

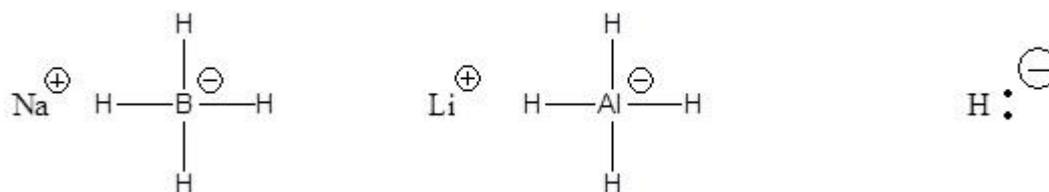
Semester – IV MJC – 6(T) Organic Chemistry

Unit – I Alcohols, Phenols, Esters and Epoxides

Preparation of alcohol by reduction of carbonyl compounds

Reduction of Aldehyde and Ketone :

The most common sources of the hydride Nucleophile are lithium aluminum hydride (LiAlH_4) and sodium borohydride (NaBH_4). Note! The hydride anion is not present during this reaction; rather, these reagents serve as a source of hydride due to the presence of a polar metal-hydrogen bond. Because aluminum is less electronegative than boron, the Al-H bond in LiAlH_4 is more polar, thereby, making LiAlH_4 a stronger reducing agent.

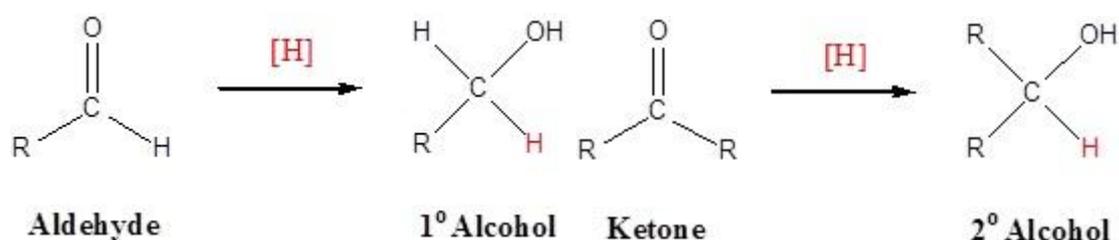


Sodium Borohydride

Lithium Aluminum Hydride

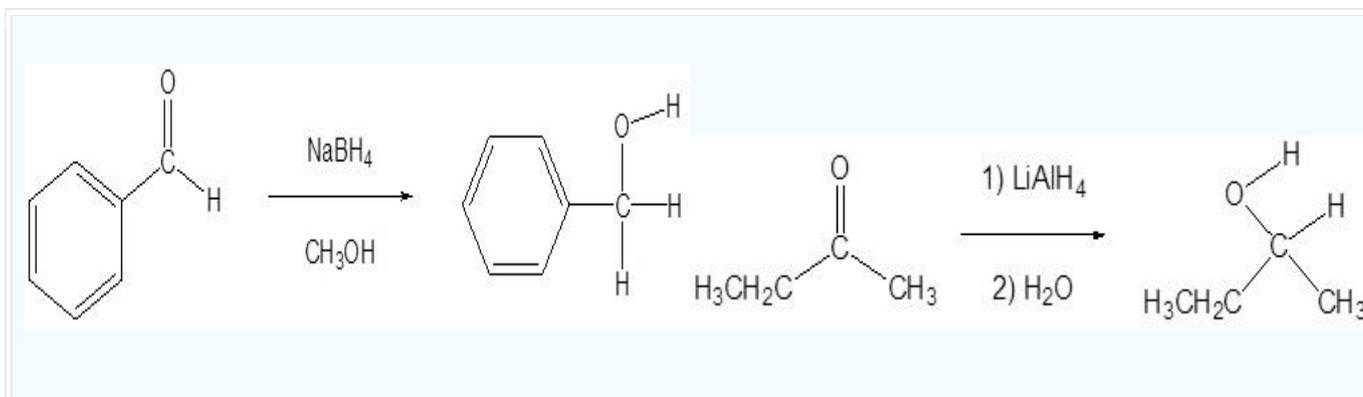
Hydride Nucleophile

Addition of a hydride anion (H^-) to an aldehyde or ketone gives an alkoxide anion, which on protonation yields the corresponding alcohol. Aldehydes produce 1° -alcohols and ketones produce 2° -alcohols.



In metal hydrides reductions the resulting alkoxide salts are insoluble and need to be hydrolyzed (with care) before the alcohol product can be isolated. In the sodium borohydride reduction the methanol solvent system achieves this hydrolysis automatically. In the lithium aluminum hydride reduction water is usually added in a second step. The lithium, sodium, boron and aluminum end up as soluble inorganic salts at the end of either reaction. Note! LiAlH_4 and NaBH_4 are both capable of reducing aldehydes and ketones to the corresponding alcohol.

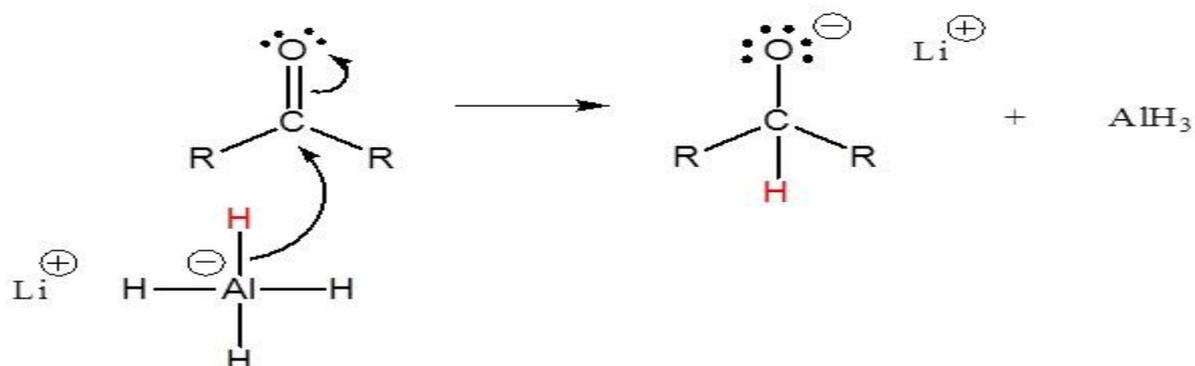
Example : 1



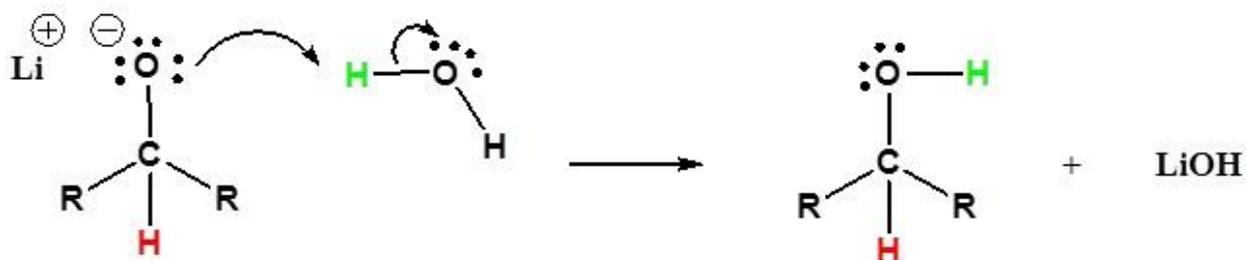
Mechanism

This mechanism is for a LiAlH_4 reduction. The mechanism for a NaBH_4 reduction is the same except methanol is the proton source used in the second step.

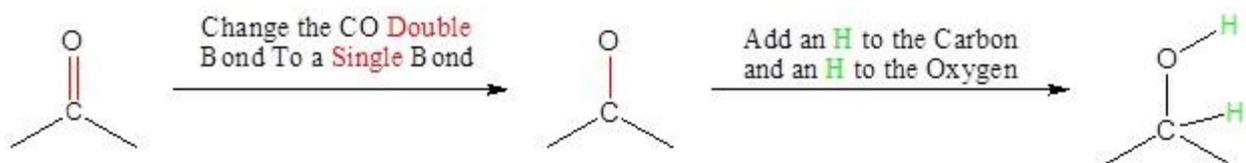
1) Nucleophilic attack by the hydride anion



2) The alkoxide is protonated



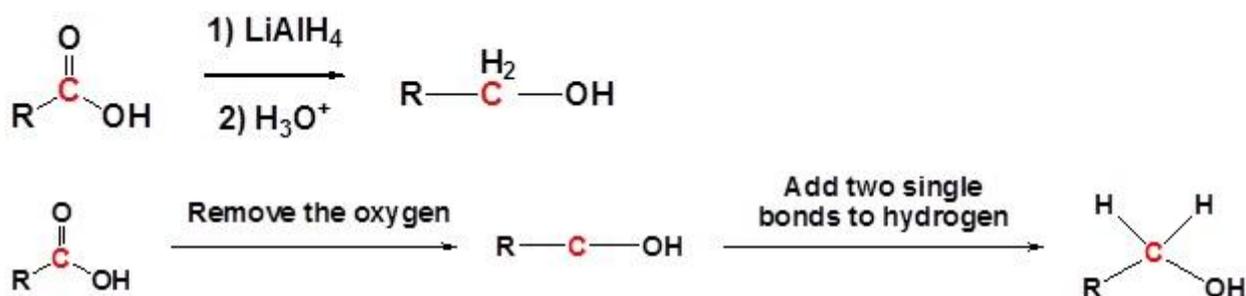
Going from Reactants to Products Simplified



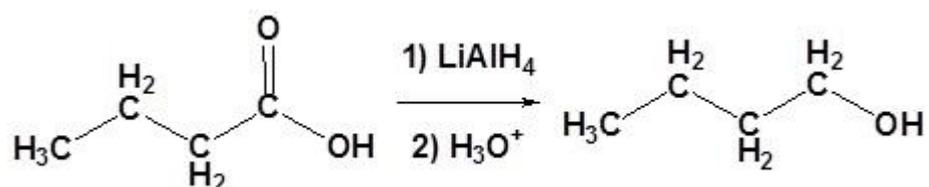
Reduction of Carboxylic acid :

Carboxylic acids can be converted to 1° alcohols using Lithium aluminum hydride (LiAlH_4). Note that NaBH_4 is not strong enough to convert carboxylic acids or esters to alcohols. An aldehyde is produced as an intermediate during this reaction, but it cannot be isolated because it is more reactive than the original carboxylic acid.

General reaction

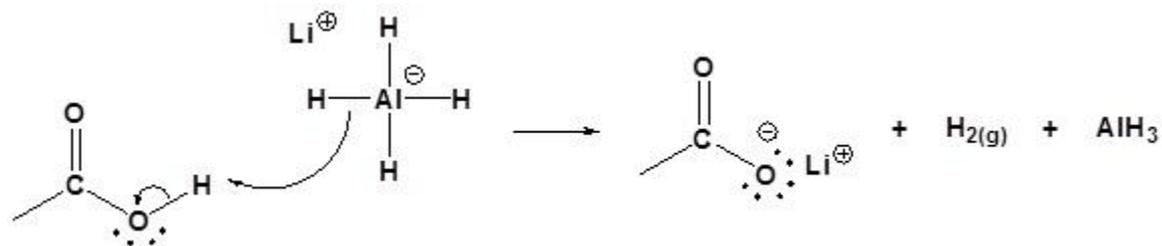


Example



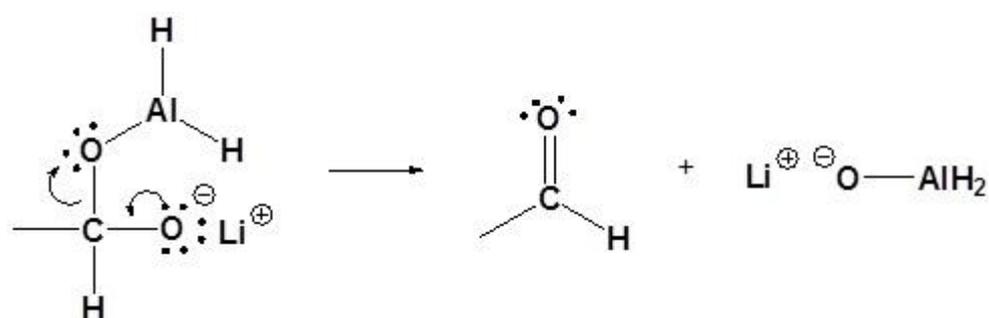
Possible Mechanism

1) Deprotonation

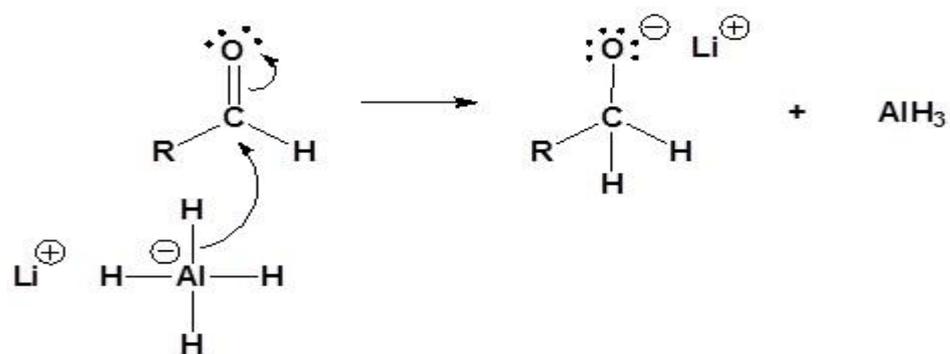


2) Nucleophilic attack by the hydride anion

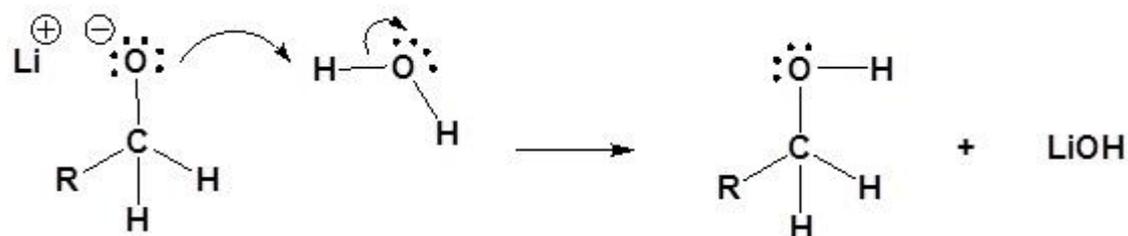
3) Leaving group removal



4) Nucleophilic attack by the hydride anion



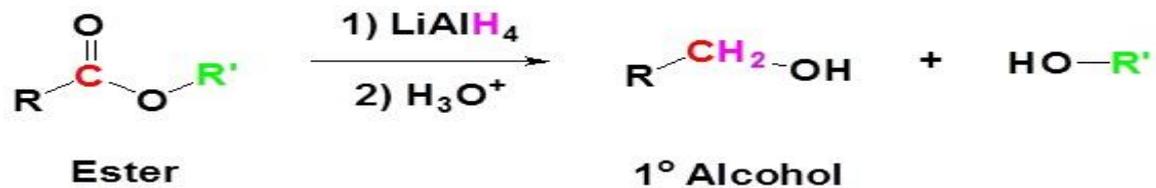
5) The alkoxide is protonated



Reduction of Esters :

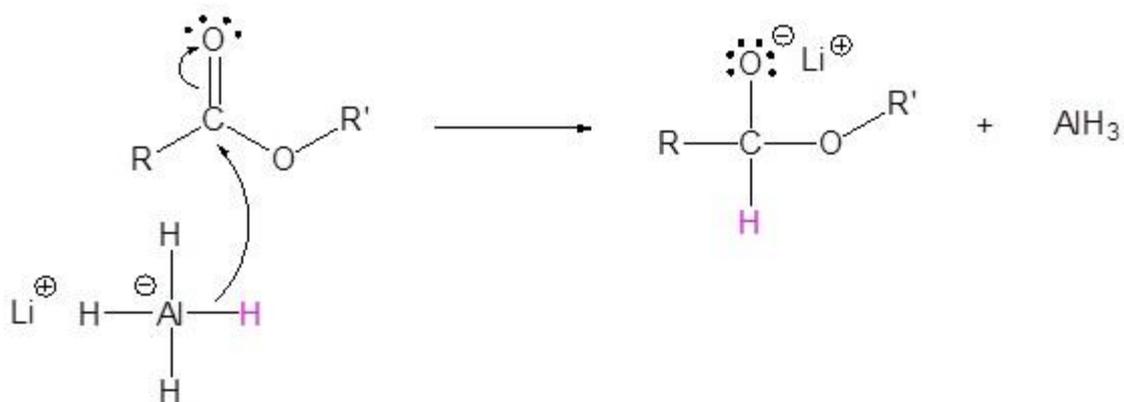
Esters can be converted to 1° alcohols using LiAlH₄, while sodium borohydride (NaBH₄) is not a strong enough reducing agent to perform this reaction.

General Reaction

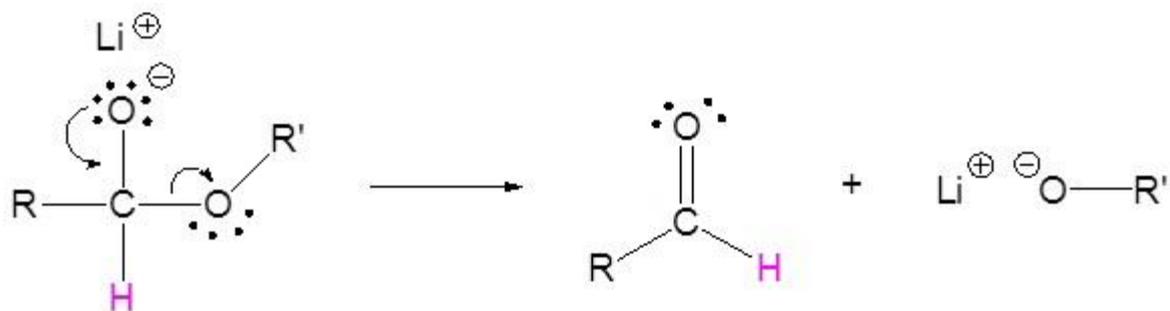


Mechanism

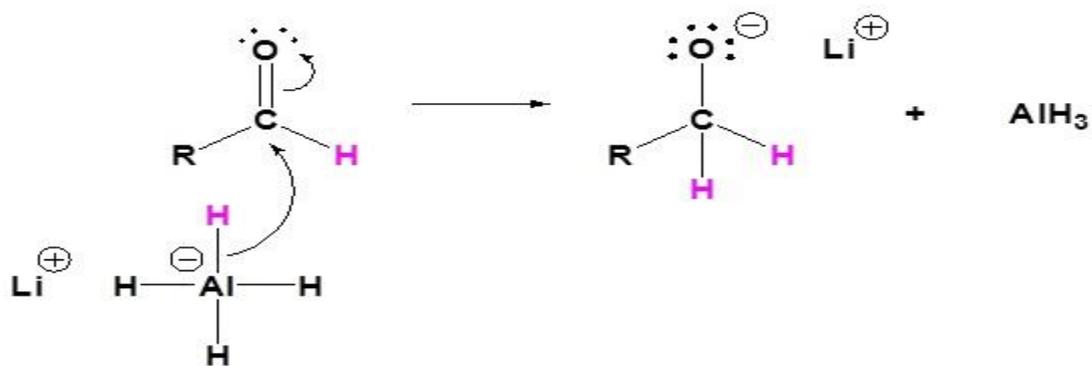
1) Nucleophilic attack by the hydride



2) Leaving group removal



3) Nucleophilic attack by the hydride anion



4) The alkoxide is protonated

