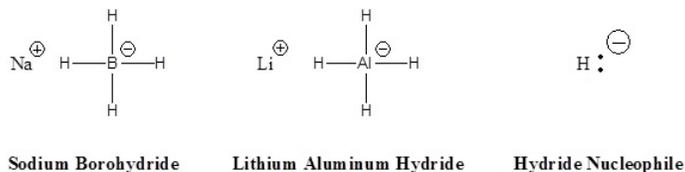
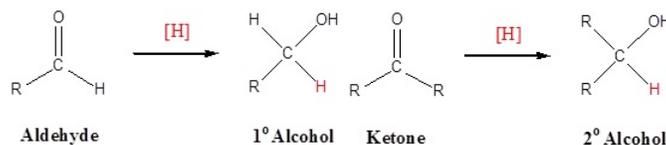


18.4: Reduction of Aldehydes and Ketones

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.

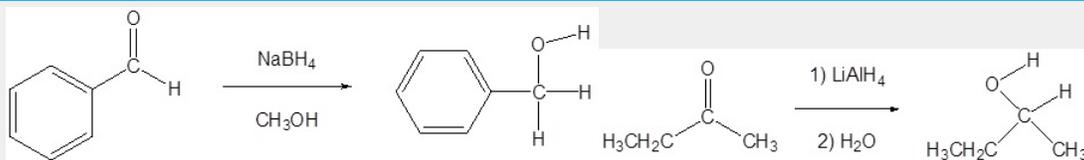


Addition of a hydride anion (H^-) to an aldehyde or ketone gives an alkoxide anion, which on protonation yields the corresponding alcohol. Aldehydes produce 1° -alcohols and ketones produce 2° -alcohols.



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.

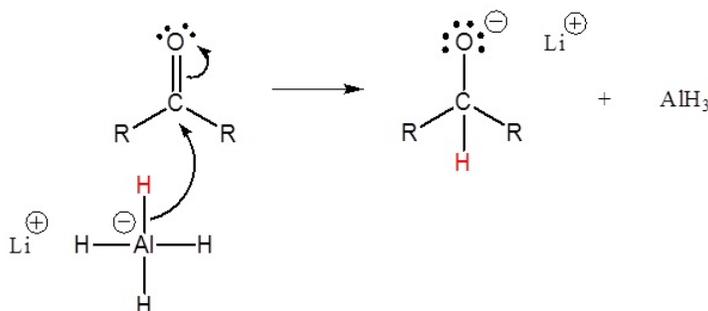
Example 1



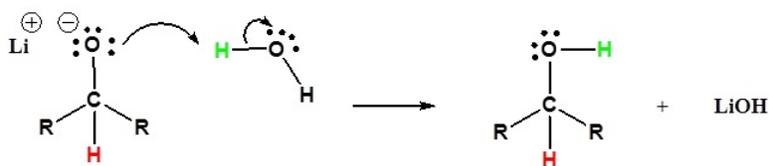
Mechanism

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.

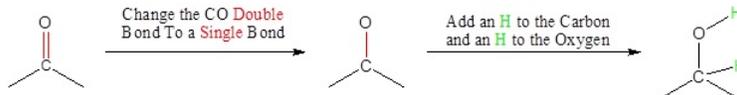
1) Nucleophilic attack by the hydride anion



2) The alkoxide is protonated



Going from Reactants to Products Simplified



Properties of Hydride Sources

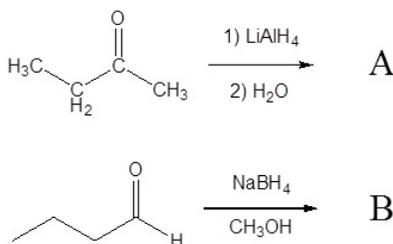
Two practical sources of hydride-like reactivity are the complex metal hydrides lithium aluminum hydride (LiAlH_4) and sodium borohydride (NaBH_4). These are both white (or near white) solids, which are prepared from lithium or sodium hydrides by reaction with aluminum or boron halides and esters. Lithium aluminum hydride is by far the most reactive of the two compounds, reacting violently with water, alcohols and other acidic groups with the evolution of hydrogen gas. The following table summarizes some important characteristics of these useful reagents.

It would be great to convert this table to text.

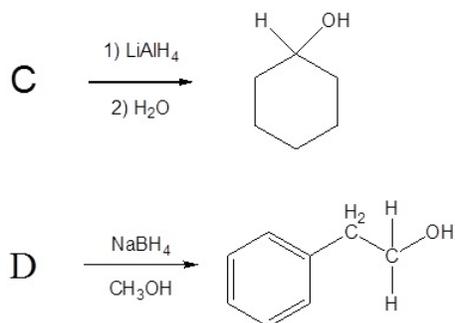
Reagent	Preferred Solvents	Functions Reduced	Reaction Work-up
Sodium Borohydride NaBH_4	ethanol; aqueous ethanol 15% NaOH ; diglyme avoid strong acids	aldehydes to 1°-alcohols ketones to 2°-alcohols inert to most other functions	1) simple neutralization 2) extraction of product
Lithium Aluminum Hydride LiAlH_4	ether; THF avoid alcohols and amines avoid halogenated compounds avoid strong acids	aldehydes to 1°-alcohols ketones to 2°-alcohols carboxylic acids to 1°-alcohols esters to alcohols epoxides to alcohols nitriles & amides to amines halides & tosylates to alkanes most functions react	1) careful addition of water 2) remove aluminum salts 3) extraction of product

Problems

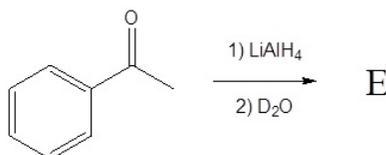
1) Please draw the products of the following reactions:



2) Please draw the structure of the molecule which must be reacted to produce the product.

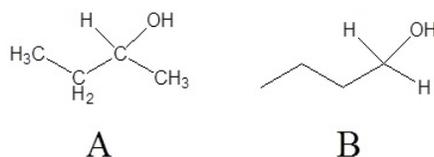


3) Deuterium oxide (D_2O) is a form of water where the hydrogens have been replaced by deuteriums. For the following LiAlH_4 reduction the water typically used has been replaced by deuterium oxide. Please draw the product of the reaction and place the deuterium in the proper location. Hint! Look at the mechanism of the reaction.

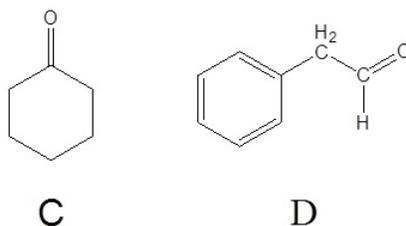


Answers

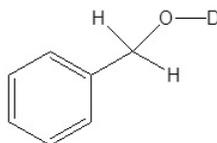
1)



2)



3)



Contributors

- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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