# CHAPTER 3

# Alkenes: The Nature of Organic Reactions

**:ene**
**hydrocarbon**
**:h one or more**
**rbon–carbon**
**uble bonds**

**Alkenes** are hydrocarbons that contain a carbon–carbon double bond functional group. They occur abundantly in nature, and many have important biological roles. For example, ethylene is a plant hormone that induces ripening in fruit, and α-pinene is the major constituent of turpentine.
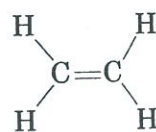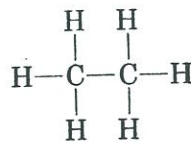


Ethylene        α-Pinene

We'll see in this chapter how and why alkenes behave the way they do, and we'll develop some general ideas about organic chemical reactivity that can be applied to all molecules.

## 3.1  NAMING ALKENES

**:nsaturated**
**containing one or**
**nore double or**
**riple bonds**

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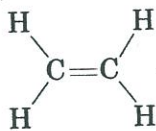


Ethylene, $C_2H_4$          Ethane, $C_2H_6$
(\_ \_drogens: *unsaturated*)   (more hydrogens: *saturated*)

Alkenes are named according to a series of rules similar to those used for naming alkanes, 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 accordingly, using the suffix *-ene*.
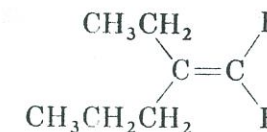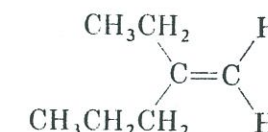


Named as a *pentene*    NOT    as a hexene, because the double bond is not contained in the six-carbon chain.

**Step 2.** Number the carbon atoms in the chain, beginning at the end nearer the double bond. If the double bond is equidistant from the two ends, begin numbering at the end nearer the first branch point:



**Step 3.** Write the full name, numbering the substituents according to their position in the chain and listing them alphabetically. Indicate the position of the double bond by giving the number of the *first* alkene carbon. If more than one double bond is present, give the position of each and use one of the suffixes *-diene*, *-triene*, and so on.
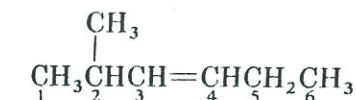


2-Hexene                2-Methyl-3-hexene
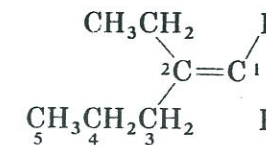


2-Ethyl-1-pentene        2-Methyl-1,3-butadiene

Cycloalkenes are named in a similar way, 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:



1-Methylcyclohexene          1,4-Cyclohexadiene          1,5-Dimethylcyclopentene

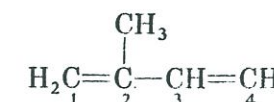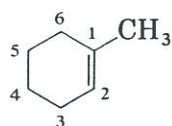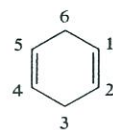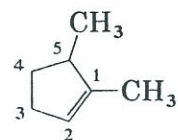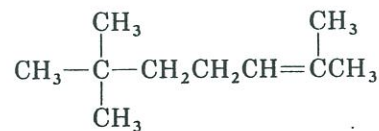For historical reasons, there are a few alkenes whose names don't conform to the rules. For example, the alkene corresponding to ethane should be called *ethene*, but the name *ethylene* has been used for so long that it is accepted by IUPAC. Table 3.1 lists some other common names.

**TABLE 3.1   Common names of some alkenes**

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

**PRACTICE PROBLEM 3.1**

What is the IUPAC name of this alkene:

$$CH_3{-}\underset{\underset{\displaystyle CH_3}{\textstyle |}}{\overset{\overset{\displaystyle CH_3}{\textstyle |}}{C}}{-}CH_2CH_2CH{=}\overset{\overset{\displaystyle CH_3}{\textstyle |}}{C}CH_3$$

SOLUTION   First, find the longest chain containing the double bond. In this case, it's 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 methyl groups at C2 and C6 (two).

$$CH_3{-}\underset{\underset{6}{\underset{\displaystyle CH_3}{\textstyle |}}}{\overset{\overset{\displaystyle CH_3}{\textstyle |}}{C}}{-}\underset{5}{CH_2}\underset{4}{CH_2}\underset{3}{CH}{=}\underset{2}{\overset{\overset{\displaystyle CH_3}{\textstyle |}}{C}}\underset{1}{CH_3}$$
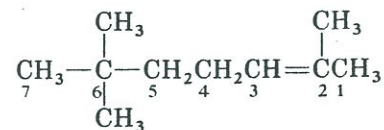
The full name is 2,6,6-trimethyl-2-heptene.

**PROBLEM  3.1**   Give IUPAC names for these compounds:

(a)   $\underset{\underset{\displaystyle }{}}{H_2C{=}CHCH_2\overset{\overset{\displaystyle CH_3}{\textstyle |}}{C}HCH_3}$

(b)   $CH_3CH_2CH{=}CHCH_2CH_2CH_3$

(c)   $H_2C{=}CHCH_2CH_2CH{=}CHCH_3$

(d)   $CH_3CH_2CH{=}CHCH(CH_3)_2$

**PROBLEM  3.2**   Name these cycloalkenes:

(a)      (b)      (c)   

**PROBLEM  3.3**   Draw structures corresponding to these IUPAC names:

(a) 2-Methyl-1-hexene          (b) 4,4-Dimethyl-2-pentene
(c) 2-Methyl-1,5-hexadiene     (d) 3-Ethyl-2,2-dimethyl-3-heptene

## 3.2   ELECTRONIC STRUCTURE OF ALKENES

We saw in Section 1.10 that the carbon atoms in a double bond are $sp^2$ hybridized and have three equivalent orbitals that lie in a plane at angles of 120° to one another. The fourth carbon orbital is an unhybridized $p$ orbital, which is perpendicular to the $sp^2$ plane. When two such carbon atoms approach each other, they form two kinds of bonds: a sigma bond, formed by head-on overlap of $sp^2$ orbitals, and a pi bond, formed by sideways overlap of $p$ orbitals. The doubly bonded carbons and the four atoms attached to them lie in a plane, with bond angles of approximately 120° (Figure 3.1).
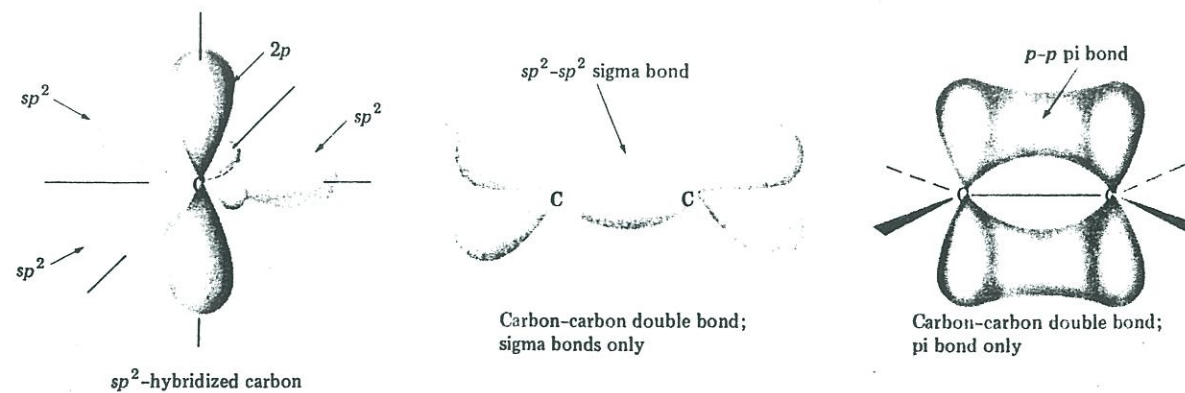


**FIGURE 3.1**   An orbital picture of the carbon–carbon double bond

We know from Section 2.5 that free rotation is possible 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. No rotation can take place around carbon–carbon double bonds because doing so would break the pi part of the bond (Figure 3.2). In fact, the energy barrier to rotation around a double bond is as large as the strength of the pi bond itself, an estimated 65 kcal/mol. (Recall that the rotation barrier for a single bond is only about 2.9 kcal/mol.)
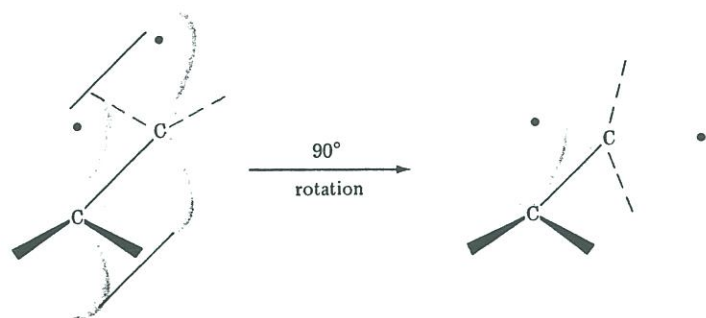


Pi bond
(*p* orbitals are parallel)

Broken pi bond after rotation
(*p* orbitals are perpendicular)

**FIGURE 3.2** Breaking the pi bond is necessary for rotation around a carbon–carbon double bond to take place

## 3 CIS–TRANS ISOMERS

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 like 2-butene. (*Disubstituted* means that two substituents other than hydrogen are linked to the double-bond carbons.) In 2-butene, the two methyl groups can be either on the same side of the double bond or on opposite sides (Figure 3.3), a situation reminiscent of substituted cycloalkanes (Section 2.7).

Since bond rotation can't occur, the two 2-butenes don't spontaneously inter-convert; they are different chemical compounds. As with disubstituted cycloalkanes (Section 2.7), we call such compounds *cis–trans isomers* because they have the same formula and overall skeleton but differ in the spatial arrangement of their atoms. The isomer with both substituents on the same side is called *cis*-2-butene, and the isomer with substituents on opposite sides is *trans*-2-butene.

Cis–trans isomerism is not limited to disubstituted alkenes: It can occur when-ever both of the double-bond carbons are attached to two different groups. If one of the double-bond carbons is attached to two identical groups, however, then cis–trans isomerism is not possible (Figure 3.4).

Although the cis–trans interconversion of alkene isomers doesn't occur spon-taneously, it can be made to happen by treating the alkene with a strong-acid ~~If ~~interconvert *cis*-2-butene with *trans*-2-butene and allow them to
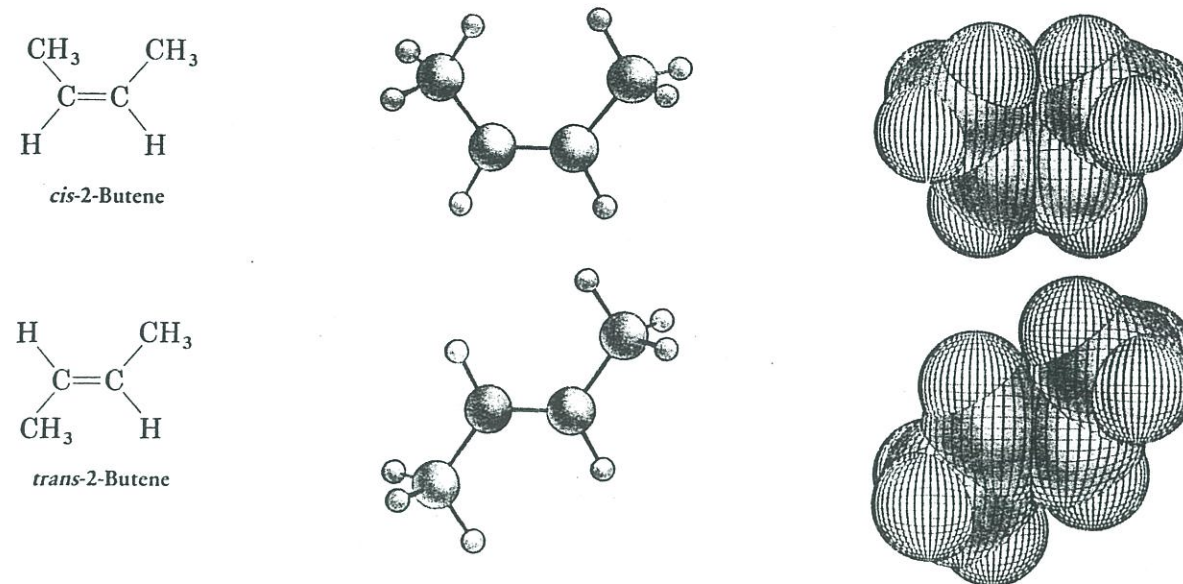


**FIGURE 3.3** Cis and trans isomers of 2-butene. The cis isomer has the substituent methyl groups on the same side of the double bond, and the trans isomer has the methyl groups on opposite sides of the double bond.
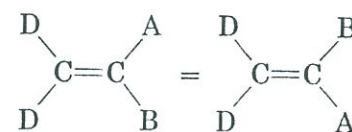


These two compounds are identical; they aren't cis–trans isomers.
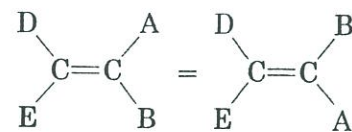
These two compounds are not identical; they are cis–trans isomers

**FIGURE 3.4** The requirement for cis–trans isomerism in alkenes. Both double-bond carbons must be attached to two different groups.

reach equilibrium, we find that they aren't of equal stability. At equilibrium, the trans isomer is more favored than the cis isomer by a ratio of 76% trans to 24% cis.



*cis*-2-Butene (24%)

*trans*-2-Butene (76%)
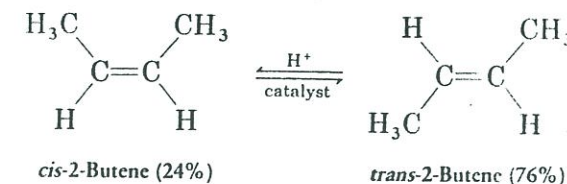
Cis alkenes are less stable than their trans isomers because of spatial inter-ference between the bulky substituents on the same side of the double bond. This

is the same kind of interference, or *steric strain*, that we saw in axial methyl-cyclohexane (Section 2.11).



Steric strain in
*cis*-2-butene

No steric strain in
*trans*-2-butene
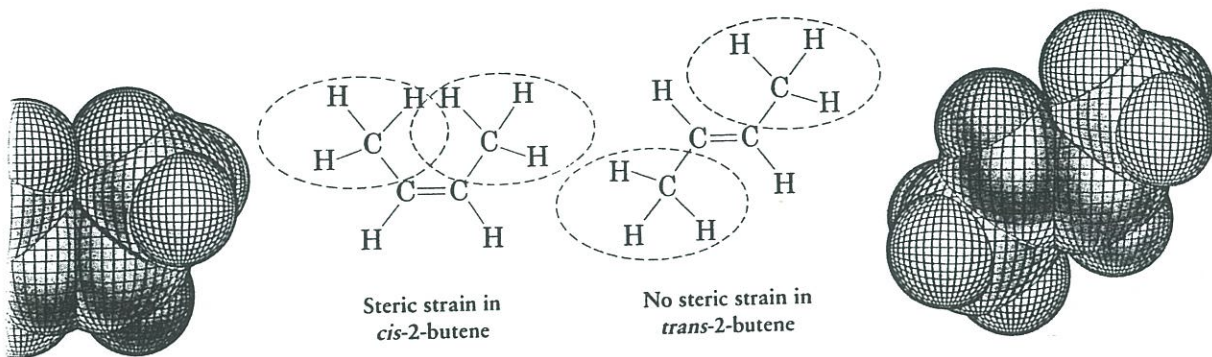
**PRACTICE PROBLEM 3.2**    Draw the cis and trans isomers of 5-chloro-2-pentene.

SOLUTION    5-Chloro-2-pentene is $ClCH_2CH_2CH=CHCH_3$. The chloroethyl and methyl groups are on the same side of the double bond in one isomer and on opposite sides in the other isomer.



*cis*-5-Chloro-2-pentene          *trans*-5-Chloro-2-pentene
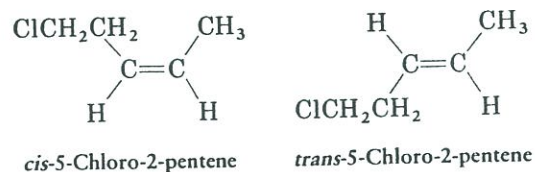
**PROBLEM 3.4**    Which of these compounds can exist as pairs of cis–trans isomers? Draw each cis–trans pair.
(a) $CH_3CH=CH_2$          (b) $(CH_3)_2C=CHCH_3$          (c) $ClCH=CHCl$
(d) $CH_3CH_2CH=CHCH_3$          (e) $CH_3CH_2CH=CBrCH_3$          (f) 3-Methyl-3-heptene

**PROBLEM 3.5**    Which is more stable, *cis*-2-methyl-3-hexene or *trans*-2-methyl-3-hexene?

**PROBLEM 3.6**    How can you account for the observation that cyclohexene does not show cis–trans isomerism?

# 3.4 SEQUENCE RULES: THE *E,Z* DESIGNATION

In the discussion of isomerism in the 2-butenes, we used the terms *cis* and *trans* to specify alkenes whose two substituents were on the same side and opposite sides of a double bond, respectively. This cis–trans naming system is unambiguous for disubstituted alkenes, but how do we denote the geometry of *tri*substituted and *tetra*substituted double bonds? (*Trisubstituted* means three substituents other than hydrogen on the double bond; *tetrasubstituted* means four substituents other than hydrogen on the double bond.)

**sequence rules**
a series of rules for assigning priorities to groups so that double-bond geometry can be specified

The answer is provided by the *E,Z* system of nomenclature, which uses a system of sequence rules to assign priorities to the groups on the double-bond carbons. Considering each of the double-bond carbons separately, we use the sequence rules to decide which of the two groups on each carbon is higher in priority. If the higher-priority groups are on the same side of the double bond, the alkene is designated *Z* (for the German *zusammen*, "together"). If the higher-priority groups are on opposite sides, the alkene is designated *E* (for the German *entgegen*, "opposite"). One way to remember which is which is to remember that Z = groups on ze zame zide (*E* = the other one). These assignments are shown in Figure 3.5.



*Z* double bond          *E* double bond
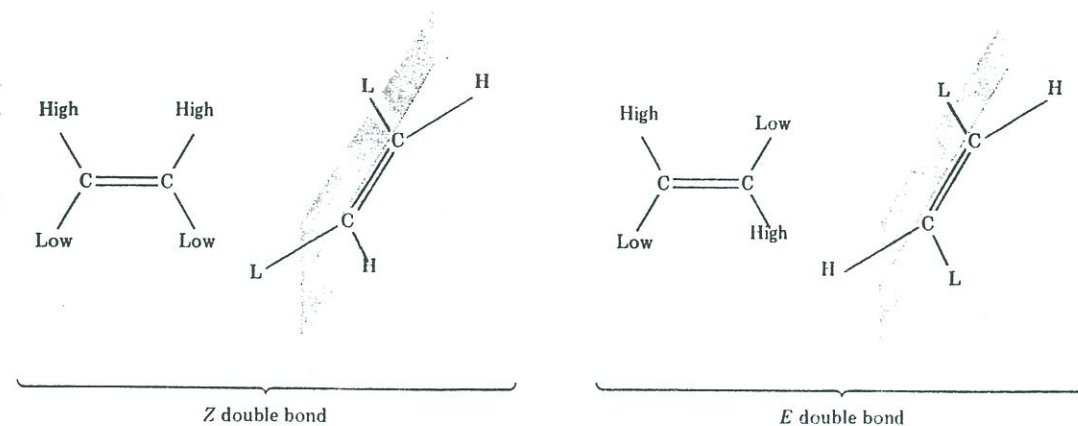
**FIGURE 3.5**    The *E,Z* system of nomenclature

The sequence rules used in assigning priorities are as follows:

**Sequence rule 1**    Look at the atoms directly attached to each of the double-bond carbons and rank them in order of decreasing atomic number. That is, an atom with a high atomic number like Cl receives higher priority than an atom with a low atomic number like H. Thus, the atoms that we commonly find attached to a double-bond carbon are assigned priorities as follows:

$$\underset{35}{Br} > \underset{17}{Cl} > \underset{8}{O} > \underset{7}{N} > \underset{6}{C} > \underset{1}{H}$$

For example:



(a) (*E*)-2-Chloro-2-butene          (b) (*Z*)-2-Chloro-2-butene
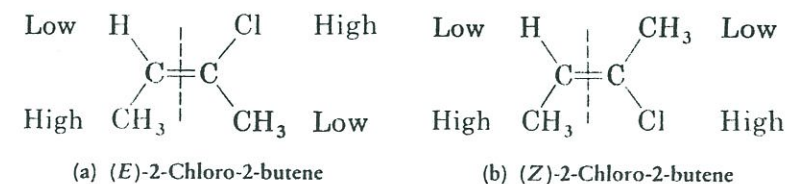
Because chlorine has a higher atomic number than carbon, it receives higher priority than a methyl ($CH_3$) group. Methyl receives higher priority than hydrogen, however, and isomer (a) is therefore assigned *E* geometry (high-priority groups on opposite sides of the double bond). Isomer (b) has *Z* geometry (high-priority groups on ze zame zide of the double bond).

**Sequence rule 2** If a decision can't be reached by ranking the first atoms in the substituents (rule 1), look at the second, third, or fourth atoms away from the double-bond carbons until a difference is found. Thus, an ethyl substituent, $-CH_2CH_3$, and a methyl substituent, $-CH_3$, are equivalent by rule 1 since both have carbon as the first atom. But by rule 2, ethyl receives higher priority than methyl because the *second* atoms are one carbon (and two hydrogens) rather than three hydrogens. Look at the following examples to see how this rule is applied:



**Sequence rule 3** Multiple-bonded atoms are considered to be 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 considered equivalent to a substituent having a carbon atom *singly* bonded to *two* oxygens.



This carbon is doubly bonded to one oxygen.    This oxygen is doubly bonded to one carbon.    is equivalent to    This carbon is singly bonded to two oxygens.    This oxygen is singly bonded to two carbons.

In the following examples, the indicated pairs are equivalent:

**PRACTICE PROBLEM 3.3**  Assign *E* or *Z* configuration to the double bond in this compound:
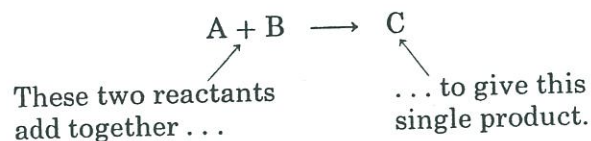


**SOLUTION**  Look at the two double-bond carbons individually. The left-hand carbon has two substituents, $-H$ and $-CH_3$, of which $-CH_3$ receives higher priority by rule 1. The right-hand carbon also has two substituents, $-CH(CH_3)_2$ and $-CH_2OH$, but rule 1 does not allow a priority assignment to be made since both groups have carbon as their first atom. By rule 2, however, $-CH_2OH$ receives higher priority than $-CH(CH_3)_2$, since $-CH_2OH$ has an *oxygen* (and two hydrogens) as its second atom whereas $-CH(CH_3)_2$ has two *carbons* (and one hydrogen) as its second atom. Thus, the two high-priority groups are on the same side of the double bond, and we assign *Z* configuration.



Low      High    Low      High    *Z* configuration

**PROBLEM 3.7**  Which member in each set is higher in priority?
(a) $-H$ or $-Br$    (b) $-Cl$ or $-Br$    (c) $-CH_3$ or $-CH_2CH_3$
(d) $-NH_2$ or $-OH$    (e) $-CH_2OH$ or $-CH_3$    (f) $-CH_2OH$ or $-CH=O$

**PROBLEM 3.8**  Which is higher in priority, $\overset{O}{\overset{\|}{-C}}-OH$ or $\overset{O}{\overset{\|}{-C}}-OCH_3$? Explain.

**PROBLEM 3.9**  Which is higher in priority, isopropyl or *n*-octyl? Explain.

**PROBLEM 3.10**  Assign *E* or *Z* configuration to these alkenes:



## 3.5  KINDS OF ORGANIC REACTIONS

Now that we know something about alkenes and the double-bond functional group, it's time to learn about their chemical reactivity. As an introduction, though, we'll first look at some of the basic principles that underlie all organic reactions. In particular, we'll develop some general notions about why compounds react the way they do and see some methods that have been developed to help understand how reactions take place.

Organic chemical reactions can be organized in two ways: by *what kinds* of reactions occur and by *how* reactions occur. We'll begin by looking at the kinds

of reactions that take place. There are four particularly important kinds of organic reactions: additions, eliminations, substitutions, and rearrangements.
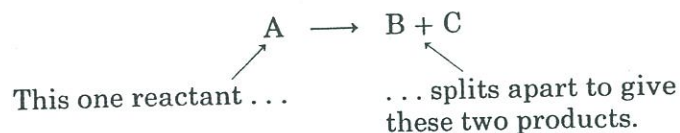
**Addition reactions** occur when two reactants add together to form a single new product with no atoms "left over." We can generalize the process as

$$A + B \longrightarrow C$$

These two reactants
add together . . .

. . . to give this
single product.

As an example of an important addition reaction that we'll be studying soon, alkenes react with HCl to yield alkyl chlorides:



Ethylene

Chloroethane

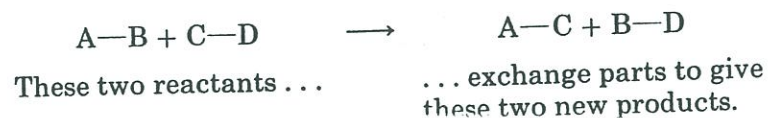These two reactants add . . .    . . . to give this product.
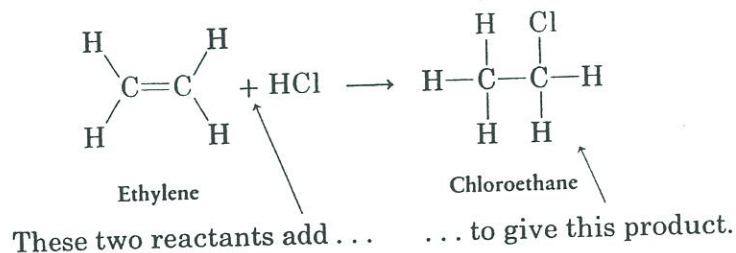
**Elimination reactions** are the opposite of addition reactions. They occur when a single reactant splits into two products, a process we can generalize as

$$A \longrightarrow B + C$$

This one reactant . . .

. . . splits apart to give
these two products.

As an example of an important elimination reaction, alkyl halides split apart into an acid and an alkene when treated with base:



Chloroethane    Ethylene

This one reactant . . .    . . . gives these two products.
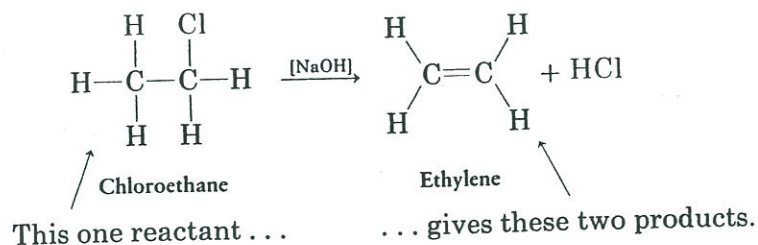
**Substitution reactions** occur when two reactants exchange parts to give two new products, a process we can generalize as

$$A—B + C—D \longrightarrow A—C + B—D$$

These two reactants . . .

. . . exchange parts to give
these two new products.

As an example of a substitution reaction, we saw in Section 2.4 that alkanes react with chlorine gas in the presence of ultraviolet light to yield alkyl chlorides. A—Cl group from chlorine replaces (substitutes for) the —H group of the alkane, and two new products result:



Methane    Chloromethane
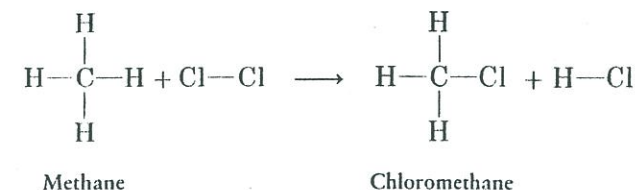
These two reactants . . .    . . . give these two products.

**Rearrangement reactions** occur when a single reactant undergoes a reorganization of bonds and atoms to yield a single isomeric product, a process we can generalize as

$$A \longrightarrow B$$

This single reactant . . .    . . . gives this isomeric product.
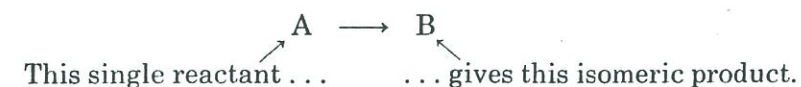
As an example of a rearrangement reaction, we saw in Section 3.3 that 1-butene can be converted into its isomer 2-butene by treatment with an acid catalyst:



*cis*-2-Butene (24%)    *trans*-2-Butene (76%)

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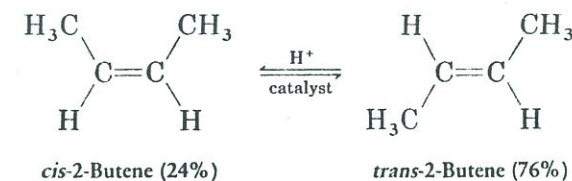
**PROBLEM 3.11**  Classify these reactions as additions, eliminations, substitutions, or rearrangements.
(a) $CH_3Br + KOH \longrightarrow CH_3OH + KBr$
(b) $CH_3CH_2OH \longrightarrow H_2C=CH_2 + H_2O$
(c) $H_2C=CH_2 + H_2 \longrightarrow CH_3CH_3$

## 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 in detail exactly what takes place at each stage of a chemical transformation. It describes which bonds are broken and in what order, which bonds are formed and in what order, and what the relative rate of each step is.

All chemical reactions involve bond breaking and bond making. When two starting materials come together, react, and yield products, certain chemical bonds in the starting materials are broken, and new bonds are formed to make the products. Fundamentally, there are only two ways in which such that one electron remains bond can break: an electronically *symmetrical* way such that one electron remains with each product fragment or an electronically *unsymmetrical* way such that both electrons remain with one product fragment, leaving the other fragment with an empty orbital. The symmetrical cleavage is called a **homolytic** process, and the unsymmetrical cleavage is called a **heterolytic** process:

$$A{:}B \longrightarrow A{\cdot} + {\cdot}B \qquad \text{Radical bond-breaking (homolytic)}$$
$$A{:}B \longrightarrow A^+ + {:}B^- \qquad \text{Polar bond-breaking (heterolytic)}$$
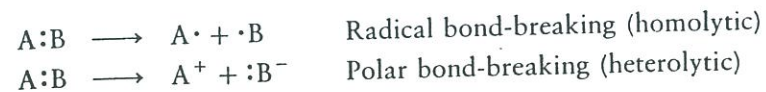
Conversely, there are two ways in which a covalent two-electron bond can form: an electronically symmetrical (**homogenic**) way, when one electron is donated to the new bond by each reactant, or an electronically unsymmetrical (**heterogenic**) way, when both bonding electrons are donated to the new bond by one reactant:

$$A{\cdot} + {\cdot}B \longrightarrow A{:}B \qquad \text{Radical bond-making (homogenic)}$$
$$A^+ + {:}B^- \longrightarrow A{:}B \qquad \text{Polar bond-making (heterogenic)}$$
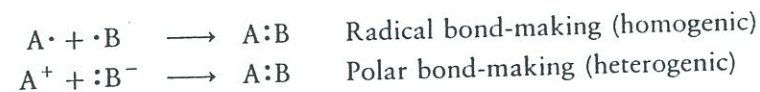
Processes that involve symmetrical bond breaking and making are called **radical reactions**. A radical is a chemical species that contains an odd number of valence electrons and thus has an orbital with only one electron. Processes that involve unsymmetrical bond breaking and making are called **polar reactions**. Polar reactions always involve species that contain an even number of valence electrons and have only electron pairs in their orbitals. Polar processes are the more common reactions always involve species that contain an even number of valence electrons description.

To see how polar reactions occur, we need to recall our discussion of polar covalent bonds and to look more deeply into the effects of bond polarity on organic molecules. We saw in Section 1.12 that certain bonds in a molecule, particularly the bonds in functional groups, often have an unsymmetrical distribution of electrons and are therefore polar. When a carbon atom bonds to an electronegative atom such as chlorine or oxygen, the bond is polarized in such a way that the carbon bears a partial positive charge ($\delta^+$) and the electronegative atom bears a partial negative charge ($\delta^-$). Conversely, when carbon bonds to an atom that is less electronegative than itself, the opposite polarity results. Such is the case with most carbon–metal (**organometallic**) bonds:
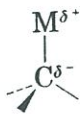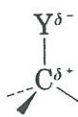
$$\underset{\text{Where } Y = O, N, Cl, Br, I}{Y^{\delta-}{-}C^{\delta+}} \qquad \underset{\text{Where } M = \text{a metal such as Mg or Li}}{M^{\delta+}{-}C^{\delta-}}$$

What does bond polarity mean with respect to chemical reactions? Because species with unlike charges attract each other, *the fundamental characteristic of all polar reactions is that the electron-rich sites in one molecule react with the electron-poor sites in another molecule.* Covalent bonds form in a polar reaction when the electron-rich reactant donates a *pair* of electrons to the electron-poor reactant; conversely, covalent bonds break in polar reactions when one of the two product fragments leaves with the electron *pair*.

Chemists usually indicate the electron movement that occurs during a polar reaction by curved arrows. By convention, a curved arrow means that an electron pair moves from the tail to the head of the arrow during the reaction. In referring to polar reactions, chemists have coined the words *nucleophile* and *electrophile*. A **nucleophile** is a reagent that is "nucleus loving"; it has an electron-rich site and forms a bond by donating an electron pair to an electron-poor site. An **electrophile**, by contrast, is "electron-loving"; it has an electron-poor site and forms a bond by accepting an electron pair from a nucleophile.

The curved arrow shows that electrons are moving from :B⁻ to A⁺.

$$\underset{\substack{\text{Electrophile} \\ \text{(electron-poor)}}}{A^+} + \underset{\substack{\text{Nucleophile} \\ \text{(electron-rich)}}}{:B^-} \longrightarrow A{:}B$$
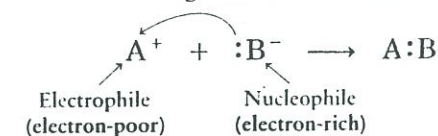
**nucleophile**
an electron-rich reagent that can donate an electron pair to an electrophile in a polar reaction

**electrophile**
an electron-poor reagent that can accept an electron pair from a nucleophile in a polar reaction

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**PRACTICE PROBLEM 3.4**  What is the direction of bond polarity in the amine functional group, $C{-}NH_2$?

**SOLUTION**  According to the electronegativity table (Table 1.4), nitrogen is more electronegative than carbon. Thus an amine is polarized with carbon as $\delta^+$ and nitrogen as $\delta^-$.

---

**PROBLEM 3.12**  What is the direction of bond polarity in these functional groups?
(a) Ketone   (b) Alkyl chloride   (c) Alcohol   (d) Alkyllithium

**PROBLEM 3.13**  Identify the functional groups and show the direction of bond polarity in each of these molecules.

(a) Acetone, $CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3$   (b) Chloroethane, $CH_3CH_2Cl$
(c) Methanethiol, $CH_3SH$   (d) Tetraethyllead, $(CH_3CH_2)_4Pb$ (the "lead" in gasoline)

**PROBLEM 3.14**  Which of the following would you expect to behave as electrophiles and which as nucleophiles? Explain.
(a) $H^+$   (b) $H\ddot{O}{:}^-$   (c) $Br^+$
(d) $:NH_3$   (e) $H{-}C{\equiv}C{-}H$   (f) $CO_2$

## 7 AN EXAMPLE OF A POLAR REACTION: ADDITION OF HCl TO ETHYLENE

Let's look in detail at a typical polar reaction, the 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 follows:



Ethylene
(nucleophile)      Hydrogen chloride
(electrophile)          Chloroethane
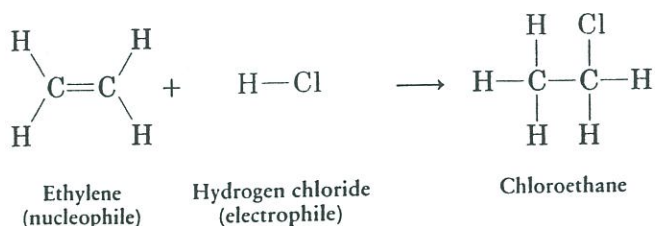
This reaction, an example of a general polar reaction type known as an **electrophilic addition**, can be understood in terms of the general concepts just discussed. We'll begin by looking at the natures of the two reactants.

What do we know about ethylene? We know from Sections 1.10 and 3.2 that a carbon–carbon double bond results from orbital overlap of two $sp^2$-hybridized carbon atoms: The sigma part of the double bond results from $sp^2$–$sp^2$ overlap, and the pi part results from $p$–$p$ overlap.

What kind of chemical reactivity might we expect of carbon–carbon double bonds? We know that alkanes are rather inert because all of their valence electrons are tied up in strong, nonpolar, carbon–carbon and carbon–hydrogen bonds. Furthermore, alkane bonding electrons are inaccessible to external reagents because they are localized in sigma orbitals between atoms.

The situation for ethylene and other alkenes is quite different. For one thing, double bonds have greater electron density than single bonds: four electrons in a double bond versus only two electrons in a single bond. Equally important, the electrons in the pi bond are accessible to external reagents because they are located above and below the plane of the double bond rather than between the nuclei (Figure 3.6).
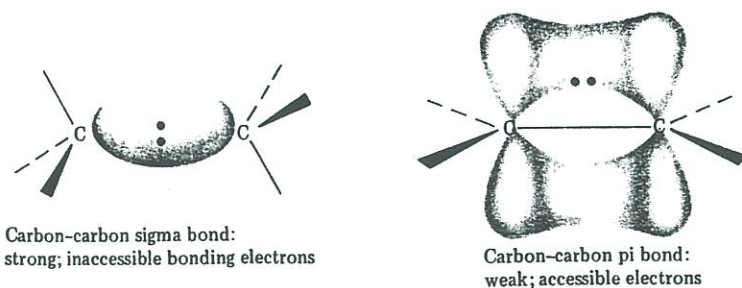


Carbon–carbon sigma bond:
strong; inaccessible bonding electrons

Carbon–carbon pi bond:
weak; accessible electrons

**FIGURE 3.6** A comparison of carbon–carbon single and double bonds. A double bond is ... electron rich and more accessible to external reagents than a single bond.

Both electron richness and electron accessibility lead us to predict high reactivity for carbon–carbon double bonds. In the terminology of polar reactions used earlier, we might predict that carbon–carbon double bonds should behave as nucleophiles. That is, the chemistry of alkenes should involve reaction of the electron-rich double bond with electron-poor reagents. This is exactly what we find: The most important reaction of alkenes is their reaction with electrophiles.

What about HCl? As a strong acid, HCl is a powerful proton ($H^+$) donor. Since a proton is positively charged and electron-poor, it is a good electrophile. Thus, the reaction between $H^+$ and ethylene is a typical electrophile–nucleophile combination, characteristic of all polar reactions.

## 3.8 THE MECHANISM OF AN ORGANIC REACTION: ADDITION OF HCl TO ETHYLENE

We can view the electrophilic addition reaction between ethylene and HCl as proceeding by the mechanism shown in Figure 3.7. The reaction takes place in two steps, beginning with an attack on the electrophile, $H^+$, by the electron pair from the nucleophilic ethylene pi bond. Two electrons from the pi bond form a new sigma bond between the entering hydrogen and one of the ethylene carbons, as shown by tracing the path of the curved arrow in Figure 3.7. (Remember: A curved arrow is used to indicate how electrons move in a polar reaction. In this case, the arrow ...

The electrophile $H^+$ is attacked by the pi electrons of the double bond, and a new C–H sigma bond is formed. This leaves the other carbon atom with a + charge and a vacant $p$ orbital.



Carbocation
intermediate

$Cl^-$ donates an electron pair to the positively charged carbon atom, forming a C–Cl sigma bond and yielding the neutral addition product.
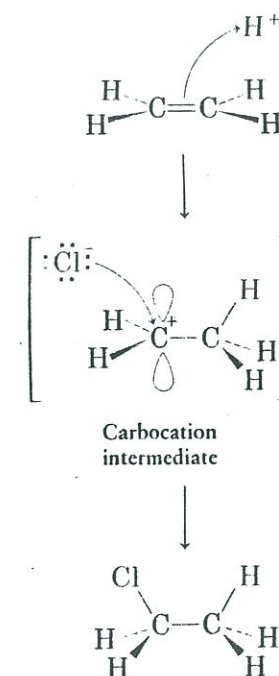
**FIGURE 3.7** The mechanism of the electrophilic addition of HCl to ethylene. The reaction takes place in two steps and involves an intermediate carbocation.

electrons move away from the carbon–carbon pi bond to form a new bond with the incoming $H^+$.) The other ethylene carbon atom, having lost its share of the pi electrons, is now trivalent and is left with a vacant $p$ orbital. Since the double-bond pi electrons were used in the formation of the new C–H bond, the trivalent carbon has only six valence electrons and therefore carries a positive charge. In the second step, this positively charged species, a carbon-cation or **carbocation**, is itself an electrophile that can accept an electron pair from the nucleophilic chloride anion to form a C–Cl bond, yielding the neutral addition product.

**carbocation**
ecies that has
sitively
ged, trivalent
on atom

**PRACTICE
PROBLEM 3.5**   What product would you expect from reaction of HCl with cyclohexene?

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



Cyclohexene                 Chlorocyclohexane
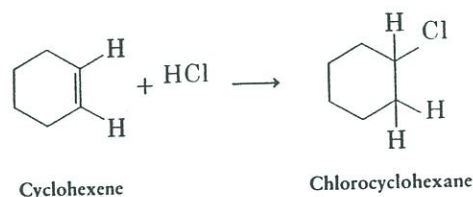
**PROBLEM 3.15**   Reaction of HCl with 2-methylpropene yields 2-chloro-2-methylpropane. Formulate the mechanism of the reaction. What is the structure of the carbocation formed during the reaction?
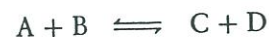
$$(CH_3)_2C=CH_2 + HCl \longrightarrow (CH_3)_3C—Cl$$

**PROBLEM 3.16**   Reaction of HCl with 2-pentene yields a mixture of two addition products. Write the reaction and show the two products.

## .9   DESCRIBING A REACTION: RATES AND EQUILIBRIA

Every chemical reaction can go in two directions. Starting materials can react to give products, and products can revert to starting materials. We usually express the resultant chemical equilibrium by an equation in which $K_{eq}$, the **equilibrium constant**, is equal to the concentration of products, divided by the concentration of starting materials. For the reaction,

$$A + B \rightleftharpoons C + D$$

we have

**quilibrium
onstant**
value that
presses the
tent to which a
ven reaction
kes place at
quilibrium

$$K_{eq} = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[C][D]}{[A][B]}$$

The equilibrium constant tells us the position of the equilibrium, that is, which side of the reaction arrow is energetically favored. If $K_{eq}$ is large, then the

and [B], and the reaction proceeds as written from left to right. Conversely, if $K_{eq}$ is small, the reaction does not take place as written but instead goes from right to left.

What the equilibrium equation does not tell us is the rate of the reaction: how fast the equilibrium is established. Some reactions are extremely slow even though they have highly favorable equilibrium constants. For example, gasoline is stable when stored because its reaction rate with oxygen is slow under normal circumstances. Under the proper reaction conditions, however (contact with a lighted match, for example), gasoline reacts rapidly with oxygen and undergoes complete conversion to water and carbon dioxide. Rates (*how fast* a reaction occurs) and equilibria (*how much* a reaction occurs) are two entirely different things.

Rate        $\longrightarrow$   Is reaction fast or slow?

Equilibrium  $\longrightarrow$   In what direction does reaction proceed?

What determines whether a reaction takes place? For a reaction to have a favorable equilibrium constant, the energy level of the products must be lower than the energy level of the reactants. In other words, energy (heat) must be given off. Such reactions are said to be **exothermic** (from the Greek *exo*, "outside," and *therme*, "heat"). Heat is produced during exothermic reactions. If the energy level of the products is higher than the energy level of the reactants, then the equilibrium constant for the reaction is unfavorable, and heat must be added to make the reaction take place. Such reactions are said to be **endothermic** (Greek *endon*, "within").

**exothermic**
a favorable
reaction that gives
off energy (heat)

**endothermic**
an unfavorable
reaction that
absorbs energy
(heat)

A good analogy for the relationship between energy and chemical reactivity (stability) is that of a rock poised near the top of a hill. The rock, in its unstable position, has stored the energy that was required to get it up there. When it rolls downhill, it releases its energy until it reaches a stable, low-energy position at the bottom of the hill. In the same way, the energy level in a chemical reaction goes downhill as the energy stored in the chemical bonds of a reactant is released and a more stable product is formed (Figure 3.8).
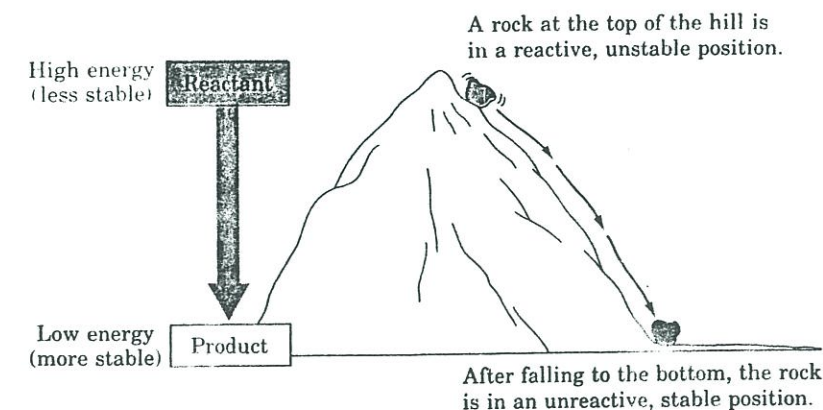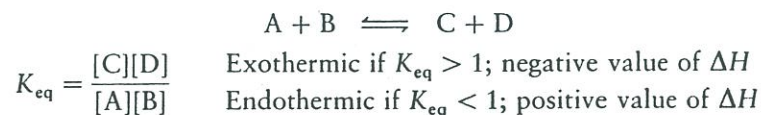


**FIGURE 3.8**  The relationship between energy and stability. Like a rock near the top of a hill, high-energy substances are unstable. They release their energy by dropping downhill

The exact amount of energy either released in an exothermic reaction or absorbed in an endothermic reaction is called the **heat of reaction**, $\Delta H$ (spoken as delta-H). By convention, $\Delta H$ has a negative value in an exothermic reaction since heat is released, and a positive value in an endothermic reaction since heat is absorbed. $\Delta H$ is a direct measure of the difference in energy between products and starting materials. As such, the size of $\Delta H$ determines the size of the equilibrium constant $K_{eq}$. Favorable reactions with large $K_{eq}$'s are highly exothermic and have negative heats of reaction whereas unfavorable reactions with small $K_{eq}$'s are endothermic and have positive heats of reaction.

$$A + B \rightleftharpoons C + D$$

$$K_{eq} = \frac{[C][D]}{[A][B]}$$

Exothermic if $K_{eq} > 1$; negative value of $\Delta H$
Endothermic if $K_{eq} < 1$; positive value of $\Delta H$

**PRACTICE PROBLEM 3.6**  Which reaction is more favorable, one with $\Delta H = -15$ kcal/mol or one with $\Delta H = +15$ kcal/mol?

SOLUTION  According to convention, reactions with negative $\Delta H$ are exothermic and thus are favorable, but reactions with positive $\Delta H$ are endothermic and unfavorable.

**PROBLEM 3.17**  Which reaction is more exothermic, one with $\Delta H = -10$ kcal/mol or one with $\Delta H = +10$ kcal/mol?

**PROBLEM 3.18**  Which reaction is more exothermic, one with $K_{eq} = 100$ or one with $K_{eq} = 0.001$?

## 0  DESCRIBING A REACTION: REACTION ENERGY DIAGRAMS AND TRANSITION STATES

For a reaction to take place, reactant molecules must collide, and reorganization of atoms and bonds must occur. Let's look again at the addition reaction between ethylene and HCl:
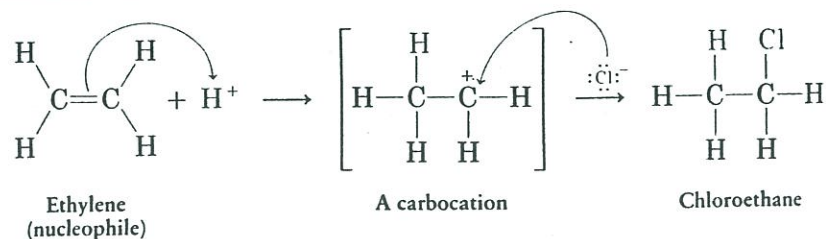
As the reaction proceeds, ethylene and HCl approach each other, the pi bond breaks, a new carbon–hydrogen bond forms in the first step, and a new carbon–chlorine bond forms in the second step.

Over the years, chemists have developed a method for depicting the energy changes that occur during a reaction using *reaction energy diagrams* of the sort shown in Figure 3.9. The vertical axis of the diagram represents the total energy of all reactants, and the horizontal axis represents the progress of the reaction from beginning (left) to end (right). Let's take a careful look at the reaction, one step at a time, and see how the addition of HCl to ethylene can be described on a reaction energy diagram.
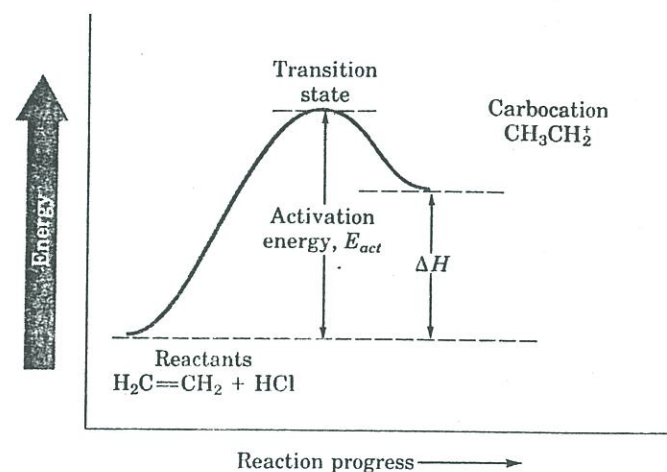
FIGURE 3.9  A reaction energy diagram for the first step in the reaction of ethylene with HCl. The energy difference between reactants and transition state, $E_{act}$, controls the reaction rate. The energy difference between reactants and carbocation product, $\Delta H$, controls the position of the equilibrium.

At the beginning of the reaction, ethylene and HCl have the total amount of energy indicated by the reactant level 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 carbon–hydrogen bond starts to form. At some point, a structure of maximum energy is reached, a structure we call the **transition state**.

The transition state represents the highest-energy structure involved in this step of the reaction and can't be isolated. Nevertheless, we can imagine the transition state to be a kind of activated complex of the two reactants in which the carbon–carbon pi bond is partially broken and the new carbon–hydrogen bond is partially formed (Figure 3.10).

The energy difference between reactants and transition state, called the **activation energy**, $E_{act}$, measures how rapidly the reaction occurs. A large activation energy corresponds to a large energy difference between reactants and transition state, and results in a slow reaction because few of the reacting molecules collide with enough energy to climb the high barrier. A small activation energy, however, results in a rapid reaction because almost all reacting molecules are energetic enough to climb to the transition state.

**transition state** a hypothetical structure of maximum energy formed during the course of a reaction

**activation energy $E_{act}$** the energy difference between starting material and transition state
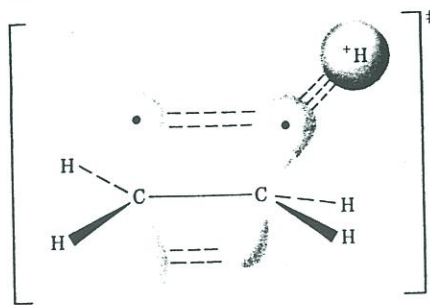
FIGURE 3.10 A hypothetical transition-state structure for the first step of the reaction of ethylene with HCl. The C–C pi bond is just beginning to break, and the C–H bond is just beginning to form.

The situation of reactants needing enough energy to climb the barrier from starting material to transition state is similar once again to the situation of a rock near the top of a hill. Although the rock would be more stable at the bottom of the hill, it is effectively trapped behind a barrier in a depression and is not able to fall spontaneously. Before the rock can release its energy in a fall, it has to be shoved up and over the barrier. In other words, energy has to be put into the rock to activate it for a fall.

Most organic reactions have activation energies in the range of 10–35 kcal/mol. Reactions with activation energies less than 20 kcal/mol take place spontaneously at room temperature or below whereas reactions with higher activation energies normally require heating. Heat provides the energy necessary for the reactants to climb the activation barrier.

Once the high-energy transition state has been reached, the reaction proceeds to the carbocation product. Energy is released as the new C–H bond forms fully, and the curve on the reaction energy diagram therefore turns downward until it reaches a minimum. This minimum point represents the energy level of the carbocation product of the first step. The energy change, $\Delta H$, between starting materials and carbocation product is simply the difference between the two levels on the diagram.[1] Since the carbocation is less stable than the starting alkene, the first step is endothermic, and energy is absorbed.

---

**PROBLEM 3.19** Which reaction is faster: one with $E_{act} = 15$ kcal/mol or one with $E_{act} = 20$ kcal/mol? Is it possible to predict which of the two has the larger $K_{eq}$?

---

## .11  DESCRIBING A REACTION: INTERMEDIATES _____

How can we describe the carbocation structure formed in the first step of the reaction of ethylene with HCl? The carbocation is clearly different from the starting materials, yet it isn't a transition state and it isn't a final product.

[1] Strictly speaking, it's not correct to say that the energy difference between starting materials and products is due entirely to the heat of the reaction, $\Delta H$. The energy difference is actually defined as the Gibbs free energy ($\Delta G$), which is equal to the heat of reaction ($\Delta H$) minus an entropy contribution $\Delta S$: ($\Delta G = \Delta H - T\,\Delta S$). Normally, though, the entropy contribution is small, and we make the simplifying

Ethylene · Reaction intermediate · Chloroethane
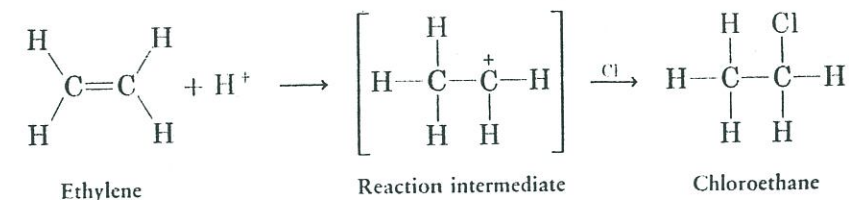
**intermediate**
a species that is formed during the course of a multistep reaction but is not the final product. Intermediates lie at minima in reaction energy diagrams

We call the carbocation, which is formed briefly during the course of the multistep reaction, a reaction **intermediate**. As soon as the intermediate is formed in the first step by reaction of ethylene with $H^+$, it reacts with $Cl^-$ in a second step to give the final product, chloroethane. This second step has its own activation energy $E_{act}$, its own transition state, and its own energy change $\Delta H$. We can view the second transition state as an activated complex between the electrophilic carbocation intermediate and nucleophilic chloride anion, a complex in which the new C–Cl bond is just starting to form.

A complete energy diagram for the overall reaction of ethylene with HCl can be constructed as in Figure 3.11. In essence, we draw diagrams for each of the individual steps and join them in the middle so that the product of step 1 (the carbocation) serves as the starting material for step 2. As indicated in Figure 3.11, the reaction intermediate lies at an energy minimum between steps 1 and 2. Since the energy level of this intermediate is higher than the level of either the starting material (ethylene + HCl) or the product (chloroethane), the intermediate is highly reactive and can't be isolated. It is, however, more stable than either of the two transition states that surround it.
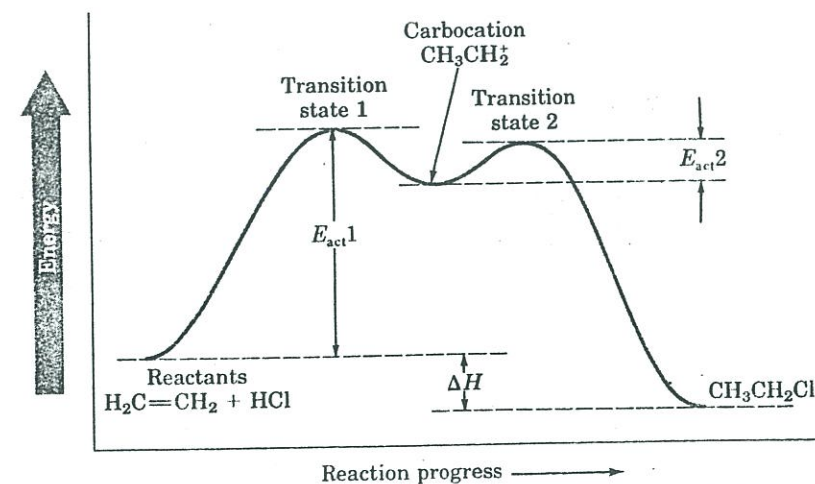


FIGURE 3.11 Overall reaction energy diagram for the reaction of ethylene with HCl. Two steps are involved, each with its own transition state. The energy minimum between the two steps represents the reaction intermediate.

Each step in a multistep process can be considered separately. Each step has its own $E_{act}$ (rate) and its own $\Delta H$ (energy change). The overall $\Delta H$ of the reaction,

however, is the energy difference between initial reactants (far left) and final products (far right). This is always true regardless of the shape of the reaction energy curve. Note, for example, that the energy diagram for the reaction of HCl with ethylene in Figure 3.11 shows the energy level of the final product to be lower than the energy level of the starting material. Thus, the overall reaction is exothermic.

**PRACTICE PROBLEM 3.7** Sketch a reaction energy diagram for a one-step reaction that is very fast and highly exothermic.

SOLUTION A very fast reaction has a small $E_{act}$, and a highly exothermic reaction has a large negative $\Delta H$. Thus, the diagram will look like this one:
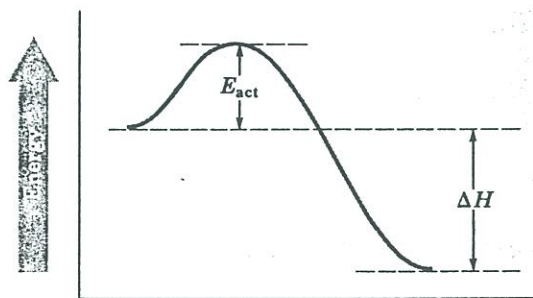


**PROBLEM 3.20** Sketch reaction energy diagrams to represent the following situations and label the parts of the diagram corresponding to starting material, product, transition state, intermediate (if any), activation energy, and $\Delta H$.
(a) An exothermic reaction that takes place in one step.
(b) An endothermic reaction that takes place in one step.

**PROBLEM 3.21** Draw a reaction energy diagram for a two-step reaction with an endothermic first step and an exothermic second step. Label the intermediate.

**NTERLUDE**

# Carrots, Alkenes, and the Chemistry of Vision

Folk medicine has long maintained that eating carrots improves night ᵗˡthough that's probably not true for healthy adults on a proper diet, ᵗestion that the chemistry of carrots and the chemistry of vision are · play a role in both.
ˑʰ in β-carotene, a purple-orange alkene that is an excellent

---

where enzymes first cut the molecule in half and then change the geometry of the C11–C12 double bond to produce 11-*cis*-retinal, the light-sensitive pigment on which the visual systems of all living things are based.



β-Carotene
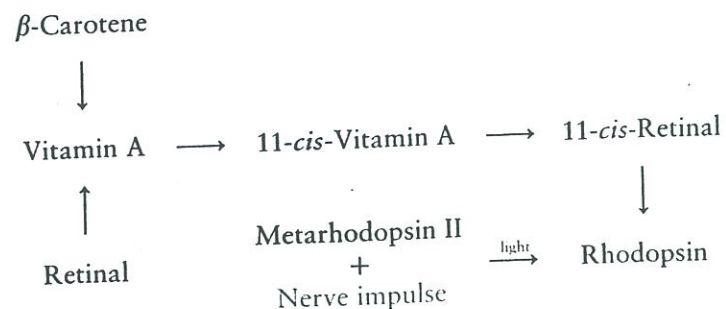


Vitamin A                    11-*cis*-Retinal
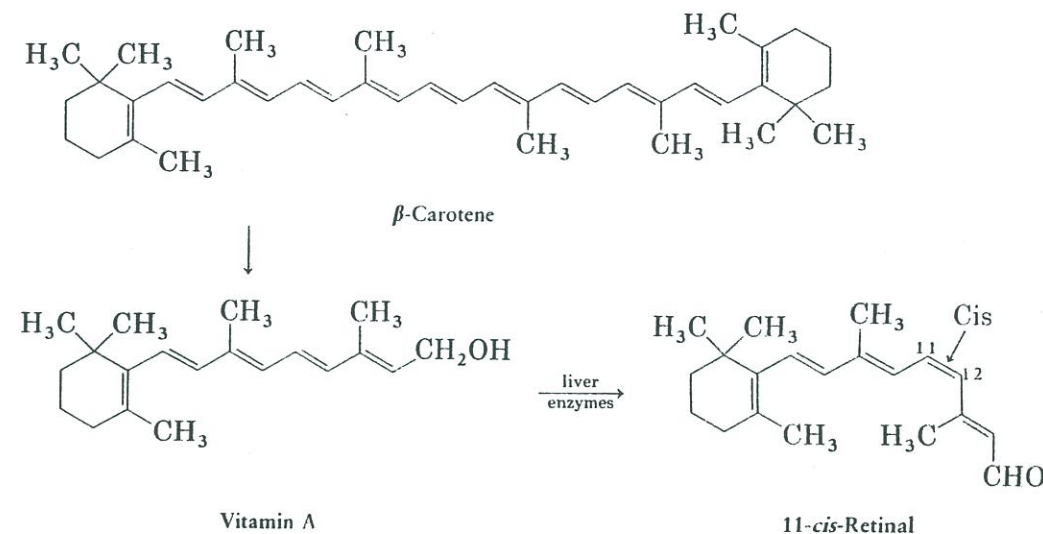
The retina of the eye contains two types of light-sensitive receptor cells, *rod* cells and *cone* cells. Rod cells are primarily responsible for seeing in dim light, whereas cone cells are responsible for seeing in bright light and for the perception of colors. In the rod cells of the eye, 11-*cis*-retinal is converted into *rhodopsin*, a light-sensitive substance formed from the protein *opsin* and 11-*cis*-retinal. When light strikes the rod cell, isomerization of the C11–C12 double bond occurs, and 11-*trans*-rhodopsin, also called metarhodopsin II, is produced. This cis–trans isomerization of rhodopsin 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.
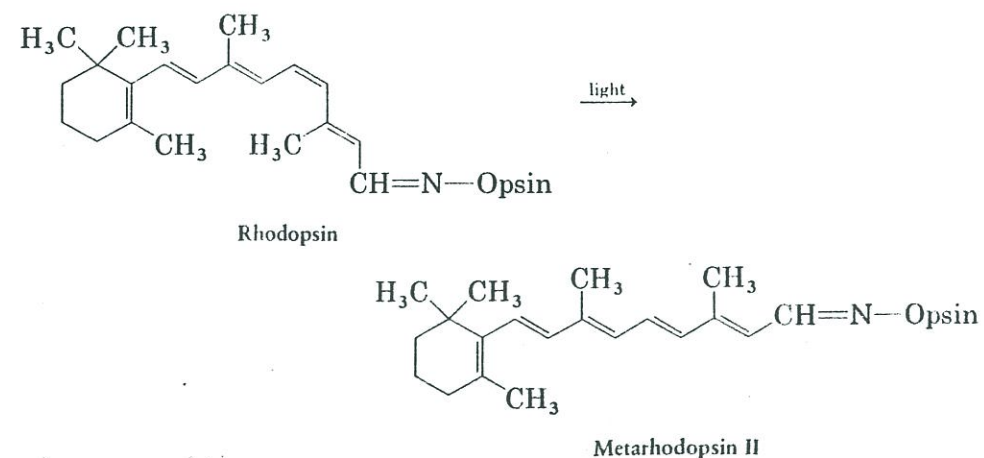


Rhodopsin



Metarhodopsin II

Metarhodopsin II is then recycled into rhodopsin by a multistep sequence involving cleavage into all-*trans*-retinal, conversion to vitamin A, cis–trans isomerization to 11-*cis*-vitamin A, and conversion back to 11-*cis*-retinal.

β-Carotene

↓

Vitamin A ⟶ 11-*cis*-Vitamin A ⟶ 11-*cis*-Retinal

↑                                              ↓

Retinal        Metarhodopsin II   —light→  Rhodopsin
                      +
                Nerve impulse

## MMARY AND KEY WORDS

Alkenes are hydrocarbons that contain carbon–carbon double bonds. A double bond consists of two parts: a **sigma bond** formed by head-on overlap of two $sp^2$ orbitals and a **pi bond** formed by sideways overlap of two $p$ orbitals. The bond strength of an alkene double bond is greater than that of a carbon–carbon single bond, with the strength of the pi part estimated to be 64 kcal/mol.

Rotation around the double bond is restricted, and substituted alkenes can therefore exist as **cis–trans isomers**. The geometry of a double bond can be described as either $Z$ (*zusammen*) or $E$ (*entgegen*) by application of a series of sequence rules.

All organic reactions involve bond making and bond breaking. Fundamentally, covalent two-electron bonds can break or form in only two ways: Bonds can break in an electronically symmetrical (**homolytic**) way such that each product retains one electron or in an electronically unsymmetrical (**heterolytic**) way such that one product retains both electrons, leaving the other product with a vacant valence orbital. Conversely, bonds can form in an electronically symmetrical (**homogenic**) way if each of two reactants donates one electron or in an electronically unsymmetrical (**heterogenic**) way if one reactant donates two electrons. Electronically symmetrical bond making and bond breaking occur in **radical reactions** whereas electronically unsymmetrical bond making and bond breaking occur in **polar reactions**:

$$A\cdot + \cdot B \longrightarrow A:B \qquad \text{Radical reactions}$$
$$A^+ + :B^- \longrightarrow A:B \qquad \text{Polar reactions}$$
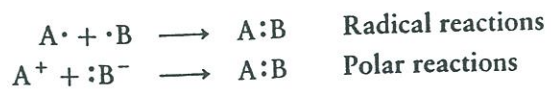
nergy changes that take place during a reaction can be described by
a reaction occurs) and **equilibria** (to what extent the reaction occurs).
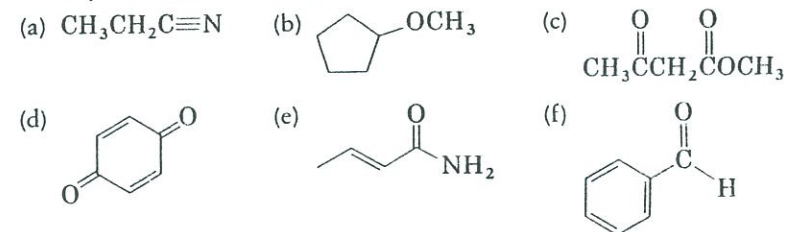osition of a reaction is determined by $\Delta H$, the energy change

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thermic, however, energy is absorbed, and the reaction has an unfavorable equilibrium constant. Reactions can be described pictorially by **reaction energy diagrams**, which follow the course of a reaction from starting material through transition state to product.

Every reaction proceeds through a **transition state**, which is the highest energy point reached. Transition-state structures can't be isolated because they are unstable, but we can imagine them to be activated complexes between starting materials, in which old bonds are beginning to break and new bonds are beginning to form. The amount of energy needed by starting materials to reach the high-energy transition state is the activation energy, $E_{act}$. The larger the magnitude of the activation energy, the slower the reaction.

Many reactions, such as the addition of HCl to ethylene, take place in more than one step and involve the formation of **intermediates**. A reaction intermediate is a structure 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.
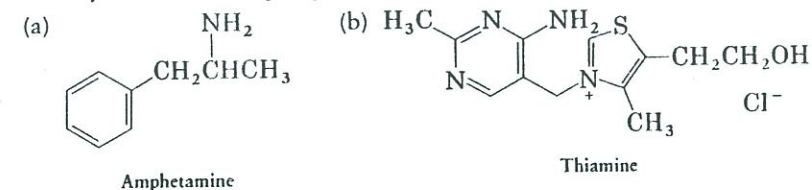
## ADDITIONAL PROBLEMS

**3.22** Identify the functional groups in these molecules:

(a) $CH_3CH_2C{\equiv}N$  (b) ⬠—$OCH_3$  (c) $CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OCH_3$

(d) [structure]  (e) [structure]—$NH_2$  (f) [structure]—$\overset{O}{\overset{\|}{C}}{\diagdown}_H$
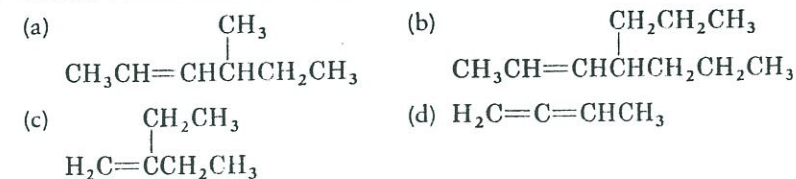
**3.23** Predict the direction of polarization of the functional groups you identified in Problem 3.22.

**3.24** Identify the functional groups in these molecules:

(a) [structure] $\overset{NH_2}{\underset{}{}}$ $CH_2\overset{}{C}HCH_3$

Amphetamine

(b) $H_3C{\diagdown}_N{\diagup}{\diagdown}^{NH_2}\ _S$ ... $CH_2CH_2OH$ ... $CH_3$ ... $Cl^-$

Thiamine

**3.25** Provide IUPAC names for these alkenes:

(a) $CH_3CH{=}CH\overset{CH_3}{\underset{|}{C}}HCH_2CH_3$

(b) $CH_3CH{=}CHCH\overset{CH_2CH_2CH_3}{\underset{|}{}}CH_2CH_2CH_3$

(c) $H_2C{=}\overset{CH_2CH_3}{\underset{|}{C}}CH_2CH_3$

(d) $H_2C{=}C{=}CHCH_3$

**3.26** Name these cycloalkenes by IUPAC rules.

(a) [structure]—$CH_3$  (b) [structure]—$CH_3$  (c) [structure]—$CH_2CH_3$  (d) [structure]—$CH_3$
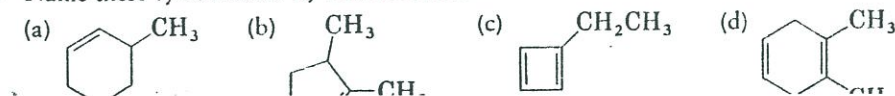
CHAPTER 3 Alkenes: The Nature of Organic Reactions

**3.27** Draw structures corresponding to these IUPAC names.

(a) 3-Propyl-2-heptene      (b) 2,4-Dimethyl-2-hexene
(c) 1,5-Octadiene      (d) 4-Methyl-1,3-pentadiene
(e) cis-4,4-Dimethyl-2-hexene      (f) (E)-3-Methyl-3-heptene

**3.28** Draw the structures of these cycloalkenes.

(a) cis-4,5-Dimethylcyclohexene      (b) 3,3,4,4-Tetramethylcyclobutene

**3.29** These names are incorrect. Draw each molecule and give its correct name.

(a) 1-Methyl-2-cyclopentene      (b) 1-Methyl-1-pentene
(c) 6-Ethylcycloheptene      (d) 3-Methyl-2-ethylcyclohexene

**3.30** Neglecting cis–trans isomers, there are five possible isomers of formula $C_4H_8$. Draw and name them.

**3.31** Which of the molecules you drew in Problem 3.30 show cis–trans isomerism? Draw and name their cis–trans isomers.

**3.32** Draw four possible structures for each of these formulas.

(a) $C_6H_{10}$      (b) $C_8H_8O$      (c) $C_7H_{10}Cl_2$

**3.33** How can you explain the fact that cyclohexene does not show cis–trans isomerism but cyclodecene does?

**3.34** Rank the following sets of substituents in order of priority according to the sequence rules.

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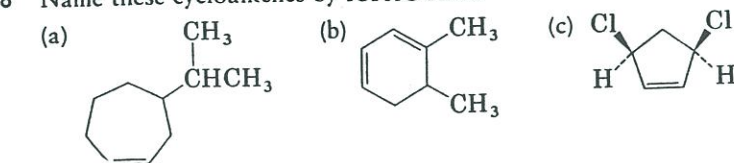(d) $-CH_3$, $-CH=CH_2$, $-CH_2CH_3$, $-CH(CH_3)_2$

**3.35** Assign E or Z configuration to these alkenes.
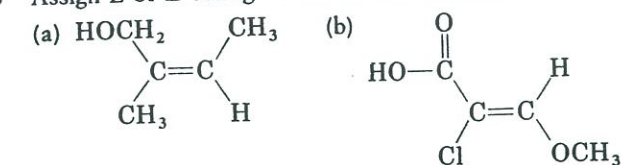


**3.36** Draw and name the five possible $C_5H_{10}$ alkene isomers. Ignore cis–trans isomers.

**3.37** Menthene, a hydrocarbon found in mint plants, has the IUPAC name 1-isopropyl-4-methylcyclohexene. What is the structure of menthene?
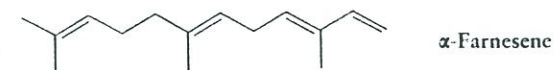
**3.38** Name these cycloalkenes by IUPAC rules.



se reagents as either electrophiles or nucleophiles.

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



α-Farnesene

**3.41** Indicate E or Z configuration for each of the double bonds in α-farnesene (Problem 3.40).

**3.42** Define these terms.

(a) Polar reaction      (b) Radical reaction
(c) Functional group      (d) Reaction intermediate

**3.43** Give an example of each of the following.

(a) An electrophile      (b) A nucleophile      (c) An oxygen-containing functional group

**3.44** If a reaction has $K_{eq} = 0.001$, is it likely to be exothermic or endothermic? Explain.

**3.45** If a reaction has $E_{act} = 5$ kcal/mol, is it likely to be fast or slow? Explain.

**3.46** If a reaction has $\Delta H = 12$ kcal/mol, is it exothermic or endothermic. Is it likely to be fast or slow? Explain.

**3.47** Draw a reaction energy diagram for a two-step exothermic reaction whose first step is faster than its second step. Label the parts of the diagram corresponding to reactants, products, transition state, activation energies, and overall $\Delta H$.

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

**3.49** Draw a reaction energy diagram for a reaction with $K_{eq} = 1$.

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

**3.51** Consider the reaction energy diagram shown here and answer the following questions.



Reaction progress ⟶
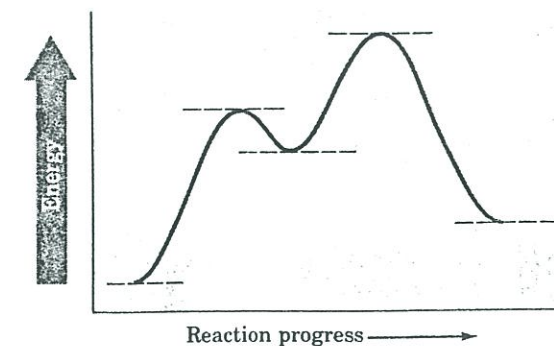
(a) Indicate the overall $\Delta H$ for the reaction. Is it positive or negative?
(b) How many steps are involved in the reaction?
(c) Which step is faster (has the lower activation energy)?
(d) How many transition states are there? Label them.