

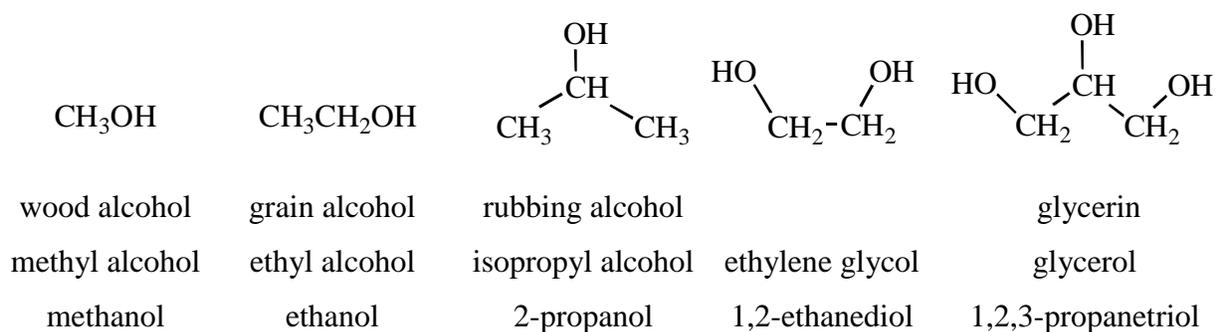
## Structure and Nomenclature of Substituted Alkanes

In the *Alkanes* notes, you learned about two systems of naming molecules. Here we expand those systems to allow us to name molecules with heteroatom (non-CH) substituents. We'll also encounter a third nomenclature method. It is the oldest of the ways to name compounds and not a system at all. It dates from the days before the existence of atoms and elements was postulated. Thus, each compound was given a unique name, frequently based on some physical characteristic (e.g. appearance, odor, or source). While most of these names have fallen out of use (e.g. sulfuric acid is no longer called *oil of vitriol* or zinc oxide = *flowers of zinc*), some survive (e.g. plaster of Paris = calcium sulfate), and a few have even been incorporated into systematic naming (e.g. benzene, which appears in a later handout).

### Alcohols

The term "alcohol" has an interesting origin. Like many words in science beginning with "al-," this term has an Arabic origin. "Al-" means "the." (Thus, alchemy is "the chemistry.") The last two syllables come from the word for an early eye shadow made of antimony powder. The word for the process by which this powder was made is very similar to the word for the powder itself. The process is essentially distillation. Medieval Europeans learned of distillation through the operation of making liquor. Of course, the active ingredient of liquors is ethanol, but at the time the name of the process by which ethanol was concentrated was given to the chemical itself. Hence, the original name of ethanol was alcohol.

Molecules containing one or more -OH groups are so common in nature that many have common names. For example:



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

- 1) Find the longest carbon chain that includes the carbon to which the –OH group(s) is attached.
- 2) Name the chain as if it were an alkane and change the final “-e” to “-ol.”
- 3) Begin counting from the end closest to the –OH group and put the –OH location prior to that chain name using numbers (if required to remove ambiguity). The examples just given also include their systematic names. When more than one –OH functionality is present, use the endings “-diol”, “-triol,” etc.

For example,  $\begin{array}{c} \text{OH} \\ | \\ \text{H}_3\text{C}-\text{CH}-\text{CH}_3 \end{array}$  contains the 3-carbon alkane, propane. The –OH group is bound to the middle (#2) carbon and, so, this alcohol is named 2-propanol.

The older systematic naming system uses the following steps and generally applies to smaller alcohols.

- 1) Identify the organic group to which the alcohol is bound and name it as an alkane substituent group under the older system.
- 2) Add the word “alcohol” to complete the name.

Thus,  $\begin{array}{c} \text{OH} \\ | \\ \text{H}_3\text{C}-\text{CH}-\text{CH}_3 \end{array}$  has the  $\text{CH}_3\text{-CH-CH}_3$  group attached to the –OH group. This group is isopropyl and so the alcohol becomes ‘isopropyl alcohol.’ A common mistake made is to combine the two systems. Thus, isopropanol is a tempting, but incorrect, name for this alcohol.

### Halide compounds

Constructing the names of these compounds follows a similar path to that of the alcohols.

Since all of the halide unknowns in this course contain bromine, will use those as our examples.

- 1) Find the longest carbon chain that includes the carbon to which the –X group(s) is attached.
- 2) Name the molecule as if it were an alkane.
- 3) Number the carbons, starting from the end closest to the –X group. The name begins with

the number of the carbon to which the halide is bound, followed by the halogen (written as halo (e.g. bromo), followed by the alkane name. Multiple halides carry the Greek prefixes di-, tri-, etc.

- 4) When multiple, different groups are bound to the alkane, they are named alphabetically.

Numbering begins with the substituent which appears closest to the end of the chain. When this is a tie, the name closest to the beginning of the alphabet gets the lower number.

Following the alcohol example,  $\begin{array}{c} \text{Br} \\ | \\ \text{H}_3\text{C}-\text{CH}-\text{CH}_3 \end{array}$  has the  $\text{CH}_3\text{-CH-CH}_3$  group attached to the  $-\text{Br}$

group. This group is isopropyl and so the alcohol becomes 'isopropyl bromide.' A slightly more complicated example would be  $\begin{array}{c} \text{Br} \\ | \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$ . This contains the 3-carbon alkane, propane. The  $-\text{Br}$  group is bound to the middle (#2) carbon, as is a methyl group and, so, this alcohol is named

2-bromo-2-methylpropane. Likewise,  $\begin{array}{c} \text{Br} \\ | \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ | \\ \text{Br} \end{array}$  is 2,2-dibromopropane.