4.2 NOMENCLATURE OF ALKENES

A. IUPAC Substitutive Nomenclature

The IUPAC substitutive nomenclature of alkenes is derived by modifying alkane nomenclature in a simple way. An unbranched alkene is named by replacing the \textit{ane} suffix in the name of the corresponding alkane with the ending \textit{ene} and specifying the location of the double bond with a number. The carbons are numbered from one end of the chain to the other so that the double bond receives the lowest number. The carbons of the double bond are numbered consecutively.

\[
\text{H}_2\text{C} = \text{CH} - \text{CH}_2\text{CH}_2\text{CH}_3
\]

1-hexene

\text{hexane} + \text{ene} = \text{hexene}

The IUPAC recognizes an exception to this rule for the name of the simplest alkene, \text{H}_2\text{C} = \text{CH}_2, which is usually called ethylene rather than ethene. (Chemical Abstracts (Sec. 2.4D, p. 66), however, uses the substitutive name ethene.)

The names of alkenes with branched chains are, like those of alkanes, derived from their principal chains. In an alkene, the principal chain is defined as the carbon chain containing the greatest number of double bonds, even if this is not the longest chain. If more than one candidate for the principal chain have equal numbers of double bonds, the principal chain is the longest of these. The principal chain is numbered from the end that results in the lowest numbers for the carbons of the double bonds.

When the alkene contains an alkyl substituent, the position of the double bond, not the position of the branch, determines the numbering of the chain. This is the main difference in the nomenclature of alkenes and alkanes. However, the position of the double bond is cited in the name \textit{after} the name of the alkyl group. Study Problem 4.2 shows how these principles are implemented.

Study Problem 4.2

Name the following compound using IUPAC substitutive nomenclature.

\[
\text{H}_2\text{C} = \text{CHCH}_2\text{CH}_2\text{CH}_3
\]

\[
\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\]
**Solution** The principal chain is the longest continuous carbon chain containing both carbons of the double bond, as shown in color in the following structure. Note in this case that the principal chain is not the longest carbon chain in the molecule. The principal chain is numbered from the end that gives the double bond the lowest number—in this case, 1. The substituent group is a propyl group. Hence, the name of the compound is 2-propyl-1-heptene:

If a compound contains more than one double bond, the *ane* ending of the corresponding alkane is replaced by *adiene* (if there are two double bonds), *atriene* (if there are three double bonds), and so on.

\[
\text{H}_2\text{C}==\text{CHCH}_2\text{CH}_2\text{CH}==\text{CH}_2
\]

1,5-hexadiene

---

**Study Problem 4.3**

Name the following compound:

\[
\begin{align*}
\text{CH}_2&-\text{CH}==\text{CH}_2 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2&-\text{C}==\text{C}==\text{CH}_3 \\
&\text{CH}_3
\end{align*}
\]

**Solution** The principal chain (color in the following structure) is the chain containing the greatest number of double bonds. One possible numbering scheme (red) gives the first-encountered carbons of the two double bonds the numbers 1 and 4, respectively; the other possible numbering scheme (blue) gives the first-encountered carbons of the double bonds the numbers 2 and 5, respectively. We compare the two possible numbering schemes pairwise—that is, (1,4) versus (2,5). The lowest number at first point of difference (1 versus 2) determines the correct numbering. The compound is a 1,4-hexadiene, with a butyl branch at carbon-4, and a methyl branch at carbon-5:

If the name remains ambiguous after determining the correct numbers for the double bonds, then the principal chain is numbered so that the lowest numbers are given to the branches at the first point of difference.
Study Problem 4.4

Name the following compound:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

\textbf{Solution} Two ways of numbering this compound give the double bond the numbers 1 and 2.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
5 & 1 & 6 & 2 \quad \text{CH}_3 \\
4 & 3 & 2 & 1 \\
\end{align*}
\]

possible names: \textbf{1,6-dimethylcyclohexene} \quad \textbf{(correct)} \\
\textbf{2,3-dimethylcyclohexene} \quad \textbf{(incorrect)}

In this situation, choose the numbering scheme that gives the lowest number for the methyl substituents \textit{at the first point of difference}. In comparing the substituent numbering schemes (1,6) with (2,3), the first point of difference occurs at the first number (1 versus 2). The (1,6) numbering scheme is correct because 1 is lower than 2. Notice that the number 1 for the double bond is not given explicitly in the name, because this is the only possible number. That is, when a double bond in a ring receives numerical priority, its carbons must be numbered consecutively with the numbers 1 and 2. That’s why the following numbering scheme is incorrect. One carbon of the double bond has the number 1, but the other is not numbered consecutively.

\[
\begin{align*}
\text{CH}_3 & \\
3 & \quad \text{CH}_3 \\
1 & 2 & 3 & 4 & 5 & 6 \\
\end{align*}
\]

\textbf{1,2-dimethylcyclohexene} \\
\textbf{(incorrect because carbons of double bond are not numbered consecutively)}

Substituent groups may also contain double bonds. Some widely occurring groups of this type have special names that must be learned:

\[
\begin{align*}
\text{H}_2\text{C} & \equiv \text{CH} & \text{H}_2\text{C} & \equiv \text{CH}_2 & \text{H}_2\text{C} & \equiv \text{C} \quad \text{CH}_3 \\
\text{vinyl} & & \text{allyl} & & \text{isopropenyl} \\
\end{align*}
\]

Other substituent groups are numbered \textit{from the point of attachment to the principal chain}.

\[
\begin{align*}
\text{CH}_3 & \equiv \text{CH}_2 & \quad \text{CH}_2 \equiv \text{CH} \equiv \text{CH} - \text{CH}_3 \\
\text{3-vinylcyclohexene} & & \text{1-(2-butenyl)cyclohexene} \\
\end{align*}
\]
The names of these groups, like the names of ordinary alkyl groups, are constructed from the name of the parent hydrocarbon by dropping the final \( e \) from the name of the corresponding alkene and replacing it with \( yl \). Thus, the substituent in the second example above is \( \text{butene}^\ddagger + yl = \text{butenyl} \). Notice the use of parentheses to set off the names of substituents with internal numbering.

Finally, some alkenes have nonsystematic traditional names that are recognized by the IUPAC. These can be learned as they are encountered. Two examples are styrene and isoprene:

\[
\begin{align*}
\text{Ph} & \text{CH} \equiv \text{CH}_2 & \text{H}_2\text{C} = \text{C} \equiv \text{CH} \equiv \text{CH}_2 \\
\text{styrene} & \quad \text{isoprene}
\end{align*}
\]

(Recall from Sec. 2.9B, p. 82, that Ph— refers to the phenyl group, a singly substituted benzene ring.)

**More Recent IUPAC Nomenclature Recommendations**

The nomenclature in this text is based on the widely used 1979 IUPAC rules. In 1993, the IUPAC recommended an alteration in nomenclature that places the number of the double bond just before the \textit{ene} suffix of the name. Thus, in the new system, \textit{1-hexene} is named \textit{hex-1-ene}, and \textit{2,4-hexadiene} is named \textit{hexa-2,4-diene}. This new system is being used by some chemists and not by others. While the system is logical, its general adoption would require chemical indexing systems either to recognize both old and new names or to cross-reference between them. Because \textit{Chemical Abstracts} has not adopted the new system, we won’t use it in this text. However, conversion between old and new names is a simple matter of moving the numerical designation.

**PROBLEMS**

4.2 Give the structure for each of the following:
(a) \( 4\text{-methyl-1,3-hexadiene} \)
(b) \( 2\text{-methylpropene} \)
(c) \( 1\text{-isopropenylcyclopentene} \)
(d) \( 5\text{-}(3\text{-pentenyl})-1,3,6,8\text{-decatetraene} \)

4.3 Name the following compounds.
(a) \( \text{CH}_3 \)
(b) \( \text{CH}_3\text{CH}_2\text{CH} \equiv \text{CHCH}_2\text{CH}_2\text{CH}_3 \)
(c) \( \text{H}_2\text{C} = \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH}_2 \equiv \text{CH} \equiv \text{CH}_3 \)

**B. Nomenclature of Double-Bond Stereoisomers: The \textit{E,Z} System**

The \textit{cis} and \textit{trans} designations for double-bond stereoisomers are unambiguous when each carbon of a double bond has a single hydrogen, as in \textit{cis-} and \textit{trans-2-butene}. However, in some important situations, the use of the terms \textit{cis} and \textit{trans} is ambiguous. For example, is the following compound, a stereoisomer of \( 3\text{-methyl-2-pentene} \), the \textit{cis-} or the \textit{trans-} stereoisomer?
One person might decide that this compound is trans, because the two identical groups are on opposite sides of the double bond. Another might decide that it is cis, because the larger groups are on the same side of the double bond. Exactly this sort of ambiguity—and the use of both conventions simultaneously in the chemical literature—brought about the adoption of an unambiguous system for the nomenclature of stereoisomers. This system, first published in 1951, is part of a general system for the nomenclature of stereoisomers called the Cahn–Ingold–Prelog system after its inventors, Robert S. Cahn (1899–1981), then editor of the Journal of the Chemical Society, the most prestigious British chemistry journal; Sir Christopher K. Ingold (1893–1970), a professor at University College, London, whose work played a very important part in the development of modern organic chemistry; and Vladimir Prelog (1906–1998), a professor at the Swiss Federal Institute of Technology, who received the 1975 Nobel Prize in Chemistry for his work in organic stereochemistry. When we apply the Cahn–Ingold–Prelog system to alkene double-bond stereochemistry, we’ll refer to it simply as the \( E, Z \) system for reasons that will be immediately apparent.

The \( E, Z \) system involves assignment of relative priorities to the two groups on each carbon of the double bond according to a set of sequence rules given in the steps to be described below. We then compare the relative locations of these groups on each alkene carbon. If the groups of higher priority are on the same side of the double bond, the compound is said to have the \( Z \) configuration (\( Z \) from the German word \textit{zusammen}, meaning “together”). If the groups of higher priority are on opposite sides of the double bond, the compound is said to have the \( E \) configuration (\( E \) from the German \textit{entgegen}, meaning “across”).

\[
\begin{align*}
&\text{high priority} & \text{high priority} & \text{high priority} & \text{low priority} \\
&\text{low priority} & \text{low priority} & \text{low priority} & \text{high priority}
\end{align*}
\]

For a compound with more than one double bond, the configuration of each double bond is specified separately.

To assign relative priorities, proceed through each of the following steps in order until a decision is reached. Study Problems 4.5 and 4.6 illustrate the use of these steps.

**Step 1** Examine the atoms directly attached to a given carbon of the double bond, and then follow the first rule that applies.

- **Rule 1a** Assign higher priority to the group containing the atom of higher atomic number.
- **Rule 1b** Assign higher priority to the group containing the isotope of higher atomic mass.

**Step 2** If the atoms directly attached to the double bond are the same, then, working outward from the double bond, consider within each group the set of attached atoms. You’ll have two sets—one for each group on the double bond.

- **Rule 2** Arrange the attached atoms within each set in descending priority order, and make a pairwise comparison of the atoms in the two sets. The higher priority is assigned to the atom of higher atomic number (or atomic mass in the case of isotopes) at the first point of difference.

**Step 3** If the sets of attached atoms are identical, move away from the double bond within each group to the next atom following the path of highest priority, and identify new sets of attached atoms. Then apply rule 2 to these new sets. Keep following this step until a decision is reached. Remember that a priority decision must be made at the first point of difference.
Study Problem 4.5

What is the configuration of the following stereoisomer of 3-methyl-2-pentene? (The numbers and letters are for reference in the solution.)

\[
\begin{align*}
\text{CH}_3 & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H}_3 & \quad \text{CH}_3
\end{align*}
\]

**Solution** First, consider the relative priorities of the groups attached to carbon-2. Applying rule 1a, the two atoms directly attached to carbon-2 are C and H. Because C has a higher atomic number (6) than H (1), the CH\(_3\) group is assigned the higher priority. Now consider the groups attached to carbon-3. Step 1 leads to no decision, because in both groups the atom directly attached to the double bond is the same—a carbon \(m\) in the case of the methyl group, and a carbon \(e\) in the case of the ethyl group. Following step 2, represent the atoms attached to these carbons as a set in descending priority order. For carbon \(e\), the set is \((C,H,H)\); notice that the carbon of the double bond is not included in the set. For carbon \(m\), the set is \((H,H,H)\). Now make a pairwise comparison of \((C,H,H)\) with \((H,H,H)\). The first point of difference occurs at the comparison of the first atoms of each set, C and H. Because C has higher priority, the group containing this atom—the ethyl group—also has higher priority. The priority pattern is therefore

\[
\begin{align*}
\text{higher priority group} & \quad \text{H}_3C \\
\text{at carbon-2} & \quad \text{C} \\
\text{lower priority group} & \quad \text{H} \\
\text{at carbon-2} & \quad \text{CH}_3 \\
\text{higher priority group} & \quad \text{CH}_3 \\
\text{at carbon-3} & \quad \text{CH}_3 \\
\text{lower priority group} & \quad \text{CH}_2CH_3 \\
\text{at carbon-3} & \quad \text{H}_3C
\end{align*}
\]

Because groups of like priority are on opposite sides of the double bond, this alkene is the \(E\) isomer; its complete name is \((E)-3\)-methyl-2-pentene.

Study Problem 4.6

Name the following alkene. (The numbers and letters are for reference in the solution.)

\[
\begin{align*}
\text{H} & \quad \text{H}_3C \\
\text{C} & \quad \text{C} \\
\text{H}_3 & \quad \text{CH}_2CH_2CH_3 \\
\text{H} & \quad \text{H}_3C
\end{align*}
\]

**Solution** At carbon-2, the methyl group has higher priority, by rule 1a. At carbon-3, rule 1a allows no decision, because atoms \(a1\) and \(b1\) are identical—both are carbons. Proceeding to step 2, the set of atoms attached to either carbons \(a1\) or \(b1\) can be represented as \((C,H,H)\); again, no decision is possible. Step 3 says that we must now consider the next atoms in each chain along the path of highest priority. We therefore move to the next carbon atom \((a2\) and \(b2)\) rather than the hydrogen in each chain, because carbon has higher priority than hydrogen. The set of atoms attached to \(a2\) is \((C,H,H)\); the set attached to \(b2\) is \((C,C,H)\). Notice that carbons \(a1\) and \(b1\) considered in the previous step are not considered as members of these sets, because we always work outward, away from the double bond, by step 2. The difference in the second atoms of each set—C versus H—dictates a decision. Because the set of atoms at carbon \(b2\) has higher priority,
the group containing carbon \( b2 \) (the isobutyl group) also has the higher priority. The process used can be summarized as follows:

\[
\begin{align*}
\text{H} & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3 \\
\text{(C,H,H)} & \quad \text{(C,H,H)} \\
\text{H}_3\text{C} & \quad \text{CH}_2 \quad \text{CH(CH}_3)_2 \\
\text{(C,H,H)} & \quad \text{(C,H,H)}
\end{align*}
\]

Because the groups of like priority are on the same side of the double bond, this alkene has the \( Z \) configuration.

Application of the nomenclature rules completes the name: \((Z)-3\text{-isobutyl-2-heptene}\).

Sometimes the groups to which we must assign priorities themselves contain double bonds. Double bonds are treated by a special convention, in which the double bond is rewritten as a single bond and the atoms at each end of the double bond are duplicated:

\[
\begin{align*}
\text{—CH\equiv CH}_2 & \text{ is treated as } \text{—CH—CH}_2 \text{ and } \text{—CH\equiv O} & \text{ is treated as } \text{—CH—O} \\
\text{C} & \quad \text{C} & \quad \text{O} & \quad \text{C}
\end{align*}
\]

Notice that the duplicated atoms bear only one bond. (The developers of this scheme preferred to say that each of these duplicated carbons “bears three phantom (that is, imaginary) atoms of priority zero.”) The treatment of triple bonds requires triplicating the atoms involved:

\[
\begin{align*}
\text{—C\equiv CH} & \text{ is treated as } \text{—C—CH} \quad \text{and } \text{—C\equiv N} & \text{ is treated as } \text{—C—N} \\
\text{C} & \quad \text{C} & \quad \text{N} & \quad \text{C}
\end{align*}
\]

**Study Problem 4.7**

Give the IUPAC name of the following compounds, including the \((E,Z)\) designation for the double-bond stereochemistry. (The carbon numbers are for reference in the solution.)

(a) \((CH_3)_2CH \quad CH_3\)  
(b) \((CH_2)_2CH \quad CH_3\)

**Solution** (a) First, give the name without the stereochemistry. By the principles discussed previously, the name is 3-isopropyl-1,3-pentadiene. Now we assign stereochemistry. Carbons 1 and 2 are not stereocenters, but carbons 3 and 4 are. At carbon-4, the methyl group receives higher pri-
ority than H. The real issue here is the relative priorities of the groups at carbon-3. We represent the two groups as follows:

(The symbol \( \Rightarrow \) means “implies.”) Notice that the carbons of the double bond are duplicated; the colors show the relationship of the replicated carbons to the original ones. The (0,0,0) next to the duplicated carbons represents the “phantom atoms” attached to these carbons—that is, imaginary atoms of priority zero. We compare carbon \( a \) of the isopropyl group with carbon \( a \) of the vinyl group. The attached groups are the same: (C,H,H). In the isopropyl group, we proceed outward to either of the methyl groups. In the vinyl group, we could proceed to carbon \( b \) or to its duplicated image, carbon \( b' \). We must choose the path of higher priority before we compare the result with the isopropyl group. Choosing the path of higher priority requires going out one more atom beyond carbons \( b \) and \( b' \)—in other words, comparing (C,H,H) for \( C_b \) with (0,0,0) for \( C_{b'} \).

Because the carbon atom attached to carbon \( b \) has a higher priority than a phantom atom on carbon \( b' \), carbon \( b \) represents the path of higher priority for vinyl. Now we are ready to compare the vinyl and isopropyl groups again. For isopropyl, carbon \( b \) is C(H,H,H), and for vinyl, carbon \( b \) is C(C,H,H). Because C has a higher priority than H, vinyl receives the higher priority. The name is therefore \((E)-3\)-isopropyl-1,3-pentadiene.

You should be able to work part (b) using the same tactics. Try it. The name is \((2E,4Z)-3\)-isopropyl-2,4-pentadiene. (Notice that the position of the isopropyl group determines the numbering of the double bonds, which is ambiguous otherwise.) Notice also that when two or more double bonds require a stereochemical designation, the number of the double bond is included with the \( E \) or \( Z \).