Reactions 8.26–8.29 are examples of protonolysis. A protonolysis is any reaction with the proton of an acid that breaks chemical bonds. For example, in the protonolysis of a Grignard reagent, the carbon–metal bond of the Grignard reagent is broken. The protonolysis reaction can be an annoyance, since, because of it, Grignard and organolithium reagents must be prepared in the absence of moisture. However, the protonolysis reaction is also useful, because it provides a method for the preparation of hydrocarbons from alkyl halides. Notice, for example, in Eq. 8.29 that ethane (a hydrocarbon) is produced from ethylmagnesium bromide, which, in turn, comes from ethyl bromide (an alkyl halide). Although one would not normally prepare an ordinary hydrocarbon by protonolysis, a particularly useful variation of this reaction is the preparation of hydrocarbons labeled with the hydrogen isotopes deuterium (D, or $^2\text{H}$) or tritium (T, or $^3\text{H}$) by reaction of a Grignard reagent with the corresponding isotopically labeled water.

\[
(\text{CH}_3)_2\text{CCH}_2\text{Br} \xrightarrow{\text{Mg, ether}} (\text{CH}_3)_2\text{CCH}_2\text{MgBr} \xrightarrow{\text{D}_2\text{O}} (\text{CH}_3)_2\text{CCH}_2\text{D}
\]

### PROBLEMS

8.23 Give the products of the following reactions. Show the curved-arrow notation for each.

(a) \(\text{H}_2\text{C} = \text{Li} + \text{CH}_3\text{OH} \rightarrow \)  
(b) \((\text{CH}_3)_2\text{CHCH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \)

8.24 (a) Give the structures of two isomeric alkylmagnesium bromides that would react with water to give propane.

(b) What compounds would be formed from the reactions of the reagents in (a) with \(\text{D}_2\text{O}\)?

### INDUSTRIAL PREPARATION AND USE OF ALKYL HALIDES, ALCOHOLS, AND ETHERS

#### A. Free-Radical Halogenation of Alkanes

Among the methods used in industry, and occasionally in the laboratory, to produce simple alkyl halides is direct halogenation of alkanes. When an alkane such as methane is treated with \(\text{Cl}_2\) or \(\text{Br}_2\), in the presence of heat or light, a mixture of alkyl halides is formed by successive chlorination reactions.

\[
\begin{align*}
\text{CH}_4 + \text{Cl}_2 & \xrightarrow{\text{heat or light}} \text{CH}_3\text{Cl} + \text{HCl} \\
\text{CH}_3\text{Cl} + \text{Cl}_2 & \xrightarrow{\text{heat or light}} \text{CH}_2\text{Cl}_2 + \text{HCl} \\
\text{CH}_2\text{Cl}_2 + \text{Cl}_2 & \xrightarrow{\text{heat or light}} \text{CHCl}_3 + \text{HCl} \\
\text{CHCl}_3 + \text{Cl}_2 & \xrightarrow{\text{heat or light}} \text{CCl}_4 + \text{HCl}
\end{align*}
\]

The relative amounts of the various products can be controlled by varying the reaction conditions.

The products in Eqs. 8.31a–d are formed in a series of substitution reactions (Sec. 7.9B). For example, \(\text{CH}_3\text{Cl}\) is formed by the substitution of a hydrogen atom in methane by a chlorine atom:

\[
\begin{align*}
\text{H} - \text{C} - \text{H} + \text{Cl}_2 & \xrightarrow{\text{heat or light}} \text{H} - \text{C} - \text{Cl} + \text{HCl}
\end{align*}
\]
8.9 INDUSTRIAL PREPARATION AND USE OF ALKYL HALIDES, ALCOHOLS, AND ETHERS

The conditions of this reaction (initiation by heat or light) suggest the involvement of free-radical intermediates (Sec. 5.6C). The mechanism of this reaction in fact follows the typical pattern of other free-radical chain reactions; it has initiation, propagation, and termination steps. The reaction is initiated when a small number of halogen molecules absorb energy from the heat or light and dissociate homolytically into halogen atoms:

\[ \text{Cl}_2 \rightarrow \text{Cl}^+ + \text{Cl}^- \]  

The ensuing chain reaction has the following propagation steps:

\[ \text{Cl}^+ + \text{CH}_3 \rightarrow \text{H} + \cdot \text{CH}_3 \]  
\[ \text{Cl}^+ + \cdot \text{CH}_3 \rightarrow \] methyl radical

The chlorine radical formed in Eq. 8.34b reacts with another CH₃ as shown in Eq. 8.34a, and thus the chain reaction continues. Termination steps result from the recombination of radical species (Problem 8.32).

The halogenation of alkanes by a free-radical mechanism is an example of a free-radical substitution reaction: a substitution reaction that occurs by a free-radical chain mechanism. (Contrast this with the free-radical addition mechanism for peroxide-mediated addition to alkenes in Sec. 5.6C.)

Free-radical halogenations with chlorine and bromine proceed smoothly, halogenation with fluorine is violent, and halogenation with iodine does not occur. These observations correlate with the \( \Delta H^\circ \) values for halogenation of methane by each halogen (see Problem 5.43 on p. 222). Halogenation by fluorine is so strongly exothermic (\( \Delta H^\circ = -424 \text{ kJ mol}^{-1}, -101 \text{ kcal mol}^{-1} \)) that the reaction is difficult to control; that is, the temperature of the reaction mixture rises more rapidly than the heat can be dissipated. Iodination is endothermic (\( \Delta H^\circ = +54 \text{ kJ mol}^{-1}, +13 \text{ kcal mol}^{-1} \)); the reaction is so unfavorable energetically that it does not proceed to a useful extent. Chlorination (\( \Delta H^\circ = -106 \text{ kJ mol}^{-1}, -25 \text{ kcal mol}^{-1} \)) and bromination (\( \Delta H^\circ = -30 \text{ kJ mol}^{-1}, -7 \text{ kcal mol}^{-1} \)) are mildly exothermic and proceed to completion without becoming violent.

**PROBLEMS**

8.31 Give the free-radical chain mechanism for the formation of ethyl bromide from ethane and bromine in the presence of light.

8.32 Explain why butane is formed as a minor by-product in the free-radical bromination of ethane.

**B. Uses of Halogen-Containing Compounds**

Of the millions of organic compounds that occur naturally, relatively few (about 5000) are halogen-containing. Most of those that do occur are produced by marine organisms that inhabit salt water, in which the concentration of halide ions is relatively high.

Alkyl halides and other halogen-containing organic compounds have many practical uses. Methylene chloride and chloroform are important solvents (see Table 8.2) that do not pose the flammability hazard of ethers. (Carbon tetrachloride was also important until its toxicity was recognized.) Tetrachloroethylene, trichlorofluoroethane, and trichloroethylene are used industrially as dry-cleaning solvents. A number of halogen-containing alkenes serve as monomers
for the synthesis of useful polymers, such as PVC, Teflon, and Kel-F (see Table 5.4). Bromotri-
fluoromethane and a number of other brominated organic compounds are used as commercial
flame retardants. The compound 2,4-dichlorophenoxyacetic acid (sold as 2,4-D) mimics a plant
growth hormone and causes broadleaved weeds to overgrow and eventually die. This is the dan-
delion killer used in commercial lawn fertilizers.

2,4-D

A few alkyl halides have medical uses. Halothane, ClBrCH—CF₃, and methoxyflurane,
Cl₂CH—CF₂—OCH₃, are safe and inert general anesthetics that have largely supplanted the
highly flammable compounds ether and cyclopropane. Certain fluorocarbons dissolve sub-
stantial amounts of oxygen, and some of these have been the subject of ongoing research as
artificial blood in surgical applications.

Because alkyl halides are rarely found in nature, and because many are not biologically de-
graded, it is perhaps not surprising that some alkyl halides released into the environment have
become the focus of concern. The chlorofluorocarbons (freons, or CFCs) such as F₂CCl₂,
HCCIF₂, and HCCl₂F, are among the most noteworthy examples. Until relatively recently, these
compounds were the only ones used as refrigerants in commercial cooling systems, and they
were also widely used as propellants in aerosol products. Nontoxic and nonflammable, and with
properties ideally suited to their applications, they seemed to be ideal industrial chemicals.
During the 1970s, a number of studies implicated them in the destruction of stratospheric ozone.
(The ozone layer provides an important shield against harmful ultraviolet solar radiation.) In Oc-
tober 1978, the United States government banned their use in virtually all but certain medically
essential aerosol products. In 1987, a number of countries, including the United States, initialed
the “Montreal Protocol on Substances That Deplete the Ozone Layer,” under which industrial
nations agreed to phase out the production of CFCs, carbon tetrachloride, and certain other sub-
stances by 2010. As a direct result, the production of CFCs by 1996 had dropped to about 16%
of its pretreaty value. CFCs in existing refrigeration systems are recycled.

The problem with CFCs stems from their chlorine content. Chlorine atoms are liberated
from these compounds in upper-atmosphere photodissociation reactions (bond-homolysis re-
actions initiated by light).

\[
\begin{align*}
\text{Cl} & \quad \text{F}_2\text{C} \quad \text{Cl} \\
\text{a freon} & \quad \xrightarrow{\text{light}} \\
& \quad \text{F}_2\text{C} \quad + \quad \cdot \text{Cl} \\
& \quad \text{a chlorine atom}
\end{align*}
\] (8.35a)

A chlorine atom reacts with ozone to give ClO⁻ and O₂:

\[
\cdot \text{Cl} + \text{O}_3 \quad \longrightarrow \quad \text{ClO}^- + \text{O}_2
\] (8.35b)

The ClO⁻ produced in Eq. 8.35b reacts with oxygen atoms (O) produced in the upper atmos-
phere by the normal photodissociation of O₂:

\[
\text{ClO}^- + \text{O} \quad \longrightarrow \quad \text{Cl}^- + \text{O}_2
\] (8.35c)

(from photodissociation
of O₂)
In this process, a chlorine atom is regenerated and is thus available to repeat the cycle. The sum of Eqs. 8.35b and 8.35c is

\[ O + O_3 \rightarrow 2O_2 \]  

(8.35d)

In effect, then, chlorine atoms catalyze the destruction of ozone; it has been estimated that a single chlorine atom can promote the destruction of 10^5 molecules of ozone.

The 1995 Nobel Prize in Chemistry was given for research into the chemical reactions that lead to the destruction of stratospheric ozone. The recipients of the prize were Mario Molina (b. 1943), a chemist then at the Massachusetts Institute of Technology; F. Sherwood Rowland (b. 1927), a chemist from The University of California, Irvine; and Paul Crutzen (b. 1933), a meteorologist-chemist from the Max-Planck Institute for Chemistry in Mainz, Germany.

One solution to this problem is to replace CFCs with related compounds that contain no chlorine. Indeed, one of the most common replacements for CFCs is the family of hydrofluorocarbons (HFCs) such as 1,1,1,2,2-pentafluoroethane (CF_3CHF_2). Although this class of compounds is less harmful to the ozone layer, HFCs nevertheless have adverse effects as greenhouse gases and ultimately exacerbate global warming.

Some potent and effective insecticides are organohalogen compounds.

![DDT and chlordane structures]

DDT was first synthesized in 1873, but it was introduced in 1939 as a pesticide by Paul Müller (1899–1965), a Swiss chemist at the Laboratorium der Farben-Fabriken J.R. Geigy A.G., Basel. So effective was this insecticide that it was viewed for about 25 years as a savior of humanity. (For example, it virtually eliminated malaria in many areas of the world, including parts of the southern United States.) Müller received the Nobel Prize Physiology or Medicine in 1948. Unfortunately, DDT, chlordane, and a number of other chlorinated broad-spectrum insecticides were subsequently found to accumulate in the fatty tissues of birds and fish, to be passed up the food chain, and to have harmful physiological effects. Hence, their use has been banned or severely curtailed.

The conflict between the use of chemistry to improve humanity’s living conditions and the generation of new problems caused by the release of chemicals into the environment finds real focus in the controversies surrounding the use of many organohalogen compounds. The great promise and public optimism that chemistry offered following World War II has given way to a public skepticism—or, at least, a period of public reflection and debate—as an increasing number of problems related to synthetic chemicals have surfaced. Is commercial organic chemistry in the end to be nothing but a Pandora’s box of problems? Perhaps a more realistic view is that few if any human technological endeavors are without risk, and chemistry is no exception. Each new generation of useful organic chemicals—whether they be pharmaceuticals, refrigerants, or insecticides—will likely bring with their benefits some new problems. These problems will provide a great research opportunity for chemists of the future who will take up the challenge of using their knowledge to improve further the benefits and to reduce or eliminate the problems.
C. Production and Use of Alcohols and Ethers

Ethanol

A number of alcohols are important in commerce. None, however, has been affected by recent events as dramatically as ethanol. In 1980, the U.S. production of ethanol was 175 million gallons. Much of it was made industrially by the hydration of ethylene (Sec. 4.9B), which in turn comes from petroleum (Sec. 5.8).

\[ \text{ethylene} + \text{H}_2\text{O} \xrightarrow{300 \degree C} \text{ethanol} \]  
\[ \text{H}_2\text{C}=\text{CH}_2 + \text{H}_2\text{O} \xrightarrow{300 \degree C} \text{CH}_3\text{CH}_2\text{OH} \]  

Ethanol obtained from this reaction, called 95% ethanol, is 95.6 mass percent pure; the remainder is water. Anhydrous ethanol, or absolute ethanol, is obtained by further drying.

In recent years, the U.S. production of ethanol has climbed rapidly, reaching more than 4 billion gallons in 2006 and likely to climb significantly higher. Most of this ethanol is produced in the U.S. by fermentation of the sugars in grain. In 2005, the world production of ethanol was 12.2 billion gallons, with the U.S. and Brazil providing about one-third each of this total, and China about 8%. (Brazil, where plants that produce fermentable sugars grow rapidly, has long operated on an ethanol-based fuel economy.) The increase in ethanol production in the United States has been driven by the demand for motor fuels that are not derived from hydrocarbons, by the phaseout of methyl tert-butyl ether (MTBE) and its replacement by ethanol as the main oxygen-containing component of gasoline, and by the notion that the use of ethanol and other plant-derived fuels will reduce the amount of CO\textsubscript{2} released into the atmosphere. (See the sidebar on p. 369).

The relatively small amount of ethanol not used for fuel is used as a starting material for the preparation of other compounds and as a solvent for inks, fragrances, and the like. Chemically pure ethanol is subject to tight federal controls to ensure that it will not be used in beverages. In many cases the ethanol used in solvent applications is denatured alcohol, which is ethanol made unfit for human consumption by the addition of certain toxic additives such as methanol.

Beverage alcohol is produced by the fermentation of malt, barley, grape juice, corn mash, or other sources of natural sugar. Beverage alcohol is not isolated; rather, alcoholic beverages are the mixtures of ethanol, water, and the natural colors and flavorings produced in the fermentation process and purified by sedimentation (as in wine) or distillation (as in brandy or whiskey). Industrial alcohol cannot be used legally to alter the alcoholic composition of beverages.

Ethanol is a drug, and, like many useful drugs, is toxic when consumed in excess. Ethanol is the most abused drug in the world.
Global Warming and Biofuels

Global warming, caused by a rapid increase in atmospheric CO$_2$ levels, was discussed in Sec. 2.7. The increase in CO$_2$ levels has resulted from the combustion of fossil fuels—oil, coal, and natural gas. The environmental impact of fossil fuels and the political instability of many of the world’s oil-producing regions have conspired to make the development of alternative fuels increasingly urgent. Ideally, the goal is to produce cheap and abundant fuels that will not, on combustion, increase the net CO$_2$ content of the atmosphere. For this reason, fuels derived from plants (biomass), termed generally biofuels, are attractive. Plants are composed largely of cellulose, the single most abundant compound on the face of the earth, and cellulose is a polymer of glucose, which in turn can be fermented to ethanol. When plants produce glucose in its various forms, they remove CO$_2$ from the atmosphere. The energy for the plant synthesis of glucose comes from the sun through photosynthesis. If we add the equations for the photosynthesis of glucose, the fermentation of glucose to ethanol, and the combustion of ethanol as a fuel, the result is no net change in atmospheric CO$_2$:

\[
\begin{align*}
6\text{CO}_2 + 6\text{H}_2\text{O} & \xrightarrow{\text{light}} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \quad \text{(biosynthesis of glucose, C}_6\text{H}_{12}\text{O}_6) \\
\text{C}_6\text{H}_{12}\text{O}_6 & \rightarrow 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2 \quad \text{(anaerobic fermentation)} \\
2\text{C}_2\text{H}_5\text{OH} + 6\text{O}_2 & \rightarrow 4\text{CO}_2 + 6\text{H}_2\text{O} \quad \text{(combustion of ethanol)}
\end{align*}
\]

Sum: No Net Change

(8.37)

This simple picture does not take into account the energy required to produce and transport the cellulosic products, run the fermentors, and deliver the ethanol-containing products to the end users. Accordingly, the net energy gain from the use of various biofuels has been a matter of debate.

Although glucose fermentation to ethanol has a prominent place in the discussion of biofuels, other fuel sources, such as biodiesel from plant oils and methane from fermentation of waste products (Fig. 2.14, p. 80), also figure into the considerations of alternative fuels. However, all of these fuels ultimately come from plants and thus depend on photosynthesis. It is interesting to think of photosynthesis in the context of solar energy as a power source, which has also been of considerable interest. Photosynthesis harnessed to produce cellulose is nature’s solar-energy collection and storage mechanism.

Putting the carbon cycle of Eq. 8.37 into practice requires decisions on which fuels to use and what plants are to be their major sources. These issues are fraught with huge political and economic ramifications. For example, the diversion of grain to ethanol production can have a major impact on the cost of food as producers who raise poultry and beef on feed grain see their feed costs rise dramatically and are forced to pass this on to the consumer. If all the corn grown in the United States were diverted to fuel, only 12% of the U.S. energy needs would be met. Hence, finding other sources of fermentable cellulose, such as silage, waste products from wood, and grasses is essential if ethanol is to become a major fuel source.

The problem of energy is one of the greatest challenges ever to face the human race. Cheap and abundant energy—and ways to store it—will make possible realistic solutions to many of the world’s problems, such as poverty, the scarcity of food, and inadequate shelter. Increasingly expensive and scarce energy will lead to wars over limited resources and to environmental disaster. Biofuels will undoubtedly be only a part of the solution to the energy problem, but they will probably fill an important niche in the ultimate solution. Although it is tempting to be discouraged by the vast scale of this problem, it is encouraging to realize that immense opportunities undoubtedly await the scientifically trained citizens who can think in new, creative ways about the solutions.
**Methanol and Methyl tert-Butyl Ether**  Methanol is formed from a mixture of carbon monoxide and hydrogen, called synthesis gas, at high temperature over special catalysts.

\[
\begin{align*}
\text{CO} + \text{H}_2 & \xrightarrow{250-400 \degree C} \text{Cr-Zn catalyst} \rightarrow \text{CH}_3\text{OH} \\
\text{(synthesis gas)} & \xrightarrow{100-600 \text{ atm}} \text{methanol}
\end{align*}
\]

(8.38)

Synthesis gas comes from the partial oxidation of methane, which is, in turn, derived from the cracking of hydrocarbons (Sec. 5.8) or from the gasification of coal. As oil supplies dwindle, coal will assume increasing importance as a fossil fuel and could become a major source for methane. Methane produced by fermentation of biological waste can also provide a link for methyl alcohol production to biofuels.

In 2005, 10.7 billion gallons of methanol was produced globally, and 0.7 billion gallons was produced in the United States. Important uses of methanol include its oxidation to formaldehyde (H\(_2\)C═O) and its reaction with carbon monoxide over special catalysts to give acetic acid (CH\(_3\)CO\(_2\)H).

In the 1990s, methanol became an important compound in the fight against urban automotive air pollution. Prior to 1990, efforts to control automotive air pollution were focused on the automobile itself—thus the “catalytic converter.” In 1990, a new strategy for reducing automotive air pollution was mandated by the Clean Air Act amendments: to add chemicals (“additives”) to gasoline itself. Chief among these additives were the so-called “oxygenates,” and the two most important of these were ethanol and methyl tert-butyl ether (MTBE). Methanol is one of the two starting materials in the industrial synthesis of MTBE.

\[
\begin{align*}
\text{H}_3\text{C} & \xrightarrow{\text{H}_2\text{SO}_4} \text{OCH}_3 \\
\text{C}═\text{CH}_2 + \text{CH}_3\text{OH} & \rightarrow \text{H}_3\text{C}—\text{C}—\text{CH}_3
\end{align*}
\]

(8.39)

The use of MTBE in gasoline significantly reduced urban air pollution from automobile exhausts. It rapidly became one of the top ten industrial organic chemicals, and it took methanol along for the ride. New methanol plants were built to feed the demand for MTBE. Then trouble started for MTBE. It was found in groundwater in California and Maine, and the source of the chemical was leakage from underground storage tanks. An advisory panel of the Environmental Protection Agency recommended in August 1999 that Congress move to substantially reduce the use of MTBE in gasoline. A controversy developed about whether MTBE should be banned, but California mandated a phaseout by 2002. Many other states followed suit, and it appears that MTBE will be completely phased out as a gasoline additive, leaving ethanol as the sole oxygenate used in gasoline. Ethanol producers are happy with this turn of events, but methanol producers were left with excess capacity. Methanol production in the U.S. has decreased by almost seven-fold in the last eight years. About 20% of the methanol produced is still used to make MTBE, but this use will decrease in importance as MTBE is phased out.

A bright spot in methanol’s future may be its use in the production of biodiesel fuel. With an octane rating of 116, methanol itself also has a largely unrealized potential for use as a motor fuel. (It has been used as a fuel in Formula-One racing engines for years.)

**Ethylene Oxide and Ethylene Glycol**  Ethylene oxide, produced by oxidation of ethylene over a silver catalyst, is one of the most important industrial derivatives of ethylene:
The worldwide annual production of ethylene oxide is about 40 billion pounds; about 9 billion pounds of ethylene oxide is produced annually in the United States.

The most important single use of ethylene oxide is its reaction with water to give ethylene glycol:

$$2 \text{H}_2\text{C}\equiv\text{CH}_2 + \text{O}_2 \xrightarrow{\text{Ag (catalyst)}} \text{H}_2\text{C}-\text{O}-\text{CH}_2$$

The ethylene oxide

(8.40)

Of the world production of ethylene glycol, 53% is used as a starting material for polyester fibers and films and 11% as automotive antifreeze. Of the world ethylene glycol production of 30.5 billion pounds, about 8 billion pounds is produced annually in the United States.

D. Safety Hazards of Ethers

Because diethyl ether and tetrahydrofuran (THF) are so commonly used in the laboratory, it is important to appreciate two safety hazards generally associated with the use of these ethers. The first is peroxide formation. On standing in air, ethers undergo autoxidation, the spontaneous oxidation by oxygen in air. Samples of ethers can accumulate dangerous quantities of explosive peroxides and hydroperoxides by autoxidation.

$$\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{O}-\text{CH}-\text{CH}_3 \rightarrow \text{other polymeric peroxides}$$

(8.42)

These peroxides can form by free-radical processes in samples of anhydrous diethyl ether, THF, and other ethers within less than two weeks. For this reason, some ethers are sold with small amounts of free-radical inhibitors, which can be removed by distilling the ether. Because peroxides are particularly explosive when heated, it is a good practice not to distill ethers to dryness. Peroxides in an ether can be detected by shaking a portion of the ether with 10% aqueous potassium iodide solution. If peroxides are present, they oxidize the iodide to iodine, which imparts a yellow tinge to the solution. Small amounts of peroxides can be removed by distillation of the ethers from lithium aluminum hydride (LiAlH$_4$), which both reduces the peroxides and removes contaminating water and alcohols.

The second ether hazard is the high flammability of diethyl ether, the ether most commonly used in the laboratory. Its flammability is indicated by its very low flash point of $-45^\circ$C. The flash point of a material is the minimum temperature at which it is ignited by a small flame.
Organic compounds are named by both common and substitutive nomenclature. In substitutive nomenclature, the name is based on the principal group and the principal chain. The principal group, specified by priority, is cited as a suffix in the name. Other groups are cited as substituents. Hydroxy (—OH) and thiol (—SH) groups can be cited as principal groups. Halogens, alkoxy (—OR) groups, and alkylthio (—SR) groups are always cited as substituents.

The noncovalent association of molecules in the liquid state raises their boiling points. Such molecular association can result from hydrogen bonding; attractive van der Waals forces, which are greatest for larger, more extended molecules; and the interaction of dipoles associated with polar molecules.

Alcohols and thiols are weakly acidic. The conjugate bases of alcohols are called alkoxides, or alcoholates; and the conjugate bases of thiols are called mercaptides, or thiolates.

Typical primary alcohols have $pK_a$ values near 15–16 in aqueous solution. The acidity of alcohols in solution is reduced (the $pK_a$ is increased) by branching near the —OH group and increased by electron-withdrawing substituents. Alkoxides are formed by the reaction of alcohols with strong bases such as sodium hydride (NaH) or by reaction with alkali metals.

Typical thiols have $pK_a$ values near 10–11. Solutions of thiolates can be formed by the reaction of thiols with NaOH in alcohol solvents.

Alcohols, thiols, and ethers are weak Bønsted bases and react with strong acids to form positively charged conjugate-acid cations that have negative $pK_a$ values. The Lewis basicities of ethers account for their formation of stable complexes with Lewis acids such as boron compounds and Grignard reagents.

A solvent is classified as protic or aprotic, depending on its ability to donate hydrogen bonds; polar or apolar, depending on the magnitude of its dielectric constant; and donor or nondonor, depending on its ability to act as a Lewis base.

The solubilities of covalent compounds follow the “like-dissolves-like” rule.

The high dielectric constant of a polar solvent contributes to the solubility of an ionic compound by reducing the attractions between oppositely charged ions. Ionic solubility is also enhanced by donor interactions, charge–dipole interactions, and hydrogen-bonding interactions of an ion with solvent molecules in its solvation shell.

Crown ethers, cryptands, and other ionophores form complexes with cations by creating artificial solvation shells for them.

Alkyl halides react with magnesium metal to give Grignard reagents; alkyl halides react with lithium to yield organolithium reagents. Both types of reagents behave as strong Bønsted bases and react readily with acids, including water and alcohols, to give alkyl halides.

Alkanes react with bromine and chlorine in the presence of heat or light in free-radical substitution reactions to give alkyl halides.