

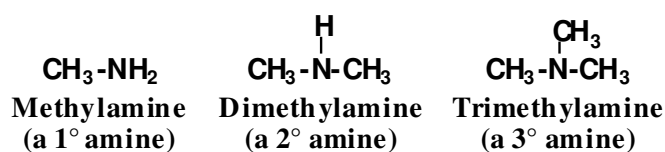
Chemistry B11
Chapters 14
Amines, aldehydes, ketones and carboxylic acids

Amines: are derivatives from ammonia (NH₃).

Aliphatic amines: an amine in which nitrogen is bonded only to alkyl group or hydrogens.

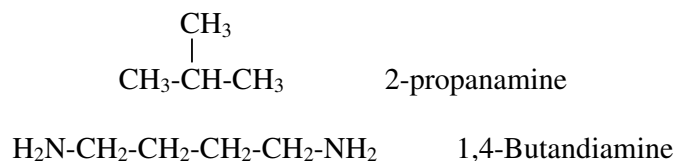
Aromatic amines: an amine in which nitrogen is bonded to one or more aromatic rings.

Note: amines are classified as **primary** (°1), **secondary** (°2) or **tertiary** (°3), depending on the number of carbon groups bonded to nitrogen.

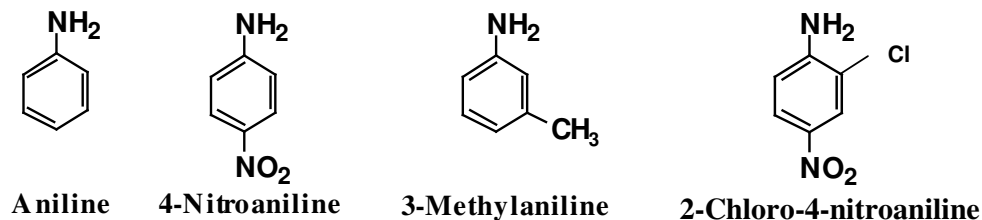


Naming of °1 amines: IUPAC names for aliphatic amines are similar to alcohols except the final “-e” of the parent alkane is dropped and replaced by “-amine”. The parent chain whether contains the nitrogen atom or amino group (NH₂).

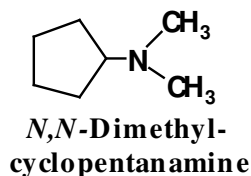
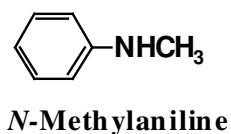
Note: The location of the amino group (-NH₂) on the parent chain is indicated by a number (as we do for the alcohols).



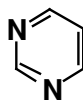
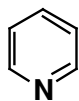
Note: Aniline is the most famous common names for aromatic amines. We begin numbering chain of aromatic by amino group (NH₂) (because it is a special substituent). We number the carbon atoms to obtain the smallest set of numbers and then list them by alphabetical order as a prefix (as we do for the alcohols).



Naming of °2 and °3 amines: when we have more than one carbon atom bonded to nitrogen atom: the largest group bonded to nitrogen is taken as the parent amine, the smaller groups bonded to nitrogen are named, and their locations are indicated by prefix N (indicating that they are bonded to nitrogen).



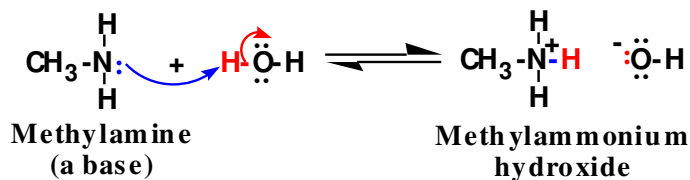
Heterocyclic amine: an amine in which the nitrogen is one of the atoms of a ring.



Pyridine Pyrimidine

Physical properties of amines: 1. They have very sharp, penetrating odors (like rotten fish). 2. They are polar compounds because of the difference in electronegativity between N and H ($3.0 - 2.1 = 0.9$). 3. Both primary and secondary amines can form hydrogen bonds with one another (because of N-H). However, the tertiary amines do not have a hydrogen bonded to nitrogen and, therefore, do not form hydrogen bond with one another (but hydrogen bonds in amines are weaker than hydrogen bonds in alcohols). 4. They have higher boiling points than hydrocarbons but lower boiling points compare to alcohols (with the same molecular weight). 5. Because of hydrogen bonding, they are more soluble in water than are hydrocarbons of comparable molecular weight.

Chemical properties of amines: they are weak bases and they can react with acids.



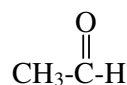
Note: Aliphatic amines are stronger bases than aromatic amines and heterocyclic amines. All aliphatic amines are slightly stronger bases than ammonia. While aliphatic amines are weak bases by comparison with inorganic bases such as NaOH, they are strong bases among organic compounds.

Note: Some amines are present in our blood and make it approximately basic (pH = 7.4).

Aldehyde: the functional group of an aldehyde is a carbonyl group (C=O) bonded to a hydrogen atom.

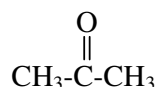


Methanal



Ethanal

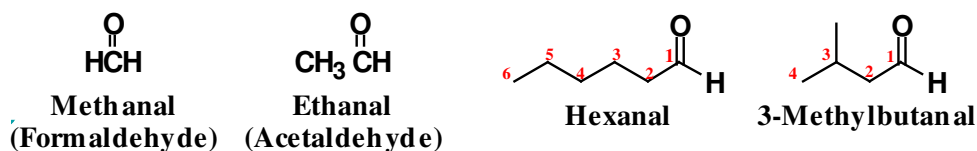
Ketone: the functional group of a ketone is a carbonyl group (C=O) bonded to two carbon atoms.



Pronanone

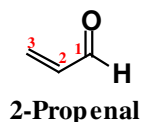
Naming of aldehydes: IUPAC names for aldehydes are similar to alcohols except the final “-e” of the parent alkane is dropped and replaced by “-al”. The parent chain should contain the carbonyl group (C=O). We number the carbon chain starting from the end nearest the carbonyl group and there is no need to use a number to locate the aldehyde group (because the carbonyl group of an aldehyde can appear only at the end of a parent chain).

Common name of aldehydes: for two first aldehydes use the prefix “form-” and “acet-” followed by “-aldehyde”.

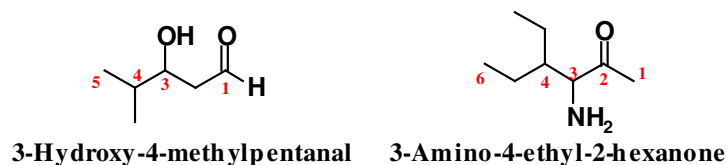


Naming of ketones: IUPAC names for ketones are similar to alcohols except the final “-e” of the parent alkane is dropped and replaced by “-one”. The parent chain should contain the carbonyl group (C=O). We start numbering the carbon chain from the end nearest the carbonyl group. For ketones, we need to show the location of the carbonyl group.

Note: In naming aldehydes or ketones that also contain the carbon-carbon double bond (C=C), we still start numbering the carbon chain from the end nearest the carbonyl group (however, we have an alkene instead of an alkane). We show the location of the carbon-carbon double bond by number of its first carbon.



Note: In naming aldehydes or ketones that also contain an -OH or -NH₂ group elsewhere in the molecule, we still start numbering the carbon chain from the end nearest the carbonyl group. Hydroxy and amino substituents are numbered and alphabetized along with any other substituents that might be present.



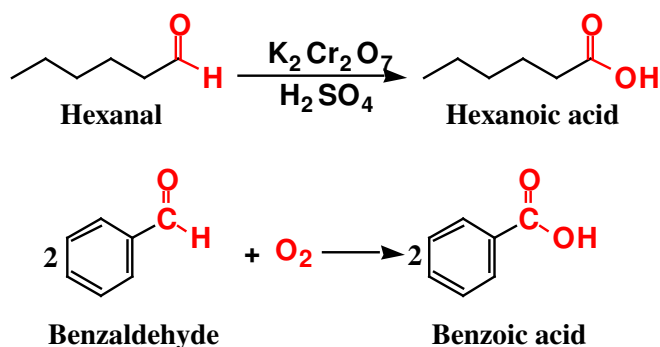
Common name of ketones: name each alkyl or aryl group bonded to the carbonyl group as a separate word, followed by the word “-ketone”. The alkyl or aryl groups are generally listed in alphabetical order. The first ketone is called acetone.



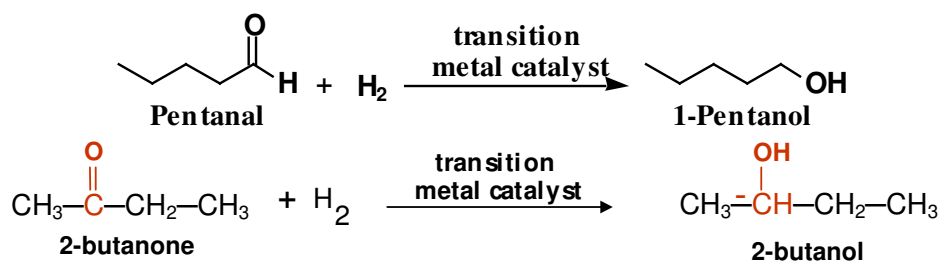
Physical properties of aldehydes and ketones: 1. Most aldehydes and ketones have strong odors (the odors of ketones are generally pleasant, and many are used in perfumes). 2. They are polar molecules (because of carbonyl group (C=O), carbon obtains the partial positive charge and oxygen obtains the partial negative charge). 3. There is only the dipole-dipole interaction between the molecules and there is no possibility for hydrogen bonding. 4. They have lower boiling points than amines and alcohols. 5. They are soluble in water (form hydrogen bonds with water - the oxygen atom of each carbonyl group is a hydrogen bond acceptor) and they are not soluble in nonpolar compounds (because they are polar).

Chemical reactions of aldehydes and ketones:

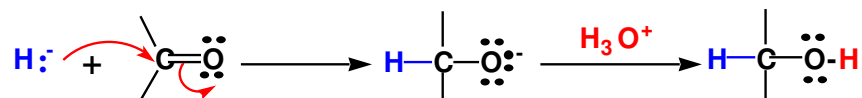
1. Oxidation: Aldehydes are oxidized to carboxylic acids by a variety of oxidizing agents, including potassium dichromate (K₂Cr₂O₇). In this reaction, a concentrated strong acid is used as a catalyst (H₂SO₄). Liquid aldehydes are so sensitive and the oxygen in air can oxidize them. They must be protected from contact with air during storage. Ketones resist oxidation by most oxidizing agents (no oxidation for ketones).



2. Reduction: we know that the C=C double bond of an alkene can be reduced by hydrogen in the presence of a transition metal catalyst (such as platinum) to a C-C single bond. The same is true of the C=O double bond of an aldehyde or ketone to the C-O. Aldehydes are reduced to primary alcohols and ketones are reduced to secondary alcohols.

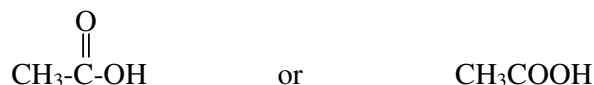


Mechanism of reduction: the reagent most commonly used in the laboratory for the reduction of an aldehyde or ketone is sodium borohydride (NaBH₄). This compound is a source of hydride ions (H⁻). In this ion, hydrogen has two valence electrons (unstable). Hydride ion is attracted to and then adds to the partially positive carbonyl carbon, which leaves a negative charge on the carbonyl oxygen. Reaction of this intermediate with aqueous acid gives the alcohol.

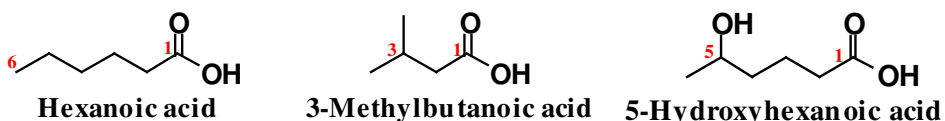


Note: An advantage of using NaBH_4 over the H_2/metal reduction is that NaBH_4 does not reduce carbon-carbon double bonds (there is no polarity –no partial positive or negative charges- on a carbon-carbon double bond to attract the negatively charged hydride ion).

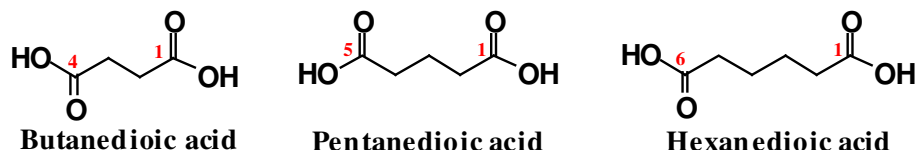
Carboxylic acid: the functional group of a carboxylic acid is a **carboxyl group** ($-\text{COOH}$), which is a carbonyl group ($\text{C}=\text{O}$) attached to a hydroxyl group ($-\text{OH}$). Carboxylic group can be represented by three ways: $-\text{COOH}$, $-\text{CO}_2\text{H}$, or the following method:



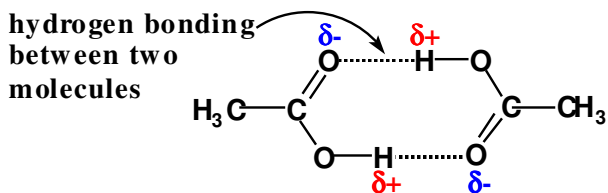
Naming of carboxylic acids: IUPAC names for carboxylic acids are similar to alcohols except the final “-e” of the parent alkane is dropped and replaced by “-oic acid”. The parent chain should contain the carboxyl group ($-\text{COOH}$). Number the chain beginning with the carbon of the carboxyl group. Because the carboxyl carbon is understood to be carbon 1, there is no need to give it a number. We consider the hydroxyl group ($-\text{OH}$) and the amino group ($-\text{NH}_2$) as a substituent (list them in alphabetical order).



Naming of dicarboxylic acids: we add the suffix “-dioic acid” to the name of the parent alkane that contains both carboxyl groups; thus, “-ane” becomes “-anedioic acid”. The numbers of the carboxyl carbons are not indicated because they can be only at the ends of the parent chain.

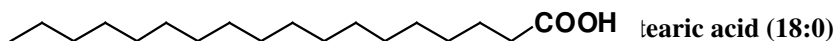


Physical properties of carboxylic acids: 1. They are so polar because they contain three polar covalent bonds ($\text{C}=\text{O}$, $\text{C}-\text{O}$, and $\text{O}-\text{H}$). 2. They have higher boiling points than other types of organic compounds of comparable molecular weight (because their polarity and the presence of the hydrogen bonding between two carboxyl groups (it creates a dimer)).

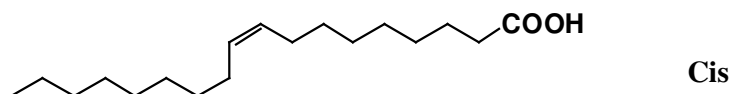


3. They are more soluble in water than other types of organic compounds (because of hydrogen bonding). 4. The liquid carboxylic acids have sharp, often disagreeable odors. 5. They have sour taste (exist in pickles, limes and lemons).

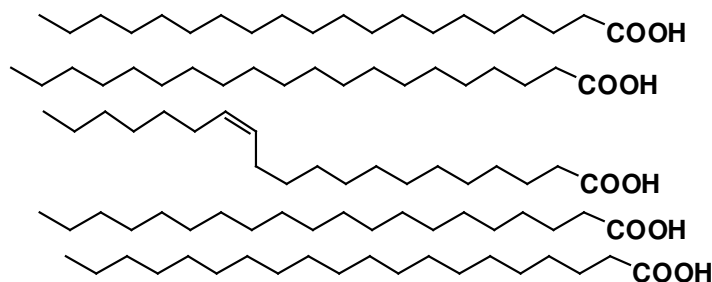
Fatty acids: long, unbranched chain carboxylic acids are found in animal fats, vegetable oils, or phospholipids of biological membranes. Nearly all fatty acids have an even number of carbon atoms, most between 12 and 20, in an unbranched chain.



Note: In most unsaturated fatty acids (with double bond C=C), the cis isomer is usually exists and the trans isomer is rare.



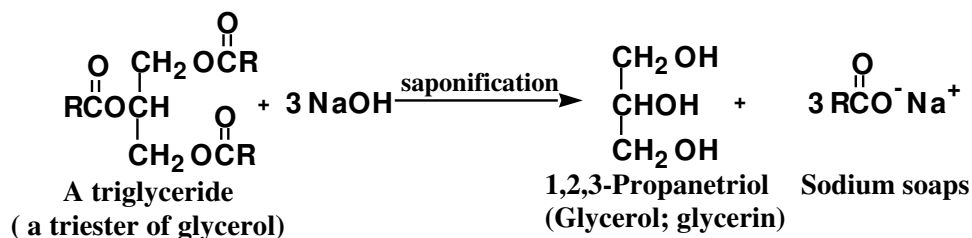
Note: the saturated fatty acids are solid at room temperature and they have higher melting points than the unsaturated fatty acids (they are liquid at room temperature). The reason is: the saturated fatty acids are linear and they can be packed together in close parallel alignment. The attractive interactions between adjacent hydrocarbon chains (London dispersion forces) are maximized. In unsaturated fatty acids, the cis double bonds interrupt the regular packing of the chains and the London dispersion forces is smaller.



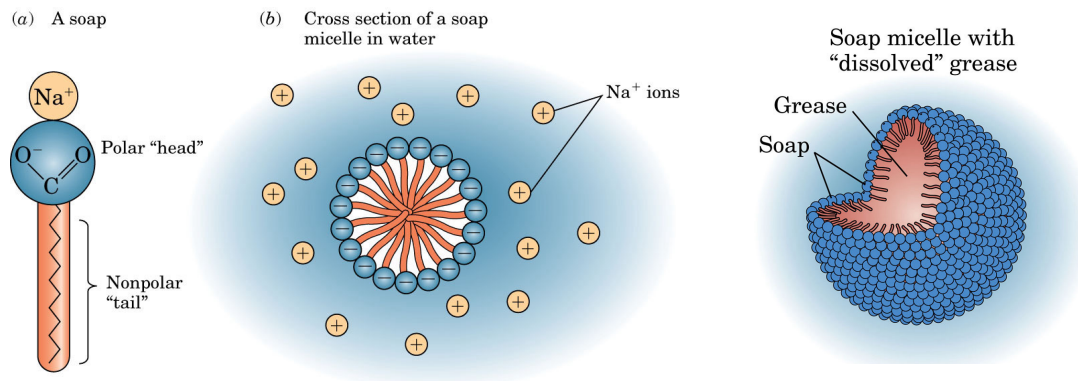
Esters: in esters the hydrogen atom in the carboxyl group is replaced with an alkyl group.



Saponification: Natural soap are sodium or potassium salts of fatty acids. They are prepared from a blend of tallow and coconut oils (**triglyceride**). Triglycerides are triesters of glycerol. The solid fats are melted with steam, and the water insoluble triglyceride layer that forms on the top is removed. the preparation of soaps begins by boiling these triglycerides with sodium hydroxide (NaOH). Boiling with potassium hydroxide (KOH), gives a potassium soap.

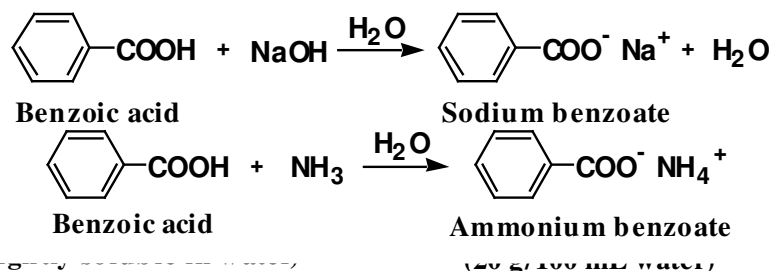


How soap cleans: soap consists of two parts: 1. Hydrophobic part, which is nonpolar and it is made of fatty acid (long hydrocarbon chain). 2. Hydrophilic part, which is polar and it is made of carboxylate group ($-\text{COO}^-$) with a negative charge and a metal ion (Na^+ or K^+). In water, nonpolar hydrocarbon chains tend to cluster in such a way as to minimize contact of their hydrocarbon chains with surrounding water molecules. The polar part stays in contact with the surrounding water molecules. Soap molecules cluster into **micelles** (a spherical arrangement of molecules). Many of the things we commonly think of as dirt, are nonpolar and insoluble in water. When the dirt and soap are mixed together, the nonpolar hydrocarbon inner parts of the soap can dissolve the dirt and they keep the dirt inside of the micelles. In this way, the dirt is washed away in the polar wash water.



Chemical reaction of carboxylic acids:

- They are weak acids ($\text{pK}_a = 4\text{-}5$). Substituents of high electronegativity (especially $-\text{OH}$, $-\text{Cl}$, and $-\text{NH}_3^+$), near the carboxyl group increase the acidity of carboxylic acids.
- As they are weak acids, they react with strong bases like NaOH , KOH , and NH_3 to form water-soluble salts.



- Fischer esterification:** reaction of a carboxylic acid with an alcohol in presence of an acid catalyst (most commonly, concentrated sulfuric acid) gives an ester.

