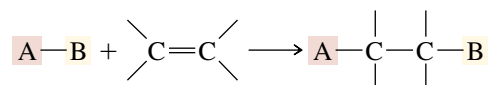


CHAPTER 6

REACTIONS OF ALKENES: ADDITION REACTIONS

Now that we're familiar with the structure and preparation of alkenes, let's look at their chemical reactions. The characteristic reaction of alkenes is **addition** to the double bond according to the general equation:

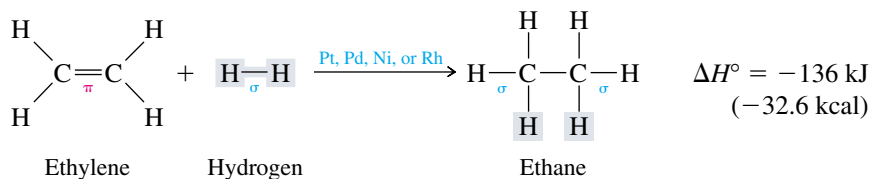


The range of compounds represented as A—B in this equation is quite large, and their variety offers a wealth of opportunity for converting alkenes to a number of other functional group types.

Alkenes are commonly described as **unsaturated hydrocarbons** because they have the capacity to react with substances which add to them. Alkanes, on the other hand, are said to be **saturated** hydrocarbons and are incapable of undergoing addition reactions.

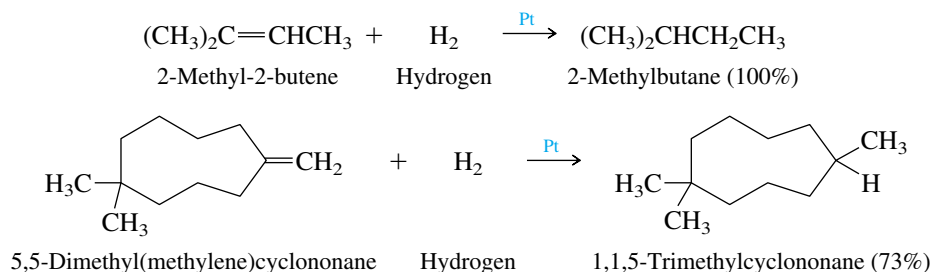
6.1 HYDROGENATION OF ALKENES

The relationship between reactants and products in addition reactions can be illustrated by the *hydrogenation* of alkenes to yield alkanes. **Hydrogenation** is the addition of H₂ to a multiple bond. An example is the reaction of hydrogen with ethylene to form ethane.



The bonds in the product are stronger than the bonds in the reactants; two C—H σ bonds of an alkane are formed at the expense of the H—H σ bond and the π component of the alkene's double bond. The overall reaction is *exothermic*, and the heat evolved on hydrogenation of one mole of an alkene is its **heat of hydrogenation**. Heat of hydrogenation is a positive quantity equal to $-\Delta H^\circ$ for the reaction.

The uncatalyzed addition of hydrogen to an alkene, although exothermic, is very slow. The rate of hydrogenation increases dramatically, however, in the presence of certain finely divided metal catalysts. *Platinum* is the hydrogenation catalyst most often used, although *palladium*, *nickel*, and *rhodium* are also effective. Metal-catalyzed addition of hydrogen is normally rapid at room temperature, and the alkane is produced in high yield, usually as the only product.



PROBLEM 6.1 What three alkenes yield 2-methylbutane on catalytic hydrogenation?

The solvent used in catalytic hydrogenation is chosen for its ability to dissolve the alkene and is typically ethanol, hexane, or acetic acid. The metal catalysts are insoluble in these solvents (or, indeed, in any solvent). Two phases, the solution and the metal, are present, and the reaction takes place at the interface between them. Reactions involving a substance in one phase with a different substance in a second phase are called **heterogeneous reactions**.

Catalytic hydrogenation of an alkene is believed to proceed by the series of steps shown in Figure 6.1. As already noted, addition of hydrogen to the alkene is very slow in the absence of a metal catalyst, meaning that any uncatalyzed mechanism must have a very high activation energy. The metal catalyst accelerates the rate of hydrogenation by providing an alternative pathway that involves a sequence of several low activation energy steps.

6.2 HEATS OF HYDROGENATION

Heats of hydrogenation are used to compare the relative stabilities of alkenes in much the same way as heats of combustion. Both methods measure the differences in the energy of *isomers* by converting them to a product or products common to all. Catalytic hydrogenation of 1-butene, *cis*-2-butene, or *trans*-2-butene yields the same product—butane. As Figure 6.2 shows, the measured heats of hydrogenation reveal that *trans*-2-butene is 4 kJ/mol (1.0 kcal/mol) lower in energy than *cis*-2-butene and that *cis*-2-butene is 7 kJ/mol (1.7 kcal/mol) lower in energy than 1-butene.

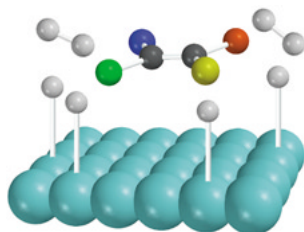
Heats of hydrogenation can be used to *estimate* the stability of double bonds as structural units, even in alkenes that are not isomers. Table 6.1 lists the heats of hydrogenation for a representative collection of alkenes.

The French chemist Paul Sabatier received the 1912 Nobel Prize in chemistry for his discovery that finely divided nickel is an effective hydrogenation catalyst.

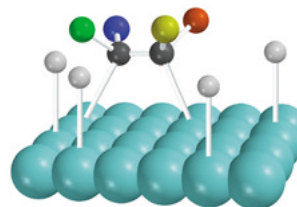
Remember that a catalyst affects the rate of a reaction but not the energy relationships between reactants and products. Thus, the heat of hydrogenation of a particular alkene is the same irrespective of what catalyst is used.

FIGURE 6.1 A mechanism for heterogeneous catalysis in the hydrogenation of alkenes.

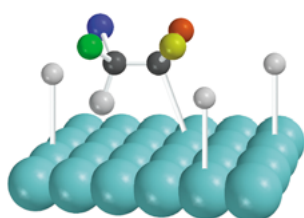
Step 1: Hydrogen molecules react with metal atoms at the catalyst surface. The relatively strong hydrogen–hydrogen σ bond is broken and replaced by two weak metal–hydrogen bonds.



Step 2: The alkene reacts with the metal catalyst. The π component of the double bond between the two carbons is replaced by two relatively weak carbon–metal σ bonds.



Step 3: A hydrogen atom is transferred from the catalyst surface to one of the carbons of the double bond.



Step 4: The second hydrogen atom is transferred, forming the alkane. The sites on the catalyst surface at which the reaction occurred are free to accept additional hydrogen and alkene molecules.

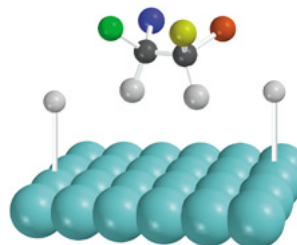


FIGURE 6.2 Heats of hydrogenation of butene isomers plotted on a common scale. All energies are in kilojoules per mole.

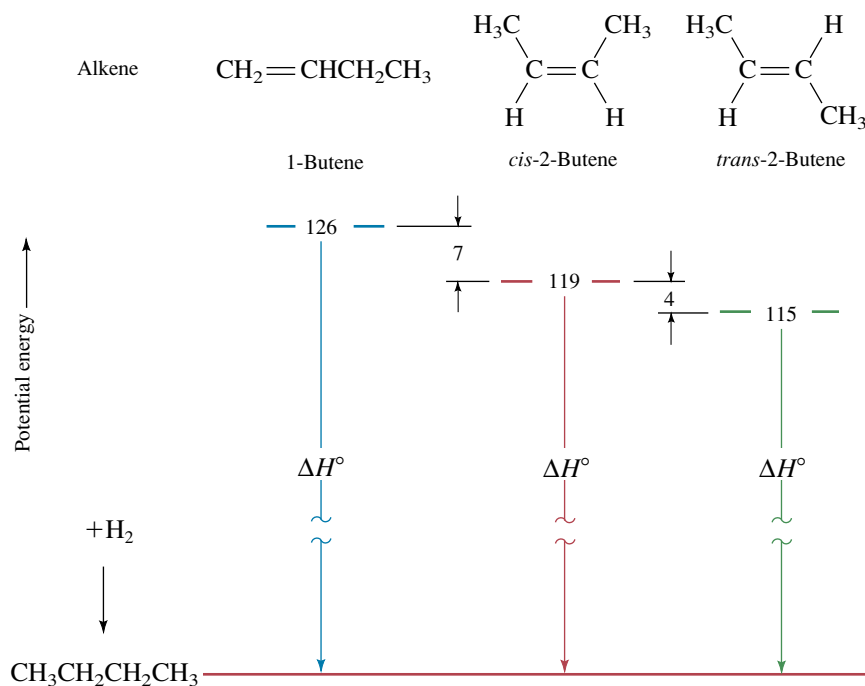
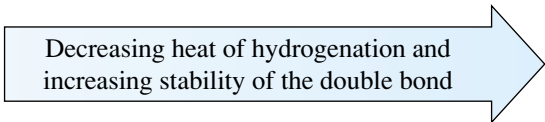
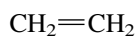


TABLE 6.1 Heats of Hydrogenation of Some Alkenes

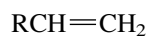
Alkene	Structure	Heat of hydrogenation	
		kJ/mol	kcal/mol
Ethylene	$\text{CH}_2=\text{CH}_2$	136	32.6
Monosubstituted alkenes			
Propene	$\text{CH}_2=\text{CHCH}_3$	125	29.9
1-Butene	$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	126	30.1
1-Hexene	$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	126	30.2
Cis-disubstituted alkenes			
<i>cis</i> -2-Butene	$\begin{array}{c} \text{H}_3\text{C} \quad \quad \text{CH}_3 \\ \quad \backslash \quad / \\ \quad \text{C}=\text{C} \\ \quad / \quad \backslash \\ \text{H} \quad \quad \quad \text{H} \end{array}$	119	28.4
<i>cis</i> -2-Pentene	$\begin{array}{c} \text{H}_3\text{C} \quad \quad \text{CH}_2\text{CH}_3 \\ \quad \backslash \quad / \\ \quad \text{C}=\text{C} \\ \quad / \quad \backslash \\ \text{H} \quad \quad \quad \text{H} \end{array}$	117	28.1
Trans-disubstituted alkenes			
<i>trans</i> -2-Butene	$\begin{array}{c} \text{H}_3\text{C} \quad \quad \text{H} \\ \quad \backslash \quad / \\ \quad \text{C}=\text{C} \\ \quad / \quad \backslash \\ \text{H} \quad \quad \quad \text{CH}_3 \end{array}$	115	27.4
<i>trans</i> -2-Pentene	$\begin{array}{c} \text{H}_3\text{C} \quad \quad \text{H} \\ \quad \backslash \quad / \\ \quad \text{C}=\text{C} \\ \quad / \quad \backslash \\ \text{H} \quad \quad \quad \text{CH}_2\text{CH}_3 \end{array}$	114	27.2
Trisubstituted alkenes			
2-Methyl-2-pentene	$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_3$	112	26.7
Tetrasubstituted alkenes			
2,3-Dimethyl-2-butene	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	110	26.4

The pattern of alkene stability determined from heats of hydrogenation parallels exactly the pattern deduced from heats of combustion.

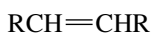




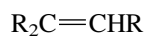
Ethylene



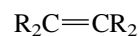
Monosubstituted



Disubstituted



Trisubstituted



Tetrasubstituted

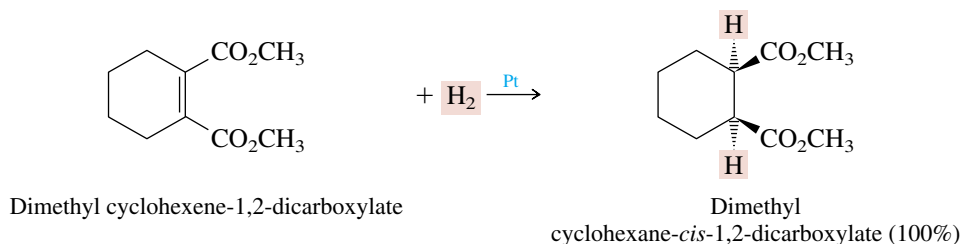
Ethylene, which has no alkyl substituents to stabilize its double bond, has the highest heat of hydrogenation. Alkenes that are similar in structure to one another have similar heats of hydrogenation. For example, the heats of hydrogenation of the monosubstituted (terminal) alkenes propene, 1-butene, 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.

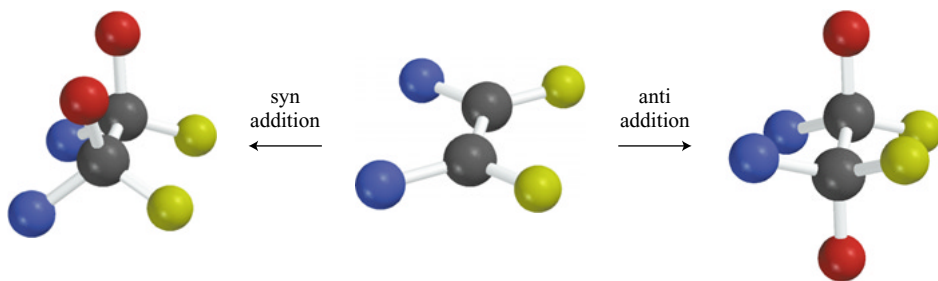
Heats of hydrogenation in kJ/mol (kcal/mol): 112 (26.7); 118 (28.2); 126 (30.2)

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.



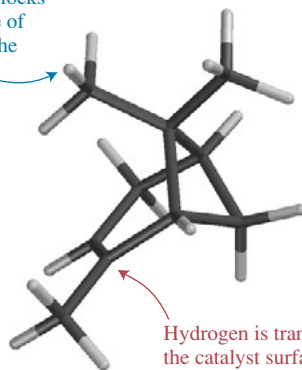
The term **syn addition** describes the stereochemistry of reactions such as catalytic hydrogenation in which two atoms or groups add to the *same face* of a double bond. When atoms or groups add to *opposite faces* of the double bond, the process is called **anti addition**.



Stereoselectivity was defined and introduced in connection with the formation of stereoisomeric alkenes in elimination reactions (Section 5.11).

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

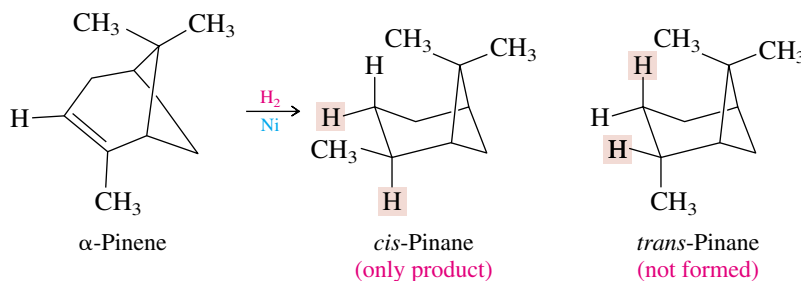


Hydrogen is transferred from the catalyst surface to the bottom face of the double bond—this is the “less hindered side”



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).



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.

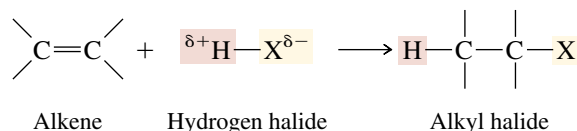
In practice, hydrogenation of α -pinene is observed to be 100% stereoselective. The only product obtained is *cis*-pinane. None of the stereoisomeric *trans*-pinane is formed.

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.

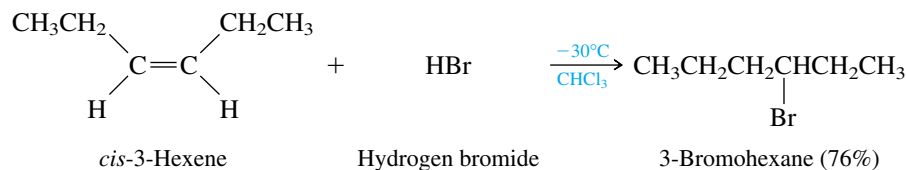
Reactions such as catalytic hydrogenation that take place at the “less hindered” side of a reactant are common in organic chemistry and are examples of steric effects on *reactivity*. We have previously seen steric effects on *structure* and *stability* in the case of *cis* and *trans* stereoisomers and in the preference for equatorial substituents on cyclohexane rings.

6.4 ELECTROPHILIC ADDITION OF HYDROGEN HALIDES TO ALKENES

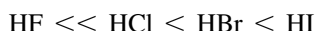
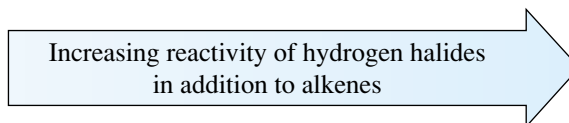
In many addition reactions the attacking reagent, unlike H_2 , is a polar molecule. Hydrogen halides are among the simplest examples of polar substances that add to alkenes.



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



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.



Slowest rate of addition;
least acidic

Fastest rate of addition;
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.

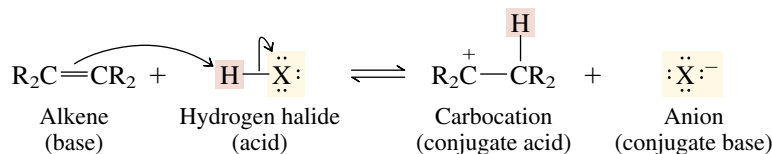
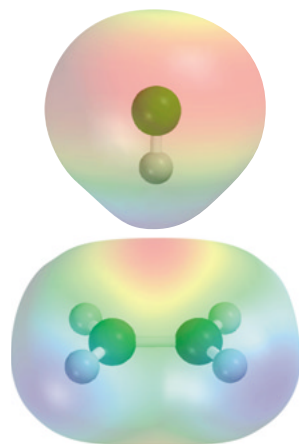


Figure 6.4 shows the complementary nature of the electrostatic potentials of an alkene and a hydrogen halide. We've also seen (Section 4.9) that carbocations, when generated in the presence of halide anions, react with them to form alkyl halides.

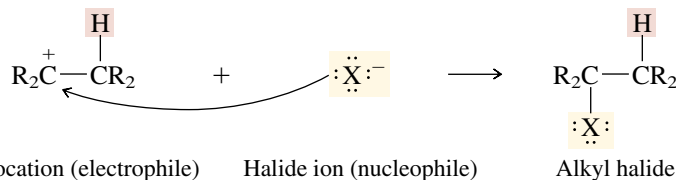
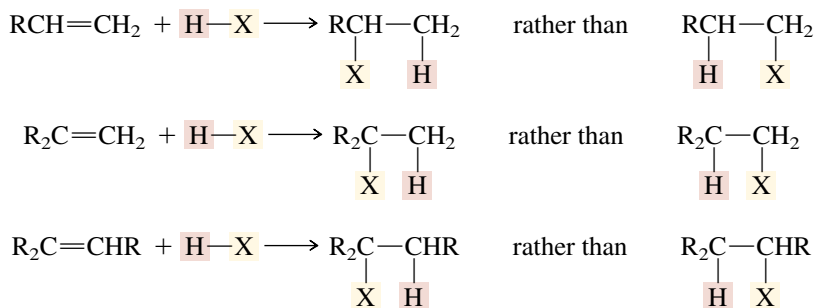


FIGURE 6.4 Electrostatic potential maps of HCl and ethylene. When the two react, the interaction is between the electron-rich site (red) of ethylene and the electron-poor region (blue) of HCl. The electron-rich region of ethylene is associated with the π electrons of the double bond, while H is the electron-poor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

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.

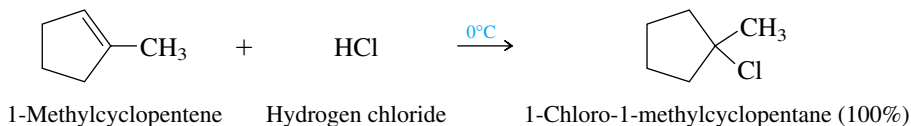
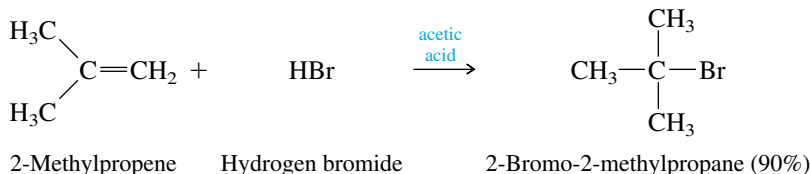
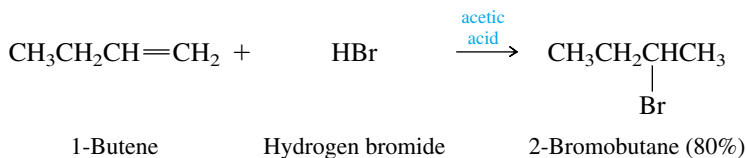
6.5 REGIOSELECTIVITY OF HYDROGEN HALIDE ADDITION: MARKOVNIKOV'S RULE

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.



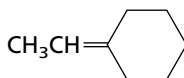
In 1870, Vladimir Markovnikov, a colleague of Alexander Zaitsev at the University of Kazan, noticed a pattern in the hydrogen halide addition to alkenes and assembled his observations into a simple statement. **Markovnikov's rule** states that *when an unsymmetrically substituted alkene reacts with a 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.

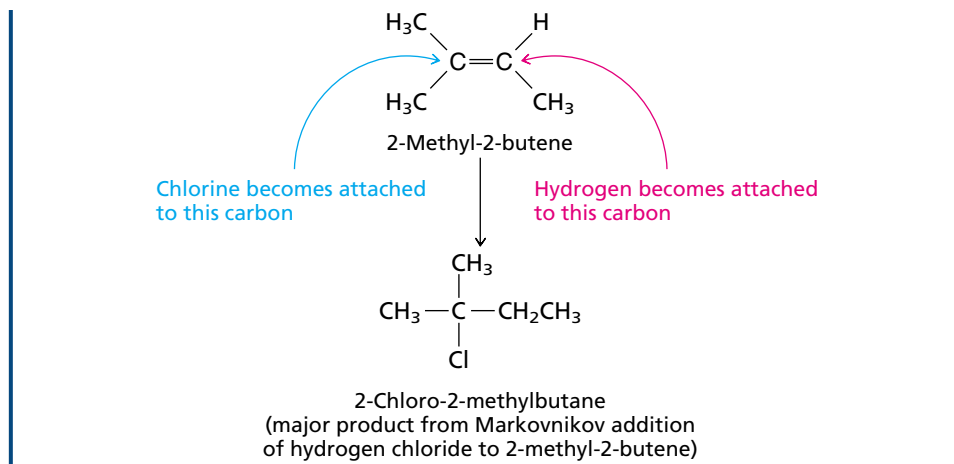


PROBLEM 6.3 Write the structure of the major organic product formed in the reaction of hydrogen chloride with each of the following:

- (a) 2-Methyl-2-butene (c) *cis*-2-Butene
 (b) 2-Methyl-1-butene (d)



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.

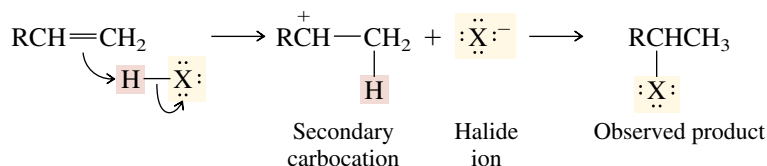


Markovnikov's rule, like Zaitsev's, organizes experimental observations in a form suitable for predicting the major product of a reaction. The reasons why it works appear when we examine the mechanism of electrophilic addition in more detail.

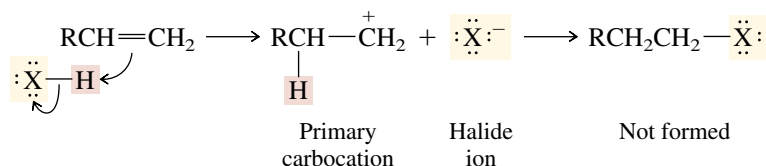
6.6 MECHANISTIC BASIS FOR MARKOVNIKOV'S RULE

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.

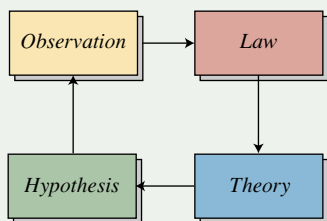
RULES, LAWS, THEORIES, AND THE SCIENTIFIC METHOD

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.

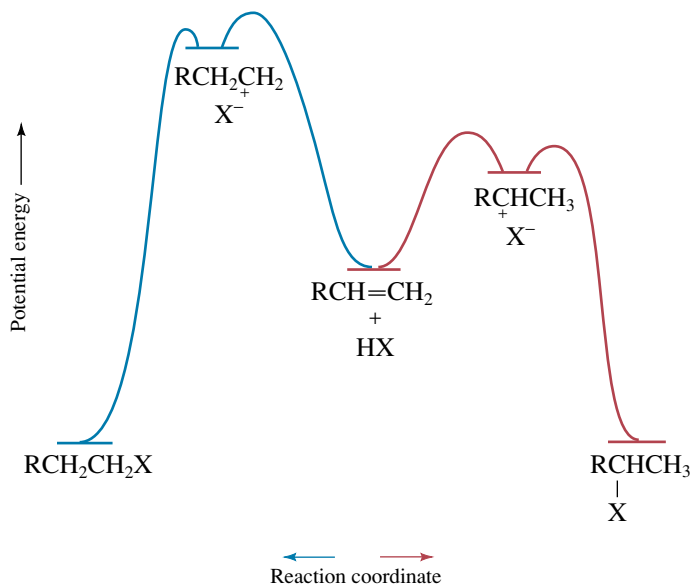
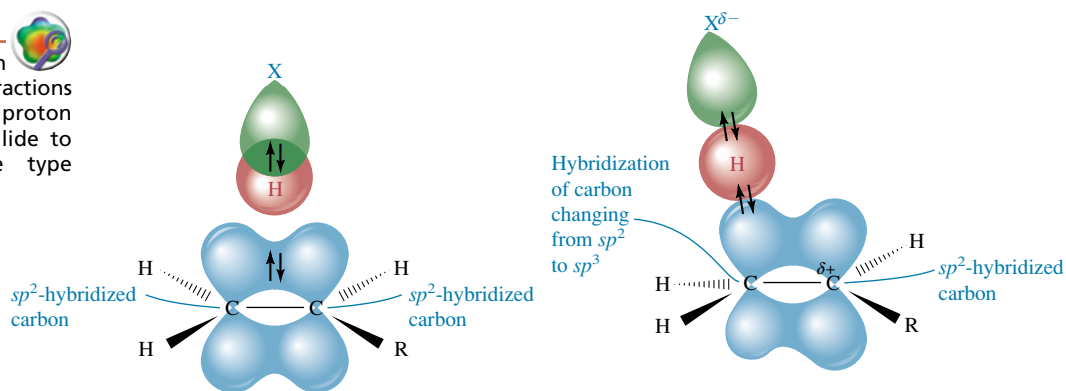


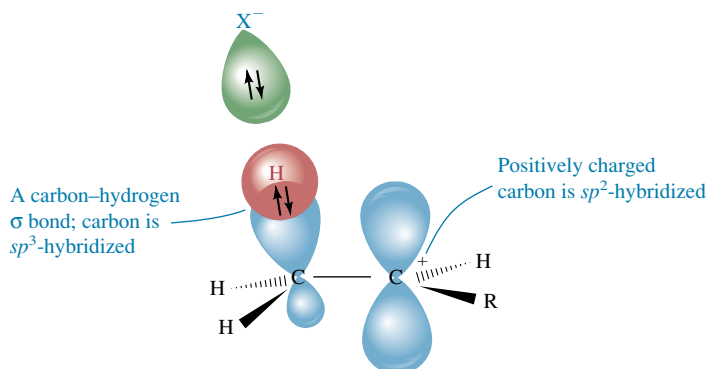
FIGURE 6.5 Energy diagram comparing addition of a hydrogen halide to an alkene according to Markovnikov's rule with addition in the direction opposite to Markovnikov's rule. The alkene and hydrogen halide are shown in the center of the diagram. The lower energy pathway that corresponds to Markovnikov's rule proceeds to the right and is shown in red; the higher energy pathway proceeds to the left and is shown in blue.

FIGURE 6.6 Electron flow and orbital interactions in the transfer of a proton from a hydrogen halide to an alkene of the type $\text{CH}_2=\text{CHR}$.



(a) The hydrogen halide (HX) and the alkene ($\text{CH}_2=\text{CHR}$) 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 $\text{C}-\text{H}$ σ bond is partially formed at the transition state.

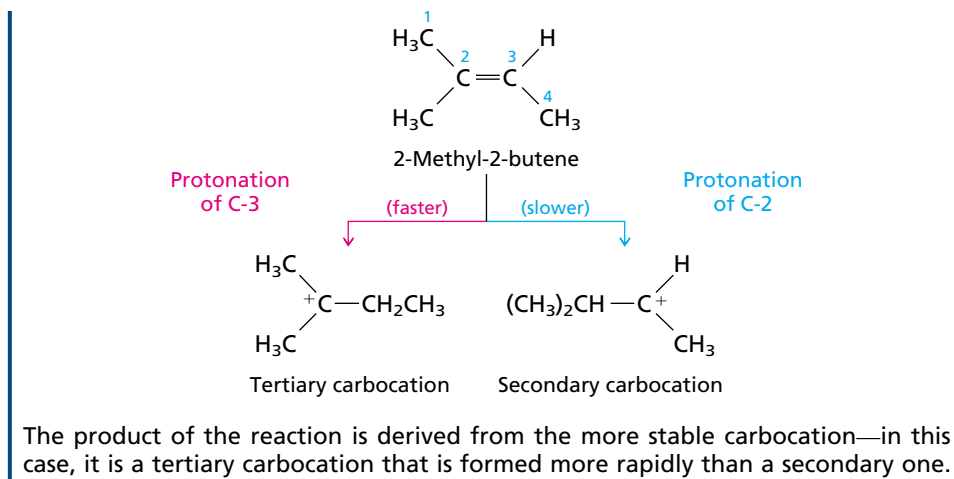


(c) Loss of the halide ion (X^-) from the hydrogen halide and $\text{C}-\text{H}$ σ bond formation complete the formation of the more stable carbocation intermediate $\text{CH}_3\dot{\text{C}}\text{HR}$.

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).

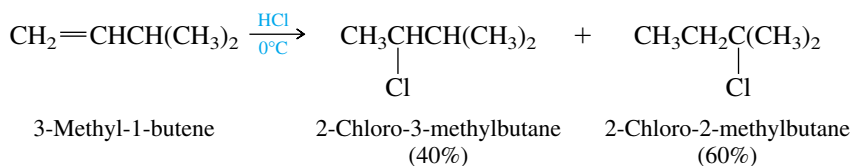
SAMPLE SOLUTION (a) Protonation of the double bond of 2-methyl-2-butene can give a tertiary carbocation or a secondary carbocation.



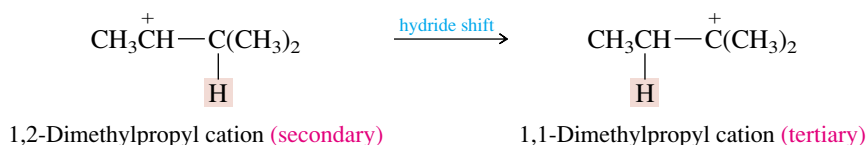
In general, alkyl substituents increase the reactivity of a double bond toward electrophilic addition. Alkyl groups are electron-releasing, and the more *electron-rich* a double bond, the better it can share its π electrons with an electrophile. Along with the observed regioselectivity of addition, this 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.



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%).

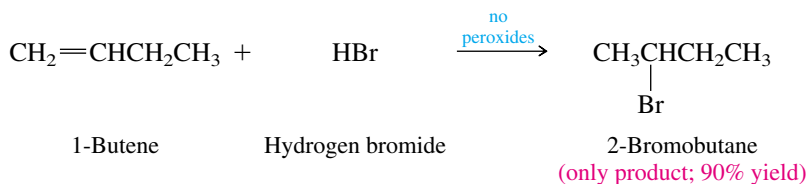


The similar yields of the two alkyl chloride products indicate that the rate of attack by chloride on the secondary carbocation and the rate of rearrangement must be very similar.

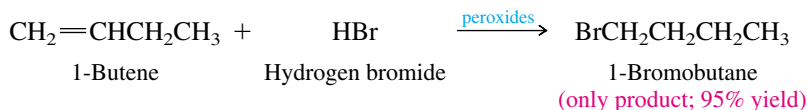
PROBLEM 6.5 Addition of hydrogen chloride to 3,3-dimethyl-1-butene gives a mixture of two isomeric chlorides in approximately equal amounts. Suggest reasonable structures for these two compounds, and offer a mechanistic explanation for their formation.

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.



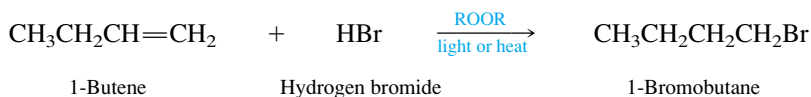
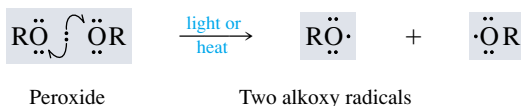
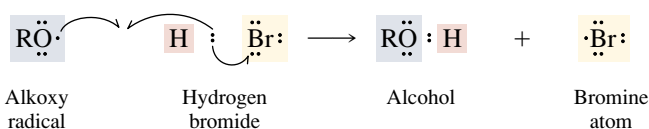
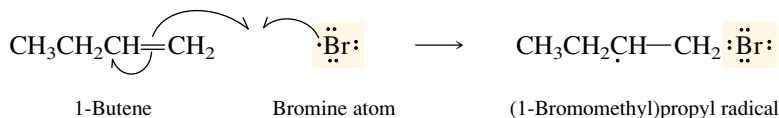
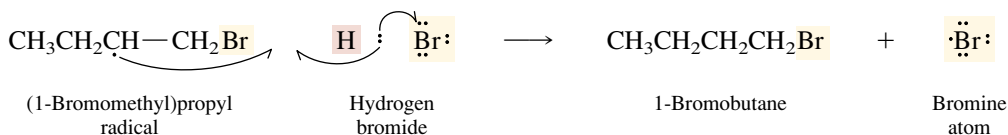
On the other hand, when the same reaction was performed in the presence of an added peroxide, only 1-bromobutane was formed.



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-

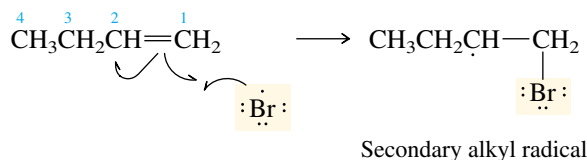
The overall reaction:**The mechanism:****(a) Initiation****Step 1:** Dissociation of a peroxide into two alkoxy radicals:**Step 2:** Hydrogen atom abstraction from hydrogen bromide by an alkoxy radical:**(b) Chain propagation****Step 3:** Addition of a bromine atom to the alkene:**Step 4:** Abstraction of a hydrogen atom from hydrogen bromide by the free radical formed in step 3:

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.

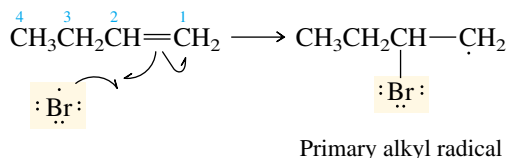
Peroxides are *initiators*; they are not incorporated into the product but act as a source of radicals necessary to get the chain reaction started. The oxygen–oxygen bond of a peroxide is relatively weak, and the free-radical addition of hydrogen bromide to alkenes begins when a peroxide molecule undergoes 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.

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

Addition of a bromine atom to C-1 gives a secondary alkyl radical.



Addition of a bromine atom to C-2 gives a primary alkyl radical.

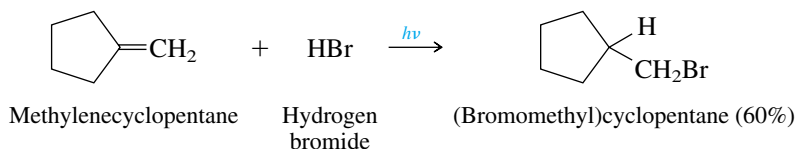


A secondary alkyl radical is more stable than a primary radical. Bromine therefore adds to C-1 of 1-butene faster than it adds to C-2. Once the bromine atom has added to the double bond, the regioselectivity of addition is set. The alkyl radical then abstracts a hydrogen atom from hydrogen bromide to give the alkyl bromide product as shown in step 4 of Figure 6.7.

The regioselectivity of addition of hydrogen bromide to alkenes under normal (ionic addition) conditions is controlled by the tendency of a *proton* to add to the double bond so as to produce the more stable *carbocation*. Under free-radical conditions the regioselectivity is governed by addition of a *bromine atom* to give the more stable *alkyl radical*.

Free-radical addition of hydrogen bromide to the double bond can also be initiated photochemically, either with or without added peroxides.

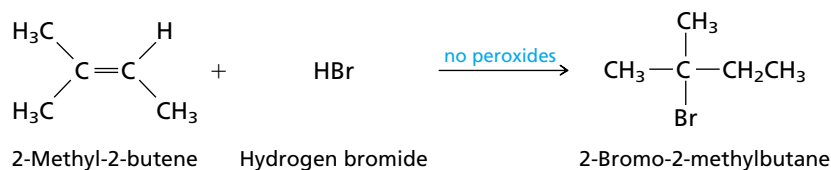
Using an sp^2 -hybridized carbon for the carbon that has the unpaired electron, make a molecular model of the free-radical intermediate in this reaction.



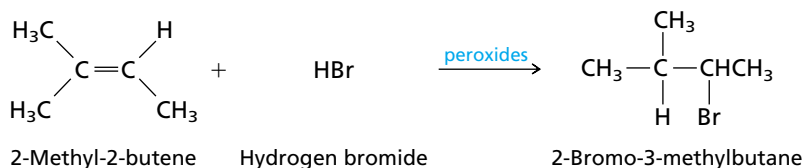
Among the hydrogen halides, only hydrogen bromide reacts with alkenes by both an ionic and a free-radical mechanism. Hydrogen iodide and hydrogen chloride always add to alkenes by an ionic mechanism and follow Markovnikov's rule. Hydrogen bromide normally reacts by the ionic mechanism, but if peroxides are present or if the reaction is initiated photochemically, the free-radical mechanism is followed.

PROBLEM 6.7 Give the major organic product formed when hydrogen bromide reacts with each of the alkenes in Problem 6.3 in the absence of peroxides and in their presence.

SAMPLE SOLUTION (a) The addition of hydrogen bromide in the absence of peroxides exhibits a regioselectivity just like that of hydrogen chloride addition; Markovnikov's rule is followed.



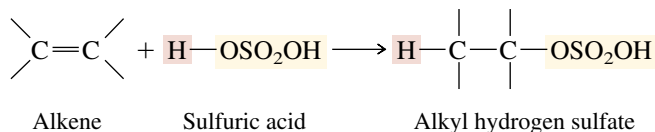
Under free-radical conditions in the presence of peroxides, addition takes place with a regioselectivity opposite to that of Markovnikov's rule.



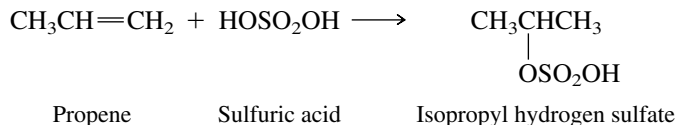
Although the possibility of having two different reaction paths available to an alkene and hydrogen bromide may seem like a complication, it can be an advantage in organic synthesis. From a single alkene one may prepare either of two different alkyl bromides, with control of regioselectivity, simply by choosing reaction conditions that favor ionic addition or free-radical addition of hydrogen bromide.

6.9 ADDITION OF SULFURIC ACID TO ALKENES

Acids other than hydrogen halides also add to the carbon-carbon bond of alkenes. Concentrated sulfuric acid, for example, reacts with certain alkenes to form alkyl hydrogen sulfates.

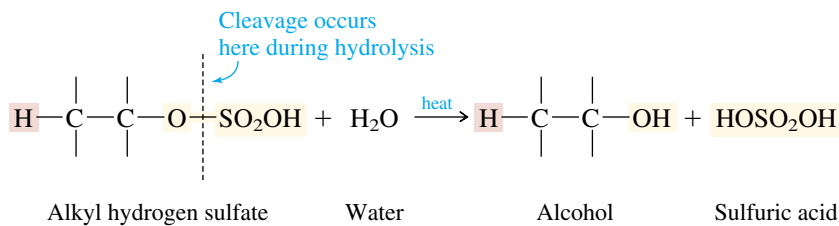


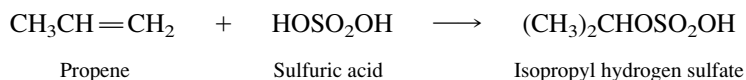
Notice in the following example that a proton adds to the carbon that has the greater number of hydrogens, and the hydrogen sulfate anion ($^-\text{OSO}_2\text{OH}$) adds to the carbon that has the fewer hydrogens.



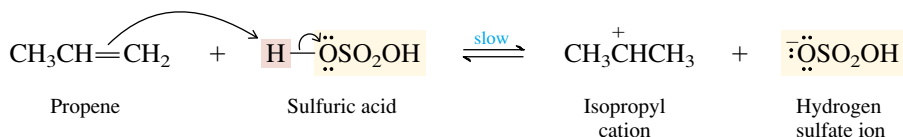
Markovnikov's rule is obeyed because the mechanism of sulfuric acid addition to alkenes, illustrated for the case of propene in Figure 6.8, is analogous to that described earlier for the ionic addition of hydrogen halides.

Alkyl hydrogen sulfates can be converted to alcohols by heating them with water or steam. This is called a **hydrolysis** reaction, because a bond is cleaved by reaction with water. (The suffix *-lysis* indicates cleavage.) It is the oxygen-sulfur bond that is broken when an alkyl hydrogen sulfate undergoes hydrolysis.



The overall reaction:**The mechanism:**

Step 1: Protonation of the carbon–carbon double bond in the direction that leads to the more stable carbocation:



Step 2: Carbocation–anion combination

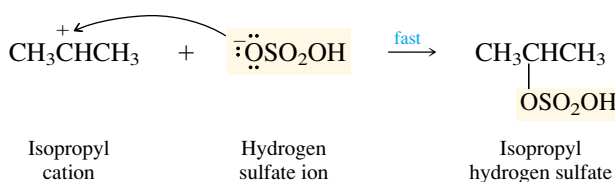
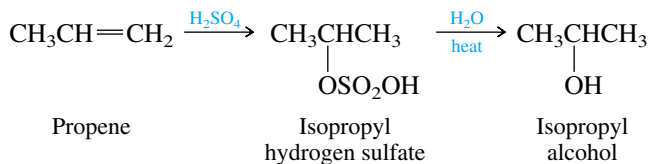


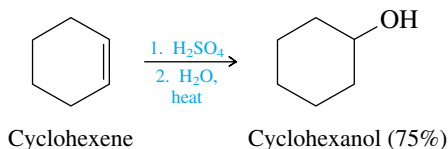
FIGURE 6.8 Mechanism of addition of sulfuric acid to propene.

The combination of sulfuric acid addition to propene, followed by hydrolysis of the resulting isopropyl hydrogen sulfate, is the major method by which over 10^9 lb of isopropyl alcohol is prepared each year in the United States.



It is convenient in synthetic transformations involving more than one step simply to list all the reagents with a single arrow. Individual synthetic steps are indicated by number. Numbering the individual steps is essential so as to avoid the implication that everything is added to the reaction mixture at the same time.

We say that propene has undergone **hydration**. Overall, H and OH have added across the carbon–carbon double bond. In the same manner, cyclohexanol has been prepared by hydration of cyclohexene:



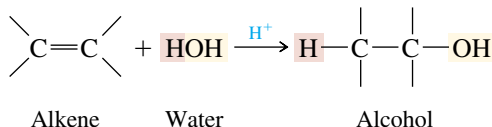
PROBLEM 6.8 Write a structural formula for the compound formed on electrophilic addition of sulfuric acid to cyclohexene (step 1 in the two-step transformation shown in the preceding equation).

Hydration of alkenes by this method, however, is limited to monosubstituted alkenes and disubstituted alkenes of the type $\text{RCH}=\text{CHR}$. Disubstituted alkenes of the

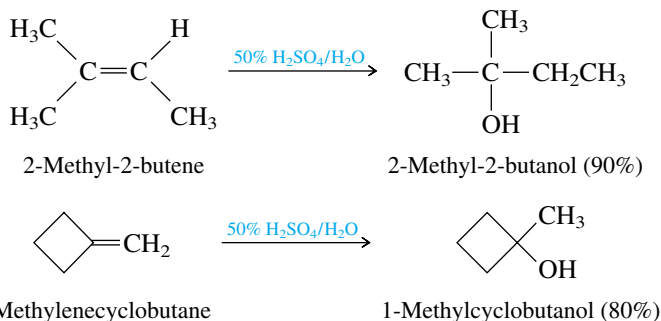
type $R_2C=CH_2$, along with trisubstituted and tetrasubstituted alkenes, do not form alkyl hydrogen sulfates under these conditions but instead react in a more complicated way with concentrated sulfuric acid (to be discussed in Section 6.21).

6.10 ACID-CATALYZED HYDRATION OF ALKENES

Another method for the hydration of alkenes is by reaction with water under conditions of acid catalysis.



Unlike the addition of concentrated sulfuric acid to form alkyl hydrogen sulfates, this reaction is carried out in a *dilute acid* medium. A 50% water/sulfuric acid solution is often used, yielding the alcohol directly without the necessity of a separate hydrolysis step. Markovnikov's rule is followed:



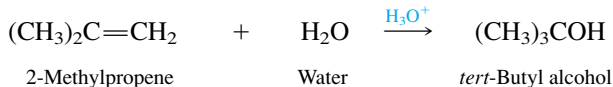
We can extend the general principles of electrophilic addition to acid-catalyzed hydration. In the first step of the mechanism shown in Figure 6.9, proton transfer to 2-methylpropene forms *tert*-butyl cation. This is followed in step 2 by reaction of the carbocation with a molecule of water acting as a nucleophile. The alkyloxonium ion formed in this step is simply the conjugate acid of *tert*-butyl alcohol. Deprotonation of the alkyloxonium ion in step 3 yields the alcohol and regenerates the acid catalyst.

PROBLEM 6.9 Instead of the three-step mechanism of Figure 6.9, the following two-step mechanism might be considered:

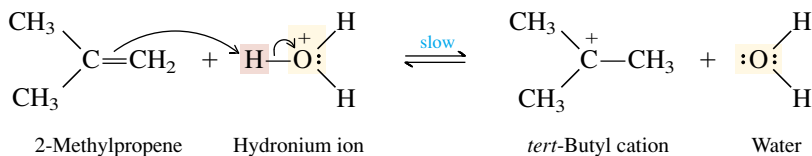
- $(\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{H}_3\text{O}^+ \xrightarrow{\text{slow}} (\text{CH}_3)_3\text{C}^+ + \text{H}_2\text{O}$
- $(\text{CH}_3)_3\text{C}^+ + \text{HO}^- \xrightarrow{\text{fast}} (\text{CH}_3)_3\text{COH}$

This mechanism cannot be correct! What is its fundamental flaw?

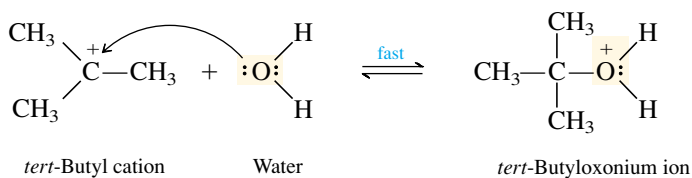
The notion that carbocation formation is rate-determining follows from our previous experience and by observing how the reaction rate is affected by the structure of the alkene. Table 6.2 gives some data showing that alkenes that yield relatively stable carbocations react faster than those that yield less stable carbocations. Protonation of ethylene, the least reactive alkene in the table, yields a primary carbocation; protonation of 2-methylpropene, the most reactive in the table, yields a tertiary carbocation. As we have seen on other occasions, the more stable the carbocation, the faster is its rate of formation.

The overall reaction:**The mechanism:**

Step 1: Protonation of the carbon–carbon double bond in the direction that leads to the more stable carbocation:



Step 2: Water acts as a nucleophile to capture *tert*-butyl cation:



Step 3: Deprotonation of *tert*-butyloxonium ion. Water acts as a Brønsted base:

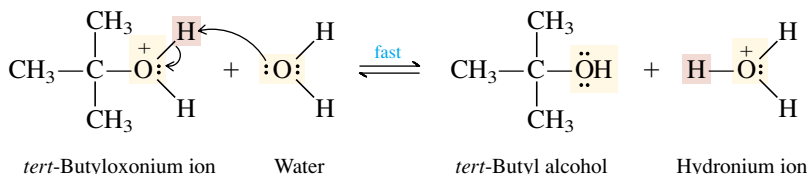


FIGURE 6.9 Mechanism of acid-catalyzed hydration of 2-methylpropene.

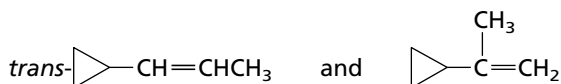
TABLE 6.2

Relative Rates of Acid-Catalyzed Hydration of Some Representative Alkenes

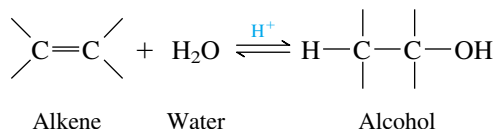
Alkene	Structural formula	Relative rate of acid-catalyzed hydration*
Ethylene	$\text{CH}_2=\text{CH}_2$	1.0
Propene	$\text{CH}_3\text{CH}=\text{CH}_2$	1.6×10^6
2-Methylpropene	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	2.5×10^{11}

*In water, 25°C.

PROBLEM 6.10 The rates of hydration of the two alkenes shown differ by a factor of over 7000 at 25°C. Which isomer is the more reactive? Why?



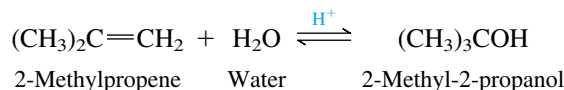
You may have noticed that the acid-catalyzed hydration of an alkene and the acid-catalyzed dehydration of an alcohol are the reverse of each other.



According to **Le Châtelier’s principle**, a system at equilibrium adjusts so as to minimize any stress applied to it. When the concentration of water is increased, the system responds by consuming water. This means that proportionally more alkene is converted to alcohol; the position of equilibrium shifts to the right. Thus, when we wish to prepare an alcohol from an alkene, we employ a reaction medium in which the molar concentration of water is high—dilute sulfuric acid, for example.

On the other hand, alkene formation is favored when the concentration of water is kept low. The system responds to the absence of water by causing more alcohol molecules to suffer dehydration, and when alcohol molecules dehydrate, they form more alkene. The amount of water in the reaction mixture is kept low by using concentrated strong acids as catalysts. Distilling the reaction mixture is an effective way of removing water as it is formed, causing the equilibrium to shift toward products. If the alkene is low-boiling, it too can be removed by distillation. This offers the additional benefit of protecting the alkene from acid-catalyzed isomerization after it is formed.

In any equilibrium process, the sequence of intermediates and transition states encountered as reactants proceed to products in one direction must also be encountered, and in precisely the reverse order, in the opposite direction. This is called the **principle of microscopic reversibility**. Just as the reaction

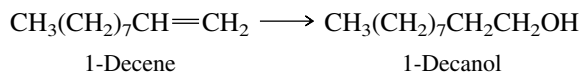


is reversible with respect to reactants and products, so each tiny increment of progress along the reaction coordinate is reversible. Once we know the mechanism for the forward phase of a particular reaction, we also know what the intermediates and transition states must be for the reverse. In particular, the three-step mechanism for the acid-catalyzed hydration of 2-methylpropene in Figure 6.9 is the reverse of that for the acid-catalyzed dehydration of *tert*-butyl alcohol in Figure 5.7.

PROBLEM 6.11 Is the electrophilic addition of hydrogen chloride to 2-methylpropene the reverse of the E1 or the E2 elimination reaction of *tert*-butyl chloride?

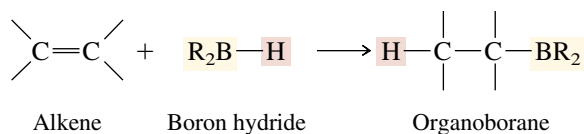
6.11 HYDROBORATION–OXIDATION OF ALKENES

Acid-catalyzed hydration converts alkenes to alcohols with Markovnikov rule regioselectivity. Frequently, however, one needs an alcohol having a structure that corresponds to hydration of an alkene with a regioselectivity apparently opposite to that of Markovnikov’s rule. The conversion of 1-decene to 1-decanol is an example of such a transformation.



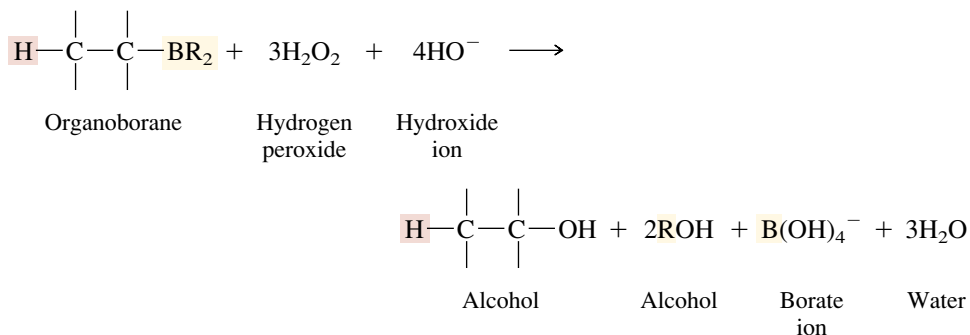
The synthetic method used to accomplish this is an indirect one, and is known as **hydroboration–oxidation**. It was developed by Professor Herbert C. Brown and his coworkers at Purdue University in the 1950s as part of a broad program designed to apply boron-containing reagents to organic chemical synthesis. The number of applications is so large (hydroboration–oxidation is just one of them) and the work so novel that Brown was a corecipient of the 1979 Nobel Prize in chemistry.

Hydroboration is a reaction in which a boron hydride, a compound of the type R_2BH , adds to a carbon–carbon bond. A new carbon–hydrogen bond and a carbon–boron bond result.



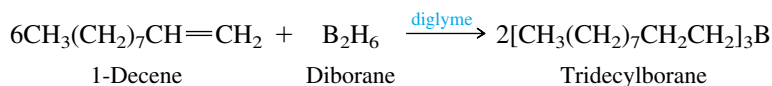
With sodium hydroxide as the base, boron of the alkylborane is converted to the water-soluble and easily removed sodium salt of boric acid.

Following hydroboration, the organoborane is oxidized by treatment with hydrogen peroxide in aqueous base. This is the **oxidation** stage of the sequence; hydrogen peroxide is the oxidizing agent, and the organoborane is converted to an alcohol.



The combination of hydroboration and oxidation leads to the overall hydration of an alkene. Notice, however, that water is not a reactant. The hydrogen that becomes bonded to carbon comes from the organoborane, and the hydroxyl group from hydrogen peroxide.

With this as introduction, let us now look at the individual steps in more detail for the case of hydroboration–oxidation of 1-decene. A boron hydride that is often used is *diborane* (B_2H_6). Diborane adds to 1-decene to give tridecylborane according to the balanced equation:

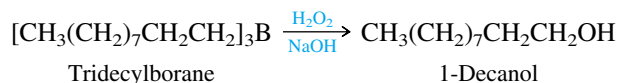


Diglyme, shown above the arrow in the equation is the solvent in this example.

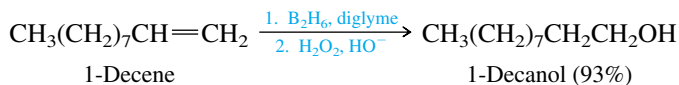
Diglyme is an acronym for *diethylene glycol dimethyl ether*, and its structure is $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$.

There is a pronounced tendency for boron to become bonded to the less substituted carbon of the double bond. Thus, the hydrogen atoms of diborane add to C-2 of 1-decene, and boron to C-1. This is believed to be mainly a steric effect, but the regioselectivity of addition does correspond to Markovnikov's rule in the sense that hydrogen is the negatively polarized atom in a B–H bond and boron the positively polarized one.

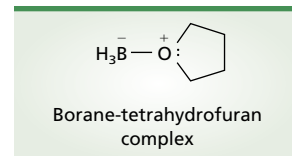
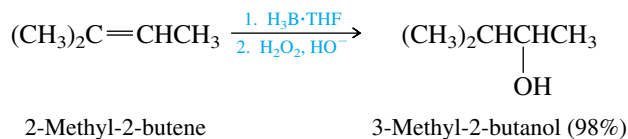
Oxidation of tridecylborane gives 1-decanol. The net result is the conversion of an alkene to an alcohol with a regioselectivity opposite to that of acid-catalyzed hydration.



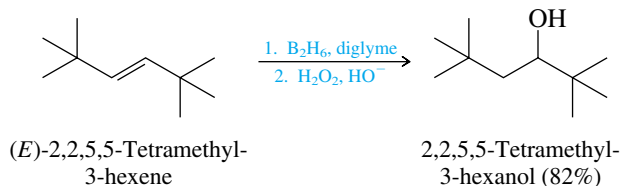
It is customary to combine the two stages, hydroboration and oxidation, in a single equation with the operations numbered sequentially above and below the arrow.



A more convenient hydroborating agent is the borane–tetrahydrofuran complex ($\text{H}_3\text{B}\cdot\text{THF}$). It is very reactive, adding to alkenes within minutes at 0°C , and is used in tetrahydrofuran as the solvent.



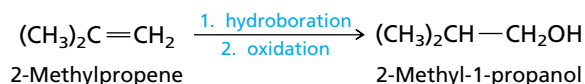
Carbocation intermediates are not involved in hydroboration–oxidation. Hydration of double bonds takes place without rearrangement, even in alkenes as highly branched as the following:



PROBLEM 6.12 Write the structure of the major organic product obtained by hydroboration–oxidation of each of the following alkenes:

- | | |
|---|-----------------------|
| (a) 2-Methylpropene | (d) Cyclopentene |
| (b) <i>cis</i> -2-Butene | (e) 3-Ethyl-2-pentene |
| (c)  | (f) 3-Ethyl-1-pentene |

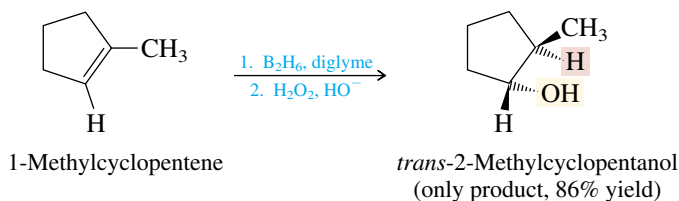
SAMPLE SOLUTION (a) In hydroboration–oxidation the elements of water (H and OH) are introduced with a regioselectivity opposite to that of Markovnikov's rule. In the case of 2-methylpropene, this leads to 2-methyl-1-propanol as the product.



Hydrogen becomes bonded to the carbon that has the fewer hydrogens, hydroxyl to the carbon that has the greater number of hydrogens.

6.12 STEREOCHEMISTRY OF HYDROBORATION–OXIDATION

A second aspect of hydroboration–oxidation concerns its stereochemistry. As illustrated for the case of 1-methylcyclopentene, H and OH add to the same face of the double bond.



Overall, the reaction leads to syn addition of the elements of water to the double bond. This fact has an important bearing on the mechanism of the process.

PROBLEM 6.13 Hydroboration–oxidation of α -pinene (page 213), like catalytic hydrogenation, is stereoselective. Addition takes place at the less hindered face of the double bond, and a single alcohol is produced in high yield (89%). Suggest a reasonable structure for this alcohol.

6.13 MECHANISM OF HYDROBORATION–OXIDATION

The regioselectivity and syn stereochemistry of hydroboration–oxidation, coupled with a knowledge of the chemical properties of alkenes and boranes, contribute to our understanding of the reaction mechanism.

We can consider the hydroboration step as though it involved borane (BH_3). It simplifies our mechanistic analysis and is at variance with reality only in matters of detail. Borane is electrophilic; it has a vacant $2p$ orbital and can accept a pair of electrons into that orbital. The source of this electron pair is the π bond of an alkene. It is believed, as shown in Figure 6.10 for the example of the hydroboration of 1-methylcyclopentene, that the first step produces an unstable intermediate called a π complex. In this π complex boron and the two carbon atoms of the double bond are joined by a *three-center two-electron bond*, by which we mean that three atoms share two electrons. Three-center two-electron bonds are frequently encountered in boron chemistry. The π complex is formed by a transfer of electron density from the π orbital of the alkene to the $2p$ orbital of boron. This leaves each carbon of the complex with a small positive charge, while boron is slightly negative. The negative character of boron in this intermediate makes it easy for one of its hydrogen substituents to migrate with a pair of electrons (a hydride shift) from boron to carbon. The transition state for this process is shown in step 2(a) of Figure 6.10; completion of the migration in step 2(b) yields the alkylborane. According to this mechanism, the carbon–boron bond and the carbon–hydrogen bond are formed on the same side of the alkene. The hydroboration step is a syn addition process.

The regioselectivity of addition is consistent with the electron distribution in the complex. Hydrogen is transferred with a pair of electrons to the carbon atom that can best support a positive charge, namely, the one that bears the methyl group.

Steric effects may be an even more important factor in controlling the regioselectivity of addition. Boron, with its attached substituents, is much larger than a hydrogen atom and becomes bonded to the less crowded carbon of the double bond, whereas hydrogen becomes bonded to the more crowded carbon.

The electrophilic character of boron is again evident when we consider the oxidation of organoboranes. In the oxidation phase of the hydroboration–oxidation sequence, as presented in Figure 6.11, the anion of hydrogen peroxide attacks boron. Hydroperoxide ion is formed in an acid–base reaction in step 1 and attacks boron in step 2. The empty $2p$ orbital of boron makes it electrophilic and permits nucleophilic reagents such as HOO^- to add to it.

Borane (BH_3) does not exist as such under normal conditions of temperature and atmospheric pressure. Two molecules of BH_3 combine to give diborane (B_2H_6), which is the more stable form.

Step 1: A molecule of borane (BH_3) attacks the alkene. Electrons flow from the π orbital of the alkene to the $2p$ orbital of boron. A π complex is formed.

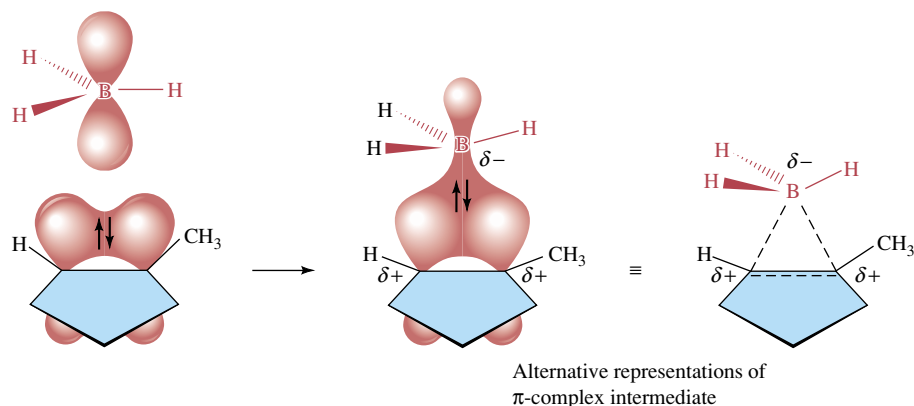
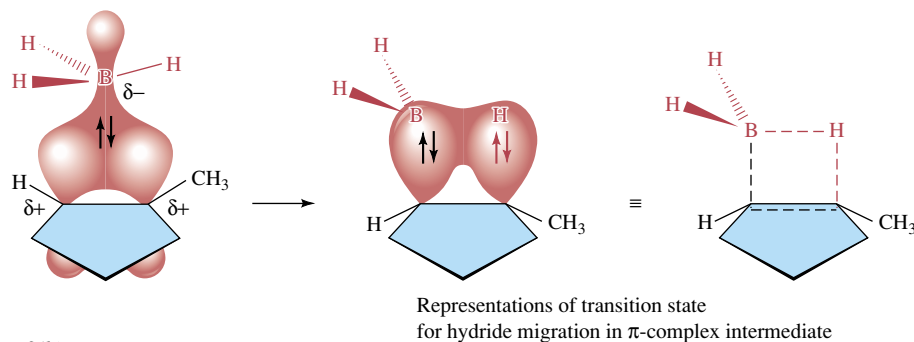


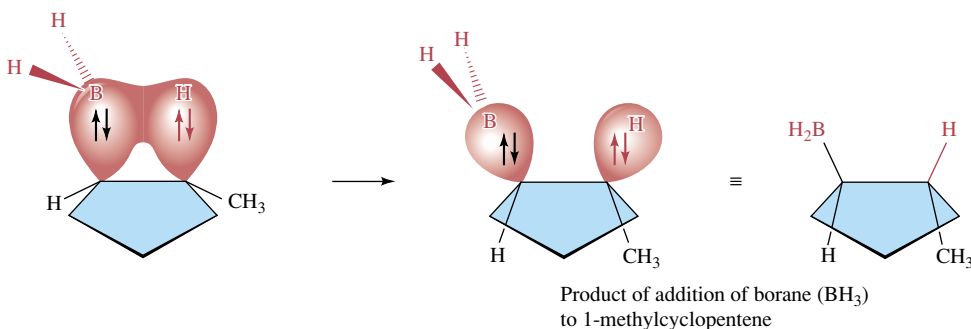
FIGURE 6.10 Orbital interactions and electron redistribution in the hydroboration of 1-methylcyclopentene.

Step 2: The π complex rearranges to an organoborane. Hydrogen migrates from boron to carbon, carrying with it the two electrons in its bond to boron. Development of the transition state for this process is shown in 2(a), and its transformation to the organoborane is shown in 2(b).

2(a)



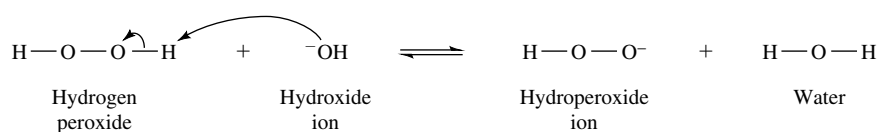
2(b)



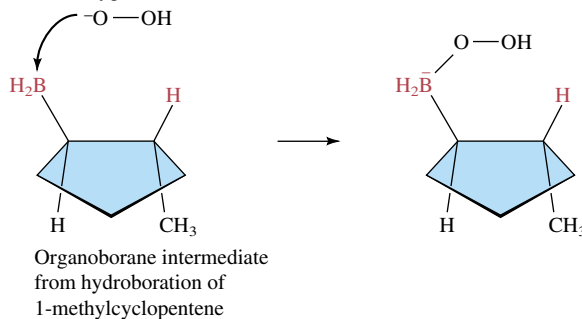
The combination of a negative charge on boron and the weak oxygen–oxygen bond causes an alkyl group to migrate from boron to oxygen in step 3. This alkyl group migration occurs with loss of hydroxide ion and is the step in which the critical carbon–oxygen bond is formed. What is especially significant about this alkyl group migration is that the stereochemical orientation of the new carbon–oxygen bond is the same as that of the original carbon–boron bond. This is crucial to the overall syn stereochemistry of

FIGURE 6.11 The oxidation phase in the hydroboration-oxidation of 1-methylcyclopentene.

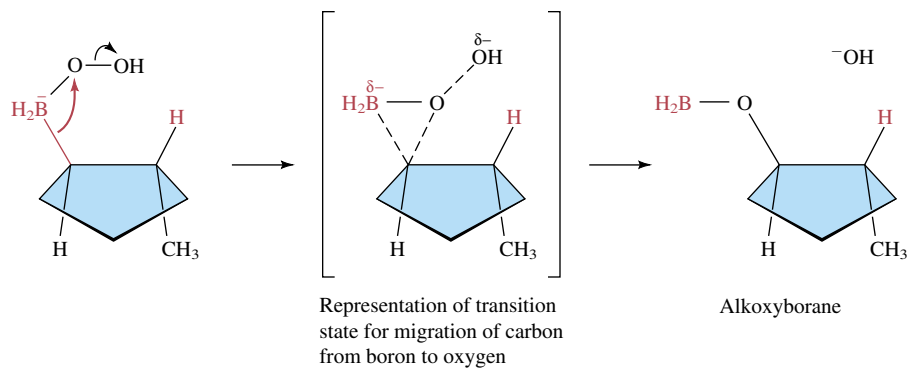
Step 1: Hydrogen peroxide is converted to its anion in basic solution:



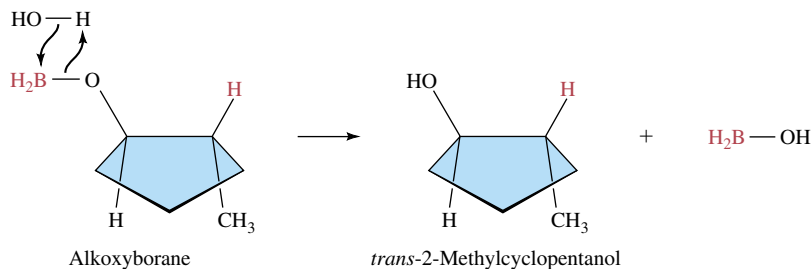
Step 2: Anion of hydrogen peroxide acts as a nucleophile, attacking boron and forming an oxygen-boron bond:



Step 3: Carbon migrates from boron to oxygen, displacing hydroxide ion. Carbon migrates with the pair of electrons in the carbon-boron bond; these become the electrons in the carbon-oxygen bond:



Step 4: Hydrolysis cleaves the boron-oxygen bond, yielding the alcohol:

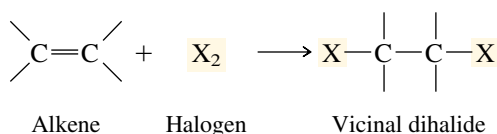


the hydroboration–oxidation sequence. Migration of the alkyl group from boron to oxygen is said to have occurred with *retention of configuration* at carbon. The alkoxyborane intermediate formed in step 3 undergoes subsequent base-promoted oxygen–boron bond cleavage in step 4 to give the alcohol product.

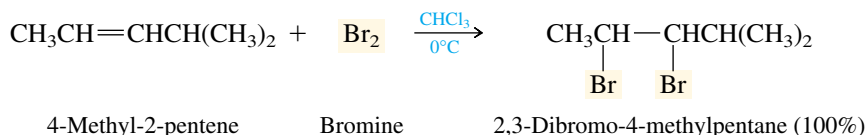
The mechanistic complexity of hydroboration–oxidation stands in contrast to the simplicity with which these reactions are carried out experimentally. Both the hydroboration and oxidation steps are extremely rapid reactions and are performed at room temperature with conventional laboratory equipment. Ease of operation, along with the fact that hydroboration–oxidation leads to syn hydration of alkenes and occurs with a regioselectivity opposite to Markovnikov’s rule, makes this procedure one of great value to the synthetic chemist.

6.14 ADDITION OF HALOGENS TO ALKENES

In contrast to the free-radical substitution observed when halogens react with *alkanes*, halogens normally react with *alkenes* by electrophilic addition.



The products of these reactions are called **vicinal** dihalides. Two substituents, in this case the halogens, are vicinal if they are attached to adjacent carbons. The word is derived from the Latin *vicinalis*, which means “neighboring.” The halogen is either chlorine (Cl₂) or bromine (Br₂), and addition takes place rapidly at room temperature and below in a variety of solvents, including acetic acid, carbon tetrachloride, chloroform, and dichloromethane.

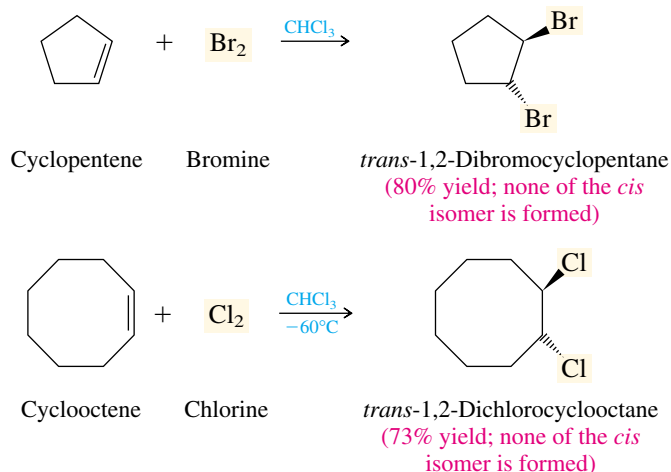


Rearrangements do not normally occur, which can mean either of two things. Either carbocations are not intermediates, or if they are, they are captured by a nucleophile faster than they rearrange. We shall see in Section 6.16 that the first of these is believed to be the case.

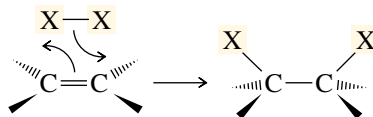
Fluorine addition to alkenes is a violent reaction, difficult to control, and accompanied by substitution of hydrogens by fluorine (Section 4.15). Vicinal diiodides, on the other hand, tend to lose I₂ and revert to alkenes, making them an infrequently encountered class of compounds.

6.15 STEREOCHEMISTRY OF HALOGEN ADDITION

The reaction of chlorine and bromine with cycloalkenes illustrates an important stereochemical feature of halogen addition. Anti addition is observed; the two bromine atoms of Br₂ or the two chlorines of Cl₂ add to opposite faces of the double bond.



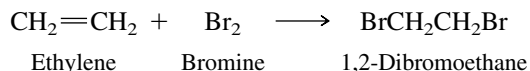
These observations must be taken into account when considering the mechanism of halogen addition. They force the conclusion that a simple one-step “bond-switching” process of the following type cannot be correct. A process of this type requires *syn* addition; it is *not* consistent with the *anti* addition that we actually see.



PROBLEM 6.14 The mass 82 isotope of bromine (^{82}Br) is radioactive and is used as a tracer to identify the origin and destination of individual atoms in chemical reactions and biological transformations. A sample of 1,1,2-tribromocyclohexane was prepared by adding $^{82}\text{Br}-^{82}\text{Br}$ to ordinary (nonradioactive) 1-bromocyclohexene. How many of the bromine atoms in the 1,1,2-tribromocyclohexane produced are radioactive? Which ones are they?

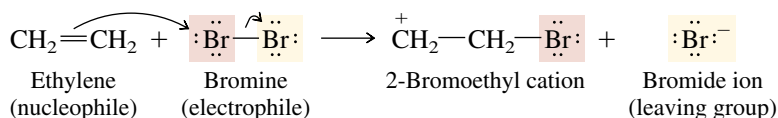
6.16 MECHANISM OF HALOGEN ADDITION TO ALKENES: HALONIUM IONS

Many of the features of the generally accepted mechanism for the addition of halogens to alkenes can be introduced by referring to the reaction of ethylene with bromine:

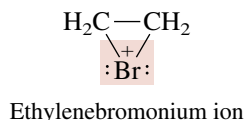


Until it was banned in the United States in 1984, 1,2-dibromoethane (ethylene dibromide, or EDB) was produced on a large scale for use as a pesticide and soil fumigant.

Neither bromine nor ethylene is a polar molecule, but both are *polarizable*, and an induced-dipole/induced-dipole force causes them to be mutually attracted to each other. This induced-dipole/induced-dipole attraction sets the stage for Br_2 to act as an electrophile. Electrons flow from the π system of ethylene to Br_2 , causing the weak bromine–bromine bond to break. By analogy to the customary mechanisms for electrophilic addition, we might represent this as the formation of a carbocation in a bimolecular elementary step.




Such a carbocation, however, has been demonstrated to be less stable than an alternative structure called a **cyclic bromonium ion**, in which the positive charge resides on bromine, not carbon.



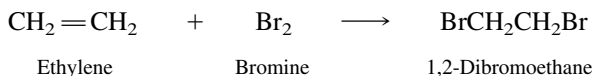
The chief reason why ethylenebromonium ion, in spite of its strained three-membered ring, is more stable than 2-bromoethyl cation is that all its atoms have octets of electrons, whereas carbon has only 6 electrons in the carbocation.

Thus, the mechanism for electrophilic addition of Br_2 to ethylene as presented in Figure 6.12 is characterized by the direct formation of a cyclic bromonium ion as its first elementary step. Step 2 is the conversion of the bromonium ion to 1,2-dibromoethane by reaction with bromide ion (Br^-).

The effect of substituents on the rate of addition of bromine to alkenes (Table 6.3) is substantial and consistent with a rate-determining step in which electrons flow from the alkene to the halogen. Alkyl groups on the carbon-carbon double bond release electrons, stabilize the transition state for bromonium ion formation, and increase the reaction rate.

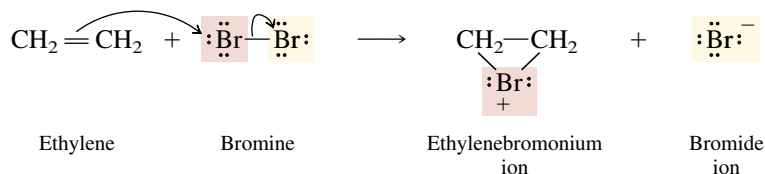
 The graphic on the first page of this chapter is an electrostatic potential map of ethylenebromonium ion.

The overall reaction:



The mechanism:

Step 1: Reaction of ethylene and bromine to form a bromonium ion intermediate:



Step 2: Nucleophilic attack of bromide anion on the bromonium ion:

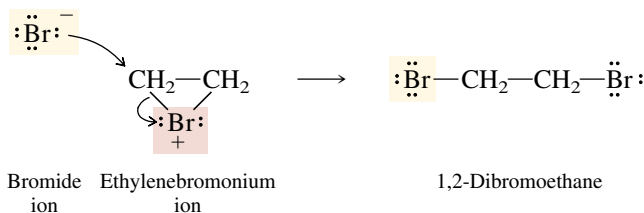


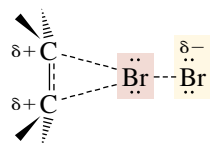
FIGURE 6.12 Mechanism of electrophilic addition of bromine to ethylene.

TABLE 6.3 Relative Rates of Reaction of Some Representative Alkenes with Bromine

Alkene	Structural formula	Relative rate of reaction with bromine*
Ethylene	$\text{CH}_2=\text{CH}_2$	1.0
Propene	$\text{CH}_3\text{CH}=\text{CH}_2$	61
2-Methylpropene	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	5,400
2,3-Dimethyl-2-butene	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	920,000

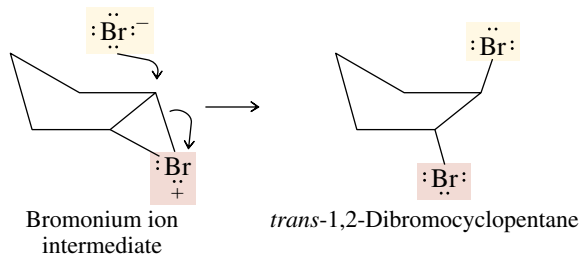
*In methanol, 25°C.

Transition state for bromonium ion formation from an alkene and bromine



PROBLEM 6.15 Arrange the compounds 2-methyl-1-butene, 2-methyl-2-butene, and 3-methyl-1-butene in order of decreasing reactivity toward bromine.

Step 2 of the mechanism in Figure 6.12 is a nucleophilic attack by Br^- at one of the carbons of the cyclic bromonium ion. For reasons that will be explained in Chapter 8, reactions of this type normally take place via a transition state in which the nucleophile approaches carbon from the side opposite the bond that is to be broken. Recalling that the vicinal dibromide formed from cyclopentene is exclusively the *trans* stereoisomer, we see that attack by Br^- from the side opposite the $\text{C}-\text{Br}$ bond of the bromonium ion intermediate can give only *trans*-1,2-dibromocyclopentane in accordance with the experimental observations.

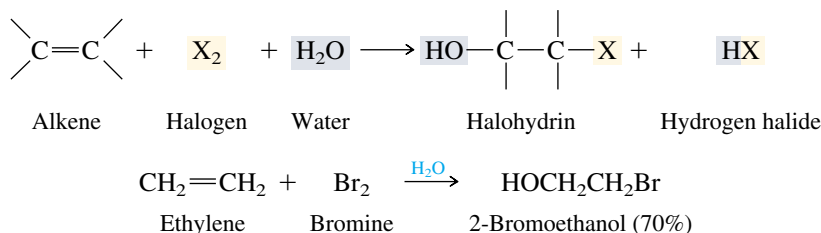


Some supporting evidence is described in the article "The Bromonium Ion," in the August 1963 issue of the *Journal of Chemical Education* (pp. 392–395).

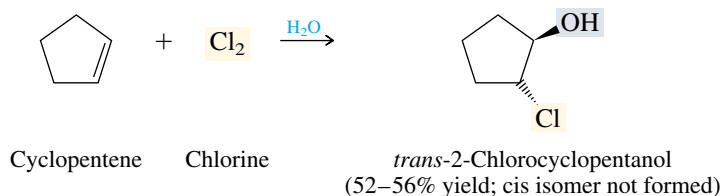
The idea that a cyclic bromonium ion was an intermediate was a novel concept at the time of its proposal in 1937. Much additional evidence, including the isolation of a stable cyclic bromonium ion, has been obtained since then to support it. Similarly, **cyclic chloronium ions** are believed to be involved in the addition of chlorine to alkenes. In the next section we shall see how cyclic chloronium and bromonium ions (**halonium ions**) are intermediates in a second reaction involving alkenes and halogens.

6.17 CONVERSION OF ALKENES TO VICINAL HALOHYDRINS

In *aqueous* solution chlorine and bromine react with alkenes to form **vicinal halohydrins**, compounds that have a halogen and a hydroxyl group on adjacent carbons.

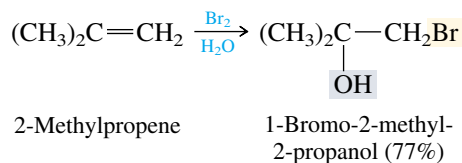


Anti addition occurs. The halogen and the hydroxyl group add to opposite faces of the double bond.



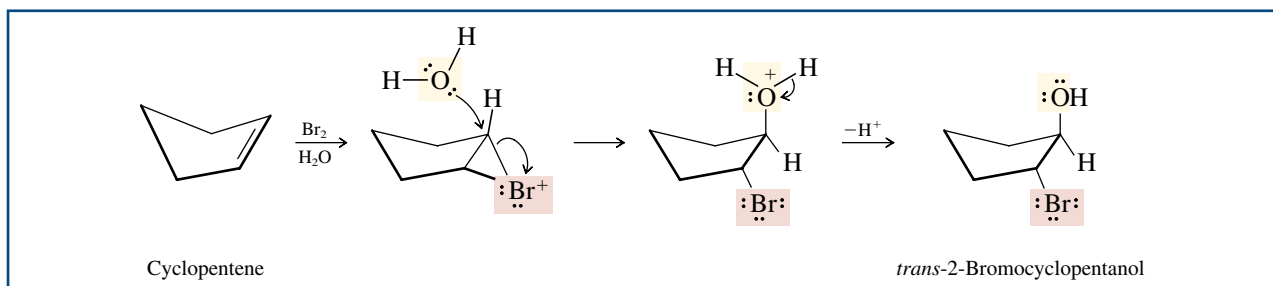
Halohydrin formation, as depicted in Figure 6.13, is mechanistically related to halogen addition to alkenes. A halonium ion intermediate is formed, which is attacked by water in aqueous solution.

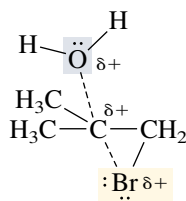
The regioselectivity of addition is established when water attacks one of the carbons of the halonium ion. In the reaction shown, the structure of the product tells us that water attacks the more highly substituted carbon.



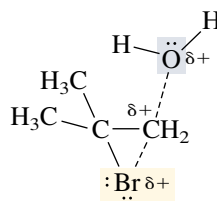
This suggests that, as water attacks the bromonium ion, positive charge develops on the carbon from which the bromine departs. The transition state has some of the character of a carbocation. We know that more highly substituted carbocations are more stable than less highly substituted ones; therefore, when the bromonium ion ring opens, it does so by breaking the bond between bromine and the more substituted carbon.

FIGURE 6.13 Mechanism of bromohydrin formation from cyclopentene. A bridged bromonium ion is formed and is attacked by a water molecule from the side opposite the carbon–bromine bond. The bromine and the hydroxyl group are trans to each other in the product.





More stable transition state;
has some of the character
of a tertiary carbocation

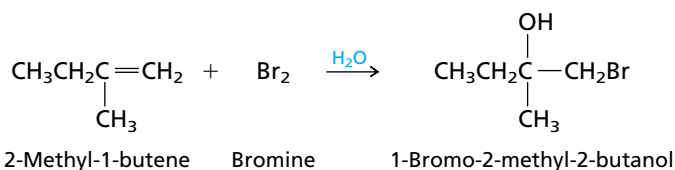


Less stable transition state;
has some of the character
of a primary carbocation

PROBLEM 6.16 Give the structure of the product formed when each of the following alkenes reacts with bromine in water:

- (a) 2-Methyl-1-butene (c) 3-Methyl-1-butene
(b) 2-Methyl-2-butene (d) 1-Methylcyclopentene

SAMPLE SOLUTION (a) The hydroxyl group becomes bonded to the more highly substituted carbon of the double bond, and bromine bonds to the less highly substituted one.



6.18 EPOXIDATION OF ALKENES

You have just seen that cyclic halonium ion intermediates are formed when sources of electrophilic halogen attack a double bond. Likewise, three-membered oxygen-containing rings are formed by the reaction of alkenes with sources of electrophilic oxygen.

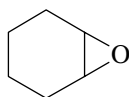
Three-membered rings that contain oxygen are called *epoxides*. At one time, epoxides were named as oxides of alkenes. Ethylene oxide and propylene oxide, for example, are the common names of two industrially important epoxides.



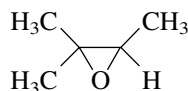
Ethylene oxide Propylene oxide

A second method for naming epoxides in the IUPAC system is described in Section 16.1.

Substitutive IUPAC nomenclature names epoxides as *epoxy* derivatives of alkanes. According to this system, ethylene oxide becomes epoxyethane, and propylene oxide becomes 1,2-epoxypropane. The prefix *epoxy-* always immediately precedes the alkane ending; it is not listed in alphabetical order like other substituents.



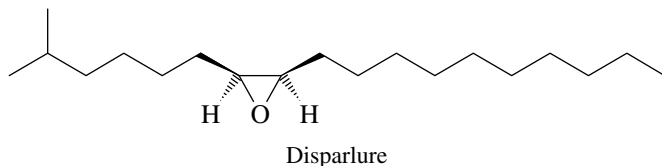
1,2-Epoxycyclohexane



2-Methyl-2,3-epoxybutane

Functional group transformations of epoxides rank among the fundamental reactions of organic chemistry, and epoxides are commonplace natural products. The female

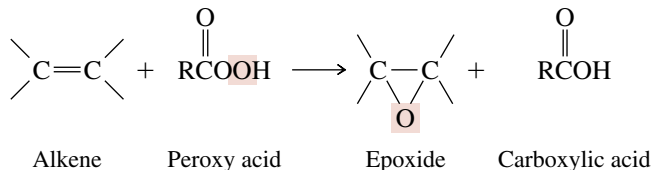
gypsy moth, for example, attracts the male by emitting an epoxide known as *disparlure*. On detecting the presence of this pheromone, the male follows the scent to its origin and mates with the female.



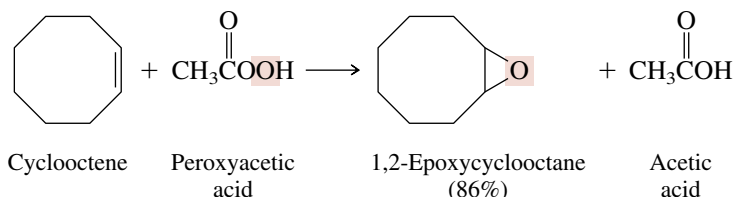
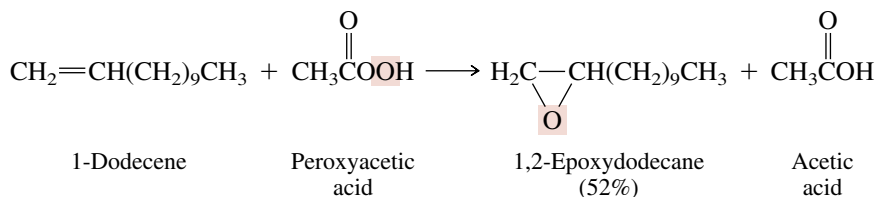
In one strategy designed to control the spread of the gypsy moth, infested areas are sprayed with synthetic disparlure. With the sex attractant everywhere, male gypsy moths become hopelessly confused as to the actual location of individual females. Many otherwise fertile female gypsy moths then live out their lives without producing hungry gypsy moth caterpillars.

PROBLEM 6.17 Give the substitutive IUPAC name, including stereochemistry, for disparlure.

Epoxides are very easy to prepare via the reaction of an alkene with a peroxy acid. This process is known as **epoxidation**.



A commonly used peroxy acid is peroxyacetic acid ($\text{CH}_3\text{CO}_2\text{OH}$). Peroxyacetic acid is normally used in acetic acid as the solvent, but epoxidation reactions tolerate a variety of solvents and are often carried out in dichloromethane or chloroform.



Epoxidation of alkenes with peroxy acids is a syn addition to the double bond. Substituents that are cis to each other in the alkene remain cis in the epoxide; substituents that are trans in the alkene remain trans in the epoxide.

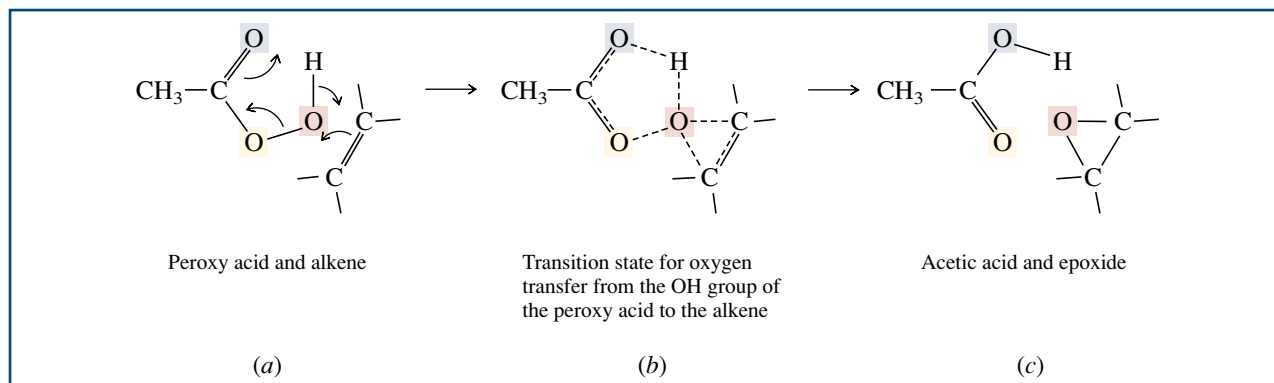


FIGURE 6.14 A one-step mechanism for epoxidation of alkenes by peroxyacetic acid. In (a) the starting peroxy acid is shown in a conformation in which the proton of the OH group is hydrogen bonded to the oxygen of the C=O group. (b) The weak O—O bond of the peroxy acid breaks, and both C—O bonds of the epoxide form in the same transition state leading to products (c).

TABLE 6.4 Relative Rates of Epoxidation of Some Representative Alkenes with Peroxyacetic Acid

Alkene	Structural formula	Relative rate of epoxidation*
Ethylene	$\text{CH}_2=\text{CH}_2$	1.0
Propene	$\text{CH}_3\text{CH}=\text{CH}_2$	22
2-Methylpropene	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	484
2-Methyl-2-butene	$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	6526

*In acetic acid, 26°C.

PROBLEM 6.18 Give the structure of the alkene, including stereochemistry, that you would choose as the starting material in a preparation of synthetic disparlure.

As shown in Table 6.4, electron-releasing alkyl groups on the double bond increase the rate of epoxidation. This suggests that the peroxy acid acts as an electrophilic reagent toward the alkene.

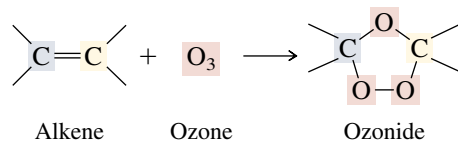
The mechanism of alkene epoxidation is believed to be a concerted process involving a single bimolecular elementary step, as shown in Figure 6.14.

6.19 OZONOLYSIS OF ALKENES

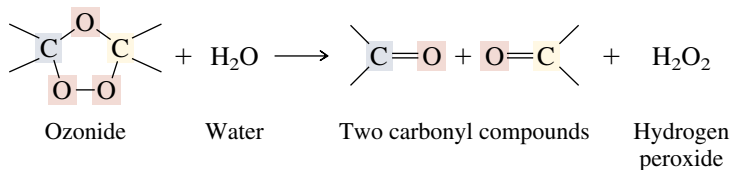
Ozone (O_3) is the triatomic form of oxygen. It is a neutral but polar molecule that can be represented as a hybrid of its two most stable Lewis structures.



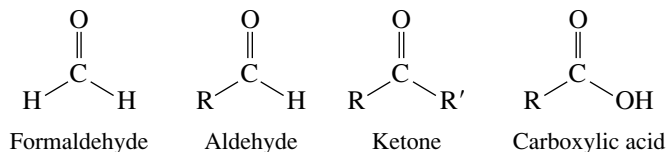
Ozone is a powerful electrophile and undergoes a remarkable reaction with alkenes in which both the σ and π components of the carbon–carbon double bond are cleaved to give a product referred to as an **ozonide**.



Ozonides undergo hydrolysis in water, giving carbonyl compounds.

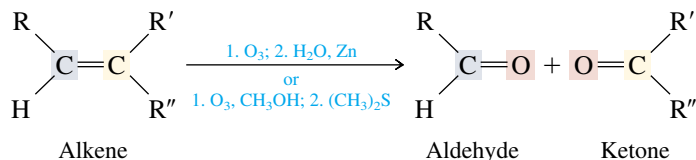


Two aldehydes, two ketones, or one aldehyde and one ketone may be formed. Let's recall the classes of carbonyl compounds from Table 2.2. Aldehydes have at least one hydrogen substituent on the carbonyl group; ketones have two carbon substituents—alkyl groups, for example—on the carbonyl. Carboxylic acids have a hydroxyl substituent attached to the carbonyl group.



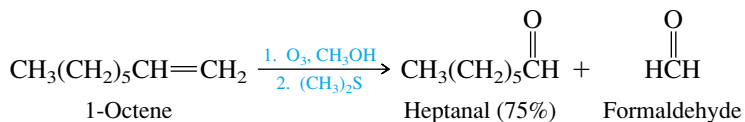
Aldehydes are easily oxidized to carboxylic acids under conditions of ozonide hydrolysis. When one wishes to isolate the aldehyde itself, a reducing agent such as zinc is included during the hydrolysis step. Zinc reacts with the oxidants present (excess ozone and hydrogen peroxide), preventing them from oxidizing any aldehyde formed. An alternative, more modern technique follows ozone treatment of the alkene in methanol with reduction by dimethyl sulfide (CH_3SCH_3).

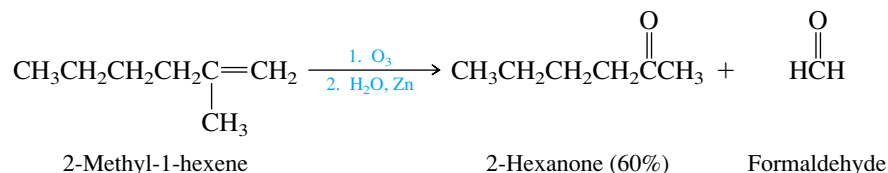
The two-stage reaction sequence is called **ozonolysis** and is represented by the general equation



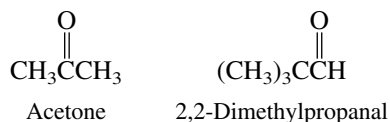
Each carbon of the double bond becomes the carbon of a carbonyl group.

Ozonolysis has both synthetic and analytical applications in organic chemistry. In synthesis, ozonolysis of alkenes provides a method for the preparation of aldehydes and ketones.





When the objective is analytical, the products of ozonolysis are isolated and identified, thereby allowing the structure of the alkene to be deduced. In one such example, an alkene having the molecular formula C_8H_{16} was obtained from a chemical reaction and was then subjected to ozonolysis, giving acetone and 2,2-dimethylpropanal as the products.



Together, these two products contain all eight carbons of the starting alkene. The two carbonyl carbons correspond to those that were doubly bonded in the original alkene. One of the doubly bonded carbons therefore bears two methyl substituents; the other bears a hydrogen and a *tert*-butyl group. The alkene is identified as 2,4,4-trimethyl-2-pentene, $(\text{CH}_3)_2\text{C}=\text{CHC}(\text{CH}_3)_3$, as shown in Figure 6.15.

PROBLEM 6.19

The same reaction that gave 2,4,4-trimethyl-2-pentene also yielded an isomeric alkene. This second alkene produced formaldehyde and 4,4-dimethyl-2-pentanone on ozonolysis. Identify this alkene.

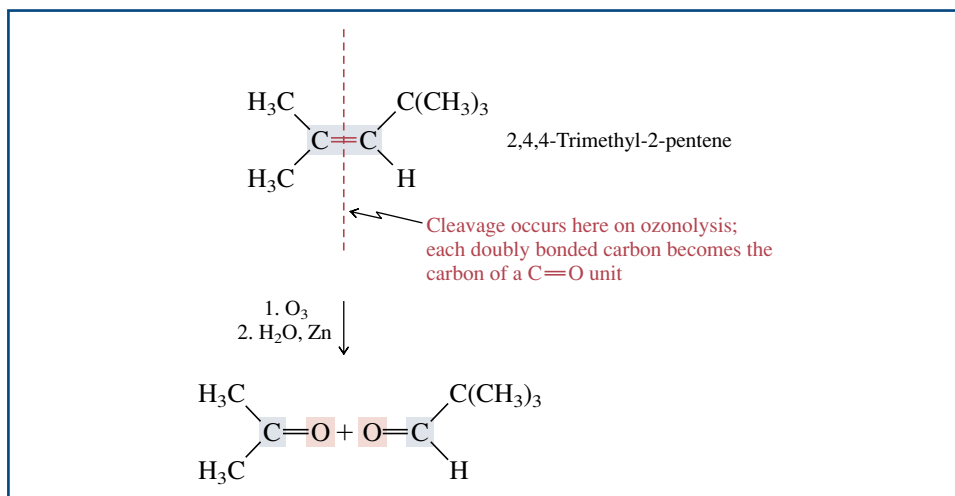
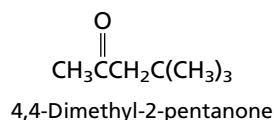


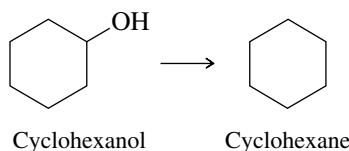
FIGURE 6.15 Ozonolysis of 2,4,4-trimethyl-2-pentene. On cleavage, each of the doubly bonded carbons becomes the carbon of a carbonyl ($\text{C}=\text{O}$) group.

6.20 INTRODUCTION TO ORGANIC CHEMICAL SYNTHESIS

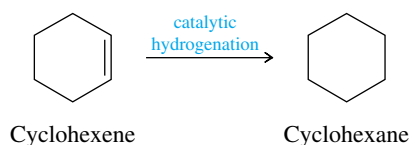
An important concern to chemists is *synthesis*, the challenge of preparing a particular compound in an economical way and with confidence that the method chosen will lead to the desired structure. In this section we will introduce the topic of synthesis, emphasizing the need for systematic planning in order to decide what is the best sequence of steps to convert a specified starting material to a desired product (the **target molecule**).

A critical feature of synthetic planning is *to reason backward from the target to the starting material*. A second is to *always use reactions that you know will work*.

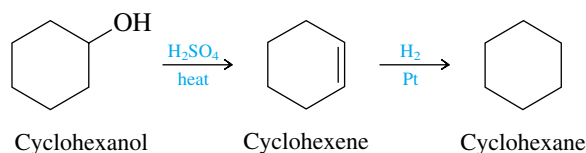
Let's begin with a simple example. Suppose you wanted to prepare cyclohexane, given cyclohexanol as the starting material. We haven't encountered any reactions so far that permit us to carry out this conversion in a single step.



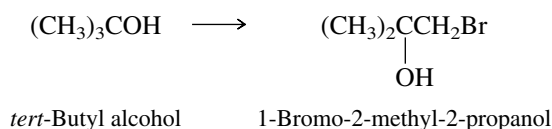
Reasoning backward, however, we know that we can prepare cyclohexane by hydrogenation of cyclohexene. We'll therefore use this reaction as the last step in our proposed synthesis.



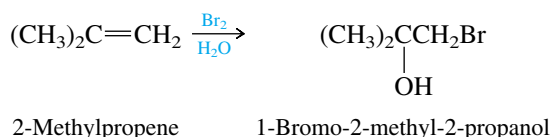
Recognizing that cyclohexene may be prepared by dehydration of cyclohexanol, a practical synthesis of cyclohexane from cyclohexanol becomes apparent.



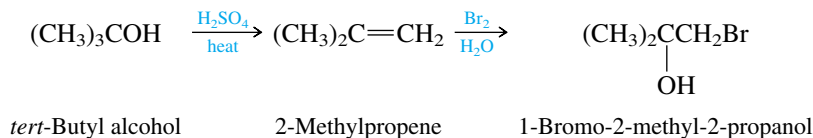
As a second example, consider the preparation of 1-bromo-2-methyl-2-propanol from *tert*-butyl alcohol.



Begin by asking the question, "What kind of compound is the target molecule, and what methods can I use to prepare that kind of compound?" The desired product has a bromine and a hydroxyl on adjacent carbons; it is a *vicinal bromohydrin*. The only method we have learned so far for the preparation of vicinal bromohydrins involves the reaction of alkenes with Br_2 in water. Thus, a reasonable last step is:



We now have a new problem: Where does the necessary alkene come from? Alkenes are prepared from alcohols by acid-catalyzed dehydration (Section 5.9) or from alkyl halides by E2 elimination (Section 5.14). Because our designated starting material is *tert*-butyl alcohol, we can combine its dehydration with bromohydrin formation to give the correct sequence of steps:

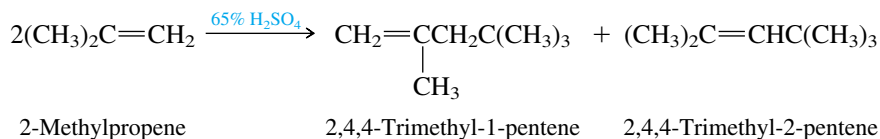


PROBLEM 6.20 Write a series of equations describing a synthesis of 1-bromo-2-methyl-2-propanol from *tert*-butyl bromide.

Often more than one synthetic route may be available to prepare a particular compound. Indeed, it is normal to find in the chemical literature that the same compound has been synthesized in a number of different ways. As we proceed through the text and develop a larger inventory of functional group transformations, our ability to evaluate alternative synthetic plans will increase. In most cases the best synthetic plan is the one with the fewest steps.

6.21 REACTIONS OF ALKENES WITH ALKENES: POLYMERIZATION

Whereas 2-methylpropene undergoes acid-catalyzed hydration in dilute sulfuric acid to form *tert*-butyl alcohol (see Section 6.10 and Figure 6.9), an unusual reaction occurs in more concentrated solutions of sulfuric acid. Rather than form the expected alkyl hydrogen sulfate (see Section 6.9), 2-methylpropene is converted to a mixture of two isomeric C₈H₁₆ alkenes.



The structures of these two C₈H₁₆ alkenes were determined by ozonolysis as described in Section 6.19.

With molecular formulas corresponding to twice that of the starting alkene, the products of this reaction are referred to as **dimers** of 2-methylpropene, which is, in turn, called the **monomer**. The suffix *-mer* is derived from the Greek *meros*, meaning “part.” Three monomeric units produce a **trimer**, four a **tetramer**, and so on. A high-molecular-weight material comprising a large number of monomer subunits is called a **polymer**.

PROBLEM 6.21 The two dimers of 2-methylpropene shown in the equation can be converted to 2,2,4-trimethylpentane (known by its common name *isooctane*) for use as a gasoline additive. Can you suggest a method for this conversion?

The two dimers of (CH₃)₂C=CH₂ are formed by the mechanism shown in Figure 6.16. In step 1 protonation of the double bond generates a small amount of *tert*-butyl cation in equilibrium with the alkene. The carbocation is an electrophile and attacks a second molecule of 2-methylpropene in step 2, forming a new carbon–carbon bond and generating a C₈ carbocation. This new carbocation loses a proton in step 3 to form a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene.

Dimerization in concentrated sulfuric acid occurs mainly with those alkenes that form tertiary carbocations. In some cases reaction conditions can be developed that favor

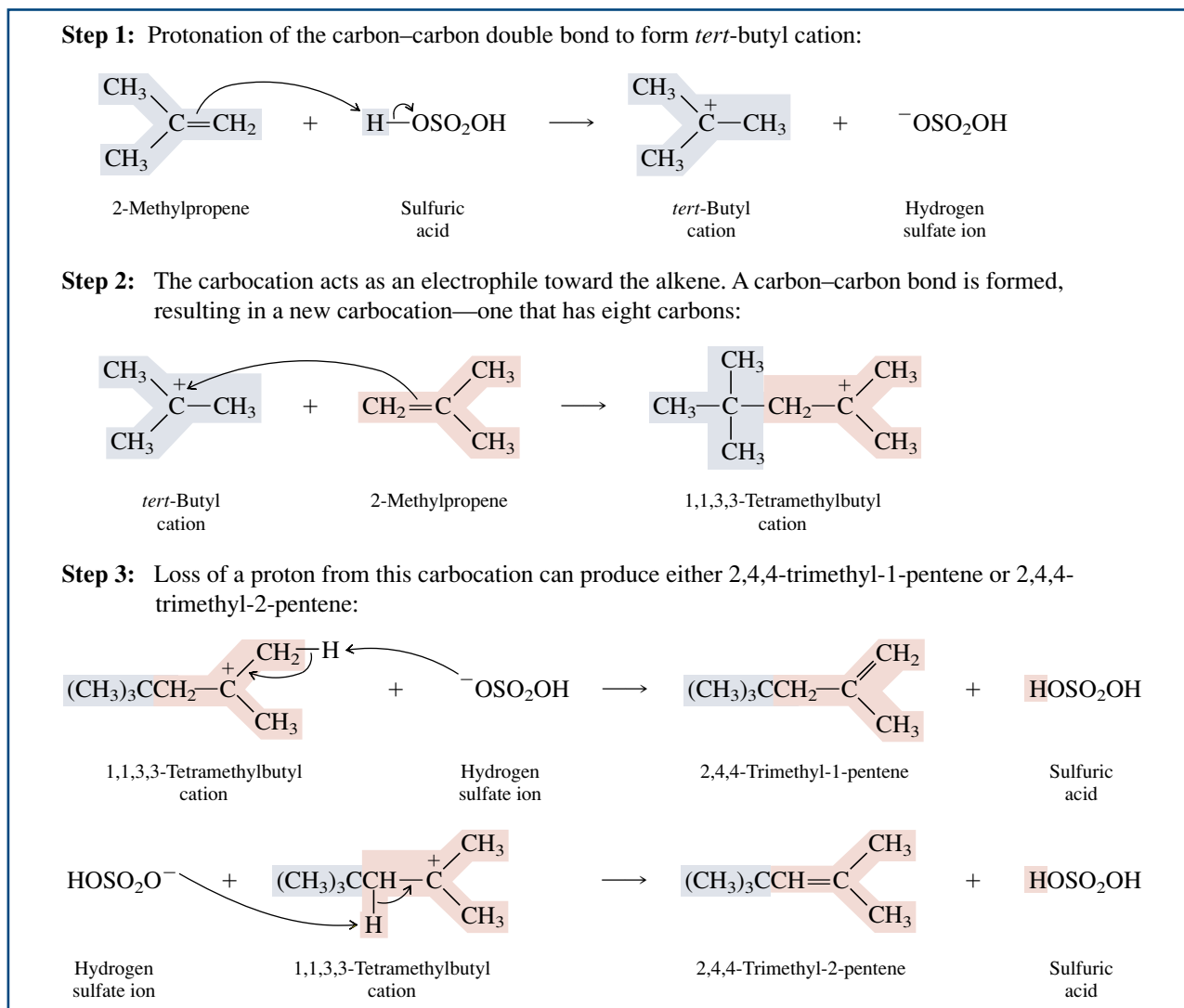
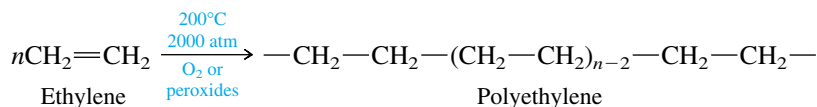


FIGURE 6.16 Mechanism of acid-catalyzed dimerization of 2-methylpropene.

the formation of higher molecular-weight polymers. Because these reactions proceed by way of carbocation intermediates, the process is referred to as **cationic polymerization**.

We made special mention in Section 5.1 of the enormous volume of ethylene and propene production in the petrochemical industry. The accompanying box summarizes the principal uses of these alkenes. Most of the ethylene is converted to **polyethylene**, a high-molecular-weight polymer of ethylene. Polyethylene cannot be prepared by cationic polymerization, but is the simplest example of a polymer that is produced on a large scale by **free-radical polymerization**.

In the free-radical polymerization of ethylene, ethylene is heated at high pressure in the presence of oxygen or a peroxide.

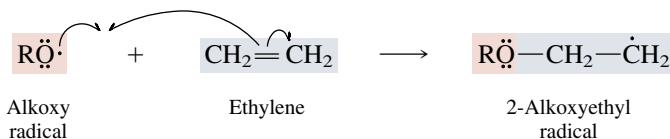


The uses to which ethylene and its relatives are put are summarized in an article entitled "Alkenes and Their Derivatives: The Alchemists' Dream Come True," in the August 1989 issue of the *Journal of Chemical Education* (pp. 670–672).

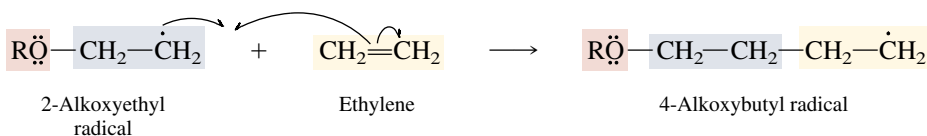
Step 1: Homolytic dissociation of a peroxide produces alkoxy radicals that serve as free-radical initiators:



Step 2: An alkoxy radical adds to the carbon–carbon double bond:



Step 3: The radical produced in step 2 adds to a second molecule of ethylene:



The radical formed in step 3 then adds to a third molecule of ethylene, and the process continues, forming a long chain of methylene groups.

FIGURE 6.17 Mechanism of peroxide-initiated free-radical polymerization of ethylene.

In this reaction n can have a value of thousands.


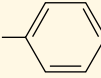
The mechanism of free-radical polymerization of ethylene is outlined in Figure 6.17. Dissociation of a peroxide initiates the process in step 1. The resulting peroxy radical adds to the carbon–carbon double bond in step 2, giving a new radical, which then adds to a second molecule of ethylene in step 3. The carbon–carbon bond-forming process in step 3 can be repeated thousands of times to give long carbon chains.

In spite of the *-ene* ending to its name, polyethylene is much more closely related to *alkanes* than to *alkenes*. It is simply a long chain of CH_2 groups bearing at its ends an alkoxy group (from the initiator) or a carbon–carbon double bond.

A large number of compounds with carbon–carbon double bonds have been polymerized to yield materials having useful properties. Some of the more important or familiar of these are listed in Table 6.5. Not all these monomers are effectively polymerized under free-radical conditions, and much research has been carried out to develop alternative polymerization techniques. One of these, **coordination polymerization**, employs a mixture of titanium tetrachloride, TiCl_4 , and triethylaluminum, $(\text{CH}_3\text{CH}_2)_3\text{Al}$, as a catalyst. Polyethylene produced by coordination polymerization has a higher density than that produced by free-radical polymerization and somewhat different—in many applications, more desirable—properties. The catalyst system used in coordination polymerization was developed independently by Karl Ziegler in Germany and Giulio Natta in Italy in the early 1950s. They shared the Nobel Prize in chemistry in 1963 for this work. The Ziegler–Natta catalyst system gives a form of **polypropylene** suitable for plastics and fibers. When propene is polymerized under free-radical conditions, the polypropylene has physical properties (such as a low melting point) that make it useless for most applications.

Coordination polymerization is described in more detail in Sections 7.15 and 14.15.

TABLE 6.5 Some Compounds with Carbon–Carbon Double Bonds Used to Prepare Polymers**A. Alkenes of the type $\text{CH}_2=\text{CH}-\text{X}$ used to form polymers of the type $(-\text{CH}_2-\underset{\text{X}}{\text{CH}}-)_n$**

Compound	Structure	—X in polymer	Application
Ethylene	$\text{CH}_2=\text{CH}_2$	—H	Polyethylene films as packaging material; “plastic” squeeze bottles are molded from high-density polyethylene.
Propene	$\text{CH}_2=\text{CH}-\text{CH}_3$	— CH_3	Polypropylene fibers for use in carpets and automobile tires; consumer items (luggage, appliances, etc.); packaging material.
Styrene	$\text{CH}_2=\text{CH}-$ 		Polystyrene packaging, housewares, luggage, radio and television cabinets.
Vinyl chloride	$\text{CH}_2=\text{CH}-\text{Cl}$	—Cl	Poly(vinyl chloride) (PVC) has replaced leather in many of its applications; PVC tubes and pipes are often used in place of copper.
Acrylonitrile	$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	— $\text{C}\equiv\text{N}$	Wool substitute in sweaters, blankets, etc.

B. Alkenes of the type $\text{CH}_2=\text{CX}_2$ used to form polymers of the type $(-\text{CH}_2-\text{CX}_2-)_n$

Compound	Structure	X in polymer	Application
1,1-Dichloroethene (vinylidene chloride)	$\text{CH}_2=\text{CCl}_2$	Cl	Saran used as air- and water-tight packaging film.
2-Methylpropene	$\text{CH}_2=\text{C}(\text{CH}_3)_2$	CH_3	Polyisobutene is component of “butyl rubber,” one of earliest synthetic rubber substitutes.

C. Others

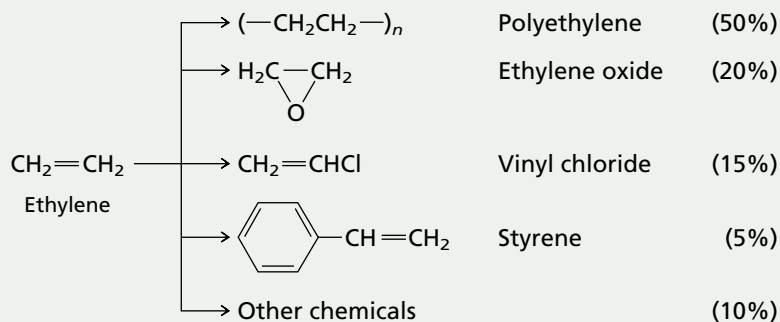
Compound	Structure	Polymer	Application
Tetrafluoroethene	$\text{CF}_2=\text{CF}_2$	$(-\text{CF}_2-\text{CF}_2-)_n$ (Teflon)	Nonstick coating for cooking utensils; bearings, gaskets, and fittings.
Methyl methacrylate	$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}\text{CO}_2\text{CH}_3$	$(-\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{CO}_2\text{CH}_3}{\text{C}}}-)_n$	When cast in sheets, is transparent; used as glass substitute (Lucite, Plexiglas).
2-Methyl-1,3-butadiene	$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}\text{CH}=\text{CH}_2$	$(-\text{CH}_2-\underset{\text{CH}_3}{\text{C}}=\text{CH}-\text{CH}_2-)_n$ (Polyisoprene)	Synthetic rubber.

Source: R. C. Atkins and F. A. Carey, *Organic Chemistry: A Brief Course*, 2nd ed. McGraw-Hill, New York, 1997, p. 251.

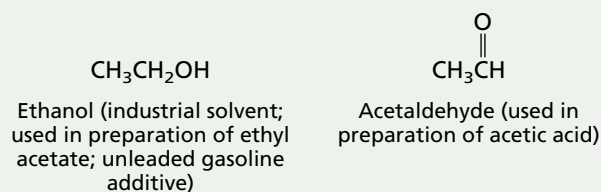
ETHYLENE AND PROPENE: THE MOST IMPORTANT INDUSTRIAL ORGANIC CHEMICALS

Having examined the properties of alkenes and introduced the elements of polymers and polymerization, let's now look at some commercial applications of ethylene and propene.

ETHYLENE We discussed ethylene production in an earlier boxed essay (Section 5.1), where it was pointed out that the output of the U.S. petrochemical industry exceeds 5×10^{10} lb/year. Approximately 90% of this material is used for the preparation of four compounds (polyethylene, ethylene oxide, vinyl chloride, and styrene), with polymerization to polyethylene accounting for half the total. Both vinyl chloride and styrene are polymerized to give poly(vinyl chloride) and polystyrene, respectively (see Table 6.5). Ethylene oxide is a starting material for the preparation of ethylene glycol for use as an antifreeze in automobile radiators and in the production of polyester fibers (see the boxed essay "Condensation Polymers: Polyamides and Polyesters" in Chapter 20).



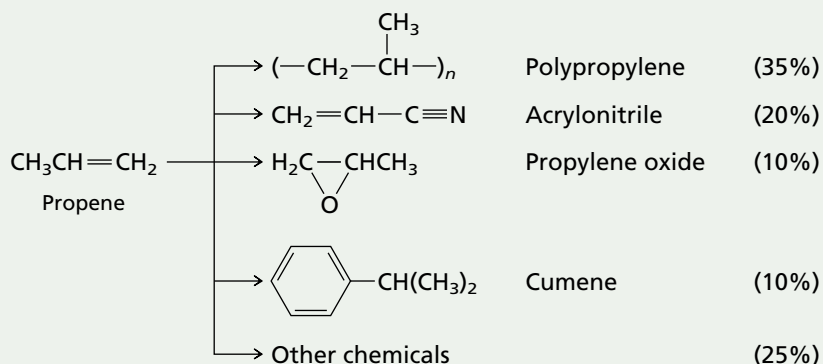
Among the "other chemicals" prepared from ethylene are ethanol and acetaldehyde:



PROPENE The major use of propene is in the production of polypropylene. Two other propene-derived organic chemicals, acrylonitrile and propylene oxide, are also starting materials for polymer synthesis. Acrylonitrile is used to make acrylic fibers (see Table 6.5), and propylene oxide is one component in the preparation of *polyurethane* polymers. Cumene itself has no direct uses but rather serves as the starting material in a process which yields two valuable industrial chemicals, acetone and phenol.

We have not indicated the reagents employed in the reactions by which ethylene and propene are converted to the compounds shown. Because of patent requirements, different companies often use different processes. Although the processes may be different, they share the common characteristic of being extremely efficient. The industrial chemist faces the challenge of producing valuable materials, at low cost. Thus, success in the industrial environment requires both an understanding of chemistry

and an appreciation of the economics associated with alternative procedures. One measure of how successfully these challenges have been met can be seen in the fact that the United States maintains a positive trade balance in chemicals each year. In 1998 that surplus amounted to \$13.4 billion in chemicals versus an overall trade deficit of \$168.6 billion.

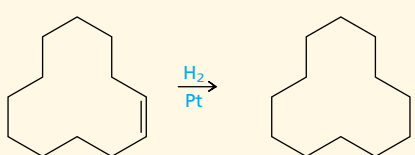
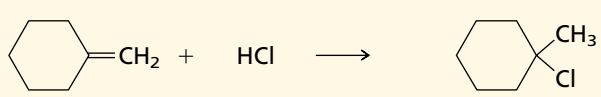


6.22 SUMMARY

Alkenes are **unsaturated hydrocarbons** and react with substances that add to the double bond.

Section 6.1 See Table 6.6.

TABLE 6.6 Addition Reactions of Alkenes

Reaction (section) and comments	General equation and specific example
<p>Catalytic hydrogenation (Sections 6.1–6.3) Alkenes react with hydrogen in the presence of a platinum, palladium, rhodium, or nickel catalyst to form the corresponding alkane.</p>	$\text{R}_2\text{C}=\text{CR}_2 + \text{H}_2 \xrightarrow{\text{Pt, Pd, Rh, or Ni}} \text{R}_2\text{CHCHR}_2$ <p>Alkene Hydrogen Alkane</p>  <p><i>cis</i>-Cyclododecene Cyclododecane (100%)</p>
<p>Addition of hydrogen halides (Sections 6.4–6.7) A proton and a halogen add to the double bond of an alkene to yield an alkyl halide. Addition proceeds in accordance with Markovnikov's rule; hydrogen adds to the carbon that has the greater number of hydrogens, halide to the carbon that has the fewer hydrogens.</p>	$\text{RCH}=\text{CR}'_2 + \text{HX} \longrightarrow \text{RCH}_2-\underset{\text{X}}{\text{CR}'_2}$ <p>Alkene Hydrogen halide Alkyl halide</p>  <p>Methylenecyclohexane Hydrogen chloride 1-Chloro-1-methylcyclohexane (75–80%)</p>
<p>Addition of sulfuric acid (Section 6.9) Alkenes react with sulfuric acid to form alkyl hydrogen sulfates. A proton and a hydrogen sulfate ion add across the double bond in accordance with Markovnikov's rule. Alkenes that yield tertiary carbocations on protonation tend to polymerize in concentrated sulfuric acid (Section 6.21).</p>	$\text{RCH}=\text{CR}'_2 + \text{HOSO}_2\text{OH} \longrightarrow \text{RCH}_2-\underset{\text{OSO}_2\text{OH}}{\text{CR}'_2}$ <p>Alkene Sulfuric acid Alkyl hydrogen sulfate</p> $\text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{HOSO}_2\text{OH} \longrightarrow \text{CH}_3-\underset{\text{OSO}_2\text{OH}}{\text{CH}}\text{CH}_2\text{CH}_3$ <p>1-Butene Sulfuric acid <i>sec</i>-Butyl hydrogen sulfate</p>
<p>Acid-catalyzed hydration (Section 6.10) Addition of water to the double bond of an alkene takes place in aqueous acid. Addition occurs according to Markovnikov's rule. A carbocation is an intermediate and is captured by a molecule of water acting as a nucleophile.</p>	$\text{RCH}=\text{CR}'_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{RCH}_2-\underset{\text{OH}}{\text{CR}'_2}$ <p>Alkene Water Alcohol</p> $\text{CH}_2=\text{C}(\text{CH}_3)_2 \xrightarrow{50\% \text{H}_2\text{SO}_4/\text{H}_2\text{O}} (\text{CH}_3)_3\text{COH}$ <p>2-Methylpropene <i>tert</i>-Butyl alcohol (55–58%)</p>

(Continued)

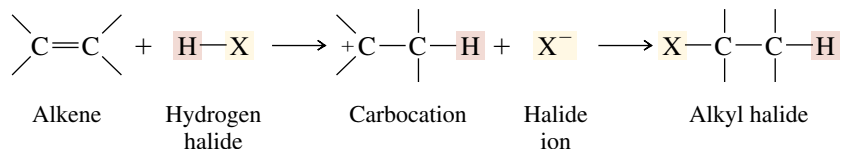
TABLE 6.6 Addition Reactions of Alkenes (Continued)

Reaction (section) and comments	General equation and specific example
Hydroboration–oxidation (Sections 6.11–6.13) This two-step sequence achieves hydration of alkenes in a stereospecific syn manner, with a regioselectivity opposite to Markovnikov's rule. An organoborane is formed by electrophilic addition of diborane to an alkene. Oxidation of the organoborane intermediate with hydrogen peroxide completes the process. Rearrangements do not occur.	$\text{RCH}=\text{CR}'_2 \xrightarrow[2. \text{H}_2\text{O}_2, \text{HO}^-]{1. \text{B}_2\text{H}_6, \text{diglyme}} \begin{array}{c} \text{RCHCHR}'_2 \\ \\ \text{OH} \end{array}$ <p style="text-align: center;">Alkene Alcohol</p> $(\text{CH}_3)_2\text{CHCH}_2\text{CH}=\text{CH}_2 \xrightarrow[2. \text{H}_2\text{O}_2, \text{HO}^-]{1. \text{H}_3\text{B}\cdot\text{THF}} (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{OH}$ <p style="text-align: center;">4-Methyl-1-pentene 4-Methyl-1-pentanol (80%)</p>
Addition of halogens (Sections 6.14–6.16) Bromine and chlorine add to alkenes to form vicinal dihalides. A cyclic halonium ion is an intermediate. Stereospecific anti addition is observed.	$\text{R}_2\text{C}=\text{CR}_2 + \text{X}_2 \longrightarrow \begin{array}{c} \text{R} \quad \text{R} \\ \quad \\ \text{X}-\text{C}-\text{C}-\text{X} \\ \quad \\ \text{R} \quad \text{R} \end{array}$ <p style="text-align: center;">Alkene Halogen Vicinal dihalide</p> $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Br}_2 \longrightarrow \begin{array}{c} \text{BrCH}_2-\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \\ \text{Br} \end{array}$ <p style="text-align: center;">1-Hexene Bromine 1,2-Dibromohexane (100%)</p>
Halohydrin formation (Section 6.17) When treated with bromine or chlorine in aqueous solution, alkenes are converted to vicinal halohydrins. A halonium ion is an intermediate. The halogen adds to the carbon that has the greater number of hydrogens. Addition is anti.	$\text{RCH}=\text{CR}'_2 + \text{X}_2 + \text{H}_2\text{O} \longrightarrow \begin{array}{c} \text{R}' \\ \\ \text{X}-\text{CH}-\text{C}-\text{OH} \\ \quad \\ \text{R} \quad \text{R}' \end{array} + \text{HX}$ <p style="text-align: center;">Alkene Halogen Water Vicinal halohydrin Hydrogen halide</p> $\begin{array}{ccc} \text{Cyclohexane ring}=\text{CH}_2 & \xrightarrow[\text{H}_2\text{O}]{\text{Br}_2} & \begin{array}{c} \text{Cyclohexane ring}-\text{CH}_2\text{Br} \\ \\ \text{OH} \end{array} \end{array}$ <p style="text-align: center;">Methylenecyclohexane (1-Bromomethyl)cyclohexanol (89%)</p>
Epoxidation (Section 6.18) Peroxy acids transfer oxygen to the double bond of alkenes to yield epoxides. The reaction is a stereospecific syn addition.	$\text{R}_2\text{C}=\text{CR}_2 + \text{R}'\text{COOH} \longrightarrow \begin{array}{c} \text{O} \\ // \\ \text{R}_2\text{C}-\text{CR}_2 \\ \backslash / \\ \text{O} \end{array} + \text{R}'\text{COH}$ <p style="text-align: center;">Alkene Peroxy acid Epoxide Carboxylic acid</p> $\begin{array}{ccc} \text{Cycloheptane ring}=\text{CH}_3 & + \text{CH}_3\text{COOH} \longrightarrow & \begin{array}{c} \text{Cycloheptane ring} \\ \backslash \quad / \\ \text{O} \end{array} + \text{CH}_3\text{COH} \end{array}$ <p style="text-align: center;">1-Methylcycloheptene Peroxyacetic acid 1-Methyl-1,2-epoxycycloheptane (65%) Acetic acid</p>

Section 6.2 Hydrogenation of alkenes is exothermic. Heats of hydrogenation can be measured and used to assess the stability of various types of double bonds. The information parallels that obtained from heats of combustion.

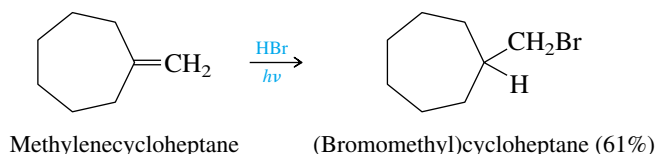
Section 6.3 Hydrogenation of alkenes is a syn addition.

Sections 6.4–6.7 See Table 6.6. Hydrogen halide addition to alkenes proceeds by electrophilic attack of the reagent on the π electrons of the double bond. Carbocations are intermediates.



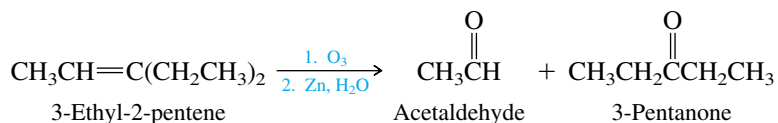
Protonation of the double bond occurs in the direction that gives the more stable of two possible carbocations.

Section 6.8 Hydrogen bromide is unique among the hydrogen halides in that it can add to alkenes either by an ionic mechanism or by a free-radical mechanism. Under photochemical conditions or in the presence of peroxides, free-radical addition is observed, and HBr adds to the double bond with a regioselectivity opposite to that of Markovnikov's rule.



Sections 6.9–6.18 See Table 6.6.

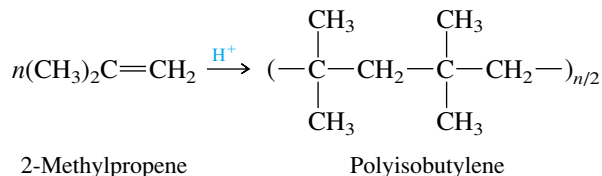
Section 6.19 Alkenes are cleaved to carbonyl compounds by **ozonolysis**. This reaction is useful both for synthesis (preparation of aldehydes, ketones, or carboxylic acids) and analysis. When applied to analysis, the carbonyl compounds are isolated and identified, allowing the substituents attached to the double bond to be deduced.



Section 6.20 The reactions described so far can be carried out sequentially to prepare compounds of prescribed structure from some given starting material. The best way to approach a synthesis is to reason backward from the desired target molecule and to always use reactions that you are sure will work. The 11 exercises that make up Problem 6.32 at the end of this chapter provide some opportunities for practice.

Section 6.21 In their **polymerization**, many individual alkene molecules combine to give a high-molecular-weight product. Among the methods for alkene

polymerization, *cationic polymerization*, *coordination polymerization*, and *free-radical polymerization* are the most important. An example of cationic polymerization is:



PROBLEMS

6.22 Write the structure of the major organic product formed in the reaction of 1-pentene with each of the following:

- Hydrogen chloride
- Hydrogen bromide
- Hydrogen bromide in the presence of peroxides
- Hydrogen iodide
- Dilute sulfuric acid
- Diborane in diglyme, followed by basic hydrogen peroxide
- Bromine in carbon tetrachloride
- Bromine in water
- Peroxyacetic acid
- Ozone
- Product of part (j) treated with zinc and water

6.23 Repeat Problem 6.22 for 2-methyl-2-butene.

6.24 Repeat Problem 6.22 for 1-methylcyclohexene.

6.25 Match the following alkenes with the appropriate heats of hydrogenation:

- 1-Pentene
- (*E*)-4,4-Dimethyl-2-pentene
- (*Z*)-4-Methyl-2-pentene
- (*Z*)-2,2,5,5-Tetramethyl-3-hexene
- 2,4-Dimethyl-2-pentene

Heats of hydrogenation in kJ/mol (kcal/mol): 151(36.2); 122(29.3); 114(27.3); 111(26.5); 105(25.1).

- 6.26**
- How many alkenes yield 2,2,3,4,4-pentamethylpentane on catalytic hydrogenation?
 - How many yield 2,3-dimethylbutane?
 - How many yield methylcyclobutane?

6.27 Two alkenes undergo hydrogenation to yield a mixture of *cis*- and *trans*-1,4-dimethylcyclohexane. A third, however, gives only *cis*-1,4-dimethylcyclohexane. What compound is this?

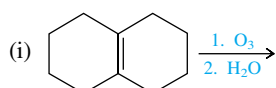
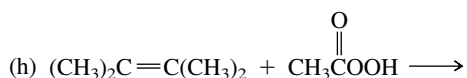
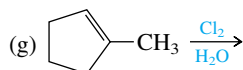
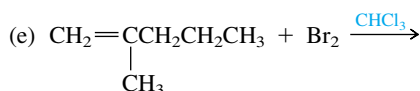
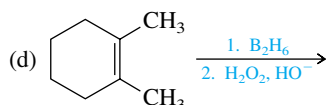
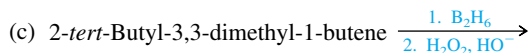
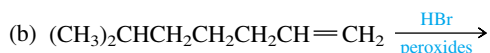
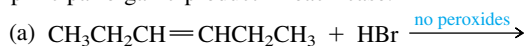
6.28 Specify reagents suitable for converting 3-ethyl-2-pentene to each of the following:

- 2,3-Dibromo-3-ethylpentane
- 3-Chloro-3-ethylpentane
- 2-Bromo-3-ethylpentane
- 3-Ethyl-3-pentanol
- 3-Ethyl-2-pentanol
- 3-Ethyl-2,3-epoxypentane
- 3-Ethylpentane

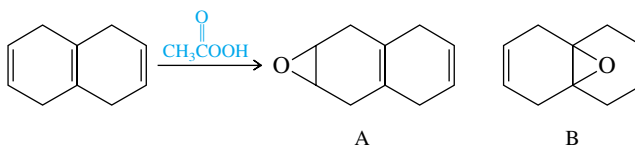
6.29 (a) Which primary alcohol of molecular formula $C_5H_{12}O$ cannot be prepared from an alkene? Why?

- Write equations describing the preparation of three isomeric primary alcohols of molecular formula $C_5H_{12}O$ from alkenes.
- Write equations describing the preparation of the tertiary alcohol of molecular formula $C_5H_{12}O$ from two different alkenes.

6.30 All the following reactions have been reported in the chemical literature. Give the structure of the principal organic product in each case.

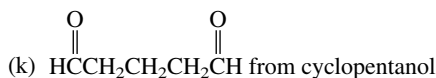


6.31 A single epoxide was isolated in 79–84% yield in the following reaction. Was this epoxide A or B? Explain your reasoning.



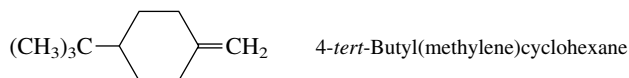
6.32 Suggest a sequence of reactions suitable for preparing each of the following compounds from the indicated starting material. You may use any necessary organic or inorganic reagents.

- 1-Propanol from 2-propanol
- 1-Bromopropane from 2-bromopropane
- 1,2-Dibromopropane from 2-bromopropane
- 1-Bromo-2-propanol from 2-propanol
- 1,2-Epoxypropane from 2-propanol
- tert*-Butyl alcohol from isobutyl alcohol
- tert*-Butyl iodide from isobutyl iodide
- trans*-2-Chlorocyclohexanol from cyclohexyl chloride
- Cyclopentyl iodide from cyclopentane
- trans*-1,2-Dichlorocyclopentane from cyclopentane



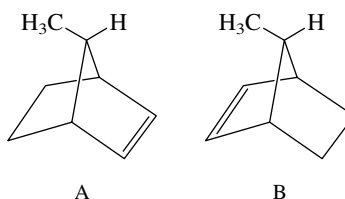
6.33 Two different compounds having the molecular formula $\text{C}_8\text{H}_{15}\text{Br}$ are formed when 1,6-dimethylcyclohexene reacts with hydrogen bromide in the dark and in the absence of peroxides. The same two compounds are formed from 1,2-dimethylcyclohexene. What are these two compounds?

6.34 On catalytic hydrogenation over a rhodium catalyst, the compound shown gave a mixture containing *cis*-1-*tert*-butyl-4-methylcyclohexane (88%) and *trans*-1-*tert*-butyl-4-methylcyclohexane (12%).



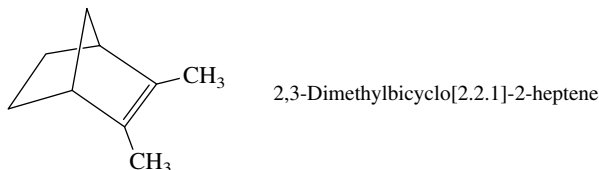
- What two products are formed in the epoxidation of 4-*tert*-butyl(methylene)cyclohexane? Which one do you think will predominate?
- What two products are formed in the hydroboration–oxidation of 4-*tert*-butyl(methylene)cyclohexane? Which one do you think will predominate?

6.35 Compound A undergoes catalytic hydrogenation much faster than does compound B. Why? Making molecular models will help.

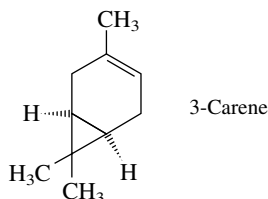


6.36 Catalytic hydrogenation of 1,4-dimethylcyclopentene yields a mixture of two products. Identify them. One of them is formed in much greater amounts than the other (observed ratio = 10:1). Which one is the major product?

6.37 There are two products that can be formed by syn addition of hydrogen to 2,3-dimethylbicyclo[2.2.1]-2-heptene. Write or make molecular models of their structures.

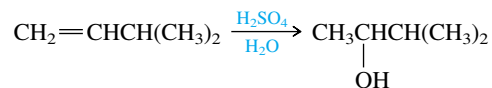


6.38 Hydrogenation of 3-carene is, in principle, capable of yielding two stereoisomeric products. Write their structures. Only one of them was actually obtained on catalytic hydrogenation over platinum. Which one do you think is formed? Explain your reasoning with the aid of a drawing or a molecular model.



6.39 In a widely used industrial process, the mixture of ethylene and propene that is obtained by dehydrogenation of natural gas is passed into concentrated sulfuric acid. Water is added, and the solution is heated to hydrolyze the alkyl hydrogen sulfate. The product is almost exclusively a single alcohol. Is this alcohol ethanol, 1-propanol, or 2-propanol? Why is this particular one formed almost exclusively?

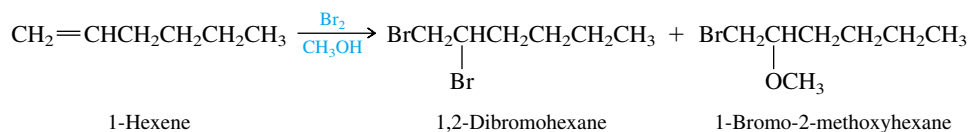
6.40 On the basis of the mechanism of acid-catalyzed hydration, can you suggest a reason why the reaction



would probably *not* be a good method for the synthesis of 3-methyl-2-butanol?

6.41 As a method for the preparation of alkenes, a weakness in the acid-catalyzed dehydration of alcohols is that the initially formed alkene (or mixture of alkenes) sometimes isomerizes under the conditions of its formation. Write a stepwise mechanism showing how 2-methyl-1-butene might isomerize to 2-methyl-2-butene in the presence of sulfuric acid.

6.42 When bromine is added to a solution of 1-hexene in methanol, the major products of the reaction are as shown:



1,2-Dibromohexane is not converted to 1-bromo-2-methoxyhexane under the reaction conditions. Suggest a reasonable mechanism for the formation of 1-bromo-2-methoxyhexane.

6.43 The reaction of thiocyanogen ($\text{N}\equiv\text{CS}-\text{SC}\equiv\text{N}$) with *cis*-cyclooctene proceeds by anti addition.



A bridged *sulfonium ion* is presumed to be an intermediate. Write a stepwise mechanism for this reaction.

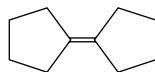
6.44 On the basis of the mechanism of cationic polymerization, predict the alkenes of molecular formula $\text{C}_{12}\text{H}_{24}$ that can most reasonably be formed when 2-methylpropene [$(\text{CH}_3)_2\text{C}=\text{CH}_2$] is treated with sulfuric acid.

6.45 On being heated with a solution of sodium ethoxide in ethanol, compound A ($\text{C}_7\text{H}_{15}\text{Br}$) yielded a mixture of two alkenes B and C, each having the molecular formula C_7H_{14} . Catalytic hydrogenation of the major isomer B or the minor isomer C gave only 3-ethylpentane. Suggest structures for compounds A, B, and C consistent with these observations.

6.46 Compound A ($\text{C}_7\text{H}_{15}\text{Br}$) is not a primary alkyl bromide. It yields a single alkene (compound B) on being heated with sodium ethoxide in ethanol. Hydrogenation of compound B yields 2,4-dimethylpentane. Identify compounds A and B.

6.47 Compounds A and B are isomers of molecular formula $\text{C}_9\text{H}_{19}\text{Br}$. Both yield the same alkene C as the exclusive product of elimination on being treated with potassium *tert*-butoxide in dimethyl sulfoxide. Hydrogenation of alkene C gives 2,3,3,4-tetramethylpentane. What are the structures of compounds A and B and alkene C?

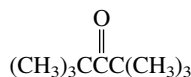
6.48 Alcohol A ($\text{C}_{10}\text{H}_{18}\text{O}$) is converted to a mixture of alkenes B and C on being heated with potassium hydrogen sulfate (KHSO_4). Catalytic hydrogenation of B and C yields the same product. Assuming that dehydration of alcohol A proceeds without rearrangement, deduce the structures of alcohol A and alkene C.



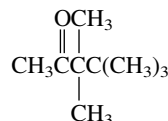
Compound B

6.49 Reaction of 3,3-dimethyl-1-butene with hydrogen iodide yields two compounds A and B, each having the molecular formula $\text{C}_6\text{H}_{13}\text{I}$, in the ratio A:B = 90:10. Compound A, on being heated with potassium hydroxide in *n*-propyl alcohol, gives only 3,3-dimethyl-1-butene. Compound B undergoes elimination under these conditions to give 2,3-dimethyl-2-butene as the major product. Suggest structures for compounds A and B, and write a reasonable mechanism for the formation of each.

6.50 Dehydration of 2,2,3,4,4-pentamethyl-3-pentanol gave two alkenes A and B. Ozonolysis of the lower boiling alkene A gave formaldehyde ($\text{CH}_2=\text{O}$) and 2,2,4,4-tetramethyl-3-pentanone. Ozonolysis of B gave formaldehyde and 3,3,4,4-tetramethyl-2-pentanone. Identify A and B, and suggest an explanation for the formation of B in the dehydration reaction.

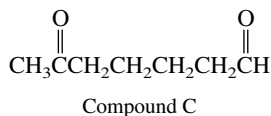


2,2,4,4-Tetramethyl-3-pentanone

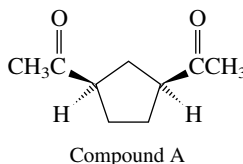


3,3,4,4-Tetramethyl-2-pentanone

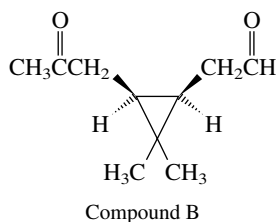
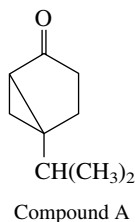
6.51 Compound A ($C_7H_{13}Br$) is a tertiary bromide. On treatment with sodium ethoxide in ethanol, A is converted into B (C_7H_{12}). Ozonolysis of B gives C as the only product. Deduce the structures of A and B. What is the symbol for the reaction mechanism by which A is converted to B under the reaction conditions?



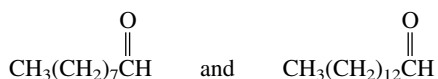
6.52 East Indian sandalwood oil contains a hydrocarbon given the name *santene* (C_9H_{14}). Ozonation of santene followed by hydrolysis gives compound A. What is the structure of santene?



6.53 *Sabinene* and Δ^3 -*carene* are isomeric natural products with the molecular formula $C_{10}H_{16}$. (a) Ozonolysis of sabinene followed by hydrolysis in the presence of zinc gives compound A. What is the structure of sabinene? What other compound is formed on ozonolysis? (b) Ozonolysis of Δ^3 -*carene* followed by hydrolysis in the presence of zinc gives compound B. What is the structure of Δ^3 -*carene*?



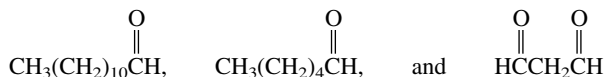
6.54 The sex attractant by which the female housefly attracts the male has the molecular formula $C_{23}H_{46}$. Catalytic hydrogenation yields an alkane of molecular formula $C_{23}H_{48}$. Ozonolysis yields



What is the structure of the housefly sex attractant?

6.55 A certain compound of molecular formula $C_{19}H_{38}$ was isolated from fish oil and from plankton. On hydrogenation it gave 2,6,10,14-tetramethylpentadecane. Ozonolysis gave $(\text{CH}_3)_2\text{C}=\text{O}$ and a 16-carbon aldehyde. What is the structure of the natural product? What is the structure of the aldehyde?

6.56 The sex attractant of the female arctiid moth contains, among other components, a compound of molecular formula $C_{21}H_{40}$ that yields



on ozonolysis. What is the constitution of this material?



6.57 Construct a molecular model of the product formed by catalytic hydrogenation of 1,2-dimethylcyclohexene. Assume syn addition occurs.



6.58 Construct a molecular model of the product formed by anti addition of Br_2 to 1,2-dimethylcyclohexene.



6.59 Examine the electrostatic potential map of $\text{H}_3\text{B}\cdot\text{THF}$ (borane–tetrahydrofuran complex) on the *Learning By Modeling* CD that accompanies this text. How does the electrostatic potential of the hydrogens bonded to boron differ from the potential of the hydrogens of the tetrahydrofuran ring?