Ethylene, which has no alkyl substituents to stabilize its double bond, has the highest heat of hydrogenation. Alkenes that are similar in structure to one another have similar heats of hydrogenation. For example, the heats of hydrogenation of the monosubstituted (terminal) alkenes propene, 1-butene, and 1-hexene are almost identical. Cis- disubstituted alkenes have lower heats of hydrogenation than monosubstituted alkenes but higher heats of hydrogenation than their more stable trans stereoisomers. Alkenes with trisubstituted double bonds have lower heats of hydrogenation than disubstituted alkenes, and tetrasubstituted alkenes have the lowest heats of hydrogenation.

> **PROBLEM 6.2** Match each alkene of Problem 6.1 with its correct heat of hydrogenation.
>
> *Heats of hydrogenation in kJ/mol (kcal/mol):* 112 (26.7); 118 (28.2); 126 (30.2)

6.3   STEREOCHEMISTRY OF ALKENE HYDROGENATION

In the mechanism for alkene hydrogenation shown in Figure 6.1, hydrogen atoms are transferred from the catalyst's surface to the alkene. Although the two hydrogens are not transferred simultaneously, it happens that both add to the same face of the double bond, as the following example illustrates.

Dimethyl cyclohexene-1,2-dicarboxylate

Dimethyl cyclohexane-*cis*-1,2-dicarboxylate (100%)
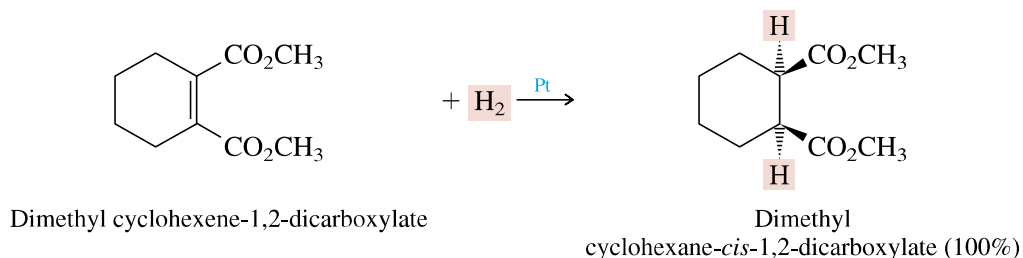
The term **syn addition** describes the stereochemistry of reactions such as catalytic hydrogenation in which two atoms or groups add to the *same face* of a double bond. When atoms or groups add to *opposite faces* of the double bond, the process is called **anti addition.**
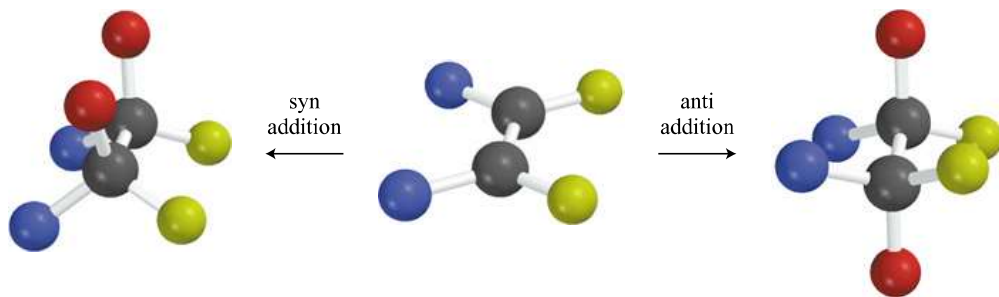
syn addition

anti addition

A second stereochemical aspect of alkene hydrogenation concerns its **stereoselectivity.** A reaction in which a single starting material can give two or more stereoisomeric products but yields one of them in greater amounts than the other (or even to the exclusion of the other) is said to be **stereoselective.** The catalytic hydrogenation of α-pinene (a constituent of turpentine) is an example of a stereoselective reaction. Syn addition of
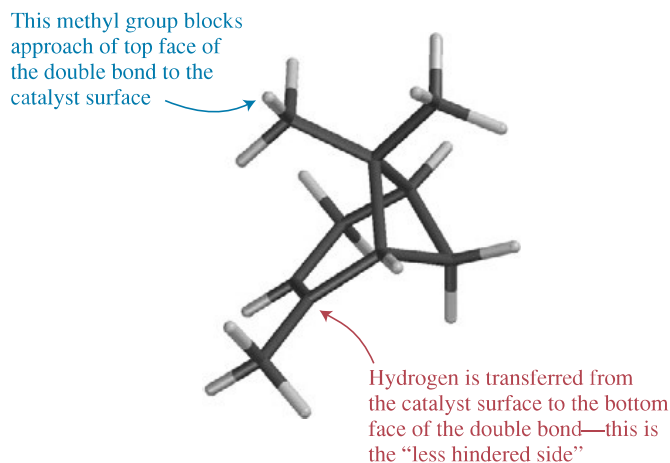
This methyl group blocks approach of top face of the double bond to the catalyst surface

Hydrogen is transferred from the catalyst surface to the bottom face of the double bond—this is the "less hindered side"

FIGURE 6.3 The methyl group that lies over the double bond of α-pinene shields one face of it, preventing a close approach to the surface of the catalyst. Hydrogenation of α-pinene occurs preferentially from the bottom face of the double bond.

hydrogen can in principle lead to either *cis*-pinane or *trans*-pinane, depending on which face of the double bond accepts the hydrogen atoms (shown in red in the equation).

α-Pinene

cis-Pinane
(only product)

trans-Pinane
(not formed)
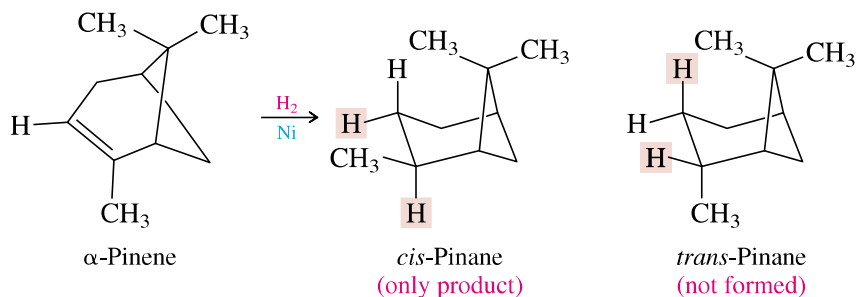
cis-Pinane and *trans*-pinane are common names that denote the relationship between the pair of methyl groups on the bridge and the third methyl group.

In practice, hydrogenation of α-pinene is observed to be 100% stereoselective. The only product obtained is *cis*-pinane. None of the stereoisomeric *trans*-pinane is formed.

The stereoselectivity of this reaction depends on how the alkene approaches the catalyst surface. As the molecular model in Figure 6.3 shows, one of the methyl groups on the bridge carbon lies directly over the double bond and blocks that face from easy access to the catalyst. The bottom face of the double bond is more exposed, and both hydrogens are transferred from the catalyst surface to that face.
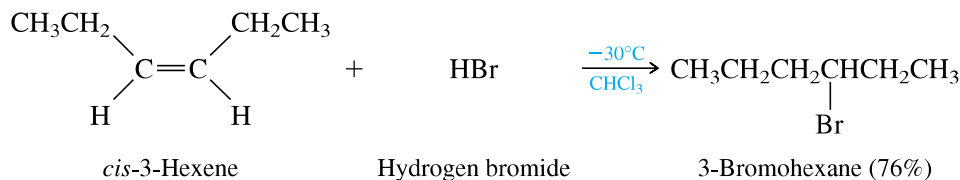
Reactions such as catalytic hydrogenation that take place at the "less hindered" side of a reactant are common in organic chemistry and are examples of steric effects on *reactivity*. We have previously seen steric effects on *structure* and *stability* in the case of *cis* and *trans* stereoisomers and in the preference for equatorial substituents on cyclohexane rings.

## 6.4 ELECTROPHILIC ADDITION OF HYDROGEN HALIDES TO ALKENES

In many addition reactions the attacking reagent, unlike H_2, is a polar molecule. Hydrogen halides are among the simplest examples of polar substances that add to alkenes.

Alkene   Hydrogen halide   Alkyl halide
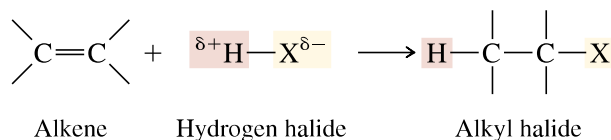
Addition occurs rapidly in a variety of solvents, including pentane, benzene, dichloromethane, chloroform, and acetic acid.

$$CH_3CH_2 \quad \quad CH_2CH_3$$
$$\underset{H}{\overset{}{\diagdown}}C=C\underset{H}{\overset{}{\diagup}} \quad + \quad HBr \quad \xrightarrow[\text{CHCl}_3]{-30°C} \quad CH_3CH_2CH_2CHCH_2CH_3$$
$$\underset{Br}{|}$$

cis-3-Hexene   Hydrogen bromide   3-Bromohexane (76%)

The reactivity of the hydrogen halides reflects their ability to donate a proton. Hydrogen iodide is the strongest acid of the hydrogen halides and reacts with alkenes at the fastest rate.

> Increasing reactivity of hydrogen halides
> in addition to alkenes

$$HF \ll HCl < HBr < HI$$
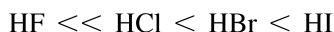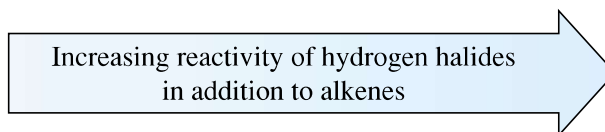
Slowest rate of addition;   Fastest rate of addition;
least acidic   most acidic

We can gain a general understanding of the mechanism of hydrogen halide addition to alkenes by extending some of the principles of reaction mechanisms introduced earlier. In Section 5.12 we pointed out that carbocations are the conjugate acids of alkenes. Acid–base reactions are reversible processes. An alkene, therefore, can accept a proton from a hydrogen halide to form a carbocation.

$$R_2C=CR_2 \; + \; H-\ddot{X}: \; \rightleftharpoons \; R_2\overset{+}{C}-\overset{\overset{H}{|}}{C}R_2 \; + \; :\ddot{X}:^-$$

Alkene   Hydrogen halide   Carbocation   Anion
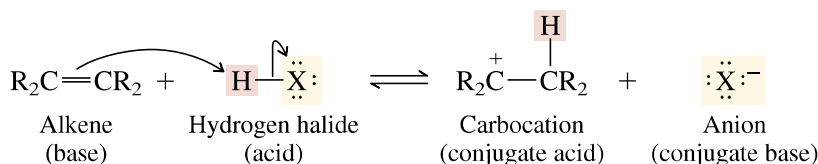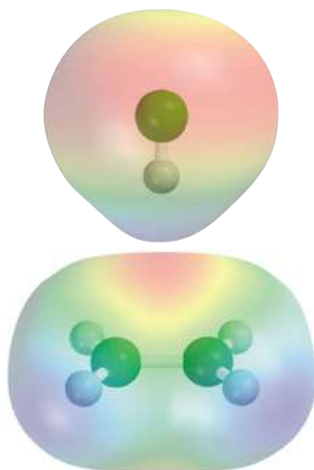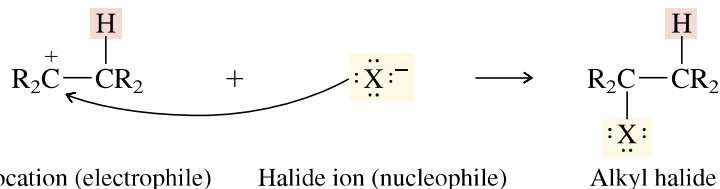(base)   (acid)   (conjugate acid)   (conjugate base)

Figure 6.4 shows the complementary nature of the electrostatic potentials of an alkene and a hydrogen halide. We've also seen (Section 4.9) that carbocations, when generated in the presence of halide anions, react with them to form alkyl halides.

$$R_2\overset{+}{C}-\overset{\overset{H}{|}}{C}R_2 \quad + \quad :\ddot{X}:^- \quad \longrightarrow \quad R_2C-\overset{\overset{H}{|}}{C}R_2$$
$$\underset{:\ddot{X}:}{|}$$

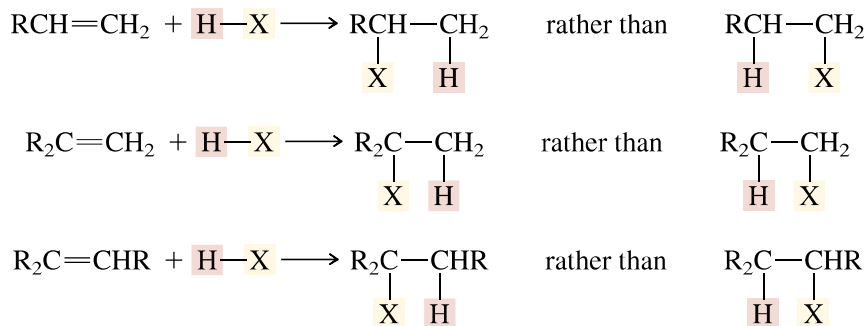Carbocation (electrophile)   Halide ion (nucleophile)   Alkyl halide

Both steps in this general mechanism are based on precedent. It is called **electrophilic addition** because the reaction is triggered by the attack of an electrophile (an acid) on the π electrons of the double bond. Using the two π electrons to form a bond to an electrophile generates a carbocation as a reactive intermediate; normally this is the rate-determining step.

6.5   REGIOSELECTIVITY OF HYDROGEN HALIDE ADDITION: MARKOVNIKOV'S RULE

In principle a hydrogen halide can add to an unsymmetrical alkene (an alkene in which the two carbons of the double bond are not equivalently substituted) in either of two directions. In practice, addition is so highly regioselective as to be considered regiospecific.

FIGURE 6.4 Electrostatic potential maps of HCl and ethylene. When the two react, the interaction is between the electron-rich site (red) of ethylene and the electron-poor region (blue) of HCl. The electron-rich region of ethylene is associated with the π electrons of the double bond, while H is the electron-poor atom (blue) of HCl.

$$\text{RCH}{=}\text{CH}_2 + \boxed{\text{H}}{-}\boxed{\text{X}} \longrightarrow \underset{\overset{|}{\boxed{\text{X}}}}{\text{RCH}}{-}\underset{\overset{|}{\boxed{\text{H}}}}{\text{CH}_2} \quad \text{rather than} \quad \underset{\overset{|}{\boxed{\text{H}}}}{\text{RCH}}{-}\underset{\overset{|}{\boxed{\text{X}}}}{\text{CH}_2}$$

$$\text{R}_2\text{C}{=}\text{CH}_2 + \boxed{\text{H}}{-}\boxed{\text{X}} \longrightarrow \underset{\overset{|}{\boxed{\text{X}}}}{\text{R}_2\text{C}}{-}\underset{\overset{|}{\boxed{\text{H}}}}{\text{CH}_2} \quad \text{rather than} \quad \underset{\overset{|}{\boxed{\text{H}}}}{\text{R}_2\text{C}}{-}\underset{\overset{|}{\boxed{\text{X}}}}{\text{CH}_2}$$

$$\text{R}_2\text{C}{=}\text{CHR} + \boxed{\text{H}}{-}\boxed{\text{X}} \longrightarrow \underset{\overset{|}{\boxed{\text{X}}}}{\text{R}_2\text{C}}{-}\underset{\overset{|}{\boxed{\text{H}}}}{\text{CHR}} \quad \text{rather than} \quad \underset{\overset{|}{\boxed{\text{H}}}}{\text{R}_2\text{C}}{-}\underset{\overset{|}{\boxed{\text{X}}}}{\text{CHR}}$$

In 1870, Vladimir Markovnikov, a colleague of Alexander Zaitsev at the University of Kazan, noticed a pattern in the hydrogen halide addition to alkenes and assembled his observations into a simple statement. **Markovnikov's rule** states that *when an unsymmetrically substituted alkene reacts with a hydrogen halide, the hydrogen adds to the carbon that has the greater number of hydrogen substituents, and the halogen adds to the carbon having fewer hydrogen substituents.* The preceding general equations illustrate regioselective addition according to Markovnikov's rule, and the equations that follow provide some examples.

An article in the December 1988 issue of the *Journal of Chemical Education* traces the historical development of Markovnikov's rule. In that article Markovnikov's name is spelled *Markownikoff,* which is the way it appeared in his original paper written in German.

$$\underset{\text{1-Butene}}{\text{CH}_3\text{CH}_2\text{CH}{=}\text{CH}_2} + \underset{\text{Hydrogen bromide}}{\text{HBr}} \xrightarrow{\overset{\text{acetic}}{\text{acid}}} \underset{\text{2-Bromobutane (80\%)}}{\underset{\overset{|}{\text{Br}}}{\text{CH}_3\text{CH}_2\text{CHCH}_3}}$$

$$\underset{\text{2-Methylpropene}}{\overset{\text{H}_3\text{C}}{\underset{\text{H}_3\text{C}}{\diagdown}}\!\!\!\text{C}{=}\text{CH}_2} + \underset{\text{Hydrogen bromide}}{\text{HBr}} \xrightarrow{\overset{\text{acetic}}{\text{acid}}} \underset{\text{2-Bromo-2-methylpropane (90\%)}}{\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}_3{-}\overset{|}{\underset{|}{\text{C}}}{-}\text{Br}}}}$$

$$\underset{\text{1-Methylcyclopentene}}{\diagup\!\!\!\!\bigcirc\!\!\!\!{-}\text{CH}_3} + \underset{\text{Hydrogen chloride}}{\text{HCl}} \xrightarrow{0°\text{C}} \underset{\text{1-Chloro-1-methylcyclopentane (100\%)}}{\diagup\!\!\!\!\bigcirc\!\!\!\!\overset{\text{CH}_3}{\underset{\text{Cl}}{<}}}$$
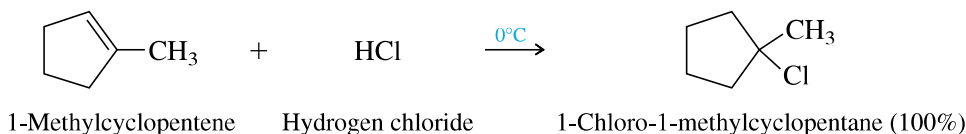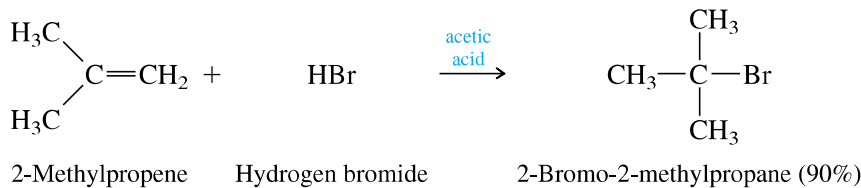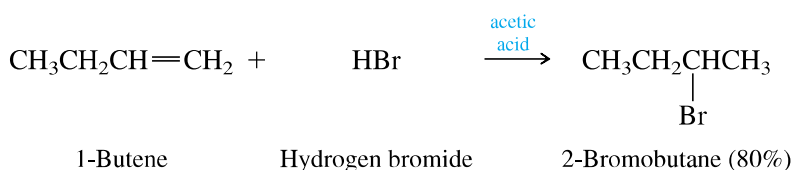
PROBLEM 6.3   Write the structure of the major organic product formed in the reaction of hydrogen chloride with each of the following:

(a) 2-Methyl-2-butene
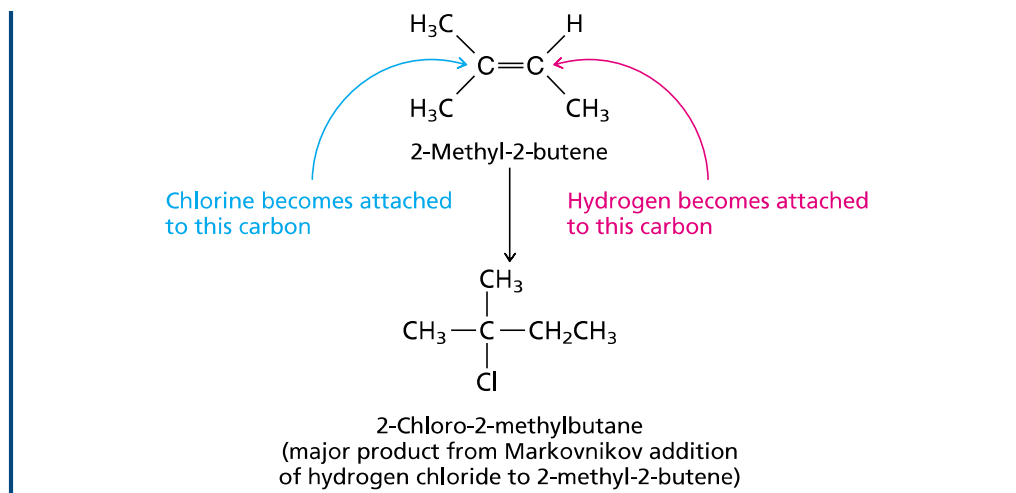
(b) 2-Methyl-1-butene

(c) *cis*-2-Butene

(d)
$$\text{CH}_3\text{CH}{=}\!\!\!\bigcirc$$
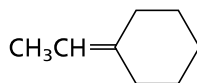
SAMPLE SOLUTION   (a) Hydrogen chloride adds to the double bond of 2-methyl-2-butene in accordance with Markovnikov's rule. The proton adds to the carbon that has one attached hydrogen, chlorine to the carbon that has none.

2-Chloro-2-methylbutane
(major product from Markovnikov addition
of hydrogen chloride to 2-methyl-2-butene)

Markovnikov's rule, like Zaitsev's, organizes experimental observations in a form suitable for predicting the major product of a reaction. The reasons why it works appear when we examine the mechanism of electrophilic addition in more detail.
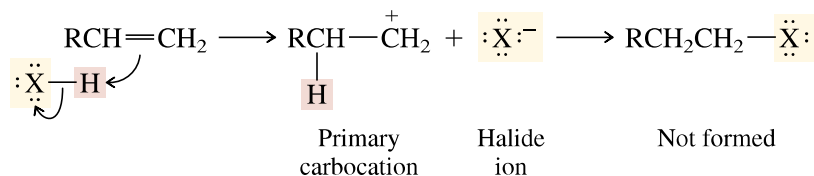
6.6   MECHANISTIC BASIS FOR MARKOVNIKOV'S RULE

Let's compare the carbocation intermediates for addition of a hydrogen halide (HX) to an unsymmetrical alkene of the type $RCH=CH_2$ (a) according to Markovnikov's rule and (b) opposite to Markovnikov's rule.

(a) *Addition according to Markovnikov's rule:*
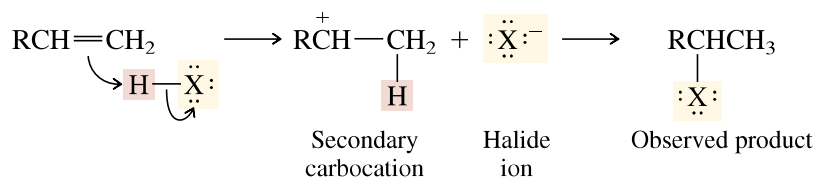
(b) *Addition opposite to Markovnikov's rule:*

The transition state for protonation of the double bond has much of the character of a carbocation, and the activation energy for formation of the more stable carbocation (secondary) is less than that for formation of the less stable (primary) one. Figure 6.5 uses a potential energy diagram to illustrate these two competing modes of addition. Both carbocations are rapidly captured by X^- to give an alkyl halide, with the major product derived from the carbocation that is formed faster. The energy difference between a primary carbocation and a secondary carbocation is so great and their rates of formation are so different that essentially all the product is derived from the secondary carbocation.

RULES, LAWS, THEORIES, AND THE SCIENTIFIC METHOD

As we have just seen, Markovnikov's rule can be expressed in two ways:

1. When a hydrogen halide adds to an alkene, hydrogen adds to the carbon of the alkene that has the greater number of hydrogens attached to it, and the halogen to the carbon that has the fewer hydrogens.

2. When a hydrogen halide adds to an alkene, protonation of the double bond occurs in the direction that gives the more stable carbocation.

The first of these statements is close to the way Vladimir Markovnikov expressed it in 1870; the second is the way we usually phrase it now. These two statements differ in an important way—a way that is related to the *scientific method.*

Adherence to the scientific method is what defines science. The scientific method has four major elements: observation, law, theory, and hypothesis.
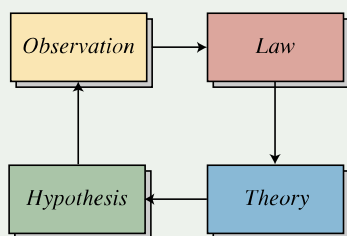
Most *observations* in chemistry come from experiments. If we do enough experiments we may see a pattern running through our observations. A *law* is a mathematical (the law of gravity) or verbal (the law of diminishing returns) description of that pattern. Establishing a law can lead to the framing of a *rule* that lets us predict the results of future experiments. This is what the 1870 version of Markovnikov's rule is: a statement based on experimental observations that has predictive value.

A *theory* is our best present interpretation of why things happen the way they do. The modern version of Markovnikov's rule, which is based on mechanistic reasoning and carbocation stability, recasts the rule in terms of theoretical ideas. Mechanisms, and explanations grounded in them, belong to the theory part of the scientific method.

It is worth remembering that a theory can never be proven correct. It can only be proven incorrect, incomplete, or inadequate. Thus, theories are always being tested and refined. As important as anything else in the scientific method is the *testable hypothesis.* Once a theory is proposed, experiments are designed to test its validity. If the results are consistent with the theory, our belief in its soundness is strengthened. If the results conflict with it, the theory is flawed and must be modified. Section 6.7 describes some observations that support the theory that carbocations are intermediates in the addition of hydrogen halides to alkenes.
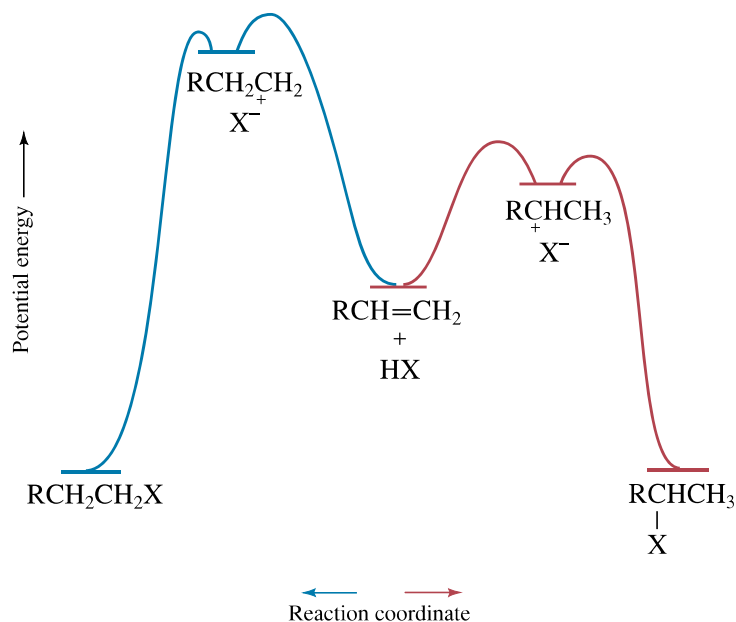
**FIGURE 6.5** Energy diagram comparing addition of a hydrogen halide to an alkene according to Markovnikov's rule with addition in the direction opposite to Markovnikov's rule. The alkene and hydrogen halide are shown in the center of the diagram. The lower energy pathway that corresponds to Markovnikov's rule proceeds to the right and is shown in red; the higher energy pathway proceeds to the left and is shown in blue.
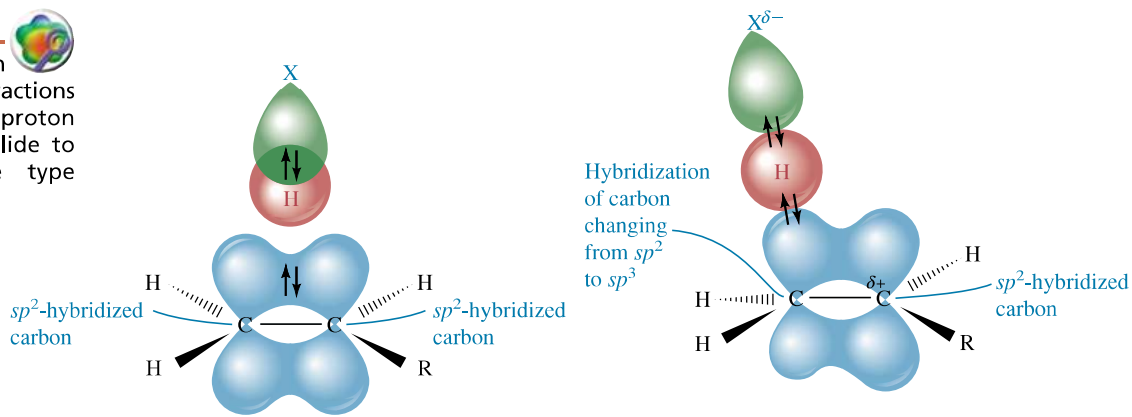
(*a*) The hydrogen halide (HX) and the alkene (CH_2=CHR) approach each other. The electrophile is the hydrogen halide, and the site of electrophilic attack is the orbital containing the σ electrons of the double bond.

(*b*) Electrons flow from the π orbital of the alkene to the hydrogen halide. The π electrons flow in the direction that generates a partial positive charge on the carbon atom that bears the electron-releasing alkyl group (R). The hydrogen–halogen bond is partially broken and a C—H σ bond is partially formed at the transition state.
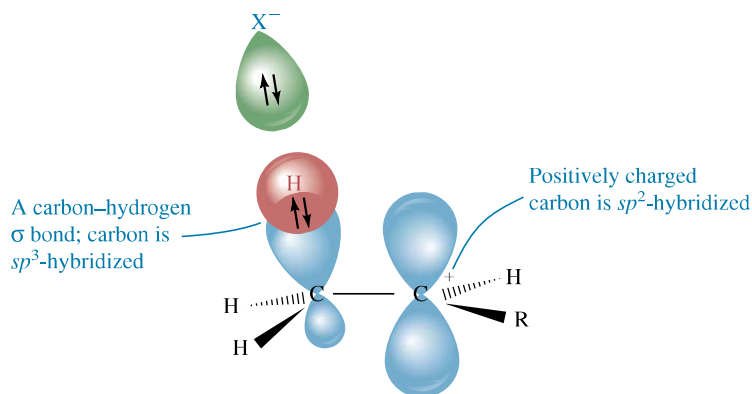
(*c*) Loss of the halide ion (X^-) from the hydrogen halide and C—H σ bond formation complete the formation of the more stable carbocation intermediate $CH_3\overset{+}{C}HR$.

Figure 6.6 focuses on the orbitals involved and shows how the π electrons of the double bond flow in the direction that generates the more stable of the two possible carbocations.

PROBLEM 6.4 Give a structural formula for the carbocation intermediate that leads to the major product in each of the reactions of Problem 6.3 (Section 6.5).

SAMPLE SOLUTION (a) Protonation of the double bond of 2-methyl-2-butene can give a tertiary carbocation or a secondary carbocation.

$$H_3C\overset{1}{}\qquad\qquad H$$

2-Methyl-2-butene

Protonation of C-3   (faster) | (slower)   Protonation of C-2

Tertiary carbocation   Secondary carbocation
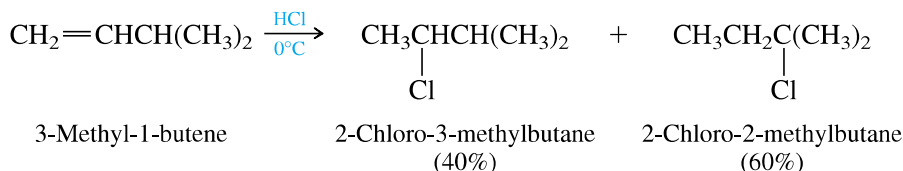
The product of the reaction is derived from the more stable carbocation—in this case, it is a tertiary carbocation that is formed more rapidly than a secondary one.
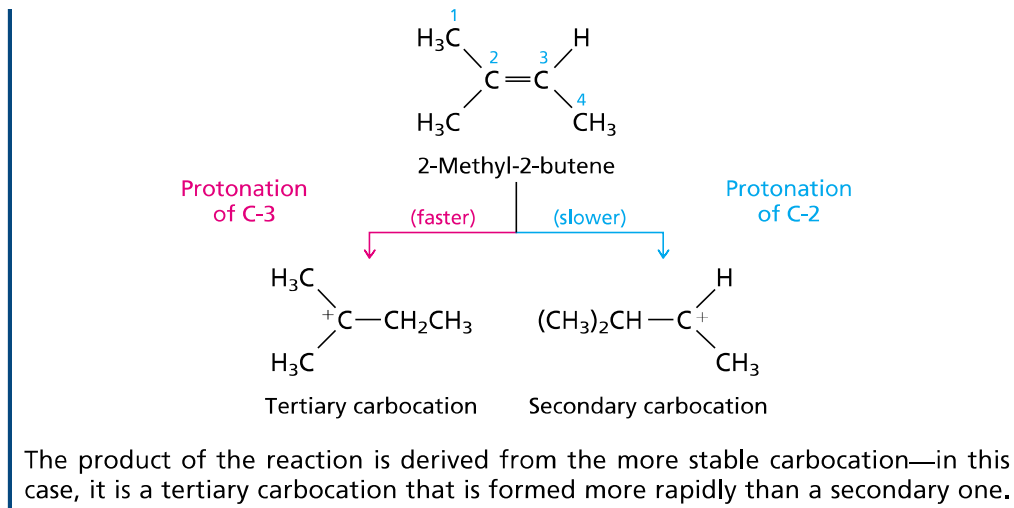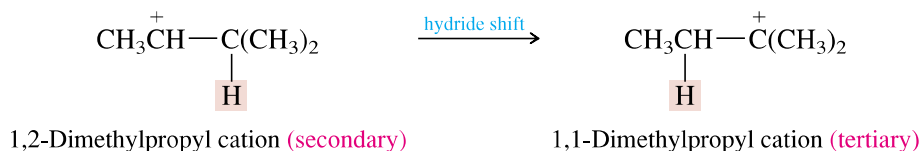
In general, alkyl substituents increase the reactivity of a double bond toward electrophilic addition. Alkyl groups are electron-releasing, and the more *electron-rich* a double bond, the better it can share its π electrons with an electrophile. Along with the observed regioselectivity of addition, this supports the idea that carbocation formation, rather than carbocation capture, is rate-determining.

6.7 CARBOCATION REARRANGEMENTS IN HYDROGEN HALIDE ADDITION TO ALKENES

Our belief that carbocations are intermediates in the addition of hydrogen halides to alkenes is strengthened by the observation that rearrangements sometimes occur. For example, the reaction of hydrogen chloride with 3-methyl-1-butene is expected to produce 2-chloro-3-methylbutane. Instead, a mixture of 2-chloro-3-methylbutane and 2-chloro-2-methylbutane results.

$$CH_2{=}CHCH(CH_3)_2 \xrightarrow[0°C]{HCl} CH_3CHCH(CH_3)_2 \;+\; CH_3CH_2C(CH_3)_2$$

3-Methyl-1-butene   2-Chloro-3-methylbutane (40%)   2-Chloro-2-methylbutane (60%)

Addition begins in the usual way, by protonation of the double bond to give, in this case, a secondary carbocation. This carbocation can be captured by chloride to give 2-chloro-3-methylbutane (40%) or it can rearrange by way of a hydride shift to give a tertiary carbocation. The tertiary carbocation reacts with chloride ion to give 2-chloro-2-methylbutane (60%).

$$CH_3\overset{+}{C}H{-}C(CH_3)_2 \xrightarrow{\text{hydride shift}} CH_3CH{-}\overset{+}{C}(CH_3)_2$$

1,2-Dimethylpropyl cation (secondary)   1,1-Dimethylpropyl cation (tertiary)
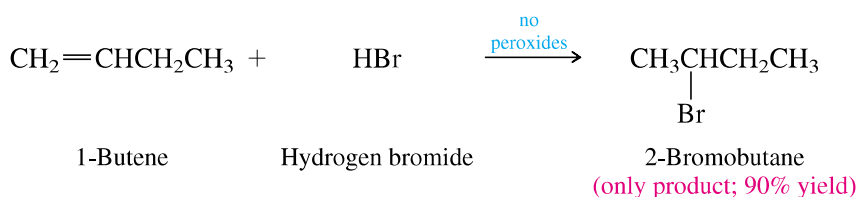
The similar yields of the two alkyl chloride products indicate that the rate of attack by chloride on the secondary carbocation and the rate of rearrangement must be very similar.
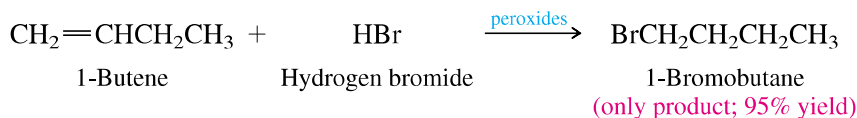
> **PROBLEM 6.5** Addition of hydrogen chloride to 3,3-dimethyl-1-butene gives a mixture of two isomeric chlorides in approximately equal amounts. Suggest reasonable structures for these two compounds, and offer a mechanistic explanation for their formation.

6.8 FREE-RADICAL ADDITION OF HYDROGEN BROMIDE TO ALKENES

For a long time the regioselectivity of addition of hydrogen bromide to alkenes was unpredictable. Sometimes addition occurred according to Markovnikov's rule, but at other times, seemingly under the same conditions, the opposite regioselectivity *(anti-Markovnikov addition)* was observed. In 1929, Morris S. Kharasch and his students at the University of Chicago began a systematic investigation of this puzzle. After hundreds of experiments, Kharasch concluded that anti-Markovnikov addition occurred when peroxides, that is, organic compounds of the type ROOR, were present in the reaction mixture. He and his colleagues found, for example, that carefully purified 1-butene reacted with hydrogen bromide to give only 2-bromobutane—the product expected on the basis of Markovnikov's rule.
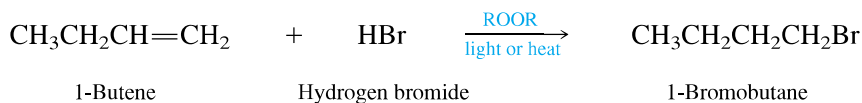
$$CH_2\!\!=\!\!CHCH_2CH_3 \; + \qquad HBr \quad \xrightarrow[\text{peroxides}]{\text{no}} \quad \underset{\underset{\displaystyle Br}{|}}{CH_3CHCH_2CH_3}$$

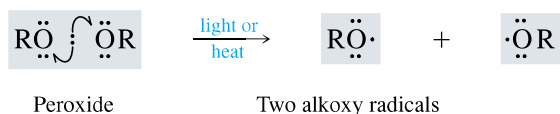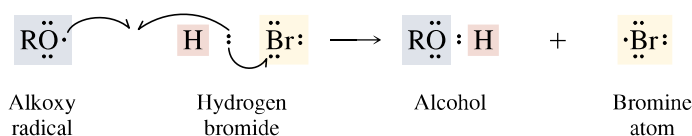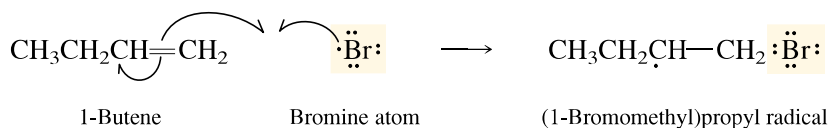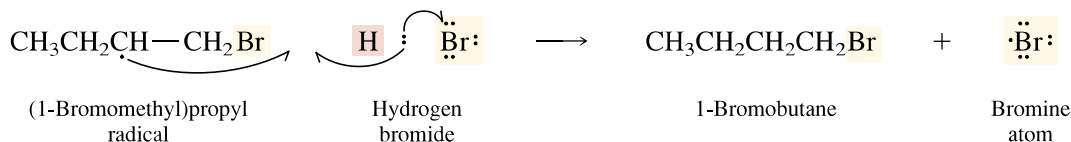| 1-Butene | Hydrogen bromide | 2-Bromobutane |
| | | (only product; 90% yield) |

On the other hand, when the same reaction was performed in the presence of an added peroxide, only 1-bromobutane was formed.

$$CH_2\!\!=\!\!CHCH_2CH_3 \; + \qquad HBr \quad \xrightarrow{\text{peroxides}} \quad BrCH_2CH_2CH_2CH_3$$

| 1-Butene | Hydrogen bromide | 1-Bromobutane |
| | | (only product; 95% yield) |

Kharasch termed this phenomenon the **peroxide effect** and demonstrated that it could occur even if peroxides were not deliberately added to the reaction mixture. Unless alkenes are protected from atmospheric oxygen, they become contaminated with small amounts of alkyl hydroperoxides, compounds of the type ROOH. These alkyl hydroperoxides act in the same way as deliberately added peroxides to promote addition in the direction opposite to that predicted by Markovnikov's rule.

> **PROBLEM 6.6** Kharasch's earliest studies in this area were carried out in collaboration with graduate student Frank R. Mayo. Mayo performed over 400 experiments in which allyl bromide (3-bromo-1-propene) was treated with hydrogen bromide under a variety of conditions, and determined the distribution of the "normal" and "abnormal" products formed during the reaction. What two products were formed? Which is the product of addition in accordance with Markovnikov's rule? Which one corresponds to addition opposite to the rule?

Kharasch proposed that hydrogen bromide can add to alkenes by two different mechanisms, both of which are, in modern terminology, regiospecific. The first mechanism is the one we discussed in the preceding section, electrophilic addition, and fol-

The overall reaction:

$$CH_3CH_2CH{=}CH_2 \quad + \quad HBr \xrightarrow[\text{light or heat}]{\text{ROOR}} \quad CH_3CH_2CH_2CH_2Br$$

1-Butene   Hydrogen bromide   1-Bromobutane

The mechanism:

(*a*) Initiation

Step 1: Dissociation of a peroxide into two alkoxy radicals:

$$R\ddot{\underset{\cdot\cdot}{O}}{\frown}\ddot{\underset{\cdot\cdot}{O}}R \xrightarrow[\text{heat}]{\text{light or}} R\ddot{\underset{\cdot\cdot}{O}}{\cdot} \quad + \quad {\cdot}\ddot{\underset{\cdot\cdot}{O}}R$$

Peroxide   Two alkoxy radicals

Step 2: Hydrogen atom abstraction from hydrogen bromide by an alkoxy radical:

$$R\ddot{\underset{\cdot\cdot}{O}}{\cdot} \quad H \; \colon \; \ddot{\underset{\cdot\cdot}{B}r}{\colon} \quad \longrightarrow \quad R\ddot{\underset{\cdot\cdot}{O}}{\colon}H \quad + \quad {\cdot}\ddot{\underset{\cdot\cdot}{B}r}{\colon}$$

Alkoxy   Hydrogen   Alcohol   Bromine
radical   bromide   atom

(*b*) Chain propagation

Step 3: Addition of a bromine atom to the alkene:

$$CH_3CH_2CH{=}CH_2 \quad {\cdot}\ddot{\underset{\cdot\cdot}{B}r}{\colon} \quad \longrightarrow \quad CH_3CH_2\overset{\cdot}{C}H{-}CH_2\ddot{\underset{\cdot\cdot}{B}r}{\colon}$$

1-Butene   Bromine atom   (1-Bromomethyl)propyl radical

Step 4: Abstraction of a hydrogen atom from hydrogen bromide by the free radical formed in step 3:

$$CH_3CH_2\overset{\cdot}{C}H{-}CH_2Br \quad H \; \colon \; \ddot{\underset{\cdot\cdot}{B}r}{\colon} \quad \longrightarrow \quad CH_3CH_2CH_2CH_2Br \quad + \quad {\cdot}\ddot{\underset{\cdot\cdot}{B}r}{\colon}$$

(1-Bromomethyl)propyl   Hydrogen   1-Bromobutane   Bromine
radical   bromide   atom

FIGURE 6.7 Initiation and propagation steps in the free-radical addition of hydrogen bromide to 1-butene.

lows Markovnikov's rule. It is the mechanism followed when care is taken to ensure that no peroxides are present. The second mechanism is the free-radical chain process, presented in Figure 6.7.

Peroxides are *initiators*; they are not incorporated into the product but act as a source of radicals necessary to get the chain reaction started. The oxygen–oxygen bond of a peroxide is relatively weak, and the free-radical addition of hydrogen bromide to alkenes begins when a peroxide molecule undergoes homolytic cleavage to two alkoxy radicals. This is depicted in step 1 of Figure 6.7. A bromine atom is generated in step 2 when one of these alkoxy radicals abstracts a proton from hydrogen bromide. Once a bromine atom becomes available, the propagation phase of the chain reaction begins. In the propagation phase as shown in step 3, a bromine atom adds to the alkene in the direction that produces the more stable alkyl radical.