CHAPTER 23: ALCOHOLS, ETHERS AND RELATED GROUPS

Organic and Biochemistry Supplement to Enhanced Introductory College Chemistry

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In this chapter, you will learn about:

- Identifying alcohols, phenols, ethers and thiols
- Naming and drawing alcohols, phenols, ethers and thiols
- Reactions that produce alcohols
- Reactions of alcohols that produce other functional groups

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- General concepts of organic chemistry and general reactions of carbon (from Chapter 19: Organic Chemistry)
- Hydrocarbon nomenclature and physical properties (Chapter 20: Alkanes and Alkyl Halides and Chapter 22: Alkenes, Alkynes, and Aromatics)

Previously, we considered several kinds of hydrocarbons. Now we examine some of the many organic compounds that contain functional groups. We first introduced the idea of the functional group, a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to the molecule. If you understand the behaviour of a particular functional group, you will know a great deal about the general properties of that class of compounds. In this chapter, we take an in-depth look at alcohols, ethers and other related groups.



Figure 23.0a. A glass of beer. Photo by Josh Olalde on Unsplash

One of the more familiar alcohols on Earth is ethyl alcohol (ethanol). As the intoxicant in alcoholic beverages, ethanol is often simply called alcohol. If ethanol is diluted, as it is in wine, beer, or mixed drinks with about 1 oz of liquor, and if it is consumed in small quantities, it is relatively safe (Figure 23.0a.). In

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excess—four or more drinks in a few hours—it causes intoxication, which is characterized by a loss of coordination, nausea and vomiting, and memory blackouts.

Excessive ingestion of ethanol over a long period of time leads to cirrhosis of the liver, alteration of brain cell function, nerve damage, and strong physiological addiction. Alcoholism—an addiction to ethanol—is the most serious drug problem in the United States. Heavy drinking shortens a person's life span by contributing to diseases of the liver, the cardiovascular system, and virtually every other organ of the body.

In small quantities—one or two drinks a day—ethanol might promote health. In addition to the possible benefits of modest amounts of ethanol, a chemical in red wines, resveratrol, is thought to lower the risk of heart disease. Resveratrol, found in red grapes, is an antioxidant. It inhibits the oxidation of cholesterol and subsequent clogging of the arteries. One need not drink wine to get the benefits of resveratrol, however. It can be obtained by eating the grapes or drinking red grape juice.

Watch More Organic Nomenclature: Heteroatom Functional Groups: Crash Course Organic Chemistry #3 (youtube.com) (https://youtu.be/VAmVdxEksxY?) (12 mins).

Attribution & References

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23.1 ALCOHOLS - STRUCTURE, NAMING AND CLASSIFICATION

Learning Objectives

By the end of this section, you will be able to:

- Identify the general structure for an alcohol.
- Identify the structural feature that classifies alcohols as primary, secondary, or tertiary.
- Name alcohols with both common names and IUPAC names

Incorporation of an oxygen atom into carbon- and hydrogen-containing molecules leads to new functional groups and new families of compounds. When the oxygen atom is attached by single bonds, the molecule is either an alcohol or ether.

Alcohols are derivatives of hydrocarbons in which an –OH group has replaced a hydrogen atom. Although all alcohols have one or more hydroxyl (–OH) functional groups, they do not behave like bases such as NaOH and KOH. NaOH and KOH are ionic compounds that contain OH⁻ ions. Alcohols are covalent molecules; the –OH group in an alcohol molecule is attached to a carbon atom by a covalent bond.

We often represent alcohols by the general formula ROH, where R is an alkyl group. Alcohols are common in nature. Most people are familiar with ethyl alcohol (ethanol) (Figure 23.1a.), the active ingredient in alcoholic beverages, but this compound is only one of a family of organic compounds known as alcohols. The family also includes such familiar substances as cholesterol and the carbohydrates. Methanol (CH₃OH) and ethanol (CH₃CH₂OH) are the first two members of the homologous series of alcohols.



Figure 23.1a. Structure of ethanol a) structural formula, b) ball and stick model, c) space-filling model. (credit a: Image by Ju, PDM; b: Image by Benjah-bmm27, PDM; c: Image by Benjah-bmm27, PDM).

Alcohols have a minimum of one -OH group in the molecule. Alcohols containing two or more hydroxyl groups can be made. Many alcohols have more than one -OH group in the structure (e.g. glucose) but rarely does any one carbon have more than one -OH group (Figure 23.1b.).



Figure 23.1b. Structure of D-glucose and L-glucose showing multiple -OH groups per molecule (credit: Image by NEUROtiker, PDM).

Alcohols with two -OH groups on adjacent carbon atoms are commonly known as glycols. Additional examples include 1,2-ethanediol (ethylene glycol, used in antifreeze, sweet colourless and somewhat viscous liquid) and 1,2,3-propanetriol (glycerin or glycerol, used as a solvent for cosmetics and medicines, sweet syrupy liquid) (Figure 23.1c.). Ethylene glycol is quite toxic. Because it is sweet, pets often lap up spills of leaked antifreeze from a garage floor or driveway. Sometimes people, especially children, drink it. The oxidation of ethylene glycol by the liver results in calcium oxalate crystals forming in the kidneys which causes renal damage and possibly death. This is not true of propylene glycol which is essentially nontoxic, and it can be used as a solvent for drugs and as a moisturizing agent for foods.



Figure 23.1c. Structure of 1,2-ethanediol and 1,2,3-propanetriol (credit: *General Chemistry 1 & 2*, CC BY 4.0).

Nomenclature of Alcohols

According to the International Union of Pure and Applied Chemistry (IUPAC), alcohols are named by changing the ending of the parent alkane name to -ol. Here are some basic IUPAC rules for naming alcohols:

- 1. The longest continuous chain (LCC) of carbon atoms containing the OH group is taken as the parent compound—an alkane with the same number of carbon atoms. The chain is numbered from the end nearest the OH group.
- 2. The number that indicates the position of the OH group is prefixed to the name of the parent hydrocarbon, and the -e ending of the parent alkane is replaced by the suffix -ol.
 - In 2013, IUPAC adopted new nomenclature guidelines that require the position number to be placed as an "infix" rather than a prefix. For example, the new name for 2-propanol would be propan-2-ol. Widespread adoption of this new nomenclature will take some time.
 - In cyclic alcohols, the carbon atom bearing the OH group is designated C1, but the 1 is not used in the name.) Substituents are named and numbered as in alkanes.
- 3. If more than one OH group appears in the same molecule (polyhydroxy alcohols), suffixes such as *-diol* and *-triol* are used. In these cases, the *-e* ending of the parent alkane is retained.

Example 23.1a

Give the IUPAC name for each compound.



Solutions:

a. Ten carbon atoms in the LCC makes the compound a derivative of decane (rule 1), and the OH on the third carbon atom makes it a 3-decanol (rule 2).

(credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

The carbon atoms are numbered from the end closest to the OH group. That fixes the two methyl (CH₃) groups at the sixth and eighth positions. The name is 6,8-dimethyl-3-decanol (not 3,5-dimethyl-8-decanol).

b. Five carbon atoms in the LCC make the compound a derivative of pentane. Two OH groups on the first and fifth carbon atoms make the compound a diol and give the name 1,5-pentanediol (rule 3).

1 2 3 4 5 HOCH₂CH₂CH₂CH₂CH₂CH₂OH

(credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

Exercise 23.1a

Name the following molecule:

OH CH3 CH₂ CH3 CH_3 H_2

Check Your Answer:1

Exercise source: *General Chemistry* 1 & 2, CC BY 4.0.

Exercise 23.1b





Check Your Answers:²

Exercise source: Introduction to Chemistry: GOB(V. 1.0)., CC BY-NC-SA 3.0.

Example 23.1b

Draw the structure for each compound.

- a. hexan-2-ol
- b. 3-methyl-2-pentanol

Solution:

a) The ending –*ol* indicates an alcohol (the OH functional group), and the *hex*– stem tells us that there are six carbon atoms in the LCC. We start by drawing a chain of six carbon atoms: –C–C–C–C–C–C–.

The 2 indicates that the OH group is attached to the second carbon atom.



(credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

Finally, we add enough hydrogen atoms to give each carbon atom four bonds.

(credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0). b) Pent- means 5 carbon chain. The numbers indicate that there is a methyl (CH₃) group on the third carbon atom and an OH group on the second carbon atom.

(credit: Intro Chem: GOB (V. 1.0)., CC BY-NC-SA 3.0).

Exercise 23.1c

Draw the structure for each compound.

a. heptan-3-ol

b. 2-methyl-3-hexanol

Check Your Answers:³

Source: Exercise 23.1c is adapted from Basics of GOB Chemistry (Ball et al.), CC BY-NC-SA 4.0, with images drawn by Samantha Sullivan Sauer using Biovia Draw, CC BY-NC 4.0.

Alcohols with one to four carbon atoms are frequently called by common names, in which the name of the alkyl group is followed by the word *alcohol* (Figure 23.1d.). Structural formula of methyl alcohol, ethyl alcohol, propyl alcohol, and isopropyl alcohol with the methyl, ethyl propyl, and isopropyl groups are highlighted in green in Figure 23.1c.

Methyl alcohol

Ethyl alcohol

Propyl alcohol

Isopropyl alcohol

Figure 23.1d.

Structure of methyl alcohol (methanol), ethyl alcohol (ethanol), Propyl alcohol (propan-1-ol), and Isopropyl alcohol (propan-2-ol) (credit: Intro Chem: GOB (V. 1.0)., CC BY-NC-SA 3.0).

Classification of Alcohols

Some of the properties of alcohols depend on the number of carbon atoms attached to the specific carbon atom that is attached to the OH group. Alcohols can be grouped into three classes on this basis.

• A **primary (1°) alcohol** is one in which the carbon atom (in red) with the OH group is attached to *one* other carbon atom (in blue) (Figure 23.1e.). Its general formula is RCH₂OH.



Figure 23.1e. Structure of primary (1^o) alcohol (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

• A secondary (2°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *two* other carbon atoms (in blue) (Figure 23.1f.). Its general formula is R₂CHOH.



Figure 23.1f. Structure of secondary (2⁰) alcohol (credit: Intro Chem: GOB (V. 1.0)., CC BY-NC-SA 3.0).

• A **tertiary (3°) alcohol** is one in which the carbon atom (in red) with the OH group is attached to *three* other carbon atoms (in blue) (Figure 23.1g.). Its general formula is R₃COH.



Figure 23.1g. Structure of tertiary (3⁰) alcohol (credit: Intro Chem: GOB (V. 1.0)., CC BY-NC-SA 3.0).

Some of the common names reflect a compound's classification as secondary (*sec-*) or tertiary (*tert-*). These designations are not used in the IUPAC nomenclature system for alcohols. There are four butyl alcohols corresponding to the four butyl groups: the butyl group (CH₃CH₂CH₂CH₂-), and three others in Figure 23.1h.



Figure 23.1h. Structure of isobutyl, sec-butyl and tert-butyl groups (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

Table 23.1a. names and classifies some of the simpler alcohols.

Table 23.1a. Classification and Nomenclature of Some Alcohols (Image Credits: Introduction to Chemistry: GOB (V. 1.0)., CC BY-NC-SA 3.0.)

Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
CH ₃ OH	_	methyl alcohol	methanol
CH ₃ CH ₂ OH	primary	ethyl alcohol	ethanol
CH ₃ CH ₂ CH ₂ OH	primary	propyl alcohol	1-propanol
(CH ₃) ₂ CHOH	secondary	isopropyl alcohol	2-propanol
CH ₃ CH ₂ CH ₂ CH ₂ OH	primary	butyl alcohol	1-butanol
CH ₃ CH ₂ CHOHCH ₃	secondary	sec-butyl alcohol	2-butanol
(CH ₃) ₂ CHCH ₂ OH	primary	isobutyl alcohol	2-methyl-1-propanol
(CH ₃) ₃ COH	tertiary	<i>tert-</i> butyl alcohol	2-methyl-2-propanol
ОН	secondary	cyclohexyl alcohol	cyclohexanol

Indigenous Perspectives: Traditional Plant-Based Remedies

Many modern medicines have their roots in Indigenous traditional plant-based remedies. One such example is salicin. Salicin is a pain killing compound derived from the willow tree. Its structure has multiple -OH groups (Figure 23.1i.). On Turtle Island, Inuit harvest dwarf willow (a tiny bush that grows in the Arctic environment and a relative of the willow tree) as a source of pain relief (Figure 23.1i.). We now know that salicin is the active ingredient which is transformed in the human body to salicylic acid. Salicylic acid is related to acetylsalicylic acid commercially known under the brand name of Aspirin (Anderson & Rayner-Canham, 2022).



Figure 23.1i. Dwarf willow (*Salix herbacea*) (left). Salicin molecule (right) (credit left: Image by El Grafo, CC BY-SA 3.0; right: Image by Fuse809; PDM).

Spotlight on Everyday Chemistry: Hand Sanitizers

Hand sanitizers use alcohol to protect against infections including from viruses and bacteria. Infographic 23.1a. shows some of the alcohols used and how the alcohol helps prevent infection.



Infographic **23.1a.** Read more about "Coronavirus: How hand sanitisers protect against infections (https://www.comp oundchem.com/ 2020/03/04/ hand-sanitisers/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 23.1a [New tab].

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Anderson, C. C., & Rayner-Canham, G. (2022, Fall). Chemistry of the cure: Case studies of some Inuit remedies. *Chem 13 News Magazine*.

Notes

- 1. 2-methyl-2-pentanol
- 2. a) 1,2-propanediol b) 1-methylcyclopentanol



23.2 PHYSICAL PROPERTIES OF ALCOHOLS

Learning Objectives

By the end of this section, you will be able to:

- Explain why the boiling points of alcohols are higher than those of ethers and alkanes of similar molar masses.
- Explain why alcohols and ethers of four or fewer carbon atoms are soluble in water while comparable alkanes are not soluble.

Alcohols can be considered derivatives of water (H_2O ; also written as HOH) (Figure 23.2a.). Refer to Appendix A: Key Element Information for more details about oxygen.



Figure 23.2a. Structure of water (left) and alcohol (right) (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

Like the H–O–H bond in water, the R–O–H bond is bent, and alcohol molecules are polar (Figure 23.2b.).



Figure 23.2b. Bent structure of alcohol showing the presence of two lone pairs of electrons on the oxygen atom and the carbon-oxygen-hydrogen bond angle of 109° (credit: Image by RamaKrishnaHare, CC BY-SA 4.0).

Boiling Point

The relationship between the structure of water and the structure of alcohols is particularly apparent in small molecules and reflected in the physical and chemical properties of alcohols with low molar mass. Replacing a hydrogen atom from an alkane with an OH group allows the molecules to associate through hydrogen bonding (Figure 23.2c.).



Figure 23.2c. Intermolecular hydrogen bonding in methanol. The OH groups of alcohol molecules make hydrogen bonding possible (credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

Recall that physical properties are determined to a large extent by the type of intermolecular forces. Table 23.2a. lists the molar masses and the boiling points of some common compounds. The table shows that substances with similar molar masses can have quite different boiling points.

Formula	Name	Molar Mass	Boiling Point (°C)
CH ₄	methane	16	-164
НОН	water	18	100
C_2H_6	ethane	30	-89
CH ₃ OH	methanol	32	65
C_3H_8	propane	44	-42
CH ₃ CH ₂ OH	ethanol	46	78
$C_{4}H_{10}$	butane	58	-1
CH ₃ CH ₂ CH ₂ OH	1-propanol	60	97

Table 23.2a. Comparison of Boiling Points and Molar Masses (Image Credits: Introductionto Chemistry: GOB (V. 1.0)., CC BY-NC-SA 3.0.)

Alkanes are nonpolar and are thus associated only through relatively weak dispersion forces. Alkanes with one to four carbon atoms are gases at room temperature. In contrast, even methanol (with one carbon atom) is a liquid at room temperature. Hydrogen bonding greatly increases the boiling points of alcohols compared to hydrocarbons of comparable molar mass. The boiling point is a rough measure of the amount of energy necessary to separate a liquid molecule from its nearest neighbours. If the molecules interact through hydrogen bonding, a relatively large quantity of energy must be supplied to break those intermolecular attractions. Only then can the molecule escape from the liquid into the gaseous state.

Adding additional -OH groups to an alcohol molecule will increase the boiling point because there are more opportunities for hydrogen bonding. Consider propan-1-ol (CH₃CH₂CHOH) which has a molar mass of 60 g/mol and a boiling point of 97° C. Now consider 1,2-ethanediol, also known as ethylene glycol, which has a molar mass of 62 g/mol and a boiling point of 197° C. The presence of one additional -OH group significantly increase the hydrogen bonding ability and as such the boiling point (National Center for Biotechnology Information, 2024a,b).

Ethylene glycol is the main ingredient in many antifreeze mixtures for automobile radiators. Because of its high boiling point, ethylene glycol does not boil away when it is used as an antifreeze. It is also completely miscible with water. A solution of 60% ethylene glycol in water freezes at -49° C (-56° F) and thus protects an automobile radiator down to that temperature.

Solubility

Alcohols can also engage in hydrogen bonding with water molecules (Figure 23.2d.). Thus, whereas the hydrocarbons are insoluble in water, alcohols with one to three carbon atoms are completely soluble.



Figure 23.2d. Intermolecular hydrogen bonding between ethanol (an alcohol) and water molecules. The OH groups of alcohol molecules allow for the hydrogen bonding to occur with the water molecules. (Credit: *Introduction to Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

As the length of the chain increases, however, the solubility of alcohols in water decreases; the molecules become more like hydrocarbons and less like water. The alcohol 1-decanol

Adding additional -OH groups to an alcohol molecule will increase the solubility because there are more opportunities for hydrogen bonding with water. Consider hexan-1-ol (CH₃CH₂CH₂CH₂CH₂CH₂OH) which has a molar mass of 102 g/mol and a solubility of 5.9 g/L at 25°C. Now consider D-glucose, also known as 2,3,4,5,6-pentahydroxyhexanal (see Figure 23.1b), which has a molar mass of 180 g/mol and a solubility of 909 g/L at 25°C. The presence of additional -OH groups significantly increase the hydrogen bonding ability with water and as such the solubility (National Center for Biotechnology Information, 2024c; "Glucose", 2023).

Spotlight on Everyday Chemistry: Glycerol

The physical properties of compounds greatly impact their everyday uses. Infographic 23.2a. highlights some key uses of glycerol (1,2,3-propanetriol).



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23.3 FORMATION OF ALCOHOLS

Learning Objectives

By the end of this section, you will be able to:

- Describe how to prepare alcohols from alkenes
- Describe other methods to prepare alcohols

Organic functional groups can be converted into other functional groups through reactions. A map of some of the more common reactions to convert functional groups can be found in Section 19.6 – General Reactions of Carbon in Infographic 19.6a.

Preparation of Methanol and Ethanol

Methanol is prepared by combining hydrogen gas and carbon monoxide at high temperatures and pressures in the presence of a catalyst composed of zinc oxide (ZnO) and chromium oxide (Cr₂O₃) catalyst (Figure 23.3a.).

$$2\mathrm{H}_2 + \mathrm{CO} \xrightarrow{200 ext{ atm, } 350\,^\circ\mathrm{C}} \mathrm{CH}_3\mathrm{OH}$$

Figure 23.3a. Preparation of methanol from carbon monoxide. (Credit: *Introduction to Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

Methanol is an important solvent and is used as an automotive fuel, either as the pure liquid—as in some racing cars—or as an additive in gasoline. Nearly 2 billion gallons of methanol are produced each year in the United States by the catalytic reduction of carbon monoxide with hydrogen gas.

Ethanol, CH₃CH₂OH, also called ethyl alcohol, is a particularly important alcohol for human use. Ethanol is the alcohol produced by some species of yeast that is found in wine, beer, and distilled drinks. It is made by

the fermentation of sugars or starch from various sources (potatoes, corn, wheat, rice, etc.). It has long been prepared by humans harnessing the metabolic efforts of yeasts in fermenting various sugars (Figure 23.3b.).



Figure 23.3b. Preparation of ethanol from glucose using yeast (credit: *Chemistry (OpenStax)* (*https://openstax.org/books/chemistry/pages/20-2-alcohols-and-ethers*), CC BY 4.0).

Organic and biochemical equations are frequently written showing only the organic reactants and products. In this way, we focus attention on the organic starting material and product, rather than on balancing complicated equations.

Spotlight on Everyday Chemistry: Physiological Effects of Alcohols

Methanol is quite poisonous to humans. Ingestion of as little as 15 mL of methanol can cause blindness, and 30 mL (1 oz) can cause death. However, the usual fatal dose is 100 to 150 mL. The main reason for methanol's toxicity is that we have liver enzymes that catalyze its oxidation to formaldehyde (methanal), the simplest member of the aldehyde family (Figure 23.3c.).



Figure 23.3c. Conversion of methanol to formaldehyde (methanal). (Credit: *Introduction to Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

Formaldehyde reacts rapidly with the components of cells, coagulating proteins in much the same way that cooking coagulates an egg. This property of formaldehyde accounts for much of the toxicity of methanol.

Ethanol is oxidized in the liver to acetaldehyde (ethanal) (Figure 23.3d.).



Figure 23.3d. Conversion of ethanol to acetaldehyde (ethanal). (Credit: *Introduction to Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

The acetaldehyde is in turn oxidized to acetic acid (HC₂H₃O₂), a normal constituent of cells, which is then oxidized to carbon dioxide and water. Even so, ethanol is potentially toxic to humans. The rapid ingestion of 1 pt (about 500 mL) of pure ethanol would kill most people, and acute ethanol poisoning kills several hundred people each year. Ethanol freely crosses into the brain, where it depresses the respiratory control center, resulting in failure of the respiratory muscles in the lungs and hence suffocation. Ethanol is believed to act on nerve cell membranes, causing a diminution in speech, thought, cognition, and judgment.

Rubbing alcohol is usually a 70% aqueous solution of isopropyl alcohol (propan-2-ol). It has a high vapor pressure, and its rapid evaporation from the skin produces a cooling effect. It is toxic when ingested but compared to methanol, is less readily absorbed through the skin.

Hydration of Alkenes

Many simple alcohols are made by the hydration of alkenes. Ethanol is made by the hydration of ethylene in the presence of a catalyst such as sulfuric acid (H_2SO_4) (Figure 23.3e.).



Figure 23.3e. Formation of ethanol from addition of water to ethene (ethylene). (Credit: *Introduction to Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

In a similar manner, isopropyl alcohol (2-propanol) is produced by the addition of water to propene (propylene) (Figure 23.3f.). In this reaction, Markovnikov's Rule applies to the carbon-carbon double bond addition (see details in Section 22.3). The -OH group of the water molecule will attach to the carbon of the carbon-carbon double bond that has more alkyl substituents. The H of the water molecule will attach to the carbon 2 rather than carbon 2.

Propylene



Isopropyl alcohol (2-propanol)

Figure 23.3f.

Formation of 2-propanol (isopropyl alcohol) from addition of water to propene (propylene). (Credit: Introduction to Chemistry: GOB (V. 1.0)., CC BY-NC-SA 3.0.)

Example 23.3a

Write the equation for the reaction of 2-butene with water to form an alcohol. What alcohol is formed? Indicate that sulfuric acid is used as a catalyst.

Solution

First write the condensed structural formula of 2-butene and indicate that it reacts with water. When water adds to the carbon-carbon double bond, 2-butanol is formed. Then write the condensed structural formula of 2-butanol after the reaction arrow to indicate that it is the product. Finally, write the formula for the catalyst above the arrow.

$CH_{3}CH = CHCH_{3} + H_{2}O \xrightarrow{H_{2}SO_{4}} CH_{3}CH_{2}CH_{2}CH_{3}$	(Credit: Introduction to Chemistry: GOB (V. 1.0)., CC BY-NC-SA 3.0.)
On	DT-NC-SASU.)

Example source: Adapted by Samantha Sullivan Sauer from *Introduction to Chemistry: GOB(V. 1.0).*, CC BY-NC-SA 3.0.

Exercise 23.3a

Write the equation for the reaction of cyclopentene with water to form an alcohol. What alcohol is formed? Indicate that phosphoric acid (H₃PO₄) is used as a catalyst.

Check Your Answer:1

Exercise source: Adapted by Samantha Sullivan Sauer from *Introduction to Chemistry: GOB(V. 1.0).*, CC BY-NC-SA 3.0, using images from Biovia Draw, licensed under CC BY-NC 4.0

Other Alcohol Producing Reactions

Alkyl Halide Substitution

In this substitution reaction, an alkyl halide is reacted with sodium hydroxide (NaOH) or potassium (KOH) for form an alcohol. This works for producing primary and, occasionally, secondary alcohols only (Figure 23.3g.). A by-product of sodium or potassium salt is formed. ("Alcohol (chemistry)", 2024).

Figure 23.3g. Alkyl halide substitution with sodium hydroxide to form primary alcohol. (credit: Samantha Sullivan Sauer / Biovia Draw, CC BY-NC 4.0)

Ester Hydrolysis

An ester is the product of an alcohol and a carboxylic acid. When this reaction is reversed, an alcohol is produced. This process will be explained in further detail in Chapter 25.



Figure 23.3h. Hydrolysis of an ester to produce an alcohol and a carboxylic acid (credit: Image by Ahazard.sciencewriter, CC BY-SA 4.0).

Reduction of Aldehydes and Ketones

An aldehyde or ketone, when reduced, will form a primary or secondary alcohol respectively (Figure 23.3i.). This process will be explained in further detail in Chapter 24.



Figure 23.3i. An aldehyde is reduced to a primary alcohol. A ketone is reduced to a secondary alcohol (*Organic Chemistry*, CC BY-NC-SA 4.0)

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- "18.2 Alcohols and Ethers (https://boisestate.pressbooks.pub/chemistry/chapter/21-2-alcohols-and-ethers/)" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction).*

References cited in-text

Alcohol (chemistry) (https://en.wikipedia.org/wiki/Alcohol_(chemistry)). (2024, January 26). In Wikipedia.

Notes



1. cyclopentanol is formed in this reaction. cyclopentene

cyclopentanol

23.4 REACTIONS OF ALCOHOLS

Learning Objectives

By the end of this section, you will be able to:

- Learn about the major types of reactions of alcohols.
- Describe the result of the oxidation of a primary and secondary alcohols.
- Draw the products from dehydration of alcohols.
- Understand the production of alcohols from esters.

Organic functional groups can be converted into other functional groups through reactions. A map of some of the more common reactions to convert functional groups can be found in Section 19.6 – General Reactions of Carbon in Infographic 19.6a.

Chemical reactions in alcohols occur mainly at the functional group, but some involve hydrogen atoms attached to the OH-bearing carbon atom or to an adjacent carbon atom. We will be discussing three major kinds of alcohol reactions – substitution, elimination and oxidation.

The versatility of the alcohol functional group is well defined as it can be transformed into many other functional groups. Figure 23.4a. highlights the formation of aldehydes, ketones, carboxylic acids, ethers, alkenes, and esters.





Oxidation

Primary and secondary alcohols are readily oxidized. We saw earlier how methanol and ethanol are oxidized by liver enzymes to form aldehydes. Because a variety of oxidizing agents can bring about oxidation, we can indicate an oxidizing agent without specifying a particular one by writing an equation with the symbol [O] above the arrow. For example, we write the oxidation of ethanol, a primary alcohol, to form acetaldehyde or ethanal, an aldehyde, as shown in Figure 23.4b.

$$CH_3CH_2OH \xrightarrow{[0]} CH_3CH=O$$

Ethanol (a primary alcohol) Acetaldehyde (an aldehyde) Figure 23.4b.

Oxidation of ethanol to ethanal (acetaldehyde). (Credit: Introduction to Chemistry: GOB (V. 1.0)., CC BY-NC-SA 3.0.)

We shall see that aldehydes are even more easily oxidized than alcohols and yield carboxylic acids. Secondary alcohols are oxidized to ketones. The oxidation of propan-2-ol (isopropyl alcohol) by potassium dichromate (K₂Cr₂O₇) gives propanone (acetone), the simplest ketone (Figure 23.4c.).



Figure 23.4c. Oxidation of propan-2-ol (isopropyl alcohol) to propanone (acetone) (Credit: *Introduction to Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0).

Unlike aldehydes, ketones are relatively resistant to further oxidation, so no special precautions are required to isolate them as they form. Note that in oxidation of both primary (RCH₂OH) and secondary (R₂CHOH) alcohols, two hydrogen atoms are removed from the alcohol molecule, one from the OH group and other from the carbon atom that bears the OH group.

Alcohol oxidation is important in living organisms. Enzyme-controlled oxidation reactions provide the energy cells need to do useful work. One step in the metabolism of carbohydrates involves the oxidation of the secondary alcohol group in isocitric acid to a ketone group (Figure 23.4d.). The overall type of reaction is the same as that in the conversion of isopropyl alcohol to acetone.





Tertiary alcohols (R₃COH) are resistant to oxidation because the carbon atom that carries the OH group does not have a hydrogen atom attached but is instead bonded to other carbon atoms. The oxidation reactions we have described involve the formation of a carbon-to-oxygen double bond. Thus, the carbon atom bearing the OH group must be able to release one of its attached atoms to form the double bond. The carbon-to-hydrogen bonding is easily broken under oxidative conditions, but carbon-to-carbon bonds are not. Therefore tertiary alcohols are not easily oxidized.

The process of oxidation of alcohols is highlighted in Infographic 23.4a.



Infographic 23.4a. Read more about "A Guide to Oxidation Reactions of Alcohols (https://www.compoundchem.com/2016/05/04/oxidation-reactions-of-alcohols/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 23.4a [New tab].

Example 23.4a

Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write "no reaction" after the arrow.



(Credit: Introduction to Chemistry: GOB (V. 1.0)., CC BY-NC-SA 3.0.)

Solution

The first step is to recognize the class of each alcohol as primary, secondary, or tertiary.

a. This alcohol has the OH group on a carbon atom that is attached to only *one* other carbon atom, so it is a primary alcohol. Oxidation forms first an aldehyde and further oxidation forms a carboxylic acid.

$$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}OH \xrightarrow{[0]} CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}C \xrightarrow{[0]} H$$

$$\xrightarrow{[0]} CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}C \xrightarrow{[0]} OH$$

(Credit: Introduction to Chemistry: GOB (V. 1.0)., CC BY-NC-SA 3.0.)

b. This alcohol has the OH group on a carbon atom that is attached to three other carbon atoms, so it is a tertiary alcohol. No reaction occurs.

$$\begin{array}{c} \mathsf{CH}_{3} \\ \mathsf{H}_{3} \\ \mathsf{CH}_{3} \\ \mathsf{CCH}_{2} \\ \mathsf{CH}_{3} \\ \mathsf{CH}_{3} \\ \mathsf{OH} \end{array} \xrightarrow{[\mathsf{O}]} \text{ no reaction}$$

(Credit: Introduction to Chemistry: GOB (V. 1.0)., CC BY-NC-SA 3.0.)

c. This alcohol has the OH group on a carbon atom that is attached to two other carbon atoms, so it is a secondary alcohol; oxidation gives a ketone.

$$\begin{array}{ccc} OH & O \\ | & & \parallel \\ CH_3CHCH_2CH_2CH_2CH_3 & \xrightarrow{(O)} & CH_3CCH_2CH_2CH_2CH_3 \end{array}$$

(Credit: Introduction to Chemistry: General, Organic, and Biological (V. 1.0)., CC BY-NC-SA 3.0.)

Spotlight on Everyday Chemistry: Chemistry of a Hangover

The process of alcohol oxidation is key to the effects of alcohol in the human body. Infographic 24.3b. highlights some of the chemistry of a hangover.



Infographic 23.4b. Read more about "What causes hangovers?

causes hangovers? A biochemical mystery (https://www.comp oundchem.com/ 2016/01/01/ hangover/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 23.4b [New tab].

Ethanol: Chemical, Drug & Poison

Ethanol is classified medically as a central nervous system (CNS) depressant. Its effects—that is, being drunk—resemble the human response to anesthetics. There is an initial excitability and increase in sociable behavior, but this results from depression of inhibition rather than from stimulation. At a blood alcohol concentration of 0.1% to 0.3%, motor coordination is affected, accompanied by loss of balance, slurred speech, and amnesia. When blood alcohol concentration rises to between 0.3% and 0.4%, nausea and loss of consciousness occur. Above 0.6%, spontaneous respiration and cardiovascular regulation are affected, ultimately leading to death. The LD₅₀ of ethanol is 10.6 g/kg.

The passage of ethanol through the body begins with its absorption in the stomach and small intestine, followed by rapid distribution to all body fluids and organs. In the pituitary gland, ethanol inhibits the production of a hormone that regulates urine flow, causing increased urine production and dehydration. In the stomach, ethanol stimulates production of acid. Throughout the body,

ethanol causes blood vessels to dilate, resulting in flushing of the skin and a sensation of warmth as blood moves into capillaries beneath the surface. The result is not a warming of the body, but an increased loss of heat at the surface.

Ethanol metabolism occurs mainly in the liver and proceeds by oxidation in two steps, first to acetaldehyde (CH₃CHO) and then to acetic acid (CH₃CO₂H). When continuously present in the body, ethanol and acetaldehyde are toxic, leading to the devastating physical and metabolic deterioration seen in people with chronic alcohol use disorder. The liver usually suffers the worst damage since it is the major site of alcohol metabolism.

Approximately 17,000 people are killed each year in the United States in alcohol-related automobile accidents. Thus, all 50 states have made it illegal to drive with a blood alcohol concentration (BAC) above 0.08%. Fortunately, simple tests have been devised for measuring blood alcohol concentration. The original breath analyzer test measured alcohol concentration in expired air by the colour change occurring when the bright-orange oxidizing agent potassium dichromate (K₂Cr₂O₇) reduced to blue-green chromium(III). Current consumer devices use a conductivity sensor, and tests used by law-enforcement agencies use IR spectroscopy to measure blood-alcohol levels in expired air. Just breathe into the machine, and let the spectrum tell the tale.

Source: "Ethanol: Chemical, Drug & Poison" is adapted from "Ch. 17 Chemistry Matters—Ethanol: Chemical, Drug, and Poison" In *Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/1-why-this-chapter)*, CC BY-NC-SA 4.0.

Exercise 23.4a

Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write "no reaction" after the arrow.



(Credit: Introduction to Chemistry: GOB (V. 1.0)., CC BY-NC-SA 3.0.)

Check Your Answers:¹

Source: Exercise 23.4a is adapted from *Introduction to Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0 with solution images by Samantha Sullivan Sauer using Biovia Draw.

Elimination – Dehydration Reactions

Formation of Alkenes

As noted in Figure 24.3a., an alcohol undergoes dehydration in the presence of a catalyst to form an alkene and water or an ether and water. It all depends on the conditions.

To form an alkene, the reaction requires a higher temperature and limited supply of alcohol. The reaction removes the OH group from the alcohol carbon atom and a hydrogen atom from an adjacent carbon atom in the same molecule (Figure 24.3e.):



Figure 23.4e. Elimination of water (dehydration) from an alcohol to form an alkene. (Credit: *Introduction to Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

The required dehydration reaction temperature is dependent on the classification of the starting alcohol. The needed temperature decreases with increasing substitution of the hydroxy-containing carbon:

- 1° alcohols: 170° 180°C
- 2° alcohols: 100°– 140 °C
- 3° alcohols: 25° 80°C

If the reaction is not sufficiently heated, the alcohols do not dehydrate to form alkenes, but react with one another to form ethers.

Example 23.4b

Draw the product of the dehydration of cyclohexanol.

Solution:



Example and image source: Supplemental Modules (Organic Chemistry), CC BY 4.0

Zaitsev's Rule

When an unsymmetrical alcohol undergoes dehydration to form an alkene, Zaitsev's rule applies. According to Zaitsev's rule, formulated in 1875 by the Russian chemist Alexander Zaitsev, elimination reactions generally (although not always) give the more stable alkene product—that is, the alkene with more alkyl substituents on the double-bond carbons. Another way to say this is the more highlysubstituted double bond isomer is favoured among the products.



Figure 23.4f. Dehydration of unsymmetrical secondary alcohol showing major and minor product according to Zaitsev's rule. (credit: *Supplemental Modules (Organic Chemistry)*, CC BY-NC-SA 4.0)

Exercise 24.3b

Draw the major product of the given reactions.



Check Your Answers:²

Source: Exercise 24.3b is adapted from *Organic Chemistry (Wade)*, images created by Samantha Sullivan Sauer using Biovia Draw, licensed under CC BY-NC-SA 4.0.

Formation of Ethers

Under the proper conditions (lower temperature and excess alcohol), it is possible for the dehydration to occur between *two* small primary alcohol molecules. The entire OH group of one molecule and only the hydrogen atom of the OH group of the second molecule are removed. The two ethyl groups attached to an oxygen atom form an ether molecule (Figure 23.4g.). Only symmetrical ethers can be prepared this way.

 $CH_{3}CH_{2}OH + HOCH_{2}CH_{3} \xrightarrow{concd H_{2}SO_{4}} CH_{3}CH_{2} - O - CH_{2}CH_{3} + H_{2}O$ Two molecules of ethanol Diethyl ether

Figure 23.4g. Elimination of water from two alcohol molecules to form an ether. (Credit: *Introduction to Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)
Example 23.4c

Write the two potential reactions from the dehydration of ethanol.

Solution:

The success of the dehydration reaction is dependent on the temperature and the amount of alcohol present. The two possible reactions are shown. You are not responsible for knowing the temperatures required.

Both reactions are dehydration reactions using sulfuric acid and result in a by-product of water. The first reaction (at lower temperature) combines two ethanol molecules to form diethyl ether (ethoxyethane). The second reaction (at higher temperature and limited alcohol) dehydrates intramolecularly resulting in ethene.

Example and image source: Synthesis of Ethers, CC BY-NC-SA 4.0

Both dehydration and hydration reactions occur continuously in cellular metabolism, with enzymes serving as catalysts and at a temperature of about 37°C. The following reaction occurs in the "Embden–Meyerhof" pathway (Figure 23.4h.).



Figure 23.4h. Dehydration of 2-phosphoglycerate into phosphoenolpyruvate. (Credit: *Introduction to Chemistry: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

Although the participating compounds are complex, the reaction is the same: elimination of water from the starting material. The idea is that if you know the chemistry of a particular functional group, you know the chemistry of hundreds of different compounds.

Esterification

Carboxylic acids can react with alcohols to form esters in a process called Fischer esterification. An acid catalyst is required and the alcohol is also used as the reaction solvent. The oxygen atoms are colour-coded in the reaction below to help understand the reaction mechanism.

Figure 23.4i. Process of esterification which combines a carboxylic acid with an alcohol (credit: *Organic Chemistry (Wade)*, CC BY-NC-SA 4.0).

For example, butanoic acid reacts with methanol to synthesize methyl butanoate. It is important to note that any proton source can be used as the catalyst. Sulfuric acid is shown in the example (Figure 23.4j.).



Figure 23.4j. Reaction of butanoic acid with methanol to form methyl butanoate (credit: *Organic Chemistry (Wade)*, CC BY-NC-SA 4.0).

Further details about esters and carboxylic acids are provided in Chapter 25.

Substitution of Alcohols

Although substitution of alcohols is not listed in Figure 23.4a., it is possible to form an alkyl halide from an alcohol.

When alcohols react with a hydrogen halide, a substitution takes place producing an alkyl halide and water:

 $R + OH + H - X \longrightarrow R - X + H_2O$

- The order of reactivity of alcohols is 3° > 2° > 1° methyl.
- The order of reactivity of the hydrogen halides is HI > HBr > HCl (HF is generally unreactive).

The reaction is acid catalyzed. Alcohols react with the strongly acidic hydrogen halides HCl, HBr, and HI, but they do not react with nonacidic NaCl, NaBr, or NaI. Primary and secondary alcohols can be

converted to alkyl chlorides and bromides by allowing them to react with a mixture of a sodium halide and sulfuric acid:

```
R-OH + NaX \xrightarrow{H_2SO_4} R-X + NaHSO<sub>4</sub> + H<sub>2</sub>O
```

Source: "17.6: Reactions of Alcohols" from *Organic Chemistry (Morsch et al)* is used under CC BY-SA 4.0.

Watch Alcohols, Ethers, and Epoxides: Crash Course Organic Chemistry #24 (youtube.com) (https://youtu.be/j04zMFwDeDU?) (12 min). Not all parts of the video apply to this text.

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Notes



23.5 PHENOLS

Learning Objectives

By the end of this section, you will be able to:

- Describe the structure and uses of some phenols
- Name phenols that contain 1 or more substituents according to the IUPAC

Structure of Phenols

Compounds in which an OH group is attached directly to an aromatic ring are designated ArOH (where Ar stands for aromatic) and called **phenols**. Phenols differ from alcohols in that they are slightly acidic in water. They react with aqueous sodium hydroxide (NaOH) to form salts.

(3.3.1)ArOH(aq)+NaOH(aq)→ArONa(aq)+H2O">ArOH $_{(aq)}$ +NaOH $_{(aq)}$ →ArONa $_{(aq)}$ +H₂O The parent compound, C₆H₅OH, is itself called phenol. (An old name, emphasizing its slight acidity, was *carbolic acid*.) Phenol is a white crystalline compound that has a distinctive ("hospital smell") odour (Figure 23.5a.).



Figure 23.5a. Structure of phenol (left). Crystal form of phenol (right). (credit: *CHEM 1152: Survey of Chemistry II (GSU – Dr. Osborne)*, CC BY-NC-SA 4.0)

Naming Phenols

In the International Union of Pure and Applied Chemistry (IUPAC) system, the rules for naming phenols are similar to naming substituted aromatics.

- 1. When naming phenols, the parent name is phenol. This accounts for the benzene ring and the hydroxyl attached to it.
- 2. The carbon atom bearing the OH group is designated C1, but the 1 is not used in the name.
- 3. The location of substituents is then determined using the shortest path. The location of all substituents (even if only one is present) must be shown. The name is then determined by indicating the location and identity of the substituents followed by the word phenol.



Solution:

According to the naming rules, the name of the molecule is 3-ethylphenol or meta-ethylphenol.

Example 23.5b

Name each compound.



Solution:

- The parent chain is phenol and C1 would represent the carbon with the OH attached. There is one substituent present on the adjacent carbon, so the parent chain would be numbered clockwise to represent the shortest path. The substituent, which is identified as a nitro group, is on C2. Therefore, the name of the molecule is 2-nitrophenol (or o-nitrophenol).
- 2. The parent chain is phenol and C1 would represent the carbon with the OH attached. There is one substituent present on the carbon opposite C1. In this position, the same number is obtained regardless of the chosen path. Therefore, the bromo substituent, is on C4. This indicates that the name of the molecule is 4-bromophenol (or p-bromophenol).

Example source: CHEM 1152: Survey of Chemistry II (GSU – Dr. Osborne), CC BY-NC-SA 4.0

Exercise 23.5a

Name the following compounds.





Check Your Answers:1

Exercise source: CHEM 1152: Survey of Chemistry II (GSU – Dr. Osborne), CC BY-NC-SA 4.0

Spotlight on Everyday Chemistry: Phenols and Us



Figure 23.5c. An operation in 1753, painted by Gaspare Traversi, of a surgery before antiseptics were used. (Credit: Oil Painting by Gaspare Traversi, Public Domain)

Phenols are widely used as antiseptics (substances that kill microorganisms on living tissue) and as disinfectants (substances intended to kill microorganisms on inanimate objects such as furniture or floors). The first widely used antiseptic was phenol (Figure 23.5c.). Joseph Lister used it for antiseptic surgery in 1867. Phenol is toxic to humans, however, and can cause severe burns when applied to the skin. In the bloodstream, it is a systemic poison—that is, one that is carried to and affects all parts of the body. Its severe side effects led to searches for safer antiseptics, a number of which have been found.

One safer phenolic antiseptic is 4-hexylresorcinol (4-hexyl-1,3-dihydroxybenzene; resorcinol is the common name for 1,3-dihydroxybenzene, and 4-hexylresorcinol has a hexyl group on the fourth carbon atom of the resorcinol ring) (Figure 23.5d.). It is much more powerful than phenol as a

germicide and has fewer undesirable side effects. Indeed, it is safe enough to be used as the active ingredient in some mouthwashes and throat lozenges.



Figure 23.5d. The compound 4-hexylresorcinol is mild enough to be used as the active ingredient in antiseptic preparations for use on the skin. (Credit: *Intro Chem: GOB* (*V. 1.0*), CC BY-NC-SA 3.0., edited by (*Ball et al.*) *CC BY-NC-SA 4.0.*)

Indigenous Perspectives: Maple Syrup

Long before Turtle Island was colonized, Indigenous Peoples of the First Nations used sap from maple trees to produce a sweet syrup or "sweet water" which could also be made into solid blocks. Maple syrup is considered to have healing and nourishing powers. Sweet water is used in ceremonies and for cooking as well. Early colonizers survived due to the gifts of maple products from the local First Nations Peoples. Infographic 23.5a. highlights some of the organic compounds found in maple syrup. Phenol based compounds are key to the flavour of the syrup (Seto, 2021; Wabanaki, n.d.).



(https://www.compoundchem.com/2016/07/01/maple-syrup/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 23.5a [New tab] .

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Wabanaki. (n.d.). Our story | Indigenous, Female Owned Maple Syrup (https://www.wabanakimaple.com/pages/our-story).

Notes

1. 1) m-chlorophenol (or 3-chlorophenol 2) o-isopropylphenol (or 2-isopropylphenol)

23.6 ETHERS - STRUCTURE AND NAMING

Learning Objectives

By the end of this section, you will be able to:

- Describe the structural difference between an alcohol and an ether that affects physical characteristics of each.
- Name simple ethers.
- Describe the structure and uses of some ethers.

With the general formula ROR', an **ether** may be considered a derivative of water in which both hydrogen atoms are replaced by alkyl or aryl groups (aryl means aromatic). It may also be considered a derivative of an alcohol (ROH) in which the hydrogen atom of the OH group is replaced by a second alkyl or aryl group (Figure 23.6a.).



Figure 23.6a. a) General structure of ethers, b) condensed structure of methoxymethane (dimethyl ether) and c) ball and stick model of methoxymethane (dimethyl ether) (credit left: Image by Hbf878, CC0; middle: Image by B Levin13, CC BY-SA 3.0; right: Image by Benjah-bmm27, PDM)

Naming Ethers

The IUPAC naming process of naming ethers involves separately naming each of the two groups attached to the oxygen atom.

1. The group that has the longest continuous carbon chain is considered the parent chain and is named accordingly. (For example, if the longest chain consists of 3 carbons, the parent chain would be

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propane).

- 2. The group attached to the oxygen that has the shorter chain is named as an alkoxy group, which replaces the "ane" ending with "oxy". For example, a one carbon chain would go from methane to methoxy.
- 3. Remaining substituents are numbered and named as in previous sections.

Example 23.6a

What is the IUPAC name for each ether?

- a. CH₃CH₂OCH₂CH₂CH₃

Solution:

- a. There is a two carbon group and a three carbon group on either side of the oxygen. The parent chain is based on the longer group (3 carbons = propane) and the alkoxy group is the shorter chain (2 carbons = ethoxy). The compound's name would be ethoxypropane.
- b. There is a six carbon group and a four carbon group on either side of the oxygen. The parent chain is based on the longer group (6 carbons = hexane) and the alkoxy group is the shorter chain (4 carbons = butoxy). The compound's name would be butoxyhexane.

Exercise 23.6a

What is the IUPAC name for each ether?

1. CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₃



(Credit: Intro Chem: GOB (V. 1.0)., CC BY-NC-SA 3.0.) Check Your Answers:1

Simple ethers also have common names, formed from the names of the groups attached to oxygen atom, followed by the generic name ether. If both groups are the same, the group name should be preceded by the prefix di-.

Example 23.6b

What is the common name for each ether?

- 1. CH₃–O–CH₂CH₂CH₃
- 2. CH₃–O–CH₃
- 3. CH₃CH₂-O-CH₂CH₃

Solutions:

- 1. methyl propyl ether
- 2. dimethyl ether
- 3. diethyl ether

Exercise 23.6b

What is the common name of this ether?

CH₃ CH₂ CH₃

Check Your Answer:²

Source: Exercise 23.6b is adapted from *General Chemistry 1 & 2*, CC BY 4.0.

Physical Properties

Ether molecules have no hydrogen atom on the oxygen atom (that is, no OH group). Therefore, there is no intermolecular hydrogen bonding between ether molecules. As a result, ethers have quite low boiling points for a given molar mass. In fact, ethers have boiling points about the same as those of alkanes of comparable molar mass and much lower than those of the corresponding alcohols (Table 23.6a.).

	-	e		
IUPAC Name	Common Name	Molar Mass	Boiling Point (°C)	Intermolecular Hydrogen B Liquid?
propane	propane	44	-42	no
methoxymethane	dimethyl ether	46	-25	no
ethanol	ethyl alcohol	46	78	yes
pentane	pentane	72	36	no
ethoxyethane	diethyl ether	74	35	no
butan-1-ol	butyl alcohol	74	117	yes
	IUPAC Name propane methoxymethane ethanol pentane ethoxyethane butan-1-ol	IUPAC NameCommon Namepropanepropanemethoxymethanedimethyl etherethanolgethyl alcoholpentanepentaneethoxyethanediethyl etherbutan-1oolbutyl alcohol	IUPAC NameCommon NameMolar Masspropanepropane44methoxymethanedimethyl ether46ethanolethyl alcohol46pentanepentane72ethoxyethanediethyl ether74butan-1-olbutyl alcohol74	IUPAC NameCommon NameMolar MassBoiling Point (°C)propanepropane44-42methoxymethanedimethyl ether46-25ethanolethyl alcohol4678pentanepentane7236ethoxyethanediethyl ether7435butan-1-olbutyl alcohol74117

Table 23.6a. Comparison of Boiling Points of Alkanes, Alcohols, and Ethers

Table source: "14.8: Ethers" In Basics of GOB (Ball et al.), CC BY-NC-SA 4.0.

Ether molecules do have an oxygen atom, however, and engage in hydrogen bonding with water molecules. Consequently, an ether has about the same solubility in water as the alcohol that is isomeric with it. For example, dimethyl ether and ethanol (both having the molecular formula C_2H_6O) are completely soluble in water, whereas diethyl ether and 1-butanol (both $C_4H_{10}O$) are barely soluble in water (8 g/100 mL of water).

Spotlight on Everyday Chemistry: General Anesthetics

A general anesthetic acts on the brain to produce unconsciousness and a general insensitivity to feeling or pain. Diethyl ether or ethoxyethane (CH₃CH₂OCH₂CH₃) was the first general anesthetic to be used. Diethyl ether is a colourless, volatile liquid that is highly flammable.



Figure 23.6b. William Morton, a Boston dentist, introduced diethyl ether into surgical practice in 1846. This painting shows an operation in Boston in 1846 in which diethyl ether was used as an anesthetic. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. (Image credit: Oil painting (V0018140) by Ernest Board, PDM).

Diethyl ether is relatively safe because there is a fairly wide gap between the dose that produces an effective level of anesthesia and the lethal dose. However, because it is highly flammable and has the added disadvantage of causing nausea, it has been replaced by newer inhalant anesthetics, including the fluorine-containing compounds halothane, enflurane, and isoflurane (Figure 23.6c.). Unfortunately, the safety of these compounds for operating room personnel has been questioned. For example, female operating room workers exposed to halothane suffer a higher rate of miscarriages than women in the general population.



Figure 23.6c. These three modern, inhalant, halogen-containing, anesthetic compounds (halothane, enflurane, and isoflurane) are less flammable than diethyl ether. (Credit: *Intro Chem: GOB (V. 1.0).*, CC BY-NC-SA 3.0.)

Ethers are produced from alcohols as previously described in this chapter. Figure 23.6d. shows an example of ether production.

Figure 23.6d. Formation of ether from intermolecular dehydration of two alcohol molecules (credit: *General Chemistry 1 & 2*, CC BY 4.0).

Spotlight on Everyday Chemistry: Foxgloves

Foxgloves are poisonous. The large biological molecules contained in the flowers have many ether functional groups. Read more about the chemistry of foxgloves in Infographic 23.6a.



Infographic 23.6a. Read more about "The Chemistry of Foxgloves – Poison & Medicine (https://www.compoundchem.com/2016/06/21/foxgloves/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 23.6a [New tab].

Link to Enhanced Learning

For more support with naming ethers and their properties, see Ether naming and introduction (video) | Khan Academy (https://www.khanacademy.org/science/organic-chemistry/alcohols-ethers-epoxides-sulfides/nomenclature-properties-ethers/v/ether-naming-and-introduction).

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Notes

- 1. 1) butoxybutane 2) ethoxycyclobutane
- 2. ethylmethyl ether. (Branches are in alphabetical order.)

23.7 THIOLS

Learning Objectives

By the end of this section, you will be able to:

- Identify and name thiols (mercaptans) by the presence of an SH group.
- Identify sulfides and disulfides.
- Understand that the mild oxidation of thiols gives disulfides.
- Recognize importance of sulfur in organic compounds.

Thiol Structure

Because sulfur is in the same group (6A) of the periodic table as oxygen, the two elements have some similar properties. We might expect sulfur to form organic compounds related to those of oxygen, and indeed it does.

Thiols (also called mercaptans), which are sulfur analogs of alcohols, have the general formula RSH. Methanethiol (also called methyl mercaptan), has the formula CH₃SH. Ethanethiol (ethyl mercaptan) is the most common odourant for liquid propane (LP) gas. Some other thiols are shown in Figure 23.7a. Because of the lack of the ability to hydrogen bond, thiols have lower boiling points than the corresponding alcohols. For example, ethanethiol is a gas at room temperature.



Figure 23.7a. Thiol structures of propanethiol, cyclopentanethiol and o-mercaptobenzoic acid (credit: *Organic Chemistry (Wade)*, CC BY-NC-SA 4.0).

The most striking characteristic of thiols is their appalling odour. Skunk scent, for instance, is caused

primarily by the simple thiols 3-methyl-1-butanethiol and 2-butene-1-thiol. Volatile thiols such as ethanethiol are also added to natural gas and liquefied propane to serve as an easily detectable warning in case of leaks.

Naming Thiols

Rules for naming thiols are similar to rules for naming alcohols.

- 1. Thiols are named by adding the word –thiol as the suffix of the parent name.
- 2. The longest carbon chain is then numbered to give the sulfhydryl group the lowest possible number.
- 3. Since the functional group has priority in numbering, if the sulhydryl (-SH) group is bonded to a ring, the carbon that it is bonded to is assigned to C1 and the number is omitted from the name.

Example 23.7a

What is the name of each thiol?



(credit: CHEM 1152: Survey of Chemistry II (GSU – Dr. Osborne), CC BY-NC-SA 4.0)

Solution:

- a. This molecule is named 2-methyl-3-pentanethiol (or 2-methylpentane-3-thiol).
- b. The longest continuous chain of carbon has four carbon atoms, so the stem name is butane. The parent name is obtained by adding the word thiol, to give butanethiol. We number from the left to give the sulfhydryl group the lowest number. Since there are no substituents present, the name of the molecule is 2-butanethiol (or butane-2-thiol).
- c. The longest continuous chain of carbon has six carbon atoms in a ring, so the stem name is cyclohexane. The parent name is obtained by adding the word thiol, to give cyclohexanethiol. The carbon that has the sulfhydryl group is assigned as C1, since any carbon in the ring can be C1. The ring is then number counterclockwise to give the methyl substituent the lowest possible number. Therefore, the name of the molecule is 2-methylcyclohexanethiol.



Sulfides and Disulfides

Sulfides, also called thioethers, have the structure R-S-R' and are sulfur analogs of ethers. Disulfides have the structure R-S-S-R'. These are both commonly found in biomolecules. Dimethylsulfide (CH₃SCH₃) which is responsible for the sometimes unpleasant odour of cooking cabbage and related vegetables.

Oxidation of thiols and other sulfur compounds changes the oxidation state of sulfur rather than carbon. The mild oxidation of thiols gives disulfides (Figure 23.7b.). An equivalent oxidation of alcohols to peroxides is not normally observed. The reasons for this different behaviour are not hard to identify. The S–S single bond is nearly twice as strong as the O–O bond in peroxides, and the O–H bond is more than 25 kcal/mole stronger than an S–H bond. Thus, thermodynamics favours disulfide formation over peroxide.

2 R-S-H
$$\left[\begin{matrix} 0 \\ H \end{matrix} \right]$$
 R-S-S-R $\left\{ \begin{matrix} [0] = mild oxidizing agents, such as iodine \\ [H] = mild reducing agents, such as zinc & acid: 2 R-S-CI $\left\{ \begin{matrix} -C_{12} \\ -20^{\circ}c \end{matrix} \right\}$ R-S-S-R $\left\{ \begin{matrix} HCO_{3}H \\ -70^{\circ}H \end{matrix} \right\}$ 2 R-SO₃H$

Figure 23.7b. Mild oxidation of thiol to disulfide (credit: *Organic Chemistry (Wade)*, CC BY-NC-SA 4.0).

The amino acids cysteine [HSCH₂CH(NH₂)COOH] and methionine [CH₃SCH₂CH₂CH(NH₂)COOH] contain sulfur atoms, as do all proteins that contain these amino acids. Disulfide linkages (-S-S-) between protein chains are extremely important in protein structure.



Figure 23.7c. Difference between thiol and disulfide in protein structures (credit: *Organic Chemistry (Wade)*, CC BY-NC-SA 4.0).

Spotlight on Everyday Chemistry: Body Odours

Many body odours are the result of organic based sulfur compounds. Halitosis (bad breath), underarm odour, flatulence and foot odour are caused by bacterial activity generating mostly organosulfur compounds. Read more in Infographic 23.7a.



Infographic 23.7a. Read more about "The Chemistry of Body Odours – Sweat, Halitosis, Flatulence & Cheesy Feet (https://www.compoundchem.com/2014/04/07/

the-chemistry-of-body-odours-sweat-halitosis-flatulence-cheesy-feet/)" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 23.7a [New tab].

Links to Enhanced Learning

Read more about the use of thiols, sulfides and disulfides in everyday compounds.

Food:

• Compound Interest: The Chemistry of Eggs & Egg Shells [New tab] (https://www.compoundchem.com/2016/03/26/eggs/)

- Compound Interest: The Chemistry of Camembert [New tab] (https://www.compoundchem.com/2016/02/10/the-chemistry-of-camembert/)
- Compound Interest: Aroma Chemistry The Smell of Freshly-Baked Bread [New tab] (https://www.compoundchem.com/2016/01/20/bread-aroma/)
- Compound Interest: Blackcurrants & Cat Urine The Chemistry of Blackcurrants [New tab] (https://www.compoundchem.com/2015/07/23/blackcurrants/)
- Compound Interest: The Chemistry of Brussels Sprouts: Bitterness & Genetics [New tab] (https://www.compoundchem.com/2014/12/04/brusselssprouts/)
- Compound Interest: What Compounds Cause Garlic Breath? The Chemistry of Garlic [New tab] (https://www.compoundchem.com/2014/05/05/what-compounds-cause-garlic-breath-the-chemistry-of-garlic/)
- Compound Interest: The Chemistry of an Onion [New tab] (https://www.compoundchem.com/2014/01/22/the-chemistry-of-an-onion/)
- Compound Interest: Why Does Asparagus Make Urine Smell? The Chemistry of Asparagus [New tab] (https://www.compoundchem.com/2014/02/10/why-does-asparagus-make-urinesmell-the-chemistry-of-asparagus/)

Waste:

- Compound Interest: Talking Trash The Chemistry Behind the Smell of Garbage [New tab] (https://www.compoundchem.com/2017/06/22/garbage/)
- Compound Interest: The Chemistry of the Smell of Toilets & Human Waste [New tab] (https://www.compoundchem.com/2015/06/02/toilets/)

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- "18.7 Thiols and Sulfides" In Organic Chemistry (OpenStax) (https://openstax.org/books/organicchemistry/pages/1-why-this-chapter) by John McMurray, CC BY-NC-SA 4.0. Access for free at Organic Chemistry (OpenStax) (https://openstax.org/books/organic-chemistry/pages/1-why-this-chapter)
- "14.8: Thiols and Disulfides" In Map: Fundamentals of General Organic and Biological Chemistry

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- "13.10: Thiols (Mercaptans)" by Dietmar Kennepohl, Steven Farmer, William Reusch, & Chris P Schaller In *Map: Organic Chemistry (Wade), Complete and Semesters I and II*, CC BY-NC-SA 4.0. / A derivative of **Thiols and Sulfides** In *Supplemental Modules*, CC BY-NC-SA 4.0. / Attributions in original source: Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
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Notes

1. a) 4-methylpentane-2-thiol, b) benzenethiol or thiophenol

CHAPTER 23 - SUMMARY

23.1 Alcohols – Structure, Naming and Classification

The –OH group is the functional group of an alcohol. Ethanol is a commonly known alcohol. Its common name is ethyl alcohol and has the formula CH₃CH₂OH. In the IUPAC system, alcohols are named by changing the ending of the parent alkane name to -ol. Alcohols are classified as primary, secondary or tertiary according to the number of carbon atoms attached to the carbon atom that is attached to the OH group. More than one -OH group can be in a molecule but typically only one -OH exists per carbon atom.

23.2 Physical Properties of Alcohols

Alcohols are bent molecules similar to water. The presence of the oxygen-hydrogen bond results in a polar molecule. Alcohols have higher boiling points than do ethers and alkanes of similar molar masses because the OH group allows alcohol molecules to engage in hydrogen bonding. Alcohols of four or fewer carbon atoms are soluble in water because the alcohol molecules engage in hydrogen bonding with water molecules; comparable alkane molecules cannot engage in hydrogen bonding. Adding more -OH groups to a molecule increases its boiling point and solubility.

23.3 Formation of Alcohols

Many alcohols are made by the hydration of alkenes. Ethanol can be made by the fermentation of sugars or starch from various sources. Alcohols can also be produced by the alkyl halide substitution, ester hydrolysis and reduction of aldehydes and ketones.

23.4 Reactions of Alcohols

Alcohols are a highly versatile functional group. Many other functional groups can be formed from alcohol molecules. Primary alcohols are oxidized to form aldehydes. Secondary alcohols are oxidized to form ketones. Tertiary alcohols are not readily oxidized. Alcohols can be dehydrated to form either alkenes (higher temperature, excess acid) or ethers (lower temperature, excess alcohol). Unsymmetrical alcohols will dehydrate to alkenes following Zaitsev's rule which says that the more highly substituted double bond isomer is favoured. Alcohols combine with carboxylic acids to form esters through esterification. In some situations, alcohols can be substituted to form alkyl halides.

23.5 Phenols

Phenols are compounds in which an OH group is attached directly to an aromatic ring. Many phenols are used as antiseptics. For the IUPAC nomenclature of phenols, the carbon bonded to the OH group is C1 and all substituents are named according to their location relative to the C1 carbon.

23.6 Ethers

The -R-O-R'- group is the functional group of an ether. It is a derivative of the alcohol and has similar shape to the water molecule. To name ethers, simply name the groups attached to the oxygen with the longest continuous carbon chain as the parent chain and the shorter carbon chain as an alkoxy group. If both groups are the same, it does not matter which side you use as the parent and alkoxy group. Ether molecules have no OH group and thus no intermolecular hydrogen bonding. Ethers therefore have quite low boiling points for a given molar mass. Ether molecules have an oxygen atom and can engage in hydrogen bonding with water molecules. An ether molecule has about the same solubility in water as the alcohol that is isomeric with it.

23.7 Thiols

Thiols, sulfides (thioethers), and disulfides are common in biological compounds that contain carbon. Thiols have a -SH group and disulfides have a -S-S- group. Thiols have strong odours like those of skunk scent and natural gas. To name thiols, the longest continuous chain is located, and the parent chain named as an alkane. The thiol suffix is added with its location.

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 "14.2: Alcohols – Nomenclature and Classification", "14.3: Physical Properties of Alcohols", "14.4: Reactions that Form Alcohols", "14.5: Reactions of Alcohols", "14.7: Phenols", "14.6: Glycols and Glycerol" and "14.8: Ethers" In *Basics of General, Organic, and Biological Chemistry (Ball et al.)* by David W. Ball, John W. Hill, and Rhonda J. Scott, CC BY-NC-SA 4.0. / A derivative of *Introduction to* Chemistry: GOB (v. 1.0), CC BY-NC 3.0

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CHAPTER 23 - REVIEW

23.1 Alcohols – Structure, Naming and Classification

1. Is isobutyl alcohol primary, secondary, or tertiary? Explain. Check answer¹

CH₃CHCH₂OH CH,

(credit: Intro Chem: GOB, CC BY-NC-SA 3.0.)

- 2. What is the longest continuous chain (LCC) in 2-ethyl-1-hexanol? What is taken as the LCC in naming the compound? Explain. Check answer²
- 3. Name each alcohol and classify it as primary, secondary, or tertiary. **Check answer**³ a. CH₃CH₂CH₂CH₂CH₂CH₂OH

```
(credit: Intro
Chem: GOB, CC
BY-NC-SA 3.0.)
```

b.



(credit: Intro Chem: GOB, CC BY-NC-SA 3.0.)

с.

4. Name each alcohol and classify it as primary, secondary, or tertiary.



- 5. Draw the structure for each alcohol. a. 3-hexanol b. 3,3-dimethyl-2-butanol c. cyclobutanol **Check** answer⁴
- 6. Draw the structure for each alcohol.
 - 1. cyclopentanol
 - 2. 4-methyl-2-hexanol
 - 3. 4,5-dimethyl-3-heptanol
- 7. What is a glycol? **Check answer**⁵
- 8. Why is ethylene glycol so much more toxic to humans than propylene glycol?
- 9. Draw the structure for each compound. **Check answer**⁶
 - a. 1,5-pentanediol
 - b. propylene glycol
- 10. Draw the structure for each compound.
 - 1. 1,3-hexanediol
 - 2. glycerol

23.2 Physical Properties of Alcohols

- 1. Why is ethanol more soluble in water than 1-hexanol? Check answer⁷
- 2. Why does 1-butanol have a lower boiling point than 1-hexanol? Check answer⁸
- 3. Arrange these alcohols in order of increasing boiling point: ethanol, methanol, and 1-propanol. **Check answer**⁹
- 4. Which has the higher boiling point —butane or 1-propanol?
- 5. Arrange these alcohols in order of increasing solubility in water: 1-butanol, methanol, and 1-octanol. **Check answer**¹⁰
- 6. Arrange these compounds in order of increasing solubility in water: 1-butanol, ethanol, and pentane.
- 7. Ethanol is used as a solvent for some drugs that are not soluble in water. Why is methanol not used in medicines?
- 8. How does the boiling point and solubility change if more OH groups are included in a molecule? Why?

23.3 Formation of Alcohols

- 1. From what alkene is ethanol made? Draw its condensed structural formula. **Check answer**¹¹
- 2. Can methanol be made from an alkene? Explain.
- 3. When water is added to ethylene in the presence of an acid catalyst, only one product—ethanol—is possible. However, when water is added to propylene, two products are possible—1-propanol and 2-propanol—but only 2-propanol is formed. In 1870, the Russian chemist Vladimir V. Markovnikov proposed a rule to predict the products of such reactions: Considering water to be HOH, the hydrogen atom of water goes on the carbon atom (of the two involved in the double bond) that has the most hydrogen atoms already bonded to it. The OH group goes on the carbon atom with fewer hydrogen atoms. Use Markovnikov's rule to predict the product of the addition of water to each compound. **Check answer**¹²
 - a. 2-methylpropene
 - b. 1-butene
 - c. 2-methyl-1-pentene
 - d. 2-methyl-2-pentene
- 4. Alcohols can be made from alkyl halides, aldehydes and ketones, and esters. Provide a description or example of each reaction.

23.4 Reactions of Alcohols

1. Name the three major types of chemical reactions of alcohols. Check answer¹³

- 2. Why do tertiary alcohols not undergo oxidation? Can a tertiary alcohol undergo dehydration?
- 3. Draw the structure of the product for each reaction.

$$\begin{array}{c} \mathsf{CH}_{3}\\ \mathsf{CH}_{3}\mathsf{CCH}_{3}\\ \mathsf{OH} \end{array} \xrightarrow[excess \ acid]{} \begin{array}{c} \mathsf{concd} \ \mathsf{H}_{2}\mathsf{SO}_{4}, 180^{\circ}\mathsf{C} \\ \mathsf{excess \ acid} \end{array} \xrightarrow[excess \ acid]{} \begin{array}{c} \mathsf{(credit: } \mathit{Intro} \\ \mathit{Chem: } \mathit{GOB}, \mathsf{CC} \\ \mathsf{BY-NC-SA \ 3.0).} \end{array}$$

a.

CH ₃ CHCH ₂ CH ₂ CH ₃	K ₂ Cr ₂ O ₇	(credit: Intro
	$\xrightarrow{H^+}$	Chem: GOB, CC
OH		BY-NC-SA 3.0).

b. Check answer¹⁴

- 4. Write an equation for the dehydration of 2-propanol to yield each compound type. **Check answer**¹⁵
 - 1. an alkene
 - 2. an ether
- 5. Draw the structure of the alkene formed by the dehydration of cyclohexanol.

Classify each conversion as oxidation, dehydration, or hydration (only the organic starting material and product are shown): **Check answer**¹⁶

- a. $CH_3OH \rightarrow HCHO$
- b. $CH_3CHOHCH_3 \rightarrow CH_3CH=CH_2$
- c. $CH_2=CHCH_2CH_3 \rightarrow CH_3CHOHCH_2CH_3$
- 6. Classify each conversion as oxidation, dehydration, or hydration (only the organic starting material and product are shown.):
 - a. $CH_3CHOHCH_3 \rightarrow CH_3COCH_3$
 - b. HOOCCH=CHCOOH \rightarrow HOOCCH₂CHOHCOOH
 - c. $2 \text{ CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3$
- 7. What does a positive result from the Tollen's test, Fehling test and Benedict test look like? **Check** answer¹⁷
- 8. For each compound, identify if the test result will be positive or negative given the listed test.
 - 1. 2-propanol Tollen's test
 - 2. 2-methyl-2-pentanol Benedict Test
 - 3. cyclopentanol Fehling Test
- 9. Draw the major product from the dehydration of each compound (assume alkene formation).

- 1. 2-methyl-2-pentanol
- 2. 2-chlorocyclopentanol
- 3. 2-methyl-4-octanol

10. Draw the product of esterification of ethanol and ethanoic acid.

23.5 Phenols

- 1. How do phenols differ from alcohols in terms of structure and properties? **Check answer**¹⁸
- 2. How do phenols differ in properties from aromatic hydrocarbons? **Check answer**¹⁹
- 3. Name each compound. **Check answer**²⁰



4. Name each compound.



- 5. Draw the structure for each compound. **Check answer**²¹
 - a) *m*-iodophenol
 - b) *p*-methylphenol (*p*-cresol)

- 6. Draw the structure for each compound.
 - 1. 2,4,6-trinitrophenol (picric acid)
 - 2. 3,5-diethylphenol

23.6 Ethers

- Identify each compound as an alcohol, a phenol, or an ether. Classify any alcohols as primary (1°), secondary (2°), or tertiary (3°).
 - a. CH₃CH₂CH₂OH

b.	CH ₃ CHCH ₃ OH	(credit: Intro Chem: GOB, CC BY-NC-SA 3.0.)
с.	ОН	(credit: <i>Intro</i> <i>Chem: GOB</i> , CC BY-NC-SA 3.0.)
d.	CH ₃ CHOCH ₃ I CH ₃	(credit: <i>Intro</i> <i>Chem: GOB</i> , CC BY-NC-SA 3.0.)

- 2. Identify each compound as an alcohol, a phenol, or an ether. Classify any alcohols as primary, secondary, or tertiary. **Check answer**²²
 - 1. CH₃CH₂OCH₂CH₃

CH₃ CH₃CCH₃ CH₃CCH₃ OH (credit: Intro Chem: GOB, CC BY-NC-SA 3.0.)



(credit: *Intro Chem: GOB*, CC BY-NC-SA 3.0.)

3.

2.



4.

- 3. Why does ethoxyethane (CH₃CH₂OCH₂CH₃) have a much lower boiling point than 1-butanol (CH₃CH₂CH₂CH₂OH)? **Check answer**²³
- Which is more soluble in water—methoxyethane (CH₃CH₂OCH₃) or 1-butanol (CH₃CH₂CH₂CH₂OH)? Explain. Check answer²⁴
- How can ethanol give two different products when heated with sulfuric acid? Name these products. Check answer²⁵
- 6. Which of these ethers is isomeric with ethanol—CH₃CH₂OCH₂CH₃, CH₃OCH₂CH₃, or CH₃OCH₃?
- 7. Name each compound. **Check answer**²⁶
 - 1. CH₃OCH₂CH₂CH₃



(credit: Intro Chem: GOB, CC BY-NC-SA 3.0).

8. Name each compound.

2.

- 1. CH₃CH₂CH₂CH₂OCH₃
- 2. CH₃CH₂OCH₂CH₂CH₃
- 9. Draw the structure for each compound. **Check answer**²⁷
 - 1. methoxyethane
 - 2. ethoxy*tert*-butane

23.7 Thiols

- 1. What is the functional group of a thiol? Write the condensed structural formula for ethanethiol (ethyl mercaptan). **Check answer**²⁸
- 2. What is the functional group of a disulfide? Write the condensed structural formula for dipropyl disulfide. **Check answer**²⁹
- 3. A common natural gas odourant is *tert*-butyl mercaptan. What is its condensed structural formula? Check answer³⁰
- 4. Write the equation for the oxidation of ethanethiol to diethyl disulfide.

(credit: Intro Chem: GOB, CC BY-NC-SA 3.0.)

Links to Enhanced Learning

Create your own organic nomenclature quiz to identify, name and draw alcohols and ethers using Organic Nomenclature (orgchem101.com). You can customize the types of questions you receive and get instant feedback.

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Notes

- 1. primary; the carbon atom bearing the OH group is attached to only one other carbon atom
- 2. 7 carbon atoms; the 6-atom chain includes the carbon atom bearing the OH group
3. a) 1-hexanol; primary b) 3-hexanol; secondary c) 3,3-dibromo-2-methyl-2-butanol; tertiary



5. an alcohol with two OH groups on adjacent carbon atoms



- 6. a. HOCH₂CH₂CH₂CH₂CH₂OH b.
- 7. Ethanol has an OH group and only 2 carbon atoms; 1-hexanol has one OH group for 6 carbon atoms and is thus more like a (nonpolar) hydrocarbon than ethanol is.
- 8. The molar mass of 1-hexanol is greater than that of 1-butanol.
- 9. methanol < ethanol < 1-propanol
- 10. 1-octanol < 1-butanol < methanol
- 11. ethylene; CH₂=CH₂
- 12. a. 2-methyl-2-propanol, b. 2-butanol, c. 2-methyl-2-pentanol, d. 2-methyl-2-pentanol
- 13. dehydration, oxidation, and esterification

14.

a.

b.

15. a. $CH_3CHOHCH_3 \rightarrow CH_3COCH_3 + H_2O$ (under conditions of conc $H_2SO_4 180^{\circ}$ C excess acid)

b. 2 CH₃CHOHCH₃ \rightarrow (CH₃)₂CHOCH(CH₃)₂ + H₂O (under conditions of conc H₂SO₄ 140° C, excess alcohol)

- 16. a. oxidation, b. dehydration, c. hydration
- 17. Tollens silver mirror finish, Fehling red precipitate, Benedict red precipitate
- 18. Phenols have an OH group attached directly to an aromatic ring. Phenols are weakly acidic.
- 19. Phenols have an OH group and are somewhat soluble in water.
- 20. 1) o-nitrophenol 2) p-bromophenol



- 21. a)
- 22. a. ether b. tertiary alcohol c. phenol d. secondary alcohol
- 23. Ethoxyethane has no intermolecular hydrogen bonding because there is no OH group; 1-butanol has an OH and engages in intermolecular hydrogen bonding.
- 24. methoxyethane (three carbon atoms, one oxygen atom) is more soluble in water than 1-butanol (four carbon atoms, one oxygen atom), even though both can engage in hydrogen bonding with water.
- 25. Intramolecular (both the H and the OH come from the same molecule) dehydration gives ethene; intermolecular (the H comes from one molecule and the OH comes from another molecule) dehydration gives ethoxyethane.
- 26. 1) methoxypropane 2) ethoxyisopropane



- 27. 1) CH₃OCH₂CH₃ 2)
- 28. SH; CH₃CH₂SH
- 29. -S-S-; CH₃CH₂CH₂SSCH₂CH₂CH₃
- 30. (CH₃)₃CSH

CHAPTER 23 - INFOGRAPHIC DESCRIPTIONS

Infographics used in Chapter 23

- 23.1a Coronavirus: How hand sanitisers protect against infections
- 23.2a Food, Cosmetics & Explosives The Versatility of Glycerol
- 23.4a A Guide to Oxidation Reactions of Alcohols
- 23.4b What causes hangovers? A biochemical mystery
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- 23.7a The Chemistry of Body Odours Sweat, Halitosis, Flatulence & Cheesy Feet

23.1a Coronavirus: How hand sanitisers protect against infections

Alcohol-based sanitizers contain 60-95% alcohol. Most contain either ethanol, n-propanol, isopropanol, or combination of these.

Chlorhexidine and benzalkonium chloride are also bound in some sanitizers. Both are also used in nonalcohol-based sanitizers.

Other ingredients include glycerol, which acts as a moisturizer to stop your skin drying out. Hydrogen peroxide is added to prevents bacterial contamination in the hand sanitizer.

Alcohols in hand sanitizers after (denature) the structure of proteins. They destroy the cell wall and membranes of bacteria cells, and the envelope of viruses (including coronavirus). They're less effective against non-enveloped viruses. Non-alcohol-based sanitizers also kill bacteria but are less effective against viruses.

Hand sanitizers with minimum of 60% alcohol are effective if applied generously. However, they don't kill all virus types and are less effective on dirty or greasy hands.

Hand washing with soap for 20 seconds washes away bacteria and viruses, and also removes dirt and grease. Antibacterial soaps are no more effective.

Read more about "Coronavirus: How hand sanitisers protect against infections [New tab] (https://www.compoundchem.com/2020/03/04/hand-sanitisers/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

23.2a Food, Cosmetics & Explosives – The Versatility of Glycerol

Also known as glycerin, glycerol is produced as a by-product of soap-making and can also be produced synthetically.

Glycerol (Propane-1,2,3-triol) is colourless, odourless, and viscous liquid. Glycerol: $C_3H_8O_3$.

In the food industry: There are a number of different uses for glycerol in the food industry. It can be used as a sweetener in drinks, as an important moistening agent for baked goods, and is also added to confectionary to prevent sugar crystallization. Additionally, it is often used as a solvent for food colourings, and higher levels can have a preservative effect.

In anti-freeze: Glycerol was historically used as an anti-freeze, since it can form strong hydrogen bonds with water, lowering the freezing point. It was succeeded by ethylene glycol, but as this is toxic to humans, glycerol is being reconsidered as an non-toxic alternative.

In personal care products: Glycerol is used as a method of improving smoothness of toothpaste, skin care products, shaving cream, soaps, and hair-care products. It serves as an emollient and lubricant in these products. It is also found in pharmaceuticals, where it is commonly used as a humectant to stop creams drying out, and as a tablet-holding agent.

As a precursor to explosives: Glycerol can be reacted with a mixture of sulfuric acid and nitric acid to produce nitroglycerin, an explosive liquid commonly used in dynamite and other propellants. This compound is also used as a medication for ischemic heart disease.

Read more about "Food, Cosmetics & Explosives – The Versatility of Glycerol [New tab] (https://www.compoundchem.com/2014/05/25/glycerol/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

23.4a A Guide to Oxidation Reactions of Alcohols

Compounds containing the alcohol functional group (-OH) can be oxidized to produce carbonyl compounds.

The reagents:

- Primary (1°) alcohol: Carbon attached to -OH has one other carbon directly attached.
- Secondary (2°) alcohol: Carbon attached to -OH has two other carbons directly attached.
- Tertiary (3°) alcohol: Carbon attached to -OH has three other carbons directly attached.

Alcohols can be oxidized to carbonyl compounds (containing a C=O bond) using an oxidizing agent. Acidified dichromate (VI) salts can be used, though due to their toxicity alternative reagents can also be utilized, such as pyridinium chlorochromate (PCC).

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- Sodium dichromate: $Na_2Cr_2O_7$
- Potassium dichromate: $K_2 C r_2 O_7$

The type of compound obtained from the reaction depends on the starting alcohol. When an oxidation reaction is carried out with a dichromate salt, the dichromate ion $(Cr_2O_7^{2^-})$ is reduced to the Cr^{3+} ion, giving a colour change from orange to dark green.

Products with different alcohols:

- Primary alcohol (orange) distils to Aldehyde (dark green) and refluxes to Carboxylic acid.
- Secondary alcohol (orange) refluxes to Ketone (dark green).
- Tertiary alcohol (orange) distils to no reaction (orange).

The apparatus:

An aldehyde can be obtained from primary alcohols using distillation. Otherwise, heating under reflux is used to make sure the alcohol is fully oxidized before distilling from the product.

- **Distillation:** Primary alcohol to aldehyde (excess alcohol used). Elevated flask of alcohol and acidified dichromate heated, water cooling tube is used to condense product and the distilled product collects in another flask.
- Heating under reflux: Primary alcohol results in carboxylic acid (excess oxidization agent used) or secondary alcohol results in ketone. Heat alcohol and acidified dichromate in a pear-shaped flask, water cooling tube is used to condense the reaction product which drops back into the pear-shaped flask.

Testing for reaction products:

Oxidizing agents can be represented simply in chemical equations as [O].

Ethanol reacts with [O] resulting in Ethanal which reacts with [O] to create Ethanoic acid. Note: In step 1, water (H_2O) is lost as a side product of the reaction.

 $3C_2H_5OH + 2Cr_2O_{7^{2-}} + 16H^+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$ Dichromate (orange) to Chromium ion (green) There are two different chemicals reactions that can be used to identify the products of oxidation reactions.

Fehling's solution: Contains complexed Cu^{2+} ions. Aldehydes reduce these ions to red copper (I) oxide. Ketones don't react with Fehling's solution.

- Aldehyde (warm) reacts changing blue to red.
- Ketone (warm) solution remains blue; no reaction.

Tollen's reagent: Contains the diamine silver ion, $\Box Ag(NH_3)_2 \exists^+$. Aldehydes reduce this to metallic silver, forming a silver mirror on the glass surface.

- Aldehyde (warm) reacts changing colourless to silver mirror (or grey silver precipitate).
- Ketone (warm) solution remains colourless; no reaction.

Read more about "A Guide to Oxidation Reactions of Alcohols [New tab] (https://www.compoundchem.com/ 2016/05/04/oxidation-reactions-of-alcohols/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

23.4b What causes hangovers? A biochemical mystery

Alcohol in your body: In the liver, the alcohol dehydrogenase enzyme converts ethanol to acetaldehyde. The dehydrogenase enzyme then converts that acetaldehyde into acetate. Acetate is broken down into carbon dioxide and water, then eliminated from the body. On average the liver breaks sown alcohol at the rate of one unit (8 grams of 10 milliliters of pure alcohol) every hour.

- 1. **Dehydration:** Alcohol has a diuretic effect: during alcohol intoxication the release of the anti-diuretic hormone (ADH) vasopressin is decreased, increasing urination. Alcohol-induced dehydration has been suggested as a cause for some hangover symptoms, but research suggest it isn't a major factor.
- 2. Acetaldehyde: Acetaldehyde is rapidly converted in the into acetate in the liver. It is produced by the breakdown of alcohol and has toxic effects that could cause hangover symptoms. Acetaldehyde concentration doesn't significantly correlate with hangover severity. Disulfiram is a drug to support treatment of alcoholism and inhibits the breakdown of acetaldehyde producing unpleasant hangover-like symptoms.
- 3. **Congeners**: Congeners are compounds other than ethanol in drinks including alcohol such as: methanol which breaks down into toxic formaldehyde and formic acid. Congers can increase hangover severity.
- 4. **Immune systems**: Cytokines are small proteins released by cells which affect other cells and play an important role in the immune system. Alcohol causes changes in cytokines concentration in the immune system. Studies have shown the effects caused by some cytokines are very similar to those of a hangover, strongly supporting their roles. IL-12 and IFN-y-concentration changes show significant correlations with hangover severity.

Read more about "What causes hangovers? A biochemical mystery [New tab] (https://www.compoundchem.com/ 2016/01/01/hangover/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

23.5a Canada Day – The Chemistry of Maple Syrup

Maple syrup is the largest commercially produced product derived from tree sap.

Sucrose is the main sugar in maple syrup, making up almost 70% of its composition.

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Maple syrup is slightly acidic due to presence of several organic acids, most abundant is malic acid (around 0.5%).

Phenolic compounds in maple syrup form from degradation of lignin in sap, though some like quebecol form in the syrup-making process. Some contribute to syrup flavour, though exact combination of compounds remains unclear.

Maple syrup is graded according to colour, but the exact compounds behind colouration is unclear. Maillard reactions, caramelization, and formation of polycarbonyl compounds have all been implicated.

Read more about "Canada Day – The Chemistry of Maple Syrup [New tab] (https://www.compoundchem.com/2016/07/01/maple-syrup/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

23.6a The Chemistry of Foxgloves – Poison & Medicine

The vibrancy of foxgloves belies their poisonous nature; but the same compounds that make them poisonous can also be used in medicine.

All parts of the foxglove contains compounds called cardiac glycosides, including the structurally similar digoxin and digitoxin. Ingestion of these compounds can cause nausea, vomiting, diarrhoea, and an irregular heart beat. They disable cell sodium-potassium ion pumps, leading to increased cell sodium and calcium ion concentration. This slows the heart rate, which can lead to a heart attack and death.

Though poisonous in large amounts, in small doses digoxin can be used to manage some heart conditions, including abnormal heat rhythms and heart failure. It increases the force of the heart's contraction and consequently the volume of blood pumped with each contracting beat, and also causes the heartbeat to slow.

- 1. Increase Na^+ Sodium ion concentration and Ca^+ Calcium ion concentration.
- 2. Results in increase force of contraction in the heart, increased volume of blood per beat, decrease in heart rate.

The therapeutic levels of digoxin don't differ greatly from those at which toxic effects are seen, and as such dosages must be carefully monitored.

- Therapeutic range: 0.8-2.0 nanograms per militlitre of blood.
- Toxic level: greater than 2.0 nanograms per militlitre of blood.

Read more about "The Chemistry of Foxgloves – Poison & Medicine [New tab] (https://www.compoundchem.com/2016/06/21/foxgloves/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

23.7a The Chemistry of Body Odours – Sweat, Halitosis, Flatulence & Cheesy Feet

Body odour is the result of bacterial activity producing odourous compounds. Here, we look at some of the main components in particular odours.

Halitosis: (from the mouth)

- Methanethiol; smells like sulfur, garlic
- Hydrogen sulfide; smells like sulfur, rotting eggs
- Dimethyl sulfide; smells like cabbage, sulfur, sweet

Underarm Odour: (from the underarms)

- (E)-3-methyl-2-hexenoic acid; smells like goat
- (S)-3-methyl-3-sulfanylhexan-1-ol; smells like onion
- 3-hydroxy-3-methylhexanoic acid; smells like cumin

Flatulence: (from the digestive system)

- Hydrogen sulfide; smells like sulfur, rotting eggs
- Methanethiol; smells like sulfur, garlic
- Dimethyl sulfide; smells like cabbage, sulfur, sweet

Foot Odour: (from the feet)

- Methanethiol; smells like sulfur, garlic
- Propanoic acid; smells like pungent, rancid, sour
- Isovaleric acid (3-methylbutanoic acid); smells like cheesy, fermented, rancid

Read more about "The Chemistry of Body Odours – Sweat, Halitosis, Flatulence & Cheesy Feet [New tab] (https://www.compoundchem.com/2014/04/07/the-chemistry-of-body-odours-sweat-halitosis-flatulence-cheesyfeet/)" by Andy Brunning / Compound Interest, CC BY-NC-ND

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