

**Chapter Objectives:**

* Learn to recognize the alcohol, phenol, and ether functional groups.
* Learn the IUPAC system for naming alcohols, phenols, and ethers.
* Learn the important physical properties of the alcohols, phenols, and ethers.
* Learn the major chemical reaction of alcohols, and learn how to predict the products of dehydration and oxidation reactions.
* Learn to recognize the thiol functional group.

Alcohols, Phenols, and Ethers

*Introduction*

* In this chapter, we will start looking at organic molecules that incorporate C—O bonds.
* Oxygen is in Group 6A of the periodic table, and in most of its compounds, contains two single bonds and two lone pairs (or one double bond and two lone pairs), and is sp3-hybridized with a **bent** molecular shape:

O

O

* The **alcohol**, **phenol**, and **ether** functional groups are found in a number of important naturally occurring molecules:

CH3CH2OH

Ethanol

OH

CH3CH2OCH2CH3

Diethyl ether

Menthol

HO

Cholesterol

2

Alcohols

3

*The Hydroxy (—OH) Functional Group*

* The **hydroxyl group** (**—OH**) is found in the **alcohol** and **phenol** functional groups. (***Note:*** that’s not the same as hydroxide, OH-, which is ionic.)
  + in **alcohols**, a hydroxyl group is connected to a carbon atom.
  + in **phenols**, —OH is connected to a benzene ring. (The “parent” molecule of this class is also named phenol: PhOH or C6H5OH.)
* When two carbon groups are connected by single bonds to an oxygen, this is classified as the **ether** functional group.

R OH

OH

R

a **phenol**

O R'

an **ether**

an **alcohol**

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*Where Does the Word “Alcohol” Come From?*

* The word “alcohol” comes from the Arabic term *al kohl* meaning “the fine powder.” Originally, this referred to an antimony sulfide (Sb2S3)compound used for eye shadow, which was ground up to form a fine powder, but then later came to refer to any finely divided powder. In the Middle Ages, this term came to mean the “essence” of anything.
* When the Europeans took up alchemy in the Middle Ages, they referred to vapors from evaporating or boiling compounds as “spirits,” since they did not believe them to be material in the same sense that solids and liquids were. Alchemists began referring to “spirits of wine,” and since an alcohol when it boils away seems to powder away to nothing, they also began to refer to “alcohol of wine” and then simply “alcohol”.

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*Some Common Alcohols*

CH3OH

**methanol** *methyl alcohol* (wood alcohol)

("methy" = wine, "hule" = wood)

Found in wood smoke; contributes to the bouqet of new wine; metabolized in the body to formaldehyde and formic acid, and can cause blindness or death (> 50 mL)

CH3CH2OH

**ethanol** *ethyl alcohol* (grain alcohol)

The acohol of alcoholic beverages; the fermentation of honey, grain, or fruit juices to yield beers and wines was probably the first chemical reaction to be discovered; metabolized in the body to produce acetaldehyde

CH3CH2CH2OH

**1-propanol**

*n*-propyl alcohol

OH

CH3CHCH3

**2-propanol**

isopropyl alcohol Rubbing alcohol is 70%

isopropyl alcohol and 30% water

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*Nomenclature of Alcohols and Phenols*

* **Step 1.** Name the longest chain to which the hydroxyl (—OH) group is attached. The name for this chain is obtained by dropping the final **-e** from the name of the hydrocarbon parent name and adding the ending **-ol**.
* **Step 2.** Number the longest chain to give the lowest possible number to the carbon bearing the hydroxyl group.
* **Step 3.** Locate the position of the hydroxyl group by the number of the C to which it is attached.
* **Step 4.** Locate and name any other substituents.
* **Step 5.** Combine the name and location for other groups, the hydroxyl group location, and the longest chain into the final name.

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CH3 CH CH2 CH3

CH3 CH CH3

OH

OH

CH3 CH2 CH2 OH

CH3 CH2 OH

CH3 OH

* Provide acceptable IUPAC names for the following compounds:

***Examples: Naming Alcohols and Phenols***

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CH3 CH2 OH

CH2 CH CH2 CH3

CH2

CH3

CH3 CH2 CH CH CH2 OH CH3

* Provide acceptable IUPAC names for the following compounds:

CH3 CH2 CH2 CH2 CH2 OH CH3 CH2 CH CH2 CH3

OH

***Examples: Naming Alcohols and Phenols***

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OH

CH2CHCH3

OH

* Provide acceptable IUPAC names for the following compounds:

OH

***Examples: Naming Alcohols and Phenols***

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* Draw and name all of the possible isomers of butanol (C4H10O)

***Examples: Naming Alcohols and Phenols***

*Nomenclature of Alcohols and Phenols*

* If there is more than one OH group, a counting prefix (di-, tri-, tetra-, etc.) is placed immediately in front of the suffix **-ol** (*di*ol, *tri*ol, *tetra*ol, etc.).
  + Usually, the final “e” of the parent hydrocarbon is not dropped (e.g., 1,2-propanediol).
  + The position of each alcohol group is indicated by carbon number, separated by commas (e.g., *1,3*- butanediol).
* For cyclic alcohols, the carbon bearing the OH is numbered as “1.”
* Phenols are named after the parent compound

**phenol**; the C bearing the OH is numbered as “1.”

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|  |  |
| --- | --- |
| ***Examples: Naming Alcohols and Phenols*** | |
| * Provide acceptable IUPAC names for the following |  |
| compounds: |  |
| OH |  |
| HO CH2 CH2 OH HO CH CH2 CH CH CH3 |  |
| CH3 CH3 |  |
| CH2 CH CH2 CH3 OH |  |
| OH OH OH CH CH2 CH |  |
| OH CH3 |  |
|  | 13 |

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CH2CH2CH3

Cl

OH

OH

OH

CH3

* Provide acceptable IUPAC names for the following compounds:

OH

***Examples: Naming Alcohols and Phenols***

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– 1-ethyl-1-hexanol (what’s wrong with this name?)

– 2,4,4,5-tetramethyl-2-heptanol

* Draw structural formulas for the following molecules:

– 3-methyl-2-pentanol

***Examples: Nomenclature of Alcohols***

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– 3-methyl-2,4-pentanediol

– 3-ethylphenol

* Draw structural formulas for the following molecules:

– 3-ethylcyclopentanol

***Examples: Nomenclature of Alcohols***

*Classification of Alcohols*

* Alcohols are classified as **primary** (**1°**), **secondary** (**2°**), or **tertiary** (**3°**) according to how many carbon groups are attached to the carbon bearing the OH group:

H

H

R''

R C OH

R C OH

R C OH

H

Primary 1°

R'

Secondary 2°

R'

Tertiary 3°

* The number of hydrogens on the carbon bearing the OH group does affect some chemical properties.

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Physical Properties of Alcohols

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*Hydrogen Bonding*

* The oxygen-hydrogen bond is an especially polar bond because oxygen is much more electronegative than hydrogen is.

H

H

+

-

O

O

O H

H

+

H

H

O

H

H

H

O

H

O

H

H

* The O—H bond is therefore a **polar bond**, and any molecule which contains an O—H bond (like an alcohol) is a **polar** molecule.

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*Physical Properties of Alcohols*

* The general rule in solubility is “like dissolves like.”
* Since the OH group makes alcohols polar, they will mix with polar solvents like water — as long as the carbon chain is fairly short.

– The longer the carbon chain, the less soluble the alcohol is.

Soluble

**Water solubility**

Insoluble

**Short chain alcohols** methanol ethanol isopropanol

butanol

pentanol

**Long chain alcohols** hexanol heptanol etc.

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*Boiling Points of Alcohols*

* Because alcohols hydrogen bond to each other, they have higher boiling points than alkanes of the same molecular weight.
* The boiling point of alcohols increases as the molecules become larger.

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*Hydrogen Bonding of Alcohols*

* Alcohols hydrogen-bond to water:

R

H

O

H

R

H

O

O

H

R

O

H

O

H

H

* Alcohols also hydrogen-bond to each other:

R

H

O

H

R

H

O

O

R

O

H

O

R

H

R

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|  |  |  |  |
| --- | --- | --- | --- |
| **Name** | **Structure** | **Molecular Weight** | **Boiling Point** |
| propane | CH3CH2CH3 | 44.09 g/mol | -42.1°C |
| dimethyl ether | CH3OCH3 | 46.07 g/mol | -24°C |
| ethanol | CH3CH2OH | 46.07 g/mol | 78.3°C |

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* Arrange the following substances in order of increasing boiling point and increasing solubility in water:
  + 2-butanol
  + 2-propanol
  + 2-methylpropane
  + 2-pentanol

***Examples: Physical Properties of Alcohols***

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Reactions of Alcohols

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*Dehydration of Alcohols to Produce Alkenes*

* Heating alcohols in concentrated sulfuric acid (**H2SO4**) at **180°C** removes the OH group and a H from an adjacent carbon to produce an **alkene**, with water as a by-product. Since water is “removed” from the alcohol, this reaction is known as a **dehydration reaction** (or an *elimination reaction*):

R R

R

R

R C C R

H2SO4 180°C

C C

+ H2O

H

OH

R

R

CH3 CH

OH

CH3

H2SO4 180°C

CH3 CH CH2 + H2O

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*Dehydration of Alcohols to Produce Alkenes*

* If there is more than one possible product of a dehydration reaction, the major product can be predicted from Zaitsev’s Rule:
* **Zaitsev’s Rule** — when an alkene is produced in an elimination reaction, the major product is the one with the more highly substituted double bond.

CH3 CH2 CH

OH

CH3

H2SO4 180°C

CH3

CH CH CH3+ H2O

90%

CH3

CH2 CH

10%

CH2

CH3 CH2 CH

OH

CH2 CH3

H2SO4 180°C

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H2SO4 180°C

CH3

CH3 CH3

CH3 C CH OH

H2SO4 180°C

CH3

CH3 CH CH CH2 CH3 OH

* Complete the following reactions:

***Examples: Dehydration of Alcohols***

|  |  |
| --- | --- |
| ***Examples: Dehydration of Alcohols*** | |
| * Complete the following reactions: |  |
| CH3 |  |
| OH |  |
| H2SO4 |  |
| 180°C |  |
| CH3 CH3 |  |
| OH |  |
| H2SO4 |  |
| 180°C |  |
| CH3 |  |
| CH3 | 29 |

*Dehydration of Alcohols to Produce Ethers*

* Heating alcohols (R—OH) in concentrated sulfuric acid (**H2SO4**) at **140°C** removes a molecule of water from two alcohol molecules, causing the two “R” groups to become attached to an oxygen atom, forming an **ether** functional group:

R OH + R OH

H2SO4 140°C

R O R + H2O

CH3CH2OH + CH3CH2OH

H2SO4 140°C

CH3CH2OCH2CH3

diethyl ether

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H2SO4 180°C

CH3CHCH2CH3

OH

H2SO4 140°C

CH3CHCH3

OH

H2SO4 140°C

CH3CH2CH2OH

* Complete the following reactions:

***Examples: Dehydration of Alcohols***

*Oxidation of Alcohols to Carbonyl Compounds*

* An oxidation reaction occurs when a molecule *loses electrons*. This is usually manifested as an *increase in the number of oxygen atoms* or a *decrease in the number of hydrogen atoms*.
* Some common oxidizing agents include potassium permanganate (KMnO4), chromic acid (H2CrO4), sodium dichromate (Na2Cr2O7), and other Cr6+ salts.
* Alcohols can be oxidized by removing two H atoms from the molecule; the exact products of the reaction will depend on the type of alcohol.
* Representation in book:

R2CHOH + (O)  R2C=O + H2O

* [O] = oxidation

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*Oxidation of Alcohols to Carbonyl Compounds*

* Primary or secondary alcohols can be oxidized to produce compounds containing the carbonyl group (a carbon-oxygen double bond, C=O):

O H

O

R C

H

[O]

C

R

R

H

1° or 2° alcohol

aldehyde or ketone

O

carbonyl group

C

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*Oxidation of 1° Alcohols*

* Primary alcohols are oxidized first to **aldehydes**, but the aldehydes are then usually oxidized into **carboxylic acids**.

O H

O

O

R C

H

[O]

C

[O]

C

R

H

1° alcohol

H

aldehyde

R

OH

carboxylic acid

CH3CH2OH

ethanol

[O]

CH

3

O

C

H

[O]

CH

3

O

C OH

acetaldehyde

acetic acid

In the body, oxidation of ethanol to acetaldehyde takes place in the liver; the acetaldehyde is further oxidized to acetyl coenzyme A, which can be used to synthesize fat or eventually be oxidized to water and carbon dioxide.

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*Oxidation of 2° Alcohols*

* Secondary alcohols are oxidized to **ketones**, which cannot be oxidized any further:

O H

O

R C

R'

[O]

C

R

R'

H

2° alcohol

ketone

OH

O

CH3

CH CH3

[O]

CH3

C

acetone

CH3

2-propanol

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*Oxidation of 3° Alcohols*

* Tertiary alcohols, because there is by definition no hydrogen on the alcoholic carbon, cannot be oxidized:

OH

[O]

R C R''

no reaction

R'

3° alcohol

OH

CH3 C

CH3

[O]

NR

CH3

*t*-butyl alcohol

36

37

[O]

OH

CH3

[O]

* Complete the following reactions:

OH

***Examples: Oxidation of Alcohols***

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[O]

[O]

CH2OH

OH

OH

* Complete the following reactions:

CH2OH

[O]

***Examples: Oxidation of Alcohols***

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CH3CH2 O CH2CH3

CH2 CH2

CH3 CH CH3

CH3 CH2 CH2

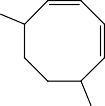
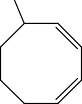
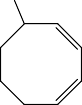
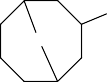
OH

OH

* Often, transformations on organic molecules must take place in more than one step.

O

***Examples: Multistep Reactions***



*Total Synthesis of Cyclooctatetraene*

R. Wilstatter and E. Waser, *Ber.*,

HO

CH3

O O

N

H

**1911**, *44*, 3423

A. C. Cope and C. G. Overberger,

*J. Amer. Chem. Soc.*, **1947**, *69*, 976;

**1948**, *70*, 1433

double

O

+ CH3NH2 +

H

O Mannich

reaction

NCH3 =

Na EtOH

O

O

pseudopelletierine

O

HO

OH

NCH3

H2SO4

NCH3

1. CH3I
2. Ag2O

N(CH3)2



OH-

(CH3)2N

(CH3)3N OH-

1. CH3I
2. Ag2O



Br2

Br

(CH3)2N

(CH3)3N

NH(CH )

OH-

3 2

1) CH I

3

2) Ag2O



OH- N(CH3)3

**Cyclooctatetraene**

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Br

N(CH3)2

Some Important Alcohols

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*Some Important Alcohols*

CH2 CH2 CH2 CH CH3

OH OH

OH OH

**Ethylene glycol**

antifreeze — pure ethylene glycol freezes at 11**°**F, but a 50:50 mixture of ethylene glycol and water freezes at -37**°**F; airplane de-icer; humectant (keeps other substances moist), used in ball point pen inks

**Propylene glycol** antifreeze, moisturizer in lotions and foods

O

OH

OH

**Cinnamic alcohol**

used in perfumes, particularly in lilac and other floral scents; flavoring agent, soaps, cosmetics

OH

**Lactic acid**

produced from fermentation of sugars during anaerobic conditions; sour taste, found in sourdough bread, pickles,

sauerkraut, sweat, etc. 42

OH

OH

OH

**-Turpineol** pine oil; perfume and bactericide used in

domestic cleaners

**Menthol**

oil of mint; has a cooling taste; found in cough drops, shaving lotion, and mentholated tobacco

**Benzyl alcohol**

used in perfumes and flavors, cosmetics, ointments, ball point pen inks

OH

**Vitamin A**

retinol

43



HO

OH

RCO2

O2CR

OH

**Glycerol / glycerin**

softening agent and moisturizer found is cosmetics and many foods; used to keep toothpaste moist

O2CR

A **triglyceride**

fats and oils

CHO

H OH

H

OH

OHO

HO

H

HO

H

H

H

H

OH

H

OH OH H OH

-D-glucose CH2OH

44



OH

O

OH

*A Few Sugars*

OH

OH

O

OH

OH

OH

O

OH

OH

OH

OH

-D-fructose -D-ribose

OH

-D-deoxyribose

OH

O

HO

HO

OH

O HO

-D-glucose OH O

OH

Sucrose

(a **disaccharide**)

OH

-D-fructose

45

O

OH

Polyoxyethylene

a *nonionic detergent*; produces less foam, and is more effective at lower temperatures than many other detergents

H O

H2N C C OH CH2

*Amino Acids containing alcohols*

H O

H O

H2N C C OH

H2N C C OH

OH

Tyrosine (Tyr)

CH3 CH OH

Threonine (Thr)

CH2OH

Serine (Ser)

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Phenols

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*Characteristics and Uses of Phenols*

* Phenols are usually weak acids:

OH O

+ H2O

+ H3O

* A solution of phenol in water (carbolic acid) can be used as an antiseptic and disinfectant. Joseph Lister introduced the use of phenol as a hospital antiseptic in 1867, which cut down drastically on deaths due to complications resulting from the use of unsterile equipment.

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“Lister and his carbolic acid ... succeeded in converting hospitals into something more than elaborate pauses on the way to the grave.” (Isaac Asimov, *Isaac Asimov’s Biographical Encyclopedia of Science and Technology*, 1972).

OH

*Important Phenols*

OH

Other phenols are also present in Lysol; they interfere with oxidation reactions to prevent the spoiling of food.

***ortho*-phenylphenol**

ingredient in Lysol

Cl

OH

OH

**2-benzyl-4-chlorophenol**

ingredient in Lysol

CH3

CH3

CH3

OH

Cl

**4-chloro-3,5-dimethylphenol**

topical antiseptic

CH2(CH2)4CH3

**4-n-hexylresorcinol**

found in mouthwash,

throat lozenges 49

*Phenols as Preservatives*

OH CH3 CH3

C

CH3

CH3

CH3

CH3 OH

C

CH3

CH3

C

CH3

O

CH3

**Antioxidants** used in preservation of foods, gasoline, lubricating oils, rubber, etc.

CH3

**BHA (butylated hydroxy anisole) BHT (butylated hydroxy toluene)**

2-*t*-butyl-4-methoxyphenol 2,6-di-*t*-butyl-4-methylphenol

CH3

HO

CH3

CH O

3 **Vitamin E**

CH3 antioxidant; prevents oxidation of lipids, red and white blood cells, polyunsaturated fatty acids, lung tissue; prevents oxidation in lungs of pollutants such as NO2 and O3

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*Phenols in Flavors and Fragrances*

OH

O

OCH3 O

**Piperine**

white and black pepper

N

CHO

**Vanillin**

oil of vanilla

O

OH

HO

O

SH

O

**2-Furylmethanethiol**

odor of coffee

OH

OH

**Pelargonidin**

a *flavonoid*; responsible for the red colors of geraniums, ripe raspberries, and strawberries

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O

CH3O

N

H

HO

**Capsaicin**

active component of red and green chili peppers, paprika

OH

OH

HO

O

**Estradiol**

**Testosterone**

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Ethers

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*Ethers*

* In the **ether** functional group, two carbon groups are connected to a single oxygen.

C O C

an **ether**

CH3 O CH3

CH3CH2 O CH2CH3

CH3 O CH2CH3

O CH CH3

CH3

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*Ether Nomenclature*

* Common names for ethers are obtained by first naming the two carbon groups attached to the oxygen (in alphabetical order) and then adding the word “ether” to the end. If the two groups are the same, the prefix “di-” is used, although sometimes this is simply dropped (“ethyl ether”).
* In the IUPAC system, ethers are named as **alkoxy** substituents (—OR = alkoxy group). The *-yl* ending of alkyl substituents is replaced by ***-oxy***

—CH3 methyl

—OCH3

methoxy

—CH2CH3 ethyl —OCH2CH3 ethoxy

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CH3

CH CH3

O

CH3CH2 O CH2CH3

CH3CH2 O CH3

CH3 O CH3

* For the following compounds, provide IUPAC names and trivial names (where possible).

***Examples: Nomenclature of Ethers***

|  |  |
| --- | --- |
| ***Examples: Nomenclature of Ethers*** | |
| * Name the following compounds: |  |
| O OH O CH3 CH3 |  |
| C |  |
| CH3 CH CH CH2 CH O CH3 |  |
| O CH3 |  |
| OCH3 O CH2 CH3 CH3 |  |
| CH3 CH CH2 O CH CH3 |  |
|  | 57 |

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O

OH

O

O

* Name the following compounds:

***Examples: Nomenclature of Ethers***

*Cyclic Ethers*

* Some ethers are found in cyclic structures. (A ring that contains elements other than carbon is called a *heterocyclic ring*.)

O

O

furan

O

tetrahydrofuran

pyran

* Tetrahydrofuran (THF) is a common solvent in organic reactions, often used in place of diethyl ether; furan and pyran turn up frequently in carbohydrate chemistry.

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*Physical Properties of Ethers*

* Alcohols hydrogen-bond to each other because they have highly polar O—H bonds.
* Ethers do not have O—H bonds, and so do **not**

hydrogen-bond to each other.

R

R

O H

H

O R

R

R

H

O

O

R

O

R

O

O

R

R

H

O

R

R

**alcohols**

R

**ethers**

*hydrogen bonding no hydrogen bonding*

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*Physical Properties of Ethers*

* Ethers are slightly polar, and **can** hydrogen-bond to water, although very weakly, through the oxygen atom:

R H H R O O O

R

R

* Ethers therefore have low boiling points, and a higher solubility in water than hydrocarbons.
* Ethers are inert to most reagents, so they make good solvent for chemical reactions.
* Some ethers make good anesthetics.

**boiling point:** alcohols > ethers > alkanes

**water solubility:** alcohols > ethers > alkanes

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O

*Some Important Ethers*

H2C CH2

**Ethylene oxide**

an *epoxide*

O

O

O

CH3

O CH3

C CH3 CH3

O

O

**methyl t-butyl ether (MTBE)**

A common gasoline additive used as an octane booster to oxygenate the gas, and make it burn with less "knocking." It has been used since 1979 as a replacement for tetraethyl lead (leaded gasoline). This additive is the subject of intense debate because of potential health hazards of drinking water contaminated with MTBE

O

**18-crown-6**

A "crown ether" (Charles J. Pedersen, Donald J. Cram, and Jean-Marie Lehn, Nobel Prize, 1987), which is capable of binding metal ions

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*Anesthetics*

N2O

**Nitrous oxide**

laughing gas

first chemical anesthetic (Sir Humphrey Davy, 1800)

CHCl3

**Chloroform**

(James Young Simpson, 1846; first to use anesthesia during childbirth)

O

**Diethyl ether**

first common anesthetic (Crawford W. Long, 1842 William T. G. Morton, Charles T. Jackson, 1844)

F

O

**Divinyl ether**

faster acting and less nauseating than diethyl ether

Br

F

Cl

H C C F

F

O

**Enflurane**

Cl F

**Halothane**

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*Polyfunctional Compounds*

* Compounds with more than one functional group are very common in nature; these polyfunctional molecules possess all of the reactivity of their individual functional groups.

O

O

O

OH

**Cholesterol**

O

HO

HN

O

O

OH

O

H H OH H

O

HO

O

H

O

O

O

**Taxol**

HO CH2

**Glucose**

C

C C C C

OH

OH H

OH

H

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Thiols

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*Thiols*

* Sulfur is in the same group on the periodic table as oxygen, and so forms many compounds which are similar to oxygen:

R OH

R SH

R S S R

an **alcohol** a **thiol** a **disulfide**

* Many thiols have strong, unpleasant odors. Ethanethiol, for instance, is added to natural gas to make it possible to detect gas leaks:

CH3CH2SH

ethanethiol

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# A Few Interesting Thiols

CH3CH2CH2SH

**Propanethiol**

CH2

CH2=CHCH2

CHCH2SH

Allyl thiol

S CH2CH=CH2

lachrymator produced when onions are cut

Allyl sulfide

These compounds are partially responsible for the odor and flavor of garlic.

O

H3N CH C O

CH2 SH

**Cysteine** (Cys)

The amino acid cysteine is found in many proteins; the SH group can link with other SH groups to form disulfide bridges.

* Disulfide linkages are important structural features of some proteins, especially those of hair.
* Enzymes containing SH groups can be damaged by complexation with heavy metals such as lead and mercury.

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*A Few Interesting Thiols*

CH3

CH2CH2CHCH3 SH

H

CH3

C C

CH3

S

S CH2

H

H

CH3

C C

HS CH2

H

68

*Gas Warfare*

O

Cl2

C

Cl Cl

Chlorine Phosgene

**Chlorine gas** and **phosgene** are among the first agents to have been used in gas warfare. Molecular chlorine is a gas at room temperature, and heavier than air; breathing chlorine gas causes pulmonary edema (swelling from excess fluid in tissues).

Phosgene is a particularly insidious poison, since symptoms may take from one to three days to appear. The gas does not have as obvious an odor as chlorine, and when inhaled, is hydrolyzed in the lungs to produce hydrochloric acid, which dissolves the membranes in the lungs. This can result in edema, blood loss, shock, and respiratory failure. Phosgene must be inhaled to be “effective,” since it cannot be absorbed through the skin.

69

*Gas Warfare*

S

Cl Cl

**Mustard gas**

**Mustard gas** is a chemical weapon first used in 1917 during World War I at the battle of Ypres. It has a sweet, agreeable odor, similar to that of mustard, but the similarity ends there.

It forms painful blisters on the skin (a *vesicant*) on contact, and in the lungs when inhaled; symptoms usually develop anywhere from 4 to 24 hours after exposure. Exposure produces deep, itching or burning blisters, swelling of the eyelids, and possibly blindness; inhalation at high concentrations damages the mucous membranes, causing bleeding and blistering within the lungs, leading to pulmonary edema.

It is also carcinogenic and mutagenic (causes damage to DNA).

Mustard gas is not very soluble in water but is very soluble in fat, contributing to its rapid absorption into the skin. It easily penetrated the early forms of protective clothing and gas masks.

Modern “improvements” include using longer carbon chains to make the molecule more hydrocarbon-like (and thus more fat-soluble). *Nitrogen mustards* have nitrogen atoms in place of the sulfur atom.

70

*Reactions of Alcohols*

**1. Dehydration of alcohols to give alkenes:**

R R

R

R

R C C R

H2SO4

180°C

C C + H2O

H

OH

R

R

**2. Dehydration of alcohols to give ethers:**

R OH

H2SO4 140°C

R O R + H2O

**3. Oxidation of a primary alcohol to give an aldehyde or carboxylic acid:**

H O O

[O] [O]

R C O H C C

R

H

1° alcohol

H

aldehyde

R

OH

carboxylic acid

71

**4. Oxidation of a secondary alcohol to give a ketone:**

H O

[O]

R C O H C

R R'

R' ketone

2° alcohol

**5. Oxidation of a tertiary alcohol — No Reaction:**

R''

[O]

R C O H NR

R'

3° alcohol

72



*Functional Groups*

R = a carbon group

R

R'''

O H

C C

CH3CH2CH3

alkane

R'

R''

alkene

R

C C

alkyne

R'

aromatic ring

phenol

O

O

O

R O R'

ether

R C H

R

C

ketone

R'

R C OH

aldehyde

carboxylic acid

73

H

H

R''

R C O H

R C O H

R C O H

H

primary (1°) alcohol

R'

secondary (2°) alcohol

R'

tertiary (3°) alcohol

OH

OR''

OH

OR'''

R C H

R C H

R C R'

R C R'

OR'

hemiacetal

OR'

acetal

OR''

hemiketal

OR''

ketal

74