I. Introduction
   A. Alcohols, Ethers and Phenols are important natural products
      1. For example:
         a. Ethanol, menthol and cholesterol are alcohols
   B. Alcohols are organic molecules containing the functional group called the hydroxyl group (-OH).
      1. This group is attached to a hydrocarbon core.
      2. Often when we want to focus our attention on the functional group refer the hydrocarbon portion of the molecule, if it is an akyl group (alkane or alkene), as the "R" group.
         a. The general structural formula for an alcohol is then
            \[ R-OH \]
      3. In some ways, an alcohol can be thought of as a water molecule in which one of the hydrogens is removed and replaced with and "R" group.
         a. As we will see, hydroxyl groups confer water-like properties to organic molecules.
   C. Phenols are obtained when the hydroxyl group is attached to an aromatic ring instead of an alkyl group.
      \[ \text{Phenol} \]
   D. Ethers are obtained with both the hydrogens of a water are replaced with alkyl groups:
      \[ R-O-R' \]
      1. The two "R" groups do not have to be the same.

II. Nomenclature of Alcohols and Phenols
   A. For this class we will focus only on the name of alcohols.
   B. Many of the simple alcohols have common names that have stuck:
      1. Methyl alcohol (wood alcohol)
      2. Ethyl alcohol (grain alcohol)
      3. Isopropyl alcohol (rubbing alcohol)
   C. We will be using the IUPAC conventions for naming alcohols:
      1. Step 1: Name the longest chain to which the hydroxyl group is attached. The chain name is obtained by dropping the final -e- from the name of the hydrocarbon that contains the same number of carbon atoms and adding the ending -ol.
      2. Step 2: Number the longest chain to give the lower number to the carbon with the attached hydroxyl group.
3. Step 3: Locate the position of the hydroxyl group by the number of the carbon atom to which it is attached.
4. Step 4: Locate and name any other groups attached to the chain.
5. Step 5: Combine the name and location for other groups, the hydroxyl group location, and the longest chain into the final name.

III. Classification of Alcohols
A. The reactions that an alcohol participates in depends on the other groups attached to the carbon to which the hydroxyl group is attached:
   1. This leads to three different classifications of alcohols
      a. *Primary alcohols* - the carbon has two or three hydrogens attached to it:

         \[
         \begin{align*}
         & C \quad -O-H \\
         & \quad \quad H
         \end{align*}
         \begin{align*}
         & C \quad -O-H \\
         & \quad \quad H
         \end{align*}

      b. *Secondary alcohols* - the carbon has only one hydrogen attached to it:

         \[
         \begin{align*}
         & C \quad -C\quad -O-H \\
         & \quad \quad \quad \quad \quad \quad \quad H
         \end{align*}
         \begin{align*}
         & C \quad -C\quad -O-H \\
         & \quad \quad \quad \quad \quad \quad \quad H
         \end{align*}

      c. *Tertiary alcohols* - the carbon has no hydrogens attached to it:

         \[
         \begin{align*}
         & C \quad -C\quad -O-H \\
         & \quad \quad \quad \quad \quad \quad \quad H
         \end{align*}
         \begin{align*}
         & C \quad -C\quad -O-H \\
         & \quad \quad \quad \quad \quad \quad \quad H
         \end{align*}

IV. Physical Properties of Alcohols
A. The hydroxyl group gives an organic molecule water-like properties.
   1. Hydrocarbons are non-polar and cannot make hydrogen bonds.
   2. Water is polar and likes to make hydrogen bonds with itself.
B. Substances that cannot form hydrogen bonds with water are usually not soluble in water.
   1. This is because in order to dissolve in water they must break some of the hydrogen bonds between the water molecule, however, they are unable to replace these broken hydrogen bonds with new hydrogen bonds.
   2. Alcohols that have short hydrocarbon chains (up to three carbons long) are quite soluble in water.
      a. They are soluble because their hydroxyl group is able to hydrogen bond to water molecules.
3. When the hydrocarbon chain gets longer than three carbons, then the alcohol becomes less soluble.
   a. This is because the non-polar hydrocarbon portion of the molecule has a greater influence on the overall properties of the molecule.
      i. A smaller portion of the hydrogen bonds between water molecules that must be broken when the molecule dissolves are replaced by the hydrogen bonds that the hydroxyl group can make.

Figure 13.2 - Compares the solubility of alcohols with different numbers of carbons to the solubilities of the corresponding alkanes.

C. Hydrogen bonding also explains why water has much higher boiling and melting points than other molecules of similar size
   1. NH₃, CH₃, and H₂S are all gases at room temperature, compared to water, which is a liquid.
   2. The hydrogen bonds that form between water molecules are also responsible for its unusually high boiling and melting points.
      a. A water molecule going from the liquid state to the gas state must break these hydrogen bonds.
      b. This requires energy, hence a higher temperature is required to break these bonds.
   3. Hydrocarbons cannot hydrogen bond to themselves.
      a. In the liquid and solid states hydrocarbon molecules are held together by very weak dispersion interactions.
      b. These interactions become larger as the molecule gets larger, which is why larger molecules have higher boiling and melting points.
   4. Alcohols have higher melting points than the corresponding hydrocarbons of similar molecular weight because, like water, they can hydrogen bond to themselves.

Figure 13.6 - Compares the boiling points of alcohols with molecular weights to the boiling points of the corresponding alkanes.
   a. All alcohols are liquids at room temperature whereas hydrocarbons with fewer than five carbons are gases.

V. Reactions of Alcohols
A. Compared to hydrocarbons, alcohols can undergo many different kinds of reactions.
   1. Like hydrocarbons, they can react with oxygen to form carbon dioxide and water.
   2. They can also undergo many other reactions that specifically involve the hydroxyl group.
      a. At this point we will only introduce two of these reactions:
         i. Dehydration of alcohols.
         ii. Oxidation of alcohols.

B. Dehydration of alcohols.
1. There are two different dehydration reactions that can occur.
   a. The first involves only a single alcohol molecule:

   \[
   \begin{align*}
   & \text{H} - \text{OH} \\
   & \text{H}_2\text{SO}_4 \\
   & 180^\circ\text{C} \\
   & \rightarrow \\
   & \text{C=O} + \text{H-OH}
   \end{align*}
   \]

   i. This reaction is reverse of the hydration reaction that we saw with alkenes.
      1) Both reactions are catalyzed by sulfuric acid, \( \text{H}_2\text{SO}_4 \).
      2) The difference is the temperature at which the reactions is carried out:
         a) At higher tempertures, 180°C, the dehydration of alcohols to form alkenes and
            water is favored.
         b) At room temperature, \( \approx 25^\circ\text{C} \), the hydration of alkenes to form alcohols is favored.

   ii. For secondary alcohols, two possible products can form, depending on which of the neighboring carbons the
       hydrogen is taken from.
      1) The more favored product is the one that is obtained when the hydrogen is removed from the carbon that
         has the fewer number of hydrogens.

   \[
   \begin{align*}
   & \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_3 \\
   & \text{OH} \\
   & \text{H}_2\text{SO}_4 \\
   & 180^\circ\text{C} \\
   & \rightarrow \\
   & \text{CH}_3\text{CH}=\text{CH}-\text{CH}_3 + \text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2 + \text{H-OH}
   \end{align*}
   \]
   90%  10%

   iii. Later we will learn that dehydration reactions are important in biochemistry.
      1) In a living cell these reactions are catalyzed by biological catalysts called enzymes, which can carry
         out the reaction at room temperature and neutral \( \text{pH} \).

   b. The second type of dehydration reaction involves two alcohol molecules reacting with one another:

   \[
   \begin{align*}
   & \text{R-OH} + \text{H-O-R} \\
   & \text{H}_2\text{SO}_4 \\
   & 140^\circ\text{C} \\
   & \rightarrow \\
   & \text{R-O-R} + \text{H-OH}
   \end{align*}
   \]

  ether

   i. The product of this reaction is an ether, \( \text{R-O-R} \), and water.

   ii. This reaction is also catalyzed by sulfuric acid, but is favored at a slightly lower temperature than the reaction
       that produces the alkene.
C. Oxidation of alcohols
1. By definition, a molecule is oxidized when it loses electrons in a reaction.
   a. When a reaction produces additional covalent bonds between carbon and oxygen, we say the carbon is oxidized.
      i. Even though in covalent bonds the bonding electrons are shared, because the oxygen is more electronegative than carbon, the electrons spend more of their time with the oxygen than with the oxygen.
      ii. The greater the number of bonds a carbon makes with oxygen, the more oxidized it is.
   1) The carbons in a hydrocarbon molecules are the least oxidized form of carbon, while the carbon in carbon dioxide is the most oxidized form for carbon.
   2) In the following series of molecules, methane is the least oxidized and carbon dioxide is the most oxidized.

      \[
      \text{H} - \text{C} - \text{H} < \text{H} - \text{C} - \text{H} < \text{H} - \text{C} - \text{H} < \text{H} - \text{C} - \text{OH} < \text{O} = \text{C} = \text{O}
      \]

   3) The second molecule in this series is methanol, which is an alcohol
      a) Though the carbon in methanol is partially oxidized, this series shows that it can become further oxidized by replacing C-H bonds with C-O bonds.
   b. There are a number of reactants that can be used to oxidize alcohol.
      i. Two commonly used ones include:
         1) Potassium permanganate - \(\text{K}_2\text{MnO}_4\).
         2) Potassium Dichromate - \(\text{K}_2\text{Cr}_2\text{O}_7\).
   c. The products of the oxidation reactions that take place with these oxidizing agents can be complex, therefore, we will not write balanced equations for the oxidation reactions
      i. Instead, we will represent the oxidizing agent as \([\text{O}]\), and will only indicate what happens to the alcohol.
   d. The product that forms from the alcohol depends on the category of the alcohol, \(i.e\). primary, secondary or tertiary.
e. Primary alcohols oxidize to form *aldehydes*:

\[
\text{R--C--H} + [\text{O}] \rightarrow \text{R--C=H}
\]

*primary alcohol* \*aldehyde*

i. The aldehyde that forms can be further oxidized to form a *carboxylic acid*:

\[
\text{R--C--H} + [\text{O}] \rightarrow \text{R--C--OH}
\]

*aldehyde* \*carboxylic acid*

f. Secondary alcohols oxidize to form ketones:

\[
\text{R--C--R'} + [\text{O}] \rightarrow \text{R--C--R'}
\]

*secondary alcohol* \*ketone*

g. Tertiary alcohols do not oxidize:

\[
\text{R--C--R'} + [\text{O}] \rightarrow \text{No reaction}
\]

*tertiary alcohol*
h. Looking at this series of reactions you will see that the ability to be oxidized requires that a hydrogen atom be bonded to the same carbon to which the oxygen is bonded:

\[ \begin{align*}
\text{primary alcohol} & \quad \text{aldehyde} \\
\text{R} & \quad \text{R'} \\
\text{O} & \quad \text{OH}
\end{align*} \]

\[ \begin{align*}
\text{alcohol} & \quad \text{carboxylic acid} \\
\text{R} & \quad \text{R'} \\
\text{OH} & \quad \text{O}
\end{align*} \]

II. Ethers

A. Earlier we saw that ethers are one of the products of the dehydration of alcohols:

\[ \begin{align*}
\text{R} & \quad \text{OH} \quad \text{HO} \quad \text{H}_2\text{SO}_4 \quad \text{140°C} \\
\text{ether} & \quad \text{R} \quad \text{O} \quad \text{HO} \\
\end{align*} \]

B. Nomenclature

1. The IUPAC rules for naming ethers are rarely used; instead, the older method of naming ethers has endured.
   a. The names for the two alkyl groups are listed followed by the word ether.
      i. If the two alkyl groups are the same, the prefix di- is used.
         \[ \begin{align*}
         \text{CH}_3\text{CH}_2\text{O} & \quad \text{CH}_3 \\
         \text{ethyl methyl ether} & \quad \text{diethyl ether}
         \end{align*} \]

C. Physical properties of ethers

1. Like alcohols, ethers can hydrogen bond to water.
   a. This makes them more soluble in water than the corresponding hydrocarbons, however they are not as soluble as alcohols because they are not able to make as many hydrogen bonds as alcohols to water.

   Compare Figure 13.13 with Figure 13.3

2. Unlike alcohols, ethers cannot form hydrogen bonds to themselves.
   a. For this reason, there boiling points are nearly the same as those for the corresponding alkanes.
Figure 13.6 - Boiling points of alcohols, ethers and alkanes

III. Phenols
A. Phenols are compounds that have hydroxyl groups attached to aromatic rings.
   1. Their chemical and physical properties are different than alcohols so they are usually treated separately from alcohols.
B. Besides being able to recognize a phenol, we will not be going into any further depth on phenols in this class.

IV. Thiols
A. Sulfur is in the same family on the periodic table as oxygen.
   1. It therefore has the same number of valence electrons as oxygen and forms the same kinds of bonds with other elements as oxygen.
B. The sulfur analogue to alcohols is called a thiol
   \[ R-SH \]

   1. The -SH group is called a sulfhydryl group.
C. Thiols have strong, sometimes disagreeable odors:
   1. Skunk odor
   2. Coffee
   3. Garlic
   4. Rotten eggs
   5. Natural gas (methane) has no odor; a thiol is added to natural gas so that its presence can be readily detected by the thiol's odor.
D. Thiols can be oxidized to form a disulfide:
   \[ R-SH + HS-R + [O] \rightarrow R-S-S-R \]

   \textit{disulfide}

   1. This reaction will become important later in our discussion of protein structure and hair permanents.