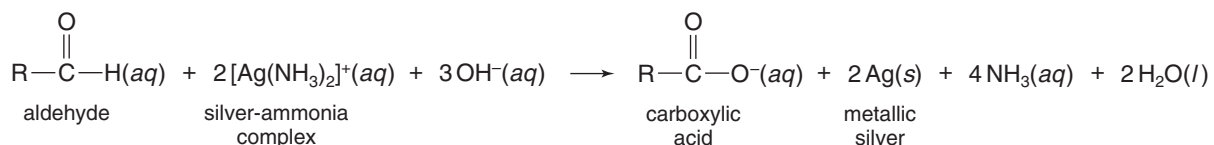


INTERCHAPTER P

Alcohols, Aldehydes, and Ketones

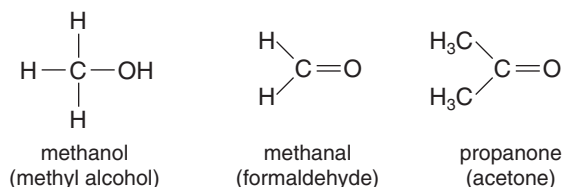


When an aldehyde is present, the Tollen's test produces a silver mirror on the inside of a test tube or flask, as shown here. The oxidation-reduction reaction that takes place is described by the equation



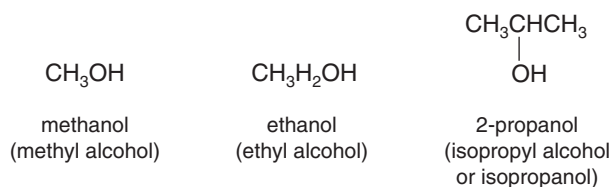
In the reaction the aldehyde functional group, R-CHO, is oxidized to a carboxylic acid functional group, R-COOH (which is deprotonated in the basic solution), while the silver ions in the silver-ammonia complex are reduced to form metallic silver. The mirror forms because a thin film of metallic silver is deposited on the inside surface of the flask and adheres to the glass. This reaction was used in Victorian times to produce mirrors on glass.

We shall continue our introduction to organic chemistry in this Interchapter. Up to now, we have learned only about hydrocarbons. We studied saturated hydrocarbons in Interchapter F, unsaturated hydrocarbons in Interchapter G, and aromatic hydrocarbons in Interchapter H. When we studied unsaturated hydrocarbons, we referred to the carbon-carbon double bond as a functional group. The chemical properties of unsaturated hydrocarbons are a result of how the double bond reacts with reagents. In this Interchapter we shall learn about alcohols, aldehydes, and ketones. Alcohols have -OH as their functional group, aldehydes have $\text{H}-\text{C}=\text{O}$, and the functional group of ketones is $\text{>C}=\text{O}$. The simplest member of each class is

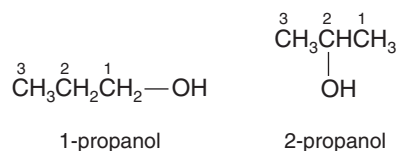


P-I. Alcohols Are Organic Compounds That Contain an -OH Group

The class of organic compounds called **alcohols** is characterized by an -OH group attached to a hydrocarbon chain. Important common alcohols (Figure P.1) are



These alcohols have both common names (given here in parentheses) and IUPAC (or systematic) names. The common names are formed by naming the alkyl group to which the -OH is attached and adding the word alcohol. The IUPAC name is formed by replacing the $-e$ from the end of the alkane name of the longest chain of carbon atoms containing the -OH group with the suffix $-ol$. Thus, we have methanol, ethanol, and propanol. If the -OH group can be attached at more than one position, then its position is denoted by a number, as in



2-propanol is also called isopropyl alcohol or isopropanol. An aqueous solution of 70% by volume of 2-propanol is sold as rubbing alcohol, the substance commonly used to clean the skin before administering an injection.

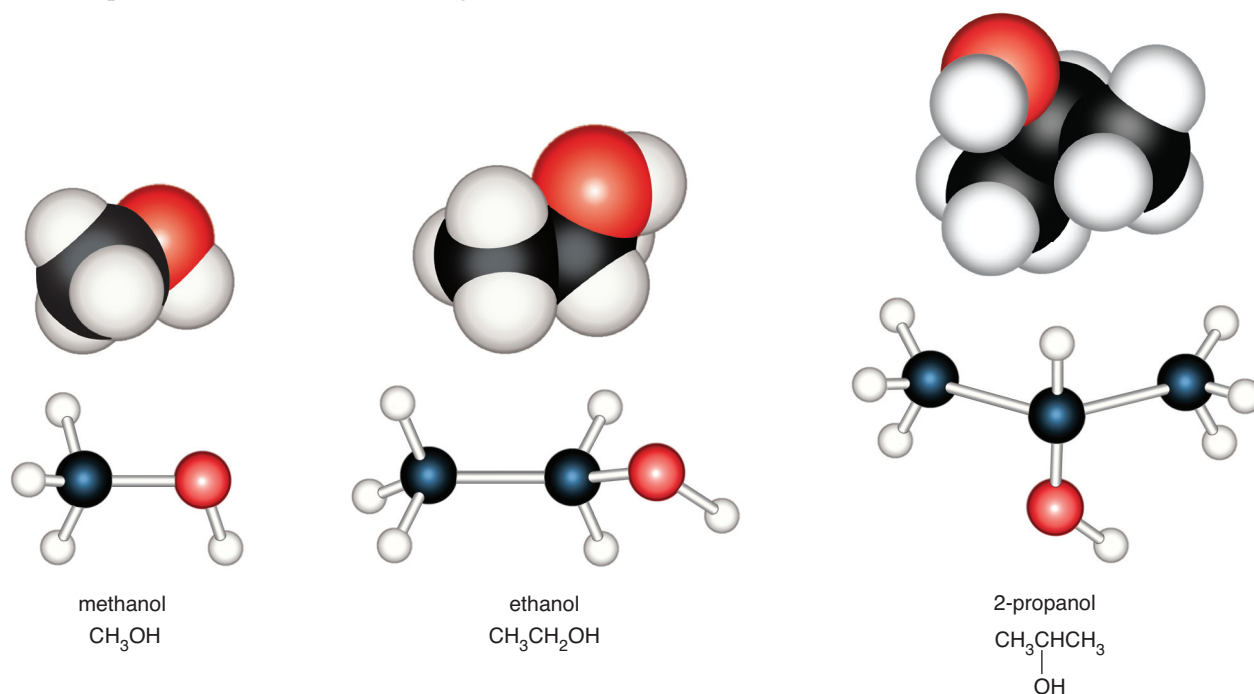
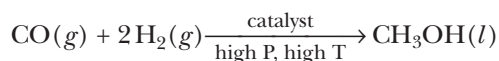


Figure P.1 Space-filling and ball-and-stick models of common alcohols: methanol, ethanol, and 2-propanol.

Methanol is sometimes called wood alcohol because it can be produced by heating wood in the absence of oxygen. Over three million metric tons of methanol are produced annually in the United States by the reaction described by



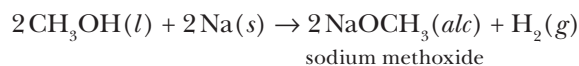
Methanol is highly toxic and can cause blindness and death if taken internally. During Prohibition in the United States, many people died or became seriously ill from drinking methanol, either because they were not aware of the difference between methanol and ethanol or because the alcohol they purchased contained methanol as a major impurity.

Ethanol is an ingredient in all fermented beverages. Various sugars and the starch in potatoes, grains, and similar substances can be used to produce ethanol by fermentation, a process in which yeast is used to convert sugar to ethanol. Although ethanol may be best known as an ingredient in alcoholic beverages, it is an important industrial chemical as well. Today most gasolines contain a certain percentage of ethanol, and special multifuel vehicles exist that can run entirely on ethanol (see Interchapter L).

It is sometimes convenient to view alcohols as derivatives of water, in which one of the hydrogen atoms is replaced by an alkyl group. This approach is most useful when the hydrocarbon portion of the alcohol is

relatively small. The low-molecular-mass alcohols form hydrogen bonds and mix completely (i.e., are miscible) with water in all proportions. As the hydrocarbon portion becomes larger, however, the solubility of alcohols in water decreases and eventually approaches the low solubility of the comparable hydrocarbon. In addition, the low-molecular-mass alcohols have much higher boiling points than their comparable hydrocarbons. For example, ethane (molecular mass 30) has a boiling point of -88.6°C , while the boiling point of methanol (molecular mass 32) is 64.6°C . The relatively high boiling points of the low-molecular-mass alcohols are due to extensive hydrogen bonding in the liquid phase.

The $-\text{OH}$ group on the relatively unreactive hydrocarbon chain accounts for the reactive properties of alcohols. We say that the $-\text{OH}$ group is a **functional group**, just as the double bond in alkenes serves as a functional group in that case. Alcohols undergo reactions analogous to those of water. For example, alcohols react with alkali metals to form **alkoxides** and liberate hydrogen:



Alkoxides are strong Lewis bases, that is, electron-pair donors (see Section 20-1).

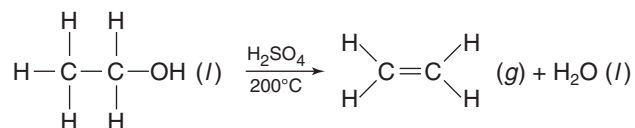
Table P.1 lists the boiling points and the solubilities in water of a number of alcohols. Note how the

TABLE P.1 Boiling points and solubilities in water of several pairs of hydrocarbons and alcohols of similar molecular masses

Name	Formula	Molecular mass	Boiling point/ $^\circ\text{C}$	Solubility in water/g per 100 g H_2O at 25°C
ethane	CH_3CH_3	30.069	-88.6	insoluble
methanol	CH_3OH	32.042	64.6	soluble in all proportions
propane	$\text{CH}_3\text{CH}_2\text{CH}_3$	44.096	-42.1	insoluble
ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	46.068	78.29	soluble in all proportions
butane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	58.122	-0.5	insoluble
1-propanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	60.095	97.2	soluble in all proportions
pentane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	72.149	36.06	insoluble
1-butanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	74.121	117.73	7.4
hexane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	86.175	68.73	insoluble
1-pentanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	88.148	137.98	2.20
heptane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	100.202	98.4	insoluble
1-hexanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	102.174	157.6	0.60

solubility decreases as the relative size of the alkyl portion of the molecule increases. Also, note that for pairs of hydrocarbons and alcohols of comparable molecular mass, the alcohols have considerably higher boiling points.

Alcohols can be converted to alkenes by acid-catalyzed dehydration. For example,



Many of the reactions that alcohols undergo depend on the number of carbon atoms that are bonded to the carbon atom bearing the $-\text{OH}$ group. For this reason we define **primary**, **secondary**, and **tertiary alcohols**. A primary alcohol has one carbon atom bonded to the carbon atom bearing the $-\text{OH}$ group; a secondary alcohol has two such carbon atoms; and a tertiary alcohol has three:

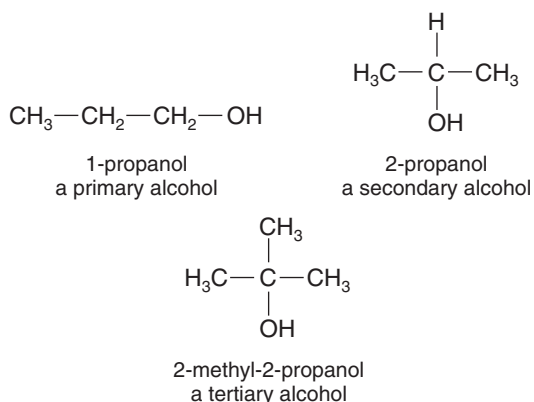
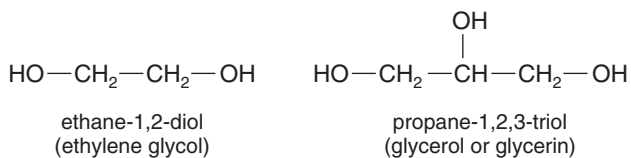


Table P.2 lists some other structural formulas of alcohols, their IUPAC names, and respective classes, just for practice. The *t*- in the common name *t*-butyl alcohol (Table P.2) stands for tertiary.

It is possible to have more than one $-\text{OH}$ group in an alcohol. Two examples are



Ethylene glycol can be obtained by a controlled oxidation of ethylene,

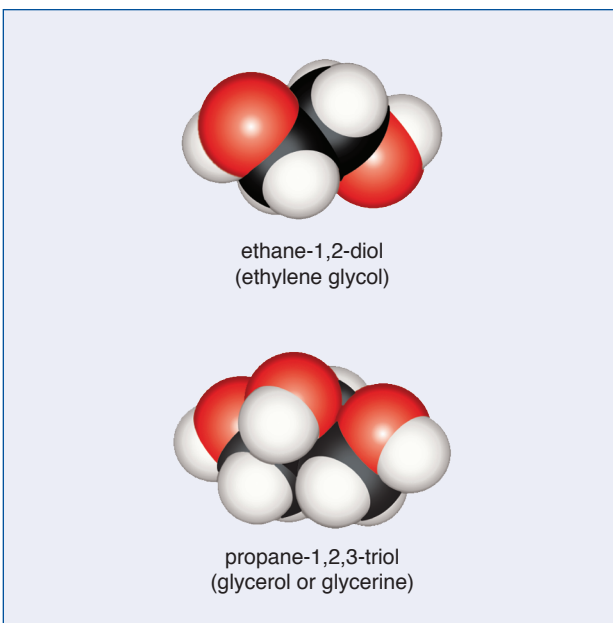
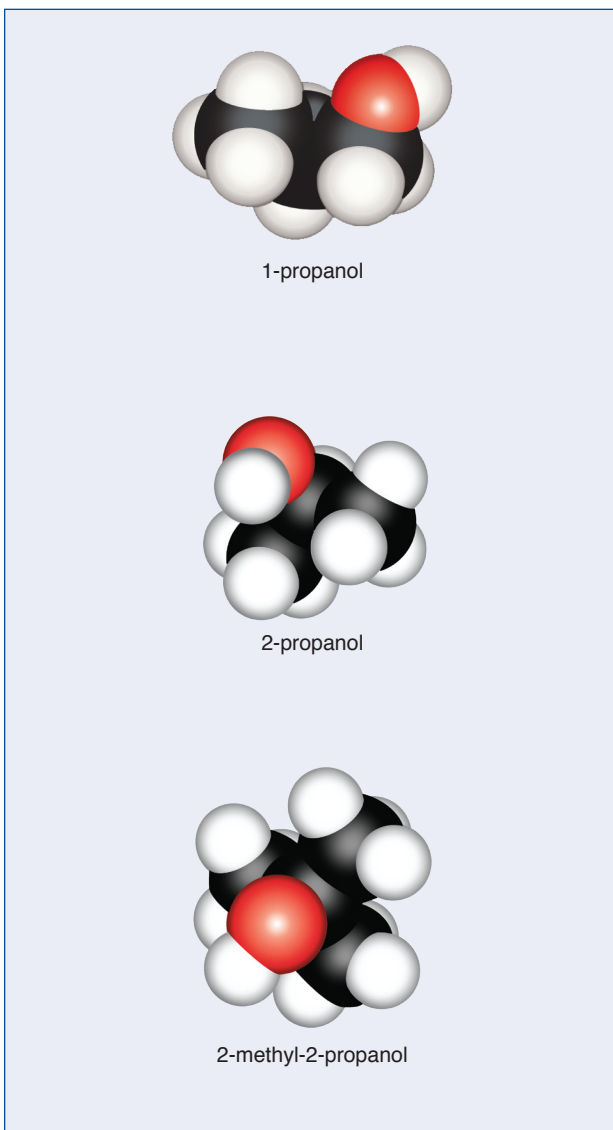
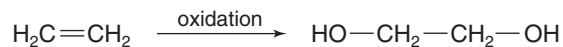


TABLE P.2 The structural formulas, corresponding IUPAC names, and classes of some alcohols

Structural formula	IUPAC name	Class
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2\text{CH}_3 \\ \\ \text{OH} \end{array}$	2-methyl-2-butanol	tertiary alcohol
$\begin{array}{c} \text{CH}_3\text{CH}_2-\text{CH}-\text{CH}_2\text{CH}_3 \\ \\ \text{OH} \end{array}$	3-pentanol	secondary alcohol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$	2-methyl-2-propanol (<i>t</i> -butyl alcohol)	tertiary alcohol

and glycerol is obtained from the hydrolysis of fats. The annual production of ethylene glycol in the United States exceeds two million metric tons. The low melting point (-11.5°C) and high boiling point (198°C) of ethylene glycol along with its complete miscibility with water make it an excellent antifreeze (Chapter 16). Glycerol, a colorless, odorless, syrupy liquid, has a wide range of uses, from medical, pharmaceutical, and cosmetic preparations to dynamite, which is a mixture of nitroglycerin (below) and an inert absorbent. Dynamite was developed and patented in 1867 by the Swedish chemist and engineer Alfred Nobel (Figure P.2), who later instituted the Nobel Prize foundation.

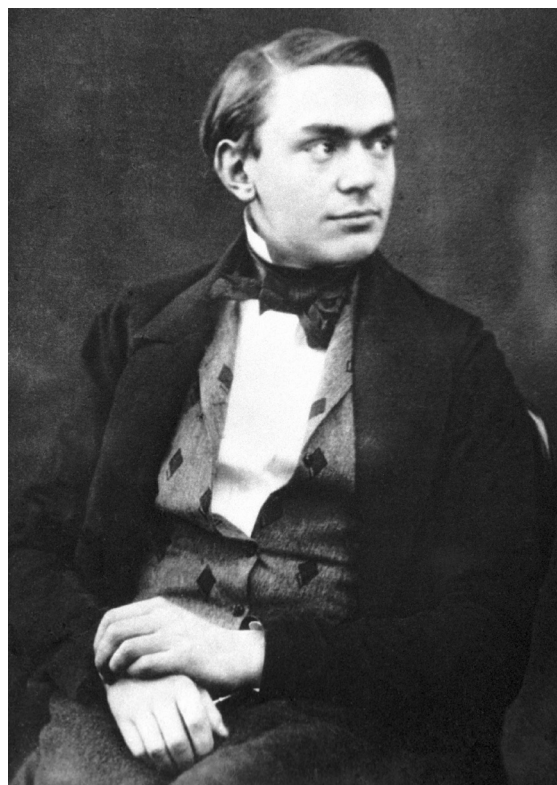
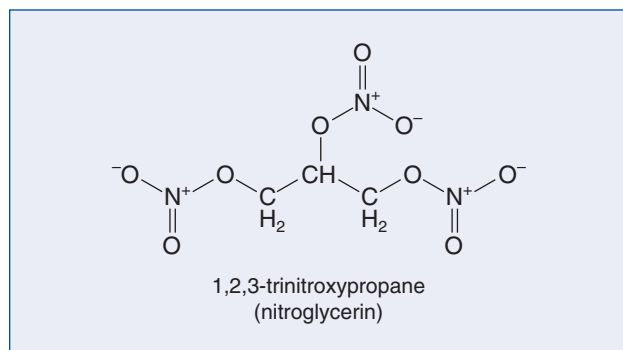
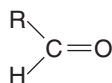


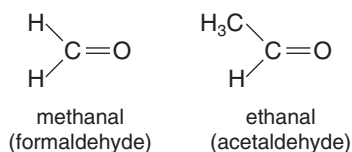
Figure P.2 Alfred Bernhard Nobel (1833–1896) was born in Stockholm, Sweden. At an early age, his father moved his family to St. Petersburg, Russia, where he set up a successful business manufacturing naval mines, armaments, and other explosive devices. Alfred was fluent in several languages and in his youth wanted to become a poet and a dramatist, but his father insisted that he study chemistry. His early education in chemistry was in St. Petersburg, although he later carried out research in several private laboratories in Europe and the United States. He returned to Sweden with his father in 1863 when his family's business went bankrupt after the Crimean War. Nobel turned his attention to making safer explosives, and in 1867 he developed dynamite, which is nitroglycerin incorporated into an absorbent. Nobel earned a large fortune from his explosives business. He was also very involved in social and peace-related issues and held views that were considered quite radical during his time. Upon his death, he willed much of his considerable fortune to institute a foundation to award prizes for contributions to the fields of physics, chemistry, physiology and medicine, literature, and peace. These awards have become one of the world's most prestigious prizes and are now known as the Nobel Prize. Although he had several loves in his life, he never married, but in 1905 the Nobel Peace Prize was awarded to Bertha von Suttner, his one-time secretary and a lifelong friend.

P-2. Aldehydes and Ketones Contain a Carbon–Oxygen Double Bond

Primary alcohols can be oxidized to produce aldehydes. **Aldehydes** are compounds that have the general formula RCHO,



where R is a hydrogen atom or an alkyl group. The –CHO functional group, called the **aldehyde group**, is characteristic of aldehydes. The two simplest aldehydes are



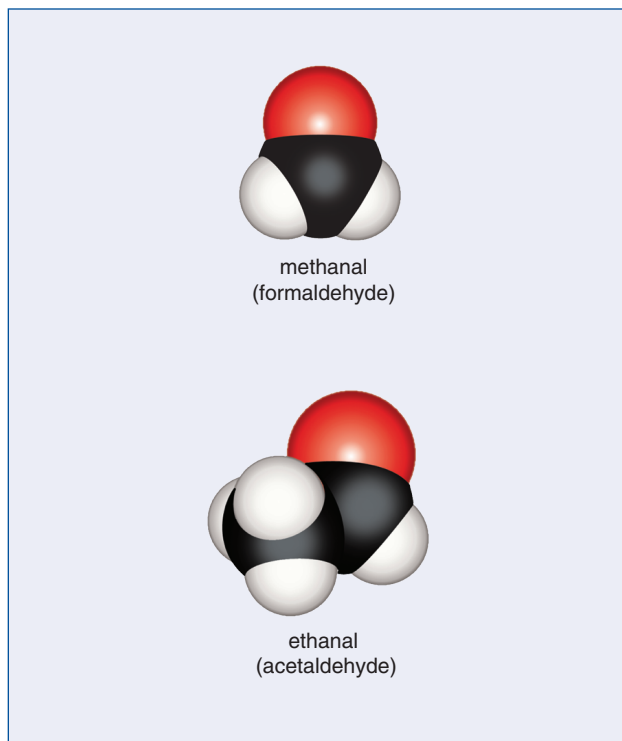
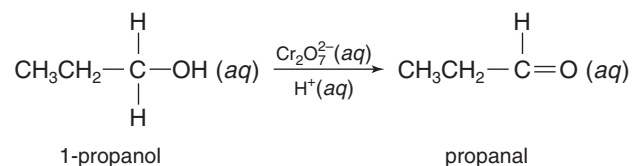
These two aldehydes are generally referred to by their common names.

Formaldehyde is a gas with an offensive and characteristic odor. It is one of the irritants in smog and

in cigarette smoke. About five million metric tons of formaldehyde are manufactured annually in the United States. Most of this goes into the production of various plastic materials. A solution of formaldehyde in water, called formalin, preserves biological specimens. However, this use is being phased out in a number of countries because formaldehyde is a carcinogen.

Acetaldehyde is a colorless, flammable liquid with a pungent, fruity odor. It is used in the manufacture of perfumes, flavors, plastics, synthetic rubbers, dyes, and a variety of other organic chemicals.

A commonly used oxidizing agent for the oxidation of primary alcohols to produce aldehydes is potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7(s)$, dissolved in an aqueous acidic solution:



Aldehydes are readily oxidized to carboxylic acids (see Interchapter R), so it is necessary to stop the oxidation of a primary alcohol at the aldehyde stage in order to prevent the aldehyde from being oxidized further to the carboxylic acid. One way to do this is to remove the aldehyde as soon as it is formed by distilling it from the reaction mixture. Reactions such as these can be used to measure alcohol content (see sidebar, page P6). Aldehydes do not hydrogen-bond and consequently have lower boiling points than the corresponding primary alcohols.

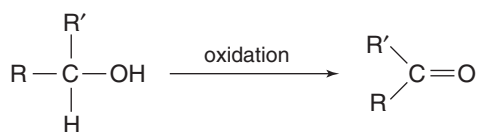
The systematic nomenclature for aldehydes uses the longest chain of consecutive carbon atoms containing the –CHO group as the parent compound. The systematic name of an aldehyde is formed by dropping the terminal *-e* and adding *-al* to the name of the corresponding alkane. For example, the IUPAC name for formaldehyde, $\text{CH}_2\text{O}(g)$, is methanal and that for acetaldehyde, $\text{CH}_3\text{CHO}(l)$, is ethanal.

Table P.3 lists the structural formulas and the IUPAC names of some aldehydes for practice.

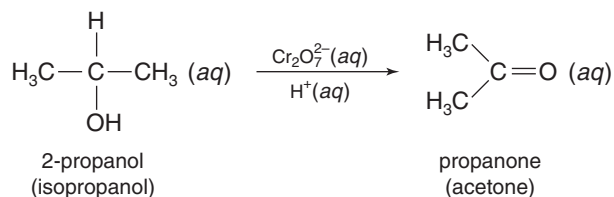
TABLE P.3 The structural formulas and the corresponding IUPAC names of some aldehydes

Structural formula	IUPAC name
$\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	propanal
$\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	butanal
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	pentanal
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} \end{array}$	3-methylbutanal
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CH}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} \\ \\ \text{CH}_3 \end{array}$	3,4-dimethylpentanal
$\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} \end{array}$	3-methylpentanal

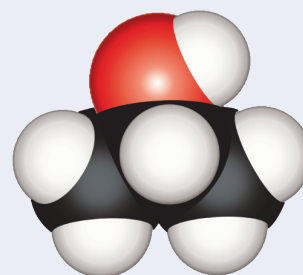
Secondary alcohols can be oxidized according to



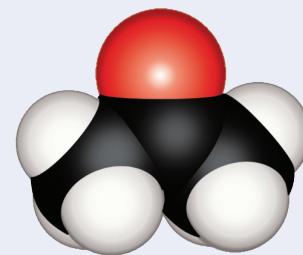
The resulting compound in this reaction is called a **ketone**. The general formula of a ketone is $\text{R}(\text{CO})\text{R}'$ where R and R' are alkyl groups and the $\text{C}=\text{O}$ group is called a **carbonyl group**. Propanone, commonly called acetone, $(\text{CH}_3)_2\text{CO}(l)$, is the simplest ketone and can be prepared from the oxidation of 2-propanol (isopropanol):



Many law enforcement agencies use a device called a breathalyzer in the field to estimate the ethanol content of the blood of someone who is suspected of being intoxicated while driving. Breathalyzers function by analyzing the extent to which the oxidation of ethanol produces either acetaldehyde or acetic acid. One type of breathalyzer uses a potassium dichromate–sulfuric acid mixture. When alcohol vapor from the breath is exhaled into the mixture, the ethanol is oxidized by the potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7(\text{acid})$. The $\text{K}_2\text{Cr}_2\text{O}_7(\text{acid})$, which is reddish-orange, is reduced to $\text{Cr}^{3+}(\text{aq})$, which is green. The greater the concentration of alcohol vapor in the breath, the more green the solution becomes. The color can be quantified spectroscopically and is directly related to the concentration of ethanol vapor in the breath. This concentration in turn can be related to the concentration of ethanol in the blood because, as blood passes through the pulmonary arteries, an equilibrium is established between the ethanol in the blood and the ethanol in the lungs.



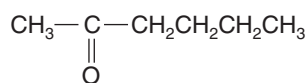
2-propanol
(isopropanol)



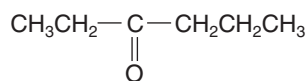
propanone
(acetone)

Acetone is a colorless, volatile liquid with a sweet odor. Over two million metric tons of acetone are produced annually in the United States. It is used extensively as a solvent because it dissolves many organic compounds yet is completely miscible with water. It dissolves fats, oils, waxes, rubber, lacquers, varnishes, rubber cements, and coatings ranging from nail polish to enamel paints.

The IUPAC nomenclature for ketones uses the longest chain of consecutive carbon atoms containing the carbonyl group as the parent compound. The ketone is named by dropping the terminal *-e* and adding *-one* to the name of the corresponding alkane, with a preceding numeral to indicate on which carbon atom in the chain the carbonyl group is located (if necessary). For example, the IUPAC name of



is 2-hexanone and that of

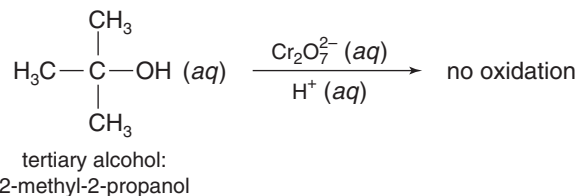


is 3-hexanone. Table P.4 lists the structural formulas and names of some ketones for practice.

TABLE P.4 The structural formulas and the corresponding IUPAC names of some ketones (common names are in parentheses)

Structural formula	IUPAC name
$\begin{array}{c} \text{CH}_3\text{CH}_2-\text{C}-\text{CH}_3 \\ \parallel \\ \text{O} \end{array}$	butanone (methyl ethyl ketone)
$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2-\text{C}-\text{CH}_3 \\ \parallel \\ \text{O} \end{array}$	2-pentanone (methyl propyl ketone)
$\begin{array}{c} \text{CH}_3\text{CH}_2-\text{C}-\text{CH}_2\text{CH}_3 \\ \parallel \\ \text{O} \end{array}$	3-pentanone (diethyl ketone)
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{C}-\text{CH}_3 \\ \parallel \\ \text{O} \end{array}$	3-methyl-2-butanone

Tertiary alcohols are resistant to oxidation. The carbon atom bearing the $-\text{OH}$ group is already bonded to three other carbon atoms and so cannot form a double bond with an oxygen atom to produce a ketone:

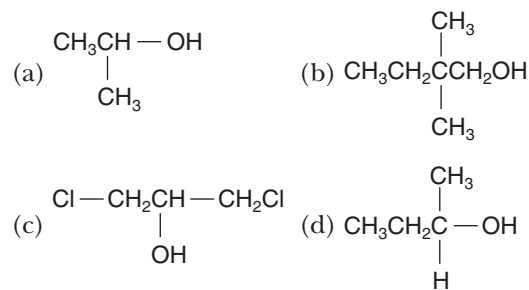


TERMS YOU SHOULD KNOW

- alcohol *P1*
- functional group *P2*
- alkoxide *P2*
- primary alcohol *P3*
- secondary alcohol *P3*
- tertiary alcohol *P3*
- aldehyde *P5*
- aldehyde group *P5*
- ketone *P6*
- carbonyl group *P6*

QUESTIONS

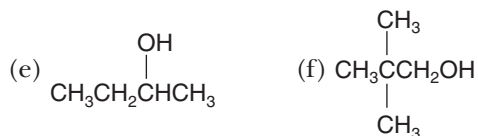
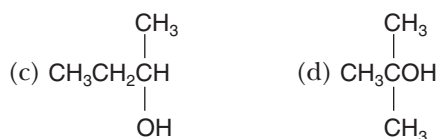
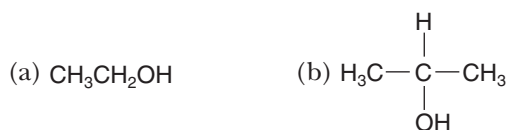
P-1. Assign IUPAC names to each of the following alcohols:



P-2. Write a structural formula for each of the following alcohols:

- (a) 2,3-dimethyl-1-butanol
- (b) 5-methyl-3-hexanol
- (c) 2-chloro-1-hexanol
- (d) 1,2-dichloro-3-pentanol

P-3. Classify the following alcohols as primary, secondary, or tertiary:



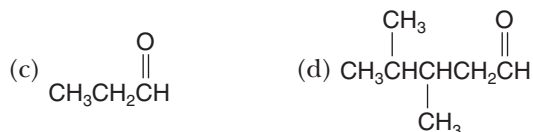
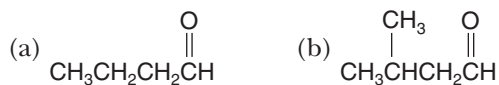
P-4. Complete and balance the following equations:



P-5. What are the products of



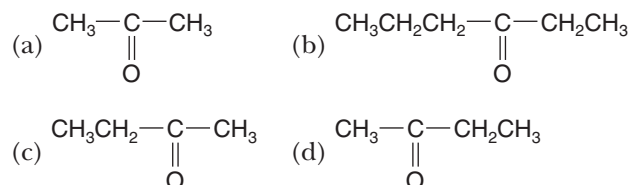
P-6. Assign IUPAC names to the following aldehydes:



P-7. Write the structural formula for each of the following aldehydes:

- (a) propanal
 (b) 2-methylpentanal
 (c) 4-methylpentanal
 (d) 3,3-dimethylhexanal

P-8. Assign IUPAC names to the following ketones:



P-9. Write Lewis formulas for

- (a) 2-methyl-3-pentanone
 (b) 3,3-dimethyl-2-hexanone
 (c) butanone

P-10. Determine which alcohol you would use to produce each of the following aldehydes:

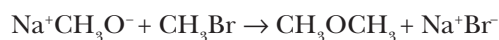
- (a) ethanal
 (b) 2-methylpropanal
 (c) 2,2-dimethylpropanal

P-11. Determine which alcohol you would use to produce each of the following ketones:

- (a) 3-pentanone
 (b) 2-pentanone
 (c) 3-hexanone

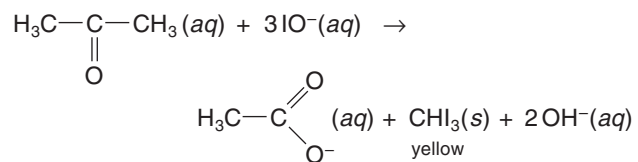
P-12. Why do we write propanone, rather than 2-propanone (dropping the number two), but *not* propanol, rather than 2-propanol?

P-13. Alkoxides react with alkyl halides to produce ethers. For example,



The product here is called dimethyl ether. Ethers are compounds with the general formula ROR' , where R and R' are alkyl groups. Devise a procedure to synthesize diethyl ether starting with ethene (ethylene) and any inorganic substances. Diethyl ether was once used as an anesthetic.

P-14. Methyl ketones such as propanone (acetone), a widely used solvent of commercial importance, can be detected by the iodoform, $\text{CHI}_3(s)$, test, in which the ketone is reacted with hypiodite in aqueous base, according to



A 5.00-mL sample of acetone ($d = 0.792 \text{ g}\cdot\text{mL}^{-1}$ at 25°C) was allowed to react with excess hypiodite

under basic conditions. After filtration, washing, and drying, the iodoform product was found to weigh 15.6 g. Calculate the theoretical yield and the percentage yield.

P-15. Aldehydes can be reduced to primary alcohols by the strong reducing agent sodium borohydride, $\text{NaBH}_4(s)$. Determine which aldehyde you would use to produce each of the following primary alcohols:

- 1-propanol
- 2-methyl-1-propanol
- 2,2-dimethyl-1-butanol