The carbon atom of a carboxyl group has a high oxidation state. It is not surprising, therefore, that many of the chemical reactions used for their preparation are oxidations. Such reactions have been discussed in previous sections of this text, and the following diagram summarizes most of these:

1. Oxidation of Arené Side-Chains

\[ \text{H}_3\text{C} \quad \text{C}_\text{H}_2 \quad \text{C}_\text{H}_3 \quad \xrightarrow{\text{KMnO}_4, \text{H}_2\text{O}, \text{H}^+} \quad \text{H}_2\text{O}_2 \quad \text{C}_\text{H}_2 \quad \text{C}_\text{O}_2 \text{H} \]

2. Oxidation of 1° Alcohols

\[ \text{H}_3\text{C} \quad \text{C}_\text{H}_3 \quad \text{H}_2\text{O} \quad \xrightarrow{\text{Jones' Reagent (H}_2\text{CrO}_4)} \quad \text{H}_3\text{C} \quad \text{C}_\text{C}_\text{C} \quad \text{OH} \]

3. Oxidation of Aldehydes

\[ \text{O} \quad \text{C} \quad \text{H} \quad \xrightarrow{\text{Tollens' Reagent (Ag}^+ \text{ in NH}_3\text{OH)} \quad \text{O} \quad \text{C} \quad \text{H}_2\text{OH} \]

4. Oxidative Cleavage of Alkenes and Alkynes

\[ \text{R} \quad \text{C} = \text{C} \quad \xrightarrow{\text{KMnO}_4, \text{H}_2\text{O}, \text{H}^+} \quad 2 \text{R} \quad \text{C} \quad \text{OH} \]

In the second procedure the electrophilic halide is first transformed into a strongly nucleophilic metal derivative, and this adds to carbon dioxide (an electrophile). The initial product is a salt of the carboxylic acid, which must then be released by treatment with strong aqueous acid.

Hydrolysis of Nitriles

\[ \text{R} = \text{CH}_2\text{Br} \quad \xrightarrow{\text{NaOH}} \quad \text{R} = \text{CH}_2\text{CN} \quad \xrightarrow{\text{H}_2\text{O}, \text{H}^+} \quad \text{R} = \text{CH}_2\text{CO}_2\text{H} \]

Carboxylation of Organometallic Reagents

\[ \text{R} = \text{Sr} \quad \xrightarrow{\text{K}_2 \text{CO}_3} \quad \text{R} = \text{SrCO}_3 \quad \xrightarrow{\text{H}_2\text{O}_2} \quad \text{R} = \text{CO}_2\text{H} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{Sr} \quad \text{OH} \]

An existing carboxylic acid may be elongated by one methylene group, using a homologation procedure called the Arndt-
Eistert reaction.

Contributors