

## CHAPTER 14

### ORGANOMETALLIC COMPOUNDS

**O**rganometallic compounds are compounds that have a carbon–metal bond; they lie at the place where organic and inorganic chemistry meet. You are already familiar with at least one organometallic compound, sodium acetylide ( $\text{NaC}\equiv\text{CH}$ ), which has an ionic bond between carbon and sodium. But just because a compound contains both a metal and carbon isn't enough to classify it as organometallic. Like sodium acetylide, sodium methoxide ( $\text{NaOCH}_3$ ) is an ionic compound. Unlike sodium acetylide, however, the negative charge in sodium methoxide resides on oxygen, not carbon.

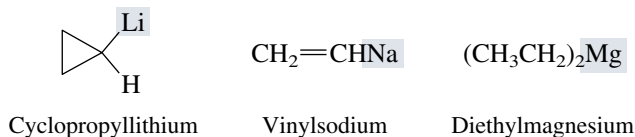


The properties of organometallic compounds are much different from those of the other classes we have studied to this point. Most important, many organometallic compounds are powerful sources of nucleophilic carbon, something that makes them especially valuable to the synthetic organic chemist. For example, the preparation of alkynes by the reaction of sodium acetylide with alkyl halides (Section 9.6) depends on the presence of a negatively charged, nucleophilic carbon in acetylide ion.

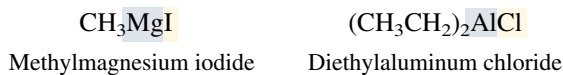
Synthetic procedures that use organometallic reagents are among the most important methods for carbon–carbon bond formation in organic chemistry. In this chapter you will learn how to prepare organic derivatives of lithium, magnesium, copper, and zinc and see how their novel properties can be used in organic synthesis. We will also finish the story of polyethylene and polypropylene begun in Chapter 6 and continued in Chapter 7 to see the unique way that organometallic compounds catalyze alkene polymerization.

## 14.1 ORGANOMETALLIC NOMENCLATURE

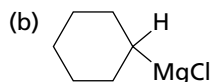
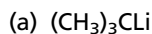
Organometallic compounds are named as substituted derivatives of metals. The metal is the base name, and the attached alkyl groups are identified by the appropriate prefix.



When the metal bears a substituent other than carbon, the substituent is treated as if it were an anion and named separately.



**PROBLEM 14.1** Both of the following organometallic reagents will be encountered later in this chapter. Suggest a suitable name for each.



**SAMPLE SOLUTION** (a) The metal lithium provides the base name for  $(\text{CH}_3)_3\text{CLi}$ . The alkyl group to which lithium is bonded is *tert*-butyl, and so the name of this organometallic compound is *tert*-butyllithium. An alternative, equally correct name is 1,1-dimethylethyllithium.

An exception to this type of nomenclature is  $\text{NaC}\equiv\text{CH}$ , which is normally referred to as *sodium acetylide*. Both sodium acetylide and ethynylsodium are acceptable IUPAC names.

## 14.2 CARBON–METAL BONDS IN ORGANOMETALLIC COMPOUNDS

With an electronegativity of 2.5 (Table 14.1), carbon is neither strongly electropositive nor strongly electronegative. When carbon is bonded to an element more electronegative than itself, such as oxygen or chlorine, the electron distribution in the bond is polarized

**TABLE 14.1** Electronegativities of Some Representative Elements

Element	Electronegativity
F	4.0
O	3.5
Cl	3.0
N	3.0
C	2.5
H	2.1
Cu	1.9
Zn	1.6
Al	1.5
Mg	1.2
Li	1.0
Na	0.9
K	0.8

so that carbon is slightly positive and the more electronegative atom is slightly negative. Conversely, when carbon is bonded to a less electronegative element, such as a metal, the electrons in the bond are more strongly attracted toward carbon.

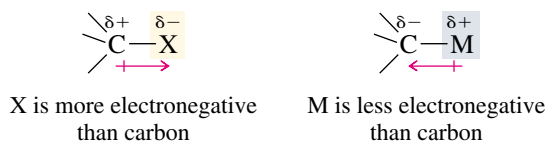
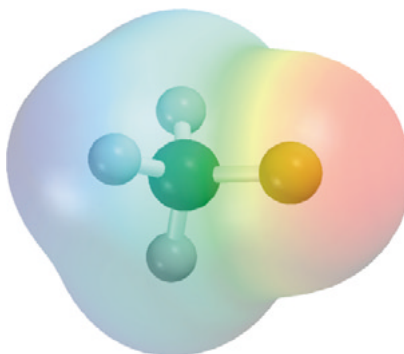
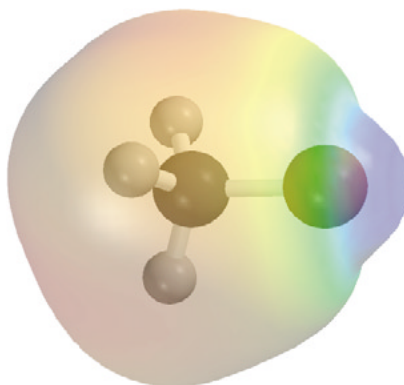


Figure 14.1 uses electrostatic potential maps to show how different the electron distribution is between methyl fluoride ( $\text{CH}_3\text{F}$ ) and methyllithium ( $\text{CH}_3\text{Li}$ ).

An anion that contains a negatively charged carbon is referred to as a **carbanion**. Covalently bonded organometallic compounds are said to have *carbanionic character*. As the metal becomes more electropositive, the ionic character of the carbon–metal bond becomes more pronounced. Organosodium and organopotassium compounds have ionic carbon–metal bonds; organolithium and organomagnesium compounds tend to have covalent, but rather polar, carbon–metal bonds with significant carbanionic character. *It is the carbanionic character of such compounds that is responsible for their usefulness as synthetic reagents.*



(a) Methyl fluoride



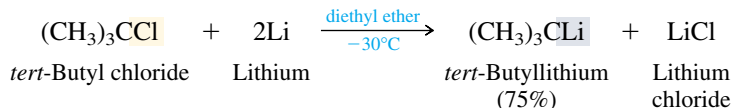
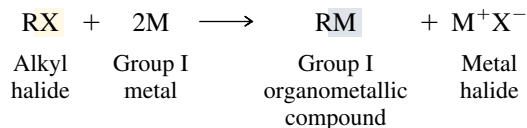
(b) Methyllithium

**FIGURE 14.1** Electrostatic potential maps of (a) methyl fluoride and of (b) methyllithium. The electron distribution is reversed in the two compounds. Carbon is electron-poor (*blue*) in methyl fluoride, but electron-rich (*red*) in methyllithium.



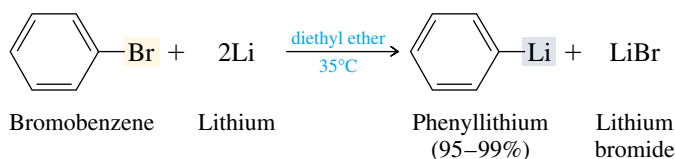
## 14.3 PREPARATION OF ORGANOLITHIUM COMPOUNDS

Before we describe the applications of organometallic reagents to organic synthesis, let us examine their preparation. Organolithium compounds and other Group I organometallic compounds are prepared by the reaction of an alkyl halide with the appropriate metal.



The alkyl halide can be primary, secondary, or tertiary. Alkyl iodides are the most reactive, followed by bromides, then chlorides. Fluorides are relatively unreactive.

Unlike elimination and nucleophilic substitution reactions, formation of organolithium compounds does not require that the halogen be bonded to  $sp^3$ -hybridized carbon. Compounds such as vinyl halides and aryl halides, in which the halogen is bonded to  $sp^2$ -hybridized carbon, react in the same way as alkyl halides, but at somewhat slower rates.



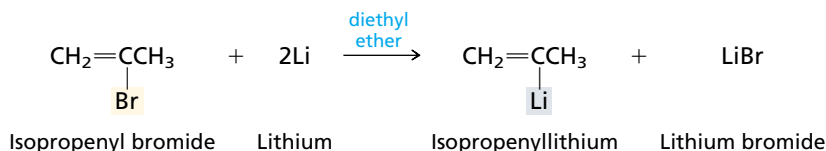
Organolithium compounds are sometimes prepared in hydrocarbon solvents such as pentane and hexane, but normally diethyl ether is used. *It is especially important that the solvent be anhydrous.* Even trace amounts of water or alcohols react with lithium to form insoluble lithium hydroxide or lithium alkoxides that coat the surface of the metal and prevent it from reacting with the alkyl halide. Furthermore, organolithium reagents are strong bases and react rapidly with even weak proton sources to form hydrocarbons. We shall discuss this property of organolithium reagents in Section 14.5.

**PROBLEM 14.2** Write an equation showing the formation of each of the following from the appropriate bromide:

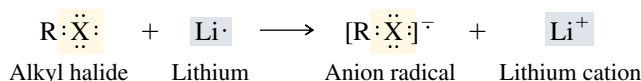
(a) Isopropenyllithium

(b) sec-Butyllithium

**SAMPLE SOLUTION** (a) In the preparation of organolithium compounds from organic halides, lithium becomes bonded to the carbon that bore the halogen. Therefore, isopropenyllithium must arise from isopropenyl bromide.

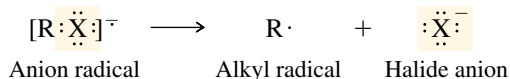


Reaction with an alkyl halide takes place at the metal surface. In the first step, an electron is transferred from the metal to the alkyl halide.

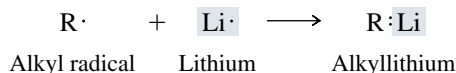


The reaction of an alkyl halide with lithium was cited earlier (Section 2.16) as an example of an *oxidation-reduction*. Group I metals are powerful reducing agents.

Having gained one electron, the alkyl halide is now negatively charged and has an odd number of electrons. It is an *anion radical*. The extra electron occupies an antibonding orbital. This anion radical fragments to an alkyl radical and a halide anion.



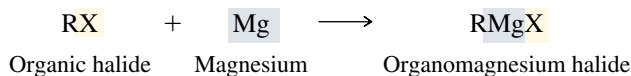
Following fragmentation, the alkyl radical rapidly combines with a lithium atom to form the organometallic compound.



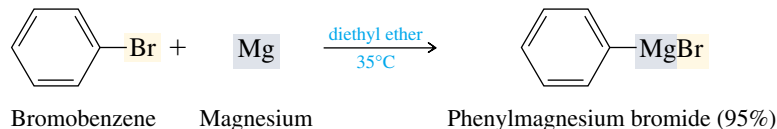
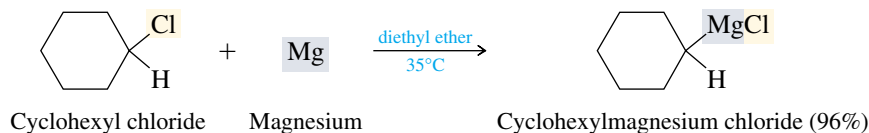
#### 14.4 PREPARATION OF ORGANOMAGNESIUM COMPOUNDS: GRIGNARD REAGENTS

The most important organometallic reagents in organic chemistry are organomagnesium compounds. They are called **Grignard reagents** after the French chemist Victor Grignard. Grignard developed efficient methods for the preparation of organic derivatives of magnesium and demonstrated their application in the synthesis of alcohols. For these achievements he was a coreipient of the 1912 Nobel Prize in chemistry.

Grignard reagents are prepared from organic halides by reaction with magnesium, a Group II metal.

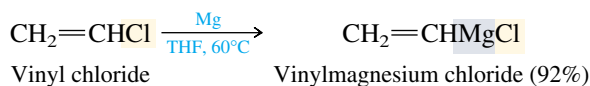


(R may be methyl or primary, secondary, or tertiary alkyl; it may also be a cycloalkyl, alkenyl, or aryl group.)



Anhydrous diethyl ether is the customary solvent used when preparing organomagnesium compounds. Sometimes the reaction does not begin readily, but once started, it is exothermic and maintains the temperature of the reaction mixture at the boiling point of diethyl ether (35°C).

The order of halide reactivity is I > Br > Cl > F, and alkyl halides are more reactive than aryl and vinyl halides. Indeed, aryl and vinyl chlorides do not form Grignard reagents in diethyl ether. When more vigorous reaction conditions are required, tetrahydrofuran (THF) is used as the solvent.



Grignard shared the prize with Paul Sabatier, who, as was mentioned in Chapter 6, showed that finely divided nickel could be used to catalyze the hydrogenation of alkenes.

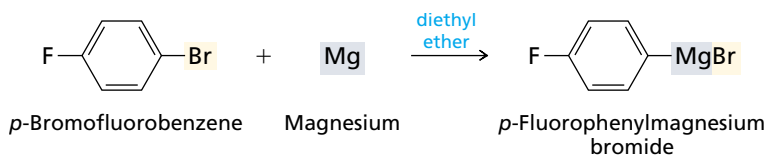
Recall the structure of tetrahydrofuran from Section 3.15:



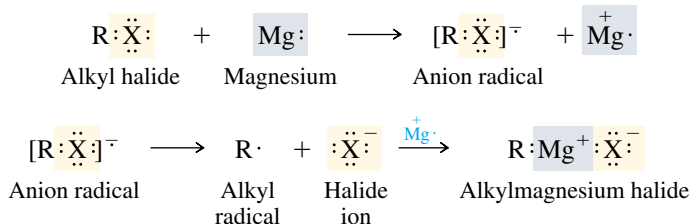
**PROBLEM 14.3** Write the structure of the Grignard reagent formed from each of the following compounds on reaction with magnesium in diethyl ether:

- (a) *p*-Bromofluorobenzene                      (c) Iodocyclobutane  
 (b) Allyl chloride                                      (d) 1-Bromocyclohexene

**SAMPLE SOLUTION** (a) Of the two halogen substituents on the aromatic ring, bromine reacts much faster than fluorine with magnesium. Therefore, fluorine is left intact on the ring, while the carbon–bromine bond is converted to a carbon–magnesium bond.



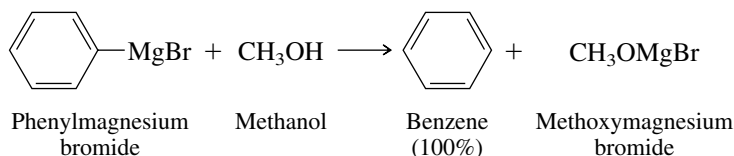
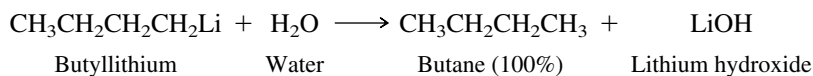
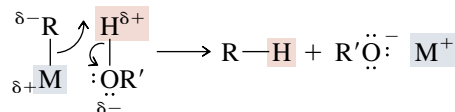
The formation of a Grignard reagent is analogous to that of organolithium reagents except that each magnesium atom can participate in two separate one-electron transfer steps:



Organolithium and organomagnesium compounds find their chief use in the preparation of alcohols by reaction with aldehydes and ketones. Before discussing these reactions, let us first examine the reactions of these organometallic compounds with proton donors.

## 14.5 ORGANOLITHIUM AND ORGANOMAGNESIUM COMPOUNDS AS BRØNSTED BASES

Organolithium and organomagnesium compounds are stable species when prepared in suitable solvents such as diethyl ether. They are strongly basic, however, and react instantly with proton donors even as weakly acidic as water and alcohols. A proton is transferred from the hydroxyl group to the negatively polarized carbon of the organometallic compound to form a hydrocarbon.



Because of their basicity organolithium compounds and Grignard reagents cannot be prepared or used in the presence of any material that bears a hydroxyl group. Nor are these reagents compatible with —NH or —SH groups, which can also convert an organolithium or organomagnesium compound to a hydrocarbon by proton transfer.

The carbon–metal bonds of organolithium and organomagnesium compounds have appreciable carbanionic character. Carbanions rank among the strongest bases that we'll see in this text. Their conjugate acids are hydrocarbons—very weak acids indeed. The equilibrium constants  $K_a$  for ionization of hydrocarbons are much smaller than the  $K_a$ 's for water and alcohols.

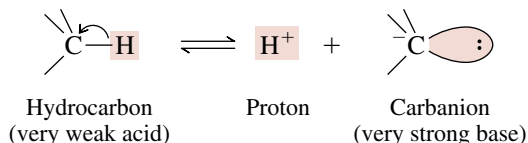
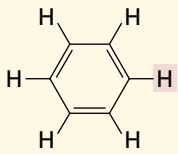
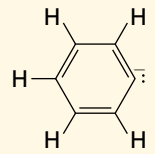


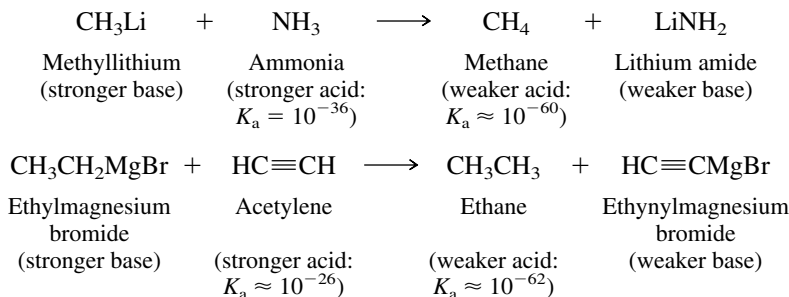
Table 14.2 presents some approximate data for the acid strengths of representative hydrocarbons.

Acidity increases in progressing from the top of Table 14.2 to the bottom. An acid will transfer a proton to the conjugate base of any acid above it in the table. Organolithium compounds and Grignard reagents act like carbanions and will abstract a proton from any substance more acidic than a hydrocarbon. Thus, N—H groups and terminal alkynes ( $\text{RC}\equiv\text{C—H}$ ) are converted to their conjugate bases by proton transfer to organolithium and organomagnesium compounds.

**TABLE 14.2** Approximate Acidities of Some Hydrocarbons and Reference Materials

Compound	Formula*	$K_a$	$\text{p}K_a$	Conjugate base
2-Methylpropane	$(\text{CH}_3)_3\text{C—H}$	$10^{-71}$	71	$(\text{CH}_3)_3\text{C}^-$
Ethane	$\text{CH}_3\text{CH}_2\text{—H}$	$10^{-62}$	62	$\text{CH}_3\text{CH}_2^-$
Methane	$\text{CH}_3\text{—H}$	$10^{-60}$	60	$\text{H}_3\text{C}^-$
Ethylene	$\text{CH}_2=\text{CH—H}$	$10^{-45}$	45	$\text{CH}_2=\text{CH}^-$
Benzene		$10^{-43}$	43	
Ammonia	$\text{H}_2\text{N—H}$	$10^{-36}$	36	$\text{H}_2\text{N}^-$
Acetylene	$\text{HC}\equiv\text{C—H}$	$10^{-26}$	26	$\text{HC}\equiv\text{C}^-$
Ethanol	$\text{CH}_3\text{CH}_2\text{O—H}$	$10^{-16}$	16	$\text{CH}_3\text{CH}_2\text{O}^-$
Water	$\text{HO—H}$	$1.8 \times 10^{-16}$	15.7	$\text{HO}^-$

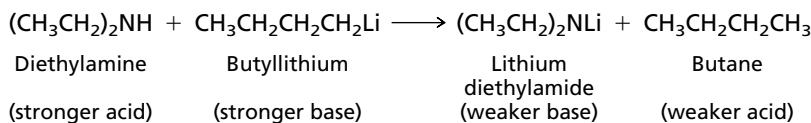
\*The acidic proton in each compound is shaded in red.



**PROBLEM 14.4** Butyllithium is commercially available and is frequently used by organic chemists as a strong base. Show how you could use butyllithium to prepare solutions containing

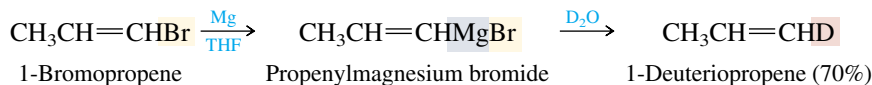
- Lithium diethylamide,  $(\text{CH}_3\text{CH}_2)_2\text{NLi}$
- Lithium 1-hexanolate,  $\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OLi}$
- Lithium benzenethiolate,  $\text{C}_6\text{H}_5\text{SLi}$

**SAMPLE SOLUTION** When butyllithium is used as a base, it abstracts a proton, in this case a proton attached to nitrogen. The source of lithium diethylamide must be diethylamine.



Although diethylamine is not specifically listed in Table 14.2, its strength as an acid ( $K_a \approx 10^{-36}$ ) is, as might be expected, similar to that of ammonia.

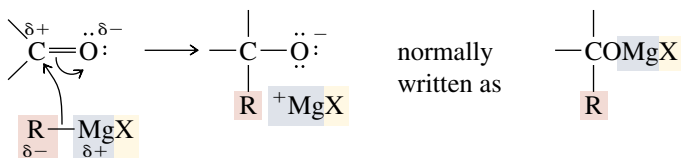
It is sometimes necessary in a synthesis to reduce an alkyl halide to a hydrocarbon. In such cases converting the halide to a Grignard reagent and then adding water or an alcohol as a proton source is a satisfactory procedure. Adding  $\text{D}_2\text{O}$  to a Grignard reagent is a commonly used method for introducing deuterium into a molecule at a specific location.



Deuterium is the mass 2 isotope of hydrogen. Deuterium oxide ( $\text{D}_2\text{O}$ ) is sometimes called "heavy water."

## 14.6 SYNTHESIS OF ALCOHOLS USING GRIGNARD REAGENTS

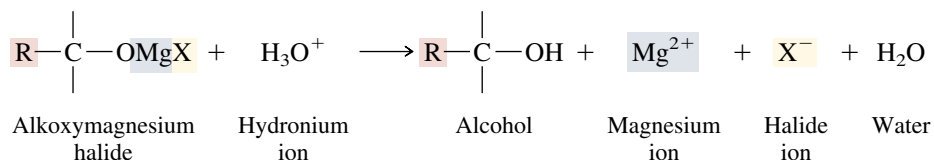
The main synthetic application of Grignard reagents is their reaction with certain carbonyl-containing compounds to produce alcohols. Carbon-carbon bond formation is rapid and exothermic when a Grignard reagent reacts with an aldehyde or ketone.



A carbonyl group is quite polar, and its carbon atom is electrophilic. Grignard reagents are nucleophilic and add to carbonyl groups, forming a new carbon-carbon bond. This

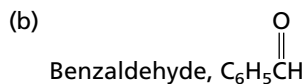
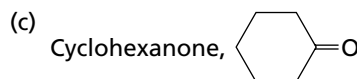


addition step leads to an alkoxymagnesium halide, which in the second stage of the synthesis is converted to an alcohol by adding aqueous acid.

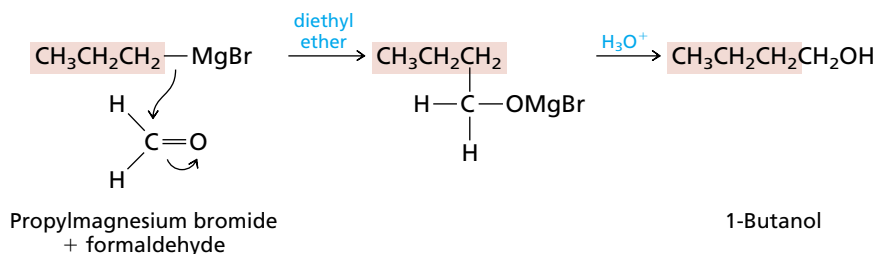


The type of alcohol produced depends on the carbonyl compound. Substituents present on the carbonyl group of an aldehyde or ketone stay there—they become substituents on the carbon that bears the hydroxyl group in the product. Thus as shown in Table 14.3, formaldehyde reacts with Grignard reagents to yield primary alcohols, aldehydes yield secondary alcohols, and ketones yield tertiary alcohols.

**PROBLEM 14.5** Write the structure of the product of the reaction of propylmagnesium bromide with each of the following. Assume that the reactions are worked up by the addition of dilute aqueous acid.



**SAMPLE SOLUTION** (a) Grignard reagents react with formaldehyde to give primary alcohols having one more carbon atom than the alkyl halide from which the Grignard reagent was prepared. The product is 1-butanol.



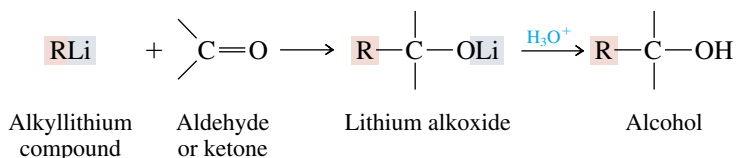
An ability to form carbon–carbon bonds is fundamental to organic synthesis. The addition of Grignard reagents to aldehydes and ketones is one of the most frequently used reactions in synthetic organic chemistry. Not only does it permit the extension of carbon chains, but since the product is an alcohol, a wide variety of subsequent functional group transformations is possible.

## 14.7 SYNTHESIS OF ALCOHOLS USING ORGANOLITHIUM REAGENTS

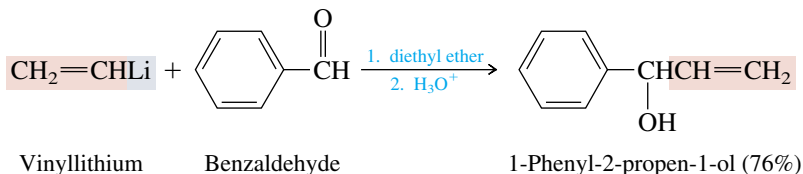
Organolithium reagents react with carbonyl groups in the same way that Grignard reagents do. In their reactions with aldehydes and ketones, organolithium reagents are somewhat more reactive than Grignard reagents.

TABLE 14.3 Reactions of Grignard Reagents with Aldehydes and Ketones

Reaction	General equation and specific example				
<b>Reaction with formaldehyde</b> Grignard reagents react with formaldehyde ( $\text{CH}_2=\text{O}$ ) to give <i>primary alcohols</i> having one more carbon than the Grignard reagent.	$\text{RMgX} + \text{HCHO} \xrightarrow{\text{diethyl ether}} \text{R}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\text{OMgX} \xrightarrow{\text{H}_3\text{O}^+} \text{R}-\underset{\text{H}}{\overset{\text{H}}{\text{C}}}-\text{OH}$	Grignard reagent	Formaldehyde	Primary alkoxy magnesium halide	Primary alcohol
		Cyclohexylmagnesium chloride	Formaldehyde		Cyclohexylmethanol (64–69%)
<b>Reaction with aldehydes</b> Grignard reagents react with aldehydes ( $\text{RCH}=\text{O}$ ) to give <i>secondary alcohols</i> .	$\text{RMgX} + \text{R}'\text{CHO} \xrightarrow{\text{diethyl ether}} \text{R}-\underset{\text{R}'}{\overset{\text{H}}{\text{C}}}-\text{OMgX} \xrightarrow{\text{H}_3\text{O}^+} \text{R}-\underset{\text{R}'}{\overset{\text{H}}{\text{C}}}-\text{OH}$	Grignard reagent	Aldehyde	Secondary alkoxy magnesium halide	Secondary alcohol
	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{MgBr} + \text{CH}_3\text{CHO} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \text{CH}_3(\text{CH}_2)_4\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_3$	Hexylmagnesium bromide	Ethanal (acetaldehyde)		2-Octanol (84%)
<b>Reaction with ketones</b> Grignard reagents react with ketones ( $\text{RCR}'\text{R}''$ ) to give <i>tertiary alcohols</i> .	$\text{RMgX} + \text{R}'\text{CR}'' \xrightarrow{\text{diethyl ether}} \text{R}-\underset{\text{R}'}{\overset{\text{R}''}{\text{C}}}-\text{OMgX} \xrightarrow{\text{H}_3\text{O}^+} \text{R}-\underset{\text{R}'}{\overset{\text{R}''}{\text{C}}}-\text{OH}$	Grignard reagent	Ketone	Tertiary alkoxy magnesium halide	Tertiary alcohol
	$\text{CH}_3\text{MgCl} + \text{Cyclopentanone} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \text{1-Methylcyclopentanol}$	Methylmagnesium chloride	Cyclopentanone		1-Methylcyclopentanol (62%)

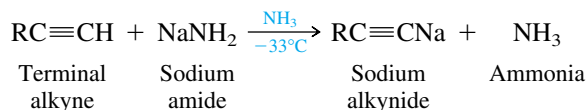


In this particular example, the product can be variously described as a *secondary* alcohol, a *benzylic* alcohol, and an *allylic* alcohol. Can you identify the structural reason for each classification?



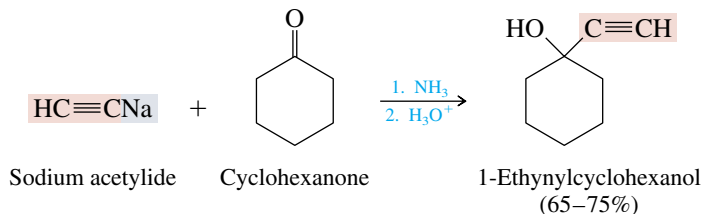
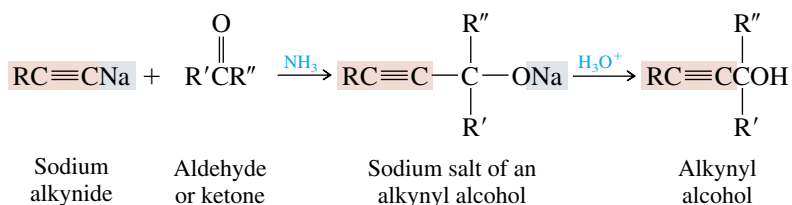
## 14.8 SYNTHESIS OF ACETYLENIC ALCOHOLS

The first organometallic compounds we encountered were compounds of the type  $\text{RC}\equiv\text{CNa}$  obtained by treatment of terminal alkynes with sodium amide in liquid ammonia (Section 9.6):

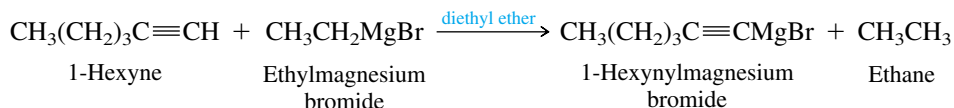


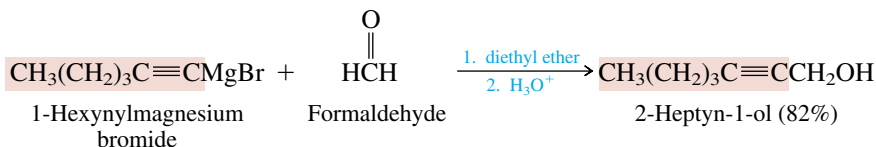
These compounds are sources of the nucleophilic anion  $\text{RC}\equiv\text{C}^-$ , and their reaction with primary alkyl halides provides an effective synthesis of alkynes (Section 9.6). The nucleophilicity of acetylide anions is also evident in their reactions with aldehydes and ketones, which are entirely analogous to those of Grignard and organolithium reagents.

These reactions are normally carried out in liquid ammonia because that is the solvent in which the sodium salt of the alkyne is prepared.



Acetylenic Grignard reagents of the type  $\text{RC}\equiv\text{CMgBr}$  are prepared, not from an acetylenic halide, but by an acid–base reaction in which a Grignard reagent abstracts a proton from a terminal alkyne.



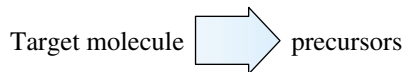


**PROBLEM 14.6** Write the equation for the reaction of 1-hexyne with ethylmagnesium bromide as if it involved ethyl anion ( $\text{CH}_3\text{CH}_2^-$ ) instead of  $\text{CH}_3\text{CH}_2\text{MgBr}$  and use curved arrows to represent the flow of electrons.

## 14.9 RETROSYNTHETIC ANALYSIS

In our earlier discussions of synthesis, we stressed the value of reasoning backward from the target molecule to suitable starting materials. A name for this process is *retrosynthetic analysis*. Organic chemists have employed this approach for many years, but the term was invented and a formal statement of its principles was set forth only relatively recently by E. J. Corey at Harvard University. Beginning in the 1960s, Corey began studies aimed at making the strategy of organic synthesis sufficiently systematic so that the power of electronic computers could be applied to assist synthetic planning.

A symbol used to indicate a retrosynthetic step is an open arrow written from product to suitable precursors or fragments of those precursors.



Often the precursor is not defined completely, but rather its chemical nature is emphasized by writing it as a species to which it is equivalent for synthetic purposes. Thus, a Grignard reagent or an organolithium reagent might be considered synthetically equivalent to a carbanion:

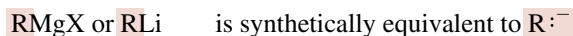
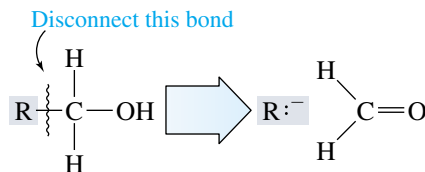


Figure 14.2 illustrates how retrosynthetic analysis can guide you in planning the synthesis of alcohols by identifying suitable Grignard reagent and carbonyl-containing precursors. In the first step, locate the carbon of the target alcohol that bears the hydroxyl group, remembering that this carbon originated in the  $\text{C}=\text{O}$  group. Next, as shown in Figure 14.2, step 2, mentally disconnect a bond between that carbon and one of its attached groups (other than hydrogen). The attached group is the group that is to be transferred from the Grignard reagent. Once you recognize these two structural fragments, the carbonyl partner and the carbanion that attacks it (Figure 14.2, step 3), you can readily determine the synthetic mode wherein a Grignard reagent is used as the synthetic equivalent of a carbanion (Figure 14.2, step 4).

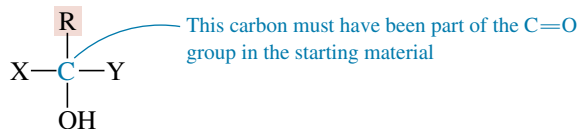
Primary alcohols, by this analysis, are seen to be the products of Grignard addition to formaldehyde:



Corey was honored with the 1990 Nobel Prize for his achievements in synthetic organic chemistry.

Problem 14.6 at the end of the preceding section introduced this idea with the suggestion that ethylmagnesium bromide be represented as ethyl anion.

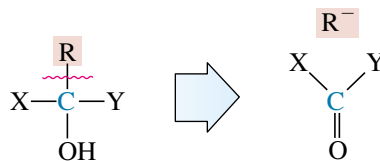
**Step 1:** Locate the hydroxyl-bearing carbon.



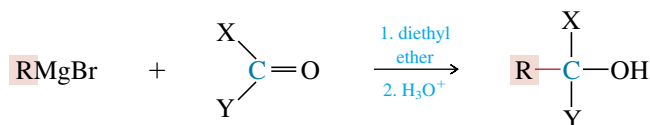
**Step 2:** Disconnect one of the organic substituents attached to the carbon that bears the hydroxyl group.



**Step 3:** Steps 1 and 2 reveal the carbonyl-containing substrate and the carbanionic fragment.

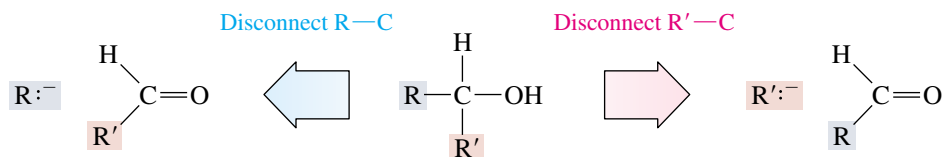


**Step 4:** Since a Grignard reagent may be considered as synthetically equivalent to a carbanion, this suggests the synthesis shown.

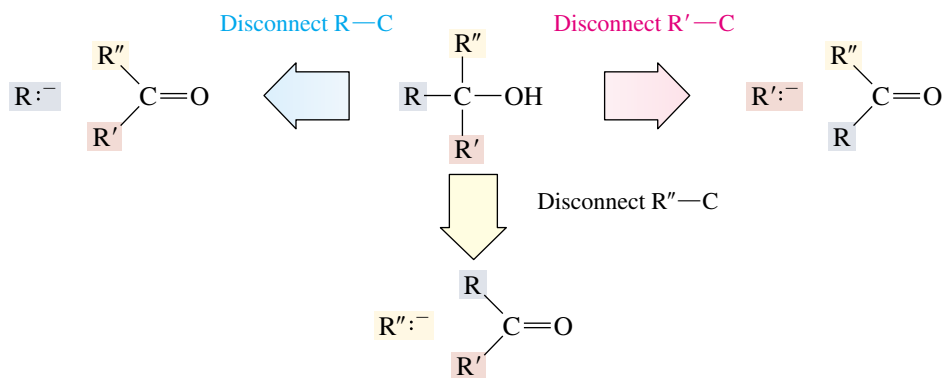


**FIGURE 14.2** A retrosynthetic analysis of alcohol preparation by way of the addition of a Grignard reagent to an aldehyde or ketone.

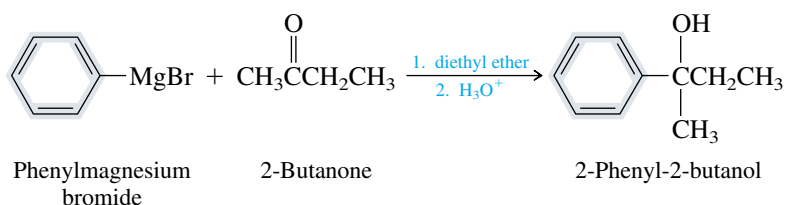
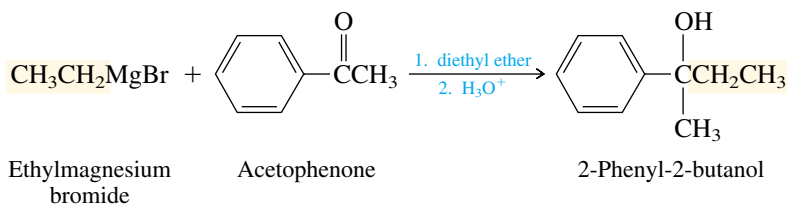
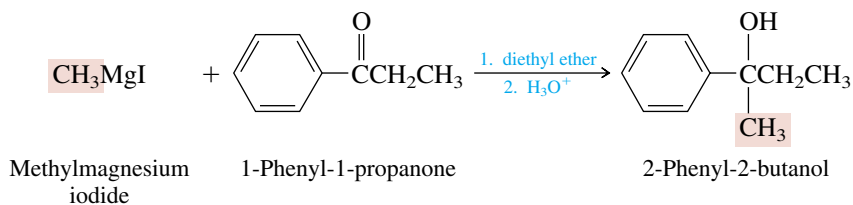
Secondary alcohols may be prepared by *two* different combinations of Grignard reagent and aldehyde:



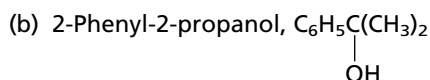
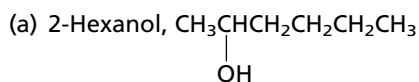
Three combinations of Grignard reagent and ketone give rise to tertiary alcohols:



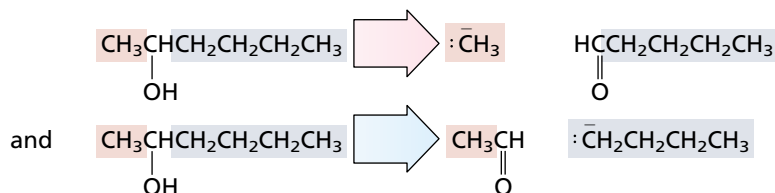
Usually, there is little to choose among the various routes leading to a particular target alcohol. For example, all three of the following combinations have been used to prepare the tertiary alcohol 2-phenyl-2-butanol:



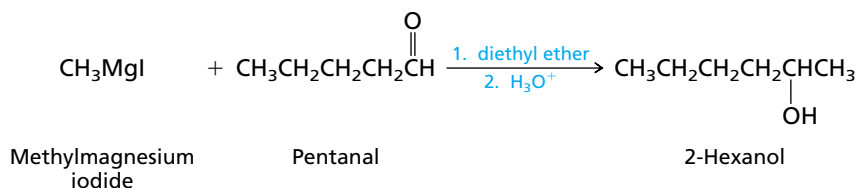
**PROBLEM 14.7** Suggest two ways in which each of the following alcohols might be prepared by using a Grignard reagent:



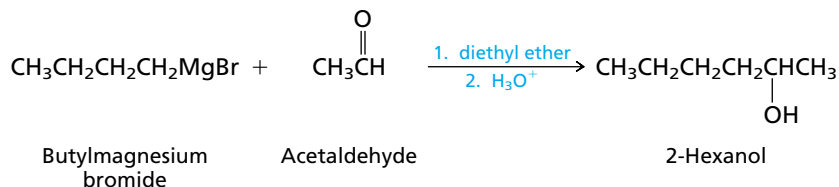
**SAMPLE SOLUTION** (a) Since 2-hexanol is a secondary alcohol, we consider the reaction of a Grignard reagent with an aldehyde. Disconnection of bonds to the hydroxyl-bearing carbon generates two pairs of structural fragments:



Therefore, one route involves the addition of a methyl Grignard reagent to a five-carbon aldehyde:



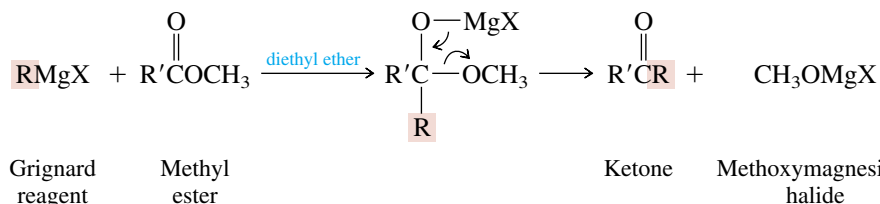
The other requires addition of a butylmagnesium halide to a two-carbon aldehyde:



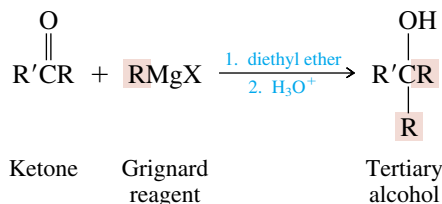
All that has been said in this section applies with equal force to the use of organolithium reagents in the synthesis of alcohols. Grignard reagents are one source of nucleophilic carbon; organolithium reagents are another. Both have substantial carbanionic character in their carbon–metal bonds and undergo the same kind of reaction with aldehydes and ketones.

### 14.10 PREPARATION OF TERTIARY ALCOHOLS FROM ESTERS AND GRIGNARD REAGENTS

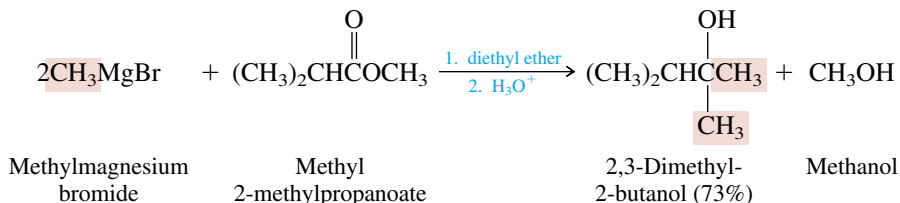
Tertiary alcohols can be prepared by a variation of the Grignard synthesis that employs an ester as the carbonyl component. Methyl and ethyl esters are readily available and are the types most often used. Two moles of a Grignard reagent are required per mole of ester; the first mole reacts with the ester, converting it to a ketone.



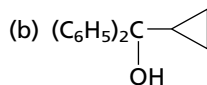
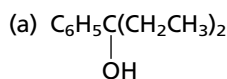
The ketone is not isolated, but reacts rapidly with the Grignard reagent to give, after adding aqueous acid, a tertiary alcohol. Ketones are more reactive than esters toward Grignard reagents, and so it is not normally possible to interrupt the reaction at the ketone stage even if only one equivalent of the Grignard reagent is used.



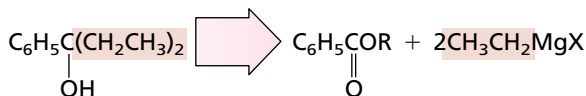
Two of the groups bonded to the hydroxyl-bearing carbon of the alcohol are the same because they are derived from the Grignard reagent. For example,



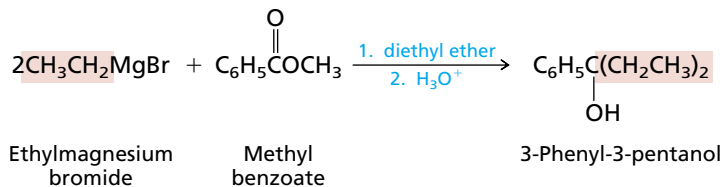
**PROBLEM 14.8** What combination of ester and Grignard reagent could you use to prepare each of the following tertiary alcohols?



**SAMPLE SOLUTION** (a) To apply the principles of retrosynthetic analysis to this case, we disconnect both ethyl groups from the tertiary carbon and identify them as arising from the Grignard reagent. The phenyl group originates in an ester of the type  $\text{C}_6\text{H}_5\text{CO}_2\text{R}$  (a benzoate ester).

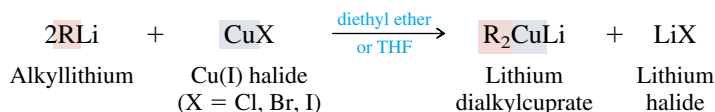


An appropriate synthesis would be



## 14.11 ALKANE SYNTHESIS USING ORGANOCOPPER REAGENTS

Organometallic compounds of copper have been known for a long time, but their versatility as reagents in synthetic organic chemistry has only recently been recognized. The most useful organocopper reagents are the lithium dialkylcuprates, which result when a copper(I) halide reacts with two equivalents of an alkyllithium in diethyl ether or tetrahydrofuran.

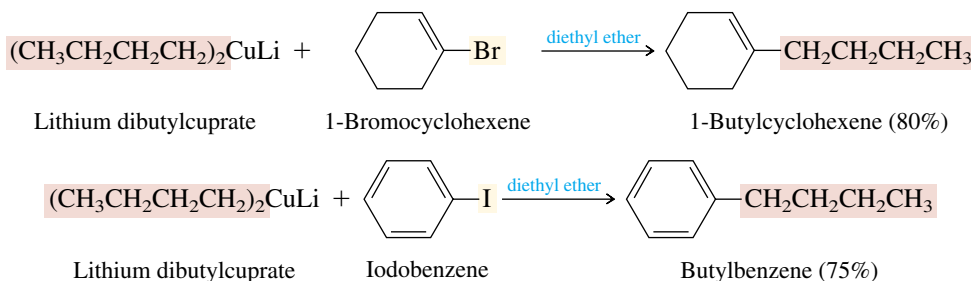


Copper(I) salts are also known as *cuprous* salts.





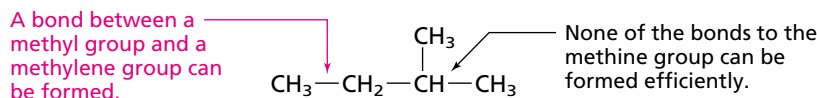
cuprates react with organic halogen compounds. Vinyl halides and aryl halides are known to be very unreactive toward nucleophilic attack, yet react with lithium dialkylcuprates:



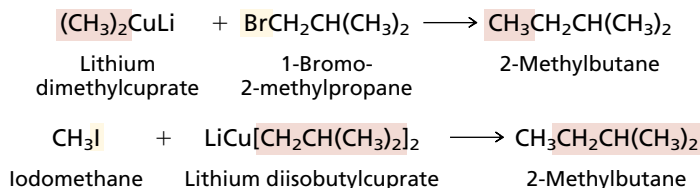
**PROBLEM 14.9** Suggest a combination of organic halide and cuprate reagent appropriate for the preparation of each of the following compounds:

- 2-Methylbutane
- 1,3,3-Trimethylcyclopentene

**SAMPLE SOLUTION** (a) First inspect the target molecule to see which bonds are capable of being formed by reaction of an alkyl halide and a cuprate, bearing in mind that neither the alkyl halide nor the alkyl group of the lithium dialkylcuprate should be secondary or tertiary.

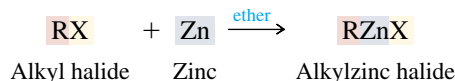


There are two combinations, both acceptable, that give the  $\text{CH}_3\text{-CH}_2$  bond:



## 14.12 AN ORGANOZINC REAGENT FOR CYCLOPROPANE SYNTHESIS

Zinc reacts with alkyl halides in a manner similar to that of magnesium.

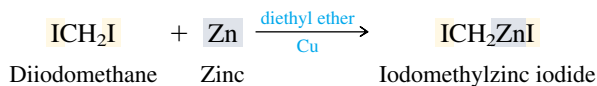


Organozinc reagents are not nearly as reactive toward aldehydes and ketones as Grignard reagents and organolithium compounds but are intermediates in certain reactions of alkyl halides.

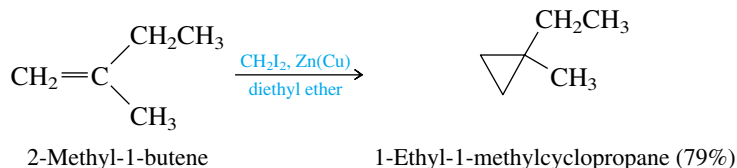
An organozinc compound that occupies a special niche in organic synthesis is *iodomethylzinc iodide* ( $\text{ICH}_2\text{ZnI}$ ), prepared by the reaction of zinc-copper couple  $[\text{Zn}(\text{Cu})$ , zinc that has had its surface activated with a little copper] with diiodomethane in ether.

Victor Grignard was led to study organomagnesium compounds because of earlier work he performed with organic derivatives of zinc.

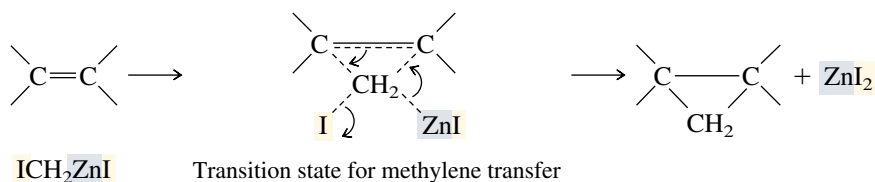
Iodomethylzinc iodide is known as the *Simmons–Smith reagent*, after Howard E. Simmons and Ronald D. Smith of Du Pont, who first described its use in the preparation of cyclopropanes.



What makes iodomethylzinc iodide such a useful reagent is that it reacts with alkenes to give cyclopropanes.



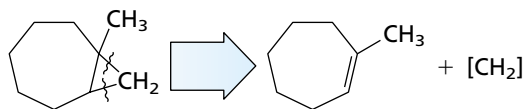
This reaction is called the *Simmons–Smith reaction* and is one of the few methods available for the synthesis of cyclopropanes. Mechanistically, the Simmons–Smith reaction seems to proceed by a single-step cycloaddition of a methylene ( $\text{CH}_2$ ) unit from iodomethylzinc iodide to the alkene:



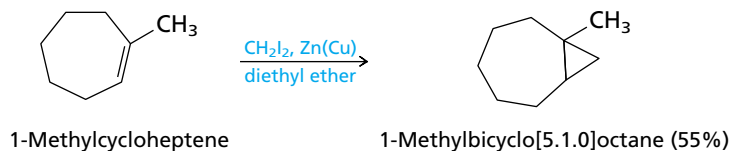
**PROBLEM 14.10** What alkenes would you choose as starting materials in order to prepare each of the following cyclopropane derivatives by reaction with iodomethylzinc iodide?



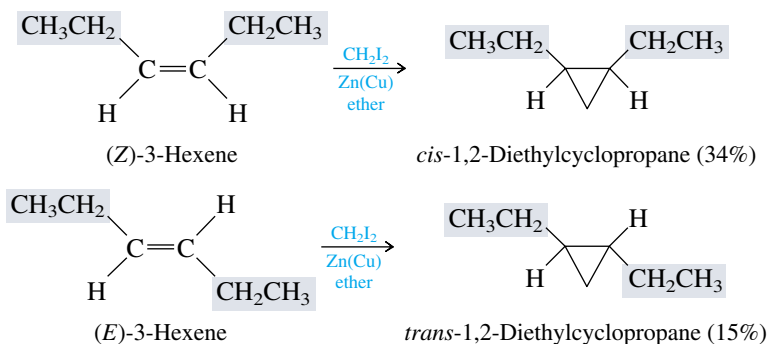
**SAMPLE SOLUTION** (a) In a cyclopropane synthesis using the Simmons–Smith reagent, you should remember that a  $\text{CH}_2$  unit is transferred. Therefore, retrosynthetically disconnect the bonds to a  $\text{CH}_2$  group of a three-membered ring to identify the starting alkene.



The complete synthesis is:



Methylene transfer from iodomethylzinc iodide is *stereospecific*. Substituents that were *cis* in the alkene remain *cis* in the cyclopropane.

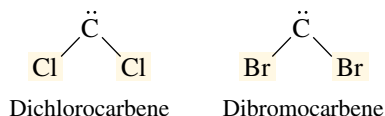


Yields in Simmons–Smith reactions are sometimes low. Nevertheless, since it often provides the only feasible route to a particular cyclopropane derivative, it is a valuable addition to the organic chemist’s store of synthetic methods.

### 14.13 CARBENES AND CARBENOIDS

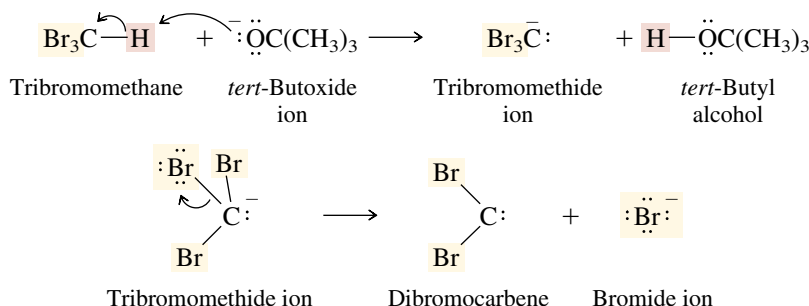
Iodomethylzinc iodide is often referred to as a **carbenoid**, meaning that it resembles a **carbene** in its chemical reactions. Carbenes are neutral molecules in which one of the carbon atoms has six valence electrons. Such carbons are *divalent*; they are directly bonded to only two other atoms and have no multiple bonds. Iodomethylzinc iodide reacts as if it were a source of the carbene  $\text{H}-\ddot{\text{C}}-\text{H}$ .

It is clear that free  $:\text{CH}_2$  is not involved in the Simmons–Smith reaction, but there is substantial evidence to indicate that carbenes are formed as intermediates in certain other reactions that convert alkenes to cyclopropanes. The most studied examples of these reactions involve dichlorocarbene and dibromocarbene.

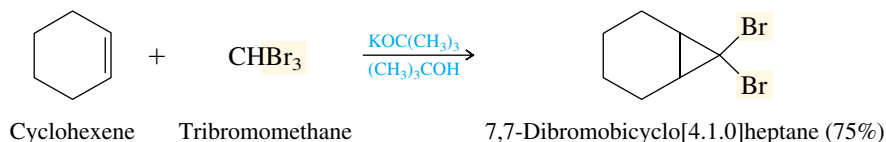


Carbenes are too reactive to be isolated and stored, but have been trapped in frozen argon for spectroscopic study at very low temperatures.

Dihalocarbenes are formed when trihalomethanes are treated with a strong base, such as potassium *tert*-butoxide. The trihalomethyl anion produced on proton abstraction dissociates to a dihalocarbene and a halide anion:



When generated in the presence of an alkene, dihalocarbenes undergo cycloaddition to the double bond to give dihalocyclopropanes:



The reaction of dihalocarbenes with alkenes is stereospecific, and syn addition is observed.

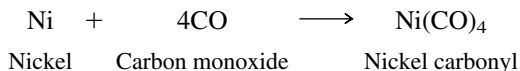
**PROBLEM 14.11** The syn stereochemistry of dibromocarbene cycloaddition was demonstrated in experiments using *cis*- and *trans*-2-butene. Give the structure of the product obtained from addition of dibromocarbene to each alkene.

The process in which a dihalocarbene is formed from a trihalomethane corresponds to an elimination in which a proton and a halide are lost from the same carbon. It is an  $\alpha$ -elimination proceeding via the organometallic intermediate  $K^+ [:\text{CX}_3]^-$ .

#### 14.14 TRANSITION-METAL ORGANOMETALLIC COMPOUNDS

A large number of organometallic compounds are based on transition metals. Examples include organic derivatives of iron, nickel, chromium, platinum, and rhodium. Many important industrial processes are catalyzed by transition metals or their complexes. Before we look at these processes, a few words about the structures of transition-metal complexes are in order.

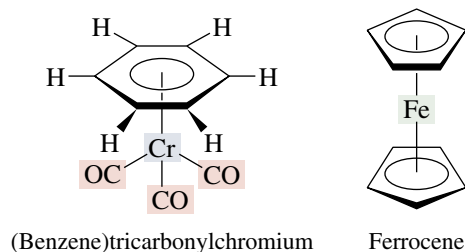
A transition-metal complex consists of a transition-metal atom or ion bearing attached groups called **ligands**. Essentially, anything attached to a metal is a ligand. A ligand can be an element ( $\text{O}_2$ ,  $\text{N}_2$ ), a compound ( $\text{NO}$ ), or an ion ( $\text{CN}^-$ ); it can be inorganic as in the examples just cited or it can be an organic ligand. Ligands differ in the number of electrons that they share with the transition metal to which they are attached. Carbon monoxide is a frequently encountered ligand in transition-metal complexes and contributes two electrons; it is best thought of in terms of the Lewis structure  $:\text{C}\equiv\overset{+}{\text{O}}:$  in which carbon is the reactive site. An example of a carbonyl complex of a transition metal is nickel carbonyl, a very toxic substance, which was first prepared over a hundred years ago and is an intermediate in the purification of nickel. It forms spontaneously when carbon monoxide is passed over elemental nickel.



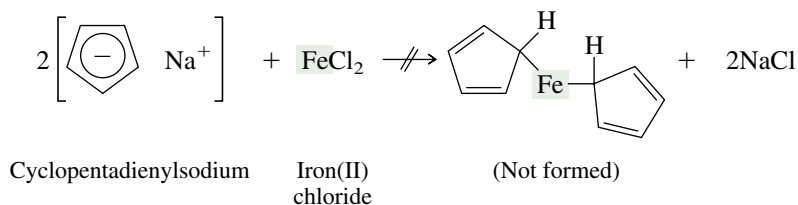
Many transition-metal complexes, including  $\text{Ni}(\text{CO})_4$ , obey what is called the **18-electron rule**, which is to transition-metal complexes as the octet rule is to main-group elements. It states that for transition-metal complexes, *the number of ligands that can be attached to a metal will be such that the sum of the electrons brought by the ligands plus the valence electrons of the metal equals 18*. With an atomic number of 28, nickel has the electron configuration  $[\text{Ar}]4s^23d^8$  (10 valence electrons). The 18-electron rule is satisfied by adding to these 10 the 8 electrons from four carbon monoxide ligands. A useful point to remember about the 18-electron rule when we discuss some reactions of transition-metal complexes is that if the number is less than 18, the metal is considered *coordinatively unsaturated* and can accept additional ligands.

**PROBLEM 14.12** Like nickel, iron reacts with carbon monoxide to form a compound having the formula  $\text{M}(\text{CO})_n$  that obeys the 18-electron rule. What is the value of  $n$  in the formula  $\text{Fe}(\text{CO})_n$ ?

Not all ligands use just two electrons to bond to transition metals. Chromium has the electron configuration  $[\text{Ar}]4s^23d^4$  (6 valence electrons) and needs 12 more to satisfy the 18-electron rule. In the compound (benzene)tricarbonylchromium, 6 of these 12 are the  $\pi$  electrons of the benzene ring; the remaining 6 are from the three carbonyl ligands.



Ferrocene has an even more interesting structure. A central iron is  $\pi$ -bonded to two cyclopentadienyl ligands in what is aptly described as a *sandwich*. It, too, obeys the 18-electron rule. Each cyclopentadienyl ligand contributes 5 electrons for a total of 10 and iron, with an electron configuration of  $[\text{Ar}]4s^23d^6$  contributes 8. Alternatively, ferrocene can be viewed as being derived from  $\text{Fe}^{2+}$  (6 valence electrons) and two aromatic cyclopentadienide rings (6 electrons each). Indeed, ferrocene was first prepared by adding iron(II) chloride to cyclopentadienylsodium. Instead of the expected  $\sigma$ -bonded species shown in the equation, ferrocene was formed.



After ferrocene, a large number of related molecules have been prepared—even some in which uranium is the metal. There is now an entire subset of transition-metal organometallic complexes known as **metallocenes** based on cyclopentadienide ligands. These compounds are not only structurally interesting, but many of them have useful applications as catalysts for industrial processes.

Naturally occurring compounds with carbon–metal bonds are very rare. The best example of such an organometallic compound is coenzyme  $\text{B}_{12}$ , which has a carbon–cobalt  $\sigma$  bond (Figure 14.3). Pernicious anemia results from a coenzyme  $\text{B}_{12}$  deficiency and can be treated by adding sources of cobalt to the diet. One source of cobalt is vitamin  $\text{B}_{12}$ , a compound structurally related to, but not identical with, coenzyme  $\text{B}_{12}$ .

## 14.15 ZIEGLER–NATTA CATALYSIS OF ALKENE POLYMERIZATION

In Section 6.21 we listed three main methods for polymerizing alkenes: cationic, free-radical, and coordination polymerization. In Section 7.15 we extended our knowledge of polymers to their stereochemical aspects by noting that although free-radical polymerization of propene gives atactic polypropylene, coordination polymerization produces a stereoregular polymer with superior physical properties. Because the catalysts responsible for coordination polymerization are organometallic compounds, we are now in a position to examine coordination polymerization in more detail, especially with respect to how the catalyst works.



The first page of this chapter displayed an electrostatic potential map of ferrocene. You may wish to view a molecular model of it on *Learning By Modeling*.

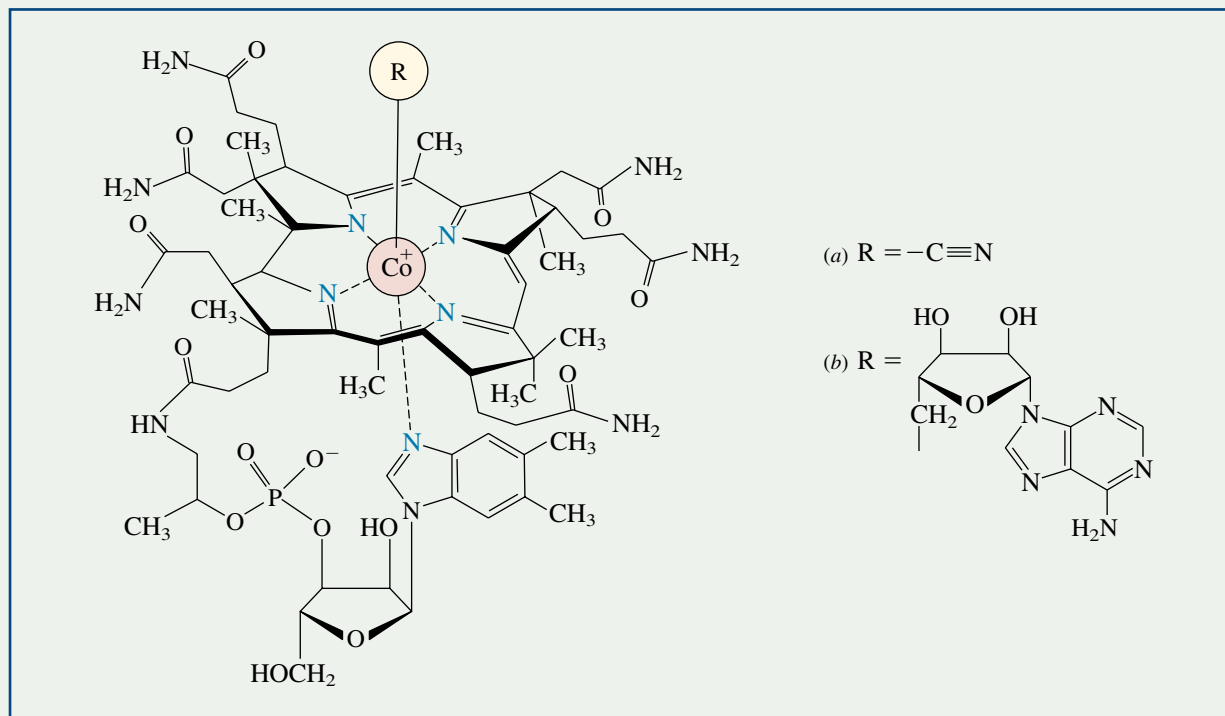
Cyclopentadienylsodium is ionic. Its anion is the cyclopentadienide ion, which contains six  $\pi$  electrons.

AN ORGANOMETALLIC COMPOUND THAT OCCURS NATURALLY: COENZYME B<sub>12</sub>

**P**ernicious anemia is a disease characterized, as are all anemias, by a deficiency of red blood cells. Unlike ordinary anemia, pernicious anemia does not respond to treatment with sources of iron, and before effective treatments were developed, was often fatal. Injection of liver extracts was one such treatment, and in 1948 chemists succeeded in isolating the "antipernicious anemia factor" from beef liver as a red crystalline compound, which they called **vitamin B<sub>12</sub>**. This compound had the formula C<sub>63</sub>H<sub>88</sub>CoN<sub>14</sub>O<sub>14</sub>P. Its complexity precluded structure determination by classical degradation techniques, and spectroscopic methods were too primitive to be of much help. The structure was solved by Dorothy Crowfoot Hodgkin of Oxford University in 1955 using X-ray diffraction techniques and is shown in Figure 14.3a. Structure determination by X-ray crystallography can be superficially considered as taking a photograph of a molecule with X-rays. It is a demanding task and earned Hodgkin the 1964 Nobel Prize in chemistry. Modern structural studies by X-ray crystal-

lography use computers to collect and analyze the diffraction data and take only a fraction of the time required years ago to solve the vitamin B<sub>12</sub> structure.

The structure of vitamin B<sub>12</sub> is interesting in that it contains a central cobalt atom that is surrounded by six atoms in an octahedral geometry. One substituent, the cyano (—CN) group, is what is known as an "artifact." It appears to be introduced into the molecule during the isolation process and leads to the synonym **cyanocobalamin** for vitamin B<sub>12</sub>. This material is used to treat pernicious anemia, but this is not the form in which it exerts its activity. The biologically active material is called **coenzyme B<sub>12</sub>** and differs from vitamin B<sub>12</sub> in the substituent attached to cobalt (Figure 14.3b). Coenzyme B<sub>12</sub> is the only known naturally occurring substance that has a carbon–metal bond. Moreover, coenzyme B<sub>12</sub> was discovered before any compound containing an alkyl group σ-bonded to cobalt had ever been isolated in the laboratory!



**FIGURE 14.3** The structures of (a) vitamin B<sub>12</sub> and (b) coenzyme B<sub>12</sub>.

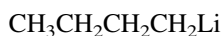




Ziegler had a working relationship with the Italian chemical company Montecatini, for which Giulio Natta of the Milan Polytechnic Institute was a consultant. When Natta used Ziegler's catalyst to polymerize propene, he discovered that the catalyst was not only effective but that it gave mainly isotactic polypropylene. (Recall from Section 7.15 that free-radical polymerization of propene gives atactic polypropylene.) Isotactic polypropylene has a higher melting point than the atactic form and can be drawn into fibers or molded into hard, durable materials. Before coordination polymerization was discovered by Ziegler and applied to propene by Natta, there was no polypropylene industry. Now, more than  $10^{10}$  pounds of it are prepared each year in the United States. Ziegler and Natta shared the 1963 Nobel Prize in chemistry: Ziegler for discovering novel catalytic systems for alkene polymerization and Natta for stereoregular polymerization.

### 14.16 SUMMARY

Section 14.1 Organometallic compounds contain a carbon–metal bond. They are named as alkyl (or aryl) derivatives of metals.

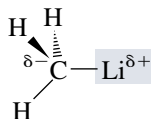


Butyllithium

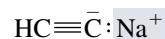


Phenylmagnesium bromide

Section 14.2 Carbon is more electronegative than metals and carbon–metal bonds are polarized so that carbon bears a partial to complete negative charge and the metal bears a partial to complete positive charge.



Methyl lithium has a polar covalent carbon–lithium bond.

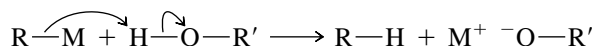


Sodium acetylide has an ionic bond between carbon and sodium.

Section 14.3 See Table 14.4

Section 14.4 See Table 14.4

Section 14.5 Organolithium compounds and Grignard reagents are strong bases and react instantly with compounds that have —OH groups.



These organometallic compounds cannot therefore be formed or used in solvents such as water and ethanol. The most commonly employed solvents are diethyl ether and tetrahydrofuran.

Section 14.6 See Tables 14.3 and 14.5

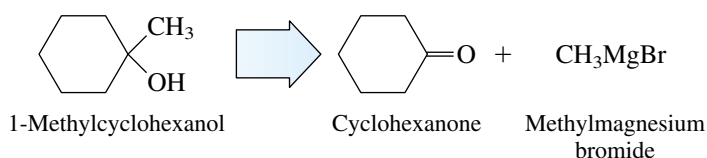
Section 14.7 See Table 14.5

Section 14.8 See Table 14.5

Section 14.9 When planning the synthesis of a compound using an organometallic reagent, or indeed any synthesis, the best approach is to reason backward from the product. This method is called **retrosynthetic analysis**. Retrosynthetic analysis of 1-methylcyclohexanol suggests it can be prepared by the reaction of methylmagnesium bromide and cyclohexanone.

TABLE 14.4 Preparation of Organometallic Reagents Used in Synthesis

Type of organometallic reagent (section) and comments	General equation for preparation and specific example
<b>Organolithium reagents (Section 14.3)</b> Lithium metal reacts with organic halides to produce organolithium compounds. The organic halide may be alkyl, alkenyl, or aryl. Iodides react most and fluorides least readily; bromides are used most often. Suitable solvents include hexane, diethyl ether, and tetrahydrofuran.	$\text{RX} + 2\text{Li} \longrightarrow \text{RLi} + \text{LiX}$ <p>Alkyl halide      Lithium      Alkyl lithium      Lithium halide</p>
	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow[\text{diethyl ether}]{\text{Li}} \text{CH}_3\text{CH}_2\text{CH}_2\text{Li}$ <p>Propyl bromide      Propyl lithium (78%)</p>
<b>Grignard reagents (Section 14.4)</b> Grignard reagents are prepared in a manner similar to that used for organolithium compounds. Diethyl ether and tetrahydrofuran are appropriate solvents.	$\text{RX} + \text{Mg} \longrightarrow \text{RMgX}$ <p>Alkyl halide      Magnesium      Alkylmagnesium halide (Grignard reagent)</p>
	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow[\text{diethyl ether}]{\text{Mg}} \text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$ <p>Benzyl chloride      Benzylmagnesium chloride (93%)</p>
<b>Lithium dialkylcuprates (Section 14.11)</b> These reagents contain a negatively charged copper atom and are formed by the reaction of a copper(I) salt with two equivalents of an organolithium reagent.	$2\text{RLi} + \text{CuX} \longrightarrow \text{R}_2\text{CuLi} + \text{LiX}$ <p>Alkyl lithium      Copper(I) halide      Lithium dialkylcuprate      Lithium halide</p>
	$2\text{CH}_3\text{Li} + \text{CuI} \xrightarrow[\text{diethyl ether}]{\text{diethyl ether}} (\text{CH}_3)_2\text{CuLi} + \text{LiI}$ <p>Methyl lithium      Copper(I) iodide      Lithium dimethylcuprate      Lithium iodide</p>
<b>Iodomethylzinc iodide (Section 14.12)</b> This is the Simmons–Smith reagent. It is prepared by the reaction of zinc (usually in the presence of copper) with diiodomethane.	$\text{CH}_2\text{I}_2 + \text{Zn} \xrightarrow[\text{Cu}]{\text{diethyl ether}} \text{ICH}_2\text{ZnI}$ <p>Diiodomethane      Zinc      Iodomethylzinc iodide</p>



Section 14.10 See Table 14.5

Section 14.11 See Tables 14.4 and 14.5

Section 14.12 See Tables 14.4 and 14.5

Section 14.13 Carbenes are species that contain a *divalent carbon*; that is, a carbon with only two bonds. One of the characteristic reactions of carbenes is with alkenes to give cyclopropane derivatives.

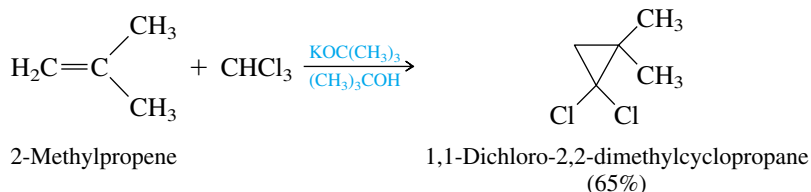


TABLE 14.5 Carbon–Carbon Bond-Forming Reactions of Organometallic Reagents

Reaction (section) and comments	General equation and specific example
<b>Alcohol synthesis via the reaction of Grignard reagents with carbonyl compounds (Section 14.6)</b> This is one of the most useful reactions in synthetic organic chemistry. Grignard reagents react with formaldehyde to yield primary alcohols, with aldehydes to give secondary alcohols, and with ketones to form tertiary alcohols.	$\text{RMgX} + \text{R}'\overset{\text{O}}{\parallel}\text{CR}'' \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \begin{array}{c} \text{R}' \\   \\ \text{RCOH} \\   \\ \text{R}'' \end{array}$ <p>Grignard reagent      Aldehyde or ketone      Alcohol</p>
	$\text{CH}_3\text{MgI} + \text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CH} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \text{CH}_3\text{CH}_2\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_3$ <p>Methylmagnesium iodide      Butanal      2-Pentanol (82%)</p>
<b>Reaction of Grignard reagents with esters (Section 14.10)</b> Tertiary alcohols in which two of the substituents on the hydroxyl carbon are the same may be prepared by the reaction of an ester with two equivalents of a Grignard reagent.	$2\text{RMgX} + \text{R}'\overset{\text{O}}{\parallel}\text{COR}'' \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \begin{array}{c} \text{R}' \\   \\ \text{RCOH} \\   \\ \text{R} \end{array}$ <p>Grignard reagent      Ester      Tertiary alcohol</p>
	$2\text{C}_6\text{H}_5\text{MgBr} + \text{C}_6\text{H}_5\overset{\text{O}}{\parallel}\text{COCH}_2\text{CH}_3 \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} (\text{C}_6\text{H}_5)_3\text{COH}$ <p>Phenylmagnesium bromide      Ethyl benzoate      Triphenylmethanol (89–93%)</p>
<b>Synthesis of alcohols using organolithium reagents (Section 14.7)</b> Organolithium reagents react with aldehydes and ketones in a manner similar to that of Grignard reagents to produce alcohols.	$\text{RLi} + \text{R}'\overset{\text{O}}{\parallel}\text{CR}'' \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \begin{array}{c} \text{R}' \\   \\ \text{RCOH} \\   \\ \text{R}'' \end{array}$ <p>Alkyl lithium      Aldehyde or ketone      Alcohol</p>
	$\text{Cyclopropyl-Li} + \text{CH}_3\overset{\text{O}}{\parallel}\text{C}(\text{CH}_3)_2 \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{diethyl ether}} \begin{array}{c} \text{OH} \\   \\ \text{C}(\text{CH}_3)_2 \\   \\ \text{CH}_3 \end{array}$ <p>Cyclopropyllithium      3,3-Dimethyl-2-butanone      2-Cyclopropyl-3,3-dimethyl-2-butanol (71%)</p>

(Continued)

Certain organometallic compounds resemble carbenes in their reactions and are referred to as **carbenoids**. Iodomethylzinc iodide (Section 14.12) is an example.

Section 14.14 Transition-metal complexes that contain one or more organic ligands offer a rich variety of structural types and reactivity. Organic ligands can be bonded to a metal by a  $\sigma$  bond or through its  $\pi$  system. **Metalloenes** are transition-metal complexes in which one or more of the ligands is a

**TABLE 14.5** Carbon–Carbon Bond-Forming Reactions of Organometallic Reagents (*Continued*)

Reaction (section) and comments	General equation and specific example
<b>Synthesis of acetylenic alcohols (Section 14.8)</b> Sodium acetylide and acetylenic Grignard reagents react with aldehydes and ketones to give alcohols of the type $\text{C}\equiv\text{C}-\text{COH}$ .	$\text{NaC}\equiv\text{CH} + \begin{array}{c} \text{O} \\ \parallel \\ \text{RCR}' \end{array} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{NH}_3, -33^\circ\text{C}} \begin{array}{c} \text{OH} \\   \\ \text{HC}\equiv\text{CCR}' \\   \\ \text{R} \end{array}$
	Sodium acetylide      Aldehyde or ketone      Alcohol
<b>Preparation of alkanes using lithium dialkylcuprates (Section 14.11)</b> Two alkyl groups may be coupled together to form an alkane by the reaction of an alkyl halide with a lithium dialkylcuprate. Both alkyl groups must be primary (or methyl). Aryl and vinyl halides may be used in place of alkyl halides.	$\text{NaC}\equiv\text{CH} + \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCH}_2\text{CH}_3 \end{array} \xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{NH}_3, -33^\circ\text{C}} \begin{array}{c} \text{OH} \\   \\ \text{HC}\equiv\text{CCCH}_2\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$
	Sodium acetylide      2-Butanone      3-Methyl-1-pentyn-3-ol (72%)
<b>The Simmons–Smith reaction (Section 14.12)</b> Methylene transfer from iodomethylzinc iodide converts alkenes to cyclopropanes. The reaction is a stereospecific syn addition of a $\text{CH}_2$ group to the double bond.	$\text{R}_2\text{CuLi} + \text{R}'\text{CH}_2\text{X} \longrightarrow \text{RCH}_2\text{R}'$
	Lithium dialkylcuprate      Primary alkyl halide      Alkane
<b>The Simmons–Smith reaction (Section 14.12)</b> Methylene transfer from iodomethylzinc iodide converts alkenes to cyclopropanes. The reaction is a stereospecific syn addition of a $\text{CH}_2$ group to the double bond.	$(\text{CH}_3)_2\text{CuLi} + \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow{\text{diethyl ether}} \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$
	Lithium dimethylcuprate      Benzyl chloride      Ethylbenzene (80%)
<b>The Simmons–Smith reaction (Section 14.12)</b> Methylene transfer from iodomethylzinc iodide converts alkenes to cyclopropanes. The reaction is a stereospecific syn addition of a $\text{CH}_2$ group to the double bond.	$\text{R}_2\text{C}=\text{CR}_2 + \text{ICH}_2\text{ZnI} \xrightarrow{\text{diethyl ether}} \begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad / \\ \text{C} \\ / \quad \diagdown \\ \text{R} \quad \text{R} \end{array} + \text{ZnI}_2$
	Alkene      Iodomethylzinc iodide      Cyclopropane derivative      Zinc iodide
<b>The Simmons–Smith reaction (Section 14.12)</b> Methylene transfer from iodomethylzinc iodide converts alkenes to cyclopropanes. The reaction is a stereospecific syn addition of a $\text{CH}_2$ group to the double bond.	$\text{Cyclopentene} \xrightarrow[\text{diethyl ether}]{\text{CH}_2\text{I}_2, \text{Zn}(\text{Cu})} \text{Bicyclo[3.1.0]hexane}$
	Cyclopentene      Bicyclo[3.1.0]hexane (53%)

cyclopentadienyl ring. Ferrocene was the first metallocene synthesized; its structure is shown on the opening page of this chapter.

**Section 14.15** Coordination polymerization of ethylene and propene has the biggest economic impact of any organic chemical process. Ziegler–Natta polymerization is carried out in the presence of catalysts derived from transition metals such as titanium.  $\pi$ -Bonded and  $\sigma$ -bonded organometallic compounds are intermediates in coordination polymerization.

## Problems

**14.13** Write structural formulas for each of the following compounds. Specify which compounds qualify as organometallic compounds.

- |                                   |                            |
|-----------------------------------|----------------------------|
| (a) Cyclopentyllithium            | (d) Lithium divinylcuprate |
| (b) Ethoxymagnesium chloride      | (e) Sodium carbonate       |
| (c) 2-Phenylethylmagnesium iodide | (f) Benzylpotassium        |

**14.14** *Dibal* is an informal name given to the organometallic compound  $[(\text{CH}_3)_2\text{CHCH}_2]_2\text{AlH}$ , used as a reducing agent in certain reactions. Can you figure out the systematic name from which “dibal” is derived?

**14.15** Suggest appropriate methods for preparing each of the following compounds from the starting material of your choice.

- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{MgI}$  (c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Li}$   
 (b)  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CMgI}$  (d)  $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{CuLi}$



**14.16** Which compound in each of the following pairs would you expect to have the more polar carbon–metal bond? Compare the models on *Learning By Modeling* with respect to the charge on the carbon bonded to the metal.

- (a)  $\text{CH}_3\text{CH}_2\text{Li}$  or  $(\text{CH}_3\text{CH}_2)_3\text{Al}$  (c)  $\text{CH}_3\text{CH}_2\text{MgBr}$  or  $\text{HC}\equiv\text{CMgBr}$   
 (b)  $(\text{CH}_3)_2\text{Zn}$  or  $(\text{CH}_3)_2\text{Mg}$

**14.17** Write the structure of the principal organic product of each of the following reactions:

- (a) 1-Bromopropane with lithium in diethyl ether  
 (b) 1-Bromopropane with magnesium in diethyl ether  
 (c) 2-Iodopropane with lithium in diethyl ether  
 (d) 2-Iodopropane with magnesium in diethyl ether  
 (e) Product of part (a) with copper(I) iodide  
 (f) Product of part (e) with 1-bromobutane  
 (g) Product of part (e) with iodobenzene  
 (h) Product of part (b) with  $\text{D}_2\text{O}$  and  $\text{DCl}$   
 (i) Product of part (c) with  $\text{D}_2\text{O}$  and  $\text{DCl}$   
 (j) Product of part (a) with formaldehyde in ether, followed by dilute acid  
 (k) Product of part (b) with benzaldehyde in ether, followed by dilute acid  
 (l) Product of part (c) with cycloheptanone in ether, followed by dilute acid

(m) Product of part (d) with  $\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_3$  in ether, followed by dilute acid

(n) Product of part (b) with  $\text{C}_6\text{H}_5\overset{\text{O}}{\parallel}\text{COCH}_3$  (2 mol) in ether, followed by dilute acid

- (o) 1-Octene with diiodomethane and zinc–copper couple in ether  
 (p) (*E*)-2-Decene with diiodomethane and zinc–copper couple in ether  
 (q) (*Z*)-3-Decene with diiodomethane and zinc–copper couple in ether  
 (r) 1-Pentene with tribromomethane and potassium *tert*-butoxide in *tert*-butyl alcohol

**14.18** Using 1-bromobutane and any necessary organic or inorganic reagents, suggest efficient syntheses of each of the following alcohols:

- (a) 1-Pentanol (d) 3-Methyl-3-heptanol  
 (b) 2-Hexanol (e) 1-Butylcyclobutanol  
 (c) 1-Phenyl-1-pentanol

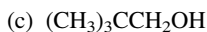
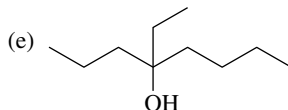
**14.19** Using bromobenzene and any necessary organic or inorganic reagents, suggest efficient syntheses of each of the following:

- (a) Benzyl alcohol (b) 1-Phenyl-1-hexanol

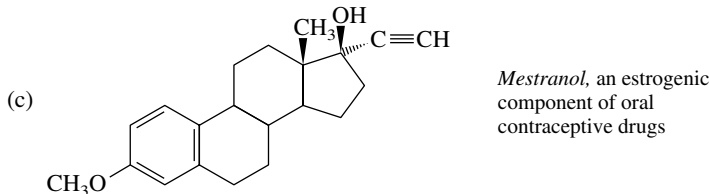
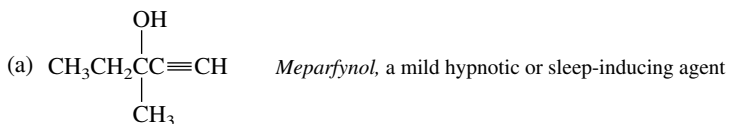
- (c) Bromodiphenylmethane  
 (d) 4-Phenyl-4-heptanol  
 (e) 1-Phenylcyclooctanol  
 (f) *trans*-2-Phenylcyclooctanol

**14.20** Analyze the following structures so as to determine all the practical combinations of Grignard reagent and carbonyl compound that will give rise to each:

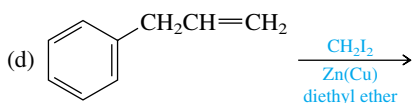
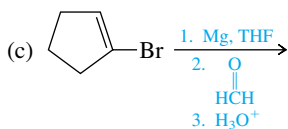
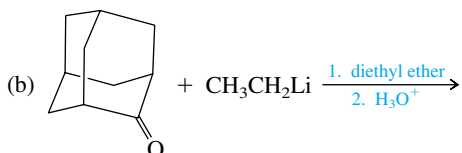
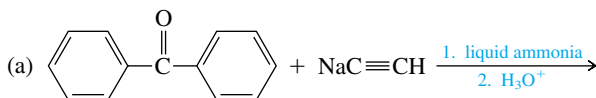
- (a)  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}(\text{CH}_3)_2$   
 (d) 6-Methyl-5-hepten-2-ol

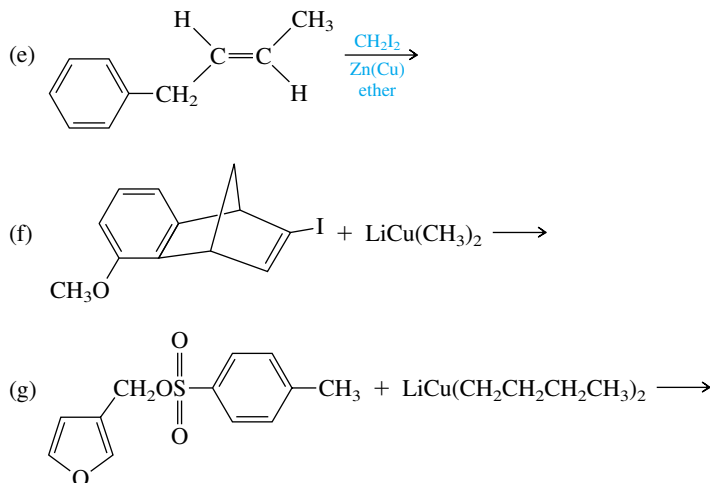


**14.21** A number of drugs are prepared by reactions of the type described in this chapter. Indicate what you believe would be a reasonable last step in the synthesis of each of the following:

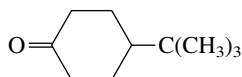


**14.22** Predict the principal organic product of each of the following reactions:





**14.23** Addition of phenylmagnesium bromide to 4-*tert*-butylcyclohexanone gives two isomeric tertiary alcohols as products. Both alcohols yield the same alkene when subjected to acid-catalyzed dehydration. Suggest reasonable structures for these two alcohols.



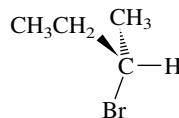
4-*tert*-Butylcyclohexanone

**14.24** (a) Unlike other esters, which react with Grignard reagents to give tertiary alcohols, ethyl

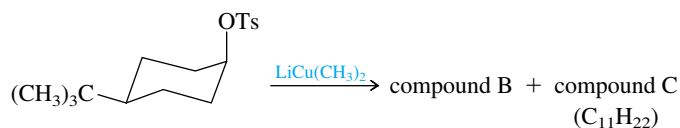
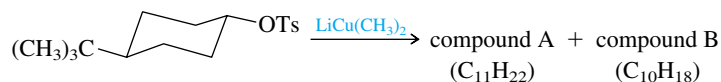
formate ( $\text{HCOCH}_2\text{CH}_3$ ) yields a different class of alcohols on treatment with Grignard reagents. What kind of alcohol is formed in this case and why?

(b) Diethyl carbonate ( $\text{CH}_3\text{CH}_2\text{OCOCCH}_2\text{CH}_3$ ) reacts with excess Grignard reagent to yield alcohols of a particular type. What is the structural feature that characterizes alcohols prepared in this way?

**14.25** Reaction of lithium diphenylcuprate with optically active 2-bromobutane yields 2-phenylbutane, with high net inversion of configuration. When the 2-bromobutane used has the stereostructure shown, will the 2-phenylbutane formed have the *R* or the *S* configuration?

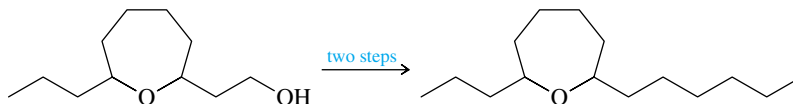


**14.26** Suggest reasonable structures for compounds A, B, and C in the following reactions:



Compound C is more stable than compound A. OTs stands for toluenesulfonate.

**14.27** The following conversion has been reported in the chemical literature. It was carried out in two steps, the first of which involved formation of a *p*-toluenesulfonate ester. Indicate the reagents for this step, and show how you could convert the *p*-toluenesulfonate to the desired product.

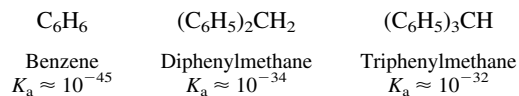


**14.28** Sometimes the strongly basic properties of Grignard reagents can be turned to synthetic advantage. A chemist needed samples of butane specifically labeled with deuterium, the mass 2 isotope of hydrogen, as shown:

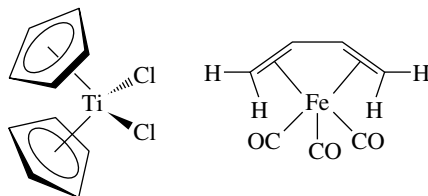


Suggest methods for the preparation of each of these using heavy water ( $\text{D}_2\text{O}$ ) as the source of deuterium, butanols of your choice, and any necessary organic or inorganic reagents.

**14.29** Diphenylmethane is significantly more acidic than benzene, and triphenylmethane is more acidic than either. Identify the most acidic proton in each compound, and suggest a reason for the trend in acidity.

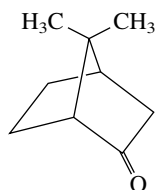


**14.30** The 18-electron rule is a general, but not universal, guide for assessing whether a certain transition-metal complex is stable or not. Both of the following are stable compounds, but only one obeys the 18-electron rule. Which one?



**14.31** One of the main uses of the “linear  $\alpha$ -olefins” prepared by oligomerization of ethylene is in the preparation of *linear low-density polyethylene*. Linear low-density polyethylene is a copolymer produced when ethylene is polymerized in the presence of a “linear  $\alpha$ -olefin” such as 1-decene [ $\text{CH}_2=\text{CH}(\text{CH}_2)_7\text{CH}_3$ ]. 1-Decene replaces ethylene at random points in the growing polymer chain. Can you deduce how the structure of linear low-density polyethylene differs from a linear chain of  $\text{CH}_2$  units?

**14.32** Make a molecular model of 7,7-dimethylbicyclo[2.2.1]heptan-2-one. Two diastereomeric alcohols may be formed when it reacts with methylmagnesium bromide. Which one is formed in greater amounts?



7,7-Dimethylbicyclo[2.2.1]heptan-2-one





**14.33** Make molecular models of the product of addition of dichlorocarbene to:

- (a) *trans*-2-Butene
- (b) *cis*-2-Butene

Which product is achiral? Which one is formed as a racemic mixture?



**14.34** Examine the molecular model of ferrocene on *Learning By Modeling*. Does ferrocene have a dipole moment? Would you expect the cyclopentadienyl rings of ferrocene to be more reactive toward nucleophiles or electrophiles? Where is the region of highest electrostatic potential?



**14.35** Inspect the electrostatic potential surface of the benzyl anion structure given on *Learning By Modeling*. What is the hybridization state of the benzylic carbon? Does the region of highest electrostatic potential lie in the plane of the molecule or perpendicular to it? Which ring carbons bear the greatest share of negative charge?