Chapter 12  Alcohols From Carbonyl Compounds. Oxidation-Reduction and Organometallic Compounds
12.1 Introduction
Carbonyl compounds are a broad group of compounds that includes aldehydes, ketones, carboxylic acids, and esters.
12.1A Structure of the Carbonyl Group

The carbonyl group is characterized by a sp² hybridization around the carbon atom. The double bond nature is evident from the 120° bond angles, indicative of a planar geometry.

Resonance structures for the carbonyl group:

- Formaldehyde ($\text{H}_2\text{C}=\text{O}$) with a dipole moment ($\mu = 2.27 \text{ D}$)
- Acetone ($\text{H}_3\text{C}=\text{O}$) with a dipole moment ($\mu = 2.88 \text{ D}$)
12.1B Reactions of Carbonyl Compounds with Nucleophiles

From a synthetic view, one of the most important reactions of carbonyl compounds is one in which the compound undergoes nucleophilic addition.

Two important nucleophiles:
- Hydride ions ($H^-$) from NaBH$_4$ or LiAlH$_4$
- Carbanions ($RCH_2^-$) from RLi or RMgX
Another related set of reactions are reactions in which alcohols and carbonyl compounds are oxidized and reduced.
12.2 Oxidation-Reduction Reactions in Organic Chemistry
Reduction

**Reduction of an organic molecules usually corresponds to increasing its hydrogen content or to decreasing its oxygen content.**

**Oxygen content decreases**

\[
\text{Carboxylic acid} \xrightarrow{[H]} \text{Aldehyde}
\]

\[
\begin{align*}
&\text{R} - \text{C} - \text{OH} \\
\rightarrow &\text{R} - \text{C} - \text{H}
\end{align*}
\]
Hydrogen content increases

\[
\begin{align*}
\text{O} & \quad \text{R} \quad \text{C} \quad \text{H} \\
\text{Aldehyde} & \quad \xrightarrow{[\text{H}] \text{ reduction}} \\
& \quad \text{R} \quad \text{CH}_2 \quad \text{OH} \quad \text{Alcohol}
\end{align*}
\]

Oxygen content decreases

\[
\begin{align*}
\text{R} \quad \text{CH}_2 \quad \text{OH} & \quad \xrightarrow{[\text{H}] \text{ reduction}} \\
\text{Alcohol} & \quad \text{R} \quad \text{CH}_3 \\
& \quad \text{Alkane}
\end{align*}
\]
Oxidation

- Increasing the oxygen content of an organic molecule or decreasing its hydrogen content is an oxidation.

\[
\begin{align*}
R-\text{CH}_3 & \quad \overset{[\text{O}]}{\underset{[\text{H}]}{\rightleftharpoons}} \quad R-\text{CH}_2\text{OH} \\
\text{Lowest oxidation state} & \\
R-\text{C-H} & \quad \overset{[\text{O}]}{\underset{[\text{H}]}{\rightleftharpoons}} \quad R-\text{C-OH} \\
\text{Highest oxidation state}
\end{align*}
\]
Oxidation of an organic compound may be broadly defined as a reaction that increases its content of any element more electronegative than carbon.
12.3 Alcohols by Reduction of Carbonyl Compounds
Primary and secondary alcohols can be synthesized by the reduction of a variety of compounds that contain the carbonyl group.

\[
\begin{align*}
\text{Aldehyde} & \quad \text{Carboxylic acid} \\
\text{R} & \quad \text{R} \\
\text{R} & \quad \text{R} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{OH} \\
\text{O} & \\
\text{Ester} & \quad \text{1°Alcohol} \\
\begin{align*}
\text{[H]} & \\
\text{R} & \quad \text{R} \\
\text{C} & \quad \text{C} \\
\text{R} & \quad \text{R} \\
\text{OH} & \quad \text{2°Alcohol} \\
\end{align*}
\end{align*}
\]
Reductions of carboxylic acids are most difficult, but can be accomplished with the powerful reducing agent lithium aluminum hydride (LiAlH₄)

\[
\text{R} \left( \overset{\text{O}}{\text{C}} \overset{\text{H}}{\text{C}} \right) \underset{\text{OH}}{\text{OH}} + 3 \text{LiAlH}_4 \xrightarrow{\text{Et}_2\text{O}} \ [\text{(RCH}_2\text{O)}_4\text{Al}]\text{Li} + 4 \text{H}_2 + 2 \text{LiAlO}_2
\]

Lithium aluminum hydride

\[
\begin{align*}
\text{H}_2\text{O} / \text{H}_2\text{SO}_4 \\
4 \text{RCH}_2\text{OH} + \text{Al}_2(\text{SO}_4)_3 + \text{Li}_2\text{SO}_4
\end{align*}
\]

(1) LiAlH₄/Et₂O
(2) H₂O/H₂SO₄

(\text{CH}_3)_3\text{C} - \text{CO}_2\text{H} \xrightarrow{\text{1 LiAlH}_4/\text{Et}_2\text{O}} (\text{CH}_3)_3\text{C} - \text{CH}_2\text{OH} \\
\text{2,2-Dimethylpropanoic acid} \xrightarrow{\text{2 H}_2\text{O}/\text{H}_2\text{SO}_4} \text{2,2-Dimethyl-1-propanol (Neopentyl alcohol)} \\
(92\%)
Esters can be reduced by high-pressure hydrogenation (hydrogenolysis) or through the use of lithium aluminum hydride.

\[ R'OH + RCH_2OH \rightarrow R'OH + RCH_2OH \]

(1) LiAlH₄/Et₂O

(2) H₂O/H₂SO₄

\[ \text{H}_2, \text{CuO-CuCr}_2\text{O}_4, 175\degree \text{C}, 5000 \text{ psi} \]
Aldehydes and ketones can also be reduced to alcohols.

\[
R\overset{O}{\text{C}}\overset{\text{H}}{\text{H}} \quad [\text{H}] \quad \text{[Reduction]} \quad R\overset{\text{CH}_2\text{OH}}{\text{C}}\overset{\text{O}}{\text{H}}
\]

Reducing agents:
- \(H_2/Pd, Pt, Ni\) …
- \(Na/EtOH\)
- \(LiAlH_4\)
- \(NaBH_4\)

Hydride transfer

Alkoxide ion

Alcohol
Reduced by LiAlH₄

\[
\begin{align*}
\text{O} & \quad \text{R} - \text{C} - \text{OH} < \quad \text{R} - \text{C} - \text{OR}' < \quad \text{R} - \text{C} - \text{R}' < \quad \text{R} - \text{C} - \text{H}
\end{align*}
\]

Reduced by NaBH₄

Ease of reduction

Sodium borohydride is a less powerful reducing agent than lithium aluminum hydride.