Reductions of carboxylic acid derivatives might be expected to lead either to aldehydes or alcohols, functional groups having a lower oxidation state of the carboxyl carbon. Indeed, carboxylic acids themselves are reduced to alcohols by lithium aluminum hydride. At this point it will be useful to consider three kinds of reductions:

i. catalytic hydrogenation
ii. complex metal hydride reductions
iii. diborane reduction.

---

**Catalytic Hydrogenation**

As a rule, the carbonyl group does not add hydrogen as readily as do the carbon-carbon double and triple bonds. Thus, it is fairly easy to reduce an alkene or alkyne function without affecting any carbonyl functions in the same molecule. By using a platinum catalyst and increased temperature and pressure, it is possible to reduce aldehydes and ketones to alcohols, but carboxylic acids, esters and amides are comparatively unreactive. The exceptional reactivity of acyl halides, on the other hand, facilitates their reduction under mild conditions, by using a poisoned palladium catalyst similar to that used for the partial reduction of alkynes to alkenes. This reduction stops at the aldehyde stage, providing us with a useful two-step procedure for converting carboxylic acids to aldehydes, as reaction #1 below demonstrates. Equivalent reductions of anhydrides have not been reported, but we might speculate that they would be reduced more easily than esters. The only other reduction of a carboxylic acid derivative that is widely used is that of nitriles to 1º-amines. Examples of these reductions are provided in the following diagram.

1. \[
\begin{align*}
\text{C}_6\text{H}_5\text{CO} & \xrightarrow{\text{H}_2, \text{Pt}-\text{BaSO}_4, \text{C}_6\text{H}_5\text{CN}} \text{C}_6\text{H}_5\text{CH}_2\text{CO} + \text{HCl} \\
\text{C}_6\text{H}_5\text{CO} & \xrightarrow{\text{H}_2, \text{Pt}-\text{BaSO}_4, \text{C}_6\text{H}_5\text{CN}} \text{C}_6\text{H}_5\text{CH}_2\text{CO} + \text{HCl}
\end{align*}
\]

2. \[
\begin{align*}
\text{C}_6\text{H}_5\text{CO} & \xrightarrow{\text{H}_2, \text{Pd}-\text{BaSO}_4, \text{C}_6\text{H}_5\text{CN}} \text{C}_6\text{H}_5\text{CH}_2\text{CO} + 2\text{C}_6\text{H}_5\text{NH}_2
\end{align*}
\]

3. \[
\begin{align*}
\text{C}_6\text{H}_5\text{CO} & \xrightarrow{\text{H}_2, \text{Ni}-\text{BaSO}_4, \text{C}_6\text{H}_5\text{CN}} \text{C}_6\text{H}_5\text{CH}_2\text{CO} + 2\text{C}_6\text{H}_5\text{NH}_2
\end{align*}
\]

4. \[
\begin{align*}
\text{C}_6\text{H}_5\text{CO} & \xrightarrow{\text{H}_2, \text{Pt}-\text{BaSO}_4, \text{C}_6\text{H}_5\text{CN}} \text{C}_6\text{H}_5\text{CH}_2\text{CO} + \text{HCl}
\end{align*}
\]

The second and third equations illustrate the extreme difference in hydrogenation reactivity between esters and nitriles. This is further demonstrated by the last reaction, in which a nitrile is preferentially reduced in the presence of a carbonyl
group and two benzene rings. The resulting 1º-amine immediately reacts with the carbonyl function to give a cyclic enamine product (colored light blue).

In most nitrile reductions ammonia is added to inhibit the formation of a 2º-amine by-product. This may occur by way of an intermediate aldehyde imine created by addition of the first equivalent of hydrogen. The following equations show how such an imine species might react with the 1º-amine product to give a substituted imine (2nd equation), which would then add hydrogen to generate a 2º-amine. Excess ammonia shifts the imine equilibrium to the left, as written below.

1. \( \text{R–C≡N} + \text{H}_2 \xrightarrow{\text{catalyst}} \text{RCH}=\text{NH} \xrightarrow{\text{H}_2} \text{RCH}_2\text{NH}_2 \) (1º-amine)

2. \( \text{RCH}=\text{NH} + \text{RCH}_2\text{NH}_2 \xrightarrow{\text{H}_2 & \text{catalyst}} \text{RCH}=\text{NCH}_2\text{R} + \text{NH}_3 \xrightarrow{\text{H}_2 & \text{catalyst}} \text{RCH}_2\text{NHCH}_2\text{R} \) (2º-amine)

Contributors