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AT THE FARM

While on vacation last summer, a student visited a friend whose family owns several horses. A veterinarian had come to take a look at one of the horses that had developed a limp. Seeing the veterinarian put on a pair of gloves and apply a pasty material to the horse's sore leg, the student asked her what the paste did. The veterinarian explained that the paste contained DMSO, an organic compound that acts as an anti-inflammatory agent.



9

Organic Reactions 2—Alcohols, Ethers, Aldehydes, and Ketones

ABOUT THIS CHAPTER

In Chapter 9 we will continue our study of the important reactions of organic compounds. Here we will look at the chemistry of four oxygen-containing families of compounds: alcohols, ethers, aldehydes, and ketones. Our discussion will also include some related sulfur-containing compounds.

CHAPTER 9 OBJECTIVES

After completing this chapter, you should be able to:

- 1 Explain how alcohols, ethers, thiols, sulfides, and disulfides are named and identify the noncovalent forces that attract like molecules to one another.
- 2 Explain how nucleophilic substitution reactions can be used to prepare alcohols, ethers, thiols, and sulfides.
- 3 Identify the products formed from the oxidation of alcohols and thiols and predict the major product of the elimination reaction that takes place when an alcohol is heated under acidic conditions.
- 4 Explain how aldehydes and ketones are named and identify the noncovalent forces that attract like molecules to one another.
- 5 Identify the oxidation reactions of aldehydes.
- 6 Explain what happens when an aldehyde or ketone is reacted with H_2 and Pt.
- 7 Describe the structure and formation of hemiacetals and acetals.

9.1 | ALCOHOLS, ETHERS, AND RELATED COMPOUNDS

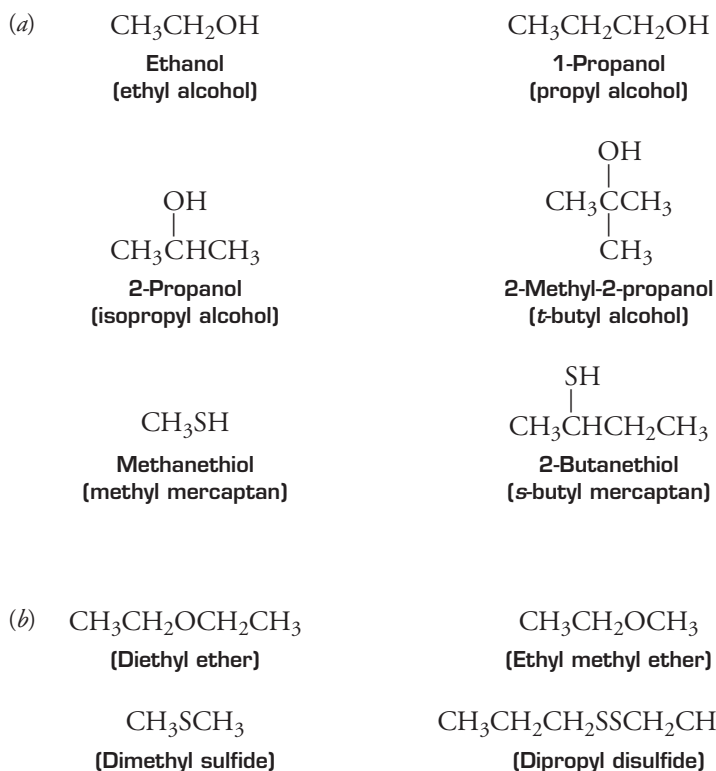
As we have seen, in alcohols an —OH group is attached to an alkane-type carbon atom, and in ethers, an oxygen atom is attached to two alkane-type or aromatic carbon atoms ($C-O-C$). The sulfur-containing families that we will consider in this chapter are thiols (contain an —SH group attached to an alkane-type or aromatic carbon atom), sulfides (contain a $C-S-C$ linkage—a sulfur atom attached to two alkane-type or aromatic carbon atoms), and disulfides (contain a $C-S-S-C$ linkage—each sulfur atom is attached to one other sulfur atom and one alkane-type or aromatic carbon atom). These sulfur compounds have been included because oxygen and sulfur belong to the same group in the periodic table and have some properties in common.

When the IUPAC rules are used to name an alcohol, the parent (the longest carbon chain carrying the —OH group) is numbered from the end nearer the —OH and named by dropping the “e” ending on the name of the corresponding hydrocarbon and adding “ol.” When a parent chain contains more than two carbon atoms, the position of the —OH group must be specified. To complete the name, any alkyl groups attached to the parent chain are identified by name, position, and number of appearances (Figure 9.1a). Smaller alcohols are often known by their common names, which are obtained by combining the name of the alkyl group attached to the —OH with the word “alcohol.” The common name of ethanol is ethyl alcohol (grain alcohol) and that of 2-propanol is isopropyl alcohol (known also as rubbing alcohol).

The IUPAC rules for naming thiols closely follow those for naming alcohols. The parent chain contains the —SH (thiol) group, is numbered from the end nearer this group, and is named by adding “thiol” to the name of the corresponding hydrocarbon (Figure 9.1a). The common names of thiols consist of the name of the alkyl group that is present plus “mercaptan,” a term that comes from the fact that thiols readily react with mercury (mercaptan for *mercury capturer*).

In this text, only the common names of ethers, sulfides, and disulfides will be described. The common names of these compounds are formed by placing the name of the organic family (ether, sulfide, or disulfide) after the names of the attached groups (Figure 9.1b).

Alcohols are categorized according to the nature of the carbon atom that is bonded directly to the —OH group. The hydroxy-carrying carbon atom is attached to only one



■ FIGURE 9.1

Naming alcohols, thiols, ethers, sulfides, and disulfides Examples of (a) IUPAC and common names (in parentheses) of alcohols and thiols and (b) common names of ethers, sulfides, and disulfides.

other carbon atom in a primary (1°) alcohol, to two other carbon atoms in a secondary (2°) alcohol, and to three other carbon atoms in a tertiary (3°) alcohol. In Figure 9.1a ethanol and 1-propanol are primary alcohols, 2-propanol is a secondary alcohol, and 2-methyl-2-propanol is a tertiary alcohol. Note that this definition of 1°, 2°, and 3° alcohols differs from that used for amines (Section 8.11).

Compared to hydrocarbons with a similar molecular weight, alcohols have relatively high boiling points (Table 9.1). Methanol (CH₃OH), for example, has a boiling point that is more than 150°C higher than that of ethane, although their molecular weights differ by only 2.0 amu. This large difference in boiling points is due to the ability of alcohol molecules to form hydrogen bonds with one another (Figure 9.2).

As we have seen for other families of organic compounds, the longer the carbon chain of an alcohol, the higher its boiling point, due to increased London force interactions between the hydrocarbon parts of the molecules (Table 9.1).

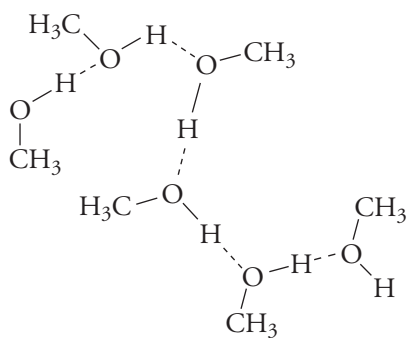
The boiling points of ethers, thiols, sulfides, and disulfides are lower than those of alcohols with similar molecular weights, because none of these compounds is able to form hydrogen bonds to like molecules. Ether molecules are slightly polar as a consequence of the C—O—C linkage, but the dipole–dipole attractions that occur between ether molecules are not strong

■ The carbon atom carrying the —OH group is attached to just one other carbon atom in a 1° alcohol, to two other carbon atoms in a 2° alcohol, and to three other carbon atoms in a 3° alcohol.

TABLE | 9.1 PHYSICAL PROPERTIES OF SELECTED ALCOHOLS, ETHERS, THIOLS, SULFIDES, DISULFIDES, AND ALKANES

Formula	IUPAC Name	Common Name	Boiling Point (°C)	Water Solubility (g/100 mL)
Alcohols				
CH ₃ OH	Methanol	Methyl alcohol	65.0	Miscible ^a
CH ₃ CH ₂ OH	Ethanol	Ethyl alcohol	78.5	Miscible
CH ₃ CH ₂ CH ₂ OH	1-Propanol	Propyl alcohol	97.4	Miscible
CH ₃ CH ₂ CH ₂ CH ₂ OH	1-Butanol	Butyl alcohol	117.3	8.0
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH	1-Pentanol	Pentyl alcohol	138	2.2
Ethers				
CH ₃ OCH ₃		Dimethyl ether	−24.9	Slight
CH ₃ CH ₂ OCH ₂ CH ₃		Diethyl ether	34.6	Very slight
CH ₃ CH ₂ CH ₂ OCH ₂ CH ₂ CH ₃		Dipropyl ether	90.5	~ 0
Thiols				
CH ₃ SH	Methanethiol	Methyl mercaptan	6	2.3
CH ₃ CH ₂ SH	Ethanethiol	Ethyl mercaptan	35	0.7
Sulfides				
CH ₃ SCH ₃		Dimethyl sulfide	38	~ 0
CH ₃ CH ₂ SCH ₂ CH ₃		Diethyl sulfide	90–92	~ 0
CH ₃ CH ₂ CH ₂ SCH ₂ CH ₂ CH ₃		Dipropyl sulfide	142–143	~ 0
Disulfides				
CH ₃ SSCH ₃		Dimethyl disulfide	107–110	~ 0
CH ₃ CH ₂ SSCH ₂ CH ₃		Diethyl disulfide	152–154	~ 0
CH ₃ CH ₂ CH ₂ SSCH ₂ CH ₂ CH ₃		Dipropyl disulfide	193–195	~ 0
Alkanes				
CH ₃ CH ₃	Ethane		−89	~ 0
CH ₃ CH ₂ CH ₃	Propane		−42	~ 0
CH ₃ CH ₂ CH ₂ CH ₃	Butane		0	~ 0
CH ₃ CH ₂ CH ₂ CH ₂ CH ₃	Pentane		36	~ 0

^a Can be mixed in all proportions.

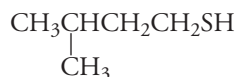


■ FIGURE 9.2

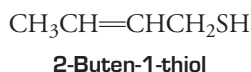
Hydrogen bonding The dashed lines represent hydrogen bonds between alcohol molecules. Their ability to form hydrogen bonds contributes to the relatively high boiling points of alcohols and to the ability of small alcohols to dissolve in water.

Did You Know?

The unpleasant odor of skunk spray is due, largely, to the thiols 3-methyl-1-butanol and 2-buten-1-thiol. Thiols are not water soluble, which is why it is difficult to remove the smell of skunk spray using soap and water.



3-Methyl-1-butanethiol



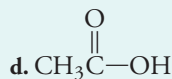
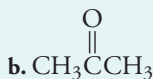
- Hydrogen bonding makes alcohols more soluble in water than are ethers, thiols, sulfides, and disulfides.

enough to raise boiling points much above those of similarly sized hydrocarbons. The relatively weak London forces that hold thiol, sulfide, and disulfide molecules to one another are responsible for their lower boiling points.

SAMPLE PROBLEM 9.1

Intermolecular forces

Which of the following molecules can form hydrogen bonds with other molecules of the same type?



STRATEGY

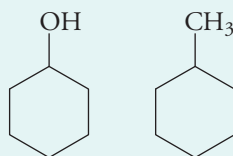
The key to solving this problem is to review the definition of hydrogen bonding. As we saw in Section 4.3, a hydrogen bond is the interaction of a nitrogen, oxygen, or fluorine atom with a hydrogen atom that is covalently bonded to a different nitrogen, oxygen, or fluorine atom.

SOLUTION

a, c, and d. Although the molecule in part b can form hydrogen bonds when different molecules provide the hydrogen atom (a hydrogen atom from H_2O , for example), two of these ketone molecules cannot hydrogen-bond with one another. Neither has a hydrogen atom covalently attached to N, O, or F.

PRACTICE PROBLEM 9.1

Which molecule has the higher boiling point?



The *like dissolves like* rule (Section 6.4) can be used to roughly predict the water solubility of a molecule. Small alcohol molecules are significantly soluble in water because, like water, they are able to form hydrogen bonds. Larger alcohol molecules have a lower solubility in water because the nonpolar hydrocarbon portion makes up an increasingly greater share of the molecular structure. Ethers are less polar than alcohols and form fewer hydrogen bonds with water molecules, so ethers are less water soluble. Thiols, sulfides, and disulfides, all of which are nonpolar, have very low solubility in water. Many thiols, sulfides, and disulfides have a strong, unpleasant odor.

SAMPLE PROBLEM 9.2

Solubility

According to Table 9.1, 1-propanol is miscible in water, while 1-pentanol has a solubility of just 2.2 g/100 mL. Account for this difference.

STRATEGY

Like dissolves like is the general rule used to understand solubility. Think about the difference in the structure of these two alcohols.

SOLUTION

Like water, all alcohols are able to form hydrogen bonds. This ability to form hydrogen bonds is what makes small alcohols soluble in water (*like dissolves like*). The solubility in water drops off with increasing alcohol size, because the nonpolar hydrocarbon part of the molecule makes up a greater percentage of the molecule. Being nonpolar, this part of the molecule is unable to interact with water molecules.

PRACTICE PROBLEM 9.2

According to Table 9.1, 1-propanol is miscible in water and ethanethiol has a water solubility of 0.7 g/100 mL. Account for the different solubility of these two molecules that have nearly the same molar mass.

9.2 | PREPARATION

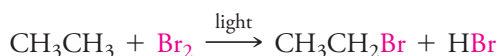
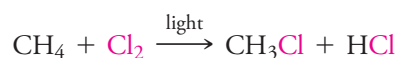
In this section we will take a look at a few of the reactions that chemists use to prepare alcohols, ethers, and related sulfur compounds. When living things manufacture these compounds, they tend to use enzyme-catalyzed versions of these same reactions.

Alcohols can be prepared using a **nucleophilic substitution reaction**, in which *an electron-rich atom or group of atoms*, called a **nucleophile**, replaces a **leaving group**, *an easily replaced atom or group of atoms* that is held to a carbon atom by a relatively weak covalent bond. Chlorine and bromine are common leaving groups used in organic chemistry.

One example of a nucleophilic substitution reaction used to prepare an alcohol is that of OH^- with methyl chloride (CH_3Cl). The electrons in the new covalent bond between carbon and oxygen are provided by OH^- , the nucleophile. The electrons in what was the carbon–chlorine bond remain with the leaving group, Cl, giving it a negative charge (Figure 9.3a). Whenever OH^- is used as the nucleophile in a substitution reaction, an alcohol is produced and the structure of the product alcohol depends on the alkyl halide reactant. The key to understanding nucleophilic substitution reactions is recognizing that the leaving group (Cl or Br) is always replaced by the nucleophile.

By changing the nucleophile, ethers, thiols, and sulfides can be prepared. In place of OH^- , a nucleophile with a $\text{C}-\text{O}^-$ linkage is used to form ethers, SH^- is used to form thiols, and a nucleophile with a $\text{C}-\text{S}^-$ linkage to form sulfides (Figure 9.3b).

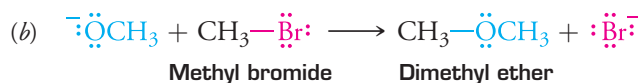
Chapter 8 described a different type of substitution reaction, one that can be used to convert an alkane into an alkyl halide. In this reaction, when an alkane is reacted with Cl_2 or Br_2 in the presence of light, one of the halogen atoms substitutes in place of a hydrogen atom.



This reaction, coupled with the nucleophilic substitution described above, allows the transformation of alkanes into alcohols, thiols, and many other types of molecules. For

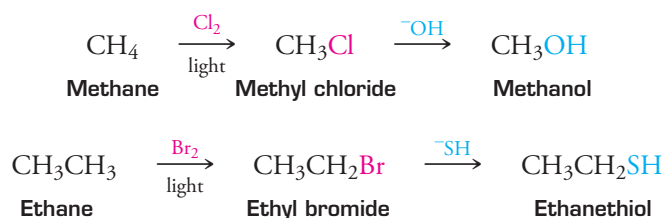
■ FIGURE 9.3

Nucleophilic substitution In a nucleophilic substitution reaction, a nucleophile (blue) replaces a leaving group (red). This reaction can be used to prepare (a) alcohols and (b) ethers, thiols, and sulfides.



Common names of alkyl halides are formed by combining the name of the alkyl group with the name of the halogen atom, whose name is changed to end in “ide.” CH_3Cl is methyl chloride and $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ is propyl bromide. IUPAC names of alkyl halides are formed by treating halogen atoms as substituents (atoms attached to the parent chain) and changing their name to end in “o.” $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ is 1-chloropropane and $(\text{CH}_3)_2\text{CHBr}$ is 2-bromopropane.

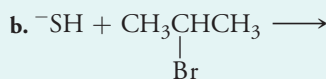
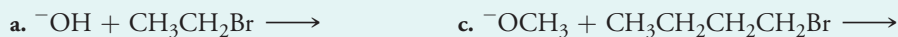
example, methane can be converted into methyl chloride, which can then undergo a nucleophilic substitution reaction to form methanol. Similarly, ethane can be transformed into ethyl bromide, which can be turned into ethanethiol.



SAMPLE PROBLEM 9.3

Predicting the product of a substitution reaction

Draw the products of each nucleophilic substitution reaction.



STRATEGY

To arrive at the product of each reaction you must decide which reactant is the nucleophile and which reactant carries the leaving group. In a nucleophilic substitution reaction, a nucleophile replaces a leaving group.

SOLUTION



PRACTICE PROBLEM 9.3

What are the products of each reaction in Sample Problem 9.3, if chlorine replaces bromine in each reactant?

9.3 | REACTIONS

Oxidation of Alcohols and Thiols

Section 5.4 showed us that an organic molecule has been oxidized if carbon atoms gain oxygen and/or lose hydrogen. The oxidizing agent potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) can be used to oxidize a number of different organic compounds, including alcohols. When an alcohol is oxidized, a carbonyl group ($\text{C}=\text{O}$) is formed when one hydrogen atom is removed from the $-\text{OH}$ group and another is removed from the carbon atom that carries the $-\text{OH}$ (Figure 9.4).

Since one of the hydrogen atoms removed during alcohol oxidation must come from the carbon that carries the $-\text{OH}$, there are limitations to the types of alcohols that can be oxidized using this reaction. A primary alcohol has two of the necessary $\text{C}-\text{H}$ bonds and can be oxidized to an aldehyde, which is immediately oxidized to a carboxylic acid by $\text{K}_2\text{Cr}_2\text{O}_7$. Secondary alcohols also carry the required $\text{C}-\text{H}$ bond and are oxidized to ketones. Tertiary alcohols have no hydrogen atom attached to the carbon atom holding the $-\text{OH}$ group, so they cannot be oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$.

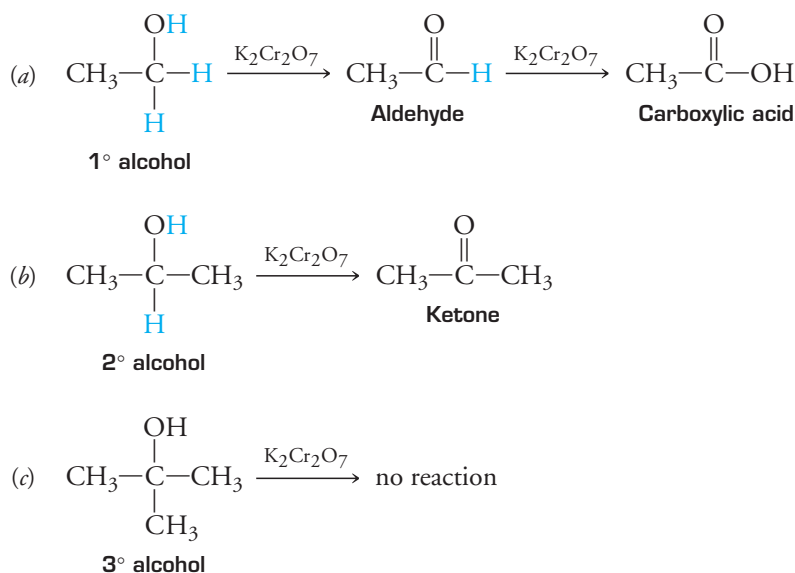


FIGURE 9.4

Alcohol oxidation Two hydrogen atoms are lost from an alcohol molecule when it is oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$: one from the $-\text{OH}$ group and one from the carbon atom that carries the $-\text{OH}$. (a) Primary alcohols are oxidized to aldehydes, which are then oxidized to carboxylic acids. (b) Secondary alcohols are oxidized to ketones. (c) Tertiary alcohols are not oxidized.

SAMPLE PROBLEM 9.4

Oxidizing alcohols

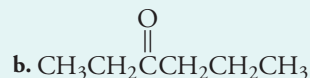
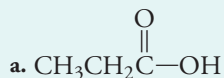
Draw the product expected from each reaction.



STRATEGY

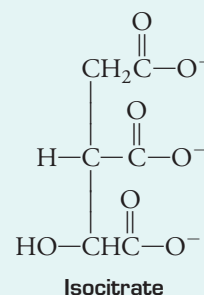
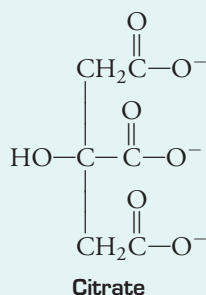
The place to begin is determining which type of alcohol (1° , 2° , or 3°) appears in each reaction. Primary alcohols are oxidized to aldehydes, which are immediately oxidized to carboxylic acids. Secondary alcohols are oxidized to ketones and tertiary alcohols are not oxidized.

SOLUTION

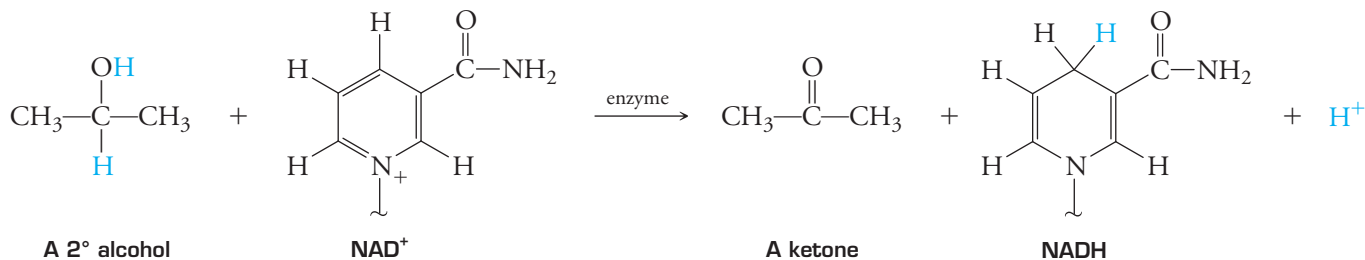


PRACTICE PROBLEM 9.4

In Chapter 14 we will study the citric acid cycle, a series of reactions involved in making compounds that can be used in a separate process to manufacture an energy-rich compound called ATP. A reaction early in the citric acid cycle involves the oxidation of an alcohol. Of the two reactants shown below (each appears somewhere in the cycle), which has an alcohol group that can be oxidized?



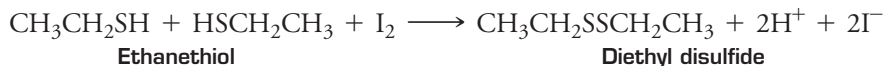
Nicotinamide adenine dinucleotide (NAD^+), an oxidizing agent used by living things, works in conjunction with certain enzymes that catalyze the oxidation of alcohols. NAD^+ assists in the oxidation of an alcohol molecule by accepting one of its hydrogen atoms, becoming NADH in the process (Figure 9.5). The second hydrogen atom released from the alcohol becomes H^+ . For example, the first step in the metabolism of the ethanol present in beer, wine, and other alcoholic beverages takes place in the liver and is catalyzed by an NAD^+ -requiring enzyme (Health Link: Aldehyde Dehydrogenase).



■ FIGURE 9.5

NAD^+ and NADH Nicotinamide adenine dinucleotide (NAD^+)—a partial structure is shown—is a common biochemical oxidizing agent. In the process of oxidizing a compound, NAD^+ is converted to NADH . The structure of NADH differs from that of NAD^+ only at the pyridine ring. For complete structures of these two compounds, see Figure 14.2.

The oxidation of thiols produces a different type of product than obtained from the oxidation of alcohols. On treatment with the oxidizing agent I_2 , two thiol molecules combine to form a disulfide. The loss of a hydrogen atom by each thiol is evidence that oxidation has taken place.



Dehydration of Alcohols

In the presence of an H^+ catalyst and heat, alcohol molecules undergo dehydration (Section 5.3), in which loss of $-\text{OH}$ and $-\text{H}$ from neighboring carbon atoms yields an alkene. When more than one alkene can be formed from a particular alcohol, the major product is the one produced by *removal of H from the neighboring carbon atom that carries fewer H atoms*. Of the possible 2-butanol dehydration products (1-butene and 2-butene), 2-butene is the major one (Figure 9.6).

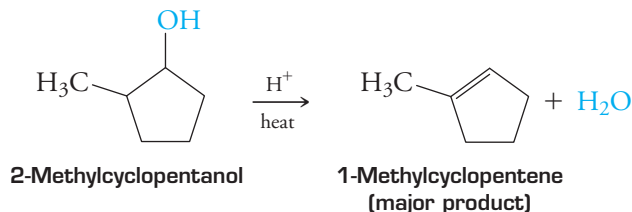
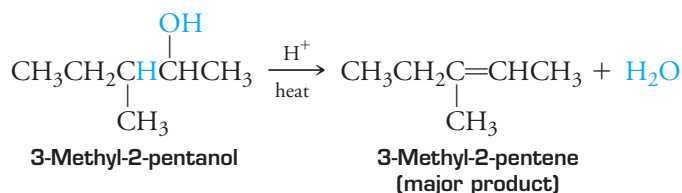
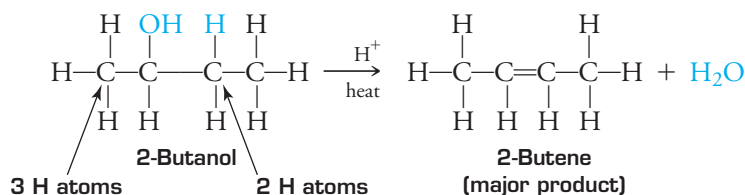


FIGURE 9.6

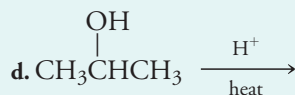
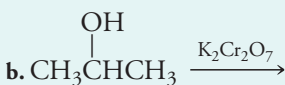
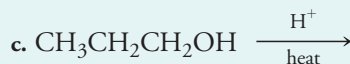
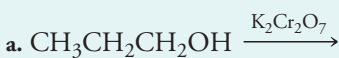
Dehydration of alcohols

When alcohols are dehydrated in the presence of H^+ and heat, the major product is that formed by removal of $-\text{OH}$ from one carbon atom and removal of $-\text{H}$ from the neighboring C atom that carries fewer H atoms.

SAMPLE PROBLEM 9.5

Oxidation and dehydration of alcohols

Draw the organic product expected from each reaction.

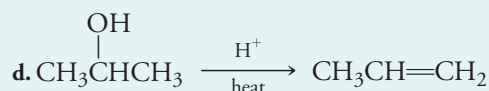
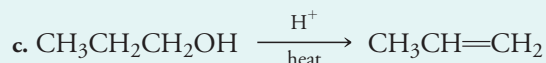
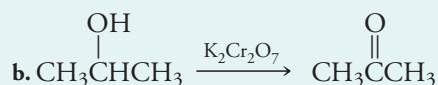
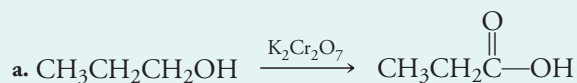


STRATEGY

Begin by checking the reactants or conditions to determine which type of reaction should be expected—two of the reactions involve oxidation and two involve dehydration. Once

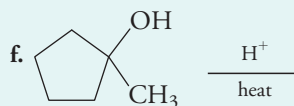
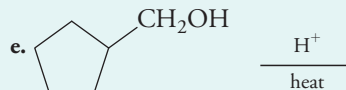
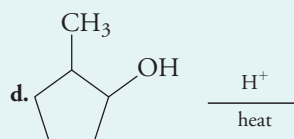
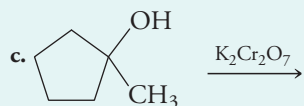
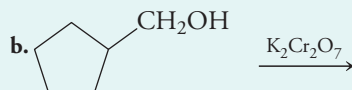
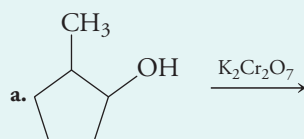
you have decided on the reaction type, think about the different rules that apply: How do different types of alcohols respond to oxidation and which is the major alkene product expected from dehydration?

SOLUTION



PRACTICE PROBLEM 9.5

Draw the organic product (if any) expected from each reaction.



9.4 | ALDEHYDES AND KETONES

Ketones and aldehydes contain a carbonyl ($\text{C}=\text{O}$) group. In a ketone the carbonyl carbon atom is attached to *two other carbon atoms* and in an aldehyde it is attached to *one carbon atom and one hydrogen atom* or to *two hydrogen atoms*.

When naming aldehydes and ketones according to the IUPAC rules, the carbonyl group ($\text{C}=\text{O}$) must be part of the parent chain, which is numbered from the end nearer this group. Since the carbonyl carbon atom of an aldehyde is always in position number 1, its position is not specified in the name. For ketones, however, the position of the carbonyl carbon is given, unless the molecule is small enough that there is no question as to carbonyl placement. Parent chains are named by dropping the final “e” from the name of the corresponding hydrocarbon and adding “al” for aldehydes or “one” for ketones (Figure 9.7).

The common names of ketones are formed by placing “ketone” after the names of the alkyl groups attached to the carbonyl carbon atom. For aldehydes and for some ketones, other common names are assigned. Three important ones to know are formaldehyde (methanal), acetaldehyde (ethanal), and acetone (propanone) (Figure 9.7).

Structural Formula	
$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{H} \end{array}$ <p>Methanal (formaldehyde)</p>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCH}_3 \end{array}$ <p>Propanone (dimethyl ketone or acetone)</p>
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{H} \end{array}$ <p>Ethanal (acetaldehyde)</p>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_3 \end{array}$ <p>2-Pentanone (methyl propyl ketone)</p>
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}-\text{C}-\text{H} \\ \\ \text{CH}_3 \end{array}$ <p>2-Methylpropanal</p>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}-\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ <p>2-Methyl-3-heptanone (butyl isopropyl ketone)</p>

■ FIGURE 9.7

Naming aldehydes and ketones IUPAC names and common names (in parentheses) are given for selected aldehydes and ketones.

Aldehydes and ketones have much lower boiling points than alcohols with a similar molecular weight. Ethanol, for example, has a boiling point of 78.5°C, while ethanal has a boiling point of 20°C (Table 9.2). The difference in boiling points is due to differences in how the molecules are attracted to one another. While alcohol molecules can form hydrogen bonds with a neighbor, aldehydes and ketones are unable to do so because hydrogen bonding requires that a hydrogen atom be covalently bonded to a nitrogen, oxygen, or fluorine atom. Aldehydes and ketones interact with like molecules through London forces, as well as through dipole–dipole forces—the carbonyl group is slightly polar. These interactions are weaker, however, than the intermolecular forces that attract alcohol molecules to one another, so aldehydes and ketones have lower boiling points than do alcohols of similar size.

The polarity of the carbonyl group and its ability to form hydrogen bonds with water molecules allow small aldehydes and ketones to be highly water soluble (*like dissolves like*). The larger an aldehyde or ketone, the less water soluble it is, because the water-insoluble hydrocarbon portion of the molecule contributes a greater share to the overall structure.

SAMPLE PROBLEM 9.6

Solubility

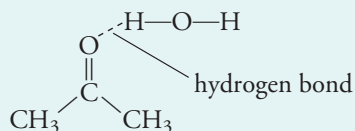
Table 9.2 shows that acetone is miscible in water. A major factor for this solubility in water is that, although hydrogen bonds do not form between two acetone molecules, they will form between an acetone molecule and a water molecule. Explain why hydrogen bonds do not form between acetone molecules and draw a picture that shows the hydrogen bond that forms between an acetone and a water molecule.

STRATEGY

Refer to Section 4.3 to review what is required for hydrogen bonding to occur.

SOLUTION

For a hydrogen bond to form, an H atom must be covalently bonded to an N, O, or F atom. The hydrogen bond is the attraction between this same hydrogen atom and a different N, O, or F atom. Acetone has no H attached to its O atom, so it cannot form hydrogen bonds to neighboring acetone molecules. The O atom of acetone can form a hydrogen bond with an H atom from water.



PRACTICE PROBLEM 9.6

1-Propanol (Table 9.1) is much more soluble in water than propanal (Table 9.2), even though they have very similar molar masses. Account for this difference in solubility.

TABLE 9.2 PHYSICAL PROPERTIES OF SELECTED ALDEHYDES AND KETONES

Formula	IUPAC Name	Common Name	Boiling Point (°C)	Water Solubility (g/100 mL)
Aldehydes				
$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	Methanal	Formaldehyde	-21	Miscible ^a
$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	Ethanal	Acetaldehyde	20	Miscible
$\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	Propanal		49	16
$\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	Butanal		76	~0
Ketones				
$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}\text{CH}_3$	Propanone	Acetone	56	Miscible
$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}\text{CH}_2\text{CH}_3$	Butanone	Methyl ethyl ketone	80	26
$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_3$	2-Pentanone	Methyl propyl ketone	102	6
$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	2-Hexanone	Methyl butyl ketone	150	2

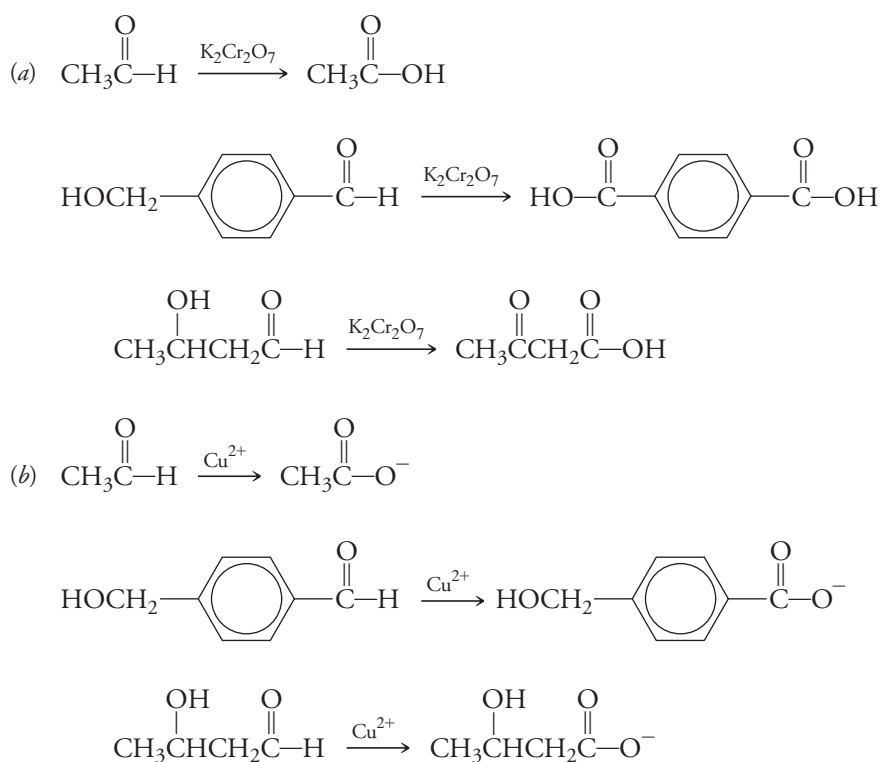
^aCan be mixed in all proportions.

9.5 | OXIDATION OF ALDEHYDES

As we saw in Section 9.3, $\text{K}_2\text{Cr}_2\text{O}_7$ will oxidize secondary alcohols into ketones and primary alcohols into aldehydes, which are further oxidized to carboxylic acids. Carboxylic acids can also be formed directly from aldehydes using $\text{K}_2\text{Cr}_2\text{O}_7$. The gain of an oxygen atom by the aldehyde is indication that oxidation has taken place (Figure 9.8a).

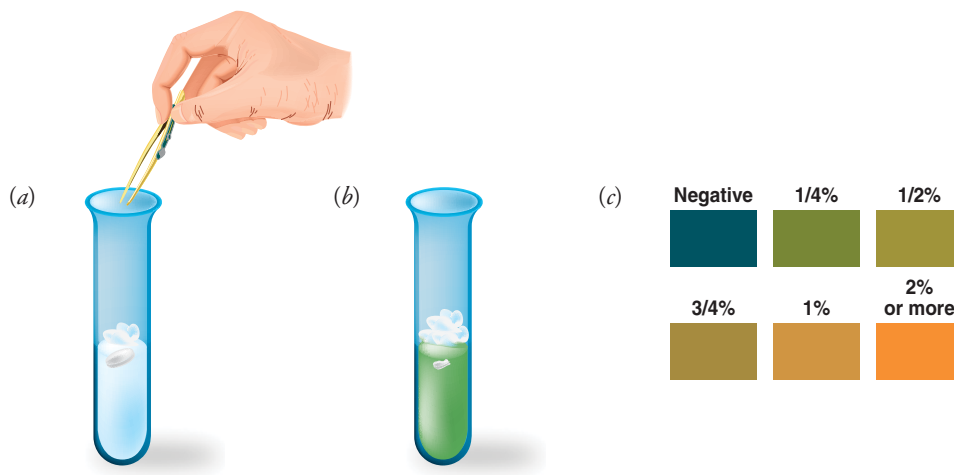
Special reagents have been developed for oxidizing aldehydes without affecting alcohols. One of these, called **Benedict's reagent**, contains Cu^{2+} as the oxidizing agent. An aldehyde will be oxidized to a carboxylic acid by Benedict's reagent, but alcohols remain unoxidized (Figure 9.8b). As Benedict's reagent oxidizes an aldehyde, its initial blue color (due to Cu^{2+}) changes as Cu^{2+} is reduced to Cu^+ . The final color of the solution depends on the amount of aldehyde initially present (Figure 9.9). Benedict's reagent has been used to monitor for diabetes by testing urine for the presence of glucose, an aldehyde-containing sugar. We will discuss other ways to measure glucose levels in Chapter 10.

■ Benedict's reagent oxidizes aldehydes but not alcohols.



■ FIGURE 9.8

Aldehyde oxidation (a) Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) oxidizes aldehydes and 1° alcohols into carboxylic acids and 2° alcohols into ketones. (b) Benedict's reagent (contains Cu^{2+}) oxidizes aldehydes into carboxylic acids, but does not oxidize 1° or 2° alcohols. Because Benedict's reagent contains a strong base, any carboxylic acids that form appear in their conjugate base form.

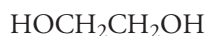


■ FIGURE 9.9

Benedict's reagent When Benedict's reagent is added to a test tube containing a glucose solution, Cu^{2+} gives the initial solution a blue color. Oxidation of glucose's aldehyde group causes a color change to take place after a few minutes. The final color of the solution depends on the initial % (w/v) concentration of glucose: blue (no glucose), green (0.25%), yellow (1%), orange (2% or higher).

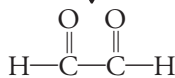
Did You Know?

Antifreeze (ethylene glycol) is very tasty to dogs and cats. Unfortunately, ingesting even small amounts of it can be fatal. The harmful effects of this alcohol come from its oxidation into the toxic compound oxalic acid. This two-step transformation is catalyzed first by alcohol dehydrogenase and then by aldehyde dehydrogenase. One of the treatment options for antifreeze poisoning is to use the drug Fomepizole, which blocks the action of alcohol dehydrogenase. Another is to administer ethyl alcohol. Alcohol dehydrogenase has a greater attraction for ethyl alcohol than ethylene glycol, so the later alcohol does not become oxidized.



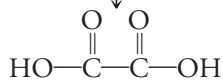
Ethylene glycol

alcohol
dehydrogenase



Oxaldehyde

aldehyde
dehydrogenase



Oxalic acid

SAMPLE PROBLEM 9.7

Oxidation reactions

Suppose that you have two test tubes, one containing propanal and the other containing 1-propanol.

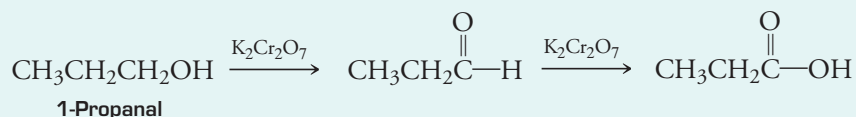
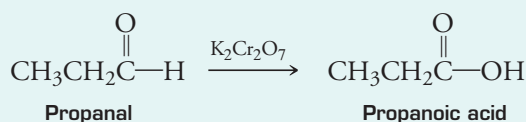
- What reactions, if any, will take place if $\text{K}_2\text{Cr}_2\text{O}_7$ is added to each tube?
- What reactions, if any, will take place if Benedict's solution is added to each tube?

STRATEGY

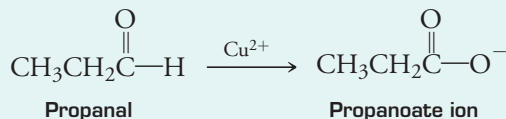
Determine which of these reagents oxidizes only aldehydes, and which oxidizes aldehydes, as well as primary and secondary alcohols.

SOLUTION

- Propanal and 1-propanol are oxidized to propanoic acid.

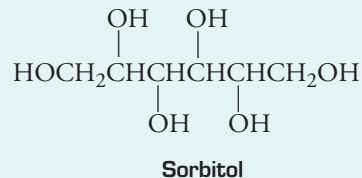
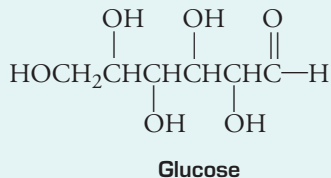


- Propanal is oxidized to propanoate ion, the conjugate base of propanoic acid. Benedict's reagent does not oxidize alcohols.



PRACTICE PROBLEM 9.7

Suppose that you have two test tubes, one containing a glucose solution and the other containing a solution of sorbitol (a sugar substitute used by diabetics). A condensed structural formula for each of these sweeteners is shown below.



- What reaction, if any, will take place if Benedict's solution is added to each tube?
- How can you tell if a reaction has occurred?

Aldehyde Dehydrogenase

HealthLink



When someone drinks beer, wine, or any other alcoholic beverage, the ethanol that it contains gets sent to their liver, where it is metabolized. The first step in the metabolism of this alcohol is its oxidation to acetaldehyde, a reaction that is catalyzed by the enzyme alcohol dehydrogenase. Acetaldehyde is subsequently oxidized to acetic acid, with the help of a different enzyme called aldehyde dehydrogenase (Figure 9.10).

Acetaldehyde is toxic, so aldehyde dehydrogenase plays the important role of catalyzing the removal of any acetaldehyde that appears in the body as a result of ethanol oxidation. If, for some reason, the acetaldehyde remains in the body for long, its effects range from an intense flushing of the face and neck to nausea and vomiting.

One of the drugs that have been used to treat chronic alcoholism interferes with the action of aldehyde dehydrogenase. If a person drinks ethanol after taking this drug (disulfiram), the ethanol is oxidized to acetaldehyde in a normal fashion, but the oxidation of acetaldehyde is considerably slowed. This causes acetaldehyde concentrations to climb, and the person soon experiences nausea and vomiting, which, in some cases, can be a deterrent to further drinking.

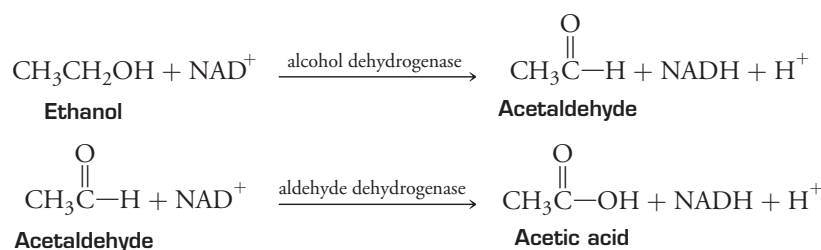
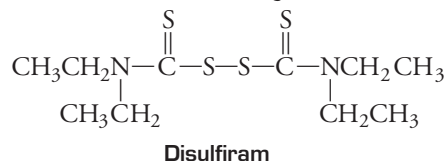


FIGURE 9.10

Metabolizing ethanol The first two steps in the metabolism of ethanol within the body are oxidation reactions. Alcohol dehydrogenase catalyzes the oxidation of ethanol to acetaldehyde and then aldehyde dehydrogenase catalyzes the oxidation of acetaldehyde to acetic acid. Each of these reactions takes place in the presence of NAD^+ , a biochemical oxidizing agent.

9.6 | REDUCTION OF ALDEHYDES AND KETONES

Catalytic hydrogenation, introduced previously in Section 5.4, involves the reaction of the carbon–carbon double bond of an alkene with H_2 , in the presence of a Pt catalyst (Figure 9.11a). Because a hydrogen atom adds to each of the double-bonded carbon atoms, hydrogenation is a reduction reaction.

In the same way, catalytic hydrogenation can reduce the carbon–oxygen double bond of an aldehyde or ketone. In the presence of H_2 and Pt, the carbon–oxygen double bond of a carbonyl is converted to a single bond (Figure 9.11b) forming an —OH group in the process. When formaldehyde is reduced using H_2 and Pt, methanol is the product. Reduction converts all other aldehydes into 1° alcohols and all ketones into 2° alcohols.

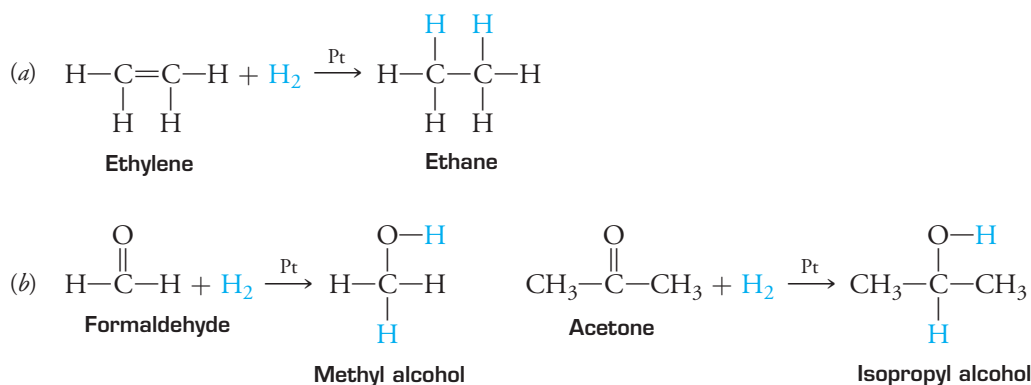


FIGURE 9.11

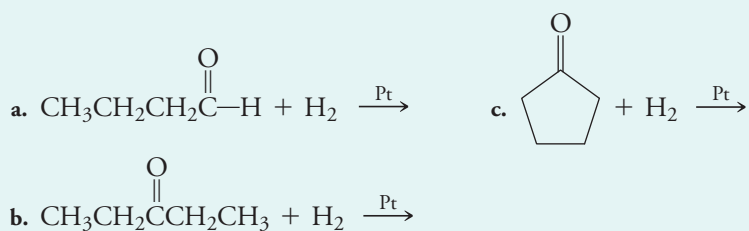
Catalytic hydrogenation

(a) Catalytic hydrogenation of an alkene produces an alkane. (b) Catalytic hydrogenation of an aldehyde or a ketone produces an alcohol.

SAMPLE PROBLEM 9.8

Predicting reduction products

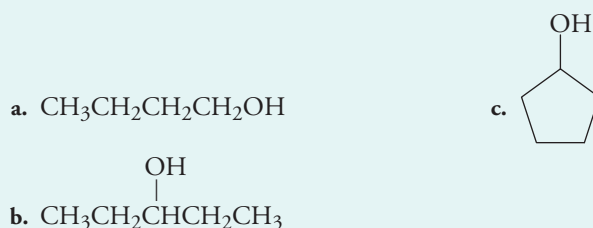
Draw the alcohol product expected from each reduction reaction.



STRATEGY

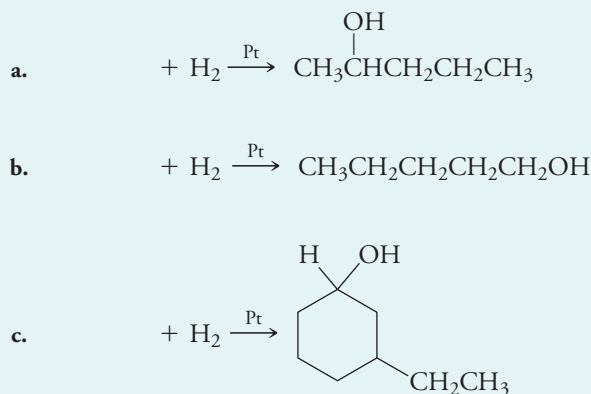
As with the reduction of a carbon–carbon double bond by H_2 and Pt, in the reduction of the carbon–oxygen double bond of an aldehyde or ketone a hydrogen atom adds to each double-bonded atom. The product of each reaction will be an alcohol.

SOLUTION

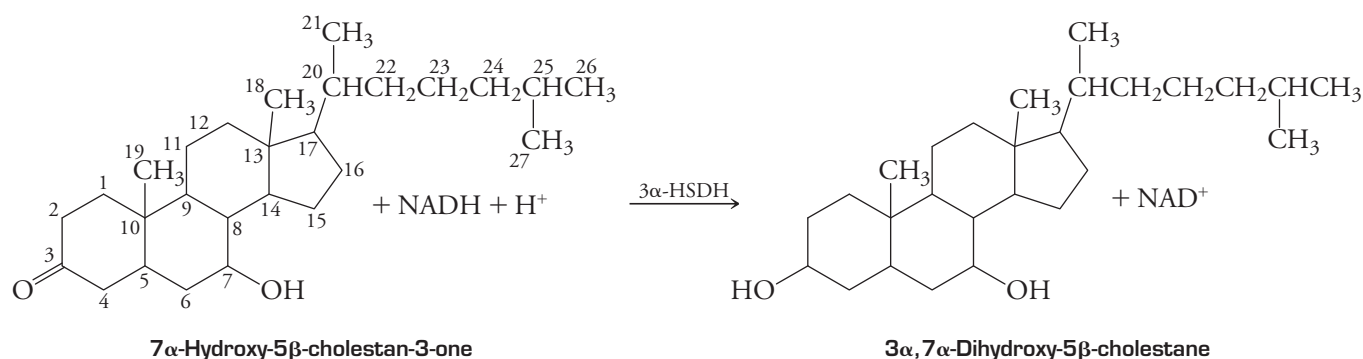


PRACTICE PROBLEM 9.8

Draw the missing reactant for each reaction.



In the presence of the biochemical reducing agent NADH, particular enzymes in your body catalyze the reduction of aldehydes and ketones into alcohols. Hydroxysteroid dehydrogenases (HSDHs), for example, are a class of enzymes that catalyze reactions involved in the synthesis of compounds known as steroids. There are a number of different HSDH enzymes, each specific for a different region of a steroid carbon skeleton. Among these is 3α -HSDH, which reduces a ketone at position 3 of a steroid ring system. This enzyme catalyzes one of the reactions in the multistep biosynthesis of bile acids (compounds that assist with the digestion of fats) from cholesterol (Figure 9.12).



■ **FIGURE 9.12**

Hydroxysteroid dehydrogenases Hydroxysteroid dehydrogenases (HSDHs) catalyze the reduction of ketone groups in steroid carbon skeletons. 3 α -HSDH acts on steroids that have a carbonyl group at ring position 3.

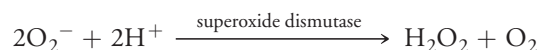
Protective Enzymes

HealthLink



Oxidation and reduction reactions are a normal part of metabolic activity. As a by-product of these reactions, O_2 is sometimes reduced to superoxide ion (O_2^-) or hydrogen peroxide (H_2O_2), two very reactive compounds that can damage proteins, nucleic acids, and other vitally important biomolecules. As a protective measure, the body manufactures superoxide dismutase, an enzyme that catalyzes the conversion of superoxide

ions into hydrogen peroxide and oxygen molecules. Catalase, another enzyme, catalyzes the breakdown of hydrogen peroxide into water and oxygen.

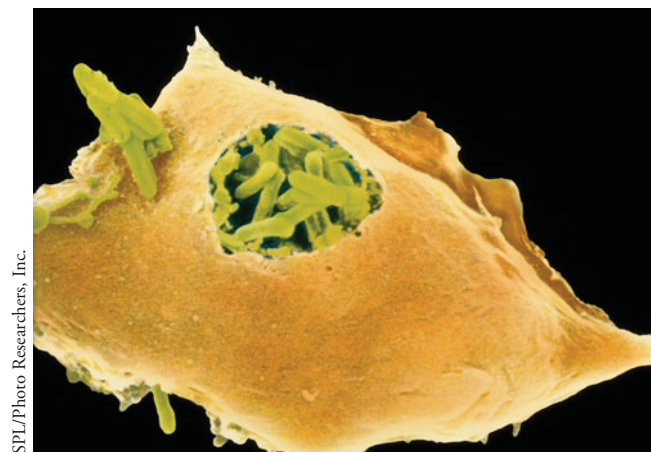


Some white blood cells use the high toxicity of superoxide and hydrogen peroxide as a way to protect the body from bacteria and other foreign substances. In a process called phagocytosis (Greek: *phago* “to eat” + *cyto* “cell”), white blood cells engulf foreign material and destroy it by releasing O_2^- and H_2O_2 (Figure 9.13).

Mutations (changes) to the gene that carries instructions for making superoxide dismutase are linked to some cases of amyotrophic lateral sclerosis (ALS). This is a disease in which nerve cells responsible for the control of muscle movement are lost. Those with ALS, also known as Lou Gehrig’s disease, may eventually become completely paralyzed.

No one knows what causes ALS, but about one case in every ten is categorized as “familial.” Of these genetically related ALS cases, about 10% are associated with a mutation in the superoxide dismutase gene. Studies are underway to try to determine why changes to this gene can affect motor neurons.

Mutations to the gene that codes for the production of catalase are also known. The symptoms of acatalasemia, a lower than normal production of catalase, can include gum infections and oral gangrene.



■ **FIGURE 9.13**

Phagocytosis A white blood cell engulfs and digests bacteria by releasing superoxide ion and hydrogen peroxide.

9.7 | REACTIONS OF ALCOHOLS WITH ALDEHYDES AND KETONES

Hemiacetals

In the presence of an H^+ catalyst, alcohols can undergo an addition reaction with the carbonyl group of an aldehyde or ketone. As with the reduction reaction described in Section 9.6, this reaction involves adding an atom or group of atoms to each of the double-bonded atoms of the $\text{C}=\text{O}$ group. In the reaction of an alcohol with an aldehyde or ketone, the alcohol's $-\text{OH}$ hydrogen atom attaches to the carbonyl oxygen atom and the remainder of the alcohol attaches to the carbonyl carbon atom (Figure 9.14a). The product that forms when an aldehyde or ketone is reacted with one alcohol molecule is called a **hemiacetal**. (Hemiacetals formed from ketones are also known as hemiketals.) A hemiacetal consists of a carbon atom that is attached to both $-\text{OH}$ and $-\text{OC}$. Although the $-\text{OH}$ group is found in alcohols and the $\text{C}-\text{O}-\text{C}$ linkage is present in ethers, the distinct chemical behavior of hemiacetals results in their not being considered members of either family.

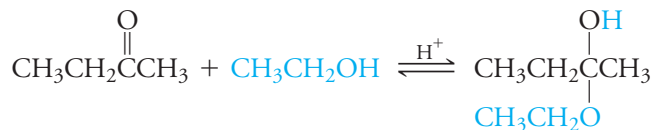
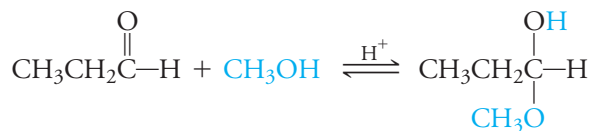
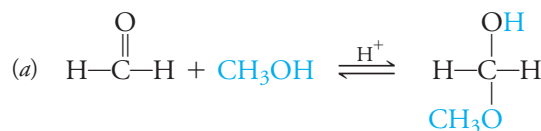
To produce a hemiacetal, an alcohol must react with an aldehyde or a ketone. Molecules that contain both an alcohol and an aldehyde or a ketone functional group can form cyclic hemiacetals when the $-\text{OH}$ reacts with a $\text{C}=\text{O}$ in the same molecule. The cyclic hemiacetal shown in Figure 9.14b is formed in the same way as any other hemiacetal—the carbonyl oxygen atom gains a hydrogen atom and the carbonyl carbon atom gains an $-\text{OC}$ group. As we will see in Chapter 10, the formation of cyclic hemiacetals is a very important part of the chemistry of sugars.

- A hemiacetal carbon atom is attached to $-\text{OH}$ and $-\text{OC}$.

Acetals

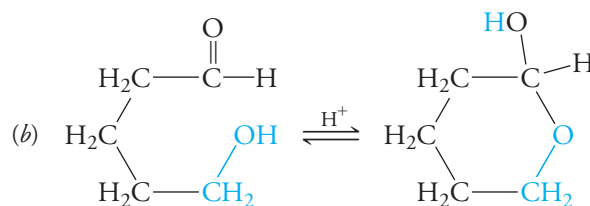
When two alcohol molecules react with an aldehyde or ketone in the presence of H^+ , an **acetal** forms (Figure 9.15a). An acetal consists of a carbon atom that is attached to two $-\text{OC}$ groups. (Acetals formed from ketones are also known as ketals.) Even though they contain $\text{C}-\text{O}-\text{C}$ linkages, acetals are not considered to be ethers. The chemistry of these two groups is entirely different. Varying the alcohol used allows for-

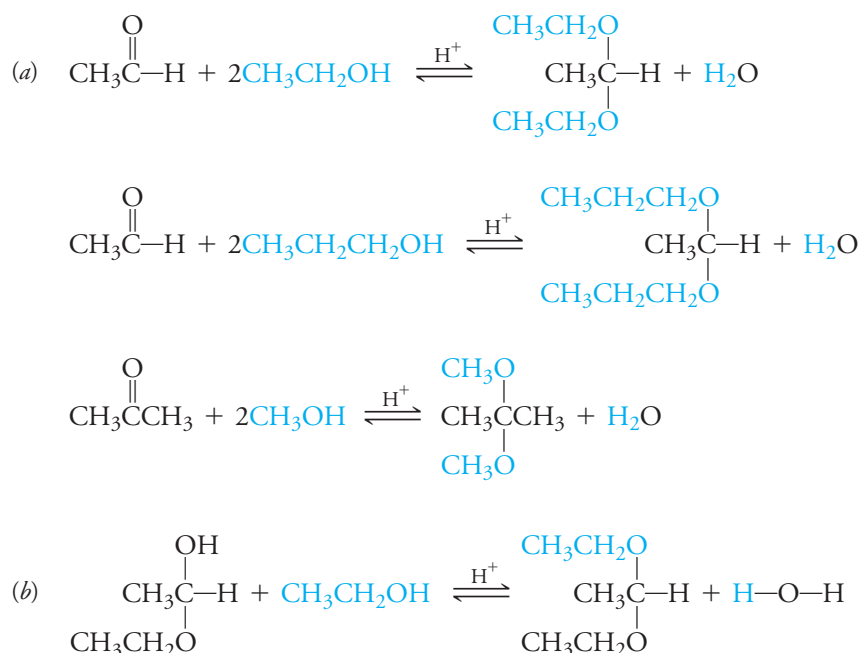
- An acetal carbon atom is attached to two $-\text{OC}$ groups.



■ FIGURE 9.14

Hemiacetals (a) The addition of an alcohol molecule to an aldehyde or ketone molecule produces a hemiacetal, in which $-\text{OH}$ and $-\text{OC}$ are attached to a single carbon atom. (b) When an alcohol group is present in the same molecule as an aldehyde or a ketone group, a cyclic hemiacetal can form.





■ **FIGURE 9.15**

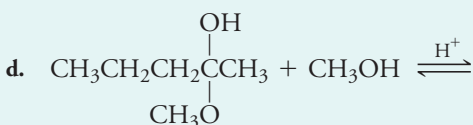
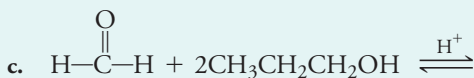
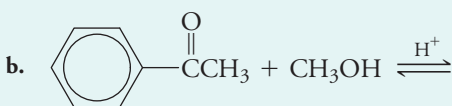
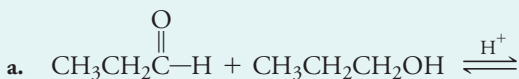
Acetals Acetals, in which two —OC groups are attached to a single carbon atom, can be produced (a) by the reaction of an aldehyde or a ketone with two alcohol molecules or (b) by the reaction of a hemiacetal with one alcohol molecule.

mation of a wide range of acetals from a given aldehyde or ketone. As shown in Figure 9.15b, acetals also can be produced directly from hemiacetals. In Chapter 10 we will see that acetals are part of the structure of starch, glycogen, cellulose, and many other carbohydrates.

SAMPLE PROBLEM 9.9

Forming hemiacetals and acetals

Draw the organic product of each reaction.

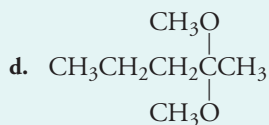
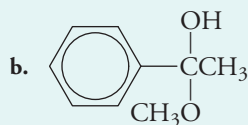
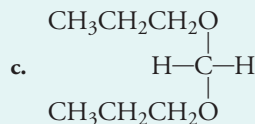
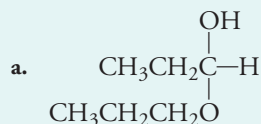


STRATEGY

The product formed depends on the reactant used and the number of alcohol molecules added. An aldehyde or a ketone molecule plus one alcohol molecule gives a hemiacetal. Adding two alcohol molecules gives an acetal. A hemiacetal plus one alcohol molecule produces an acetal.

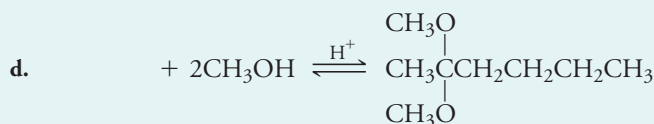
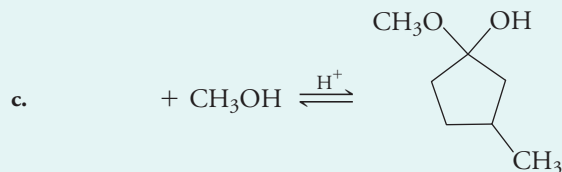
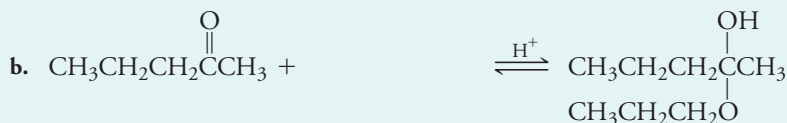
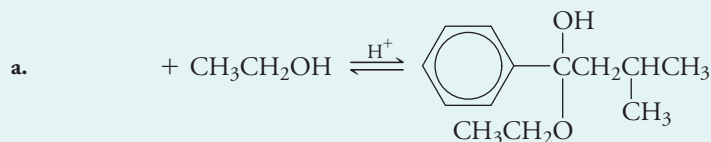


SOLUTION



PRACTICE PROBLEM 9.9

Draw the missing reactant for each reaction.



Drugs in the Environment

HealthLink

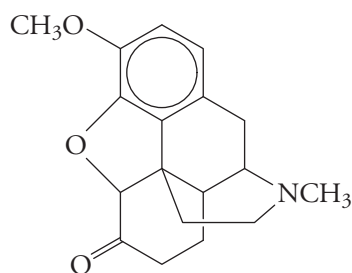


Each day, millions of gallons of liquid and solid human waste arrive at sewage treatment plants. After removal of solids, the liquid waste is cleaned to remove disease-causing organisms such as bacteria and viruses, and is then released into surface or ground water. The sanitized solids end up as biosolids (sludge), about half of which are used as fertilizer for gardens and farmland.

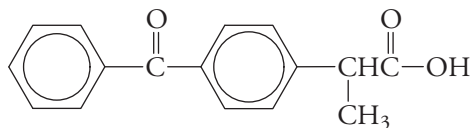
Not all traces of human activity are removed from these treated liquids and solids and, through them, pharmaceuticals and other chemicals are introduced into the environment. When a drug is flushed down the toilet, either directly as a means of quick disposal or indirectly in human waste, some of that drug is likely to end up being present in the water or biosolids that leave a sewage treatment plant.

Among the pharmaceuticals that have been detected in rivers, lakes, and biosolids are the painkiller hydrocodone, the anti-inflammatory ketoprofen, the antiepileptic carbamazepine (Figure 9.16), and the antidepressant fluoxetine (Prozac; see Problem 9.109). The disinfectant triclosan (used in antibacterial soaps), the steroid hormone estrone (used in birth control pills; see Problem 9.110), and caffeine and nicotine (Figure 9.16) are among the other chemicals that have been detected.

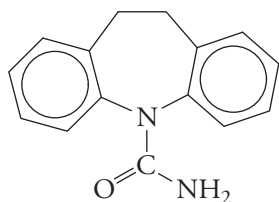
Scientists question whether these compounds introduced into the environment via sewage treatment plants have any adverse effects. At this time, the concentration of these drugs and other chemicals is below that believed to be harmful to organisms in the environment.



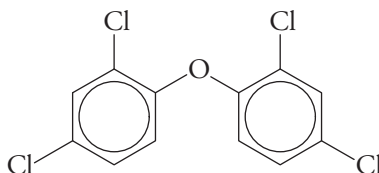
Hydrocodone



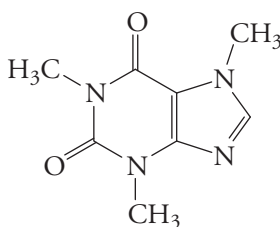
Ketoprofen



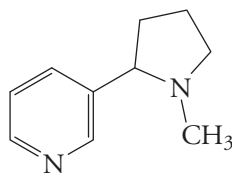
Carbamazepine



Triclosan



Caffeine



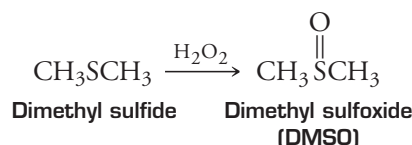
Nicotine

FIGURE 9.16

Compounds present in water and biosolids released from sewage treatment plants Hydrocodone (painkiller), ketoprofen (anti-inflammatory), carbamazepine (antiepileptic), triclosan (disinfectant), caffeine, and nicotine are among the compounds that make it through sewage treatment and into the environment.

AT THE FARM . . . REVISITED

In Section 9.3 we saw that thiols can be oxidized to form disulfides. The oxidation of sulfides follows a different path. For example, when dimethyl sulfide reacts with the oxidizing agent hydrogen peroxide (H_2O_2), dimethyl sulfoxide (DMSO) is formed. DMSO has anti-inflammatory properties and is approved by the U.S. Food and Drug Administration for veterinary use on horses and dogs. On horses, for example, it is applied as a paste directly to the legs—DMSO rapidly penetrates the skin and reaches the affected area.

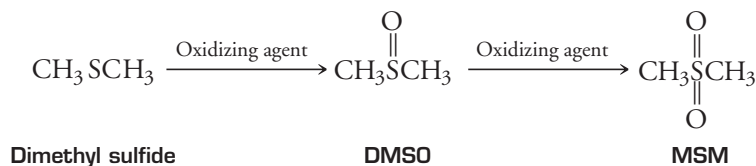


Some thought has been given to using DMSO as a solvent to dissolve therapeutic drugs and to transport them directly through the skin of humans. Studies using laboratory animals, however, have shown that DMSO can damage vision, so its use on humans is not approved.

One unpleasant side effect of using DMSO is that once this odorless compound is absorbed by the body of an animal (humans included) it is readily reduced to dimethyl sulfide, which has a very strong garlic-like odor. To overcome this drawback, veterinarians have found that DMSO's oxidation product, methylsulfonylmethane (MSM), is a

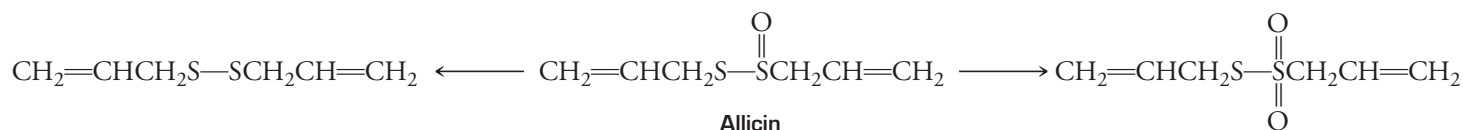


good replacement for DMSO. MSM has the same anti-inflammatory effect as DMSO, but is not reduced to dimethyl sulfide.



THINKING IT THROUGH

A sulfur-containing compound called alliin is present in garlic. When a garlic clove is crushed or cut, an enzyme catalyzes the conversion of alliin into allicin (below). Allicin is one of the compounds responsible for the odor of garlic. Allicin can undergo two additional reactions. In which of these reactions is allicin oxidized and in which is it reduced?



CHAPTER 9 OBJECTIVES

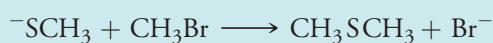
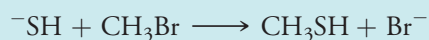
OBJECTIVE	SUMMARY	SECTION	SAMPLE AND PRACTICE PROBLEMS	END OF CHAPTER PROBLEMS
1. Explain how alcohols, thiols, ethers, sulfides, and disulfides are named and identify the noncovalent forces that attract like molecules to one another.	For IUPAC names of alcohols and thiols, the parent chain contains the functional group and is numbered from the end nearer that group. IUPAC names of alcohols end in “ol” and thiol names end in “thiol.” Common names of alcohols, thiols, ethers, sulfides, and disulfides are formed by giving the name of the group or groups attached to O or S, followed by the name of the family (except for thiols, which are called mercaptans). Alcohol molecules are held to one another primarily by hydrogen bonds. Also, the larger the alcohol molecule, the greater the contribution of London forces. Ethers interact through dipole–dipole and London forces, while thiols, sulfides, and disulfides are attracted to like molecules only through London forces.	9.1	9.1, 9.2	9.3–9.38
2. Explain how nucleophilic substitution reactions can be used to prepare alcohols, ethers, thiols, and sulfides.	In a nucleophilic substitution reaction an electron-rich nucleophile displaces a leaving group from a carbon atom. When certain alkyl halides are reacted with (a) OH^- an alcohol is produced, (b) a nucleophile containing $\text{C}-\text{O}^-$ an ether is produced, (c) SH^- a thiol is formed, and (d) with a nucleophile containing $\text{C}-\text{S}^-$ a sulfide is created.	9.2	9.3	9.39–9.52

OBJECTIVE	SUMMARY	SECTION	SAMPLE AND PRACTICE PROBLEMS	END OF CHAPTER PROBLEMS
3. Identify the products formed from the oxidation of alcohols and thiols and predict the major product for the elimination reaction that takes place when an alcohol is heated under acidic conditions.	When reacted with $\text{K}_2\text{Cr}_2\text{O}_7$, 1° alcohols are converted into aldehydes, which are further oxidized to become carboxylic acids, and 2° alcohols are converted into ketones. 3° alcohols are not oxidized by this reagent. In the oxidation of thiols by I_2 , two thiol molecules react to form a disulfide. In the presence of H^+ and heat, alcohols are dehydrated to form alkenes. When more than one alkene can be produced from an alcohol, the major product formed is identified by locating the carbon atom adjacent to the $\text{C}-\text{OH}$ that carries the fewest H atoms and removing H from it.	9.3	9.4, 9.5	9.53–9.64
4. Explain how aldehydes and ketones are named, and identify the noncovalent forces that attract like molecules to one another.	When assigning IUPAC names to aldehydes and ketones, the parent chain contains the functional group and is numbered from the end nearer that group. IUPAC names of aldehydes end in “al” and those of ketones end in “one.” Common names of ketones can be formed by giving the names of the groups attached to the $\text{C}=\text{O}$ followed by “ketone.” Aldehydes and ketones are attracted to like molecules by dipole–dipole and London forces.	9.4	9.6	9.65–9.72
5. Identify the oxidation reactions of aldehydes.	When reacted with $\text{K}_2\text{Cr}_2\text{O}_7$, aldehydes are converted into carboxylic acids. 1° and 2° alcohols are also oxidized by this reagent. Benedict’s reagent (contains Cu^{2+}) oxidizes aldehydes, but not alcohols.	9.5	9.7	9.73–9.76
6. Explain what happens when an aldehyde or ketone is reacted with H_2 and Pt.	H_2/Pt converts formaldehyde into CH_3OH , other aldehydes into 1° alcohols, and ketones into 2° alcohols.	9.6	9.8	9.77–9.80
7. Describe the structure and formation of hemiacetals and acetals .	Hemiacetals contain a $\text{C}-\text{O}-\text{C}-\text{O}-\text{H}$ linkage and acetals contain a $\text{C}-\text{O}-\text{C}-\text{O}-\text{C}$ linkage. Under acidic conditions, reacting an aldehyde or ketone with an alcohol produces a hemiacetal. Under these same conditions, reacting an aldehyde or ketone with two alcohols or reacting a hemiacetal with one alcohol gives an acetal.	9.7	9.9	9.81–9.88

Summary of Reactions

Section 9.2

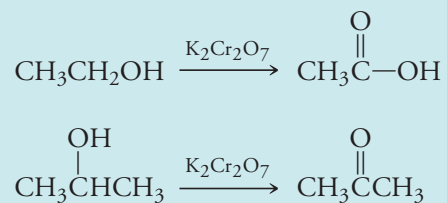
Nucleophilic substitution





Section 9.3

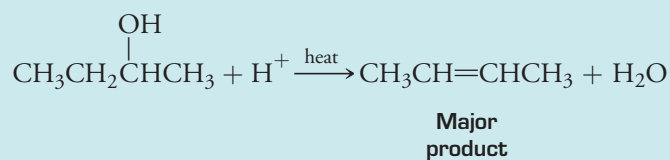
Oxidation of alcohols



Oxidation of thiols

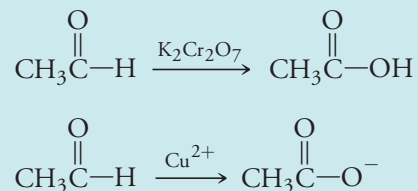


Dehydration of alcohols



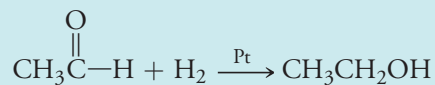
Section 9.5

Oxidation of aldehydes



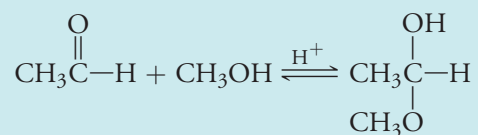
Section 9.6

Reduction of aldehydes and ketones

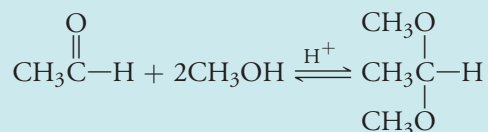


Section 9.7

Hemiacetal formation



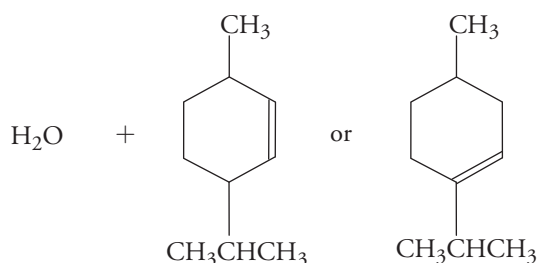
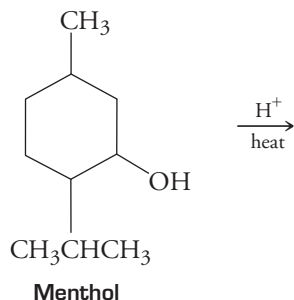
Acetal formation



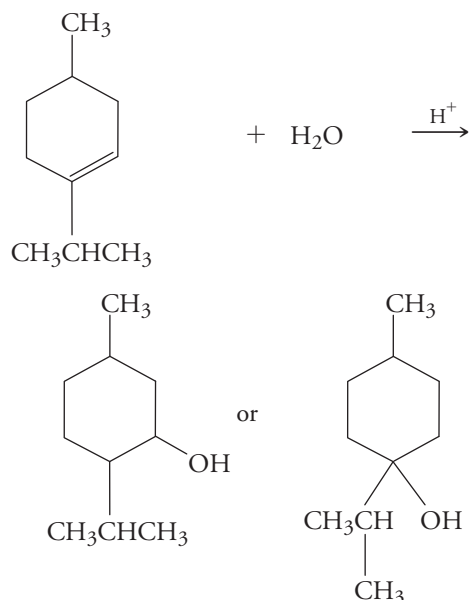
END OF CHAPTER PROBLEMS

Answers to problems whose numbers are printed in color are given in Appendix C. More challenging questions are marked with an asterisk.

- 9.1 a.** Add the missing hydrogen atoms to the ring on each molecule.



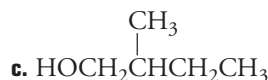
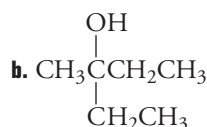
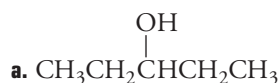
- b.** When heated in the presence of H^+ , menthol reacts to form two alkenes. In the reaction above, which alkene is the major product?
- c.** Circle the atoms in menthol that are the source of the water molecule that appears as one of the reaction products.
- 9.2 a.** Add the missing hydrogen atoms to the ring on each molecule.



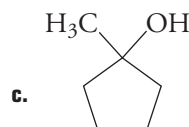
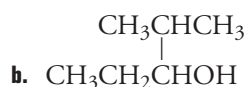
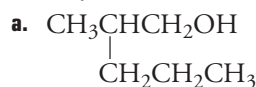
- b.** When reacted with water in the presence of H^+ , two alcohol products are formed. In the reaction above, which alcohol is the major product?
- c.** Circle the atoms in the major product that were provided by the water molecule.

9.1 ALCOHOLS, ETHERS, AND RELATED COMPOUNDS

- 9.3** Identify each alcohol as being 1° , 2° , or 3° .



- 9.4** Identify each alcohol as being 1° , 2° , or 3° .



- 9.5** Give the IUPAC name of each alcohol in Problem 9.3.

- 9.6** Give the IUPAC name of each alcohol in Problem 9.4.

- 9.7** Draw each alcohol molecule.

- a.** 2-hexanol **c.** 4-isopropylcyclohexanol
b. 3-methyl-1-pentanol

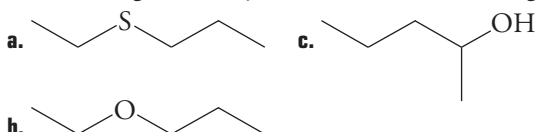
- 9.8** Draw each alcohol molecule.

- a.** 2,3-dimethyl-3-hexanol
b. 4,4-dimethyl-2-hexanol
c. *cis*-3-methylcyclohexanol

- 9.9** Identify each alcohol in Problem 9.7 as being 1° , 2° , or 3° .

- 9.10** Identify each alcohol in Problem 9.8 as being 1° , 2° , or 3° .

9.11 To which organic family does each molecule belong?



9.12 To which organic family does each molecule belong?



9.13 Name each molecule in Problem 9.11.

9.14 Name each molecule in Problem 9.12.

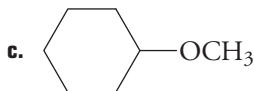
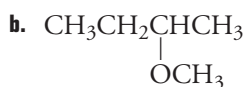
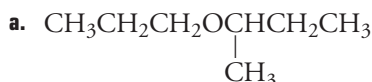
***9.15** Are the compounds in parts a and b of Problem 9.11 identical molecules, different conformations of the same molecule, *cis/trans* isomers, constitutional isomers, or entirely different molecules?

***9.16** Are the compounds in parts b and c of Problem 9.11 identical molecules, different conformations of the same molecule, *cis/trans* isomers, constitutional isomers, or entirely different molecules?

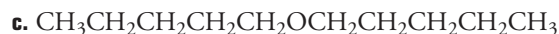
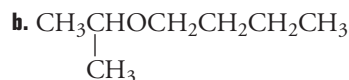
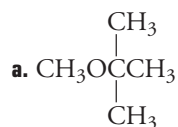
***9.17** a. What is the shape around the S atom for the molecule in Problem 9.11a?
 b. What is the shape around the O atom for the molecule in Problem 9.11b?
 c. One of the molecules in parts a and b of Problem 9.11 is polar and the other is not. Which is which?

9.18 a. Of the molecules in parts b and c of Problem 9.11, one has a boiling point of 117.3°C and the other has a boiling point of 39.6°C. Which is which?
 b. Account for this difference in boiling point.

9.19 Give the common name of each ether.



9.20 Give the common name of each ether.



9.21 Draw each molecule.

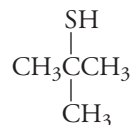
- a. dimethyl ether c. butyl ethyl ether
 b. dicyclopentyl ether

9.22 Draw each molecule.

- a. dipropyl ether c. isobutyl isopropyl ether
 b. cyclopentyl ethyl ether

9.23 The molecule $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$ is partly responsible for the strong odor that is associated with onions. Give its IUPAC and common name.

9.24 Give the IUPAC and common name of the molecule.



9.25 a. Allyl mercaptan is the major compound that can be detected on the breath immediately after eating garlic. Draw this compound (allyl = $-\text{CH}_2\text{CH}=\text{CH}_2$).
 *b. Give the IUPAC name for allyl mercaptan.

9.26 a. Diallyl disulfide is the compound second highest in concentration in the breath immediately after eating garlic. Draw this compound (allyl = $-\text{CH}_2\text{CH}=\text{CH}_2$).
 b. Allyl propyl disulfide is one of the compounds responsible for the odor of onions. Draw this compound.

***9.27** a. Which of the following is a liquid at STP: $\text{CH}_3\text{CH}_2\text{OH}$ or CH_3OCH_3 ? (See Table 9.1)
 b. Account for this difference in boiling points.

9.28 Account for the fact that dipropyl ether has a higher boiling point than diethyl ether.

9.29 Explain why $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ is less soluble in water than its constitutional isomer $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$.

9.30 Account for the fact that dipropyl ether has a lower solubility in water than diethyl ether.

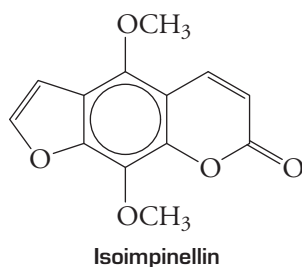
9.31 Ethanol (molecular weight = 46.0 amu) has a boiling point of 75.5°C and propane (molecular weight = 44.0 amu) has a boiling point of -42°C. Account for the difference in boiling point.

9.32 Ethanol (molecular weight = 46.0 amu) is miscible in water, while propane (molecular weight = 44.0 amu) is insoluble. Account for the difference in water solubility.

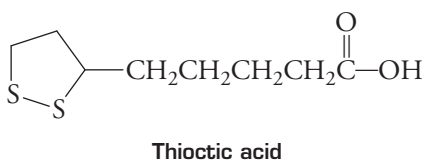
9.33 1-Propanol has a boiling point of 97.4°C, and 1-butanol has a boiling point of 117.3°C. Account for the difference in boiling point.

9.34 1-Propanol is miscible in water and 1-butanol has a water solubility of 8.0 g/100 mL. Account for this difference in water solubility.

- 9.35** Methanethiol (molecular weight = 48.0 amu) has a boiling point of 6°C and ethanol (molecular weight = 46.0 amu) has a boiling point of 78.5°C. Account for the difference in boiling point.
- 9.36** Methanethiol (molecular weight = 48.0 amu) has a water solubility of 2.3 g/100 mL and ethanol (molecular weight = 46.0 amu) is miscible in water. Account for the difference in water solubility.
- 9.37** Isoimpinellin, a naturally occurring ether, is found at very low levels in celery. Tests have shown that at high concentrations this compound can be a carcinogen (cancer-causing agent). This is not cause to avoid eating celery, however, because many foods naturally contain toxic substances at very low levels.

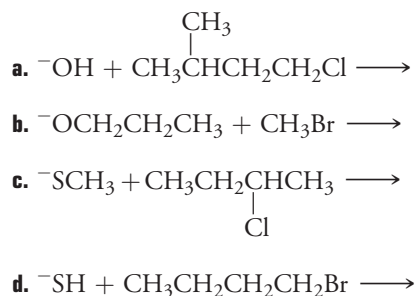


- a. How many ether groups does isoimpinellin contain?
- *b. What other functional groups are present in this molecule?
- 9.38** Thiocetic acid is a growth factor for many bacteria. Which functional groups does this molecule contain?

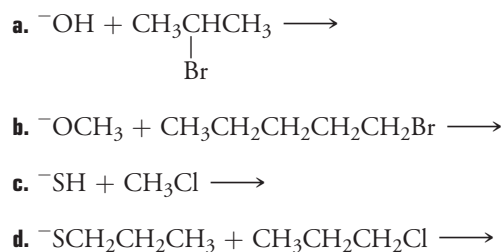


9.2 PREPARATION

- 9.39** Draw the products of each nucleophilic substitution reaction.



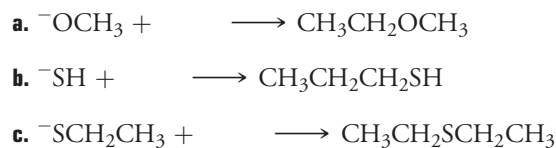
- 9.40** Draw the products of each nucleophilic substitution reaction.



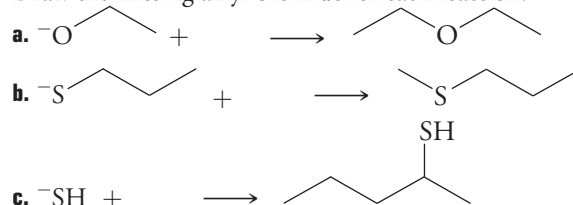
- 9.41** Name each of the organic products in Problem 9.39.

- 9.42** Name each of the organic products in Problem 9.40.

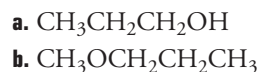
- 9.43** Draw the missing alkyl bromide for each reaction.



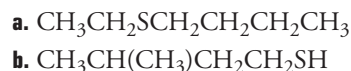
- 9.44** Draw the missing alkyl bromide for each reaction.



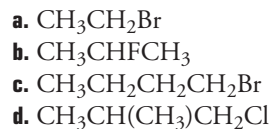
- 9.45** Write a chemical reaction equation that shows how each compound can be produced from an alkyl bromide.



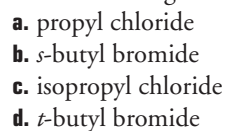
- 9.46** Write a chemical reaction equation that shows how each compound can be produced from an alkyl bromide.



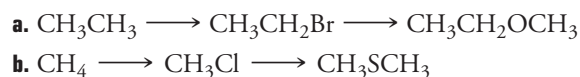
- 9.47** The molecule CH_3Cl is named methyl chloride. Name each of the following molecules:



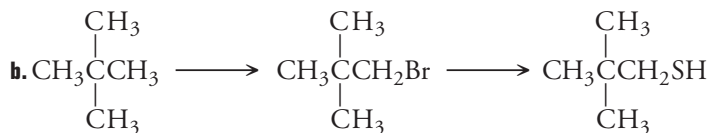
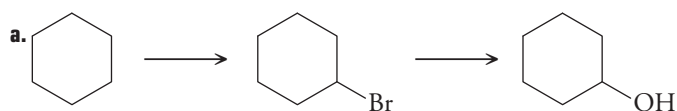
- 9.48** Methyl chloride has the formula CH_3Cl . Draw each of the following molecules:



- ***9.49** Complete the series of reactions by adding the necessary reactants or conditions to the reaction arrows.

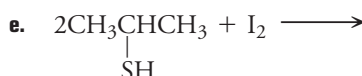
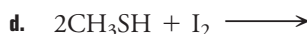
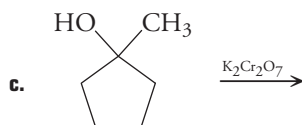
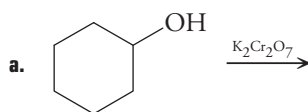


***9.50** Complete the series of reactions by adding the necessary reactants or conditions to the reaction arrows.

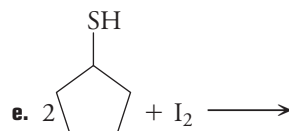
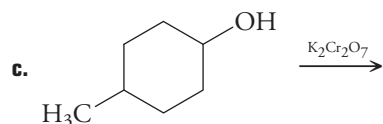
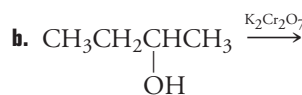


9.3 REACTIONS

9.51 Draw the organic product (if any) expected from each reaction.



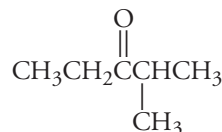
9.52 Draw the organic product (if any) expected from each reaction.



9.53 Describe the difference in the products obtained when 1-butanol and 1-butanethiol are oxidized.

9.54 Describe the difference in the products obtained when 1-butanol and 2-butanol are oxidized.

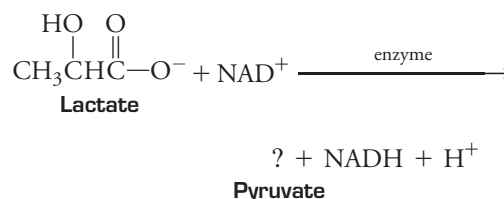
***9.55** When oxidized, which alcohol produces the ketone shown below?



***9.56** When oxidized, which thiol produces the disulfide shown below?



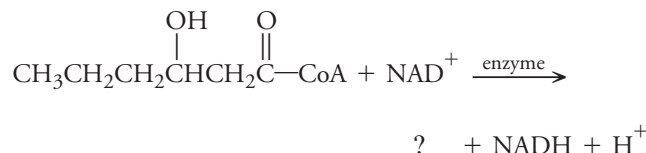
***9.57** a. Lactate, which builds up in muscle cells during exercise, is sent to the liver where an enzyme catalyzes the oxidation of this 2° alcohol to pyruvate. Draw pyruvate.



b. Lactate and pyruvate are the conjugate bases of lactic acid and pyruvic acid, respectively. Draw these carboxylic acids.

c. At pH 7, why does each of these acids appear in its conjugate base form?

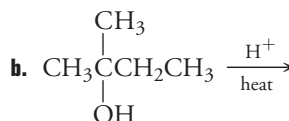
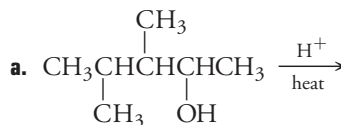
***9.58** a. One step in the breakdown of fatty acids by the body involves the enzyme catalyzed oxidation of a 2° alcohol group present in a carboxylic acid derivative. In this compound, “CoA” is coenzyme A, whose structure will be introduced in Chapter 14. Draw the oxidation product.



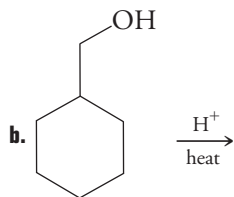
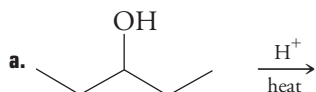
b. Name the carboxylic acid that provides the carboxylic acid residue present in the reactant.

c. To which carbon atom in the reactant is the —OH group attached, α or β?

9.59 Draw the major product of each reaction.



9.60 Draw the major product of each reaction.



***9.61** Draw each molecule named below and draw the major organic product expected when each is reacted with H^+ and heat.

- 2,3-dimethyl-2-butanol
- 2,3-dimethyl-3-hexanol
- 2-methylcyclopentanol

***9.62** Draw each molecule named below and draw the major organic product expected when each is reacted with H^+ and heat.

- 2,3-dimethyl-3-pentanol
- 2-hexanol
- 1-methylcyclopentanol

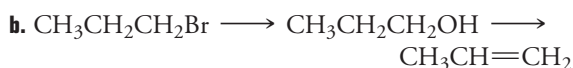
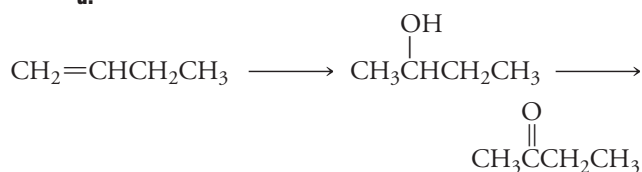
***9.63** a. When a particular alcohol is heated in the presence of H^+ , 2-methyl-2-butene is the major product. Draw and name this alcohol.

b. When a different alcohol is heated in the presence of H^+ , 2-methyl-2-butene is the major product. Draw and name this alcohol.

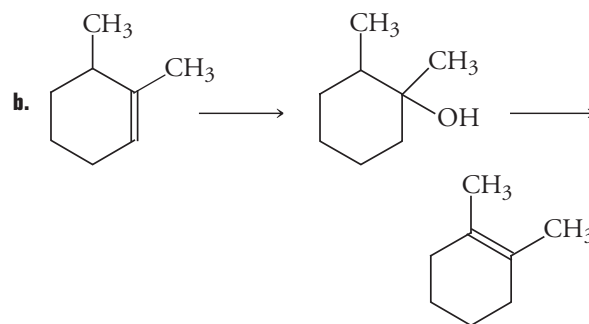
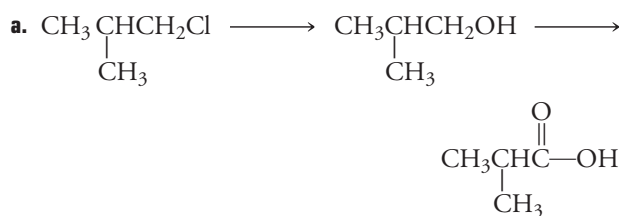
***9.64** a. When a particular alcohol is heated in the presence of H^+ , 1-methylcyclopentene is the major product. Draw and name this alcohol.

b. When a different alcohol is heated in the presence of H^+ , 1-methylcyclopentene is the major product. Draw and name this alcohol.

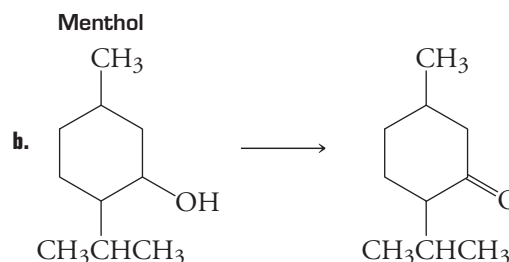
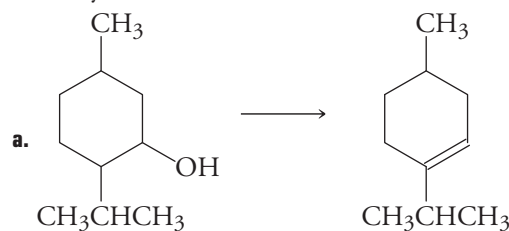
***9.65** Complete the series of reactions by adding the necessary reactants or conditions to the reaction arrows.



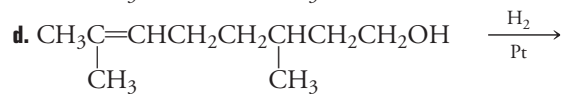
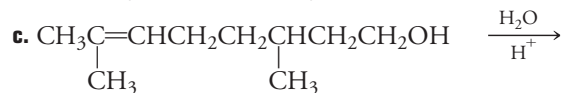
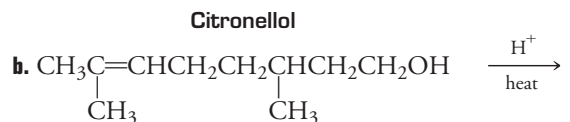
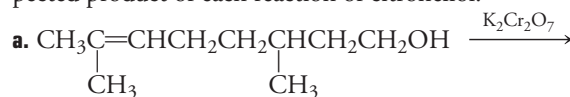
***9.66** Complete the series of reactions by adding the necessary reactants or conditions to the reaction arrows.



***9.67** Menthol flavor is due to the alcohol named menthol (below). Complete each reaction of menthol by adding the necessary reactants or conditions to the reaction arrows.

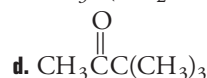
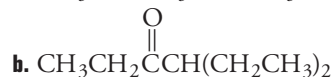


***9.68** Citronellol is a component of rose oil. Give the expected product of each reaction of citronellol.

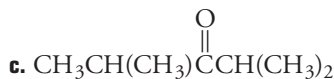
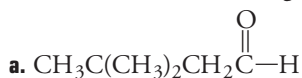


9.4 ALDEHYDES AND KETONES

9.69 Name each of the following molecules.



9.70 Name each of the following molecules.



9.71 Draw each molecule.

- a. pentanal c. dipropyl ketone
b. 3-bromohexanal d. 2,5-dibromocyclohexanone

9.72 Draw each molecule.

- a. octanal
b. 2,5-dimethylcyclopentanone
c. 2-octanone
d. 2-isopropylpentanal

9.73 2-Hexanone has a boiling point of 150°C and 2-pentanone has a boiling point of 102°C .

- a. Draw each molecule.
b. Account for the difference in boiling point.

9.74 Acetone has a boiling point of 56°C and isopropyl alcohol has a boiling point of 82°C .

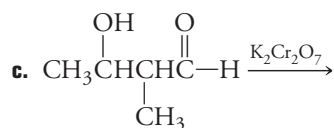
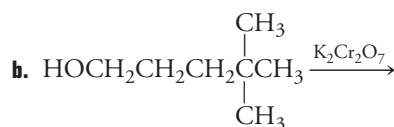
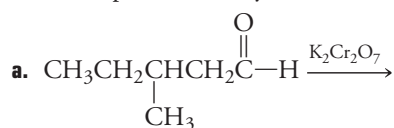
- a. Draw each molecule.
b. Account for the difference in boiling point.

9.75 Propanone (molecular weight = 58.0 amu) has a boiling point of 56°C and 1-propanol (molecular weight = 60.0 amu) has a boiling point of 97.4°C . Account for the difference in boiling point.

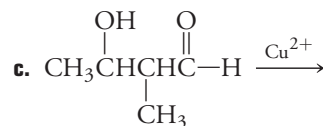
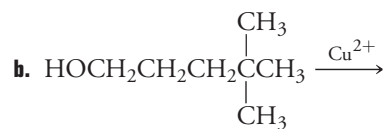
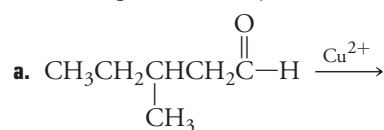
9.76 Propanone (molecular weight = 58.0 amu) has a boiling point of 56°C and butane (molecular weight = 58.0 amu) has a boiling point of 0°C . Account for the difference in boiling point.

9.5 OXIDATION OF ALDEHYDES

9.77 Draw the product (if any) of each reaction.



9.78 Draw the product (if any) of each reaction.



9.79 Draw each molecule. Draw the product (if any) obtained when each is reacted with $\text{K}_2\text{Cr}_2\text{O}_7$.

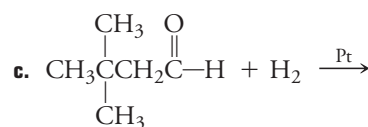
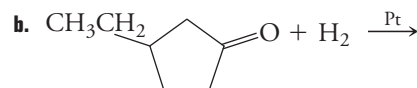
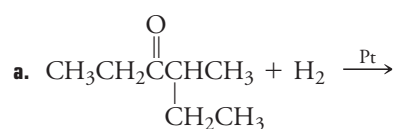
- a. propanal d. 3-chloro-3-methylpentanal
b. butanone e. 3-hydroxybutanal
c. 1-butanol

9.80 Draw each molecule. Draw the product (if any) obtained when each is reacted with Benedict's reagent.

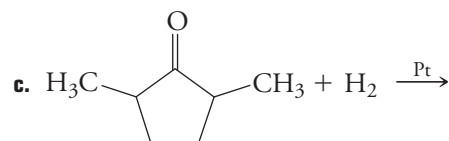
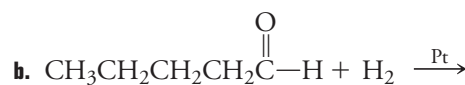
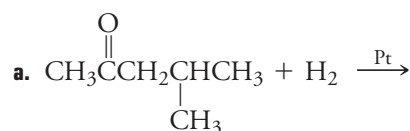
- a. propanal d. 3-chloro-3-methylpentanal
b. butanone e. 3-hydroxybutanal
c. 1-butanol

9.6 REDUCTION OF ALDEHYDES AND KETONES

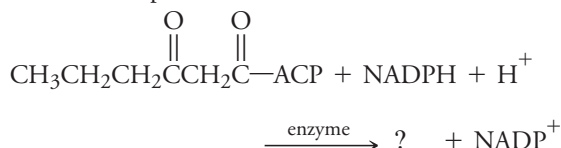
9.81 Draw the product of each reaction.



9.82 Draw the product of each reaction.

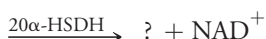
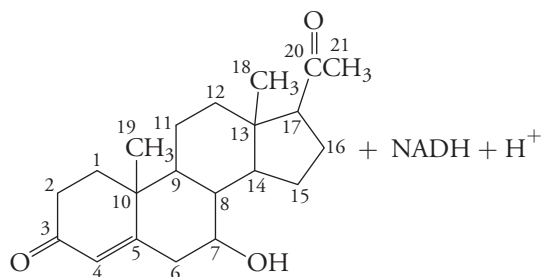


- 9.83** One step in the biochemical synthesis of fatty acids is the enzyme-catalyzed reduction of a ketone group present in a carboxylic acid derivative. In this compound, “ACP” is acyl carrier protein (Chapter 14), and the carbonyl-ACP group is similar to an ester. Draw the reduction product.



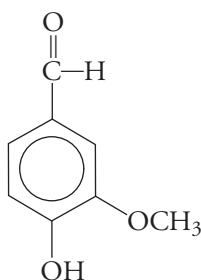
- *9.84** The first step in the biochemical breakdown of progesterone is a reaction involving 20 α -hydroxysteroid dehydrogenase (20 α -HSDH), an enzyme which catalyzes the reduction of a ketone group at position 20 of steroids.

- a.** Draw the product that forms when progesterone is reduced by the action of 20 α -HSDH and NADH.



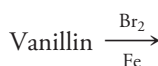
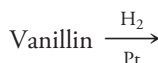
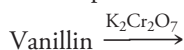
- b.** Draw the product that forms when 1 mol progesterone is reacted with 3 mol of H_2 in the presence of Pt.

- *9.85** The flavor of vanilla is largely due the molecule named vanillin.

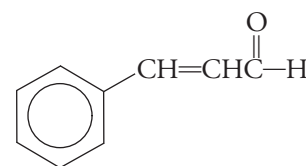


Vanillin

- a.** Which organic families are present in vanillin?
b. Draw a product of each reaction.

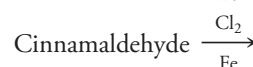
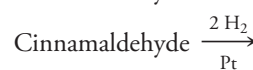


- *9.86** The flavor of cinnamon is largely due to the molecule named cinnamaldehyde.



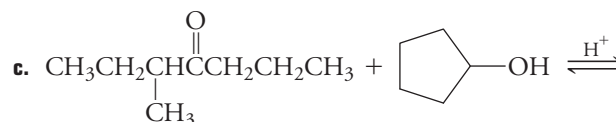
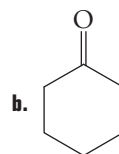
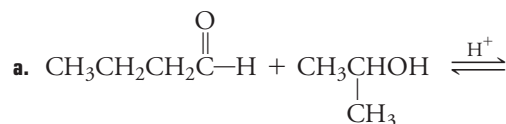
Cinnamaldehyde

- a.** Which organic families are present in cinnamaldehyde?
b. Draw a product of each reaction.

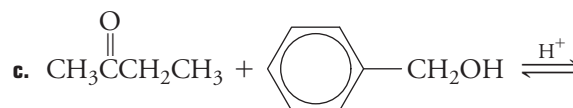
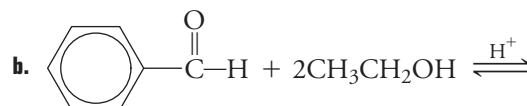


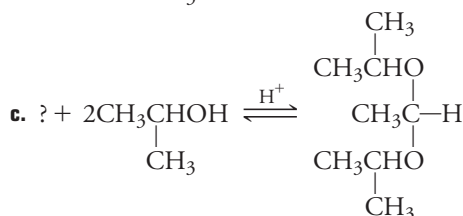
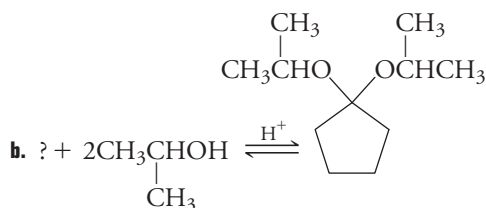
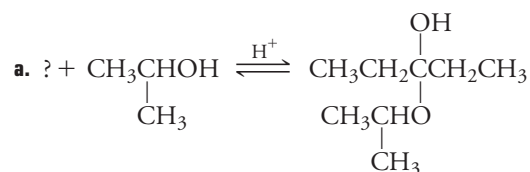
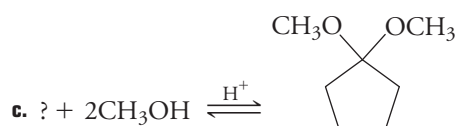
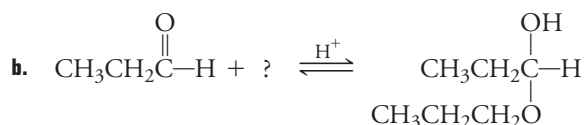
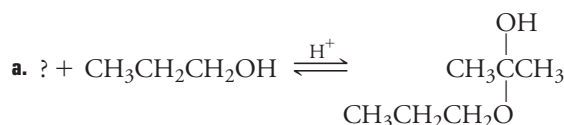
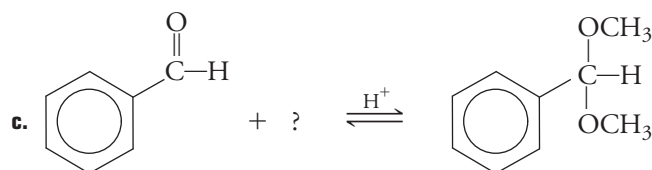
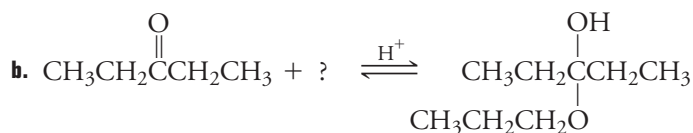
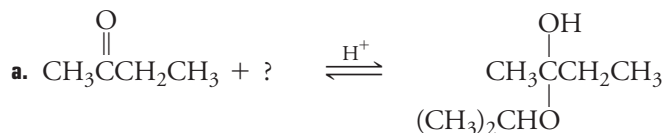
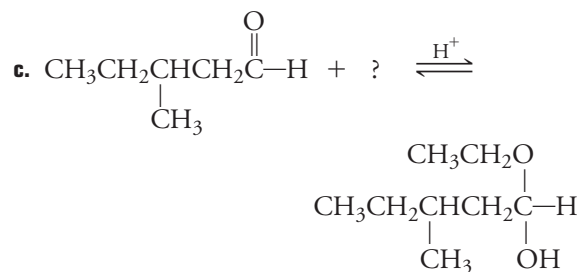
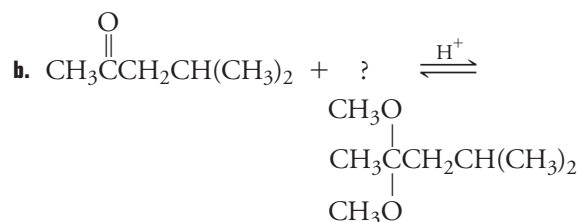
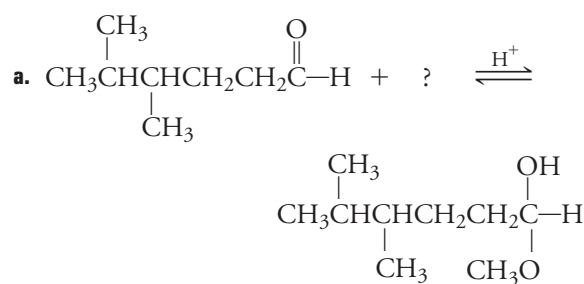
9.7 REACTIONS OF ALCOHOLS WITH ALDEHYDES AND KETONES

- 9.87** Draw the product of each reaction.



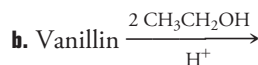
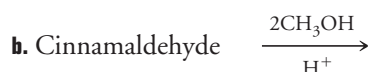
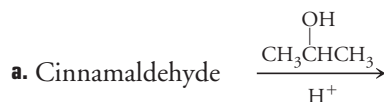
- 9.88** Draw the product of each reaction.



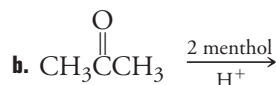
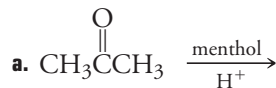
9.89 Draw the missing reactant for each reaction.**9.90** Draw the missing reactant for each reaction.**9.91** Draw the missing reactant for each reaction.**9.92** Draw the missing reactant for each reaction.

***9.93** a. How are cyclic hemiacetals similar to lactones (Figure 8.32)?
b. How are cyclic hemiacetals different from lactones?

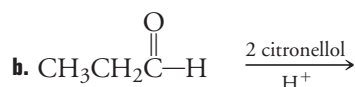
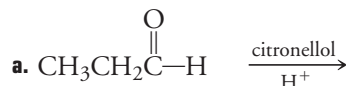
***9.94** What product is formed in the presence of H^+ when an alcohol molecule is reacted with each of the following?
a. an aldehyde
b. a carboxylic acid

9.95** Draw the product of each reaction. The structure of vanillin is given in Problem 9.85.9.96** Draw the product of each reaction. The structure of cinnamaldehyde is given in Problem 9.86.

- *9.97** Draw the product of each reaction. The structure of menthol is given in Problem 9.67.



- *9.98** Draw the product of each reaction. The structure of citronellol is given in Problem 9.68.



HealthLink | ALDEHYDE DEHYDROGENASE

- 9.99** The toxicity of methanol is mainly due to the aldehyde produced when it is oxidized in the liver. Draw methanol, then draw and name the aldehyde formed on its oxidation.

- 9.100** Describe the physiological action of disulfiram.



HealthLink | PROTECTIVE ENZYMES

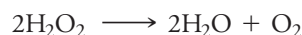
- 9.101** O_2 is reduced when it is converted into H_2O_2 . Explain.

- 9.102** O_2 is reduced when it is converted into O_2^- . Explain.

- *9.103** In the breakdown of superoxide, which product results from the oxidation of O_2^- and which product results from the reduction of O_2^- ? Explain.

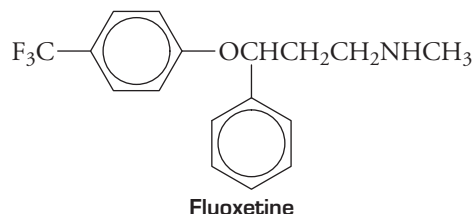


- 9.104** In the breakdown of hydrogen peroxide, which product results from the oxidation of H_2O_2 and which product results from the reduction of H_2O_2 ? Explain.

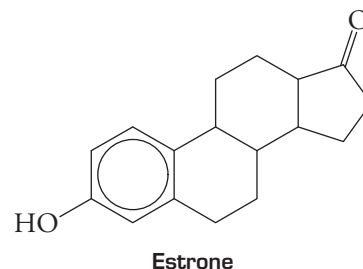


HealthLink | DRUGS IN THE ENVIRONMENT

- *9.105** The antidepressant fluoxetine (Prozac), which has been detected in biosolids, is typically sold as the hydrochloride salt. Draw this salt.



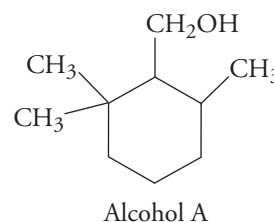
- 9.106** The steroid hormone estrone has been detected in river, stream, and well water. Draw the product formed when the ketone group in estrone is reduced by H_2 and Pt.



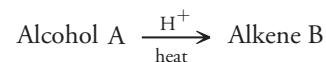
- *9.107** The antidepressant venlafaxine has been detected in ground water at concentrations of $50 \mu\text{g/L}$.
- At this concentration, how many grams of this drug are present in 3.0 L of water?
 - Convert $50 \mu\text{g/L}$ into parts per million.
 - Convert $50 \mu\text{g/L}$ into parts per billion.
- *9.108** Paraxanthine, a product of caffeine metabolism in humans, has been detected in ground water at concentrations of $150 \mu\text{g/L}$.
- At this concentration, how many grams of paraxanthine are present in 25.0 mL of water?
 - Convert $150 \mu\text{g/L}$ into parts per million.
 - Convert $150 \mu\text{g/L}$ into parts per billion.

LEARNING GROUP PROBLEMS

- 9.109 a.** An alkyl halide is converted into the alcohol below. Write the chemical equation for this reaction.



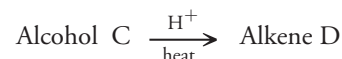
- b.** Draw the reaction product, Alkene B.



- c.** Draw the reaction product, Alcohol C.



- d.** Draw the reaction product, Alkene D.



- e.** Give the IUPAC name of Alkene D.

f. Draw the reaction product.



g. Draw the reaction product.



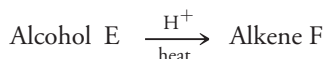
9.110 a. Draw butyl bromide.

b. Draw the reaction product, Alcohol E.



c. Give the IUPAC and common name of Alcohol E.

d. Draw the reaction product, Alkene F.

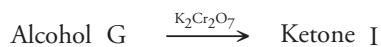
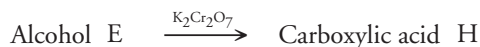


e. Name alkene F.

f. Draw the reaction product, Alcohol G.



g. Draw the reaction products, carboxylic acid H and ketone I.

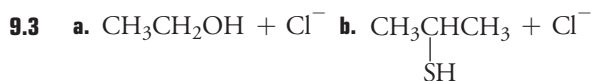
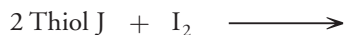


h. Draw the product formed when Ketone I is reacted with H_2/Pt .

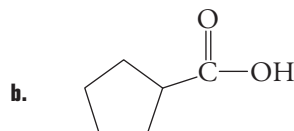
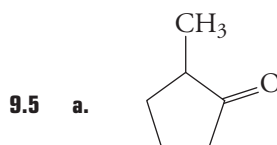
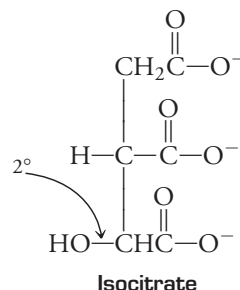
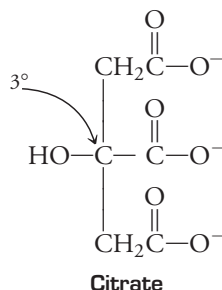
i. Draw the reaction product, Thiol J.



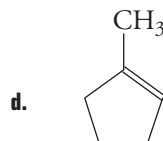
j. Draw the reaction product.



9.4 Citrate contains a 3° alcohol and cannot be oxidized. Isocitrate contains a 2° alcohol and can.

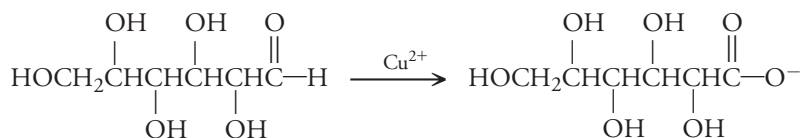


c. No reaction.



9.6 1-Propanol is more capable of forming hydrogen bonds with water molecules.

9.7 a. Benedict's solution oxidizes only aldehydes. Glucose will react, but sorbitol will not.



b. There will be a color change from the initial light blue color.

SOLUTIONS TO PRACTICE PROBLEMS

9.1 The alcohol molecule.

9.2 1-Propanol is polar and can form hydrogen bonds with water molecules. Ethanethiol is nonpolar and will not form hydrogen bonds with water molecules.

