Carboxylic Acids 2 - Synthesis and Reactions

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Synthesis of Carboxylic Acids

Carboxylic acids can be synthesized in many different ways from various functional groups.

1) Oxidation of Alkenes

2) Oxidation of Alkynes

3) Oxidation of Primary Alcohols

$$\frac{\text{KMnO}_4}{\text{OH}}$$

Synthesis of Carboxylic Acids – contd...

4) Oxidation of Alkylbenzenes

5) Oxidation of Aldehydes

6) <u>Hydrolysis of Cyanohydrins and Other Nitriles</u> – note that one carbon is added in this reaction.

Synthesis of Carboxylic Acids - contd...

7) <u>Carbonation of Grignard Reagent</u>. Note that one carbon is added during this reaction.

$$\frac{\text{Mg}}{\text{Br}} \xrightarrow{\text{Mg}} \frac{1) \text{CO}_2}{2) \text{H}_3 \text{O}^+}$$

$$\frac{\text{Br}_2}{\text{FeBr}_3} \xrightarrow{\text{Mg}} \frac{1) \text{CO}_2}{2) \text{H}_3 \text{O}^+}$$

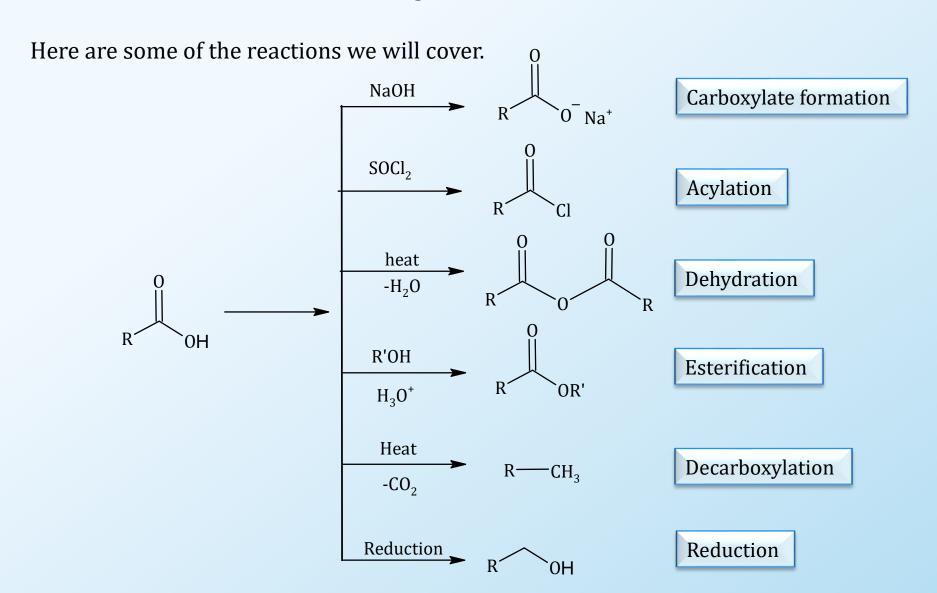
You will note that in all these syntheses, the common theme was oxidation. Carboxylic acids are the highest oxidized of all the functional groups and for most of the syntheses a strong oxidizing agent, KMnO₄, is used.

A simple and common reaction of acid is the acid – base reaction to form salts.

Most of the other reactions are nucleophilic addition reactions just like all carbonyls. In some conditions carboxylic acids can also undergo nucleophilic substitution where – OH is the leaving group. This is in the acylation and esterification reactions.

A number of reactions involve converting the carboxylic acid into other derivatives.

And finally, decarboxylation can be done to remove the carboxyl group.



1) **Neutralization**: Reaction with a base will give a carboxylate.

$$CH_3COOH + NaOH \longrightarrow CH_3COO^+Na^- + H_2O$$

2) <u>Acid chlorides</u> are prepared by treating a carboxylic acid with thionyl chloride, SOCl₂ or PCl₃ or PCl₃.

3) <u>Dehydration</u>: Anhydrides can be prepared by heating a carboxylic acid enough to dehydrate it. The heat needed is very high so only acetic acid and diacids can be dehydrated. Two molecules of acids are needed to form an anhydride. The diacids will give a cyclic anhydride.

4) **Esterification**: Esters can be prepared by treating a carboxylic acid with an alcohol in the presence of an acid catalyst, commonly H₂SO₄ or gaseous HCl. (Mechanism will be covered later.)

$$H_{3}0^{+}$$
 OH $H_{2}0$ $H_{3}0^{+}$ $H_{2}0$

5) **<u>Decarboxylation</u>**: loss of CO₂ from a carboxyl group. Most carboxylic acids, if heated to a very high temperature, undergo thermal decarboxylation.

6) Reduction: Lithium aluminum hydride reduces a carboxyl group to a 1° alcohol. A better way to carry out reduction is by converting acid to acyl chloride first. Another good reagent to use is borane, BH₃. This is specially good if there are other functional groups that can be reduced by LAH. Acids can be reduced to aldehydes using diisobutyllithium hydride (DIBAL)

Key Concepts

- Synthesis
 - Oxidations
 - Hydrolysis of nitriles
 - Carboxylation using Grignard
- Reactions
 - Acid base reactions
 - Carboxylic acid interconversion to other derivatives.
 - Reductions
 - Esterification