

## WHAT'S AHEAD

- 26.1 ► The Structure of Unsaturated Hydrocarbons
- 26.2 ► Isomerism and Nomenclature
- 26.3 ► Arrow Notation and Resonance Structures: Electron Counting
- 26.4 ► Electrophilic Addition Reactions
- 26.5 ► Alkanes from Alkenes: Catalytic Hydrogenation
- 26.6 ► Addition Polymerization

# 26

## CHEMISTRY OF ALKENES AND ALKYNES

### 26.1 | The Structure of Unsaturated Hydrocarbons



Unsaturated hydrocarbons contain a double or triple bond between two carbon atoms, and they differ greatly from alkanes in much of their chemistry. Understanding the molecular basis of this different reactivity allows us to predict what reactions may occur and enhances our ability to use basic chemicals to synthesize more complex substances. These, in turn, may be built into the modern materials that surround us and used, for example, in construction, medicine and technology.

When you finish this section, you should be able to:

- Recognize alkene and alkyne functional groups
- Understand the characteristics of a  $\pi$ -bond including the effect it has on the geometry of a molecule

**Alkenes**, also known as olefins, are unsaturated hydrocarbons that contain a carbon-carbon double bond. They have the general formula:



The simplest alkene is  $\text{CH}_2=\text{CH}_2$ , called ethene (IUPAC name) or ethylene (common name). Ethene is a plant hormone that plays important roles in seed germination and fruit ripening. The carbon-carbon double bond makes ethene much more reactive than ethane.

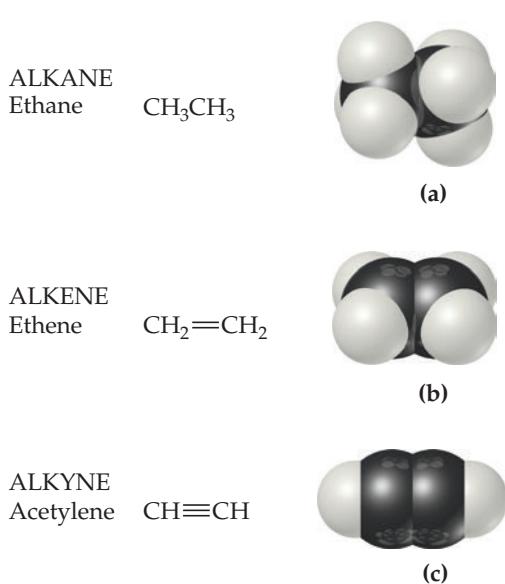
**Alkynes** are hydrocarbons that contain a carbon-carbon triple bond, as in acetylene ( $\text{HC}\equiv\text{CH}$ ), whose systematic name is ethyne. When acetylene is burned in a stream of oxygen, as in an oxy-acetylene torch, the flame reaches about 3200 K. The oxy-acetylene torch is used widely in welding, which requires high temperatures. Acetylene, and alkynes in general, are highly reactive molecules. Because of their higher reactivity, they are not as widely distributed in nature as alkenes; alkynes are, however, important intermediates in many industrial processes. Alkynes have the general molecular formula



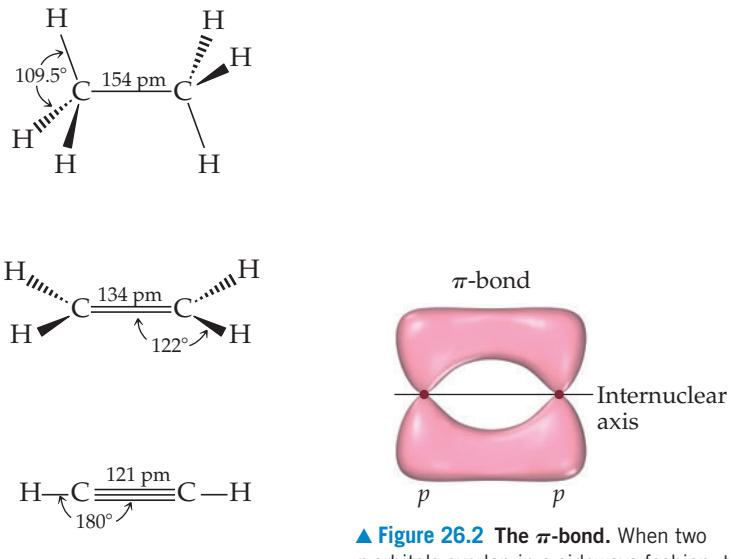
### The $\pi$ -bond

In the types of covalent bonds we have considered so far, the electron density is concentrated symmetrically about the line connecting the nuclei (the *internuclear axis*). In other words, the line joining the two nuclei passes through the middle of the electron overlap region. These bonds are all called **sigma ( $\sigma$ )-bonds**.

To describe the bonding in unsaturated hydrocarbons, we must consider a second kind of bond, one that results from the overlap between two  $p$  orbitals perpendicular to the internuclear axis (Figure 26.2). This “sideways” overlap of  $p$  orbitals produces a **pi ( $\pi$ )-bond**. A  $\pi$ -bond is a covalent bond in which the electron overlap regions lie above and below the internuclear axis. Unlike a  $\sigma$ -bond, in a  $\pi$ -bond there is no probability of finding an electron on the internuclear axis. Because the  $p$  orbitals in a  $\pi$ -bond overlap sideways rather than directly facing each other, the total overlap in a  $\pi$ -bond



▲ Figure 26.1 Three hydrocarbon types for a two-carbon system.



▲ Figure 26.2 The  $\pi$ -bond. When two  $p$  orbitals overlap in a sideways fashion, the result is a  $\pi$ -bond. Note that the two regions of overlap constitute a *single*  $\pi$ -bond.

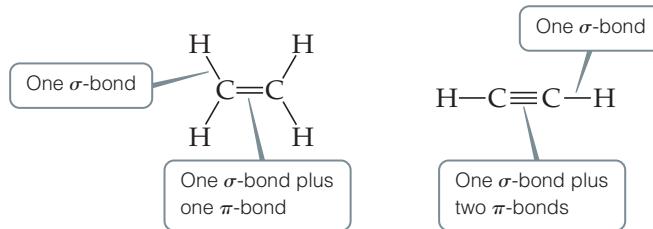
tends to be less than that in a  $\sigma$ -bond. As a consequence,  $\pi$ -bonds are generally weaker than  $\sigma$ -bonds.

We can summarize unsaturation in the following way:

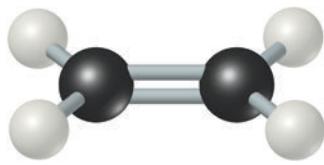
C—C single bonds are  $\sigma$ -bonds.

C=C double bonds consist of one  $\sigma$ -bond and one  $\pi$ -bond.

C≡C triple bonds consists of one  $\sigma$ -bond and two  $\pi$ -bonds.



### Bonding in Alkenes



**▲ Figure 26.3** The molecular geometry of ethene. Ethene,  $C_2H_4$ , has one carbon–carbon  $\sigma$ -bond and one  $\pi$ -bond.

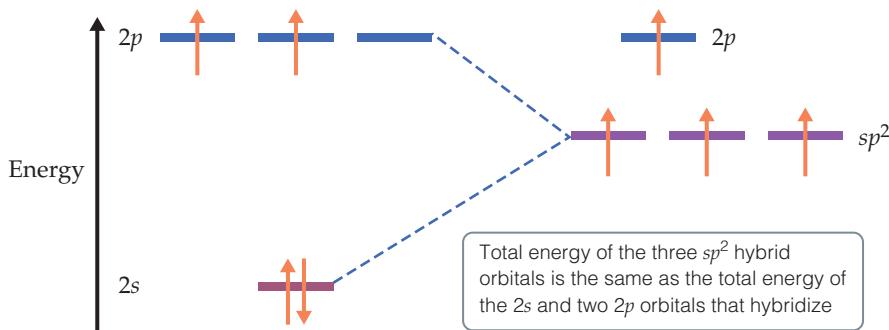
In order to rationalize the bonding and geometry of an alkene (Figure 26.3), let us consider ethene ( $C_2H_4$ ). The bond angles about carbon in ethene are all approximately  $120^\circ$  (Figure 26.3), suggesting that each carbon atom uses  $sp^2$  hybrid orbitals (Figure 9.18) to form  $\sigma$ -bonds with the other carbon and with two hydrogens. Because carbon has four valence electrons, after  $sp^2$  hybridization carbon still has one electron remaining in the unhybridized  $2p$  orbital (Figure 26.4).

The unhybridized  $2p$  orbital is directed perpendicular to the plane that contains the three  $sp^2$  hybrid orbitals. The hybrid orbitals separate within the same plane to give inter-orbital angles of  $120^\circ$ . This orbital pattern gives rise to a trigonal planar arrangement of  $\sigma$ -bonds.

Each  $sp^2$  hybrid orbital on a carbon atom contains one electron. Figure 26.5 shows how the four C—H  $\sigma$ -bonds are formed by overlap of  $sp^2$  hybrid orbitals on C with the 1s orbitals on each H atom. We use eight electrons to form these four electron-pair bonds. The C—C  $\sigma$ -bond is formed by the overlap of two  $sp^2$  hybrid orbitals, one on each carbon atom, and requires two more electrons. Thus 10 of the 12 valence electrons in  $C_2H_4$  are used to form five  $\sigma$ -bonds.

The remaining two valence electrons reside in the unhybridized  $2p$  orbitals, one electron on each carbon atom. These two  $2p$  orbitals can overlap with each other in a sideways fashion, as shown in Figure 26.2. The resultant electron density is concentrated above and below the C—C bond axis, forming a single  $\pi$ -bond. Thus the carbon–carbon double bond in ethene consists of one  $\sigma$ -bond and one  $\pi$ -bond. Note carefully that the unhybridized  $p$ -orbital overlap above and below the plane forms a single  $\pi$ -bond and not two  $\pi$ -bonds.

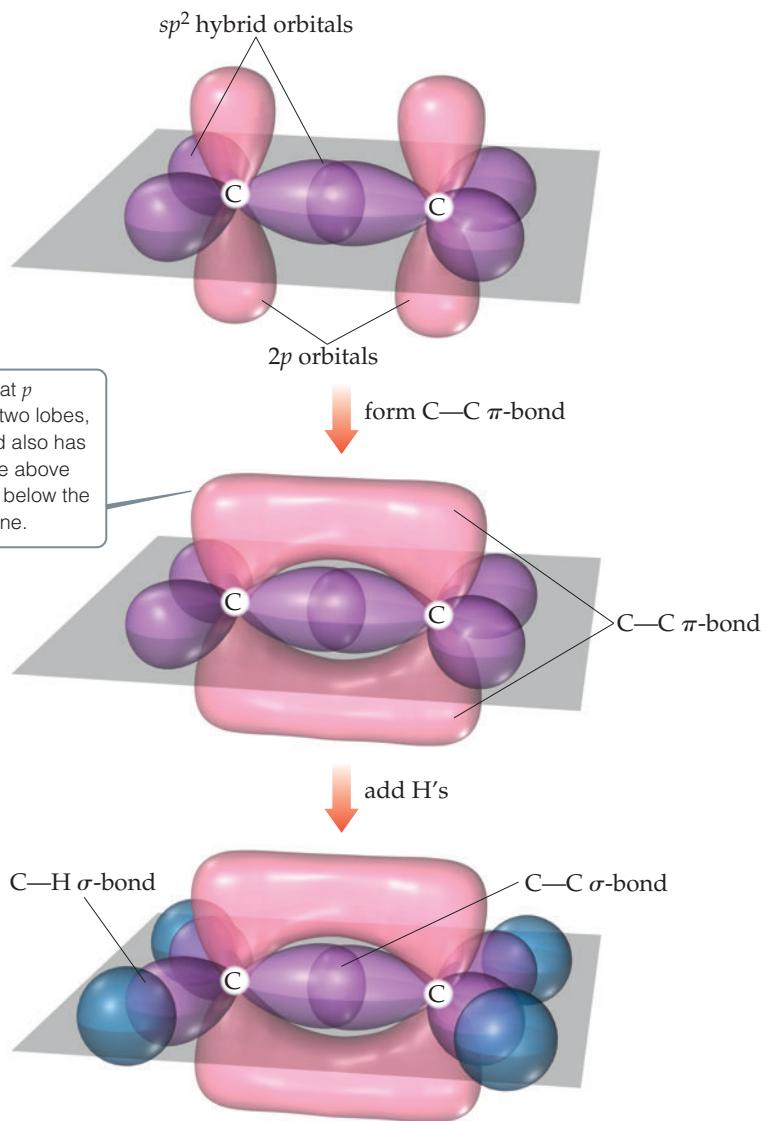
Although we cannot experimentally observe a  $\pi$ -bond directly (all we can observe are the positions of the atoms), the structure of ethene provides strong support for its presence. First, the carbon–carbon bond length in ethene (134 pm) is much shorter than in compounds with carbon–carbon single bonds (154 pm), consistent with the presence



**◀ Figure 26.4** Degeneracy of hybrid orbitals. Mixing 2s and two 2p orbitals yields hybrid orbitals whose energies lie between those of the original atomic orbitals.

**Go Figure**

Why is it important that the  $sp^2$  hybrid orbitals of the two carbon atoms lie in the same plane?



**▲ Figure 26.5 Hybridization in ethene.** The  $\sigma$ -bonding framework is formed from  $sp^2$  hybrid orbitals on the carbon atoms. The unhybridized  $2p$  orbitals on the C atoms are used to make a  $\pi$ -bond.

of a stronger carbon-carbon double bond (Table 26.1). Second, all six atoms lie in the same plane, and stay in the same plane (Figures 26.3 and 26.5). If the  $\pi$ -bond were absent, there would be no reason for the two  $CH_2$  fragments of ethene to lie in the same

**TABLE 26.1 Carbon–carbon bond lengths, general molecular formulas and bond enthalpies for ethane, ethene and ethyne**

| Molecule | General formula of class | C—C bond length (pm) | Approximate bond enthalpy (kJ mol <sup>-1</sup> ) |
|----------|--------------------------|----------------------|---|
| Ethane   | $CH_3-CH_3$              | 154                  | 350   |
| Ethene   | $CH_2=CH_2$              | 134                  | 620   |
| Ethyne   | $CH \equiv CH$           | 121                  | 840   |

plane, as they could rotate with respect to each other in a similar way to alkanes. As a result, the introduction of one or more  $\pi$ -bonds introduces a degree of rigidity into molecules.

Note the difference in bond strength (bond enthalpy) between ethane and ethene in Table 26.1. The C—C double bond is not twice as strong (meaning twice as hard to break) as a single bond, nor is a triple bond three times as strong as a single bond. The fact that each  $\pi$ -bond is weaker than a  $\sigma$ -bond is part of the reason why alkenes and alkynes are far more reactive than alkanes.

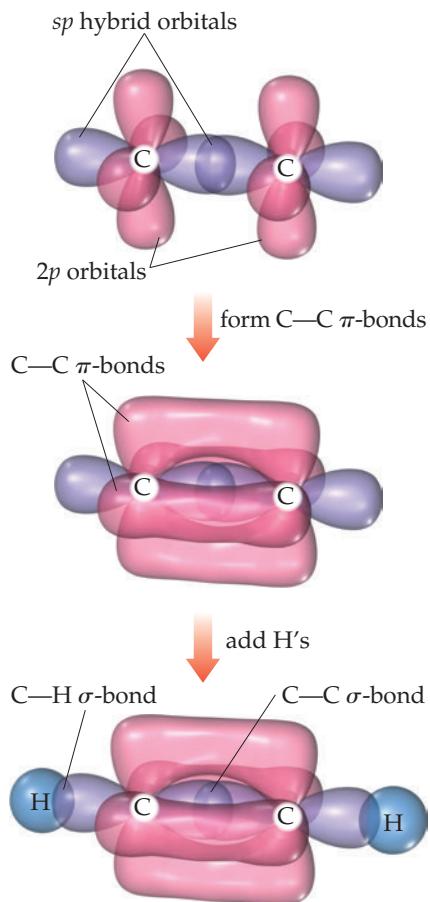
### Bonding in Alkynes

The bonding and geometry of carbon–carbon triple bonds can also be explained by hybridization. Ethyne (more commonly known as acetylene,  $C_2H_2$ ), for example, is a linear molecule containing a triple bond:  $H—C\equiv C—H$ . The linear geometry about the triple bond suggests that each carbon atom uses  $sp$  hybrid orbitals to form  $\sigma$ -bonds with the other carbon and with one hydrogen. Each carbon atom thus has two remaining unhybridized  $2p$  orbitals at right angles to each other and to the axis of the  $sp$  hybrid set (Figure 26.6). These  $p$  orbitals overlap to form a pair of  $\pi$ -bonds. Thus the triple bond in acetylene consists of one  $\sigma$ -bond and two  $\pi$ -bonds.



### Go Figure

Based on the models of bonding in ethene and acetylene, which molecule should have the higher carbon–carbon bond energy?

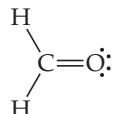


**▲ Figure 26.6 Formation of two  $\pi$ -bonds.** In acetylene,  $C_2H_2$ , the overlap of two sets of unhybridized carbon  $2p$  orbitals leads to the formation of two  $\pi$ -bonds.

## Sample Exercise 26.1

### Describing $\sigma$ -bonds and $\pi$ -bonds in a molecule

Formaldehyde has the Lewis structure



Describe how the bonds in formaldehyde are formed in terms of overlap of appropriate hybridized and unhybridized orbitals.

### SOLUTION

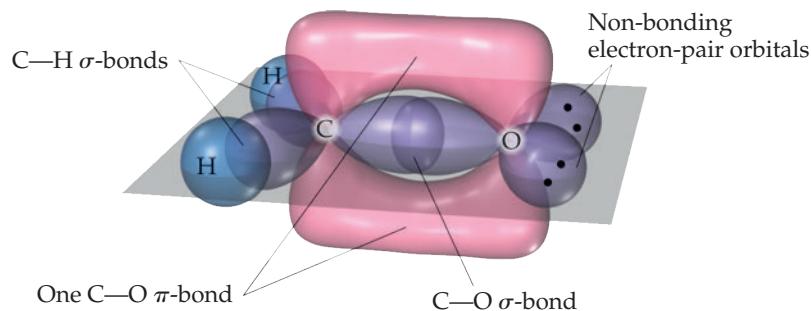
**Analyse** We are given a structure containing several types of bonds and are asked to interpret these bonds in terms of hybrid orbitals.

**Plan** Single bonds are of the  $\sigma$  type, whereas double bonds consist of one  $\sigma$ -bond and one  $\pi$ -bond. The ways in which these bonds form can be deduced from the geometry of the molecule, which we predict using the VSEPR model.

**Solve** The C atom has three electron domains around it, which suggests a trigonal planar geometry with bond angles of about  $120^\circ$ . This geometry implies  $sp^2$  hybrid orbitals on C.

These hybrids are used to make the two C—H and one C—O  $\sigma$ -bonds to C. There remains an unhybridized  $2p$  orbital on carbon, perpendicular to the plane of the three  $sp^2$  hybrids.

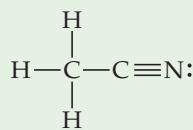
The O atom also has three electron domains around it, so we assume that it has  $sp^2$  hybridization as well. One of these hybrids participates in the C—O  $\sigma$ -bond, while the other two hybrids hold the two non-bonding electron pairs of the O atom. Like the C atom, therefore, the O atom has an unhybridized  $2p$  orbital that is perpendicular to the plane of the molecule. The unhybridized  $2p$  orbitals on the C and O atoms overlap to form a C—O  $\pi$ -bond, as illustrated in **Figure 26.7**.



▲ **Figure 26.7** Formation of  $\sigma$ -bonds and  $\pi$ -bonds in formaldehyde,  $\text{H}_2\text{CO}$ .

### ► Practice Exercise

Consider the acetonitrile molecule:



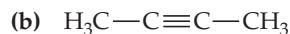
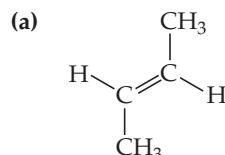
- (a) Predict the bond angles around each carbon atom;
- (b) describe the hybridization at each of the carbon atoms;
- (c) determine the total number of  $\sigma$ -bonds and  $\pi$ -bonds in the molecule.



## Sample Exercise 26.2

### Determining hybridization

Locate the  $sp^3$ ,  $sp^2$  and  $sp$  hybridized carbon atoms in the following compounds.

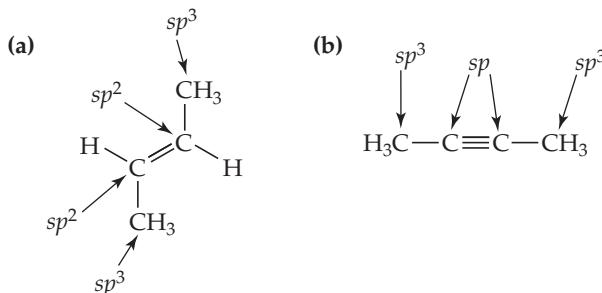


**SOLUTION**

**Analyse** We are given two compounds and are asked to relate the bonding types to a level of hybridization.

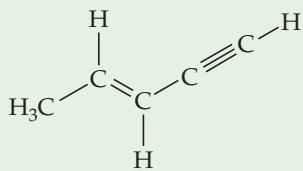
**Plan** This type of question is made easier by remembering that all carbons are  $sp^3$  hybridized, except for those containing a double bond (in which case they are  $sp^2$  hybridized) and those containing a triple bond (which are  $sp$  hybridized).

**Solve** Using these observations:

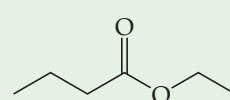
**► Practice Exercise**

Locate the  $sp^3$ ,  $sp^2$  and  $sp$  hybridized carbon atoms in the following compounds.

(a)



(b)



## CHEMISTRY AND LIFE Terpenes and Isoprene

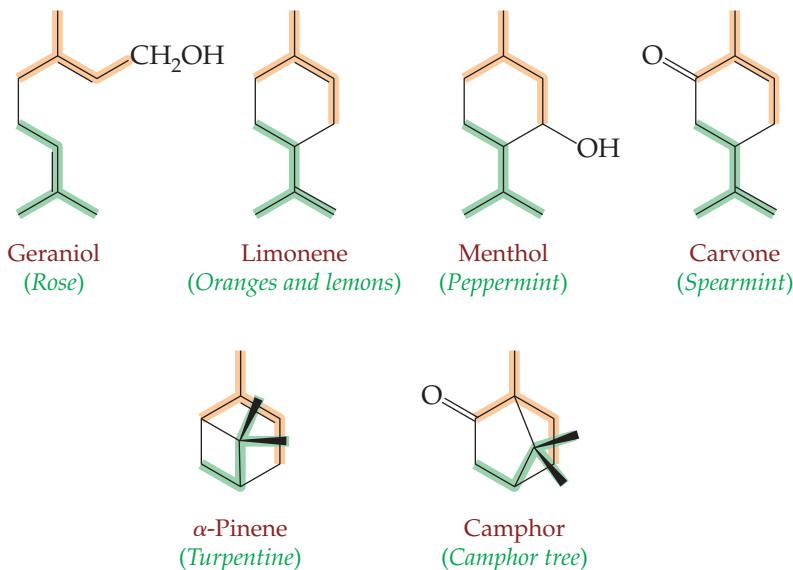
Terpenes are a class of naturally occurring compounds whose carbon skeleton can be divided into two or more isoprene units—a five-carbon unit whose systematic name is 2-methyl-1,3-butadiene (**Figure 26.8**). Terpenes are among the most widely distributed and utilized of all compound classes. Compounds such as camphor, menthol, pinene, geraniol, carvone and limonene are terpenes and each is divisible into two isoprene units.

Distant forest covered hills often appear to have a bluish haze, particularly on hot days. Isoprene is partly responsible for this. This haze

is rich in isoprene, oxidized derivatives of isoprene, and other simple terpenes. The worldwide emission rate of these natural hydrocarbons by vegetation has been estimated to be  $5 \times 10^{11}$  kg / year. Eucalyptus trees are a particularly rich source of isoprene and are found covering the Blue Mountains, just west of Sydney, Australia (**Figure 26.9**).

Isoprene is a colourless liquid with a distinct aromatic odour. Large petroleum-based companies such as Shell Chemicals manufacture large quantities of it as a by-product of ethene production. The polymer polyisoprene is used in a wide variety of rubber applications including medical equipment, baby bottle teats/nipples, toys, shoe soles, tyres and the elastic films used inside golf balls. It is also used in adhesives and in paints and coatings.

As shown in the Chemistry and Life box in Section 26.3, several biologically important terpenes, such as vitamin A, play a large role in vision. The terpenes demonstrate effectively how nature uses simple building blocks such as isoprene to construct larger and more complex molecules with even more complex functions.



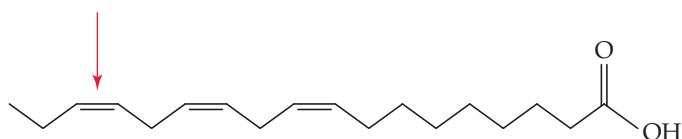
▲ **Figure 26.8 Well-known terpenes.** Geraniol, limonene, menthol, pinene and camphor are common terpenes. The positions of the isoprene units are highlighted. Note that the isoprene units are “linked” head-to-tail.



▲ **Figure 26.9 The Blue Mountains in Australia.** The blue haze is caused in part by isoprene emitted by the plants of the region.

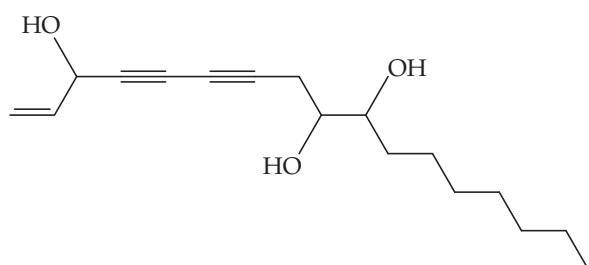
## Self-Assessment Exercises

- 26.1** Many plant oils contain unsaturated fats, of which linolenic acid is an example of an omega-3 fatty acid.



Identify the functional group indicated by an arrow in linolenic acid? (a) alkane (b) alkene (c) alkyne (d) alcohol

- 26.2** Panaxytriol is a natural product found in ginseng. It has the following structure:



How many  $\pi$ -bonds are present in panaxytriole? (a) 1 (b) 2 (c) 3 (d) 5

## Exercises

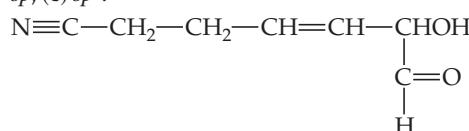
- 26.3** What structural features help us identify a compound as  
(a) an alkene, (b) an alkyne?

**26.4** Give the molecular formula of a hydrocarbon containing five carbon atoms that is (a) an alkane, (b) an alkene, (c) an alkyne. Which are saturated and which are unsaturated hydrocarbons?

**26.5** Give the molecular formula of a cyclic alkane, a cyclic alkene and a linear alkyne that in each case contains six carbon atoms. Which are saturated and which are unsaturated hydrocarbons?

- 26.6** What are the approximate bond angles (**a**) about carbon in an alkane, (**b**) about a C—C double bond in an alkene, (**c**) about a C—C triple bond in an alkyne?

**26.7** Identify the carbon atom/s in the following structure that has/have each of the following hybridizations: (**a**)  $sp^3$ , (**b**)  $sp$ , (**c**)  $sp^2$



26.1 (b) 26.2 (d)

Answers to Self-Assessment Exercises

## 26.2 | Isomerism and Nomenclature



The  $\pi$ -bond of an alkene introduces a rigidity to the carbon–carbon chain at the double bond, which is not seen in an alkane. It is rather like the crosspiece of a five-barred gate lending strength to the structure. The consequence of this is that we may have two distinct

geometries resulting from a molecule of a single constitution. This is another example of the wonderful variety that arises from even simple molecules. The two different shapes of a double bond in the protein rhodopsin are central to the way we see and, in the area of polymers, we have a single monomer producing rubber with its elastic nature or gutta percha, which is a rigid material used as a filler in dental root canal therapy.

When you finish this section, you should be able to:

- Name simple alkene and alkyne molecules
- Recognize where geometric isomers arise and be able to assign a stereochemical descriptor to the name of the structure

Alkene nomenclature is based on the longest continuous chain of carbon atoms that *contains* the double bond. The name given to this longest chain is obtained from the name of the corresponding alkane (Table 24.3), by noting the position of unsaturation, and by changing the ending from *-ane* to *-ene*. Examples of an alkene and cycloalkene and their systematic names are shown in **Figure 26.10**. Note that the longest carbon chain in 2-ethyl-3-methylpent-1-ene is not the one that contains the double bond. This chain is ignored because the longest chain *containing the double bond* takes precedence in naming. Note too that the double bond is always given the lowest position number possible.

The general formula for a cycloalkene is



which is the same as that of an alkyne. Hence, cycloalkenes and alkynes with the same number of carbon atoms are constitutional isomers.

The location of the double bond along an alkene chain is indicated by a prefix number. The chain is always numbered from the end that brings us to the double bond sooner and hence gives the smallest-numbered prefix. In propene the only possible location for the double bond is between the first and second carbons; thus a prefix indicating its location is unnecessary. For butene (**Figure 26.11**) there are two possible positions for the double bond: either after the first carbon (but-1-ene) or after the second carbon (but-2-ene).

If a substance contains two or more double bonds, each one is located by a numerical prefix. The ending of the name is altered to identify the number of double bonds: diene (two), triene (three) and so forth. For example,  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$  is named penta-1,4-diene.

► **Figure 26.10** Nomenclature of alkenes.

Alkene nomenclature is derived from the longest carbon chain containing the double bond. The position of the double bond is always assigned the lowest position number possible. The position of the double bond in a cycloalkene is arbitrarily assigned as spanning positions 1 and 2.



2-Ethyl-3-methylpent-1-ene

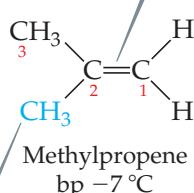
3-Methylcyclopentene



### Go Figure

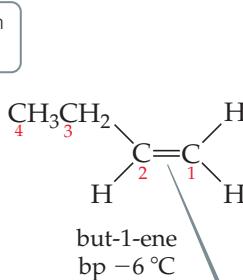
How many isomers are there for propene,  $\text{C}_3\text{H}_6$ ?

Red numbers mark longest chain containing a  $\text{C}-\text{C}$  double bond



Methylpropene  
bp  $-7^\circ\text{C}$

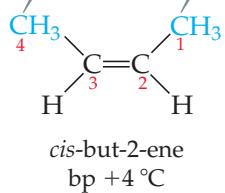
Methyl group branching off longest chain



but-1-ene  
bp  $-6^\circ\text{C}$

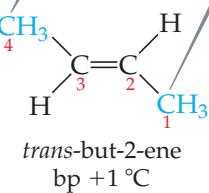
No methyl group branching off

Methyl groups on same side of double bond



cis-but-2-ene  
bp  $+4^\circ\text{C}$

Methyl groups on opposite sides of double bond



trans-but-2-ene  
bp  $+1^\circ\text{C}$

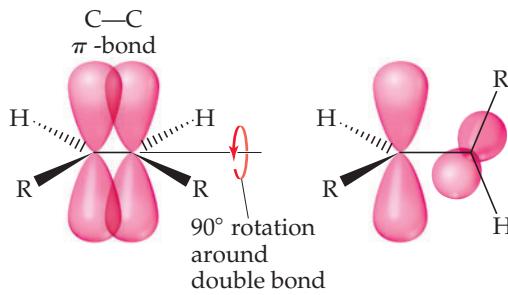
▲ **Figure 26.11**  $\text{C}_4\text{H}_8$  structural isomers. Full structural formulas, names and boiling points of alkenes with the molecular formula  $\text{C}_4\text{H}_8$ .

## Isomerism in Alkenes—The E, Z System

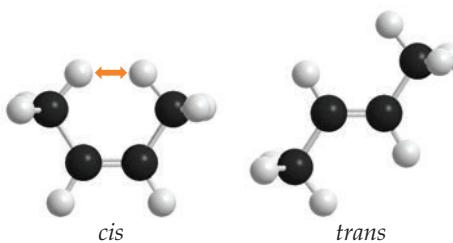
Alkenes with two or more different substituents that lie on either side of the carbon–carbon double bond occur as geometrical isomers. For example, the two structures *cis*-but-2-ene and *trans*-but-2-ene (Figure 26.11) are geometric isomers. Their molecular formula and connectivity are the same; they differ only by the spatial arrangement of the two methyl groups. Geometric isomers, like diastereomers, possess distinct physical properties, such as boiling point, and often differ significantly in their chemical behaviour. This isomerism is a result of the restricted rotation about the carbon–carbon double bond, which in turn is caused by the *p*-orbital overlap required for formation of the  $\pi$ -bond (Figure 26.12). The carbon–carbon bond axis and the bonds to the hydrogen atoms and to the alkyl groups (designated R) are all in a plane. The *p* orbitals that overlap sideways to form the  $\pi$ -bond are perpendicular to the molecular plane. As Figure 26.12 shows, rotation around the carbon–carbon double bond requires the  $\pi$ -bond to be broken, a process that requires considerable energy (about 250 kJ/mol). Although rotation about a double bond doesn't occur easily, it is a key process in the chemistry of vision (see Chemistry and Life box later in Section 26.3).

*Cis*-alkenes tend to be less stable than *trans*-alkenes because of the extra steric interactions that occur when both alkyl substituents are on the same side of the double bond.

Figure 26.13 illustrates this point using the geometric isomers of but-2-ene.



▲ **Figure 26.12** Rotation about a carbon–carbon double bond. In an alkene, the overlap of the *p* orbitals that form the  $\pi$ -bond is lost in the rotation. For this reason, rotation about carbon–carbon double bonds does not occur readily, usually requiring the absorption of energy.



▲ **Figure 26.13** Steric interactions in alkenes. Alkenes such as *cis*-but-2-ene are less stable than their *trans* counterpart due to added steric interactions.

### Sample Exercise 26.3

#### Drawing isomers

Draw all the structural and geometric isomers of pentene,  $C_5H_{10}$ , that have an unbranched hydrocarbon chain.

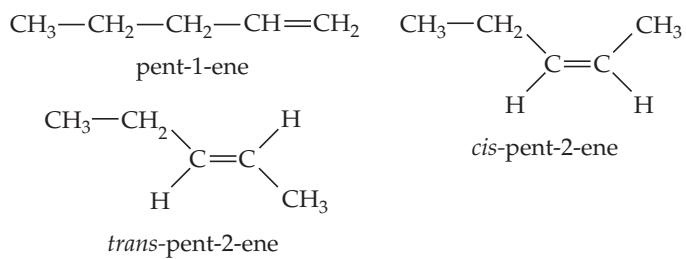
#### SOLUTION

**Analyse** We are given the name of an alkene and asked to derive all possible isomer permutations.

**Plan** Because the compound is named pentene and not pentadiene or pentatriene, we know that the five-carbon chain contains only one carbon–carbon double bond. Thus we can begin by first placing the double bond in various locations along the chain, remembering that the chain can be numbered from either end. After finding the different distinct locations for the double bond, we can consider whether the molecule can have *cis* and *trans* isomers.

**Solve** There can be a double bond after either the first carbon (pent-1-ene) or second carbon (pent-2-ene). These are the only two possibilities because the chain can be numbered from either end. (Thus what we might erroneously call pent-4-ene is actually pent-1-ene, as seen by numbering the carbon chain from the other end.) Because the first C atom in pent-1-ene is bonded to two H atoms, there are no *cis-trans* isomers. However, there are

*cis* and *trans* isomers for pent-2-ene. Thus the three isomers for pentene are



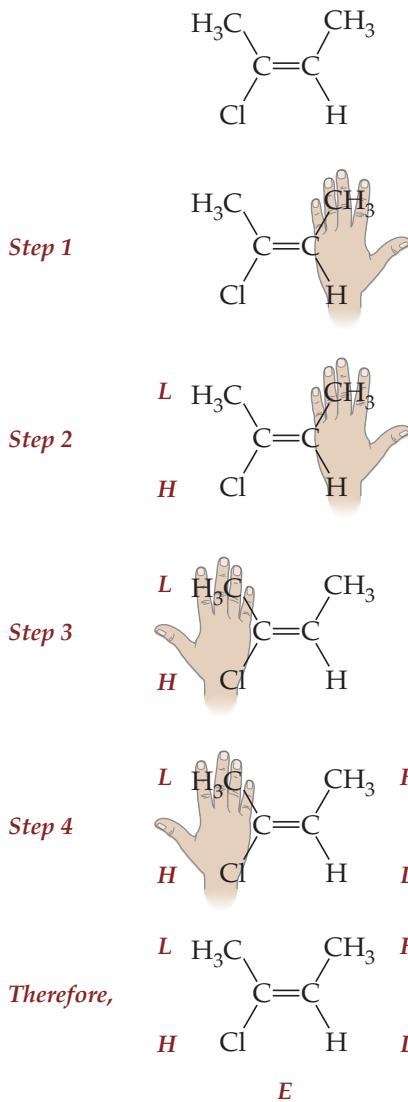
(You should convince yourself that *cis*- or *trans*-pent-3-ene is identical to *cis*- or *trans*-pent-2-ene, respectively.)

#### ► Practice Exercise

How many straight-chain isomers are there of hexene,  $C_6H_{12}$ ?


**Go Figure**

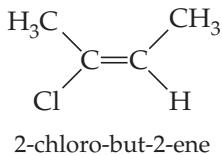
What stereoisomer would you get if you replaced Cl with H in this example? E or Z?



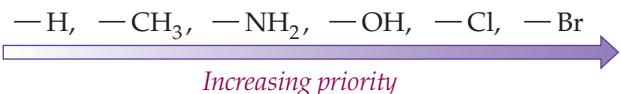
▲ **Figure 26.14** Assignment of **E** and **Z** isomers. The hand acts to remove one side of the molecular structure from consideration.

Although *cis* and *trans* nomenclature is useful to describe simple geometric isomers, it fails to describe more complex isomers accurately. To remove any ambiguity in naming geometric isomers, the IUPAC has established a set of priority rules similar to the Cahn–Ingold–Prelog priority rules used for determining stereochemistry.

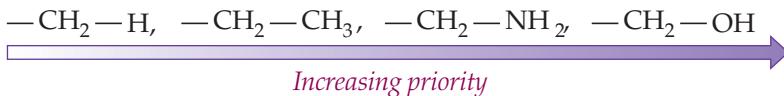
The system for naming isomers is known as the ***E, Z* system**. An alkene is designated *E* (from German *entgegen*, meaning “opposite”) or *Z* (from German *zusammen*, meaning “together”) based on specific priority rules. The priority rules are listed and their application to the geometric isomer of 2-chloro but-2-ene is shown in **Figure 26.14**.



1. Split the molecule through the C—C double bond into two parts and concentrate on setting the priority for one side at a time.
2. Assign a priority to each substituent using H for highest priority and L for lowest priority, based on the *atomic number* of the two atoms directly attached to the  $sp^2$  carbon atom. The higher the atomic number, the higher the priority. A representative set of groups in increasing priority order is:



If two atoms are identical in terms of priority, you need to move out along the respective chains until you encounter a difference in priority. Reapply rule 2 to determine priority. If no difference is found, the two substituents must be identical and no *E/Z* isomerism is possible. An example of increasing priority fragments is:



3. Repeat step 2 for the other side of the C—C double bond.
4. If the two higher-priority groups are on the same side of the double bond, the alkene is the *Z* isomer. If they occur on opposite sides, as in the example shown in Figure 26.14, the alkene is the *E* isomer.

### Alkynes

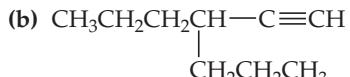
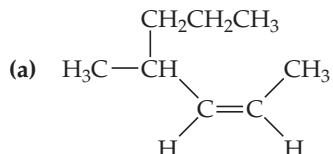
Alkynes are unsaturated hydrocarbons containing one or more C—C triple bonds. Alkynes are named by identifying the longest continuous chain in the molecule *containing the triple bond* and modifying the ending of the name, as listed in Table 24.3, from *-ane* to *-yne*, as shown in Sample Exercise 26.4. Alkynes are linear about the C—C triple bonds, so geometric isomerism is not possible about the triple bond. Alkynes are, however, constitutional isomers of cycloalkenes.



### Sample Exercise 26.4

#### Naming unsaturated hydrocarbons

Name the following compounds:



*Continued*

**SOLUTION**

**Analyse** We are given the structural formulas for two compounds—the first an alkene and the second an alkyne—and asked to name them.

**Plan** In each case, the name is based on the number of carbon atoms in the longest continuous carbon chain that contains the multiple bond. In the case of (a), care must be taken to indicate whether *E*, *Z* isomerism is possible and, if so, which isomer is given.

**Solve**

(a) The longest continuous chain of carbons that contains the double bond is seven carbons in length. The parent compound is therefore heptene. Because the double bond begins at carbon 2 (numbering from the end closest to the double bond), the parent hydrocarbon chain is named hept-2-ene. A methyl group is located at carbon atom 4. Thus the

compound is 4-methylhept-2-ene. The geometrical configuration at the double bond is *Z* (that is, the alkyl groups are bonded to the double bond on the same side). Thus the full name is *Z*-4-methylhept-2-ene.

(b) The longest continuous chain of carbon atoms containing the triple bond is six, so this compound is a derivative of hexyne. The triple bond comes after the first carbon (numbering from the right), making it a derivative of hex-1-yne. The branch from the hexyne chain contains three carbon atoms, making it a propyl group. Because it is located on the third carbon atom of the hexyne chain, the molecule is 3-propylhex-1-yne.

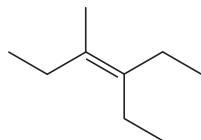
**► Practice Exercise**

Draw the condensed structural formula for 4-methylpent-2-yne.

In Chapter 32, we will discuss the techniques used to determine the molecular structure of alkenes and alkynes—namely nuclear magnetic resonance spectroscopy, infrared spectroscopy and mass spectrometry.

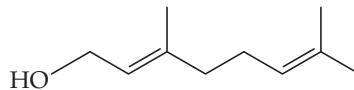
## Self-Assessment Exercises

**26.8** What is the correct name for this structure?



- (a) 2,3-diethylpent-2-ene (b) 3-ethyl-4-methylhex-3-ene  
(c) 3,4-diethylpent-3-ene

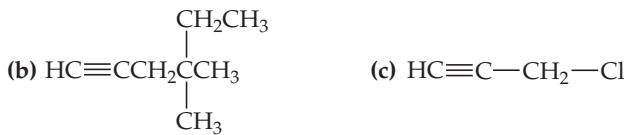
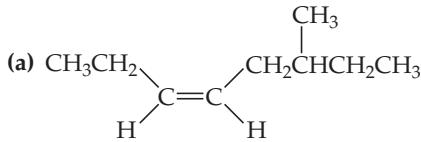
**26.9** What is the correct descriptor (*E* or *Z*) for the double bonds in geraniol, a component in citronella oil.



- (a) both *E* (b) both *Z* (c) one *E* and one *Z* (d) only one double bond has stereochemistry and that is *E* (e) only one double bond has stereochemistry and that is *Z*

## Exercises

**26.10** Name the following compounds systematically:



**26.11** Why is geometric isomerism possible for alkenes, but not for aliphatic alkanes and alkynes?

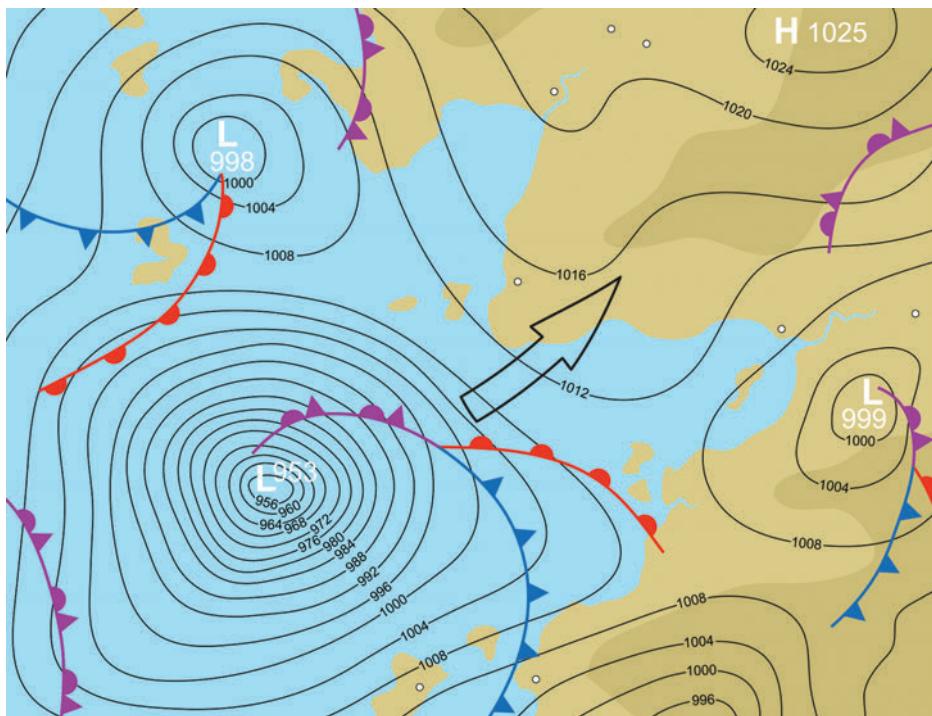
**26.12** Draw the condensed structural formulas for the *E* and *Z* isomers of pent-2-ene. Can cyclopentene exhibit *E*, *Z* isomerism? Explain.

26.8 (b) 26.9 (e)

Answers to Self-Assessment Exercises



## 26.3 | Arrow Notation and Resonance Structures: Electron Counting



From the results of many experiments, we can learn the product we get from mixing two chemicals together. However, if we understand how the molecules interact to give this product, then our knowledge allows us to predict the outcome of reactions that have yet to be tried. Using a few basic rules, we can construct a likely *mechanism* for the reaction. While it is very difficult to see individual molecules reacting with one another (and even that through the use of highly advanced technology), the reaction mechanism can help us visualize what is going on at a molecular level. One tool we use to aid us with this is the drawing of “curved arrows”. These arrows represent the movement of electrons either within a molecule or between two molecules and allow us to keep track of what is going on. Rather like predicting the weather, we use a combination of observations of past events with a model of how change occurs to predict outcomes.

When you finish this section, you should be able to:

- Draw curved arrows to show the electron movements in a resonance structure
- Extend the concept of curved arrows to a reaction between an electron donor and an electron acceptor

A “straight” arrow indicates the transformation of a reactant into a product in a chemical equation. Arrows can also be used to track the flow of electrons that is occurring. In this case a curved arrow is used so there is no confusion about which process we are showing. The curved arrows always start from where the electrons are coming from and end where the electrons are going to. Curved arrows are used for three common types of electron redistribution:

1. From a bond to an adjacent atom—this forms a lone pair on the receiving atom, or joins two molecules together.
2. From an atom to an adjacent bond—this uses a lone pair on the donor atom to form a  $\pi$ -bond.
3. From one bond to an adjacent bond—this redistributes the electrons although, overall, the same number of  $\sigma$ - and  $\pi$ -bonds is retained.

## CHEMISTRY AND LIFE The Chemistry of Vision

Scientists have begun to understand the complex chemistry of vision. Vision begins when light is focused by the lens onto the retina, the layer of cells lining the interior of the eyeball. The retina contains *photoreceptor* cells known as rods and cones (Figure 26.15). The human retina contains about 3 million cones and 100 million rods. The rods are sensitive to dim light and are used in night vision. The cones are sensitive to colours. The tops of the rods and cones contain a substance called *rhodopsin*. Rhodopsin consists of a protein, called *opsin*, bonded to a reddish-purple pigment called *retinal*, which is similar in structure to  $\beta$ -carotene. Structural

changes around a double bond in the retinal portion of the molecule trigger a series of chemical reactions that result in vision. Our recent discussions now allow us to appreciate another aspect of double bonds: the rigidity that they introduce into molecules.

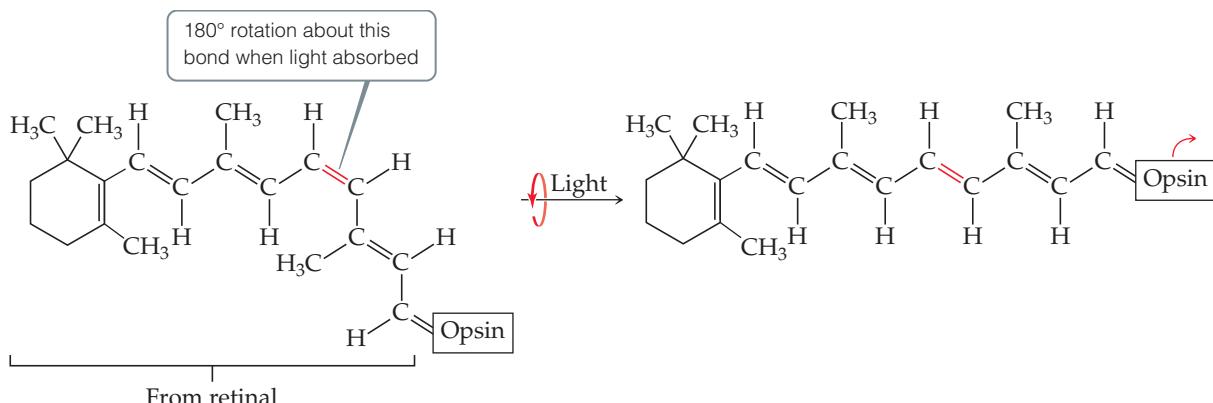
Imagine taking the  $-\text{CH}_2$  group of the ethene molecule and rotating it relative to the other  $-\text{CH}_2$  group, as shown in Figure 26.12. This rotation destroys the overlap of  $p$  orbitals, breaking the  $\pi$ -bond, a process that requires considerable energy. Thus the presence of a double bond restricts the rotation of the bonds in a molecule.

Our vision depends on this rigidity in retinal. In its normal form, retinal is held rigid by its double bonds, as shown on the left in Figure 26.16. Light entering the eye is absorbed by rhodopsin, and the energy is used to break the  $\pi$ -bond portion of the indicated double bond. The molecule then rotates around this bond, changing its geometry. The retinal then separates from the opsin, leading to conformational changes that trigger the reactions producing a nerve impulse. The brain interprets this impulse as the sensation of vision. It takes as few as five closely spaced molecules reacting in this fashion to produce the sensation of vision. Thus only five photons of light are necessary to stimulate the eye.

Enzymes in the retina revert the retinal to its original form and reattach it to the opsin. The slowness of this process helps to explain why intense bright light causes temporary blindness. The light causes all the retinal to separate from the opsin, leaving no further molecules to absorb light.



▲ Figure 26.15 Inside the eye. A colour-enhanced scanning electron micrograph of the rods (yellow) and cones (blue) in the retina of the human eye.

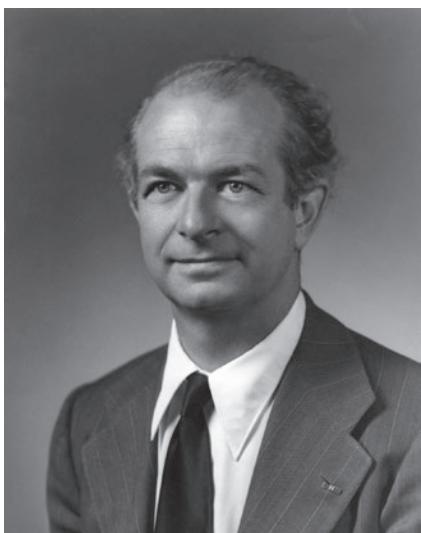


▲ Figure 26.16 The chemical basis of vision. When rhodopsin absorbs visible light, the  $\pi$  component of the double bond (shown in red) breaks, allowing rotation that produces a change in molecular geometry.

The use of curved arrows is a useful way to rationalize all your organic reactions or to demonstrate stability. Following this set of simple rules will help you master this technique. All structures generated using curved arrows must:

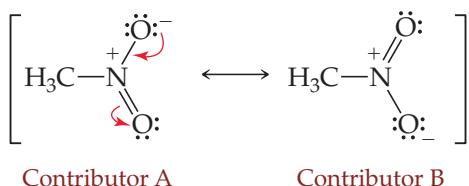
1. have the same number of valence electrons as the starting structure,
2. obey the rules of covalent bonding—for example, no more than four formal bonds to carbon,
3. differ only in the distribution of valence electrons,
4. have the same number of paired or unpaired electrons.

The concept of resonance was advanced in the 1930s by Linus Pauling (1901–1994) (Figure 26.17). He rationalized that many molecules and ions are best described by writing two or more Lewis structures, and that individual Lewis structures are *contributing structures*.



**▲ Figure 26.17** Linus Pauling, a scientist of the highest calibre who won a Nobel Prize in 1954 for his contributions to chemistry. He was also very socially aware, using his scientific knowledge and his influence to combat nuclear testing in the 1950s and 1960s. For this effort, he was awarded the Nobel Peace Prize in 1962 and is still the only person in history to have won two unshared Nobel Prizes.

Let us consider the two contributing (resonance) structures of nitromethane using curved arrow notation to interconvert contributor A and contributor B:



The curved arrows, shown in red, are placed on the first structure to show how the electrons move during the transformation into the second structure. In this case a lone pair on one oxygen atom becomes the new  $\pi$ -bond while the electron pair of the  $\pi$ -bond in contributor A shifts to become a lone pair on the second oxygen atom. Note that the curved arrow indicates the movement of an electron *pair* and not of single electrons.

The two different contributing structures of nitromethane are linked by a double-headed (resonance) arrow as opposed to a set of equilibrium arrows ( $\rightleftharpoons$ ) and are grouped together in square brackets since they both contribute to the same structure. This means that the actual molecule (or ion) is a hybrid of the various contributing structures. In other words the “real” structure of nitromethane is neither contributor A nor contributor B, but something in between—that is, a structure in which the negative charge is spread across both oxygens. We say that the negative charge is *delocalized* across the two N—O bonds. We can observe this delocalization experimentally by looking at the N—O bond lengths in *nitro* compounds. The two bond lengths are equal at 121 pm and lie between the size of a single N—O bond and a double N—O bond.

The presence, or absence, of contributing resonance structures plays a large part in the reactivity of molecules and ions. We will see a lot more of this, especially when discussing what constitutes a good leaving group and the reactivity of phenols.

## A CLOSER LOOK

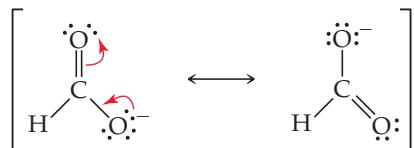
### Describing Charge

$\oplus$  or  $+$ ? Organic chemists tend to circle positive and negative signs on molecules to distinguish charge from bonds and plus signs. It also helps when describing electron redistribution. From here on, we will use this form of notation in our mechanistic considerations.

## Sample Exercise 26.5

## Resonance and curved arrows

Draw two equivalent resonance structures for the formate ion,  $\text{HCO}_2^-$  using curved arrows to indicate movement of electrons.



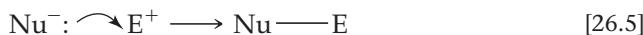
## ► Practice Exercise

Which of the following molecules or ions will exhibit delocalized bonding:  $\text{SO}_3^{2-}$ ,  $\text{H}_2\text{CO}$ ,  $\text{O}_3$ ,  $\text{NH}_4^+$ ?

Arrow notation can also be used to rationalize a reaction's pathway or *mechanism*. A simple and general reaction may look like this:



where "Nu" is not the fictional element "nubrium" but a nucleophile—that is, any molecule or ion with a lone pair of electrons available for reaction. We can use the arrow notation to describe pictorially how the lone pair on Nu is able to form a new covalent bond with an electrophile E (electro, meaning *negative*; phile, meaning *loving*), which is an electron-pair acceptor:



An example of this type of reaction is



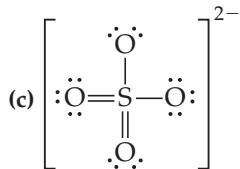
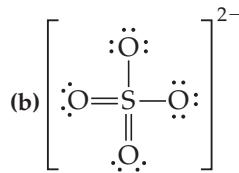
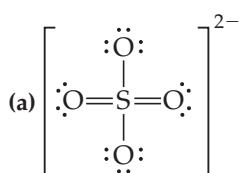
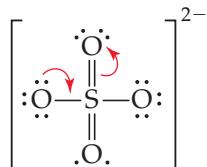
We will gain significant experience at using arrow notation in the next section and throughout the next five chapters as we discuss the reactivity of functional groups.

## Self-Assessment Exercises

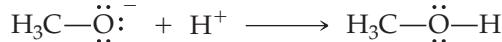
**26.13** What does a curved arrow represent?

- (a) The transformation of reactants into products
- (b) The movement of a single electron
- (c) The movement of a pair of electrons

**26.14** Which resonance structure results from the curved arrows shown in this contributor to the sulfate ion:



**26.15** Which curved arrow correctly represents the following reaction:



- (a)  $\text{H}_3\text{C}-\ddot{\text{O}}^- + \text{H}^+ \curvearrowright \text{H}_3\text{C}-\ddot{\text{O}}-\text{H}$
- (b)  $\text{H}_3\text{C}-\ddot{\text{O}}^- + \text{H}^+ \curvearrowright \text{H}_3\text{C}-\ddot{\text{O}}-\text{H}$
- (c)  $\text{H}_3\text{C}-\ddot{\text{O}}^- + \text{H}^+ \curvearrowright \text{H}_3\text{C}-\ddot{\text{O}}-\text{H}$

## Exercises

**26.16** (a) Write a single Lewis structure for acetate,  $\text{CH}_3\text{COO}^-$ . (b) Are there other equivalent Lewis structures for the molecule? (c) Would you expect  $\text{CH}_3\text{COO}^-$  to exhibit delocalized  $\pi$ -bonding? (d) Draw the curved arrows that represent the electron movement linking the two resonance contributors of the acetate ion. Explain.

**26.17** Draw the curved arrows representing the electron pair movement in the neutralization reaction of the acetate ion,  $\text{CH}_3\text{COO}^-$ , with  $\text{H}^+$ .

26.13 (c)    26.14 (b)    26.15 (b)

Answers to Self-Assessment Exercises



## 26.4 | Electrophilic Addition Reactions



A synthetic organic research chemist is someone whose focus is to transform chemicals that are cheap and readily available into new molecules that have a specific purpose, for example as pharmaceuticals or a new type of glue or a material with a high strength to weight ratio. In this section, we see how the process may start as we look at reactions of unsaturated hydrocarbons. A few different combinations of chemicals can lead to a wide variety of products. While this may seem confusing at first, we find that the reactions all occur by the same basic mechanism so by visualizing what happens on a molecular level enables us to predict the outcome of all electrophilic addition reactions. There is a distinct pattern to what is occurring!

When you finish this section, you should be able to:

- Predict the outcome of any electrophilic addition reaction
- Understand the mechanism by which these reactions occur
- Use your knowledge of the reaction mechanism to rationalize the regioselective and stereoselective characteristics of the reaction

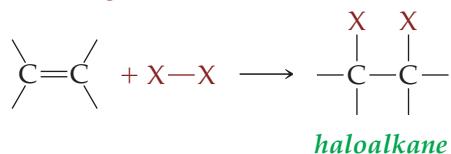
The presence of carbon–carbon double or triple bonds in a compound markedly increases its chemical reactivity. The most characteristic reactions of alkenes and alkynes are **addition reactions**, in which a reactant is added across the two carbon atoms that form the multiple bond. Three main types of addition reactions are typical of alkenes and alkynes, leading to increasing the degree of functionality within a hydrocarbon: **halogenation**, **hydrohalogenation** and **hydration**. These reactions involve the addition of  $X_2$  ( $X = Cl, Br$ ),  $HX$  ( $X = Cl, Br, I$ ) and  $HOH$  (water), respectively. [Figure 26.18](#) shows a general representation of each reaction.

The reason why alkenes and alkynes are so reactive is twofold. In both cases, the unhybridized  $p$  orbitals that form the  $\pi$ -bonds are electron-rich, so would be expected to attract electron-deficient species. Also, we have seen that in carbon,  $\pi$ -bonds are weaker than  $\sigma$ -bonds, so would be expected to react to form  $\sigma$ -bonds wherever possible. Moreover, the shape of alkenes and alkynes make them easily accessible to reagents ([Figure 26.19](#)). The electron-rich nature of a multiple bond leads to enhanced reactivity with electrophiles. Hence, **electrophiles** are molecules that accept a pair of electrons in a chemical reaction. Reactions of alkenes and alkynes with electrophiles are called electrophilic addition reactions.

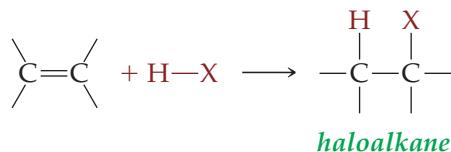
### Addition Reactions Involving $HX$ ( $X = Cl, Br, I$ )

Let's consider the addition reaction between HBr and but-2-ene as a representative of this reaction type. The reaction proceeds in two steps. In the first step, which is

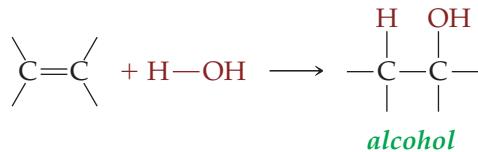
## (a) Halogenation



## (b) Hydrohalogenation

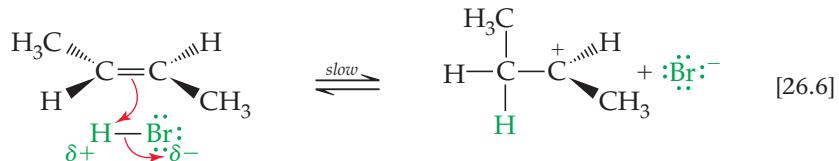


## (c) Hydration



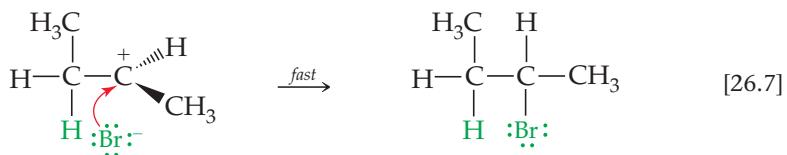
▲ **Figure 26.18** Addition reactions of alkenes and alkynes ( $\text{X} = \text{halogen}$ ). Halogenation, hydrohalogenation and hydration of an alkene are useful and efficient ways of preparing alkyl halides and alcohols. The addition reactions of alkynes follow those of the alkenes.

rate-determining, the electron-rich double bond attacks the hydrogen of  $\text{HBr}$  (the electrophile), which transfers a proton to one of the two alkene carbons and produces a bromide ion in the process:



The pair of electrons that formed the  $\pi$ -bond between the carbon atoms in the alkene are used to form the new  $\text{C}-\text{H}$  bond. As a result, one carbon has fewer valence electrons associated with it. This carbon is now electron-deficient, as indicated by the positive charge. Organic molecules bearing a positive charge on carbon are called **carbocations**. Carbocations are classified as *primary* ( $1^\circ$ ), *secondary* ( $2^\circ$ ) or *tertiary* ( $3^\circ$ ), depending on the number of carbon units bonded to the positively charged carbon. For example, the carbocation formed on the right-hand side in Equation 26.6 is secondary, as the carbon bearing the positive charge has two other carbons bonded directly to it.

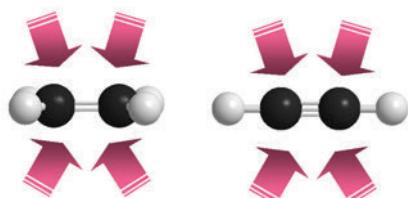
The second step, involving the addition of  $\text{Br}^-$  to the carbocation, is faster:



In this step the bromide ion donates a pair of electrons to the carbocation, forming the new  $\text{C}-\text{Br}$  bond. The bromide ion is behaving as a **nucleophile** (*nucleus-loving*). A nucleophile is a species that donates a pair of electrons in a chemical reaction. Nucleophiles are electron-rich species.

Since the first step in the reaction involves both the alkene and hydrogen halide, the rate law for the reaction is second order, first order in both the alkene and  $\text{HBr}$ :

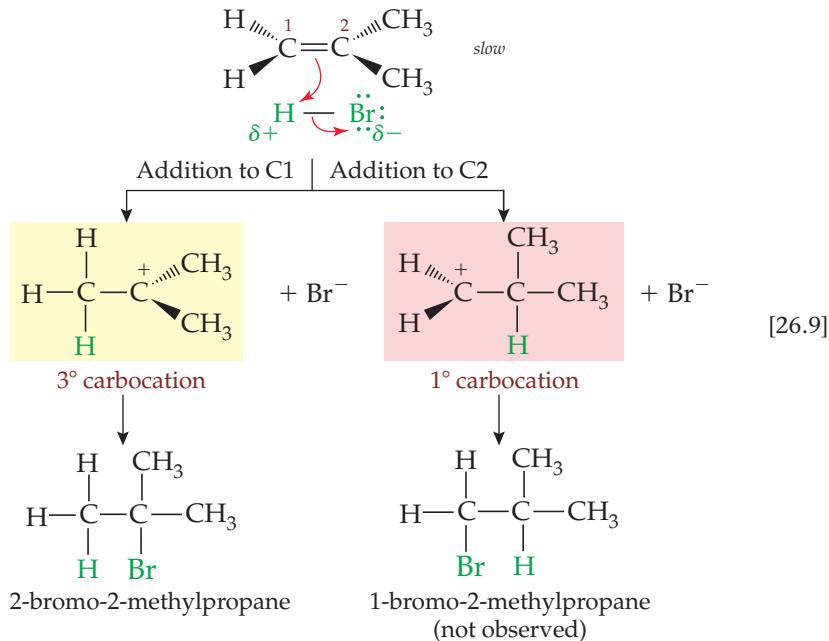
$$\text{Rate} = -\frac{\Delta[\text{CH}_3\text{CH}=\text{CHCH}_3]}{\Delta t} = k[\text{CH}_3\text{CH}=\text{CHCH}_3][\text{HBr}] \quad [26.8]$$



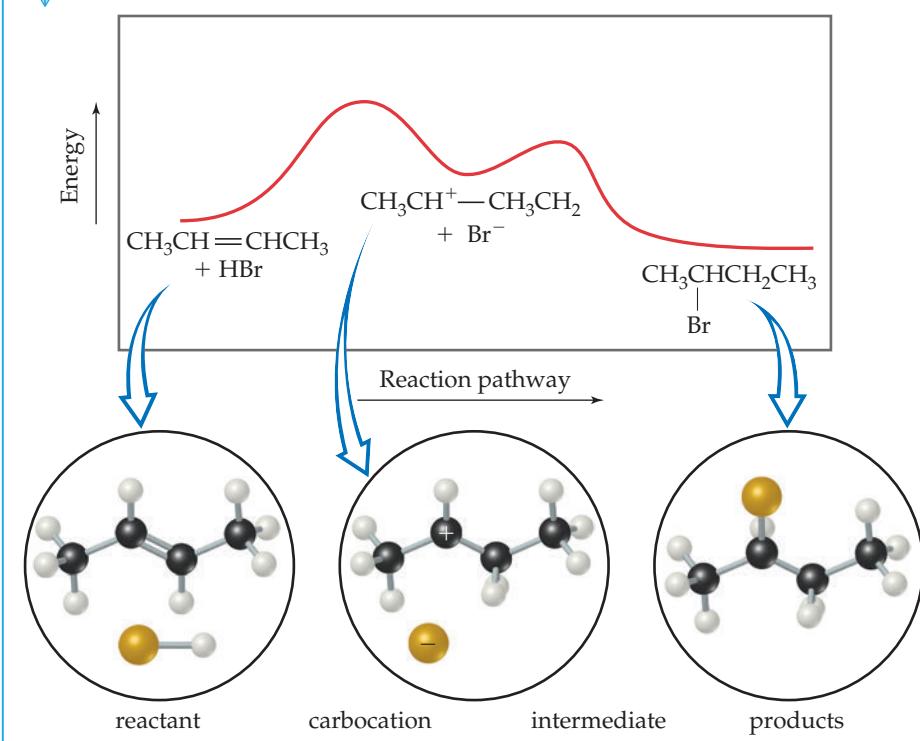
▲ **Figure 26.19** The accessibility of alkenes and alkynes. The trigonal planar and linear geometries of alkenes and alkynes makes the addition of halogens easier through the exposed faces, as indicated by the arrows. Alkynes have two additional regions of accessibility, one directed out of the page and the other into the page.

The energy profile for the reaction is shown in **Figure 26.20**. The first energy maximum represents the transition state in the first step of the mechanism. The second maximum represents the transition state for the second step. Notice that there is an energy minimum between the first and second steps of the reaction. This energy minimum corresponds to the intermediate carbocation.

Let us now consider the reaction of 2-methylpropene with HBr. This reaction is a *regioselective reaction* meaning that one product, 2-bromo-2-methylpropane, is formed predominantly. The first step of the addition leads to the possible formation of two intermediate carbocations:



**Go Figure** As shown, is this reaction endothermic or exothermic?



▲ **Figure 26.20** Energy profile for addition of HBr to but-2-ene.

From a large body of experiments, we know that  $3^\circ$  carbocations are more stable and require a lower activation barrier to formation than either  $1^\circ$  or  $2^\circ$  carbocations. Hence the product distribution can be rationalized based on which intermediate is formed in preference.

The relative stability of primary, secondary and tertiary carbocations is:



and is based on how easily the alkyl groups around the positive charge can spread the charge away. This is known as an *inductive effect*. The larger the area the positive charge is spread over, the more stable the carbocation. In the case of hydrocarbons, as the number of alkyl groups increases so too does the stability of the carbocation increase.

The first person to note the regioselectivity in hydrohalogenations (and hydrations) was Vladimir Markovnikov (1837–1904). The general rule for electrophilic additions to alkenes bears his name. **Markovnikov's rule** states:

*In the addition of HX to an alkene, the hydrogen adds to the carbon atom of the double bond bearing the greater number of hydrogen atoms bonded directly to it.*

This can also be written:

*In the addition of HX to an alkene, the hydrogen adds to the least substituted carbon atom of the double bond.*

This rule provides an easy way to predict the major product of an addition reaction involving HX.

Returning to Equation 26.9, C1 has two hydrogens directly attached whereas C2 has none (those on the methyl group hydrogens do not count because they are not directly attached to the  $sp^2$  hybridized carbon of the double bond). The product predicted by using Markovnikov's rule is certainly the one predicted on the basis of carbocation stability.

## Sample Exercise 26.6

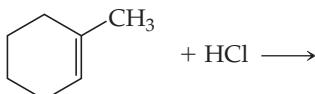
### Addition of HX to alkenes

Name and draw the structural formula for the major product formed when 1-methylcyclohexene reacts with HCl. Justify your choice for the major product.

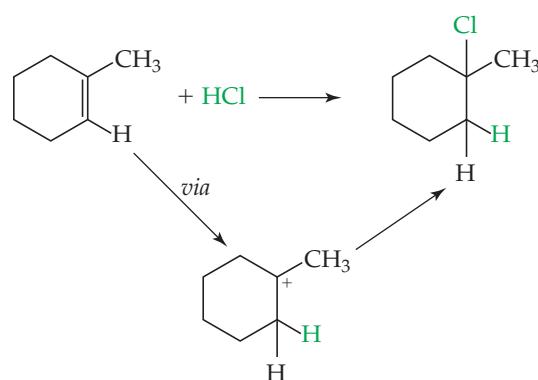
#### SOLUTION

**Analyse** We are asked for several things here, including knowing something about nomenclature and converting names into structures, as well as the reactivity of alkenes.

**Plan** Begin by drawing the structure of the reactants and identify the reaction as the addition of HCl to the double bond:



**Solve** Using Markovnikov's rule, the hydrogen atom of HX should add to the double bond on the side with the most number of hydrogens:

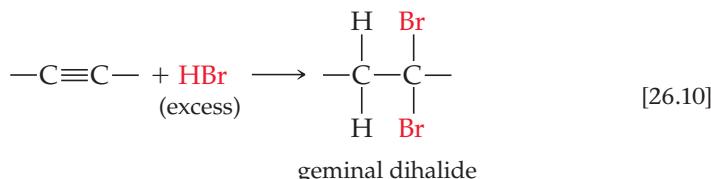


Hence our answer is *1-chloro-1-methylcyclohexane*. Our justification comes from the relative stabilities of the possible carbocation intermediates. Our chosen product forms a  $3^\circ$  carbocation intermediate over the alternative  $2^\circ$  carbocation intermediate because it is more stable due to enhanced inductive effects. To say "because Markovnikov said so" is not satisfactory.

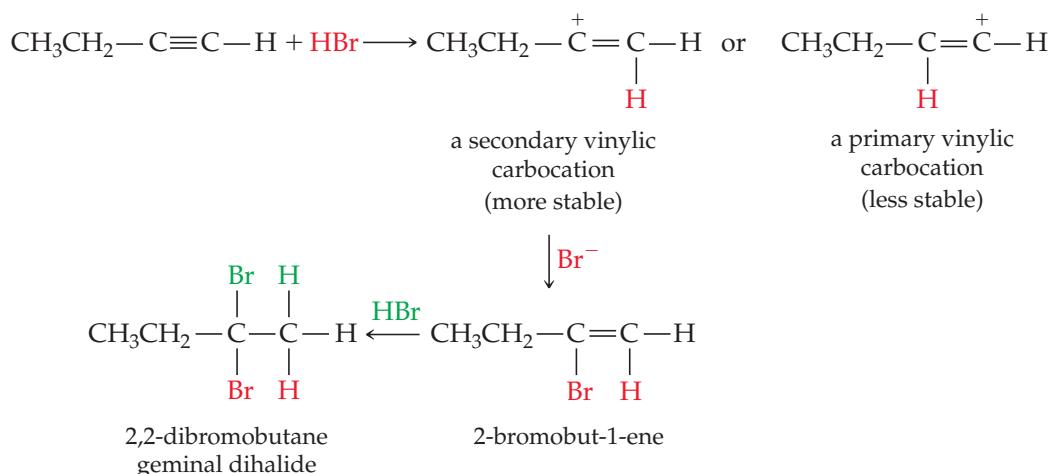
#### ► Practice Exercise

Addition of HCl to an alkene forms 2-chloro-3-methylbutane. What is the alkene?

The addition of HX across an alkyne forms a *geminal* dihalide. The term *geminal* refers to two groups occupying the same carbon. Equation 26.10 demonstrates reactions of this class.



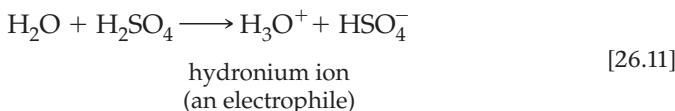
In the case of a terminal alkyne, for example but-1-yne, protonation occurs at the terminal carbon due to the formation of a stabilized secondary vinylic carbocation, which is relatively more stable than the alternative primary carbocation. Notice that the trend of carbocation stability is the same as that discussed for the addition of HBr to alkenes. Further reaction of this carbocation with the bromide nucleophile leads to 2-bromobut-1-ene as the sole product. Further addition of HBr to the alkene follows Markovnikov's rule, leading to the geminal dibromide 2,2-dibromobutane.



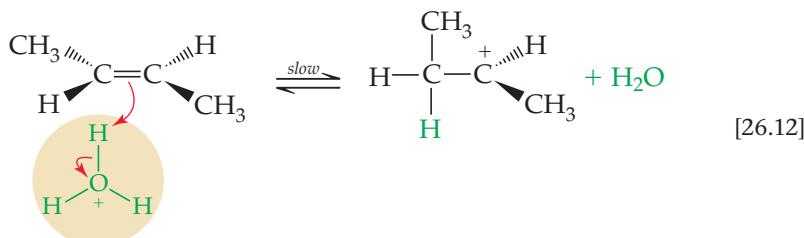
## Addition Reactions Involving $\text{H}_2\text{O}$

The *hydration* of alkenes and alkynes is not as easy to accomplish as either the halogenation or hydrohalogenation of the same compounds. Hydration reactions need to be catalysed by a small amount of a strong acid, such as  $\text{H}_2\text{SO}_4$ . The reason is easily demonstrated mechanistically. Again, we can use but-2-ene as our alkene to illustrate this example.

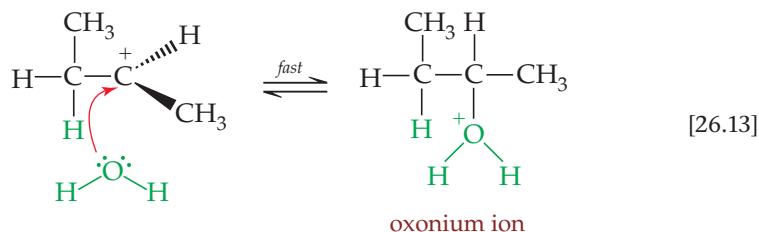
The addition of a few drops of sulfuric acid to a reaction mixture containing but-2-ene and water leads to the formation of the hydronium ion, as shown:



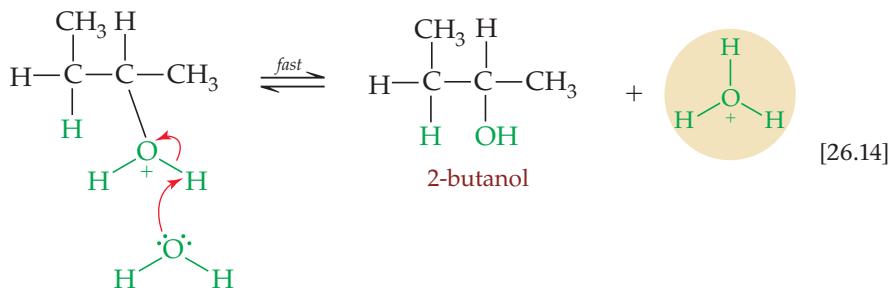
In terms of the addition of water, the hydronium species is the active electrophile. The reaction proceeds as shown in Equations 26.12 to 26.14. The first step involves the addition of a proton from the hydronium ion to one of the carbons that make up the double bond. This step is slow and rate-determining.



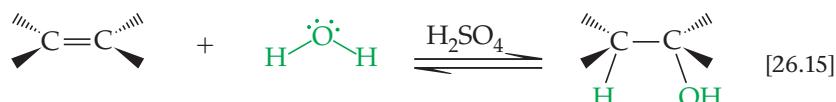
A molecule of water can then act as a nucleophile forming a C—O bond with the valence electrons of one of its two lone pairs. Note that a nucleophile need not be negatively charged; it just needs to be a species capable of donating a pair of electrons. In this case, an oxonium ion is formed.



Loss of a proton from the oxonium ion yields the final alcohol product. The other product formed is a new hydronium ion. This ion is capable of reacting further with another alkene in the same way described in Equations 26.12 to 26.14. Theoretically, an amount of sulfuric acid large enough to initiate the formation of a single hydronium ion is enough to allow the reaction to proceed. In practice, more is required to make sure the reaction is completed in a timely manner.



You may have noticed in Equations 26.12 to 26.14 that equilibrium arrows are used to describe each step of the reaction mechanism. This is because the reverse reaction—that is, the *dehydration* of alcohols—is also catalysed by  $\text{H}_2\text{SO}_4$ . In fact, this reverse method is a very useful way of preparing alkenes.

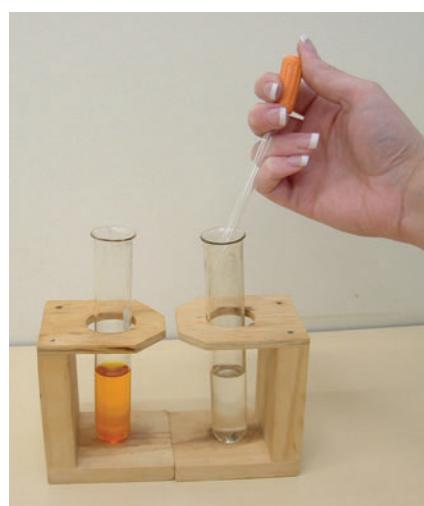


The direction of the equilibrium, shown in equation 26.15—that is, to maximize the yield of the alkene from the alcohol (right to left) or the alcohol from the alkene (left to right)—can be manipulated by adjusting the amount of water present in the reaction mixture. Large amounts of water (usually as aqueous acid) favour alcohol formation, whereas using concentrated acid and eliminating water favour alkene formation. By using these simple techniques, the alkene prepared in high yield.

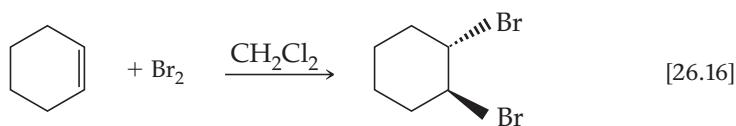
## Halogenation: Addition of $\text{Br}_2$ and $\text{Cl}_2$

One of the easiest and most dramatic reactions in organic chemistry has to be the reaction of  $\text{Br}_2$  with an alkene. Bromine is a dense orange liquid, whose colour persists if made into a solution in hexane. The addition of a slight excess of an alkene to this solution (Figure 26.21) at room temperature immediately turns the solution colourless. Undertaking this reaction in the presence of an alkane also demonstrates the large difference in reactivity between alkanes and alkenes towards bromination. This reaction and its dramatic colour change is a useful qualitative test for the presence of a  $\text{C}=\text{C}$  double bond in a compound.

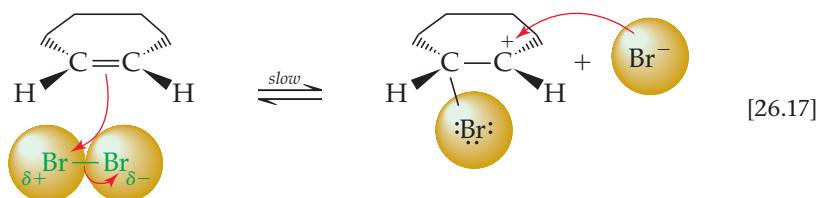
The addition of bromine or chlorine to an alkene is an example of a **stereoselective reaction**: a reaction in which the product has one particular geometry in preference over another. Observe how in Equation 26.16 the two bromine atoms add to opposite sides of the plane of the cyclohexene molecule. Let us now investigate the reaction of bromine with cyclohexene, as an example of a halogenation, in more detail.



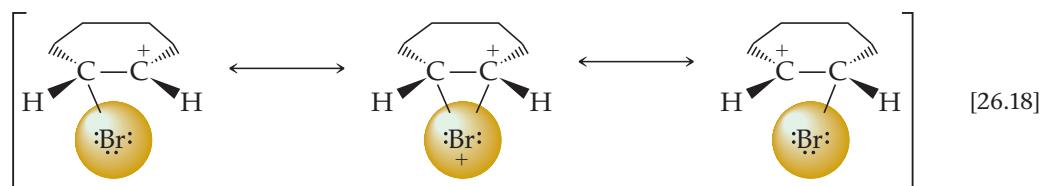
**▲ Figure 26.21** Bromine test for alkenes. The bright orange colour of bromine solution is in contrast to the colourless solution produced by the addition of an alkene to the same solution.



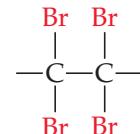
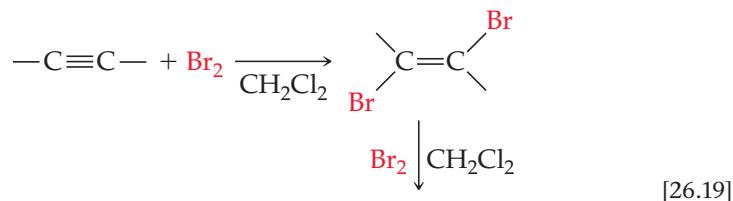
The reasons for the stereoselectivity observed in the bromination of alkenes involve both steric and electronic components. The enormous size of a bromine atom compared with a hydrogen atom means that the incoming nucleophile ( $\text{Br}^-$ ) cannot attack the carbocation from the same face as the initial electrophile (as shown in Equation 26.17). In the case of a cyclic structure, restricted rotation about the C—C bonds ensures that only the *trans*-dihaloalkane is formed. Chlorination is not as stereoselective because of chlorine's comparatively smaller size.



Three contributors to the resonance structure of the intermediate carbocation are possible because of the electron-rich nature of the bromine atom and its accessibility to the carbocation due to its size. Of these, the middle structure bearing the *bromonium ion* is the largest contributor to the intermediate's overall structure.



The bromination and chlorination of alkynes follows a similar mechanism. The stepwise addition of bromine, by way of example, is shown in Equation 26.19. In each step, dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) is the solvent.

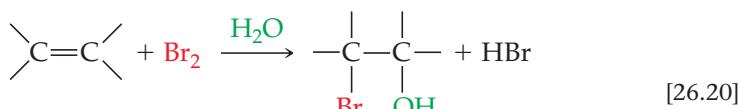


Addition of one equivalent of bromine leads to the formation of the dibromo-alkene in which the two bromo groups occupy a *trans* arrangement across the double bond as a result of the bromonium intermediate formed. A further equivalent of bromine leads to the tetrabrominated alkane in which all four positions around the carbon-carbon triple bond are occupied by halogen. Tetrahalogenation occurs when an excess of bromine or chlorine to the alkyne is used.

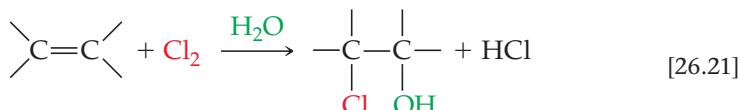
### Halohydrin Formation

Let us now extend what we have learned about the mechanisms associated with the bromination and hydration of alkenes to more complicated additions. To do this, we will investigate the formation of the *halohydrins*—a class of compound containing halogen and OH functional groups. If the halogen and OH groups are on adjacent carbon atoms,

the compound is called a *vicinal haloalcohol*. Equations 26.20 and 26.21 illustrate the reaction type:



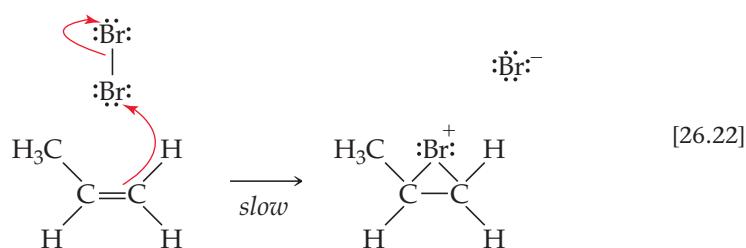
*a vicinal haloalcohol*



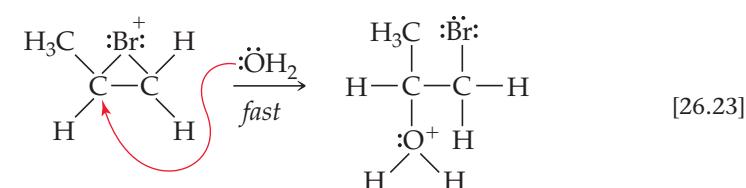
The halogen of the haloalcohol originates from the source you are familiar with (being  $\text{Br}_2$  or  $\text{Cl}_2$ ) and the OH group of the haloalcohol occurs typically through the introduction of water to the reaction. This can be achieved either by adding water to the solvent of choice or as the solvent, depending on practicality.

The mechanism of bromohydrin formation has three steps. Here we look at the formation of the bromohydrin derived from propene in more detail:

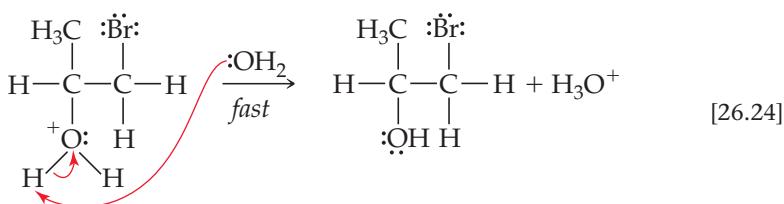
**Step 1**



**Step 2**



**Step 3**

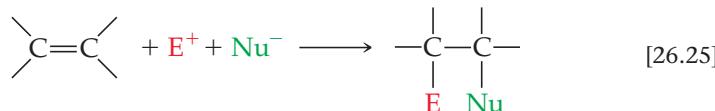


A cyclic bromonium ion is formed in the first step because  $\text{Br}^+$  is the only electrophile in the reaction mixture (the corresponding cyclic chloronium ion would form if chlorine is used). This cyclic bromonium ion rapidly reacts with any nucleophile present. In the present case, two nucleophiles are present in solution. The two nucleophiles are  $\text{Br}^-$  and  $\text{H}_2\text{O}$ . But because  $\text{H}_2\text{O}$  is in the solvent, it is present in a higher concentration than  $\text{Br}^-$ . Consequently, reaction between the cyclic bromonium ion and  $\text{H}_2\text{O}$  is more likely. The protonated bromohydrin is a strong acid, and so reacts readily with water to form the haloalcohol.

Notice throughout Equations 26.23–26.24 that the *regioselectivity* is well-defined with very little of the alternative bromohydrin formed. The product distribution follows *Markovnikov's rule*, as do all the additions we have studied so far. You may recall that for the addition of  $\text{HCl}$  across a double bond, the hydrogen adds to the side of the double bond with the most hydrogens. In the example of  $\text{HCl}$  addition,  $\text{H}^+$  is considered to be the electrophile. In the case of haloalcohol formation, the electrophile is  $\text{Br}^+$ , yet the outcome is still the same, that is, the electrophile adds to the side of the double bond with the most hydrogens.

While the major organic product of the reactions shown in Equations 26.20 and 26.21 is the vicinal haloalcohol (called a bromohydrin or chlorohydrin, respectively), the corresponding dihalides are also formed to some extent. This is due to the competition between the two nucleophiles present, bromide ion and water.

Halohydrin formation suggests we can generalize addition reactions in the following way:



where the requisite nucleophile and electrophile can come from different starting materials. This means that provided you are able to identify a range of electrophiles ( $\text{E}^+$ ) and nucleophiles ( $\text{Nu}^-$ ) from a broad range of reagents, you will be able to convert alkenes into many highly functionalized compounds. **Table 26.2** lists some common electrophile ( $\text{E}^+$ ) and nucleophile ( $\text{Nu}^-$ ) combinations and the addition products.

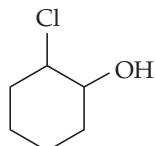
**TABLE 26.2 Summary of addition reactions to an alkene by electrophile ( $\text{E}^+$ ) and nucleophile ( $\text{Nu}^-$ ) from Equation 26.25**

| Reagents                                   | Electrophile           | Nucleophile            | Product  |
|--|------------------------|------------------------|--|
| $\text{Br}_2$                              | $\text{Br}_2$          | $\text{Br}^-$          | $\begin{array}{c}   &   \\ -\text{C}-\text{C}- \\   &   \\ \text{Br} & \text{Br} \end{array}$    |
| $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ | $\text{H}_3\text{O}^+$ | $\text{H}_2\text{O}$   | $\begin{array}{c}   &   \\ -\text{C}-\text{C}- \\   &   \\ \text{H} & \text{OH} \end{array}$     |
| $\text{Cl}_2$                              | $\text{Cl}_2$          | $\text{Cl}^-$          | $\begin{array}{c}   &   \\ -\text{C}-\text{C}- \\   &   \\ \text{Cl} & \text{Cl} \end{array}$    |
| $\text{Br}_2/\text{H}_2\text{O}$           | $\text{Br}_2$          | $\text{H}_2\text{O}$   | $\begin{array}{c}   &   \\ -\text{C}-\text{C}- \\   &   \\ \text{Br} & \text{OH} \end{array}$    |
| $\text{NBS}/\text{H}_2\text{O}$            | $\text{Br}_2$          | $\text{H}_2\text{O}$   | $\begin{array}{c}   &   \\ -\text{C}-\text{C}- \\   &   \\ \text{Br} & \text{OH} \end{array}$    |
| $\text{Cl}_2/\text{CH}_3\text{OH}$         | $\text{Cl}_2$          | $\text{CH}_3\text{OH}$ | $\begin{array}{c}   &   \\ -\text{C}-\text{C}- \\   &   \\ \text{Cl} & \text{OCH}_3 \end{array}$ |
| $\text{Br}_2/\text{NaCl}$                  | $\text{Br}_2$          | $\text{Cl}^-$          | $\begin{array}{c}   &   \\ -\text{C}-\text{C}- \\   &   \\ \text{Br} & \text{Cl} \end{array}$    |
| $\text{Cl}_2/\text{NaBr}$                  | $\text{Cl}_2$          | $\text{Br}^-$          | $\begin{array}{c}   &   \\ -\text{C}-\text{C}- \\   &   \\ \text{Cl} & \text{Br} \end{array}$    |
| $\text{NBS}/\text{NH}_4\text{Cl}$          | $\text{Br}_2$          | $\text{Cl}^-$          | $\begin{array}{c}   &   \\ -\text{C}-\text{C}- \\   &   \\ \text{Br} & \text{Cl} \end{array}$    |
| $\text{NBS}/\text{NH}_4\text{F}$           | $\text{Br}_2$          | $\text{F}^-$           | $\begin{array}{c}   &   \\ -\text{C}-\text{C}- \\   &   \\ \text{Br} & \text{F} \end{array}$     |

## Sample Exercise 26.7

### Addition reactions leading to halohydrins

Indicate how the following alcohol can be prepared from an alkene:

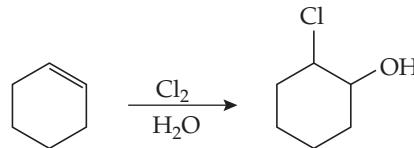


### SOLUTION

**Analyse** We are asked to work backwards from a given structure to determine how we could make it from an alkene.

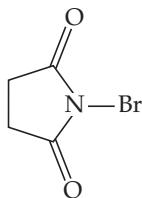
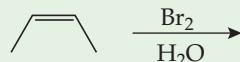
**Plan** Understand the differences between the starting alkene and the chlorohydrin product. Use our general equation [26.25] to determine from what reagents the electrophile and nucleophile are derived.

**Solve** The alkene required for this reaction is cyclohexene. This is deduced by placing the double bond between the positions occupied by the introduced Cl and OH functional groups. To get the addition of Cl and OH to the alkene, the reagents of choice must be  $\text{Cl}_2$  and water. The water acts as both solvent and nucleophile.



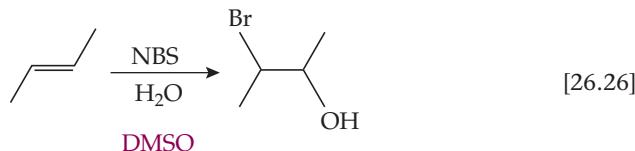
### ► Practice Exercise

What are the major and minor products of the following reaction?



▲ **Figure 26.22** *N*-Bromosuccinimide, or NBS, can act as an electrophilic source of bromine by decomposing slowly in the presence of water to form a tiny amount of  $\text{Br}_2$ .

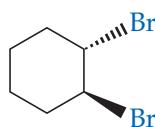
To develop the concept shown in Equation 26.22 further, let us now investigate another source of electrophilic bromine, which is *N*-bromosuccinimide (Figure 26.22). A general reaction utilizing *N*-bromosuccinimide (abbreviated NBS) as an electrophilic source of bromine is shown in Equation 26.26.



Here, the NBS reacts with an alkene in the presence of water and dimethylsulfoxide (DMSO) ( $(\text{CH}_3)_2\text{S}=\text{O}$ ), which is a polar organic solvent miscible with water. Under these conditions, the NBS decomposes slowly to form a small amount of  $\text{Br}_2$ , which then undergoes reaction to form the bromohydrin. Because only a small amount of  $\text{Br}^-$  is ever generated, the concentration of water is always in excess and so the bromohydrin is always formed in high yield.

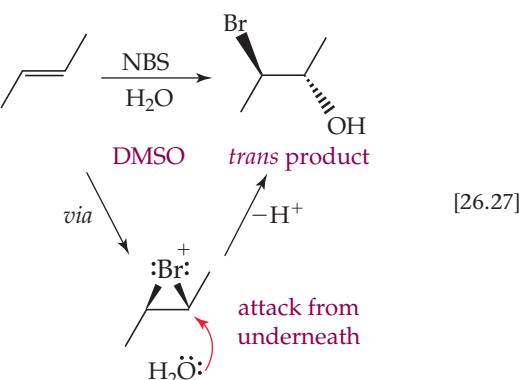
### A CLOSER LOOK Stereochemistry in Halohydrin Formation

Stereoselectivity plays a part in the formation of the bromohydrin. Recall from Equation 26.16 that the product of the bromination of cyclohexene is the *trans* dibromide.

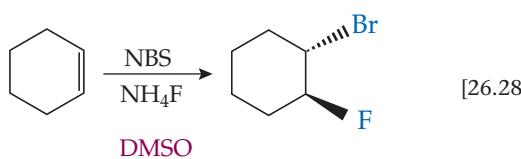


*trans*-1,2-dibromocyclohexane

Because the bridged halonium ion ring is opened by backside attack of  $\text{H}_2\text{O}$  in the halohydrin formation, addition of X and OH occurs in an *anti* (opposite) fashion and the *trans* product is most often formed.

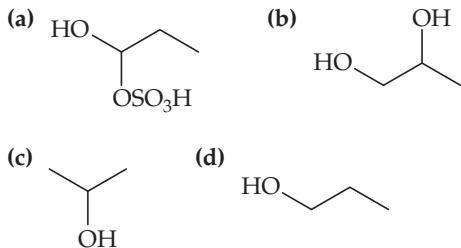


We can see the similarity more clearly in the following example where ammonium fluoride ( $\text{NH}_4\text{F}$ ) provides a source of fluoride, which acts as the nucleophile, and DMSO acts as the solvent. Again, the *trans* product is formed.

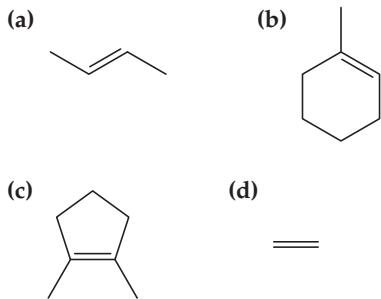


## Self-Assessment Exercises

- 26.18** What is product formed from the addition of water in the presence of dilute sulfuric acid to propene?



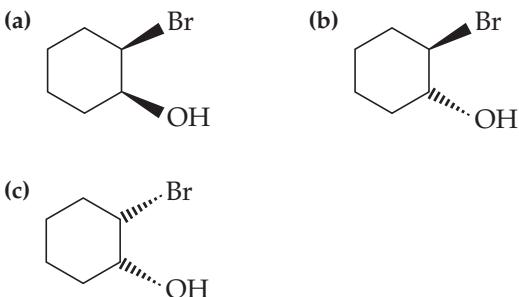
- 26.19** In the addition of HBr to the following alkenes, in which case do we need to apply Markovnikov's rule?



- 26.20** Which alkyne, when treated with excess HI, gives the exclusively 2,2-diiodopentane?



- 26.21** What product is formed when cyclohexene is treated with NBS in the presence of water?



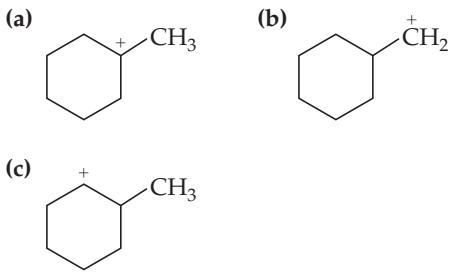
## Exercises

- 26.22** (a) Suggest a method of preparing *trans*-1,2-dichlorocyclohexane. (b) Suggest a method of preparing 1-chloro-2-fluorocyclohexane from cyclohexene.

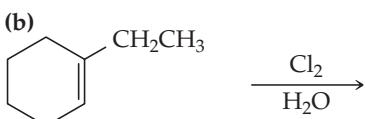
- 26.23** In the hydrohalogenation of but-1-ene with HCl, two alkyl halides can be formed. (a) Draw them. (b) Circle the major organic product and give an explanation for your choice, taking into account the stability of any intermediates.

- 26.24** Draw the intermediate that is thought to form in the addition of a hydrogen halide to an alkene, showing how it is formed and how it reacts, using cyclohexene as the alkene in your description.

- 26.25** Place the following carbocations in an increasing order of relative stability:



- 26.26** What is the major product of the following reactions?



- 26.27** Consider the dehydration and rehydration of 1-propanol. Is the product of the two reactions the same as the starting alcohol?

**26.28** What would be the major organic product for the reaction of but-2-yne with excess bromine?

26.18 (c) 26.19 (b) 26.20 (a) 26.21 (b)

**Answers to Self-Assessment Exercises**

## 26.5 | Alkanes from Alkenes: Catalytic Hydrogenation



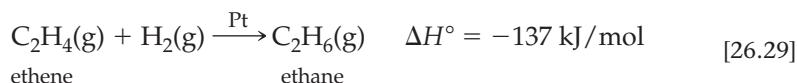
Catalysts play a very important role in hydrocarbon chemistry. “Catalytic cracking” is used in oil refineries to convert high molecular weight hydrocarbons to the more useful, lower molecular weight, feedstock for the chemical industry. Catalysts are also used in the addition of hydrogen to alkenes and alkynes both in the research laboratory as well as for the manufacture of margarine from plant oils.

When you finish this section, you should be able to:

- Identify the conditions required to add hydrogen gas to an alkene or alkyne
  - Understand the stereochemical outcome of hydrogenation of disubstituted cyclic alkenes

The reaction between an alkene and molecular hydrogen ( $H_2$ ), referred to as hydrogenation, does not occur readily under ordinary conditions of temperature and pressure. One reason for the lack of reactivity of  $H_2$  towards alkenes is the high bond enthalpy of the  $H_2$  molecule. To promote the reaction, it is necessary to use a catalyst that assists in rupturing the  $H-H$  bond. The most widely used catalysts are finely divided metals capable of adsorbing  $H_2$ , such as Pt, Pd and Ni. The hydrogenation reaction is often called a **catalytic hydrogenation**, since only a small amount of the solid metal is necessary to promote the reduction of the alkene to the corresponding alkane in solution. Because the alkene and catalyst exist in different phases, this type of reaction undergoes *heterogeneous catalysis*.

The reaction of hydrogen gas with ethene gas to form ethane gas provides an example of heterogeneous catalysis:

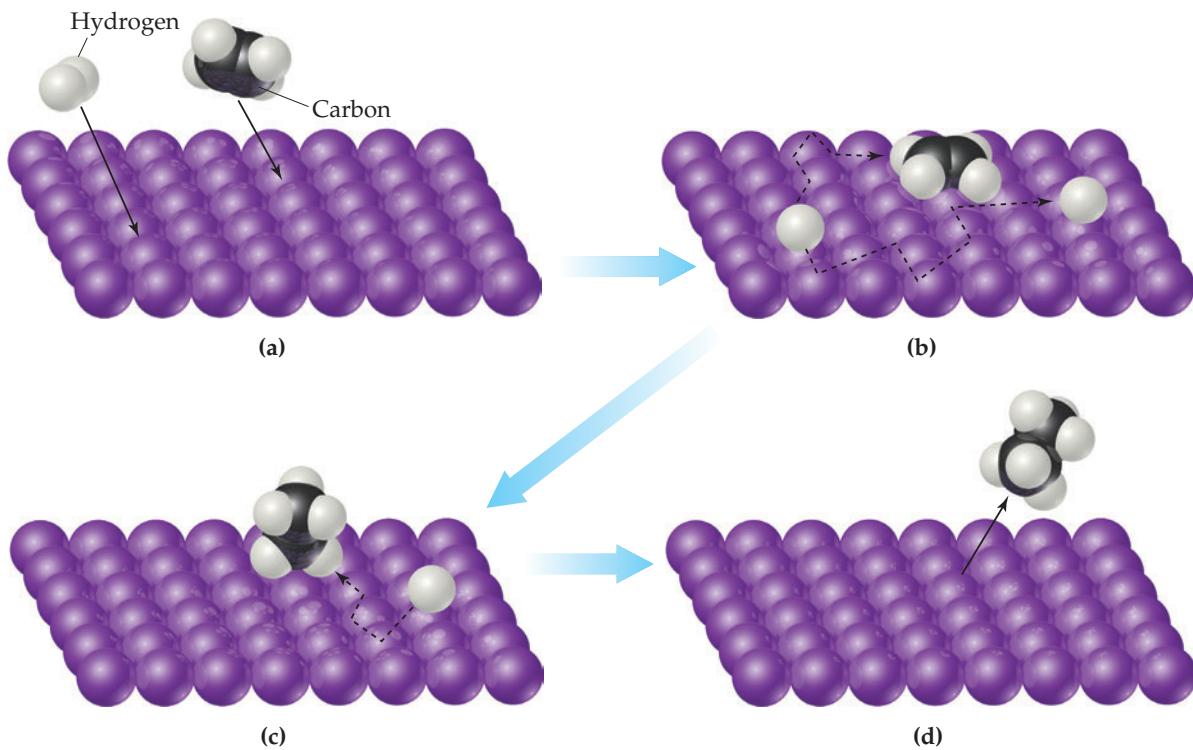


We can understand the role of the catalyst in this process by considering the bond enthalpies involved (Table 8.3). In the course of the hydrogenation reaction, the H—H  $\sigma$ -bond and the carbon-carbon  $\pi$ -bond must be broken, and to do so requires the input of energy, which we can liken to the activation energy of the reaction. The formation of the new C—H  $\sigma$ -bonds *releases* an even greater amount of energy, making the reaction *exothermic*. When H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> are bonded to the surface of the catalyst, less energy is required to break the bonds, lowering the activation energy of the reaction.

### A CLOSER LOOK Hydrogenation

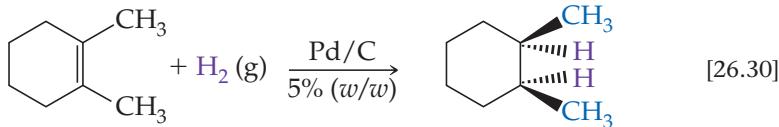
The mechanism by which the reaction is thought to occur is shown schematically in Figure 26.23. Both ethene and hydrogen are adsorbed on the metal surface (Figure 26.23(a)). Upon adsorption the H—H bond of H<sub>2</sub> breaks, leaving two H atoms that are bonded to the metal surface, as shown in Figure 26.23(b). The hydrogen atoms are relatively free to move about the surface. When a hydrogen atom encounters an adsorbed ethene molecule, it can form a  $\sigma$ -bond to one of the

carbon atoms, effectively destroying the C—C  $\pi$ -bond and leaving an *ethyl group* (C<sub>2</sub>H<sub>5</sub>) bonded to the surface *via* a metal-to-carbon bond (Figure 26.23(c)). This bond is relatively weak, and when the other carbon atom also encounters a hydrogen atom, a second C—H  $\sigma$ -bond is readily formed and the resulting ethane molecule is released from the metal surface (Figure 26.23(d)). The site is ready to adsorb another ethene molecule and thus begin the cycle again.



▲ **Figure 26.23** Mechanism for reaction of ethene with hydrogen on a catalytic surface. (a) The hydrogen and ethene are adsorbed at the metal surface. (b) The H—H bond is broken to give two adsorbed hydrogen atoms. (c) These hydrogens migrate to the adsorbed ethene and bond to the carbon atoms. (d) As C—H bonds are formed, the adsorption of the molecule to the metal surface is decreased and ethane is released.

Catalytic hydrogenations favour a *cis* stereochemistry. For example, the reaction of 1,2-dimethylcyclohexene with hydrogen in the presence of 5% (w/w) palladium on carbon (Pd/C) yields the alkane in 100% yield, with >75% of the alkane having the *cis* stereochemistry. Palladium on carbon is a standard synthetic catalyst for hydrogenation.



## Sample Exercise 26.8

### Identifying the product of a hydrogenation reaction

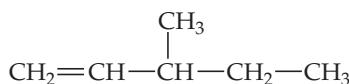
Write the structural formula for the product of the hydrogenation of 3-methyl-1-pentene.

#### SOLUTION

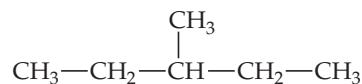
**Analyse** We are asked to predict the compound formed when a particular alkene undergoes hydrogenation (reaction with H<sub>2</sub>).

**Plan** To determine the structural formula of the reaction product, we must first write the structural formula or Lewis structure of the reactant. In the hydrogenation of the alkene, H<sub>2</sub> adds to the double bond, producing an alkane. (That is, each carbon atom of the double bond forms a bond to an H atom, and the double bond is converted to a single bond.)

**Solve** The name of the starting compound tells us that we have a chain of five C atoms with a double bond at one end (position 1) and a methyl group on the third C from that end (position 3):



Hydrogenation—the addition of two H atoms to the carbons of the double bond—leads to the following alkane:



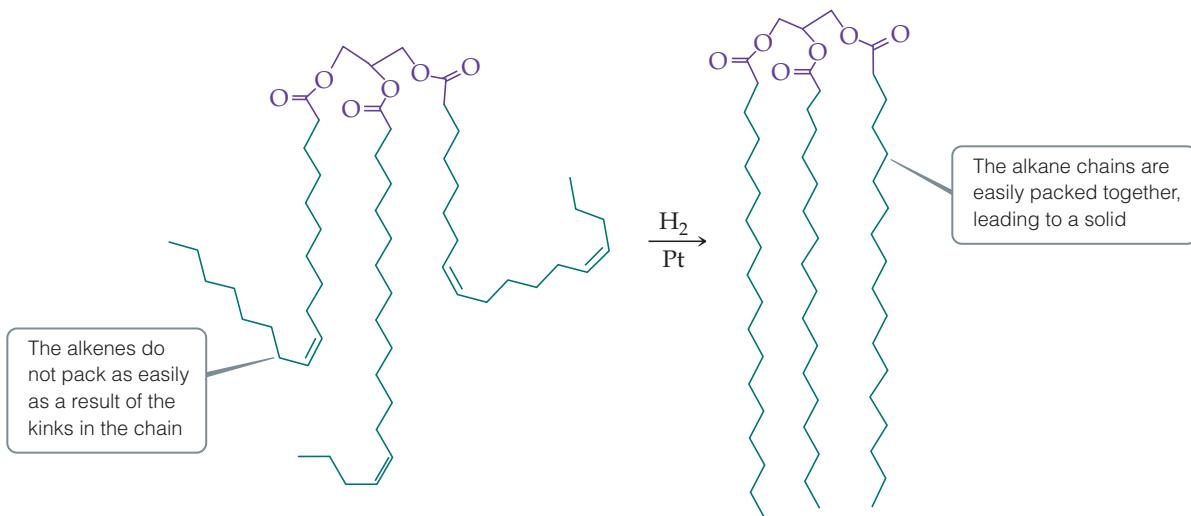
**Comment** The longest chain in the product alkane has five carbon atoms; its name is therefore 3-methylpentane.

#### ► Practice Exercise

Draw all the possible products (including stereochemistry) for the complete hydrogenation of the theoretical compound hexamethylcyclohexatriene, assuming 100% *cis* addition per double bond. Do not account for chair and boat conformations.

Hydrogenation is a useful commercial process for the preparation of fats from *polyunsaturated oils*. These oils, as the name suggests, contain many alkenes. Oils are generally **triglycerides** rich in linoleic (C<sub>18</sub>H<sub>32</sub>O<sub>2</sub>), oleic (C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>), arachidonic (C<sub>20</sub>H<sub>32</sub>O<sub>2</sub>) and other unsaturated fatty esters which, because of their structure, are liquids at room temperature (Section 26.2). Their conversion to stearic (C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>) and arachidic esters (C<sub>20</sub>H<sub>40</sub>O<sub>2</sub>) by hydrogenation leads to **fats**, whose properties are more those of solids or semi-solids at room temperature. The reason for the change in physical properties has to do with the ease of packing the long alkyl chains over those chains that are “kinked” by the introduction of double bonds (Figure 26.24).

The process of converting oils to fats is called **hardening**. This process is especially relevant to the manufacture of margarine and cooking fats. The final hardened product is typically white. In the past, β-carotene was added to colour the margarine so that it looks like butter.



▲ Figure 26.24 Hydrogenation of vegetable oil leads to a more solid product.

## Self-Assessment Exercises

**26.29** What catalyst is required in the hydrogenation reaction of an alkene?

- (a) H<sup>+</sup> (b) Fe (c) Pd/C

**26.30** Partial hydrogenation of but-2-yne produces but-2-ene. What is the stereochemistry of the product?

- (a) *Z* (b) *E* (c) a mixture of *Z* and *E* isomers

## Exercises

- 26.31** Draw the products resulting from the catalytic hydrogenation of the following molecules.



- 26.32** How many moles of hydrogen are required to completely hydrogenate pent-1-en-3-yne?

- 26.33** Draw the structures of all possible alkenes and alkynes that could be used in a catalytic hydrogenation to form 2-methylbutane.

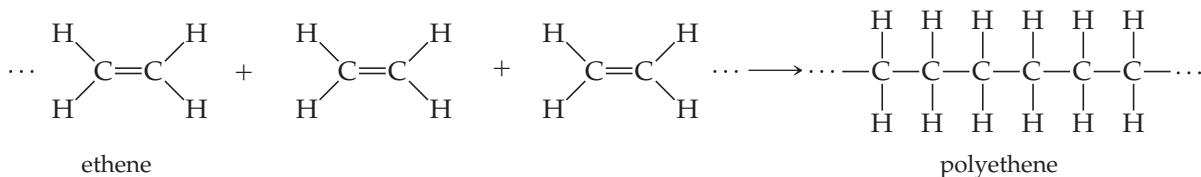
26.29 (c) 26.30 (a)

**Answers to Self-Assessment Exercises**

## 26.6 | Addition Polymerization



In nature, we find many substances of very high molecular mass that make up much of the structure of living organisms and tissues. Some examples include starch and cellulose (which abound in plants) and proteins (found in both plants and animals). In 1827 Jons Jakob Berzelius (1779–1848) coined the word **polymer** (from the Greek *poly*, “many”, and *meros*, “parts”) to denote molecular substances of high molecular mass formed by the *polymerization* (joining together) of **monomers**, that is, molecules with low molecular mass. An example is the reaction of ethene monomers to form polyethene:



When you finish this section, you should be able to:

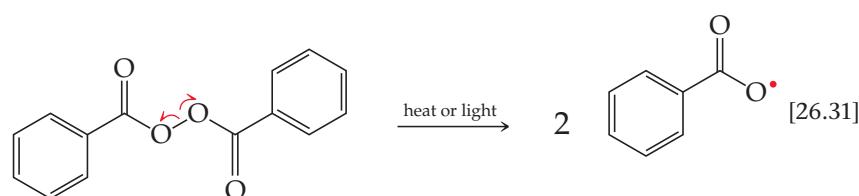
- Recognize the relationship between a monomer and a polymer
- Understand the three stages of addition polymerization
- Make the link between macroscopic properties such as density and the molecular level properties of crystallinity and cross linking

For a long time, humans have processed naturally occurring polymers, such as wool, leather, silk and natural rubber, into usable materials. Over the last century, however, chemists have learned to form synthetic polymers by polymerizing compounds through controlled chemical reactions. A great many of these synthetic polymers have a backbone of carbon–carbon bonds because carbon atoms have an exceptional ability to form strong stable bonds with one another.

**Plastics** are materials that can be formed into various shapes, usually by the application of heat and pressure. **Thermoplastic** materials can be reshaped. For example, plastic milk containers are made from a polymer known as *Polyethene*, which has a high molecular mass. These containers can be melted down and the polymer recycled for some other use. In contrast, a **thermosetting plastic** is shaped through irreversible chemical processes and thus cannot be readily reshaped.

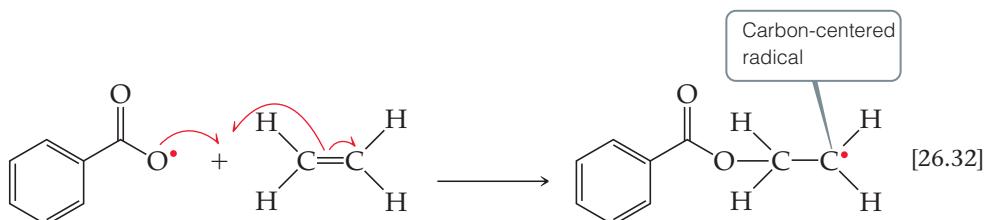
## Making Polymers

Polyethene (**Figure 26.25**) is a solid substance that is used to make thousands of plastic products, such as plastic bags, food containers and laboratory equipment. In making polyethene, a reactive center is formed that adds sequentially to the double bond in each ethene, extending the polymer chain and regenerating the reactive center. Such reactions are classified as chain-growth or **addition polymerizations** and polyethene is an **addition polymer**. In ethene polymerization, the reactive center is frequently a free radical, which can be derived from a radical initiator such as lauroyl peroxide. Peroxides dissociate to form two radicals upon heating or irradiation with light because of the very weak O—O bond:

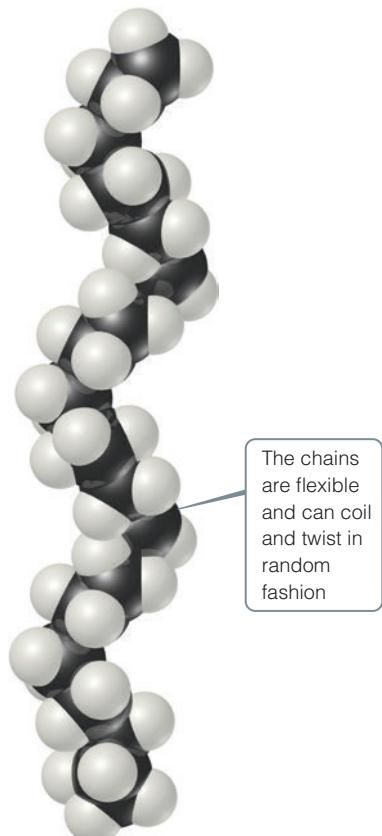


Note the use of *fishhook arrows* in Equation 26.31. They differ from the arrows we have studied to date, which were “arrow”-headed. Fishhook arrows represent the movement of a single electron rather than an electron pair.

Once formed, the benzoyl radical can react with ethene to form a new carbon-centered radical. This step is called the **initiation** step. The relative stabilities of alkyl radicals follow a similar pattern to that of carbocations, namely  $3^\circ > 2^\circ > 1^\circ$  alkyl radicals.

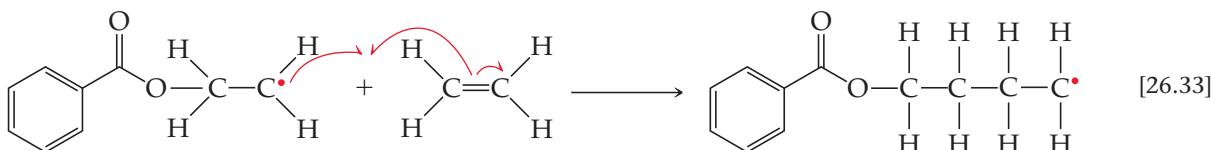


The next stage of reaction is known as **propagation**. In this stage, the chain is extended by the consecutive addition of more ethene units through C—C bond formation:



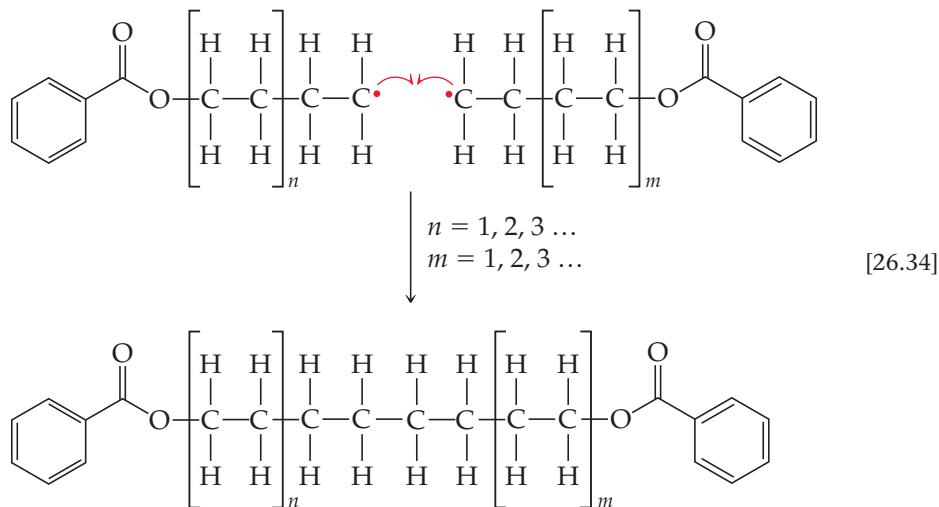
▲ **Figure 26.25** A segment of a polyethene chain. The segment shown here consists of 28 carbon atoms. In commercial polyethene, the chain lengths range from about  $10^3$  to  $10^5$   $\text{CH}_2$  units.

### Propagation



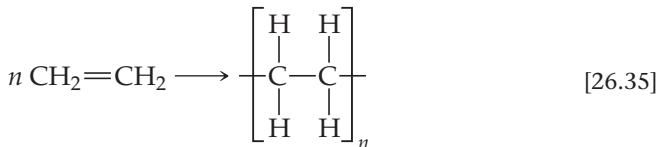
The propagation continues until two radical polymer chains react to form a completed polymer by a final C—C bond formation that terminates the radical. This is known as the **termination** step. In Equation 26.34,  $n$  and  $m$  are normally large integers, which may or may not have the same value.

### Termination



The reactive center in a chain-growth polymerization need not be a radical: depending on the monomer used, it may be an anion, cation or coordination complex. The most common process for polyethene production is *Ziegler-Natta* polymerization, named after the two scientists who developed the reaction in the 1950s. This process typically involves titanium and aluminum complexes, with a coordination complex as the reactive center, and is used in the formation of high-density polyethene (HDPE), a hard plastic. Radical polymerization of polyethene gives a polymer with occasional long branches, rather than simple straight chains, which makes it harder to pack the molecules together—this is low-density polyethene (LDPE), used in stretchy plastic wrap.

We can write the overall equation for the polymerization of ethene as follows:



Here,  $n$  represents the large number—ranging from hundreds to many thousands—of monomer molecules (ethene, in this case) that react to form one large polymer molecule. Within the polymer, a repeat unit (the unit shown in brackets in Equation 26.35) appears along the entire chain.

Polyethene is a very important commercial material; more than 10 billion kilograms are produced globally each year. Although its composition is simple, the polymer is not easy to make. Only after many years of research were the right conditions identified for manufacturing it. Today many different forms of polyethene, varying widely in physical properties, are known. Polymers of other chemical compositions provide still greater variety in physical and chemical properties. **Table 26.3** lists several other common polymers obtained by addition polymerization.

**TABLE 26.3** Addition polymers of commercial importance

| Monomers   | Addition Polymer           | Structure  | Uses  |
|--|----------------------------|--|---|
| $\text{CH}_2=\text{CH}_2$  | Polyethene                 | $\left[ \text{CH}_2-\text{CH}_2 \right]_n$                           | Films, packaging, bottles                         |
| $\begin{array}{c} \text{CH}_2=\text{CH} \\   \\ \text{CH}_3 \end{array}$                       | Polypropylene              | $\left[ \text{CH}_2-\text{CH}(\text{CH}_3) \right]_n$                | Kitchenware, fibres, appliances                   |
| $\begin{array}{c} \text{CH}_2=\text{CH} \\   \\ \text{C}_6\text{H}_5 \end{array}$              | Polystyrene                | $\left[ \text{CH}_2-\text{CH}(\text{C}_6\text{H}_5) \right]_n$       | Packaging, disposable food containers, insulation |
| $\begin{array}{c} \text{CH}_2=\text{CH} \\   \\ \text{Cl} \end{array}$                         | Poly(vinyl chloride) (PVC) | $\left[ \text{CH}_2-\text{CH}(\text{Cl}) \right]_n$                  | Pipe fittings, clear film for meat packaging      |
| $\begin{array}{c} \text{COOCH}_3 \\   \\ \text{CH}_2=\text{C} \\   \\ \text{CH}_3 \end{array}$ | Poly(methyl methacrylate)  | $\left[ \text{CH}_2-\text{C}(\text{CH}_3)(\text{COOCH}_3) \right]_n$ | Perspex, paints, moulded articles                 |

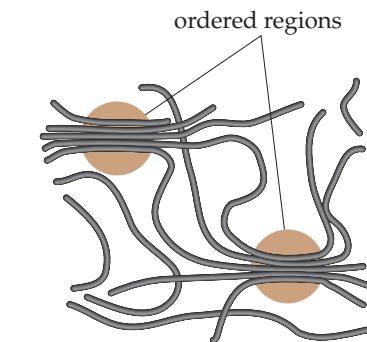
The names of polymers are simply derived from the monomers employed (Table 26.3). Poly(vinyl chloride) (PVC), for example, is made from vinyl chloride, poly(methyl methacrylate) is made from methyl methacrylate and polystyrene is made from styrene.

## Structure and Physical Properties of Addition Polymers

The simple structural formulas given for polyethene and other polymers are deceptive. Since each carbon atom in polyethene is surrounded by four bonds, the atoms are arranged in a tetrahedral fashion, so that the chain is not straight as we sometimes depict it. Furthermore, the atoms are relatively free to rotate around the C—C single bonds. Thus rather than being straight and rigid, the chains of an addition polymer are very flexible, folding readily. The flexibility in the molecular chains can cause the polymer material itself to be very flexible.

Both synthetic and naturally occurring polymers consist commonly of a collection of *macromolecules* (large molecules) of different molecular weights. Depending on the conditions of formation, the molecular weights may be distributed over a wide range or be closely clustered around an average value. In part, because of this distribution in molecular weights, polymers are largely amorphous (non-crystalline) materials. Rather than exhibiting a well-defined crystalline phase with a sharp melting point, they soften over a range of temperatures. They may, however, possess short-range order in some regions of the solid, with chains lined up in regular arrays, as shown in **Figure 26.26**. The extent of such ordering is indicated by the degree of **crystallinity** of the polymer. The crystallinity of a polymer can be enhanced with mechanical stretching, which aligns the polymer chains as the molten polymer is drawn out. Intermolecular forces between the polymer chains hold the chains together in the ordered crystalline regions, making the polymer denser, harder, less soluble and more resistant to heat. **Table 26.4** shows how the properties of polyethene change as the degree of crystallinity increases.

The simple linear structure of polyethene is conducive to intermolecular interactions that lead to crystallinity. However, the degree of crystallinity in polyethene strongly



▲ **Figure 26.26** Interactions between polymer chains. In the circled regions, the forces that operate between adjacent polymer-chain segments lead to ordering analogous to the ordering in crystals, though less regular.

**TABLE 26.4 Properties of polyethene as a function of crystallinity**

|                               | Crystallinity |      |      |      |      |
|-------------------------------|---------------|------|------|------|------|
|                               | 55%           | 62%  | 70%  | 77%  | 85%  |
| Melting point (°C)            | 109           | 116  | 125  | 130  | 133  |
| Density (g cm <sup>-3</sup> ) | 0.92          | 0.93 | 0.94 | 0.95 | 0.96 |
| Stiffness* (MPa)              | 12            | 17   | 13   | 29   | 35   |
| Yield stress* (MPa)           | 170           | 320  | 520  | 830  | 1140 |

\* These test results show that the mechanical strength of the polymer increases with increased crystallinity. Discussion of the exact meaning and significance of these tests is beyond the scope of this text.

## CHEMISTRY AND LIFE Recycling Plastics

If you look at the bottom of a plastic container, you are likely to see a recycle symbol (**Figure 26.27**) containing a number, as shown in **Table 26.5**. The number and letter abbreviation below it indicate the kind of polymer from which the container is made, as summarized

in Table 26.5. These symbols make it possible to sort containers by composition. In general, the lower the number, the greater the ease with which the material can be recycled.



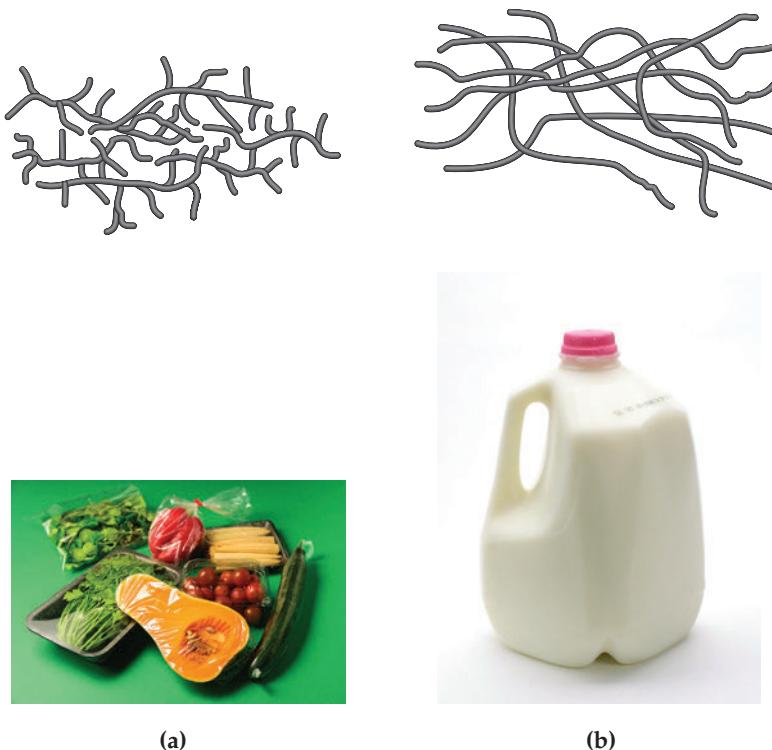
▲ **Figure 26.27** Recycling symbols.

**TABLE 26.5 Categories used for recycling polymeric materials**

| Recycling number | Abbreviation | Polymer                    |
|------------------|--------------|----------------------------|
| 1                | PET or PETE  | Polyethylene terephthalate |
| 2                | HDPE         | High-density polyethene    |
| 3                | V            | Polyvinyl chloride (PVC)   |
| 4                | LDPE         | Low-density polyethene     |
| 5                | PP           | Polypropylene              |
| 6                | PS           | Polystyrene                |
| 7                | —            | Others                     |

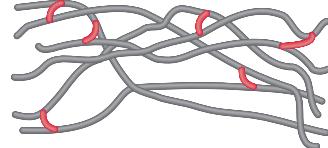
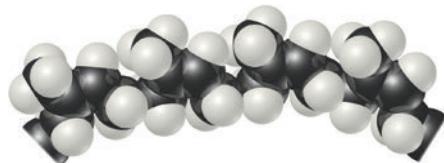
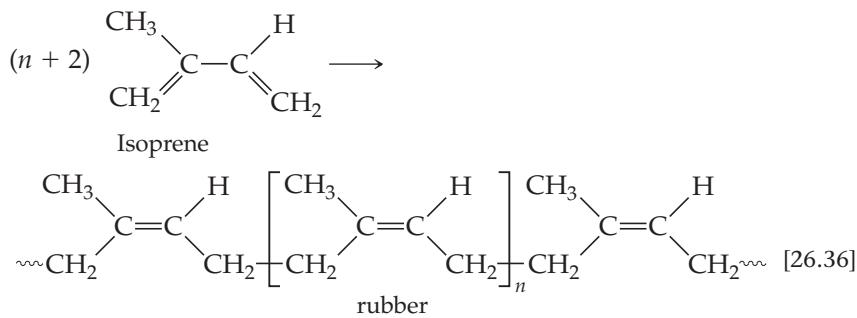
depends on the average molecular mass. Polymerization results in a mixture of macromolecules with varying values of  $n$  and hence varying molecular masses. So-called low-density polyethene (LDPE), used in forming films and sheets, has an average molecular mass in the range of  $10^4$  u and has substantial chain branching. That is, side chains occur off the main chain of the polymer, much like spur lines that branch from a main railway line. These branches inhibit the formation of crystalline regions, reducing the density of the material. High-density polyethene (HDPE), used to form bottles, drums and pipes, has an average molecular mass in the range of  $10^6$  u. This form has less branching and thus a higher degree of crystallinity. Low-density and high-density polyethene are illustrated in **Figure 26.28**. Thus the properties of polyethene can be “tuned” by varying the average length, crystallinity and branching of the chains, making it a very versatile material.

The physical properties of polymeric materials can be modified extensively by adding substances with lower molecular mass, called *plasticizers*, to reduce the extent of interactions between chains and thus to make the polymer more pliable. Poly(vinyl chloride) (PVC) (Table 26.3), for example, is a hard, rigid material of high molecular mass that is used to manufacture drainpipes. When blended with a suitable substance of lower molecular mass, however, it forms a flexible polymer that can be used to make rainboots and doll parts. In some applications, the plasticizer in a plastic object may be lost over time because of evaporation. As this happens, the plastic loses its flexibility and becomes subject to cracking.



**▲ Figure 26.28** Two types of polyethene. (a) Schematic illustration of the structure of low-density polyethene (LDPE) and food-storage bags made of LDPE film. (b) Schematic illustration of the structure of high-density polyethene (HDPE) and containers formed from HDPE.

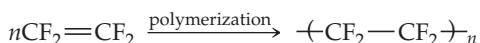
Polymers can be made stiffer by introducing chemical bonds between the polymer chains, as illustrated in **Figure 26.29**. Forming bonds between chains is called **cross-linking**. The greater the number of cross-links in a polymer, the more rigid the material. Whereas thermoplastic materials consist of independent polymer chains, thermosetting materials become cross-linked when heated. The cross-links allow them to hold their shapes. An important example of cross-linking is the **vulcanization** of natural rubber, a process discovered by Charles Goodyear in 1839 (see the Chemistry and Life, page 1246). Natural rubber is formed from a liquid resin derived from the inner bark of *Hevea brasiliensis*, or rubber tree. Chemically, it is a terpene, a polymer of isoprene, C<sub>5</sub>H<sub>8</sub>. In the process of vulcanization a controlled number of sulfur cross-links are introduced by reacting the carbon-carbon double bonds of adjacent chains with elemental sulfur in the presence of an accelerator and activator compound.



**▲ Figure 26.29** Cross-linking of polymer chains. The cross-linking groups (red) constrain the relative motions of the polymer chains, making the material harder and less flexible than when the cross-links are not present.

## CHEMISTRY AND LIFE The Accidental Discovery of Teflon®

In 1938 a scientist at Du Pont named Roy J. Plunkett (1910–1994) made a rather curious observation: a tank of gaseous tetrafluoroethene ( $\text{CF}_2=\text{CF}_2$ ) that was supposed to be full seemed to have no gas in it. Rather than discard the tank, Plunkett decided to cut it open. He found that the inside of the tank was coated with a waxy white substance that was remarkably unreactive towards even the most corrosive reagents. That compound was formed by the addition polymerization of tetrafluoroethylene:



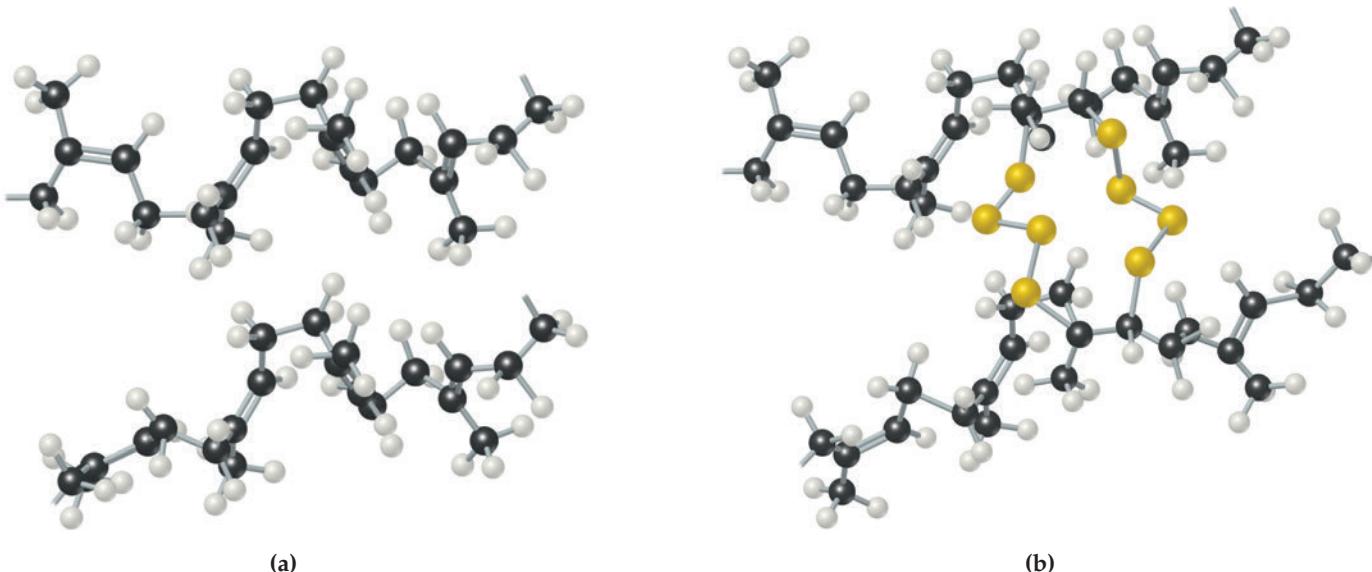
As it turned out, the properties of this material, called Teflon®, were ideal for an immediate and important application in the development of the first atomic bomb. Uranium hexafluoride ( $\text{UF}_6$ ), which was used to separate fissionable  $^{235}\text{U}$  by gaseous diffusion, is an extremely corrosive material. Teflon® was used as a gasket material in the gaseous diffusion plant. It is now used in a variety of applications, from non-stick cookware to space suits.

Plunkett's desire to know more about something that just didn't seem right is a wonderful example of how natural scientific curiosity can lead to remarkable discoveries.

## CHEMISTRY AND LIFE Vulcanization

Natural rubber is not a useful polymer because it is too soft and too chemically reactive. Charles Goodyear (1800–1860) accidentally discovered that adding sulfur to rubber and then heating the mixture makes the rubber harder and reduces its susceptibility to oxidation or other chemical attack. The sulfur changes rubber into a thermosetting polymer by cross-linking the polymer chains through reactions

at some of the double bonds, as shown schematically in **Figure 26.30**. Cross-linking of about 5% of the double bonds creates a flexible, resilient rubber. When the rubber is stretched, the cross-links help to prevent the chains from slipping, so that the rubber retains its elasticity. Nature also uses a sulfide crosslink to rigidify and preserve certain protein structures, such as insulin.



**▲ Figure 26.30** Vulcanization of rubber. (a) In natural rubber, carbon–carbon double bonds occur at regular intervals along the chain. (b) Chains of sulfur atoms have been added across two polymer chains, by the opening of a carbon–carbon double bond on each chain.

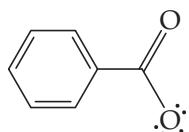
## Self-Assessment Exercises

- 26.34** Identify the monomer unit in poly(vinyl acetate) from this fragment of the polymer chain.



- (a)  $\text{CH}_2=\text{CH}-\overset{\text{O}}{\underset{\text{C}}{\text{||}}} \text{O}-\text{CH}_3$
- (b)  $\text{CH}_2=\text{CH}-\overset{\text{O}}{\underset{\text{C}}{\text{||}}} \text{O}-\text{CH}_3$
- (c)  $\text{CH}_3-\overset{\text{O}}{\underset{\text{C}}{\text{||}}} \text{O}-\text{CH}_3$

- 26.35** A radical such as the benzyloxy radical is often used in which stage of polymerization?



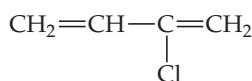
- (a) Initiation (b) Propagation (c) Termination

- 26.36** A polymer with a high degree of cross-linking is likely to show which characteristics? (a) a soft flexible material (b) elasticity (c) a low melting point (d) a rigid structure

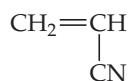
## Exercises

- 26.37** Draw the structure of the monomer(s) employed to form each of the following polymers: (a) poly(vinyl chloride), (b) polystyrene, (c) polypropylene.

- 26.38** Write the chemical equation that represents the formation of (a) polychloroprene (neoprene) from chloroprene



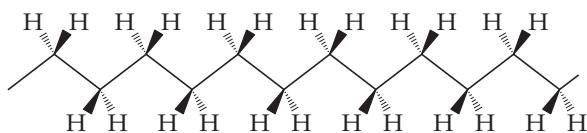
(Neoprene is used in road pavement seals, expansion joints, conveyor belts and wire and cable jackets.); (b) polyacrylonitrile



(Polyacrylonitrile is used in home furnishings, craft yarns, clothing and many other items.)

- 26.39** What molecular features make a polymer flexible? Explain how cross-linking affects the chemical and physical properties of the polymer.

- 26.40** Although polyethene can twist and turn in random ways, the most stable form is a linear one with the carbon backbone oriented as shown in this figure:

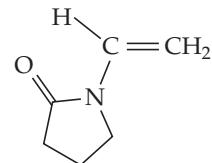


- (a) What is the hybridization of orbitals at each carbon atom? What angles do you expect between the bonds?

(b) Now imagine that the polymer is polypropylene rather than polyethene. Draw the structures for polypropylene in which (i) the  $\text{CH}_3$  groups lie on the same side of the plane of the paper (this form is called isotactic polypropylene), (ii) the  $\text{CH}_3$  groups lie on alternating sides of the plane (syndiotactic polypropylene), and (iii) the  $\text{CH}_3$  groups are randomly distributed on either side (atactic polypropylene). Which of these forms would you expect to have the highest crystallinity and melting point, and which the lowest? Explain in terms of intermolecular interactions and molecular shapes.

(c) Polypropylene fibres have been employed in athletic wear. The product is said to be superior to cotton clothing in wicking moisture away from the body through the fabric to the outside. Explain the difference between polypropylene and cotton (which has many  $-\text{OH}$  groups along the molecular chain), in terms of intermolecular interactions with water.

- 26.41** Poly(vinyl pyrrolidone) is commonly used in cosmetics and in wine clarification. Draw a representative segment of the polymer prepared from *N*-vinyl pyrrolidone:



- 26.42** How would you expect the properties of vulcanized rubber to vary as the percentage of sulfur increases?

26.34 (b) 26.35 (a) 26.36 (d)

Answers to Self-Assessment Exercises



### Sample Integrative Exercise

Putting concepts together

In an example of an electrophilic addition reaction 1-butene reacts with hydrogen bromide to give 2-bromobutane. (a) Draw out the mechanism of this reaction including the carbocation intermediate. Show all the atoms attached to the double bond and use curved arrows to indicate electron-pair movements. (b) What are the hybridization and molecular geometry of the two atoms C1 and C2 in the starting material, intermediate and product? (c) Indicate the stereogenic carbon center in the product with \*. (d) Explain why the product is formed as a racemic mixture.

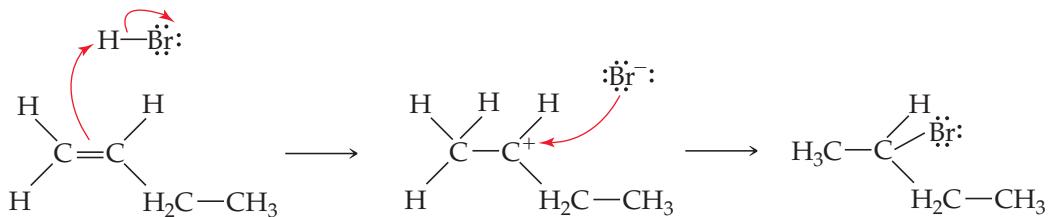
### SOLUTION

**Analyse** In this problem we examine the mechanism of an electrophilic addition reaction and how the shape of the intermediate relates to the chirality of the product.

**Plan** First identify the structure of the starting material and product from the names given. Then draw the mechanism of the reaction and identify how the molecular geometry of C1 and C2 changes as the reaction progresses. Finally identify the features of the geometry change that result in a racemic mixture being produced.

**Solve**

(a)

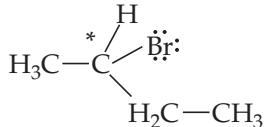


(b)

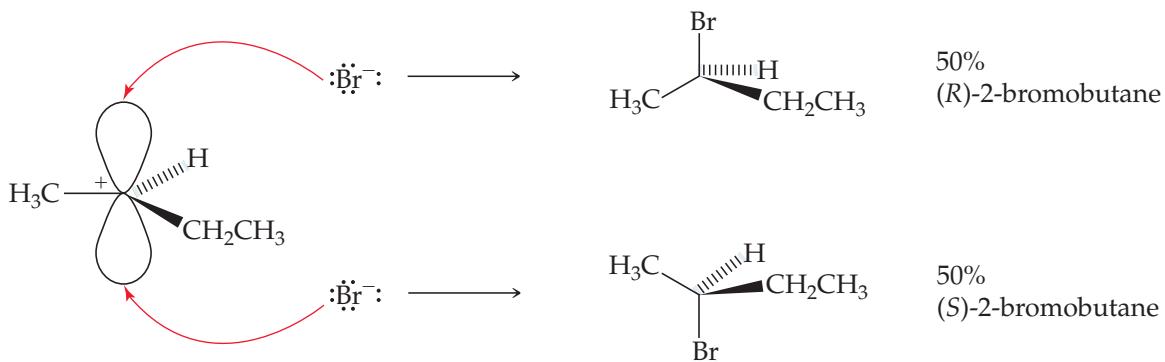
|  | Hybridization—C1 | Geometry—C1 | Hybridization—C2 | Geometry—C2 |
|--|------------------|-------------|------------------|-------------|
|--|------------------|-------------|------------------|-------------|

|                   |        |                 |        |                 |
|-------------------|--------|-----------------|--------|-----------------|
| Starting material | $sp^2$ | Trigonal planar | $sp^2$ | Trigonal planar |
| Intermediate      | $sp^3$ | Tetrahedral     | $sp^2$ | Trigonal planar |
| Product           | $sp^3$ | Tetrahedral     | $sp^3$ | Tetrahedral     |

(c)



(d) The carbocation is  $sp^2$  hybridized and trigonal planar in shape. The positive charge may be thought of as an empty  $p$  orbital pointing above and below the plane containing the carbocation. The final stage of this reaction involves attack by the bromide ion on the carbocation and there is equal probability of this occurring to the top or the bottom face of the intermediate.



## Chapter Summary and Key Terms

**SECTION 26.1** Unsaturated hydrocarbons are those hydrocarbons that contain multiple bonds. Two main classes—**alkenes** and **alkynes**—are dealt with in this chapter. Alkenes contain one or more double bonds. Each double bond consists of one  $\sigma$ -bond and one  $\pi$ -bond. The  $\pi$ -bond is formed by the overlap of the unhybridized  $p$  orbitals on adjacent  $sp^2$  hybridized carbon atoms. Alkynes contain one or more triple bonds. Each triple bond consists of one  $\sigma$ -bond and two  $\pi$ -bonds. The order of bond lengths is triple bond < double bond < single bond.

**SECTION 26.2** The names of alkenes and alkynes are based on the longest continuous chain of carbon atoms that contains the multiple bond, and the location of the multiple bond is specified by a numerical prefix. The **E,Z system** is used to name the geometric isomers of alkenes and is based on the same priority system used in *R,S* nomenclature.

**SECTION 26.3** Organic chemists use **curved arrow notation** to describe the redistribution of valence electrons. Arrow notation can also be used to describe resonance structures or to rationalize a reaction mechanism.

**SECTION 26.4** Alkenes and alkynes readily undergo **addition reactions** to the carbon–carbon multiple bonds. There are three main classes

of addition reactions: **halogenation**, **hydrohalogenation** and **hydration**. Additions of acids, such as  $\text{HBr}$ , proceed via a rate-determining step in which a proton is transferred to one of the alkene or alkyne carbon atoms, forming a **carbocation**. This addition follows **Markovnikov's rule**, which states that the hydrogen of  $\text{HX}$  ( $\text{X} = \text{halogen, OH}$ ) adds to the side of the double bond with the most hydrogens. The carbocation is a form of **electrophile** that readily reacts with a **nucleophile**, in this case  $\text{Br}^-$ , to form the product. The addition of bromine to cyclohexene is an example of a **stereoselective reaction**.

**SECTION 26.5** **Catalytic hydrogenation** can be used to convert alkenes or alkynes to alkanes using molecular hydrogen and a metal catalyst such as Ni, Pd or Pt. Oils are **triglycerides** that contain double bonds. They may be hydrogenated to **fats** in a process called **hardening**.

**SECTION 26.6** **Polymers** are molecules of high molecular mass formed by joining together large numbers of smaller molecules, called **monomers**. In a chain growth or **addition polymerization** reaction, the molecules form new linkages by opening existing bonds. Polyethene is an example of an **addition polymer**. Three stages exist in this type of polymerization: **initiation**, **propagation** and **termination**.

**Plastics** are materials that can be formed into various shapes, usually by the application of heat and pressure. **Thermoplastics** can be reshaped, perhaps by heating, in contrast to **thermosetting plastics**, which are formed through an irreversible chemical process and cannot be reshaped.

Polymers are largely amorphous, but some materials possess a degree of **crystallinity**. High-density polyethylene, for example, with

not much side-chain branching and a high molecular mass, has a higher degree of crystallinity than low-density polyethylene, which has a lower molecular mass and a higher relative degree of branching. Polymer properties are also strongly affected by **cross-linking**, in which short chains of atoms connect the long polymer chains. Rubber is cross-linked by short chains of sulfur atoms in the process called **vulcanization**.

## Key Skills

- Understand how to name alkenes and alkynes. In the case of alkenes, be able to determine *E*, *Z* isomerism. (Sections 26.1 and 26.2)
  - Describe and understand the rules for using curved arrow notation and their application to describe the mechanism of a chemical reaction. (Section 26.3)
  - Be able to draw the products of addition reactions using a range of reactants (e.g. Br<sub>2</sub>, HCl) and understand their product distribution. (Sections 26.4 and 26.5)

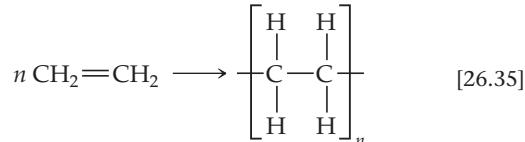
- Understand the importance of alkenes to the industrial manufacturing of plastics. (Section 26.6)
  - Be able to draw polymers formed by the addition polymerization of alkene monomers and understand some of their properties. (Section 26.6)

## Key Equations

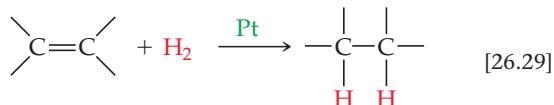
- Addition reactions



- Addition polymerization



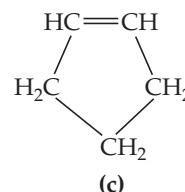
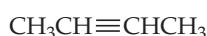
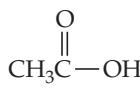
- Hydrogenation



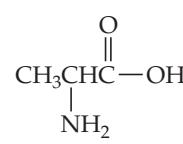
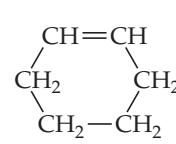
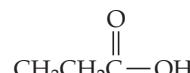
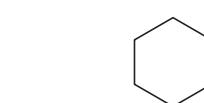
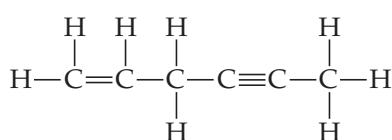
## Exercises

## Visualizing concepts

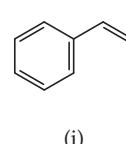
- 26.43** Which of the following molecules is unsaturated?  
[Section 26.1]



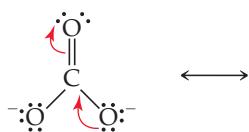
- 26.44** Consider the hydrocarbon drawn here. **(a)** What is the hybridization at each carbon atom in the molecule? **(b)** How many  $\sigma$ -bonds are there in the molecule? **(c)** How many  $\pi$ -bonds? [Section 26.1]



- 26.46** Consider the molecules shown here. Which of these would be most likely to form an addition polymer? [Section 26.4]

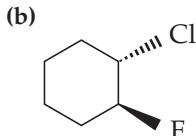
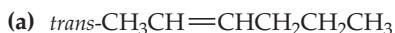


- 26.47** Draw the product of the following valence electron movements. [Section 26.3]



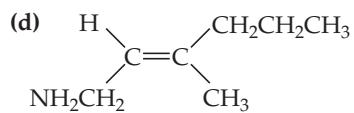
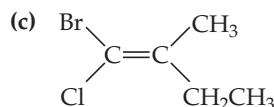
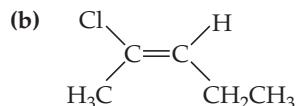
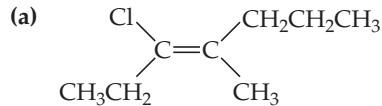
### Structure, Bonding and Naming (Sections 26.1, 26.2 and 26.3)

- 26.48** Give the general molecular formula for any cyclic alkene. What other general class of hydrocarbon has the same general formula?
- 26.49** What are the characteristic hybrid orbitals employed by **(a)** carbon in an alkane, **(b)** carbon in a double bond in an alkene, **(c)** carbon in a triple bond in an alkyne?
- 26.50** Name the following compounds systematically:

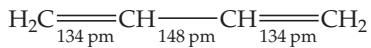


- 26.51** **(a)** Using butene as an example, distinguish between structural (constitutional) and geometric isomers. **(b)** The compound 4-chloropent-2-ene exists as four stereoisomers. Explain how these four isomers arise by drawing the structures of all four stereoisomers and showing the relationship between them.

- 26.52** Systematically name the following alkenes, assigning their geometry as *E* or *Z* where appropriate.



- 26.53** 1,3-butadiene, C<sub>4</sub>H<sub>6</sub>, is a planar molecule that has the following carbon–carbon bond lengths:

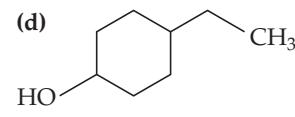
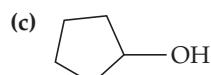
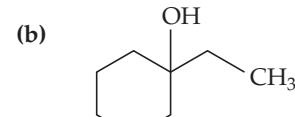
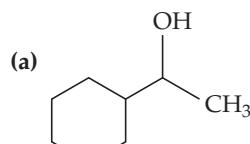


- (a)** Predict the bond angles around each of the carbon atoms, and sketch the molecule. **(b)** Compare the bond lengths with the average bond lengths listed in Table 26.1. Can you explain any differences?

- 26.54** **(a)** What is the difference between a localized  $\pi$ -bond and a delocalized one? **(b)** How can you determine whether a molecule or ion will exhibit delocalized  $\pi$ -bonding? **(c)** Is the  $\pi$ -bond in NO<sub>2</sub><sup>-</sup> localized or delocalized?

### Addition Reactions of Unsaturated Hydrocarbons (Sections 26.4 and 26.5)

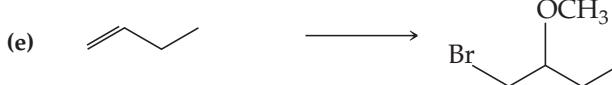
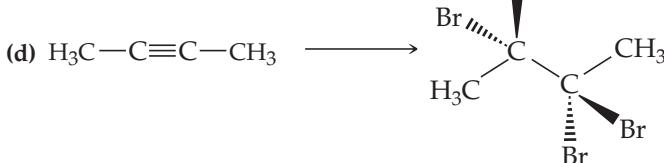
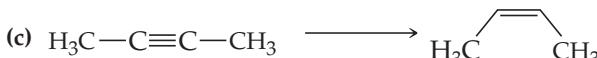
- 26.55** Using condensed structural formulas, write a chemical equation for each of the following reactions: **(a)** hydrogenation of cyclohexene; **(b)** addition of H<sub>2</sub>O to *trans*-pent-2-ene, using H<sub>2</sub>SO<sub>4</sub> as a catalyst (draw both likely products); **(c)** reaction of propene with bromine in water solvent.
- 26.56** The rate law for the addition of Br<sub>2</sub> to an alkene is first order in Br<sub>2</sub> and first order in alkene. Does this fact prove that the mechanism of addition of Br<sub>2</sub> to an alkene proceeds in the same manner as for addition of HBr? Explain.
- 26.57** What alkenes would you hydrate to obtain the following alcohols?



- 26.58** **(a)** When but-1-yne is hydrohalogenated with HCl a geminal dichloride is formed in preference. Draw its structure. **(b)** Give a reason for your choice.

- 26.59** **(a)** In the bromination of propene, a cyclic bromonium ion is formed in the first step. Draw it. **(b)** The addition of a nucleophile (Nu<sup>⊖</sup>) to this bromonium ion yields a single major product. Why is this the case and what product is formed? **(c)** Is this product chiral if Nu = OH? **(d)** What if Nu = Br?

- 26.60** Suggest suitable reagents for the following reactions:



- 26.61** (a) Write the structural formula for the product of the hydrogenation of 3-methyl pent-1-ene. What is the systematic name of the product? (b) When D<sub>2</sub> reacts with ethene (C<sub>2</sub>H<sub>4</sub>) in the presence of a finely divided catalyst, ethane with two deuteriums, CH<sub>2</sub>D—CH<sub>2</sub>D, is formed. (Deuterium, D, is an isotope of hydrogen of mass 2.) Very little ethane forms in which two deuteriums are bound to one carbon (for example, CH<sub>3</sub>—CHD<sub>2</sub>). Use the sequence of steps involved in the reaction to explain why this is so.

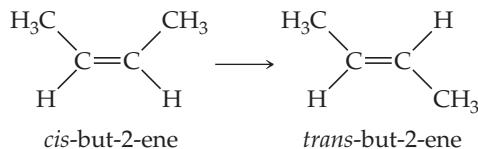
### Addition Polymerization (Section 26.6)

- 26.62** The structure of decane is shown in Table 24.3. Decane is not considered to be a polymer, whereas polyethene is. What is the distinction?

- 26.63** What is a monomer? Give three examples of monomers, taken from the examples given in this chapter.
- 26.64** Teflon® is a polymer formed by the polymerization of F<sub>2</sub>C=CF<sub>2</sub>. Draw the structure of a section of this polymer. What type of polymerization reaction is required to form it?
- 26.65** What molecular structural features cause high-density polyethene (HDPE) to be denser than low-density polyethene (LDPE)?
- 26.66** Are high molecular masses and a high degree of crystallinity always desirable properties of a polymer? Explain.

## Integrative Exercises

- 26.67** But-2-ene, C<sub>4</sub>H<sub>8</sub>, can undergo *cis-trans* isomerization:



As discussed in the Chemistry and Life box on the chemistry of vision, such transformations can be induced by light and are the key to human vision. (a) What is the hybridization at the two central carbon atoms of but-2-ene? (b) The isomerization occurs by rotation about the central C—C bond. With reference to Figure 26.5, explain why the  $\pi$ -bond between the two central carbon atoms is destroyed halfway through the rotation from *cis*- to *trans*-but-2-ene. (c) Based on average bond enthalpies (Table 8.3), how much energy per molecule must be supplied to break the C—C  $\pi$ -bond? (d) What is the longest wavelength of light that will provide photons of sufficient energy to break the C—C  $\pi$ -bond and cause the isomerization? (e) Is the wavelength in your answer to part (d) in the visible portion of the electromagnetic spectrum? Comment on the importance of this result for human vision.

- 26.68** Ethene (CH<sub>2</sub>=CH<sub>2</sub>) reacts with hydrogen gas in the presence of a catalyst to give ethane (CH<sub>3</sub>CH<sub>3</sub>). (a) Draw the structures of the reactants and the product for this reaction and indicate the number of  $\sigma$ - and  $\pi$ -bonds that have been broken and have been formed in this reaction. Use average bond enthalpies in Table 8.3 to estimate (b) the enthalpy change for this reaction and (c) the average energy of a carbon–carbon  $\sigma$ -bond and  $\pi$ -bond. (d) Draw the electron distribution in a  $\pi$ -bond and explain why it is weaker than a  $\sigma$ -bond between the same atoms.

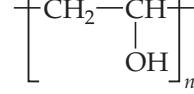
- 26.69** Consider the electrophilic addition of hydrogen chloride to propene. (a) Draw the reaction showing the primary and secondary carbocation intermediates and the products that

arise from each intermediate. (b) Sketch an energy profile, similar to Figure 26.20, for the two possible pathways in this reaction showing the relative energies of the intermediates and indicating which carbocation is the more stable. (c) If the temperature of the reaction mixture was increased would the relative proportions of the two possible products change?

- 26.70** A sample of a polyunsaturated oil is hydrolysed to give either linoleic acid (C<sub>18</sub>H<sub>32</sub>O<sub>2</sub>) or arachidonic acid (C<sub>20</sub>H<sub>32</sub>O<sub>2</sub>) and you have to find out which one. You take a 1.0 g sample of the unknown acid and perform a hydrogenation reaction under catalytic conditions. This will hydrogenate the carbon–carbon double bonds present but not the carbon–oxygen double bond of the carboxylic acid group. (a) Calculate the double bond equivalents in linoleic acid and arachidonic acid. (b) Determine the number of carbon–carbon double bonds present in each of the acids. Your sample of unknown acid absorbs 299 cm<sup>3</sup> of hydrogen gas under STP conditions. (c) Calculate the number of moles of hydrogen gas used and identify which acid you have.

- 26.71** Acetylene (H—C≡C—H) can explosively form benzene (C<sub>6</sub>H<sub>6</sub>). (a) Write a chemical equation for this reaction and (b) calculate the heat of reaction given  $\Delta_f H^\circ$  (benzene) = 83 kJ mol<sup>-1</sup> and  $\Delta_f H^\circ$  (acetylene) = 227 kJ mol<sup>-1</sup>.

- 26.72** Polyvinyl alcohol is a polymer with the following structure.



(a) What intermolecular forces exist between polymer chains in polyvinyl alcohol? (b) Do you expect polyvinyl alcohol to be water soluble?

## Design an Experiment

Many nuts, seeds and some fish are a good source of polyunsaturated fats in which the fat molecule contains two or more double bonds. These fats are liquid at room temperature (oils). Hydrogenation of some of the double bonds present increases the melting point of the fat and produces a semi-solid product that is easier to spread than a fully saturated fat such as butter. Imagine that you are an industrial chemist charged with monitoring the hydrogenation of an oil and stopping the reaction when some, but not all, of the double bonds

have been saturated. In your experiment you take a small sample from the reaction mixture at regular time intervals after the hydrogenation commenced. (a) How would you ensure you took the same sized sample each time? (b) what type of solvent would you use to dissolve the sample? (c) What reagent can you think of that changes colour when it reacts with a double bond? (e) Can you think of a way of quantifying the amount of reagent you add and so relating it to the number of double bonds remaining in the sample.