ALCOHOLS

Preparation of Alcohols- From haloalkanes
From carbonyl compounds
From carboxylic acids
From ester

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Preparation of Alcohols

1. ***By hydrolysis of haloalkanes:*** in presence of aqueous sodium or potassium hydroxide or moist silver oxide.

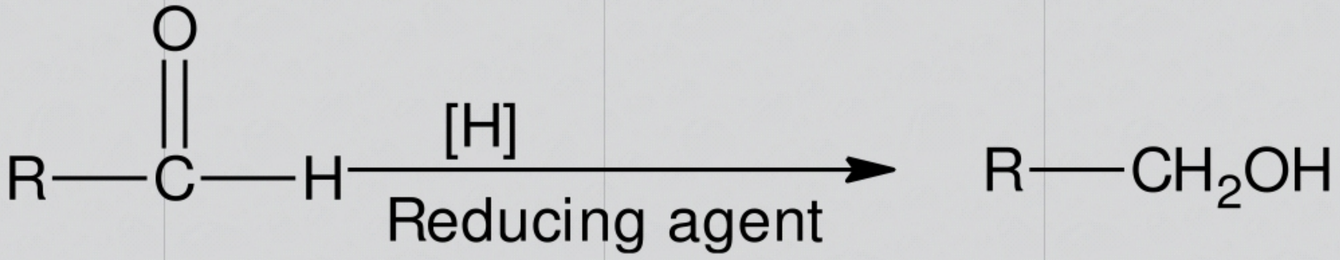
$$R - X + KOH(aq) \longrightarrow R - OH + KX$$

Reaction will follow either S_N1 or S_N2 mechanism.

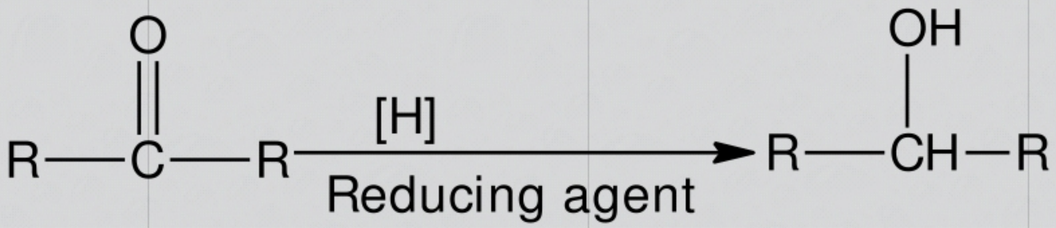
2. ***Reduction of Carbonyl Compounds***

(a) **Reduction by reducing agents**

(i) Aldehyde gives primary alcohol



(ii) Ketone gives secondary alcohol



Reducing agents

(i) $LiAlH_4$ (ii) $NaBH_4$

(iii) Na/C_2H_5OH (iv) Metal (Zn, Fe or Sn)/Acid (HCl, dil H_2SO_4 or CH_3COOH)

(v) (a) Aluminium isopropoxide/isopropylalcohol (b) H_2O

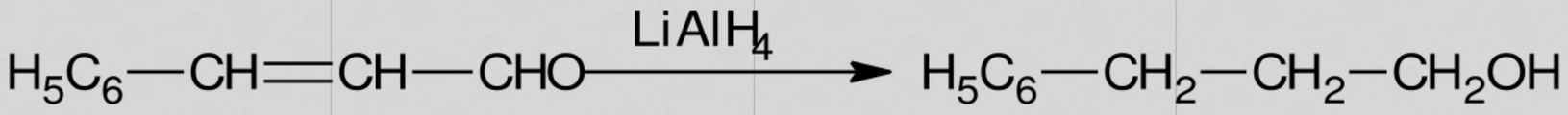
(vi) H_2/Ni

- $NaBH_4$ and aluminium isopropoxide reduces only carbonyl group and has no effect on any other group.

$$CH_3-CH=CH-CHO \xrightarrow{NaBH_4} CH_3-CH=CH-CH_2OH$$

- Reduction with aluminium isopropoxide is known as Meerwein – Ponndorf Verley (MPV) reduction.

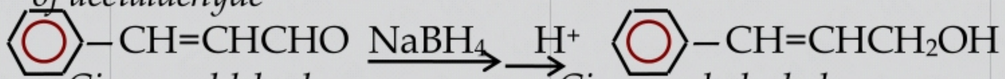
- $LiAlH_4$ has no effect on double and triple bonds but if compound is β - aryl, α, β - unsaturated carbonyl compound then double bond also undergoes reduction.



Aldehydes can be reduced to primary alcohols, and ketones to secondary alcohols, either by catalytic hydrogenation or by use of chemical reducing agents like lithium aluminum hydride, $LiAlH_4$. Such reduction is useful for the preparation of certain alcohols that are less available than the corresponding carbonyl compounds, in particular carbonyl compounds that can be obtained by the aldol condensation. For example:

$$\underset{\textit{Crotonaldehyde}}{CH_3CH{=}CHCHO} \xrightarrow{H_2,\ Ni} \underset{\textit{n-Butyl alcohol}}{CH_3CH_2CH_2CH_2OH}$$

From aldol condensation of acetaldehyde



Cinnamaldehyde — *Cinnamyl alcohol*

From aldol condensation of benzaldehyde and acetaldehyde

In the reduction process choice of reducing agent is very important most commonly used reducing agents are $LiAlH_4$ and $NaBH_4$.

Sodium borohydride, $NaBH_4$, does not reduce carbon-carbon double bonds, not even those conjugated with carbonyl groups, and is thus useful for the reduction of such unsaturated carbonyl compounds to unsaturated alcohols.

Let us look a little more closely at reduction by metal hydrides. Alcohols are formed from carbonyl compounds, smoothly and in high yield, by the action of such compounds as lithium aluminum hydride, $LiAlH_4$.

$$4R_2C{=}O + LiAlH_4 \rightarrow (R_2CHO)_4AlLi \xrightarrow{H_2O} 4R_2CHOH + LiOH + Al(OH)_3$$

Reduction of acids to alcohols

Lithium aluminum hydride, $LiAlH_4$, is one of the few reagents that can reduce an acid to an alcohol; the inital product is an alkoxide from which the alcohol is liberated by hydrolysis:

$$4RCOOH + 3LiAlH_4 \rightarrow 4RCH_2OH \quad \textbf{1}^{o}\textbf{alcohol}$$

Because of the excellent yield it gives, $LiAlH_4$ is widely used in the laboratory for the reduction of not only acids but many other classes of compounds.

- **Reduction of esters**

Like many organic compounds, esters can be reduced in two ways: *(a)* by catalytic hydrogenation using molecular hydrogen, or *(b)* chemical reduction. In either case, the ester is cleaved to yield (in addition to the alcohol or phenol from which it was derived) *a primary alcohol corresponding to the acid portion of the ester.*

$$\underset{\textit{Ester}}{RCOOR'} \xrightarrow{\text{reduction}} \underset{1^o\ \textit{alcohol}}{RCH_2OH} + R'OH$$

Hydrogenolysis (cleavage by hydrogen) of an ester requires more severe conditions than simple hydrogenation of (addition of hydrogen to) a carbon-carbon double bond. High pressures and elevated temperatures are required: the catalyst used most often is a mixture of oxides known as copper chromite, of approximately the composition $CuO.CuCr_2O_4$. For example:

$$\underset{\textit{(Methyl dodecanoate)}}{CH_3(CH_2)_{10}COOCH_3} \xrightarrow[150^o,\ 5000\ lb/in.^2]{H_2,CuO.CuCr_2O_4} \underset{\textit{(1-Dodecanol)}}{CH_3(CH_2)_{10}CH_2OH} + CH_3OH$$

Chemical reduction is carried out by use of sodium metal and alcohol, or more usually by use of lithium aluminium hydride. *For example:*

$CH_3(CH_2)_{14}COOC_2H_5 \xrightarrow{LiAlH_4} CH_3(CH_2)_{14}CH_2OH$

(Ethyl hexadecanoate) *1-Hexadecanol*