05

Reactions of Alkenes and Alkynes

Polyethylene is the most widely used plastic, making up items such as packing foam, plastic bottles, and plastic utensils (top: © Jon Larson/iStockphoto; middle: GNL Media/Digital Vision/Getty Images, Inc.; bottom: © Lakhesis/iStockphoto). Inset: A model of ethylene.

IN THIS CHAPTER, we begin our systematic study of organic reactions and their mechanisms. Reaction mechanisms are step-by-step descriptions of how reactions proceed and are one of the most important unifying concepts in organic chemistry. We use the reactions of alkenes as the vehicle to introduce this concept.

5.1 What Are the Characteristic Reactions of Alkenes?

The most characteristic reaction of alkenes is **addition to the carbon–carbon double bond** in such a way that the pi bond is broken and, in its place, sigma bonds are formed to two new atoms or groups of atoms. Several examples of reactions at the carbon–carbon double bond are shown in Table 5.1, along with the descriptive name(s) associated with each.

TABLE 5.1 Characteristic Reactions of Alkenes	
Reaction	Descriptive Name(s)
$>C=C< + HX \longrightarrow -\overset{\mid}{\underset{\mid}{C}}-\overset{\mid}{\underset{\mid}{C}}-$ $X = Cl, Br, I$ H $Cl (X)$	Hydrochlorination (hydrohalogenation)
$>C=C< + H_2O \longrightarrow -\overset{\mid}{\underset{\mid}{C}}-\overset{\mid}{\underset{\mid}{C}}-$ H OH	Hydration
$>C=C< + X_2 \longrightarrow -\overset{\mid}{\underset{\mid}{C}}-\overset{\mid}{\underset{\mid}{C}}-$ $X_2 = Cl_2, Br_2$ $(X) Br$ $Br (X)$	Bromination (halogenation)
$>C=C< + BH_3 \longrightarrow -\overset{\mid}{\underset{\mid}{C}}-\overset{\mid}{\underset{\mid}{C}}-$ H BH_2	Hydroboration
$>C=C< + H_2 \longrightarrow -\overset{\mid}{\underset{\mid}{C}}-\overset{\mid}{\underset{\mid}{C}}-$ H H	Hydrogenation (reduction)

From the perspective of the chemical industry, the single most important reaction of ethylene and other low-molecular-weight alkenes is the production of **chain-growth polymers** (Greek: *poly*, many, and *meros*, part). In the presence of certain catalysts called *initiators*, many alkenes form polymers by the addition of **monomers** (Greek: *mono*, one, and *meros*, part) to a growing polymer chain, as illustrated by the formation of polyethylene from ethylene:

$$n\text{CH}_2 = \text{CH}_2 \xrightarrow{\text{initiator}} +\text{CH}_2\text{CH}_2+_n$$

In alkene polymers of industrial and commercial importance, n is a large number, typically several thousand. We discuss this alkene reaction in Chapter 16.
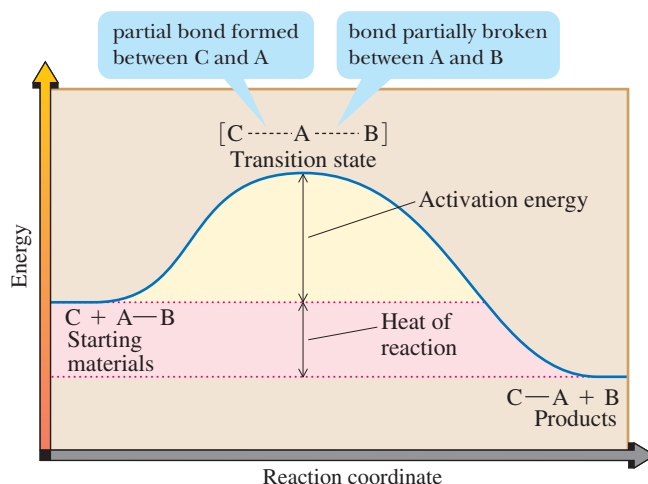
5.2 What Is a Reaction Mechanism?

Reaction mechanism A step-by-step description of how a chemical reaction occurs.

A **reaction mechanism** describes in detail how a chemical reaction occurs. It describes which bonds break and which new ones form, as well as the order and relative rates of the various bond-breaking and bond-forming steps. If the reaction takes place in solution, the reaction mechanism describes the role of the solvent; if the reaction involves a catalyst, the reaction mechanism describes the role of the catalyst.

A. Energy Diagrams and Transition States

To understand the relationship between a chemical reaction and energy, think of a chemical bond as a spring. As a spring is stretched from its resting position, its energy increases. As

partial bond formed
between C and A

bond partially broken
between A and B

$[C \text{-----} A \text{-----} B]$
Transition state

Activation energy

C + A—B
Starting
materials

Heat of
reaction

C—A + B
Products

Energy

Reaction coordinate

FIGURE 5.1
An energy diagram for a one-step reaction between C and A — B. The dashed lines in the transition state indicate that the new C — A bond is partially formed and the A — B bond is partially broken. The energy of the reactants is higher than that of the products—the reaction is exothermic.

it returns to its resting position, its energy decreases. Similarly, during a chemical reaction, bond breaking corresponds to an increase in energy, and bond forming corresponds to a decrease in energy. We use an **energy diagram** to show the changes in energy that occur in going from reactants to products. Energy is measured along the vertical axis, and the change in position of the atoms during a reaction is measured on the horizontal axis, called the **reaction coordinate**. The reaction coordinate indicates how far the reaction has progressed, from no reaction to a completed reaction.

Figure 5.1 shows an energy diagram for the reaction of C + A—B to form C—A + B. This reaction occurs in one step, meaning that bond breaking in reactants and bond forming in products occur simultaneously.

The difference in energy between the reactants and products is called the **heat of reaction**, **Δ*H***. If the energy of the products is lower than that of the reactants, heat is released and the reaction is called **exothermic**. If the energy of the products is higher than that of the reactants, heat is absorbed and the reaction is called **endothermic**. The one-step reaction shown in Figure 5.1 is exothermic.

A **transition state** is the point on the reaction coordinate at which the energy is at a maximum. At the transition state, sufficient energy has become concentrated in the proper bonds so that bonds in the reactants break. As they break, energy is redistributed and new bonds form, giving products. Once the transition state is reached, the reaction proceeds to give products, with the release of energy.

A transition state has a definite geometry, a definite arrangement of bonding and non-bonding electrons, and a definite distribution of electron density and charge. Because a transition state is at an energy maximum on an energy diagram, we cannot isolate it and we cannot determine its structure experimentally. Its lifetime is on the order of a picosecond (the duration of a single bond vibration). As we will see, however, even though we cannot observe a transition state directly by any experimental means, we can often infer a great deal about its probable structure from other experimental observations.

For the reaction shown in Figure 5.1, we use dashed lines to show the partial bonding in the transition state. At the same time, as C begins to form a new covalent bond with A, the covalent bond between A and B begins to break. Upon completion of the reaction, the A—B bond is fully broken and the C—A bond is fully formed.

The difference in energy between the reactants and the transition state is called the **activation energy**. The activation energy is the minimum energy required for a reaction to occur; it can be considered an energy barrier for the reaction. The activation energy determines the rate of a reaction—that is, how fast the reaction occurs. If the activation energy is large, a very few molecular collisions occur with sufficient energy to reach the transition state, and the reaction is slow. If the activation energy is small, many collisions generate sufficient energy to reach the transition state and the reaction is fast.

Energy diagram A graph showing the changes in energy that occur during a chemical reaction; energy is plotted on the *y*-axis, and the progress of the reaction is plotted on the *x*-axis.

Reaction coordinate A measure of the progress of a reaction, plotted on the *x*-axis in an energy diagram.

Heat of reaction The difference in energy between reactants and products.

Exothermic reaction A reaction in which the energy of the products is lower than the energy of the reactants; a reaction in which heat is liberated.
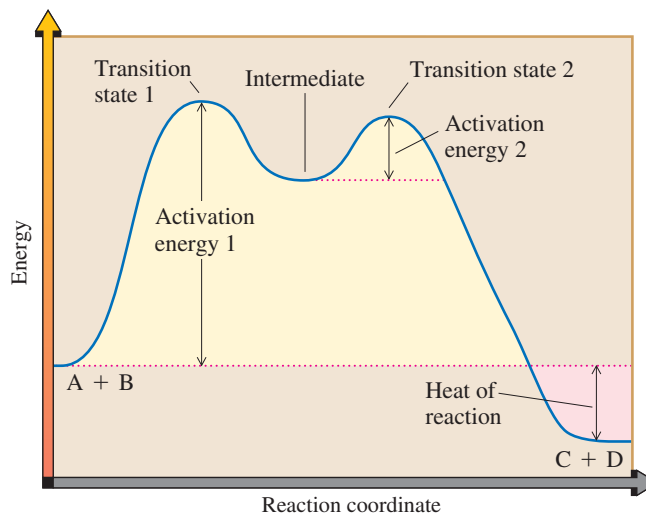
Endothermic reaction A reaction in which the energy of the products is higher than the energy of the reactants; a reaction in which heat is absorbed.

Transition state An unstable species of maximum energy formed during the course of a reaction; a maximum on an energy diagram.

Activation energy The difference in energy between reactants and the transition state.

FIGURE 5.2
Energy diagram for a two-step reaction involving the formation of an intermediate. The energy of the reactants is higher than that of the products, and energy is released in the conversion of A + B to C + D.

In a reaction that occurs in two or more steps, each step has its own transition state and activation energy. Shown in Figure 5.2 is an energy diagram for the conversion of reactants to products in two steps. A **reaction intermediate** corresponds to an energy minimum between two transition states, in this case an intermediate between transition states 1 and 2. Note that because the energies of the reaction intermediates we describe are higher than the energies of either the reactants or the products, these intermediates are highly reactive, and rarely, if ever, can one be isolated.

Reaction intermediate An unstable species that lies in an energy minimum between two transition states.

The slowest step in a multistep reaction, called the **rate-determining step**, is the step that crosses the highest energy barrier. In the two-step reaction shown in Figure 5.2, Step 1 crosses the higher energy barrier and is, therefore, the rate-determining step.

Rate-determining step The step in a reaction sequence that crosses the highest energy barrier; the slowest step in a multistep reaction.

EXAMPLE 5.1

Draw an energy diagram for a two-step exothermic reaction in which the second step is rate determining.

STRATEGY

A two-step reaction involves the formation of an intermediate. In order for the reaction to be exothermic, the products must be lower in energy than the reactants. In order for the second step to be rate determining, it must cross the higher energy barrier.

SOLUTION
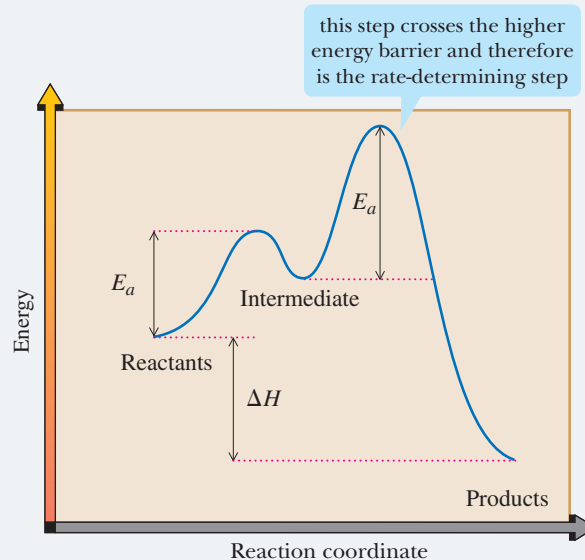
See problems 5.12, 5.13

PROBLEM 5.1

In what way would the energy diagram drawn in Example 5.1 change if the reaction were endothermic?

Chemical Connections 5A
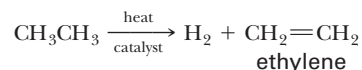
CATALYTIC CRACKING AND THE IMPORTANCE OF ALKENES

By far, the largest source of hydrocarbons is crude oil, which contains mostly alkanes. This is unfortunate because, as we learned in Chapter 3, alkanes are relatively inert and would not be very useful as starting materials for organic reactions to produce the myriad of compounds used in society today.

Fortunately, crude oil is readily converted to alkenes, compounds with a reactive functional group (the C—C double bond), through the process of catalytic cracking. In catalytic cracking, the hydrocarbon feedstocks of crude oil are mixed with solid catalysts and heated to temperatures above 500 °C. These conditions allow C—C single bonds to be broken, forming reactive intermediates that eventually react to form smaller alkanes and alkenes.

$$CH_3CH_2CH_2CH_2CH_2CH_3 \xrightarrow[\text{catalyst}]{\text{heat}}$$
$$CH_3CH_2CH_2CH_3 + CH_2{=}CH_2$$
$$\text{ethylene}$$
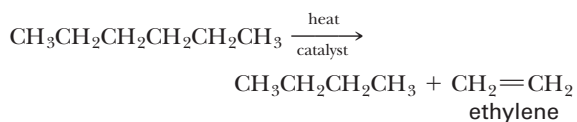
The smaller hydrocarbons formed in the initial reactions react again to form even smaller hydrocarbons.

After several cracking cycles, the major alkene product formed is ethylene, the smallest possible alkene.

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{catalyst}]{\text{heat}} CH_3CH_3 + CH_2{=}CH_2$$
$$\text{ethylene}$$

$$CH_3CH_3 \xrightarrow[\text{catalyst}]{\text{heat}} H_2 + CH_2{=}CH_2$$
$$\text{ethylene}$$

The ethylene is then collected and subjected to other reactions, such as hydration to give ethanol.

$$CH_2{=}CH_2 \xrightarrow{\text{hydration}} CH_3CH_2OH$$
$$\text{ethanol}$$
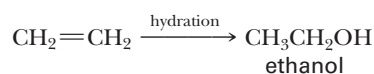
Through this process, crude oil is converted to functionalized organic compounds which can, in turn, be used for many of the organic reactions presented in this text.

Question

Would you predict the catalytic cracking reactions to be exothermic or endothermic?

B. Developing a Reaction Mechanism

To develop a reaction mechanism, chemists begin by designing experiments that will reveal details of a particular chemical reaction. Next, through a combination of experience and intuition, they propose one or more sets of steps or mechanisms, each of which might account for the overall chemical transformation. Finally, they test each proposed mechanism against the experimental observations to exclude those mechanisms that are not consistent with the facts.
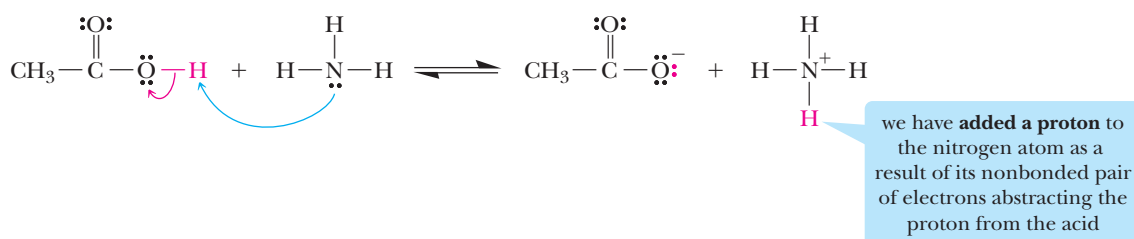
A mechanism becomes generally established by excluding reasonable alternatives and by showing that it is consistent with every test that can be devised. This, of course, does not mean that a generally accepted mechanism is a completely accurate description of the chemical events, but only that it is the best chemists have been able to devise. It is important to keep in mind that, as new experimental evidence is obtained, it may be necessary to modify a generally accepted mechanism or possibly even discard it and start all over again.

Before we go on to consider reactions and reaction mechanisms, we might ask why it is worth the trouble to establish them and your time to learn about them. One reason is very practical. Mechanisms provide a theoretical framework within which to organize a great deal of descriptive chemistry. For example, with insight into how reagents add to particular alkenes, it is possible to make generalizations and then predict how the same reagents might add to other alkenes. A second reason lies in the intellectual satisfaction derived from constructing models that accurately reflect the behavior of chemical systems. Finally, to a creative scientist, a mechanism is a tool to be used in the search for new knowledge and new understanding. A mechanism consistent with all that is known about a reaction can be used to make predictions about chemical interactions as yet unexplored, and experiments can be designed to test these predictions. Thus, reaction mechanisms provide a way not only to organize knowledge, but also to extend it.
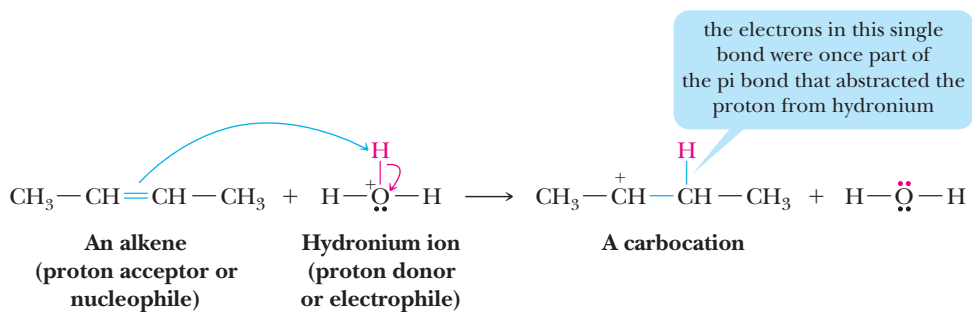
C.　Some Common Patterns in Reaction Mechanisms

At this point, let us stop for a moment and analyze several of the common reaction mechanism patterns to be seen in the mechanisms we will present in this and following chapters. You may notice that some of these mechanisms are similar to each other. It is the result of the reaction and the mechanistic steps involved that are being highlighted because of their prevalence in organic chemistry.

Pattern 1:　Add a proton. In Section 2.2, we learned that an acid is a proton donor, a base is a proton acceptor, and an acid–base reaction is a proton-transfer reaction. In addition, we saw that we can use curved arrows to show how a proton-transfer reaction takes place, as for example, in the acid–base reaction between acetic acid and ammonia to form acetate ion and ammonium ion. This is an example of a *nonbonded pair of electrons being used to add a proton* to a compound.
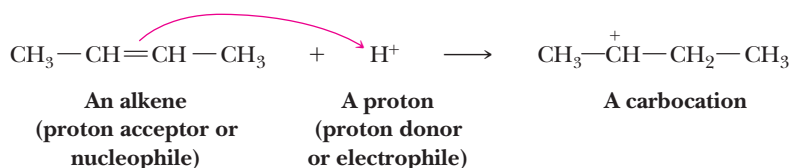
we have **added a proton** to the nitrogen atom as a result of its nonbonded pair of electrons abstracting the proton from the acid

Following is another example of **adding a proton**. Here, the *proton is added* across the pi bond of the C—C double bond. The compounds below are labeled as "proton donor" and "proton acceptor," terms used to describe Brønsted acids and bases. They can also be labeled according to Lewis acid–base theory as "electrophile" and "nucleophile."

the electrons in this single bond were once part of the pi bond that abstracted the proton from hydronium

$CH_3—CH{=}CH—CH_3$ + $H—\overset{+}{\underset{\cdot\cdot}{O}}—H$ $\longrightarrow$ $CH_3—\overset{+}{CH}—CH—CH_3$ + $H—\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}—H$

An alkene　　　　**Hydronium ion**　　　　**A carbocation**
(proton acceptor or　**(proton donor**
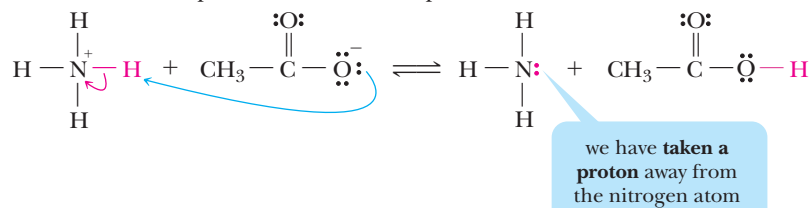**nucleophile)**　　　**or electrophile)**

This pattern is typical in all reactions in which the reaction is catalyzed by an acid. Remember that in a carbon–carbon double bond, two pairs of electrons are shared between the two carbon atoms. An acid–base reaction in which a double bond provides the pair of electrons for the hydrogen transfer creates a carbocation. And remember that, as shown in Section 2.2, a proton, H^+, does not exist as such in aqueous solution. Instead it immediately combines with a water molecule to form the hydronium ion, H_3O^+.

While the above equation is the most accurate way to write the proton transfer in aqueous solution, we will simplify the equation to show just the proton and formation of the new covalent bond.
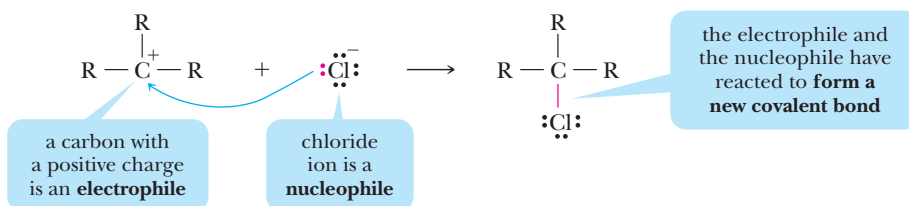
$CH_3—CH{=}CH—CH_3$ + H^+ $\longrightarrow$ $CH_3—\overset{+}{CH}—CH_2—CH_3$

An alkene　　　　　**A proton**　　　　　**A carbocation**
(proton acceptor or　**(proton donor**
nucleophile)　　　　**or electrophile)**

Pattern 2: Take a proton away. If we run the "add a proton" reaction in reverse, then it corresponds to "take a proton away" from the ammonium ion and transfer it to the acetate ion. We can also use curved arrows to show the flow of electron pairs in this type of reaction as well. The mechanism for taking a proton away is similar to adding a proton, only we focus our attention on the compound that loses the proton.
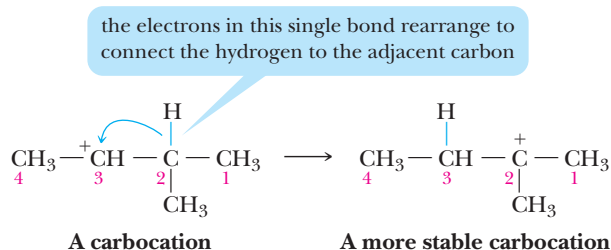
we have **taken a proton** away from the nitrogen atom

Pattern 3: Reaction of an electrophile and a nucleophile to form a new covalent bond. Another characteristic pattern is the reaction between an **electrophile** (an electron-poor species that can accept a pair of electrons to form a new covalent bond) and a **nucleophile** (an electron-rich species that can donate a pair of electrons to form a new covalent bond). An example of this type of reaction is that between a carbocation and halide ion. The driving force behind this reaction is the strong attraction between the positive and negative charges of the reacting species and the energy released when the new covalent bond forms. The following equation shows the flow of electron pairs in this type of reaction.

the electrophile and the nucleophile have reacted to **form a new covalent bond**

a carbon with a positive charge is an **electrophile**

chloride ion is a **nucleophile**

Pattern 4: Rearrangement of a bond. A common reaction that occurs in carbocations is the shift of a hydrogen or an alkyl group to place the positive charge at a more stable position. A rearrangement occurs when the electrons in a sigma bond break their bond from one carbon atom to form a new bond to another carbon atom as shown. The driving force for this process is the greater stability of the newly formed carbocation over the original. We will have more to say about rearrangements in Section 5.4.

the electrons in this single bond rearrange to connect the hydrogen to the adjacent carbon

A carbocation   **A more stable carbocation**

Pattern 5: Break a bond to form a stable ion or molecule. A carbocation can also be formed when a chemical species breaks off from a molecule, taking the electrons from the former single bond with it. The chemical species that broke off is called a leaving group, and the bond breaks because it forms one or more stable ions or molecules. We will have more to say about leaving groups in Section 7.5C.

bromide ion, the leaving group, is a stable ion in solution
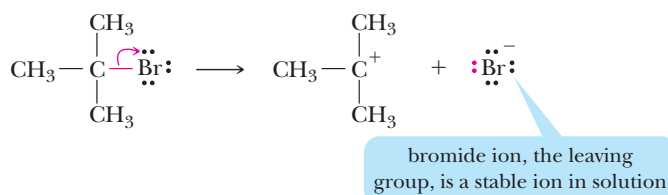
5.3 What Are the Mechanisms of Electrophilic Additions to Alkenes?
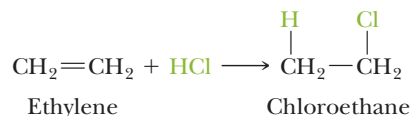
We begin our introduction to the chemistry of alkenes with an examination of three types of addition reactions: the addition of hydrogen halides (HCl, HBr, and HI), water (H_2O), and halogens (Cl_2, Br_2). We first study some of the experimental observations about each addition reaction and then its mechanism. By examining these particular reactions, we develop a general understanding of how alkenes undergo addition reactions.

As we will show for the addition reactions of alkenes and for the reactions of many other classes of organic compounds, high-electron-density regions of molecules or ions react with low-electron-density regions of other molecules or ions, often resulting in the formation of a new covalent bond. We call an electron-rich species a **nucleophile** (nucleus loving), meaning that it seeks a region of low electron density. We call a low-electron-density species an **electrophile** (electron loving), meaning that it seeks a region of high electron density. Note that nucleophiles are Lewis bases and electrophiles are Lewis acids (Section 2.6).

Electrophile An electron-poor species that can accept a pair of electrons to form a new covalent bond; alternatively, a Lewis acid (Section 2.6).

A. Addition of Hydrogen Halides

The hydrogen halides HCl, HBr, and HI add to alkenes to give haloalkanes (alkyl halides). These additions may be carried out either with the pure reagents or in the presence of a polar solvent such as acetic acid. The addition of HCl to ethylene gives chloroethane (ethyl chloride):

$$CH_2{=}CH_2 + HCl \longrightarrow \underset{\text{Chloroethane}}{CH_2{-}CH_2}$$

(with H and Cl added to the carbons)

Ethylene

The addition of HCl to propene gives 2-chloropropane (isopropyl chloride); hydrogen adds to carbon 1 of propene and chlorine adds to carbon 2. If the orientation of addition were reversed, 1-chloropropane (propyl chloride) would be formed. The observed result is that 2-chloropropane is formed to the virtual exclusion of 1-chloropropane:

$$CH_3CH{=}CH_2 + HCl \longrightarrow CH_3CH{-}CH_2 + CH_3CH{-}CH_2$$

Propene   2-Chloropropane   1-Chloropropane (not observed)
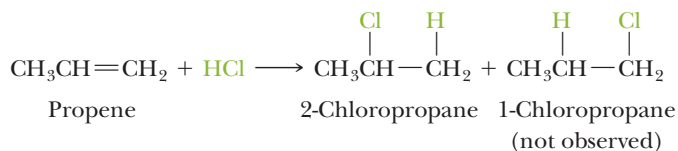
Regioselective reaction A reaction in which one direction of bond forming or bond breaking occurs in preference to all other directions.
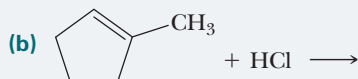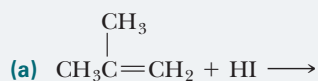
Markovnikov's rule In the addition of HX or H_2O to an alkene, hydrogen adds to the carbon of the double bond having the greater number of hydrogens.

We say that the addition of HCl to propene is highly regioselective and that 2-chloropropane is the major product of the reaction. A **regioselective reaction** is a reaction in which one direction of bond forming or breaking occurs in preference to all other directions.

Vladimir Markovnikov observed this regioselectivity and made the generalization, known as **Markovnikov's rule**, that, in the addition of HX to an alkene, hydrogen adds to the doubly bonded carbon that has the greater number of hydrogens already bonded to it. Although Markovnikov's rule provides a way to predict the product of many alkene addition reactions, it does not explain why one product predominates over other possible products.
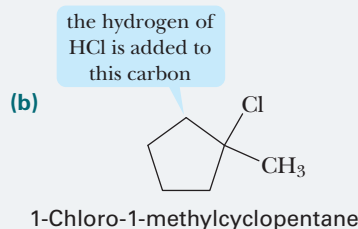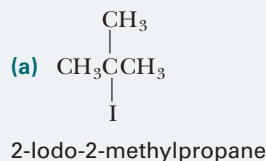
EXAMPLE 5.2

Name and draw a structural formula for the major product of each alkene addition reaction:

(a)
$$\underset{\substack{| \\ CH_3}}{CH_3C}{=}CH_2 + HI \longrightarrow$$

(b) [cyclopentene ring with —CH_3 substituent] + HCl $\longrightarrow$
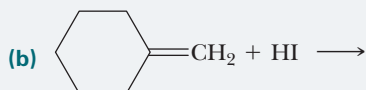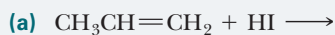
STRATEGY

Use Markovnikov's rule, which predicts that H adds to the least substituted carbon of the double bond and halogen adds to the more substituted carbon.

SOLUTION

(a)
$$CH_3\overset{\underset{|}{CH_3}}{\underset{\underset{I}{|}}{CH_3\overset{}{C}CH_3}}$$

2-Iodo-2-methylpropane

(b)

the hydrogen of HCl is added to this carbon

Cl

CH₃

1-Chloro-1-methylcyclopentane

See problems 5.17–5.20, 5.28

── **PROBLEM 5.2** ──────────────────

Name and draw a structural formula for the major product of each alkene addition reaction:

(a) $CH_3CH{=\!=}CH_2 + HI \longrightarrow$

(b) ⬡$={=}CH_2 + HI \longrightarrow$

Chemists account for the addition of HX to an alkene by a two-step mechanism, which we illustrate by the reaction of 2-butene with hydrogen chloride to give 2-chlorobutane. Let us first look at this two-step mechanism in general and then go back and study each step in detail.

Mechanism

Electrophilic Addition of HCl to 2-Butene

STEP 1: **Add a proton.** The reaction begins with the transfer of a proton from HCl to 2-butene, as shown by the two curved arrows on the left side of Step 1:

$$CH_3CH{=\!=}CHCH_3 \ + \ H{-}\overset{\delta+}{}\underset{}{\overset{\delta-}{Cl}}: \ \underset{\text{slow, rate}}{\overset{\text{determining}}{\rightleftharpoons}} \ CH_3\overset{+}{CH}{-}\overset{\overset{H}{|}}{CHCH_3} \ + \ :\overset{..}{\underset{..}{Cl}}:^{-}$$

(a nucleophile)   (an electrophile)   *sec*-Butyl cation (a 2° carbocation intermediate)
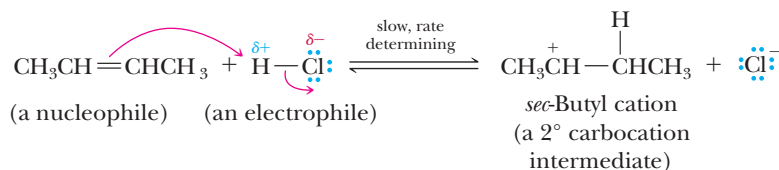
The first curved arrow shows the breaking of the pi bond of the alkene and its electron pair now forming a new covalent bond with the hydrogen atom of HCl. In this step, the carbon–carbon double bond of the alkene is the nucleophile (the electron-rich, nucleus-seeking species) and HCl is the electrophile (the electron-poor, electron-seeking species). The second curved arrow shows the breaking of the polar covalent bond in HCl and this electron pair being given entirely to chlorine, forming chloride ion. Step 1 in this mechanism results in the formation of an organic cation and chloride ion.

STEP 2: **Reaction of an electrophile and a nucleophile to form a new covalent bond.** The reaction of the *sec*-butyl cation (an electrophile and a Lewis acid) with chloride ion (a nucleophile and a Lewis base) completes the valence shell of carbon and gives 2-chlorobutane:

$$:\overset{..}{\underset{..}{Cl}}:^{-} + \ CH_3\overset{+}{CH}CH_2CH_3 \ \overset{\text{fast}}{\longrightarrow} \ CH_3\overset{\overset{\displaystyle :\overset{..}{Cl}:}{|}}{CH}CH_2CH_3$$

Chloride ion   *sec*-Butyl cation   2-Chlorobutane
(a Lewis base)   (a Lewis acid)
(a nucleophile)   (an electrophile)
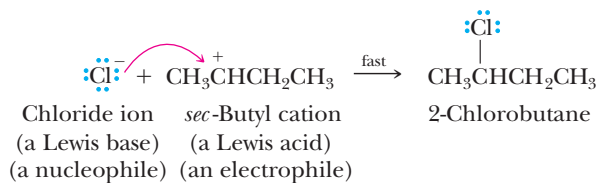
Draw Mechanisms

Mechanisms show how bonds are broken and formed. Although individual atoms may change positions in a reaction, the curved arrows used in a mechanism are only for the purpose of showing electron movement. Therefore, it is important to remember that curved arrow notation always shows the arrow originating from a bond or from an unshared electron pair (not the other way around).

Correct use of curved arrows...

Incorrect use of curved arrows...
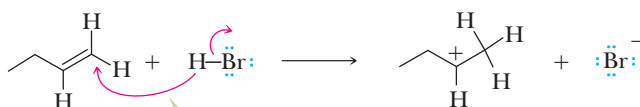
a common mistake is to use curved arrows to indicate the movement of atoms rather than electrons

Now let us go back and look at the individual steps in more detail. There is a great deal of important organic chemistry embedded in these two steps, and it is crucial that you understand it now.

Step 1 results in the formation of an organic cation. One carbon atom in this cation has only six electrons in its valence shell and carries a charge of +1. A species containing a positively charged carbon atom is called a **carbocation** (*carbon* + *cation*). Carbocations are classified as primary (1°), secondary (2°), or tertiary (3°), depending on the number of carbon atoms bonded directly to the carbon bearing the positive charge. All carbocations are Lewis acids (Section 2.6) and electrophiles.

In a carbocation, the carbon bearing the positive charge is bonded to three other atoms, and, as predicted by valence-shell electron-pair repulsion (VSEPR), the three bonds about that carbon are coplanar and form bond angles of approximately 120°. According to the orbital overlap model of bonding, the electron-deficient carbon of a carbocation uses its sp^2 hybrid orbitals to form sigma bonds to three groups. The unhybridized $2p$ orbital lies perpendicular to the sigma bond framework and contains no electrons. A Lewis structure and an orbital overlap diagram for the *tert*-butyl cation are shown in Figure 5.3.

Figure 5.4 shows an energy diagram for the two-step reaction of 2-butene with HCl. The slower, rate-determining step (the one that crosses the higher energy barrier) is Step 1, which leads to the formation of the 2° carbocation intermediate. This intermediate lies in an energy minimum between the transition states for Steps 1 and 2. As soon as the carbocation intermediate (a Lewis acid) forms, it reacts with chloride ion (a Lewis base) in a Lewis acid–base reaction to give 2-chlorobutane. Note that the energy level for 2-chlorobutane (the product) is lower than the energy level for 2-butene and HCl (the reactants). Thus, in this alkene addition reaction, heat is released; the reaction is, accordingly, exothermic.

Carbocation A species containing a carbon atom with only three bonds to it and bearing a positive charge.

FIGURE 5.3
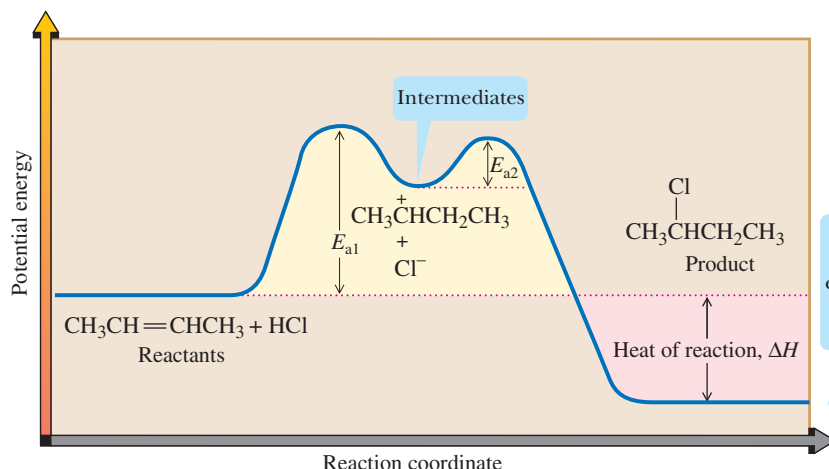The structure of the *tert*-butyl cation. (a) Lewis structure and (b) an orbital picture.

tert-Butyl cation
(a)

vacant $2p$ orbital

σ bonds formed by overlap of sp^2-sp^3 hybrid orbitals
(b)
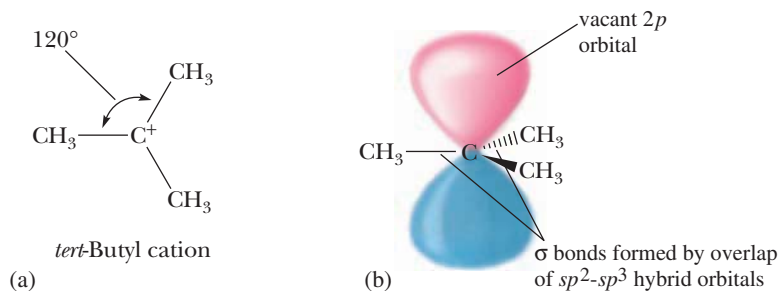
FIGURE 5.4
Energy diagram for the two-step addition of HCl to 2-butene. The reaction is exothermic.

Relative Stabilities of Carbocations: Regioselectivity and Markovnikov's Rule

The reaction of HX and an alkene can, at least in principle, give two different carbocation intermediates, depending on which of the doubly bonded carbon atoms forms a bond with H^+, as illustrated by the reaction of HCl with propene:
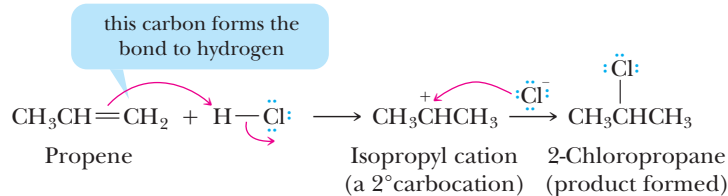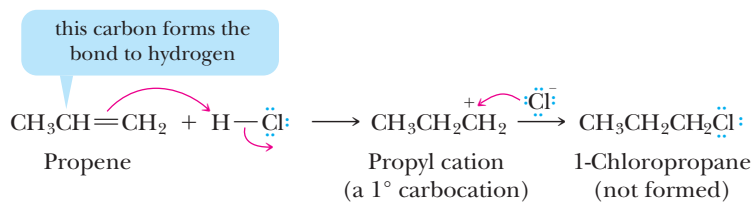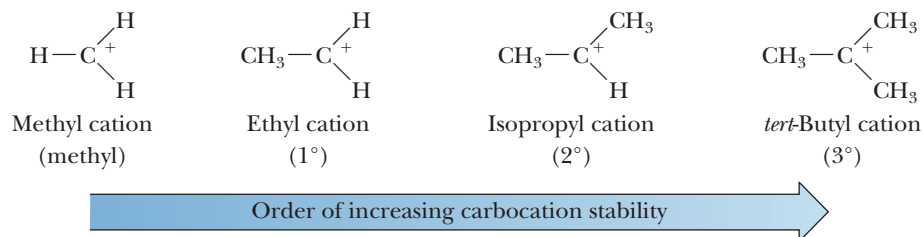

The observed product is 2-chloropropane. Because carbocations react very quickly with chloride ions, the absence of 1-chloropropane as a product tells us that the 2° carbocation is formed in preference to the 1° carbocation.

Similarly, in the reaction of HCl with 2-methylpropene, the transfer of a proton to the carbon–carbon double bond might form either the isobutyl cation (a 1° carbocation) or the *tert*-butyl cation (a 3° carbocation):
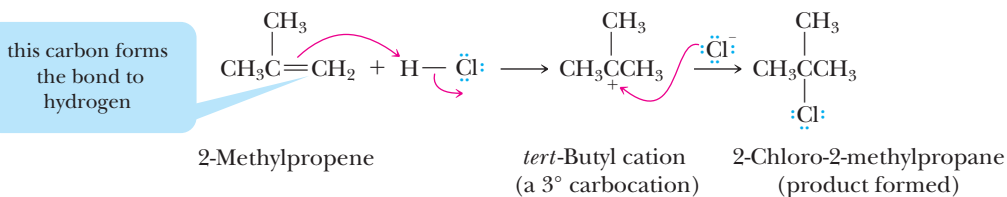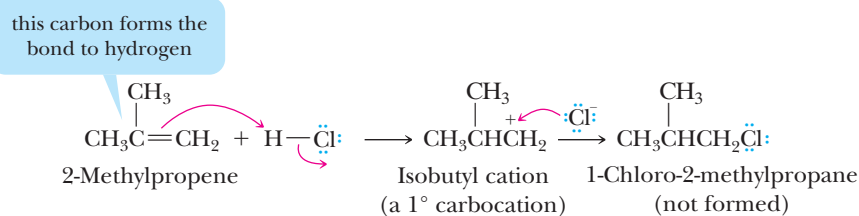
In this reaction, the observed product is 2-chloro-2-methylpropane, indicating that the 3° carbocation forms in preference to the 1° carbocation.

From such experiments and a great amount of other experimental evidence, we learn that a 3° carbocation is more stable and requires a lower activation energy for its formation than a 2° carbocation. A 2° carbocation, in turn, is more stable and requires a lower activation energy for its formation than a 1° carbocation. In fact, 1° carbocations are so unstable and so difficult to form that they are never observed in solution; they should never be proposed as a reaction intermediate when other more stable carbocations are an option. It follows that a more stable carbocation intermediate forms faster than a less stable carbocation intermediate. Following is the order of stability of four types of alkyl carbocations:

Methyl cation (methyl)	Ethyl cation (1°)	Isopropyl cation (2°)	tert-Butyl cation (3°)

Order of increasing carbocation stability

Although the concept of the relative stabilities of carbocations had not been developed in Markovnikov's time, their relative stabilities are the underlying basis for his rule; that is, the proton of H—X adds to the less substituted carbon of a double bond because this mode of addition produces the more stable carbocation intermediate.

Now that we know the order of stability of carbocations, how do we account for it? The principles of physics teach us that a system bearing a charge (either positive or negative) is more stable if the charge is delocalized. Using this principle, we can explain the order of stability of carbocations if we assume that alkyl groups bonded to a positively charged carbon release electrons toward the cationic carbon and thereby help delocalize the charge on the cation. The electron-releasing ability of alkyl groups bonded to a cationic carbon is accounted for by the **inductive effect** (Section 2.5C).

The inductive effect operates in the following way: The electron deficiency of the carbon atom bearing a positive charge exerts an electron-withdrawing inductive effect that polarizes electrons from adjacent sigma bonds toward it. Thus, the positive charge of the cation is not localized on the trivalent carbon, but rather is delocalized over nearby atoms as well. The larger the volume over which the positive charge is delocalized, the greater is the stability of the cation. Thus, as the number of alkyl groups bonded to the cationic carbon increases, the stability of the cation increases as well. Figure 5.5 illustrates the electron-withdrawing inductive effect of the positively charged carbon and the resulting delocalization of charge. According to quantum mechanical calculations, the charge on carbon in the methyl cation is approximately +0.645, and the charge on each of the hydrogen atoms is +0.118. Thus, even in the methyl cation, the positive charge is not localized on carbon. Rather, it is delocalized over the volume of space occupied by the entire ion. The polarization of electron density and the delocalization of charge are even more extensive in the *tert*-butyl cation.

FIGURE 5.5
Methyl and *tert*-butyl cations. Delocalization of positive charge by the electron-withdrawing inductive effect of the trivalent, positively charged carbon according to molecular orbital calculations.

the methyl groups donate electron density toward the carbocation carbon, thus delocalizing the positive charge
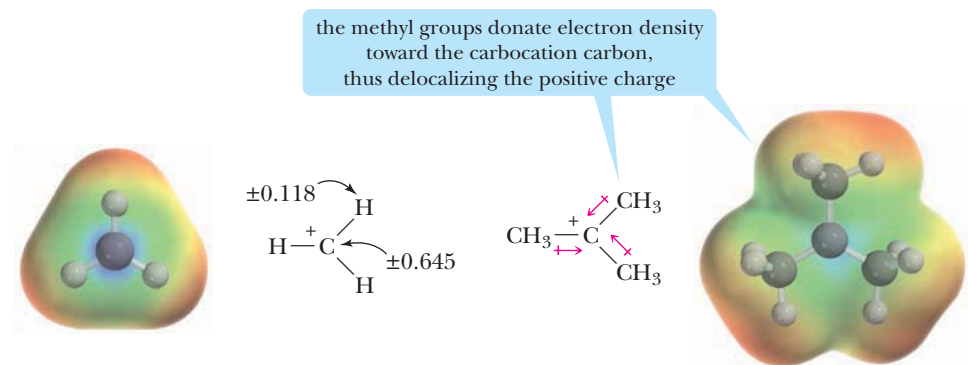
EXAMPLE 5.3

Arrange these carbocations in order of increasing stability:

(a)   **(b)**   **(c)**
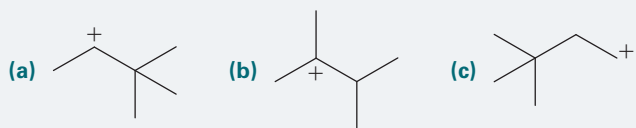
STRATEGY

Determine the degree of substitution of the positively charged carbon and then consider the order of decreasing stability of alkyl carbocations is 3° > 2° > 1°.
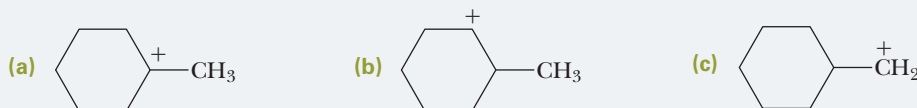
SOLUTION

Carbocation (a) is secondary, (b) is tertiary, and (c) is primary. In order of increasing stability, they are $c < a < b$.
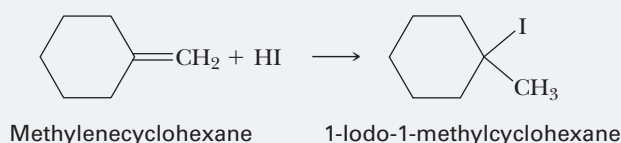
See problems 5.15, 5.16

PROBLEM 5.3

Arrange these carbocations in order of increasing stability:

(a)   **(b)**   **(c)**

EXAMPLE 5.4

Propose a mechanism for the addition of HI to methylenecyclohexane to give 1-iodo-1-methylcyclohexane:

Methylenecyclohexane   1-Iodo-1-methylcyclohexane

Which step in your mechanism is rate determining?

STRATEGY

Propose a two-step mechanism similar to that proposed for the addition of HCl to propene. Formation of the carbocation intermediate is rate determining.

SOLUTION

STEP 1: Add a proton. A rate-determining proton transfer from HI to the carbon–carbon double bond gives a 3° carbocation intermediate:
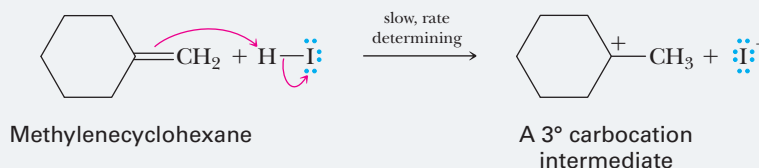
Methylenecyclohexane   A 3° carbocation intermediate

STEP 2: Reaction of a nucleophile and an electrophile to form a new covalent bond. Reaction of the 3° carbocation intermediate (a Lewis acid) with iodide ion (a Lewis base) completes the valence shell of carbon and gives the product:

(an electrophile)   (a nucleophile)   1-Iodo-1-methylcyclohexane
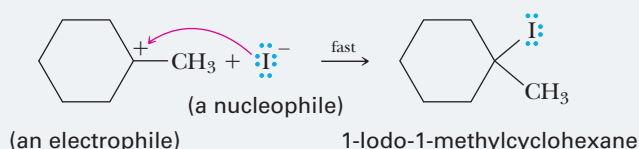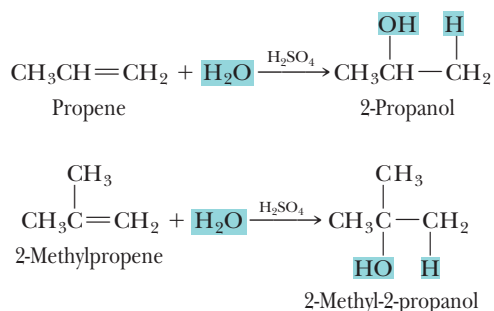
See problem 5.29

PROBLEM 5.4

Propose a mechanism for the addition of HI to 1-methylcyclohexene to give 1-iodo-1-methylcyclohexane. Which step in your mechanism is rate determining?

B. Addition of Water: Acid-Catalyzed Hydration

Hydration Addition of water.

In the presence of an acid catalyst—most commonly, concentrated sulfuric acid—water adds to the carbon–carbon double bond of an alkene to give an alcohol. The addition of water is called **hydration**. In the case of simple alkenes, H adds to the carbon of the double bond with the greater number of hydrogens and OH adds to the carbon with the lesser number of hydrogens. Thus, H—OH adds to alkenes in accordance with Markovnikov's rule:

$$CH_3CH{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3CH{-}CH_2$$

Propene   2-Propanol
(OH H)

$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_2$$

2-Methylpropene   (HO H)
2-Methyl-2-propanol

EXAMPLE 5.5

Draw a structural formula for the product of the acid-catalyzed hydration of 1-methylcyclohexene.

STRATEGY

Use Markovnikov's rule, which states that the H adds to the carbon of the carbon–carbon double bond bearing the greater number of hydrogens and that OH adds to the carbon bearing the lesser number of hydrogens.

SOLUTION

1-Methylcyclohexene   1-Methylcyclohexanol
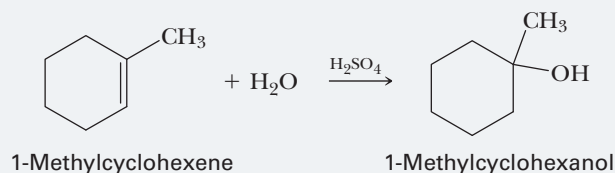
See problems 5.19, 5.20, 5.28, 5.32

PROBLEM 5.5

Draw a structural formula for the product of each alkene hydration reaction:

(a) + H₂O $\xrightarrow{H_2SO_4}$ (b) + H₂O $\xrightarrow{H_2SO_4}$
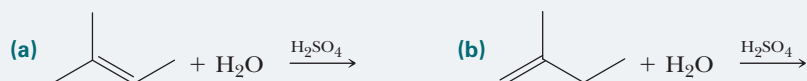
The mechanism for the acid-catalyzed hydration of alkenes is quite similar to what we have already proposed for the addition of HCl, HBr, and HI to alkenes and is illustrated by the hydration of propene to 2-propanol. This mechanism is consistent with the fact that acid is a catalyst. An H_3O^+ is consumed in Step 1, but another is generated in Step 3.
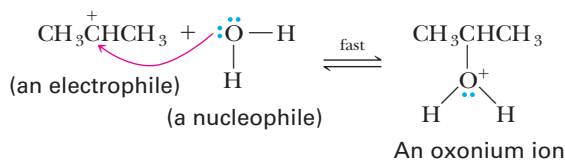
Mechanism

Acid-Catalyzed Hydration of Propene

STEP 1: Add a proton. Proton transfer from the acid catalyst, in this case, the hydronium ion, to propene gives a 2° carbocation intermediate (a Lewis acid):

$$CH_3CH=CH_2 + H-\overset{+}{O}-H \underset{}{\overset{\text{slow, rate}}{\rightleftharpoons}} CH_3\overset{+}{C}HCH_3 + :\overset{}{O}-H$$

(a nucleophile)   (an electrophile)   A 2° carbocation intermediate
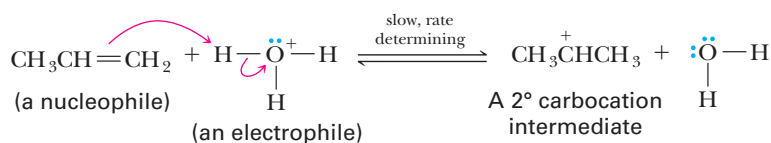
In this step, the carbon–carbon double bond of the alkene functions as a nucleophile and the hydronium ion functions as an electrophile.

STEP 2: Reaction of a nucleophile and an electrophile to form a new covalent bond. Reaction of the carbocation intermediate (a Lewis acid) with water (a Lewis base) completes the valence shell of carbon and gives an **oxonium ion:**

$$CH_3\overset{+}{C}HCH_3 + :\overset{}{O}-H \overset{\text{fast}}{\rightleftharpoons} CH_3CHCH_3$$

(an electrophile)   (a nucleophile)   An oxonium ion

Oxonium ion An ion that contains an oxygen atom that bears a positive charge and with three bonds to oxygen.

STEP 3: Take a proton away. Proton transfer from the oxonium ion to water gives the alcohol and generates a new molecule of the catalyst:

$$CH_3CHCH_3 + H-\overset{}{O}-H \overset{\text{fast}}{\rightleftharpoons} CH_3CHCH_3 + H-\overset{+}{O}-H$$
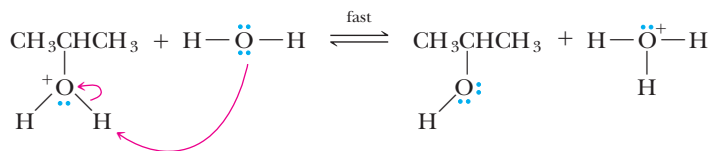
EXAMPLE 5.6

Propose a mechanism for the acid-catalyzed hydration of methylenecyclohexane to give 1-methylcyclohexanol. Which step in your mechanism is rate determining?

STRATEGY

Propose a three-step mechanism similar to that for the acid-catalyzed hydration of propene.

SOLUTION

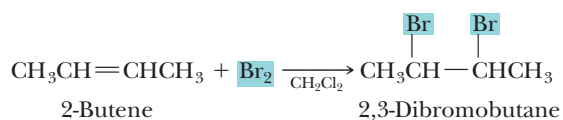The formation of the 3° carbocation intermediate in Step 1 is rate determining.

STEP 1: Add a proton. Proton transfer from the acid catalyst to the alkene gives a 3° carbocation intermediate (a Lewis acid):
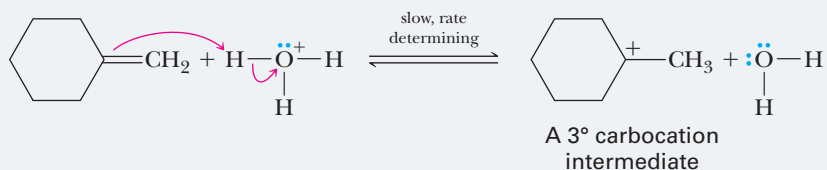
A 3° carbocation
intermediate

STEP 2: Reaction of a nucleophile and an electrophile to form a new covalent bond. Reaction of the carbocation intermediate (a Lewis acid) with water (a Lewis base) completes the valence shell of carbon and gives an oxonium ion:
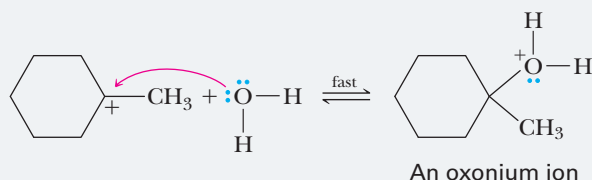
An oxonium ion

STEP 3: Take a proton away. Proton transfer from the oxonium ion to water gives the alcohol and regenerates the acid catalyst:
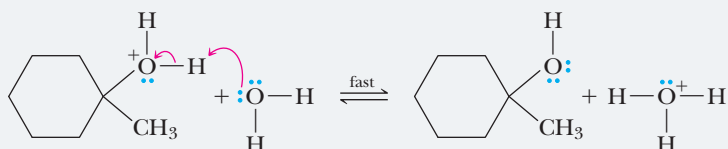
See problems 5.29–5.31, 5.38

PROBLEM   5.6

Propose a mechanism for the acid-catalyzed hydration of 1-methylcyclohexene to give 1-methylcyclohexanol. Which step in your mechanism is rate determining?

C.   Addition of Bromine and Chlorine

Chlorine (Cl_2) and bromine (Br_2) react with alkenes at room temperature by the addition of halogen atoms to the two carbon atoms of the double bond, forming two new carbon–halogen bonds:

$$CH_3CH=CHCH_3 + Br_2 \xrightarrow{CH_2Cl_2} CH_3CH-CHCH_3$$

with Br and Br substituents.

2-Butene   2,3-Dibromobutane

Stereoselective reaction
A reaction in which one stereoisomer is formed or destroyed in preference to all others that might be formed or destroyed.

Anti stereoselectivity
Addition of atoms or groups of atoms from opposite sides or faces of a carbon–carbon double bond.

Fluorine, F_2, also adds to alkenes, but because its reactions are very fast and difficult to control, addition of fluorine is not a useful laboratory reaction. Iodine, I_2, also adds, but the reaction is not preparatively useful.

The addition of bromine and chlorine to a cycloalkene gives a *trans* dihalocycloalkane. For example, the addition of bromine to cyclohexene gives *trans*-1,2-dibromocyclohexane; the *cis* isomer is not formed. Thus, the addition of a halogen to a cycloalkene is stereoselective. A **stereoselective reaction** is a reaction in which one stereoisomer is formed or destroyed in preference to all others that might be formed or destroyed. We say that addition of bromine to an alkene occurs with **anti stereoselectivity**.

in anti stereoselectivity, the reactants add to opposite sides of the former C—C double bond. We know this because one Br is bonded with a solid wedge, while the other Br is bonded with a dashed wedge

Cyclohexene   *trans*-1,2-Dibromocyclohexane
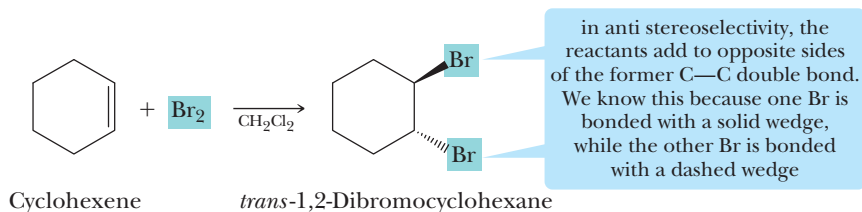
The reaction of bromine with an alkene is a particularly useful qualitative test for the presence of a carbon–carbon double bond. If we dissolve bromine in dichloromethane, the solution turns red. Both alkenes and dibromoalkanes are colorless. If we now mix a few drops of the bromine solution with an alkene, a dibromoalkane is formed, and the solution becomes colorless.

A solution of bromine in dichloromethane is red. Add a few drops of an alkene and the red color disappears.

EXAMPLE   5.7

Complete these reactions, showing the stereochemistry of each product:

(a) + Br$_2$ $\xrightarrow{\text{CH}_2\text{Cl}_2}$

(b) + Cl$_2$ $\xrightarrow{\text{CH}_2\text{Cl}_2}$
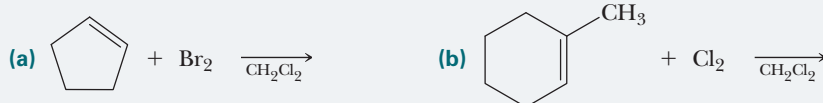
STRATEGY

The addition of both Br$_2$ and Cl$_2$ to cycloalkenes occurs with anti stereoselectivity; the two halogen atoms are *trans* to each other in the product.

SOLUTION

(a) + Br$_2$ $\xrightarrow{\text{CH}_2\text{Cl}_2}$

(b) + Cl$_2$ $\xrightarrow{\text{CH}_2\text{Cl}_2}$
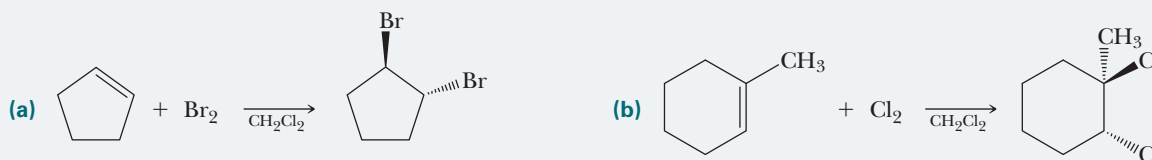
See problem 5.21

PROBLEM   5.7

Complete these reactions:

(a) CH$_3$CCH=CH$_2$ + Br$_2$ $\xrightarrow{\text{CH}_2\text{Cl}_2}$
(with CH$_3$ groups above and below the central C)

(b) + Cl$_2$ $\xrightarrow{\text{CH}_2\text{Cl}_2}$

Halonium ion   An ion in which a halogen atom bears a positive charge.

Stereoselectivity and Bridged Halonium Ion Intermediates

We explain the addition of bromine and chlorine to cycloalkenes, as well as their anti stereoselectivity (they always add *trans* to each other), by a two-step mechanism that involves a halogen atom bearing a positive charge, called a **halonium ion**. The cyclic structure of which this ion is a part is called a **bridged halonium ion**. The bridged bromonium ion shown in the mechanism that follows might look odd to you, but it is an acceptable Lewis structure. A calculation of formal charge places a positive charge on bromine. Then, in Step 2, a bromide ion reacts with the bridged intermediate from the side opposite that occupied by the bromine atom, giving the dibromoalkane. Thus, bromine atoms add from opposite faces of the carbon–carbon double bond.

Mechanism

Addition of Bromine with Anti Selectivity

STEP 1: Reaction of a nucleophile and an electrophile to form a new covalent bond. Reaction of the pi electrons of the carbon–carbon double bond (a nucleophile) with bromine (an electrophile) forms a bridged bromonium ion intermediate in which bromine bears a positive formal charge:

A bridged bromonium ion intermediate
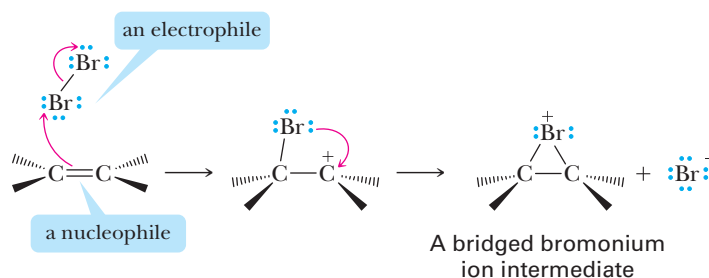
STEP 2: Reaction of a nucleophile and an electrophile to form a new covalent bond. A bromide ion (a nucleophile and a Lewis base) attacks carbon (an electrophile and a Lewis acid) from the side opposite the bridged bromonium ion, opening the three-membered ring:

Anti (coplanar) orientation of added bromine atoms

A Newman projection of the product viewed from the left
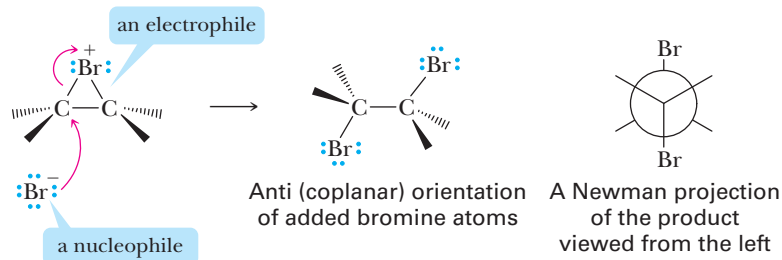
The addition of chlorine or bromine to cyclohexene and its derivatives gives a *trans* diaxial product because only axial positions on adjacent atoms of a cyclohexane ring are anti and coplanar. The initial *trans* diaxial conformation of the product is in equilibrium with the *trans* diequatorial conformation, and, in simple derivatives of cyclohexane, the latter is the more stable conformation and predominates.

trans Diaxial   *trans* Diequatorial (more stable)
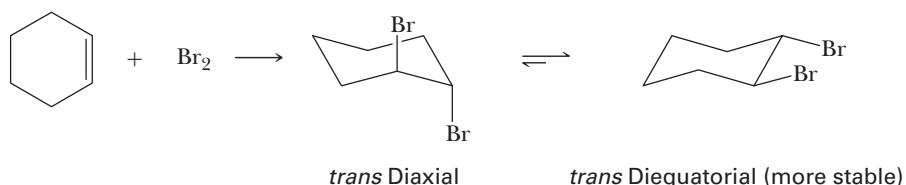
5.4 What Are Carbocation Rearrangements?

As we have seen in the preceding discussion, the expected product of electrophilic addition to a carbon–carbon double bond involves rupture of the π bond and formation of two new σ bonds in its place. In the addition of HCl to 3,3-dimethyl-1-butene, however, only 17% of 2-chloro-3, 3-dimethylbutane, the expected product, is formed. The major product is 2-chloro-2,3-dimethylbutane, a compound with a different connectivity of its carbon atoms than that in the starting material. We say that the formation of 2-chloro-2,3-dimethylbutane involves a **rearrangement**. Typically, either an alkyl group or a hydrogen atom migrates, with its bonding pair of electrons, from an adjacent atom to an electron-deficient atom. In the rearrangements we examine in this chapter, migration is to an adjacent electron-deficient carbon atom bearing a positive charge. In other words, rearrangement is to the positively charged carbon of a carbocation.

Rearrangement A reaction in which a carbon or hydrogen atom has shifted its connectivity to another atom within the molecule.

| 3,3-Dimethyl-1-butene | 2-Chloro-3,3-dimethylbutane (the expected product 17%) | 2-Chloro-2,3-dimethylbutane (the major product 83%) |
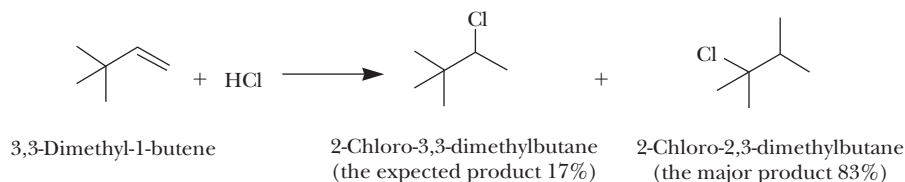
Formation of the rearranged product in this reaction can be accounted for by the following mechanism, the key step of which is a type of rearrangement called a **1,2-shift**. In the rearrangement shown in Step 2, the migrating group is a methyl group with its pair of bonding electrons.

Mechanism

Rearrangement by a 1,2-Shift

STEP 1: **Add a proton.** Proton transfer from the HCl (an electrophile) to the alkene (a nucleophile) gives a 2° carbocation intermediate.

3,3-Dimethyl-1-butene
(a nucleophile)

(an electrophile)

A 2° carbocation
intermediate
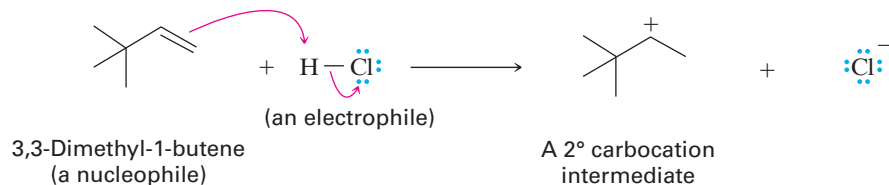
STEP 2: **Rearrangement of a bond.** Migration of a methyl group with its bonding electrons from an adjacent carbon gives a more stable 3° carbocation intermediate. The major movement is that of the bonding electron pair with the methyl group following.
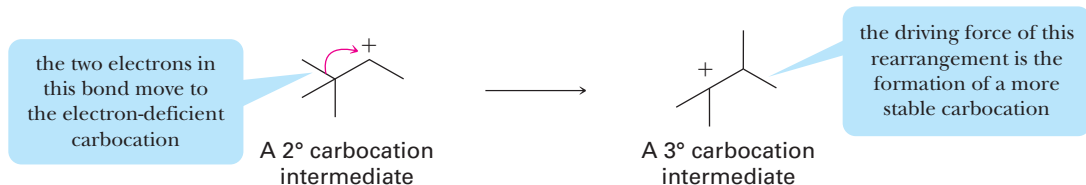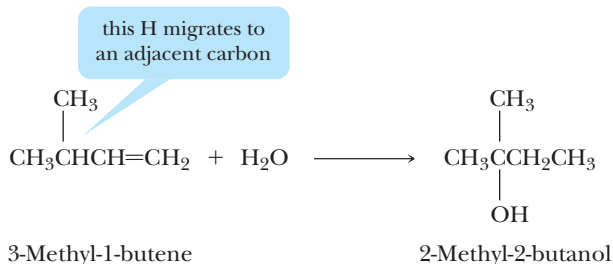
the two electrons in this bond move to the electron-deficient carbocation

the driving force of this rearrangement is the formation of a more stable carbocation

A 2° carbocation
intermediate

A 3° carbocation
intermediate

STEP 3: **Reaction of a nucleophile and an electrophile to form a new covalent bond.** Reaction of the 3° carbocation intermediate (an electrophile and a Lewis acid) with chloride ion (a nucleophile and a Lewis base) gives the rearranged product.

(a nucleophile)

A 3° carbocation
intermediate
(an electrophile)
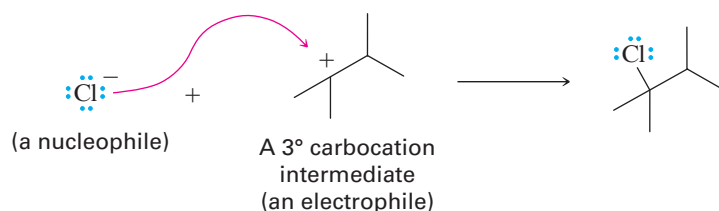
The driving force for this rearrangement is the fact that the less stable 2° carbocation is converted to a more stable 3° carbocation. From the study of this and other carbocation rearrangements, we find that 2° carbocations rearrange to 3° carbocations. 1° Carbocations are never observed for reactions taking place in solution and should not be proposed as reaction intermediates.

Rearrangements also occur in the acid-catalyzed hydration of alkenes, especially when a carbocation formed in the first step can rearrange to a more stable carbocation. For example, the acid-catalyzed hydration of 3-methyl-1-butene gives 2-methyl-2-butanol. In this example, the group that migrates is a hydrogen with its bonding pair of electrons, in effect, a hydride ion H:⁻.

this H migrates to an adjacent carbon

$$CH_3CHCH{=}CH_2 \ + \ H_2O \ \longrightarrow \ CH_3CCH_2CH_3$$

3-Methyl-1-butene   2-Methyl-2-butanol

In summary, a rearrangement is likely to occur when a secondary carbocation forms and can rearrange by a 1,2-shift to a more stable tertiary carbocation.

EXAMPLE 5.8

Propose a mechanism for the acid-catalyzed hydration of 3-methyl-1-butene to give 2-methyl-2-butanol.

STRATEGY

Propose a mechanism similar to that proposed for the acid-catalyzed hydration of an alkene involving proton transfer from the acid catalyst to form a carbocation intermediate, rearrangement of the carbocation intermediate to a more stable intermediate, reaction of the more stable carbocation with water to form an oxonium ion, and finally proton transfer from the oxonium ion to water to give the product and regenerate the acid catalyst. Lest you be tempted to use H⁺ to initiate the reaction, remember that ionization of a strong acid in water generates a hydronium ion and an anion. Hydronium ion and not H⁺ is the true catalyst in this reaction.

SOLUTION

STEP 1: Add a proton. Proton transfer from the hydronium ion (the acid catalyst and electrophile) to the carbon–carbon double bond (the nucleophile) gives a 2° carbocation intermediate.

there is one hydrogen bonded to the carbocation carbon that is not drawn

3-Methyl-1-butene   Hydronium ion   A 2° carbocation
(a nucleophile)   (an electrophile)   intermediate
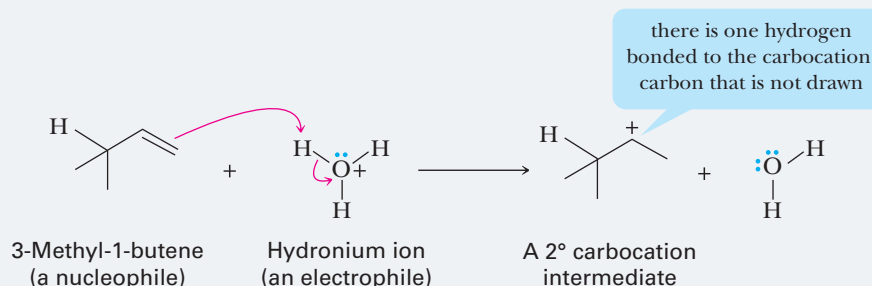
STEP 2: Rearrangement of a bond. A 1,2-shift of a hydrogen from an adjacent carbon with its bonding pair of electrons to the positively charged carbon gives a more stable 3° carbocation intermediate.

A 2° carbocation
intermediate

A 3° carbocation
intermediate

STEP 3: Reaction of a nucleophile and an electrophile to form a new covalent bond. Reaction of the 3° carbocation (an electrophile and a Lewis acid) with a water molecule (a nucleophile and a Lewis base) completes the valence shell of carbon and gives an oxonium ion.

(a nucleophile)　　A 2° carbocation
intermediate
(an electrophile)

An oxonium
ion

STEP 4: Take a proton away. Proton transfer from the oxonium ion to water gives the alcohol and regenerates the acid catalyst.

An oxonium
ion

Hydronium
ion
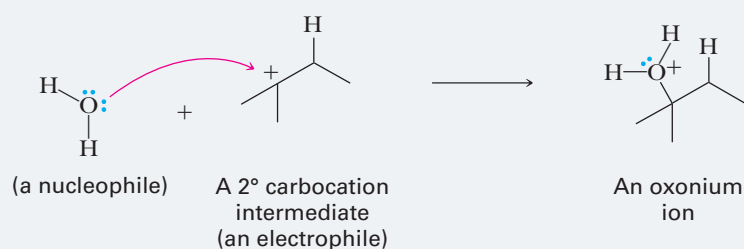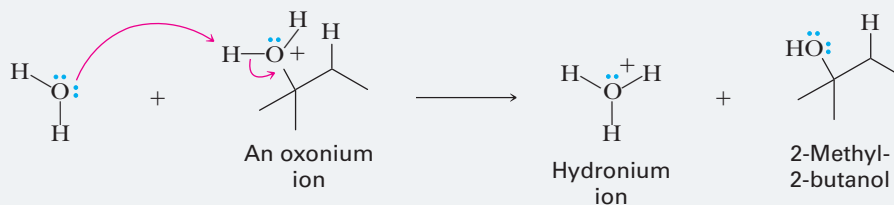
2-Methyl-
2-butanol

See problems 5.29–5.31, 5.38

PROBLEM 5.8

The acid-catalyzed hydration of 3,3-dimethyl-1-butene gives 2,3-dimethyl-2-butanol as the major product. Propose a mechanism for the formation of this alcohol.

$$CH_2{=}CH{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 \;+\; H_2O \xrightarrow{\;H_2SO_4\;} CH_3{-}\underset{}{\overset{\overset{CH_3}{|}}{CH}}{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}OH$$

3,3-Dimethyl-1-butene

2,3-Dimethyl-2-butanol
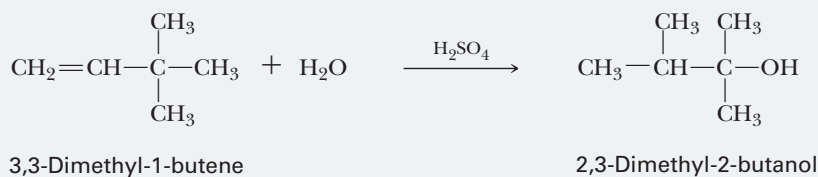
5.5 What Is Hydroboration–Oxidation of an Alkene?

The result of hydroboration and subsequent oxidation of an alkene is hydration of the carbon–carbon double bond, here illustrated by the hydroboration–oxidation of 1-hexene to give 1-hexanol.

the net result of hydroboration–oxidation is the addition of H and OH across the C—C double bond

contrary to Markovnikov's rule, the hydrogen has added to the former double-bond carbon with the fewer hydrogens

$$\xrightarrow[\text{2) NaOH, } H_2O_2]{\text{1) } BH_3 \cdot THF}$$
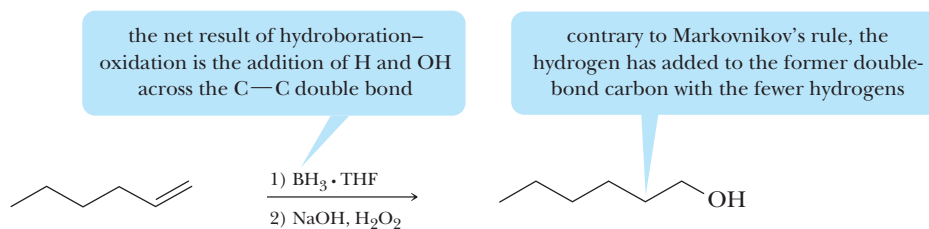
Because hydrogen is added to the more substituted carbon of the double bond and —OH to the less substituted carbon, we refer to the regiochemistry of hydroboration and subsequent oxidation as **anti-Markovnikov hydration**.

Note by way of comparison that acid-catalyzed hydration of 1-hexene follows Markovnikov's rule and gives 2-hexanol.

$$+ \quad H_2O \quad \xrightarrow{H_2SO_4}$$

1-Hexene   2-Hexanol
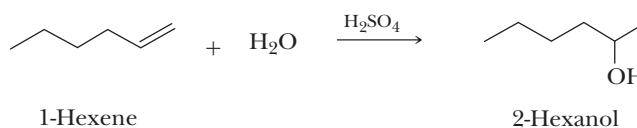
The special value of hydration of an alkene by the combination of hydroboration–oxidation is that its regioselectivity is opposite that of acid-catalyzed hydration.

Hydroboration is the addition of borane, BH_3, to an alkene to form a trialkylborane. Borane cannot be prepared as a pure compound because it reacts with itself ($2BH_3 \rightarrow B_2H_6$) to form diborane B_2H_6, a toxic gas that ignites spontaneously in air. However, BH_3 forms a stable Lewis acid–base complex with ethers and is most commonly used as a commercially available solution of BH_3 in tetrahydrofuran (THF).

$$2 \quad \overset{..}{\underset{..}{O}} \quad + \quad B_2H_6 \quad \rightleftharpoons \quad 2 \quad \overset{+}{\underset{..}{O}} - \overset{-}{BH_3}$$

Tetrahydrofuran $BH_3 \cdot$ THF
(THF)
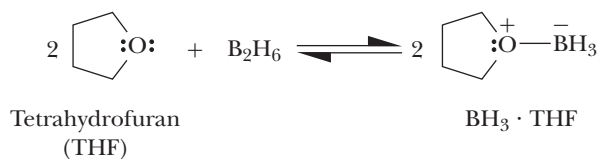
The overall reaction of BH_3 with a C—C double bond occurs in three steps. Borane reacts first with one molecule of the alkene to form an alkylborane, then with a second molecule of alkene to form a dialkylborane, and finally with a third molecule of alkene to form a trialkylborane. Although borane reacts with three equivalents of alkene to form the trialkylborane, we will focus on just the reaction of the first equivalent of C=C to explain the selectivities of the reaction.

Borane $\xrightarrow{CH_2=CH_2}$ Ethylborane
(an alkylborane) $\xrightarrow{CH_2=CH_2}$ Diethylborane
(a dialkylborane) $\xrightarrow{CH_2=CH_2}$ Triethylborane
(a trialkylborane)

we will focus on just this first reaction to explain the selectivities of the hydroboration reaction
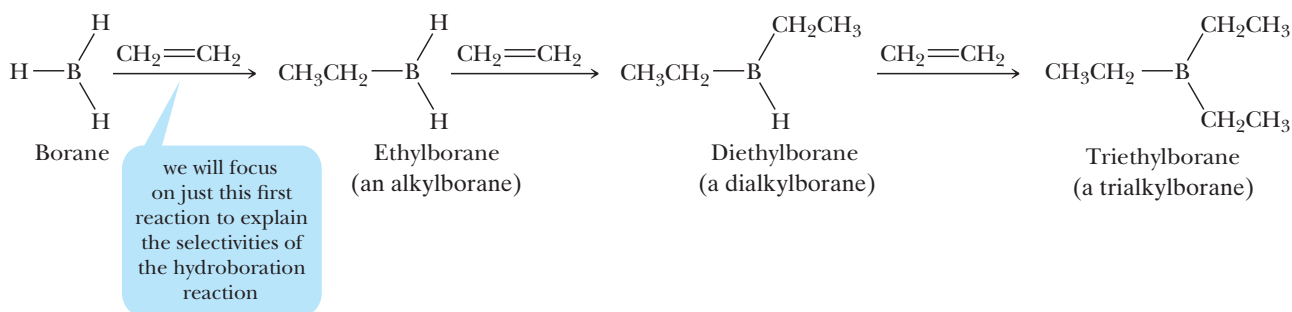
Boron, atomic number 5, has three electrons in its valence shell. To bond with three other atoms, boron uses sp^2 hybrid orbitals. Study the orbital model of BH_3 and take note of its types of orbitals and their geometrical arrangement. Because of the vacant $2p$ orbital in the valence shell of boron, BH_3, BF_3, and other tricovalent compounds of boron are electrophiles and closely resemble carbocations, except that they are electrically neutral.

an empty p orbital
(contains no electrons)
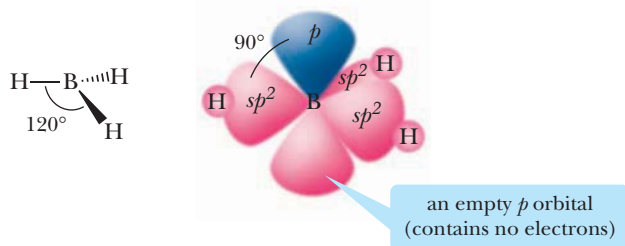
Addition of borane to alkenes is regioselective and stereoselective in the following ways:

- Regioselective: In the addition of borane to an unsymmetrical alkene, boron becomes bonded predominantly to the less substituted carbon of the double bond.
- Stereoselective: Hydrogen and boron add from the same face of the double bond; that is, the reaction is **syn** (from the same side) **stereoselective**.

Both the regioselectivity and syn stereoselectivity are illustrated by hydroboration of 1-methylcyclopentene.

1-Methylcyclopentene $\quad + \quad BH_3 \longrightarrow$

(Syn addition of BH_3)
(R = 2-methylcyclopentyl)
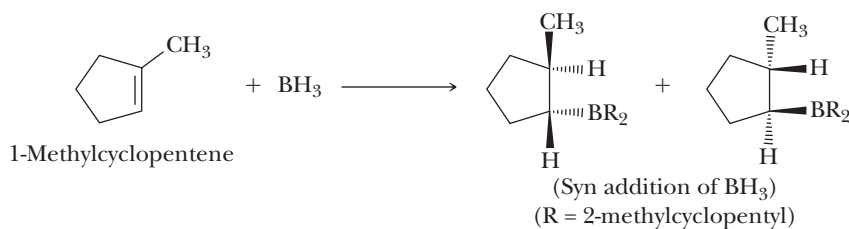
Mechanism

Hydroboration of an Alkene

STEP 1. **Reaction of a nucleophile and an electrophile to form a new covalent bond**. The addition of borane to an alkene is initiated by coordination of the vacant $2p$ orbital of boron (an electrophile) with the electron pair of the pi bond (a nucleophile). Chemists account for the stereoselectivity of hydroboration by proposing the formation of a cyclic, four-center transition state. Boron and hydrogen add simultaneously and from the same face of the double bond, with boron adding to the less substituted carbon atom of the double bond. This accounts for the syn stereoselectivity of the reaction. As shown in the mechanism, there is a slight polarity (about 5%) to the B—H bond because hydrogen (2.1) is slightly more electronegative than boron (2.0).

this transition state, with the positive charge on the more substituted carbon, is lower in energy and therefore favored in the reaction mechanism

$\delta-$ $\delta+$
H—B

+

$CH_3CH_2CH_2CH{=}CH_2$
Starting reagents

$\longrightarrow$

$CH_3CH_2CH_2{-}\overset{\displaystyle}{\underset{H}{C}}{=}CH_2$

$CH_3CH_2CH_2{-}\overset{\displaystyle}{\underset{H}{C}}{=}CH_2$

Two possible transition states
(some carbocation character
exists in both transition states)
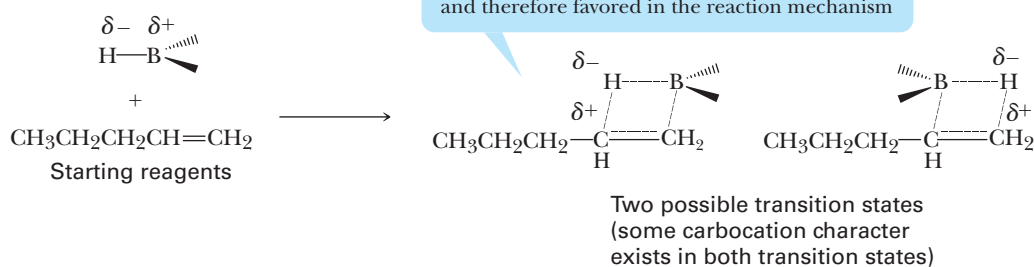
We account for the regioselectivity by steric factors. Boron, the larger part of the reagent, adds selectively to the less hindered carbon of the double bond, and hydrogen, the smaller part of the reagent, adds to the more hindered carbon. It is believed that the observed regioselectivity is due largely to steric effects.

Step 2 and beyond. Step 1 in this mechanism explains why the proton ends up on the less substituted carbon of the former C—C double bond and why the newly added boron and proton are added

syn. The boranes that are formed in the hydroboration reaction are typically oxidized using hydrogen peroxide under basic conditions. Oxidation by hydrogen peroxide results in the replacement of the boron group with an —OH group. In fact, the hydroxyl group replaces the boron such that the newly added —OH group is still syn to the proton from the previous reaction. There are many steps in the mechanism of the oxidation reaction which are beyond the scope of this text. However, we summarize the oxidation reaction below:

the —OH replaces the boron group and retains the syn orientation with the originally added proton

$$\underset{\substack{\text{(product after two steps)}}}{\underset{H_2O}{\overset{NaOH,\ H_2O_2}{\longrightarrow}}}$$

(product after two steps)   (product after three steps) $+$ $NaBO_3$
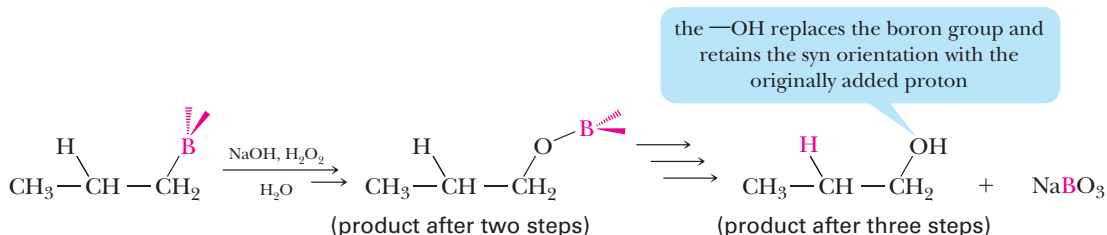
EXAMPLE 5.9

Draw structural formulas for the alcohol formed by hydroboration–oxidation of each alkene.

(a) $CH_3\overset{\underset{\displaystyle CH_3}{|}}{C}{=}CHCH_3$

(b)
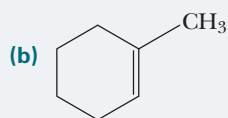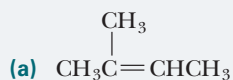
STRATEGY

Hydroboration–oxidation is regioselective (—OH adds to the more substituted carbon of the carbon–carbon double bond, and —H adds to the more substituted carbon). It is also stereoselective (—H and —OH add to the same face of the double bond).

SOLUTION

(a)

3-Methyl-2-butanol

(b)
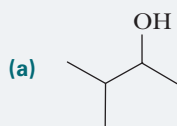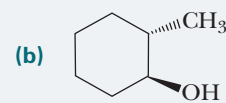
trans-2-Methylcylohexanol

See problem 5.36

PROBLEM 5.9

Draw a structural formula for the alkene that gives each alcohol on hydroboration followed by oxidation.

(a)

(b)
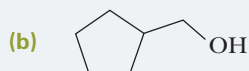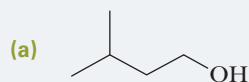
5.6 How Can an Alkene Be Reduced to an Alkane?

Most alkenes react quantitatively with molecular hydrogen, H_2 in the presence of a transition metal catalyst to give alkanes. Commonly used transition metal catalysts include platinum, palladium, ruthenium, and nickel. Yields are usually quantitative or nearly so. Because the conversion of an alkene to an alkane involves reduction by hydrogen in the presence of a catalyst, the process is called **catalytic reduction** or, alternatively, **catalytic hydrogenation**.

$$\text{Cyclohexene} + H_2 \xrightarrow[25°C,\ 3\ atm]{Pd} \text{Cyclohexane}$$
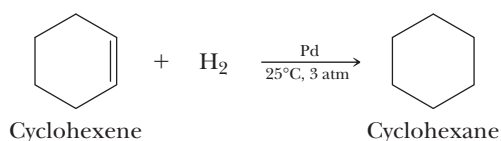
The metal catalyst is used as a finely powdered solid, which may be supported on some inert material such as powdered charcoal or alumina. The reaction is carried out by dissolving the alkene in ethanol or another nonreacting organic solvent, adding the solid catalyst, and exposing the mixture to hydrogen gas at pressures from 1 to 100 atm. Alternatively, the metal may be chelated with certain organic molecules and used in the form of a soluble complex.

Catalytic reduction is stereoselective, the most common pattern being the **syn addition** of hydrogens to the carbon–carbon double bond. The catalytic reduction of 1,2-dimethylcyclohexene, for example, yields *cis*-1,2-dimethylcyclohexane along with lesser amounts of *trans*-1,2-dimethylcyclohexane.

1,2-Dimethyl-cyclohexene $+ H_2 \xrightarrow{Pt}$ 70% to 85% *cis*-1,2-Dimethyl-cyclohexane $+$ 30% to 15% *trans*-1,2-Dimethyl-cyclohexane
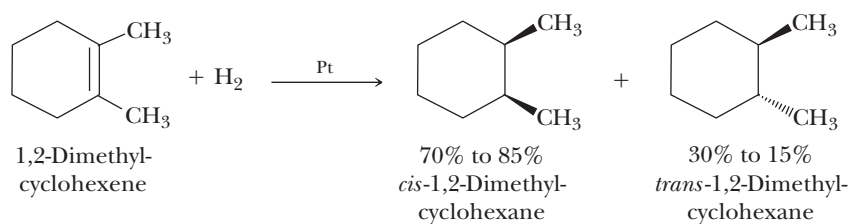
The transition metals used in catalytic reduction are able to adsorb large quantities of hydrogen onto their surfaces, probably by forming metal–hydrogen sigma bonds. Similarly,
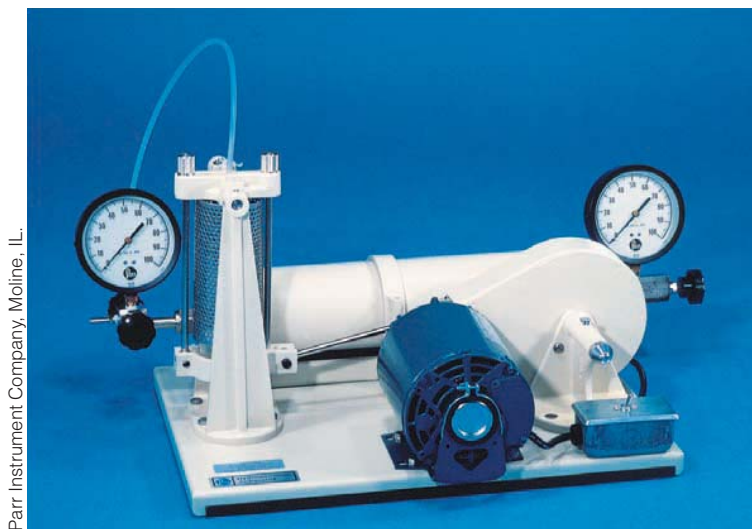
A Parr shaker-type hydrogenation apparatus.

(a)

(b)

(c)
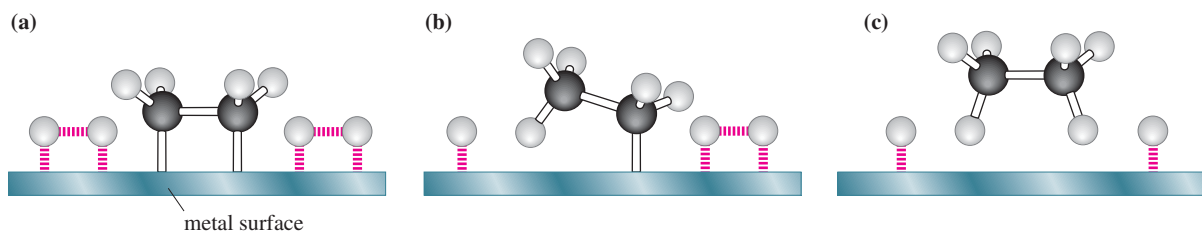
metal surface

FIGURE 5.6

Syn addition of hydrogen to an alkene involving a transition metal catalyst. (a) Hydrogen and alkene are adsorbed on the metal surface, and (b) one hydrogen atom is transferred to the alkene, forming a new C—H bond. The other carbon remains adsorbed on the metal surface. (c) A second C—H bond forms, and the alkane is desorbed.

these transition metals adsorb alkenes on their surfaces, with the formation of carbon–metal bonds [Figure 5.6(a)]. Hydrogen atoms are added to the alkene in two steps.
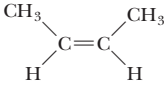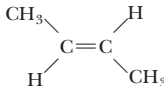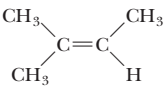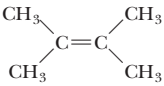
Heats of Hydrogenation and the Relative Stabilities of Alkenes

The **heat of hydrogenation** of an alkene is defined as its heat of reaction, $\Delta H°$, with hydrogen, to form an alkane. Table 5.2 lists the heats of hydrogenation of several alkenes.

Three important points follow from the information given in the table.

1. The reduction of an alkene to an alkane is an exothermic process. This observation is consistent with the fact that, during hydrogenation, there is net conversion of a weaker pi bond to a stronger sigma bond; that is, one sigma bond (H—H) and one pi bond (C=C) are broken, and two new sigma bonds (C—H) are formed.

2. The heat of hydrogenation depends on the degree of substitution of the carbon–carbon double bond: The greater the substitution, the lower is the heat of hydrogenation. Compare, for example, the heats of hydrogenation of ethylene (no substituents), propene (one substituent), 1-butene (one substituent), and the *cis* and *trans* isomers of 2-butene (two substituents each).

3. The heat of hydrogenation of a *trans* alkene is lower than that of the isomeric *cis* alkene. Compare, for example, the heats of hydrogenation of *cis*-2-butene and *trans*-2-butene. Because the reduction of each alkene gives butane, any difference in their heats of hydrogenation

TABLE 5.2   Heats of Hydrogenation of Several Alkenes

Name	Structural Formula	ΔH [kJ (kcal/mol)]	
Ethylene	$CH_2{=}CH_2$	−137 (−32.8)	
Propene	$CH_3CH{=}CH_2$	−126 (−30.1)	
1-Butene	$CH_3CH_2CH{=}CH_2$	−127 (−30.3)	Ethylene
cis-2-Butene		−120 (−28.6)	
trans-2-Butene		−115 (−27.6)	*trans*-2-Butene
2-Methyl-2-butene		−113 (−26.9)	
2,3-Dimethyl-2-butene		−111 (−26.6)	2,3-Dimethyl-2-butene
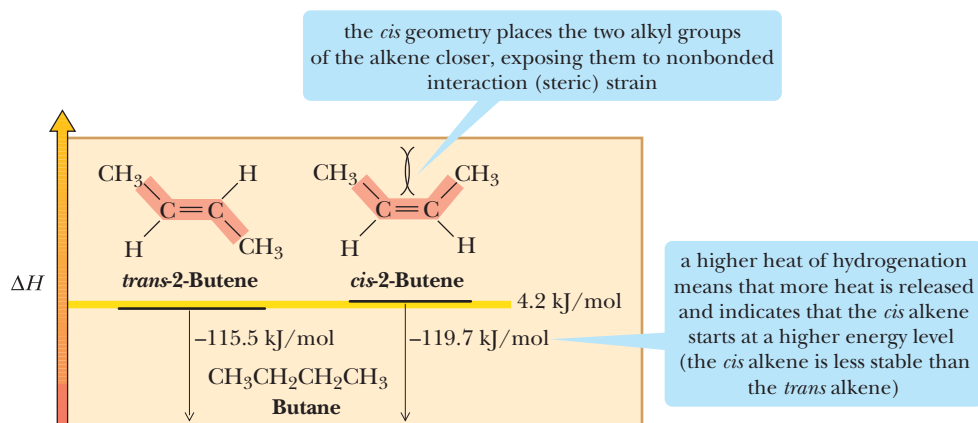
FIGURE 5.7
Heats of hydrogenation of *cis*-2-butene and *trans*-2-butene. *trans*-2-Butene is more stable than *cis*-2-butene by 4.2 kJ/mol (1.0 kcal/mol).

must be due to a difference in relative energy between the two alkenes (Figure 5.7). The alkene with the lower (less negative) value of $\Delta H°$ is the more stable alkene.

These features of a hydrogenation reaction allow us to compare the stabilities and reactivities of any two alkenes that would yield the same product upon hydrogenation. Thus we explain the greater stability of *trans* alkenes relative to *cis* alkenes in terms of non-bonded interaction strain. In *cis*-2-butene, the two —CH_3 groups are sufficiently close to each other that there is repulsion between their electron clouds. This repulsion is reflected in the larger heat of hydrogenation (decreased stability) of *cis*-2-butene compared with that of *trans*-2-butene (approximately 4.2 kJ/mol).

5.7 How Can an Acetylide Anion Be Used to Create a New Carbon–Carbon Bond?

In this section, we cover one of two very important reactions of alkynes for organic synthesis. As we have seen (Section 4.4) an acetylide anion is a strong base. It is also a nucleophile—it has an unshared pair of electrons that it can donate to an electrophilic carbon atom to form a new carbon–carbon bond.

To see how the use of an acetylide anion can lead to the formation of a new carbon–carbon bond, consider chloromethane, CH_3Cl. The C—Cl bond of chloromethane is polar covalent, with carbon bearing a partial positive charge because of the difference in electronegativity between carbon and chlorine.
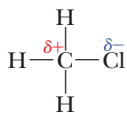
In this instance, an acetylide anion donates its unshared pair of electrons to the carbon of chloromethane and in so doing displaces the halogen atom. Notice that this mechanism follows one of our common patterns, **the reaction of a nucleophile with an electrophile to form a new covalent bond**:
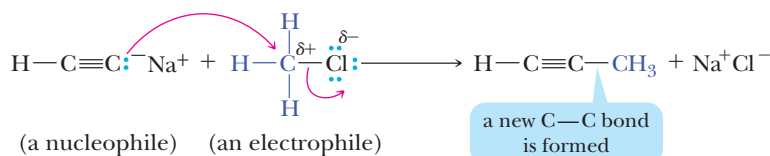
The important result is the formation of a new carbon–carbon bond. As is the case with so many organic reactions, this is an instance where reaction is brought about by the interaction of positive and negative charges of interacting molecules.
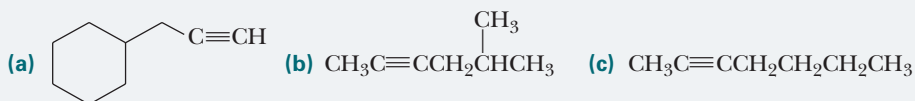
Because an alkyl group is added to the original alkyne molecule, this type of reaction is called an **alkylation reaction**. We limit our discussion in this chapter to reactions of acetylide anions with methyl and primary haloalkanes. We will discuss the scope and limitation of this type of nucleophilic substitution in more detail in Chapter 7. For reasons we will discuss there, alkylation of nucleophilic acetylide anions is practical only for methyl and primary halides. While this alkylation reaction can be used with limited success with secondary haloalkanes, it fails altogether for tertiary haloalkanes.

Because of the ready availability of acetylene and the ease with which it is converted to a nucleophile, alkylation of acetylide anions is the most convenient laboratory method used for the synthesis of other alkynes. The process can be repeated, and a terminal alkyne in turn can be converted to an internal alkyne. An important feature of this reaction is that a new carbon–carbon skeleton can be made, allowing for the construction of larger carbon skeletons from smaller ones. In the following scheme, the carbon skeleton of 3-heptyne is constructed from acetylene and two lower-molecular-weight haloalkanes.

$$HC\equiv CH \xrightarrow[\text{2) } CH_3CH_2Br]{\text{1) } NaNH_2} CH_3CH_2C\equiv CH \xrightarrow[\text{4) } CH_3CH_2CH_2Br]{\text{3) } NaNH_2} CH_3CH_2C\equiv CCH_2CH_2CH_3$$

Acetylene   1-Butyne   3-Heptyne
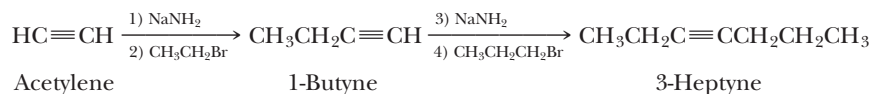
EXAMPLE   5.10

Propose a synthesis for each alkyne starting with acetylene and any necessary organic and inorganic reagents.

(a) [cyclohexyl-CH₂-C≡CH structure]

(b) $CH_3C\equiv CCH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$

(c) $CH_3C\equiv CCH_2CH_2CH_2CH_3$

STRATEGY

Each alkyne can be synthesized by alkylation of an appropriate alkyne anion. First decide which new carbon–carbon bond or bonds must be formed by alkylation and which alkyne anion nucleophile and haloalkane pair is required to give the desired product. Synthesis of a terminal alkyne from acetylene requires only one nucleophilic substitution, and synthesis of an internal alkyne from acetylene requires two nucleophilic substitutions.
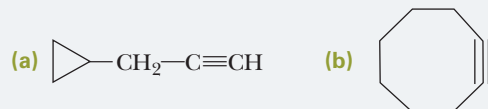
SOLUTION

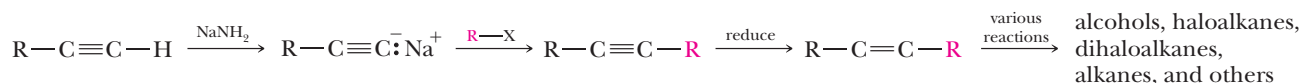(a) $HC\equiv CH \xrightarrow[\text{2) } [\text{cyclohexyl-CH}_2\text{-Br}]]{\text{1) } NaNH_2}$ [cyclohexyl-CH₂-C≡CH]

(b) $HC\equiv CH \xrightarrow[\text{2) } BrCH_3]{\text{1) } NaNH_2} CH_3C\equiv CH \xrightarrow[\substack{\text{4) } BrCH_2\overset{\overset{CH_3}{|}}{C}HCH_3}]{\text{3) } NaNH_2} CH_3C\equiv CCH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$

(c) $HC\equiv CH \xrightarrow[\text{2) } BrCH_3]{\text{1) } NaNH_2} CH_3C\equiv CH \xrightarrow[\text{4) } BrCH_2CH_2CH_2CH_3]{\text{3) } NaNH_2} CH_3C\equiv CCH_2CH_2CH_2CH_3$
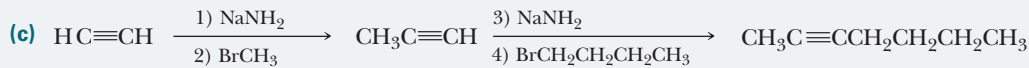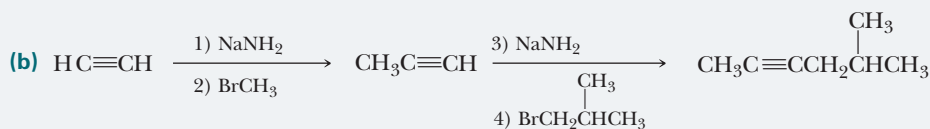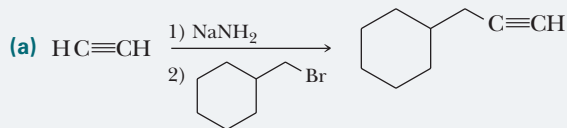
See problem 5.50

PROBLEM 5.10

Propose a synthesis for each alkyne starting with acetylene and any necessary organic and inorganic reagents.

(a) $\triangleright$—CH_2—$C\equiv CH$ **(b)**
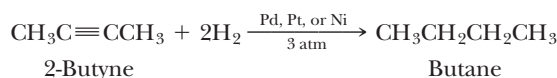

5.8 How Can Alkynes Be Reduced to Alkenes and Alkanes?
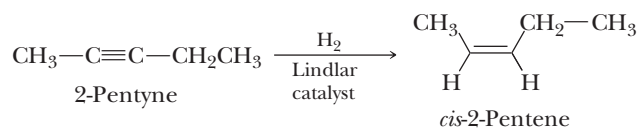
In the previous section, we saw how terminal alkynes can be used to form C—C bonds and synthesize larger alkynes. In this section, we will learn how alkynes can be reduced to alkanes and alkenes. Because of the rich number of reactions available to alkenes, we can now use these two reactions in tandem to synthesize a large variety of compounds:

$$R-C\equiv C-H \xrightarrow{NaNH_2} R-C\equiv \overset{-}{C}\text{:}Na^+ \xrightarrow{R-X} R-C\equiv C-R \xrightarrow{reduce} R-C=C-R \xrightarrow[reactions]{various} \begin{array}{l}\text{alcohols, haloalkanes,}\\ \text{dihaloalkanes,}\\ \text{alkanes, and others}\end{array}$$

Treatment of an alkyne with H_2 in the presence of a transition metal catalyst, most commonly Pd, Pt, or Ni, results in the addition of two moles of H_2 to the alkyne and its conversion to an alkane. Catalytic reduction of an alkyne can be brought about at or slightly above room temperature and with moderate pressures of hydrogen gas.

$$CH_3C\equiv CCH_3 + 2H_2 \xrightarrow[\text{3 atm}]{\text{Pd, Pt, or Ni}} CH_3CH_2CH_2CH_3$$
$$\text{2-Butyne} \qquad\qquad\qquad\qquad \text{Butane}$$

Reduction of an alkyne occurs in two stages: first, addition of one mole of H_2 to form an alkene and then addition of the second mole of H_2 to the alkene to form the alkane. In most cases, it is not possible to stop the reaction at the alkene stage. However, by careful choice of catalyst, it is possible to stop the reaction at the addition of one mole of hydrogen. The catalyst most commonly used for this purpose consists of finely powdered palladium metal deposited on solid calcium carbonate that has been specially modified with lead salts. This combination is known as the **Lindlar catalyst**. Reduction (hydrogenation) of alkynes over a Lindlar catalyst is stereoselective: **syn addition** of two hydrogen atoms to the carbon–carbon triple bond gives a *cis* alkene:

$$CH_3-C\equiv C-CH_2CH_3 \xrightarrow[\substack{\text{Lindlar}\\\text{catalyst}}]{H_2} \begin{array}{c}CH_3\qquad CH_2-CH_3\\ \diagdown\ \diagup\\ \\ H\qquad\quad H\end{array}$$
$$\text{2-Pentyne} \qquad\qquad\qquad\qquad \textit{cis}\text{-2-Pentene}$$

Because addition of hydrogen in the presence of the Lindlar catalyst is stereoselective for syn addition, it has been proposed that reduction proceeds by simultaneous or nearly simultaneous transfer of two hydrogen atoms from the surface of the metal catalyst to the alkyne. Earlier we presented a similar mechanism for the catalytic reduction of an alkene to an alkane (Section 5.6).

Organic chemistry is the foundation for the synthesis of new compounds such as medicines, agrochemicals, and plastics, to name just a few. In order to make these compounds, organic chemists must rely on a vast collection of reactions. The reactions presented in this

chapter will already allow you to achieve the synthesis of complex molecules that may require multiple steps to make. As you continue your studies of organic chemistry, new reactions will be presented, the same reactions that have allowed for the creation of the millions of compounds that have contributed to the progress of civilization.

SUMMARY OF KEY QUESTIONS

5.1 What Are the Characteristic Reactions of Alkenes?

- A characteristic reaction of alkenes is **addition**, during which a pi bond is broken and sigma bonds are formed to two new atoms or groups of atoms. Alkene addition reactions include addition of halogen acids, H—Cl, acid-catalyzed addition of H_2O to form an alcohol, addition of halogens, X_2, hydroboration followed by oxidation to give an alcohol, and transition metal-catalyzed addition of H_2 to form an alkane.

5.2 What Is a Reaction Mechanism?

- A **reaction mechanism** is a description of (1) how and why a chemical reaction occurs, (2) which bonds break and which new ones form, (3) the order and relative rates in which the various bond-breaking and bond-forming steps take place, and (4) the role of the catalyst if the reaction involves a catalyst.
- **Transition state theory** provides a model for understanding the relationships among reaction rates, molecular structure, and energetics.
- A key postulate of transition state theory is that a **transition state** is formed in all reactions.
- The difference in energy between reactants and the transition state is called the **activation energy**.

- An **intermediate** is an energy minimum between two transition states.
- The slowest step in a multistep reaction, called the **rate-determining step**, is the one that crosses the highest energy barrier.
- There are many patterns that occur frequently in organic reaction mechanisms. These include **adding a proton, taking a proton away**, the **reaction of a nucleophile and electrophile to form a new bond**, and **rearrangement of a bond**.

5.3 What Are the Mechanisms of Electrophilic Additions to Alkenes?

- An **electrophile** is any molecule or ion that can accept a pair of electrons to form a new covalent bond. All electrophiles are Lewis acids.
- A **nucleophile** is an electron-rich species that can donate a pair of electrons to form a new covalent bond. All nucleophiles are Lewis bases.
- The rate-determining step in **electrophilic addition** to an alkene is reaction of an electrophile with a carbon–carbon double bond to form a **carbocation**, an ion that contains a carbon with only six electrons in its valence shell and has a positive charge.
- Carbocations are planar with bond angles of 120° about the positive carbon.
- The order of stability of carbocations is 3° > 2° > 1° > methyl. Primary carbocations, however, are so unstable and

have such a high energy of activation for their formation that they are never formed in solution.
- **Electrophilic addition of a hydrogen halide** to an alkene is the addition of a halogen (Cl, Br, or I) and H across the carbon–carbon double bond. The reaction occurs with **Markovnikov regioselectivity** with the H adding to the carbon with the greater number of hydrogens.
- **Acid-catalyzed hydration** of an alkene is the addition of OH and H across the carbon–carbon double bond. The reaction occurs with Markovnikov regioselectivity.
- **Addition of bromine and chlorine** to an alkene is the addition of two halogens across the carbon–carbon double bond. The mechanism involves a **bridged halonium ion** as an intermediate and is an **anti stereoselective**.

5.4 What Are Carbocation Rearrangements?

- The driving force for a **carbocation rearrangement** is conversion of an initially formed carbocation to a more stable 2° or 3° carbocation.

- Rearrangement is by a **1,2-shift** in which an atom or group of atoms with its bonding electrons moves from an adjacent carbon to an electron-deficient carbon.

5.5 What Is Hydroboration–Oxidation of an Alkene?

- **Hydroboration** of an alkene is the addition of BH_2 and H across a C—C double bond.

- Hydroboration occurs with **anti-Markovnikov** regioselectivity with the H adding to the carbon with the fewer number of hydrogens.

- **Oxidation** of the hydroboration product results in the replacement of the boron group with an —OH group.

- **Hydroboration–oxidation** is **syn stereoselective**.

5.6 How Can an Alkene Be Reduced to an Alkane?

- The reaction of an alkene with H_2 in the presence of a transition metal catalyst converts all C—C double bonds in the alkene to C—C single bonds via the syn stereoselective addition of a hydrogen to each carbon of the former double bond.

- The **heats of reaction**, ΔH, of **hydrogenation reactions** can be used to compare the relative stabilities of alkenes.

5.7 How Can an Acetylide Anion Be Used to Create a New Carbon–Carbon Bond?

- **Acetylide anions** are both strong bases and nucleophiles. As nucleophiles, they can be alkylated by treatment with a methyl, primary, or secondary haloalkane. In this way,

acetylene serves as a two-carbon building block for the synthesis of larger carbon skeletons.

5.8 How Can Alkynes Be Reduced to Alkenes and Alkanes?

- Treatment of alkyne with H_2 in the presence of a transition metal catalyst, most commonly Pd, Pt, or Ni, results in the addition of two moles of H_2 to the alkyne and its conversion to an alkane.

- Reduction of an alkyne using the **Lindlar catalyst** results in syn-stereoselective addition of one mole of H_2 to an alkyne. With this reagent, a disubstituted alkyne can be reduced to a *cis*-alkene.

QUICK QUIZ

Answer true or false to the following questions to assess your general knowledge of the concepts in this chapter. If you have difficulty with any of them, you should review the appropriate section in the chapter (shown in parentheses) before attempting the more challenging end-of-chapter problems.

1. Catalytic reduction of an alkene is syn stereoselective. (5.6)
2. Borane, BH_3, is a Lewis acid. (5.5)
3. All electrophiles are positively charged. (5.3)
4. Catalytic hydrogenation of cyclohexene gives hexane. (5.6)
5. A rearrangement will occur in the reaction of 2-methyl-2-pentene with HBr. (5.4)
6. All nucleophiles are negatively charged. (5.3)
7. In hydroboration, BH_3 behaves as an electrophile. (5.5)
8. In catalytic hydrogenation of an alkene, the reducing agent is the transition metal catalyst. (5.6)
9. Alkene addition reactions involve breaking a pi bond and forming two new sigma bonds in its place. (5.3)
10. The foundation for Markovnikov's rule is the relative stability of carbocation intermediates. (5.3)
11. Acid-catalyzed hydration of an alkene is regioselective. (5.3)
12. The mechanism for addition of HBr to an alkene involves one transition state and two reactive intermediates. (5.3)
13. Hydroboration of an alkene is regioselective and stereoselective. (5.5)
14. According to the mechanism given in the text for acid-catalyzed hydration of an alkene, the —H and —OH groups added to the double bond both arise from the same molecule of H_2O. (5.3)
15. Acid-catalyzed addition of H_2O to an alkene is called *hydration*. (5.3)
16. If a compound fails to react with Br_2, it is unlikely that the compound contains a carbon–carbon double bond. (5.3)
17. Addition of Br_2 and Cl_2 to cyclohexene is anti-stereoselective. (5.3)
18. A carbocation is a carbon that has four bonds to it and bears a positive charge. (5.3)
19. The geometry about the positively charged carbon of a carbocation is best described as trigonal planar. (5.3)
20. The carbocation derived by proton transfer to ethylene is $CH_3CH_2^+$. (5.3)
21. Alkyl carbocations are stabilized by the electron-withdrawing inductive effect of the positively charged carbon of the carbocation. (5.3)

22. The oxygen atom of an oxonium ion obeys the octet rule. (5.3)

23. Markovnikov's rule refers to the regioselectivity of addition reactions to carbon–carbon double bonds. (5.3)

24. A rearrangement, in which a hydride ion shifts, will occur in the reaction of 3-methyl-1-pentene with HCl. (5.4)

25. Acid-catalyzed hydration of 1-butene gives 1-butanol, and acid-catalyzed hydration of 2-butene gives 2-butanol. (5.3)

26. Alkenes are good starting materials for reactions in which it is necessary to form a C—C bond. (5.7)

27. Alkynes can be reduced to *cis* alkenes. (5.8)

(1) T (2) T (3) F (4) F (5) F (6) F (7) T (8) F (9) F (10) T (11) T (12) F
(13) T (14) F (15) T (16) T (17) T (18) F (19) T (20) T (21) T (22) T
(23) T (24) T (25) F (26) F (27) F

Detailed explanations for many of these answers can be found in the accompanying Solutions Manual.

KEY REACTIONS

1. **Addition of H—X to an Alkene (Section 5.3A)**

The addition of H—X is regioselective and follows Markovnikov's rule. Reaction occurs in two steps and involves the formation of a carbocation intermediate:
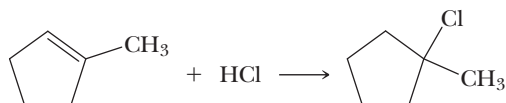
2. **Acid-Catalyzed Hydration of an Alkene (Section 5.3B)**

Hydration of an alkene is regioselective and follows Markovnikov's rule. Reaction occurs in two steps and involves the formation of a carbocation intermediate:

$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}CH_3$$
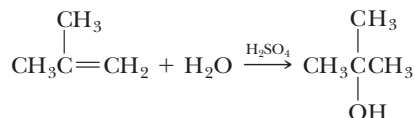
3. **Addition of Bromine and Chlorine to an Alkene (Section 5.3C)**

Addition of halogen occurs in two steps and involves anti-stereoselective addition by way of a bridged bromonium or chloronium ion intermediate:
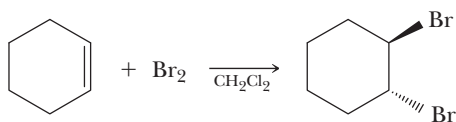
4. **Carbocation Rearrangements (Section 5.4)**

Rearrangement is from a less stable carbocation intermediate to a more stable one by a 1,2-shift. Rearrangements often occur during the hydrochlorination and acid-catalyzed hydration of alkenes.
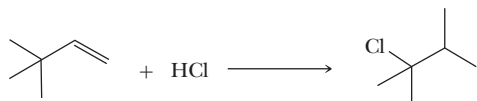
3,3-Dimethyl-1-butene   2-Chloro-2,3-dimethylbutane

5. **Hydroboration–Oxidation of an Alkene (Section 5.5)**

Addition of BH$_3$ to an alkene is syn-stereoselective and regioselective: boron adds to the less substituted carbon of the double bond, and hydrogen adds to the more substituted carbon. Hydroboration–oxidation results in anti-Markovnikov hydration of the alkene.
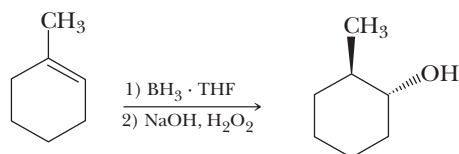
6. **Reduction of an Alkene: Formation of Alkanes (Section 5.6)**

Catalytic reduction involves predominantly the syn-stereoselective addition of hydrogen:
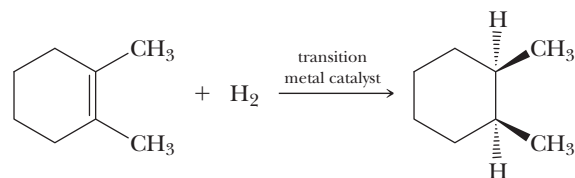
7. **Alkylation on an Acetylide Anion (Section 5.7)**

Acetylide anions are nucleophiles and displace halogen from methyl and 1° haloalkanes. Alkylation of acetylide anions is a valuable way to assemble a larger carbon skeleton.
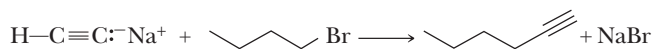
8. **Reduction of an Alkyne (Section 5.8)**

Several different reagents reduce alkynes. Catalytic reduction using a transition metal catalyst gives an alkane. Catalytic reduction using a specially prepared catalyst called the Lindlar catalyst gives a *cis* alkene.
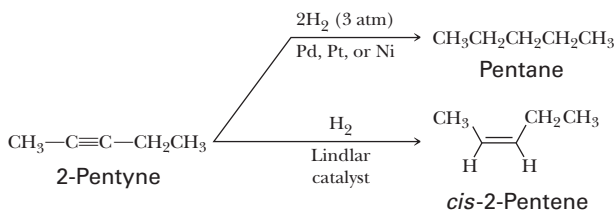
PROBLEMS

A problem marked with an asterisk indicates an applied "real-world" problem. Answers to problems whose numbers are printed in blue are given in Appendix D.

Section 5.2 Energy Diagrams

5.11 Describe the differences between a transition state and a reaction intermediate.

5.12 Sketch an energy diagram for a one-step reaction that is very slow and only slightly exothermic. How many transition states are present in this reaction? How many intermediates are present? **(See Example 5.1)**

5.13 Sketch an energy diagram for a two-step reaction that is endothermic in the first step, exothermic in the second step, and exothermic overall. How many transition states are present in this two-step reaction? How many intermediates are present? **(See Example 5.1)**

5.14 Determine whether each of the following statements is true or false, and provide a rationale for your decision:

(a) A transition state can never be lower in energy than the reactants from which it was formed.
(b) An endothermic reaction cannot have more than one intermediate.
(c) An exothermic reaction cannot have more than one intermediate.

Sections 5.3–5.5 Electrophilic Additions to Alkenes, Rearrangements, and Hydroboration–Oxidation

5.15 From each pair, select the more stable carbocation: **(See Example 5.3)**

(a) $CH_3CH_2CH_2^+$ or $CH_3\overset{+}{C}HCH_3$

(b) $CH_3\overset{CH_3}{\underset{+}{C}H}CHCH_3$ or $CH_3\overset{CH_3}{\underset{+}{C}}CH_2CH_3$
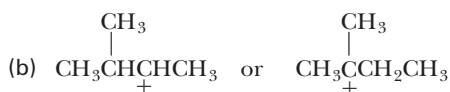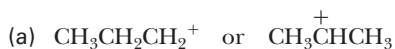
5.16 From each pair, select the more stable carbocation: **(See Example 5.3)**

(a)

(b)
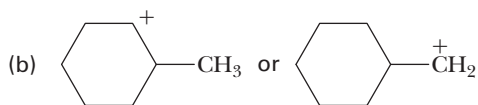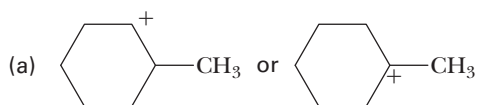
5.17 Draw structural formulas for the isomeric carbocation intermediates formed by the reaction of each alkene with HCl. Label each carbocation as primary, secondary, or tertiary, and state which, if either, of the isomeric carbocations is formed more readily. **(See Example 5.2)**
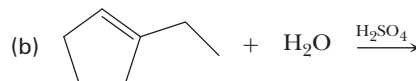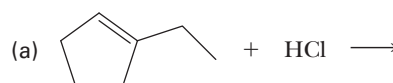
(a) (b)

(c) (d)
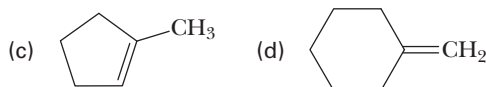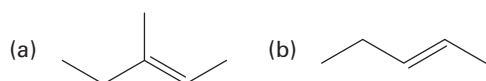
5.18 From each pair of compounds, select the one that reacts more rapidly with HI, draw the structural for-

mula of the major product formed in each case, and explain the basis for your ranking: **(See Example 5.2)**

(a) and

(b) and
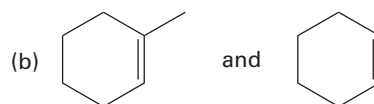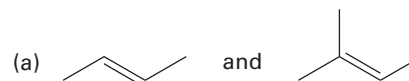
5.19 Complete these equations by predicting the major product formed in each reaction: **(See Examples 5.2, 5.5)**

(a) + HCl ⟶

(b) + H_2O $\xrightarrow{H_2SO_4}$

(c) + HI ⟶

(d) + HCl ⟶

(e) + H_2O $\xrightarrow{H_2SO_4}$

(f) + H_2O $\xrightarrow{H_2SO_4}$
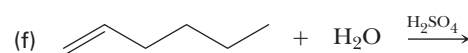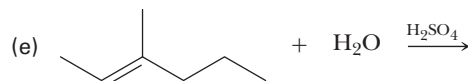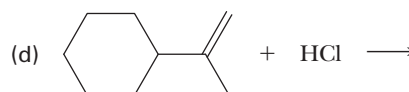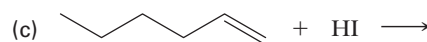
5.20   The reaction of 2-methyl-2-pentene with each reagent is regioselective. Draw a structural formula for the product of each reaction, and account for the observed regioselectivity. **(See Examples 5.2, 5.5, 5.9)**

(a)   HI
(b) H_2O in the presence of H_2SO_4
(c) BH_3 followed by H_2O_2, NaOH

5.21   The addition of bromine and chlorine to cycloalkenes is stereoselective. Predict the stereochemistry of the product formed in each reaction: **(See Example 5.7)**

(a)   1-Methylcyclohexene + Br_2
(b)   1,2-Dimethylcyclopentene + Cl_2

5.22   Draw a structural formula for an alkene with the indicated molecular formula that gives the compound shown as the major product. Note that more than one alkene may give the same compound as the major product.

(a) $C_5H_{10} + H_2O \xrightarrow{H_2SO_4}$

(b) $C_5H_{10} + Br_2 \longrightarrow$

(c) $C_7H_{12} + HCl \longrightarrow$
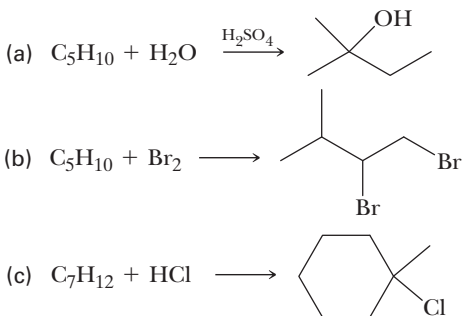
5.23   Draw the structural formula for an alkene with the molecular formula C_5H_{10} that reacts with Br_2 to give each product:

(a)   (b)

(c)
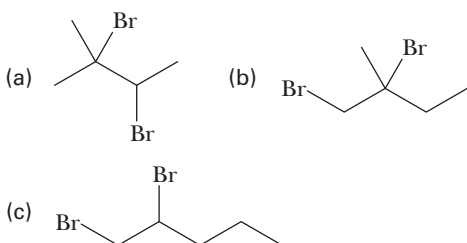
5.24   Draw the structural formula for a cycloalkene with the molecular formula C_6H_{10} that reacts with Cl_2 to give each compound:

(a)   (b)

(c)   (d)
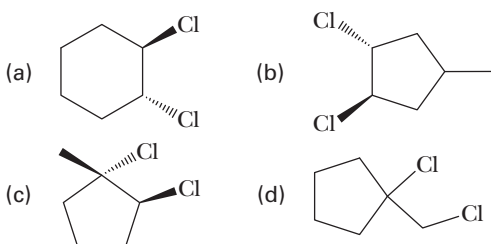
5.25   Draw the structural formula for an alkene with the molecular formula C_5H_{10} that reacts with HCl to give the indicated chloroalkane as the major product:

(a)   (b)   (c)
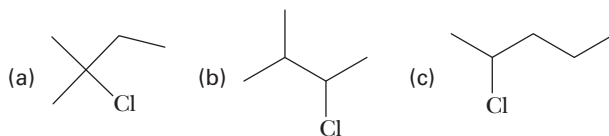
5.26   Draw the structural formula of an alkene that undergoes acid-catalyzed hydration to give the indicated alcohol as the major product. More than one alkene may give each compound as the major product.

(a)   3-Hexanol   (b)   1-Methylcyclobutanol
(c)   2-Methyl-2-butanol   (d)   2-Propanol

5.27   Draw the structural formula of an alkene that undergoes acid-catalyzed hydration to give each alcohol as the major product. More than one alkene may give each compound as the major product.

(a)   Cyclohexanol
(b)   1,2-Dimethylcyclopentanol
(c)   1-Methylcyclohexanol
(d)   1-Isopropyl-4-methylcyclohexanol

5.28   Complete these equations by predicting the major product formed in each reaction. Note that certain of these reactions involve rearrangements. **(See Examples 5.2, 5.5)**
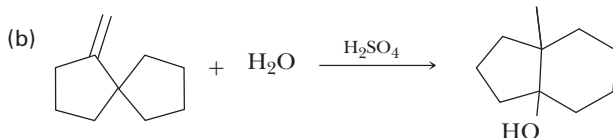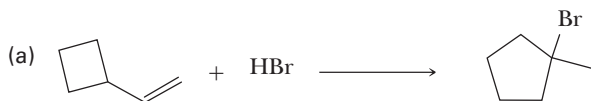
(a)   + HBr $\longrightarrow$

(b)   + H_2O $\xrightarrow{H_2SO_4}$

(c)   + H_2O $\xrightarrow{H_2SO_4}$

(d)   + HI $\longrightarrow$

(e)   + HCl $\longrightarrow$

(f)   + H_2O $\xrightarrow{H_2SO_4}$
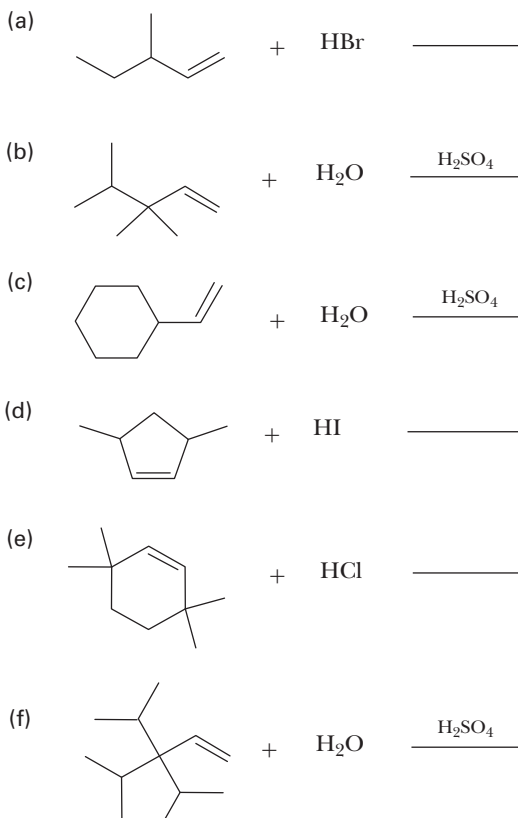
5.29 Propose a mechanism for each reaction in Problem 5.28. **(See Examples 5.4, 5.6, 5.8)**
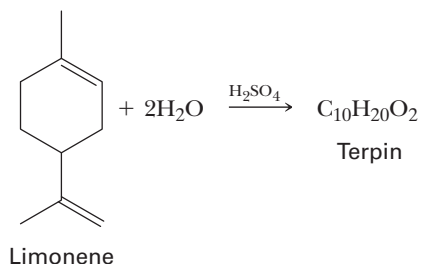
5.30 Propose a mechanism for the following acid-catalyzed dehydration. **(See Examples 5.6, 5.8)**
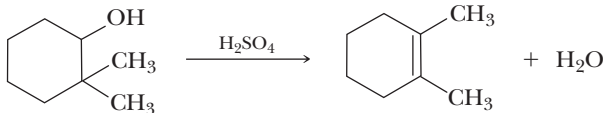
5.31 Propose a mechanism for each of the following transformations. **(See Examples 5.4, 5.6, 5.8)**

(a)

(b)

**5.32** Terpin is prepared commercially by the acid-catalyzed hydration of limonene: **(See Example 5.5)**

Limonene

(a) Propose a structural formula for terpin and a mechanism for its formation.
(b) How many *cis–trans* isomers are possible for the structural formula you propose?
(c) Terpin hydrate, the isomer in terpin in which the one-carbon and three-carbon substituents are *cis* to each other, is used as an expectorant in cough medicines. Draw the alternative chair conformations for terpin hydrate, and state which of the two is the more stable.

5.33 Propose a mechanism for this reaction and account for its regioselectivity.

5.34 The treatment of 2-methylpropene with methanol in the presence of a sulfuric acid catalyst gives *tert*-butyl methyl ether:
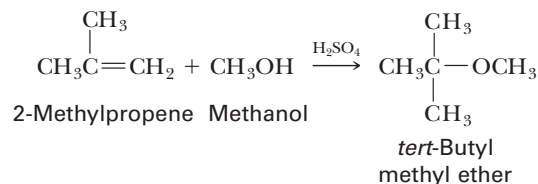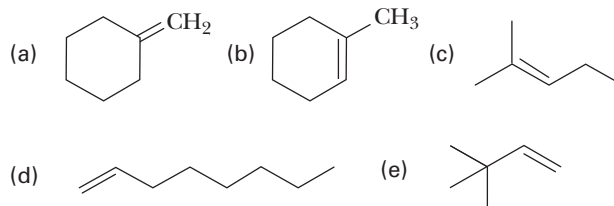

Propose a mechanism for the formation of this ether.

5.35 Treating cyclohexene with HBr in the presence of acetic acid gives a mixture of bromocyclohexane and cyclohexyl acetate.
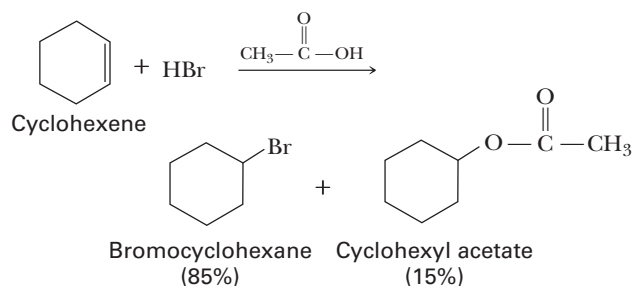

Account for the formation of each product but do not be concerned with the relative percentages of each.

5.36 Draw a structural formula for the alcohol formed by treating each alkene with borane in tetrahydrofuran (THF), followed by hydrogen peroxide in aqueous sodium hydroxide, and specify the stereochemistry where appropriate. **(See Example 5.9)**

5.37 Treatment of 1-methylcyclohexene with methanol in the presence of a sulfuric acid catalyst gives a compound with the molecular formula $C_8H_{16}O$. Propose a structural formula for this compound and a mechanism for its formation.
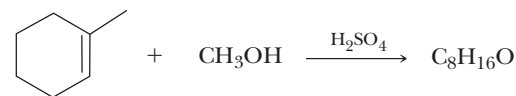

1-Methylcyclohexene   Methanol

5.38 *cis*-3-Hexene and *trans*-3-hexene are different compounds and have different physical and chemical properties. Yet, when treated with H_2O/H_2SO_4, each gives the same alcohol. What is the alcohol, and how do you account for the fact that each alkene gives the same one? **(See Examples 5.6, 5.8)**

Section 5.6 Oxidation–Reduction

5.39 Write a balanced equation for the combustion of 2-methylpropene in air to give carbon dioxide and water. The oxidizing agent is O_2, which makes up approximately 20% of air.

**5.40** Draw the product formed by treating each alkene with H_2/Ni:

(a) (b) (c) (d)
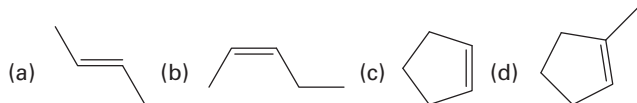
5.41 Hydrocarbon A, C_5H_8, reacts with 2 moles of Br_2 to give 1,2,3,4-tetrabromo-2-methylbutane. What is the structure of hydrocarbon A?
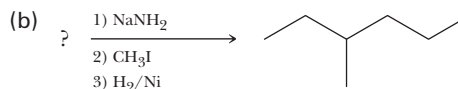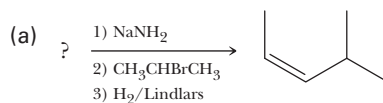
5.42 Two alkenes, A and B, each have the formula C_5H_{10}. Both react with H_2/Pt and with HBr to give identical products. What are the structures of A and B?

Sections 5.7–5.8 Reactions of Alkynes

5.43 Complete these equations by predicting the major products formed in each reaction. If more than one product is equally likely, draw both products.

(a)

(b)

(c) $(CH_3)_2CH_2CCH$ $\xrightarrow[\text{2) } CH_3(CH_2)_4Br]{\text{1) NaNH}_2}$
3) $H_2/Pd \cdot C$
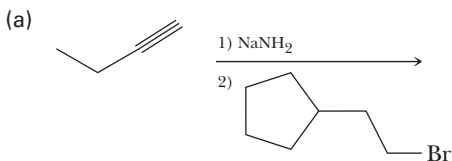
5.44 Determine the alkyne that would be required in the following sequences of reactions.

(a) ? $\xrightarrow[\text{2) } CH_3CHBrCH_3]{\text{1) NaNH}_2}$
3) $H_2/Lindlars$

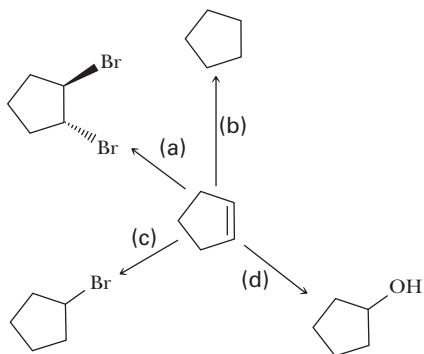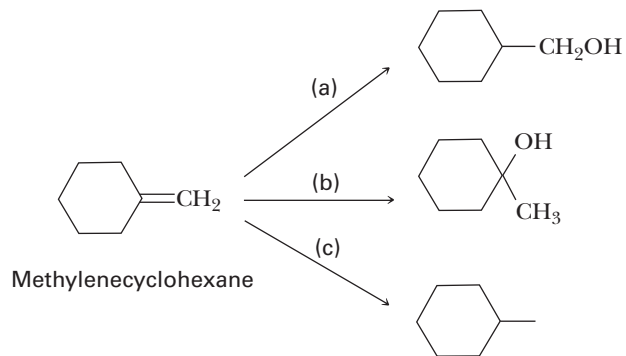(b) ? $\xrightarrow[\text{2) } CH_3I]{\text{1) NaNH}_2}$
3) H_2/Ni

Synthesis

5.45 Show how to convert ethylene into these compounds:
(a) Ethane
(b) Ethanol
(c) Bromoethane
(d) 1,2-Dibromoethane
(e) Chloroethane

**5.46** Show how to convert cyclopentene into these compounds:

5.47 Show how to convert methylenecyclohexane into each of these compounds.

Methylenecyclohexane

5.48 Show how to convert 1-butene into these compounds:
(a) Butane
(b) 2-Butanol
(c) 1-Butanol
(d) 2-Bromobutane
(e) 1,2-Dibromobutane

**5.49** Show how the following compounds can be synthesized in good yields from an alkene:

(a)

(b)

(c)

(d)
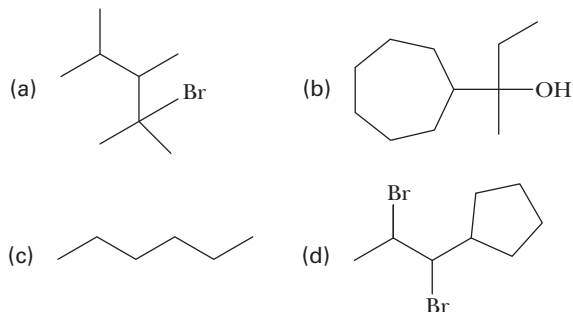
5.50 How would you prepare *cis*-3-hexene using only acetylene as the source of carbon atoms, and using any necessary inorganic regents? **(See Example 5.10)**

5.51 Test your cumulative knowledge of the reactions learned thus far by completing the following chemical transformations. Note that some will require more than one step.

(a)

(b) H———H ⟶

(c)

(d)

(e)

(f)
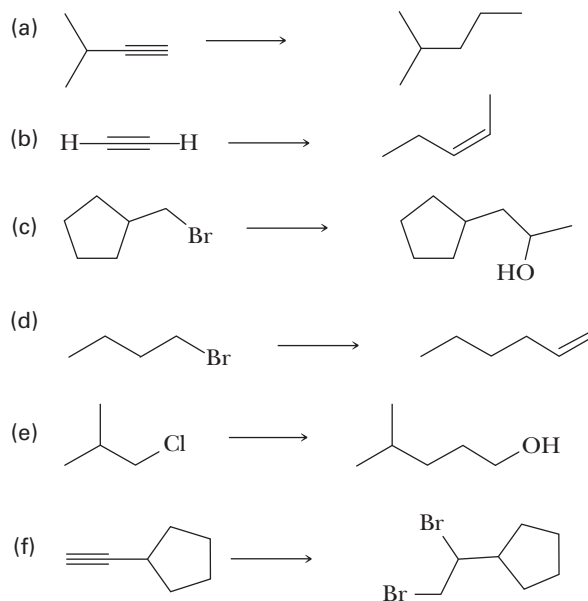
LOOKING AHEAD

5.52 Each of the following 2° carbocations is more stable than the tertiary-butyl carbocation shown:


a tertiary carbocation

(a)

(b)

(c)
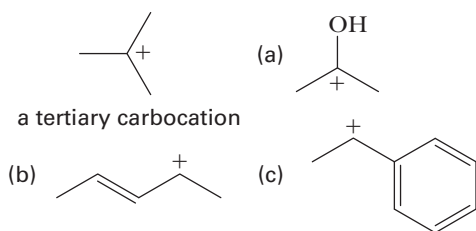
Provide an explanation for each cation's enhanced stability.

5.53 Recall that an alkene possesses a π cloud of electrons above and below the plane of the C=C bond. Any reagent can therefore react with either face of the double bond. Determine whether the reaction of each of the given reagents with the top face of *cis*-2-butene will produce the same product as the reaction of the same reagent with the bottom face. (*Hint:* Build molecular models of the products and compare them.)

(a) H_2/Pt

(b) $\dfrac{1) \ BH_3 \cdot THF}{2) \ NaOH, \ HOOH}$

(c) Br_2/CH_2Cl_2
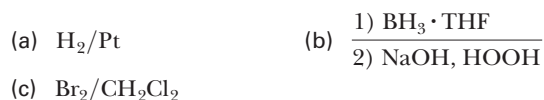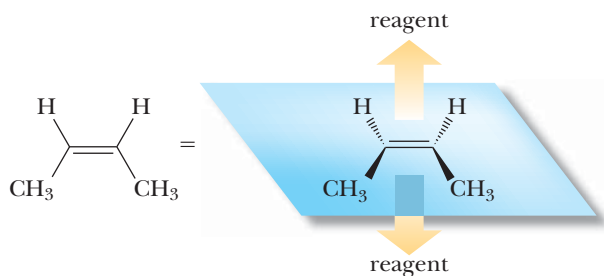
5.54 This reaction yields two products in differing amounts:
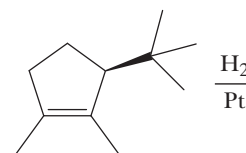
Draw the two products and predict which product is favored.

GROUP LEARNING ACTIVITIES

5.55 Take turns quizzing each other on the reactions presented in this chapter in the following ways:

(a) Say the name of a reaction and ask each other to come up with the reagents and products of that reaction. For example, if you say "catalytic hydrogenation of an alkene" the answer should be "H_2/Pt reacts to give an alkane."

(b) Describe a set of reagents and ask each other what functional group(s) the reagents react with. For example, if you say "H_2/Pt," the answer should be "alkenes" and "alkynes."

(c) Name a functional group or class of compound as a product of a reaction and ask what functional group or class of compound could be used to synthesize that product. For example, if you say "alkene," the answer should be "alkyne."

5.56 Using a piece of paper or, preferably, a whiteboard or chalkboard, take turns drawing the mechanisms of each reaction in this chapter from memory. If you forget a step or make a mistake, another member of the group should step in and finish it.

5.57 With the exception of ethylene to ethanol, the acid-catalyzed hydration of alkenes cannot be used for the synthesis of primary alcohols. Explain why this is so.