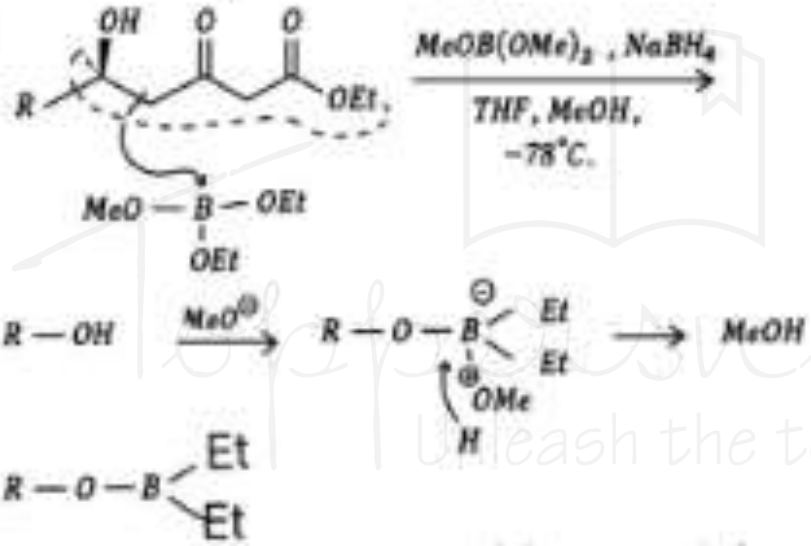

∴ chelation, attack from anti side.

∴ chelation increases electrophiicity in carbonyl carbon.

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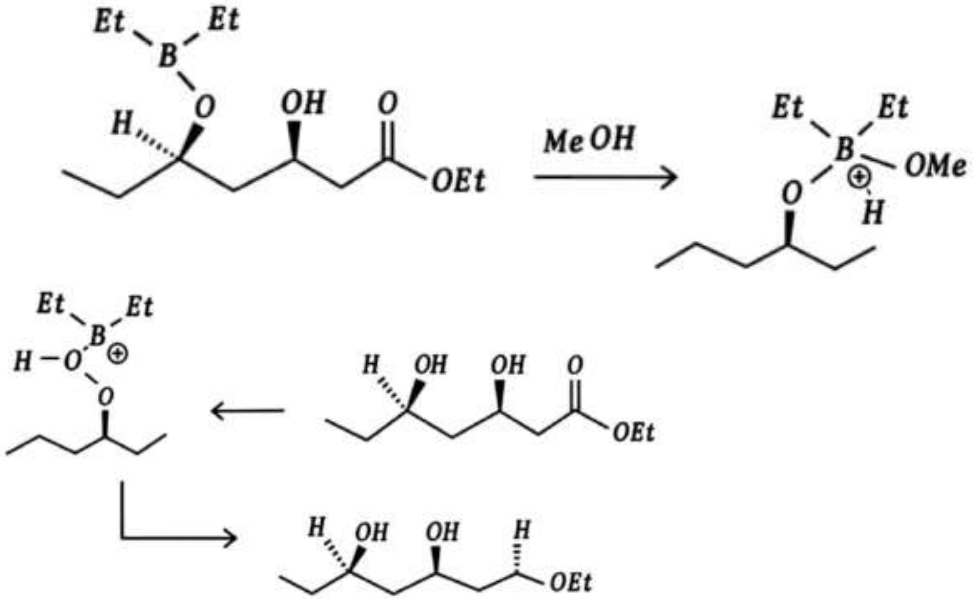
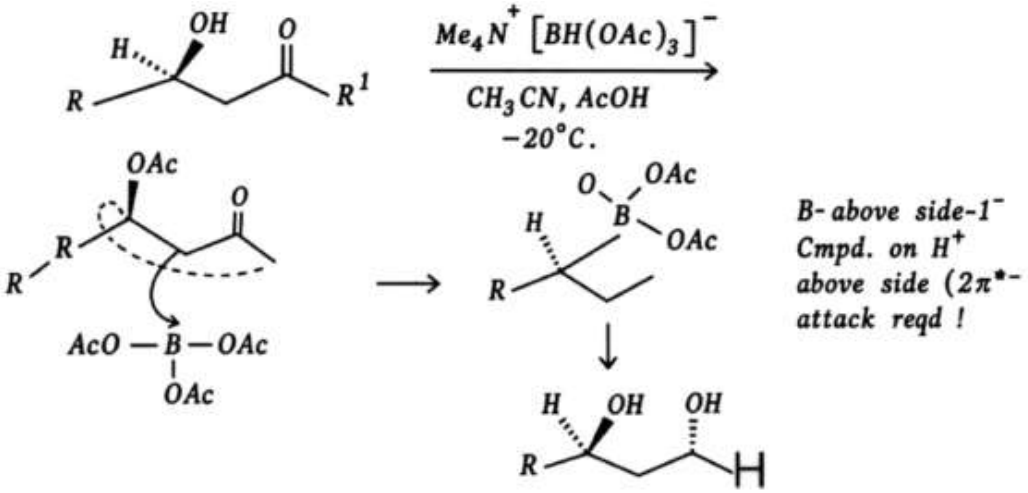
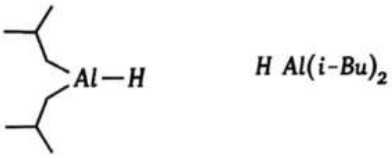


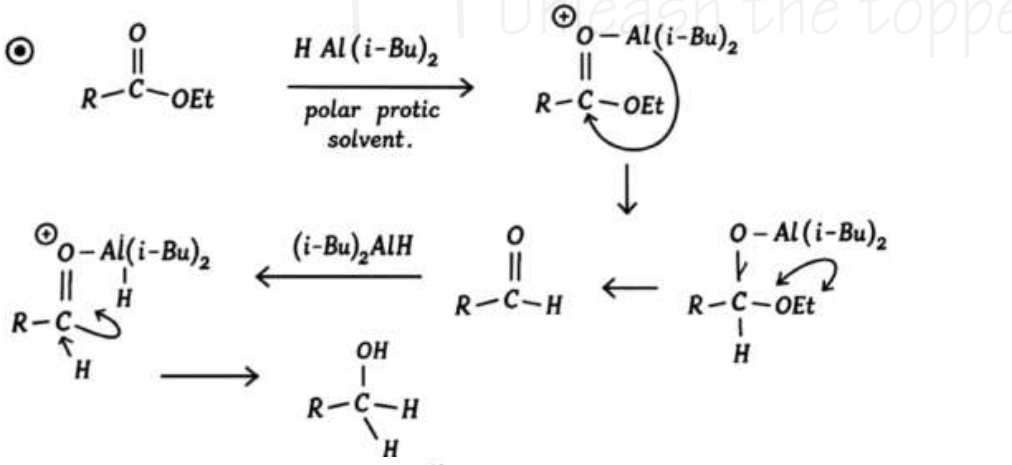


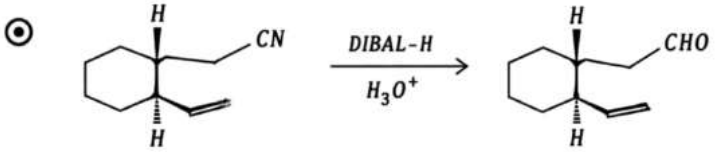
DIBAL – H (Reducing agent)

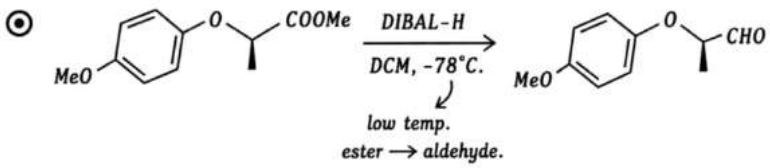
(Diisobutyl Aluminium hydride)

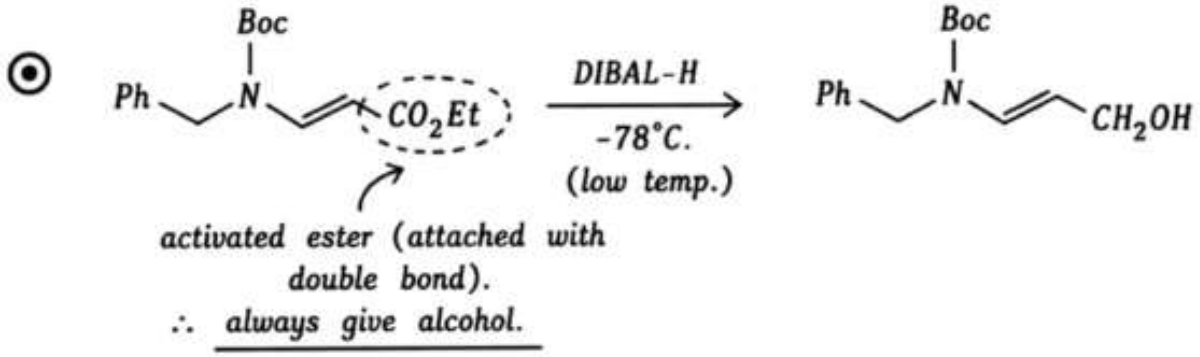


- internal alkyne ⟶ cis alkene.
- ester $\xrightarrow{Low\ temperature}$ aldehyde.
  $\xrightarrow{High\ temperature}$ alcohol.
- cyanide ⟶ aldehyde.
- R – COCl ⟶ aldehyde.
- $R - CONH_2/N_2$ ⟶ aldehyde.

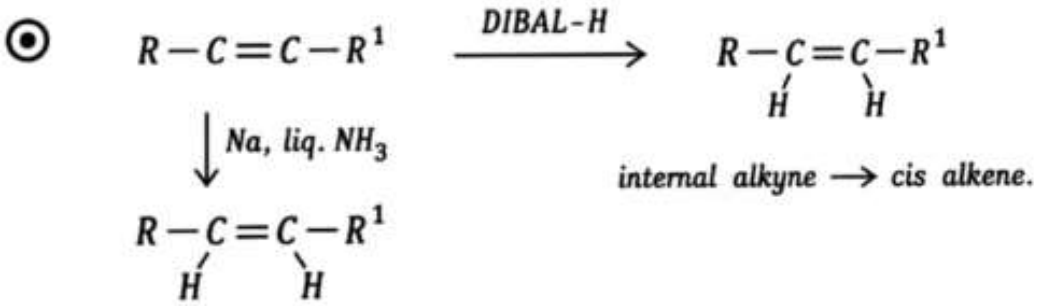




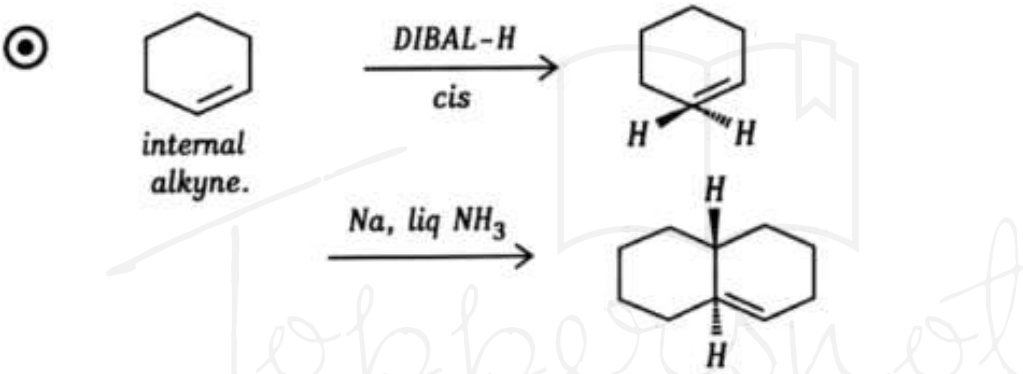




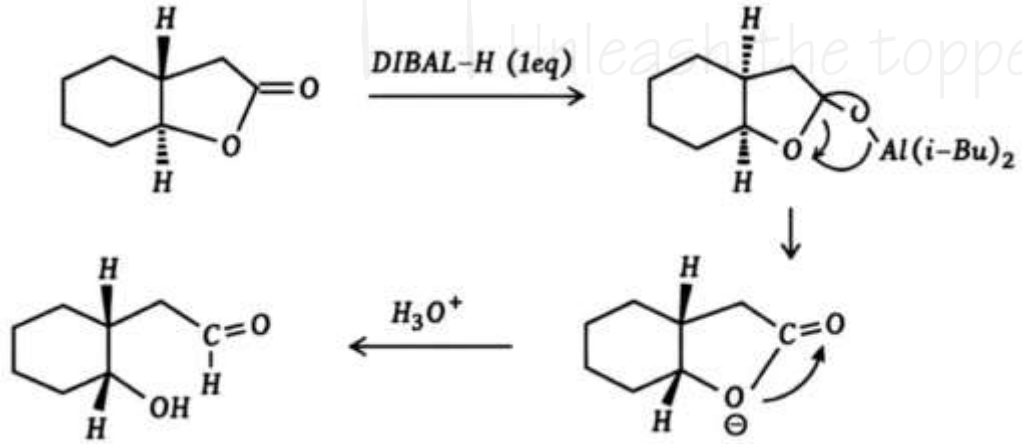
activated ester (attached with double bond).
∴ always give alcohol.

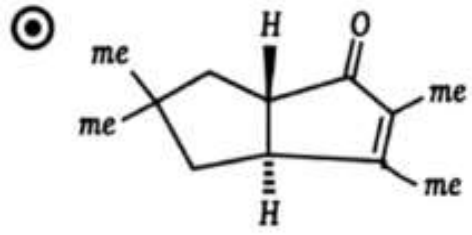


internal alkyne → cis alkene.



internal alkyne.





i) DIBAL-H
ii) Cl-CH_2-COOT /DBAD/ PPh_3
iii) $LiAlH_4$

⇒ if two five membered ring are fused together, the stereochemistry of group present at the junction will be the stereochemistry of incoming group.

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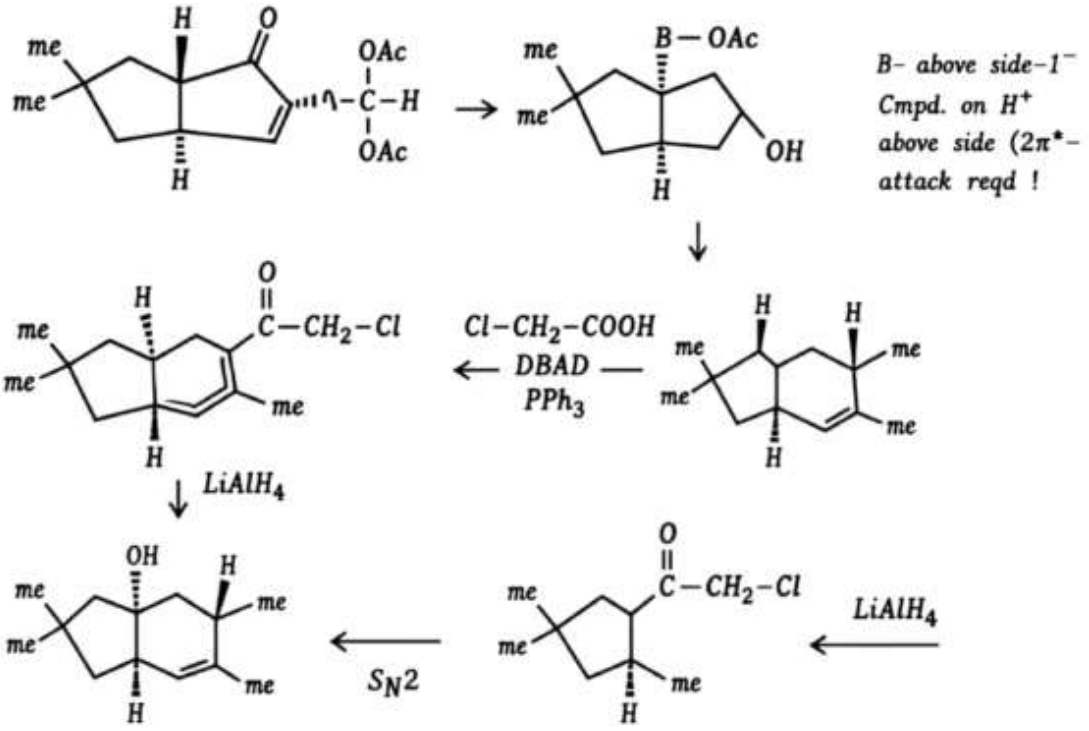
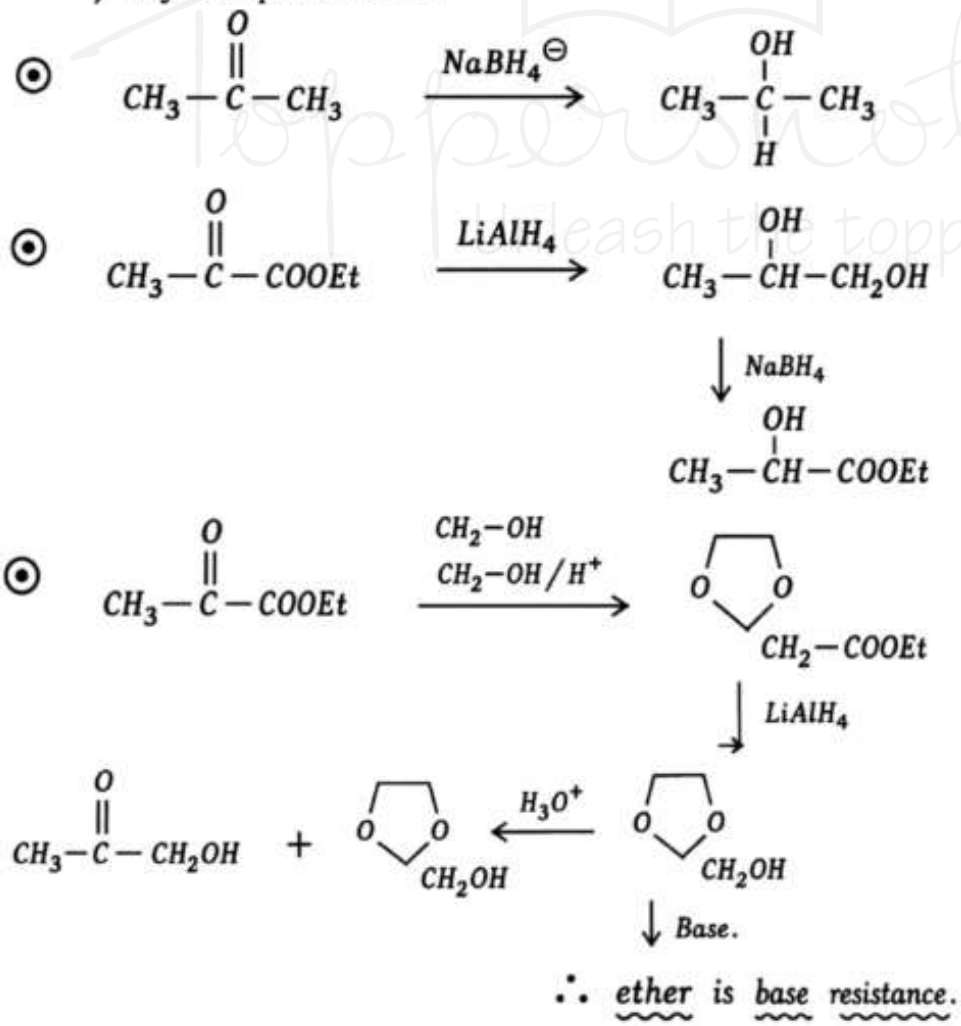


$NaBH_4$:

- Selective reduction for reduction of aldehydes and ketone.
- $Na^+ BH_4^-$ $Li^+ AlH_4^-$

  ↳ *Soft Comparison to* Li^+



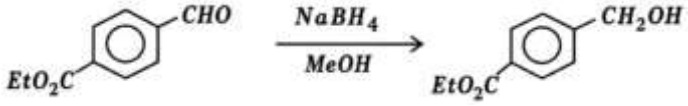
∴ ether is base resistance.

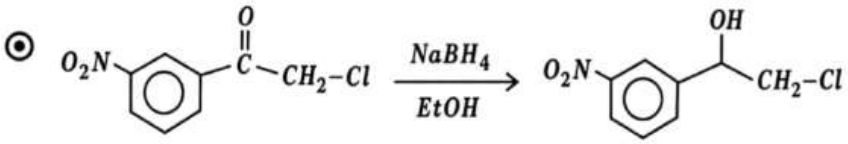
$NaBH_4$:-

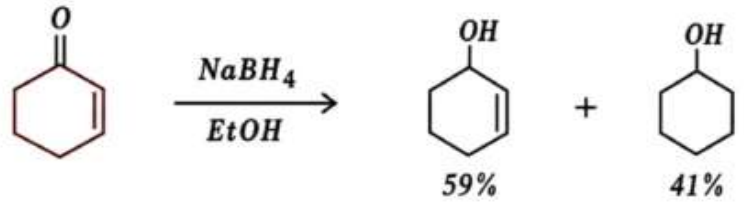
Ketone/aldehyde ⟶ alcohol.

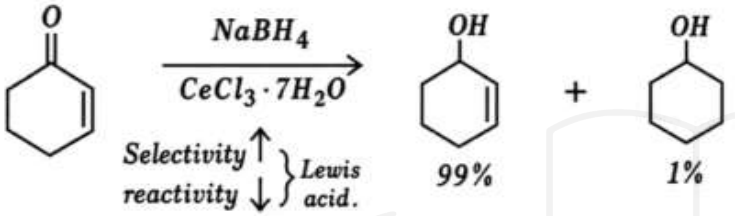
Tosyl hydrozone ⟶ -CH2.

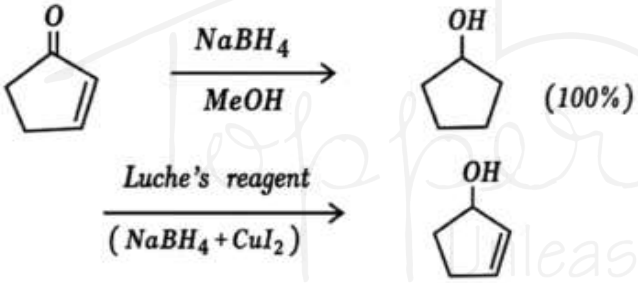
Alkyl azide (RN_3) ⟶ AMINE (RNH_2)



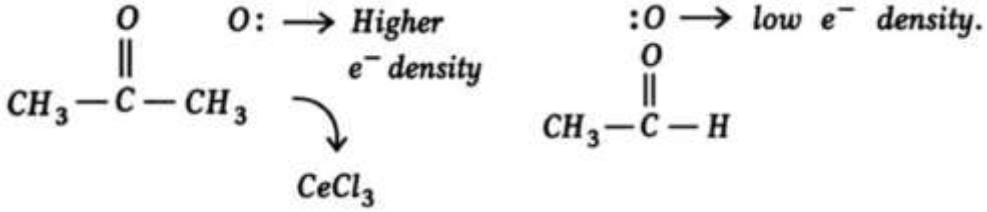








Luche's reagent ⇒ Ketone is reduced in presence of aldehyde.



i.e, Ketone reduced in presence of aldehyde.