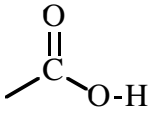
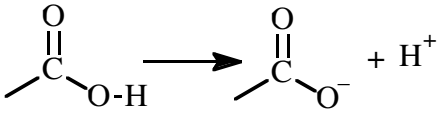
Carboxylic Acids and their Derivatives: Many important compounds are all synthesized from one specific type of carbonyl compound. These carbonyl compounds that are used as the starting material fall into the category of **carboxylic acids**, and the compounds made are referred to as **derivatives** of the carboxylic acids.

All carboxylic acids contain the **carboxylic group**:

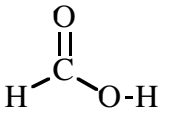


This is also called the "organic acid" group. The reason it is acidic is that the H on the oxygen readily comes off (in the form of H^+), leaving the conjugate base behind, i.e.

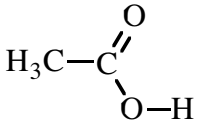


A common carboxylic acid is acetic acid (old name, but almost always used), vinegar is typically 4% – 8% CH_3COOH. As we will see, the bio-molecules known as fatty acids are nothing more than long chain carboxylic acids.

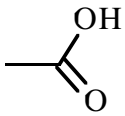
Naming Carboxylic Acids: Except for common names, carboxylic acids are named after the longest hydrocarbon chain that includes the acid group, but with the suffix "**oic acid**". For example:

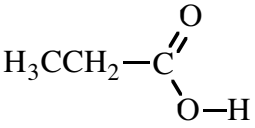


methanoic acid (formic acid)

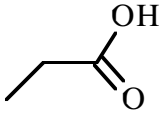


ethanoic acid (acetic acid)

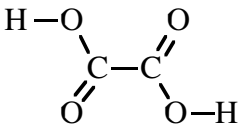




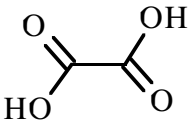
propanoic acid

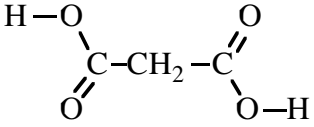


There are also compounds that have two acid groups, the so-called **dicarboxylic acids**. They are given names that end in "**dioic acid**":

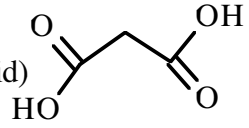


ethanedioic acid (oxalic acid)

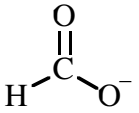




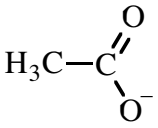
propanedioic acid (malonic acid)

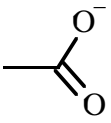


Conjugate Base Names: The ionic form of carboxylic acids (i.e. the conjugate base) is also very important. They appear generally as alkali salts, and are given the suffix "**oate**" in lieu of the "oic acid":



methanoate ion (formate ion)

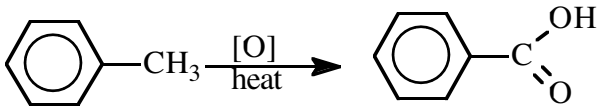


ethanoate ion (acetate ion)


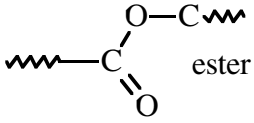
The "oate" name is also used in describing esters, as we will see later.

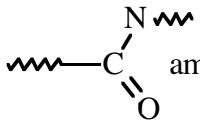
Synthesis of Carboxylic Acids: When we discussed aldehydes and ketones, we mentioned that when 1˚ alcohols are oxidized, the product is not usually the aldehyde. The oxidation tends to proceed past the carbonyl all the way to the carboxylic group. Of course, for 2˚ alcohols, the oxidation does stop at the ketone. This is the most common method of making non-aromatic carboxylic acids.

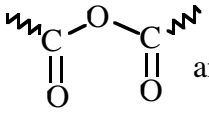
The most common method of making aromatic carboxylic acids is by oxidizing methyl substituted benzenes (i.e. **toluene** derivatives). The aromatic ring makes the methyl group very susceptible to oxidation:

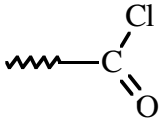


Derivatives of Carboxylic Acids: The reactions of carboxylic acids with other types of molecules produce derivatives. The main derivatives are:



ester


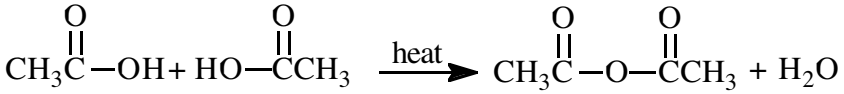
amide


anhydride


acyl (acid) chloride

The common derivatives of carboxylic acids are the **esters** and the **amides**. The **acyl chlorides** and **anhydrides** are important from a practical synthetic aspect. In fact, they are often used to make esters and amides (instead of going directly from the acid). We will start our discussion of the reactions from these. The naming will be treated as we go along.

Anhydride Synthesis: As the name implies, an anhydride is the product when two carboxylic acids join by "losing" a water molecule. This is accomplished by heating a pure sample of the acid, until the water is driven off. For example:



This reaction is reversible; all that needs to be done is that the anhydride is heated with water.

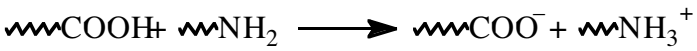
The name of the anhydride is based on the carboxylic acid (or acids) that are used in its synthesis. The name is basically the name of the acid where "acid" is replaced by "anhydride". So, for example, the molecule above would be "acetic anhydride".

The usefulness of these two derivatives lies mainly in their use as synthetic reagents for amides and esters.

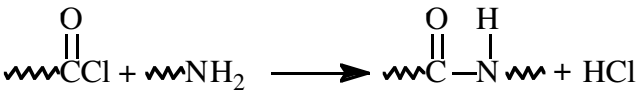
Amide Synthesis: The amide linkage:

is so prevalent in proteins that it is also called the **peptide bond**, where peptide refers to a protein. The natural fibers (silk, wool, cotton) are all proteins. Therefore, when chemists wanted to develop "synthetic" fibers, like nylon, they had to develop methods of making amides.

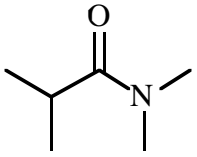
The difficulty in making amides stems from the acidic nature of carboxylic acids and the basic nature of amines. When you mix the two together, instead of forming a covalent bond, an acid base neutralization would occur:



So, instead of doing the reaction directly, the acid is first converted into an acyl chloride, which then reacts with the amine to form the amide:



The naming of these compounds is similar to naming amines. The root name is based on the carboxylic acid, where the suffix "oic acid" is replaced by "amide". The side chains on the nitrogen are given the prefix ***N***. So, if we were to name the following compound:



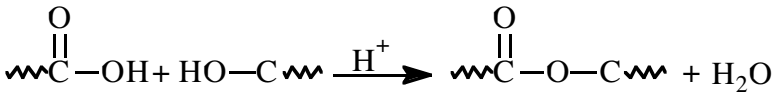
we would notice the acid from which it was synthesized was 2-methylpropanoic acid. We would also see that there are two methyl groups on the nitrogen (i.e. the amine was dimethyl amine). Thus, the name of this compound must be:

***N*,*N*,2 trimethyl propanamide**.

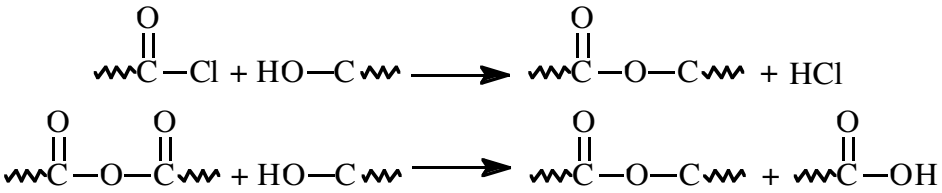
{cyclic amides are called **lactams**, though we won't really go into them here}

Esters: One of the "nicest" classes of molecules are the esters. Like aldehydes, they are quite fragrant, and the fragrance is usually pleasant. The smell of bananas, vanilla, rum and wintergreen are all due to esters. Unlike aldehydes, esters tend to be fairly stable (recall aldehydes oxidize readily), though they do break down under very acidic conditions. Esters represent a molecule formed when an alcohol and a carboxylic acid combine.

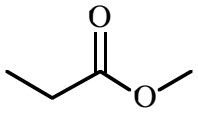
Depending on the relative reactivity of the carboxylic acid, esters can be made in several ways. In the first method, the carboxylic acid and the alcohol are heated in the presence of strong acid:



Though this is the simplest method, it does not always work. Another method is to use the ionic form of the acid and a halo alkane. Again, this does not always work. A sure fire method is to treat an acyl chloride OR an anhydride with the alcohol:



The names of esters are based on the IONIC form of the acid. Thus, the name of the molecule



would be **methyl propanoate**. {Cyclic esters are called **lactones**, though we won't really go into them here}

Hydrolysis of Esters - Saponification: Natural fats are all esters between polyols (usually 1,2,3 propanetriol). When esters are treated with strong base (like NaOH or KOH), the ester linkage is broken, and the alcohol is reformed. The other product is the ionic form of the carboxylic acid (i.e. the carboxylate ion). This is the process that occurs when soap is made from fat and lye (NaOH). This process, therefore, is called **saponification**.