This field of switch grass is a prime source of biomass for ethanol production.
22.1 Functional Groups
22.2 Classification of Alcohols
22.3 Naming Alcohols
22.4 Physical Properties of Alcohols
22.5 Chemical Properties of Alcohols
22.6 Common Alcohols
22.7 Phenols
Chapter Outline

22.8 Properties of Phenols
22.9 Production of Phenol
22.10 Ethers
22.11 Structures and Properties of Ethers
22.12 Preparation of Ethers
22.13 Thiols

Chapter 22 Summary
A functional group is a group of atoms (or atom) in an organic compound that has specific behavioral characteristics.

For example the hydroxyl (–OH) group is the characteristic functional group for alcohols and phenols.

\[ R-OH \quad \text{alcohol} \]
\[ \text{phenol} \]
Alcohols, ethers, and phenols are organic compounds that are structural derivatives of water formed by replacing a hydrogen atom with an alky group or aromatic ring.
Classification of Alcohols

Structurally, an alcohol is derived from an aliphatic (non-aromatic) hydrocarbon by the replacement of at least one hydrogen atom with a hydroxyl group (–OH).

Alcohols are represented by the general formula ROH, with methanol (CH₃OH) being the first member of the homologous series. (R represents an alkyl or substituted alkyl group.)
Classification of Alcohols

Models illustrating the structural arrangements of the atoms in methanol and ethanol are shown in Figure 22.1 below.
Classification of Alcohols

Alcohols are classified by the number of R groups attached to the hydroxyl carbon as shown here.

- Primary (1°)
  \[ R - \text{C} - \text{OH} \]
- Secondary (2°)
  \[ R - \text{C} - \text{OH} \]
- Tertiary (3°)
  \[ R - \text{C} - \text{OH} \]
Classification of Alcohols

Formulas of specific examples of these classes of alcohols are shown in Table 22.1 on the next slide. Methanol (CH₃OH) is grouped with the primary alcohols . . .
<table>
<thead>
<tr>
<th>Class</th>
<th>Formula</th>
<th>IUPAC name</th>
<th>Common name*</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td>CH₃OH</td>
<td>Methanol</td>
<td>Methyl alcohol</td>
<td>65.0</td>
</tr>
<tr>
<td>Primary</td>
<td>CH₃CH₂OH</td>
<td>Ethanol</td>
<td>Ethyl alcohol</td>
<td>78.5</td>
</tr>
<tr>
<td>Primary</td>
<td>CH₃CH₂CH₂OH</td>
<td>1-Propanol</td>
<td>n-Propyl alcohol</td>
<td>97.4</td>
</tr>
<tr>
<td>Primary</td>
<td>CH₃CH₂CH₂CH₂OH</td>
<td>1-Butanol</td>
<td>n-Butyl alcohol</td>
<td>118</td>
</tr>
<tr>
<td>Primary</td>
<td>CH₃(CH₂)₃CH₂OH</td>
<td>1-Pentanol</td>
<td>n-Pentyl alcohol (n-amyl)</td>
<td>138</td>
</tr>
<tr>
<td>Primary</td>
<td>CH₃CHCH₂OH</td>
<td>2-Methyl-1-propanol</td>
<td>Isobutyl alcohol</td>
<td>108</td>
</tr>
<tr>
<td>Primary</td>
<td>CH₃C=CH₂OH</td>
<td>Phenylmethanol</td>
<td>Benzyl alcohol</td>
<td>205.0</td>
</tr>
<tr>
<td>Secondary</td>
<td>CH₃CHCH₃</td>
<td>2-Propanol</td>
<td>Isopropyl alcohol</td>
<td>82.5</td>
</tr>
<tr>
<td>Secondary</td>
<td>CH₃CH₂CHCH₃</td>
<td>2-Butanol</td>
<td>sec-Butyl alcohol</td>
<td>91.5</td>
</tr>
<tr>
<td>Tertiary</td>
<td>CH₃C(CH₃)=OH</td>
<td>2-Methyl-2-propanol</td>
<td>t-Butyl alcohol</td>
<td>82.9</td>
</tr>
<tr>
<td>Dihydroxy</td>
<td>HOCH₂CH₂OH</td>
<td>1,2-Ethanediol</td>
<td>Ethylene glycol</td>
<td>197</td>
</tr>
<tr>
<td>Trihydroxy</td>
<td>HOCH₂CHCH₂OH</td>
<td>1,2,3-Propanetriol</td>
<td>Glycerol or glycerine</td>
<td>290</td>
</tr>
</tbody>
</table>
The –OH group of a 2\textsuperscript{o} alcohol like 2-butanol can be written as a single-line formula by enclosing the OH in parentheses. Single-line formulas for 3\textsuperscript{o} alcohols can also drawn this way.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CHCH}_3 & \quad \text{CH}_3\text{CH}_2\text{CH(OH)CH}_3 \\
\text{2-butanol} & \quad \text{2-butanol (written as a single-line formula)}
\end{align*}
\]
Alcohols with more than one –OH group are known as polyhydroxy alcohols. These include diols, triols, and carbohydrates like D-galactose and D-glucose.

\[
\text{D-Galactose} \quad \text{D-Glucose}
\]

\[
\begin{align*}
\text{HO} & \quad \text{HO} \\
\text{HO} & \quad \text{HO} \\
\text{H} & \quad \text{CH}_2\text{OH} \\
\end{align*}
\]
Each hydroxyl group in a polyhydroxyl alcohol can be classified as 1°, 2° or 3°. Classify each hydroxyl group in D-galactose.
Each hydroxyl group in a polyhydroxyl alcohol can be classified as 1º, 2º or 3º. Classify each hydroxyl group in D-galactose.
IUPAC Rules for Naming Alcohols

1. Select the longest continuous chain of carbon atoms containing the hydroxyl group.

2. Number the carbon atoms in this chain so that the carbon atom bearing the –OH group has the lowest possible number.
IUPAC Rules for Naming Alcohols

3. Form the parent alcohol name by replacing the final -e of the corresponding alkane name by -ol.

When isomers are possible (alcohols with three or more carbon atoms) indicate the position of the hydroxyl in the name by placing the number of the carbon atom to which the –OH is bonded immediately before the parent alcohol name.
IUPAC Rules for Naming Alcohols

4. Name each alkyl side chain (or other group), and designate its position by number.
See how the following examples are named with the use of the IUPAC System.

- 2-propanol: \( \text{CH}_3\text{CHCH}_3\text{OH} \)
- Cyclohexanol: \( \text{cyclic hexane with one OH group} \)
- 1,3-cyclohexanediol: \( \text{cyclic hexane with two OH groups} \)
- 3-methyl-1-butanol: \( \text{CH}_3\text{CHCH}_2\text{CH}_2\text{OH} \)
- 1,2-ethanediol: \( \text{HOCH}_2\text{CH}_2\text{OH} \)
Your Turn!

Name the following alcohol using the IUPAC method.

\[
\text{CH}_3\text{CH}_2\text{CCH}_2\text{CHCH}_2\text{CH}_3
\]

OH

\[
\text{CH}_3
\]

\[
\text{CH}_3\text{CH}_2\text{CCH}_2\text{CHCH}_2\text{CH}_3
\]
Your Turn!

Name the following alcohol using the IUPAC method.

5,5-dimethyl-3-heptanol
Your Turn!

Write the structural formula of 2,4-dimethyl-2-hexanol.
Your Turn!

Write the structural formula of 2,4-dimethyl-2-hexanol.
Physical Properties of Alcohols

Alcohols contain the polar hydroxyl group (–OH).

The –OH group can undergo hydrogen bonding which affects the solubility and boiling point of alcohols.
Hydrogen bonding between alcohol molecules explains the increase in boiling points of alcohols compared to alkanes.
Physical Properties of Alcohols

Hydrogen bonding between alcohol and water molecules explains the increased solubility of alcohols in water as compared to alkanes.

![Diagram of hydrogen bonding between water and alcohol molecules]

water–alcohol
Table 22.2 shows that the boiling point of an alcohol is much higher than the parent alkane. This difference is because of hydrogen bonding.

Table 22.2  Comparison of Boiling Points of Alkanes and Monohydroxy Alcohols

<table>
<thead>
<tr>
<th>Name</th>
<th>Boiling point (°C)</th>
<th>Name</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>36</td>
<td>1-Pentanol</td>
<td>138</td>
</tr>
<tr>
<td>Hexane</td>
<td>69</td>
<td>1-Hexanol</td>
<td>157</td>
</tr>
<tr>
<td>Octane</td>
<td>126</td>
<td>1-Octanol</td>
<td>195</td>
</tr>
<tr>
<td>Decane</td>
<td>174</td>
<td>1-Decanol</td>
<td>233</td>
</tr>
</tbody>
</table>
Increasing the number of –OH groups in a molecule increases the boiling point and water solubility of the molecule.
Notice in Table 22.3 that the boiling point of 1,2-ethanediol is 100°C higher than the boiling point of 1-propanol because of an additional –OH group.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Molar mass</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>CH₃CH₂OH</td>
<td>46</td>
<td>78</td>
</tr>
<tr>
<td>1,2-Ethanediol</td>
<td>CH₂(OH)CH₂OH</td>
<td>62</td>
<td>197</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>CH₃CH₂CH₂OH</td>
<td>60</td>
<td>97</td>
</tr>
</tbody>
</table>
Physical Properties of Alcohols

The effect of added –OH groups on solubility is most noticeable when you consider a carbohydrate like glucose . . .
Physical Properties of Alcohols

Notice the difference in solubility of hexanol (only one –OH group) and glucose (five –OH groups).

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \]

1-hexanol

(solubility = 0.6g/100g H\(_2\)O)

\[ \text{H} \quad \text{C} \quad \text{=O} \]

\[ \text{H} \quad \text{OH} \]

\[ \text{HO} \quad \text{H} \]

\[ \text{H} \quad \text{OH} \]

\[ \text{H} \quad \text{OH} \]

\[ \text{CH}_2\text{OH} \]

D-glucose

(solubility = 95g/10g H\(_2\)O)
Branching also affects boiling points. A branched-chain alcohol will have a lower boiling point than the corresponding straight-chain alcohol.

For example 2-butanol is branched and has a boiling point of 91.5°C versus 118°C for 1-butanol which is a straight-chain molecule.

\[
\begin{align*}
\text{2-butanol} & : \text{CH}_3\text{CH}_2\text{CHCH}_3 \quad \text{OH} \\
\text{1-butanol} & : \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}
\end{align*}
\]
Physical Properties of Alcohols

Alcohols with three carbon atoms or fewer are infinitely soluble in water while those with four or more carbon atoms have limited solubility in water.

Recall that all hydrocarbons are insoluble in water.
List the alcohols below in order of increasing boiling point.

a) 1-butanol  b) 1-propanol  c) methanol  d) 1-pentanol
Your Turn!

List the alcohols below in order of increasing boiling point.

a) 1-butanol  b) 1-propanol  c) methanol  d) 1-pentanol

methanol → 1-propanol → 1-butanol → 1-pentanol

Lowest boiling point  Highest boiling point
Chemical Properties of Alcohols

Alcohols undergo many reactions including these five.

- **Protonation** to form an oxonium ion
- **Deprotonation** to form an alkoxide ion
- **Oxidation** to form aldehydes, ketones, and carboxylic acids
- **Dehydration** to form alkenes and ethers
- **Esterification** to form carboxylic esters
Acid-base properties of alcohols

Alcohols can act as weak acids or weak bases (undergo protonation and deprotonation) due to the nature of the –OH group as shown here.
Chemical Properties of Alcohols

Alcohols form oxonium ions in the presence of a strong acid. Here methanol reacts with sulfuric acid and behaves like a base.

A protonated alcohol is called an oxonium ion.
Alcohols form alkoxide ions (RO\(^{-}\)) in the presence of strong bases or an alkali metal. Here ethanol reacts with sodium and behaves like an acid.

\[
\begin{align*}
2\text{H}_2\text{O} + 2\text{Na} & \rightarrow 2\text{Na}^+ + \text{OH}^- + \text{H}_2(\text{g}) \\
\text{sodium hydroxide} \\
2\text{CH}_3\text{CH}_2\text{OH} + 2\text{Na} & \rightarrow 2\text{Na}^+ + \text{OCH}_2\text{CH}_3^- + \text{H}_2(\text{g}) \\
\text{sodium ethoxide}
\end{align*}
\]

This is an example of an alkoxide ion.

The order of reactivity of alcohols with alkali metals is 1° > 2° > 3°.
Chemical Properties of Alcohols

Oxidation

The oxidation state of carbon is determined by the functional group.

Alkanes → Alcohols → \{Aldehydes, Ketones\} → Carboxylic acids → Carbon dioxide

Increasing oxidation state

Notice that aldehydes, ketones and carboxylic acids are more oxidized than alcohols.
The oxidation states of several compounds with different functional groups are shown in Table 22.4.

**Table 22.4 Oxidation States of Carbon in One-Carbon Compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number of C—O bonds</th>
<th>Oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0</td>
<td>−4</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>1</td>
<td>−2</td>
</tr>
<tr>
<td>H₂C═O</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>O[\text{HCO}]</td>
<td>3</td>
<td>+2</td>
</tr>
<tr>
<td>O═C═O</td>
<td>4</td>
<td>+4</td>
</tr>
</tbody>
</table>
Chemical Properties of Alcohols

Alcohols are oxidized to form aldehydes, ketones, or carboxylic acids. \([O]\) is the general symbol for oxidizing agents in reactions.

Some common oxidizing agents are \(\text{KMnO}_4\), \(\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4\), and \(\text{O}_2\).
Chemical Properties of Alcohols

• Primary alcohols oxidize to form aldehydes which then oxidize to form carboxylic acids.

• Secondary alcohols oxidize to form ketones.

• Tertiary alcohols do not oxidize under these conditions.
Chemical Properties of Alcohols

Chemical reactions:

1. Primary alcohol: $R-\text{CH-OH} \xrightarrow{[O]} R-\text{C-H} + \text{H}_2\text{O} \xrightarrow{[O]} R-\text{C-OH}$
   - Primary alcohol
   - Aldehyde
   - Carboxylic acid

2. Secondary alcohol: $R-\text{C-R} \xrightarrow{[O]} R-\text{C-R} + \text{H}_2\text{O}$
   - Secondary alcohol
   - Ketone

3. Tertiary alcohol: $R-\text{C-R} \xrightarrow{[O]} \text{No reaction}$
   - Tertiary alcohol

Chemical reactions illustrate the reactivity of alcohols under the influence of oxygen.
Chemical Properties of Alcohols

An application of the oxidation of alcohols is the oxidation of ethanol used in the alcohol breath analyzer test.

The orange color of $\text{K}_2\text{Cr}_2\text{O}_7$ in the picture on the left partially changes to green in the picture on the right when it reacts with ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) in the balloon indicating the presence of alcohol.
Chemical Properties of Alcohols

The human body metabolizes ethanol by oxidizing it. Ethanol is oxidized in the liver producing ethanal.

\[
\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{[O]} \text{CH}_3\text{C}==\text{H} \quad \text{ethanol} \quad \text{acetaldehyde (ethanal)}
\]

Ethanal is toxic and can damage the liver. Excess alcohol consumption can cause cirrhosis of the liver.
Chemical Properties of Alcohols

Ethanal is then oxidized to acetic acid during the metabolism of ethanol which can be used as a source of biochemical energy and thus contributes to overall caloric intake and can contribute to obesity.

\[
\begin{align*}
\text{CH}_3\text{-CH} & \xrightarrow{[O]} \text{CH}_3\text{-C- OH} \\
\text{acetaldehyde} & \quad \text{acetic acid}
\end{align*}
\]
Your Turn!

What are the products when 2-butanol is oxidized with $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$?
Your Turn!

What are the products when 2-butanol is oxidized with K$_2$Cr$_2$O$_7$/H$_2$SO$_4$?

2-Butanol is a 2° alcohol so the oxidation produces a ketone.
Dehydration

Alcohols are dehydrated to form alkenes when heated with sulfuric acid.

\[
\text{H--C--C--H} \quad \xrightarrow{96\% \, \text{H}_2\text{SO}_4 \, 180^\circ\text{C}} \quad \text{CH}_2\text{=CH}_2 + \text{H}_2\text{O}
\]

(only possible alkene product)
Some alcohols can form two alkenes when dehydrated as shown here.

Minor product due to one R group substituted on the double bond

Major product due to two R groups substituted on the double bond
Saytzeff’s rule can be used to predict the major product in a dehydration reaction. Saytzeff’s rule states that . . .

During intramolecular dehydration, if there is a choice of positions for the carbon–carbon double bond, the preferred location is the one that generally gives the more highly substituted alkene—that is, the alkene with the most alkyl groups attached to the double-bonded carbons.
Ethers can be prepared by a dehydration reaction between two primary alcohol molecules when heated with sulfuric acid.

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{96\% \text{H}_2\text{SO}_4, 140^\circ\text{C}} \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{H}_2\text{O} \]

diethyl ether
Chemical Properties of Alcohols

A reaction in which two molecules are combined by removing a small molecule is known as a condensation reaction. This reaction is an example of a condensation.

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{96\% H}_2\text{SO}_4, 140^\circ\text{C}} \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{H}_2\text{O}
\]

diethyl ether
Esterification

Alcohols also react with carboxylic acids to form esters in a reaction known as esterification.

\[
\text{R} - \text{C} - \text{OH} + \text{H} - \text{OR'} \rightleftharpoons \text{R} - \text{C} - \text{OR'} + \text{HOH}
\]

- Carboxylic acid
- Alcohol
- Ester

\[
\text{CH}_3\text{C} - \text{OH} + \text{HOCH}_2\text{CH}_3 \rightleftharpoons \text{CH}_3\text{C} - \text{OCH}_2\text{CH}_3 + \text{HOH}
\]

- Acetic acid
- Ethanol
- Ethyl acetate
Utility of the Hydroxyl Functional Group

The hydroxyl group is a particularly important functional group. It introduces a myriad of possible reactions leading to a variety of valuable organic compounds.
Figure 22.2 below shows three important reactions involving the hydroxyl functional group.
The introduction of the –OH is an important part of the metabolism of fat molecules in the body. First fat molecules are oxidized to form carbon-carbon double bonds.

\[
W \text{–CH}_2\text{–CH}_2\text{–Z} \rightarrow W \text{–CH} \equiv \text{CH} \text{–Z}
\]

part of a fat
(W and Z abbreviate the rest of the fat molecule)

an alkene
Chemical Properties of Alcohols

A –OH is added to the double bond which is then oxidized to form a ketone. The introduction of the hydroxyl group and the formation of the ketone are important steps in the metabolism of fat molecules.

\[ W-\text{CH} = \text{CH}-Z + H_2O \xrightarrow{H^+} W-\text{CH}-\text{CH}_2-Z \]  
an alcohol

\[ W-\text{CH}-\text{CH}_2-Z \xrightarrow{[O]} W-\text{C} = \text{CH}_2-Z \]  
a ketone
Your Turn!

Show the organic products for the following reactions.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(_2\text{CHCH}_3) \xrightarrow{60\% \text{ H}_2\text{SO}_4} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(_2\text{C}(_2\text{OH}) + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(_2\text{OH}) \xrightarrow{100^\circ \text{C}} \text{CH}_3\text{CH}_2\text{CH}_2\text{C}(_2\text{OH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{C}(_2\text{OH}) \xrightarrow{\text{H}^+} \text{H}^+
\]
Your Turn!

Show the organic products for the following reactions.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_3 \quad \xrightarrow{\text{60\% H}_2\text{SO}_4, 100^\circ\text{C}} \quad \text{CH}_3\text{CH}_2\text{CH}\equiv\text{CHCH}_3 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_3
\]

Major product \quad Minor product

Your Turn!

Show the organic product for the following reaction.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C} \quad \text{OH} \quad + \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \quad \text{H}^+ \quad \rightleftharpoons
\]
Your Turn!

Show the organic product for the following reaction.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(-\text{OH}) + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightleftharpoons[\text{H}^+]{\text{H}^+} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(-\text{O})-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3
\]

Esterification reaction to form an ester.
Common Alcohols

There are three general methods for synthesizing an alcohol.

1. Hydrolysis of an ester.

2. Alkaline hydrolysis of an alkyl halide (*1° and 2° alcohols only*).

3. Catalytic reduction of aldehydes and ketones.
Common Alcohols

Hydrolysis of an Ester

An ester can be hydrolyzed to form an alcohol and a carboxylic acid which is the reverse of esterification.

\[
\text{ester} \quad \text{RC} \text{--OR'} + \text{HOH} \xrightarrow{\Delta \text{H}^+} \text{RC} \text{--OH} + \text{R'}\text{OH}
\]

ester \quad \text{carboxylic acid} \quad \text{alcohol}
Alkaline hydrolysis of an alkyl halide to form $1^\circ$ or $2^\circ$ alcohols

Alkyl halides can be hydrolyzed to form an alcohol and a salt.

$$RX + NaOH(aq) \rightarrow ROH + NaX$$

alkyl halide \hspace{1cm} \text{alcohol}

$$CH_3CH_2Cl + NaOH(aq) \rightarrow CH_3CH_2OH + NaCl$$
Common Alcohols

Catalytic reduction of aldehydes and ketones

Aldehydes and ketones can be reduced to form $1^\circ$ and $2^\circ$ alcohols.

\[
\begin{align*}
\text{O} & \quad \parallel \\
R-C-H & \xrightarrow{\Delta} \quad \text{RCH}_2\text{OH} \\
1^\circ \text{alcohol} \\
\text{O} & \quad \parallel \\
R-C-R & \xrightarrow{\Delta} \quad \text{RCH-CH-R} \\
2^\circ \text{alcohol}
\end{align*}
\]
Common Alcohols

The preceding general methods can be used to make many alcohols, but these methods may not be practical for a specific alcohols.

Hence, for economic reasons, most of the widely used alcohols are made on an industrial scale by special methods that have been developed for specific alcohols as described on the following slides . . .
Common Alcohols

Preparation of Methanol

Methanol is a common industrial solvent prepared by the high-pressure catalytic hydrogenation of carbon monoxide.

\[ \text{CO} + 2\text{H}_2 \quad \xrightarrow{\text{ZnO–Cr}_2\text{O}_3, 300–400^\circ\text{C}, 200\text{ atm}} \quad \text{CH}_3\text{OH} \]
Common Alcohols

Properties of Methanol

Methanol has a boiling point of 65°C making it a highly flammable liquid.

Methanol is poisonous and can cause blindness or death when taken internally.
Common Alcohols

Properties of Methanol

Methanol is primarily used as a feedstock to produce the intermediate formaldehyde.

It is also used as an industrial solvent and as a denaturant for ethanol.
Common Alcohols

Preparation of Ethanol

Ethanol can be prepared by fermentation.

\[
\text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O} \xrightarrow{\text{yeast}} 2 \text{CH}_3\text{CH}_2\text{OH} + 2 \text{CO}_2
\]

glucose

ethanol
Common Alcohols

Preparation of Ethanol

Ethanol can also be prepared by the \textit{acid-catalyzed addition} of water to ethylene.

\[
\text{CH}_2\text{═CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{OH}
\]
Ethanol Properties and Applications

Pure ethanol has a boiling point of 78°C and is very hygroscopic. 100% ethanol takes up water very quickly until a stable concentration of 95.6% ethanol is reached.

Ethanol can act in the body as a food, drug, or a poison depending on the quantity consumed.
Ethanol Properties and Applications

Ethanol is used commercially as an intermediate in the manufacture of other chemicals such as acetic acid.

It is also used as a solvent for many organic substances, as a compounding ingredient for pharmaceuticals, perfumes, flavorings, etc., and as a major component in alcoholic beverages.
Common Alcohols

Preparation of 2-Propanol (isopropyl alcohol, isopropanol, rubbing alcohol)

2-Propanol is a secondary alcohol prepared from propene.

\[
\text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{CHCH}_3
\]

(propene) \hspace{2cm} \text{OH} \hspace{2cm} \text{2-propanol}
Common Alcohols

2-Propanol Applications

Commercial uses include the manufacture of chemicals like acetone, as an industrial solvent, and in rubbing-alcohol formulations.
Common Alcohols

Preparation of Ethylene Glycol (1,2-ethanediol)

Ethylene Glycol is a diol obtained from petroleum or prepared from ethylene oxide.

\[
2 \text{CH}_2\text{=CH}_2 + \text{O}_2 \xrightarrow{\text{Ag catalyst}} 200-300^\circ\text{C} 2 \text{CH}_2\text{=CH}_2 \quad \text{ethylene oxide (oxirane)}
\]

\[
\text{HOCH}_2\text{CH}_2\text{OH} \quad \text{1,2-ethanediol (ethylene glycol)}
\]
Common Alcohols

Ethylene Glycol Applications

Commercial uses of ethylene glycol include the manufacture of Dacron polyester fiber and Mylar film, explosives, antifreeze, as a solvent for paints, plastics, and ink applications.
Common Alcohols

Glycerol Applications (1,2,3-propanetriol, *glycerine*)

Glycerol is a polyhydroxy alcohol. It is a desirable commercial chemical because of its attraction for water which is due to the polarity of its hydroxyl groups.
Common Alcohols

Glycerol Applications (1,2,3-propanetriol, glycerine)

Commercial uses include the manufacture of polymers and explosives (see reaction below), as an emollient in cosmetics, as a humectant in tobacco products, and as a sweetener.

\[
\begin{align*}
\text{glycerol} & \quad + \quad 3\ \text{HONO}_2 \quad \xrightarrow{\text{nitric acid}} \quad \text{glyceryltribinitrate (nitroglycerine)} \\
\text{CH}_2\text{OH} & \quad + \quad 3\ \text{CH}_2\text{ONO}_2 \quad \xrightarrow{\text{glyceryltribinitrate (nitroglycerine)}} \quad 3\ \text{H}_2\text{O} + \quad \text{CH}_2\text{OONO}_2
\end{align*}
\]
**Phenols**

Phenols are organic compounds that have a hydroxy group attached to an aromatic ring.

![phenol structure](image)
Phenols

Naming Phenols

Derivatives of phenols are named using the general methods for naming aromatic compounds as shown here.

- \( m \)-bromophenol
- \( p \)-aminophenol
- 2,4,6-trinitrophenol (picric acid)
Your Turn!

Name the following phenol derivatives.
Your Turn!

Name the following phenol derivatives.

- 2,5-dibromophenol
- \( p \)-ethylphenol
- 4-chloro-3-nitrophenol
Some phenol derivatives are known by **common names** as shown here.

- **catechol**
  - 1,2-dihydroxybenzene
- **resorcinol**
  - 1,3-dihydroxybenzene
- **hydroquinone**
  - 1,4-dihydroxybenzene
Some phenol derivatives are used as flavoring agents like these and some are used in the manufacture of other useful derivatives.

vanilla  eugenol  thymol
vanilllin  eugenol  thymol

Chapter Outline
Phenols

BHT is a phenol and an antioxidant preservative for food. Urushiol is a phenol that is the active irritant in poison ivy and poison oak.

2,6-di-t-butyl-4-methylphenol (butylated hydroxytoluene, BHT)

Urushiol
These methylphenol derivatives are effective disinfectants
Phenols occur naturally in plants like marijuana (tetrahydrocannabinol) and some phenols are used as pH indicators (phenolphthalein).
Adrenalin is a phenol derivative and a hormone.
Phenol is a weak acid with a melting point of 41°C.

The table below is a comparison of the pH of phenol with the pH of water and acetic acid.

<table>
<thead>
<tr>
<th>Substance</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>7.0</td>
</tr>
<tr>
<td>Phenol (0.1M)</td>
<td>5.5</td>
</tr>
<tr>
<td>Acetic acid (0.1M)</td>
<td>2.87</td>
</tr>
</tbody>
</table>
Properties of Phenols

Phenols will react with a strong base like NaOH but not with weaker bases like NaHCO₃.

\[
\text{phenol} + \text{NaOH} \rightarrow \text{sodium phenoxide} + \text{H}_2\text{O}
\]
Properties of Phenols

Alcohols do not react with either NaOH or NaHCO₃. Phenols are stronger acids than alcohols.

\[
\text{ROH} + \text{NaOH} \rightarrow \text{no reaction}
\]

alcohol
The toxicity of phenols to microorganisms make them excellent antiseptics. For example 4-hexylresorcinol is used as an antiseptic in many pharmaceutical preparations.

\[
\text{OH} \\
\text{CH}_2\text{(CH}_2\text{)}_4\text{CH}_3
\]

4-hexylresorcinol
Phenol is obtained from coal tar but it is also produced synthetically by the process shown below.
Ethers are organic compounds that have the general formula ROR' where both R groups (alkyl or aromatic) can be the same or different.

Common names of ethers are formed from the names of the groups attached to the oxygen atom, followed by the word *ether* as shown on the next slide . . .
Ethers

The alkyl groups are listed in alphabetical order followed by the word *ether* as shown here.

![Chemical structure of CH₃-O-CH₂CH₃]

- methyl
- ether
- ethyl

Use a prefix if both alkyl groups are the same.

![Chemical structure of CH₃-O-CH₃]

- methyl
- ether
- methyl

dimethyl ether
To name ethers by the IUPAC System, you need to learn how to name alkoxy groups (RO–).

An alkoxy group consists of an alkyl or aryl group and an oxygen atom. It is named by dropping the -yl of the alkyl or aryl name and adding the suffix -oxy.

\[ \text{CH}_3\text{O} \text{ is called methoxy (meth + oxy)} \]
\[ \text{CH}_3\text{CH}_2\text{O} \text{ is called ethoxy (eth + oxy)} \]
\[ \text{is called phenoxy (phen + oxy)} \]
In the IUPAC System, ethers are named as alkoxy (RO–) derivatives of the alkane corresponding to the longest carbon–carbon chain in the molecule . . .
Ethers

1. Name the longest continuous carbon chain corresponding to the parent alkane.

2. Name the remaining part as an alkoxy group.

For example…

\[
\begin{array}{c}
\text{CH}_3\text{O} \\
\text{CH}_2\text{CH}_3
\end{array}
\]

This is the longest C—C chain, so call it ethane.

\[
\text{CH}_3\text{O}
\]

is the alkoxy group.

…would be named methoxyethane
Ethers

More examples . . .

\[
\text{CH}_3\text{CH}_2\text{O} \text{CH}_2\text{CH}_3 \text{ is ethoxyethane}
\]

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{O} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \text{ is 1-propoxybutane}
\]

Additional examples are shown on Table 22.5 on the next slide . . .
### Table 22.5 Names and Structural Formulas of Ethers

<table>
<thead>
<tr>
<th>Name*</th>
<th>Formula</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl ether (methoxymethane)</td>
<td>CH(_3)—O—CH(_3)</td>
<td>−25</td>
</tr>
<tr>
<td>Ethyl methyl ether (methoxyethane)</td>
<td>CH(_3)CH(_2)—O—CH(_3)</td>
<td>8</td>
</tr>
<tr>
<td>Diethyl ether (ethoxyethane)</td>
<td>CH(_3)CH(_2)—O—CH(_2)CH(_3)</td>
<td>35</td>
</tr>
<tr>
<td>Ethyl isopropyl ether (2-ethoxypropane)</td>
<td>CH(_3)CH(_2)—O—CHCH(_3)</td>
<td>54</td>
</tr>
<tr>
<td>Divinyl ether (ethenyloxyethene)</td>
<td>CH(_2)=CH—O—CH=CH(_2)</td>
<td>39</td>
</tr>
<tr>
<td>Anisole, methyl phenyl ether (methoxybenzene)</td>
<td>[Image] OCH(_3)</td>
<td>154</td>
</tr>
<tr>
<td>Diphenyl ether (phenoxybenzene)</td>
<td>[Image] O</td>
<td>259</td>
</tr>
<tr>
<td>Ethylene oxide (oxirane)</td>
<td>CH(_2)=CH(_2)</td>
<td>11</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF) (1,4-epoxybutane)</td>
<td>CH(_2)—CH(_2)</td>
<td>66</td>
</tr>
</tbody>
</table>
Your Turn!

Give common names and IUPAC names for the following ethers.

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3 \]

\[ \text{C}_6\text{H}_5\text{OCH}_2\text{CH}_3 \]
Your Turn!

Give common names and IUPAC names for the following ethers.

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>−O−CH<sub>2</sub>CH<sub>3</sub>

- **Common name:** ethyl propyl ether
- **IUPAC name:** 1-ethoxypropane

CH<sub>2</sub>=CH−O−CH<sub>2</sub>CH<sub>3</sub>

- **Common name:** ethyl phenyl ether
- **IUPAC name:** ethoxybenzene
Ethers have a bent shape similar to water and alcohols.
Ethers are polar enough to dissolve some polar substances like water but also nonpolar enough to dissolve many nonpolar organic compounds.
The slight solubility of ether in water and sulfuric can be explained by hydrogen bonding as shown here.
Because no –OH group is present, hydrogen bonding does not occur between ether molecules. This lack of hydrogen bonding can be seen by comparing the boiling points of a hydrocarbon, an ether, and an alcohol of similar molar mass, as in Table 22.6 on the next slide.

Notice that the boiling point of the ether is somewhat above that of the hydrocarbon but much lower than that of the more polar alcohol . . .
## Structures and Properties of Ethers

### Table 22.6 Boiling Points of Ethers, Alkanes, and Alcohols

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Molar mass</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl ether</td>
<td>CH$_3$OCH$_3$</td>
<td>46</td>
<td>−24</td>
</tr>
<tr>
<td>Propane</td>
<td>CH$_3$CH$_2$CH$_3$</td>
<td>44</td>
<td>−42</td>
</tr>
<tr>
<td>Ethanol</td>
<td>CH$_3$CH$_2$OH</td>
<td>46</td>
<td>78</td>
</tr>
<tr>
<td>Ethyl methyl ether</td>
<td>CH$_3$OCH$_2$CH$_3$</td>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>Butane</td>
<td>CH$_3$CH$_2$CH$_2$CH$_3$</td>
<td>58</td>
<td>−0.6</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>CH$_3$CH$_2$CH$_2$OH</td>
<td>60</td>
<td>97</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>CH$_3$CH(OH)CH$_3$</td>
<td>60</td>
<td>83</td>
</tr>
</tbody>
</table>
Ethers are common solvents found in laboratories because they are good solvents for polar and nonpolar compounds and have low chemical reactivity.

However, their use can be dangerous, since low-molar-mass ethers are volatile and highly flammable.
Another hazard of ethers is that, despite their generally low chemical reactivity, oxygen in the air slowly reacts with them to form unstable peroxides that are subject to explosive decomposition.

\[
\text{CH}_3\text{CH}_2\text{O} \text{CH}_2\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{CH} = \text{O} \text{CH}_2\text{CH}_3
\]

\[
\uparrow \quad \text{O} \quad \text{O} \quad \text{H}
\]

diethyl ether hydroperoxide
We have seen that ethers can be made by dehydration of alcohols by heating them in the presence of an acid.

Ethers are also be made from alkyl halides and sodium alkoxides or sodium phenoxides via a substitution reaction known as the Williamson synthesis.

\[
RX + R'ONa \rightarrow ROR' + NaX
\]

alkyl halide alkoxide ether
This synthesis is often used to prepare mixed ethers where \( R \neq R' \).
Write the equation for the preparation of phenyl propyl ether by the Williamson synthesis reaction.
Write the equation for the preparation of phenyl propyl ether by the Williamson synthesis reaction.

\[
\text{Ph-O-Na} \quad + \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \quad \rightarrow \quad \text{Ph-O-CH}_2\text{CH}_2\text{CH}_3 \quad + \quad \text{NaBr}
\]
Thiols are organic compounds that contain the –SH group as shown below. Thiols are also called mercaptans.

Thiols are named by adding the suffix -thiol to the alkane parent name.

\[
\begin{align*}
\text{CH}_3\text{SH} & \quad \text{methanethiol} \\
& \quad (\text{methyl mercaptan}) \\
\text{CH}_3\text{CH}_2\text{CHCH}_3 \quad \text{SH} & \quad \text{2-butanethiol} \\
& \quad (\text{sec-butyl mercaptan})
\end{align*}
\]
Thiols have several characteristic properties including:

- Foul odors
- Lower boiling points than alcohols
- Readily oxidized to form disulfides
Thiols

Thiols have strong offensive odors. For example the scent of a skunk is due to thiol components.

The strong odor associated with natural gas is due to the additive methanethiol ($CH_3SH$).
Thiol

Thiols have lower boiling points than alcohols.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} & \quad \text{CH}_3\text{CH}_2\text{SH} \\
\text{ethanol} & \quad \text{ethanethiol} \\
(b.p. \ is \ 78^\circ C) & \quad (b.p. \ is \ 36^\circ C)
\end{align*}
\]

Thiols boil at lower temperatures than alcohols because hydrogen bonds can’t form between thiol molecules but can form between alcohol molecules.
Thiols readily oxidize to form disulfides. A disulfide is a molecule containing a S–S bond.

\[ \text{K}_2\text{H} + \text{K}_2\text{H} \xrightarrow{[O]} \text{K} – \overset{\text{2}}{\text{2}} – \overset{\text{2}}{\text{2}} – \text{K} \]  

This is a disulfide.

\[ \text{CH}_3\text{SH} \quad \text{CH}_3\text{S-SCH}_3 \]
Thiols are important biological molecules

Thiol derivatives are found in proteins like insulin. The disulfide bond in insulin helps to create the three-dimensional shape of the protein.

The thioester group is found in acetyl coenzyme A which serves an important role in metabolism.
Chapter 22 Summary

- An alcohol is an organic compound that contains the hydroxyl functional group.

- A hydroxyl-group carbon of a primary alcohol is bonded to one other carbon. For a secondary alcohol, two carbons are bonded to the hydroxyl-group carbon; three carbons are bonded to the hydroxyl-group carbon for a tertiary alcohol.

- Polyhydroxy alcohols (or polyols) have more than one hydroxyl group per molecule.
Chapter 22 Summary

• Naming alcohols follows a similar process to that used for alkanes. Several alcohols are generally known by their common names.

• Because of the hydroxyl group, alcohols have higher boiling points than corresponding alkanes. Alcohols become more like hydrocarbons as the alkyl chain is made longer.
Chapter 22 Summary

• Hydrogen bonding between water and alcohol molecules accounts for their solubility. Hydrogen bonding between alcohol molecules accounts for their relatively high boiling points.

• Aliphatic alcohols, like water, can be protonated or deprotonated.

• Alcohols can be oxidized to form many different organic compounds.
Chapter 22 Summary

- Alcohols lose water in the presence of a strong acid. 1°, 2°, and 3° alcohols will undergo an intramolecular dehydration to form alkenes.

- 1° alcohols can be easily dehydrated to form ethers.

- Alcohols react with carboxylic acids to form esters in an esterification reaction.
Chapter 22 Summary

- Three general methods for making alcohols are hydrolysis of esters, alkaline hydrolysis of alkyl halides, and catalytic reduction of aldehydes and ketones.

- A phenol contains a hydroxyl group bound to an aromatic ring. Phenol is a weak acid, stronger than alcohol or water but weaker than acetic or carbonic acids.

- Ethers have the general formula ROR′. Because of the oxygen, ethers are more polar than alkanes.
Chapter 22 Summary

• Ethers can be synthesized by intermolecular dehydration of alcohols. Ethers are also formed by the Williamson synthesis.

• Thiols or mercaptans are organic compounds that contain the –SH group.