3. Carbonation of a Grignard reagent (Section 17.5) Adding  $CO_2$  to a Grignard reagent followed by acidification provides a useful route to carboxylic acids.

Cyclopentanecarboxylic acid

R



**6. Fischer Esterification (Section 17.7A)** An ester can be prepared by treating a carboxylic acid with an alcohol in the presence of an acid catalyst.

$$OH + HO \longrightarrow H_2SO_4 \longrightarrow O \longrightarrow + H_2CO$$

Fischer esterification is reversible. To achieve high yields of ester, it is necessary to force the equilibrium to the right. One way to accomplish this is to use an excess of alcohol; another is to remove water by azeotropic distillation using a Dean-Stark trap.

8. Conversion to Acid Halides (Section 17.8) Acid chlorides, the most common and widely used of the acid halides, are prepared by treating a carboxylic acid with thionyl chloride. The mechanism, similar to that of the conversion of alcohols to chloroalkanes, involves initial chlorosulfite formation, followed by nucleophilic attack of chloride ion on the carbonyl carbon to give a tetrahedral carbonyl addition intermediate, which decomposes to give the acid chloride, SO<sub>2</sub>, and chloride ion.

$$OH + SOCl_2 \xrightarrow{\text{ether}} Cl + SO_2 + HCl$$

g. Decarboxylation of  $\beta$ -Ketoacids (Section 17.9A)  $\beta$ -Ketoacids decarboxylate upon heating. The mechanism involves redistribution of electrons in a six-membered transition state to give  $CO_2$  and the enol of a ketone, which tautomerizes to give a ketone. The reaction is facilitated by a hydrogen bond between the carboxyl hydrogen atom and  $\beta$ -carbonyl oxygen.