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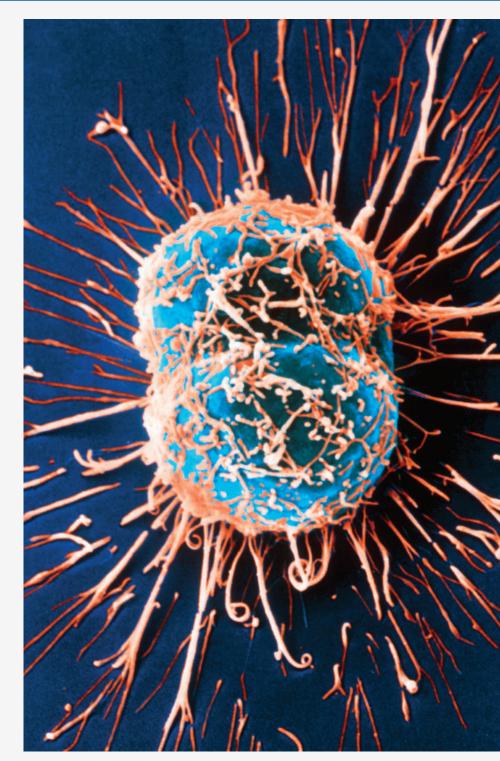
Alkenes, Alkynes, and Aromatic Compounds

CONTENTS

- 13.1 Alkenes and Alkynes
- 13.2 Naming Alkenes and Alkynes
- 13.3 The Structure of Alkenes: Cis-Trans Isomerism
- 13.4 Properties of Alkenes and Alkynes
- 13.5 Types of Organic Reactions
- 13.6 Addition Reactions of Alkenes
- 13.7 Alkene Polymers
- 13.8 Aromatic Compounds and the Structure of Benzene
- 13.9 Naming Aromatic Compounds
- 13.10 Reactions of Aromatic Compounds

CONCEPTS TO REVIEW

- A. VSEPR and Molecular Shapes (Section 4.8)
- B. Families of Organic Molecules: Functional Groups (Section 12.2)
- C. Drawing Organic Structures (Section 12.4)
- D. The Shapes of Organic Molecules (Section 12.5)
- E. Naming Alkanes (Section 12.6)



▲ In the war on cancer, potent new drugs containing carbon—carbon triple bonds are providing hope for the treatment of diseases such as cervical cancer.

unctional groups give organic molecules their characteristic physical, chemical, and biological properties. In Chapter 12, we examined the simplest hydrocarbons, alkanes, which provide the scaffolding upon which the complicated molecules responsible for life are built. Now we will look at the chemistry of molecules that contain carbon—carbon multiple bonds, or *unsaturated* hydrocarbons. While alkenes and aromatic systems are found in many naturally occurring biomolecules, alkynes are not as commonly observed. However, when

alkynes are found in biological systems, they show surprising physiological activity. Chemists quite often take biologically active molecules that nature provides and use them as starting points in the laboratory to design new drugs to treat disease. Using this strategy, complex alkynes have been isolated from a number of natural sources such as bacterial cultures; these have subsequently shown promise as antitumor agents. Out of this work, the discovery of an extremely interesting class of molecules known as the *enedigne* antibiotics has arisen, a family of naturally occurring compounds that are proving to be among the most potent antitumor agents known. Discussed in more detail in the Chemistry in Action "Enedigne Antibiotics: A Newly Emerging Class of Antitumor Agents" later in the chapter, these toxic molecules, isolated from the bacteria *Micromonospora*, cut deoxyribonucleic acid (DNA) strands, which keeps a cell from reproducing, and could lead to the development of new drugs in the treatment of cancer as well as other diseases.

The last group of unsaturated hydrocarbons we will discuss are known as the aromatic hydrocarbons. *Aromatic compounds* contain a six-membered ring of carbon atoms, have alternating single and double bonds, and possess resonance, which gives aromatic compounds their unique reactivity. If one or more of the carbons in an aromatic ring is replaced by an atom other than C, we obtain what are known as *aromatic heterocyclic* molecules, many of which have unique biological properties. While only alkenes and aromatic compounds are widespread in nature, all of these unsaturated functional groups (including alkynes) are found in many biologically important molecules.

13.1 Alkenes and Alkynes

Learning Objectives:

- · Identify the functional groups present in alkenes and alkynes.
- Differentiate between saturated and unsaturated molecules.

Alkanes, introduced in Chapter 12, are **saturated** because each carbon atom has four single bonds. Because this is the maximum number of single bonds a carbon can have, no more atoms can be added to any of the carbons in an alkane—in other words, the molecule is saturated. Alkenes and alkynes, however, are **unsaturated** because they contain carbon—carbon multiple bonds. Atoms can be added to an alkene or alkyne by converting these multiple bonds to single bonds. **Alkenes** are hydrocarbons that contain carbon—carbon double bonds, **cycloalkenes** are hydrocarbons that contain a double bond in a ring system, and **alkynes** are hydrocarbons that contain carbon—carbon triple bonds (cycloalkynes are rare and unknown for rings containing less than eight carbons). As you continue your study of organic and biochemistry, the term *unsaturated* will generically be used to indicate the presence of double bonds; for example, the unsaturated fatty acids (discussed in Chapter 23).

Unsaturated carbons are marked with an *

Most of the organic chemicals used in making drugs, explosives, paints, plastics, and pesticides are synthesized by routes that begin with alkenes. Ethene is one of these alkene building blocks that is in tremendous demand, with much of it used for making polyethene, the most common type of plastic in the world. In fact, ethene

Saturated A molecule in which each carbon atom has the maximum number of single bonds possible (four).

Unsaturated A molecule that contains one or more carbon–carbon multiple bonds.

Alkene A hydrocarbon that contains a carbon–carbon double bond.

Cycloalkene A cyclic hydrocarbon that contains a double bond.

Alkyne A hydrocarbon that contains a carbon–carbon triple bond.



▲ An elephant weighs five metric tons, while a blue whale weighs 200 metric tons. That means that the amount of ethene produced worldwide is equal to the weight of 40 million elephants, or 1 million blue whales!

CONCEPTS TO REVIEW Review the IUPAC naming system introduced in Section 12.6.

production worldwide is expected to be at a staggering 175 million tons by the end of 2015 and 200 million metric tons by 2020, demonstrating just how important an industrial starting material it is.

Ethene is also formed in the leaves, flowers, and roots of plants, where it acts as a hormone to control seedling growth, stimulate root formation, and regulate fruit ripening; it is thought of as the aging hormone in plants. In its role as a hormone, ethene causes death by signaling the plant to rapidly drop its leaves, effectively shutting down photosynthesis.

13.2 Naming Alkenes and Alkynes

Learning Objectives:

- Name a simple alkene or alkyne given its condensed or line structure.
- Draw the condensed or line structure of an alkene or alkyne given its name.

In the International Union of Pure and Applied Chemistry (IUPAC) system, alkenes and alkynes are named by a series of rules identical to those used for alkanes, with one major addition: the main chain must include all the atoms that are part of the multiple bonds. The parent names indicating the number of carbon atoms in the main chain are the same as those for alkanes, with the *-ene* suffix used in place of *-ane* for alkenes and the *-yne* suffix used for alkynes. The names of alkenes and alkynes also contain a number, called an *index number*, indicating the position of the multiple bond. The main chain in any unsaturated molecule is numbered so that the molecule's name has the lowest index number possible for that multiple bond. This indexing rule for functional groups will be used again and again throughout the remaining chapters of this text.

STEP 1: Name the parent compound. Find the longest chain containing the double or triple bond, and name the parent compound by adding the suffix *-ene* or *-yne* to the name for the main chain. If there is more than one double or triple bond, the number of multiple bonds is indicated using a numerical prefix (*diene* = two double bonds, *tri*ene = three double bonds, and so forth).

STEP 2: Number the carbon atoms in the main chain so that those with multiple bonds have the lowest index numbers possible. Thus, begin numbering at the end nearer the multiple bond (Examples 1 and 3). If the multiple bond is an equal distance from both ends, begin numbering at the end nearer the first branch point (Example 2).

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_4 \\ \text{CH}_2 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_2 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_2 \\ \text{CH}_3 \\$$

McMurry, John, et al. Fundamentals of General, Organic and Biological Chemistry, SI Edition, Pearson Education, Limited, 2017. ProQuest Ebook Central http://ebookcentral.proquest.com/lib/rcsidublin/detail.action?docID=5186171.

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Cycloalkenes are quite common. The double-bonded carbon atoms in substituted cycloalkenes are assigned index numbers of 1 and 2 so as to give the first substituent the next lowest possible index number.

(Cyclic alkynes are rare, and even those that are known are far too reactive to be readily available. For these reasons, we will spend no time discussing them.)

STEP 3: Write the full name. Assign numbers to the branching substituents, and list the substituents alphabetically. Use commas to separate numbers and hyphens to separate words from numbers. Indicate the position of the multiple bond in the chain by giving the number of the *first* multiple-bonded carbon. If more than one double bond is present, identify the position of each and use the appropriate name ending (e.g., 1,3-buta*diene* and 1,3,6-hepta*triene*).

Common Names. For historical reasons, there are a few alkenes and alkynes whose names do not conform to the IUPAC rules. For instance, the 2-carbon alkene $H_2C = CH_2$ should properly be called *ethene*, but the name *ethylene* has been used for so long that it is now accepted by the IUPAC. Similarly, the 3-carbon alkene *propene* ($CH_3CH = CH_2$) is commonly called *propylene*, and the 4-carbon diene 2-methylbuta-1,3-diene (see above) is more commonly known as *isoprene*. The simplest alkyne, HC = CH, should be known as *ethyne* but is almost always called *acetylene*.

Worked Example 13.1 Naming Organic Compounds: Alkenes

What is the IUPAC name of the following alkene?

$$H_{3}C CH_{2}CH_{3}$$
 $CH_{3}CH_{2}CH_{2}-C=C-CH_{3}$

ANALYSIS Identify the parent compound as the longest continuous chain that contains the double bond. The location of the double bond and any substituents are identified by numbering the carbon chain from the end nearer the double bond.

-continued on next page

—continued from previous page

SOLUTION

STEP 1: The longest continuous chain containing the double bond has seven carbons—*heptene*. In this case, we have to turn a corner to find the longest chain.

$$H_3C$$
 CH_2CH_3 $CH_3CH_2CH_2-C=C-CH_3$ Name as a heptene.

STEP 2: Number the chain from the end nearer the double bond. The first double-bond carbon is C4 starting from the left end but C3 starting from the right.

$$H_3C$$
 CH_2CH_3
 7 6 5 4 | 3 Name as a substituted hept-3-ene.

STEP 3: Two methyl groups are attached at C3 and C4.

$$\begin{array}{cccc} & & 2 & 1 \\ & & H_3C & CH_2CH_3 & Substituents: 3-Methyl, 4-Methyl \\ 7 & 6 & 5 & 4 & | & | 3 \\ CH_3CH_2CH_2 - C = C - CH_3 & Name: 3,4-Dimethylhept-3-ene \\ \end{array}$$

Worked Example 13.2 Molecular Structures: Alkenes

Draw the structure of 3-ethyl-4-methylpent-2-ene using both condensed and line structure.

ANALYSIS Identify the parent name (*pent*) and the location of the double bond and other substituents by numbering the carbons in the parent chain.

SOLUTION

STEP 1: The parent compound is a five-carbon chain with the double bond between C2 and C3.

STEP 2: Add the ethyl and methyl substituents on C3 and C4, and write in the additional hydrogen atoms so that each carbon atom has four bonds.

$$\begin{array}{c|cccc}
CH_2CH_3 \\
1 & 2 & 3 & 4 & 5 \\
CH_3 & CH = C - CH - CH_3 & 3-Ethyl-4-methylpent-2-ene \\
 & CH_3
\end{array}$$

Using line structures we can draw it in the following ways:

In this particular case either is correct. The two structures differ in the position of the CH₃ with respect to the CH₂CH₃; they are examples of cis–trans isomers (Section 13.3).

PROBLEM 13.1

What are the IUPAC names of the following compounds?

(b)
$$H_2C = CHCH_2CH_2C = CH_2$$

PROBLEM 13.2

Draw both condensed and line structures corresponding to the following IUPAC names:

(a) 3-Methylhept-1-ene

(b) 4,4-Dimethylpent-2-yne

(c) 2-Methylhex-3-ene

(d) 1,3,3-Trimethylcyclohexene

KEY CONCEPT PROBLEM 13.3 —

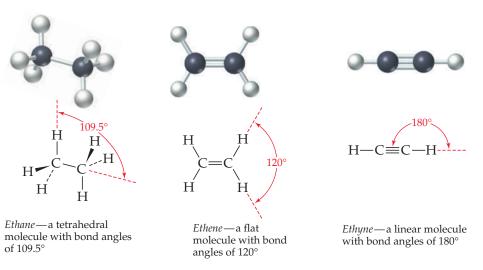
What are the IUPAC names of the two alkenes shown in the margin? Redraw each in line structure format.

13.3 The Structure of Alkenes: Cis-Trans Isomerism

Learning Objective:

• Identify cis-trans isomers of alkenes.

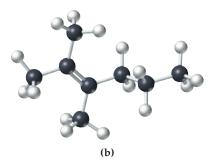
Alkenes and alkynes differ from alkanes in shape because of their multiple bonds. Methane is tetrahedral, but ethene is flat (planar), and ethyne is linear (straight), as predicted by the valence-shell electron-pair repulsion (VSEPR) model discussed in Section 4.8.

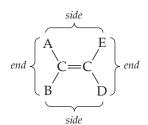


In ethene, the two carbons and four attached atoms that make up the double-bond functional group lie in a plane. Unlike in alkanes, where free rotation around the C—C single bond occurs, there is no rotation around a double bond, and the molecules are more rigid. However, their restricted freedom of rotation makes a new kind of isomerism possible for alkenes. As a consequence of their rigid nature, alkenes possess *ends* and *sides*.

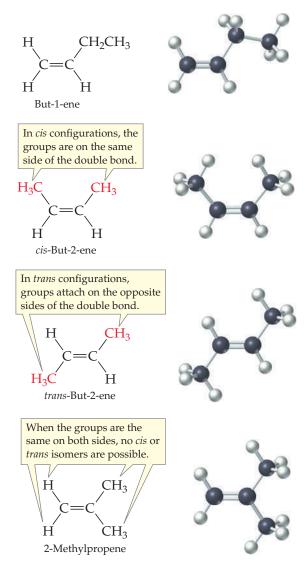
To see this new kind of isomerism, look at the four C_4H_8 compounds shown on the next page. When written as condensed structures, there appear to be only three alkene isomers of formula C_4H_8 : but-1-ene ($CH_2 = CHCH_2CH_3$), but-2-ene ($CH_3CH = CHCH_3$), and 2-methylpropene ((CH_3)₂ $C = CH_2$). The compounds but-1-ene and but-2-ene are conetal, Fundamentals of General, Granicand Biological Chemistry, 61 Edition, Pearson, Education, Limited, 2017: ProQuest Ebook Central.







and 2-methylpropene ((CH₃)₂C = CH₂). The compounds but-1-ene and but-2-ene are con-McMurry, John, et al. Fyndamentals of General Organicand Highgingal Chamistry, file dition, Pearson Education, Limited 2017; Produest Ebook Central http://ebookcentral.produest.com/librosidubiin/detail.action/doc/D=5/185171. It is in the compound of the compou along the chain, and 2-methylpropene is a constitutional isomer of both but-1-ene and but-2-ene because it has the same molecular formula but a different connection of carbon atoms (see Section 12.3). In fact, though, there are *four* isomers of C_4H_8 . Because rotation cannot occur around carbon–carbon double bonds, *there are two different but-2-enes*. In one isomer, the two — CH_3 groups are on the same side of the double bond; in the other isomer, they are on opposite sides of the double bond.



Cis-trans isomer Alkenes that have the same connections between atoms but differ in their three-dimensional structures because of the way those groups attach to different sides of the double bond. The two but-2-enes are called **cis-trans isomers.** They have the same formula and connections between atoms but have different three-dimensional structures because of the way those groups attach to different sides of the double bond. In this case, the isomer with its methyl groups on the same side of the double bond is named *cis*-but-2-ene, and the isomer with its methyl groups on opposite sides of the double bond is named *trans*-but-2-ene.

Cis—trans isomerism is possible whenever an alkene has two *different* s ubstituent groups on each of its ends. (This means that in the earlier drawing illustrating the sides and ends of an alkene molecule, $A \neq B$ and $D \neq E$.) If one of the carbons composing the double bond is attached to two identical groups, cis—trans isomerism cannot exist. In 2-methylbut1-ene, for example, cis—trans isomerism is not possible because C1 is bonded to two identical groups (hydrogen atoms). To convince yourself of this, mentally flip either one of these two structures top to bottom; note that it becomes identical to the other structure.

$$C=C$$
 and $C=C$ CH_3 CH_3 CH_3 CH_3

These compounds are identical. Because the carbon left of the double bond has two H atoms attached, cis—trans isomerism is impossible.

In pent-2-ene, however, the structures do not become identical when one of them is flipped, so cis-trans isomerism does occur.

$$H$$
 $C=C$
and
 H_3C
 H_3C
 $C+C$
 H_3C
 $C+C$
 H
 $C+C$
 C

These compounds are not identical. Neither carbon of the double bond has two identical groups attached to it.

It is important to note that the molecule must remain intact when you perform this analysis; you cannot break and reform any bonds when flipping and comparing the two structures.

The two substituents that are on the same side of the double bond in an alkene are said to be cis to each other, and those on opposite sides of the double bond are said to be trans to each other. In our generic molecule on the previous page showing ends and sides, for example, A and E are cis to each other, B and D are cis to each other, B and E are trans to each other, and A and D are trans to each other. Thus, in alkenes, the terms cis and trans are used in two ways: (1) as a *relative* term to indicate how various groups are attached to the double-bond carbons (e.g., "groups A and E are cis") and (2) in nomenclature as a way to indicate how the longest chain in the molecule goes in, through, and out of the double bond (e.g., *cis*-but-2-ene and *trans*-but-2-ene). Alkynes, because of their linear structure, cannot have cis—trans isomerism; while the triple bond does have ends, it does not have sides, a necessary requirement of this type of isomer.

Recall from Section 12.5 that rotation around C—C single bonds allows a molecule to exist in multiple conformations.

Worked Example 13.3 Molecular Structure: Cis and Trans Isomers

Draw structures for both the cis and trans isomers of hex-2-ene.

ANALYSIS First, draw a condensed structure of hex-2-ene to see which groups are attached to the double-bond carbons.

Next, begin to draw the two isomers. Choose one end of the double bond, and attach its groups in the *same* way to generate two identical partial structures.

$$H_3C$$
 H_3C $C=C$

Finally, attach groups to the other end in the two possible different ways.

SOLUTION

Trace the longest chain in each structure. In the structure on the left, the longest chain comes in on one side of the double bond and exits on the same side; thus, the two hydrogens are on the same side of the double bond and this is the cis isomer. The structure on the left is the trans isomer because the longest chain comes in on one side of the double bond and exits on the opposite side, and the two hydrogens are on opposite sides of the double bond. It is common in line structures to show the hydrogens attached to the double bond, but not necessary.

PROBLEM 13.4

Which of the following substances exist as can cis-trans isomers? Draw both isomers for those that do.

- (a) 2,3-Dimethylpent-2-ene (condensed structures only)
- **(b)** 2-Methylhex-2-ene (both condensed and line structures)
- (c) Hex-2-ene (line structures only)

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HANDS-ON CHEMISTRY 13.1

Models are an invaluable tool in organic chemistry when discussing structure. In this exercise, you are going to look at double bonds and how they restrict rotation when present in an organic molecule. You will also look at how they can crucially change the shape of a molecule. To accomplish all of this you are going to use models, but you do not need a model kit to carry out this exercise. If you have a model kit, follow the instructions included with it to make the "building blocks" described next. If you do not have access to a model kit, follow the instructions next to make "gumdrop building blocks." You will need a box of toothpicks and a bag of multicolored gumdrops (preferred), gummy bears, or mini marshmallows; it does not matter as long as you can insert a toothpick in it and it will stay in place. Throughout this exercise, remember that carbon is tetravalent (forms four bonds) and that hydrogen and chlorine are monovalent (form one bond).

Building Blocks—for this exercise, you will need the following (use the color coding of atoms listed in Table 4.2 as your guide if possible):

Six tetrahedral carbon units—make these by placing four toothpicks into a gumdrop in a tetrahedral array. Use gumdrops of whatever color you have assigned to being carbon (black or some other dark color). Note: There will be times you will have to remove toothpicks to make connections to other units; when you do, make the new connection in the same location as the toothpick you removed.

Three carbon alkene units—to make these, connect two carbon-colored gumdrops to one another using two toothpicks.



Be sure that there is some space between them so that they look like an alkene model.

Six "one group" units—simply stick a toothpick into a gumdrop. The gumdrops should all be the same color, although the color should vary from what you've already used.



Note: You may want to take pictures of each model you make with your phone for review later. Once finished with a question, you can disassemble your models for use in the next question.

- a. Start by assembling butane by connecting four of your tetrahedral units (you will have to remove toothpicks as necessary to make connections). Add gumdrops at the end of the toothpicks to represent Hs if you wish. By rotating around the single bonds, write down all the conformations possible. Is any one higher in energy than the others? See Section 12.5 for help.
- b. Now, using your alkene units, build models of 2-methylpropene, cis-but-2-ene, and trans-but-2-ene (see Section 13.3). Confirm that these three are all different molecules. Notice that you cannot rotate around the double bond to convert the cis molecule into the trans without breaking the double bond. The cis isomer is slightly higher in energy than the trans; can you come up with a possible reason why?
- **c.** Repeat part b for 2-chlorobut-1-ene, showing that there is only one possible isomer for this compound.

d. Cis double bonds are found in many biological molecules, such as the unsaturated fatty acids (see Section 23.2), despite them being of slightly higher energy than the trans. Build two molecules with the following structure, one where all the double bonds are cis and one where they are all trans. Can you come up with a reasonable explanation as to why the all-cis molecule might be more advantageous to have in an aqueous environment over the all-trans molecule?

PROBLEM 13.5

Draw both the condensed and line structures for the cis and trans isomers of 3,4-dimethylhex-3-ene.

KEY CONCEPT PROBLEM 13.6 -

Name the compounds shown below, including the appropriate *cis-* or *trans-* prefix. Redraw each in line structure format.



13.4 Properties of Alkenes and Alkynes

Learning Objective:

• Identify the physical properties of alkenes and alkynes.

The properties of alkenes and alkynes resemble those of alkanes in many respects (Section 12.7). The bonds in alkenes and alkynes are nonpolar, and the physical properties of these compounds are influenced mainly by weak London dispersion forces. Alkenes and alkynes with 1–4 carbon atoms are gases at room temperature, and boiling points increase with the size of the molecules.

Like alkanes, alkenes and alkynes are insoluble in water, soluble in nonpolar solvents, and less dense than water. They are flammable; those that are gases present explosion hazards when mixed with air. Unlike alkanes, alkenes are more reactive because of their double bonds. As we will see in the next section, alkenes undergo addition of various reagents to their double bonds to yield saturated products. Alkynes, as you might expect, are more reactive since they have two double bonds to react.

Properties of Alkenes and Alkynes

- Nonpolar; insoluble in water; soluble in nonpolar organic solvents; less dense than water
- Flammable; nontoxic
- Alkenes display cis-trans isomerism when each double-bond carbon atom has different substituents
- Cis-trans isomers can have different physical and biological properties.
- Multiple bonds are chemically reactive.

13.5 Types of Organic Reactions

Learning Objective:

· Identify the different types of organic reactions.

Before looking at the chemistry of alkenes and alkynes, we should first discuss some general reactivity patterns that make the task of organizing and categorizing organic reactions much simpler. Four particularly important kinds of organic reactions are discussed in this section: *additions*, *eliminations*, *substitutions*, and *rearrangements*.

 Addition Reactions Additions occur when two reactants add together to form a single product with no atoms "left over." We can generalize the process as

These two reactants
$$A + B \longrightarrow C$$
 ... to give this single product.

The most common addition reactions encountered in organic chemistry are those in which a reagent adds across a carbon–carbon multiple bond (an unsaturated molecule) to give a product that contains two (for alkenes) or four (for alkynes) new single bonds (a saturated system). This process can be generalized as

Intermolecular forces were described in Section 8.2.

Addition reaction A general reaction type in which a substance X—Y adds to the multiple bond of an unsaturated reactant to yield a saturated product that has only single bonds.

We'll explore the mechanism of addition reactions further in the Mastering Reactions: How Addition Reactions Occur feature on page 456. An example of an addition reaction is the reaction of an alkene, such as ethene, with H₂ to yield an alkane.

Elimination reaction A general reaction type in which a saturated reactant yields an unsaturated product by losing groups from two adjacent atoms.

Elimination Reactions Eliminations are the opposite of addition reactions. Eliminations occur when a single reactant splits into two or more products, a process we can generalize as

This one reactant ...
$$X Y A = B + X + Y \dots$$
 splits apart to give these two products.

In almost all cases, an elimination reaction converts the starting material to a product that has two fewer single bonds and a carbon–carbon multiple bond in their place.

$$C - C \longrightarrow C = C + X - Y$$

As an example of an elimination reaction, we will see in the next chapter that an alcohol, such as ethanol, eliminates to give water and an alkene when treated with an acid catalyst. This specific process is known as a *dehydration reaction* and can be seen in further detail in the Mastering Reactions: How Eliminations Occur feature on page 483.

Water was eliminated from the reactant.

H OH

$$H = C - C - H = \frac{H_2SO_4}{catalyst}$$
 $H = H = H_2O$
 $H = H$

• Substitution Reactions Substitutions occur when two reactants exchange parts to give two new products, a process we can generalize as

These two reactants exchange parts ...
$$AB + C \longrightarrow AC + B$$
 ... to give these two products.

As an example of a substitution reaction, we saw in Section 12.8 that alkanes, such as methane, react with Cl_2 in the presence of ultraviolet (UV) light to yield alkyl chlorides (the UV light is needed due to the low reactivity of alkanes). Here, a — Cl group substitutes for the — H group of the alkane, and two new products result:

Substitution reaction A general reaction type in which an atom or group of atoms in a molecule is replaced by another atom or group of atoms.

A much more common type of substitution reaction is one that involves alkylhalides and Lewis bases, such as the reaction shown here:

$$CH_3CH_2CH_2CI + CH_3O^-Na^+ \longrightarrow CH_3CH_2CH_2OCH_3 + Na^+CI^-$$

We previously saw another example of this type of substitution reaction in Chapter 12 in Mastering Reactions: Organic Chemistry and the Curved Arrow Formalism on page 420. We'll learn more about alkyl halides and Lewis bases in Chapters 14 and 16.

Rearrangement Reactions Rearrangement occurs when bonds and atoms in the
reactant are reorganized to yield a single product that is an isomer of the reactant.
A generalized example of one type of rearrangement seen in organic chemistry is

Rearrangement reaction A general reaction type in which a molecule undergoes bond reorganization to yield an isomer.

$$C = C \longrightarrow C - C$$

Rearrangement reactions are important in organic chemistry as well as biochemistry. Because of their complex nature, however, we will not discuss them in detail in this book. An example of a rearrangement is the conversion of *cis*-but-2-ene into its isomer *trans*-but-2-ene by treatment with an acid catalyst:

This simple-looking interconversion involves the breaking of the C = C bond followed by rotation and reformation of the double bond; this is a key process in vision (see the Chemistry in Action "The Chemistry of Vision and Color" p. 448).

LOOKING AHEAD The conversion of glucose to fructose (Chapter 22) is an example of tautomerization, converting one carbohydrate into another.

Worked Example 13.4 Identifying Reactions of Alkenes

Classify the following alkene reactions as addition, elimination, or substitution reactions:

(a)
$$CH_3CH = CH_2 + H_2 \longrightarrow CH_3CH_2CH_3$$

(b)
$$CH_3CH_2CH_2OH \xrightarrow{H_2SO_4} CH_3CH = CH_2 + H_2O$$

(c)
$$CH_3CH_2CI + KOH \longrightarrow CH_3CH_2OH + KCI$$

ANALYSIS Determine whether atoms have been added to the starting compound (addition), removed from the starting compound (elimination), or switched with another reactant (substitution).

SOLUTION

- (a) Two H atoms have been added in place of the double bond, so this is an addition reaction.
- **(b)** A water molecule (H₂O) has been formed by *removing* an H atom and an —OH group from adjacent C atoms, forming a double bond in the process, so this is an *elimination* reaction.
- (c) The reactants (CH₃CH₂Cl and KOH) have *traded* the —OH and the —Cl substituent groups, so this is a *substitution* reaction.

PROBLEM 13.7

Classify the following reactions as an addition, elimination, or substitution:

(a)
$$CH_3Br + NaOH \longrightarrow CH_3OH + NaBr$$

(b)
$$H_2C = CH_2 + HC1 \longrightarrow CH_3CH_2C1$$

(c)
$$CH_3CH_2Br \longrightarrow H_2C = CH_2 + HBr$$

CHEMISTRY IN ACTION

The Chemistry of Vision and Color

Our vision, from the vibrant colors we see to the ability of our eyes to adapt to both bright sunlight and pitch darkness, is one of our key sensory systems, but what is the role of chemistry in this system? A critical player in the ability to see is vitamin A, an important biological alkene.

A vitamin is an organic molecule required by the body in trace amounts and usually obtained through diet (Section 19.9). Beta-carotene, a purple-orange alkene, found in carrots and other yellow vegetables provides our main dietary source of vitamin A (also known as retinol). The enzymatic conversion of beta-carotene to vitamin A

takes place in the mucosal cells of the small intestine; vitamin A is then stored in the liver, from which it can be transported to the eye. In the eye, vitamin A is oxidized to retinal, which undergoes cis-trans isomerization of its C11-C12 double bond to produce 11-cis-retinal. Reaction with the protein opsin then produces the light-sensitive substance rhodopsin.

The human eye has two kinds of light-sensitive cells, rod cells and cone cells. The 3 million rod cells are primarily responsible for seeing in dim light, whereas the 100 million cone cells are responsible for seeing in bright light and for the perception of bright colors. When light strikes the rod cells, cis-trans isomerization of the C11 — C12 double bond occurs

$$\beta$$
-Carotene

$$CH_2OH$$

$$Opsin-NH_2$$

$$I1-cis$$

$$CH=O$$

$$I1-cis$$
-Retinal
$$N-Opsin$$

$$H$$

$$CH=N-Opsin$$

$$Rhodopsin$$

$$II$$

PROBLEM 13.8

Many biological transformations can be simply classified as additions, eliminations, or substitutions. How would you classify the following reactions?

(a) Fumaric acid to malic acid (found in the citric acid cycle, Section 21.8)

$$HO \longrightarrow OH \longrightarrow HO \longrightarrow OH$$

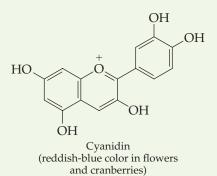
(b) 2-Phosphoglyceric acid to phosphoenolpyruvic acid (found in glycolysis, Section 22.3)

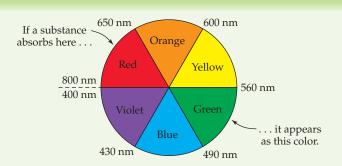
$$H_2O_3P$$
 OH \longrightarrow H_2O_3P OH

via a rearrangement reaction, and 11-trans-rhodopsin, also called *meta*rhodopsin II, is produced. This cis—trans isomerization is accompanied by a change in molecular geometry, which in turn causes a nerve impulse to be sent to the brain, where it is perceived as vision. Metarhodopsin II is then changed back to 11-cis-retinal for use in another vision cycle.

While this explains how we see, it does not tell us what causes the actual colors themselves. Other organic compounds such as the plant pigment cyanidin are also brightly colored. This is due to the fact that they are extended conjugated systems.

Conjugated systems are molecules that contain arrays of alternating double and single bonds, and the electrons within the double bonds are spread out, or *delocalized*, over the whole molecule. Whenever there is conjugation in a molecule, a delocalized region of electron density is formed that is in turn capable of absorbing light. Compounds with extended stretches of alternating double and single bonds (10 or more) absorb in the visible region. The presence of a charged atom in the conjugated system, such as the oxygen in cyanidin, allows absorption in the visible range to occur with fewer conjugated double bonds.





▲ Using an artist's color wheel, it is possible to determine the observed color of a substance by knowing the color of the light absorbed. Observed and absorbed colors are complementary. Thus, if a substance absorbs red light, it has a green color.

The color that we see is complementary to the color that is absorbed; that is, we see what is left of the white light after certain colors have been absorbed. For example, the plant pigment cyanidin absorbs greenish-yellow light and thus appears reddish-blue. It is speculated that this is also the reason that red-colored mulch seems to promote plant growth: the reflected red color is absorbed by the green plant, creating the effect of additional incoming sunlight for photosynthesis.

- **CIA Problem 13.1** (a) After the reaction of 11-cis-retinal with opsin, classify the reaction rhodopsin undergoes in the presence of light to produce 11-trans-rhodopsin. (b) How many hydrogens are present in 11-cis-retinal? (c) What are the functional groups present in this molecule?
- **CIA Problem 13.2** What is the difference in the purpose of the rod cells and the cone cells in the eye?
- **CIA Problem 13.3** Tetrabromofluorescein is a purple dye often used in lipsticks. If the dye is purple, what color does it absorb?

13.6 Addition Reactions of Alkenes

Learning Objectives:

- Predict the addition products obtained when alkenes react with H₂, Cl₂, HCl, or H₂0.
- Identify "unsymmetrically substituted" and "symmetrically substituted" alkenes.
- Utilize Markovnikov's rule when addition reactions to unsymmetrically substituted alkenes occur.

Most of the reactions of alkenes and alkynes are *addition reactions*, where reagent X—Y adds to the multiple bond in the unsaturated reactant to yield a saturated product that has only single bonds.

Addition reactions of alkenes are often used to prepare large quantities of industrially important compounds (such as ethanol). Addition reactions of alkenes and alkynes are similar in many ways. Since alkynes are rarely found in nature, and because addition to an alkyne can generally be thought of as a "double addition" of an alkene, we will limit our discussion in this section to the reactions of alkenes, even though alkynes will do the exact same reactions.

Addition of H2 to Alkenes: Hydrogenation

Alkenes and alkynes react with hydrogen, a process called **hydrogenation**, in the presence of a metal catalyst such as palladium to yield the corresponding alkane product.

(An alkene)
$$C = C + H_2 \xrightarrow{Catalyst} - C - C - (An alkane)$$

For example,

$$\begin{array}{c|cccc} CH_3 & & CH_3 \\ H & + & H_2 & \xrightarrow{Pd \ catalyst} & & H \\ H & & H & & H \end{array}$$

1-Methylcyclohexene

Methylcyclohexane (85% yield)

The addition of hydrogen to an alkene is used commercially to convert unsaturated vegetable oils, which contain numerous double bonds, to the saturated fats used in margarine and cooking fats. This process has come under intense scrutiny in recent years because it also creates *trans*-fatty acids in the product (which, in the diet, has been associated with increased risk of heart disease). We will see the structures of these fats and oils in Chapter 23.

Worked Example 13.5 Organic Reactions: Addition

Hydrogenation The addition of H₂

product.

to a multiple bond to give a saturated

What product would you obtain from the following reaction? Draw both the condensed structure and the line structure of the product.

$$CH_3CH_2CH = CHCH_3 + H_2 \xrightarrow{Pd} ?$$

ANALYSIS Rewrite the reactant, showing a single bond and two partial bonds in place of the double bond.

$$\substack{\text{CH}_3\text{CH}_2\text{CH}-\text{CHCH}_3\\|}$$

Then, add a hydrogen to each carbon atom of the double bond, and rewrite the product in condensed form.

SOLUTION

The reaction is

$$CH_3CH_2CH = CHCH_3 + H_2 \xrightarrow{Pd} CH_3CH_2CH_2CH_2CH_3$$

In line structure format, this reaction would look as follows:

$$\begin{array}{cccc}
& & & & \\
& & & \\
& & & \\
& & & \\
& & & \\
\end{array}$$

PROBLEM 13.9

Write the structures of the products from the following hydrogenation reactions:

(a)
$$\rightarrow$$
 + H₂ \xrightarrow{Pd} ?

(b) *cis*-But-2-ene +
$$H_2 \xrightarrow{Pd}$$

(c) trans-Hept-3-ene +
$$H_2 \xrightarrow{Pd}$$
?

(a)
$$\longrightarrow$$
 + H₂ \xrightarrow{Pd} ? (b) cis-But-2-ene + H₂ \xrightarrow{Pd} ? (c) trans-Hept-3-ene + H₂ \xrightarrow{Pd} ? (d) \longrightarrow CH₃ + H₂ \xrightarrow{Pd} ?

Addition of Cl₂ and Br₂ to Alkenes: Halogenation

Alkenes react with the halogens Br₂ and Cl₂ to give 1,2-dihaloalkane addition products in a halogenation (alkene) reaction.

$$C = C + X_2 \longrightarrow C - C - (A 1,2-dihaloalkane where X = Br or Cl)$$

Halogenation (alkene) The addition of Cl2 or Br2 to a multiple bond to give a dihalide product.

For example,

The addition of Br₂ and Cl₂ to an alkene occurs in an analogous way to that shown in Worked Example 13.5. This reaction is used to manufacture nearly 8 million tons of 1,2-dichloroethane each year in the United States. It is the first step in making the widely used poly(vinyl chloride) plastics (PVC).

Another halogen, Br₂, provides a convenient test for the presence of a carboncarbon double or triple bond in a molecule (Figure 13.1). A few drops of a reddishbrown solution of Br₂ are added to a sample of an unknown compound; the immediate disappearance of the color reveals the presence of a carbon-carbon multiple bond, because the bromine reacts with the compound to form a colorless dibromide. This test can also be used to determine the level of unsaturation of fats (Chapter 23).





▲ Figure 13.1 Testing for unsaturation with bromine.

(a) No color change results when the bromine solution is added to hexane (C_6H_{14}) . (b) Disappearance of the bromine color when it is added to 1-hexene (C₆H₁₂) indicates the presence of a double bond.

Hydrohalogenation The addition of HCl or HBr to a multiple bond to give an alkyl halide product.

PROBLEM 13.10

What products would you expect from the following halogenation reactions?

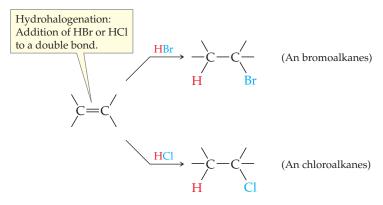
(a) 2-Methylpropene +
$$Br_2 \longrightarrow$$
?

(b) Pent-1-ene +
$$Cl_2 \longrightarrow$$

(a) 2-Methylpropene +
$$Br_2 \longrightarrow$$
? (b) Pent-1-ene + $Cl_2 \longrightarrow$? (c) CH_3 | C

Addition of HBr and HCl to Alkenes

Alkenes react with hydrogen bromide (HBr) to yield bromoalkanes (R-Br) and with hydrogen chloride (HCl) to yield chloroalkanes (R—Cl), in what are called **hydrohalogenation** reactions.



The addition of HBr to 2-methylpropene is an example.

2-Methylpropene

2-Bromo-2-methylpropane

Look carefully at the above example. Only one of the two possible addition products is obtained. 2-Methylpropene *could* add HBr to give 1-bromo-2-methylpropane, but it does not; it gives only 2-bromo-2-methylpropane as the major product.

This result is typical of what happens when HBr and HCl add to an alkene in which one of the double-bond carbons has more hydrogens than the other (an unsymmetrically substituted alkene). The results of such additions can be predicted using Markovnikov's **rule,** formulated in 1869 by the Russian chemist Vladimir Markovnikov.

Markovnikov's rule In the addition of HX to an alkene, the major product arises from the H attaching to the double-bond carbon that has the larger number of H atoms directly attached to it and the X attaching to the carbon that has the smaller number of H atoms attached.

2 hydrogens already on this carbon, so —H attaches here.

No hydrogens on this carbon, so —Br attaches here.
$$H_3C$$
 — CH_2 — CH_3 — CCH_3 — $CCCH_4$ — CCH_3 — $CCCH_4$ — $CCCH_4$ — $CCCCH_4$ — $CCCCCCCC$ — $CCCCCCCCC$ — $CCCCCCCC$ — $CCCCCCC$ — $CCCCCC$ — $CCCCCC$ — $CCCCCC$ — $CCCCCC$ — $CCCCC$ — $CCCC$ — $CCCCC$ — $CCCCC$

Note that the terms "unsymmetrically substituted" and "symmetrically substituted" here refer only to the *number* of hydrogens and carbons attached to each carbon engaged in the double bond and not to the *identity* of the carbon groups attached.

"Unsymmetrically substituted"

"Symmetrically substituted"

In the examples above, R, R', and R" can be any group except H and do not have to be different in this context.

The scientific reason behind Markovnikov's rule is a powerful and important principle in organic chemistry. The Mastering Reactions: How Addition Reactions Occur feature on page 456 discusses Markovnikov's rule in further detail, including the stability of intermediates known as *carbocations* that form during the reaction.

Both possible products form in equal amounts if an alkene has equal numbers of H atoms attached to the double-bond carbons (a symmetrically substituted double bond).

Worked Example 13.6 Organic Reactions: Markovnikov's Rule

What major product do you expect from the following reaction?

$$CH_3$$

 $CH_3CH_2C = CHCH_3 + HCI \longrightarrow ?$

ANALYSIS The reaction of an alkene with HCl leads to the formation of an alkyl chloride addition product according to Markovnikov's rule. To make a prediction, look at the starting alkene and count the number of hydrogens attached to each double-bond carbon. Then write the product by attaching H to the carbon with more hydrogens and attaching Cl to the carbon with fewer hydrogens.

SOLUTION

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3}\text{CH}_{2}\text{C} = \text{CHCH}_{3} \\ \text{No hydrogens on this carbon, so} \\ \text{-Cl attaches here.} \end{array} \\ \begin{array}{c} \text{One hydrogen already} \\ \text{on this carbon, so} \\ \text{-H attaches here.} \end{array} \\ \\ \text{Same as} \quad \begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \\ \text{Same as} \end{array} \\ \end{array}$$

McMurry, John, et al. Fundamentals of General, Organic and Biological Chemistry, SI Edition, Pearson Education, Limited, 2017. ProQuest Ebook Central http://ebookgentral.proquest.com/lib/rcsidublin/detail.action?docID≕5186171....

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Worked Example 13.7 Organic Reactions: Markovnikov's Rule

From what two different alkenes can 2-chloro-3-methylbutane be made?

2-Chloro-3-methylbutane

ANALYSIS 2-Chloro-3-methylbutane is an alkyl chloride that might be made by addition of HCl to an alkene. To generate the possible alkene precursors, remove the —Cl group and an —H atom from adjacent carbons and replace with a double bond.

Look at the possible alkene addition reactions to see which is compatible with Markovnikov's rule. In this case, addition to 3-Methylbut-1-ene is compatible. Note that if HCl is added to 2-Methylbut-2-ene, the major product will have the Cl attached to the wrong carbon (the carbon with the methyl group on it).

SOLUTION

PROBLEM 13.11

Draw all possible products formed when 2-methylbut-2-ene undergoes addition with HCl. Label them as being either the major or the minor product.

PROBLEM 13.12

What major products do you expect from the following reactions?

(a)
$$CH_3$$
 + HCl \longrightarrow ? (b) \longrightarrow + HBr \longrightarrow ?

PROBLEM 13.13

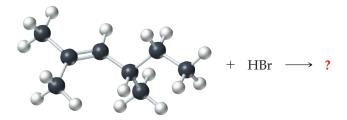
In the following addition reactions, are the given alkyl halides obtained as the major products? Give a reason for your answer.

(a) 3-Chloro-3-ethylpentane from addition of HCl to 3-ethylpent-2-ene

$$(b) \xrightarrow{\text{HBr}} \xrightarrow{\text{Br}}$$

KEY CONCEPT PROBLEM 13.14 -

What product do you expect from the following reaction? Draw your answer in both condensed and line structure formats.



Addition of Water to Alkenes: Hydration

Although a water molecule (H—OH) could be considered as another type of H—X, an alkene will not react with pure water alone. If, however, a small amount of a strong acid catalyst such as H_2SO_4 is added, an addition reaction takes place to yield an *alcohol* (R—OH); a reaction known as a **hydration** reaction. In fact, the United States produces nearly 100 million gallons of ethanol each year by this method.

Hydration The addition of water to a multiple bond to give an alcohol product.

$$C = C + H - O - H \xrightarrow{H_2SO_4} C - C - C$$
An alcohol

For example,

$$\begin{array}{c} H \\ C = C \\ H \end{array} + \begin{array}{c} H_2O \\ H \end{array} \xrightarrow{H_2SO_4} \begin{array}{c} H \\ C = C \\ H \end{array} + \begin{array}{c} H \\ OH \end{array}$$

$$\begin{array}{c} H \\ OH \end{array}$$

As with the addition of HBr and HCl, we can use Markovnikov's rule to predict the product when water adds to an unsymmetrically substituted alkene. Hydration of 2-methylpropene, for example, gives 2-methylpropan-2-ol as the major product:

No hydrogens on this carbon, so —OH attaches here. Two hydrogens already on this carbon, so —H attaches here.
$$\begin{array}{c} \text{CH}_3 \\ \text{C} = \text{CH}_2 \\ \text{H}_3\text{C} \end{array} + \begin{array}{c} \text{H} = \text{O} - \text{H} \\ \frac{\text{H}_2\text{SO}_4}{250^{\circ}\text{C}} > \begin{array}{c} \text{CH}_3 \\ \text{OH} \\ \text{H} \end{array}$$

MASTERING REACTIONS

How Addition Reactions Occur

How do alkene addition reactions take place? Do two molecules, say ethene and HBr, simply collide and immediately form a product molecule of bromoethane, or is the process more complex? In Chapter 12, we presented a useful and convenient way for organic chemists to visualize reactions (see Mastering Reactions: Organic Chemistry and the Curved Arrow Formalism on p. 420). Here, we apply this to the study of addition reactions, specifically those involving H⁺. Detailed studies show that alkene addition reactions take place in two distinct steps, as illustrated in the following figure for the addition of HBr to ethene.

$$\begin{array}{c} H \\ H \\ C = C \\ H \end{array} \xrightarrow{Step 1} \begin{bmatrix} H & H \\ H \\ H \\ C = C \\ H \end{bmatrix} \xrightarrow{Step 2} \begin{array}{c} H & H \\ H \\ H \\ Br & H \end{array}$$

$$\begin{array}{c} Step 2 \\ H - C - C - H \\ H \\ Br & H \end{array}$$

$$\begin{array}{c} Br \\ Bromoethane \end{array}$$

▲ The mechanism of the addition of HBr to an alkene. The reaction takes place in two steps and involves a carbocation intermediate. In the first step, two electrons move from the C = C double bond to form a C = H bond. In the second step, Br^- uses two electrons to form a bond to the positively charged carbon.

To begin, recognize that almost all organic reactions can be visualized as occurring between an electron-rich species and an electron-poor species. In the first step, the electron-rich alkene reacts with H⁺ from the acid HBr. The carbon—carbon double bond partially breaks, and two electrons move from the double bond to form a new single bond (indicated by the curved red arrow in the figure). The remaining double-bond carbon, having had electrons that were being shared removed from it, now has only six electrons in its outer shell and bears a positive charge. Carbons that possess a positive charge, or *carbocations*, are highly reactive. As soon as this carbocation is formed, it immediately reacts with Br⁻ to form a neutral product.

For ethene both carbons have identical substitution. What about the case where the double bond is unsymmetrically substituted, say, with 2-methylbut-2-ene? Here, we perform the same analysis as the one we did for ethene.

$$\begin{array}{c} H \\ H_3C-C-CH-CH_3 \\ H_3C-C=CH-CH_3 \\ \end{array} \begin{array}{c} Path \ 1 \\ Path \ 1 \\ Path \ 2 \\ Path \ 3 \\ Path \ 2 \\ Path \ 3 \\ Path \ 2 \\ Path \ 3 \\ Path \ 4 \\ Pat$$

The double bond, being electron rich, attacks the electron-poor H⁺ and in doing so, causes a carbocation to form; however, here we have two possibilities. If the H⁺ attaches to C2, the carbocation will form on C3 (Path 1); if the H⁺ attaches to C3, the carbocation will form on C2 (Path 2). Since this is an equilibrium process (the H⁺ can just as easily be removed to regenerate the alkene) we should see both, but is one favored over the other? The answer to that can be arrived at by examining the two carbocations. Carbocations are electron-deficient species, so anything that can help stabilize one over another will cause a preference for that species to be seen. Car-

bons are known to donate electron density through the single bond; therefore, the more carbons attached to a carbocation, the less electron poor it is the more stable it will be, making it more favorable. The more favorable the carbocation, the more product will arise from it. Studies have shown that tertiary (3°) carbocations are more stable than secondary (2°) carbocations, which are much more stable than primary (1°) carbocations (which are almost never formed).

Thus, when the bromide reacts, two possible products are formed, with the major product arising from the more stable carbocation.

A tertiary (3°) carbocation

Markovnikov Product (Major)

A secondary (2°) carbocation

Anti-Markovnikov Product (Minor)

You should notice that the major product is that predicted by Markovnikov's rule. This now shows you the scientific basis for his observations: The major product arises because the intermediate it is derived from is more stable than any other intermediate (here, the 3° carbocation). This concept of the stability of intermediates lies at the very core of organic chemistry and is so powerful that it allows chemists to successfully predict the outcomes of diverse organic reactions.

A description of the individual steps by which old bonds are broken and new bonds are formed in a reaction is called a **reaction mechanism**. Mechanisms allow chemists to classify thousands of seemingly unrelated organic reactions into only a few categories and help us to understand what is occurring during a reaction. Their study is essential to our ever-expanding ability to understand biochemistry and the physiological effects of drugs.

Reaction mechanism A description of the individual steps by which old bonds are broken and new bonds are formed in a reaction.

MR Problem 13.1 Remembering Markovnikov's rule, draw the structure of the carbocation formed during the reaction of 2-methylpropene with HCI.

MR Problem 13.2 Refer to Problem 13.62: Assuming that Markovnikov's rule is followed, predict which of the two structures you drew is formed, and draw the carbocation involved as an intermediate.

MR Problem 13.3 Consider the molecule buta-1,3-diene (shown next). When this is reacted with HBr at 25 °C, the major product obtained is 1-bromobut-2-ene. Given that the first step is the formation of a carbocation and assuming that Markovnikov's rule is initially followed, propose an explanation for the formation of the product seen. (Hint: Think about resonance.)

$$+ HBr \longrightarrow H$$



Worked Example 13.8 Reaction of Alkenes: Hydration

What products do you expect from the following hydration reaction?

$$CH_3CH = CHCH_2CH_3 + H_2O \xrightarrow{H_2SO_4} ?$$

ANALYSIS Water is added to the double bond, with an H atom added to one carbon and an —OH group added to the other carbon of the double bond.

SOLUTION

Because this is *not* an unsymmetrically substituted alkene, we can add the —OH group to either carbon:

PROBLEM 13.15

What products do you expect from the following hydration reactions? Label them as major and minor if more than one is formed.

PROBLEM 13.16

Draw the structures of the two different alkenes from which 3-methylpentan-3-ol, shown in the margin, can be made. Draw them in both condensed and line format.

13.7 Alkene Polymers

Learning Objective:

Predict what polymer forms given an alkene monomer.

Polymer A large molecule formed by the repetitive bonding together of many smaller molecules (or monomers).

Monomer A small molecule that is used to prepare a polymer.

A **polymer** is a large molecule formed by the repetitive bonding together of many smaller molecules called **monomers**. As we will see in later chapters, biological polymers such as cellulose, starch, proteins, and DNA occur throughout nature. Although the basic idea is the same, synthetic polymers are much simpler than biopolymers because the starting monomer units are usually small, simple organic molecules.

Many simple alkenes undergo *polymerization* reactions when treated with the proper catalyst. Ethene yields polyethene upon polymerization, propene yields polypropene, and styrene yields polystyrene. The polymer product might have anywhere from a few hundred to a few thousand monomer units incorporated into a long, repeating chain.

$$\begin{array}{c} H_2C=CH_2\\ \text{Ethene} \end{array} \begin{array}{c} CH_3CH=CH_2\\ \text{Propene} \end{array} \begin{array}{c} CH=CH_2\\ \text{Styrene} \end{array}$$

The fundamental reaction in the polymerization of an alkene monomer resembles the addition reactions of a carbon–carbon double bond described in the preceding sections. One of the most common methods used to make polymers involves the use of radicals (see Section 12.8). The reaction begins by addition of a species called an *initiator* to an alkene; this results in the breaking of one of the bonds making up the double bond. A reactive intermediate that contains an unpaired electron (known as a *radical*) is formed in this step, and it is this reactive intermediate that adds to a second alkene molecule. This produces another reactive intermediate, which adds to a third alkene molecule, and so on. Because the result is continuous addition of one monomer after another to the end of the growing polymer chain, polymers formed in this way are *chain-growth polymers*. The basic repeating unit is enclosed in parentheses, and the subscript *n* indicates how many repeating units are in the polymer.

Variations in the substituent group Z attached to the double bond impart different properties to the product, as illustrated by the alkene polymers listed in Table 13.1. Polymer rigidity is controlled by addition of a small amount of a cross-linking agent, typically 1–2% of a dialkene (an alkene containing two double bonds), whose role is to covalently link two chains of monomer units together.

The properties of a polymer depend not only on the monomer but also on the average size of the huge molecules in a particular sample and on how extensively they cross-link and branch. The long molecules in straight-chain polyethene pack closely together, giving a rigid material called *high-density polyethene*, which is mainly used in bottles for products such as milk and motor oil. When polyethene molecules contain many branches (due to the Z groups present), they cannot pack together as tightly and instead form a flexible material called *low-density polyethene*, which is used mainly in packaging materials.

The use of polymers has changed the nature of activities ranging from plumbing and clothing to items such as skis and snowboards. In the health-care fields, the use of inexpensive, disposable equipment is now common.



▲ These disposable polypropene medical supplies are used once and then discarded.

reactive, electron poor

Table 13.1 Some Alkene Polymers and Their Uses

| | · · · J | | |
|------------------------------|---|-----------------------------------|---|
| Monomer Name | Monomer Structure | Polymer Name | Uses |
| Ethene | $H_2C = CH_2$ | Polyethene | Packaging, bottles |
| Propene | $H_2C = CH - CH_3$ | Polypropene | Bottles, rope, pails, medical tubing |
| Vinyl chloride | $H_2C = CH - CI$ | Poly(vinyl chloride) | Insulation, plastic pipe |
| Styrene | $H_2C=CH$ | Polystyrene | Foams, molded plastics |
| Styrene and 1,3-butadiene | H ₂ C=CH- and H ₂ C=CHCH=CH ₂ | Styrene-butadiene rubber (SBR) | Synthetic rubber for tires |
| Acrylonitrile | $H_2C = CH - C \equiv N$ | Orlon, Acrilan | Fibers, outdoor carpeting |
| Methyl methacrylate | $\begin{array}{c} O \\ \parallel \\ H_2C = CCOCH_3 \\ CH_3 \end{array}$ | Plexiglas, Lucite | Windows, contact lenses, fiber optics |
| Tetrafluoroethylene | F ₂ C=CF ₂ | Teflon | Nonstick coatings, bearings, replacement heart valves and blood vessels |

Worked Example 13.9 Reactions of Alkenes: Polymerization

Write the structure of a segment of polystyrene, used in foams and molded plastics. The monomer is

-continued from previous page

ANALYSIS The polymerization reaction resembles the addition of two monomer units to either end of the double bond.

SOLUTION

Draw three molecules of styrene with the double bonds aligned next to each other; then add the monomer units together with single bonds, eliminating the double bonds in the process.

PROBLEM 13.17

The structure of vinyl acetate is shown below (the partial structure $H_2C = CH$ is known as a *vinyl group*). When polymerized it produces poly(vinyl acetate), a polymer used for the springy soles in running shoes. Draw the structure of the polymer obtained if three vinyl acetate units underwent polymerization.

$$O$$
 \parallel
 H_2C =CHOCCH₃ Vinyl acetate

PROBLEM 13.18

Polychlorotrifluoroethylene (PCTFE (Kel-F)) is a polymer that has the lowest water vapor transmission rate of any plastic, making it an excellent moisture barrier. It can also be used for injection molding of plastic items, while polytetrafluoroethylene (PTFE (Teflon)) cannot. Given the monomer shown below, draw a representative structure for PCTFE.

$$F \subset F$$

13.8 Aromatic Compounds and the Structure of Benzene

Learning Objectives:

- Identify the structures of aromatic compounds.
- Explain the importance and function of resonance in aromatic compounds.

Chemists initially used the word *aromatic* to describe fragrant substances from fruits, trees, and other natural sources, but they soon realized, however, that many of the substances grouped as aromatic behave differently from most other organic compounds. Today, chemists use the term **aromatic** to refer to the class of compounds that contain benzene-like rings.

Benzene, the simplest aromatic compound, is a flat, symmetrical molecule with the molecular formula C_6H_6 . It is often represented as cyclohexatriene, a 6-membered carbon ring with three double bonds. Though useful, the problem with this representation is that it gives the wrong impression about benzene's chemical reactivity and bonding. Because benzene appears to have three double bonds, you might expect it to react with H_2 , Br_2 , HCl, and H_2O to give the same kinds of addition products that alkenes do. But this expectation would be wrong. Benzene and other aromatic compounds are



Aromatic The class of compounds containing benzene-like rings.

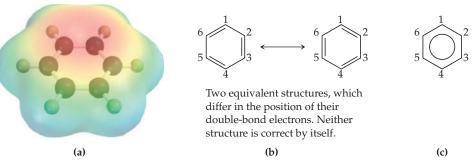
much less reactive than alkenes and do not undergo the usual addition reactions seen in alkenes.

$$\begin{array}{c}
 & H_2, Pd \\
\hline
 & Br_2 \\
\hline
 & HCl \\
\hline
 & H_3O^+
\end{array}$$
No reaction

Benzene's relative lack of chemical reactivity is a consequence of its structure. If you were to draw a six-membered ring with alternating single and double bonds, where would you place the double bonds? There are two equivalent possibilities (Figure 13.2b), neither of which is fully correct by itself. Experimental evidence shows that all six carbon–carbon bonds in benzene are identical, so a picture with three double bonds and three single bonds cannot be correct.

The properties of benzene are best explained by assuming that its true structure is an *average* of the two equivalent conventional Lewis structures. Rather than being held between specific pairs of atoms, the double-bond electrons are instead free to move over the entire ring. Each carbon–carbon bond is thus intermediate between a single bond and a double bond. This is known as **resonance**, where the true structure of a molecule is an average among two or more possible conventional structures, and a special double-headed arrow (\longleftrightarrow) is used to show the resonance relationship. Resonance allows the electrons in the double bonds to be *delocalized* over the entire molecule, thus lowering the reactivity of the double bonds. It is important to note that *no atoms move between resonance structures*, *only pairs of electrons* (in this case, double bonds).

Because the real structure of benzene is intermediate between the two forms shown in Figure 13.2b, it is difficult to represent benzene with the standard conventions using lines for covalent bonds. Thus, we sometimes represent the double bonds as a circle inside the six-membered ring, as shown in Figure 13.2c. It is more common, though, to draw the ring with three double bonds, with the understanding that it is an aromatic ring with equivalent bonding all around. We use this convention in this book.



▲ Figure 13.2 Some representations of benzene.

(a) An electrostatic potential map shows the equivalency of the carbon–carbon bonds. Benzene is usually represented by the two equivalent structures in (b) or by the single structure in (c).

Simple aromatic hydrocarbons like benzene are nonpolar, insoluble in water, volatile, and flammable. Unlike alkanes and alkenes, however, several aromatic hydrocarbons have biological effects. Benzene itself has been implicated as a cause of leukemia, and the dimethyl-substituted benzenes are central nervous system depressants.

Everything we have said about the structure and stability of the benzene ring also applies to the ring when it has substituents, such as in the germicidal agent hexachlorophene and the flavoring ingredient vanillin.

The benzene ring is also present in many biomolecules (including plant dyes and pigments, see the Chemistry in Action on p. 448) and retains its characteristic properties in these compounds as well. In addition, aromaticity is not limited to rings that



▲ Benzaldehyde, an aromatic compound, gives cherries their odor.

Resonance The phenomenon where the true structure of a molecule is an average among two or more conventional Lewis structures that differ only in the placement of double bonds.

Vanillin (vanilla flavoring)

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contain only carbon. For example, many compounds classified as aromatics have one or more nitrogen atoms in the ring. Pyridine, indole, and adenine are three examples:

These and all other compounds that contain a substituted benzene ring, or a similarly stable six-membered ring in which double-bond electrons are equally shared around the ring, are classified as aromatic compounds. While the rules regarding exactly what makes a molecule aromatic are not as simple as we discuss here, for the purposes of this text, we say that a 6-membered ring with alternating single and double bonds will be aromatic.

13.9 Naming Aromatic Compounds

Learning Objective:

Name simple monosubstituted or disubstituted aromatic compounds.

Substituted benzenes are named using *-benzene* as the parent. Thus, C₆H₅Br is bromobenzene, C₆H₅CH₂CH₃ is ethylbenzene, and so on. No number is needed for monosubstituted benzenes because all the ring positions are identical.

When a benzene has more than one substituent present, the positions of those substituents are indicated by numbers, just as in naming cycloalkanes. Disubstituted benzenes (and only disubstituted benzenes) are unique in that the relational descriptors *o-(ortho), m- (meta),* and *p- (para)* may be used in place of 1,2-, 1,3-, and 1,4-, respectively. The terms *ortho-, meta-,* or *para-* (or their single-letter equivalents) are then used as prefixes.

Table 13.2 Common Names of Some Aromatic Compounds

| · · · · · · · · · · · · · · · · · · · | | |
|---|---------------------------|--|
| Structure | Name | |
| \sim CH ₃ | Toluene | |
| —ОН | Phenol | |
| NH_2 | Aniline | |
| H_3C \sim | para-Xylene (p-Xylene) | |
| | Benzoic acid | |
| О - - | Benzaldehyde | |

While any one of these three nomenclature schemes are acceptable, we will almost exclusively use o-, m-, and p- in naming these disubstituted compounds.

Many substituted aromatic compounds have common names in addition to their systematic names. For example, methylbenzene is familiarly known as *toluene*, hydroxybenzene as *phenol*, aminobenzene as *aniline*, and so on, as shown in Table 13.2. Frequently, these common names are also used together with *o-* (*ortho*), *m-* (*meta*), or *p-* (*para*) prefixes. For example,

$$Cl$$
— CH_3 MO_2 NO_2 NH_2 p -Chlorotoluene m -Nitrophenol o -Bromoaniline

Occasionally, the benzene ring itself may be considered a substituent group attached to another parent compound. When this happens, the name **phenyl** (pronounced *fen*-nil and commonly abbreviated Ph—) is used for the C_6H_5 — unit.

Phenyl The C_6H_5 — group.

Worked Example 13.10 Naming Organic Compounds: Aromatic Compounds

Name the following aromatic compound:

ANALYSIS First, identify the parent organic compound, then identify the location of substituent groups on the benzene ring either by number or by ortho(o-), meta(m-), or para(p-).

SOLUTION

The parent compound is a benzene ring with an amine group (*aminobenzene*, which is commonly known as *aniline*). The substituent group is attached at the C4, or para, position relative to the amino group. The propyl group is attached to the benzene ring by the middle carbon, so it is *isopropyl*.

Name: para-isopropylaniline, or 4-isopropylaminobenzene

Worked Example 13.11 Molecular Structures: Aromatic Compounds

Draw the structure of *m*-chloroethylbenzene.

ANALYSIS *m*-Chloroethylbenzene has a benzene ring with two substituents, chloro and ethyl, in a meta relationship (i.e., on C1 and C3).

SOLUTION

Since all carbons in the benzene ring are equivalent, draw a benzene ring and attach one of the substituents—for example, chloro—to any position.

—continued from previous page

Now go to a meta position two carbons away from the chloro-substituted carbon, and attach the second (ethyl) substituent.

PROBLEM 13.19

What are the IUPAC names for the following compounds?

(a)
$$HO$$
 CH_2CH_3 (b) CH_3

PROBLEM 13.20

Draw structures corresponding to the following names (refer to Table 13.2 if necessary):

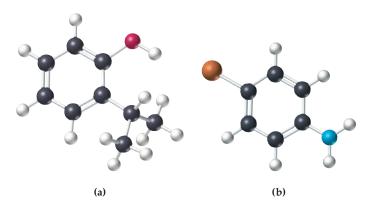
- (a) *m*-Chloronitrobenzene
- **(b)** *o*-Nitrotoluene

(c) p-Methylaniline

(d) p-Nitrophenol

KEY CONCEPT PROBLEM 13.21 —

Name the following compounds (red = O, blue = N, brown = Br):



13.10 Reactions of Aromatic Compounds

Learning Objective:

• Predict the products obtained when aromatic compounds react with concentrated HNO_3 , Cl_2 , Br_2 , or concentrated H_2SO_4 .

Unlike alkenes, which undergo addition reactions, aromatic compounds usually undergo a special type of substitution reaction known as an *electrophilic aromatic substitution* (EAS) reaction. That is, a group Y substitutes for one hydrogen atom on the

aromatic ring without changing the ring itself. It does not matter which of the six ring hydrogens in benzene is replaced because all six are equivalent.

Substitution: H replaced with Y.

H

$$C=C$$
 $H-C$
 $C-C$
 H
 $C=C$
 $C-C$
 $C-C$

The mechanism responsible for this type of reaction is similar to that seen for alkenes, with the key difference being regeneration of the extremely stable aromatic ring.

Nitration is the substitution of a *nitro group* (—NO₂) for one of the ring hydrogens. The reaction occurs when benzene reacts with nitric acid in the presence of sulfuric acid as catalyst.

Nitration The substitution of a nitro group (—NO₂) for a hydrogen on an aromatic ring.

H H Nitration: Substitution of H with nitro group.

$$C = C$$
 $C = C$
 $C =$

Nitration of aromatic rings is a key step in the synthesis both of explosives like TNT (trinitrotoluene) and of many important pharmaceutical agents, since the $-NO_2$ group can be readily converted to an $-NH_2$. Nitrobenzene itself is the industrial starting material for the preparation of aniline, which is used to make many of the brightly colored dyes in clothing.

Halogenation (aromatic) The substitution of a halogen group (—X) for a hydrogen on an aromatic ring.

Halogenation (aromatic) is the substitution of a halogen atom, usually bromine or chlorine, for one of the ring hydrogens. The reaction occurs when benzene reacts with Br₂ or Cl₂ in the presence of FeBr₃ or FeCl₃ as catalyst.

Sulfonation The substitution of a sulfonic acid group ($-SO_3H$) for a hydrogen on an aromatic ring.

Sulfonation is the substitution of a sulfonic acid group ($-SO_3H$) for one of the ring hydrogens. The reaction occurs when benzene reacts with concentrated sulfuric acid and SO_3 .

CHEMISTRY IN ACTION

Enedigne Antibiotics: A Newly Emerging Class of Antitumor Agents

While we discuss alkynes only briefly in this chapter and this text as a whole, it is not because alkynes are not important in organic chemistry. Alkynes are not usually found in nature; however, when they are isolated from natural sources, such as plants and bacteria, they have unexpected physiological properties, including toxicity. For example, ichthyothereol, a trialkyne, isolated from the leaves of a small herb found in the Amazon and Central America, inhibits energy production in mitochondria, and while being toxic to fish, mice, and dogs, has no effect on humans. This has caused chemists to investigate what might happen if the alkyne function were introduced into other biologically active molecules, which has led to the discovery of pharmaceuticals such as Rasagiline, a monoamine oxidase inhibitor effective in treating Parkinson's disease. This compound, due to its neuroprotective nature, is also offering a novel approach to Alzheimer's drug therapy. Rasagiline seems to enhance memory and learning, while also improving mood, motivation, and age-related memory decline and provides a great lead for the discovery of new medicines to treat this debilitating disease. Due to successes such as Rasagiline, chemists and biochemists have intensified the hunt for naturally occurring alkynes. This expanding pursuit for new alkyne-containing natural products has led to the discovery of a very unlikely class of antitumor antibiotics known as the enediques, which we first learned about at the beginning of the chapter. Initially discovered in a fermentation broth derived from the bacteria *Micromonospora*, they represent a new chemical structure class for antibiotics.

The enedigne family of compounds represents the most potent antitumor agents known. The toxic nature of these compounds arises from their ability to cause scission of DNA strands in their target. The enedigne antibiotics fall into three basic families: the calicheamicins, the dynemicins (shown next), and the most complex of the group, the chromoproteins. All members have three distinct regions within them: (1) an anthraquinone-like portion; (2) a chemical "warhead" comprised of two triple

Rasagiline

Aromatic-ring sulfonation is a key step in the synthesis of such compounds as the sulfa-drug family of antibiotics:

$$H_2N$$
 SO_2NH_2

Sulfanilamide—a sulfa antibiotic

PROBLEM 13.22

What products will be formed when toluene is reacted with the reagents shown here?

- (a) Br₂ and FeBr₃
- (b) HNO₃ and H₂SO₄ catalyst
- (c) SO₃ in H₂SO₄

PROBLEM 13.23

Reaction of Br₂ and FeBr₃ with phenol can lead to *three* possible substitution products. Show the structure of each and name them.

Dynemicin A

bonds, conjugated through a double bond, within a 9–10-membered ring; and (3) a "trigger." In Dynemicin A (shown above), that trigger is the three-membered epoxide ring (highlighted in red). The anthraquinone portion intercalates into the major groove of DNA; the trigger is then activated by some nucleophilic species (such as an oxygen, nitrogen, or sulfur atom) that attacks and then opens the epoxide ring. Once opened, the warhead undergoes a rearrangement reaction, producing an extremely reactive diradical aromatic species, which then induces the breakage of the DNA strands.

All of the enedignes are very toxic, as are all antitumor agents. One way to utilize them in the war on cancer would be to attach them to an antibody specifically prepared to target the tumor cells the doctor wishes to destroy. This method, known as

"immunotargeting," would allow the preparation of a "magic bullet," which would attack only the tumor cells and nothing else. One of the reasons that the enedigne antibiotics are so attractive is that they have activity against drug-resistant tumors. Many cancer cells have natural resistance to a number of the drugs usually used to treat them or will develop resistance over the course of a treatment. This, coupled with a lack of selectivity to antitumor agents (antitumor drugs affect all cells, not just cancer) is one

of the major causes of the ineffectiveness of anticancer therapies. Compounds such as Dynemicin A and others discovered through studies of the enedignes could represent a new weapon in our assault on an old and deadly foe: cancer.

The meaning of the wedged and dashed bonds will be clarified in Section 14.10 when we discuss stereochemistry.

- **CIA Problem 13.4** What beneficial properties of Rasagiline make it useful for the treatment of Alzheimer's disease?
- **CIA Problem 13.5** Why would attaching an enedigne-containing molecule to an antibody be an attractive way to treat cancer cells?
- **CIA Problem 13.6** What are the major causes of the ineffectiveness of anticancer therapies?

SUMMARY REVISITING THE CHAPTER LEARNING OBJECTIVES

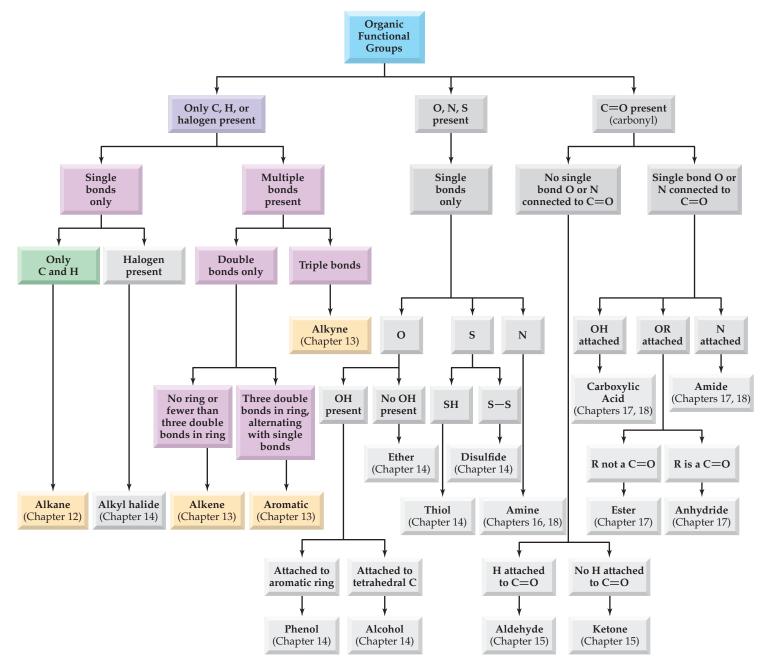
- Identify the functional groups present in alkenes and alkynes. Alkenes are hydrocarbons that contain a carbon—carbon double bond, and alkynes are hydrocarbons that contain a carbon—carbon triple bond (see Problems 27, 29—31, 34, 35, and 43).
- **Differentiate between saturated and unsaturated molecules.** A *saturated* molecule is one that contains only tetravalent carbon atoms and no double or triple bonds. Compounds are said to be *unsaturated* because they have fewer hydrogens than corresponding alkanes. The term is usually used to indicate the presence of double or triple bonds (see Problems 30 and 31).
- Name a simple alkene or alkyne given its condensed or line structure. Alkenes and alkynes are named in a manner almost identical to that used for naming alkanes (Section 12.6), except now the functional group takes priority in numbering the carbon chain. Alkenes are named using the family ending -ene; alkynes use the family ending -yne (see Problems 34–37).
- Draw the condensed or line structure of an alkene or alkyne given its name. Organic compounds can be represented by structural formulas in which all atoms and bonds are shown, by condensed structures in which not all bonds are drawn, or by line structures in which the carbon skeleton is represented by lines and the locations of C and H atoms are understood (see Problems 38, 39, 48, 61, and 70).
- Identify cis—trans isomers of alkenes. Alkenes can be thought of as having sides and ends. Cis—trans isomers are seen in substituted alkenes as a consequence of the lack of rotation around carbon—carbon double bonds. In the cis isomer, the two substituents are on the same side of the double bond; in the trans isomer, they are on opposite sides of the double bond (see Problems 44–51, 71, 81, 82, and 84).
- Identify the physical properties of alkenes and alkynes. Alkenes and alkynes are generally nonpolar, insoluble in water (hydrophobic), and unreactive. They possess low melting and/or boiling points due to their weak intermolecular forces. Alkenes are generally nontoxic and therefore have limited physiological effects (see Problems 72 and 73).
- Identify the different types of organic reactions. Addition reactions occur when two reactants add together to form a single product with no atoms left over. Elimination reactions occur when a single reactant breaks into two products, forming an alkene or an alkyne in the process. Substitution reactions occur when two reactants exchange atoms or groups to give two new products. Rearrangement reactions occur when a single reactant undergoes a reorganization of bonds and atoms to yield a single isomeric product (see Problems 52–57).
- Predict the addition products obtained when alkenes react with H_2 , CI_2 , HCI, or H_2O . Alkenes and alkynes undergo addition reactions to their multiple bonds. Addition of hydrogen to an alkene(hydrogenation) yields an alkane product, addition of CI_2 or Br_2 (halogenation) yields a 1,2-dihaloalkane product, addition of HBr and HCl (hydrohalogenation) yields an alkyl halide product, and addition of water (hydration) yields an alcohol product (see Problems 58–62 and 76–80).

- Identify "symmetrically substituted" and "unsymmetrically substituted" alkenes. Alkenes can be classified as symmetrically substituted if each carbon of the double bond has the same number of hydrogens directly attached to each carbon and unsymmetrically substituted if the carbons do not (see Problems 46–48, 50, 70, and 71).
- Utilize Markovnikov's rule when addition reactions to unsymmetrically substituted alkenes occur. Markovnikov's rule predicts that in the addition of HX or H_2O to a double bond, the H becomes attached to the carbon with more hydrogens and the X or OH becomes attached to the carbon with fewer Hs (see Problems 58 and 60).
- Predict what polymer forms given an alkene monomer. Many simple alkenes undergo polymerization, a reaction that resembles addition to a carbon—carbon double bond, as described in the preceding sections. An *initiator* adds to an alkene to form a radical; this results in the breaking of one of the bonds making up the double bond. This reactive intermediate adds to a second alkene molecule to produce another reactive intermediate, which adds to a third alkene molecule, and so on. The resulting polymer is the result of the continuous addition of one monomer after another to the end of the growing polymer chain (see Problems 63, 64, and 83).
- Identify the structures of aromatic compounds. Aromatic compounds contain six-membered, benzene-like rings and are usually written with three double bonds. In fact, however, there is equal bonding between neighboring carbon atoms in benzene rings because the double-bond electrons are symmetrically spread around the entire ring (see Problems 31–33, 37, and 39).
- Explain the importance and function of resonance in aromatic compounds. Aromatic compounds exhibit resonance: Lewis structures that are interconvertable by only the movement of pairs of electrons; no atoms can move. Resonance allows for the delocalization of electrons by spreading electron density over the entire molecule. Because of this, delocalized electrons are less reactive than those found in a normal alkene or alkyne (see Problems 29 and 31).
- Name simple monosubstituted or disubstituted aromatic compounds. Disubstituted benzenes have the suffix *-benzene* as the parent name, and positions of the substituents are indicated with the prefixes *ortho-* (1,2 substitution), *meta-* (1,3 substitution), or *para-* (1,4 substitution) (see Problems 26, 33, 37, 39, and 69).
- Predict the products obtained when aromatic compounds react with concentrated HNO $_3$, Cl $_2$, Br $_2$, or concentrated H $_2$ SO $_4$. Aromatic compounds are unusually stable but can be made to undergo substitution reactions, in which one of the ring hydrogens is replaced by another group (C $_6$ H $_6 \rightarrow C_6$ H $_5$ Y). Among these substitutions are nitration (substitution of NO $_2$ for H), halogenation (substitution of Br or Cl for H), and sulfonation (substitution of SO $_3$ H for H) (see Problems 42 and 65–68).

KEY WORDS

Addition reaction, p. 445 Alkene, p. 437 Alkyne, p. 437 Aromatic, p. 460 Cis–trans isomer, p. 442 Cycloalkene, p. 437 Elimination reaction, p. 446 Halogenation (alkene), p. 451 Halogenation (aromatic), p. 466 Hydration, p. 455 Hydrogenation, p. 450 Hydrohalogenation, p. 452

Markovnikov's rule, p. 452 Monomer, p. 458 Nitration, p. 465 Phenyl, p. 463 Polymer, p. 458 Reaction mechanism, p. 457 Rearrangement reaction, p. 447 Resonance, p. 461 Saturated, p. 437 Substitution reaction, p. 446 Sulfonation, p. 466 Unsaturated, p. 437



▲ Figure 13.3 Functional Group Concept Map. This is the same concept map we saw at the end of Chapter 12, except the functional groups discussed in this chapter, alkenes, alkynes, and aromatic compounds, have now been colorized.

SUMMARY OF REACTIONS

- 1. Reactions of alkenes and alkynes (Section 13.6):
 - (a) Addition of H₂ to yield an alkane (hydrogenation):

An alkene:
$$\begin{array}{c} H & H & H & H & H \\ C = C & \frac{H_2}{Catalyst} \rightarrow H - C - C - H \\ H & H & H & H \end{array}$$

An alkyne:
$$H-C\equiv C-H$$
 $\xrightarrow{2H_2}$ $H-C-C-H$

(b) Addition of
$$Cl_2$$
 or Br_2 to yield a dihalide (halogenation):

$$\begin{array}{c} H \\ C = C \\ H \end{array} \xrightarrow{\begin{array}{c} Cl_2 \text{ (or Br}_2) \\ H \end{array}} H \xrightarrow{\begin{array}{c} Cl \\ - C \\ - C \\ H \end{array}} H \xrightarrow{\begin{array}{c} Cl \\ - C \\ H \end{array}} H$$

McMurry, John, et al. Fundamentals of General, Organic and Biological Chemistry, SI Edition Pearson Education, Limited, 2017. ProQuest Ebook Central, http://ebookcentral.proquest.com/lib/rcsidublin/detail.action?docID=5186171.

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$$\begin{array}{c}
H \\
C = C \\
H
\end{array}
\xrightarrow{HCl (or HBr)}
\xrightarrow{H}
\xrightarrow{Cl}
\xrightarrow{| | | | |}
H
\xrightarrow{H}
\xrightarrow{Cl}$$

$$H - C - C - H
\xrightarrow{| | | |}
H
\xrightarrow{H}$$

(d) Addition of H₂O to yield an alcohol (hydration):

2. Reactions of aromatic compounds (Section 13.10):

(a) Substitution of an —NO₂ group to yield a nitrobenzene (nitration):

$$\frac{\text{HNO}_3}{\text{H}_2\text{SO}_4 \text{ catalyst}} \longrightarrow \frac{\text{NO}_2}{\text{NO}_2}$$

(b) Substitution of a Cl or Br atom to yield a halobenzene (halogenation):

$$\frac{\text{Cl}_2 \text{ (or Br}_2)}{\text{FeCl}_3 \text{ (or FeBr}_3)}$$

(c) Substitution of an — SO₃H group to yield a benzenesulfonic acid (sulfonation):

$$\frac{SO_3}{H_2SO_4 \text{ catalyst}} \longrightarrow \frac{SO_3H}{H_2SO_4 \text{ catalyst}}$$

UNDERSTANDING KEY CONCEPTS

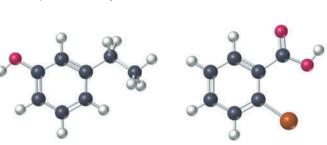
13.24 Name the following alkenes, and predict the products of their reaction with (1) HBr, (2) H_2O , and (3) an acid catalyst.



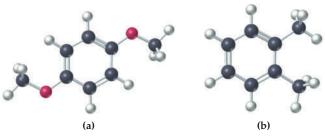
13.25 Name the following alkynes:



13.26 Give IUPAC names for the following substances (red = O, brown = Br):



13.27 Draw the product from reaction of the following substances with (1) Br_2 and $FeBr_3$ and (2) SO_3 and H_2SO_4 catalyst (red = 0):



13.28 Alkynes undergo hydrogenation to give alkanes, just as alkenes do. Draw and name the products that would result from hydrogenation of the alkynes shown in Problem 13.25.

13.29 We saw in Section 13.8 that benzene can be represented by either of two resonance forms, which differ in the positions of the double bonds in the aromatic ring. Naphthalene, a polycyclic aromatic compound, can be represented by *three* forms with different double-bond positions. Draw all three structures, showing the double bonds in each (the following numbered skeletal structure of naphthalene shows only the connections among atoms).

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ADDITIONAL PROBLEMS

NAMING ALKENES, ALKYNES, AND AROMATIC COMPOUNDS (SECTIONS 13.1, 13.2, 13.9)

- **13.30** (a) What do the terms saturated and unsaturated mean?
 - **(b)** Draw an example of a saturated four carbon compound and an unsaturated four carbon compound.
- **13.31** (a) What does the term "aromatic" refer to when discussing organic molecules?
 - **(b)** What is resonance and why is it important in aromatic compounds?
- **13.32** What family-name endings are used for alkenes, alkynes, and substituted benzenes?
- **13.33** What prefixes are used in naming the following?
 - (a) A 1,3-disubstituted benzene
 - (b) A 1,4-disubstituted benzene
- **13.34** Write structural formulas for compounds that meet the following descriptions:
 - (a) A 6-carbon alkene whose longest chain is 4 carbons in length (three possibilities)
 - **(b)** An alkyne with 5 carbons total (three possibilities)
 - (c) A monosubstituted benzene with a total of 8 carbons (one possibility)
 - (d) A disubstituted benzene with a total of 8 carbons (three possibilities)
- **13.35** Write structural formulas for compounds that meet the following descriptions:
 - (a) An alkene, C₆H₁₂, that cannot have cis-trans isomers and whose longest chain is 5 carbons long
 - **(b)** An alkene with a chemical formula of $C_{10}H_{12}$ that has cis–trans isomers and contains a benzene ring.
- **13.36** What are the IUPAC names of the following compounds?
 - (a) CH₃CH=CHCH₂CH





13.37 Give IUPAC names for the following aromatic compounds:

- **13.38** Draw structures corresponding to the following IUPAC names:
 - (a) trans-Pent-2-ene
 - (b) trans-3,4-Dimethylhex-3-ene
 - (c) 2-Methylbuta-1,3-diene
 - (d) trans-Hept-3-ene
 - (e) p-Nitrotoluene
 - (f) o-Chlorophenol
 - (g) 1,2-Dimethylcyclobutene
 - (h) 3,3-Diethyl-6-methylnon-4-ene
- **13.39** Draw structures corresponding to the following names:
 - (a) Aniline
 - (b) Phenol
 - (c) o-Xylene
 - (d) 2,4,6-Trinitrobenzene
 - (e) p-Chlorobenzoic acid
 - (f) m-Nitroaniline
 - (g) o-Chlorobenzaldehyde
 - (h) Anisole (methoxybenzene)
- **13.40** Seven alkynes have the formula C_6H_{10} . Draw them, using line structures.
- **13.41** Draw and name all phenols with the formula C_7H_8O .
- **13.42** When ethylbenzene is reacted with nitric acid, three possible benzenes containing both a nitro group and an ethyl group are obtained. Draw and name them.
- **13.43** There are four different pentenes having the following general structure:

The four differ only in the placement of the double bond. Draw and name all four. Ignore cis-trans isomers.

ALKENE CIS-TRANS ISOMERS (SECTION 13.3)

- **13.44** What requirement(s) must be met for an alkene to show cis–trans isomerism?
- **13.45** Why do alkynes not show cis–trans isomerism?
- **13.46** Draw line structures for the following alkenes. Which can exist as cis–trans isomers? For those that can, draw both isomers.
 - (a) 2-Methyloct-2-ene
- (b) Hept-3-ene
- (c) 3,4-Dimethylhex-3-ene
- **13.47** Which compound(s) in Problem 13.43 can exist as cistrans isomers? Label each as being either a symmetrically or unsymmetrically substituted alkene.

- **13.48** Draw structures of the following compounds:
 - (a) cis-Hept-3-ene
 - **(b)** *cis*-4-Methylpent-2-ene
 - (c) trans-2,5-Dimethylhex-3-ene
- **13.49** Each of the following has a cis or trans isomeric form. Draw it.

a)
$$H$$
 Cl CH

13.50 Which of the following pairs are isomers, and which are identical?

(a)
$$H_3C$$
 Br Br $C=C$ And $C=C$ H

(b)
$$CH_3CH_2$$
 $C=C$ and $C=C$ CH_2CH_3

13.51 Draw the other cis–trans isomer for the following molecules:

(a)
$$CH_3$$
 CH_3 CH_3 CH_3

b)
$$H$$
 Cl CH_2Pl

KINDS OF REACTIONS (SECTION 13.5)

- **13.52** What is the difference between a substitution reaction and an addition reaction?
- **13.53** Give an example of an addition reaction.
- **13.54** If 2-methylpent-2-ene were converted into hex-1-ene, what kind of reaction would that be?
- **13.55** If bromocyclohexane were converted into cyclohexene, what kind of reaction would that be?
- **13.56** Identify the type of reaction for the following:

(a)
$$CH_3 \xrightarrow{Br_2} CH_2Br + HBr$$

$$(\mathbf{b}) \xrightarrow{\mathrm{CH}_3} \xrightarrow{\mathrm{CH}_3}$$

13.57 Identify the type of reaction for the following:

$$\begin{array}{c} \mathsf{CH_3} \\ | \\ \mathsf{(a)} \ \mathsf{CH_3} \mathsf{CHCH_2} \mathsf{CH_2} \mathsf{CH_2} \mathsf{Br} \ + \ \mathsf{NaI} \ \longrightarrow \\ & \mathsf{CH_3} \\ | \\ & \mathsf{CH_3} \mathsf{CHCH_2} \mathsf{CH_2} \mathsf{I} \ + \ \mathsf{NaBr} \\ \end{array}$$

REACTIONS OF ALKENES AND ALKYNES (SECTIONS 13.6-13.7)

- **13.58** Write equations for the reaction of pent-2-ene with the following:
 - (a) H₂ and Pd catalyst
- **(b)** Br₂

- (c) HCl
- (d) H₂O and H₂SO₄ catalyst
- **13.59** Write equations for the reaction of 1-methylcyclohexene with the reagents shown in Problem 13.58.
- 13.60 What alkene could you use to make the following products? Draw the structure of the alkene, and tell what other reagent is also required for the reaction to occur.

(b) CH₃CH₂CH₃

Br (c) CH₃CHCH₂CH₂

- **13.61** 2,2,3,3-Tetrabromopentane can be prepared by an addition reaction of excess Br2 with an alkyne. Draw the structure of the alkyne and name it.
- 13.62 4-Methylpent-1-yne reacts with HBr in a 1:1 molar ratio to yield two different addition products, both being bromopentenes and having the chemical formula C₅H₉Br. Draw the structures of two possible products.
- **13.63** Polyvinylpyrrolidone (PVP) is often used in hair sprays to hold hair in place. Draw a few units of the PVP polymer. The vinylpyrrolidone monomer unit has the following structure:

Saran, used as a plastic wrap for foods, is a polymer with the following structure. What is the monomer unit of Saran?

REACTIONS OF AROMATIC COMPOUNDS (SECTION 13.10)

- 13.65 For each of the following reagents, decide whether chlorobenzene will react with it or not, and, if it does, draw and name the products expected from the reaction.
 - (a) Br₂ and FeBr₃
- (b) HBr
- (c) HNO₃ and H₂SO₄ catalyst
- **13.66** Write equations for the reaction of p-dichlorobenzene with the following:
 - (a) Br₂ and FeBr₃
 - (b) HNO₃ and H₂SO₄ catalyst
- (d) Cl₂ and FeCl₃

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- **13.67** Aromatic compounds do not normally react with hydrogen in the presence of a palladium catalyst but will if very high pressures (200 atm) and high temperatures are used. Under these conditions, toluene adds three molecules of H₂ to give an alkane addition product. What is a likely structure for the product?
- **13.68** The explosive trinitrotoluene (TNT) is made by carrying out three successive nitration reactions on toluene. If these nitrations only occur in the ortho and para positions relative to the methyl group, what is the structure of TNT?

CONCEPTUAL PROBLEMS

- **13.69** Salicylic acid (*o*-hydroxybenzoic acid) is used as starting material to prepare aspirin. Draw the structure of salicylic acid.
- **13.70** The following names are incorrect by IUPAC rules. Draw the structures represented by the following names, and write their correct names. Label each as being symmetrically or unsymmetrically substituted.
 - (a) 2-Methyl-4-hexene
 - **(b)** 1,3-Dimethyl-1-hexyne
 - (c) 2-Isopropyl-1-propene
 - (d) 1,4,6-Trinitrobenzene
 - (e) 1,2-Dimethyl-3-cyclohexene
 - (f) 3-Methyl-2,4-pentadiene
- **13.71** Which of the compounds in Problem 13.70 are capable of cis-trans isomerism? Draw each isomer.
- **13.72** Assume that you have two unlabeled bottles, one with cyclohexane and one with cyclohexene. How could you tell them apart by carrying out chemical reactions?
- **13.73** Assume you have two unlabeled bottles, one with cyclohexene and one with benzene. How could you tell them apart by carrying out chemical reactions?
- **13.74** The compound p-dichlorobenzene has been used as an insecticide. Draw its structure.
- **13.75** Menthene, a compound found in mint plants, has the formula C₁₀H₁₈ and the IUPAC name 1-isopropyl-4-methylcyclohexene. What is the structure of menthene?
- 13.76 Cinnamaldehyde, the pleasant-smelling substance found in cinnamon oil, has the following structure:

$$\begin{array}{c}
 & O \\
 & \parallel \\
 & -CH = CH - C - H
\end{array}$$

What products would you expect to obtain from reaction of cinnamaldehyde with water and sulfuric acid catalyst?

13.77 Predict the products of the following reactions:

(a)
$$CH_3CH_2CH = CHCHCH_3 \xrightarrow{H_2, Pd}$$
?

$$(\mathbf{b}) \stackrel{\text{HNO}_3}{\longrightarrow} -\text{OH} \quad \xrightarrow{\text{H}_2\text{SO}_4} \rightarrow$$

(c)
$$\frac{H_2O}{H_2SO_4} ?$$

$$(\mathbf{d}) \xrightarrow{\mathrm{H}_2\mathrm{O}} ?$$

(e)
$$CH_3C \equiv CCH_2CH_3 \xrightarrow{H_2, Pd}$$
?

- 13.78 Two products are possible when pent-2-ene is treated with HBr. Write the structures of the possible products, and explain why they are made in about equal amounts.
- **13.79** Ocimene, a compound isolated from the herb basil, has three double bonds and the IUPAC name 3,7-dimethylocta-1,3,6-triene.
 - (a) Draw its structure.
 - (b) Draw the structure of the compound formed if enough HBr is added to react with all the double bonds in ocimene.
- **13.80** Describe how you could prepare the following compound from an alkene. Draw the formula of the alkene, name it, and list the inorganic reactants or catalysts needed for the conversion.

13.81 Which of the following compounds are capable of cis-trans isomerism?

$$CH_3$$
 $CH=CI$
(a) $CH_3CHCH=CHCH_3$ (b) $CH_3CH_2CHCH_3$

GROUP PROBLEMS

- **13.82** Why do you suppose small-ring cycloalkenes like cyclohexene do not exist as cis-trans isomers, whereas large ring cycloalkenes like cyclodecene do show isomerism?
- "Superglue" is an alkene polymer made from the monomer 13.83 unit.

Draw a representative segment of the structure of superglue.

13.84 Draw all possible C₅H₁₀ alkene isomers having a longest chain of four carbons and a methyl group. (Hint: Adapt the method described in Worked Example 12.12 to arrive at your answers.)