

The pink color of flamingo feathers is caused by the presence in the bird's diet of β -carotene, a polyalkene.

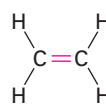


Steve Allen/Digital Images

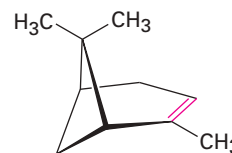
Alkenes and Alkynes: The Nature of Organic Reactions

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 - 3.2** Electronic Structure of Alkenes
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- Interlude*—Terpenes: Naturally Occurring Alkenes

Alkenes, sometimes called *olefins*, are hydrocarbons that contain a carbon-carbon double bond, $C=C$, and **alkynes** are hydrocarbons that contain a carbon-carbon triple bond, $C\equiv C$. Alkenes occur abundantly in nature, but alkynes are much less common. Ethylene, for instance, is a plant hormone that induces ripening in fruit, and α -pinene is the major component of turpentine. Life itself would be impossible without such compounds as β -carotene, a *polyalkene* that contains 11 double bonds. An orange pigment responsible for the color of carrots, β -carotene is a valuable dietary source of vitamin A. It was once thought to offer some protection against some types of cancer, but that has now been shown not to be true.



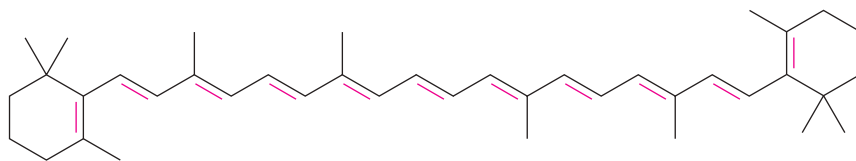
Ethylene



α -Pinene



Online homework for this chapter can be assigned in OWL, an online homework assessment tool.



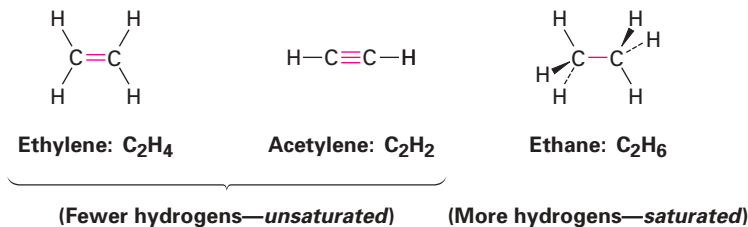
β -Carotene
(orange pigment and vitamin A precursor)

WHY THIS CHAPTER?

Carbon–carbon double bonds are present in most organic and biological molecules, so a good understanding of their behavior is needed. In this chapter, we'll look at some consequences of alkene stereoisomerism and then focus in detail on the broadest and most general class of alkene reactions, the electrophilic addition reaction. Carbon–carbon *triple* bonds, by contrast, occur less commonly than double bonds, so we'll not spend much time on their chemistry.

3.1 Naming Alkenes and Alkynes

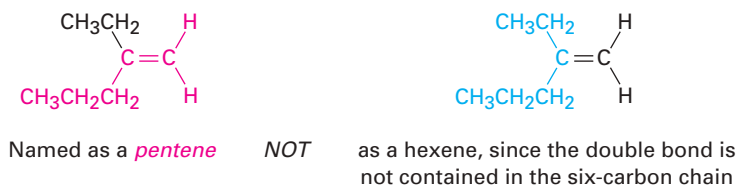
Because of their multiple bond, alkenes and alkynes have fewer hydrogens per carbon than related alkanes and are therefore referred to as **unsaturated**. Ethylene, for example, has the formula C_2H_4 , and acetylene has the formula C_2H_2 , whereas ethane has the formula C_2H_6 .



Alkenes are named using a series of rules similar to those for alkanes (Section 2.3), with the suffix *-ene* used in place of *-ane* to identify the family. There are three steps.

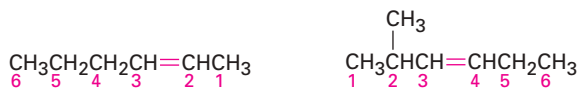
STEP 1 Name the parent hydrocarbon.

Find the longest carbon chain that contains the double bond, and name the compound using the suffix *-ene* in place of *-ane*.

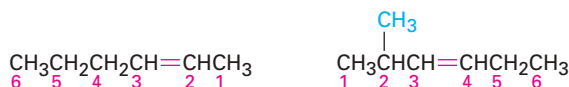


STEP 2 Number the carbon atoms in the chain.

Begin numbering at the end nearer the double bond, or, if the double bond is equidistant from the two ends, begin at the end nearer the first branch point. This rule ensures that the double-bond carbons receive the lowest possible numbers.

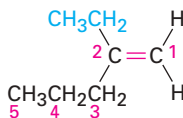
**STEP 3** Write the full name.

Number the substituents on the main chain according to their position, and list them alphabetically. Indicate the position of the double bond by giving the number of the first alkene carbon and placing that number directly before the *-ene* suffix. If more than one double bond is present, give the position of each and use the appropriate multiplier suffix *-diene*, *-triene*, *-tetraene*, and so on.

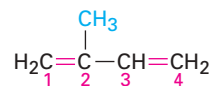


Hex-2-ene

2-Methylhex-3-ene

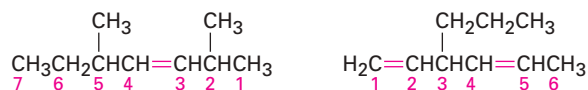


2-Ethylpent-1-ene



2-Methylbuta-1,3-diene

We should also note that IUPAC changed its naming rules in 1993. Prior to that time, the locant, or number locating the position of the double bond, was placed before the parent name rather than before the *-ene* suffix: 2-butene rather than but-2-ene, for instance. Changes always take time to be fully accepted, so the new rules have not yet been adopted universally and some texts have not yet been updated. We'll use the new naming system in this book, although you may encounter the old system elsewhere. Fortunately, the difference between old and new is minor and rarely causes problems.



New naming system: 2,5-Dimethylhept-3-ene

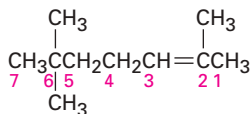
3-Propylhexa-1,4-diene

(Old naming system: 2,5-Dimethyl-3-heptene)

3-Propyl-1,4-hexadiene)

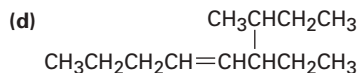
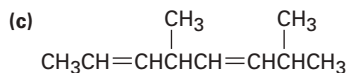
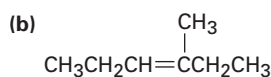
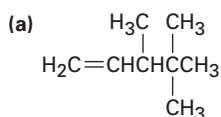
Cycloalkenes are named similarly, but because there is no chain end to begin from, we number the cycloalkene so that the double bond is between C1 and C2 and the first substituent has as low a number as possible. Note

Strategy First, find the longest chain containing the double bond—in this case, a heptene. Next, number the chain beginning at the end nearer the double bond, and identify the substituents at each position. In this case, there are three methyl groups, one at C2 and two at C6.

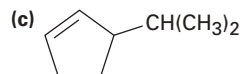
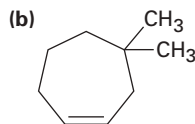
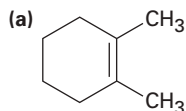


Solution Write the full name, listing the substituents alphabetically and giving the position of each. Identify the position of the double bond by placing the number of the first alkene carbon before the *-ene* suffix: 2,6,6-trimethylhept-2-ene.

Problem 3.1 Give IUPAC names for the following compounds:



Problem 3.2 Name the following cycloalkenes:



Problem 3.3 Draw structures corresponding to the following IUPAC names:

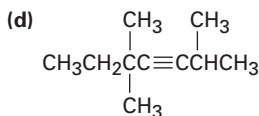
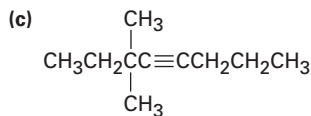
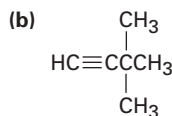
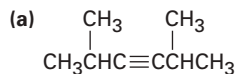
(a) 2-Methylhex-1-ene

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

(c) 2-Methylhexa-1,5-diene

(d) 3-Ethyl-2,2-dimethylhept-3-ene

Problem 3.4 Name the following alkynes:



Problem 3.5 Change the following old names to new, post-1993 names, and draw the structure of each compound:

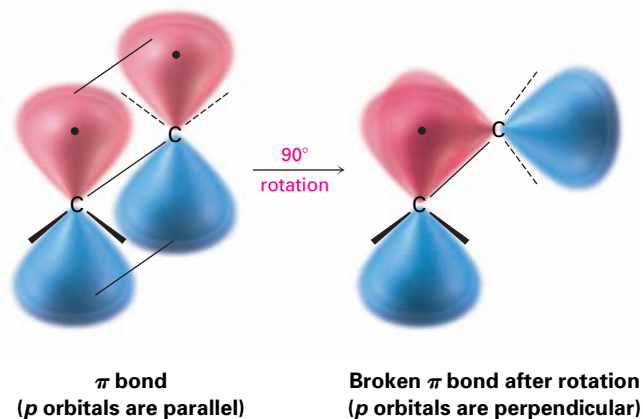
- (a) 2,5,5-Trimethyl-2-hexene (b) 2,2-Dimethyl-3-hexyne
 (c) 2-Methyl-2,5-heptadiene (d) 1-Methyl-1,3-cyclopentadiene

3.2 Electronic Structure of Alkenes

We saw in Section 1.8 that the carbon atoms in a double bond have three equivalent sp^2 hybrid orbitals, which lie in a plane at angles of 120° to one another. The fourth carbon orbital is an unhybridized p orbital perpendicular to the sp^2 plane. When two sp^2 -hybridized carbon atoms approach each other, they form a σ bond by head-on overlap of sp^2 orbitals and a π bond by sideways overlap of p orbitals. The doubly bonded carbons and the four attached atoms lie in a plane, with bond angles of approximately 120° (Figure 3.1).

We also know from Section 2.5 that rotation can occur around single bonds and that open-chain alkanes like ethane and propane therefore have many rapidly interconverting conformations. The same is not true for double bonds, however. For rotation to take place around a double bond, the π part of the bond must break momentarily (Figure 3.1). Thus, the energy barrier to rotation around a double bond must be at least as great as the strength of the π bond itself, an estimated 350 kJ/mol (84 kcal/mol). Recall that the rotation barrier for a single bond is only about 12 kJ/mol.

Figure 3.1 The π bond must break momentarily for rotation around a carbon-carbon double bond to take place, requiring a large amount of energy.

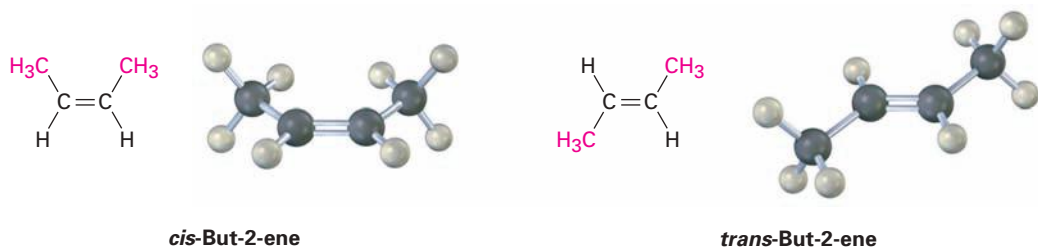


3.3 Cis-Trans Isomers of Alkenes

The lack of rotation around carbon-carbon double bonds is of more than just theoretical interest; it also has chemical consequences. Imagine the situation for a disubstituted alkene such as but-2-ene. (*Disubstituted* means that two substituents other than hydrogen are bonded to the double-bond carbons.) The two methyl groups in but-2-ene can be either on the same side of the double bond or on opposite sides, a situation similar to that in substituted cycloalkanes (Section 2.8).

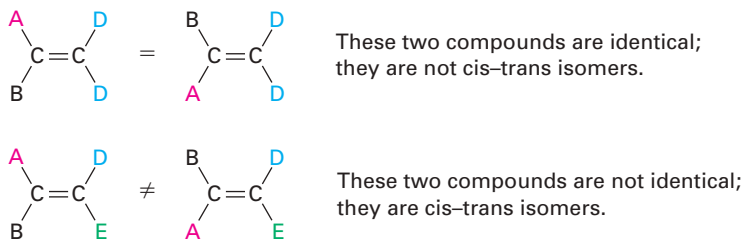
Because bond rotation can't occur, the two but-2-enes can't spontaneously interconvert and are different chemical compounds. As with disubstituted cycloalkanes, we call such compounds *cis-trans isomers*. The isomer with both substituents on the same side of the double bond is *cis*-but-2-ene, and the isomer with substituents on opposite sides is *trans*-but-2-ene (Figure 3.2).

Figure 3.2 Cis and trans isomers of but-2-ene. The *cis* isomer has the two methyl groups on the same side of the double bond, and the *trans* isomer has the methyl groups on opposite sides.

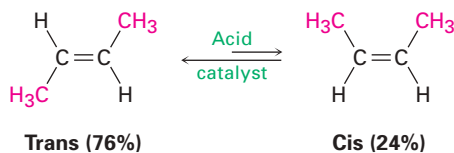


Cis–trans isomerism is not limited to disubstituted alkenes. It occurs whenever each double-bond carbon is attached to two different groups. If one of the double-bond carbons is attached to two identical groups, however, then cis–trans isomerism is not possible (Figure 3.3).

Figure 3.3 The requirement for cis–trans isomerism in alkenes. Compounds that have one of their carbons bonded to two identical groups can't exist as cis–trans isomers. Only when both carbons are bonded to two different groups are cis–trans isomers possible.

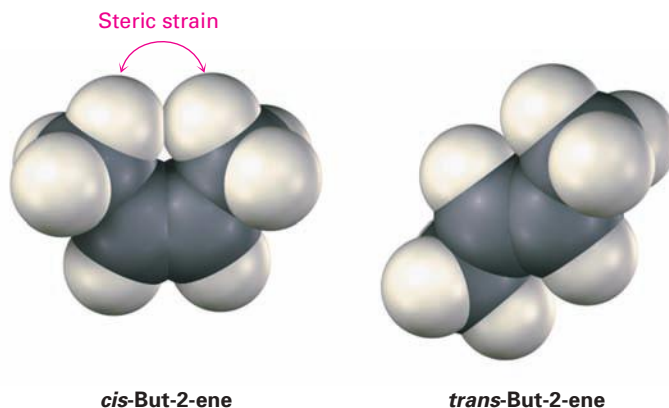


Although the interconversion of *cis* and *trans* alkene isomers doesn't occur spontaneously, it can be brought about by treating the alkene with a strong acid catalyst. If we do, in fact, interconvert *cis*-but-2-ene with *trans*-but-2-ene and allow them to reach equilibrium, we find that they aren't of equal stability. The *trans* isomer is more favored than the *cis* isomer by a ratio of 76:24.



Cis alkenes are less stable than their *trans* isomers because of steric (spatial) interference between the large substituents on the same side of the

double bond. This is the same kind of interference, or *steric strain*, that we saw in the axial conformation of methylcyclohexane (Section 2.11).



Worked Example 3.2

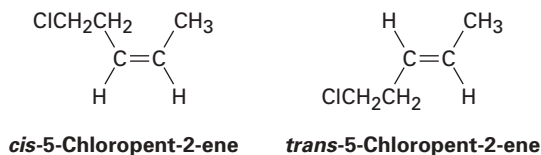
Drawing Cis and Trans Alkene Isomers

Draw the cis and trans isomers of 5-chloropent-2-ene.

Strategy

First, draw the molecule without indicating isomers to see the overall structure: $\text{ClCH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$. Then locate the two substituent groups on the same side of the double bond for the cis isomer and on opposite sides for the trans isomer.

Solution



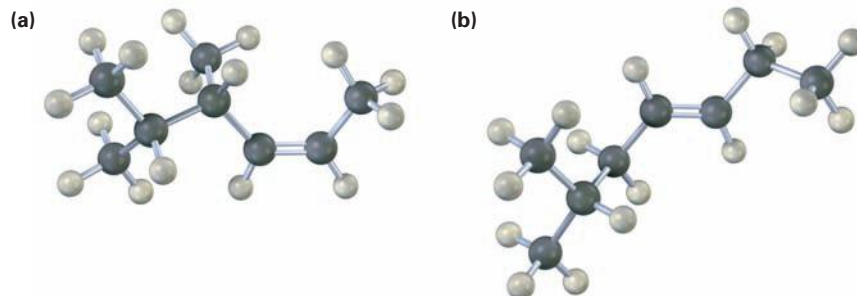
Problem 3.6

Which of the following compounds can exist as cis-trans isomers? Draw each cis-trans pair.

- (a) $\text{CH}_3\text{CH}=\text{CH}_2$ (b) $(\text{CH}_3)_2\text{C}=\text{CHCH}_3$
 (c) $\text{ClCH}=\text{CHCl}$ (d) $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$
 (e) $\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{Br})\text{CH}_3$ (f) 3-Methylhept-3-ene

Problem 3.7

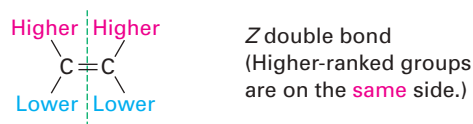
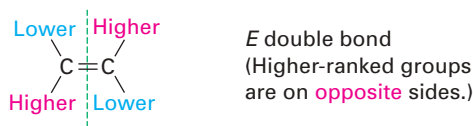
Name the following alkenes, including the cis or trans designation:



3.4 Sequence Rules: The *E,Z* Designation

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

According to the ***E,Z* system**, a set of *sequence rules* is used to rank the two substituent groups on each double-bond carbon. If the higher-ranked groups on each carbon are on opposite sides of the double bond, the alkene is said to have *E* stereochemistry, for the German *entgegen*, meaning “opposite.” If the higher-ranked groups are on the same side, the alkene has *Z* stereochemistry, for the German *zusammen*, meaning “together.” (You can remember which is which by noting that the groups are on “ze zame zide” in the *Z* isomer.)

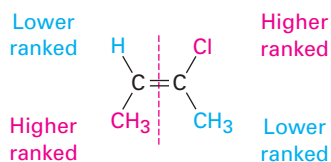


Called the *Cahn–Ingold–Prelog rules* after the chemists who proposed them, the sequence rules are as follows:

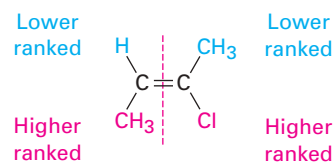
RULE 1 Considering the double-bond carbons separately, look at the atoms directly attached to each carbon and rank them according to atomic number. The atom with the higher atomic number has the higher ranking, and the atom with the lower atomic number (usually hydrogen) has the lower ranking. Thus, the atoms commonly found attached to a double-bond carbon are assigned the following rankings. When different isotopes of the same element are compared, such as deuterium (^2H) and protium (^1H), the heavier isotope ranks higher than the lighter isotope.

Atomic number	35	17	16	15	8	7	6	(2)	(1)	
Higher ranking	Br	> Cl	> S	> P	> O	> N	> C	> ^2H	> ^1H	Lower ranking

For example:



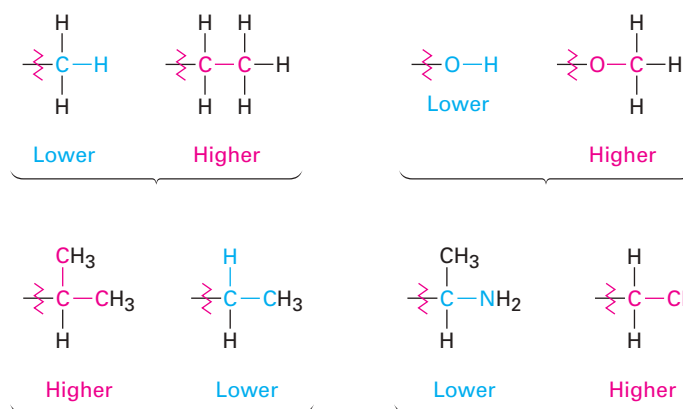
(a) (*E*)-2-Chlorobut-2-ene



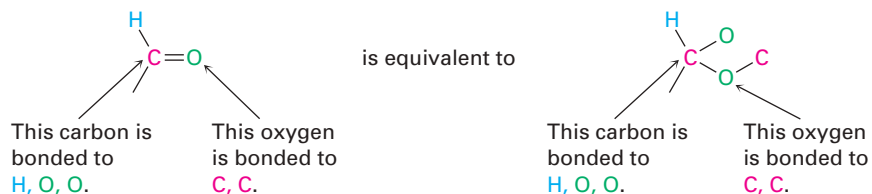
(b) (*Z*)-2-Chlorobut-2-ene

Because chlorine has a higher atomic number than carbon, it ranks higher than a methyl (CH₃) group. Methyl ranks higher than hydrogen, however, and isomer (a) is therefore assigned *E* stereochemistry (higher-ranked groups on opposite sides of the double bond). Isomer (b) has *Z* stereochemistry (higher-ranked groups on “ze zame zide” of the double bond).

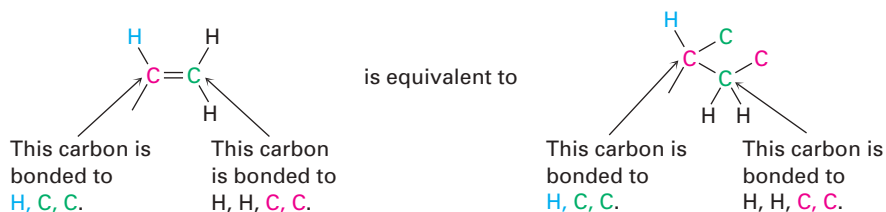
RULE 2 If a decision can't be reached by ranking the first atoms in the substituents, look at the second, third, or fourth atoms away from the double-bond carbons until the first difference is found. Thus, a -CH₂CH₃ substituent and a -CH₃ substituent are equivalent by rule 1 because both have carbon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

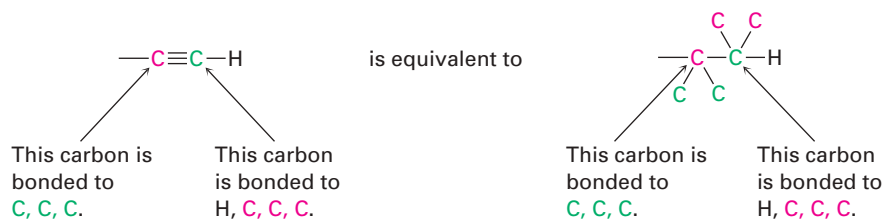


RULE 3 Multiple-bonded atoms are equivalent to the same number of single-bonded atoms. For example, an aldehyde substituent (-CH=O), which has a carbon atom *doubly* bonded to *one* oxygen, is equivalent to a substituent having a carbon atom *singly* bonded to *two* oxygens.

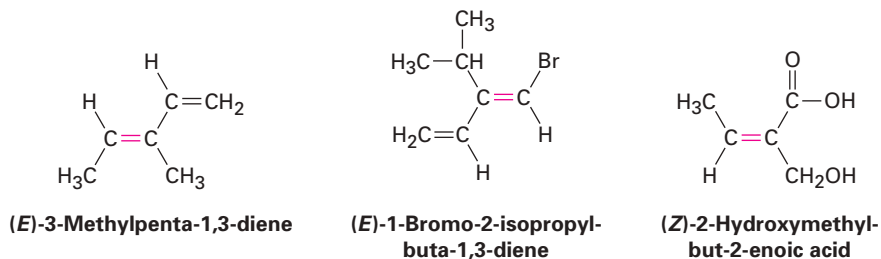


As further examples, the following pairs are equivalent:





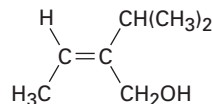
By applying the sequence rules, we can assign the stereochemistry shown in the following examples. Work through each one to convince yourself the assignments are correct.



Worked Example 3.3

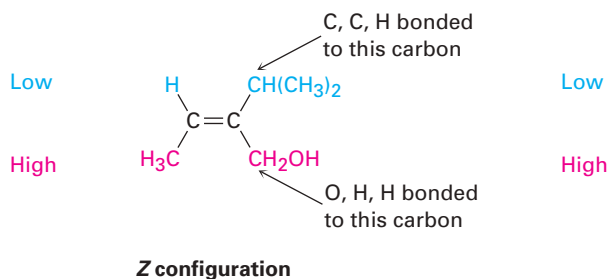
Assigning *E,Z* Stereochemistry to an Alkene

Assign *E* or *Z* stereochemistry to the double bond in the following compound:

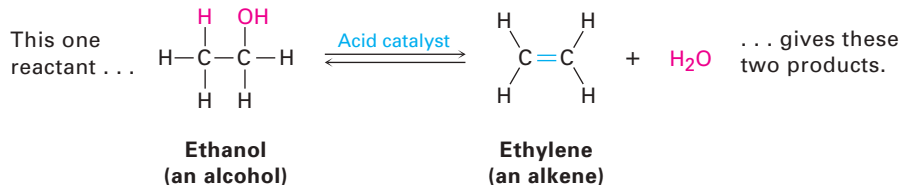


Strategy Look at each double-bond carbon individually, and assign rankings. Then see whether the two higher-ranked groups are on the same or opposite sides of the double bond.

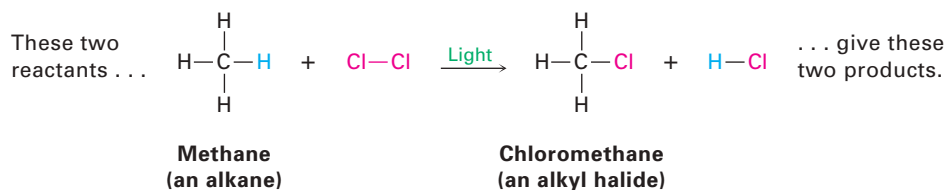
Solution The left-hand carbon has two substituents, -H and -CH_3 , of which -CH_3 ranks higher by rule 1. The right-hand carbon also has two substituents, $\text{-CH}(\text{CH}_3)_2$ and $\text{-CH}_2\text{OH}$, which are equivalent by rule 1. By rule 2, however, $\text{-CH}_2\text{OH}$ ranks higher than $\text{-CH}(\text{CH}_3)_2$ because $\text{-CH}_2\text{OH}$ has an *oxygen* as its highest second atom, whereas $\text{-CH}(\text{CH}_3)_2$ has *carbon* as its highest second atom. The two higher-ranked groups are on the same side of the double bond, so the compound has *Z* stereochemistry.



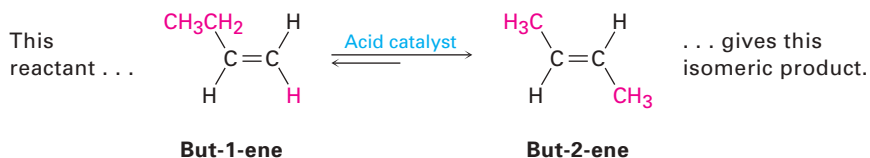
- **Elimination reactions** are, in a sense, the opposite of addition reactions. They occur when a single organic reactant splits into two products, often with formation of a small molecule such as H_2O or HCl . An example is the acid-catalyzed reaction of an alcohol to yield water and an alkene.



- **Substitution reactions** occur when two reactants exchange parts to give two new products. An example that we saw in Section 2.4 is the reaction of an alkane with Cl_2 in the presence of ultraviolet light to yield an alkyl chloride. A $-\text{Cl}$ group substitutes for the $-\text{H}$ group of the alkane, and two new products result.



- **Rearrangement reactions** occur when a single organic reactant undergoes a reorganization of bonds and atoms to yield a single isomeric product. An example that we saw in Section 3.3 is the conversion of *cis*-but-2-ene into its isomer *trans*-but-2-ene by treatment with an acid catalyst.

**Problem 3.11**

Classify the following reactions as additions, eliminations, substitutions, or rearrangements:

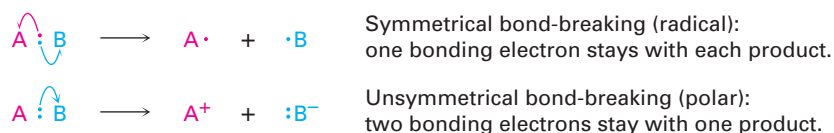
- (a) $\text{CH}_3\text{Br} + \text{KOH} \rightarrow \text{CH}_3\text{OH} + \text{KBr}$
 (b) $\text{CH}_3\text{CH}_2\text{Cl} + \text{NaOH} \rightarrow \text{H}_2\text{C}=\text{CH}_2 + \text{NaCl}$
 (c) $\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_3$

3.6 How Reactions Occur: Mechanisms

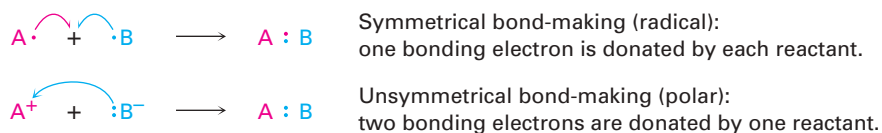
Having looked at the kinds of reactions that take place, let's now see *how* reactions occur. An overall description of how a reaction occurs is called a **reaction mechanism**. A mechanism describes what takes place at each stage of a chemical transformation—which bonds are broken and in what order, which bonds are formed and in what order, and what the relative rates of the steps are.

All chemical reactions involve bond-breaking in the reactant molecules and bond-making in the product molecules, which means that the electrons in those bonds must move about and reorganize. Fundamentally, a covalent two-electron bond can break in two ways: a bond can break in an electronically *symmetrical* way so that one electron remains with each product fragment, or a bond can break in an electronically *unsymmetrical* way so that both electrons remain with one product fragment, leaving the other fragment with a vacant orbital. The symmetrical cleavage is said to be *homolytic*, and the unsymmetrical cleavage is said to be *heterolytic*.

We'll develop the point in more detail later, but you might note for now that the movement of *one* electron in the symmetrical process is indicated using a half-headed, or “fishhook,” arrow (\frown), while the movement of *two* electrons in an unsymmetrical process is indicated using a full-headed curved arrow (\curvearrowright), as noted previously in Section 1.12.



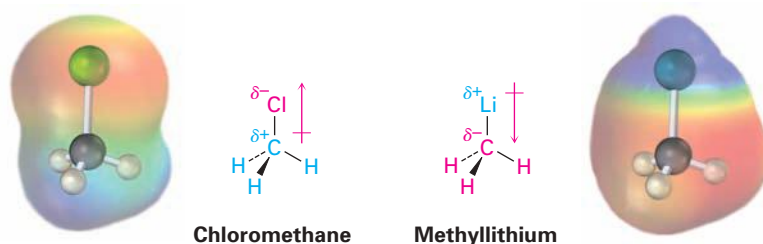
Just as there are two ways in which a bond can break, there are two ways in which a covalent two-electron bond can form. A bond can form in an electronically symmetrical way if one electron is donated to the new bond by each reactant or in an electronically unsymmetrical way if both bonding electrons are donated by one reactant.



Processes that involve symmetrical bond-breaking and bond-making are called **radical reactions**. A **radical**, often called a *free radical*, is a neutral chemical species that contains an odd number of electrons and thus has a single, unpaired electron in one of its orbitals. Processes that involve unsymmetrical bond breaking and making are called **polar reactions**. Polar reactions involve species that have an even number of electrons and thus have only electron pairs in their orbitals. Polar processes are by far the more

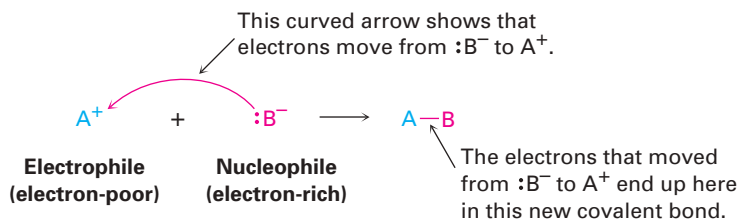
common reaction type in both organic and biological chemistry, and much of this book is devoted to their description.

To see how polar reactions occur, we first need to look more deeply into the effects of bond polarity on organic molecules. We saw in Section 1.9 that certain bonds in a molecule, particularly the bonds in functional groups, are often polar. When carbon bonds to a more electronegative atom, such as chlorine or oxygen, the bond is polarized so that the carbon bears a partial positive charge (δ^+) and the electronegative atom bears a partial negative charge (δ^-). When carbon bonds to a less electronegative atom, such as a metal, the opposite polarity results. As always, electrostatic potential maps show electron-rich regions of a molecule in red and electron-poor regions in blue.



What effect does bond polarity have on chemical reactions? Because unlike charges attract, the fundamental characteristic of all polar reactions is that electron-rich sites in one molecule react with electron-poor sites in another molecule (or within the same molecule). Bonds are made when an electron-rich atom shares a pair of electrons with an electron-poor atom, and bonds are broken when one atom leaves with both electrons from the former bond.

As noted previously, chemists normally indicate the movement of an electron pair during a polar reaction by using a curved, full-headed arrow. A curved arrow shows where electrons move when reactant bonds are broken and product bonds are formed. It means that an electron pair moves *from* the atom (or bond) at the tail of the arrow *to* the atom at the head of the arrow during the reaction.



In referring to the electron-rich and electron-poor species involved in polar reactions, chemists use the words *nucleophile* and *electrophile*. A **nucleophile** is a substance that is “nucleus loving” and thus attracted to a positive charge. A nucleophile has a negatively polarized, electron-rich atom

and can form a bond by donating an electron pair to a positively polarized, electron-poor atom. Nucleophiles can be either neutral or negatively charged and usually have lone-pairs of electrons: ammonia, water, hydroxide ion, and chloride ion are examples. An **electrophile**, by contrast, is “electron-loving.” An electrophile has a positively polarized, electron-poor atom and can form a bond by accepting a pair of electrons from a nucleophile. Electrophiles can be either neutral or positively charged. Acids (H^+ donors), alkyl halides, and carbonyl compounds are examples (Figure 3.4).

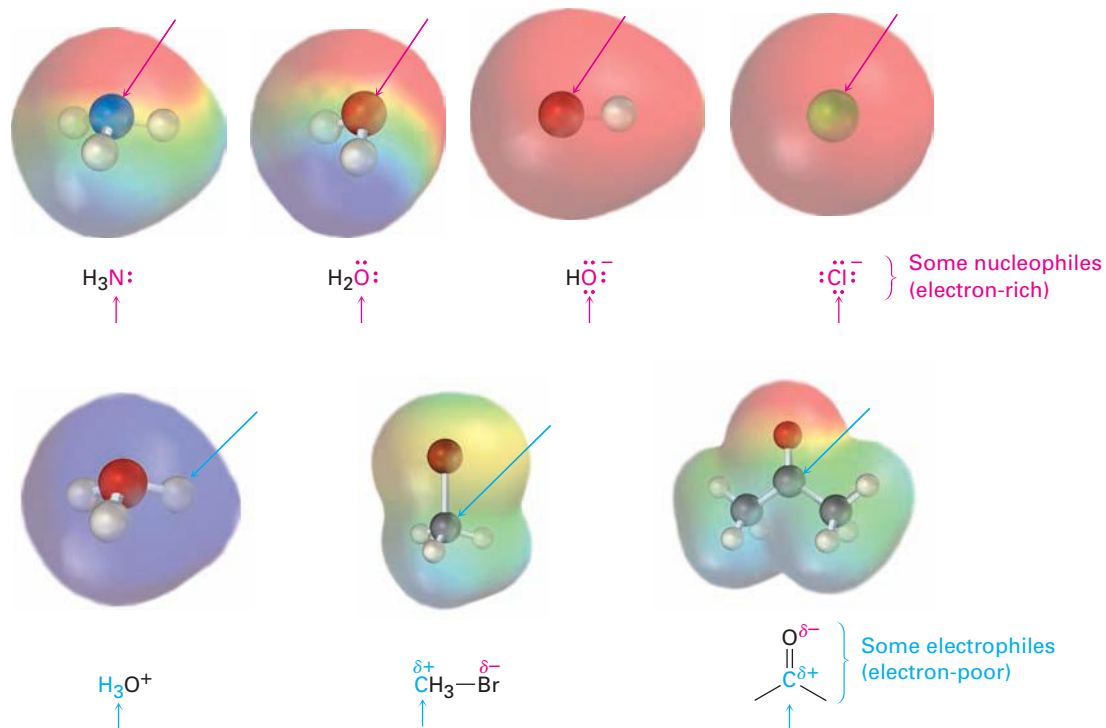


Figure 3.4 Some nucleophiles and electrophiles. Electrostatic potential maps identify the nucleophilic (red; negative) and electrophilic (blue; positive) atoms.

Note that neutral compounds can often react either as nucleophiles or as electrophiles, depending on the circumstances. After all, if a compound is neutral yet has an *electron-rich* nucleophilic site within it, it must also have a corresponding *electron-poor* electrophilic site. Water, for instance, acts as an electrophile when it donates H^+ but acts as a nucleophile when it donates a nonbonding pair of electrons. Similarly, a carbonyl compound acts as an electrophile when it reacts at its positively polarized carbon atom, yet acts as a nucleophile when it donates a pair of electrons from its negatively polarized oxygen atom.

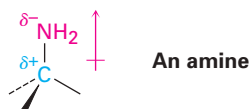
If the definitions of nucleophiles and electrophiles sound similar to those given in Section 1.12 for Lewis acids and Lewis bases, that's because there is indeed a correlation. Lewis bases are electron donors and behave as nucleophiles, whereas Lewis acids are electron acceptors and behave as electrophiles. Thus, much of organic chemistry is explainable in terms of acid–base reactions. The main difference is that the words *acid* and *base* are used broadly in all fields of chemistry, while the words *nucleophile* and *electrophile* are used primarily in organic chemistry when bonds to carbon are involved.

Worked Example 3.4**Predicting the Polarity of a Bond**

What is the direction of bond polarity in the amine functional group, C—NH₂?

Strategy Look at the electronegativity values in Figure 1.14 on page 16 to see which atoms withdraw electrons more strongly.

Solution Nitrogen (EN = 3.0) is more electronegative than carbon (EN = 2.5) according to Figure 1.14, so an amine is polarized with carbon δ^+ and nitrogen δ^- .

**Worked Example 3.5****Identifying Electrophiles and Nucleophiles**

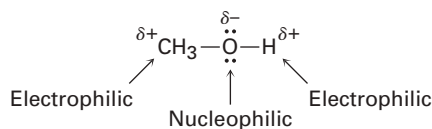
Which of the following species is likely to behave as a nucleophile and which as an electrophile?

- (a) NO₂⁺ (b) CH₃O⁻ (c) CH₃OH

Strategy A nucleophile has an electron-rich site, either because it is negatively charged or because it has a functional group containing an atom that has a lone pair of electrons. An electrophile has an electron-poor site, either because it is positively charged or because it has a functional group containing an atom that is positively polarized.

Solution

- (a) NO₂⁺ (nitronium ion) is likely to be an electrophile because it is positively charged.
 (b) CH₃O⁻ (methoxide ion) is likely to be a nucleophile because it is negatively charged.
 (c) CH₃OH (methyl alcohol) can be either a nucleophile, because it has two lone pairs of electrons on oxygen, or an electrophile, because it has polar C—O and O—H bonds.

**Problem 3.12**

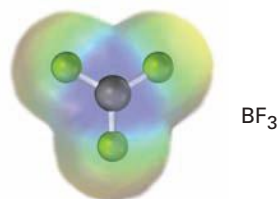
What is the direction of bond polarity in the following functional groups? (See Figure 1.14 on page 16 for electronegativity values.)

- (a) Aldehyde (b) Ether
 (c) Ester (d) Alkylmagnesium bromide, R—MgBr

Problem 3.13 Which of the following are most likely to behave as electrophiles, and which as nucleophiles? Explain.

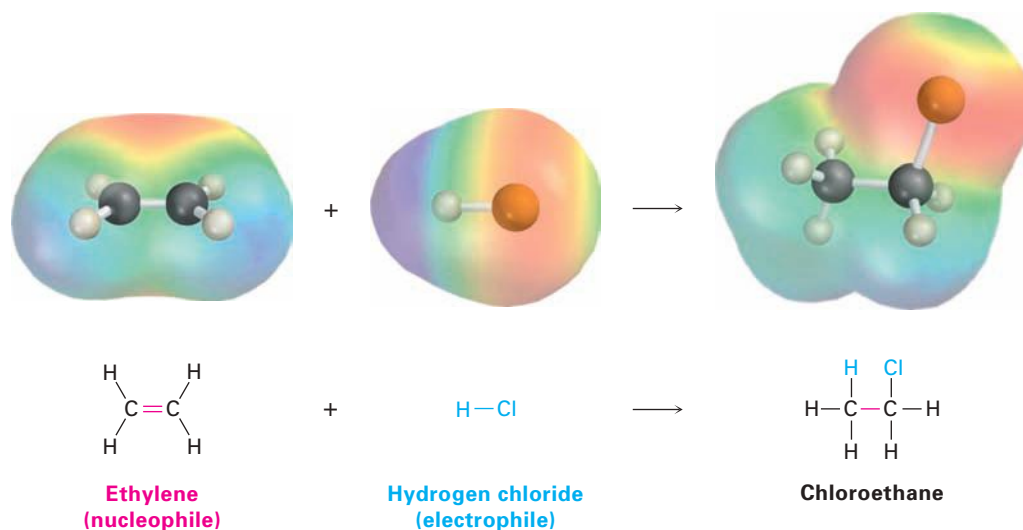
- (a) NH_4^+ (b) $\text{C}\equiv\text{N}^-$ (c) Br^+ (d) CH_3NH_2 (e) $\text{H}-\text{C}\equiv\text{C}-\text{H}$

Problem 3.14 An electrostatic potential map of boron trifluoride is shown. Is BF_3 likely to be an electrophile or a nucleophile? Draw an electron-dot structure for BF_3 , and explain the result.



3.7 The Mechanism of an Organic Reaction: Addition of HCl to Ethylene

Let's look in detail at a typical polar reaction, the addition reaction of ethylene with HCl. When ethylene is treated with hydrogen chloride at room temperature, chloroethane is produced. Overall, the reaction can be formulated as:



The reaction is an example of a general polar reaction type known as an *electrophilic addition reaction* and can be understood using the general ideas discussed in the previous section. Let's begin by looking at the nature of the two reactants.

What do we know about ethylene? We know from Sections 1.8 and 3.2 that a carbon-carbon double bond results from orbital overlap of two sp^2 -hybridized carbon atoms. The σ part of the double bond results from sp^2-sp^2 overlap, and the π part results from $p-p$ overlap.

What kind of chemical reactivity might we expect of a $\text{C}=\text{C}$ bond? Unlike the valence electrons in alkanes, which are relatively inaccessible because they are tied up in strong, nonpolar $\text{C}-\text{C}$ and $\text{C}-\text{H}$ σ bonds between nuclei, the

π electrons in alkenes are accessible to external reagents because they are located above and below the plane of the double bond rather than between the nuclei (Figure 3.5). Furthermore, an alkene π bond is much weaker than an alkane σ bond, so an alkene is more reactive. As a result, C=C bonds behave as nucleophiles in much of their chemistry. That is, alkenes typically react by donating an electron pair from the double bond to form a new bond with an electron-poor, electrophilic partner.

What about HCl? As a strong acid, HCl is a powerful proton (H^+) donor and thus a good electrophile. The reaction of HCl with ethylene is therefore a typical electrophile–nucleophile combination as in all polar reactions.

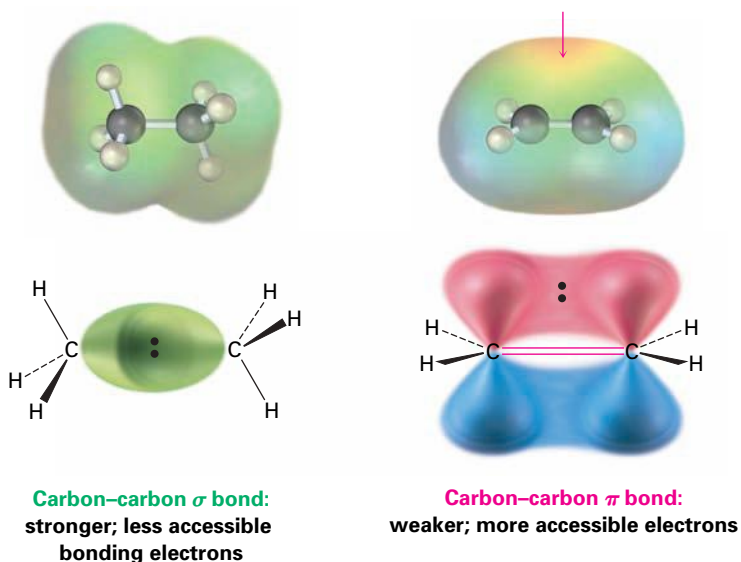


Figure 3.5 A comparison of carbon–carbon single and double bonds. A double bond is both more accessible to approaching reactants than a single bond and more electron-rich (more nucleophilic). An electrostatic potential map of ethylene indicates that the double bond is the region of highest negative charge (red).

We can view the electrophilic addition reaction between ethylene and HCl as taking place in two steps by the pathway shown in Figure 3.6. The reaction begins when the alkene donates a pair of electrons from its C=C bond to HCl to form a new C–H bond plus Cl^- , as indicated by the path of the curved arrows in the first step of Figure 3.6. One curved arrow begins at the middle of the double bond (the source of the electron pair) and points to the hydrogen atom in HCl (the atom to which a bond will form). This arrow indicates that a new C–H bond forms using electrons from the former C=C bond. A second curved arrow begins in the middle of the H–Cl bond and points to the Cl, indicating that the H–Cl bond breaks and the electrons remain with the Cl atom, giving Cl^- .

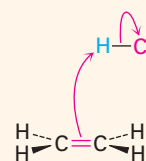
When one of the alkene carbon atoms bonds to the incoming hydrogen, the other carbon atom, having lost its share of the double-bond electrons, now has only six valence electrons and is left with a positive charge. This positively charged species—a carbon-cation, or **carbocation**—is itself an electrophile

that can accept an electron pair from nucleophilic Cl^- anion in a second step, forming a C–Cl bond and yielding the neutral addition product. Once again, a curved arrow in Figure 3.6 shows the electron-pair movement from Cl^- to the positively charged carbon.

MECHANISM

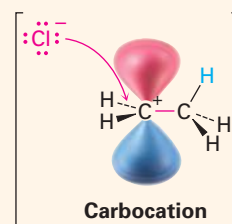
Figure 3.6 The mechanism of the electrophilic addition of HCl to ethylene. The reaction takes place in two steps and involves an intermediate carbocation.

- 1 A hydrogen atom on the electrophile HCl is attacked by π electrons from the nucleophilic double bond, forming a new C–H bond. This leaves the other carbon atom with a + charge and a vacant p orbital. Simultaneously, two electrons from the H–Cl bond move onto chlorine, giving chloride anion.



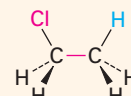
Ethylene

1 ↓



Carbocation

2 ↓



Chloroethane

© John McMurry

Worked Example 3.6

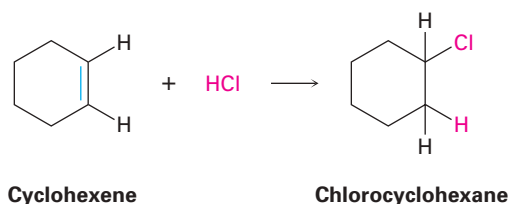
Predicting the Product of an Electrophilic Addition Reaction

What product would you expect from reaction of HCl with cyclohexene?

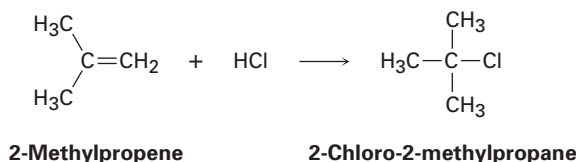
Strategy

HCl adds to the double-bond functional group in cyclohexene in exactly the same way it adds to ethylene, yielding an addition product.

Solution



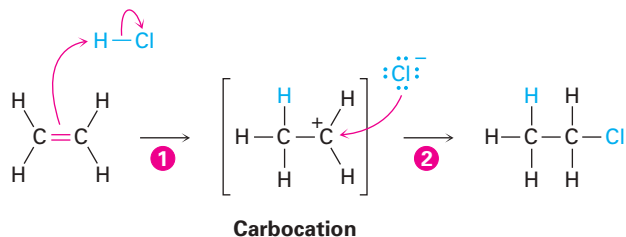
Problem 3.15 Reaction of HCl with 2-methylpropene yields 2-chloro-2-methylpropane. What is the structure of the carbocation formed during the reaction? Show the mechanism of the reaction.



Problem 3.16 Reaction of HCl with pent-2-ene yields a mixture of two addition products. Write the reaction, and show the two products.

3.8 Describing a Reaction: Transition States and Intermediates

For a reaction to take place, reactant molecules must collide and a reorganization of atoms and bonds must occur. In the addition reaction of HCl and ethylene, for instance, the two reactants approach each other, the C=C π bond and H-Cl bond break, a new C-H bond forms in the first step, and a new C-Cl bond forms in the second step.

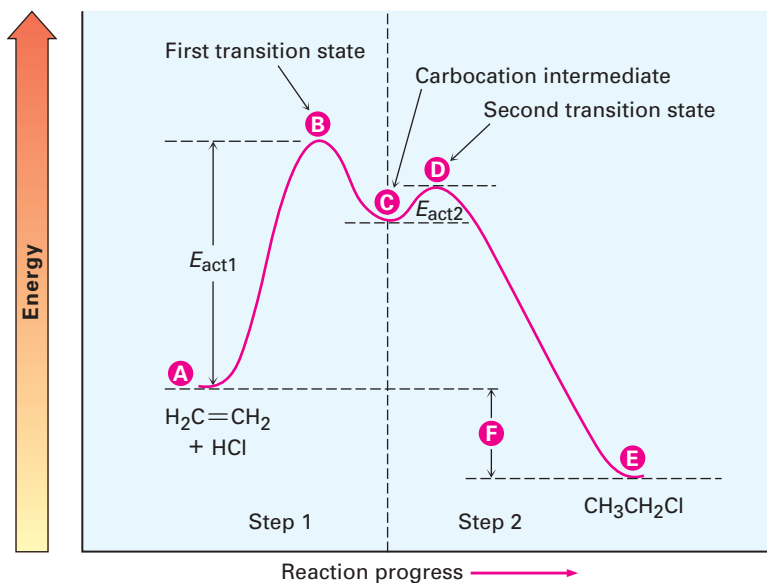


To depict graphically the energy changes that occur during a reaction, chemists use *energy diagrams* of the sort shown in Figure 3.7. The vertical axis of the diagram represents the total energy of all reactants, and the horizontal axis, called the *reaction coordinate*, represents the progress of the reaction from beginning to end.

At the beginning of the reaction, ethylene and HCl have the total amount of energy indicated by the reactant level at point **A** on the left side of the diagram. As the two molecules crowd together, their electron clouds repel each other, causing the energy level to rise. If the collision has occurred with sufficient force and proper orientation, the reactants continue to approach each other despite the repulsion until the new C-H bond starts to form and the H-Cl bond starts to break. At some point (**B** on the diagram), a structure

of maximum energy is reached, a structure called the **transition state**. The transition state represents the highest-energy structure involved in this step of the reaction and can't be isolated or directly observed. Nevertheless, we can imagine it to be a kind of activated complex of the two reactants in which the C=C π bond is partially broken and the new C-H bond is partially formed.

Figure 3.7 An energy diagram for the reaction of ethylene with HCl. Two separate steps are involved, each with its own activation energy, transition state, and energy change. The energy minimum between the two steps represents the carbocation reaction intermediate.



The energy difference between reactants **A** and transition state **B** is called the **activation energy, E_{act}** , and is a measure of how rapidly the reaction occurs. A large activation energy results in a slow reaction because few of the reacting molecules collide with enough energy to reach the transition state. A small activation energy results in a rapid reaction because almost all reacting molecules are energetic enough to climb to the transition state. As an analogy, think about hikers climbing over a mountain pass. If the pass is a high one, the hikers need a lot of energy and surmount the barrier slowly. If the pass is low, however, the hikers need less energy and reach the top quickly.

Most organic reactions have activation energies in the range 40 to 125 kJ/mol (10–30 kcal/mol). Reactions with activation energies less than 80 kJ/mol take place at or below room temperature, while reactions with higher activation energies often require heating to give the molecules enough energy to climb the activation barrier.

Once the high-energy transition state **B** has been reached, energy is released as the new C-H bond forms fully, so the curve in Figure 3.7 turns downward until it reaches a minimum at point **C**, representing the energy level of the carbocation. We call the carbocation, which is formed transiently during the course of the multistep reaction, a **reaction intermediate**. As soon as the carbocation intermediate is formed in the first step, it immediately reacts with Cl^- in a second step to give the final product, chloroethane. This

second step has its own activation energy, $E_{\text{act}2}$, and its own transition state (**D**), which we can think of as an activated complex between the electrophilic carbocation intermediate and nucleophilic Cl^- anion in which the new C–Cl bond is partially formed. Finally, the curve turns downward as the C–Cl bond forms fully to give the final addition product at point **E**.

Each individual step in the reaction has its own energy change, represented by the difference in levels between reactant and intermediate (step 1) or intermediate and product (step 2). The *overall* energy change for the reaction, however, is the energy difference between initial reactants (far left) and final products (far right), as represented by **F** in Figure 3.7. Because the energy level of the final products is lower than that of the reactants, energy is released and the reaction is favorable. If the energy level of the final products were higher than that of the reactants, energy would be absorbed and the reaction would not be favorable.

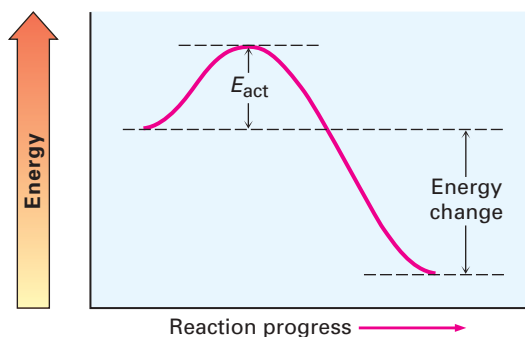
Worked Example 3.7

Drawing an Energy Diagram

Sketch an energy diagram for a one-step reaction that is fast and releases a large amount of energy.

Strategy A fast reaction has a low E_{act} , and a reaction that releases a large amount of energy forms products that are much lower in energy and more stable than reactants.

Solution



- Problem 3.17** Which reaction is faster, one with $E_{\text{act}} = 60 \text{ kJ/mol}$ or one with $E_{\text{act}} = 80 \text{ kJ/mol}$?
- Problem 3.18** Sketch an energy diagram to represent each of the following situations.
- A reaction that releases energy and takes place in one step
 - A reaction that absorbs energy and takes place in one step
- Problem 3.19** Draw an energy diagram for a two-step reaction whose first step absorbs energy and whose second step releases energy. Label the intermediate.

3.9 Describing a Reaction: Catalysis

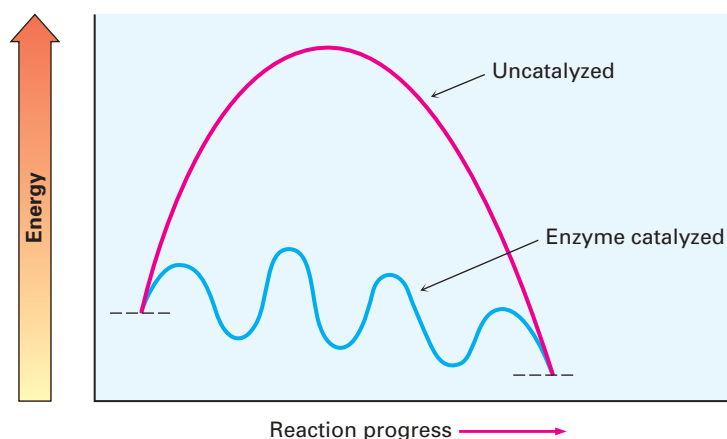
How fast a reaction occurs depends on the value of its activation energy, E_{act} , as noted in the previous section. Unfortunately, there is no way to predict the size of the activation energy for a reaction, and it may well happen that the E_{act} of a process is too large for the reaction to occur easily, even at high temperature. The only solution in such a situation is to find a way to change the reaction mechanism to an alternative pathway that occurs through different steps with lower activation energies.

A **catalyst** is a substance that increases the rate of a chemical transformation by providing an alternative mechanism. The catalyst *does* take part in the reaction, but it is regenerated at some point and thus undergoes no net change. An example that we'll see in the next chapter, for instance, is the use of a metal catalyst such as palladium to effect the reaction of an alkene with H_2 gas and produce an alkane. In the absence of palladium, an alkene undergoes no reaction with H_2 gas even at high temperature, but in the presence of palladium, reaction occurs rapidly at room temperature. Called a *hydrogenation* reaction, the process is used industrially to convert liquid vegetable oil to solid cooking fats.



The hundreds of thousands of biological reactions that take place in living organisms almost all involve catalysts. Biological reactions use the same mechanisms as reactions that take place in the laboratory and can be described in similar ways, but they are constrained by the fact that they must have low enough activation energies to occur at moderate temperatures. This constraint is met through the use of large, structurally complex catalysts called *enzymes*, which provide reaction mechanisms that proceed through a series of small steps rather than through one or two large steps. Thus, a typical energy diagram for an enzyme-catalyzed biological reaction might look like that in Figure 3.8.

Figure 3.8 An energy diagram for a typical, enzyme-catalyzed biological reaction (blue curve) versus an uncatalyzed laboratory reaction (red curve). The biological reaction takes place in several steps, each of which has a relatively small activation energy.





Terpenes: Naturally Occurring Alkenes

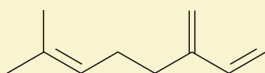


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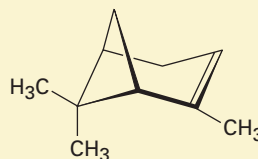
The wonderful fragrance of leaves from the California bay laurel is due primarily to myrcene, a simple terpene.

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

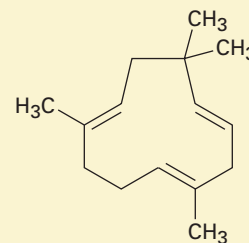
Chemically, plant essential oils consist largely of mixtures of compounds known as *terpenoids*—small organic molecules with an immense diversity of structure. More than 35,000 different terpenoids are known. Some are open-chain molecules, and others contain rings; some are hydrocarbons, and others contain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



Myrcene
(oil of bay)

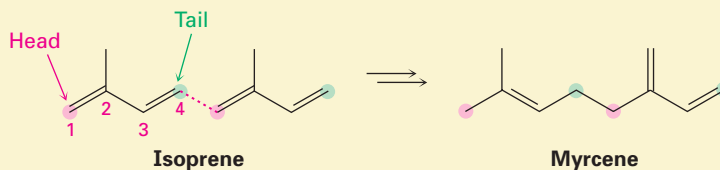


α -Pinene
(turpentine)



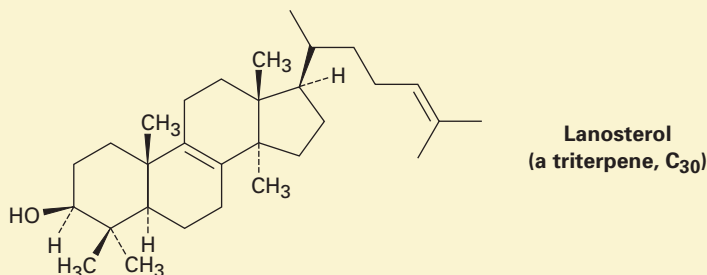
Humulene
(oil of hops)

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

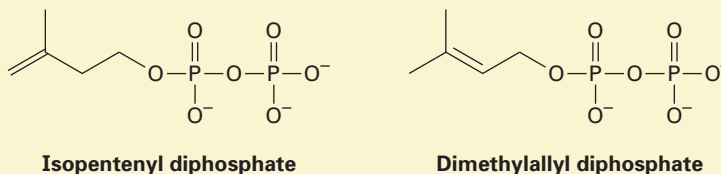


Terpenes (and terpenoids) are further classified according to the number of 5-carbon units they contain. Thus, *monoterpenes* are 10-carbon substances derived from two isoprene units, *sesquiterpenes* are 15-carbon molecules derived from three isoprene units, *diterpenes* are 20-carbon

substances derived from four isoprene units, and so on. Monoterpenes and sesquiterpenes are found primarily in plants, but the higher terpenoids occur in both plants and animals, and many have important biological roles. The triterpenoid lanosterol, for example, is the precursor from which all steroid hormones are made.



Isoprene itself is not the true biological precursor of terpenoids. Nature instead uses two “isoprene equivalents”—isopentenyl diphosphate and dimethylallyl diphosphate—which are themselves made by two different routes depending on the organism. Lanosterol, in particular, is biosynthesized from acetic acid by a complex pathway that has been worked out in great detail.



Summary and Key Words

activation energy, E_{act} 99
 addition reaction 89
 alkene 78
 alkyne 78
 carbocation 96
 catalyst 101
 electrophile 93
 elimination reaction 90
E,Z system 86
 nucleophile 92
 polar reaction 91
 radical 91
 radical reaction 91
 reaction intermediate 99
 reaction mechanism 91
 rearrangement reaction 90
 substitution reaction 90
 transition state 99
 unsaturated 79

All chemical reactions, whether in the laboratory or in living organisms, follow the same “rules.” To understand both organic and biological chemistry, it’s necessary to know not just *what* occurs but also *why* and *how* chemical reactions take place. In this chapter, we’ve taken a brief look at the fundamental kinds of organic reactions. We’ve looked first at alkene stereoisomerism and then we’ve used alkene chemistry as a vehicle to see why reactions occur and how they can be described.

Alkenes are hydrocarbons that contain a carbon–carbon double bond, C=C, and **alkynes** are hydrocarbons that contain a carbon–carbon triple bond, C≡C. Because they contain fewer hydrogens than related alkanes, alkenes are often referred to as **unsaturated**.

A double bond consists of two parts: a σ bond formed by head-on overlap of two sp^2 orbitals and a π bond formed by sideways overlap of two p orbitals. Because rotation around the double bond is not possible, substituted alkenes can exist as *cis*–*trans* isomers. The geometry of a double bond can be described by the ***E,Z* system** as either *E* (*entgegen*) or *Z* (*zusammen*) by application of a series of sequence rules that rank the substituent groups on the double-bond carbons.

A full description of how a reaction occurs is called its **mechanism**. There are two kinds of organic mechanisms: polar and radical. **Polar reactions**, the most common kind, involve even-electron species and occur when an electron-rich reagent, or **nucleophile**, donates an electron pair to an electron-poor reagent, or **electrophile**, in forming a new bond. **Radical reactions** involve odd-electron species and occur when each reactant donates one electron in forming a new bond.

A reaction can be described pictorially by using an energy diagram, which follows the course of the reaction from reactant to product. Every reaction proceeds through a **transition state**, which represents the highest-energy point reached and is a kind of activated complex between reactants. The amount of energy needed by reactants to reach the transition state is the **activation energy, E_{act}** . The larger the activation energy, the slower the reaction. A **catalyst** can sometimes be used to increase the rate of a reaction by providing an alternative mechanistic pathway.

Many reactions take place in more than one step and involve the formation of an **intermediate**. An intermediate is a species that is formed during the course of a multistep reaction and that lies in an energy minimum between two transition states. Intermediates are more stable than transition states but are often too reactive to be isolated.

Exercises

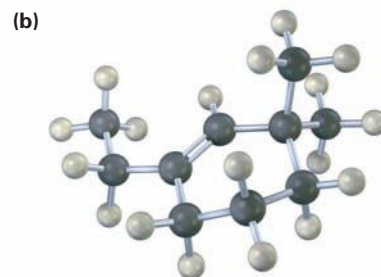
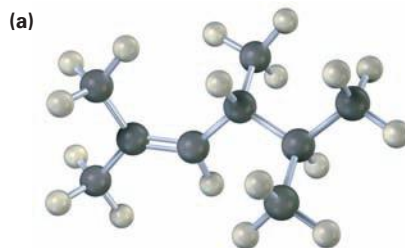
Visualizing Chemistry

(Problems 3.1–3.19 appear within the chapter.)

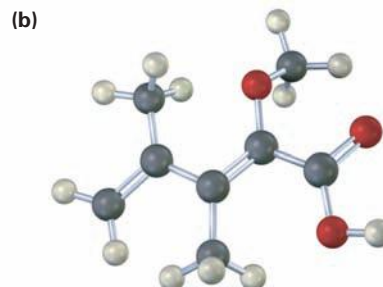
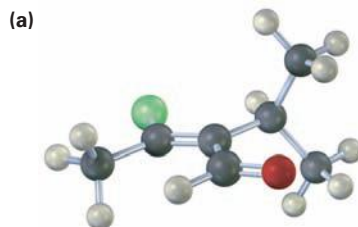


Interactive versions of these problems are assignable in OWL.

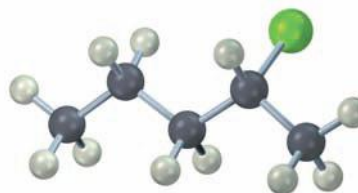
3.20 Name the following alkenes, and convert each drawing into a skeletal structure.



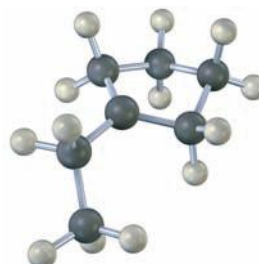
3.21 Assign *E* or *Z* stereochemistry to each of the following alkenes, and convert each drawing into a skeletal structure (red = O, yellow-green = Cl).



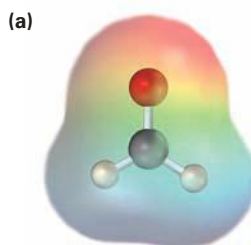
- 3.22 The following alkyl chloride can be prepared by addition of HCl to two different alkenes. Name and draw the structures of both (yellow-green = Cl).



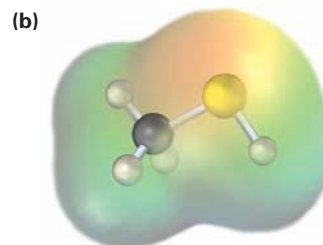
- 3.23 The following carbocation is a possible intermediate in the electrophilic addition of HCl with two different alkenes. Write structures for both.



- 3.24 Electrostatic potential maps of (a) formaldehyde (CH_2O) and (b) methanethiol (CH_3SH) are shown. Is the formaldehyde carbon atom likely to be electrophilic or nucleophilic? What about the methanethiol sulfur atom? Explain.



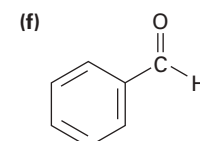
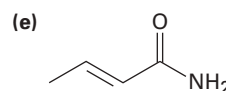
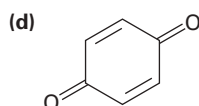
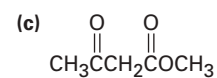
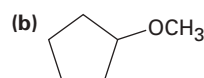
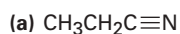
Formaldehyde



Methanethiol

Additional Problems

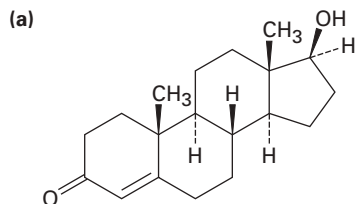
- 3.25 Predict the direction of polarization of the functional groups in each of the following molecules.



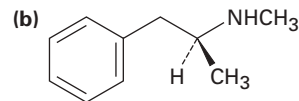
3.26 Which of the following are likely to behave as electrophiles and which as nucleophiles?

- (a) Cl^- (b) $\text{N}(\text{CH}_3)_3$ (c) Hg^{2+} (d) CH_3S^- (e) CH_3^+

3.27 Identify the likely electrophilic and nucleophilic sites in each of the following molecules:

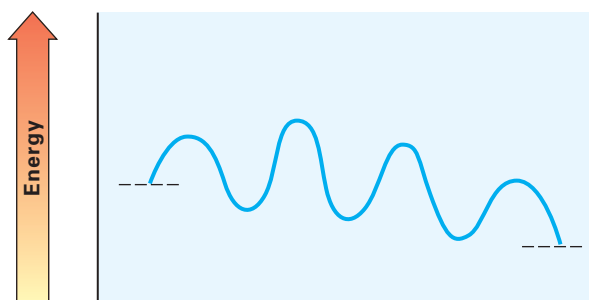


Testosterone



Amphetamine

3.28 Look at the following energy diagram for an enzyme-catalyzed reaction:

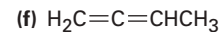
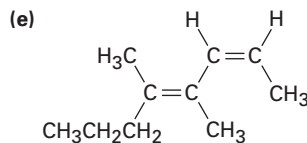
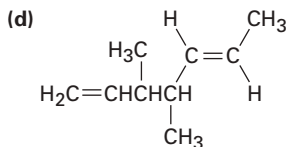
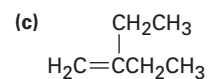
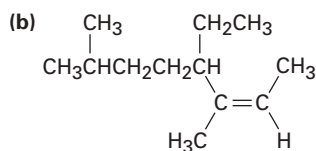
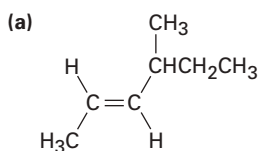


(a) How many steps are involved?

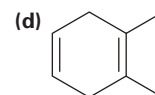
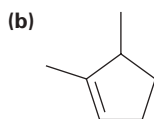
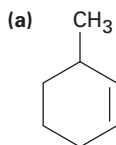
(b) Which is the fastest step, and which is the slowest?

NAMING ALKENES, ALKYNES, AND CYCLOALKENES

3.29 Name the following alkenes:

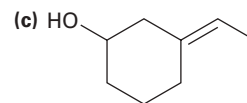
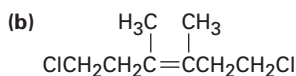
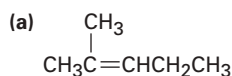


3.30 Name the following cycloalkenes:



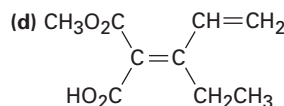
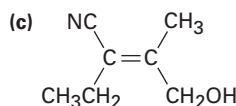
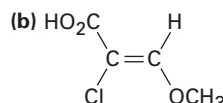
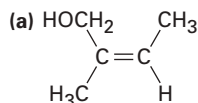
- 3.31** Draw structures corresponding to the following IUPAC names:
 (a) 3-Propylhept-2-ene (b) 2,4-Dimethylhex-2-ene
 (c) Octa-1,5-diene (d) 4-Methylpenta-1,3-diene
 (e) *cis*-4,4-Dimethylhex-2-ene (f) (*E*)-3-Methylhept-3-ene
- 3.32** Draw the structures of the following cycloalkenes:
 (a) *cis*-4,5-Dimethylcyclohexene (b) 3,3,4,4-Tetramethylcyclobutene
- 3.33** The following names are incorrect. Draw each molecule, tell why its name is wrong, and give its correct name.
 (a) 1-Methylcyclopent-2-ene (b) 1-Methylpent-1-ene
 (c) 6-Ethylcycloheptene (d) 3-Methyl-2-ethylcyclohexene
- 3.34** Correct the following pre-1993 names to current names, and draw each structure:
 (a) 2,5-Dimethyl-3-hexyne (b) (*Z*)-3-Methyl-2-pentene
- 3.35** Which of the following molecules show *cis*–*trans* isomerism?

DOUBLE-BOND ISOMERS



- 3.36** Draw and name molecules that meet the following descriptions:
 (a) An alkene, C_6H_{12} , that does not show *cis*–*trans* isomerism
 (b) The *E* isomer of a trisubstituted alkene, C_6H_{12}
 (c) A cycloalkene, C_7H_{12} , with a tetrasubstituted double bond
- 3.37** Neglecting *cis*–*trans* isomers, there are five substances with the formula C_4H_8 . Draw and name them.
- 3.38** Which of the molecules you drew in Problem 3.37 show *cis*–*trans* isomerism? Draw and name their *cis*–*trans* isomers.
- 3.39** Cyclodecene can exist in both *cis* and *trans* forms, but cyclohexene cannot. Explain.
- 3.40** Rank the following pairs of substituents according to the sequence rules:
- (a) $-\text{CH}_2\text{CH}_3$ $-\text{CH}_2\text{CH}_2\text{CH}_3$ (b) $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{CH}_3 \end{array}$ $-\text{CH}_2\text{OH}$
- (c) $-\text{CH}(\text{CH}_3)_2$ (d) $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{CH}_2\text{CHCH}_2\text{Cl} \end{array}$ $-\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
- 3.41** Rank the following sets of substituents according to the sequence rules:
 (a) $-\text{CH}_3$, $-\text{Br}$, $-\text{H}$, $-\text{I}$
 (b) $-\text{OH}$, $-\text{OCH}_3$, $-\text{H}$, $-\text{CO}_2\text{H}$
 (c) $-\text{CH}_3$, $-\text{CO}_2\text{H}$, $-\text{CH}_2\text{OH}$, $-\text{CHO}$
 (d) $-\text{CH}_3$, $-\text{CH}=\text{CH}_2$, $-\text{CH}_2\text{CH}_3$, $-\text{CH}(\text{CH}_3)_2$

3.42 Assign *E* or *Z* stereochemistry to the following alkenes:



3.43 Draw and name the six C_5H_{10} alkene isomers, including *E,Z* isomers.

3.44 Draw and name all possible stereoisomers of hepta-2,4-diene.

3.45 Menthene, a hydrocarbon found in mint plants, has the IUPAC name 1-isopropyl-4-methylcyclohexene. What is the structure of menthene?

ENERGY DIAGRAMS

3.46 If a reaction has $E_{act} = 15$ kJ/mol, is it likely to be fast or slow at room temperature? Explain.

3.47 Draw an energy diagram for a two-step reaction that releases energy and whose first step is faster than its second step. Label the parts of the diagram corresponding to reactants, products, transition states, intermediate, activation energies, and overall energy change.

3.48 Draw an energy diagram for a two-step reaction whose second step is faster than its first step.

3.49 Draw an energy diagram for a reaction whose products and reactants are of equal stability.

3.50 Describe the difference between a transition state and a reaction intermediate.

3.51 Consider the energy diagram shown:



(a) Indicate the overall energy change for the reaction. Is it positive or negative?

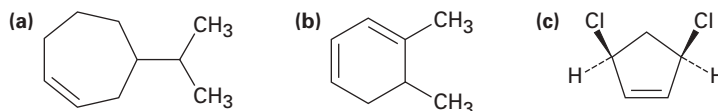
(b) How many steps are involved in the reaction?

(c) Which step is faster?

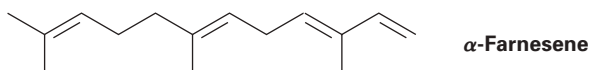
(d) How many transition states are there? Label them.

GENERAL PROBLEMS

3.52 Name the following cycloalkenes:



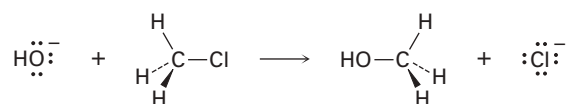
3.53 α -Farnesene is a constituent of the natural waxy coating found on apples. What is its IUPAC name?



3.54 Indicate *E* or *Z* stereochemistry for each of the double bonds in α -farnesene (see Problem 3.53).

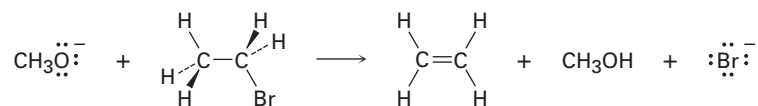
3.55 Reaction of 2-methylpropene with HCl might, in principle, lead to a mixture of two products. Draw them.

3.56 Hydroxide ion reacts with chloromethane in a single step according to the following equation:



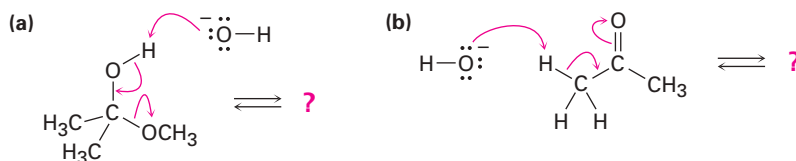
Identify the bonds broken and formed, and draw curved arrows to represent the flow of electrons during the reaction.

3.57 Methoxide ion ($\text{CH}_3\text{O}^{\ominus}$) reacts with bromoethane in a single step according to the following equation:

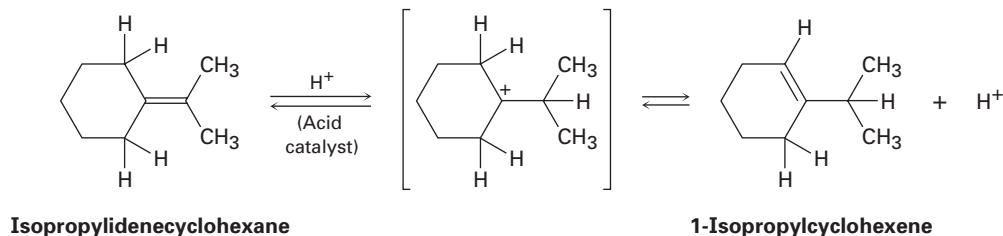


Identify the bonds broken and formed, and draw curved arrows to represent the flow of electrons during the reaction.

3.58 Follow the flow of electrons indicated by the curved arrows in each of the following reactions, and predict the products that result:



- 3.59 When isopropylidenecyclohexane is treated with strong acid at room temperature, isomerization occurs by the mechanism shown below to yield 1-isopropylcyclohexene:

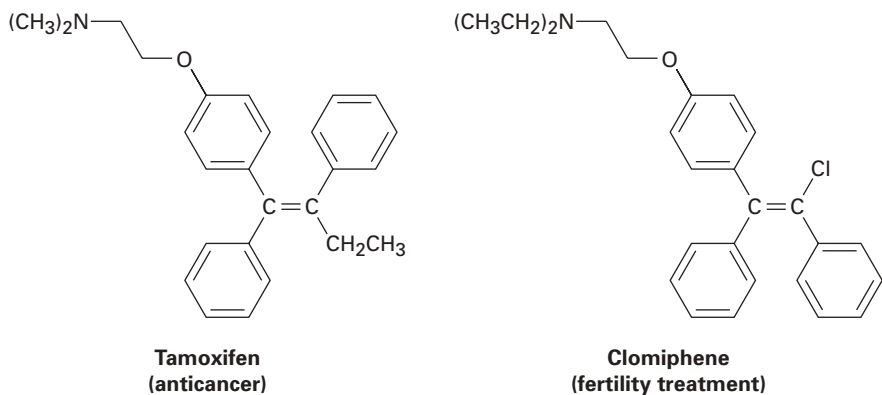


At equilibrium, the product mixture contains about 30% isopropylidenecyclohexane and about 70% 1-isopropylcyclohexene.

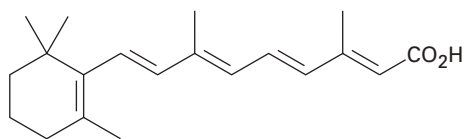
- (a) What kind of reaction is occurring? Is the mechanism polar or radical?
- (b) Draw curved arrows to indicate electron flow in each step.
- 3.60 We'll see in the next chapter that the stability of carbocations depends on the number of alkyl groups attached to the positively charged carbon—the more alkyl groups, the more stable the cation. Draw the two possible carbocation intermediates that might be formed in the reaction of HCl with 2-methylpropene (Problem 3.55), tell which is more stable, and predict which product will form.

IN THE MEDICINE CABINET

- 3.61 Tamoxifen and clomiphene have similar structures but very different medical uses. Tell whether the alkene double bond in each is *E* or *Z*.



- 3.62 Retin A, or retinoic acid, is a medication commonly used to reduce wrinkles and treat severe acne. How many different isomers arising from double bond isomerizations are possible?



Retin A (retinoic acid)

IN THE FIELD 3.63 Lycopene, the pigment that gives tomatoes their red color, is a terpene derived formally by the joining together of numerous isoprene units (see the *Interlude* in this chapter). Start at one end of the molecule, and identify all the contiguous isoprene groupings.

