6

Alkenes: Structure and Reactivity

An **alkene**, sometimes called an *olefin,* is a hydrocarbon that contains a carbon–carbon double bond. Alkenes occur abundantly in nature. Ethylene, for instance, is a plant hormone that induces ripening in fruit, and α-pinene is the major component of turpentine. Life itself would be impossible without such alkenes as β-carotene, a compound that contains 11 double bonds. An orange pigment responsible for the color of carrots, β-carotene is a valuable dietary source of vitamin A and is thought to offer some protection against certain types of cancer.
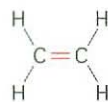
Ethylene
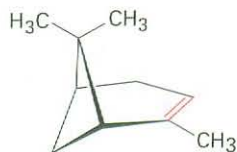
α-Pinene
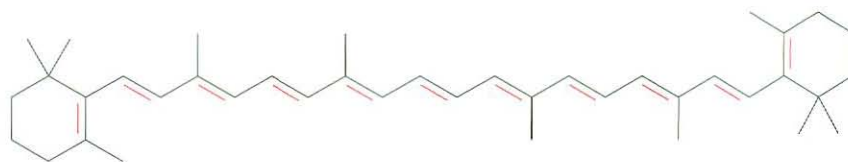
β-Carotene
**(orange pigment and vitamin A precursor)**

WHY THIS CHAPTER?

Carbon–carbon double bonds are present in most organic and biological molecules, so a good understanding of their behavior is needed. In this chapter, we'll look at some consequences of alkene stereoisomerism and then focus on the broadest and most general class of alkene reactions, the electrophilic addition reaction.
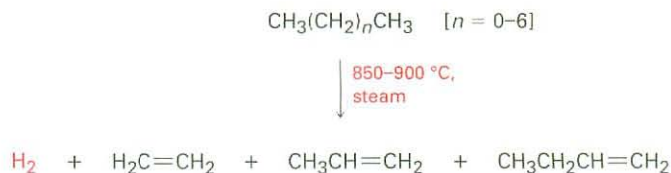
6.1 | Industrial Preparation and Use of Alkenes

Ethylene and propylene, the simplest alkenes, are the two most important organic chemicals produced industrially. Approximately 26 million tons of ethylene and 17 million tons of propylene are produced each year in the United States for use in the synthesis of polyethylene, polypropylene, ethylene glycol, acetic acid, acetaldehyde, and a host of other substances (Figure 6.1).

Figure 6.1 Compounds derived industrially from ethylene and propylene.
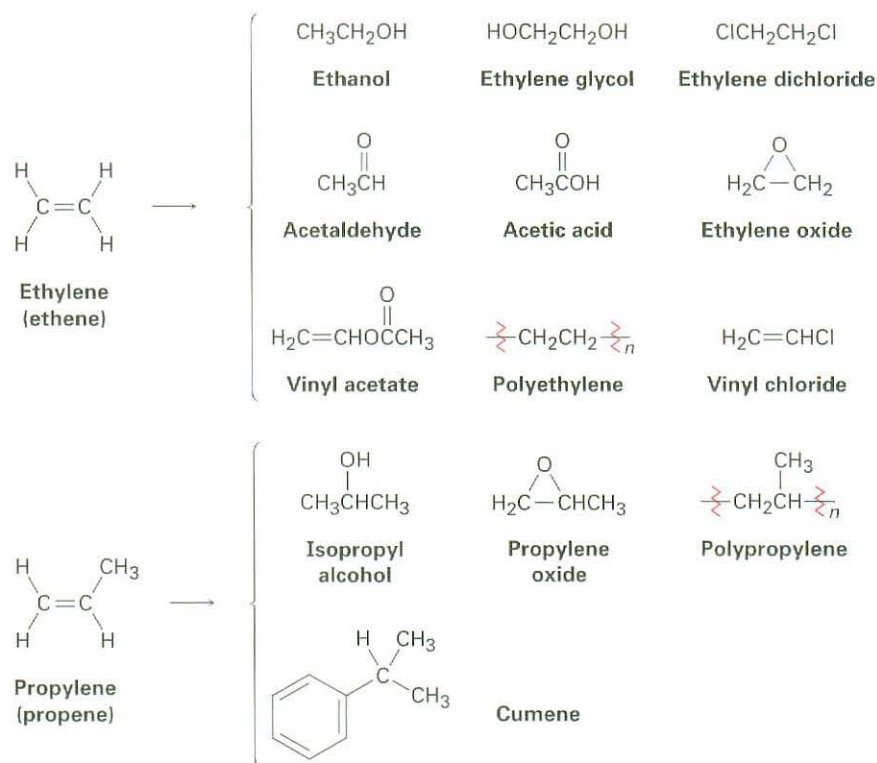

Ethylene, propylene, and butene are synthesized industrially by thermal cracking of light (C_2–C_8) alkanes.

$$CH_3(CH_2)_nCH_3 \quad [n = 0-6]$$

850–900 °C, steam

$$H_2 \ + \ H_2C{=}CH_2 \ + \ CH_3CH{=}CH_2 \ + \ CH_3CH_2CH{=}CH_2$$

Thermal cracking takes place without a catalyst at temperatures up to 900 °C. The exact processes are complex, although they undoubtedly involve radical reactions. The high-temperature reaction conditions cause spontaneous homolytic breaking of C–C and C–H bonds, with resultant formation of smaller fragments. We might imagine, for instance, that a molecule of butane

splits into two ethyl radicals, each of which then loses a hydrogen atom to generate two molecules of ethylene.
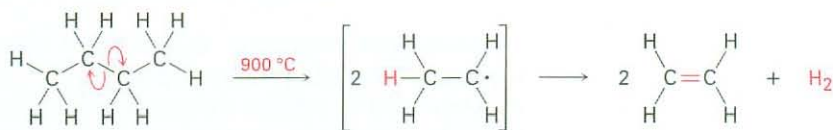
Thermal cracking is an example of a reaction whose energetics are dominated by entropy ($\Delta S°$) rather than by enthalpy ($\Delta H°$) in the free-energy equation $\Delta G° = \Delta H° - T\Delta S°$. Although the bond dissociation energy D for a carbon–carbon single bond is relatively high (about 375 kJ/mol) and cracking is highly endothermic, the large positive entropy change resulting from the fragmentation of one large molecule into several smaller pieces, together with the extremely high temperature, makes the $T\Delta S°$ term larger than the $\Delta H°$ term, thereby favoring the cracking reaction.

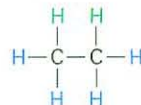## 6.2 | Calculating Degree of Unsaturation

Because of its double bond, an alkene has fewer hydrogens than an alkane with the same number of carbons—C_nH_{2n} for an alkene versus C_nH_{2n+2} for an alkane—and is therefore referred to as **unsaturated**. Ethylene, for example, has the formula C_2H_4, whereas ethane has the formula C_2H_6.


Ethylene: C_2H_4
(fewer hydrogens—*unsaturated*)

Ethane: C_2H_6
(more hydrogens—*saturated*)

In general, each ring or double bond in a molecule corresponds to a loss of two hydrogens from the alkane formula C_nH_{2n+2}. Knowing this relationship, it's possible to work backward from a molecular formula to calculate a molecule's **degree of unsaturation**—the number of rings and/or multiple bonds present in the molecule.

Let's assume that we want to find the structure of an unknown hydrocarbon. A molecular weight determination on the unknown yields a value of 82, which corresponds to a molecular formula of C_6H_{10}. Since the saturated C_6 alkane (hexane) has the formula C_6H_{14}, the unknown compound has two fewer pairs of hydrogens ($H_{14} - H_{10} = H_4 = 2 H_2$), and its degree of unsaturation is two. The unknown therefore contains two double bonds, one ring and one double bond, two rings, or one triple bond. There's still a long way to go to establish structure, but the simple calculation has told us a lot about the molecule.
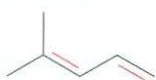
4-Methyl-1,3-pentadiene
(two double bonds)

Cyclohexene
(one ring, one double bond)
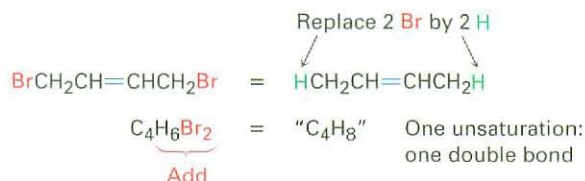
Bicyclo[3.1.0]hexane
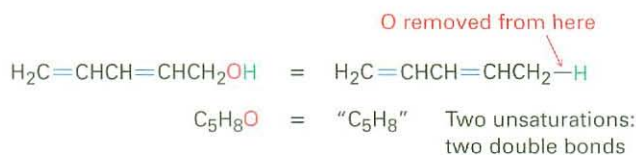(two rings)

4-Methyl-2-pentyne
(one triple bond)

C_6H_{10}

Similar calculations can be carried out for compounds containing elements other than just carbon and hydrogen.

▌ **Organohalogen compounds (C, H, X, where X = F, Cl, Br, or I)**   A halogen substituent acts simply as a replacement for hydrogen in an organic molecule, so we can add the number of halogens and hydrogens to arrive at an equivalent hydrocarbon formula from which the degree of unsaturation can be found. For example, the organohalogen formula $C_4H_6Br_2$ is equivalent to the hydrocarbon formula C_4H_8 and thus has one degree of unsaturation.

Replace 2 Br by 2 H

$$BrCH_2CH{=}CHCH_2Br \quad = \quad HCH_2CH{=}CHCH_2H$$

$$C_4H_6Br_2 \quad = \quad \text{``}C_4H_8\text{''} \qquad \text{One unsaturation:}$$
$$\text{one double bond}$$

Add

▌ **Organooxygen compounds (C, H, O)**   Oxygen forms two bonds, so it doesn't affect the formula of an equivalent hydrocarbon and can be ignored when calculating the degree of unsaturation. You can convince yourself of this by seeing what happens when an oxygen atom is inserted into an alkane bond: $C-C$ becomes $C-O-C$ or $C-H$ becomes $C-O-H$, and there is no change in the number of hydrogen atoms. For example, the formula C_5H_8O is equivalent to the hydrocarbon formula C_5H_8 and thus has two degrees of unsaturation.

O removed from here

$$H_2C{=}CHCH{=}CHCH_2OH \quad = \quad H_2C{=}CHCH{=}CHCH_2{-}H$$

$$C_5H_8O \quad = \quad \text{``}C_5H_8\text{''} \qquad \text{Two unsaturations:}$$
$$\text{two double bonds}$$

▌ **Organonitrogen compounds (C, H, N)**   Nitrogen forms three bonds, so an organonitrogen compound has one more hydrogen than a related hydrocarbon; we therefore *subtract* the number of nitrogens from the number of hydrogens to arrive at the equivalent hydrocarbon formula. Again, you can convince yourself of this by seeing what happens when a nitrogen atom is inserted into an alkane bond: $C-C$ becomes $C-NH-C$ or $C-H$ becomes $C-NH_2$, meaning that one additional hydrogen atom has been added. We must therefore subtract this extra hydrogen atom to arrive at the equivalent hydrocarbon formula. For example, the formula C_5H_9N is equivalent to C_5H_8 and thus has two degrees of unsaturation.

$$C_5H_9N \quad = \quad \text{``}C_5H_8\text{''} \qquad \text{Two unsaturations: one ring}$$
$$\text{and one double bond}$$
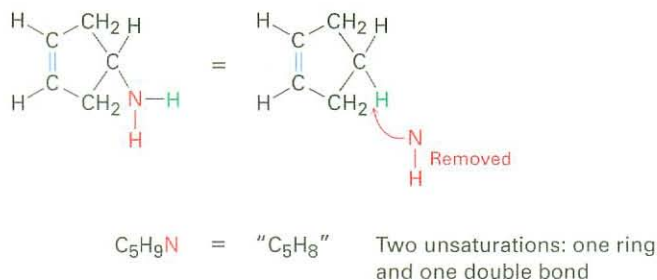
To summarize:

▌ **Add** the number of halogens to the number of hydrogens.

▌ **Ignore** the number of oxygens.

▌ **Subtract** the number of nitrogens from the number of hydrogens.

Problem 6.1 | Calculate the degree of unsaturation in the following formulas, and then draw as many structures as you can for each:
(a) C_4H_8 (b) C_4H_6 (c) C_3H_4

Problem 6.2 | Calculate the degree of unsaturation in the following formulas:
(a) C_6H_5N (b) $C_6H_5NO_2$ (c) $C_8H_9Cl_3$
(d) $C_9H_{16}Br_2$ (e) $C_{10}H_{12}N_2O_3$ (f) $C_{20}H_{32}ClN$

Problem 6.3 | Diazepam, marketed as an antianxiety medication under the name Valium, has three rings, eight double bonds, and the formula $C_{16}H_?ClN_2O$. How many hydrogens does diazepam have? (Calculate the answer; don't count hydrogens in the structure.)
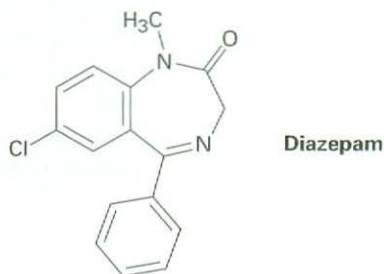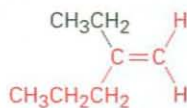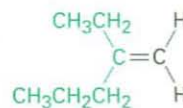

Diazepam

6.3 | Naming Alkenes

Alkenes are named using a series of rules similar to those for alkanes (Section 3.4), with the suffix *-ene* used instead of *-ane* to identify the family. There are three steps.

Step 1 **Name the parent hydrocarbon.** Find the longest carbon chain containing the double bond, and name the compound accordingly, using the suffix *-ene*:
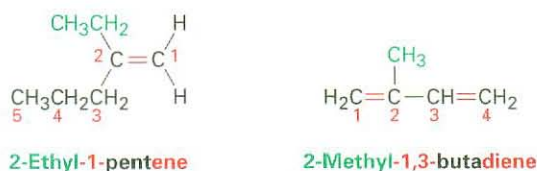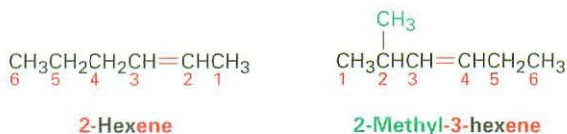

Named as a *pentene*   *NOT*   as a hexene, since the double bond is not contained in the six-carbon chain

Step 2 **Number the carbon atoms in the chain.** Begin at the end nearer the double bond or, if the double bond is equidistant from the two ends, begin at the end nearer the first branch point. This rule ensures that the double-bond carbons receive the lowest possible numbers.

Step 3   **Write the full name.** Number the substituents according to their positions in the chain, and list them alphabetically. Indicate the position of the double bond by giving the number of the first alkene carbon and placing that number directly before the parent name. If more than one double bond is present, indicate the position of each and use one of the suffixes *-diene, -triene,* and so on.

$$CH_3CH_2CH_2CH=CHCH_3$$
$$\quad 6 \quad 5 \quad 4 \quad 3 \quad\; 2 \;\; 1$$

2-Hex*ene*

$$\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$$
$$CH_3CHCH=CHCH_2CH_3$$
$$\;1 \quad 2 \quad 3 \quad\;\; 4 \quad 5 \quad 6$$

2-Methyl-3-hex*ene*

$$\overset{\displaystyle CH_3CH_2}{} \quad \overset{\displaystyle H}{}$$
$$\underset{2}{} C = \underset{}{} C^{\,1}$$
$$CH_3CH_2CH_2 \quad\quad H$$
$$\;5 \quad\; 4 \quad\; 3$$

2-Ethyl-1-pent*ene*

$$\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$$
$$H_2C=C-CH=CH_2$$
$$\;1 \quad 2 \quad\; 3 \quad\;\; 4$$

2-Methyl-1,3-buta*diene*

We should also note that IUPAC changed their naming recommendations in 1993 to place the locant indicating the position of the double bond immediately before the *-ene* suffix rather than before the parent name: but-2-ene rather than 2-butene, for instance. This change has not been widely accepted by the chemical community, however, so we'll stay with the older but more commonly used names. Be aware, though, that you may occasionally encounter the newer system.

$$\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}} \quad\quad \overset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$$
$$CH_3CH_2CHCH=CHCHCH_3$$
$$\;7 \quad\; 6 \quad\; 5 \quad\; 4 \quad\quad 3 \quad 2 \quad 1$$

$$\overset{\displaystyle CH_2CH_2CH_3}{}$$
$$H_2C=CHCHCH=CHCH_3$$
$$\;1 \quad\; 2 \quad 3 \quad 4 \quad\;\; 5 \quad 6$$

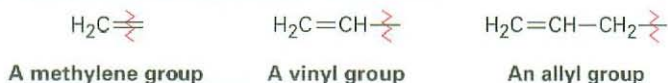|		
Older naming system:	2,5-Dimethyl-3-hept*ene*	3-Propyl-1,4-hexa*diene*
(Newer naming system:	2,5-Dimethylhept-3-ene	3-Propylhexa-1,4-diene)

Cycloalkenes are named similarly to open-chain alkenes but, because there is no chain end to begin from, we number the cycloalkene so that the double bond is between C1 and C2 and the first substituent has as low a number as possible. Note that it's not necessary to indicate the position of the double bond in the name because it is always between C1 and C2. As with open-chain alkenes, newer but not yet widely accepted naming rules place the locant immediately before the suffix in a diene.

1-Methylcyclohex*ene*   **1,4-Cyclohexa*diene***   **1,5-Dimethylcyclopent*ene***
                                  (New: Cyclohexa-1,4-diene)

For historical reasons, there are a few alkenes whose names are firmly entrenched in common usage but don't conform to the rules. For example, the alkene derived from ethane should be called *ethene,* but the name *ethylene* has
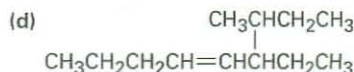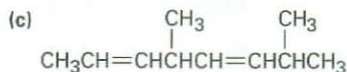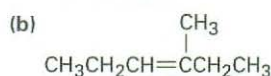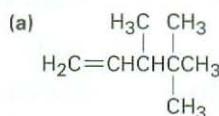
been used so long that it is accepted by IUPAC. Table 6.1 lists several other common names that are often used and are recognized by IUPAC. Note also that a $=CH_2$ substituent is called a **methylene group**, a $H_2C=CH-$ substituent is called a **vinyl group**, and a $H_2C=CHCH_2-$ substituent is called an **allyl group**.

$$H_2C\overset{\displaystyle\rightleftharpoons}{}\qquad H_2C=CH\overset{\displaystyle\rightleftharpoons}{}\qquad H_2C=CH-CH_2\overset{\displaystyle\rightleftharpoons}{}$$

A methylene group   **A vinyl group**   **An allyl group**

Table 6.1 **Common Names of Some Alkenes**

Compound	Systematic name	Common name
$H_2C=CH_2$	Ethene	Ethylene
$CH_3CH=CH_2$	Propene	Propylene
$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle \vert}{C}}=CH_2$	2-Methylpropene	Isobutylene
$H_2C=\overset{\displaystyle CH_3}{\underset{\displaystyle \vert}{C}}-CH=CH_2$	2-Methyl-1,3-butadiene	Isoprene

Problem 6.4 Give IUPAC names for the following compounds:

(a)
$$\overset{\displaystyle H_3C\;\;CH_3}{\underset{\displaystyle \vert\;\;\;\;\vert}{H_2C=CHCHCCH_3}}$$
$$\underset{\displaystyle \underset{\displaystyle CH_3}{\vert}}{}$$

(b)
$$\overset{\displaystyle CH_3}{\underset{\displaystyle \vert}{CH_3CH_2CH=CCH_2CH_3}}$$

(c)
$$\overset{\displaystyle CH_3\;\;\;\;\;\;\;\;CH_3}{\underset{\displaystyle \vert\;\;\;\;\;\;\;\;\;\;\vert}{CH_3CH=CHCHCH=CHCHCH_3}}$$

(d)
$$\overset{\displaystyle CH_3CHCH_2CH_3}{\underset{\displaystyle \vert}{CH_3CH_2CH_2CH=CHCHCH_2CH_3}}$$

Problem 6.5 Draw structures corresponding to the following IUPAC names:
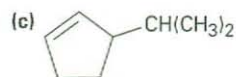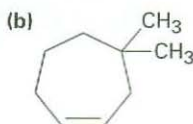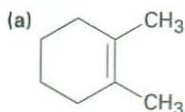(a) 2-Methyl-1,5-hexadiene   (b) 3-Ethyl-2,2-dimethyl-3-heptene
(c) 2,3,3-Trimethyl-1,4,6-octatriene   (d) 3,4-Diisopropyl-2,5-dimethyl-3-hexene
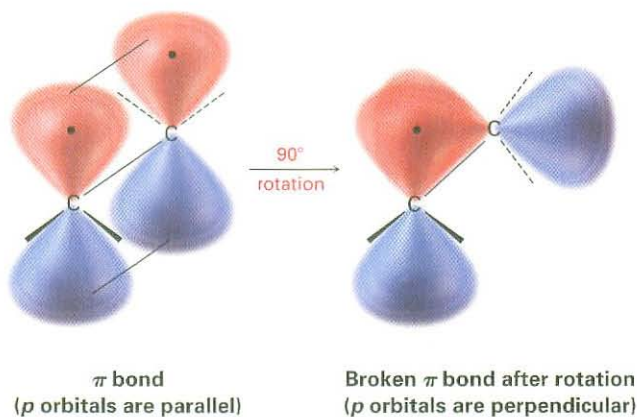
Problem 6.6 Name the following cycloalkenes:

(a)

(b)

(c)

6.4 | Cis–Trans Isomerism in Alkenes

We saw in Chapter 1 that the carbon–carbon double bond can be described in two ways. In valence bond language (Section 1.8), the carbons are sp^2-hybridized and have three equivalent hybrid orbitals that lie in a plane at angles of 120° to one another. The carbons form a σ bond by head-on overlap of sp^2 orbitals and a π bond by sideways overlap of unhybridized p orbitals oriented

perpendicular to the sp^2 plane, as shown in Figure 1.14 on page 16. In molecular orbital language (Section 1.11), interaction between the p orbitals leads to one bonding and one antibonding π molecular orbital. The π bonding MO has no node between nuclei and results from a combination of p orbital lobes with the same algebraic sign. The π antibonding MO has a node between nuclei and results from a combination of lobes with different algebraic signs, as shown in Figure 1.18, page 22.

Although essentially free rotation is possible around single bonds (Section 3.6), the same is not true of double bonds. For rotation to occur around a double bond, the π bond must break and re-form (Figure 6.2). Thus, the barrier to double-bond rotation must be at least as great as the strength of the π bond itself, an estimated 350 kJ/mol (84 kcal/mol). Recall that the barrier to bond rotation in ethane is only 12 kJ/mol.

Figure 6.2 The π bond must break for rotation to take place around a carbon–carbon double bond.

90°
rotation

π bond
(p orbitals are parallel)

Broken π bond after rotation
(p orbitals are perpendicular)

The lack of rotation around carbon–carbon double bonds is of more than just theoretical interest; it also has chemical consequences. Imagine the situation for a disubstituted alkene such as 2-butene. (*Disubstituted* means that two substituents other than hydrogen are bonded to the double-bond carbons.) The two methyl groups in 2-butene can be either on the same side of the double bond or on opposite sides, a situation similar to that in disubstituted cycloalkanes (Section 4.2).

Since bond rotation can't occur, the two 2-butenes can't spontaneously interconvert; they are different, isolable compounds. As with disubstituted cycloalkanes, we call such compounds *cis–trans stereoisomers*. The compound with substituents on the same side of the double bond is called *cis*-2-butene, and the isomer with substituents on opposite sides is *trans*-2-butene (Figure 6.3).
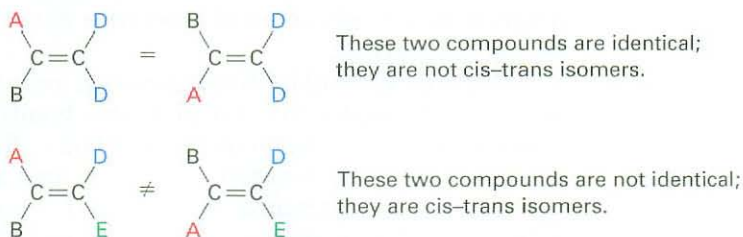

cis-2-Butene
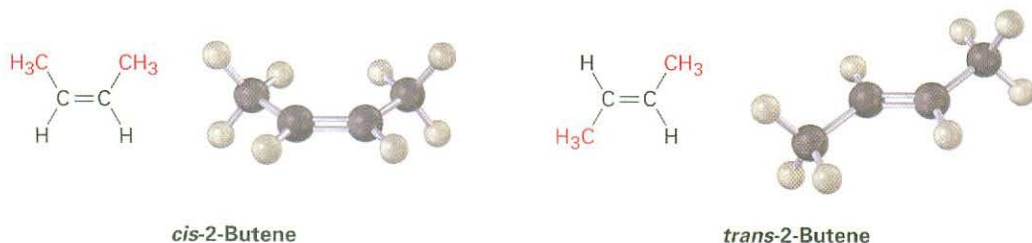
trans-2-Butene

Figure 6.3 Cis and trans isomers of 2-butene. The cis isomer has the two methyl groups on the same side of the double bond, and the trans isomer has the methyl groups on opposite sides.

Cis–trans isomerism is not limited to *di*substituted alkenes. It can occur whenever both double-bond carbons are attached to two different groups. If one of the double-bond carbons is attached to two identical groups, however, then cis–trans isomerism is not possible (Figure 6.4).

Figure 6.4 The requirement for cis–trans isomerism in alkenes. Compounds that have one of their carbons bonded to two identical groups can't exist as cis–trans isomers. Only when both carbons are bonded to two different groups are cis–trans isomers possible.

These two compounds are identical; they are not cis–trans isomers.

These two compounds are not identical; they are cis–trans isomers.

Problem 6.7 Which of the following compounds can exist as pairs of cis–trans isomers? Draw each cis–trans pair, and indicate the geometry of each isomer.
(a) $CH_3CH=CH_2$
(b) $(CH_3)_2C=CHCH_3$
(c) $CH_3CH_2CH=CHCH_3$
(d) $(CH_3)_2C=C(CH_3)CH_2CH_3$
(e) $ClCH=CHCl$
(f) $BrCH=CHCl$

Problem 6.8 Name the following alkenes, including the cis or trans designation:

(a)

(b)
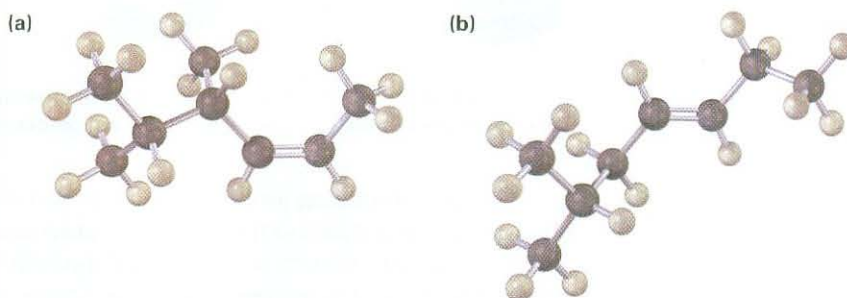
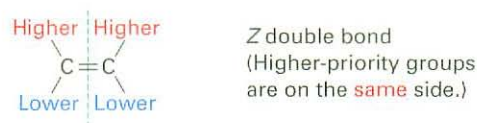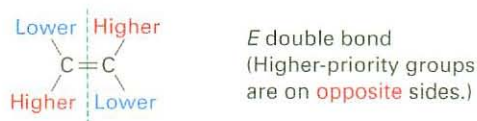

6.5 | Sequence Rules: The *E,Z* Designation

The cis–trans naming system used in the previous section works only with *disubstituted* alkenes—compounds that have two substituents other than hydrogen on the double bond. With trisubstituted and tetrasubstituted double bonds, a more general method is needed for describing double-bond geometry. (*Trisubstituted* means three substituents other than hydrogen on the double bond; *tetrasubstituted* means four substituents other than hydrogen.)

According to the *E,Z* **system** of nomenclature, a set of *sequence rules* is used to assign priorities to the substituent groups on the double-bond carbons. Considering each doubly bonded carbon atom separately, the sequence rules are used to decide which of the two attached groups is higher in priority. If the higher-priority groups on each carbon are on the same side of the double bond, the alkene is designated **Z**, for the German *zusammen*, meaning "together." If the higher-priority groups are on opposite sides, the alkene is designated **E**, for
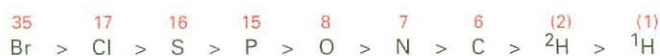
the German *entgegen,* meaning "opposite." (A simple way to remember which is which is to note that the groups are on "ze zame zide" in the *Z* isomer.)
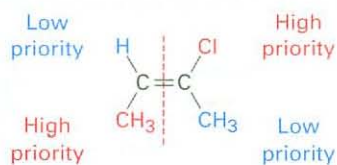
Lower | Higher
C=C
Higher | Lower

E double bond
(Higher-priority groups are on opposite sides.)

Higher | Higher
C=C
Lower | Lower

Z double bond
(Higher-priority groups are on the same side.)

Called the *Cahn–Ingold–Prelog rules* after the chemists who proposed them, the sequence rules are as follows:

Rule 1 **Considering the double-bond carbons separately, look at the two atoms directly attached to each and rank them according to atomic number.** An atom with higher atomic number receives higher priority than an atom with lower atomic number. Thus, the atoms commonly found attached to a double bond are assigned the following order. Note that when different isotopes of the same element are compared, such as deuterium (^2H) and protium (^1H), the heavier isotope receives priority over the lighter isotope.
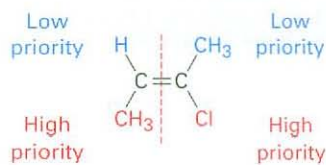
$$\underset{Br}{35} > \underset{Cl}{17} > \underset{S}{16} > \underset{P}{15} > \underset{O}{8} > \underset{N}{7} > \underset{C}{6} > \underset{^2H}{(2)} > \underset{^1H}{(1)}$$

| Robert Sidney Cahn	Sir Christopher Kelk Ingold	Vladimir Prelog
Robert Sidney Cahn (1899–1981) was born in England and received a doctoral degree in France. Although not specifically trained as a chemist, he became editor of the British *Journal of the Chemical Society.*	**Sir Christopher Kelk Ingold** (1893–1970) was born in Ilford, England, and received his D.Sc. at the University of London. After 6 years as professor at the University of Leeds, he spent his remaining career at University College, London (1930–1961). Ingold published more than 400 scientific papers and, along with Linus Pauling, was instrumental in developing the theory of resonance.	**Vladimir Prelog** (1906–1998) was born in Sarajevo, Bosnia, where, as a young boy, he was close enough to hear the shots that killed Archduke Ferdinand and ignited World War I. After receiving a Dr.Ing. degree in 1929 at the Institute of Technology in Prague, Czechoslovakia, he taught briefly at the University of Zagreb before becoming professor of chemistry at the Swiss Federal Institute of Technology (ETH) in Zürich (1941–1976). He received the 1975 Nobel Prize in chemistry for his lifetime achievements on the stereochemistry of antibiotics, alkaloids, enzymes, and other naturally occurring molecules.

For example:

Low priority		High priority		Low priority		Low priority

H — Cl
C=C
CH₃ — CH₃
High priority / Low priority

H — CH₃
C=C
CH₃ — Cl
High priority / High priority

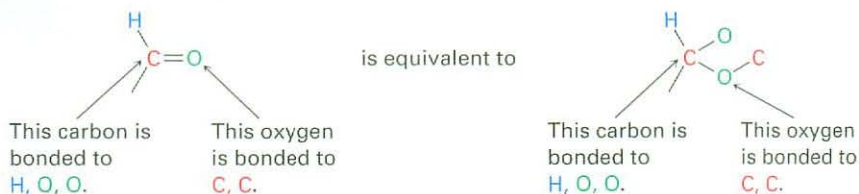(a) **(E)-2-Chloro-2-butene**   (b) **(Z)-2-Chloro-2-butene**

Because chlorine has a higher atomic number than carbon, a −Cl substituent receives higher priority than a −CH₃ group. Methyl receives higher priority than hydrogen, however, and isomer (a) is assigned E geometry because its high-priority groups are on opposite sides of the double bond. Isomer (b) has Z geometry because its high-priority groups are on "ze zame zide" of the double bond.

Rule 2   If a decision can't be reached by ranking the first atoms in the substituent, look at the second, third, or fourth atoms away from the double-bond carbons until the first difference is found. A −CH₂CH₃ substituent and a −CH₃ substituent are equivalent by rule 1 because both have carbon as the first atom. By rule 2, however, ethyl receives higher priority than methyl because ethyl has a *carbon* as its highest second atom, while methyl has only *hydrogen* as its second atom. Look at the following examples to see how the rule works:
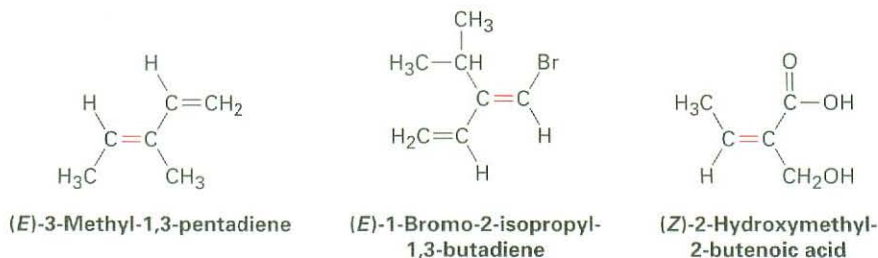
Lower   Higher   Lower   Higher

Higher   Lower   Lower   Higher
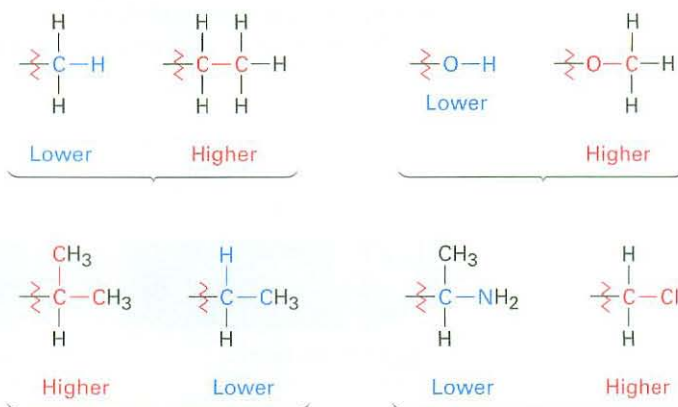
Rule 3   Multiple-bonded atoms are equivalent to the same number of single-bonded atoms. For example, an aldehyde substituent (−CH=O), which has a carbon atom *doubly* bonded to *one* oxygen, is equivalent to a substituent having a carbon atom *singly* bonded to *two* oxygens.

is equivalent to

This carbon is bonded to H, O, O.

This oxygen is bonded to C, C.

This carbon is bonded to H, O, O.

This oxygen is bonded to C, C.

As further examples, the following pairs are equivalent:

This carbon is bonded to H, C, C.   This carbon is bonded to H, H, C, C.   is equivalent to   This carbon is bonded to H, C, C.   This carbon is bonded to H, H, C, C.

This carbon is bonded to C, C, C.   This carbon is bonded to H, C, C, C.   is equivalent to   This carbon is bonded to C, C, C.   This carbon is bonded to H, C, C, C.
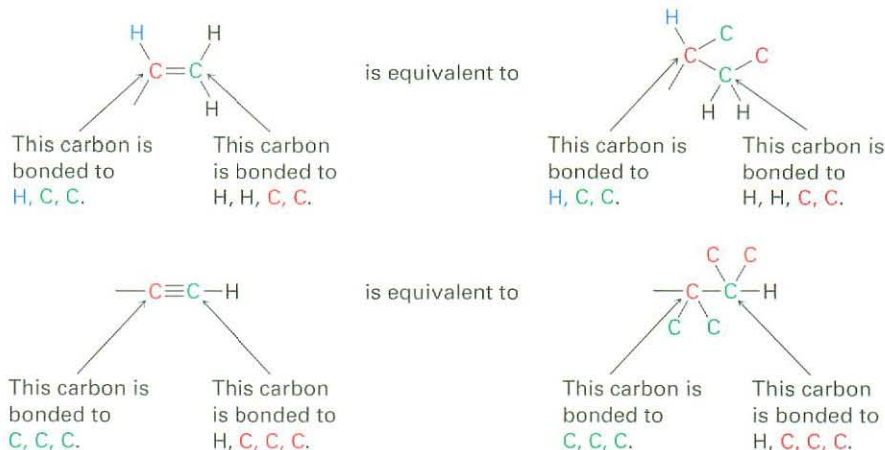
Taking all the sequence rules into account, we can assign the configurations shown in the following examples. Work through each one to convince yourself that the assignments are correct.

(*E*)-3-Methyl-1,3-pentadiene   (*E*)-1-Bromo-2-isopropyl-1,3-butadiene   (*Z*)-2-Hydroxymethyl-2-butenoic acid

---

WORKED EXAMPLE 6.1

Assigning E and Z Configurations to Substituted Alkenes

Assign *E* or *Z* configuration to the double bond in the following compound:
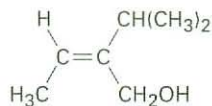
Strategy   Look at the two substituents connected to each double-bond carbon, and determine their priorities using the Cahn–Ingold–Prelog rules. Then see whether the two high-priority groups are on the same or opposite sides of the double bond.

Solution   The left-hand carbon has −H and −CH$_3$ substituents, of which −CH$_3$ receives higher priority by sequence rule 1. The right-hand carbon has −CH(CH$_3$)$_2$ and −CH$_2$OH substituents, which are equivalent by rule 1. By rule 2, however, −CH$_2$OH receives higher priority than −CH(CH$_3$)$_2$. The substituent −CH$_2$OH has an *oxygen* as

its highest second atom, but $-CH(CH_3)_2$ has a *carbon* as its highest second atom. The two high-priority groups are on the same side of the double bond, so we assign *Z* configuration.


Z configuration
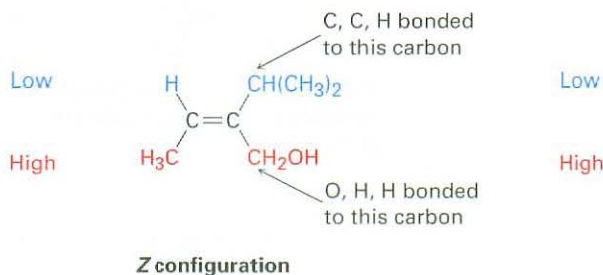
Problem 6.9   Which member in each of the following sets has higher priority?
(a) $-H$ or $-Br$ (b) $-Cl$ or $-Br$ (c) $-CH_3$ or $-CH_2CH_3$
(d) $-NH_2$ or $-OH$ (e) $-CH_2OH$ or $-CH_3$ (f) $-CH_2OH$ or $-CH=O$

Problem 6.10   Rank the following sets of substituents in order of Cahn–Ingold–Prelog priorities:
(a) $-CH_3$, $-OH$, $-H$, $-Cl$
(b) $-CH_3$, $-CH_2CH_3$, $-CH=CH_2$, $-CH_2OH$
(c) $-CO_2H$, $-CH_2OH$, $-C\equiv N$, $-CH_2NH_2$
(d) $-CH_2CH_3$, $-C\equiv CH$, $-C\equiv N$, $-CH_2OCH_3$

Problem 6.11   Assign *E* or *Z* configuration to the following alkenes:

(a)

(b)

(c)

(d)
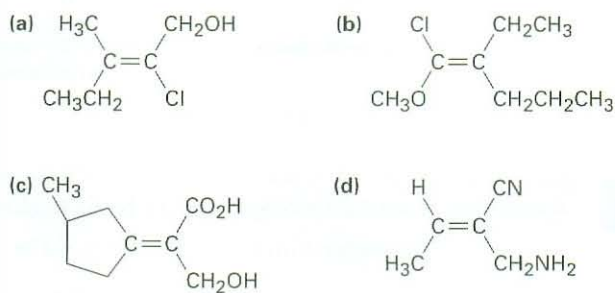
Problem 6.12   Assign stereochemistry (*E* or *Z*) to the double bond in the following compound, and convert the drawing into a skeletal structure (red = O):
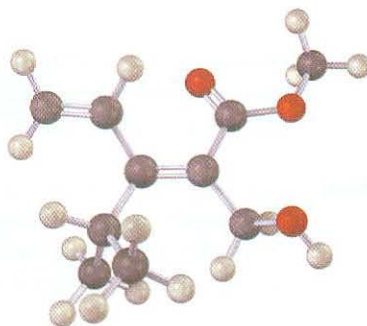
6.6 | Stability of Alkenes

Although the cis–trans interconversion of alkene isomers does not occur spontaneously, it can often be brought about by treating the alkene with a strong acid catalyst. If we interconvert *cis*-2-butene with *trans*-2-butene and allow them to reach equilibrium, we find that they aren't of equal stability. The trans isomer is more stable than the cis isomer by 2.8 kJ/mol (0.66 kcal/mol) at room temperature, leading to a 76:24 ratio.


Trans (76%)   **Cis (24%)**
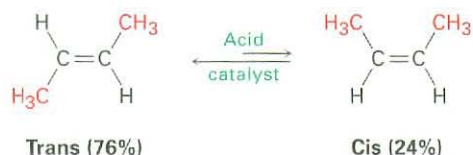
Using the relationship between equilibrium constant and free energy shown previously in Figure 4.12, p. 122, we can calculate that *cis*-2-butene is less stable than *trans*-2-butene by 2.8 kJ/mol (0.66 kcal/mol) at room temperature.

Cis alkenes are less stable than their trans isomers because of steric strain between the two larger substituents on the same side of the double bond. This is the same kind of steric interference that we saw previously in the axial conformation of methylcyclohexane (Section 4.7).


Steric strain

cis-2-Butene   *trans*-2-Butene
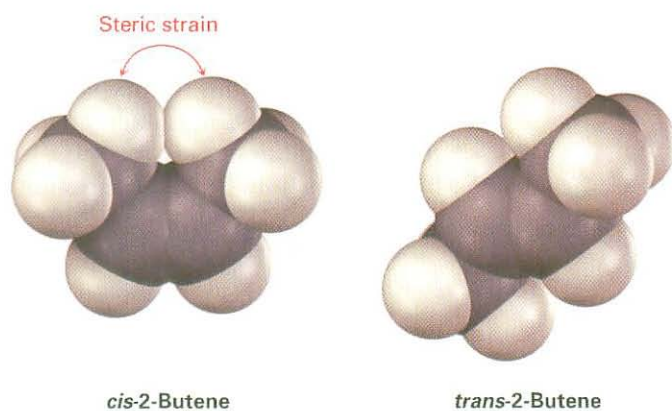
Although it's sometimes possible to find relative stabilities of alkene isomers by establishing a cis–trans equilibrium through treatment with strong acid, a more general method is to take advantage of the fact that alkenes undergo a *hydrogenation* reaction to give the corresponding alkane on treatment with H_2 gas in the presence of a catalyst such as palladium or platinum.

trans-2-Butene   Butane   *cis*-2-Butene
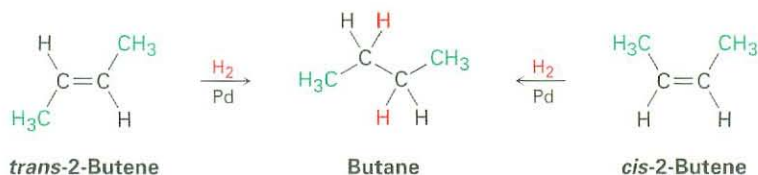
Energy diagrams for the hydrogenation reactions of *cis*- and *trans*-2-butene are shown in Figure 6.5. Since *cis*-2-butene is less stable than *trans*-2-butene by 2.8 kJ/mol, the energy diagram shows the cis alkene at a higher energy level. After reaction, however, both curves are at the same energy level (butane). It therefore follows that $\Delta G°$ for reaction of the cis isomer must be larger than $\Delta G°$ for reaction of the trans isomer by 2.8 kJ/mol. In other words, more energy is released in the hydrogenation of the cis isomer than the trans isomer because the cis isomer has more energy to begin with.

Figure 6.5 Energy diagrams for hydrogenation of *cis*- and *trans*-2-butene. The cis isomer is higher in energy than the trans isomer by about 2.8 kJ/mol and therefore releases more energy in the reaction.
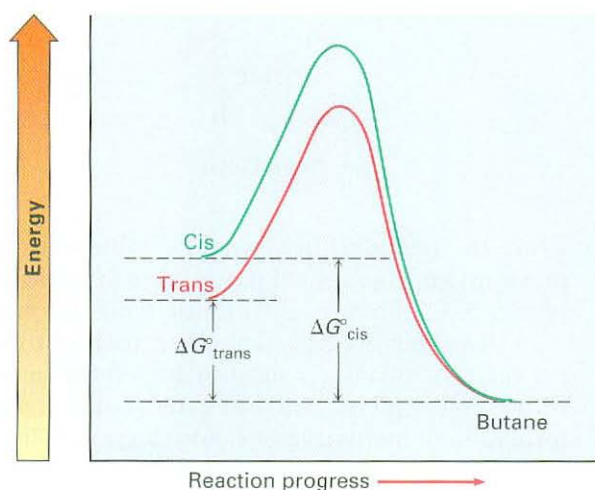
If we were to measure what are called *heats of hydrogenation* ($\Delta H°_{hydrog}$) for the two double-bond isomers and find their difference, we could determine the relative stabilities of cis and trans isomers without having to measure an equilibrium position. In fact, the results bear out our expectation. For *cis*-2-butene, $\Delta H°_{hydrog} = -120$ kJ/mol (-28.6 kcal/mol); for the trans isomer, $\Delta H°_{hydrog} = -116$ kJ/mol (-27.6 kcal/mol).

Cis isomer
$\Delta H°_{hydrog} = -120$ kJ/mol

Trans isomer
$\Delta H°_{hydrog} = -116$ kJ/mol

The energy difference between the 2-butene isomers as calculated from heats of hydrogenation (4 kJ/mol) agrees reasonably well with the energy difference calculated from equilibrium data (2.8 kJ/mol), but the numbers aren't exactly the same for two reasons. First, there is probably some experimental error, since heats of hydrogenation require skill and specialized equipment to measure accurately. Second, heats of reaction and equilibrium constants don't measure exactly the same thing. Heats of reaction measure enthalpy changes, $\Delta H°$, whereas equilibrium constants measure free-energy changes, $\Delta G°$, so we might expect a slight difference between the two.

Table 6.2 lists some representative data for the hydrogenation of different alkenes, showing that alkenes become more stable with increasing substitution.

For example, ethylene has $\Delta H°_{hydrog} = -137$ kJ/mol (-32.8 kcal/mol), but when one alkyl substituent is attached to the double bond, as in 1-butene, the alkene becomes approximately 10 kJ/mol more stable ($\Delta H°_{hydrog} = -126$ kJ/mol). Further increasing the degree of substitution leads to still further stability. As a general rule, alkenes follow the stability order:

Tetrasubstituted > Trisubstituted > Disubstituted > Monosubstituted
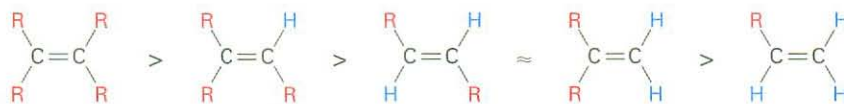
Table 6.2 | **Heats of Hydrogenation of Some Alkenes**

Substitution	Alkene	$\Delta H°_{hydrog}$ (kJ/mol)	(kcal/mol)
Ethylene	$H_2C=CH_2$	−137	−32.8
Monosubstituted	$CH_3CH=CH_2$	−126	−30.1
Disubstituted	$CH_3CH=CHCH_3$ (cis)	−120	−28.6
	$CH_3CH=CHCH_3$ (trans)	−116	−27.6
	$(CH_3)_2C=CH_2$	−119	−28.4
Trisubstituted	$(CH_3)_2C=CHCH_3$	−113	−26.9
Tetrasubstituted	$(CH_3)_2C=C(CH_3)_2$	−111	−26.6

The stability order of alkenes is due to a combination of two factors. One is a stabilizing interaction between the C=C π bond and adjacent C−H σ bonds on substituents. In valence-bond language, the interaction is called **hyperconjugation**. In a molecular orbital description, there is a bonding MO that extends over the four-atom C=C−C−H grouping, as shown in Figure 6.6. The more substituents that are present on the double bond, the more hyperconjugation there is and the more stable the alkene.
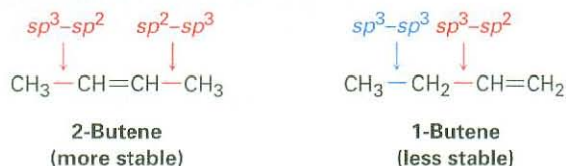
Figure 6.6 Hyperconjugation is a stabilizing interaction between an unfilled π orbital and a neighboring filled C−H σ bond on a substituent. The more substituents there are, the greater the stabilization of the alkene.
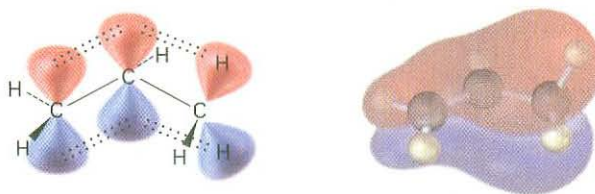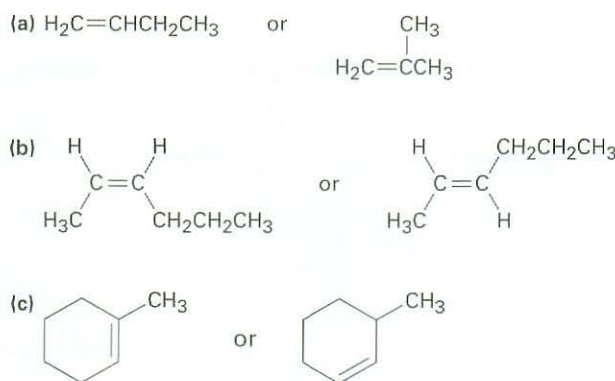

A second factor that contributes to alkene stability involves bond strengths. A bond between an sp^2 carbon and an sp^3 carbon is somewhat stronger than a bond between two sp^3 carbons. Thus, in comparing 1-butene and 2-butene, the monosubstituted isomer has one sp^3–sp^3 bond and one sp^3–sp^2 bond, while

the disubstituted isomer has two sp^3–sp^2 bonds. More highly substituted alkenes always have a higher ratio of sp^3–sp^2 bonds to sp^3–sp^3 bonds than less highly substituted alkenes and are therefore more stable.

$$\overset{\color{red}{sp^3\text{–}sp^2 \quad sp^2\text{–}sp^3}}{\color{red}{\downarrow \qquad\quad \downarrow}}$$
$$CH_3-CH=CH-CH_3$$

2-Butene
(more stable)

$$\overset{\color{red}{sp^3\text{–}sp^3 \quad sp^3\text{–}sp^2}}{\color{red}{\downarrow \qquad\quad \downarrow}}$$
$$CH_3-CH_2-CH=CH_2$$

1-Butene
(less stable)

Problem 6.13 | Name the following alkenes, and tell which compound in each pair is more stable:

(a) $H_2C=CHCH_2CH_3$ or $\underset{\displaystyle H_2C=CCH_3}{\overset{\displaystyle CH_3}{|}}$

(b)

$$\underset{H_3C}{\overset{H}{}}C=C\underset{CH_2CH_2CH_3}{\overset{H}{}}$$ or $$\underset{H_3C}{\overset{H}{}}C=C\underset{H}{\overset{CH_2CH_2CH_3}{}}$$

(c)

[structure with CH₃] or [structure with CH₃]

6.7 | Electrophilic Addition Reactions of Alkenes

Before beginning a detailed discussion of alkene reactions, let's review briefly some conclusions from the previous chapter. We said in Section 5.5 that alkenes behave as nucleophiles (Lewis bases) in polar reactions. The carbon–carbon double bond is electron-rich and can donate a pair of electrons to an electrophile (Lewis acid). For example, reaction of 2-methylpropene with HBr yields 2-bromo-2-methylpropane. A careful study of this and similar reactions by Christopher Ingold and others in the 1930s led to the generally accepted mechanism shown in Figure 6.7 for **electrophilic addition reactions**.

The reaction begins with an attack on the electrophile, HBr, by the electrons of the nucleophilic π bond. Two electrons from the π bond form a new σ bond between the entering hydrogen and an alkene carbon, as shown by the curved arrow at the top of Figure 6.7. The carbocation intermediate that results is itself an electrophile, which can accept an electron pair from nucleophilic Br^- ion to form a C–Br bond and yield a neutral addition product.

The energy diagram for the overall electrophilic addition reaction (Figure 6.8) has two peaks (transition states) separated by a valley (carbocation intermediate). The energy level of the intermediate is higher than that of the starting alkene, but the reaction as a whole is exergonic (negative $\Delta G°$). The first step, protonation of the alkene to yield the intermediate cation, is relatively slow but, once formed, the cation intermediate rapidly reacts further to yield the final alkyl bromide product. The relative rates of the two steps are indicated in Figure 6.8 by the fact that $\Delta G^{\ddagger}_1$ is larger than $\Delta G^{\ddagger}_2$.

Figure 6.7 MECHANISM:
Mechanism of the electrophilic addition of HBr to 2-methyl-propene. The reaction occurs in two steps and involves a carbocation intermediate.

1. A hydrogen atom on the electrophile HBr is attacked by π electrons from the nucleophilic double bond, forming a new C–H bond. This leaves the other carbon atom with a + charge and a vacant p orbital. Simultaneously, two electrons from the H–Br bond move onto bromine, giving bromide anion.
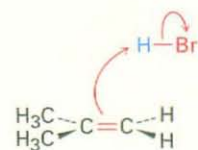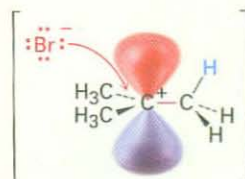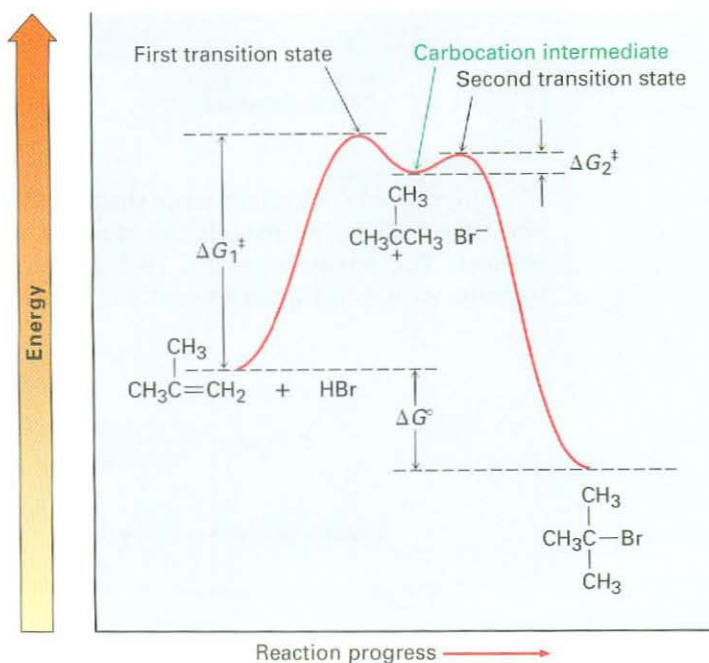
2. Bromide ion donates an electron pair to the positively charged carbon atom, forming a C–Br bond and yielding the neutral addition product.

2-Methylpropene

Carbocation intermediate

2-Bromo-2-methylpropane

© John McMurry

Figure 6.8 Energy diagram for the two-step electrophilic addition of HBr to 2-methylpropene. The first step is slower than the second step.

Electrophilic addition of HX to alkenes is successful not only with HBr but with HCl and HI as well. Note that HI is usually generated in the reaction mixture by treating potassium iodide with phosphoric acid.

2-Methylpropene → 2-Chloro-2-methylpropane (94%)

1-Pentene   (HI)   2-Iodopentane
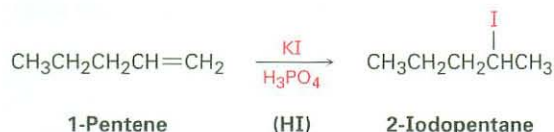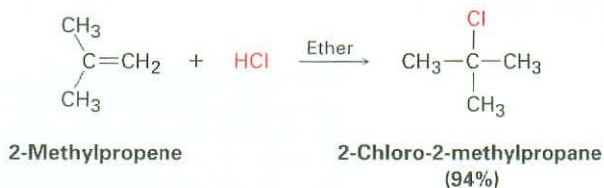
Writing Organic Reactions

This is a good time to mention that organic reaction equations are sometimes written in different ways to emphasize different points. In describing a laboratory process, for example, the reaction of 2-methylpropene with HCl just shown might be written in the format A + B → C to emphasize that both reactants are equally important for the purposes of the discussion. The solvent and notes about other reaction conditions, such as temperature, are written either above or below the reaction arrow.

2-Methylpropene → 2-Chloro-2-methyl-propane
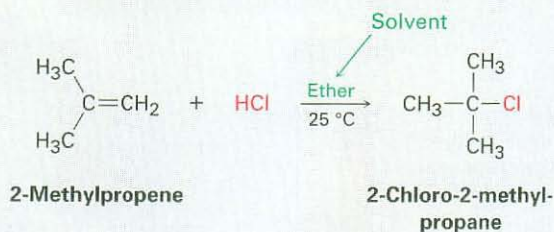
Alternatively, we might write the same reaction in a format to emphasize that 2-methylpropene is the reactant whose chemistry is of greater interest. The second reactant, HCl, is placed above the reaction arrow together with notes about solvent and reaction conditions.

2-Methylpropene   Solvent   2-Chloro-2-methyl-propane
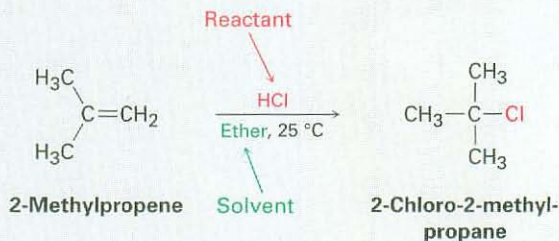
In describing a biological process, the reaction is usually written to show only the structure of the primary reactant and product, while abbreviating the structures of various biological "reagents" and by-products by using a curved arrow that intersects the straight reaction arrow. As discussed in Section 5.11, the reaction of glucose with ATP to give glucose 6-phosphate plus ADP would be written as

Glucose   **Glucose 6-phosphate**
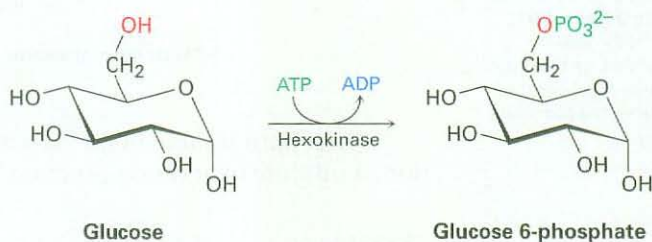
6.8 | Orientation of Electrophilic Additions: Markovnikov's Rule

Look carefully at the reactions shown in the previous section. In each case, an unsymmetrically substituted alkene has given a single addition product, rather than the mixture that might have been expected. As another example, 1-pentene *might* react with HCl to give both 1-chloropentane and 2-chloropentane, but it doesn't. Instead, the reaction gives only 2-chloropentane as the sole product. We say that such reactions are **regiospecific** (**ree**-jee-oh-specific) when only one of two possible orientations of addition occurs.

$$CH_3CH_2CH_2CH{=}CH_2 \ + \ HCl \longrightarrow CH_3CH_2CH_2\overset{\overset{\textstyle Cl}{|}}{C}HCH_3 \quad \left[CH_3CH_2CH_2CH_2CH_2Cl \right.$$

1-Pentene   **2-Chloropentane**   **1-Chloropentane**
                                       (sole product)   *(NOT formed)*
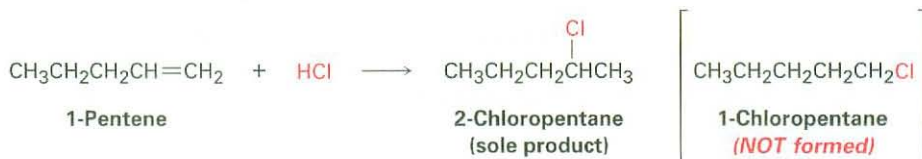
After looking at the results of many such reactions, the Russian chemist Vladimir Markovnikov proposed in 1869 what has become known as **Markovnikov's rule.**

Markovnikov's rule   In the addition of HX to an alkene, the H attaches to the carbon with fewer alkyl substituents and the X attaches to the carbon with more alkyl substituents.
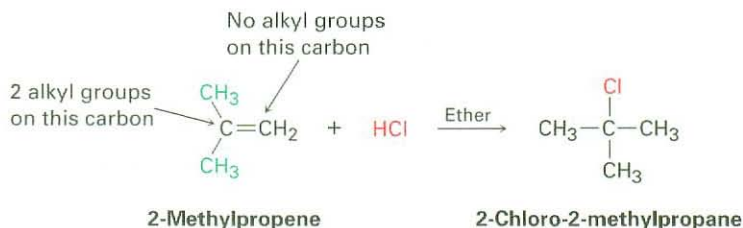
2-Methylpropene   **2-Chloro-2-methylpropane**

2 alkyl groups on this carbon

1 alkyl group on this carbon

1-Methylcyclohexene   **1-Bromo-1-methylcyclohexane**
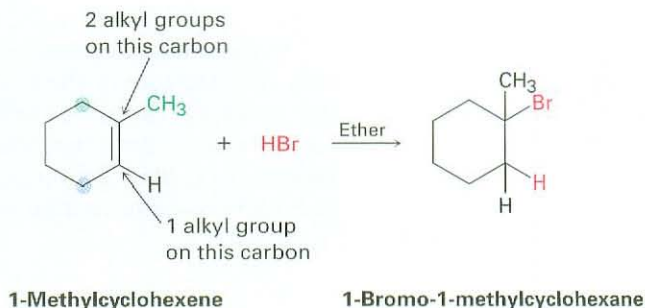
When both double-bond carbon atoms have the same degree of substitution, a mixture of addition products results.

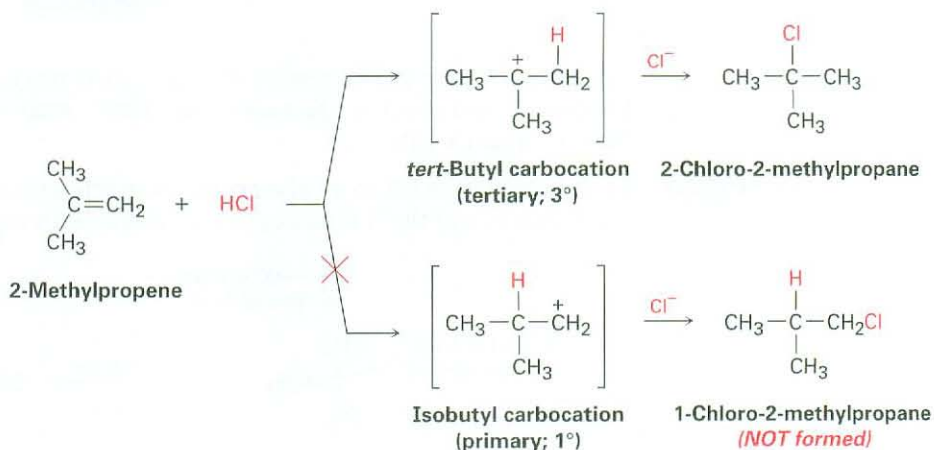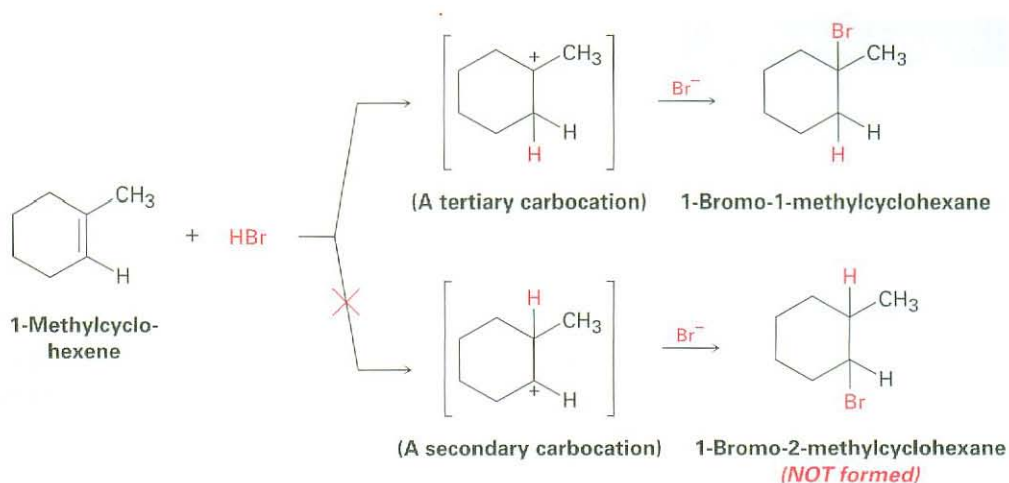1 alkyl group on this carbon   1 alkyl group on this carbon

$CH_3CH_2CH=CHCH_3$ + HBr $\xrightarrow{\text{Ether}}$ $CH_3CH_2CH_2CHCH_3$ + $CH_3CH_2CHCH_2CH_3$

2-Pentene   **2-Bromopentane**   **3-Bromopentane**
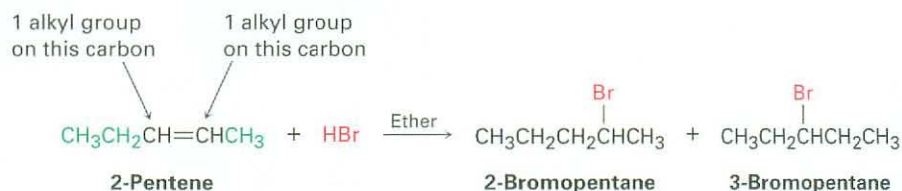
Since carbocations are involved as intermediates in these reactions, Markovnikov's rule can be restated.

Markovnikov's rule (restated)   In the addition of HX to an alkene, the more highly substituted carbocation is formed as the intermediate rather than the less highly substituted one.

For example, addition of H^+ to 2-methylpropene yields the intermediate *tertiary* carbocation rather than the alternative primary carbocation, and addition to 1-methylcyclohexene yields a tertiary cation rather than a secondary one. Why should this be?

2-Methylpropene

tert-**Butyl carbocation** (tertiary; 3°)   **2-Chloro-2-methylpropane**

Isobutyl carbocation (primary; 1°)   **1-Chloro-2-methylpropane** *(NOT formed)*

WORKED EXAMPLE 6.2   *Predicting the Product of an Electrophilic Addition Reaction*

What product would you expect from reaction of HCl with 1-ethylcyclopentene?
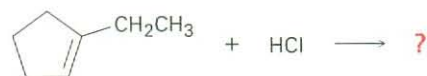
Strategy   When solving a problem that asks you to predict a reaction product, begin by look-
ing at the functional group(s) in the reactants and deciding what kind of reaction is
likely to occur. In the present instance, the reactant is an alkene that will probably
undergo an electrophilic addition reaction with HCl. Next, recall what you know
about electrophilic addition reactions, and use your knowledge to predict the prod-
uct. You know that electrophilic addition reactions follow Markovnikov's rule, so H^+
will add to the double-bond carbon that has one alkyl group (C2 on the ring) and
the Cl will add to the double-bond carbon that has two alkyl groups (C1 on the ring).

Solution   The expected product is 1-chloro-1-ethylcyclopentane.
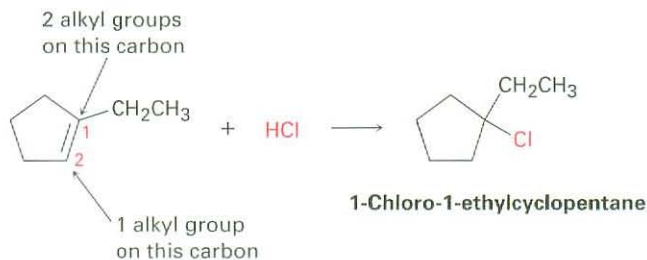
WORKED EXAMPLE 6.3

Synthesizing a Specific Compound

What alkene would you start with to prepare the following alkyl halide? There may be more than one possibility.

$$? \longrightarrow CH_3CH_2\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2CH_2CH_3$$
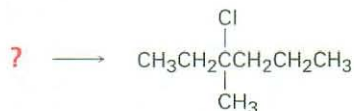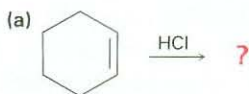
Strategy When solving a problem that asks how to prepare a given product, *always work backward*. Look at the product, identify the functional group(s) it contains, and ask yourself, "How can I prepare that functional group?" In the present instance, the product is a tertiary alkyl chloride, which can be prepared by reaction of an alkene with HCl. The carbon atom bearing the −Cl atom in the product must be one of the double-bond carbons in the reactant. Draw and evaluate all possibilities.

Solution There are three possibilities, any one of which could give the desired product.
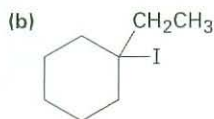
$$\overset{\overset{\displaystyle CH_3}{|}}{CH_3CH=C}CH_2CH_2CH_3 \quad or \quad \overset{\overset{\displaystyle CH_3}{|}}{CH_3CH_2C=CHCH_2CH_3} \quad or \quad \overset{\overset{\displaystyle CH_2}{||}}{CH_3CH_2C}CH_2CH_2CH_3$$

$$\Big\downarrow HCl$$

$$CH_3CH_2\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2CH_2CH_3$$
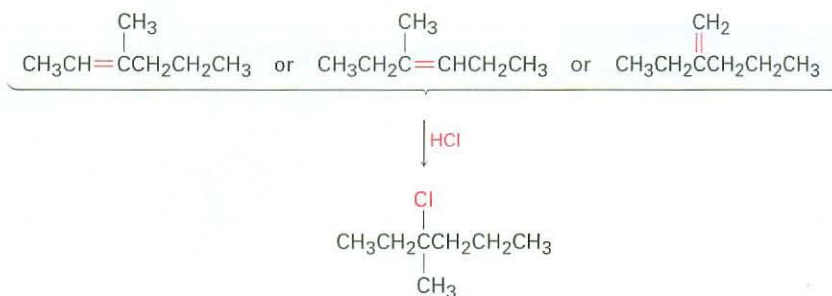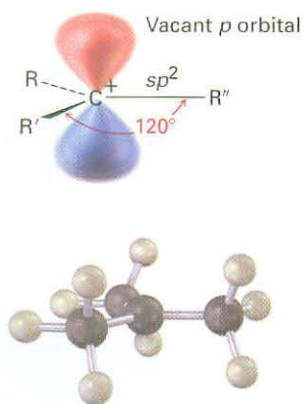

Problem 6.14 Predict the products of the following reactions:

(a)

  $\xrightarrow{\text{HCl}}$ **?**

(b) $\overset{\overset{\displaystyle CH_3}{|}}{CH_3C=CHCH_2CH_3} \xrightarrow{\text{HBr}}$ **?**

(c) $\overset{\overset{\displaystyle CH_3}{|}}{CH_3CHCH_2CH=CH_2} \xrightarrow[\text{H}_2\text{SO}_4]{\text{H}_2\text{O}}$ **?**

(Addition of H_2O occurs.)

(d)

  $\xrightarrow{\text{HBr}}$ **?**
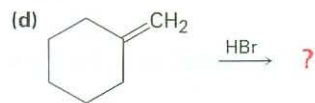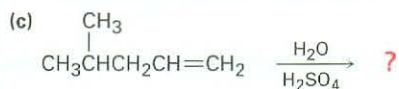
Problem 6.15 What alkenes would you start with to prepare the following alkyl halides?

(a)

(b)

(c) $\overset{\overset{\displaystyle Br}{|}}{CH_3CH_2CHCH_2CH_2CH_3}$

(d)
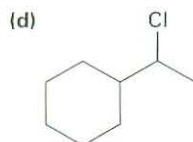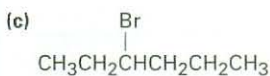
6.9 | Carbocation Structure and Stability

To understand why Markovnikov's rule works, we need to learn more about the structure and stability of carbocations and about the general nature of reactions and transition states. The first point to explore involves structure.

A great deal of evidence has shown that carbocations are *planar*. The trivalent carbon is sp^2-hybridized, and the three substituents are oriented to the corners of an equilateral triangle, as indicated in Figure 6.9. Because there are only six valence electrons on carbon and all six are used in the three σ bonds, the p orbital extending above and below the plane is unoccupied.

The second point to explore involves carbocation stability. 2-Methylpropene might react with H^+ to form a carbocation having three alkyl substituents (a tertiary ion, 3°), or it might react to form a carbocation having one alkyl substituent (a primary ion, 1°). Since the tertiary alkyl chloride, 2-chloro-2-methylpropane, is the only product observed, formation of the tertiary cation is evidently favored over formation of the primary cation. Thermodynamic measurements show that, indeed, the stability of carbocations increases with increasing substitution so that the stability order is tertiary > secondary > primary > methyl.

Vacant *p* orbital

Figure 6.9 The structure of a carbocation. The trivalent carbon is sp^2-hybridized and has a vacant *p* orbital perpendicular to the plane of the carbon and three attached groups.

ThomsonNOW™ Click *Organic Interactive* to **rank the stability of carbocation intermediates.**

Methyl | Primary (1°) | Secondary (2°) | Tertiary (3°)

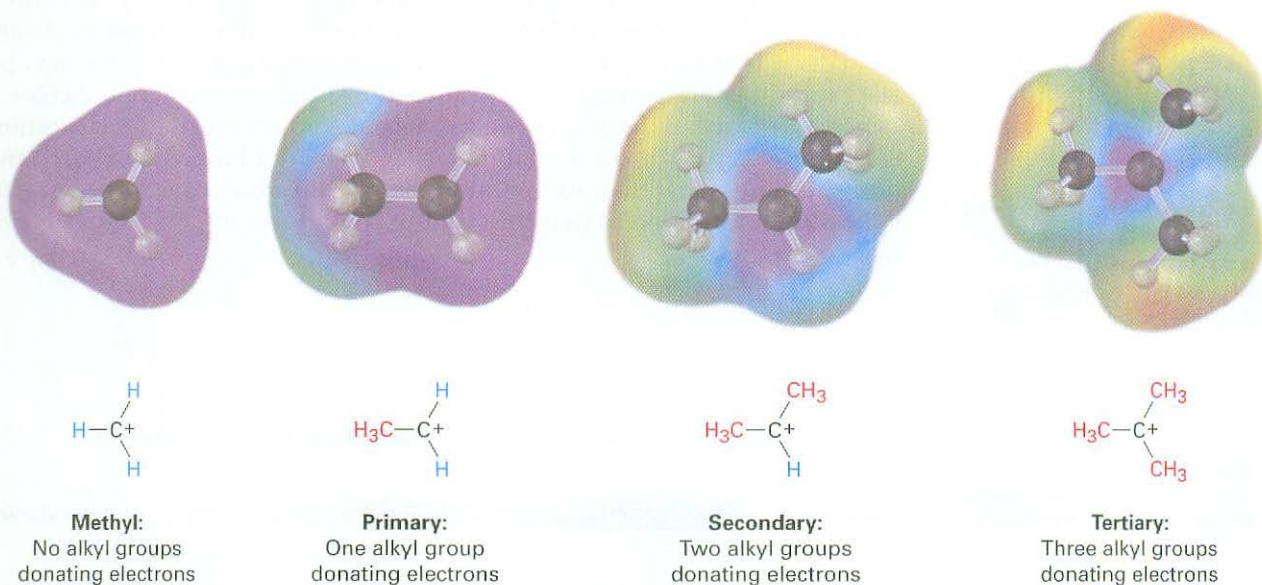Less stable ← Stability → More stable

One way of determining carbocation stabilities is to measure the amount of energy required to form the carbocation by dissociation of the corresponding alkyl halide, $R-X \rightarrow R^+ + :X^-$. As shown in Figure 6.10, tertiary alkyl halides dissociate to give carbocations more easily than secondary or primary ones. As a result, trisubstituted carbocations are more stable than disubstituted ones, which are more stable than monosubstituted ones. The data in Figure 6.10 are taken from measurements made in the gas phase, but a similar stability order is found for carbocations in solution. The dissociation enthalpies are much lower in solution because polar solvents can stabilize the ions, but the order of carbocation stability remains the same.

Figure 6.10 A plot of dissociation enthalpy versus substitution pattern for the gas-phase dissociation of alkyl chlorides to yield carbocations. More highly substituted alkyl halides dissociate more easily than less highly substituted ones.
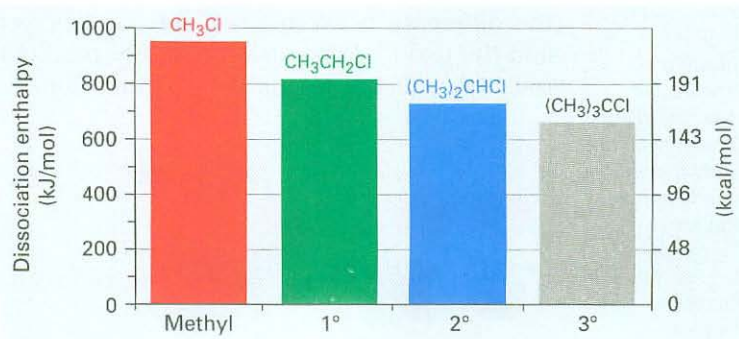
Why are more highly substituted carbocations more stable than less highly substituted ones? There are at least two reasons. Part of the answer has to do with inductive effects, and part has to do with hyperconjugation. Inductive effects, discussed in Section 2.1 in connection with polar covalent bonds, result from the shifting of electrons in a σ bond in response to the electronegativity of nearby atoms. In the present instance, electrons from a relatively larger and more polarizable alkyl group can shift toward a neighboring positive charge more easily than the electron from a hydrogen. Thus, the more alkyl groups there are attached to the positively charged carbon, the more electron density shifts toward the charge and the more inductive stabilization of the cation occurs (Figure 6.11).

Methyl:	Primary:	Secondary:	Tertiary:
No alkyl groups donating electrons	One alkyl group donating electrons	Two alkyl groups donating electrons	Three alkyl groups donating electrons

Figure 6.11 A comparison of inductive stabilization for methyl, primary, secondary, and tertiary carbocations. The more alkyl groups there are bonded to the positively charged carbon, the more electron density shifts toward the charge, making the charged carbon less electron-poor (blue in electrostatic potential maps).

Hyperconjugation, discussed in Section 6.6 in connection with the stabilities of substituted alkenes, is the stabilizing interaction between a vacant p orbital and properly oriented C—H σ bonds on neighboring carbons. The more alkyl groups there are on the carbocation, the more possibilities there are for hyperconjugation and the more stable the carbocation. Figure 6.12 shows the molecular orbital involved in hyperconjugation for the ethyl carbocation, $CH_3CH_2^+$, and indicates the difference between the C—H bond perpendicular to the cation p orbital and the two C—H bonds more nearly parallel to the cation p orbital. Only the roughly parallel C—H bonds are oriented properly to take part in hyperconjugation.

Figure 6.12 Stabilization of the ethyl carbocation, $CH_3CH_2^+$, through hyperconjugation. Interaction of neighboring C—H σ bonds with the vacant p orbital stabilizes the cation and lowers its energy. The molecular orbital shows that only the two C—H bonds more nearly parallel to the cation p orbital are oriented properly for hyperconjugation. The C—H bond perpendicular to the cation p orbital cannot take part.
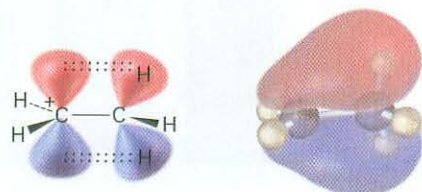
Problem 6.16   Show the structures of the carbocation intermediates you would expect in the following reactions:

(a)

$$CH_3CH_2C(CH_3)=CHCH(CH_3)CH_3 \xrightarrow{\text{HBr}} \text{?}$$

(b) (cyclopentylidene)=CHCH_3 $\xrightarrow{\text{HI}}$ **?**

Problem 6.17   Draw a skeletal structure of the following carbocation. Identify it as primary, secondary, or tertiary, and identify the hydrogen atoms that have the proper orientation for hyperconjugation in the conformation shown.
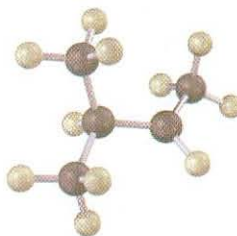
6.10 | The Hammond Postulate

Let's summarize our knowledge of electrophilic addition reactions up to this point. We know that:

■ **Electrophilic addition to an unsymmetrically substituted alkene gives the more highly substituted carbocation intermediate.** A more highly substituted carbocation forms faster than a less highly substituted one and, once formed, rapidly goes on to give the final product.

■ **A more highly substituted carbocation is more stable than a less highly substituted one.** That is, the stability order of carbocations is tertiary > secondary > primary > methyl.

What we have not yet seen is how these two points are related. Why does the *stability* of the carbocation intermediate affect the *rate* at which it's formed and thereby determine the structure of the final product? After all, carbocation stability is determined by the free-energy change $\Delta G°$, but reaction rate is determined by the activation energy $\Delta G^{\ddagger}$. The two quantities aren't directly related.

Although there is no simple quantitative relationship between the stability of a carbocation intermediate and the rate of its formation, there *is* an intuitive relationship. It's generally true when comparing two similar reactions that the more stable intermediate forms faster than the less stable one. The situation is shown graphically in Figure 6.13, where the reaction energy profile in part (a) represents the typical situation rather than the profile in part (b). That is, the curves for two similar reactions don't cross one another.

An explanation of the relationship between reaction rate and intermediate stability was first advanced in 1955. Known as the **Hammond postulate**, the argument goes like this: transition states represent energy maxima. They are high-energy activated complexes that occur transiently during the course of a reaction and immediately go on to a more stable species. Although we can't
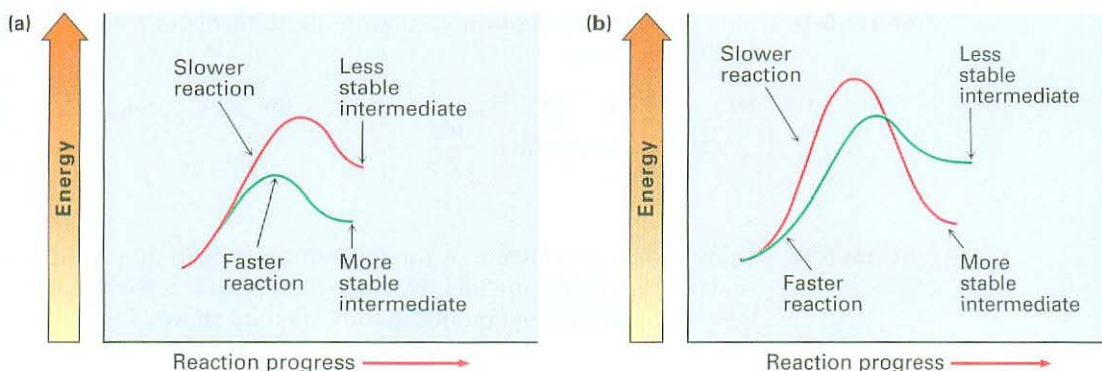
Figure 6.13 Energy diagrams for two similar competing reactions. In **(a)**, the faster reaction yields the more stable intermediate. In **(b)**, the slower reaction yields the more stable intermediate. The curves shown in **(a)** represent the typical situation.

actually observe transition states because they have no finite lifetime, the Hammond postulate says that we can get an idea of a particular transition state's structure by looking at the structure of the nearest stable species. Imagine the two cases shown in Figure 6.14, for example. The reaction profile in part (a) shows the energy curve for an endergonic reaction step, and the profile in part (b) shows the curve for an exergonic step.

Figure 6.14 Energy diagrams for endergonic and exergonic steps. **(a)** In an endergonic step, the energy levels of transition state and *product* are closer. **(b)** In an exergonic step, the energy levels of transition state and *reactant* are closer.
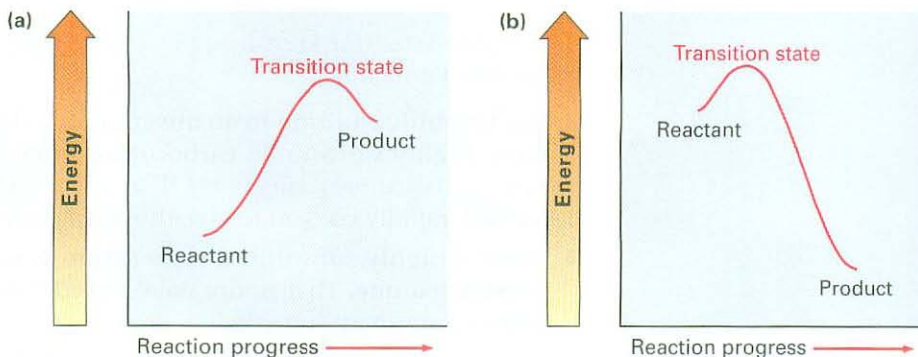
In an endergonic reaction (Figure 6.14a), the energy level of the transition state is closer to that of the product than to that of the reactant. Since the transition state is closer energetically to the product, we make the natural assumption that it's also closer structurally. In other words, *the transition state for an endergonic reaction step structurally resembles the product of that step.* Conversely, the transition state for an exergonic reaction (Figure 6.14b) is closer energetically, and thus structurally, to the reactant than to the product. We therefore say that *the transition state for an exergonic reaction step structurally resembles the reactant for that step.*

Hammond postulate The structure of a transition state resembles the structure of the nearest stable species. Transition states for endergonic steps structurally resemble products, and transition states for exergonic steps structurally resemble reactants.

How does the Hammond postulate apply to electrophilic addition reactions? The formation of a carbocation by protonation of an alkene is an endergonic step. Thus, the transition state for alkene protonation structurally resembles the

carbocation intermediate, and any factor that stabilizes the carbocation will stabilize the nearby transition state. Since increasing alkyl substitution stabilizes carbocations, it also stabilizes the transition states leading to those ions, thus resulting in a faster reaction. More stable carbocations form faster because their greater stability is reflected in the lower-energy transition state leading to them (Figure 6.15).

Figure 6.15 Energy diagrams for carbocation formation. The more stable tertiary carbocation is formed faster (green curve) because its increased stability lowers the energy of the transition state leading to it.
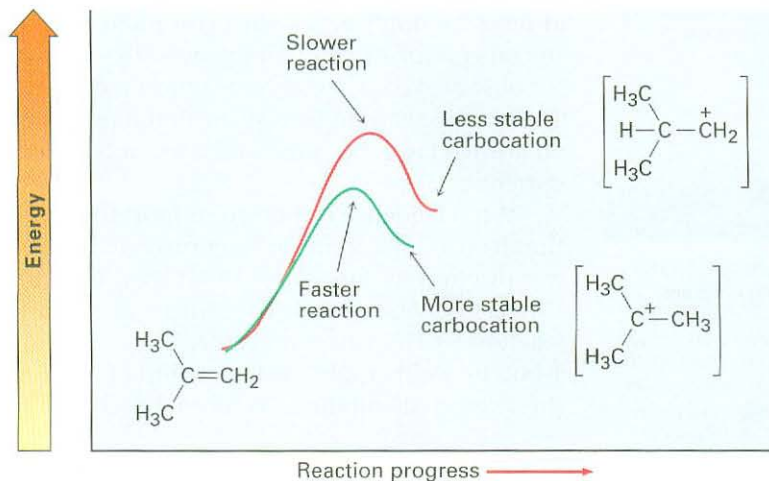
We can imagine the transition state for alkene protonation to be a structure in which one of the alkene carbon atoms has almost completely rehybridized from sp^2 to sp^3 and in which the remaining alkene carbon bears much of the positive charge (Figure 6.16). This transition state is stabilized by hyperconjugation and inductive effects in the same way as the product carbocation. The more alkyl groups that are present, the greater the extent of stabilization and the faster the transition state forms.

Alkene   **Productlike transition state**   **Carbocation**
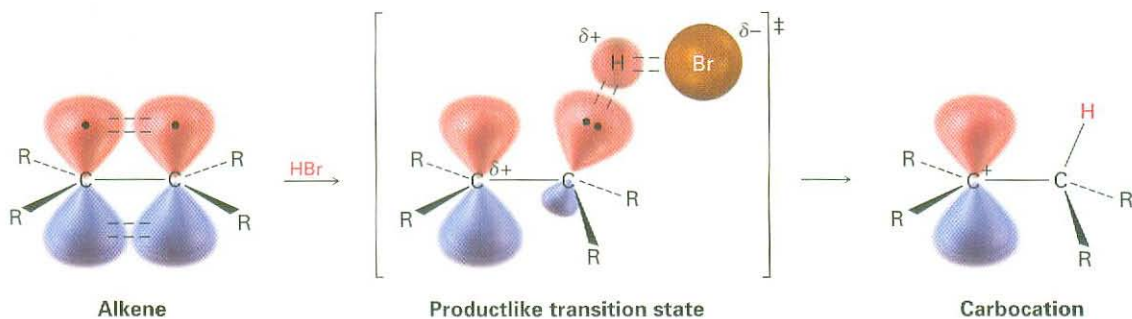
Figure 6.16 The hypothetical structure of a transition state for alkene protonation. The transition state is closer in both energy and structure to the carbocation than to the alkene. Thus, an increase in carbocation stability (lower $\Delta G°$) also causes an increase in transition-state stability (lower $\Delta G^{\ddagger}$), thereby increasing the rate of its formation.

Problem 6.18   What about the second step in the electrophilic addition of HCl to an alkene—the reaction of chloride ion with the carbocation intermediate? Is this step exergonic or endergonic? Does the transition state for this second step resemble the reactant (carbocation) or product (alkyl chloride)? Make a rough drawing of what the transition-state structure might look like.

6.11 | Evidence for the Mechanism of Electrophilic Additions: Carbocation Rearrangements

How do we know that the carbocation mechanism for electrophilic addition reactions of alkenes is correct? The answer is that we *don't* know it's correct; at least we don't know with complete certainty. Although an incorrect reaction mechanism can be disproved by demonstrating that it doesn't account for observed data, a correct reaction mechanism can never be entirely proved. The best we can do is to show that a proposed mechanism is consistent with all known facts. If enough facts are accounted for, the mechanism is probably correct.

What evidence is there to support the carbocation mechanism proposed for the electrophilic addition reaction of alkenes? One of the best pieces of evidence was discovered during the 1930s by F. C. Whitmore of the Pennsylvania State University, who found that structural rearrangements often occur during the reaction of HX with an alkene. For example, reaction of HCl with 3-methyl-1-butene yields a substantial amount of 2-chloro-2-methylbutane in addition to the "expected" product, 2-chloro-3-methylbutane.

Frank C. Whitmore

Frank C. Whitmore (1887–1947) was born in North Attleboro, Massachusetts, and received his Ph.D. at Harvard working with E. L. Jackson. He was professor of chemistry at Minnesota, Northwestern, and the Pennsylvania State University. Nicknamed "Rocky," he wrote an influential advanced textbook in organic chemistry.

3-Methyl-1- butene   **2-Chloro-3-methylbutane** (approx. 50%)   **2-Chloro-2-methylbutane** (approx. 50%)

If the reaction takes place in a single step, it would be difficult to account for rearrangement, but if the reaction takes place in several steps, rearrangement is more easily explained. Whitmore suggested that it is a carbocation intermediate that undergoes rearrangement. The secondary carbocation intermediate formed by protonation of 3-methyl-1-butene rearranges to a more stable tertiary carbocation by a **hydride shift**—the shift of a hydrogen atom and its electron pair (a hydride ion, :H⁻) between neighboring carbons.

3-Methyl-1- butene   **A 2° carbocation**   Hydride shift   **A 3° carbocation**

2-Chloro-3-methylbutane   **2-Chloro-2-methylbutane**
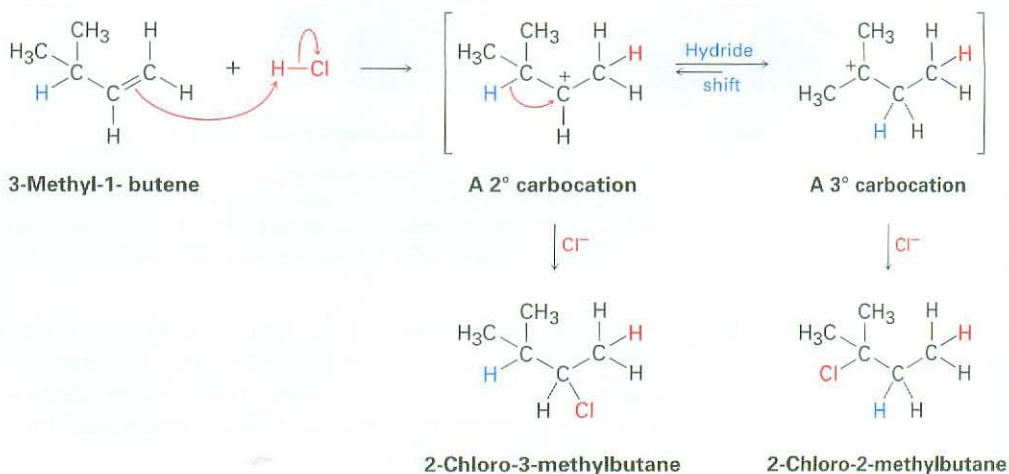
Carbocation rearrangements can also occur by the shift of an alkyl group with its electron pair. For example, reaction of 3,3-dimethyl-1-butene with HCl leads to an equal mixture of unrearranged 2-chloro-3,3-dimethylbutane and rearranged 2-chloro-2,3-dimethylbutane. In this instance, a secondary carbocation rearranges to a more stable tertiary carbocation by the shift of a methyl group.

3,3-Dimethyl-1-butene   **A 2° carbocation**   **A 3° carbocation**

2-Chloro-3,3-dimethylbutane   **2-Chloro-2,3-dimethylbutane**
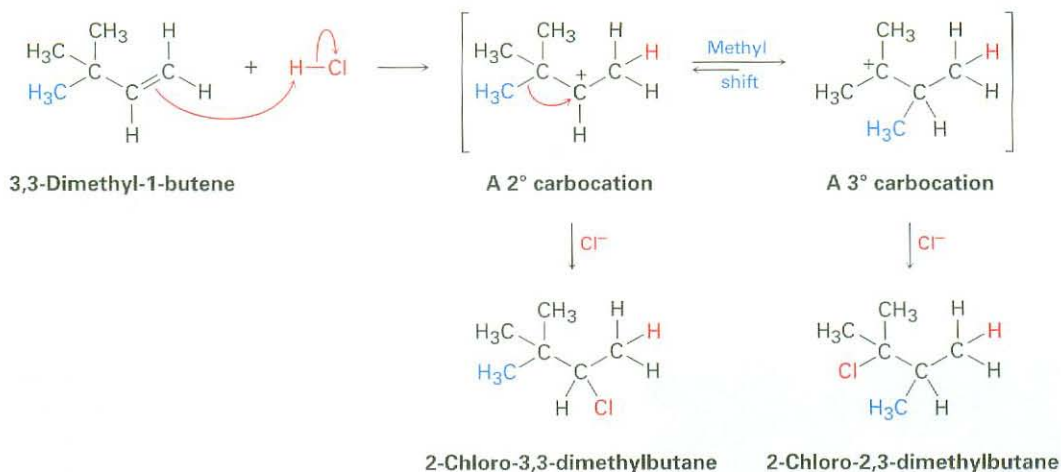
Note the similarities between the two carbocation rearrangements: in both cases, a group (:H⁻ or :CH₃⁻) moves to an adjacent positively charged carbon, taking its bonding electron pair with it. Also in both cases, a less stable carbocation rearranges to a more stable ion. Rearrangements of this kind are a common feature of carbocation chemistry and are particularly important in the biological pathways by which steroids and related substances are synthesized. An example is the following hydride shift that occurs during the biosynthesis of cholesterol.

A tertiary carbocation   **An isomeric**
tertiary carbocation
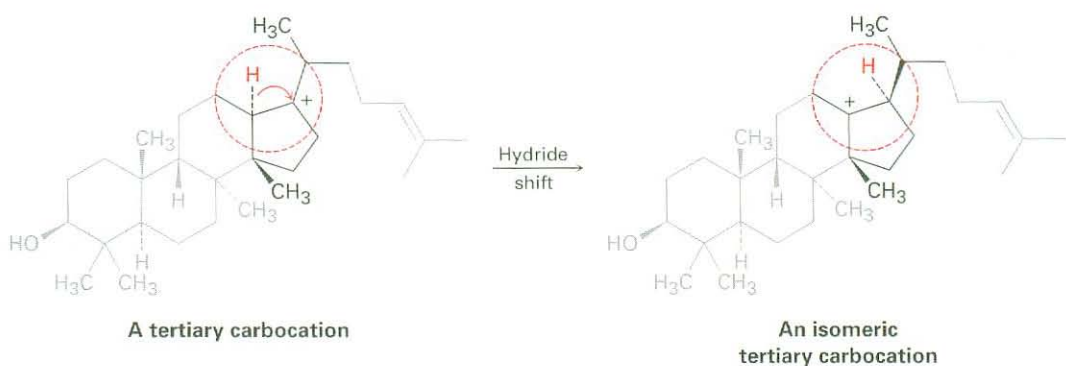
A word of advice that we'll repeat on occasion: biological molecules are often larger and more complex in appearance than the molecules chemists work with in the laboratory, but don't be intimidated. When looking at *any* chemical transformation, focus only on the part of the molecule where the change is occurring and don't worry about the rest. The tertiary carbocation just pictured looks complicated, but all the chemistry is taking place in the small part of the molecule inside the red circle.

Problem 6.19 | On treatment with HBr, vinylcyclohexane undergoes addition and rearrangement to yield 1-bromo-1-ethylcyclohexane. Using curved arrows, propose a mechanism to account for this result.

Vinylcyclohexane   **1-Bromo-1-ethylcyclohexane**
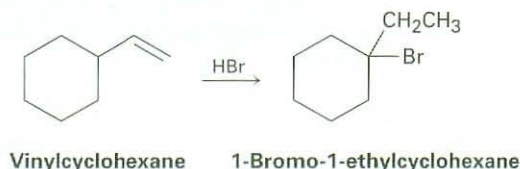
Focus On . . .

Terpenes: Naturally Occurring Alkenes

The wonderful fragrance of leaves from the California bay tree is due primarily to myrcene, a simple terpene.

© 2006 San Marcos Growers

It has been known for centuries that codistillation of many plant materials with steam produces a fragrant mixture of liquids called *essential oils*. For hundreds of years, such plant extracts have been used as medicines, spices, and perfumes. The investigation of essential oils also played a major role in the emergence of organic chemistry as a science during the 19th century.

Chemically, plant essential oils consist largely of mixtures of compounds known as *terpenoids*—small organic molecules with an immense diversity of structure. More than 35,000 different terpenoids are known. Some are open-chain molecules, and others contain rings; some are hydrocarbons, and others contain oxygen. Hydrocarbon terpenoids, in particular, are known as *terpenes*, and all contain double bonds. For example:

Myrcene
(oil of bay)
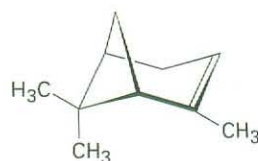
α-Pinene
(turpentine)
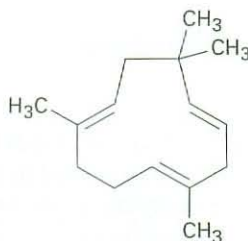
Humulene
(oil of hops)

(continued)

Regardless of their apparent structural differences, all terpenoids are related. According to a formalism called the *isoprene rule,* they can be thought of as arising from head-to-tail joining of 5-carbon isoprene units (2-methyl-1,3-butadiene). Carbon 1 is the head of the isoprene unit, and carbon 4 is the tail. For example, myrcene contains two isoprene units joined head to tail, forming an 8-carbon chain with two 1-carbon branches. α-Pinene similarly contains two isoprene units assembled into a more complex cyclic structure, and humulene contains three isoprene units. See if you can identify the isoprene units in α-pinene and humulene.

Isoprene   **Myrcene**
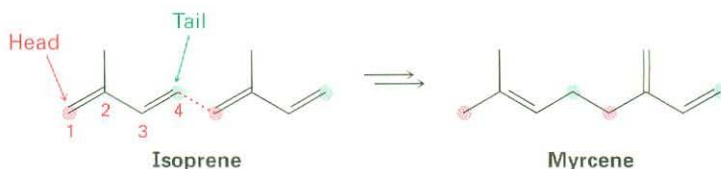
Terpenes (and terpenoids) are further classified according to the number of 5-carbon units they contain. Thus, *monoterpenes* are 10-carbon substances biosynthesized from two isoprene units, *sesquiterpenes* are 15-carbon molecules from three isoprene units, *diterpenes* are 20-carbon substances from four isoprene units, and so on. Monoterpenes and sesquiterpenes are found primarily in plants, but the higher terpenoids occur in both plants and animals, and many have important biological roles. The triterpenoid lanosterol, for example, is the precursor from which all steroid hormones are made.

Lanosterol
(a triterpene, C_{30})
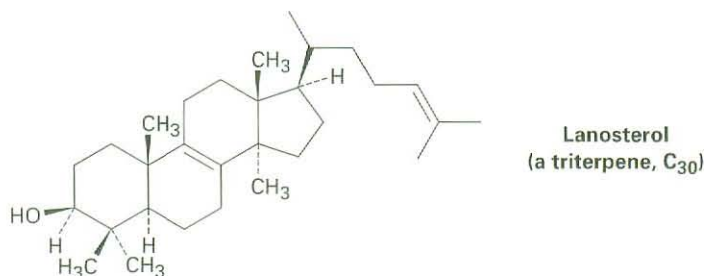
Isoprene itself is not the true biological precursor of terpenoids. As we'll see in Chapter 27, nature instead uses two "isoprene equivalents"—isopentenyl diphosphate and dimethylallyl diphosphate—which are themselves made by two different routes depending on the organism. Lanosterol, in particular, is biosynthesized from acetic acid by a complex pathway that has been worked out in great detail.
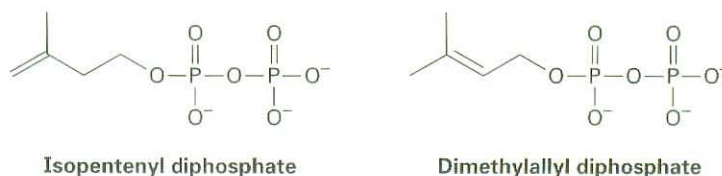
Isopentenyl diphosphate   **Dimethylallyl diphosphate**

SUMMARY AND KEY WORDS

An **alkene** is a hydrocarbon that contains a carbon–carbon double bond. Because they contain fewer hydrogens than alkanes with the same number of carbons, alkenes are said to be **unsaturated**.

Because rotation around the double bond can't occur, substituted alkenes can exist as cis–trans stereoisomers. The geometry of a double bond can be specified by application of the Cahn–Ingold–Prelog sequence rules, which assign priorities to double-bond substituents. If the high-priority groups on each carbon are on the same side of the double bond, the geometry is **Z** (*zusammen,* "together"); if the high-priority groups on each carbon are on opposite sides of the double bond, the geometry is **E** (*entgegen,* "apart").

Alkene chemistry is dominated by **electrophilic addition reactions**. When HX reacts with an unsymmetrically substituted alkene, **Markovnikov's rule** predicts that the H will add to the carbon having fewer alkyl substituents and the X group will add to the carbon having more alkyl substituents. Electrophilic additions to alkenes take place through carbocation intermediates formed by reaction of the nucleophilic alkene π bond with electrophilic H^+. Carbocation stability follows the order

$$\text{Tertiary (3°)} \; > \; \text{Secondary (2°)} \; > \; \text{Primary (1°)} \; > \; \text{Methyl}$$

$$R_3C^+ \quad > \quad R_2CH^+ \quad > \quad RCH_2{}^+ \quad > \quad CH_3{}^+$$

Markovnikov's rule can be restated by saying that, in the addition of HX to an alkene, the more stable carbocation intermediate is formed. This result is explained by the **Hammond postulate**, which says that the transition state of an exergonic reaction step structurally resembles the reactant, whereas the transition state of an endergonic reaction step structurally resembles the product. Since an alkene protonation step is endergonic, the stability of the more highly substituted carbocation is reflected in the stability of the transition state leading to its formation.

Evidence in support of a carbocation mechanism for electrophilic additions comes from the observation that structural rearrangements often take place during reaction. Rearrangements occur by shift of either a hydride ion, :H⁻ (a **hydride shift**), or an alkyl anion, :R⁻, from a carbon atom to the adjacent positively charged carbon. The result is isomerization of a less stable carbocation to a more stable one.

EXERCISES

Organic KNOWLEDGE TOOLS

ThomsonNOW™ Sign in at **www.thomsonedu.com** to assess your knowledge of this chapter's topics by taking a pre-test. The pre-test will link you to interactive organic chemistry resources based on your score in each concept area.

Online homework for this chapter may be assigned in Organic OWL.

■ indicates problems assignable in Organic OWL.

▲ denotes problems linked to Key Ideas of this chapter and testable in ThomsonNOW.

VISUALIZING CHEMISTRY

(Problems 6.1–6.19 appear within the chapter.)

6.20 ■ Name the following alkenes, and convert each drawing into a skeletal structure:
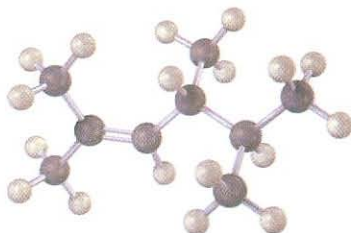
(a)   (b)
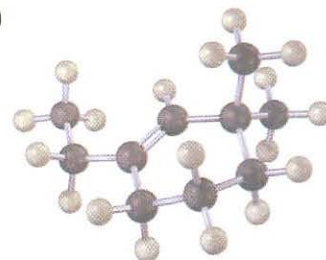
6.21 ■ Assign stereochemistry (*E* or *Z*) to the double bonds in each of the following compounds, and convert each drawing into a skeletal structure (red = O, yellow-green = Cl):
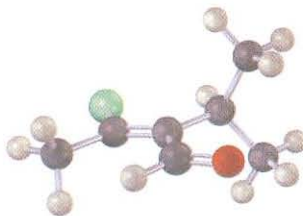
(a)   (b)
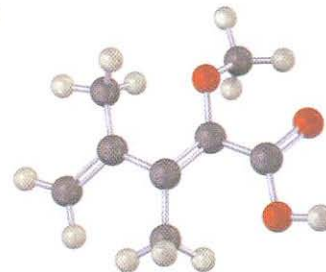
6.22 ■ The following carbocation is an intermediate in the electrophilic addition reaction of HCl with two different alkenes. Identify both, and tell which C—H bonds in the carbocation are aligned for hyperconjugation with the vacant *p* orbital on the positively charged carbon.

ADDITIONAL PROBLEMS

6.23 ■ Calculate the degree of unsaturation in the following formulas, and draw five possible structures for each:
(a) $C_{10}H_{16}$ (b) C_8H_8O (c) $C_7H_{10}Cl_2$
(d) $C_{10}H_{16}O_2$ (e) $C_5H_9NO_2$ (f) $C_8H_{10}ClNO$

6.24 How many hydrogens does each of the following compounds have?
(a) $C_8H_?O_2$, has two rings and one double bond
(b) $C_7H_?N$, has two double bonds
(c) $C_9H_?NO$, has one ring and three double bonds

6.25 Loratadine, marketed as an antiallergy medication under the name Claritin, has four rings, eight double bonds, and the formula $C_{22}H_?ClN_2O_2$. How many hydrogens does loratadine have? (Calculate your answer; don't count hydrogens in the structure.)

Loratadine
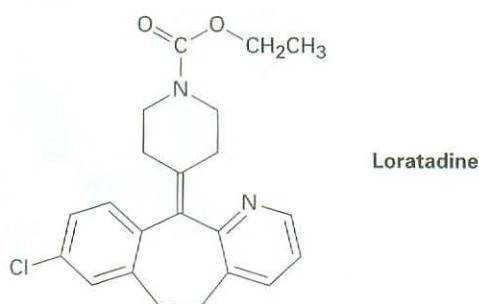
6.26 ■ Name the following alkenes:

(a)

(b)

(c)

(d)

(e)

(f) H_2C=C=CHCH$_3$
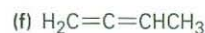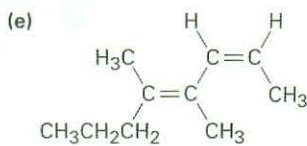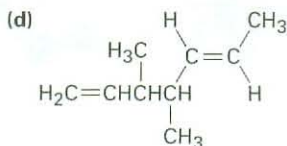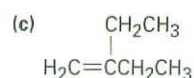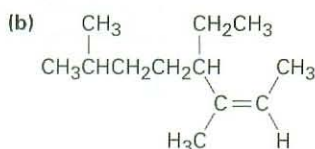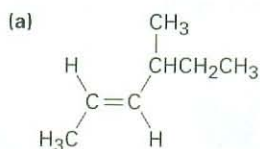
6.27 ■ Ocimene is a triene found in the essential oils of many plants. What is its IUPAC name, including stereochemistry?

Ocimene
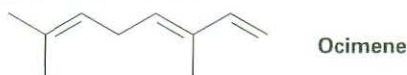
6.28 α-Farnesene is a constituent of the natural wax found on apples. What is its IUPAC name, including stereochemistry?

α-Farnesene

■ Assignable in OWL   ▲ Key Idea Problems
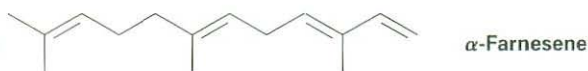
6.29 ■ Draw structures corresponding to the following systematic names:

(a) (4E)-2,4-Dimethyl-1,4-hexadiene
(b) *cis*-3,3-Dimethyl-4-propyl-1,5-octadiene
(c) 4-Methyl-1,2-pentadiene
(d) (3E,5Z)-2,6-Dimethyl-1,3,5,7-octatetraene
(e) 3-Butyl-2-heptene
(f) *trans*-2,2,5,5-Tetramethyl-3-hexene

6.30 ■ Menthene, a hydrocarbon found in mint plants, has the systematic name 1-isopropyl-4-methylcyclohexene. Draw its structure.

6.31 Draw and name the 6 pentene isomers, C_5H_{10}, including *E,Z* isomers.

6.32 Draw and name the 17 hexene isomers, C_6H_{12}, including *E,Z* isomers.

6.33 *trans*-2-Butene is more stable than *cis*-2-butene by only 4 kJ/mol, but *trans*-2,2,5,5-tetramethyl-3-hexene is more stable than its cis isomer by 39 kJ/mol. Explain.

6.34 Cyclodecene can exist in both cis and trans forms, but cyclohexene cannot. Explain. (Making molecular models is helpful.)

6.35 Normally, a trans alkene is *more* stable than its cis isomer. *trans*-Cyclooctene, however, is *less* stable than *cis*-cyclooctene by 38.5 kJ/mol. Explain.

6.36 *trans*-Cyclooctene is less stable than *cis*-cyclooctene by 38.5 kJ/mol, but *trans*-cyclononene is less stable than *cis*-cyclononene by only 12.2 kJ/mol. Explain.

6.37 Allene (1,2-propadiene), $H_2C=C=CH_2$, has two adjacent double bonds. What kind of hybridization must the central carbon have? Sketch the bonding π orbitals in allene. What shape do you predict for allene?

6.38 The heat of hydrogenation for allene (Problem 6.37) to yield propane is -295 kJ/mol, and the heat of hydrogenation for a typical monosubstituted alkene such as propene is -126 kJ/mol. Is allene more stable or less stable than you might expect for a diene? Explain.

6.39 ■ Predict the major product in each of the following reactions:

(a)

$$CH_3CH_2CH=\overset{\overset{\displaystyle CH_3}{|}}{C}CH_2CH_3 \quad \xrightarrow[H_2SO_4]{H_2O} \quad ?$$

(Addition of H_2O occurs.)

(b)
 $\xrightarrow{HBr}$?

(c)
 $\xrightarrow{HBr}$?

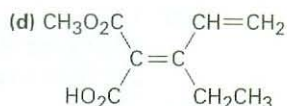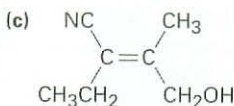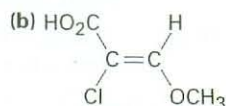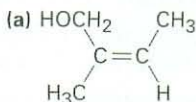(d) $H_2C=CHCH_2CH_2CH_2CH=CH_2 \quad \xrightarrow{2\ HCl} \quad ?$
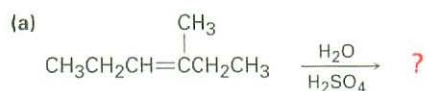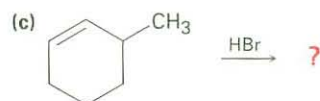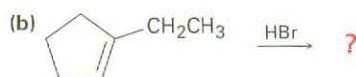
6.40 ■ Predict the major product from addition of HBr to each of the following alkenes:

(a)

(b)

(c)
$$CH_3CH=\overset{\overset{\displaystyle CH_3}{|}}{C}HCHCH_3$$
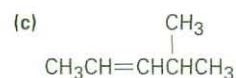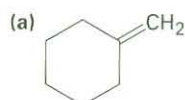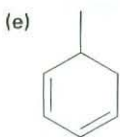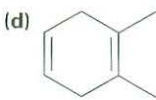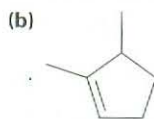

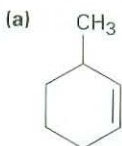
6.41 ■ Rank the following sets of substituents in order of priority according to the Cahn–Ingold–Prelog sequence rules:

(a) $-CH_3$, $-Br$, $-H$, $-I$

(b) $-OH$, $-OCH_3$, $-H$, $-CO_2H$

(c) $-CO_2H$, $-CO_2CH_3$, $-CH_2OH$, $-CH_3$

(d) $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2OH$, $-\overset{\overset{\displaystyle O}{\|}}{C}CH_3$

(e) $-CH=CH_2$, $-CN$, $-CH_2NH_2$, $-CH_2Br$

(f) $-CH=CH_2$, $-CH_2CH_3$, $-CH_2OCH_3$, $-CH_2OH$
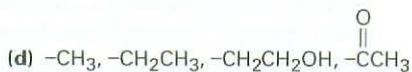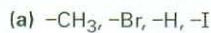
6.42 ▲ Assign E or Z configuration to each of the following alkenes:

(a)
$$\begin{array}{ccc} HOCH_2 & & CH_3 \\ & C{=}C & \\ H_3C & & H \end{array}$$

(b)
$$\begin{array}{ccc} HO_2C & & H \\ & C{=}C & \\ Cl & & OCH_3 \end{array}$$

(c)
$$\begin{array}{ccc} NC & & CH_3 \\ & C{=}C & \\ CH_3CH_2 & & CH_2OH \end{array}$$

(d)
$$\begin{array}{ccc} CH_3O_2C & & CH{=}CH_2 \\ & C{=}C & \\ HO_2C & & CH_2CH_3 \end{array}$$

6.43 ■ Name the following cycloalkenes:

(a)

(b)

(c)

(d)

(e)

(f)
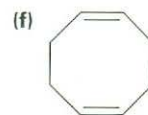
6.44 Fucoserraten, ectocarpen, and multifidene are sex pheromones produced by marine brown algae. What are their systematic names? (The latter two are a bit difficult; make your best guess.)
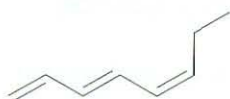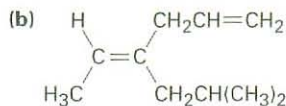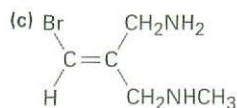

Fucoserraten
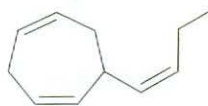
Ectocarpen
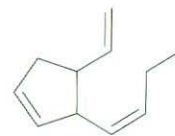
Multifidene

6.45 ▲ Which of the following *E,Z* designations are correct, and which are incorrect?

(a) CH₃


Z

(b) H CH₂CH=CH₂

E

(c) Br CH₂NH₂

Z

(d) NC CH₃

E

(e) Br

Z

(f) HOCH₂ CO₂H
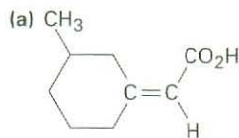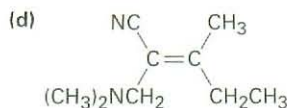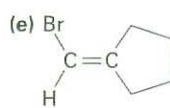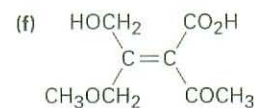
E

6.46 ▲ *tert*-Butyl esters [RCO₂C(CH₃)₃] are converted into carboxylic acids (RCO₂H) by reaction with trifluoroacetic acid, a reaction useful in protein synthesis (Section 26.7). Assign *E,Z* designation to the double bonds of both reactant and product in the following scheme, and explain why there is an apparent change of double-bond stereochemistry:
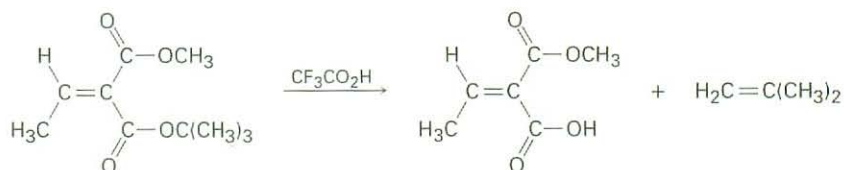

6.47 ■ Each of the following carbocations can rearrange to a more stable ion. Propose structures for the likely rearrangement products.

(a) $CH_3CH_2CH_2CH_2{}^+$ (b) $CH_3\overset{+}{C}HCHCH_3$ (c)
                                              |
 CH_3
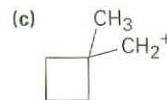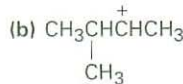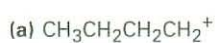
6.48 Addition of HCl to 1-isopropylcyclohexene yields a rearranged product. Propose a mechanism, showing the structures of the intermediates and using curved arrows to indicate electron flow in each step.

6.49   Addition of HCl to 1-isopropenyl-1-methylcyclopentane yields 1-chloro-1,2,2-trimethylcyclohexane. Propose a mechanism, showing the structures of the intermediates and using curved arrows to indicate electron flow in each step.
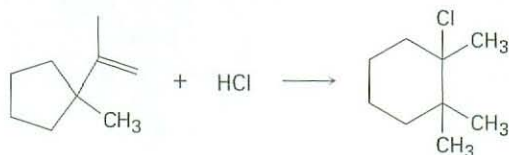
6.50   Vinylcyclopropane reacts with HBr to yield a rearranged alkyl bromide. Follow the flow of electrons as represented by the curved arrows, show the structure of the carbocation intermediate in brackets, and show the structure of the final product.
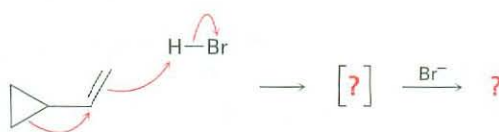
Vinylcyclopropane

6.51   ■ Calculate the degree of unsaturation in each of the following formulas:
   (a) Cholesterol, $C_{27}H_{46}O$ (b) DDT, $C_{14}H_9Cl_5$
   (c) Prostaglandin E_1, $C_{20}H_{34}O_5$ (d) Caffeine, $C_8H_{10}N_4O_2$
   (e) Cortisone, $C_{21}H_{28}O_5$ (f) Atropine, $C_{17}H_{23}NO_3$

6.52   The isobutyl cation spontaneously rearranges to the *tert*-butyl cation by a hydride shift. Is the rearrangement exergonic or endergonic? Draw what you think the transition state for the hydride shift might look like according to the Hammond postulate.


Isobutyl cation   ***tert*-Butyl cation**

6.53   Draw an energy diagram for the addition of HBr to 1-pentene. Let one curve on your diagram show the formation of 1-bromopentane product and another curve on the same diagram show the formation of 2-bromopentane product. Label the positions for all reactants, intermediates, and products. Which curve has the higher-energy carbocation intermediate? Which curve has the higher-energy first transition state?

6.54   Make sketches of the transition-state structures involved in the reaction of HBr with 1-pentene (Problem 6.53). Tell whether each structure resembles reactant or product.

■ Assignable in OWL   ▲ Key Idea Problems

6.55 Limonene, a fragrant hydrocarbon found in lemons and oranges, is bio-synthesized from geranyl diphosphate by the following pathway. Add curved arrows to show the mechanism of each step. Which step involves an alkene electrophilic addition? (The ion $OP_2O_6^{4-}$ is the diphosphate ion, and "Base" is an unspecified base in the enzyme that catalyzes the reaction.)

$$+ \ OP_2O_6^{4-}$$

Geranyl diphosphate   **H**   **Limonene**
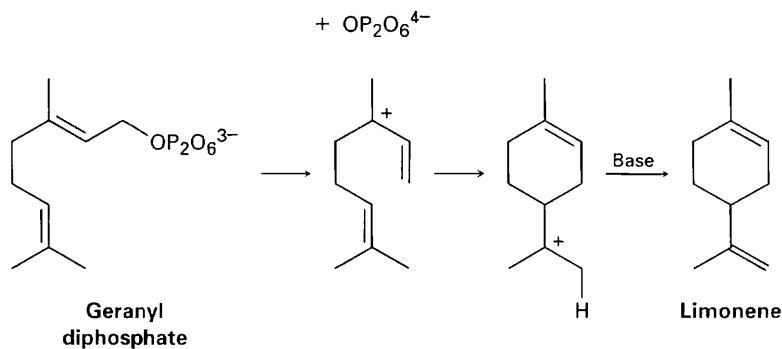
6.56 *epi*-Aristolochene, a hydrocarbon found in both pepper and tobacco, is bio-synthesized by the following pathway. Add curved arrows to show the mecha-nism of each step. Which steps involve alkene electrophilic addition(s), and which involve carbocation rearrangement(s)? (The abbreviation H−A stands for an unspecified acid, and "Base" is an unspecified base in the enzyme.)


epi-**Aristolochene**
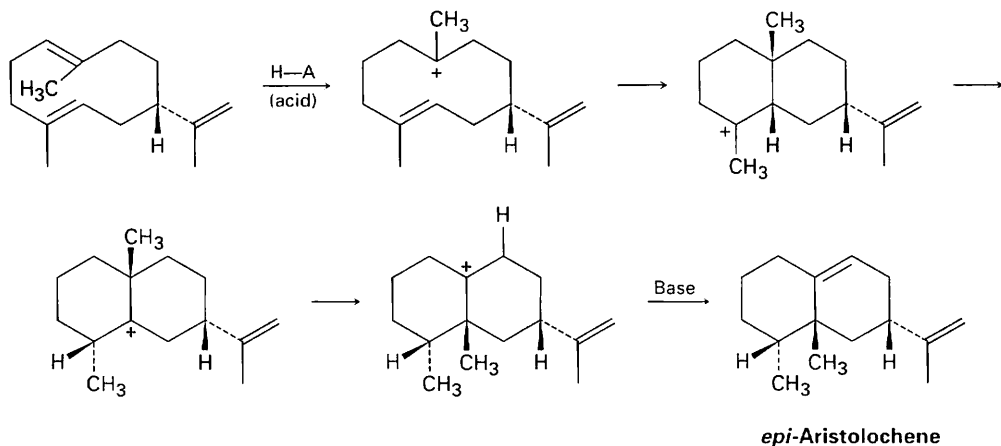
6.57 Aromatic compounds such as benzene react with alkyl chlorides in the pres-ence of $AlCl_3$ catalyst to yield alkylbenzenes. The reaction occurs through a carbocation intermediate, formed by reaction of the alkyl chloride with $AlCl_3$ ($R-Cl + AlCl_3 \rightarrow R^+ + AlCl_4^-$). How can you explain the observation that reaction of benzene with 1-chloropropane yields isopropylbenzene as the major product?
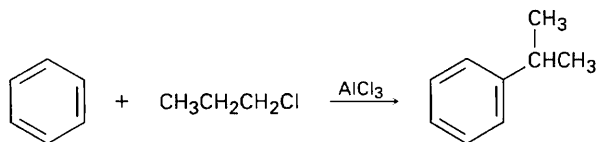
6.58 ▲ Alkenes can be converted into alcohols by acid-catalyzed addition of water. Assuming that Markovnikov's rule is valid, predict the major alcohol product from each of the following alkenes.

(a)
$$CH_3$$
$$CH_3CH_2C=CHCH_3$$

(b)
$$=CH_2$$

(c)
$$CH_3$$
$$CH_3CHCH_2CH=CH_2$$
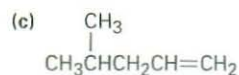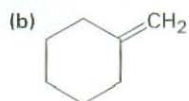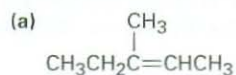
6.59 Reaction of 2,3-dimethyl-1-butene with HBr leads to an alkyl bromide, $C_6H_{13}Br$. On treatment of this alkyl bromide with KOH in methanol, elimination of HBr to give an alkene occurs and a hydrocarbon that is isomeric with the starting alkene is formed. What is the structure of this hydrocarbon, and how do you think it is formed from the alkyl bromide?