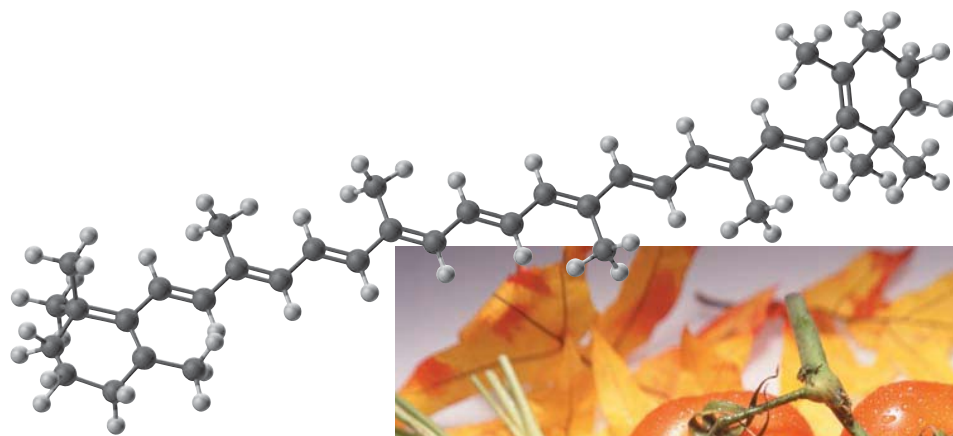# 04

Alkenes and Alkynes

Carotene and carotene-like molecules are partnered with chlorophyll in nature to assist in the harvest of sunlight. In autumn, green chlorophyll molecules are destroyed and the yellows and reds of carotene and related molecules become visible. The red color of tomatoes comes from lycopene, a molecule closely related to carotene. See Problems 4.37 and 4.38. Inset: A model of β-carotene. (Charles D. Winters)

IN THIS CHAPTER, we begin our study of unsaturated hydrocarbons. An unsaturated hydrocarbon is a hydrocarbon that has fewer hydrogens bonded to carbon than an alkane has. There are three classes of unsaturated hydrocarbons: alkenes, alkynes, and arenes. **Alkenes** contain one or more carbon–carbon double bonds, and **alkynes** contain one or more carbon–carbon triple bonds. Ethene (ethylene) is the simplest alkene, and ethyne (acetylene) is the simplest alkyne:

Alkene   An unsaturated hydrocarbon that contains a carbon–carbon double bond.

Alkyne   An unsaturated hydrocarbon that contains a carbon–carbon triple bond.
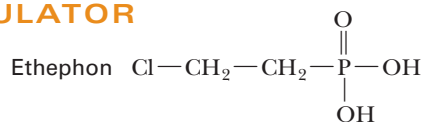

Ethene
(an alkene)

Ethyne
(an alkyne)

108
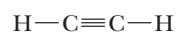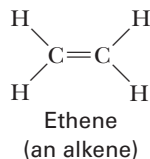
Chemical Connections 4A

ETHYLENE, A PLANT GROWTH REGULATOR

Ethylene occurs only in trace amounts in nature. Still, scientists have discovered that this small molecule is a natural ripening agent for fruits. Thanks to this knowledge, fruit growers can pick fruit while it is green and less susceptible to bruising. Then, when they are ready to pack the fruit for shipment, the growers can treat it with ethylene gas to induce ripening. Alternatively, the fruit can be treated with ethephon (Ethrel), which slowly releases ethylene and initiates ripening.

$$\text{Ethephon} \quad \text{Cl}-\text{CH}_2-\text{CH}_2-\overset{\displaystyle \overset{O}{\|}}{\underset{\displaystyle \underset{OH}{|}}{P}}-\text{OH}$$

The next time you see ripe bananas in the market, you might wonder when they were picked and whether their ripening was artificially induced.

Question

Explain the basis for the saying "A rotten apple can spoil the barrel."

Arenes are the third class of unsaturated hydrocarbons. The characteristic structural feature of an arene is the presence of one or more benzene rings. The simplest arene is benzene:

although benzene and other arenes contain C–C double bonds, we must remember that their double bonds are not reactive in the ways we will describe in Chapters 5–8 (i.e., we will leave them unreacted in reactions that we cover in these chapters)

**Arene** A compound containing one or more benzene rings.
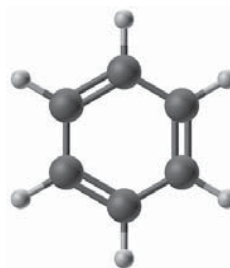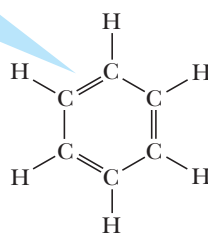
Benzene
(an arene)

The chemistry of benzene and its derivatives is quite different from that of alkenes and alkynes. Even though we do not study the chemistry of arenes until Chapter 9, we will show structural formulas of compounds containing benzene rings in earlier chapters. What you need to remember at this point is that a benzene ring is not chemically reactive under any of the conditions we describe in Chapters 4–8.

Compounds containing carbon–carbon double bonds are especially widespread in nature. Furthermore, several low-molecular-weight alkenes, including ethylene and propene, have enormous commercial importance in our modern, industrialized society. The organic chemical industry produces more pounds of ethylene worldwide than any other chemical. Annual production in the United States alone exceeds 20 billion kg (45 billion pounds).

What is unusual about ethylene is that it occurs only in trace amounts in nature. The enormous amounts of it required to meet the needs of the chemical industry are derived the world over by thermal cracking of hydrocarbons. In the United States and other areas of the world with vast reserves of natural gas, the major process for the production of ethylene is thermal cracking of the small quantities of ethane extracted from natural gas. In **thermal cracking**, a saturated hydrocarbon is converted to an unsaturated hydrocarbon plus H_2. Heating ethane in a furnace to 800–900 °C for a fraction of a second cracks it to ethylene and hydrogen.

$$\text{CH}_3\text{CH}_3 \xrightarrow[\text{(thermal cracking)}]{800–900\,°C} \text{CH}_2{=}\text{CH}_2 + \text{H}_2$$

Ethane   Ethylene
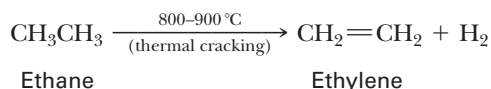
Europe, Japan, and other areas of the world with limited supplies of natural gas depend almost entirely on thermal cracking of petroleum for their ethylene.

The crucial point to recognize is that ethylene and all of the commercial and industrial products made from it are derived from either natural gas or petroleum—both nonrenewable natural resources!

4.1 What Are the Structures and Shapes of Alkenes and Alkynes?
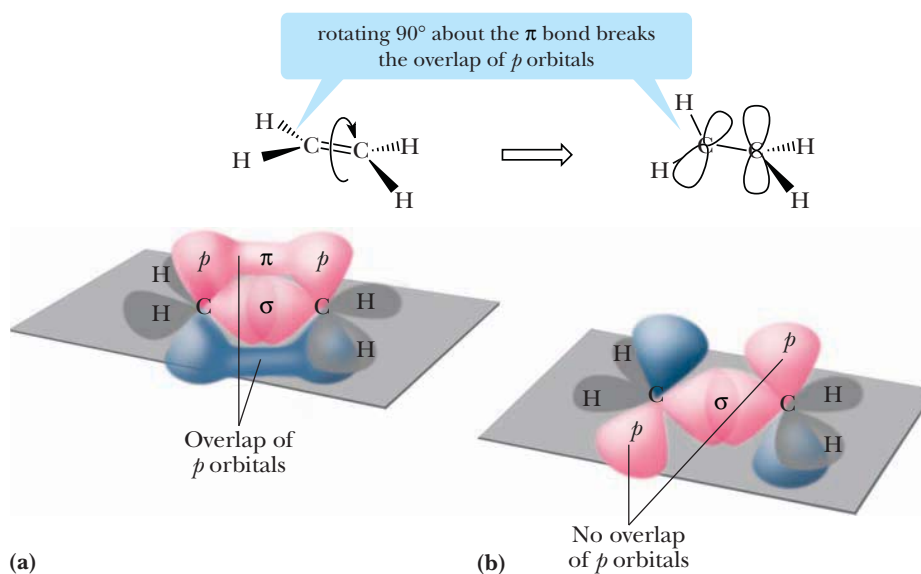
A. Shapes of Alkenes

Using valence-shell electron-pair repulsion (VSEPR; Section 1.3), we predict a value of 120° for the bond angles about each carbon in a double bond. The observed H—C—C bond angle in ethylene is 121.7°, a value close to that predicted by VSEPR. In other alkenes, deviations from the predicted angle of 120° may be somewhat larger as a result of strain between groups bonded to one or both carbons of the double bond. The C—C—C bond angle in propene, for example, is 124.7°.

Ethylene Propene
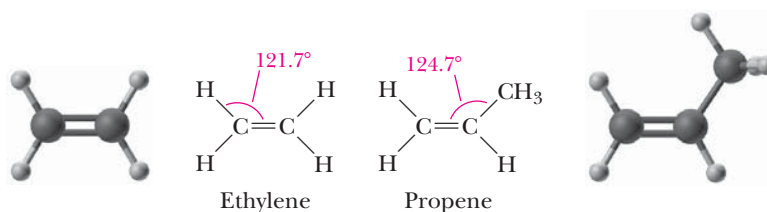
B. Orbital Overlap Model of a Carbon–Carbon Double Bond

In Section 1.6D, we described the formation of a carbon–carbon double bond in terms of the overlap of atomic orbitals. A carbon–carbon double bond consists of one sigma bond and one pi bond. Each carbon of the double bond uses its three sp^2 hybrid orbitals to form sigma bonds to three atoms. The unhybridized $2p$ atomic orbitals, which lie perpendicular to the plane created by the axes of the three sp^2 hybrid orbitals, combine to form the pi bond of the carbon–carbon double bond.

It takes approximately 264 kJ/mol (63 kcal/mol) to break the pi bond in ethylene—that is, to rotate one carbon by 90° with respect to the other so that no overlap occurs between $2p$ orbitals on adjacent carbons (Figure 4.1). This energy is considerably greater than
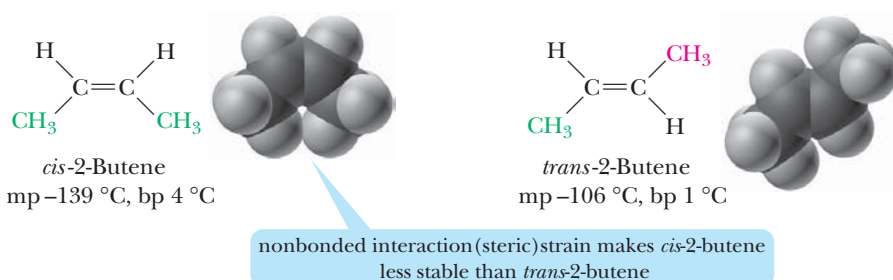
rotating 90° about the π bond breaks the overlap of p orbitals

Overlap of p orbitals

No overlap of p orbitals

(a)

(b)

the thermal energy available at room temperature, and, as a consequence, rotation about a carbon–carbon double bond is severely restricted. You might compare rotation about a carbon–carbon double bond, such as the bond in ethylene, with that about a carbon–carbon single bond, such as the bond in ethane (Section 3.6A). Whereas rotation about the carbon–carbon single bond in ethane is relatively free (the energy barrier is approximately 13 kJ/mol), rotation about the carbon–carbon double bond in ethylene is restricted (the energy barrier is approximately 264 kJ/mol).

C. *Cis–Trans* Isomerism in Alkenes

Because of restricted rotation about a carbon–carbon double bond, an alkene in which each carbon of the double bond has two different groups bonded to it shows *cis–trans* isomerism.

Cis–trans isomerism
Isomers that have the same order of attachment of their atoms, but a different arrangement of their atoms in space due to the presence of either a ring (Chapter 3) or a carbon–carbon double bond (Chapter 4).

cis-2-Butene
mp –139 °C, bp 4 °C

trans-2-Butene
mp –106 °C, bp 1 °C

nonbonded interaction (steric) strain makes *cis*-2-butene less stable than *trans*-2-butene

Consider, for example, 2-butene: In *cis*-2-butene, the two methyl groups are on the same side of the double bond; in *trans*-2-butene, the two methyl groups are on opposite sides of the double bond. These two compounds cannot be converted into one another at room temperature because of the restricted rotation about the double bond; they are different compounds, with different physical and chemical properties.

It takes approximately 264 kJ (63 kcal/mol) to break the π bond of ethylene—that is, to rotate one carbon by 90° with respect to the other where there is zero overlap between the $2p$ orbitals of adjacent carbons (Figure 4.1). This energy is considerably greater than the thermal energy available at room temperature; consequently, rotation about a carbon–carbon double bond does not occur under normal conditions.

Cis alkenes are less stable than their *trans* isomers because of nonbonded interaction strain between alkyl substituents on the same side of the double bond in the *cis* isomer, as can be seen in space-filling models of the *cis* and *trans* isomers of 2-butene. This is the same type of steric strain that results in the preference for equatorial methylcyclohexane over axial methylcyclohexane (Section 3.6B).

Charles D. Winters

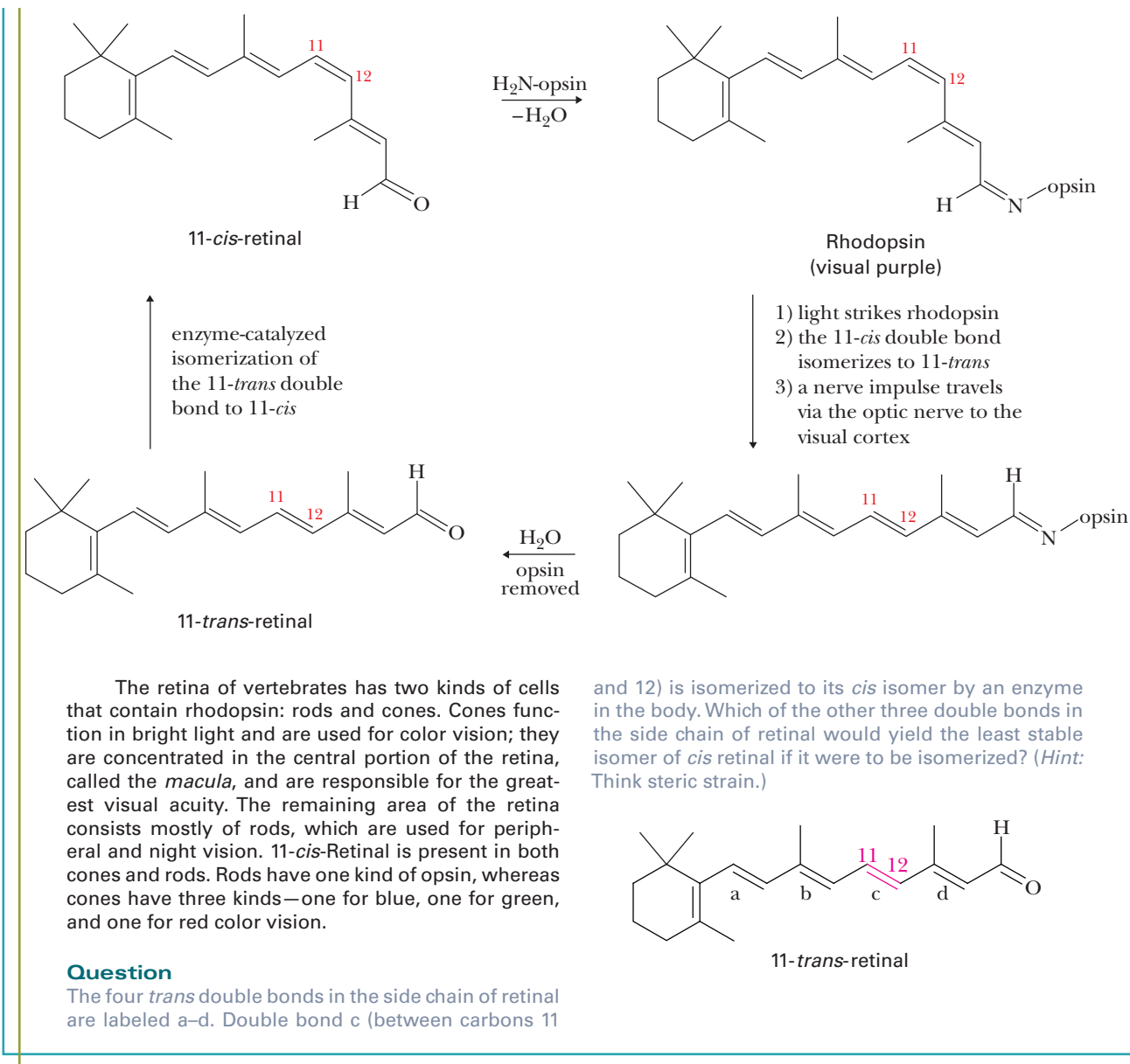The combustion of acetylene yields energy that produces the very hot temperatures of an oxyacetylene torch.

Chemical Connections 4B

CIS–TRANS ISOMERISM IN VISION

The retina—the light-detecting layer in the back of our eyes—contains reddish compounds called *visual pigments*. Their name, *rhodopsin*, is derived from the Greek word meaning "rose colored." Each rhodopsin molecule is a combination of one molecule of a protein called opsin and one molecule of 11-*cis*-retinal, a derivative of vitamin A in which the CH₂OH group of the vitamin is converted to an aldehyde group, —CHO, and the double bond between carbons 11 and 12 of the side chain is in the less stable *cis* configuration. When rhodopsin absorbs light energy, the less stable 11-*cis* double bond is converted to the more stable 11-*trans* double bond. This isomerization changes the shape of the rhodopsin molecule, which in turn causes the neurons of the optic nerve to fire and produce a visual image.

11-*cis*-retinal

H₂N-opsin
−H₂O

Rhodopsin
(visual purple)

enzyme-catalyzed
isomerization of
the 11-*trans* double
bond to 11-*cis*

1) light strikes rhodopsin
2) the 11-*cis* double bond
   isomerizes to 11-*trans*
3) a nerve impulse travels
   via the optic nerve to the
   visual cortex

11-*trans*-retinal

H₂O
opsin
removed

The retina of vertebrates has two kinds of cells that contain rhodopsin: rods and cones. Cones function in bright light and are used for color vision; they are concentrated in the central portion of the retina, called the *macula*, and are responsible for the greatest visual acuity. The remaining area of the retina consists mostly of rods, which are used for peripheral and night vision. 11-*cis*-Retinal is present in both cones and rods. Rods have one kind of opsin, whereas cones have three kinds—one for blue, one for green, and one for red color vision.

Question
The four *trans* double bonds in the side chain of retinal are labeled a–d. Double bond c (between carbons 11

and 12) is isomerized to its *cis* isomer by an enzyme in the body. Which of the other three double bonds in the side chain of retinal would yield the least stable isomer of *cis* retinal if it were to be isomerized? (*Hint:* Think steric strain.)

11-*trans*-retinal

D.   Structure of Alkynes

The functional group of an alkyne is a **carbon–carbon triple bond**. The simplest alkyne is ethyne, C_2H_2. Ethyne is a linear molecule; all of its bond angles are 180° (Figure 1.10).
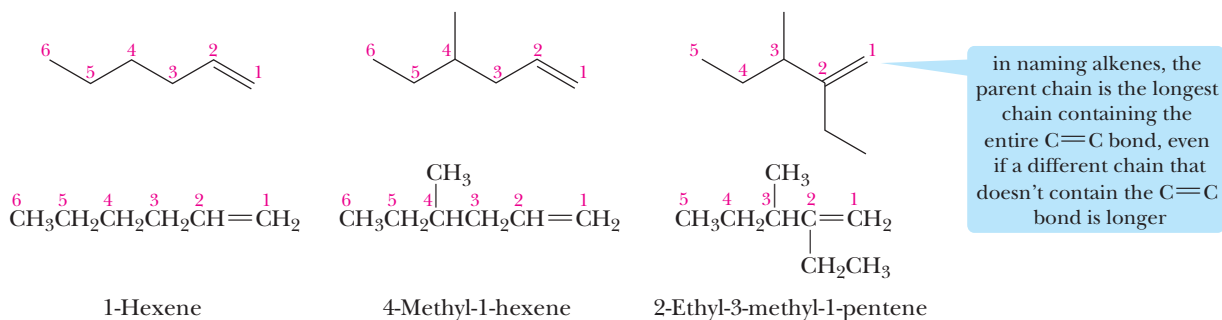
According to the orbital overlap model (Section 1.6F), a triple bond is described in terms of the overlap of sp hybrid orbitals of adjacent carbons to form a sigma bond, the overlap of parallel $2p_y$ orbitals to form one pi bond, and the overlap of parallel $2p_z$ orbitals to form the second pi bond. In ethyne, each carbon forms a bond to a hydrogen by the overlap of an sp hybrid orbital of carbon with a $1s$ atomic orbital of hydrogen.

4.2   How Do We Name Alkenes and Alkynes?

Alkenes are named using the IUPAC system, but, as we shall see, some are still referred to by their common names.
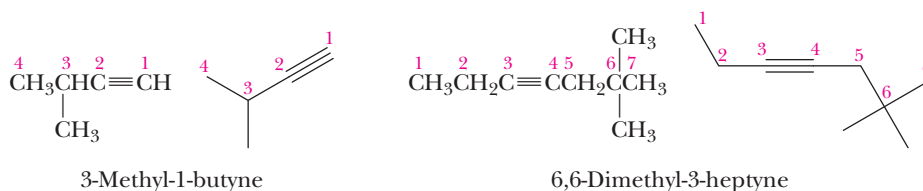
A. IUPAC Names

We form IUPAC names of alkenes by changing the **-an-** infix of the parent alkane to **-en-** (Section 3.5). Hence, $CH_2\!=\!CH_2$ is named ethene, and $CH_3CH\!=\!CH_2$ is named propene. In higher alkenes, where isomers exist that differ in the location of the double bond, we use a numbering system. We number the longest carbon chain that contains the double bond in the direction that gives the carbon atoms of the double bond the lower set of numbers. We then use the number of the first carbon of the double bond to show its location. We name branched or substituted alkenes in a manner similar to the way we name alkanes (Section 3.3). We number the carbon atoms, locate the double bond, locate and name substituent groups, and name the main (parent) chain.
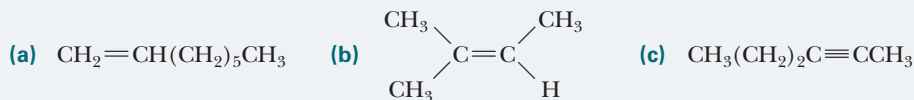

> in naming alkenes, the parent chain is the longest chain containing the entire C=C bond, even if a different chain that doesn't contain the C=C bond is longer

$$6 \quad 5 \quad 4 \quad 3 \quad 2 \quad 1$$
$$CH_3CH_2CH_2CH_2CH\!=\!CH_2$$

1-Hexene

$$CH_3$$
$$6 \quad 5 \quad 4 \quad | \quad 3 \quad 2 \quad 1$$
$$CH_3CH_2CHCH_2CH\!=\!CH_2$$

4-Methyl-1-hexene

$$CH_3$$
$$5 \quad 4 \quad 3 \quad | \quad 2 \quad 1$$
$$CH_3CH_2CHC\!=\!CH_2$$
$$|$$
$$CH_2CH_3$$

2-Ethyl-3-methyl-1-pentene

Note that there is a six-carbon chain in 2-ethyl-3-methyl-1-pentene. However, because the longest chain that contains the carbon–carbon double bond has only five carbons, the parent hydrocarbon is pentane, and we name the molecule as a disubstituted 1-pentene.

We form IUPAC names of alkynes by changing the **-an-** infix of the parent alkane to **-yn-** (Section 3.5). Thus, $HC\!\equiv\!CH$ is named ethyne, and $CH_3C\!\equiv\!CH$ is named propyne. The IUPAC system retains the name *acetylene*; therefore, there are two acceptable names for $HC\!\equiv\!CH$: *ethyne* and *acetylene*. Of these two names, *acetylene* is used much more frequently. For larger molecules, we number the longest carbon chain that contains the triple bond from the end that gives the triply bonded carbons the lower set of numbers. We indicate the location of the triple bond by the number of the first carbon of the triple bond.

$$4 \quad 3 \quad 2 \quad 1$$
$$CH_3CHC\!\equiv\!CH$$
$$|$$
$$CH_3$$

3-Methyl-1-butyne

$$CH_3$$
$$1 \quad 2 \quad 3 \quad 4 \; 5 \quad 6 | 7$$
$$CH_3CH_2C\!\equiv\!CCH_2CCH_3$$
$$|$$
$$CH_3$$

6,6-Dimethyl-3-heptyne

EXAMPLE 4.1

Write the IUPAC name of each unsaturated hydrocarbon:

(a) $CH_2\!=\!CH(CH_2)_5CH_3$

(b)
$$CH_3 \qquad CH_3$$
$$\diagdown \qquad \diagup$$
$$C\!=\!C$$
$$\diagup \qquad \diagdown$$
$$CH_3 \qquad H$$

(c) $CH_3(CH_2)_2C\!\equiv\!CCH_3$

STRATEGY

First look for the longest carbon chain that contains the multiple bond. This chain determines the root name. Number the carbon chain to give the placement of the multiple bond the lowest possible set of numbers. Then identify substituents and give each a name and a number. Locate the position of the multiple bond by the number of its first carbon.
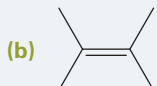
SOLUTION

(a) 1-Octene (b) 2-Methyl-2-butene (c) 2-Hexyne
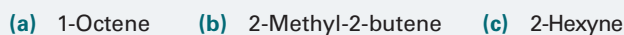
See problems 4.15–4.20

PROBLEM   4.1

Write the IUPAC name of each unsaturated hydrocarbon:

(a)   (b)   (c)

B.   Common Names

Despite the precision and universal acceptance of IUPAC nomenclature, some alkenes, particularly those with low molecular weight, are known almost exclusively by their common names, as illustrated by the common names of these alkenes:

$$CH_2{=}CH_2 \qquad CH_3CH{=}CH_2 \qquad CH_3\overset{CH_3}{\underset{|}{C}}{=}CH_2$$

IUPAC name: Ethene   Propene   2-Methylpropene
Common name: Ethylene   Propylene   Isobutylene

Furthermore, the common names **methylene** (a CH_2 group), **vinyl**, and **allyl** are often used to show the presence of the following alkenyl groups.

Alkenyl Group	Common Name	Example	Common Name
$CH_2{=}CH{-}$	Vinyl	$-CH{=}CH_2$	Vinylcyclopentane
$CH_2{=}CHCH_2{-}$	Allyl	$-CH_2CH{=}CH_2$	Allylcyclopentane

C.   Systems for Designating Configuration in Alkenes

The *Cis–Trans* System

The most common method for specifying the configuration of a disubstituted alkene uses the prefixes *cis* and *trans*. In this system, the orientation of the atoms of the parent chain determines whether the alkene is *cis* or *trans*. Following are structural formulas for the *cis* and *trans* isomers of 4-methyl-2-pentene:

cis-4-Methyl-2-pentene   *trans*-4-Methyl-2-pentene
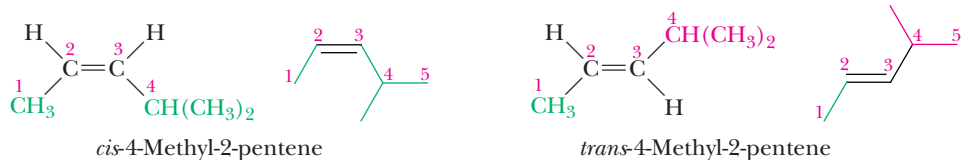
In the *cis* example, carbon atoms of the main chain (carbons 1 and 4) are on the same side of the double bond. In the *trans* example, the same carbon atoms of the main chain are on opposite sides of the double bond.

EXAMPLE   4.2

Name each alkene, and, using the *cis–trans* system, show the configuration about each double bond:

(a)   (b)
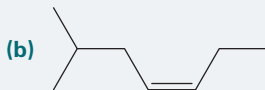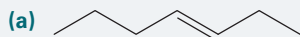
STRATEGY

Locate the longest carbon chain that contains the multiple bond and number it from the end that gives the lower set of numbers to the carbon atoms of the multiple bond. Indicate the location of the multiple bond by the number of its first

carbon atom. Configuration of a carbon–carbon double bond (*cis* or *trans*) in a common name is determined by the orientation of the carbon atoms of the parent chain relative to each other. If you are having difficulty discerning the orientation of the carbon atoms, draw in the hydrogen atoms on the C=C bond and determine their orientation relative to each other.

SOLUTION

(a) The chain contains seven carbon atoms and is numbered from the end that gives the lower number to the first carbon of the double bond. The carbon atoms of the parent chain are on opposite sides

of the double bond. The compound's name is *trans*-3-heptene.

(b) The longest chain contains seven carbon atoms and is numbered from the right, so that the first carbon of the double bond is carbon 3 of the chain. The carbon atoms of the parent chain are on the same side of the double bond. The compound's name is *cis*-6-methyl-3-heptene.

See problems 4.21, 4.22

PROBLEM 4.2

Name each alkene, and, using the *cis–trans* system, specify its configuration:

(a)

(b)
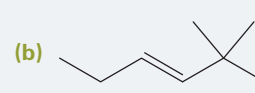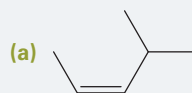
The E,Z System

The **E,Z system** must be used for tri- and tetrasubstituted alkenes. This system uses a set of rules to assign priorities to the substituents on each carbon of a double bond. If the groups of higher priority are on the same side of the double bond, the configuration of the alkene is **Z** (German: *zusammen*, together). If the groups of higher priority are on opposite sides of the double bond, the configuration is **E** (German: *entgegen*, opposite).
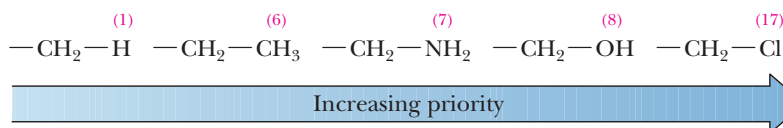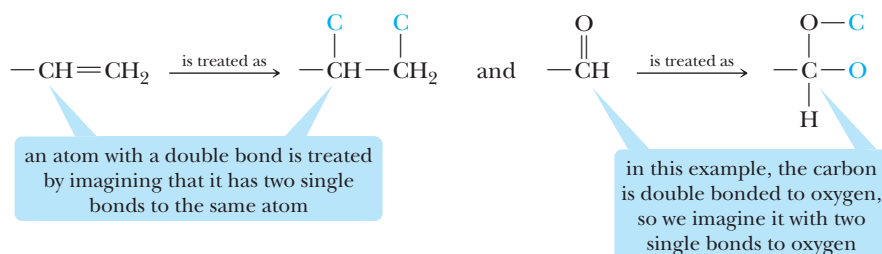
E,Z system A system used to specify the configuration of groups about a carbon–carbon double bond.

Z From the German *zusammen*, meaning together; specifies that groups of higher priority on the carbons of a double bond are on the same side.

higher   higher   higher   lower

$$\text{C}=\text{C}$$

lower   lower   lower   higher

Z (*zusammen*)   **E** (*entgegen*)
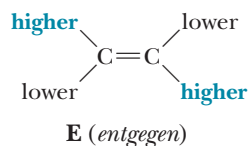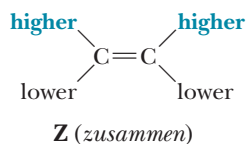
The first step in assigning an E or a Z configuration to a double bond is to label the two groups bonded to each carbon in order of priority.

E From the German *entgegen*, meaning opposite; specifies that groups of higher priority on the carbons of a double bond are on opposite sides.

Priority Rules

1. Priority is based on atomic number: The higher the atomic number, the higher is the priority. Following are several substituents arranged in order of increasing priority (the atomic number of the atom determining priority is shown in parentheses):

(1)   (6)   (7)   (8)   (16)   (17)   (35)   (53)
—H, —CH$_3$, —NH$_2$, —OH, —SH, —Cl, —Br, —I

Increasing priority →
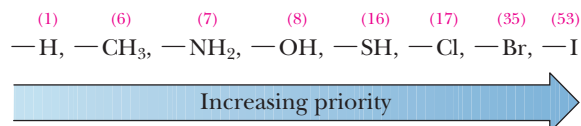
2. If priority cannot be assigned on the basis of the atoms that are bonded directly to the double bond, look at the next set of atoms, and continue until a priority can be assigned. Priority is assigned at the first point of difference. Following is a series of groups, arranged in order of increasing priority (again, numbers in parentheses give the atomic number of the atom on which the assignment of priority is based):

(1)   (6)   (7)   (8)   (17)
—CH$_2$—H   —CH$_2$—CH$_3$ —CH$_2$—NH$_2$ —CH$_2$—OH   —CH$_2$—Cl
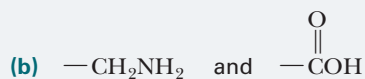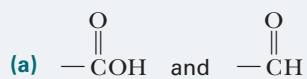
Increasing priority →

3. In order to compare carbons that are not sp^3 hybridized, the carbons must be manipulated in a way that allows us to maximize the number of groups bonded to them. Thus, we treat atoms participating in a double or triple bond as if they are bonded to an equivalent number of similar atoms by single bonds; that is, atoms of a double bond are replicated. Accordingly,

$$-CH{=}CH_2 \xrightarrow{\text{is treated as}} \begin{array}{c} C \quad C \\ | \quad | \\ -CH-CH_2 \end{array} \quad \text{and} \quad \begin{array}{c} O \\ \| \\ -CH \end{array} \xrightarrow{\text{is treated as}} \begin{array}{c} O-C \\ | \\ -C-O \\ | \\ H \end{array}$$

an atom with a double bond is treated by imagining that it has two single bonds to the same atom

in this example, the carbon is double bonded to oxygen, so we imagine it with two single bonds to oxygen

---

EXAMPLE 4.3

Assign priorities to the groups in each set:

(a)
$$\begin{array}{c} O \\ \| \\ -COH \end{array} \quad \text{and} \quad \begin{array}{c} O \\ \| \\ -CH \end{array}$$

(b)
$$-CH_2NH_2 \quad \text{and} \quad \begin{array}{c} O \\ \| \\ -COH \end{array}$$

STRATEGY

Priority is based on atomic number; the higher the atomic number, the higher the priority. If priority cannot be determined on the basis of the atoms bonded directly to the carbon–carbon double bond, continue to the next set of atoms and continue in this manner until a priority can be assigned.

See problems 4.23, 4.27, 4.28, 4.32

SOLUTION

(a) The first point of difference is the O of the —OH in the carboxyl group, compared with the —H in the aldehyde group. The carboxyl group is higher in priority:

$$\begin{array}{c} O \\ \| \\ -C-O-H \end{array} \qquad \begin{array}{c} O \\ \| \\ -C-H \end{array}$$

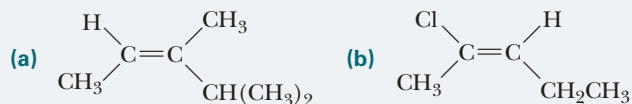Carboxyl group (higher priority)   Aldehyde group (lower priority)
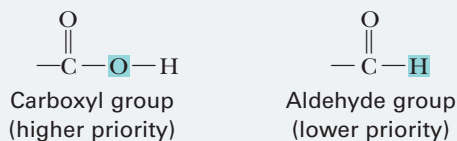
(b) Oxygen has a higher priority (higher atomic number) than nitrogen. Therefore, the carboxyl group has a higher priority than the primary amino group:

$$-CH_2NH_2 \qquad \begin{array}{c} O \\ \| \\ -COH \end{array}$$

lower priority   higher priority
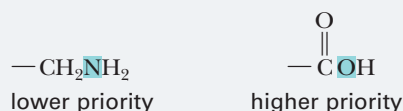
EXAMPLE 4.4

Name each alkene and specify its configuration by the E,Z system:

(a)
$$\begin{array}{c} H \\ \diagdown \\ CH_3 \end{array} C{=}C \begin{array}{c} CH_3 \\ \diagup \\ CH(CH_3)_2 \end{array}$$

(b)
$$\begin{array}{c} Cl \\ \diagdown \\ CH_3 \end{array} C{=}C \begin{array}{c} H \\ \diagup \\ CH_2CH_3 \end{array}$$

STRATEGY

Assign a priority to each atom or group of atoms on the carbon–carbon double bond. If the groups of higher priority are on the same side of the double bond, the alkene has the Z configuration; if they are on opposite sides, the alkene has the E configuration.

SOLUTION

(a) The group of higher priority on carbon 2 is methyl; that of higher priority on carbon 3 is isopropyl. Because the groups of higher priority are on the same side of the carbon–carbon double bond, the alkene has the Z configuration. Its name is (Z)-3,4-dimethyl-2-pentene.

(b) Groups of higher priority on carbons 2 and 3 are —Cl and —CH_2CH_3. Because these groups are on opposite sides of the double bond, the configuration of this alkene is E, and its name is (E)-2-chloro-2-pentene.

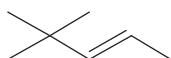See problems 4.23, 4.27, 4.28, 4.32

PROBLEM 4.3

Name each alkene and specify its configuration by the E,Z system:

(a) (b) (c)
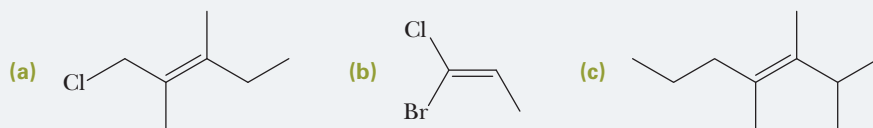
Name an Alkene

HOW TO 4.1

As an example of how to name an alkene, consider the following alkene, drawn here as a line-angle formula.

1. *Determine the parent chain, that is, the longest chain of carbon atoms that contains the functional group.*

   In this example, the parent chain is five carbon atoms, making the compound a disubstituted pentene.

2. *Number the parent chain from the end that gives the carbon atoms of the double bond the lower set of numbers.*

   In this example, the parent chain is a disubstituted 2-pentene.

   when numbering an alkene, give the C=C bond priority over any alkyl substituents
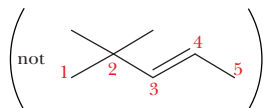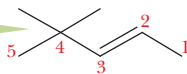
3. *Name and locate the substituents on the parent chain.*

There are two methyl substituents on carbon 4 of the parent chain, and they are named 4,4-dimethyl-. The name to this point is 4,4-dimethyl-2-pentene.

4. *Determine whether the molecule shows* cis–trans *isomerism. If it does, use either the* cis–trans *or the E,Z system to specify the configuration.*

   In this example, the molecule shows *cis–trans* isomerism, and the double bond has the *trans* configuration. Therefore, the IUPAC name is *trans*-4,4-dimethyl-2-pentene.

   Note that the double bond locator may be placed either before the parent name, as in the name just given, or immediately before the infix specifying the double bond to give the name *trans*-4,4-dimethylpent-2-ene.
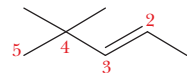
   ***trans*-4,4-Dimethyl-2-pentene**
   or
   ***trans*-4,4-Dimethylpent-2-ene**
   or
   (E)-4,4-Dimethyl-2-pentene

D. Naming Cycloalkenes

In naming **cycloalkenes**, we number the carbon atoms of the ring double bond 1 and 2 in the direction that gives the substituent encountered first the smaller number. We name and locate substituents and list them in alphabetical order, as in the following compounds:
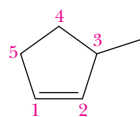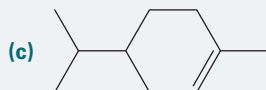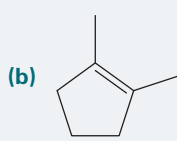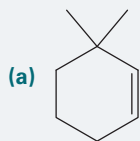
3-Methylcyclopentene
(not 5-methylcyclopentene)
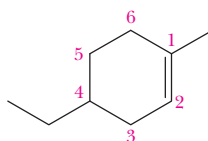
4-Ethyl-1-methylcyclohexene
(not 5-ethyl-2-methylcyclohexene)

EXAMPLE 4.5

Write the IUPAC name for each cycloalkene:

(a) **(b)**

(c)

STRATEGY

The parent name of a cycloalkene is derived from the name of the alkene with the same number of carbon atoms (e.g.,

for a 6-carbon cycloalkene, use "cyclohexene" as the parent name). Number the carbon atoms of the ring 1 and 2 in the direction that gives the substituent encountered first the smaller number. Finally, name and number all substituents and list them in alphabetical order.

SOLUTION

(a) 3,3-Dimethylcyclohexene
(b) 1,2-Dimethylcyclopentene
(c) 4-Isopropyl-1-methylcyclohexene
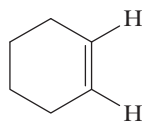
See problems 4.15–4.20

PROBLEM 4.4

Write the IUPAC name for each cycloalkene:

(a) **(b)** **(c)**
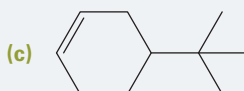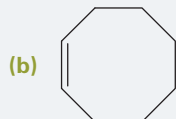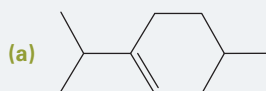
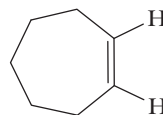### E. *Cis–Trans* Isomerism in Cycloalkenes

Following are structural formulas for four cycloalkenes:
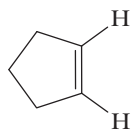
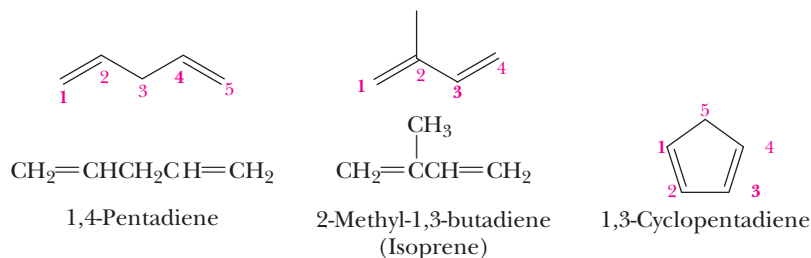Cyclopentene   Cyclohexene   Cycloheptene   Cyclooctene
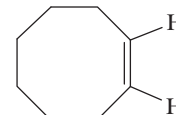
In these representations, the configuration about each double bond is *cis*. Because of angle strain, it is not possible to have a *trans* configuration in cycloalkenes of seven or fewer carbons. To date, *trans*-cyclooctene is the smallest *trans*-cycloalkene that has been prepared in pure form and is stable at room temperature. Yet, even in this *trans*-cycloalkene, there is considerable intramolecular strain. *cis*-Cyclooctene is more stable than its *trans* isomer by 38 kJ/mol (9.1 kcal/mol).
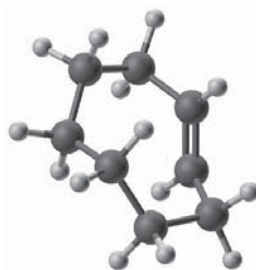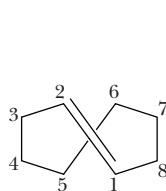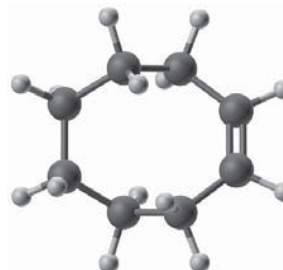
trans-Cyclooctene   *cis*-Cyclooctene
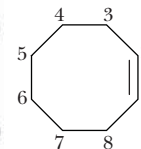
F. Dienes, Trienes, and Polyenes

We name alkenes that contain more than one double bond as alkadienes, alkatrienes, and so forth. We refer to those that contain several double bonds more generally as polyenes (Greek: *poly*, many). Following are three examples of dienes:

CH_2=$CHCH_2CH$=CH_2

1,4-Pentadiene

CH_2=CCH=CH_2 with CH_3 substituent

**2-Methyl-1,3-butadiene
(Isoprene)**

1,3-Cyclopentadiene

G. *Cis–Trans* Isomerism in Dienes, Trienes, and Polyenes

Thus far, we have considered *cis–trans* isomerism in alkenes containing only one carbon–carbon double bond. For an alkene with one carbon–carbon double bond that can show *cis–trans* isomerism, two *cis–trans* isomers are possible. For an alkene with **n** carbon–carbon double bonds, each of which can show *cis–trans* isomerism, 2^n *cis–trans* isomers are possible.

EXAMPLE   4.6

How many *cis–trans* isomers are possible for 2,4-heptadiene?

STRATEGY

Determine which of the carbon–carbon double bonds can show *cis–trans* isomerism. The number of *cis–trans* isomers possible is 2^n. *n* is the number of double bonds that may exhibit this type of isomerism.

SOLUTION

This molecule has two carbon–carbon double bonds, each of which exhibits *cis–trans* isomerism. As the following table shows, $2^2 = 4$ *cis–trans* isomers are possible (below the table are line-angle formulas for two of these isomers):

Double bond	
C_2-C_3	C_4-C_5
trans	*trans*
trans	*cis*
cis	*trans*
cis	*cis*

trans,trans-2,4-Heptadiene   *trans,cis*-2,4-Heptadiene
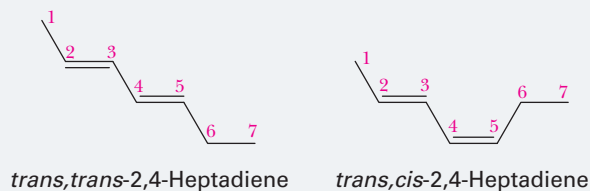
See problem 4.36

PROBLEM   4.5

Draw structural formulas for the other two *cis–trans* isomers of 2,4-heptadiene.

EXAMPLE   4.7

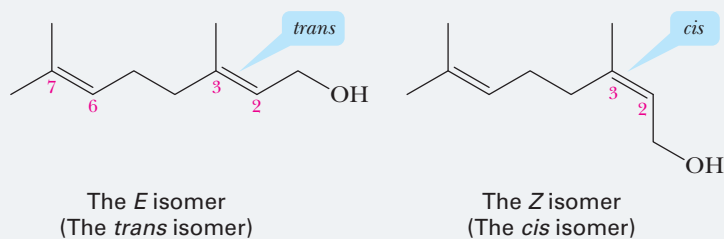Draw all possible *cis–trans* isomers for the following unsaturated alcohol:

CH_3C=$CHCH_2CH_2C$=$CHCH_2OH$ with CH_3 substituents

STRATEGY

Identify the number of C–C double bonds, *n*, that exhibit *cis–trans* isomerism. The number of possible *cis–trans* isomers will then be equal to 2^n. Alkene carbons that are bonded to two identical groups do not exhibit *cis–trans* isomerism.

SOLUTION

Cis–trans isomerism is possible only for the double bond between carbons 2 and 3 of the chain. It is not possible for the other double bond because carbon 7 has two identical groups on it. Thus, $2^1 = 2$ *cis–trans* isomers are possible. Each isomer may be named by the *cis–trans* system, but as noted earlier, for structures containing a tri- or tetrasubstituted double bond, it is preferable to use the E,Z system.

trans

OH

The *E* isomer
(The *trans* isomer)
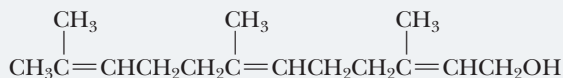
cis

OH

The *Z* isomer
(The *cis* isomer)

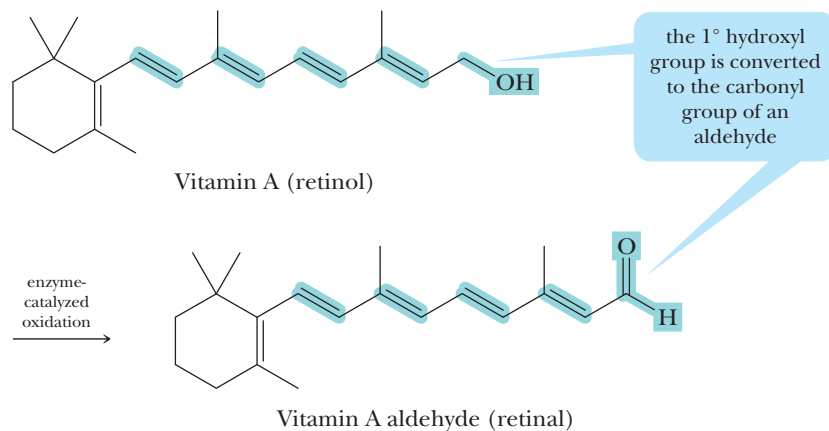The *E* isomer of this alcohol, named geraniol, is a major component of the oils of rose, citronella, and lemongrass.

See problem 4.36

PROBLEM 4.6

How many *cis–trans* isomers are possible for the following unsaturated alcohol?

$$CH_3C\!=\!CHCH_2CH_2C\!=\!CHCH_2CH_2C\!=\!CHCH_2OH$$

with CH_3 groups on the three double-bonded carbons

Vitamin A is an example of a biologically important compound for which a number of *cis–trans* isomers are possible. There are four carbon–carbon double bonds in the chain of carbon atoms bonded to the substituted cyclohexene ring, and each has the potential for *cis–trans* isomerism. Thus, $2^4 = 16$ *cis–trans* isomers are possible for this structural formula. Vitamin A is the all *trans* isomer. The enzyme-catalyzed oxidation of vitamin A converts the primary hydroxyl group to a carbonyl group of an aldehyde to give retinal, the biologically active form of the vitamin:

OH

the 1° hydroxyl group is converted to the carbonyl group of an aldehyde

Vitamin A (retinol)

enzyme-catalyzed oxidation

O

H

Vitamin A aldehyde (retinal)

4.3   What Are the Physical Properties of Alkenes and Alkynes?

Alkenes and alkynes are nonpolar compounds, and the only attractive forces between their molecules are dispersion forces (Section 3.8B). Therefore, their physical properties are similar to those of alkanes (Section 3.8) with the same carbon skeletons. Alkenes and alkynes that are liquid at room temperature have densities less than 1.0 g/mL. Thus, they are less dense than water. Like alkanes, alkenes and alkynes are nonpolar and are soluble in each other. Because of their contrasting polarity with water, they do not dissolve in water. Instead, they form two layers when mixed with water or another polar organic liquid such as ethanol.

CH₃—C≡C—CH₃
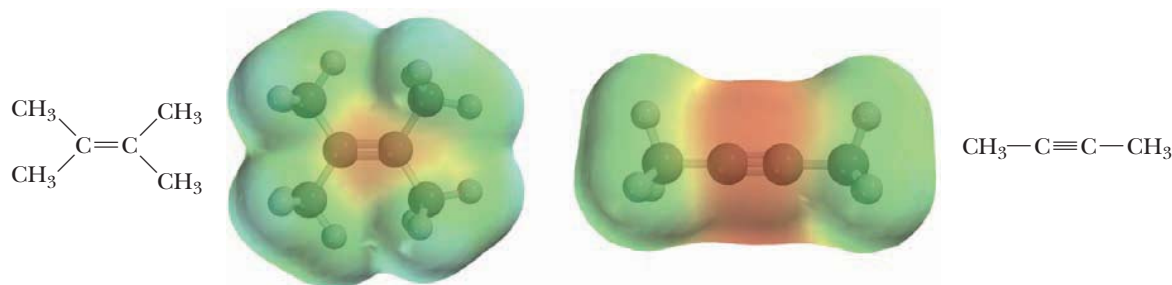
Tetramethylethylene and dimethylacetylene. Both a carbon–carbon double bond and a carbon–carbon triple bond are sites of high electron density and, therefore, sites of chemical reactivity.

EXAMPLE 4.8

Describe what will happen when 1-nonene is added to the following compounds:

(a) Water

(b) 8-Methyl-1-nonyne

STRATEGY

First determine the polarity of the solvent and the solute. Then apply the generalization, "like dissolves like."
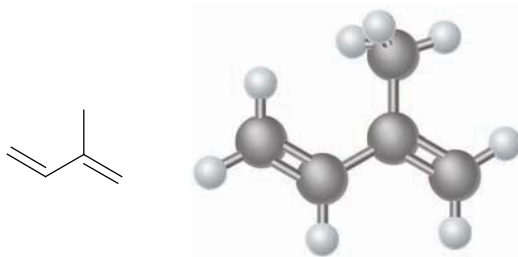
SOLUTION

(a) 1-Nonene is an alkene and, therefore, nonpolar. It will not dissolve in a polar solvent such as water. Water and 1-nonene will form two layers; water, which has the higher density, will be the lower layer, and 1-nonene will be the upper layer.

(b) Because alkenes and alkynes are both nonpolar, they will dissolve in one another.

Chemical Connections 4C

WHY PLANTS EMIT ISOPRENE

Names like Virginia's *Blue Ridge*, Jamaica's *Blue Mountain Peak*, and Australia's *Blue Mountains* remind us of the bluish haze that hangs over wooded hills in the summertime. In the 1950s, it was discovered that this haze is rich in isoprene, which means that isoprene is far more abundant in the atmosphere than anyone thought. The haze is caused by the scattering of light from an aerosol produced by the photooxidation of isoprene and other hydrocarbons. Scientists now estimate that the global emission of isoprene by plants is 3×10^{11} kg/yr (3.3×10^8 ton/yr), which represents approximately 2% of all carbon fixed by photosynthesis.

Why do plants emit so much isoprene into the atmosphere rather than use it for the synthesis of terpenes and other natural products? Tom Starkey, a University of Wisconsin plant physiologist, found that the emission of isoprene is extremely sensitive to temperature. Plants grown at 20 °C do not emit isoprene,

Isoprene

A recent study of hydrocarbon emissions in the Atlanta area revealed that plants are by far the largest emitters of hydrocarbons, with plant-derived isoprene accounting for almost 60% of the total.
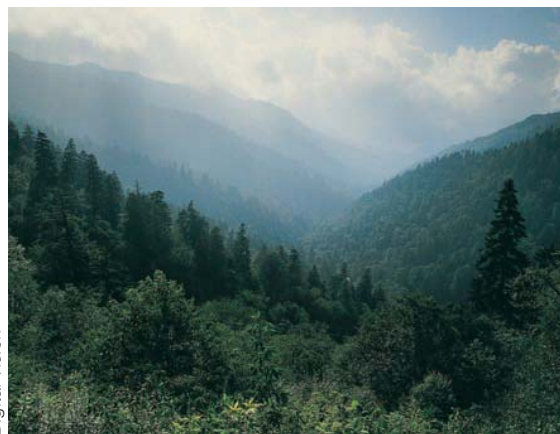
Digital Vision

The haze of the Smoky Mountains is caused by light-scattering from the aerosol produced by the photooxidation of isoprene and other hydrocarbons.

but they begin to emit it when the temperature of their leaves increases to 30°C. In certain plants, isoprene emission can increase as much as tenfold for a 10°C increase in leaf temperature. Starkey studied the relationship between temperature-induced leaf damage and isoprene concentration in leaves of the kudzu plant, a nonnative invasive vine. He discovered that leaf damage, as measured by the destruction of chlorophyll, begins to occur at 37.5°C in the absence o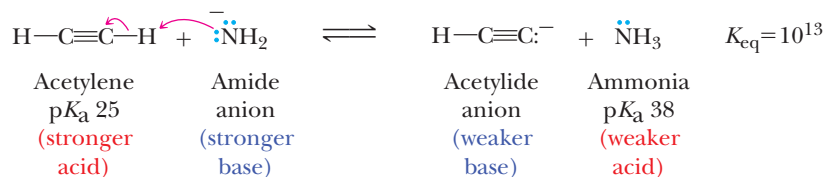f isoprene, but not until 45°C in its presence. Starkey speculates that isoprene dissolves in leaf membranes and in some way increases their tolerance to heat stress. Because isoprene is made rapidly and is also lost rapidly, its concentration correlates with temperature throughout the day.

Question

Based on the information in this Chemical Connections what can you deduce about the physical properties of leaf cell membranes?
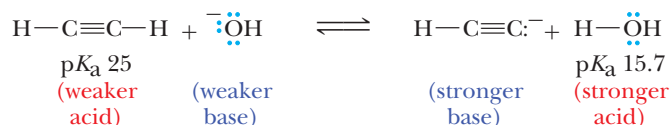
4.4   Why Are 1-Alkynes (Terminal Alkynes) Weak Acids?

One of the major differences between the chemistry of alkynes and that of alkenes and alkanes is that a hydrogen bonded to a carbon atom of a terminal alkyne is sufficiently acidic (pK_a 25) that it can be removed by a strong base, such as sodium amide, $NaNH_2$, to give an acetylide anion.

$$H-C\equiv C-H + :NH_2^- \rightleftharpoons H-C\equiv C:^- + NH_3 \qquad K_{eq}=10^{13}$$

Acetylene	Amide	Acetylide	Ammonia
pK_a 25	anion	anion	pK_a 38
(stronger acid)	(stronger base)	(weaker base)	(weaker acid)

In this equilibrium, acetylene is the stronger acid and sodium amide is the stronger base, and the position of equilibrium lies considerably toward the right and favors formation of the acetylide anion and ammonia (Section 2.4). Table 4.1 gives pK_a values for an alkane, alkene, and an alkyne hydrogen. Also given for comparison is the value for water.

Because water (pK_a 15.7) is a stronger acid than acetylene (pK_a 25), the hydroxide ion is not a strong enough base to convert a terminal alkyne to an alkyne anion. The position of equilibrium for this acid–base reaction lies toward the left.

$$H-C\equiv C-H + :OH^- \rightleftharpoons H-C\equiv C:^- + H-OH$$

pK_a 25			pK_a 15.7
(weaker acid)	(weaker base)	(stronger base)	(stronger acid)

The pK_a values for alkene hydrogens (pK_a approximately 44) and alkane hydrogens (pK_a approximately 51) are so large (they are so weakly acidic) that neither the commonly used alkali metal hydroxides nor sodium amide are strong enough bases to remove a proton from an alkene or an alkane.

TABLE 4.1   Acidity of Alkanes, Alkenes, and Alkynes

Weak Acid		Conjugate Base	pK_a
Water	$HO-H$	HO^-	15.7
Alkyne	$HC\equiv C-H$	$HC\equiv C^-$	25
Alkene	$CH_2=CH-H$	$CH_2=CH^-$	44
Alkane	CH_3CH_2-H	$CH_3CH_2^-$	51

Increasing acidity →

Why is the acidity of a hydrogen bonded to a triple-bonded carbon so much more acidic than one bonded to a double-bonded carbon of an alkene or to an alkane? We explain these relative acidities in the following way. The lone pair of electrons on a carbon anion lies in a hybrid orbital: an sp^3 hybrid orbital for an alkane, an sp^2 hybrid orbital for an alkene, and an sp hybrid orbital for an alkyne. An sp hybrid orbital has 50% s character, an sp^2 hybrid orbital has 33% s character, and an sp^3 hybrid orbital has 25% s character. Recall from your course in general chemistry and from Chapter 1 of this text that a 2s orbital is lower in energy than a 2p orbital. Consequently, electrons in a 2s orbital are held more tightly to the nucleus than those in a 2p orbital. The more s character in a hybrid orbital of carbon, the more electronegative the carbon atom will be, resulting in a greater stability of the anion and thus a more acidic hydrogen. Of the three types of organic compounds in the series alkyne, alkene, and alkane, the carbon in an alkyne (sp hybridized with 50% s character) is the most electronegative. Therefore, an alkyne anion is the most stable of the series, and an alkyne is the strongest acid of the series. By similar reasoning, the alkane carbon (sp^3 hybridized and 25% s character) is the least electronegative, and an alkane is the weakest acid of the series. An alkene, with 33% s character, is intermediate. Finally, it is only the hydrogen of a 1-alkyne that shows this type of acidity. No other hydogens of an alkyne have comparable acidity, and no other hydrogens are removed by $NaNH_2$.

these hydrogens are much lower in acidity and are not deprotonated by $NaNH_2$

only this hydrogen is acidic enough to be deprotonated by $NaNH_2$

$$CH_3-CH_2-CH_2-C\equiv C-H$$

SUMMARY OF KEY QUESTIONS

4.1 What Are the Structures and Shapes of Alkenes and Alkynes?

- An **alkene** is an **unsaturated hydrocarbon** that contains a carbon–carbon double bond.

- Alkenes have the general formula C_nH_{2n}.

- An **alkyne** is an unsaturated hydrocarbon that contains a carbon–carbon triple bond.

- Alkynes have the general formula C_nH_{2n-2}.

- According to the **orbital overlap model**, a carbon–carbon double bond consists of one sigma bond formed by the overlap of sp^2 hybrid orbitals and one pi bond formed by the overlap of parallel 2p atomic orbitals. It takes approximately 264 kJ/mol (63 kcal/mol) to break the pi bond in ethylene.

- A carbon–carbon triple bond consists of one sigma bond formed by the overlap of sp hybrid orbitals and two pi bonds formed by the overlap of pairs of parallel 2p orbitals.

- The structural feature that makes ***cis–trans* isomerism** possible in alkenes is restricted rotation about the two carbons of the double bond.

- To date, *trans*-cyclooctene is the smallest *trans*-cycloalkene that has been prepared in pure form and is stable at room temperature.

4.2 How Do We Name Alkenes and Alkynes?

- According to the IUPAC system, we show the presence of a **carbon–carbon double bond** by changing the infix of the parent hydrocarbon from **-an-** to **-en-**.

- The names *vinyl* and *allyl* are commonly used to show the presence of $-CH=CH_2$ and $-CH_2CH=CH_2$ groups.

- We show the presence of a **carbon–carbon triple bond** by changing the infix of the parent alkane from **-an-** to **-yn-**.

- The orientation of the carbon atoms of the parent chain about the double bond determines whether an alkene is *cis* or *trans*. If atoms of the parent are on the same side of the double bond, the configuration of the alkene is *cis*; if they are on opposite sides, the configuration is *trans*.

- Using a set of priority rules, we can also specify the configuration of a carbon–carbon double bond by the **E,Z system**.

- If the two groups of higher priority are on the same side of the double bond, the configuration of the alkene is **Z** (German: *zusammen*, together); if they are on opposite sides, the configuration is **E** (German: *entgegen*, opposite).

- To name an alkene containing two or more double bonds, we change the infix to -adien-, -atrien-, and so forth. Compounds containing several double bonds are called polyenes.

4.3   What Are the Physical Properties of Alkenes and Alkynes?

- Alkenes and alkynes are nonpolar compounds, and the only interactions between their molecules are **dispersion forces**.

- The physical properties of alkenes and alkynes are similar to those of alkanes.

4.4   Why Are 1-Alkynes (Terminal Alkynes) Weak Acids?

- Terminal alkynes are weakly acidic (pK_a 25) and can be converted to alkyne anions by strong bases such as sodium amide, $NaNH_2$.

QUICK QUIZ

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

1. Ethylene and acetylene are constitutional isomers. (4.2)
2. Alkanes that are liquid at room temperature are insoluble in water and when added to water will float on water. (4.3)
3. The bulk of the ethylene used by the chemical industry worldwide is obtained from nonrenewable resources. (4.1)
4. Alkenes and alkynes are nonpolar molecules. (4.3)
5. The IUPAC name of $CH_3CH=CHCH_3$ is 1,2-dimethylethylene. (4.2)
6. Cyclohexane and 1-hexene are constitutional isomers. (4.1)
7. The IUPAC name of an alkene is derived from the name of the longest chain of carbon atoms that contains the double bond. (4.2)
8. There are two classes of unsaturated hydrocarbons, alkenes and alkynes. (4.1)

9. Both geraniol and menthol (pp. 258–259) show *cis–trans* isomerism. (4.4)
10. 1,2-Dimethylcyclohexene shows *cis–trans* isomerism. (4.2)
11. 2-Methyl-2-butene shows *cis–trans* isomerism. (4.2)
12. Both ethylene and acetylene are planar molecules. (4.1)
13. The physical properties of alkenes are similar to those of alkanes with the same carbon skeletons. (4.3)
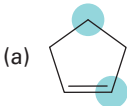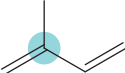14. Isoprene is the common name for 2-methyl-1,3-butadiene. (4.4)

Answers: (1) F (2) T (3) T (4) T (5) F (6) T (7) T (8) T (9) T (10) F (11) F (12) T (13) T (14) T

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

PROBLEMS

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

### Section 4.1   Structure of Alkenes and Alkynes

4.7   Describe what will happen when *trans*-3-heptene is added to the following compounds:

   (a) Cyclohexane   (b) Ammonia (*l*)

4.8   Each carbon atom in ethane and in ethylene is surrounded by eight valence electrons and has four bonds to it. Explain how VSEPR (Section 1.3) predicts a bond angle of 109.5° about each carbon in ethane, but an angle of 120° about each carbon in ethylene.

4.9   Explain the difference between saturated and unsaturated.

4.10   Use valence-shell electron-pair repulsion (VSEPR) to predict all bond angles about each of the following highlighted carbon atoms.

(c) $HC\equiv C-CH=CH_2$ (d)

4.11   For each highlighted carbon atom in Problem 4.10, identify which orbitals are used to form each sigma bond and which are used to form each pi bond.

4.12 Predict all bond angles about each highlighted carbon atom:

(a)

(b)

OH

(c)

(d)

Br

Br
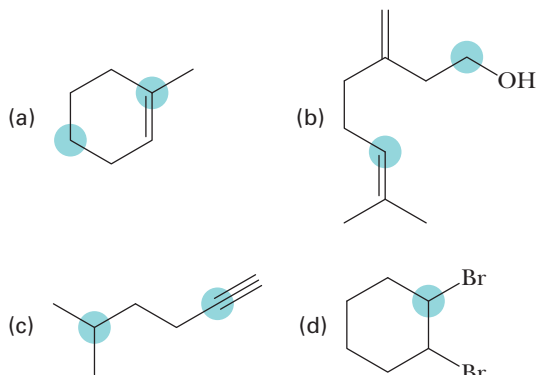
4.13 For each highlighted carbon atom in Problem 4.12, identify which orbitals are used to form each sigma bond and which are used to form each pi bond.

4.14 Following is the structure of 1,2-propadiene (allene). In it, the plane created by H—C—H of carbon 1 is perpendicular to that created by H—C—H of carbon 3.

H
H
C=C=C
H
H
1   2   3

1,2-Propadiene   Ball-and-stick model
(Allene)
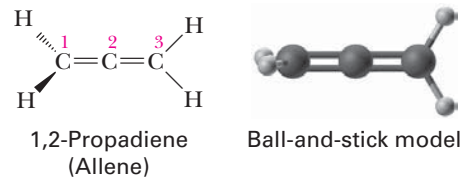
(a) State the orbital hybridization of each carbon in allene.
(b) Account for the molecular geometry of allene in terms of the orbital overlap model. Specifically, explain why all four hydrogen atoms are not in the same plane.

## Section 4.2 Nomenclature of Alkenes and Alkynes

4.15 Draw a structural formula for each compound: **(See Examples 4.1, 4.5)**

(a) *trans*-2-Methyl-3-hexene
(b) 2-Methyl-3-hexyne
(c) 2-Methyl-1-butene
(d) 3-Ethyl-3-methyl-1-pentyne
(e) 2,3-Dimethyl-2-butene
(f) *cis*-2-Pentene
(g) (*Z*)-1-Chloropropene
(h) 3-Methylcyclohexene

4.16 Draw a structural formula for each compound: **(See Examples 4.1, 4.5)**

(a) 1-Isopropyl-4-methylcyclohexene
(b) (6*E*)-2,6-Dimethyl-2,6-octadiene
(c) *trans*-1,2-Diisopropylcyclopropane
(d) 2-Methyl-3-hexyne
(e) 2-Chloropropene
(f) Tetrachloroethylene

4.17 Write the IUPAC name for each compound: **(See Examples 4.1, 4.5)**

(a)

(b)

(c)

(d)
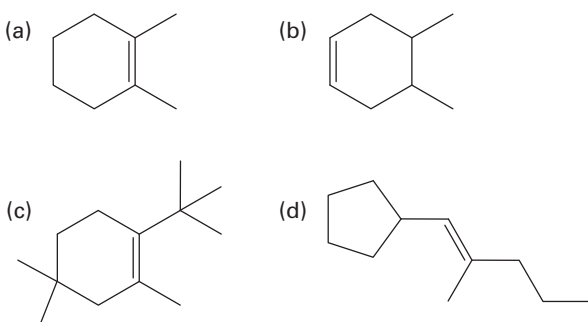
4.18 Write the IUPAC name for each compound: **(See Examples 4.1, 4.5)**

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)
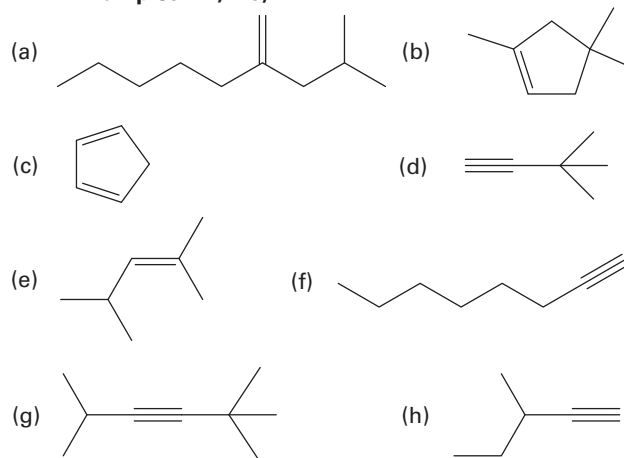
4.19 Explain why each name is incorrect, and then write a correct name for the intended compound: **(See Examples 4.1, 4.5)**

(a) 1-Methylpropene   (b) 3-Pentene
(c) 2-Methylcyclohexene   (d) 3,3-Dimethylpentene
(e) 4-Hexyne   (f) 2-Isopropyl-2-butene

4.20 Explain why each name is incorrect, and then write a correct name for the intended compound: **(See Examples 4.1, 4.5)**

(a) 2-Ethyl-1-propene
(b) 5-Isopropylcyclohexene
(c) 4-Methyl-4-hexene
(d) 2-*sec*-Butyl-1-butene
(e) 6,6-Dimethylcyclohexene
(f) 2-Ethyl-2-hexene

Sections 4.2 and 4.3 *Cis–Trans* (E/Z) Isomerism in Alkenes and Cycloalkenes

4.21 Which of these alkenes show *cis–trans* isomerism? For each that does, draw structural formulas for both isomers. **(See Example 4.2)**

(a) 1-Hexene   (b) 2-Hexene
(c) 3-Hexene   (d) 2-Methyl-2-hexene
(e) 3-Methyl-2-hexene   (f) 2,3-Dimethyl-2-hexene

4.22 Which of these alkenes show *cis–trans* isomerism? For each that does, draw structural formulas for both isomers. **(See Example 4.2)**

(a) 1-Pentene
(b) 2-Pentene
(c) 3-Ethyl-2-pentene
(d) 2,3-Dimethyl-2-pentene
(e) 2-Methyl-2-pentene
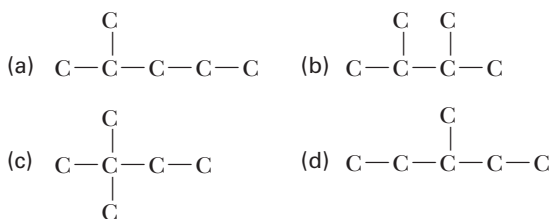(f) 2,4-Dimethyl-2-pentene

4.23 Which alkenes can exist as pairs of E/Z isomers? For each alkene that does, draw both isomers. **(See Examples 4.3, 4.4)**

(a) CH_2=CHBr   (b) CH_3CH=CHBr
(c) $(CH_3)_2C$=$CHCH_3$ (d) $(CH_3)_2CHCH$=$CHCH_3$

4.24 There are three compounds with the molecular formula $C_2H_2Br_2$. Two of these compounds have a dipole greater than zero, and one has no dipole. Draw structural formulas for the three compounds, and explain why two have dipole moments but the third one has none.

4.25 Name and draw structural formulas for all alkenes with the molecular formula C_5H_{10}. As you draw these alkenes, remember that *cis* and *trans* isomers are different compounds and must be counted separately.

4.26 Name and draw structural formulas for all alkenes with the molecular formula C_6H_{12} that have the following carbon skeletons (remember *cis* and *trans* isomers):

(a)
$$C-C-C-C-C$$
with C above second carbon

(b)
$$C-C-C-C$$
with C above second and third carbons

(c)
$$C-C-C-C$$
with C above and below second carbon

(d)
$$C-C-C-C-C$$
with C above third carbon

4.27 Arrange the groups in each set in order of increasing priority: **(See Examples 4.3, 4.4)**

(a) $-CH_3, -Br, -CH_2CH_3$
(b) $-OCH_3, -CH(CH_3)_2, -CH_2CH_2NH_2$
(c) $-CH_2OH, -COOH, -OH$
(d) $-CH$=$CH_2, -CH$=$O, -CH(CH_3)_2$

4.28 Name each alkene and specify its configuration using the E,Z system. **(See Examples 4.3, 4.4)**
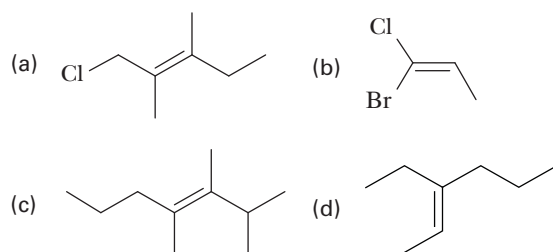
4.29 Draw the structural formula for at least one bromoalkene with molecular formula C_5H_9Br that **(a)** shows E,Z isomerism and **(b)** does not show E,Z isomerism.

4.30 Is *cis–trans* isomerism possible in alkanes? Is it possible in alkynes? Explain.

4.31 For each molecule that shows *cis–trans* isomerism, draw the *cis* isomer:
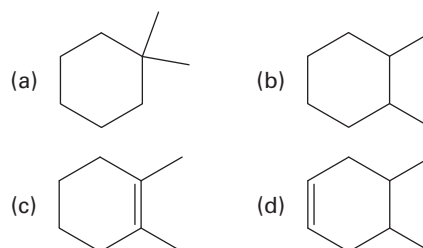
4.32 Explain why each name is incorrect or incomplete, and then write a correct name: **(See Examples 4.3, 4.4)**

(a) (*Z*)-2-Methyl-1-pentene
(b) (*E*)-3,4-Diethyl-3-hexene
(c) *trans*-2,3-Dimethyl-2-hexene
(d) (1*Z*,3*Z*)-2,3-Dimethyl-1,3-butadiene

4.33 Draw structural formulas for all compounds with the molecular formula C_5H_{10} that are

(a) Alkenes that do not show *cis–trans* isomerism.
(b) Alkenes that do show *cis–trans* isomerism.
(c) Cycloalkanes that do not show *cis–trans* isomerism.
(d) Cycloalkanes that do show *cis–trans* isomerism.

***4.34** β-Ocimene, a triene found in the fragrance of cotton blossoms and several essential oils, has the IUPAC name (3*Z*)-3,7-dimethyl-1,3,6-octatriene. Draw a structural formula for β-ocimene.

***4.35** Oleic acid and elaidic acid are, respectively, the *cis* and *trans* isomers of 9-octadecenoic acid. One of these fatty acids, a colorless liquid that solidifies at 4 °C, is a major component of butterfat. The other, a white solid with a melting point of 44–45 °C, is a major component of partially hydrogenated vegetable oils. Which of these two fatty acids is the *cis* isomer and which is the *trans* isomer? (*Hint*: Think about the geometry of packing and the relative strengths of the resulting dispersion forces.)

4.36 Determine whether the structures in each set represent the same molecule, *cis–trans* isomers, or constitutional isomers. If they are the same molecule, determine whether they are in the same or different conformations as a result of rotation about a carbon–carbon single bond. **(See Examples 4.6, 4.7)**

(a)   and   (b)   and

(c)   and   (d)   and
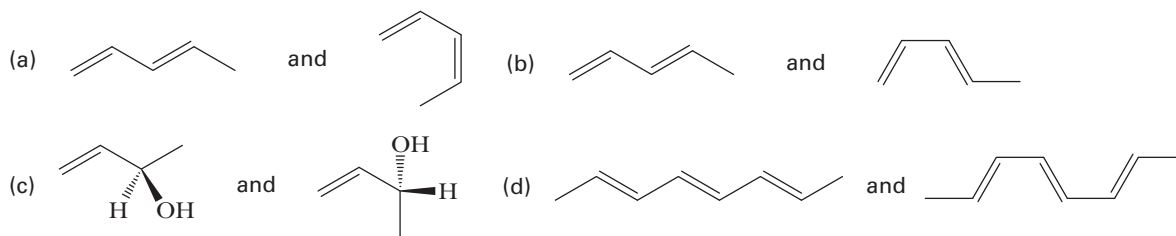
*4.37 Following is the structural formula of lycopene, a deep-red compound that is partially responsible for the red color of ripe fruits, especially tomatoes:
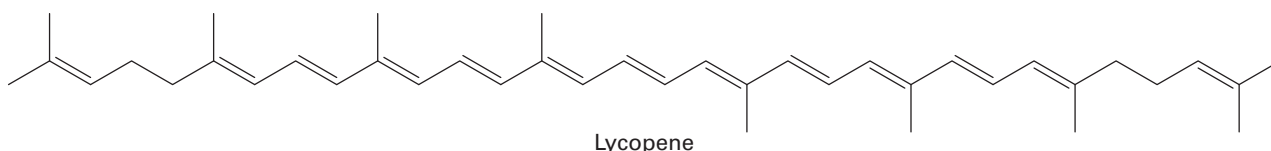
Lycopene

Approximately 20 mg of lycopene can be isolated from 1 kg of fresh, ripe tomatoes. How many of the carbon–carbon double bonds in lycopene have the possibility for *cis–trans* isomerism? Use the E,Z system to assign the configuration of all applicable double bonds.

*4.38 As you might suspect, β-carotene, a precursor of vitamin A, was first isolated from carrots. Dilute solutions of β-carotene are yellow—hence its use as a food coloring. In plants, it is almost always present in combination with chlorophyll to assist in harvesting the energy of sunlight. As tree leaves die in the fall, the green of their chlorophyll molecules is replaced by the yellows and reds of carotene and carotene-related molecules.

(a) Compare the carbon skeletons of β-carotene and lycopene. What are the similarities? What are the differences?
(b) Use the E,Z system to assign the configuration of all applicable double bonds.

β-Carotene
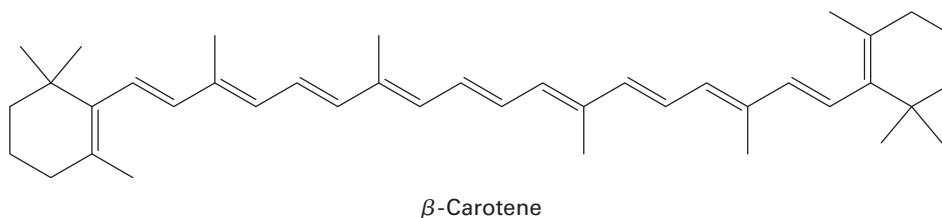
*4.39 In many parts of South America, extracts of the leaves and twigs of *Montanoa tomentosa* are used as a contraceptive, to stimulate menstruation, to facilitate labor, and as an abortifacient. The compound responsible for these effects is zoapatanol:
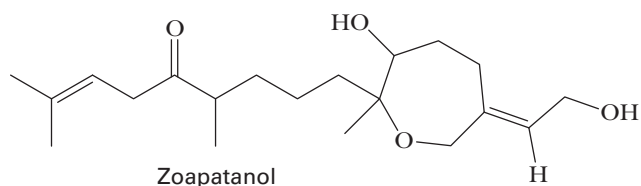
Zoapatanol

(a) Specify the configuration about the carbon–carbon double bond to the seven-membered ring, according to the E,Z system.
(b) How many *cis–trans* isomers are possible for zoapatanol? Consider the possibilities for *cis–trans* isomerism in cyclic compounds and about carbon–carbon double bonds.

*4.40 Pyrethrin II and pyrethrosin are natural products isolated from plants of the chrysanthemum family:


Chrysanthemum blossoms.

Pyrethrin II is a natural insecticide and is marketed as such.

(a) Label all carbon–carbon double bonds in each about which *cis–trans* isomerism is possible.

(b) Why are *cis–trans* isomers possible about the three-membered ring in pyrethrin II, but not about its five-membered ring?
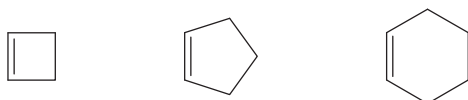

Pyrethrin II

Pyrethrosin
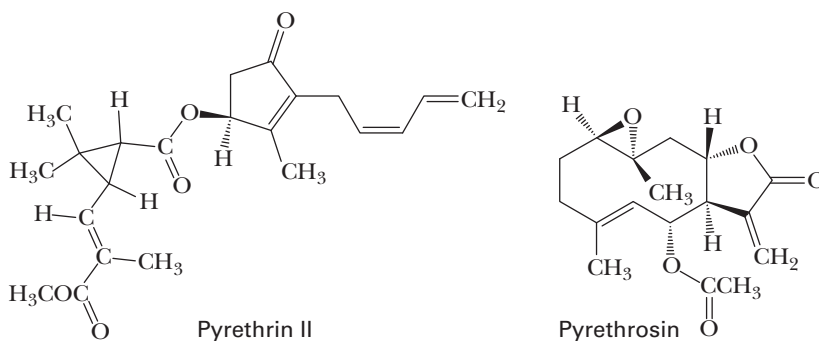
LOOKING AHEAD

4.41 Explain why the central carbon–carbon single bond in 1,3-butadiene is slightly shorter than the central carbon–carbon single bond in 1-butene:

1.47 Å   1.51 Å

1,3-Butadiene   1-Butene
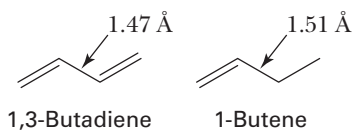
4.42 What effect might the ring size in the following cyclo-alkenes have on the reactivity of the $C=C$ double bond in each?
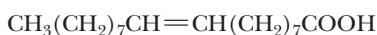
4.43 What effect might each substituent have on the electron density surrounding the alkene $C=C$ bond; that is, how does each substituent affect whether each carbon of the $C-C$ double bond is partially positive or partially negative?

(a) $\diagup\!\!\diagup OCH_3$ (b) $\diagup\!\!\diagup CN$

(c) $\diagup\!\!\diagup Si(CH_3)_3$
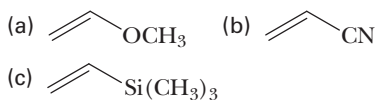
*4.44 In Section 19.1 on the biochemistry of fatty acids, we will study the following three long-chain unsaturated carboxylic acids:

Oleic acid

$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$

Linoleic acid

$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$

Linolenic acid

$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$

Each has 18 carbons and is a component of animal fats, vegetable oils, and biological membranes. Because of their presence in animal fats, they are called fatty acids.

(a) How many *cis–trans* isomers are possible for each fatty acid?

(b) These three fatty acids occur in biological membranes almost exclusively in the *cis* configuration. Draw line-angle formulas for each fatty acid, showing the *cis* configuration about each carbon–carbon double bond.

*4.45 Assign an E or a Z configuration and a *cis* or a *trans* configuration to these carboxylic acids, each of which is an intermediate in the citric acid cycle. Under each is given its common name.

(a)

Fumaric acid

(b)

Aconitic acid
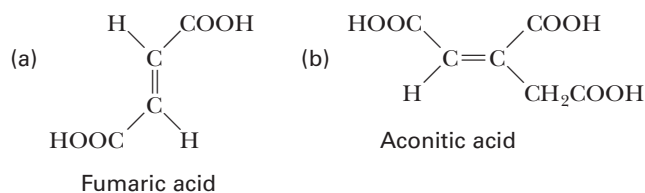
GROUP LEARNING ACTIVITIES

4.46 Take turns coming up with structures that fit the following criteria. For each structure you come up with, explain to the group why your answer is correct.

(a) An alkene with the formula C_6H_{12} that cannot be named using *cis–trans* or E,Z.

(b) A compound with the formula C_7H_{12} that does not contain a pi bond.

(c) A compound with the formula C_6H_{10} that does not contain a methylene group.

(d) An alkene that uses "vinyl" in its IUPAC name.

(e) A compound that can be named with the E,Z system but not with the *cis–trans* system.

(f) A compound that can be named with the *cis–trans* system but not with the E,Z system.

(g) A *trans*-cycloalkene that has no ring or angle strain. (*Hint:* You may need to use a model kit to explain.)