

Chapter 3

Alcohols, Phenols, and Ethers

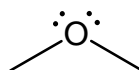
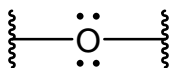
Chapter Objectives:

- 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.

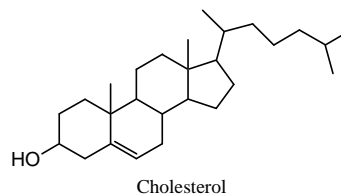
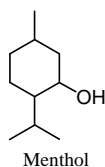
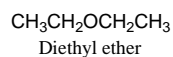
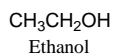
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 CHEM 2353 Fundamentals of Organic Chemistry
Organic and Biochemistry for Today (Seager & Slabaugh)
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Introduction

- 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 sp^3 -hybridized with a **bent** molecular shape:



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

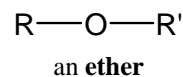
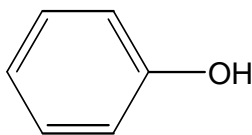
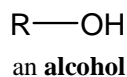


Alcohols

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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.



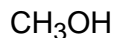
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Where Does the Word “Alcohol” Come From?

- The word “alcohol” comes from the Arabic term *al kohl* meaning “the fine powder.” Originally, this referred to an antimony sulfide (Sb_2S_3) 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



methanol

methyl alcohol
(wood alcohol)

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

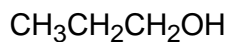
Found in wood smoke; contributes to the bouquet of new wine; metabolized in the body to formaldehyde and formic acid, and can cause blindness or death (> 50 mL)



ethanol

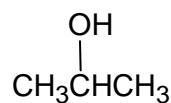
ethyl alcohol
(grain alcohol)

The alcohol 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



1-propanol

n-propyl alcohol



2-propanol

isopropyl alcohol

Rubbing alcohol is 70% isopropyl alcohol and 30% water

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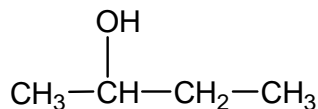
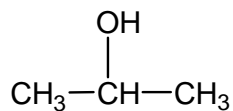
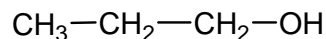
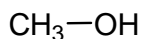
Nomenclature of Alcohols and Phenols

- **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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Examples: Naming Alcohols and Phenols

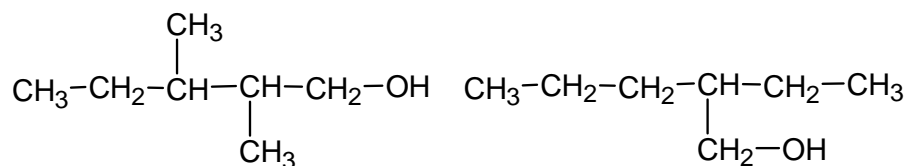
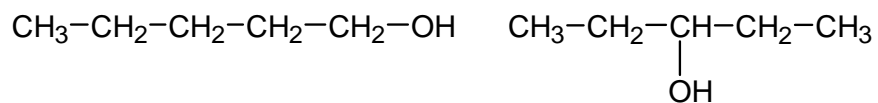
- Provide acceptable IUPAC names for the following compounds:



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Examples: Naming Alcohols and Phenols

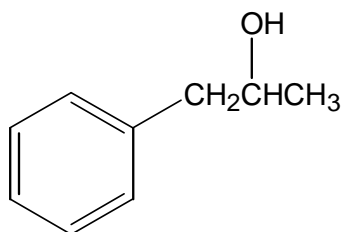
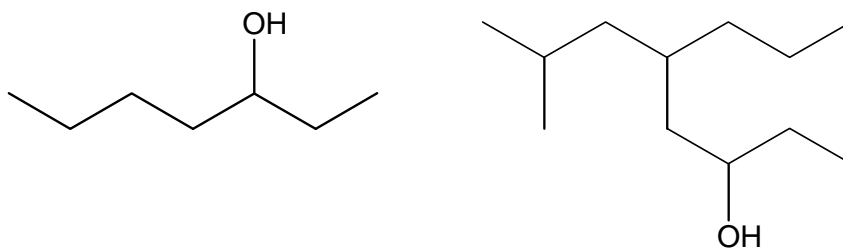
- Provide acceptable IUPAC names for the following compounds:



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Examples: Naming Alcohols and Phenols

- Provide acceptable IUPAC names for the following compounds:



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Examples: Naming Alcohols and Phenols

- Draw and name all of the possible isomers of butanol ($C_4H_{10}O$)

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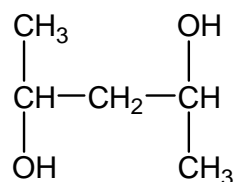
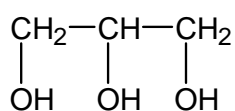
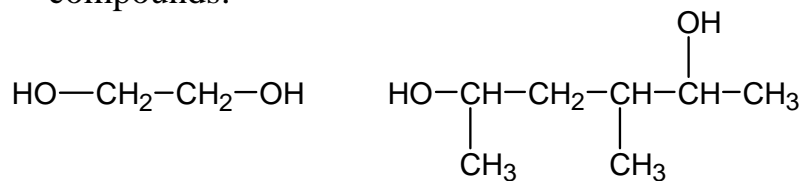
Nomenclature of Alcohols and Phenols

- If there is more than one OH group, a counting prefix (di-, tri-, tetra-, etc.) is placed immediately in front of the suffix **-ol** (*diol, triol, tetraol*, 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

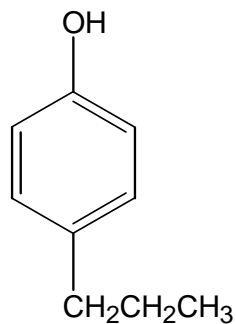
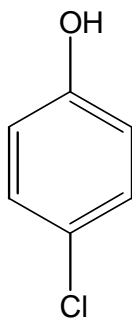
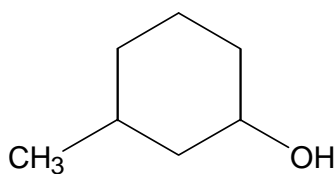
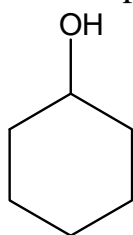
- Provide acceptable IUPAC names for the following compounds:



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Examples: Naming Alcohols and Phenols

- Provide acceptable IUPAC names for the following compounds:



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Examples: Nomenclature of Alcohols

- Draw structural formulas for the following molecules:
 - 3-methyl-2-pentanol

 - 2,4,4,5-tetramethyl-2-heptanol

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

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Examples: Nomenclature of Alcohols

- Draw structural formulas for the following molecules:
 - 3-ethylcyclopentanol

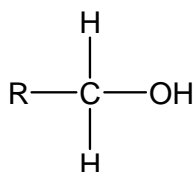
 - 3-ethylphenol

 - 3-methyl-2,4-pentanediol

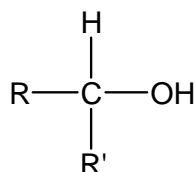
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Classification of Alcohols

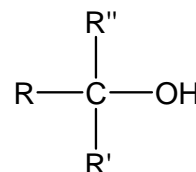
- Alcohols are classified as **primary** (1°), **secondary** (2°), or **tertiary** (3°) according to how many carbon groups are attached to the carbon bearing the OH group:



Primary
 1°



Secondary
 2°



Tertiary
 3°

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

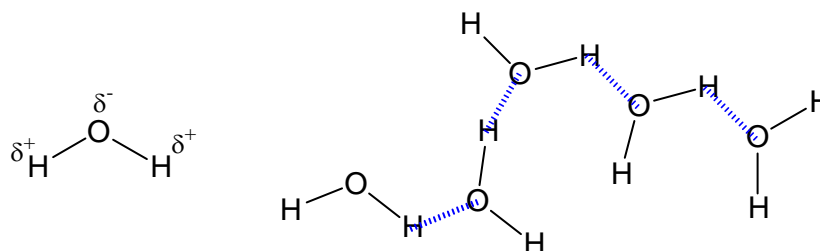
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Physical Properties of Alcohols

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Hydrogen Bonding

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

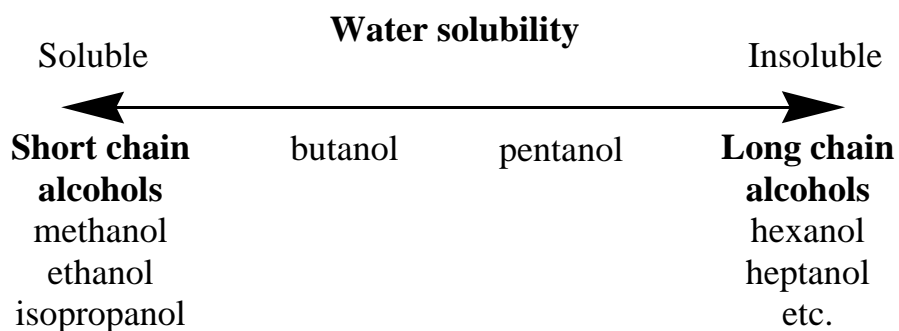


- The O—H bond is therefore a **polar bond**, and any molecule which contains an O—H bond (like an alcohol) is a **polar molecule**.

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Physical Properties of Alcohols

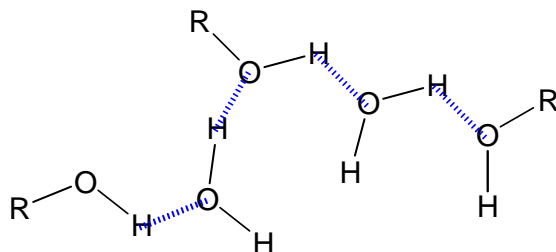
- The general rule in solubility is “like dissolves like.”
- Since the OH group makes alcohols polar, they will mix with polar solvents like water — as long as the carbon chain is fairly short.
 - The longer the carbon chain, the less soluble the alcohol is.



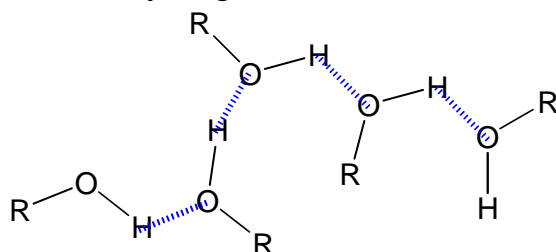
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Hydrogen Bonding of Alcohols

- Alcohols hydrogen-bond to water:



- Alcohols also hydrogen-bond to each other:



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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.

Name	Structure	Molecular Weight	Boiling Point
propane	$\text{CH}_3\text{CH}_2\text{CH}_3$	44.09 g/mol	-42.1°C
dimethyl ether	CH_3OCH_3	46.07 g/mol	-24°C
ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	46.07 g/mol	78.3°C

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Examples: Physical Properties of Alcohols

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

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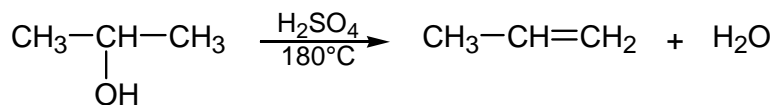
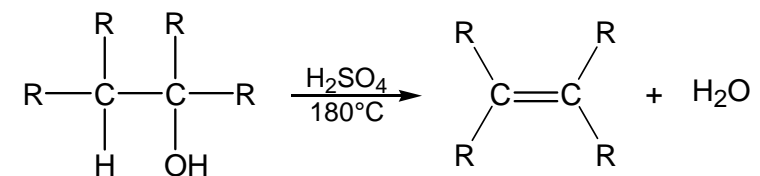
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Reactions of Alcohols

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Dehydration of Alcohols to Produce Alkenes

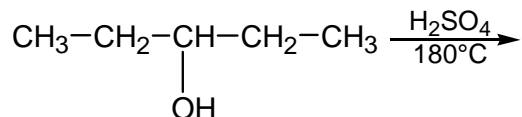
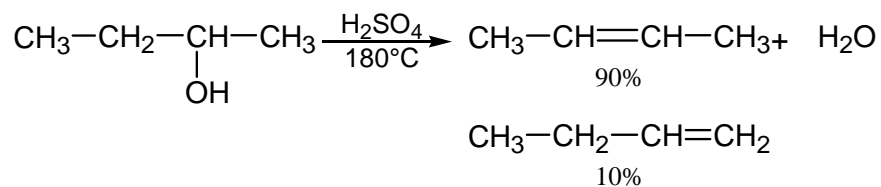
- Heating alcohols in concentrated sulfuric acid (H_2SO_4) at 180°C removes the OH group and a H from an adjacent carbon to produce an **alkene**, with water as a by-product. Since water is “removed” from the alcohol, this reaction is known as a **dehydration reaction** (or an *elimination reaction*):



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Dehydration of Alcohols to Produce Alkenes

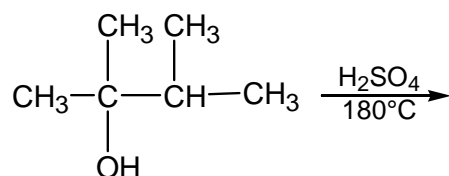
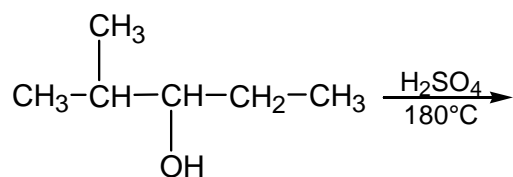
- If there is more than one possible product of a dehydration reaction, the major product can be predicted from Zaitsev's Rule:
- **Zaitsev's Rule** — when an alkene is produced in an elimination reaction, the major product is the one with the more highly substituted double bond.



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Examples: Dehydration of Alcohols

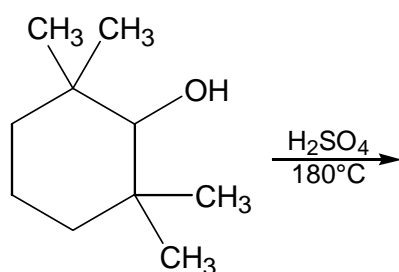
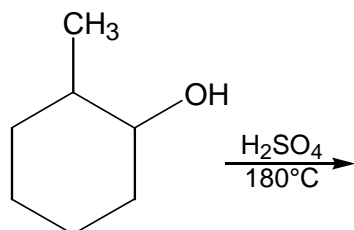
- Complete the following reactions:



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Examples: Dehydration of Alcohols

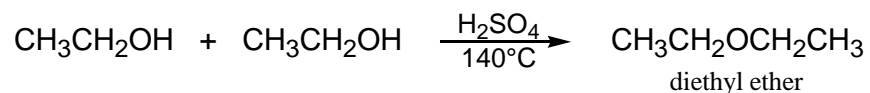
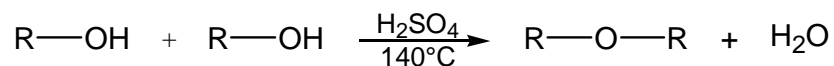
- Complete the following reactions:



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Dehydration of Alcohols to Produce Ethers

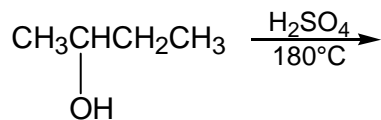
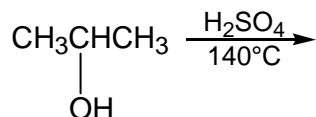
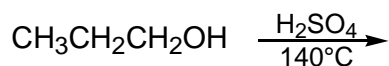
- Heating alcohols ($\text{R}-\text{OH}$) in concentrated sulfuric acid (H_2SO_4) at 140°C removes a molecule of water from two alcohol molecules, causing the two “R” groups to become attached to an oxygen atom, forming an **ether** functional group:



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Examples: Dehydration of Alcohols

- Complete the following reactions:



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Oxidation of Alcohols to Carbonyl Compounds

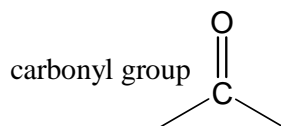
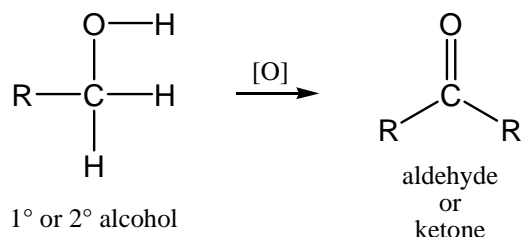
- An oxidation reaction occurs when a molecule *loses electrons*. This is usually manifested as an *increase in the number of oxygen atoms* or a *decrease in the number of hydrogen atoms*.
- Some common oxidizing agents include potassium permanganate (KMnO_4), chromic acid (H_2CrO_4), sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$), and other Cr^{6+} 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:

$$\text{R}_2\text{CHOH} + (\text{O}) \rightarrow \text{R}_2\text{C}=\text{O} + \text{H}_2\text{O}$$
- [O] = oxidation

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Oxidation of Alcohols to Carbonyl Compounds

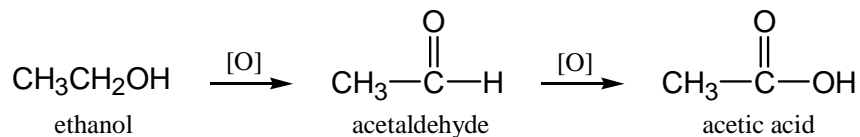
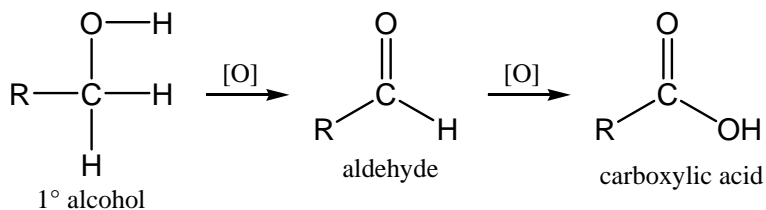
- Primary or secondary alcohols can be oxidized to produce compounds containing the carbonyl group (a carbon-oxygen double bond, C=O):



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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**.

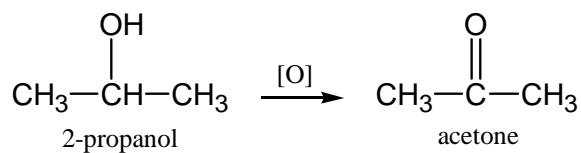
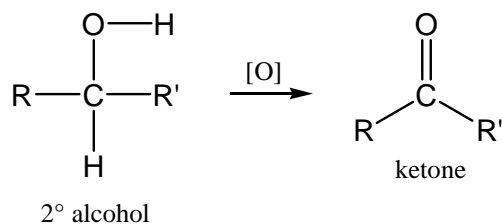


In the body, oxidation of ethanol to acetaldehyde takes place in the liver; the acetaldehyde is further oxidized to acetyl coenzyme A, which can be used to synthesize fat or eventually be oxidized to water and carbon dioxide.

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Oxidation of 2° Alcohols

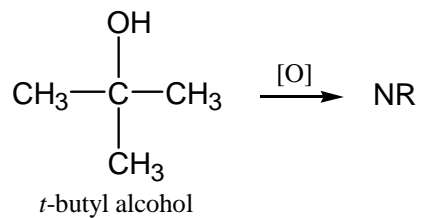
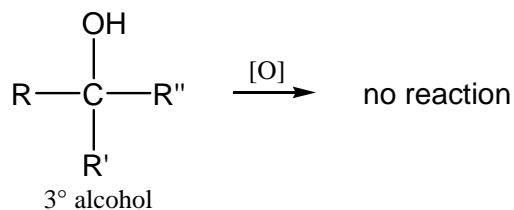
- Secondary alcohols are oxidized to **ketones**, which cannot be oxidized any further:



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Oxidation of 3° Alcohols

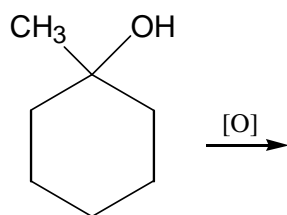
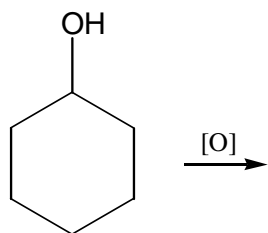
- Tertiary alcohols, because there is by definition no hydrogen on the alcoholic carbon, cannot be oxidized:



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Examples: Oxidation of Alcohols

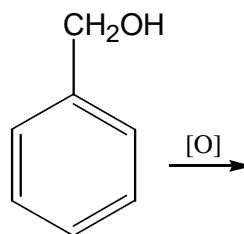
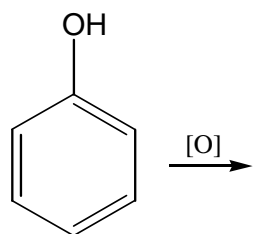
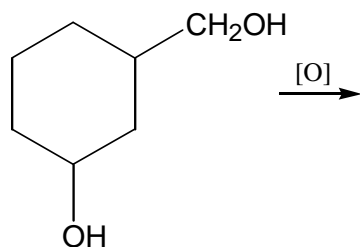
- Complete the following reactions:



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Examples: Oxidation of Alcohols

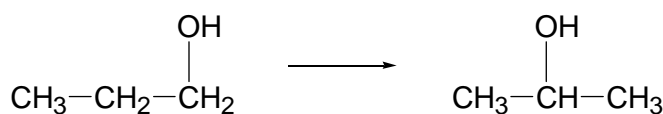
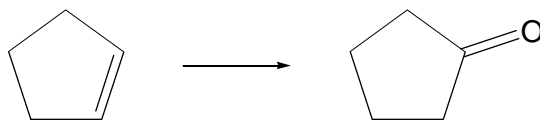
- Complete the following reactions:



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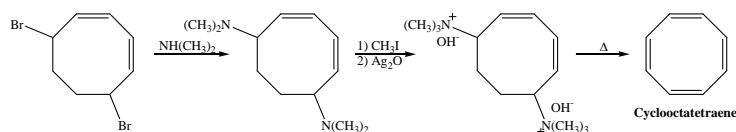
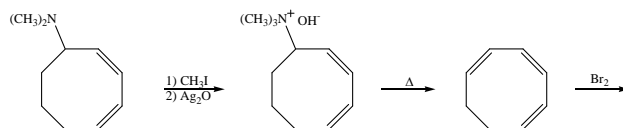
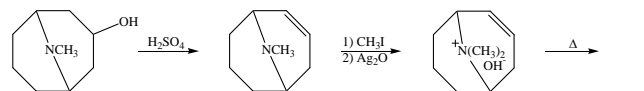
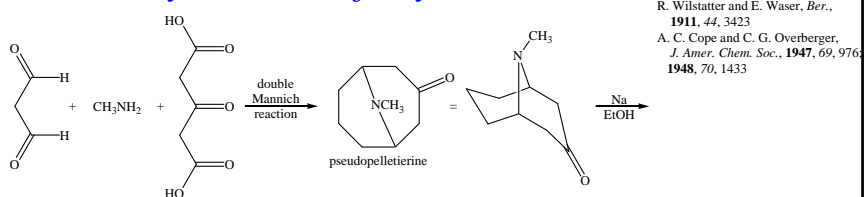
Examples: Multistep Reactions

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



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Total Synthesis of Cyclooctatetraene

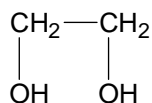


40

Some Important Alcohols

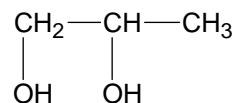
41

Some Important Alcohols



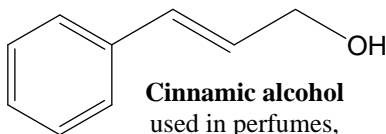
Ethylene glycol

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



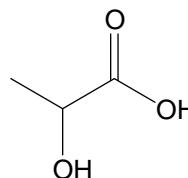
Propylene glycol

antifreeze, moisturizer in lotions and foods



Cinnamic alcohol

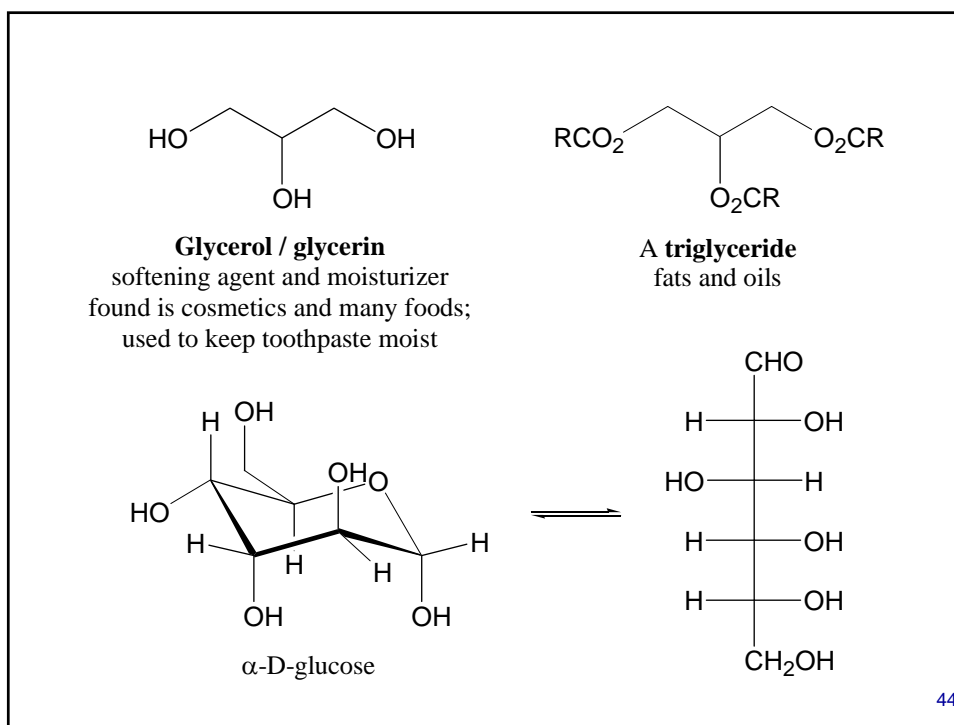
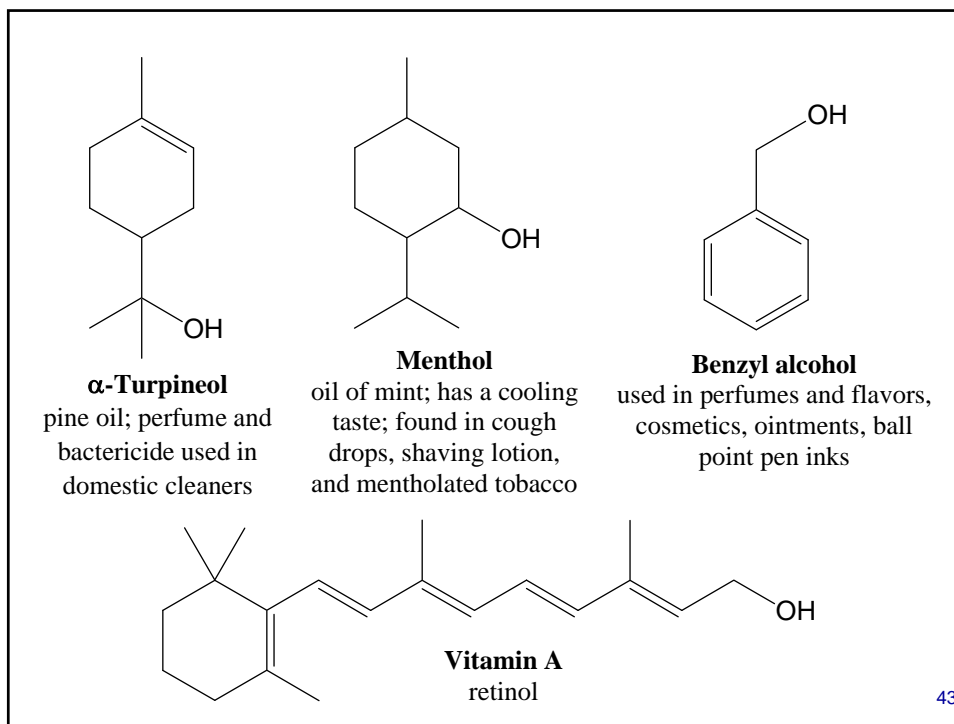
used in perfumes, particularly in lilac and other floral scents; flavoring agent, soaps, cosmetics

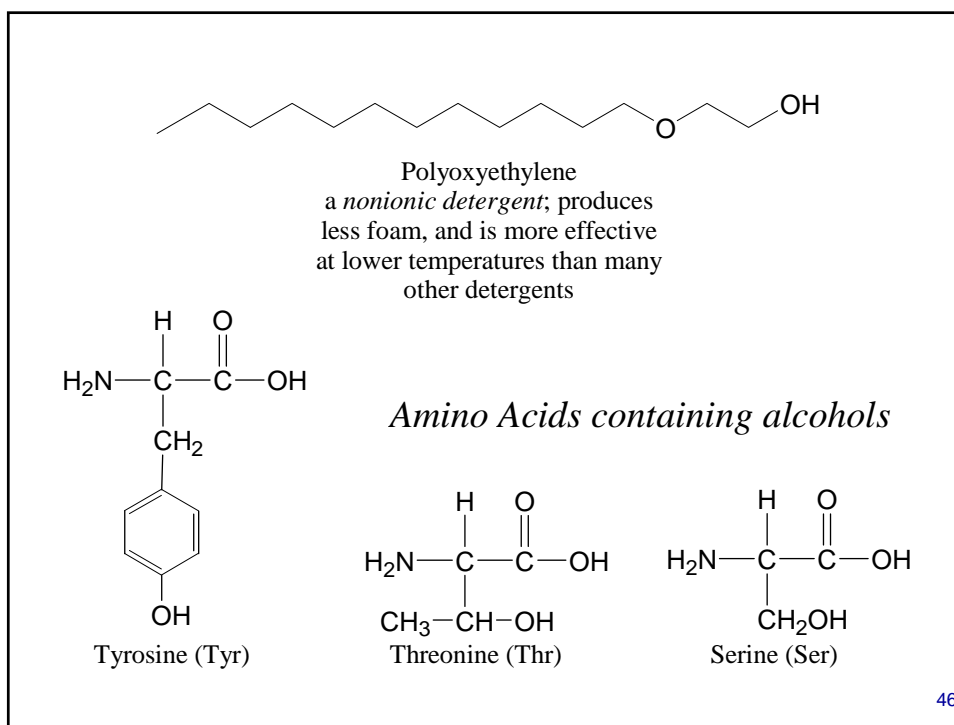
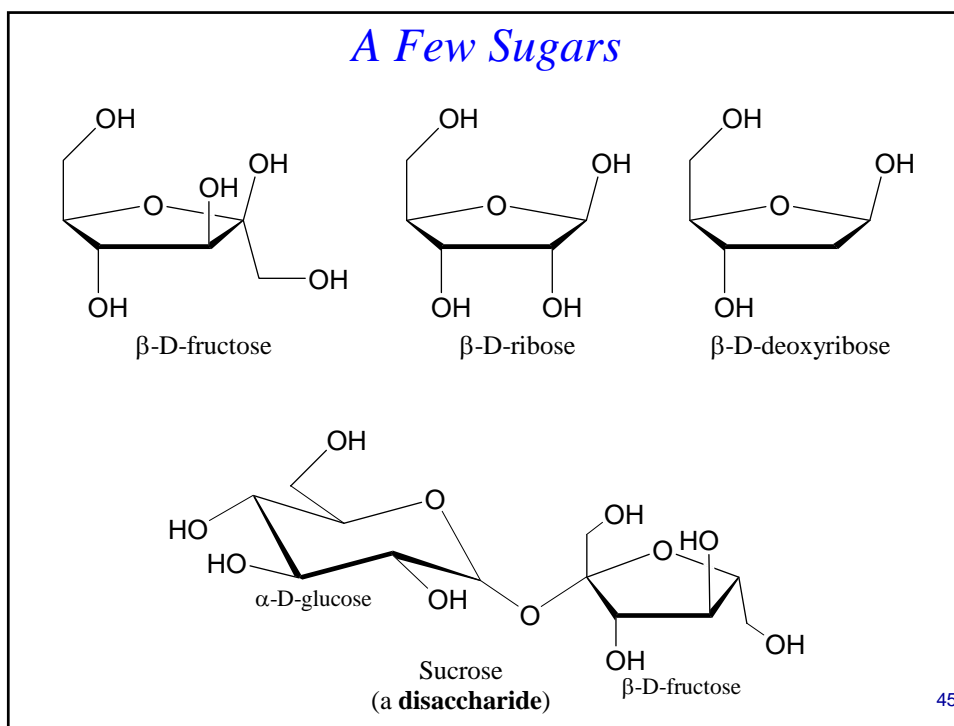


Lactic acid

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

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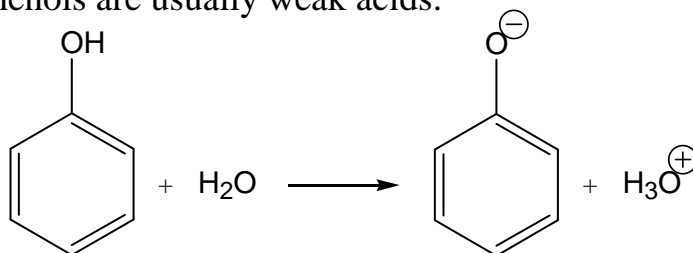


Phenols

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Characteristics and Uses of Phenols

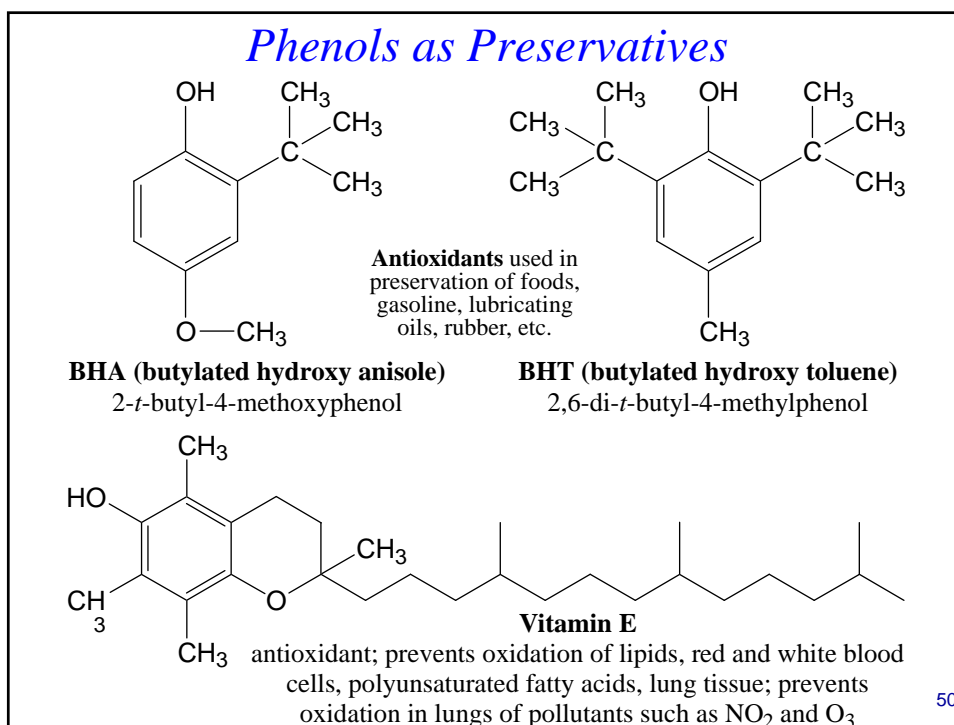
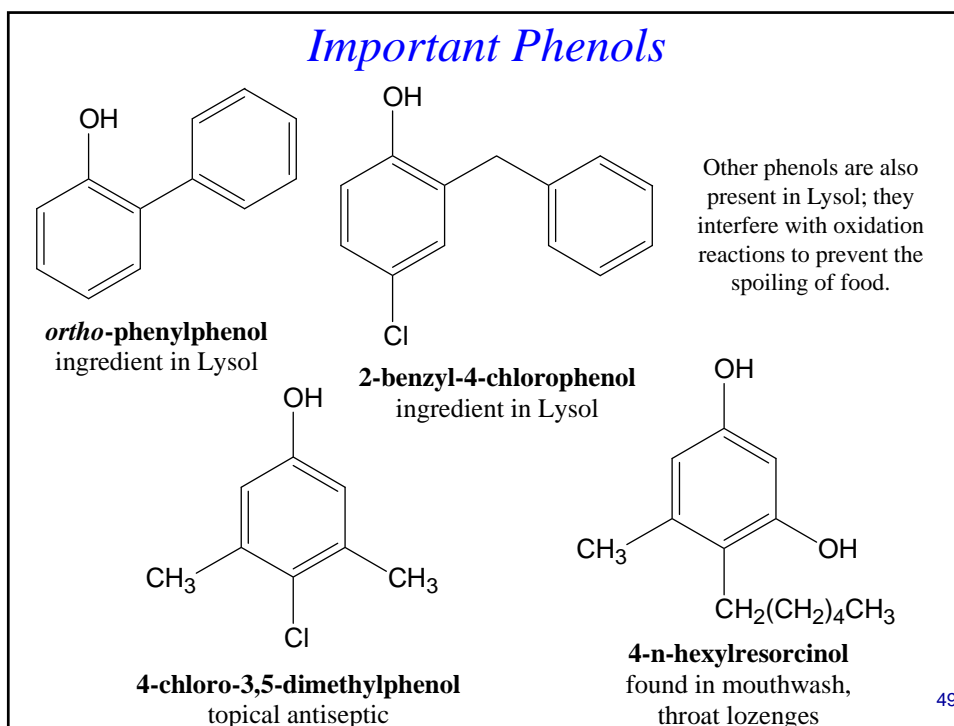
- Phenols are usually weak acids:



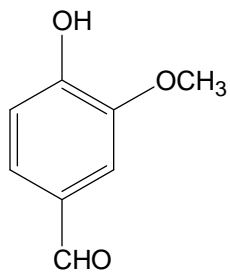
- A solution of phenol in water (carbolic acid) can be used as an antiseptic and disinfectant. Joseph Lister introduced the use of phenol as a hospital antiseptic in 1867, which cut down drastically on deaths due to complications resulting from the use of unsterile equipment.

“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).

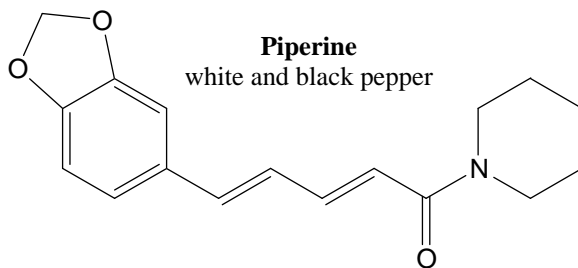
48



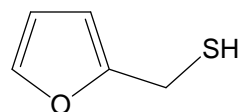
Phenols in Flavors and Fragrances



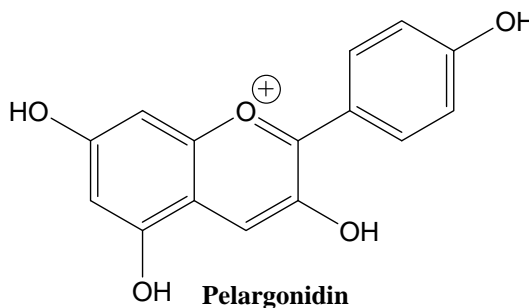
Vanillin
oil of vanilla



Piperine
white and black pepper

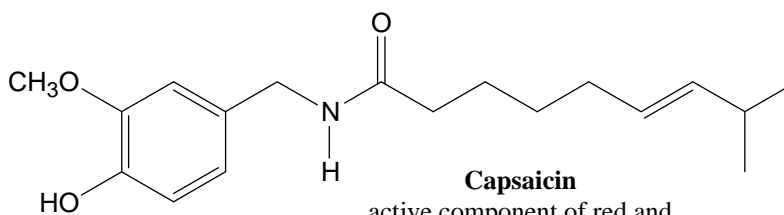


2-Furylmethanethiol
odor of coffee

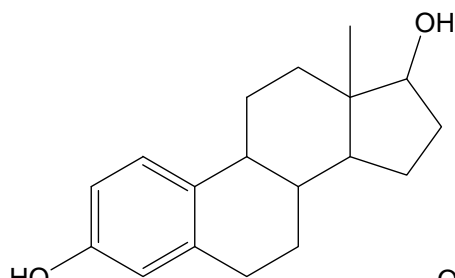


Pelargonidin
a flavonoid; responsible for the red colors of geraniums, ripe raspberries, and strawberries

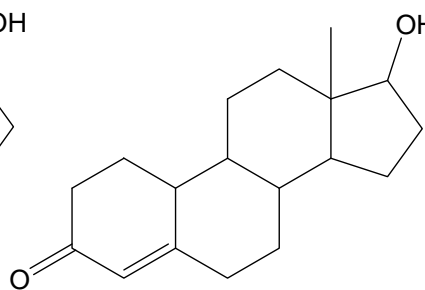
51



Capsaicin
active component of red and green chili peppers, paprika



Estradiol



Testosterone

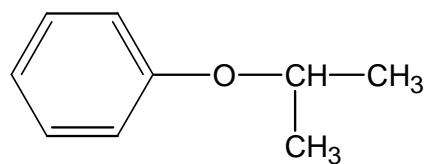
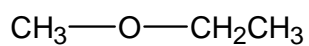
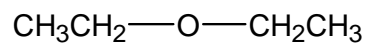
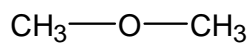
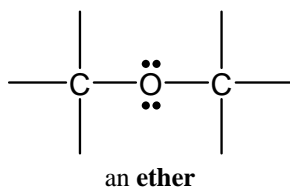
52

Ethers

53

Ethers

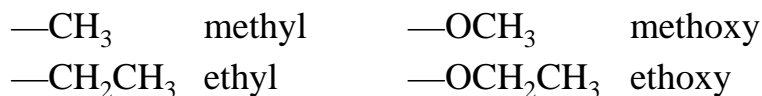
- In the **ether** functional group, two carbon groups are connected to a single oxygen.



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Ether Nomenclature

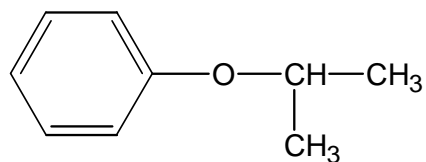
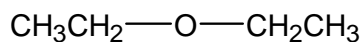
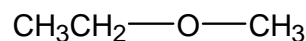
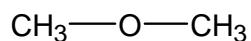
- Common names for ethers are obtained by first naming the two carbon groups attached to the oxygen (in alphabetical order) and then adding the word “ether” to the end. If the two groups are the same, the prefix “di-” is used, although sometimes this is simply dropped (“ethyl ether”).
- In the IUPAC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



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Examples: Nomenclature of Ethers

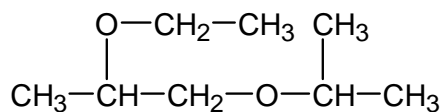
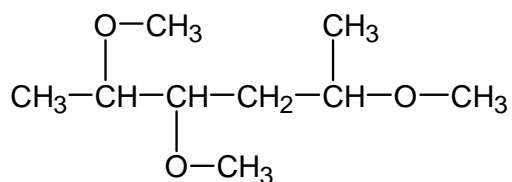
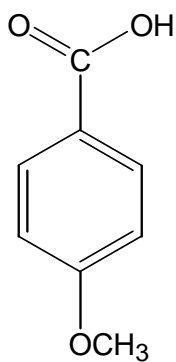
- For the following compounds, provide IUPAC names and trivial names (where possible).



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Examples: Nomenclature of Ethers

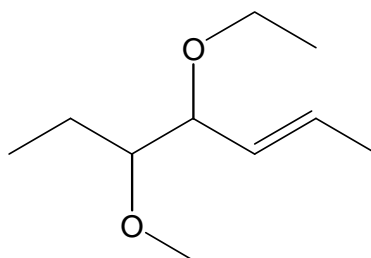
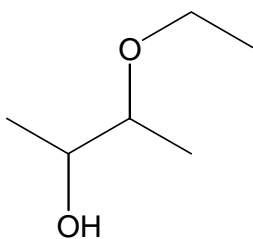
- Name the following compounds:



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Examples: Nomenclature of Ethers

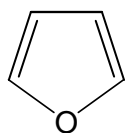
- Name the following compounds:



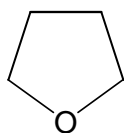
58

Cyclic Ethers

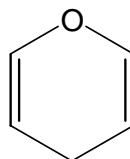
- Some ethers are found in cyclic structures. (A ring that contains elements other than carbon is called a *heterocyclic ring*.)



furan



tetrahydrofuran



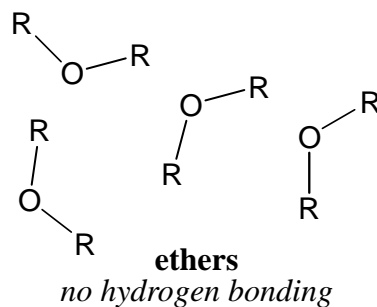
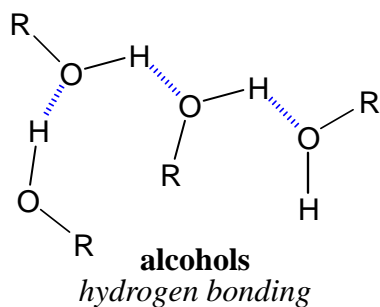
pyran

- 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

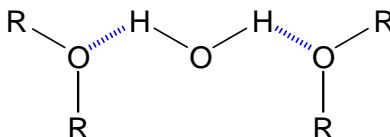
- Alcohols hydrogen-bond to each other because they have highly polar O—H bonds.
- Ethers do not have O—H bonds, and so do **not** hydrogen-bond to each other.



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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:



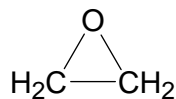
- Ethers therefore have low boiling points, and a higher solubility in water than hydrocarbons.
- Ethers are inert to most reagents, so they make good solvent for chemical reactions.
- Some ethers make good anesthetics.

boiling point: alcohols > ethers > alkanes

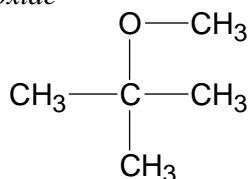
water solubility: alcohols > ethers > alkanes

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Some Important Ethers

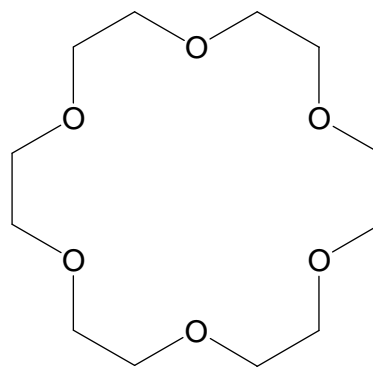


Ethylene oxide
an epoxide



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



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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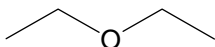
Anesthetics



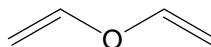
Nitrous oxide
laughing gas
first chemical anesthetic
(Sir Humphrey Davy, 1800)



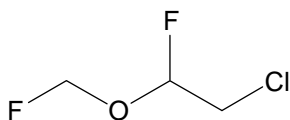
Chloroform
(James Young Simpson,
1846; first to use anesthesia
during childbirth)



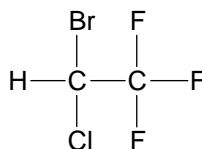
Diethyl ether
first common anesthetic
(Crawford W. Long, 1842
William T. G. Morton,
Charles T. Jackson, 1844)



Divinyl ether
faster acting and less
nauseating than diethyl ether



Enflurane

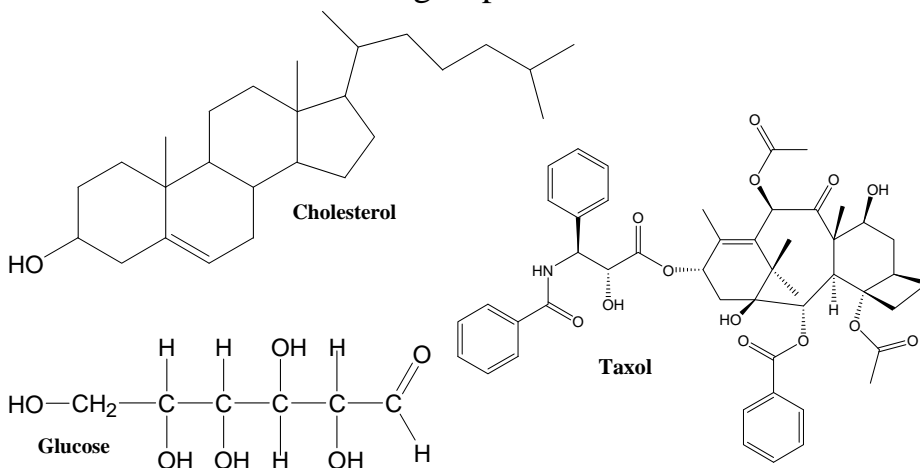


Halothane

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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.



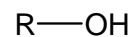
64

Thiols

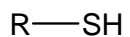
65

Thiols

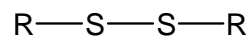
- Sulfur is in the same group on the periodic table as oxygen, and so forms many compounds which are similar to oxygen:



an **alcohol**



a **thiol**



a **disulfide**

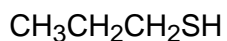
- Many thiols have strong, unpleasant odors. Ethanethiol, for instance, is added to natural gas to make it possible to detect gas leaks:



ethanethiol

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A Few Interesting Thiols

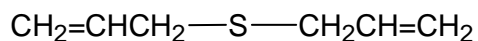


Propanethiol

lachrymator produced
when onions are cut

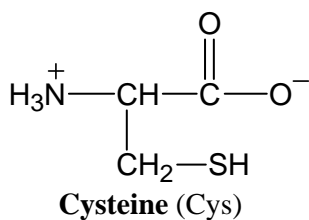


Allyl thiol



Allyl sulfide

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

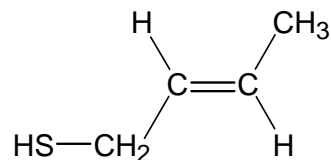
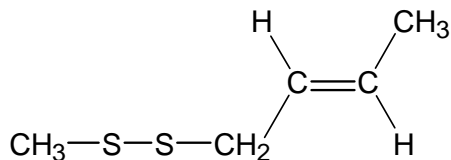
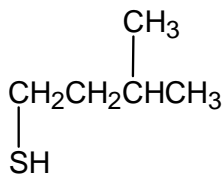


The amino acid cysteine is found in many proteins; the SH group can link with other SH groups to form disulfide bridges.

- 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.

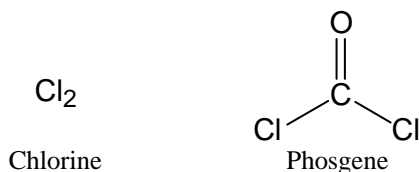
67

A Few Interesting Thiols



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Gas Warfare

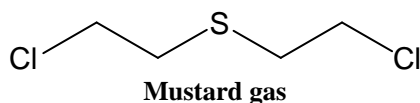


Chlorine gas and **phosgene** are among the first agents to have been used in gas warfare. Molecular chlorine is a gas at room temperature, and heavier than air; breathing chlorine gas causes pulmonary edema (swelling from excess fluid in tissues).

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.

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Gas Warfare



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).

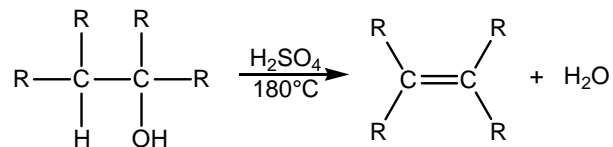
Mustard gas is not very soluble in water but is very soluble in fat, contributing to its rapid absorption into the skin. It easily penetrated the early forms of protective clothing and gas masks.

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.

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Reactions of Alcohols

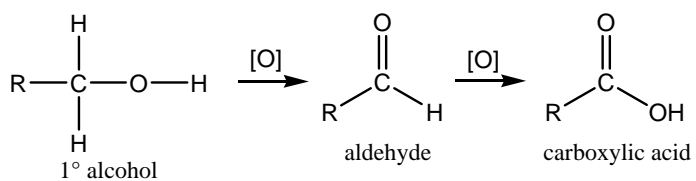
1. Dehydration of alcohols to give alkenes:



2. Dehydration of alcohols to give ethers:

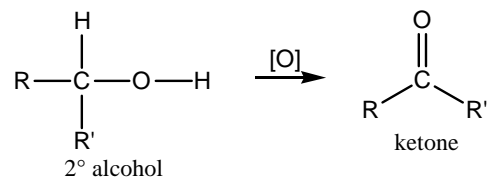


3. Oxidation of a primary alcohol to give an aldehyde or carboxylic acid:

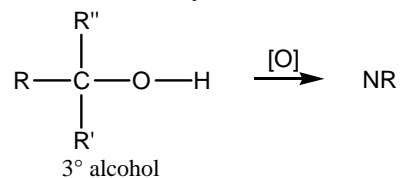


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4. Oxidation of a secondary alcohol to give a ketone:



5. Oxidation of a tertiary alcohol — No Reaction:



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