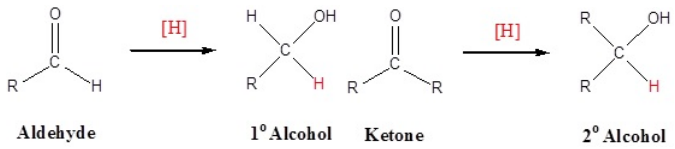
19.16: Nucleophilic Addition of H– and R——A Review

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

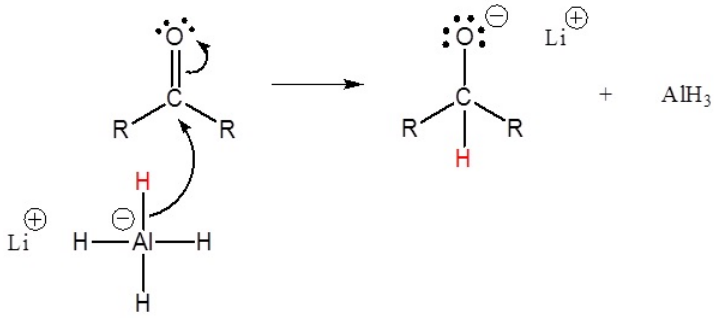


In metal hydrides reductions the resulting alkoxide salts are insoluble and need to be hydrolyzed (with care) before the alcohol product can be isolated. In the sodium borohydride reduction the methanol solvent system achieves this hydrolysis automatically. In the lithium aluminum hydride reduction water 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.

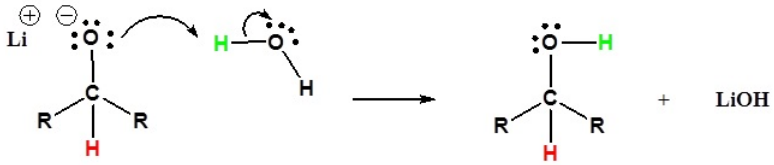
Mechanism

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) Nucleopilic attack by the hydride anion

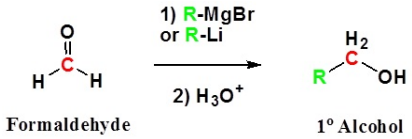


2) The alkoxide is protonated

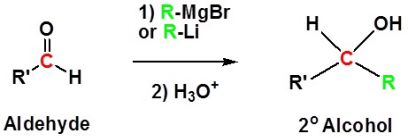


Addition of a organometallic reagent to an aldehyde or ketone gives an alkoxide anion, which on protonation yields the corresponding alcohol. Aldehydes produce 2º-alcohols and ketones produce 3º-alcohols.

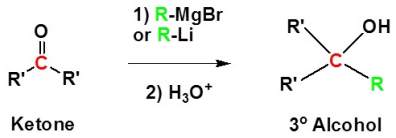
Addition to formaldehyde gives 1o alcohols



Addition to aldehydes gives 2º alcohols

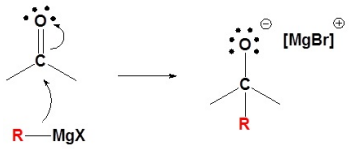


Addition to ketones gives 3^{o} alcohols

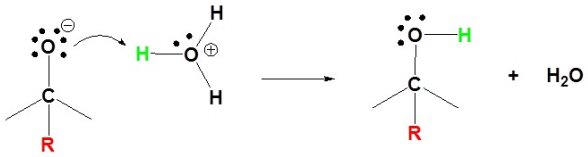


Mechanism

1) Nucleophilic attack



2) Protonation



Contributors

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