Reagents

1) Reducing reagents.
2) Oxidising reagents.
3) OMC reagents
4) Miscellaneous

CSIR NET – (20-25 M)*

⇒ Reagent + I + Rx^n $mech^m$

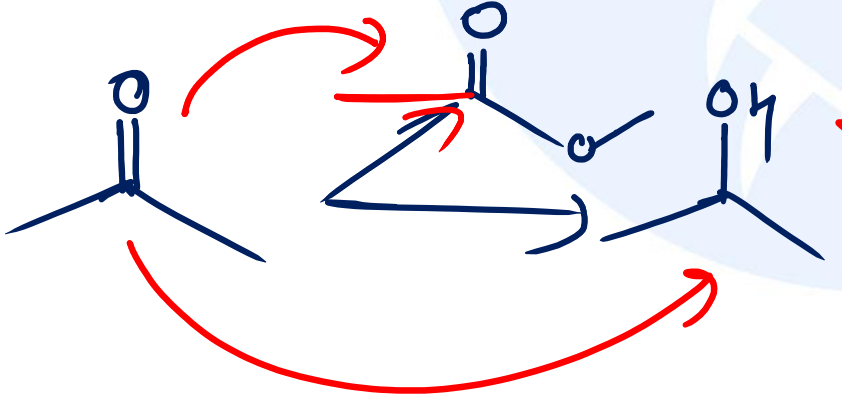
SET – (10-15 M)*

GATE – (8-10 M)*

BARC – Q^s (2-3)

GSI Pre. – 10 Q^s

*GSI Mains – (20-30 M)



* Functional group interconversion

Reducing Reagents

1) **Hydride Based Reducing Reagent**

Eg $NaBH_4$, $LiAlH_4$, BH_3 etc...

2) **Metal dissolved in solvent**

Eg - Birch Reduction

Na in liq-NH_3

3) **Metal Based Reduction**

Eg H_2 Pd/C

* WcCo

4) **Oxygen Removal Based Reduction**

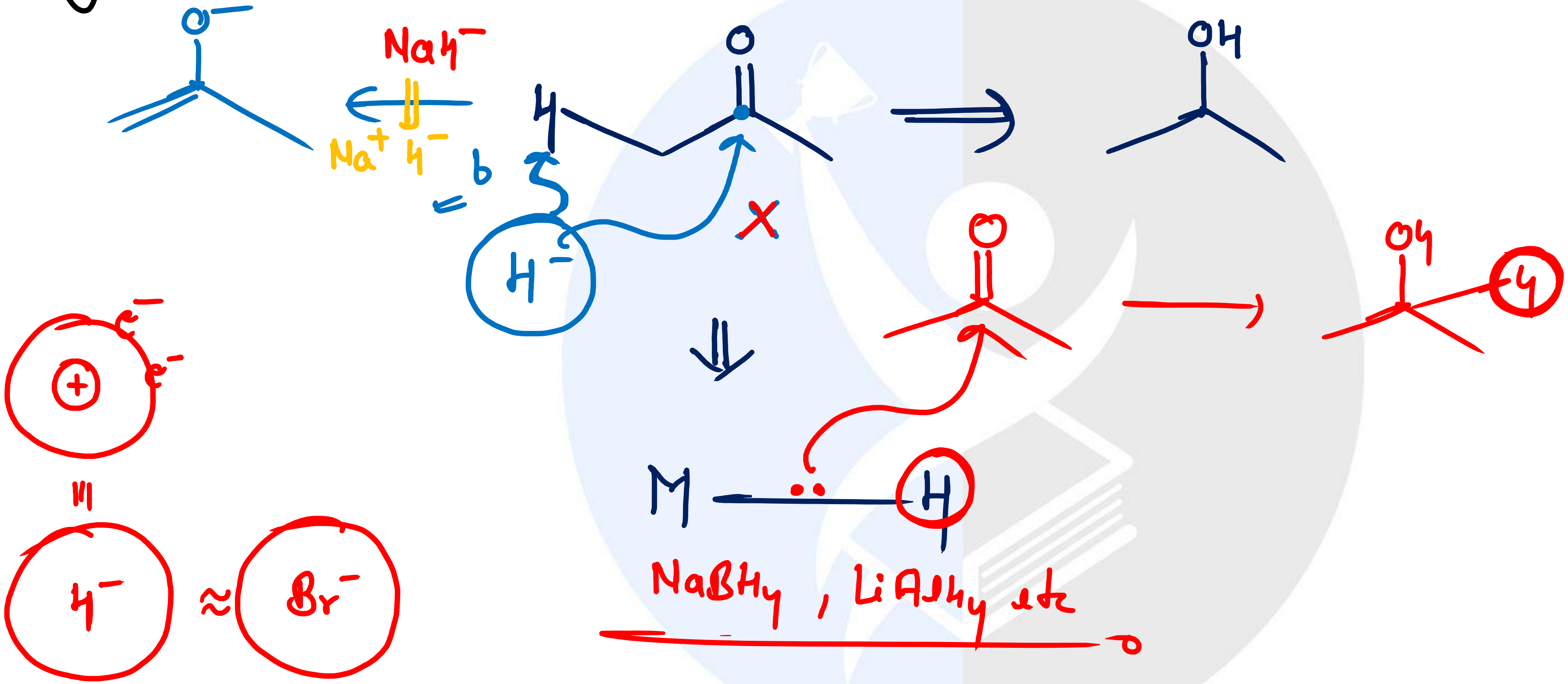
Eg NH_2-NH_2/OH^-

$\Rightarrow$ Oxidation $\equiv$ Add^n of [O]

$\equiv M \longrightarrow M^+ + \bar{e}$

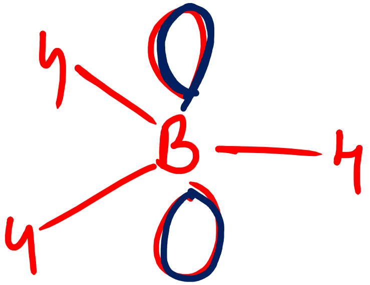
$\equiv$ Removal of H

"Hydride Based' Reducing Reagents.



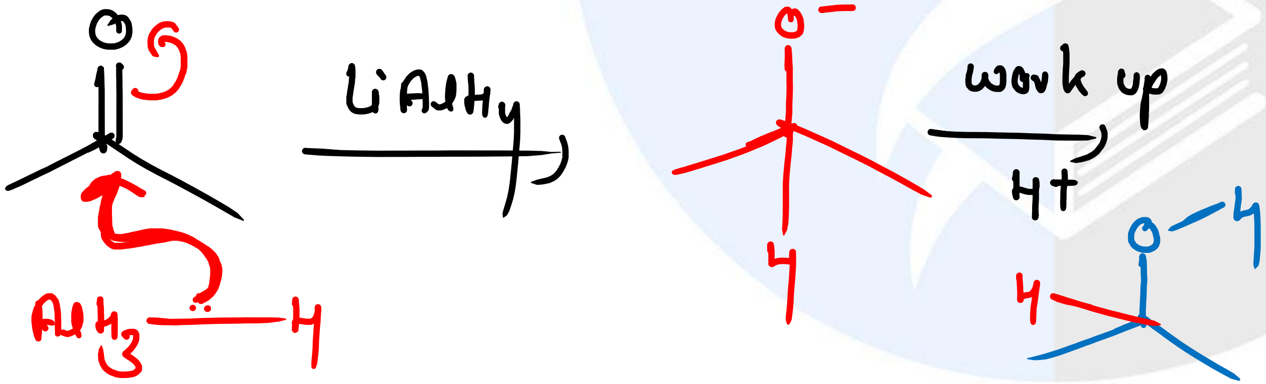
NaBH$_4$, LiAlH$_4$ etc.

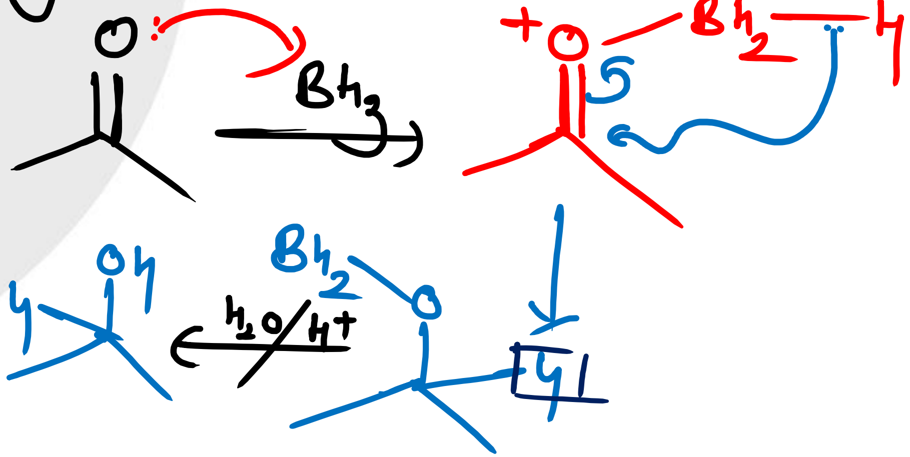
Hydride Based Reagents.

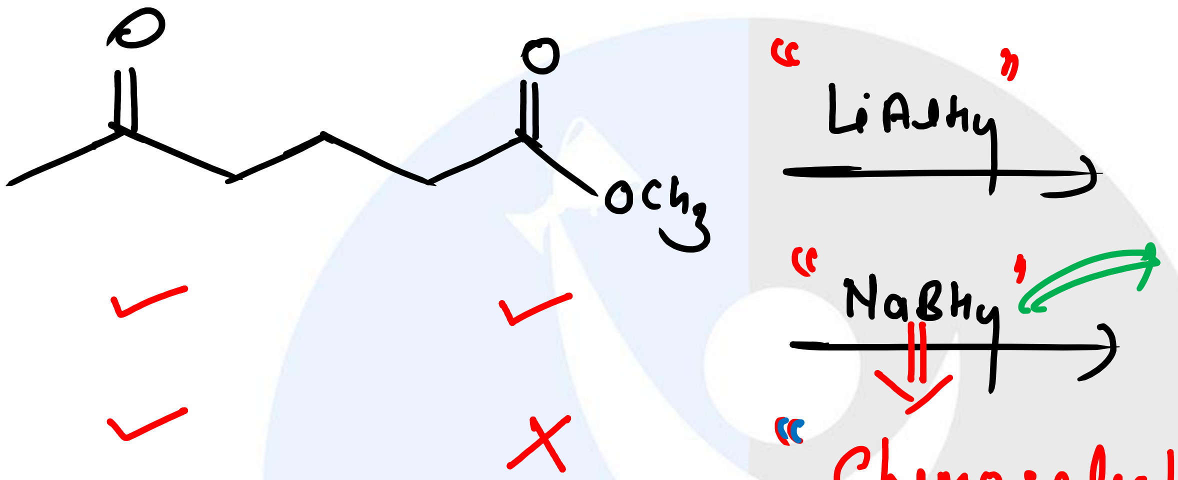


"Direct Attack" ⇐ Nucleophilic Hydride Donor

Electrophilic Hydride Donor ⟹ "Indirect attack"

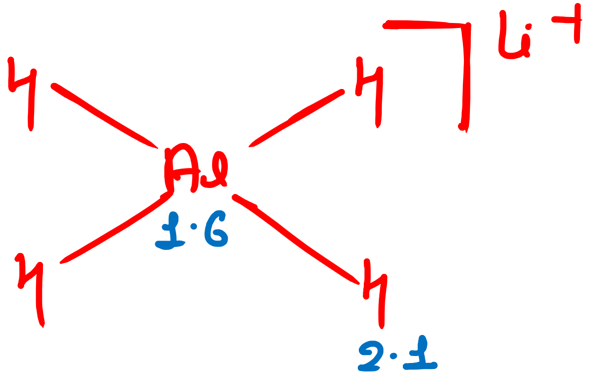


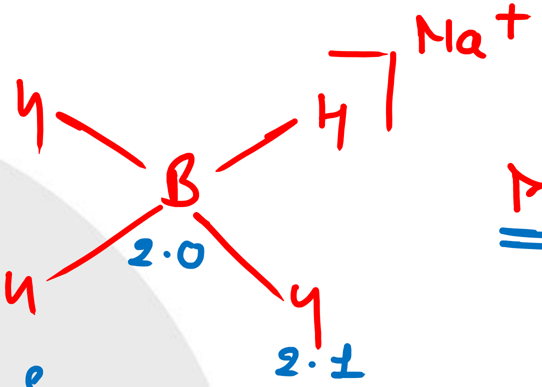




'chemoselective Reagent'

"Chemoselectivity" *





Mild RA

$\overset{\delta+}{Al}-\overset{\delta-}{H}$ Polarity ↑ ΔE.N. ↑

charge density ↑

⇓

* Nucleophilicity ↑↑

⇓

chemoselectivity ↓↓

$B-\overset{\delta-}{H}$ Polarity ↓ ΔE.N. ↓

charge density ↓

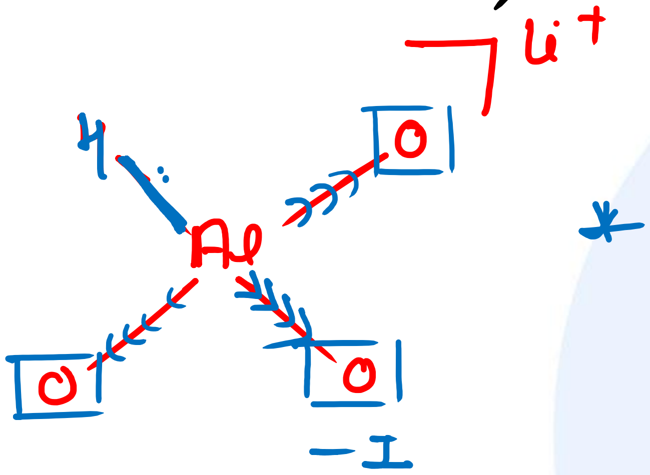
⇓

Nucleophilicity ↓↓

⇓

* chemoselective ↑↑

Effect of EDG / EWG.



* Polarity of Al—H bond decreases.

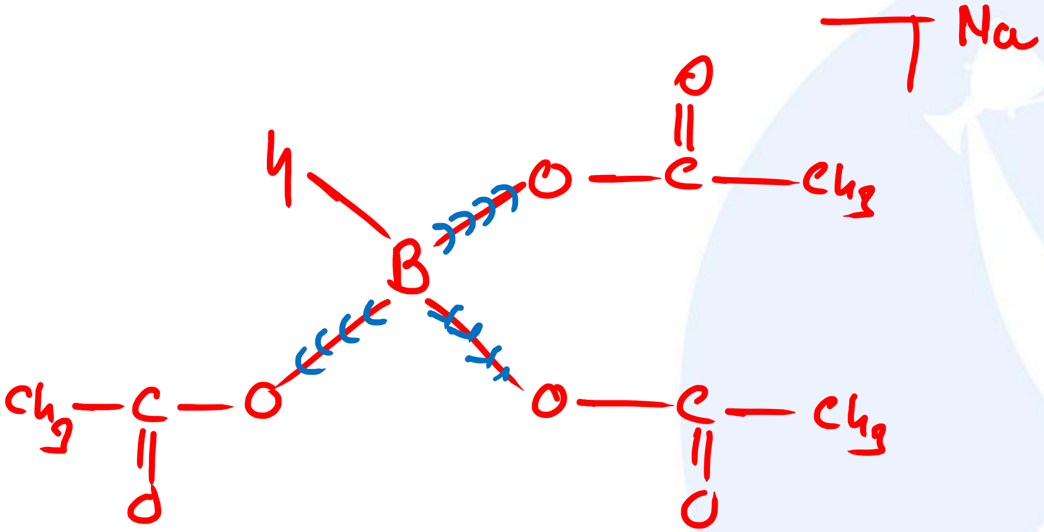
⇓

Nucleophilicity ↓↓

⇓

chemoselectivity ↑↑.

$Na[BH(OAc)_3]$



B—H Polarity ↓ses

⇓

Nucleophilicity ↓

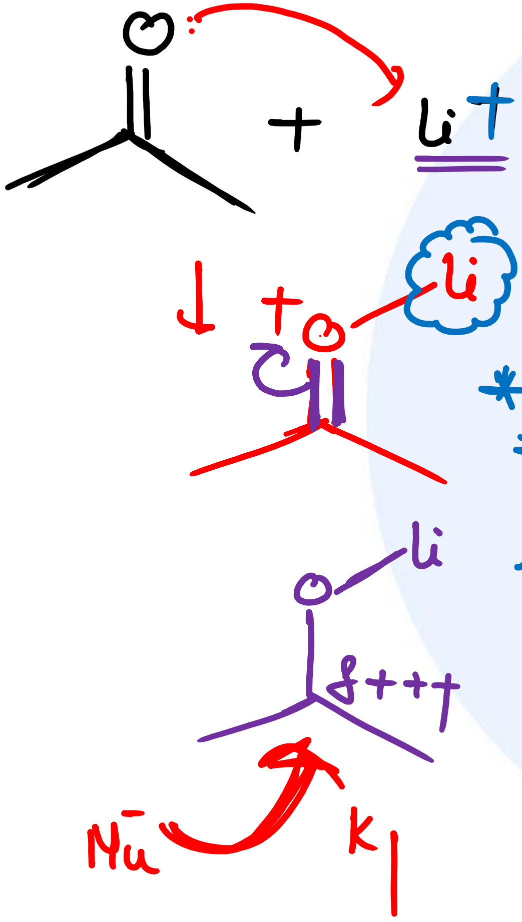
⇓

Chemoselectivity ↑

"EWG" ⇒ Nucleophilicity ↓↓ ⇒ chemoselectivity ↑↑

EDG ⇒ " " ↑↑" ⇒ " ↓↓

Role of Metals.

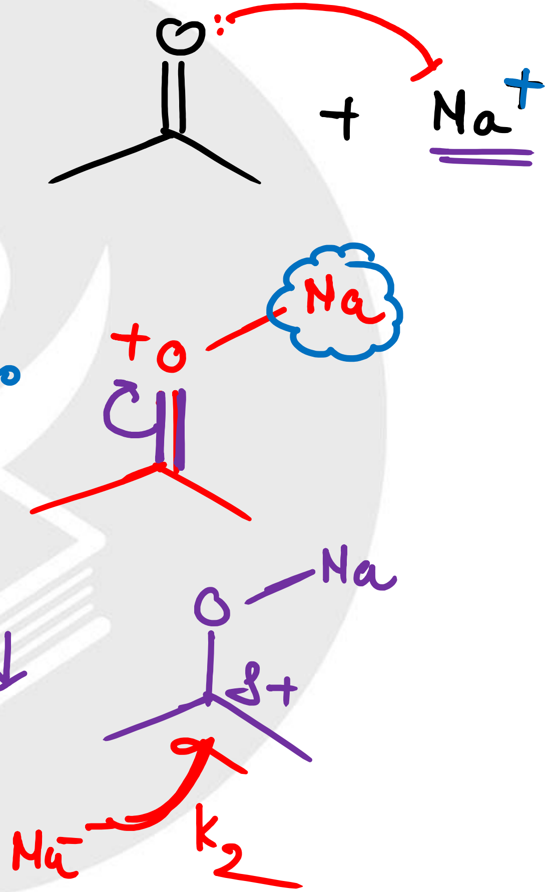


* Fajan Rule.

* 1) $PP \propto$ charge

2) $\uparrow PP \propto \dfrac{1}{\text{size}\downarrow}$

* $\boxed{k_1 > k_2}$



Q. Rate of Reduction for following metal?

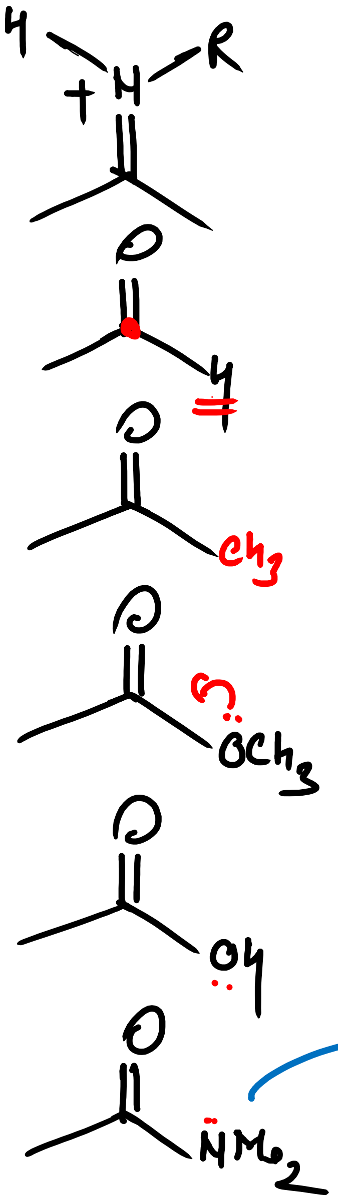
Zn^{+2} Li^{+} Na^{+}

k_1 k_2 k_3

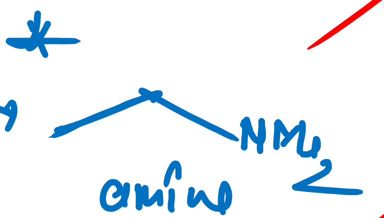
* $\boxed{k_1 > k_2 > k_3}$

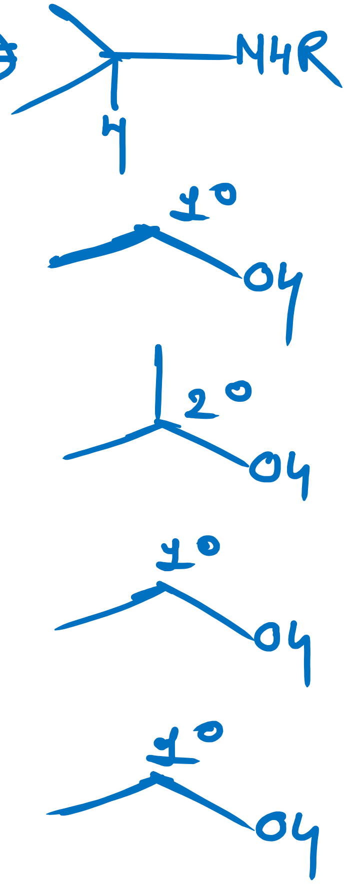
$LiAlH_4 \rightarrow NaBH_4 \rightarrow LiBH_4 \rightarrow ZnBH_4$

*Note: Unique chemoselectivity.

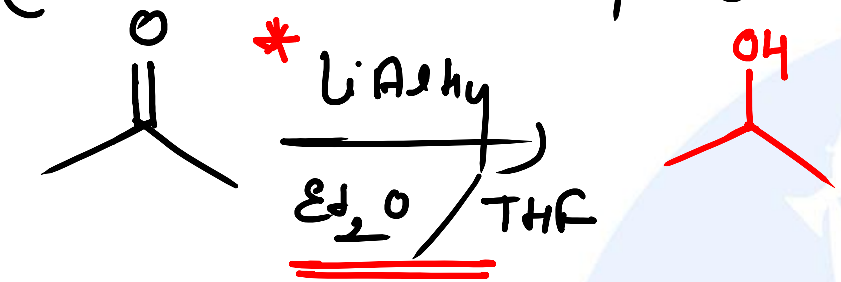


	$LiAlH_4$	$NaBH_4$	$LiBH_4$	$ZnBH_4$	
Imine	✓	✓	✓	✓	⇒ amine
Aldehyde	✓	✓	✓	✓	⇒ 1°
Ketone	✓	✓	✓	✓	⇒ 2°
Ester	✓	✗	✓	✓	⇒ 1°
Acid	✓	✗	✗	✓	⇒ 1°
Amide	✓	✗	✗	✗	⇒





Reduction via $LiAlH_4$

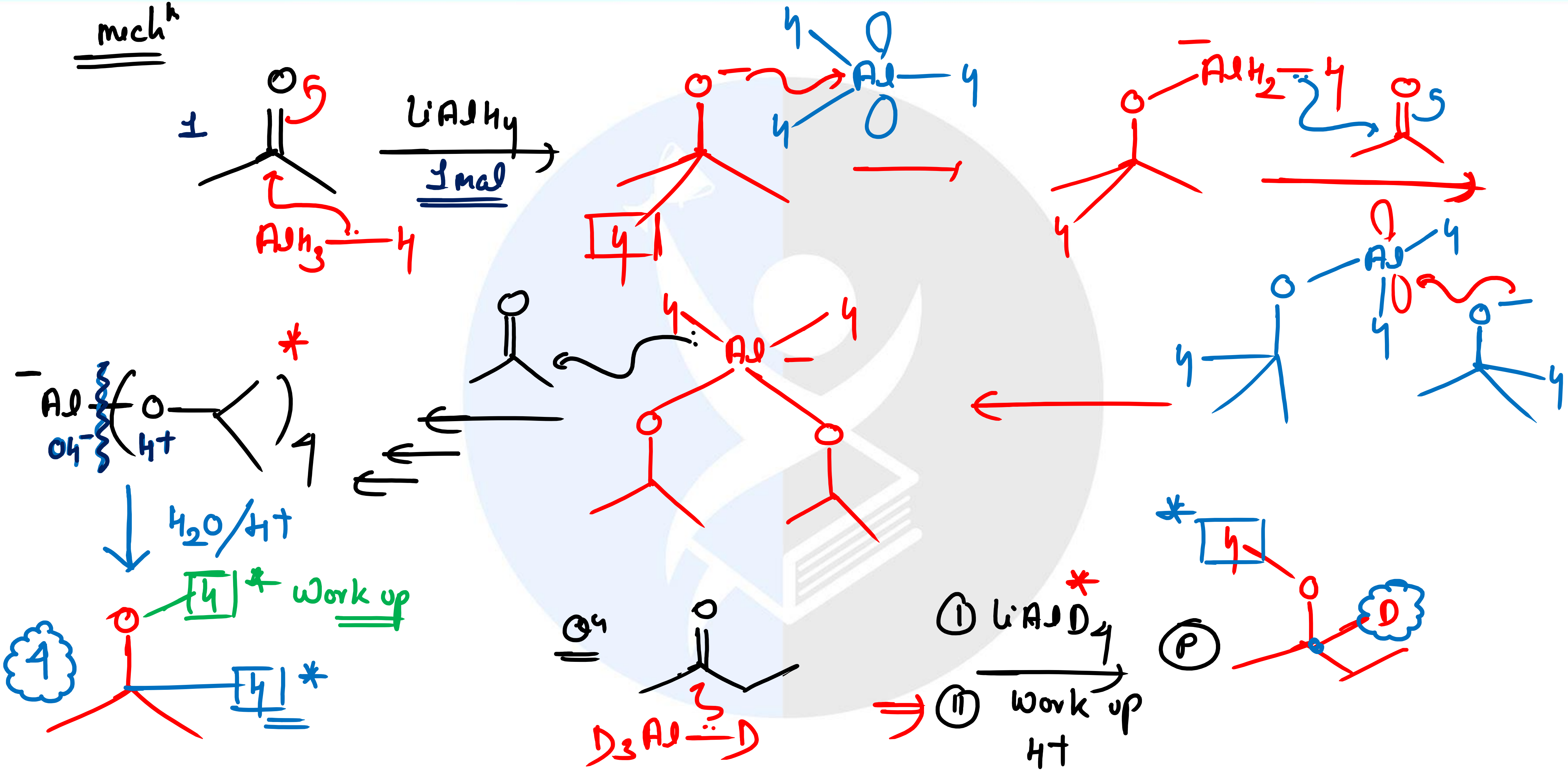


* Never use "Polar solvent" with $LiAlH_4$

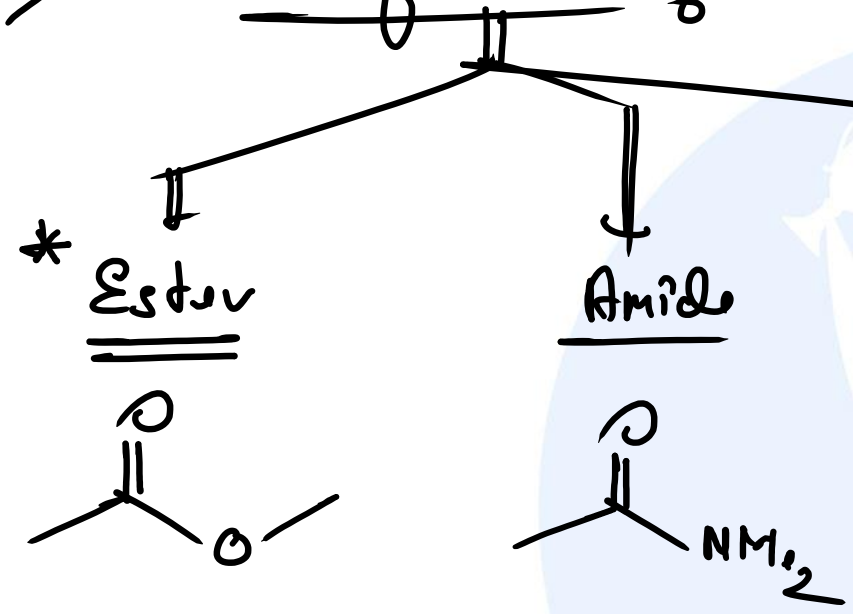
$$\Rightarrow R{-}\underline{OH}^{*} + LiAlH_4 \longrightarrow \underline{H_2}\uparrow$$

$$Al{-}\overset{\delta-}{\underline{H}}$$

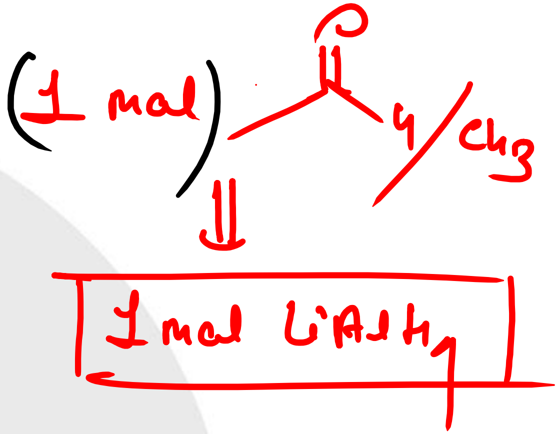
mech^n


1
$LiAlH_4$
1 mol
AlH_3—H
Al
H
H_2O/H^+
Work up
4
OH^-
H^+
Q
D_3Al—D
① $LiAlD_4$
② Work up H^+
P
D

Derivative of Acid

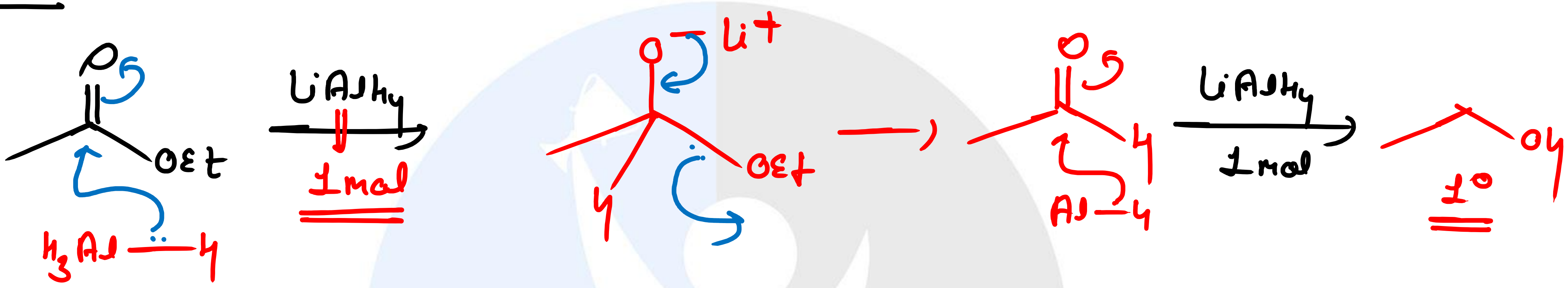


#



$\boxed{1\ \text{mol}\ LiAlH_4}$

Ester



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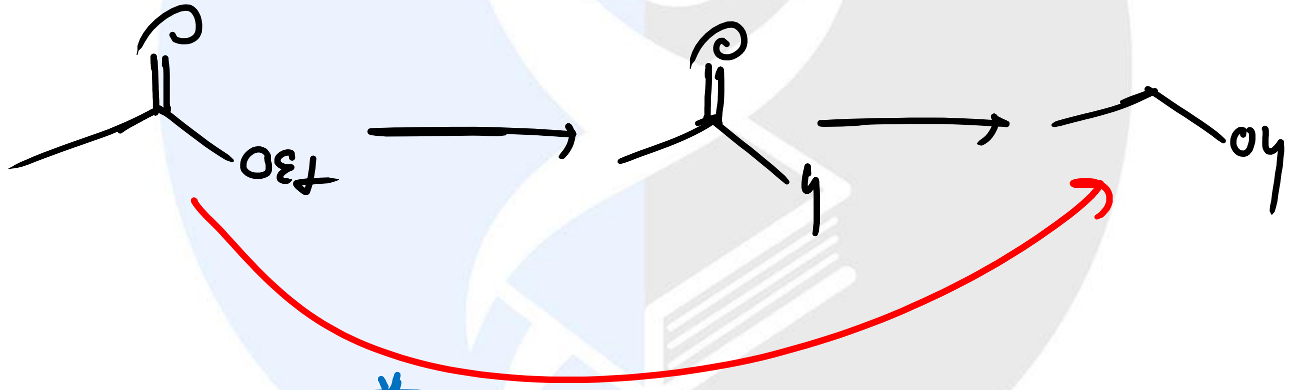
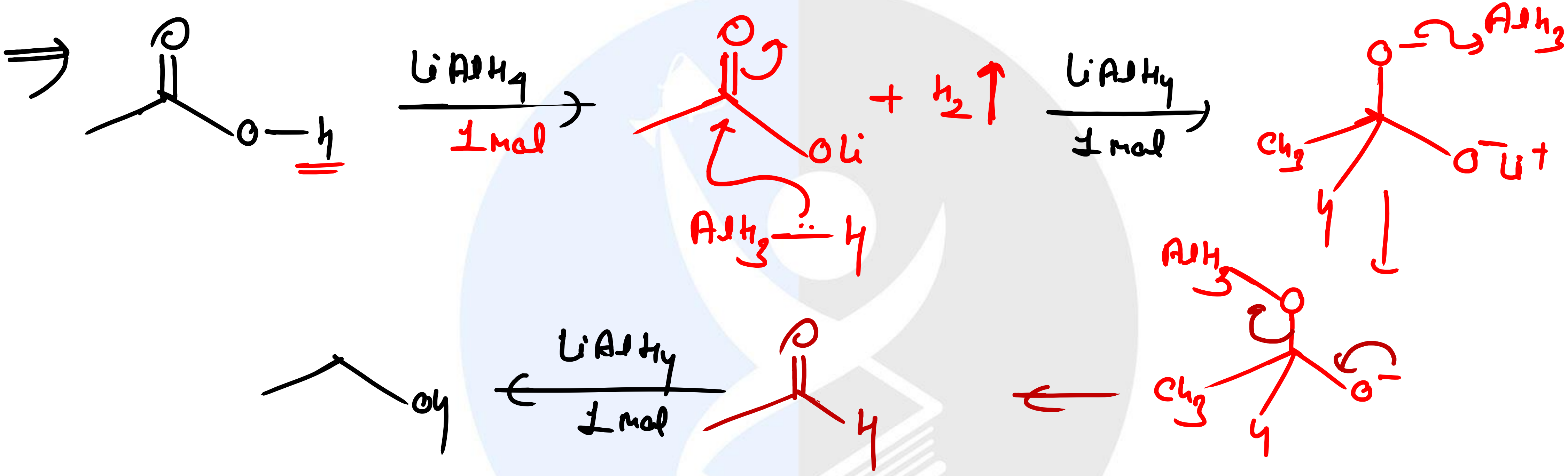
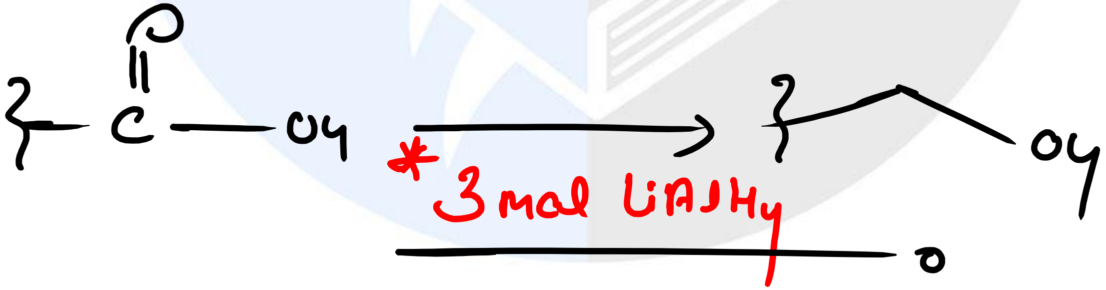


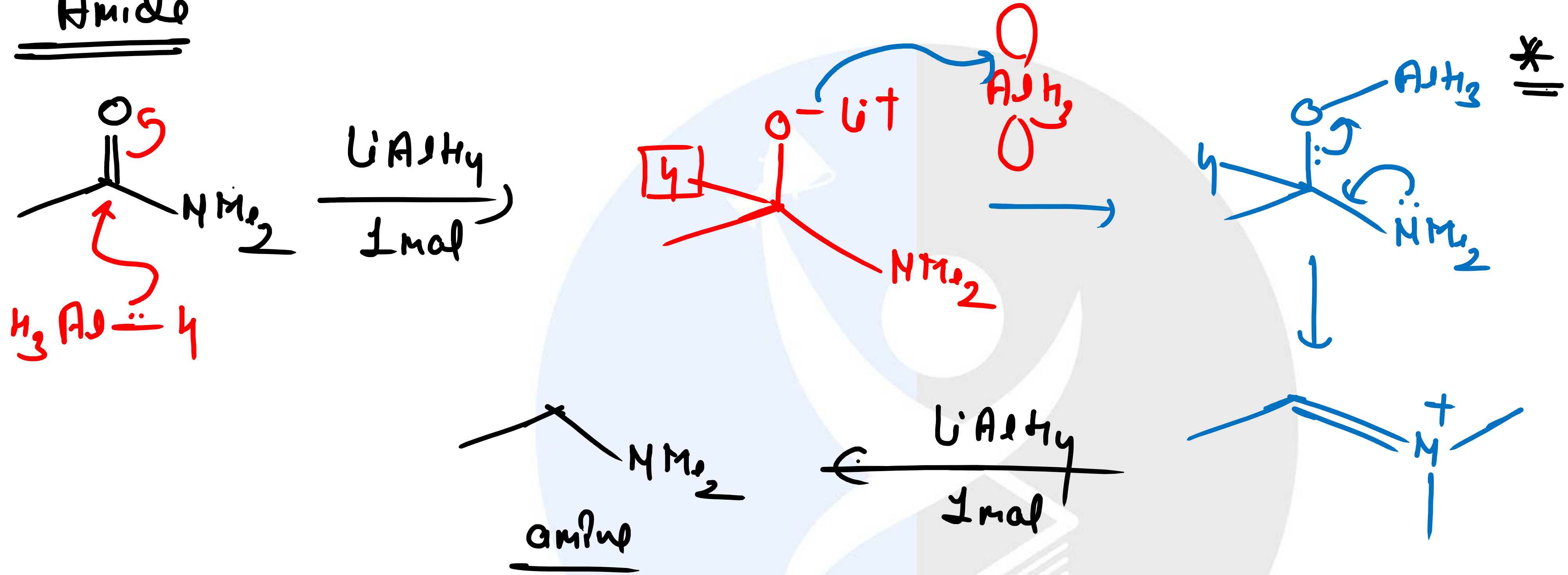
* 2 mol $LiAlH_4$

"Acids"

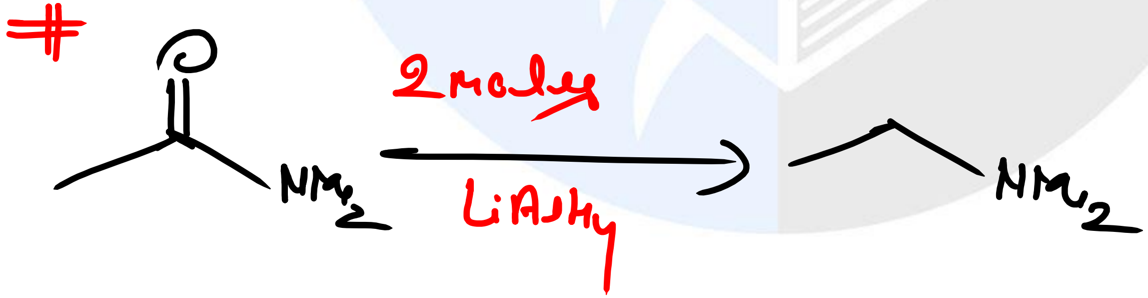

⇒
LiAlH4
1 mol
OLi
+ H2↑
AlH3—H
LiAlH4
1 mol
O—AlH3
CH3
O⁻ Li⁺
H
AlH3
CH3
O⁻
H
LiAlH4
1 mol
OH
H


C
O
OH
* 3 mol LiAlH4
OH

“Amide”

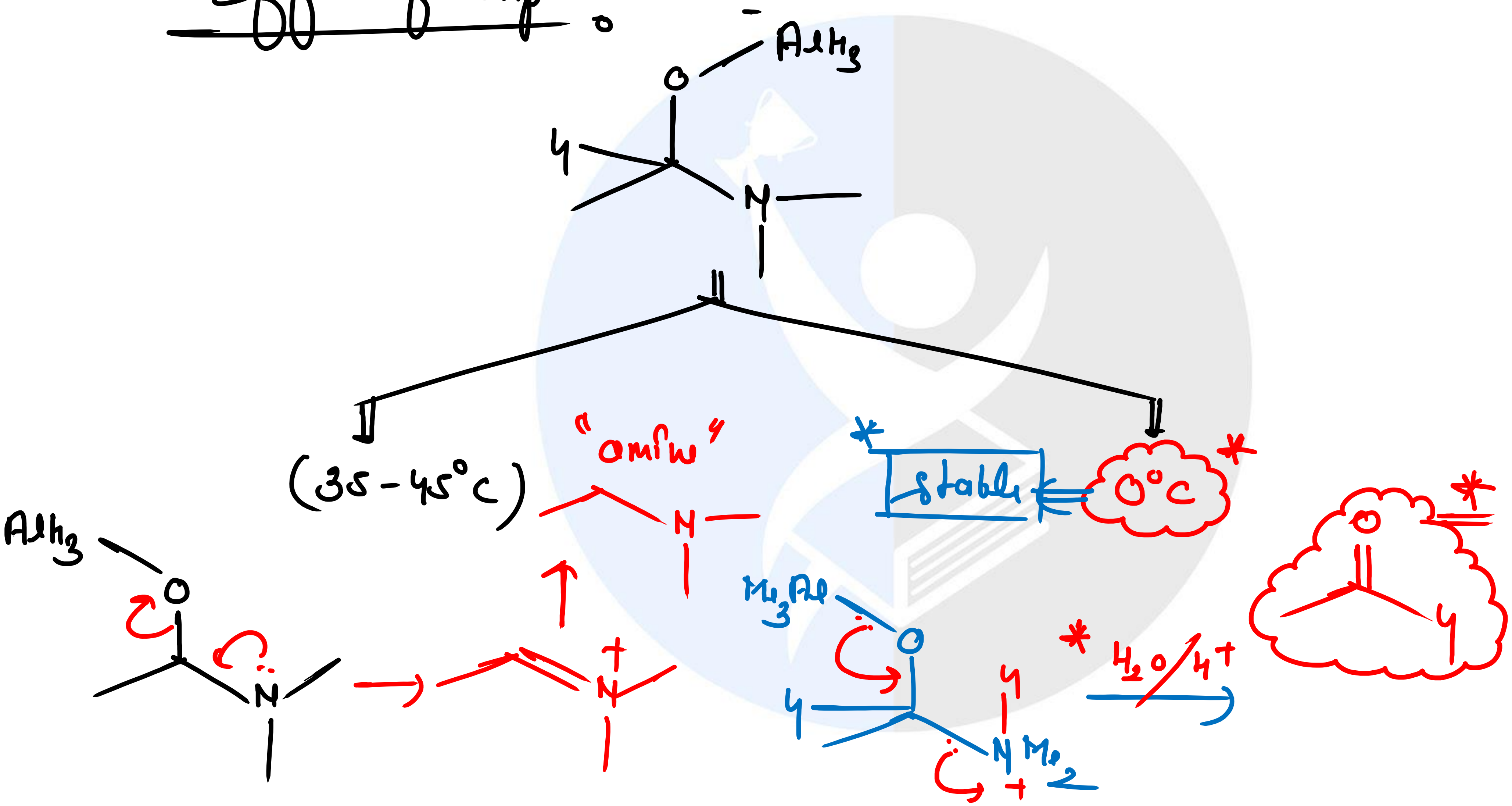


LiAlH4
1 mol
H3Al–H
O⁻ Li⁺
H
AlH3
NMe2
AlH3 *
H
NMe2
LiAlH4
1 mol
+
N
NMe2
amine

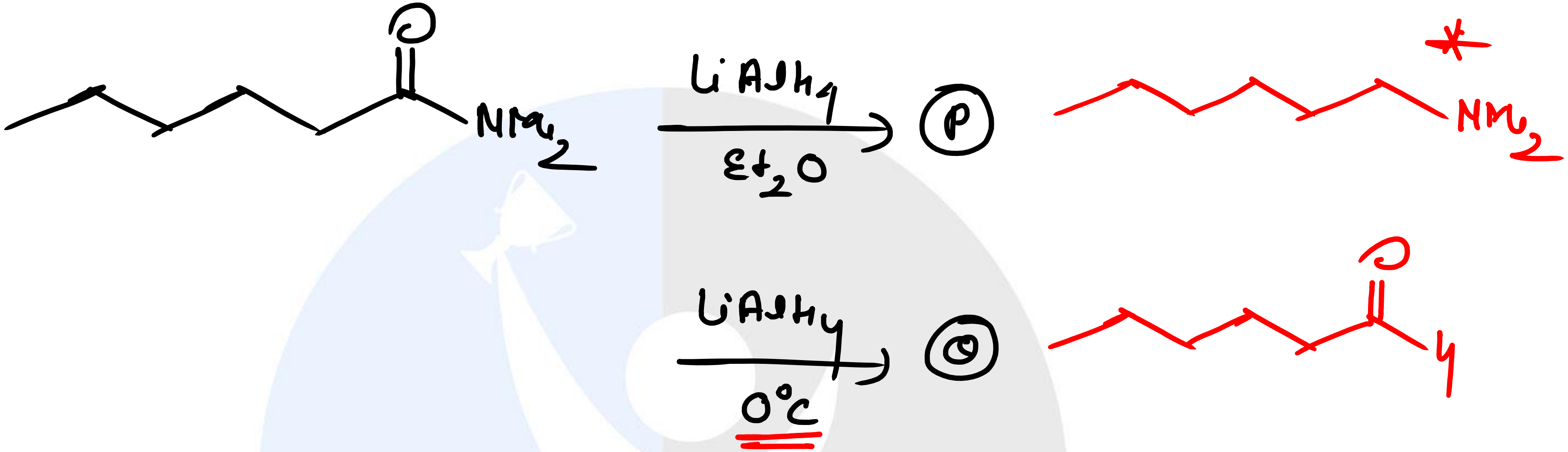


#
NMe2
2 moles
LiAlH4
NMe2

Effect of Tempr.



Q4



Q4

*Carruthers