carboxylic acids and carboxylic acid derivatives are attached to weaker bases than are the acyl groups of aldehydes and ketones. (Remember that the lower the pK_a , the stronger the acid and the weaker its conjugate base.) The hydrogen of an aldehyde and the alkyl group of a ketone are too basic to be replaced by another group.

This chapter discusses the reactions of carboxylic acids and carboxylic acid derivatives. We will see that these compounds undergo substitution reactions because they have an acyl group attached to a group that can be replaced by a nucleophile. The reactions of aldehydes and ketones are discussed in Chapter 16, where we will see that these compounds do not undergo substitution reactions because their acyl group is attached to a group that cannot be replaced by a nucleophile.

THE NOMENCLATURE OF CARBOXYLIC ACIDS AND CARBOXYLIC ACID DERIVATIVES

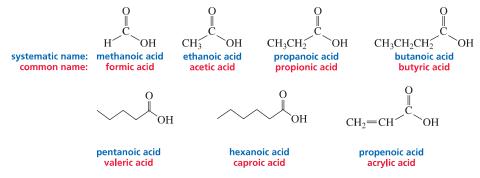
Let's start by looking at how carboxylic acids are named, because their names form the basis of the names of the other carbonyl compounds.

Naming Carboxylic Acids

The functional group of a carboxylic acid is called a **carboxyl group**.

LEARN THE STRATEGY

In systematic (IUPAC) nomenclature, a carboxylic acid is named by replacing the terminal "e" of the alkane name with "oic acid." For example, the one-carbon alkane is methane, so the one-carbon carboxylic acid is methanoic acid.





valerian flowers

Carboxylic acids containing six or fewer carbons are frequently called by their common names. These names were chosen by early chemists to describe some feature of the compound, usually its origin.

- Formic acid is found in ants, bees, and other stinging insects; its name comes from formica, which is Latin for "ant."
- Acetic acid—contained in vinegar—got its name from acetum, the Latin word for "vinegar."
- Propionic acid is the smallest acid that shows some of the characteristics of the larger fatty acids (Section 25.1); its name comes from the Greek words pro ("the first") and pion ("fat").
- Butyric acid is found in rancid butter; the Latin word for "butter" is butyrum.
- Valeric acid got its name from valerian, an herb that has been used as a sedative since Greco/ Roman times.
- Caproic acid is found in goat's milk. If you have ever smelled a goat, then you know what caproic acid smells like. Caper is the Latin word for "goat."



happy goat

 $\alpha =$ alpha $\beta =$ beta $\gamma =$ gamma $\delta =$ delta $\varepsilon =$ epsilon

In systematic nomenclature, the position of a substituent is designated by a number. The carbonyl carbon is always the C-1 carbon. In common nomenclature, the position of a substituent is designated by a lowercase Greek letter, and the carbonyl carbon is not given a designation. Thus, the carbon adjacent to the carbonyl carbon is the α -carbon, the carbon adjacent to the α -carbon is the β -carbon, and so on.

$$\begin{array}{c} O \\ \parallel \\ CH_3CH_2CH_2CH_2CH_2CH_2 \\ 6 \end{array} \\ \begin{array}{c} O \\ \parallel \\ C \\ OH \end{array} \\ \begin{array}{c} CH_3CH_2CH_2CH_2CH_2CH_2 \\ \epsilon \\ \delta \\ \gamma \\ \end{array} \\ \begin{array}{c} OH \\ CC \\ OH \\ CC \\ OH \\ COmmon nomenclature \\ \end{array}$$

Take a careful look at the following examples to make sure that you understand the difference between systematic (IUPAC) and common nomenclature:

Carboxylic acids in which a carboxyl group is attached to a ring are named by adding "carboxylic acid" to the name of the cyclic compound.

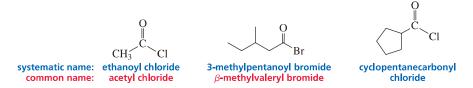


Hamiltonia Hamiltonia Management Manage

 α -Hydroxycarboxylic acids are found in skin products that claim to reduce wrinkles by penetrating the top layer of the skin, causing it to flake off.

Naming Acyl Chlorides

Acyl chlorides have a Cl in place of the OH group of a carboxylic acid. Acyl chlorides are named by replacing "ic acid" of the acid name with "yl chloride." For cyclic acids that end with "carboxylic acid," "carboxylic acid" is replaced with "carbonyl chloride." (Acyl bromides exist too, but are less common than acyl chlorides.)



Naming Esters

An **ester** has an OR' group in place of the OH group of a carboxylic acid. In naming an ester, the name of the group (R') attached to the **carboxyl oxygen** is stated first, followed by the name of the acid, with "ic acid" replaced by "ate." (The prime on R' indicates that the alkyl group it designates does not have to be the same as the alkyl group designated by R.) Recall that a benzene ring is called a phenyl group and a benzene ring attached to a methylene group is called a benzyl group (see the top of the next page).

systematic name: common name:

ethyl ethanoate ethyl acetate

phenyl propanoate phenyl propionate

methyl 3-bromobutanoate methyl β-bromobutyrate

LEARN THE STRATEGY

The double-bonded oxygen is the carbonyl oxygen.

The single-bonded oxygen is the carboxyl oxygen.