1.4 Alcohols, Ethers, and Thiols

Figure 1 Flambé is a cooking technique in which alcohol is added to food and heated until the alcohol ignites.

The flammability of alcohol was used in the past to determine whether producers of distilled alcoholic beverages were watering down their product. Ethanol, which contains 2 carbon atoms, is the alcohol in alcoholic beverages. To determine whether a beverage contained a certain concentration of ethanol, a small quantity of gunpowder was mixed with the beverage. If a spark ignited the gunpowder, the liquid contained at least 57 % alcohol by volume and the beverage was considered to be full strength: not watered down. Beverages that passed this test were labelled "100 percent proof." If the gunpowder did not ignite, the alcohol concentration was under proof and the water concentration too high. Most modern alcoholic-beverage containers still list the proof of the contents, but today the numerical value is typically based on the percentage of ethanol by volume. The mention of proof on the label of alcoholic drinks is for historical reasons. These days, the flammability of ethanol is more often used in the cooking technique known as flambé (**Figure 1**).

Although there are many important alcohols, the two simplest, methanol and ethanol, have the greatest commercial value. Methanol, also known as *wood alcohol* because it was originally obtained by heating wood in the absence of air, is now generally manufactured from methane. Ethanol can be manufactured by an addition reaction of ethene, although most ethanol, including beverage alcohol, is produced by fermentation of sugars from plants. Although ethanol is legally consumed in Canada, it has serious health effects and is toxic in large quantities.

Alcohols

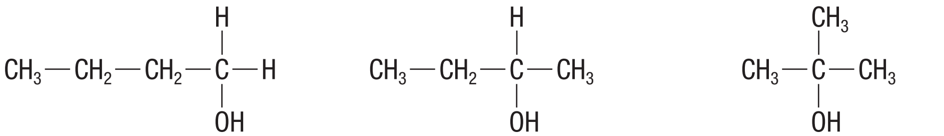
alcohol organic compound that contains the hydroxyl (–OH) functional group

primary alcohol an alcohol in which the hydroxyl group is bonded to a terminal carbon atom

secondary alcohol an alcohol in which the hydroxyl group is bonded to a carbon atom with two alkyl groups bonded to it

tertiary alcohol an alcohol in which the hydroxyl group is bonded to a carbon atom with three alkyl groups bonded to it

An **alcohol** is an organic compound that contains the hydroxyl group (–OH). Alcohols are classified according to the number of other carbon atoms that are directly bonded to the carbon atom attached to the hydroxyl group. For example, the 4-carbon alcohol, butanol, has three different isomers. Their properties depend on the arrangement of the carbon atoms within the molecule. Butan-1-ol (**Figure 2(a)**) is a **primary alcohol** because the –OH group is attached to the carbon atom at the end of the carbon chain, which has only 1 carbon atom attached to it. Butan-2-ol (**Figure 2(b)**) is a **secondary alcohol** because the –OH group is bonded to a carbon atom that is attached to 2 other carbon atoms. In a **tertiary alcohol**, such as 2-methylpropan-2-ol (**Figure 2(c)**), the carbon atom is bonded to the –OH group and 3 carbon atoms from alkyl groups.



(a) butan-1-ol
a primary alcohol (1°)

(b) butan-2-ol
a secondary alcohol (2°)

(c) 2-methyl-propan-2-ol
a tertiary alcohol (3°)

Figure 2 Examples of the three classes of alcohols

The presence of the electronegative oxygen atom in the –OH group affects the polarity of the molecule. The C–O bond is significantly more polar than the C–H bond based on the electronegativity difference between carbon and oxygen compared to that between carbon and hydrogen. The bond between oxygen and hydrogen is also polar. Therefore, alcohols (unlike hydrocarbons) are polar molecules.

Naming and Drawing Alcohols

IUPAC conventions for naming alcohols are similar to those for naming alkenes. We name an alcohol by replacing the final *-e* of the parent hydrocarbon with *-ol*. The name includes the number of the carbon atom to which the hydroxyl group is attached. If the chain also has hydrocarbon or halide constituents, we assign the lowest number to the carbon atom with the hydroxyl group.

The isomers of alcohols have different properties. For example, there are two isomers of propanol (**Figure 3**). Propan-1-ol is used as a solvent for lacquers and waxes, and as brake fluid. The other isomer, propan-2-ol (isopropyl alcohol), is also known as rubbing alcohol. It is used as an antiseptic to clean the skin before injections and in the manufacture of oils, gums, and propanone (also known as acetone). Both isomers of propanol are toxic to humans and many other animals if ingested.

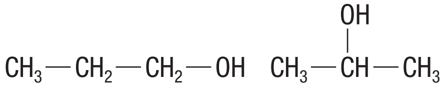
Alcohols containing more than one –OH group are referred to as polyalcohols. The suffix *-diol* (for two –OH groups) or *-triol* (for three –OH groups) is added to the alkane name instead of *-ol*. A common example of a polyalcohol is ethane-1,2-diol (**Figure 4(a)**), commonly known as ethylene glycol. This compound is widely used as antifreeze in automobile engines. Another common polyalcohol is propane-1,2,3-triol, commonly called glycerol or glycerine (**Figure 4(b)**). Since glycerine has a low toxicity and is soluble in water, it is frequently used in pharmaceutical preparations to help dissolve less polar compounds. The solubility in water is due to the three –OH groups, which increase the polarity.

Cyclic hydrocarbons may also form alcohols. The naming conventions for cyclic alcohols are the same as for straight-chain alcohols: Use the root name of the cyclic hydrocarbon, drop the ending, and add the suffix *-ol*. For example, the addition of an –OH group to cyclooctane results in cyclooctanol (**Figure 5(a)**).

When numbering the atoms in a cyclic hydrocarbon, the –OH functional group takes precedence over other substituents in naming. An example is 2,2-dimethylcyclohexanol. Even though there are two methyl groups, the number starts with the hydroxyl group (**Figure 5(b)**).

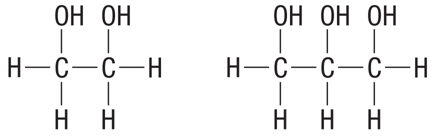
An aromatic hydrocarbon can have a bonded –OH group added, forming an aromatic alcohol. The simplest aromatic alcohol is a benzene ring with one hydroxyl group bonded to it. The IUPAC name for this compound is phenol (**Figure 5(c)**). If the benzene ring has two –OH groups, the name is based on benzene and includes the numbers for the –OH groups. An example is benzene-1,2-diol (**Figure 5(d)**).

In some cases, a different functional group takes precedence over the alcohol in naming. In this case, the –OH group is treated as a substituent, called *hydroxyl*. This convention applies to carboxylic acids, aldehydes, and ketones, which will be discussed later. When there is a multiple bond in the chain, the –OH group takes precedence (for example: pent-4-ene-1-ol).



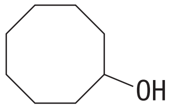
propan-1-ol propan-2-ol

Figure 3 The two isomers of propanol

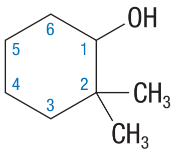


(a) ethane-1,2-diol **(b)** propane-1,2,3-triol

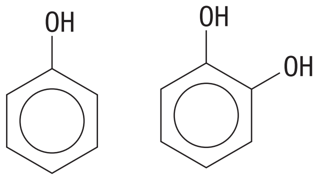
Figure 4 Two commonly used polyalcohols



(a) cyclooctanol



(b) 2,2-dimethylcyclohexanol



(c) phenol **(d)** benzene-1,2-diol

Figure 5 Four cyclic alcohols

Tutorial 1 Naming and Drawing Alcohols

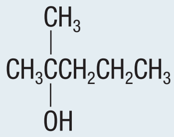
In this tutorial, you will first practise using the structure of an alcohol to determine its name. Then, you will practise drawing the structure of an alcohol from its name.

Naming alcohols follows many of the same steps that you have already learned:

1. Identify the longest carbon chain or ring.
2. If there is only one –OH group, the compound has the suffix *-ol*. If more than one group, use the suffixes *-diol* or *-triol*.
3. Number the parent chain from the end so that the –OH group is attached to the carbon atom with the lowest possible number.
4. Identify any other substituents and their locations.
5. If you are required to identify the type of alcohol, count the number of carbon atoms bonded to the atom to which the –OH group is attached.

Sample Problem 1: Naming Alcohols from Structural Formulas

Name the following alcohol and identify it as a primary, secondary, or tertiary alcohol:



Solution

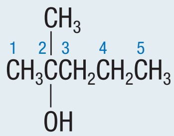
Step 1. Identify the longest carbon chain or ring.

In this compound, the longest chain has 5 carbon atoms: pentane.

Step 2. If there is only one –OH group, the compound has the suffix *-ol*. If more than one group, use the suffixes *-diol* or *-triol*.

There is one –OH group, so this compound is a pentanol.

Step 3. Number the parent chain from the end so that the –OH group is attached to the carbon atom with the lowest possible number.



The –OH group is attached to the second carbon atom: pentan-2-ol.

Step 4. Identify any other substituents and their locations.

There is also a methyl group attached to the second carbon atom.

This compound is 2-methylpentan-2-ol.

Step 5. Count the number of carbon atoms bonded to the atom to which the –OH group is attached.

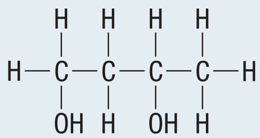
The carbon atom to which the hydroxyl group is attached is also bonded to 3 other carbon atoms, so this is a tertiary alcohol.

Sample Problem 2: Drawing Alcohols

Draw the structure of butane-1,3-diol.

Solution

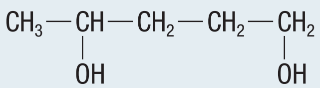
The name "butanediol" indicates that this alcohol consists of a 4-carbon chain with two hydroxyl groups attached to it. The hydroxyl groups are attached to the first and third carbon atoms. Therefore, the structure of this alcohol is



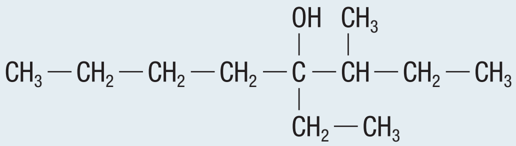
Practice

1. Write the name for each of the following compounds: K/U

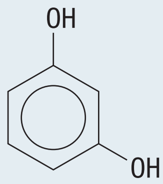
(a)



(b)



(c)



2. Draw the structural formula for each of the following alcohols: K/U C

(a) 2-chloro-2,5-dimethylheptan-3-ol

(b) propane-1,3-diol

(c) phenol

(d) pent-2-ene-1,4-diol

Properties of Alcohols

Alcohols typically have much higher boiling points than the corresponding unsubstituted alkanes. For example, the boiling point of methanol is 65 °C while the boiling point of methane is –162 °C. Consider the intermolecular forces that occur in the compounds in order to understand the differences in properties.

UNIT TASK **BOOKMARK**

Alcohols are relatively environmentally benign solvents for non-polar solutes. For the Unit Task (page 116), consider whether alcohols would be suitable alternatives to more toxic solvents.

Methane molecules are non-polar and exhibit only weak van der Waals forces. The polarity of methanol molecules, however, results in very strong dipole–dipole forces. These dipole interactions allow hydrogen bonding between the hydroxyl groups of adjacent molecules. As you may recall, **hydrogen bonding** is a type of dipole interaction in which the hydrogen atom attached to a highly electronegative atom on one molecule is strongly attracted to an electronegative atom on another molecule. In methanol, a hydroxyl hydrogen atom on one molecule forms a hydrogen bond with the oxygen atom of a neighbouring molecule (**Figure 6**). Hydrogen bonding between alcohol molecules means that more energy is needed in order to separate molecules from one another. This additional energy must be added to change the liquid into vapour, so the boiling point is higher.

hydrogen bonding a strong dipole–dipole force between a hydrogen atom attached to a highly electronegative atom (N, O, or F) in one molecule and a highly electronegative atom in another molecule

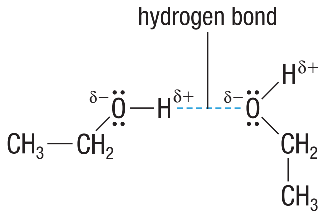


Figure 6 Hydrogen bonds form between the hydroxyl groups of adjacent alcohol molecules.

Simple alcohols with short carbon chains are more soluble in water than those with longer carbon chains. The addition of the –OH group increases the polarity of the alcohol molecule and, therefore, its solubility in water. However, as the size of the carbon chain grows, alcohols are less soluble in water. Because the hydrocarbon region of an alcohol molecule is non-polar, alcohols tend to be able to dissolve both polar and non-polar substances. This makes alcohols very useful as solvents.

Reactions Involving Alcohols

Recall from Section 1.2 that an alkene may react with water to produce an alcohol. This hydration reaction is a form of addition reaction. Many alcohols are manufactured commercially by the addition reaction of an alkene and water. An example is the formation of an alcohol from but-1-ene and water, using sulfuric acid as a catalyst. There are two possible products of this reaction: butan-1-ol and butan-2-ol. The reaction follows Markovnikov's rule, however: the hydrogen atom tends to bond to the carbon atom at the end of the butene chain, leaving the –OH group to attach to the second carbon atom. The production of butan-2-ol is therefore favoured. (**Figure 7**).

Investigation **1.4.1**

Properties of Alcohols (page 63)
In this controlled experiment you will make and test predictions about the properties of alcohols.

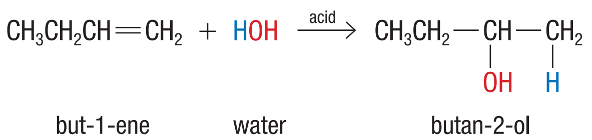


Figure 7 The reaction of but-1-ene with water produces butan-2-ol.

The modern method for production of methanol, CH_3OH, combines carbon monoxide with hydrogen gas at high temperature and pressure, using a catalyst. The chemical equation for this reaction is

$$CO(g) + 2\ H_2(g) \xrightarrow{\text{catalyst}} CH_3OH(l)$$

Ethanol or beverage alcohol, CH_3CH_2OH, is traditionally prepared by fermenting an aqueous sugar solution, usually from fruit or grains. This reaction requires the presence of yeast and the absence of oxygen. The chemical equation for this reaction is shown below.

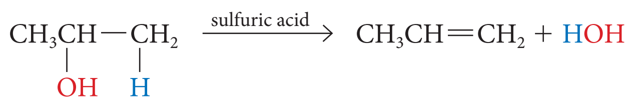
$$C_6H_{12}O_6(aq) \rightarrow 2\ CO_2(g) + 2\ C_2H_5OH(aq)$$

Like many organic compounds, alcohols undergo combustion with oxygen. This reaction, similar to the combustion of hydrocarbons, produces carbon dioxide and water. For example, the following equation represents the combustion of propanol:

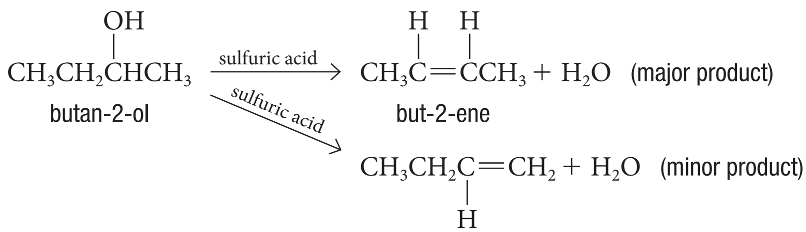
$$2\ CH_3CH_2CH_2OH(l) + 9\ O_2(g) \rightarrow 8\ H_2O(g) + 6\ CO_2(g)$$

The reverse of the addition reaction that produces an alcohol is a **dehydration reaction** to form an alkene and water. The reaction is catalyzed by sulfuric acid, which removes

dehydration reaction a reaction that involves the removal of a hydrogen atom and a hydroxyl group from the reactant, producing a slightly smaller molecule and water the hydrogen atom and hydroxyl group. The two adjacent carbon atoms form a double bond. An example of a dehydration reaction is the dehydration of propanol.



In dehydration reactions of secondary or tertiary alcohols containing more than 3 carbon atoms, more than one alkene may potentially be produced. Predicting the major product is beyond the scope of this course.



In the following tutorial, you will study examples of reactions involving alcohols: addition and dehydration. Addition reactions will be familiar, as you encountered them in Section 1.2.

Tutorial 2 Predicting Reactions Involving Alcohols

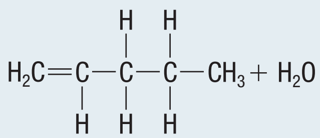
In this tutorial, you will learn to predict the products of two different reactions involving alcohols.

Sample Problem 1: Addition Reaction to Form an Alcohol

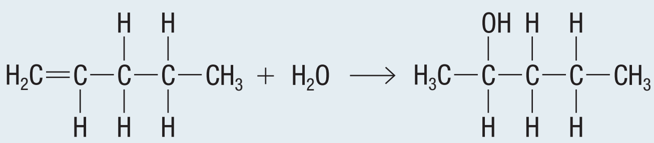
Write the chemical equation for the addition reaction of pent-1-ene and water.

Solution

First, draw the reactants, pent-1-ene and water.



As the molecule being added is water, this is a hydration reaction. During the hydration reaction, the double bond will break. According to Markovnikov's rule, a hydrogen atom from the water molecule will tend to bond to the carbon atom that is already bonded to the greatest number of hydrogen atoms. In pent-1-ene, that is the first carbon atom.



Therefore, the main product of the reaction is pentan-2-ol.

Sample Problem 2: Dehydration Reaction of an Alcohol

Write the chemical equation for the dehydration of ethanol.

Solution

During a dehydration reaction, a water molecule is removed from an alcohol to form an alkene. Ethanol contains only 2 carbon atoms, so there is only one possibility for the position of the double bond; the resulting alkene is ethene. The chemical reaction is

$$C_2H_5OH(l) \xrightarrow{H_2SO_4} C_2H_4(g) + H_2O(g)$$

Practice

1. Draw the chemical equation, showing structural formulas, for the addition reaction that forms butan-2-ol. T/I
2. Write the chemical equation for the dehydration of pentanol. T/I

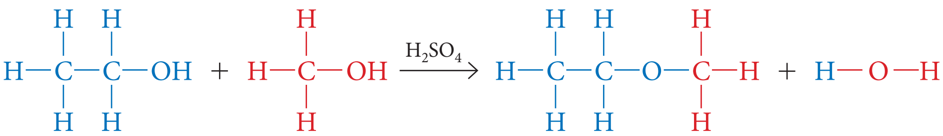
Ethers

Physicians and chemists have long searched for substances that would eliminate pain during medical procedures. A Boston dentist demonstrated the use of dinitrogen monoxide as an anesthetic in 1844. Around the same time, another organic compound was being tested. The compound ethoxyethane (also named diethyl ether or, at that time, simply "ether") is an effective anesthetic. Although ethoxyethane has been used successfully for decades, it is very volatile and flammable. Because of this hazard, ethoxyethane has largely been replaced by safer compounds. Currently, its major use is as a solvent for fats and oils.

An **ether** is an organic compound that contains a functional group in which an oxygen atom is bonded between 2 carbon atoms within a chain. Ethers can be synthesized from the reaction of alcohols. When the alcohols react, a molecule of water is produced in a **condensation reaction**:

ether an organic compound containing an oxygen atom between 2 carbon atoms in a chain

condensation reaction a chemical reaction in which two molecules combine to form a larger molecule and a small molecule, such as water



$$CH_3CH_2OH + CH_3OH \xrightarrow{H_2SO_4} CH_3CH_2OCH_3 + HOH$$

ethanol, methanol, methoxyethane, water

Experimental evidence shows that the boiling points of ethers tend to be slightly higher than those of similar-sized alkanes but lower than the boiling points of similar-sized alcohols. We can explain this by comparing the intermolecular forces in each type of compound. Ethers do not contain hydroxyl groups and they cannot form hydrogen bonds as alcohols do. However, the C–O bond is polar. Furthermore, unbonded electron pairs on the oxygen atom give the molecule a V shape. As a result, we can conclude that ether molecules are somewhat polar. The intermolecular forces in ethers are stronger than those in hydrocarbons but weaker than those in alcohols.

Ethers are useful solvents. The C–O bond allows them to dissolve highly polar substances, while the alkyl group allows them to dissolve less polar substances.

UNIT TASK BOOKMARK

Could we use ethers as solvents, to reduce toxic VOCs? Consider this question as you work on the Unit Task, described on page 116.

Naming Ethers

The IUPAC method to name an ether is to add the suffix *-oxy* to the smaller hydrocarbon group that is bonded to the larger alkane group. For example, an ether made up of a methyl group and an ethyl group joined by an oxygen molecule is called methoxyethane. A commonly used alternative nomenclature uses the names of the two hydrocarbon groups followed by the word "ether:" methylethyl ether. If the two alkane groups are the same size, the prefix *di-* is used. Thus, methoxymethane would be called dimethyl ether.

Tutorial 3 Naming and Drawing Ethers

In this tutorial, you will first practise naming ethers according to the IUPAC convention. Then, you will practise drawing structural formulas of ethers.

When naming ethers, follow these steps:

1. Identify the two alkyl groups.
2. Write the name of the shorter alkyl group, then the suffix -*oxy*, then the name of the longer alkyl group as if it were an alkane.

Sample Problem 1: Naming an Ether Given the Structural Formula

Write the name of the ether shown below.

$$H_3C—CH_2—CH_2—O—CH_3$$

Solution

Step 1. Identify the two alkyl groups.

This ether has a propyl group on one side of the oxygen atom and a methyl group on the other.

Step 2. Write the name of the shorter alkyl group, then the suffix -*oxy*, then the name of the longer alkyl group as if it were an alkane. In this case, a number is required to indicate the carbon atom in the propyl group to which the methoxy group is attached.

This ether is 1-methoxypropane.

Sample Problem 2: Drawing an Ether from Its Name

Draw the structural formula for 1-ethoxybutane.

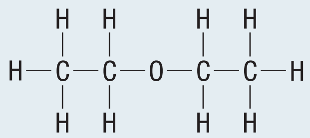
Solution

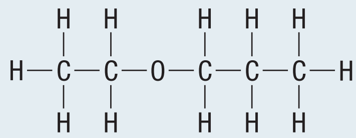
The longer carbon chain is butane, which has 4 carbon atoms. The shorter chain is ethyl, which has 2 carbon atoms. Therefore, 1-ethoxybutane has the following structure:

$$H_3C—CH_2—O—CH_2—CH_2—CH_2—CH_3$$

Practice

1. Name each of the following ethers: K/U

(a)


(b)


2. Draw the structural formula of each of the following ethers: K/U C

(a) 2-methoxypropane (b) 3-ethoxypentane

Thiols

thiol an organic compound that contains the sulfhydryl (–SH) group

A **thiol** is an organic compound that includes the sulfhydryl functional group, –SH. The sulfhydryl group is similar to the hydroxy group, –OH. Thiols generally have strong odours. For example, a thiol gives garlic its strong odour. The smell associated with the spray of a skunk is also caused by a thiol. Since sulfur is present in the products of digested proteins, thiols are also responsible for the strong stench of sewage.

Gas delivery companies add thiols to natural gas to make leaks easier to detect, since natural gas itself (mostly methane) has no odour.

Hydrogen peroxide reacts with thiols to form odourless disulfide compounds. Hence, hydrogen peroxide is sometimes used to neutralize the odours of many thiols.

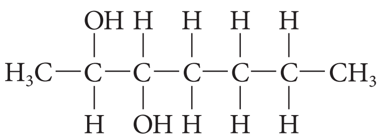
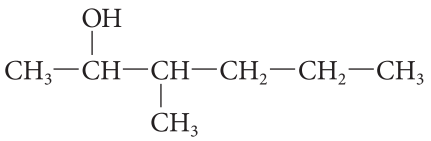
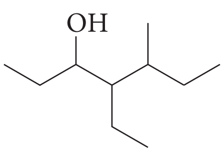
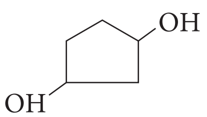
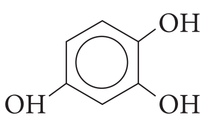
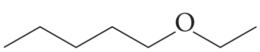
To name thiols, the suffix -*thiol* is added to the end of the alkane name. For example, $HSCH_3$ is methanethiol.

1.4 Review

Summary

- Alcohols contain a hydroxyl group, —OH. The hydroxyl group allows alcohols to form hydrogen bonds. Alcohols can be further classified as primary, secondary, and tertiary.
- Alcohols can be produced by hydration reactions of alkenes. Dehydration reactions use a catalyst and acid to change the alcohol back to an alkene and water. In a combustion reaction an alcohol reacts with oxygen, producing carbon dioxide and water.
- Ethers can be produced from the condensation reaction of alcohols. Ethers are widely used as solvents because of their ability to dissolve both polar and non-polar substances.
- Thiols contain the sulfhydryl functional group —SH. They typically have strong odours.

Questions

1. Write the name of each of the following compounds: K/U
   (a) 
   (b) 
   (c) 
   (d) 
   (e) 
   (f) $H_3C—CH_2—CH_2—CH_2—O—CH_2—CH_2—CH_3$
   (g) 
   (h) $H_3C—CH_2—SH$
2. Draw the structural formula for each of the following compounds: K/U C
   (a) 5-bromohexan-3-ol
   (b) 2-methylpentan-3-ol
   (c) 3,5-dichloropentan-2-ol
   (d) cyclobutane-1,2-dithiol
   (e) 2-methoxyheptane
   (f) cyclohex-4-ene-1,3-diol
3. If you were given two samples and told that one was ethanol and one was heptan-2-ol, describe two tests that you could run on the samples to identify them. T/I
4. Predict the product(s) of each of the following chemical reactions: T/I
   (a) hept-1-ene + water
   (b) butan-1-ol with sulfuric acid catalyst
   (c) propan-1-ol + ethanol
5. Write the chemical equation for the complete combustion of methanol. T/I
6. A chemist needs to synthesize 1-ethoxypentane. She has the following substances available: ethene, pent-1-ene, and water. Describe how the chemist could synthesize 1-ethoxypentane. (Assume that the chemist can use reaction conditions that allow her to overcome Markovnikov's rule.) T/I A
7. Rotten eggs have a distinct odour. Based on your reading in this section, what type(s) of compounds do you think are present in rotten eggs? Conduct research to check your reasoning. A

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