



Alcohols & Ethers

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Lecture 8

2020-2021

Lecture Goals

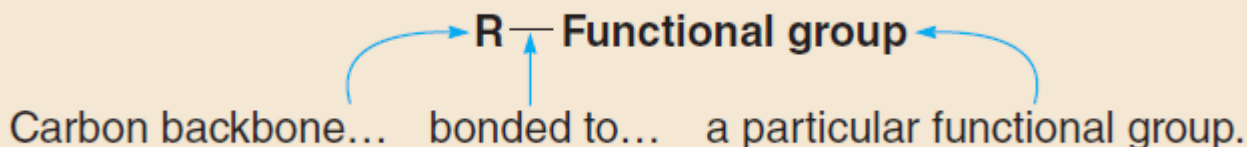
- In this chapter you will learn how to:
 - Recognize the common functional groups and understand their importance.
 - Identify alcohols and Ethers
 - Determine the properties of each functional group

1. Functional Groups

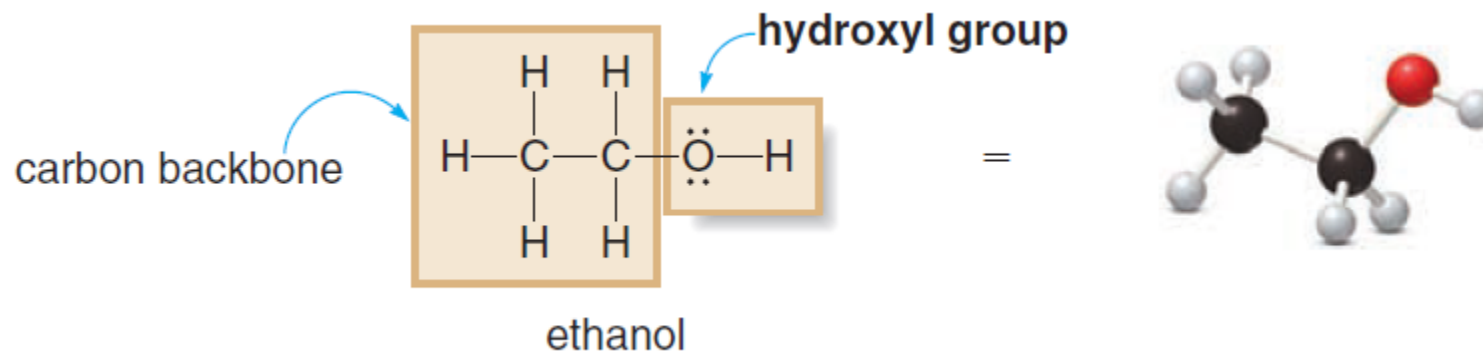
- In addition to strong C-C and C-H bonds, organic molecules may have other structural features as well. Although over 20 million organic compounds are currently known, only a limited number of common structural features, **called functional groups**, are found in these molecules.

- A **functional group** is an atom or a group of atoms with characteristic chemical and physical properties.
- A **functional group** contains a heteroatom, a multiple bond, or sometimes both a heteroatom *and* a multiple bond.

- A functional group determines a molecule's shape, properties, and the type of reactions it undergoes. A functional group behaves the same whether it is bonded to a carbon backbone.



For Example



The most common functional groups can be subdivided into three types.

- **Hydrocarbons**
- **Compounds containing a single bond to a heteroatom**
- **Compounds containing a C=O group**

Table 10.4 Compounds Containing a Carbon–Heteroatom Single Bond

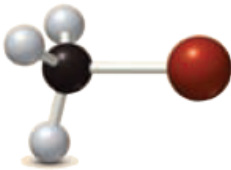
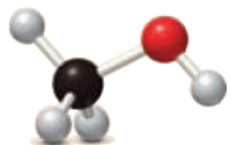
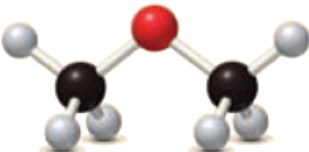
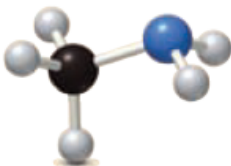
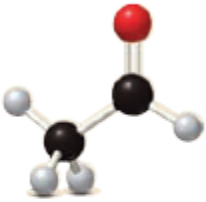
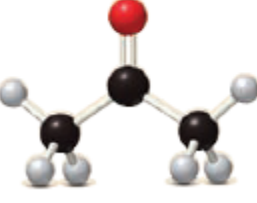
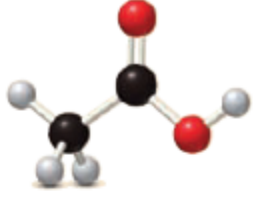
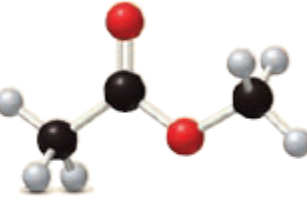
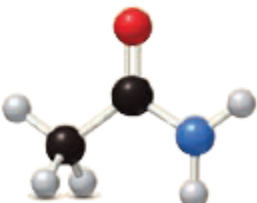
Type of Compound	General Structure	Example	3-D Structure	Functional Group
Alkyl halide	$\text{R}-\ddot{\text{X}}:$ <p>(X = F, Cl, Br, I)</p>	$\text{CH}_3-\ddot{\text{Br}}:$		-X
Alcohol	$\text{R}-\ddot{\text{O}}\text{H}$	$\text{CH}_3-\ddot{\text{O}}\text{H}$		-OH hydroxyl group
Ether	$\text{R}-\ddot{\text{O}}-\text{R}$	$\text{CH}_3-\ddot{\text{O}}-\text{CH}_3$		-OR
Amine	$\text{R}-\ddot{\text{N}}\text{H}_2 \text{ or}$ $\text{R}_2\ddot{\text{N}}\text{H} \text{ or } \text{R}_3\ddot{\text{N}}$	$\text{CH}_3-\ddot{\text{N}}\text{H}_2$		-NH ₂ amino group

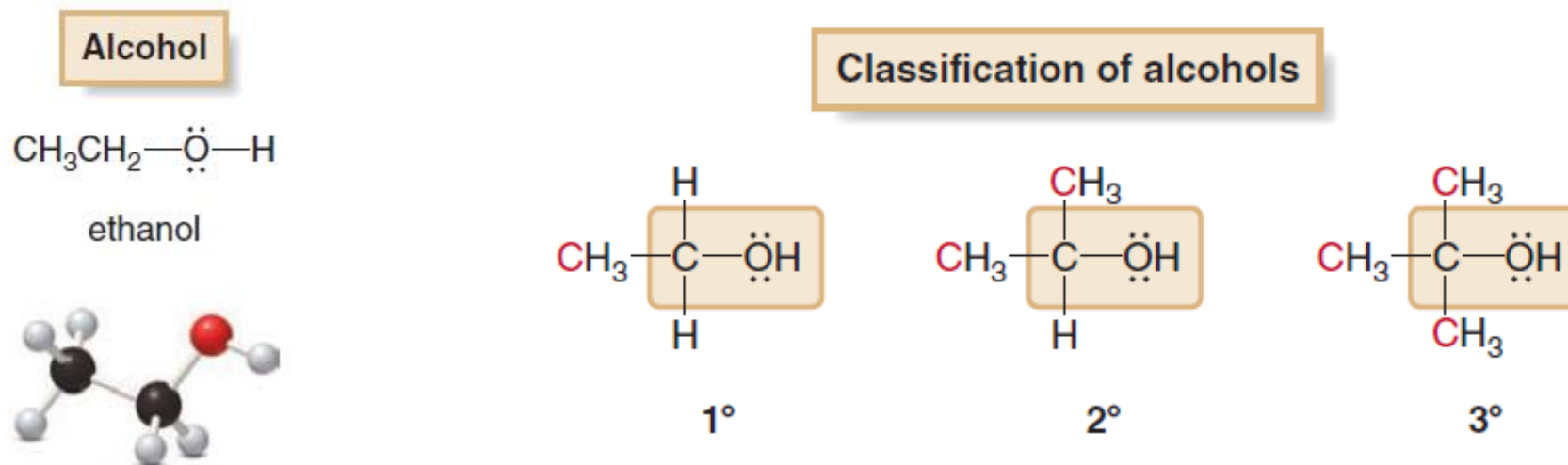
Table 10.5 Compounds Containing a C=O Group

Type of Compound	General Structure	Example	3-D Structure	Functional Group
Aldehyde	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\text{H} \end{array}$		$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{C}-\text{H} \end{array}$
Ketone	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\text{R} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\text{CH}_3 \end{array}$		$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{C} \end{array}$
Carboxylic acid	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{O}}\text{H} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\ddot{\text{O}}\text{H} \end{array}$		$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{C}-\ddot{\text{O}}\text{H} \\ \text{carboxyl group} \end{array}$
Ester	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{O}}\text{R} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\ddot{\text{O}}\text{CH}_3 \end{array}$		$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{C}-\ddot{\text{O}}\text{R} \end{array}$
Amide	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{N}}\text{H} \text{ (or R)} \\ \text{H (or R)} \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3-\text{C}-\ddot{\text{N}}\text{H}_2 \end{array}$		$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{C}-\ddot{\text{N}} \end{array}$

2. Alcohols

- Alcohols contain a **hydroxyl group (OH)** bonded to carbon.

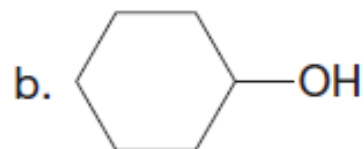
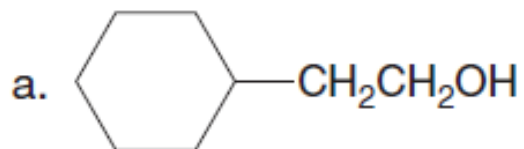
Alcohols (ROH) are classified as **primary (1°)**, **secondary (2°)**, or **tertiary (3°)** based on the number of carbon atoms bonded to the carbon with the OH group.



- A **primary (1°)** alcohol has an OH group on a carbon bonded to one carbon.
- A **secondary (2°)** alcohol has an OH group on a carbon bonded to two carbons.
- A **tertiary (3°)** alcohol has an OH group on a carbon bonded to three carbons.

PROBLEM

Classify each alcohol as 1°, 2°, or 3°.

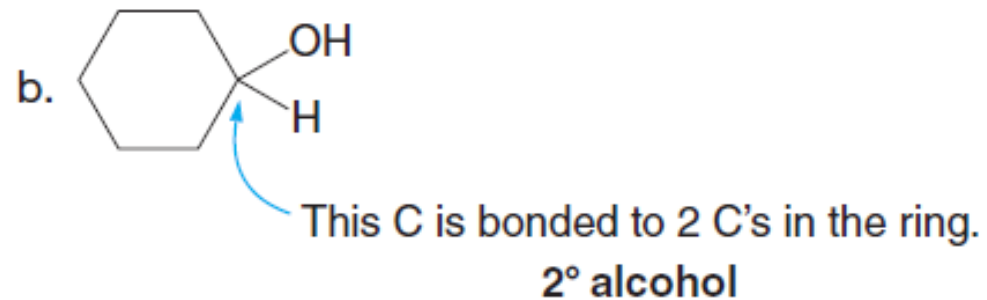
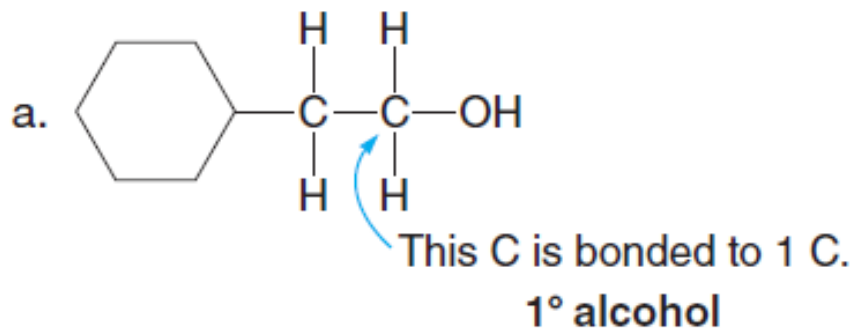


Analysis

To determine whether an alcohol is 1°, 2°, or 3°, locate the C with the OH group and count the number of C's bonded to it. A 1° alcohol has the OH group on a C bonded to one C, and so forth.

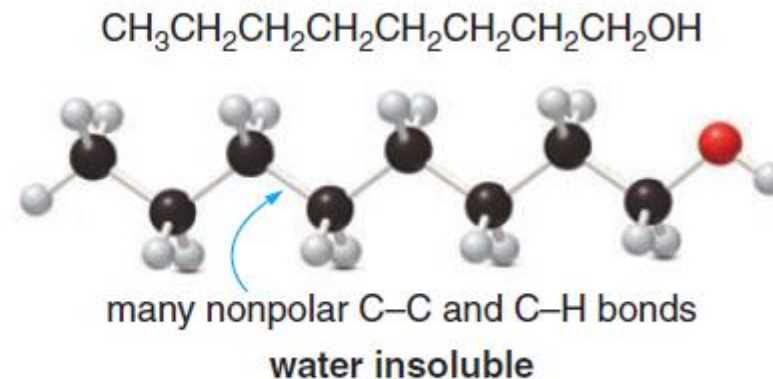
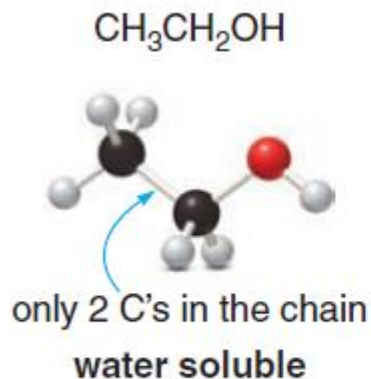
Solution

Draw out the structure or add H's to the skeletal structure to clearly see how many C's are bonded to the C bearing the OH group.



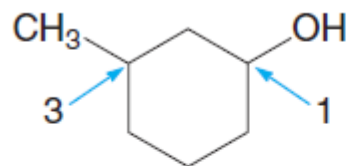
2.1. The Physical Properties of Alcohols

1. An alcohol contains an oxygen atom with a **bent shape** like H_2O .
2. Alcohols are capable of intermolecular **hydrogen bonding**.
3. Alcohols have **higher boiling points** and **melting points** than **hydrocarbons** of comparable size and shape.
4. Alcohols are soluble in **organic solvents**.
5. Low molecular weight alcohols (**those having less than six carbons**) are **soluble in water**.
6. Higher molecular weight alcohols (**those having six carbons or more**) are **not soluble in water**.



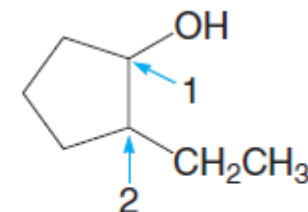
2.2. Nomenclature of Alcohols

- ❑ In the IUPAC system, alcohols are identified by the suffix **-ol**. To name an alcohol:
- ❑ Find the longest carbon chain containing the carbon bonded to the OH group.
- ❑ Number the carbon chain to give the OH group the lower number, and apply all other rules of nomenclature.
- ❑ When an OH group is bonded to a ring, the ring is numbered beginning with the OH group, and the “1” is usually omitted from the name. The ring is then numbered in a clockwise or counterclockwise fashion to give the next substituent the lower number.



3-methylcyclohexanol

[The OH group is at C1; the second substituent (CH₃) gets the lower number.]



2-ethylcyclopentanol

[The OH group is at C1; the second substituent (CH₃CH₂) gets the lower number.]

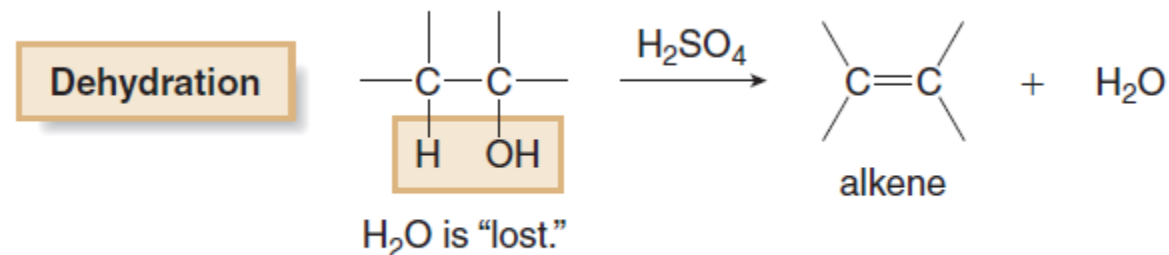
2.3. Reactions of Alcohols

- Alcohols undergo two useful reactions—**dehydration** and **oxidation**.

2.3A. Dehydration:

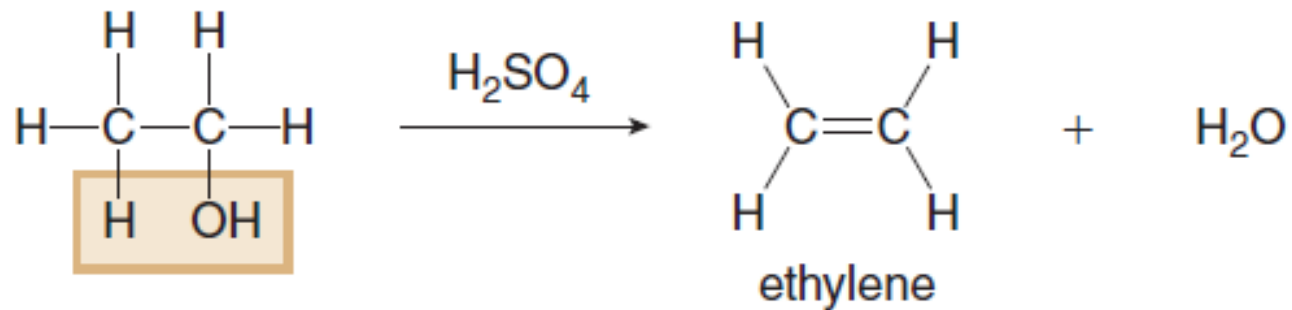
- When an alcohol is treated with a strong acid such as H_2SO_4 , the elements of **water** are lost and an **alkene is formed** as product. *Loss of H_2O from a starting material is called dehydration.*
- Dehydration takes place by breaking bonds on two adjacent atoms—the C-OH bond and an adjacent C-H bond.

Dehydration is an example of a general type of organic reaction called an **elimination reaction**.

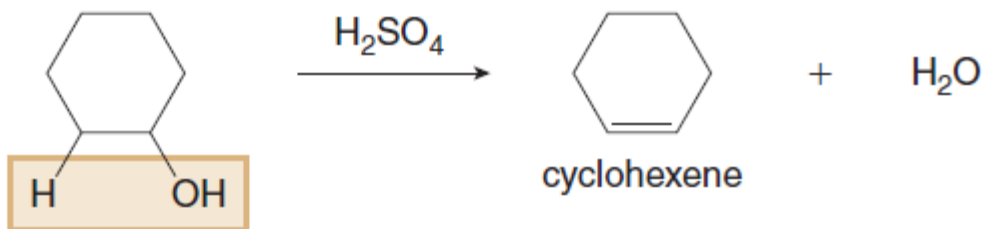


Elimination is a reaction in which elements of the starting material are "lost" and a new multiple bond is formed.

Examples

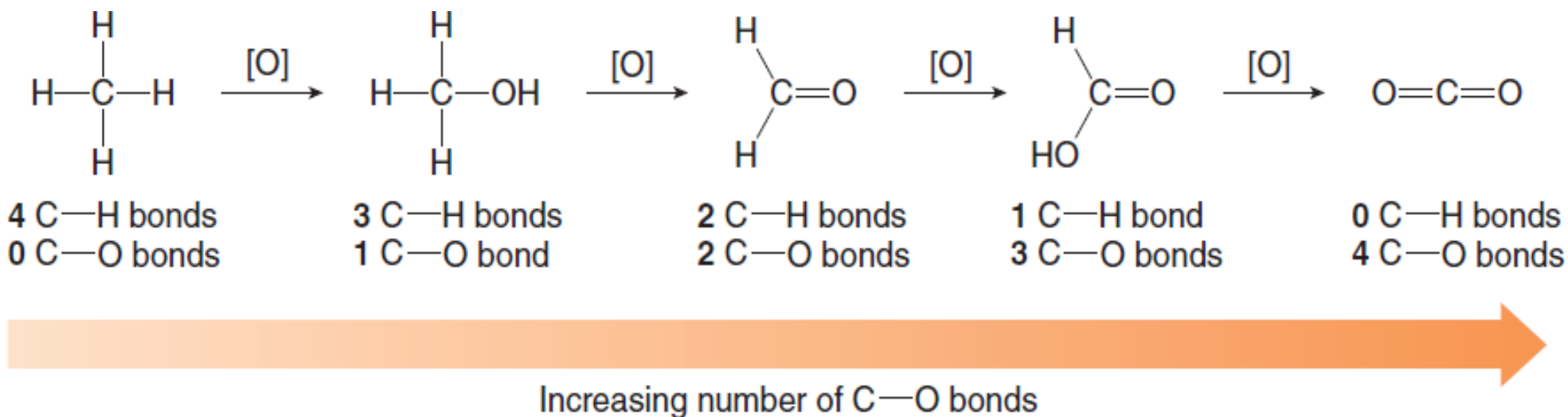


Elimination of H and OH from two adjacent atoms forms cyclohexene.



2.3B. Oxidation:

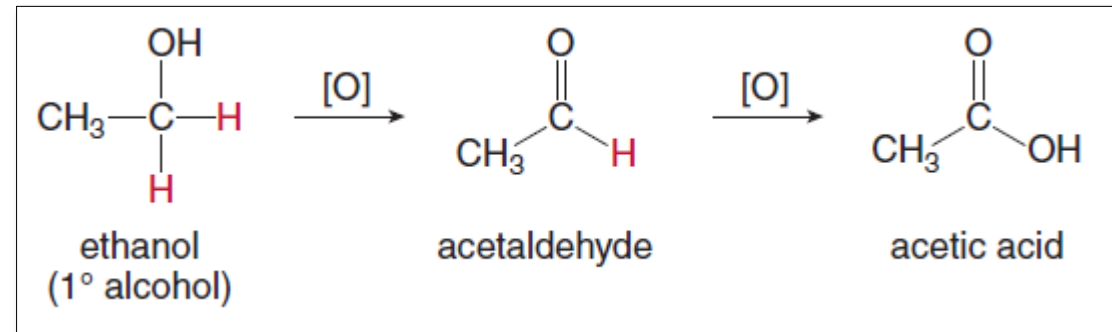
- To determine if an organic compound has been oxidized, we compare the relative number of C-H and C-O bonds in the starting material and product.
- ❖ Oxidation results in an increase in the number of C—O bonds or a decrease in the number of C—H bonds.
- Thus, an organic compound like CH₄ can be oxidized by replacing C-H bonds with C-O bonds. Organic chemists use the symbol [O] to indicate oxidation.



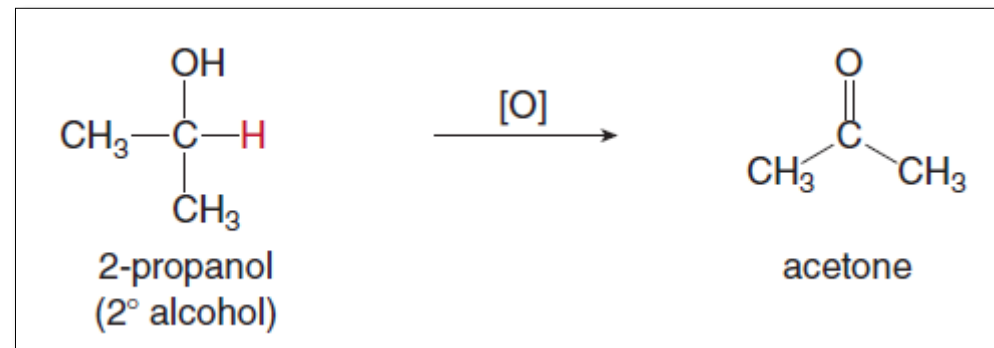
2.3B. Oxidation:

- Alcohols can be oxidized to a variety of compounds, depending on the type of alcohol and the reagent. **Oxidation occurs by replacing the C-H bonds on the carbon bearing the OH group by C-O bonds.** All oxidation products from alcohol starting materials contain a C=O, a **carbonyl group**.

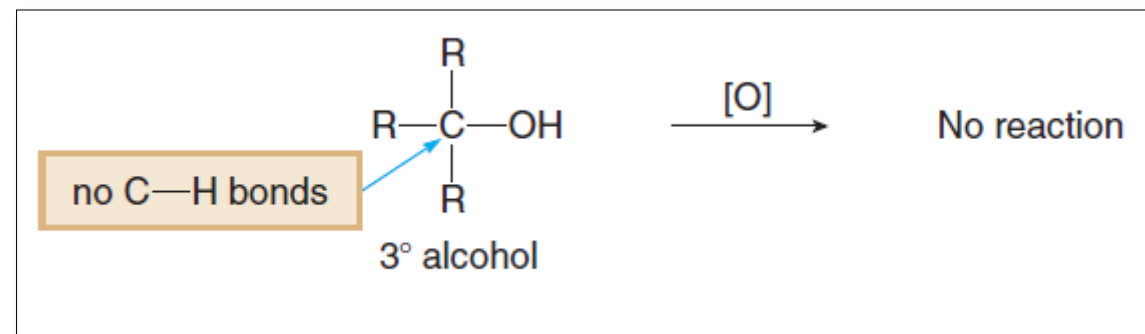
Primary (1°) alcohols are first oxidized to aldehydes (RCHO), which are further oxidized to carboxylic acids (RCOOH) by replacing one and then two C—H bonds by C—O bonds.



Secondary (2°) alcohols are oxidized to ketones (R₂CO), by replacing one C—H bond by one C—O bond.

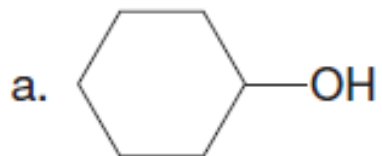


Tertiary (3°) alcohols have no H atoms on the carbon with the OH group, so they are not oxidized.

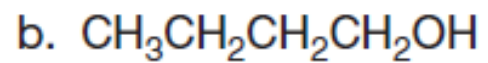


PROBLEM

Draw the carbonyl products formed when each alcohol is oxidized.



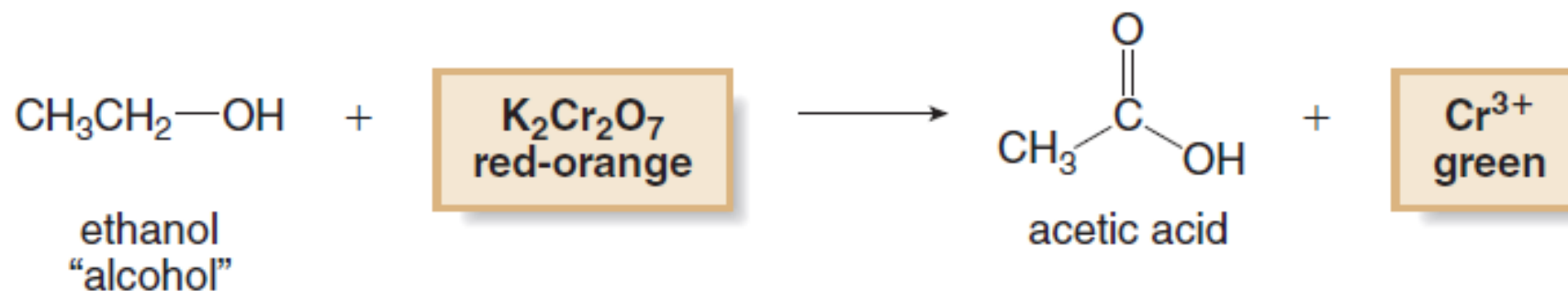
cyclohexanol



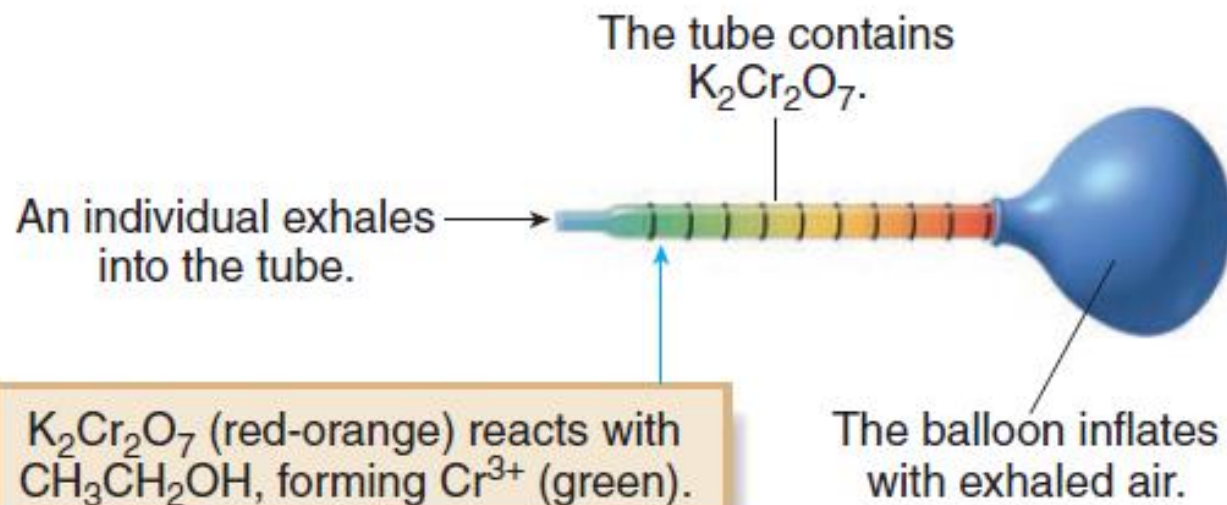
1-butanol

2.4. Oxidation and Blood Alcohol Screening

- ❖ A common reagent for alcohol oxidation is potassium dichromate, $K_2Cr_2O_7$, a **red-orange** solid.
- ❖ Oxidation with this chromium reagent is characterized by a color change, as the **red-orange reagent** is reduced to a **green Cr^{3+}** product.
- ❖ The first devices used to measure blood alcohol content in individuals suspected of “**driving under the influence**” made use of this color change.
- ❖ Oxidation of CH_3CH_2OH , the 1° alcohol in alcoholic beverages, with red-orange $K_2Cr_2O_7$ forms CH_3COOH and green Cr^{3+} .



Schematic of an alcohol testing device



Consumer product



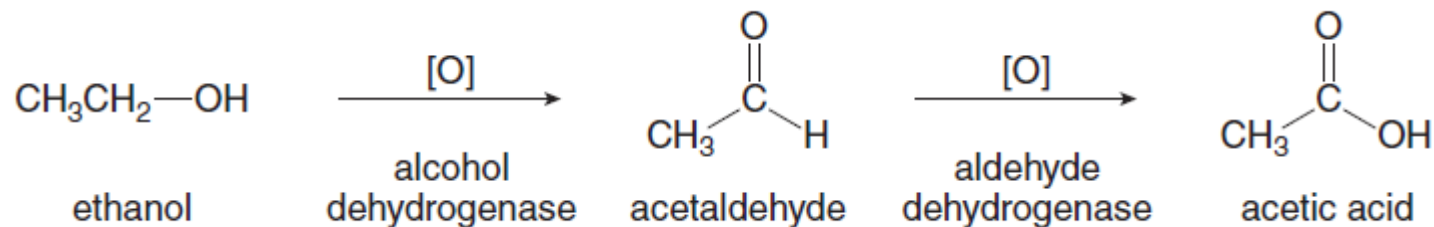
$K_2Cr_2O_7$

- The oxidation of CH_3CH_2OH with $K_2Cr_2O_7$ to form CH_3COOH and Cr^{3+} was the first available method for the routine testing of alcohol concentration in exhaled air. Some consumer products for alcohol screening are still based on this technology.
- A driver is considered “under the influence” in most states with a blood alcohol concentration of 0.08%.

2.5. The Metabolism of Ethanol

(FOCUS ON HEALTH & MEDICINE)

- When ethanol is consumed, it is quickly absorbed in the **stomach** and **small intestines** and then rapidly transported in the **bloodstream** to other organs.
- Ethanol is metabolized in the **liver**, by a two-step oxidation sequence. *The body does not use chromium reagents as oxidants.* Instead, high molecular weight enzymes, **alcohol dehydrogenase** and **aldehyde dehydrogenase**, and a small molecule called a **coenzyme** carry out these oxidations.

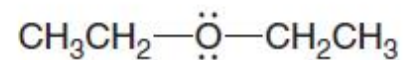


- If more ethanol is ingested than can be metabolized in a given time period, the concentration of acetaldehyde accumulates. This toxic compound is responsible for the feelings associated with a hangover.

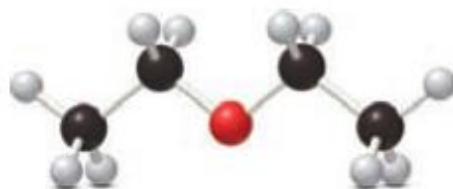
3. Ethers

- □ Ethers contain two alkyl groups bonded to an oxygen atom.

Ether



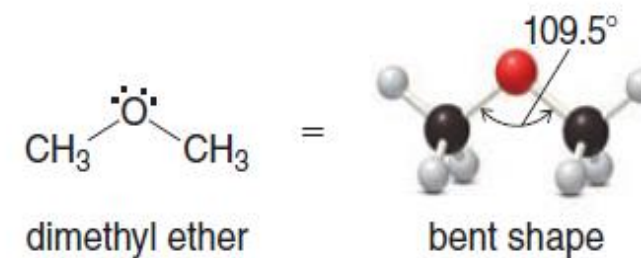
diethyl ether



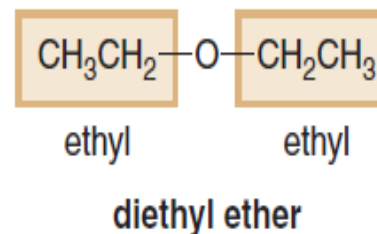
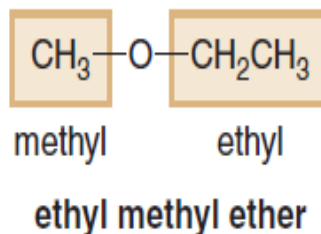
- The oxygen atom in ethers have two lone pairs of electrons, so each heteroatom is surrounded by eight electrons.

3.1. Structure and Properties of Ethers

1. Ethers (ROR) are organic compounds that have two alkyl groups bonded to an oxygen atom.
2. The oxygen atom of an ether is surrounded by two carbon atoms and two lone pairs of electrons, giving it a bent shape like the oxygen in H₂O. The C-O-C bond angle is similar to the tetrahedral bond angle of 109.5°.

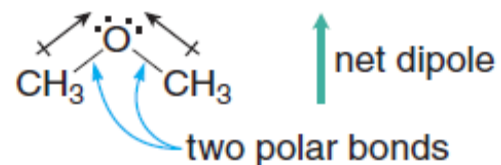


3. Simple ethers are usually assigned common names. To do so, name both alkyl groups bonded to the oxygen, arrange these names alphabetically, and add the word ether. For ethers with identical alkyl groups, name the alkyl group and add the prefix di-.



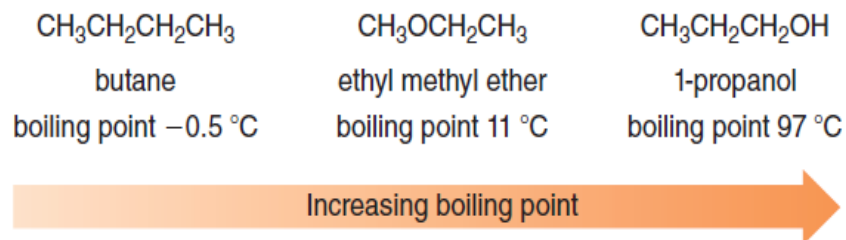
3.1. Structure and Properties of Ethers

4. Because oxygen is more electronegative than carbon, the C-O bonds of an ether are both polar. Since an ether contains two polar bonds and a bent shape, it has a net dipole.



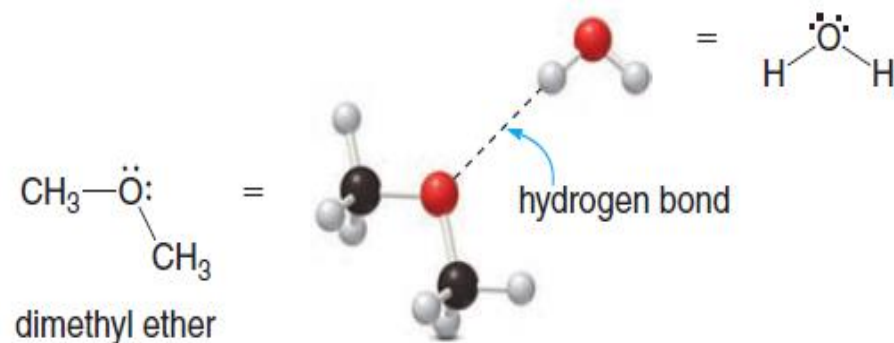
5. Ethers do not contain a hydrogen atom bonded to oxygen, so unlike alcohols, two ether molecules cannot intermolecularly hydrogen bond to each other. This gives ethers stronger intermolecular forces than alkanes but weaker intermolecular forces than alcohols. As a result:

- Ethers have higher melting points and boiling points than hydrocarbons of comparable size and shape.
- Ethers have lower melting points and boiling points than alcohols of comparable size and shape.



3.1. Structure and Properties of Ethers

- All ethers are soluble in organic solvents. Like alcohols.
- Ether with low molecular weight ethers are water soluble, because the oxygen atom of the ether can hydrogen bond to one of the hydrogens of water.



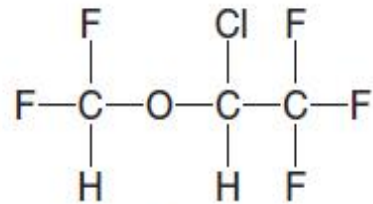
- When the alkyl groups of the ether have more than a total of five carbons, the nonpolar portion of the molecule is too large, so the ether is water insoluble.

3.2. Ethers as Anesthetics

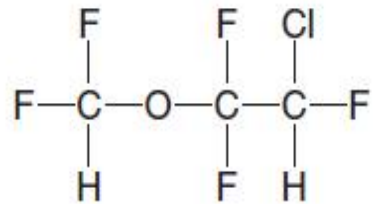
A general anesthetic is a drug that interferes with nerve transmission in the brain, resulting in a loss of consciousness and the sensation of pain. The discovery that diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$) is a general anesthetic dramatically changed surgery in the nineteenth century.

Diethyl ether is an imperfect anesthetic, but considering the alternatives at the time, it was considered revolutionary. It is safe and easy to administer with low patient mortality, but it is highly flammable, and it causes nausea in many patients.

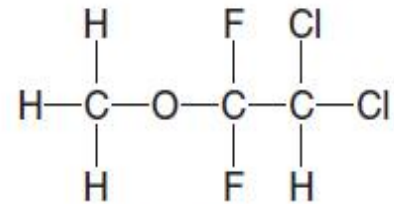
For these reasons, alternatives to diethyl ether are now widely used. Many of these newer general anesthetics, which cause little patient discomfort, are also ethers. These include isoflurane, enflurane, and methoxyflurane. Replacing some of the hydrogen atoms in the ether by halogens results in compounds with similar anesthetic properties but decreased flammability.



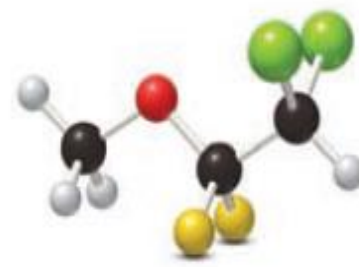
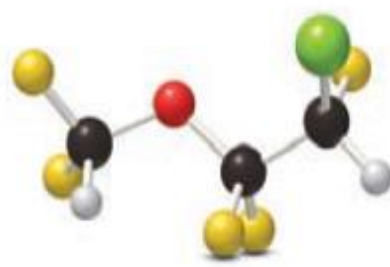
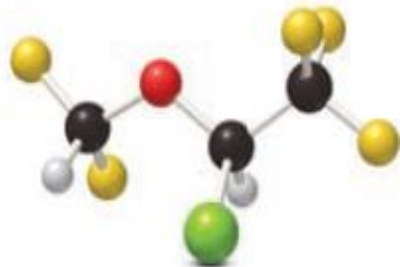
isoflurane
(Trade name: Forane)



enflurane
(Trade name: Ethrane)

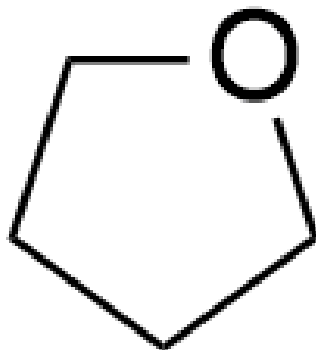


methoxyflurane
(Trade name: Penthrane)



3.3. Reaction of Ethers

Compared to other organic molecules, ethers are not very reactive. This is very advantageous to chemists, because this means we can use them as solvents. One of the most common ether solvents used in industry is tetrahydrofuran (THF).



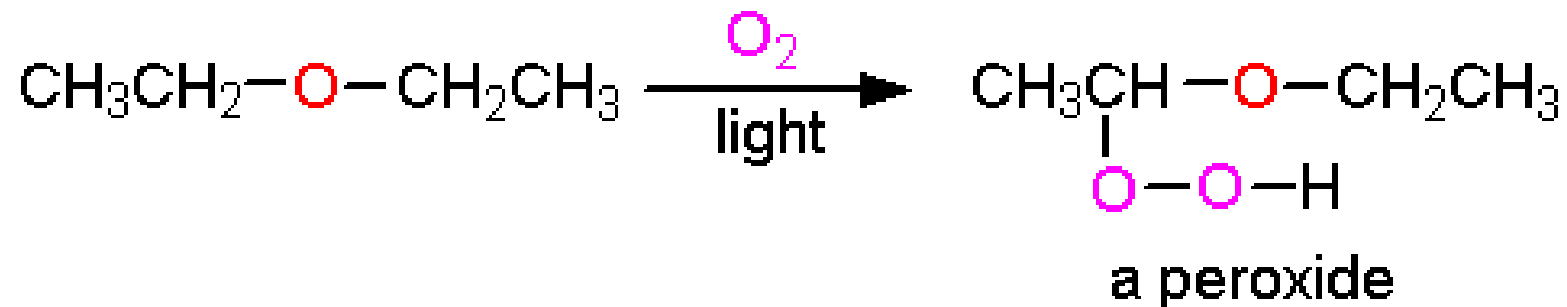
Tetrahydrofuran

3.3. Reaction of Ethers

1. Oxidation of ethers

Ethers will slowly react with oxygen in the air in an oxidation reaction, forming peroxides. Peroxides are molecules that have a functional group with two oxygens attached to each other.

This is a particularly dangerous reaction because the peroxides are so unstable, they tend to explode! Bomb squads have been summoned to universities to remove old bottles of ether because they have formed peroxides.

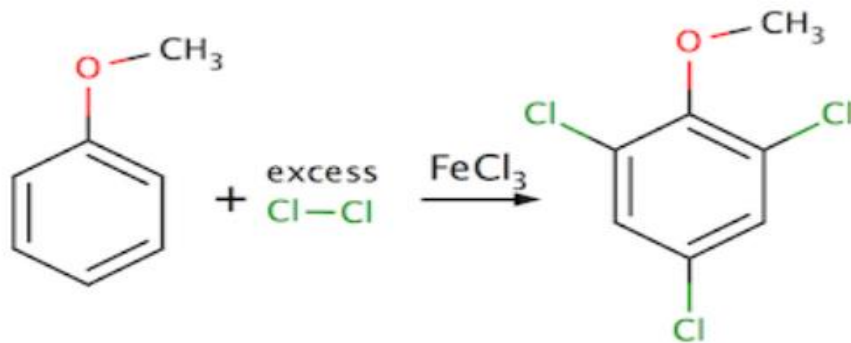


3.3. Reaction of Ethers

2. Chlorination

If an ether is part of an aromatic ring, it can react with chlorine to produce 2,4,6-trichloroanisole. This molecule causes wines to have 'cork taint', or a moldy smell.

In this reaction, the presence of the ether directs the chlorine to specific positions on the aromatic ring. Chlorine will only add to the carbon adjacent to the ether, known as the ortho position, or directly across from the ether, known as the para position. Because of this really specific reactivity, the ether group is known as an ortho/para director.



End