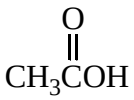
Structure and Nomenclature of Molecules Possessing Carbonyl Groups

There are a number of molecular types in organic chemistry that include the C=O (carbonyl) group. In this module, we will discuss four of them (ketones, aldehydes, esters, and carboxylic acids). This module is done last because each has a different, although related, nomenclature system. A commonality to all of these molecular types is how the first two molecules in the series are named. As you have seen, one and two carbon alkanes are named methane and ethane, respectively. Each molecule can be named based on this system. All can also be named using an older nomenclature system (much like the arenes have two systems). Some also have a non-systematic common name (like 'grain alcohol' for ethanol). The systematic names are based on the names for the carboxylic acids and so that is where we begin.

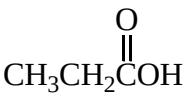
Carboxylic acids

Carboxylic acids have been known for millennia and so many received common names that were then used to develop systematic names for other carbonyl containing molecules. Carboxylic acids typically have low volatility because of strong hydrogen bonding, but their vapors are typically sharp and unpleasant. They are also generally toxic. For example, formic acid is the sting in an ant bite.

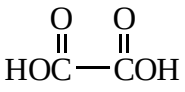
methanoic acid
formic acid



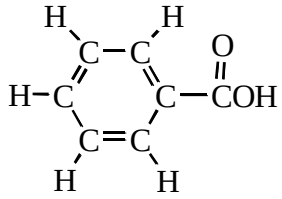
ethanoic acid
acetic acid



propanoic acid
propionic acid



ethanedioic acid
oxalic acid



benzoic acid

In general, the modern system of nomenclature is used for all monocarboxylic acids consisting of 3 carbons or more (the terms methanoic and ethanoic acid are rarely used). In contrast, the common names are used almost exclusively for the 2-6 carbon dicarboxylic acids. For benzene rings with functional groups, the "benz" beginning is always used (although there is

a very clunky IUPAC name).

The modern system of naming acids begins by using the names of alkanes as their base.

1) Find the longest carbon chain that includes the carbon to which the –C(O)OH group is attached.
2) Name the molecule as if it were an alkane; starting from the carbon in the –C(O)OH group. This is an important point: **you must include the carbonyl acid carbon in the counting**.
3) Change the final "-e" to "-ic acid." Numbering is unnecessary because the –C(O)OH group is always a terminal group.
4) If the carboxylic acid contains other attached groups, the molecule is <u>always</u> named as a carboxylic acid and numbering begins with the carbonyl carbon. Unsubstituted carboxylic acids never need numbers since the acid group appears on the end of the chain.

hexanoic acid 2-hydroxypentanoic acid

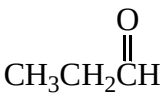
<u>Aldehydes</u>

Aldehydes are molecules that end in C(O)H (i.e. the –OH group in an acid is replaced by an -H). They typically result in nature from the oxidation of alcohols and usually have a sharp, disagreeable odor. Formaldehyde is a typical example of this. Cinnamonaldehyde represents an aldehyde with a sharp, pleasant odor (picture provided in Arenes notes). Substituted aldehydes are named as in the case for carboxylic acids.

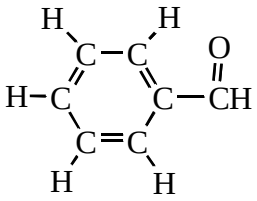
1) Name the corresponding carboxylic acid by any system.
2) For IUPAC naming, replace "-oic acid" with "-al."
3) For the older system, replace "-ic acid" with "aldehyde."

Preferred names are underlined.

methanal



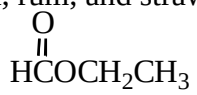
propanal



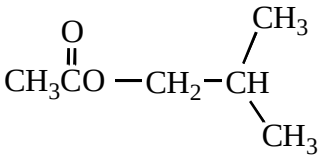
formaldehyde propionaldehyde benzaldehyde

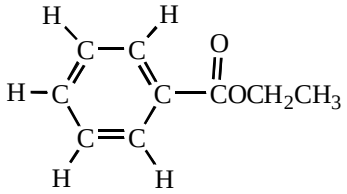
Esters

In esters, the "-OH" is replaced by an "-OR" group, where "R" is some organic group. Thus, they have the general formula: RC(O)OR', where the R groups may be the same or different. Esters generally produce pleasant odors (scents) that are mild. The scents associated with fruits are frequently either an ester or a mixture of esters. That scents are frequently blends of several compounds accounts for the fact that fruit flavored things (e.g. gum) rarely taste exactly like the real thing. Wikipedia lists many examples (http://en.wikipedia.org/wiki/Ester), several of which are used as nomenclature examples below. We'll begin with ethyl formate, $HC(O)OCH_2CH_3$, a component of lemon, rum, and strawberry flavors.



1) Name the portion of the molecule containing the carbonyl group as if it was a carboxylic acid. In this case, the acid would be formic acid. Replace "-ic acid" by "-oate." Now, we have "formate."
2) Name the "R" group as if it were a substituent on another molecule. In this case, the "R" group is ethyl.
3) The ester is named by placing the "R" group name first, and ester group second, in this case: ethyl formate.





ethyl acetate isobutylacetate ethylbenzoate

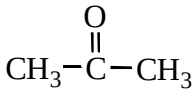
peach, pineapple, raspberry cherry, raspberry, strawberry "essence di Niobe"

Essence di Niobe is a 'fruity' ester used in the manufacture of perfumes. Ethyl acetate is also sold as "acetone-free" nail polish remover.

Ketones

Ketones are molecules whose carbonyls occur along the inside of a carbon chain. They have the general formula R-C(O)-R', where the R groups may be the same or different. Ketones are frequently fragrant and are considered between esters and aldehydes in terms of pleasantness. They are frequently used as solvents and are found in nature in a number of places. For example, muscone is the primary contributor to the odor of musk, while acetophenone is found in apple, cheese, apricot, banana, beef, and cauliflower. As you have probably guessed, ketones are indicated by the "-one" ending.

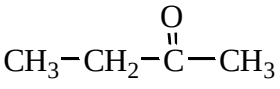
1) IUPAC system: Name the parent alkane by the standard rules replacing the "-e" ending with "-one."
2) In molecules that require numbering, numbering should begin such that the carbonyl carbon gets the lowest possible number, unless there is an aldehyde or carboxylic acid group. Those always occupy the number 1 position.
3) Common system: Name each group bound to the carbonyl as a substituent. Then use those substituent names as prefixes to the word "ketone." Usually, they are placed in order of increasing size.



propanone

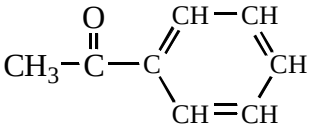
dimethyl ketone

acetone



butanone

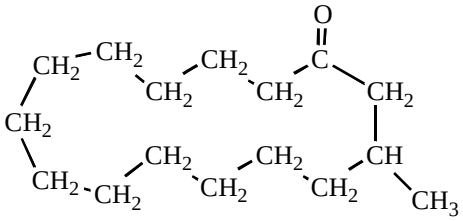
methylethylketone



phenylethanone

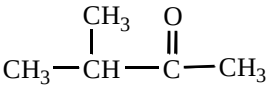
methylphenylketone

acetophenone



3-methylcyclopentadecanone

muscone



3-methylbutanone

methylisopropylketone