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 Arene Side-Chains**

```
        H3C\-C=CH2
        CH2CH2CH3

        KMnO4
        H2O, Heat

        H2C\=CH2
        CO2H
        CO2H
```

2. **Oxidation of 1° Alcohols**

```
        H3C\-C\-H
        H3C\-C\-H

        Jones' Reagent
        (H2CrO4)

        H3C\-C\-C\-H
        H3C\-C\-H
```

3. **Oxidation of Aldehydes**

```
        O
        \=O

        Tollens' Reagent
        (Ag+ in NH4OH)

        OH
```

4. **Oxidative Cleavage of Alkenes and Alkynes**

```
        C\=C\-CH2-CH=CH2
        NC

        KMnO4
        H2O, Heat

        2 \=C\-CH3
        NC
```

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**

```
        R-CH2-CN
        NaOH, H2O

        R-CHO + HCN
```

**Carboxylation of Organometallic Reagents**

```
        R-SnR3
        (or R-Cl or R-Br)

        KO2
        (t-BuOK or other)

        R-CHO + H2O
```

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

Contributors