Complex metal hydride reductions: LiAlH4 and NaBH4

TOPICS COVERED

- Lithium Aluinium Hydride (LAH)
- Mechanism of Reduction using LAH
- Reduction of carbonyl compounds, carboxylic acid using LAH
- Reduction of amides, esters, epoxides using LAH
- Comparative analysis of LiAlH4 and NaBH4
- Stereochemistry of Ketone Reduction and Problems

Lithium Aluminum Hydride (LAH)

Lithium aluminum hydride (LAH) is a strong reducing agent with chemical formula $LiAlH_4$. It can reduce a variety of functional groups such as aldehydes, esters, acids, ketones, nitriles, epoxides and azides. It vigorously reacts with water and all the reactions are performed in polar aprotic solvents.

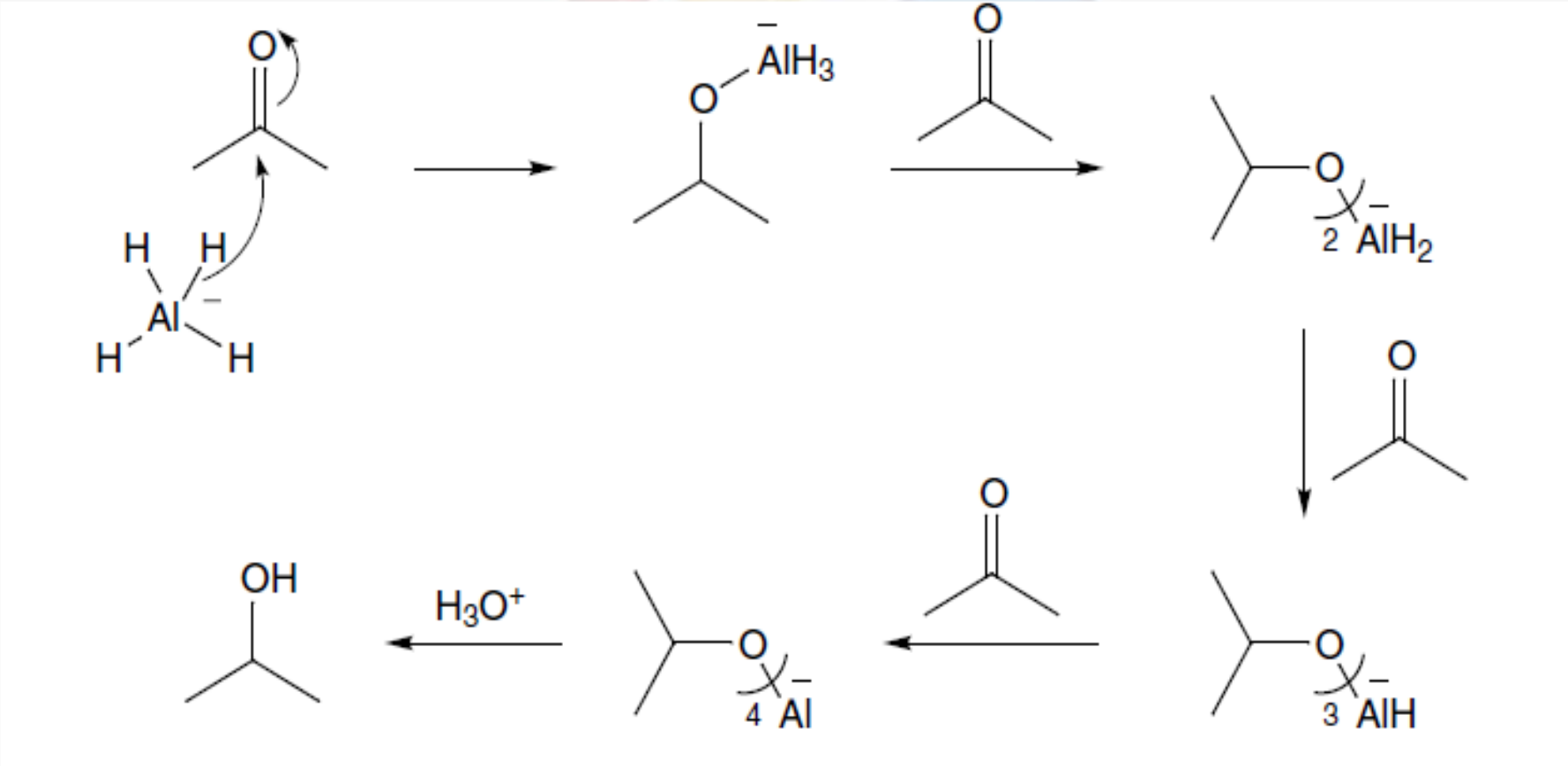
Preparation

It was first prepared by treating lithium hydride (LiH) with aluminum chloride ($AlCl_3$)

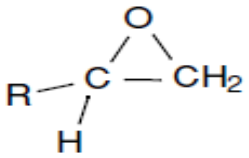
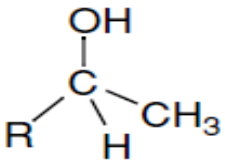
$$4LiH + AlCl3 \rightarrow LiAlH_4 + 3LiCl$$

In industrial scale, it is prepared from sodium aluminum hydride which is prepared by reaction of sodium, aluminum and hydrogen at high temperature and pressure

Mechanism of Ketone Reduction Using LAH

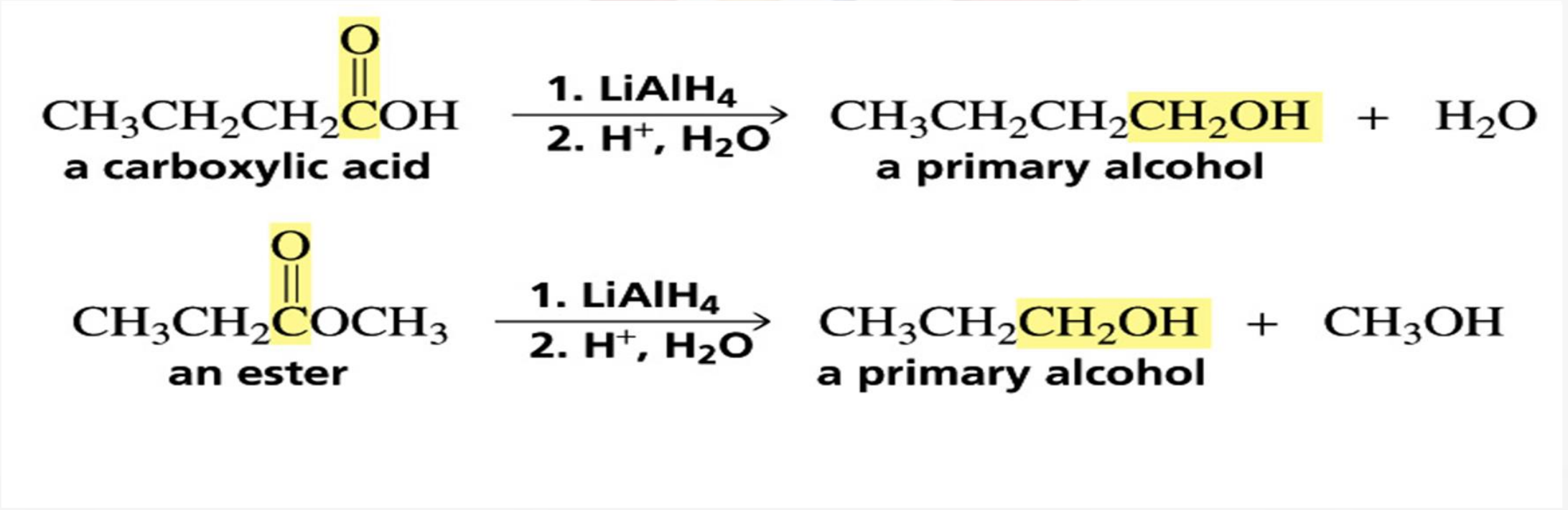


Functional group reduced by LAH

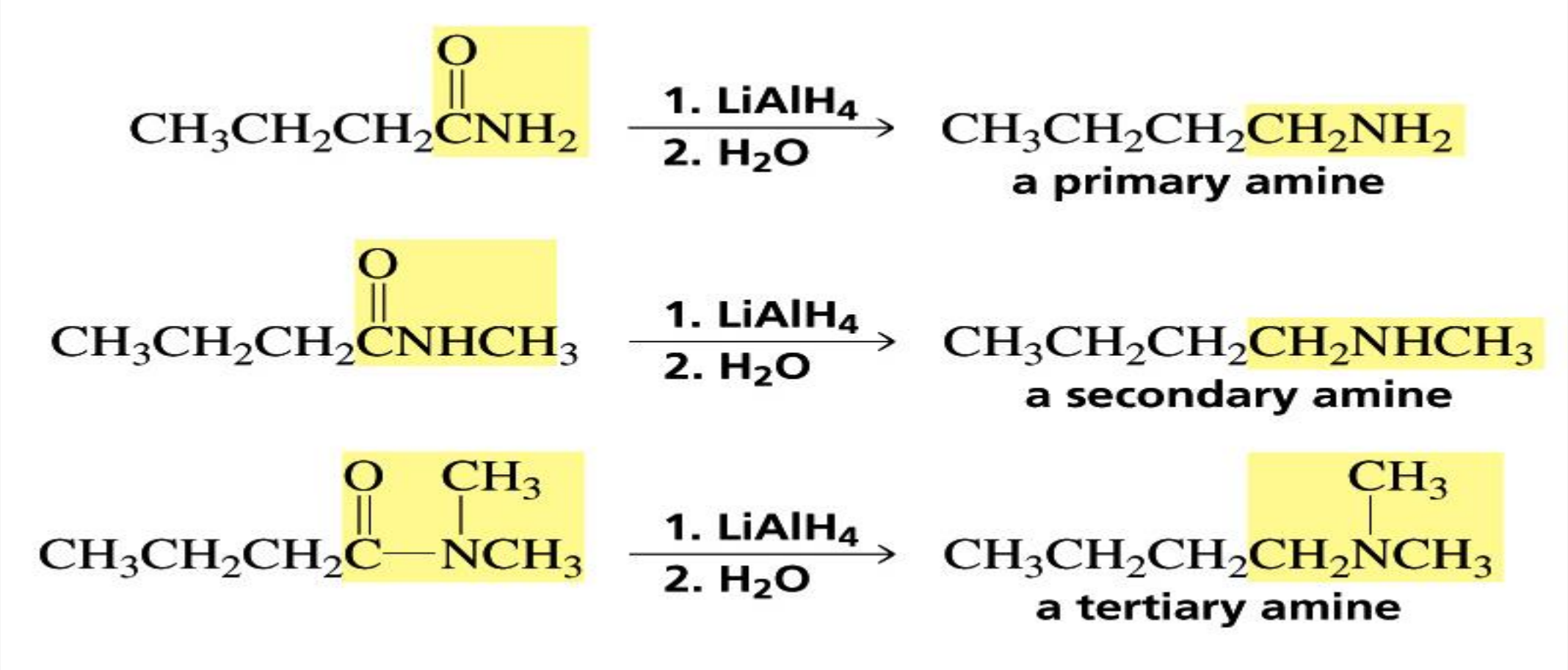
Functional group	Reduction product
RCHO	RCH_2OH
$R_2C{=}O$	RCH(OH)R
RCO_2R'	$RCH_2OH + R'OH$
RCO_2H	RCH_2OH
RCONHR′	RCH_2NHR'
$RCONR'_2$	$RCH_2NR'_2$ or $RCH(OH)NR'_2$ (→ RCHO + R'_2NH)
$RC{\equiv}N$	RCH_2NH_2 or RCH=NH (→ RCHO)
RCH=NOH	RCH_2NH_2
RNO_2	RNH_2
$ArNO_2$	ArNHNHAr or ArN=NAr
RCH_2Br	RCH_3
RCH_2OSO_2Ar	RCH_3
	

$LiAlH_4$ is a stronger reducing agent than $NaBH_4$

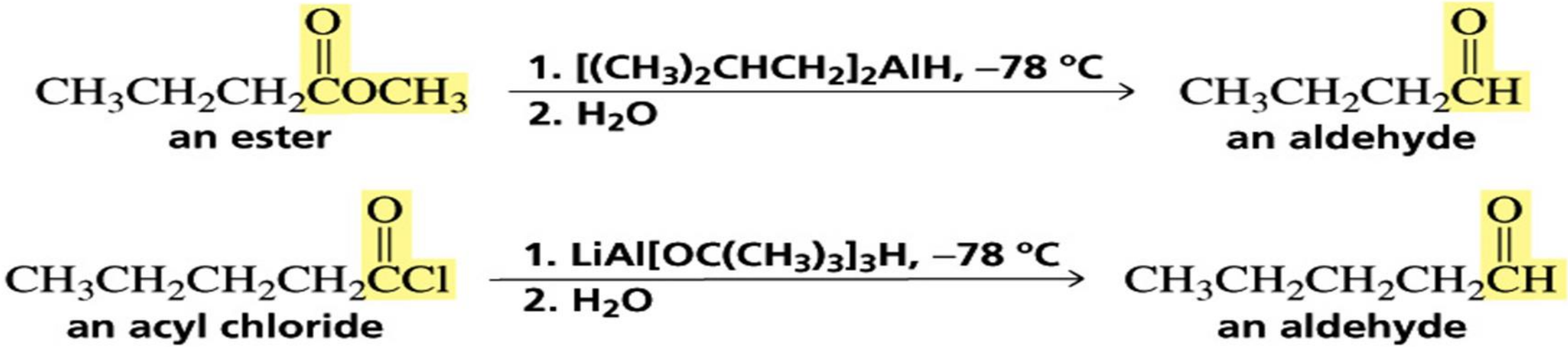
$LiAlH_4$ is used to reduce compounds that are nonreactive toward $NaBH_4$



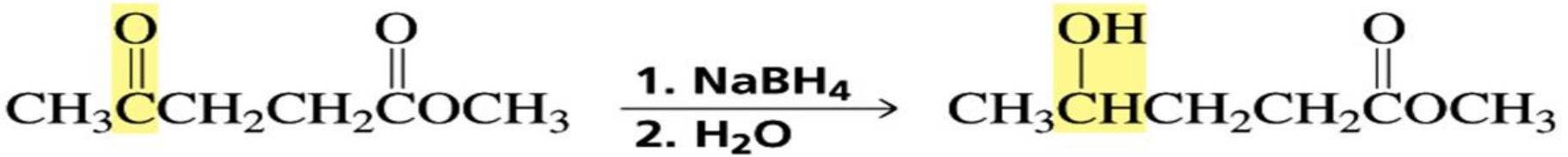
Formation of Amines by Reduction

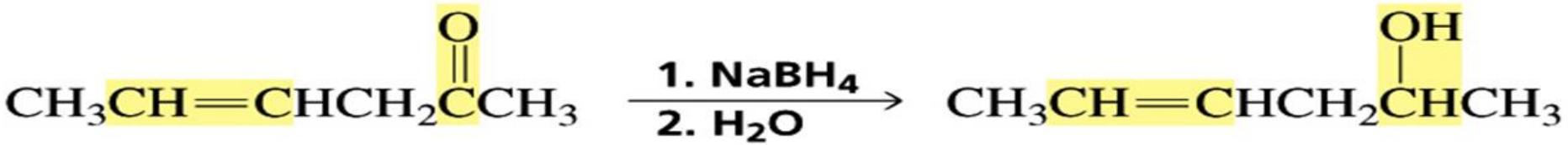


DIBAL allows the addition of one equivalent of hydride to an ester
Replacing some of hydrogens of $LiAlH_4$ with OR groups decreases the reactivity of the metal hydride



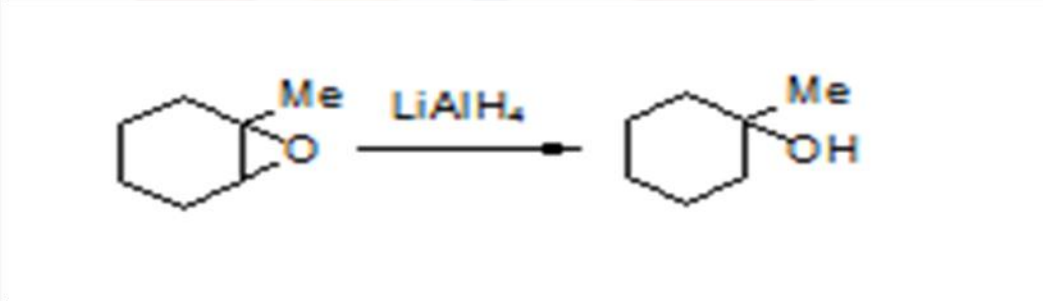
$NaBH_4$ can be used to selectively reduce an aldehyde or a keto group in a compound

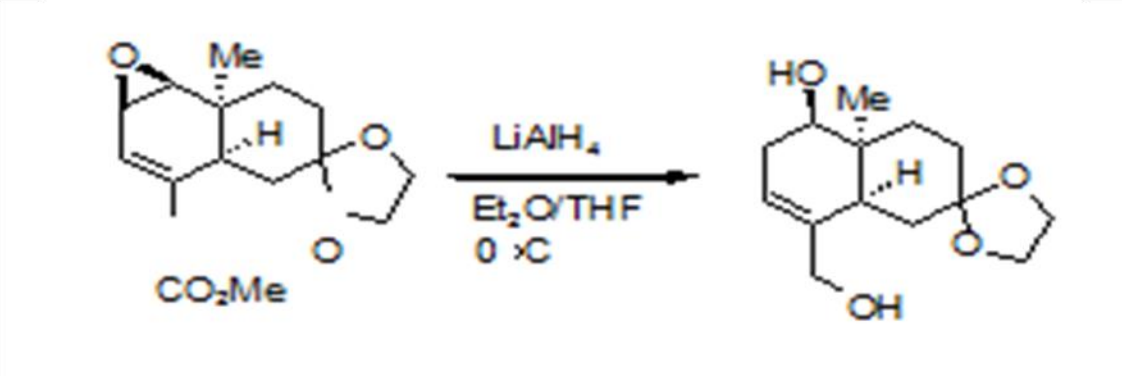




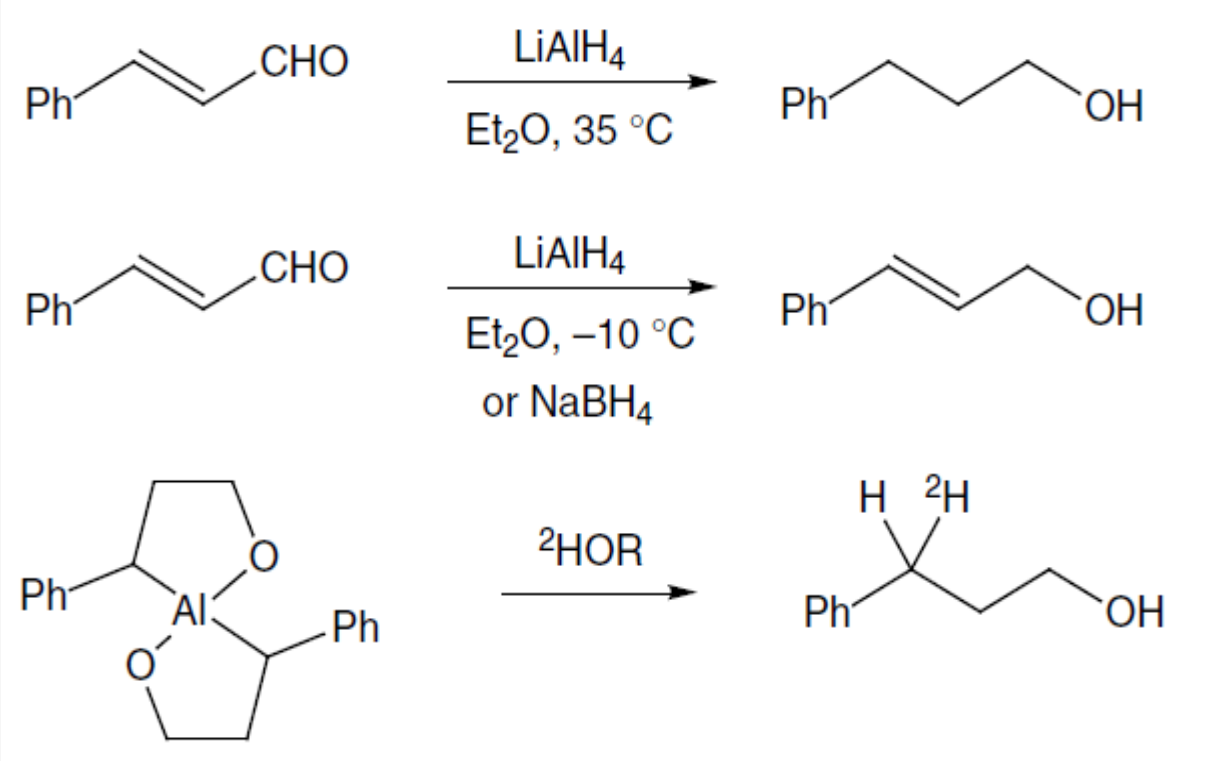
Reduction of Epoxides

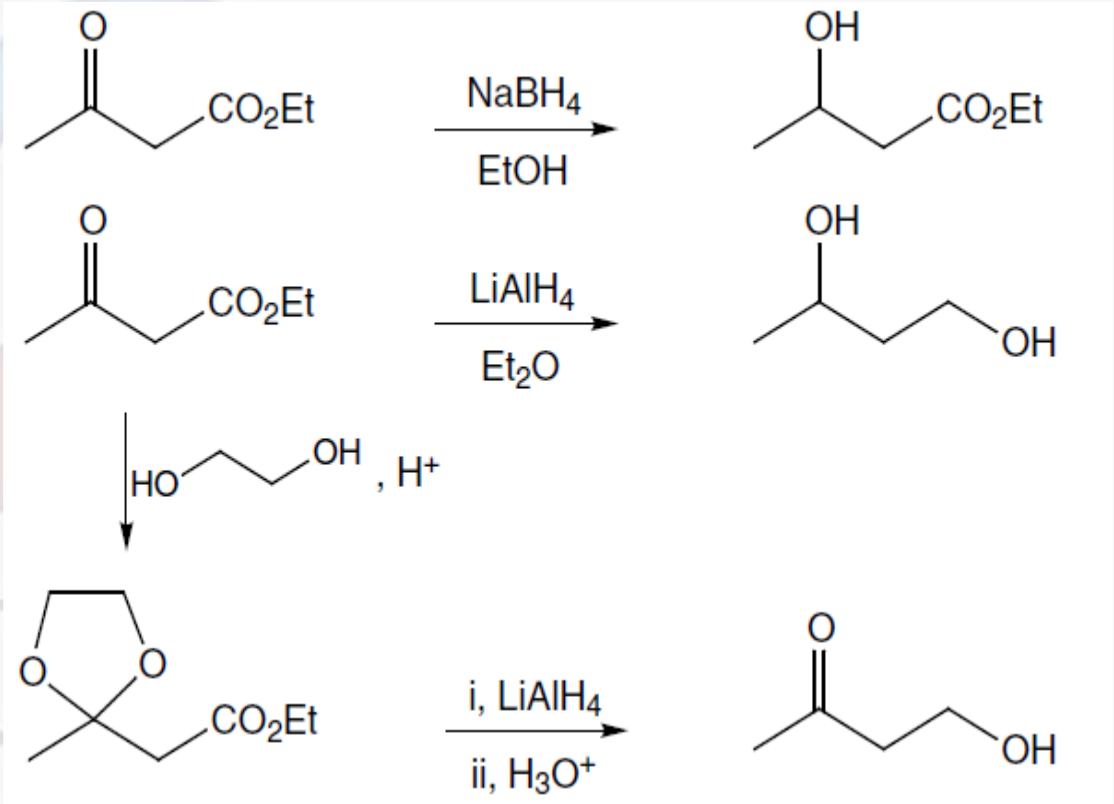
The epoxides are reduced to the corresponding alcohols . The hydride ion is transferred to the less hindered side of the epoxides.





More Examples of Reduction by LAH





References

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THANK YOU