Chapter 10 Lecture Notes: Alcohols, Ethers, Aldehydes, and Ketones

Educational Goals

1. Given the structure of an alcohol, ether, thiol, sulfide, aldehyde, or ketone molecule, be able to give the systemic names and vice versa.

2. Know and understand the intermolecular forces that attract alcohol, ether, thiol, sulfide, disulfide, aldehyde, and ketone molecules to one another, and how these forces affect boiling points and melting points.

3. Identify alcohols as primary (1°), secondary (2°), or tertiary (3°).

4. Predict the products of the reactions in chapter 10 that involve alcohols, thiols, aldehydes, and/or ketones:
   - oxidation of thiols to produce disulfides
   - nucleophilic substitution reaction of alkyl halides and hydroxide
   - hydration of alkenes
   - dehydration of alcohols
   - oxidation of alcohols
   - oxidation of aldehydes
   - reduction of aldehydes and ketones
   - hemiacetal and acetal formation

5. Predict the major and minor products for the hydration of an alkene.

6. Predict the major and minor products for the dehydration of an alcohol.

Alcohols

The Structure of Alcohols

Alcohols contain one or more ************ functional groups (-OH) attached to a hydrocarbon (alkyl group) part. The general form of an alcohol is shown below.

A specific example of an alcohol is ethanol. Condensed structural formulas and a ball-and-stick model for ethanol are shown below.

CH\textsubscript{3}CH\textsubscript{2}OH or CH\textsubscript{3}CH\textsubscript{2}OH

The skeletal structure of ethanol is shown below. I have added large dots to indicate the carbon atom positions.

\[ \text{black sphere = carbon} \]
\[ \text{red sphere = oxygen} \]
\[ \text{white sphere = hydrogen} \]
Alcohols are classified as primary (1\textsuperscript{o}), secondary (2\textsuperscript{o}), or tertiary (3\textsuperscript{o}) based on the number of R groups attached to the carbon that is “______________” (bonded to) the hydroxyl group.

In primary (1\textsuperscript{o}) alcohols, the carbon that is “carrying” the hydroxyl group is bonded to one R group. An example of a primary alcohol is 1-propanol.

In secondary (2\textsuperscript{o}) alcohols, the carbon “carrying” the hydroxyl group is bonded to two R groups. An example of a secondary alcohol is 2-butanol:

In tertiary (3\textsuperscript{o}) alcohols, the carbon “carrying” the hydroxyl group is bonded to three R groups. An example of a tertiary alcohol is 2-methyl-2-propanol:
Naming Alcohols

The systematic method for naming alcohols is based on the hydrocarbon naming method.

**Step 1: Find and name the parent chain.**

The parent chain is the longest, continuous chain of carbon atoms that contains the \[ \text{__________} \] of \[ \text{____________} \] to the \[ \text{____________} \] group (OH).

- Count the number of carbon atoms in the parent chain. Starting with the alkane name that corresponds to the number of carbon atoms in the parent chain, replace the “e” at the end of the alkane name with “ol.”
  - For example, if the parent chain of an alcohol contains two carbons, it would be called ethanol.

  ethane ➔ ethanol

- For alcohols with more than two carbons, the position of the point of attachment to the hydroxyl group must be indicated by adding a number before the parent chain.
  - Assign position numbers to the carbons in the parent chain. Position number 1 is assigned to the carbon at the _____ of the parent chain that is _____ to the hydroxyl group.
    - If the hydroxyl group is bonded to carbon number 1 of the parent chain, then “1-” is used as a prefix to the parent chain name. For example, in the molecule below, the parent chain is called 1-pentanol.

Understanding Check
Identify each of the alcohols shown below as either primary (1\(^\circ\)), secondary (2\(^\circ\)), or tertiary (3\(^\circ\)).

<table>
<thead>
<tr>
<th>Number</th>
<th>Structure</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH(_3)CH(_2)CH(_2)-OH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>2</td>
<td>CH(_3)-CH(_2)-CH(_2)-CH(_3)-OH</td>
<td>2-pentanol</td>
</tr>
<tr>
<td>3</td>
<td>CH(_2)-CH(_2)-CH(_2)-CH(_3)-OH</td>
<td>3-pentanol</td>
</tr>
<tr>
<td>4</td>
<td>CH(_3)-CH(_2)-CH(_3)-OH</td>
<td>2-methylpropan-2-ol</td>
</tr>
<tr>
<td>5</td>
<td>CH(_3)-CH(_2)-CH(_2)-CH(_2)-CH(_2)-OH</td>
<td>1-hexanol</td>
</tr>
</tbody>
</table>

For example, in the molecule below, the parent chain is called 1-pentanol.
• If the hydroxyl group is bonded to carbon number 2 of the parent chain, then “2-” is used as a prefix to the parent chain name. For example, in the molecule below, the parent chain is called 2-pentanol.

\[
\begin{align*}
\text{OH} \\
\text{CH}_3 \quad \text{CH} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3 \\
1 & \quad 2 & \quad 3 & \quad 4 & \quad 5
\end{align*}
\]

Steps 2, 3, and 4 are done the same way as you did when naming other organic molecules.

Step 2: Name any alkyl group substituents.

Step 3: Determine the point of attachments of alkyl groups to the parent chain.

Step 4: Construct the name of the alcohol by placing the alkyl groups in alphabetical order and specifying their position number, followed by the name of the parent chain.

Example: Name the molecule that is shown below.

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{OH}
\end{align*}
\]

Solution:

Step 1: Find and name the parent chain.

- The parent chain is the longest, continuous chain of carbon atoms that contains the point of attachment to the hydroxyl group (OH).

The hydroxyl group is bonded to carbon number 1 of the parent chain, so “1-” is used as a prefix to the parent chain name. The parent chain is called 1-hexanol.

Step 2: Name any alkyl group substituents. methyl

Step 3: Determine the point of attachments of alkyl groups to the parent chain. 4-methyl

Step 4: Construct the name of the alcohol by placing the alkyl groups in alphabetical order and specifying their position number, followed by the name of the parent chain.

The name of the molecule is 4-methyl-1-hexanol.

Understanding Check

Write the systematic name for each of alcohol molecules that are shown here.
Let’s do a problem where we are given the name of an alcohol, and wish to draw its structural formula.

**Example:** Draw the line bond structure of 3-methyl-2-butanol.

**Solution:**
First draw the **carbons** of the parent chain. The parent chain is 2-butanol, therefore it contains **four** carbons.

\[
\text{C} \quad \text{C} \quad \text{C} \quad \text{C}
\]

The “2-” prefix in 2-butanol indicates that the hydroxyl group is bonded to carbon number **2** of the parent chain. Since we are drawing a line bond structure, we must include the bonds to all atoms **and** all lone pairs. Remember to add the lone pairs to the **oxygens** on the hydroxyl group.

Next, add the **carbon** of the methyl substituent.

- Since we are drawing the structure of 3-methyl-2-butanol, the methyl group’s carbon is attached to carbon number **3** of the parent chain.

To finish, add enough hydrogens to each carbon in order to satisfy the octet rule.

**Understanding Check:** We just drew the line bond structure of 3-methyl-2-butanol. Draw the **condensed** and the **skeletal** structural formula of 3-methyl-2-butanol.

**Understanding Check:** Draw the line bond structure of 4-methyl-3-heptanol.
Polyhydroxy Alcohols
Molecules with more than one hydroxyl group are called ________________ alcohols.

- An example of a polyhydroxy alcohol is glycerol (also known as glycerin).
  - Glycerol is an important biomolecule because it is one of the precursors to triglycerides (fats and vegetable oils) and some of the compounds found in cell membranes (glycerophospholipids and glycerooglycolipids).
  - The condensed structure and the ball-and-stick model of glycerol are shown below.

Cyclic Alcohols
When the hydroxyl group of an alcohol is bound to a __________ structure it is called a cyclic alcohol.

Cyclic alcohols can be secondary (2°) or tertiary (3°).
Cyclic alcohols are named in a manner similar to that for cycloalkanes.
- Starting with the cycloalkane name that corresponds to the number of carbon atoms in the ring structure, cyclic alcohols are named by replacing the “e” at the end of the cycloalkane name with “ol.”
- The ring-carbon that is carrying the OH is always designated as position number 1. Note the names of the cyclic alcohols that are shown above.

Understanding Check
Draw a skeletal structural formula for cyclopropanol and for cyclobutanol.
Properties of Alcohols

Water Solubility of Alcohols

Smaller alcohol molecules have significant water solubility because of their ability to interact with water through \textit{\underline{bonding}} and \underline{interactions}. As their nonpolar (hydrocarbon) parts get larger, the water solubilities of alcohols decrease.

Melting and Boiling Points of Alcohols

Alcohol molecules have higher melting and boiling points than alkanes of similar size because of their ability to interact with each other through \textit{hydrogen bonding} and \textit{dipole-dipole interactions}. As their nonpolar (hydrocarbon) parts get larger, the melting and boiling points of alcohols \textit{increase} because of increasing \underline{forces}.

<table>
<thead>
<tr>
<th>Molecule Name</th>
<th>Condensed Structure</th>
<th>Water Solubility (g/100 mL)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>CH₂OH</td>
<td>miscible*</td>
<td>65.0</td>
</tr>
<tr>
<td>ethanol</td>
<td>CH₃CH₂OH</td>
<td>miscible</td>
<td>78.5</td>
</tr>
<tr>
<td>1-propanol</td>
<td>CH₃CH₂CH₂OH</td>
<td>miscible</td>
<td>97.4</td>
</tr>
<tr>
<td>1-butanol</td>
<td>CH₃CH₂CH₂CH₂OH</td>
<td>8.0</td>
<td>117</td>
</tr>
<tr>
<td>1-pentanol</td>
<td>CH₃CH₂CH₂CH₂CH₂OH</td>
<td>2.2</td>
<td>138</td>
</tr>
</tbody>
</table>

*miscible indicates that the substance will mix/dissolve at any alcohol to water ratio.

Alcohols have biological, industrial, and medical applications. Alcohols are used as fuels, medications, recreational drugs, antiseptic agents, industrial solvents, antifreeze, detergents, and preservatives. Humans have consumed ethanol as a recreational drug since the Neolithic age (stone age).

Annual Per Capita Ethanol Consumption (liters) by Country

Annual per capita recorded ethanol consumption (liters) by country in 2004. Based on the data of WHO Global Status Report on Alcohol 2004 and Statistical Information System.
Ethanol, 1-propanol, and 2-propanol are used, with about 10-30% water, as antiseptic (surface antimicrobial) agents. One or more of these three alcohols serve as the active ingredients in many hand sanitizers, such as Purell.

Methanol is added to automotive windshield washer fluid, de-icers, and gasoline additive products as an antifreeze agent. Antifreeze agents lower the melting points of liquids.

Aqueous ethylene glycol (50% v/v), a polyhydroxy alcohol, is used as engine antifreeze. It is quite effective as an antifreeze because of its ability to disrupt water-water hydrogen bonding (because of its own ability to hydrogen bond with water). A trace of fluorescent color is added to antifreeze to facilitate in leak detection.

Methanol, ethanol, and some other small alcohol molecules are used as fuel. This includes use in internal combustion engine automobiles. Since alcohol can be produced by renewable resources and lowers pollutant emissions, many countries require the addition of alcohol to gasoline. In the United States, many states mandate that alcohol be added to gasoline.

Alcohols are used as preservatives for specimens in biological sciences, and as solvents for medical drugs, perfumes, and the preparation of plant extracts, such as vanilla.

**Formation of Alcohols**

1) Alcohol Fermentation

![Picture of Louis Pasteur]

Ethanol is produced in nature in a process called *alcohol fermentation*.

In the 1850s and 1860s, Louis Pasteur discovered that fermentation involved living organisms.

It was not until 1897 that Eduard Buchner found that ground fragments of dead yeast could produce ethanol and CO$_2$.

- As a result of Buchner’s work, the term “enzyme” was applied to materials that enabled fermentation, and the understanding that fermentation was a result of enzymatic processes gained acceptance.
  - Buchner’s results are often regarded as the birth of *biochemistry*, and he was awarded the Nobel Prize in chemistry for this work in 1907.

Alcohol fermentation is a series of chemical reactions that convert sugar molecules, such as glucose, into ethanol and CO$_2$.

- The final step in this reaction series involves an enzyme which is only present in yeast and some bacteria.

The overall reaction of ethanol formation from a sugar molecule (glucose) is shown below.

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

*glucose*  **→**  *ethanol*  +  *carbon dioxide*
2) Alcohol Formation in Nucleophilic Substitution Reactions

If you were a chemistry major, you would take a year-long organic chemistry class in which you would study the mechanisms of all of the reactions that we cover in this course.

A reaction mechanism is a description of the sequence of bond-breaking and bond-formation that occurs in a chemical reaction.

Since the intention of this course is to cover general, organic, and biochemistry in just one semester, we don’t have the time - or need - to study the reaction mechanisms for all of the chemical reactions that I present. However, I do wish to introduce you to one very commonly observed reaction mechanism - the “nucleophilic substitution II” (SN2) reaction mechanism.

In the nucleophilic substitution (SN2) reaction for the formation of an alcohol, a hydroxide ion reacts with an __________ __________ molecule.

- An alkyl halide is a hydrocarbon that had one of its hydrogens replaced with a halogen (group VII element: F, Cl, Br, or I).

\[
\begin{align*}
\text{alkyl halide} & \quad + \quad \text{OH}^- \\ & \quad \Leftrightarrow \\ & \quad \text{alcohol} \\ & \quad + \quad \text{halogen ion}
\end{align*}
\]

\(X\) represents F, Cl, Br, or I

- Specific examples of nucleophilic substitution reactions for the formation of alcohols are shown below.

\[
\begin{align*}
\text{CH}_3\text{Cl} & \quad + \quad \text{OH}^- \\ & \quad \Leftrightarrow \\ & \quad \text{CH}_3\text{-OH} \\ & \quad + \quad \text{Cl}^-
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{Br} & \quad + \quad \text{OH}^- \\ & \quad \Leftrightarrow \\ & \quad \text{CH}_3\text{-OH} \\ & \quad + \quad \text{Br}^-
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{-I} & \quad + \quad \text{OH}^- \\ & \quad \Leftrightarrow \\ & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{-OH} \\ & \quad + \quad \text{I}^-
\end{align*}
\]

The negative charge of the hydroxide ion is quite attracted to the partial positive charge of the carbon that is bonded to the halogen atom.

The reaction mechanism is called nucleophilic substitution because the nucleophile (OH\(^-\)) is attracted to the nucleus of the partially positive carbon, and then substitutes for (replaces) the halogen (X).
The S<sub>N</sub>2 chemical reaction involves *making one new bond and breaking one old bond*. First, a lone pair from the hydroxide nucleophile forms a bond to the carbon that is carrying the halogen.

The species which is formed by the newly-made bond is called a __________ __________. The transition state is a *high-energy molecule* because there are ten electrons (five single bonds) around a carbon atom instead of the lower-energy octet.

The transition state has a *high energy*, which means that it is __________. The weakest of the five bonds (the bond to the halogen) will quickly break. When this bond breaks, the halogen takes with it the two electrons that were in its bond to the carbon, and an alcohol is produced.

Let’s consider the energy reaction diagram for this S<sub>N</sub>2 reaction:

**Understanding Check:** Predict the products of the following nucleophilic substitution reaction.

\[ \text{CH}_3\text{CH}_2\text{Br} + \text{OH}^- \rightleftharpoons \]
3) Hydration of Alkenes

In chapter 6, you learned that an __________ can react with water to produce an alcohol.

- A hydrogen from $\text{H}_2\text{O}$ is added to one of the double-bonded carbon atoms and $\text{OH}$ from the $\text{H}_2\text{O}$ is added to the other double-bonded carbon atom in the alkene, to produce the corresponding alcohol.

General Form of the Chemical Equation for the Hydration of an Alkene:

In chapter 6, I showed you a bond flipping method to help you predict the structure of the alcohol that is produced when you add $\text{H}_2\text{O}$ “across a double bond.”

**Step 1:** Draw the $\text{H}_2\text{O}$ to be added across the double bond and the alkene as shown below.

**Steps 2 and 3:** *Flip* the bonds, as shown below, to get the alcohol product of the reaction.

In chapter 6, we always began with symmetric alkenes when doing hydration reactions.

An alkene is __________ when a line drawn perpendicular to, and through, the middle of the double bond of its structural formula results in __________ parts on each side of the line.
Another example of a symmetric alkene is 2-butene.

Note that parts of the molecule on each side of the dashed line bisecting the carbon-carbon double bond are identical.

When a symmetric alkene undergoes a hydration reaction, there is only ______ possible product.

Example: The hydration of 2-butene. \[ \text{CH}_3\text{CH} \rightleftharpoons \text{CHCH}_3 + \text{H}_2\text{O} \]

The ______ alcohol molecule is produced regardless of which of 2-butene’s double-bonded carbons gets the added OH group.

The reason that the addition of the OH to either double-bonded carbon results in the same alcohol (2-butanol) is that the 2-butene is symmetric.

An example of an _____________ alkene is propene.

Note that the dashed line bisecting the carbon-carbon double bond results in _____ identical parts on each side of the line.
When an asymmetric alkene undergoes a hydration reaction, there are _______ different alcohol molecules produced.

**Example:** The hydration of propene.

The addition of the **OH** group to propene’s **right-most** double-bonded carbon produces 2-propanol.

The addition of the **OH** group to the **left-most** double-bonded carbon produces 1-propanol.

The hydration of an asymmetric alkene **does ____ produce an ______ amount of each alcohol product.**
- For example, in the hydration of propene, there is **more** 2-propanol than 1-propanol produced.

The product made in **greater** quantity is called the “__________ product.”

The product made in **lesser** quantity is called the “__________ product.”
It is possible to predict the major and minor products for the hydration of an asymmetric alkene using Markovnikov’s Rule.

- This rule says that, the major product is formed by adding the H - from water - to the alkene’s double-bonded carbon that originally carried the most hydrogens, and adding the OH to the other double-bonded carbon.
  - An easy way to remember this rule is by using the old saying, “the rich get richer,” where the H’s represent money.

\[ \text{H} \quad \text{C} \quad \text{C} \quad \text{CH}_3 + \text{HO} - \text{H} \]

The minor product is formed by adding the H and OH in a manner opposite to that described for the major product.

**Understanding Check**

Draw and name the major and minor products for the hydration of 2-methyl-2-butene.

\[ \text{CH}_3\text{CH} \quad \text{CCH}_3 + \text{H}_2\text{O} \]

**Compounds that are Related to Alcohols**

Water and alcohols are said to be “structurally ________” because of their bonding patterns. If one of the hydrogens from water is replaced by an alkyl group (R), then an alcohol is obtained.

\[ \text{H} \quad \text{O} \quad \text{H} \quad \text{water} \quad \text{R} \quad \text{O} \quad \text{H} \quad \text{alcohol} \]

Ethers and alcohols are structurally related compounds. If the hydrogen from an alcohol is replaced by an alkyl group (R’), then an ________ is obtained.

\[ \text{R} \quad \text{O} \quad \text{H} \quad \text{alcohol} \quad \text{R} \quad \text{O} \quad \text{R'} \quad \text{ether} \]

Peroxides are structurally related to water, ethers, and alcohols. If a ________ oxygen is added to water, ethers, or alcohols, as in the arrangement shown below, then a ________ is obtained.

\[ \text{R} \quad \text{or} \quad \text{H} \quad \text{O} \quad \text{O} \quad \text{R'} \quad \text{or} \quad \text{H} \quad \text{general form of a peroxide} \]
Ethers

The Structure of Ethers

Ethers contain an __________ atom that is attached to _____ alkyl (R) groups.

A specific example of an ether is diethyl ether.

- Diethyl ether was introduced as a surgical anesthetic in the 1840s. It is rarely used as an anesthetic currently because of the availability of more desirable substances.

Both of the alkyl (R) groups in diethyl ether are ethyl groups (-CH₂CH₃).

\[
\text{CH}_3\text{CH}_2\text{O}-\text{CH}_2\text{CH}_3 \quad \text{or} \quad \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3
\]

Cyclic Ethers

A cyclic compound that has an oxygen atom in one of the ring positions is called a __________ ether.

Cyclic ethers are heterocyclic compounds because their rings contain more than one type of element.

- Examples of cyclic ethers:

Naming Ethers

We will use what is referred to as the “__________ names” for ethers.

- This trivial method for naming ethers is not based on the IUPAC hydrocarbon naming method.

Step 1. Identify the alkyl group names for the two alkyl (R) groups.

- If the two R groups are identical use the “di” prefix before alkyl group name.

Step 2. Construct the name of the ether by placing the alkyl groups in alphabetical order followed by the word “ether.”

- Use a space between the alkyl group names and before the word “ether.”

Examples:
Water Solubility of Ethers

Smaller ethers have significant water solubility because of their ability to interact with water through hydrogen bonding and dipole-dipole interactions. As their nonpolar (hydrocarbon) parts get larger, the water solubilities of ethers decrease.

Melting and Boiling Points of Ethers

Ethers have higher melting and boiling points than hydrocarbons of similar size because they can interact with each other through dipole-dipole interactions - they are polar molecules. As their nonpolar (hydrocarbon) parts get larger, the melting and boiling points of ethers increase because of increasing London forces. Ethers are unable to hydrogen bond with each other, and therefore, they have lower melting and boiling points than alcohols and carboxylic acids of similar size.

Ethers in Nature and Industry

Ethers have natural, industrial, and biochemical applications. Dimethyl ether and ethyl methyl ether are used as aerosol spray propellants. Dimethyl ether is used as an industrial solvent and in the perfume industry for the extraction of fragrant compounds from their natural sources. Ethylene oxide, a cyclic ether, is used in the medical industry and hospitals as a disinfectant or sterilization agent for heat sensitive equipment.

- For example, disposable plastic syringes are sterilized using pure ethylene oxide.

Peroxides

Peroxides contain two oxygen atoms that are single-bonded to each other and situated between hydrogens, alkyl groups, or any other organic groups.

Peroxides are quite reactive because of the two oxygen atoms that are single-bonded to each other. A much more stable configuration (lower energy) results when the oxygen-oxygen single bond breaks, and the oxygen atoms acquire more electrons by oxidizing another molecule. It is for this reason that peroxides are very effective oxidizing agents, and are frequently used as disinfectants and bleaching agents.
A specific example of a peroxide is *hydrogen peroxide*.

![Hydrogen peroxide](image)

Hydrogen peroxide is important in human and animal metabolism. An extremely toxic byproduct of the production of ATP in the mitochondria is the superoxide ion \((O_2^-)\) ion. This is not the *monoatomic* oxide ion \((O^-)\); it is an unstable *diatomic* ion with a \(1^-\) charge. The superoxide ion is extremely toxic to cells because it can react with and damage (oxidize) DNA, proteins, and membrane component compounds. Almost all organisms have evolved enzymes called superoxide dismutases (SOD) to quickly remove superoxide ions. These enzymes are *antioxidant agents*. SOD enzymes catalyze the reaction of superoxide ions and water to produce hydrogen peroxide, oxygen, and hydroxide ions.

\[
2 O_2^- + 2 H_2O \xrightarrow{\text{SOD}} H_2O_2 + O_2 + 2 OH^- 
\]

Though not quite as strong an oxidizer as superoxide, hydrogen peroxide is also an oxidizing agent, and is therefore quite toxic to cells. However, the hydrogen peroxide produced from superoxide is quickly converted to oxygen and water by an enzyme called catalase.

\[
2 H_2O_2 \xrightarrow{\text{catalase}} 2 H_2O + O_2 
\]

**Sulfur Analogs**

When the oxygen atom(s) of water, alcohol, ether, or peroxide is replaced by _________, the resulting compound is called a *sulfur analog*.

- For example, the *sulfur analog of water*, dihydrogen sulfide, is obtained if the oxygen in a water molecule is replaced by sulfur.

![H2O and H2S](image)

Dihydrogen sulfide \((H_2S)\) is often called hydrogen sulfide. Although \(H_2S\) is heavier than \(H_2O\), it is a gas at room temperature. The reason for this difference is that, unlike water, \(H_2S\) molecules are unable to hydrogen bond with each other. \(H_2S\) has the foul odor of rotten eggs. It is toxic and very reactive (explosive, flammable, and corrosive). \(H_2S\) occurs in nature when bacteria metabolize organic matter in the absence of oxygen. This often happens in sewers and swamps. It is also found in natural gas, some water wells, and volcanic gases. It is found in very low concentration in humans, where it acts as a chemical signaling molecule.

**Thiols**

The *sulfur analog of an alcohol* is obtained if the oxygen in an alcohol is replaced by sulfur.

The resulting molecule is called a _________.

![Alcohol and thiol](image)

Thiols are often referred to as *mercaptans*. Many thiols have the aroma of garlic. Thiol aromas can be pungent and annoying. There are several thiols in the spray of skunks.
A specific example of a thiol is 2-methyl-2-propanethiol.

![2-methyl-2-propanethiol](image)

2-methyl-2-propanethiol is added, in very small amounts, to natural gas as an odorant in order to help detect gas leaks or mistakenly-opened valves.

The -SH functional group, which defines the thiol family of organic compounds, is referred to as a thiol group or a sulfhydryl group.

**Naming Thiols**

Thiols are systematically named in the same way as alcohols with only one exception:

- The term “thiol” is added to the end the alkane name that indicates the number of carbons in the parent chain (instead of replacing the “e” from the alkane name with “ol,” as we did for alcohols).

- **Examples:**

![ethanethiol](image)

![3-methyl-1-butanethiol](image)

As was the case for alcohols, the point of attachment of the thiol group (-SH) must be indicated for thiols with more than two carbons in their parent chain. The point of attachment to the thiol group is indicated by writing the position number in front of the parent chain name.

<table>
<thead>
<tr>
<th>Understanding Check: Name the molecule that is shown here.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SH} )</td>
</tr>
</tbody>
</table>

**Sulfides**

The sulfur analog of an ether is obtained if the oxygen in an ether molecule is replaced by sulfur. The resulting molecule is called a ______________. Sulfides are also referred to as thioethers.
A specific example of a sulfide is *dimethyl sulfide* (DMS).

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

dimethyl sulfide (DMS)

DMS is found in the atmosphere in greater concentration than any other organic sulfur-containing compound because it is produced by phytoplankton. It is also produced by bacteria in sewers. DMS has a characteristic cabbage-like odor. It is produced from cooking certain vegetables - corn, cabbage, beetroot - and seafood.

**Naming Sulfides**

We will use *common* names for sulfides, as we did for ethers.

**Step 1. Identify the alkyl group names for each of the R groups.**
- If the two R groups are *identical* use the “di” prefix before the alkyl group name.

**Step 2. Name the sulfide by placing the alkyl groups in alphabetical order followed by the word “sulfide.”**
- Use a space between the alkyl group names and before the word “sulfide.”

**Examples:**

<table>
<thead>
<tr>
<th>CH₃SCH₃</th>
<th>CH₃SCH₂CH₃</th>
<th>CH₃CH₂SCH₂CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethyl sulfide</td>
<td>ethyl methyl sulfide</td>
<td>diethyl sulfide</td>
</tr>
</tbody>
</table>

**Understanding Check:** Name the molecule that is shown here.

\[
\text{CH}_3\text{CH}_2\text{S} - \text{CH}_2\text{CH}_2\text{CH}_3
\]

**Disulfides**

The *sulfur analog of a peroxide* is obtained if the two oxygens in a peroxide molecule are replaced by two sulfurs.

The resulting molecule is called a ____________.

The S-S bond is called a **disulfide bond**.

Disulfides can be made from the reaction of *two thiols*. In this reaction, the thiols are oxidized to form a disulfide.

\[
\text{RSH} + \text{R'SH} \rightarrow \text{RSSR} + 2\text{H}
\]

You can recognize that the thiol reactants were ____________ because they __________ hydrogen in the reaction.
The disulfide bond is important in protein biochemistry.

**Cysteine** is one of the twenty common amino acid molecules that make up proteins. **Cysteine**, shown on the right, contains a thiol group that is capable of forming disulfide bonds with other cysteine-thiols.

**Two thiol (SH) groups on the same protein molecule or** two thiol groups on two different protein molecules can react to form disulfide bonds. The disulfide bonds in protein play an important role in how many proteins maintain their shape, which is critical in their biological function. This concept is illustrated (on the right) in a large protein molecule - represented as a thick orange ribbon - that is held into a particular shape with the help of some disulfide bonds. You will learn more details of protein structure and function in chapter 15.

**Understanding Check**
Draw the condensed structure of the disulfide that is formed by the reaction of two methanethiol molecules.

---

**Aldehydes and Ketones**

**The Structure of Aldehydes and Ketones**
The general forms of aldehydes and ketones are shown below.

In aldehydes, the carbonyl carbon is bonded to ________ R group and ________ hydrogen (H).

- **Exception:** the simplest aldehyde, **formaldehyde**, which has the carbonyl carbon bonded to *two* hydrogens.

In ketones, the carbonyl carbon is bonded to ________ R groups.
An example of an aldehyde and a ketone:

Sometimes a shorthand notation “CHO” is used for the carbonyl group and the hydrogen that is bonded to the carbonyl carbon when drawing aldehydes, as shown below.

Any molecule that contains a carbonyl group (C=O) is called a ______________ _____________.

So far, you have been introduced to several carbonyl compounds: aldehydes, ketones, carboxylic acids, esters, and amides.

As a review, and for comparison, the general form for each of these families is shown below.

Understanding Check: Classify each of the following molecules as either an aldehyde or a ketone.

a. \( \text{CH}_3\text{CH}_2\text{CH}_2 - C - H \)  

b. \( \text{CH}_3\text{CH}_2\text{CH}_2 - C - \text{CH}_2\text{CH}_3 \)  

c. \( \text{benzene} - C - H \)
Naming Aldehydes and Ketones

**Common Names for Aldehydes and Ketones**

*Small* aldehydes and ketones, those with a relatively few number of carbon atoms, are often identified by common names.

- Examples of *common names* used for aldehydes:

  ![Formaldehyde](formaldehyde.png)
  ![Acetaldehyde](acetaldehyde.png)
  ![Benzaldehyde](benzaldehyde.png)

Sometimes, *common names* for *ketones* list the names of the alkyl groups bonded to the *carbonyl group* followed by the word *ketone*.

- Examples:

  ![Dimethyl ketone](dimethyl_ketone.png)
  ![Ethyl methyl ketone](ethyl_methyl_ketone.png)

**Systematic Names for Aldehydes and Ketones**

The systematic method for naming aldehydes and ketones is based on the hydrocarbon naming method.

**Step 1: Find and name the parent chain.**

The *parent chain is the longest, continuous chain of carbon atoms that contains the ________ carbon.*

- **For aldehydes**, starting with the alkane name that corresponds to the number of carbon atoms in the parent chain, replace the “e” at the end of the alkane name with “al.” For example, if the parent chain of an aldehyde contains two carbons, it would be called ethanal.

  ethane \[\rightarrow\] ethanal

- **For aldehydes**, the carbonyl carbon will *always* be at the _____ of the parent chain and is assigned position number 1.

- **For ketones**, starting with the alkane name that corresponds to the number of carbon atoms in the parent chain, replace the “e” at the end of the alkane name with “one.” For example, if the parent chain of a ketone contains three carbons, it would be called propanone.

  propane \[\rightarrow\] propanone

- **For ketones** with *more than four carbons*, the position of the *carbonyl carbon* must be indicated by adding a number as a prefix to the parent chain name.
  - Position number 1 is assigned to the carbon at the *end of the parent chain* that is ________ to the *carbonyl carbon*.
  - For example, if the carbonyl carbon is in position number 2 of a parent chain that contains five carbon atoms, then the parent chain is called 2-pentanone.

  ![2-Pentanone](2-pentanone.png)
Steps 2, 3, and 4 are done the same way as you did when systematically naming other organic molecules.

**Step 2:** Name any alkyl group substituents.

**Step 3:** Determine the point of attachments of alkyl groups to the parent chain.

**Step 4:** Construct the name of the molecule by placing the alkyl groups in alphabetical order and specifying their position number, followed by the name of the parent chain.

**Aldehyde Systematic Name Examples:**

- \[
\begin{array}{c}
\text{O} \\
\text{H} \quad \text{C} \quad \text{H}
\end{array}
\]

  - methanal

- \[
\begin{array}{c}
\text{O} \\
\text{CH₃C} \quad \text{H}
\end{array}
\]

  - ethanal

- \[
\begin{array}{c}
\text{O} \\
\text{CH₃CHC} \quad \text{H} \\
\text{CH₃}
\end{array}
\]

  - 2-methylpropanal

**Ketone Systematic Name Examples:**

- \[
\begin{array}{c}
\text{O} \\
\text{CH₃CCH₃}
\end{array}
\]

  - propanone

- \[
\begin{array}{c}
\text{O} \\
\text{CH₃CCH₂CH₂CH₃}
\end{array}
\]

  - 2-pentanone

- \[
\begin{array}{c}
\text{O} \\
\text{CH₃CCH₂CH₂CH₂CCH₃} \\
\text{CH₃}
\end{array}
\]

  - 2-methyl-3-pentanone

**Understanding Check:** Write the systematic names for each of the molecules shown here.

a. \[
\begin{array}{c}
\text{O} \\
\text{CH₃CHCH₂C} \quad \text{H} \\
\text{CH₃}
\end{array}
\]

b. \[
\begin{array}{c}
\text{CH₃} \\
\text{CH₃CCH₂CH₂CH₂CCH₃} \\
\text{CH₃}
\end{array}
\]

c. \[
\begin{array}{c}
\text{O} \\
\text{CH₃CCH₂CH₂CH₂CH₃} \\
\text{CH₃}
\end{array}
\]

**Understanding Check:** Draw the condensed and skeletal structure for each of these molecules.

a. 4-methyl-2-pentanone  

b. 5,5-dimethylhexanal  

c. 3-ethyl-4-octanone
Cyclic Ketones

A cyclic ketone is a molecule in which a carbonyl carbon occupies a position between two other carbons in a ring structure.

- Examples:

![cyclic pentanone and cyclohexanone](image)

Cyclic ketones are named in a manner similar to that for cyclic alcohols.

- Starting with the cycloalkane name that corresponds to the number of carbon atoms in the ring structure chain, replace the “e” at the end of the cycloalkane name with “one.”

Frequently Encountered Aldehydes and Ketones

\[
\begin{align*}
\text{methanal (or formaldehyde)} & : \quad \text{O} \\
& \quad \text{H} \quad \text{C} \quad \text{H}
\end{align*}
\]

Methanal, (common name formaldehyde) is quite toxic; however, it is frequently used because of its ability to kill viruses, fungi, and bacteria. It is used to disinfect and sterilize equipment. Formaldehyde will react with other compounds, and chemically bond multiple molecules together into “polymers.” Polymers are molecules composed of multiple repeated subunits. The polymers that are formed using formaldehyde as linking agents are used to make plastics and adhesives, and for binding plywood. Formaldehyde-linked polymers may “out-gas” formaldehyde in the curing process, therefore it is important to use safety precautions when handling these materials. In 2011, the US National Toxicology Program categorized formaldehyde as "known to be a human carcinogen".

\[
\begin{align*}
\text{ethanal (or acetaldehyde)} & : \quad \text{O} \\
& \quad \text{CH}_3\text{C} \quad \text{H}
\end{align*}
\]

Ethanal (common name acetaldehyde) has a sweet aroma. It is narcotic if taken in large enough amounts. It occurs in smaller quantities, naturally, in coffee, bread, and ripe fruit, especially in apples. Its use is widespread in industry, notably in the formation of polymer adhesives such as carpenter’s glue (also known as white glue or Elmer’s glue). I will discuss acetaldehyde's biological significance later in this chapter.

\[
\begin{align*}
\text{propanone (or acetone)} & : \quad \text{O} \\
& \quad \text{CH}_3\text{C CH}_3
\end{align*}
\]

Propanone (common name acetone) is often used as a solvent and cleaning agent. It has the ability to dissolve many organic compounds and is also miscible with water. It is used as household nail-polish remover. Acetone has a high vapor pressure, and is highly flammable. It is not significantly toxic and is not currently regarded as a carcinogen, a mutagenic chemical, or a concern for chronic neurotoxicity issues.
Properties of Aldehydes and Ketones

### Water Solubility of Aldehydes and Ketones

Smaller aldehyde and ketone molecules have significant water solubility because of their ability to interact with water through hydrogen bonding and dipole-dipole interactions. As their nonpolar parts get larger, the solubilities of aldehydes and ketones decrease.

### Boiling Points of Aldehydes and Ketones

As their nonpolar parts get larger, the boiling points of aldehydes and ketones increase because of increasing London forces.

<table>
<thead>
<tr>
<th>Aldehyde Name</th>
<th>Condensed Structure</th>
<th>Water Solubility (g/100 mL)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanal</td>
<td>CH₃CHO</td>
<td>miscible</td>
<td>21</td>
</tr>
<tr>
<td>propanal</td>
<td>CH₃CH₂CHO</td>
<td>16</td>
<td>49</td>
</tr>
<tr>
<td>butanal</td>
<td>CH₃CH₂CH₂CHO</td>
<td>7</td>
<td>76</td>
</tr>
<tr>
<td>pentanal</td>
<td>CH₃CH₂CH₂CH₂CHO</td>
<td>1</td>
<td>103</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ketone Name</th>
<th>Condensed Structure</th>
<th>Water Solubility (g/100 mL)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>propanone</td>
<td>CH₃COCH₃</td>
<td>miscible</td>
<td>56</td>
</tr>
<tr>
<td>2-butanone</td>
<td>CH₃COCH₂CH₃</td>
<td>26</td>
<td>80</td>
</tr>
<tr>
<td>2-pentanone</td>
<td>CH₃COCH₂CH₂CH₃</td>
<td>6</td>
<td>102</td>
</tr>
</tbody>
</table>

Water Solubility of Aldehydes and Ketones

Smaller aldehyde and ketone molecules have significant water solubility because of their ability to interact with water through hydrogen bonding and dipole-dipole interactions. As their nonpolar parts get larger, the solubilities of aldehydes and ketones decrease.

Boiling Points of Aldehydes and Ketones

As their nonpolar parts get larger, the boiling points of aldehydes and ketones increase because of increasing London forces.

![Butane, Propanal, Propanone, Propanol](image)

Aldehydes and ketones have higher boiling points than hydrocarbons of similar size because of their ability to interact with each other through dipole-dipole interactions.

Aldehydes and ketones have lower boiling points than alcohols or carboxylic acids of similar size because aldehydes and ketones are not capable of interacting with each other through hydrogen bonding.

- Although aldehydes and ketones do have lone pairs of electrons on their oxygen atoms, they do not contain a hydrogen bonded to an N, O, or F that would be needed for hydrogen bonding with each other.
Reactions Involving Alcohols, Aldehydes, and Ketones

Reactions of Alcohols

1. The Dehydration of Alcohols

I introduced you to the *dehydration of alcohols* reaction in chapter 6. Dehydration of alcohols is the *reverse* of the hydration of alkenes. \( \text{H}_2\text{O} \) is __________ from an alcohol to form an alkene.

- In the dehydration of an alcohol, a hydroxyl group (OH) is removed from one carbon, and an H is removed from *another carbon* that is __________ to the carbon from which the hydroxyl group was removed. A __________ bond forms between these two carbons.

- This reaction is catalyzed by a strong acid (H_3O^+) or an enzyme.

*The general form* of the equation for the dehydration of an alcohol reaction.

\[
\begin{array}{ccc}
\text{Hydrocarbon} & \text{OH} & \text{Hydrocarbon} \\
\text{or H} & \text{or H} & \text{or H} \\
\text{Hydrocarbon} & \text{Hydrocarbon} & \text{Hydrocarbon} \\
\text{or H} & \text{or H} & \text{or H} \\
\text{H}_2\text{O} & \text{C} & \text{C} \\
\text{C} & \text{C} & \text{C} \\
\text{alkene} & \text{alcohol} & + \\
\end{array}
\]

In chapter 6, I showed you a *bond flipping method* to help you predict the structure of the alkene that is produced when you “remove \( \text{H}_2\text{O} \)” to form a double bond.” Let’s review that method now by removing \( \text{H}_2\text{O} \) from 1-propanol (dehydration of 1-propanol). Beginning with the structure of the alcohol, perform the following steps:

**Step #1:** Flip the bond between the C and OH up to an H on an adjacent carbon.

**Step #2:** Flip the C-H bond from the adjacent carbon down to make a double bond to the C that originally carried the OH

For the dehydration of a *primary (1°) alcohol* there is only one carbon that is adjacent to the carbon carrying the OH, therefore there is only ______ possible alkene product.

[Diagram showing bond flipping method for dehydration of 1-propanol]
The dehydration of a ______________ secondary (2°) or a symmetric tertiary (3°) alcohol only produces a single alkene product.

- A 2° or 3° alcohol is symmetric if the alkyl groups bonded to the carbon carrying the OH are identical.
  - For example, 2-propanol, shown below, is symmetric. Note that the alkyl groups bonded to the carbon carrying the OH are identical; they are both methyl groups.

When a symmetric alcohol is dehydrated, it makes no difference from which adjacent carbon a hydrogen is removed to form the double bond; the alkene product is the same.

When an ______________ 2° or 3° alcohol undergoes a dehydration reaction, there are ______ different alkene molecules produced.

- 2° and 3° alcohols are asymmetric when the alkyl groups bonded to the carbon carrying the OH are ______ identical.
  - An example of an asymmetric alcohol is 2-butanol, shown here.

- Note that the alkyl groups that are bonded to the carbon carrying the OH, are not identical; one is a methyl group and the other is an ethyl group.
Let’s have a look at the **two different alkenes that are produced** when 2-butanol undergoes a dehydration reaction.

You have previously learned that the *hydration* of an asymmetric alkene does not produce equal amounts of both alcohol products. A similar situation occurs for the *dehydration* of alcohols.

For example, in the dehydration of 1-butanol, about *four times* as much 2-butene (major product) as 1-butene (minor product) is produced.

It is possible to predict the major and minor products for the dehydration of an alcohol; in the **major product**, the double bond is formed between the carbon that was carrying the OH and the adjacent carbon that **originally carried fewer hydrogens**.

The **minor product** is formed between the carbon that was carrying the OH and the adjacent carbon that **originally carried more hydrogens**.
29

In the formation of the _______ alkene product, the adjacent carbon that originally contained _______ hydrogens will ______ another hydrogen when the double bond is formed.

• An easy way to remember the alcohol dehydration rule for the major product is with the old saying, “the poor get poorer,” where hydrogen atoms (H) represent money.

Understanding Check

Draw and name the major and minor products for the dehydration of 3-ethyl-4-octanol.

\[
\begin{align*}
\text{OH} & \quad \text{H}_2\text{O} + \\
\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \quad \text{CH}_2\text{CH}_3
\end{align*}
\]

Major Product | Minor Product

2) The Oxidation of Alcohols

An oxidation can only occur when it is accompanied by a reduction.

• The reactant that is oxidized loses one or more electrons and the reactant that is reduced gains those electrons.

You learned that the oxidation of an organic compound in a reaction can be identified by the addition of oxygen and/or loss of hydrogen.

For the reduction of an organic compound, the opposite occurs; the addition of hydrogen and/or loss of oxygen.
When an alcohol is oxidized, the hydrogen from the hydroxyl group (OH) and a hydrogen (H) attached to the carbon that is carrying the hydroxyl group are both removed, and the C-O single bond is changed to a __________ bond.

The reason that this reaction is classified as an oxidation (loss of electrons) is that the hydrogen that is bonded to the hydroxyl-carrying carbon, leaves the alcohol and takes ________ of the electrons from the bond with it.

A hydrogen with two electrons is called a ____________ ion (H:). The “[O],” drawn above (or below) the arrows in a chemical equation, is often used to indicate that the reactant is being oxidized, and should not be confused with the presence of a catalyst.

When oxidation is indicated by using “[O],” then the identity of the oxidizing agent - which is actually a reactant - and the destination of the hydrogens are often omitted from the chemical equation.

- When doing so, it is acceptable - and expected - that the equation is not balanced.

The structure of the alcohol determines the identity of its oxidation product.

a) **Oxidation of Primary (1°) Alcohols**

Oxidation of a primary (1°) alcohol produces an ____________.

The oxidation of a primary alcohol produces an aldehyde because the hydroxyl group of a primary alcohol is attached to a carbon at an end of the parent chain, and therefore the carbonyl group in the product is at the end of the chain.

A specific example of the oxidation of a primary alcohol is the oxidation of ethanol:

The H⁺ that is produced will quickly react with water to form a hydronium ion (H₃O⁺). The evolution of the alcohol dehydrogenase enzyme for this reaction was important in order to remove naturally-occurring ethanol that we consume in some foods. Ethanol is toxic to cells. Although not an evolutionary requirement, the existence of this enzyme allows for the consumption of alcoholic beverages. The drug disulfiram (sold as Antabuse), is designed to deter individuals from drinking. It works by inhibiting the alcohol dehydrogenase enzyme, and thereby produces very undesirable effects when alcohol is consumed.
Certain organic molecules and inorganic oxidizing agents, such as MnO$_4^-$, can _______ oxidize aldehydes to produce __________.  

![Diagram of oxidation reaction]

Example: For humans (and many animals) the conversion of the ethanal (an aldehyde) to acetic acid (a carboxylic acid) in the second step of the alcohol oxidation reaction, shown below, is catalyzed by an enzyme called **acetaldehyde dehydrogenase**.

![Diagram of enzyme catalysis]

Most individuals of Asian descent have one of two variations in their DNA that each result in an **especially efficient** form of the *alcohol dehydrogenase* enzyme that catalyzes the first reaction (ethanol to ethanal). These individuals convert ethanol to ethanal very quickly. About half of the Asian individuals who have one of those DNA variants, also have a **second DNA variation** that results in a **less functional** acetaldehyde dehydrogenase enzyme to catalyze the second reaction above. For individuals with both of these DNA variants, **high ethanol levels** occur when consuming alcoholic beverages, which cause the red blotches/flushes (erythema) on the face, neck, shoulders, and, sometimes, the entire body. This condition is known as **alcohol flush**. Alcohol flush has been correlated with a greatly-increased risk of esophageal cancer for those who drink. The DNA variants leading to alcohol flush are most common among individuals of Asian descent, but do also occur, though much less frequently, in individuals of other geographical descents.

**b) Oxidation of Secondary (2º) Alcohols**

The oxidation of a secondary alcohol produces a __________.  

![Diagram of oxidation reaction]

A *ketone* is produced because the hydroxyl group of a secondary alcohol is attached to a carbon *that is not at the end of the parent chain*, and therefore the carbonyl group in the product is *not at the end of the parent chain*.

A specific example of the oxidation of a secondary alcohol is the oxidation of 2-propanol.
c) Oxidation of Tertiary (3°) Alcohols

A tertiary alcohol ______________ be oxidized to an aldehyde or a ketone because tertiary alcohols do not have a hydrogen attached to the carbon that is carrying the hydroxyl group.

Understanding Check
MnO₄⁻ will first oxidize a primary alcohol to an aldehyde, and then it will oxidize the aldehyde to produce a carboxylic acid.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} & \quad \overset{[O]}{\longrightarrow} \quad \text{an aldehyde} \\
\text{butanol} & \quad \overset{[O]}{\longrightarrow} \quad \text{a carboxylic acid}
\end{align*}
\]

Draw and name the aldehyde that is initially formed, and then the carboxylic acid that is subsequently formed in the oxidation of butanol when MnO₄⁻ is used as the oxidizing agent.

Understanding Check
Draw and name the organic molecule that is formed in the reaction shown here.

\[
\begin{align*}
\text{OH} & \quad \overset{[O]}{\longrightarrow} \\
\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 & \quad \text{[O]}
\end{align*}
\]
Reactions of Aldehydes and Ketones

1. The Oxidation of Aldehydes

*Aldehydes* can be oxidized to *carboxylic acids*.

- I told you about the oxidation of aldehydes when I discussed the oxidation of *primary alcohols* to form *aldehydes*, which, under certain conditions are further oxidized to *carboxylic acids*.

![Diagram of oxidation reaction]

A specific example of the *oxidation of an aldehyde* is a reaction that my students do in a laboratory activity. They use the permanganate ion (MnO₄⁻) to oxidize *benzaldehyde*.

In the following review problem, I would like you to draw the carboxylic acid that is produced when this reaction occurs.

**Understanding Check**

Draw the structure of the *carboxylic acid* that is formed in the *oxidation* of benzaldehyde.

- The *R* group in benzaldehyde is a *benzene ring*.

![Diagram of benzaldehyde and its oxidation]

2) The Reduction of Aldehydes and Ketones

Reduction of an aldehyde or a ketone produces an ____________.

- This is the ______________ of the *oxidation* of alcohols reaction.

![Diagram of general form of reduction equation]

As was the case for “[O],” an “[R]” is often written above the arrows in a chemical equation to indicate that the reactant is being *reduced*.

- When reduction is indicated by using “[R],” then the identity of the reducing agent reactant and the source of the hydrogens (or destination of oxygens) are often omitted from the chemical equation. In this case, the equation need not be balanced.
Reduction of aldehydes or ketones involves the formation of a bond to the *carbonyl carbon* by a
____________ ______ (*H*:), accompanied by the bonding of an *H*⁺ ion to the carbonyl-oxygen atom,
and the conversion of the carbon-oxygen *double* bond into a *single* bond.

![Diagram of reduction process](image)

**Aldehydes** are reduced to ____________(1⁰) *alcohols*.

![Diagram of aldehyde conversion](image)

**Ketones** are reduced to ____________(2⁰) *alcohols*.

![Diagram of ketone conversion](image)

In *biological systems*, the *hydride ion* (*H*:⁻) used in the reduction of aldehydes or ketones is supplied by
*nicotinamide adenine dinucleotide hydride* (NADH) or other organic hydride ion sources.

- For example, the final reaction in yeast’s alcohol fermentation process is the reaction of ethanal
  with NADH and an *H*⁺ to form ethanol and NAD⁺.

![Chemical reaction](image)
In the laboratory, hydride ions from aluminum hydride (AlH₄⁻), or borohydride (BH₄⁻) are used as reducing agents.

Hydrogen gas (H₂) is used as a reducing agent in laboratory and industrial applications.

- Reductions that use hydrogen gas (H₂) are called ____________ reactions.

They occur at high temperatures and in the presence of metal catalysts - often platinum (Pt) metal surfaces. Hydrogenation reactions do not use the mechanism of the addition of hydride (H⁻) and H⁺ ions that I previously described. A discussion of the mechanism for catalytic hydrogenation is beyond the scope of this book; however, you can predict the products for the reduction/hydrogenation of aldehydes or ketones by adding H₂ “across” the carbon-oxygen double bond (the carbonyl group), as we did for adding H₂ and H₂O “across” a C=C double bond.

To more easily visualize the addition of H₂ across the carbonyl group, it is convenient to redraw the aldehyde or ketone reactant with the R’ or H group flipped downward, as shown below.

\[
\begin{align*}
\text{R} & \quad \text{C} & R' \text{ or } H \\
\text{H₂} & \quad & \\
\text{R'} \text{ or } H & \\
\end{align*}
\]

Next, draw the H₂ molecule to the side of the carbonyl group, and then flip the bond between the hydrogens downward to make a new bond to the carbonyl carbon:

\[
\begin{align*}
\text{R} & \quad \text{C} & \overset{\text{H}}{\text{R'}} \text{ or } H \\
\text{H} & \quad \overset{\text{H}}{\text{R'}} \text{ or } H \\
\text{R'} \text{ or } H & \\
\end{align*}
\]

Finally, flip one pair of electrons from the carbonyl group’s double bond upward to form a bond with the remaining unbound hydrogen (H).

\[
\begin{align*}
\text{R} & \quad \text{C} & \overset{\text{OH}}{\text{H}} \\
\text{R'} \text{ or } H & \\
\end{align*}
\]

- A specific example of the hydrogenation of a ketone is the reaction of propanone with H₂.

\[
\begin{align*}
\text{CH₃} & \quad \text{C} & \quad \text{CH₃} + \overset{\text{Pt}}{\overset{\text{H₂}}{\overset{\text{H}}{\text{H}}} \quad \text{CH₃} & \quad \text{CH} & \quad \text{CH₃} \rightarrow \text{CH₃} & \quad \text{CH} & \quad \text{CH₃} \\
\text{propanone} & & \\
\text{H₂} & & \\
2\text{-propanol} & & \\
\end{align*}
\]
3) The Reaction of Aldehydes or Ketones with Alcohols: Hemiacetal and Acetal Production

A ___________ is a molecule that contains both an OR group and OH group that are bonded to the __________ carbon.

An ___________ is a molecule that contains ________ OR groups, where both OR groups are bonded to the same carbon.
An **aldehyde or a ketone** will react with an **alcohol** to form a **hemiacetal**.

The **OR** from the **alcohol** forms a bond to the **carbonyl-carbon** of the aldehyde or ketone, the **H** from the **alcohol** bonds to the **carbonyl-oxygen**, and the carbonyl group’s double bond is changed to a single bond.

![Hemiacetal Formation Diagram]

The **hemiacetal** that is formed can react with an *alcohol* molecule to form an **acetal** and an **H₂O** molecule. The structure of the **acetal** that is produced is drawn by **exchanging** the **R”** group of the **alcohol** and the **H** from the **hemiacetal**’s hydroxyl group (**OH**), as shown below.

![Acetal Formation Diagram]

**Example:** Draw the structure of the hemiacetal - and then the acetal - that is formed by the reaction of ethanol with ethanal.

![Example Diagram]

**Solution:** To form the **hemiacetal**, the **OR** from the **alcohol** forms a bond to the carbonyl carbon of the aldehyde or ketone, the **H** from the alcohol bonds to the carbonyl **oxygen**, and the carbonyl group’s double bond is changed to a single bond. A simple way to do this is to add the alcohol “across” the carbonyl double bond.

To add the alcohol (**CH₃CH₂OH**) across the carbonyl group, it is convenient to redraw the aldehyde as shown below.

![Aldehyde Redraw Diagram]

Next, draw the **alcohol molecule** to the side of the carbonyl group, as shown below, and then flip the bond from the **alcohol’s hydroxyl group** downward to make a new bond to the carbonyl carbon.
Finally, flip one pair of electrons from the carbonyl group upward to form a bond to the remaining unbound hydrogen (H).

```
CH₂₃C—OCH₂CH₃  →  CH₂₃C—OCH₂CH₃ — H
                  hemiacetal
```

The hemiacetal that is formed can react with a second ethanol molecule to form an acetal and an H₂O molecule. The structure of the acetal can be drawn by exchanging the R group of the alcohol (CH₃CH₂) and the H from the hemiacetal’s hydroxyl group:

```
CH₃C—OCH₂CH₃ + HOCH₂CH₃  →  CH₂₃C—OCH₂CH₃ + HOH
                  hemiacetal ethanol acetal H₂O
```

**Understanding Check**

Draw the hemiacetal, and then the acetal, that are formed in the reaction shown below.

```
CH₃CH₂C—H + CH₃OH  ⇌
```

**Understanding Check**

Draw the hemiacetal, and then the acetal, that are formed in the reaction shown below.

```
CH₃CH₂C CH₂CH₃ + CH₃OH  ⇌
```