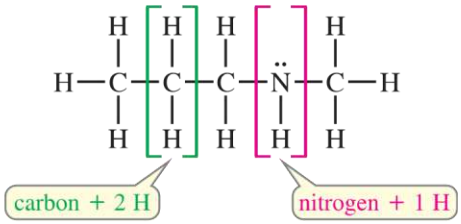
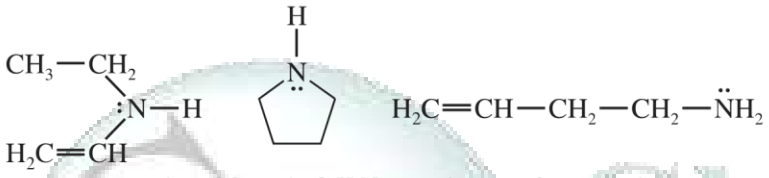
Nitrogen A nitrogen atom can take the place of a carbon atom in the chain, but nitrogen is trivalent, having only one additional hydrogen atom, compared with two hydrogens for each additional carbon atom. In computing the elements of unsaturation, *count nitrogen as half a carbon atom.*



The formula C_4H_9N is like a formula with $4\frac{1}{2}$ carbon atoms, with saturated formula $C_{4.5}H_{9+2}$. The formula C_4H_9N has one element of unsaturation, because it is two hydrogen atoms short of the saturated formula.



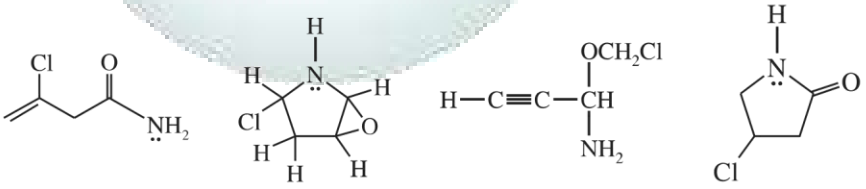
examples of formula C_4H_9N, one element of unsaturation

SOLVED PROBLEM 7-1

Draw at least four compounds of formula C_4H_6NOCl.

SOLUTION

Counting the nitrogen as $\frac{1}{2}$ carbon, ignoring the oxygen, and counting chlorine as a hydrogen shows the formula is equivalent to $C_{4.5}H_7$. The saturated formula for 4.5 carbon atoms is $C_{4.5}H_{11}$, so C_4H_6NOCl has two elements of unsaturation. These could be two double bonds, two rings, one triple bond, or a ring and a double bond. There are many possibilities, four of which are listed here.



two double bonds | two rings | one triple bond | one ring, one double bond

Problem-solving Hint

In figuring elements of unsaturation:
Count halogens as hydrogens.
Ignore oxygen.
Count nitrogen as half a carbon.

PROBLEM 7-3

Draw five more compounds of formula C_4H_6NOCl.

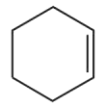
PROBLEM 7-4

For each of the following molecular formulas, determine the number of elements of unsaturation, and draw three examples.

(a) $C_4H_4Cl_2$ **(b)** C_4H_8O **(c)** $C_6H_8O_2$ **(d)** $C_5H_5NO_2$ **(e)** C_6H_3NClBr

7-4 Nomenclature of Alkenes

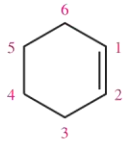
Simple alkenes are named much like alkanes, using the root name of the longest chain containing the double bond. The ending is changed from *-ane* to *-ene*. For example, "ethane" becomes "ethene," "propane" becomes "propene," and "cyclohexane" becomes "cyclohexene."



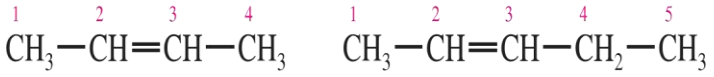
	$CH_2{=}CH_2$	$CH_2{=}CH{-}CH_3$	
IUPAC names:	ethene	propene	cyclohexene
Common names:	ethylene	propylene	

When the chain contains more than three carbon atoms, a number is used to give the location of the double bond. The chain is numbered starting from the end closest to the double bond, and the double bond is given the *lower* number of its two double-bonded carbon atoms. Cycloalkenes are assumed to have the double bond in the number 1 position.

	$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H_2{-}\overset{4}{C}H_3$	$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H_2{-}\overset{4}{C}H_2{-}\overset{5}{C}H_3$
old IUPAC names:	1-butene	1-pentene
new IUPAC names:	but-1-ene	pent-1-ene



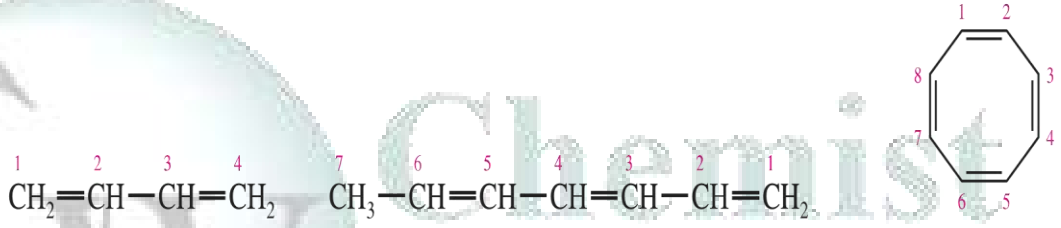
cyclohexene



old IUPAC names: 2-butene 2-pentene
new IUPAC names: but-2-ene pent-2-ene

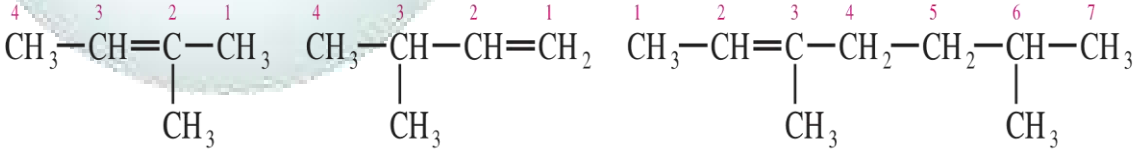
In 1993, the IUPAC recommended a logical change in the positions of the numbers used in names. Instead of placing the numbers before the root name (1-butene), they recommended placing them immediately before the part of the name they locate (but-1-ene). The new placement is helpful for clarifying the names of compounds containing multiple functional groups. You should be prepared to recognize names using either placement of the numbers, because both are widely used. In this section, names using the old number placement are printed in blue, and those using the new number placement are printed in green. Throughout this book, we will generally use the new number placement.

A compound with two double bonds is a **diene.** A **triene** has three double bonds, and a **tetraene** has four. Numbers are used to specify the locations of the double bonds.



old IUPAC names: 1,3-butadiene 1,3,5-heptatriene 1,3,5,7-cyclooctatetraene
new IUPAC names: buta-1,3-diene hepta-1,3,5-triene cycloocta-1,3,5,7-tetraene

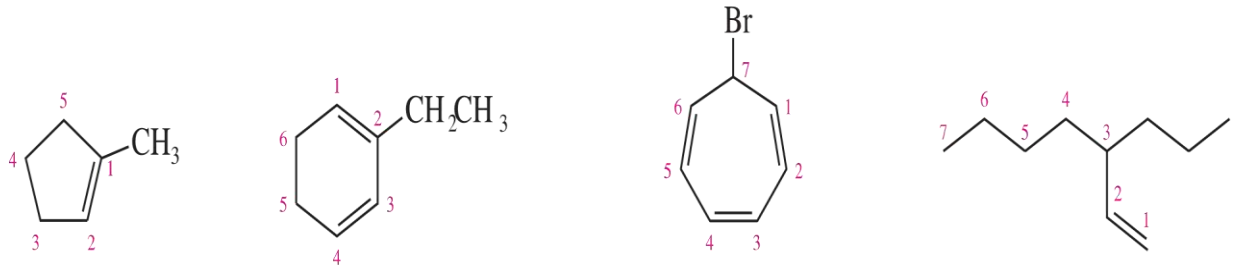
Each alkyl group attached to the main chain is listed with a number to give its location. Note that the double bond is still given preference in numbering, however.



2-methyl-2-butene
2-methylbut-2-ene

3-methyl-1-butene
3-methylbut-1-ene

3,6-dimethyl-2-heptene
3,6-dimethylhept-2-ene



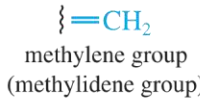
1-methylcyclopentene
1-methylcyclopentene

2-ethyl-1,3-cyclohexadiene
2-ethylcyclohexa-1,3-diene

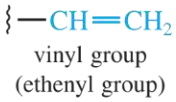
7-bromo-1,3,5-cycloheptatriene
7-bromocyclohepta-1,3,5-triene

3-propyl-1-heptene
3-propylhept-1-ene

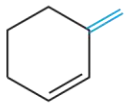
Alkenes as Substituents Alkenes named as substituents are called *alkenyl groups*. They can be named systematically (ethenyl, propenyl, etc.), or by common names. Common alkenyl substituents are the vinyl, allyl, methylene, and phenyl groups. The phenyl group (Ph) is different from the others because it is aromatic (see Chapter 16) and does not undergo the typical reactions of alkenes.



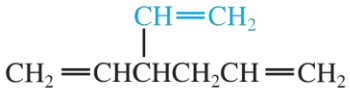
methylene group
(methylidene group)



vinyl group
(ethenyl group)

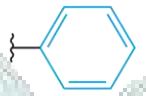


3-methylenecyclohexene



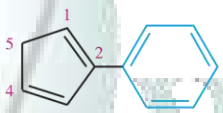
3-vinyl-1,5-hexadiene
3-vinylhexa-1,5-diene

allyl group
2-propenyl group



phenyl group
(Ph)

allyl chloride
3-chloropropene

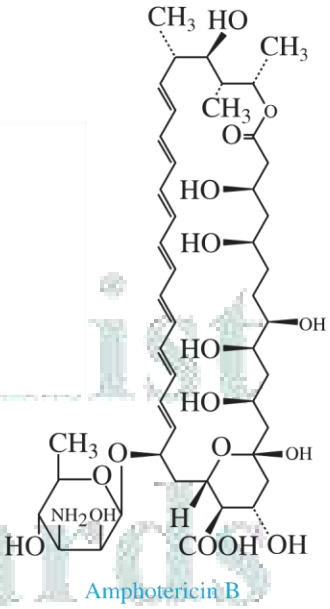


2-phenyl-1,3-cyclopentadiene
2-phenylcyclopenta-1,3-diene

Application: Antifungal Drugs

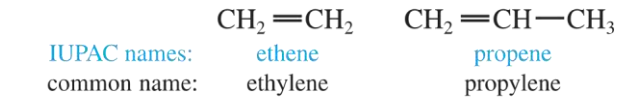
The polyene antifungals are a group of drugs with a nonpolar region consisting of 4–7 sets of alternating single and double bonds. They insert themselves in the cell membranes of fungi, causing disruption and leakiness that results in fungal cell death.

The best-known polyene antifungal drug is Amphotericin B, whose structure is shown below.

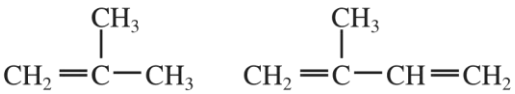


Amphotericin B

Common Names Most alkenes are conveniently named by the IUPAC system, but common names are sometimes used for the simplest compounds.

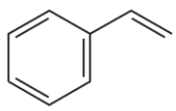


IUPAC names: ethene, propene
common name: ethylene, propylene



2-methylpropene
isobutylene

2-methylbuta-1,3-diene
isoprene



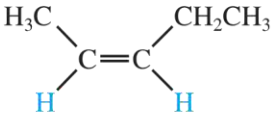
ethenylbenzene
styrene
(vinylbenzene)

7-5 Nomenclature of Cis-Trans Isomers

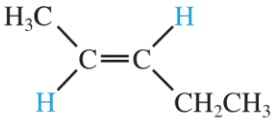
7-5A Cis-Trans Nomenclature

In Chapters 2 and 5, we saw how the rigidity and lack of rotation of carbon–carbon double bonds give rise to **cis-trans isomerism,** also called **geometric isomerism.** If two similar groups bonded to the carbons of the double bond are on the same side of

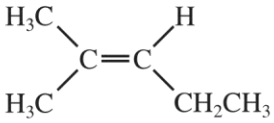
the bond, the alkene is the **cis** isomer. If the similar groups are on opposite sides of the bond, the alkene is **trans.** Not all alkenes are capable of showing cis-trans isomerism. If either carbon of the double bond holds two identical groups, the molecule cannot have cis and trans forms. Following are some cis and trans alkenes and some alkenes that cannot show cis-trans isomerism.



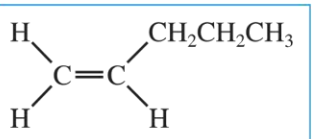
cis-2-pentene
cis-pent-2-ene



trans-2-pentene
trans-pent-2-ene



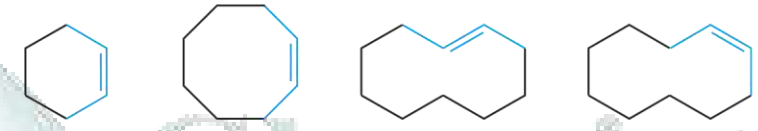
2-methyl-2-pentene
2-methylpent-2-ene



1-pentene
pent-1-ene

(neither cis nor trans)

Trans cycloalkenes are unstable unless the ring is large enough (at least eight carbon atoms) to accommodate the trans double bond (Section 7-7D). Therefore, all cycloalkenes are assumed to be cis unless they are specifically named trans. The cis name is rarely used with cycloalkenes, except to distinguish a large cycloalkene from its trans isomer.



cyclohexene cyclooctene *trans*-cyclodecene *cis*-cyclodecene

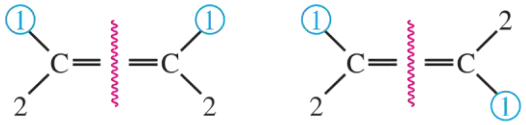
7-5B *E-Z* Nomenclature

The cis-trans nomenclature for geometric isomers sometimes gives an ambiguous name. For example, the isomers of 1-bromo-1-chloropropene are not clearly cis or trans because it is not obvious which substituents are referred to as being cis or trans.

geometric isomers of 1-bromo-1-chloropropene

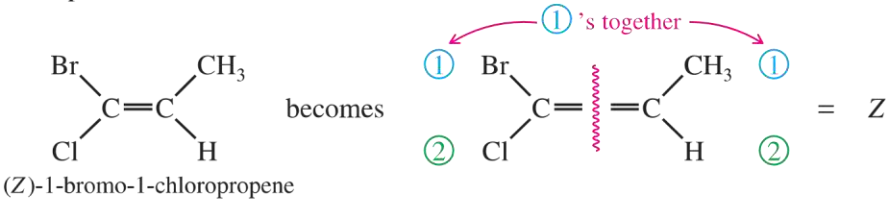
To deal with this problem, we use the ***E-Z* system** of nomenclature (pun intended) for cis-trans isomers, which is patterned after the Cahn–Ingold–Prelog convention for asymmetric carbon atoms (Section 5-3). It assigns a unique configuration of either *E* or *Z* to any double bond capable of geometric isomerism.

To name an alkene by the *E-Z* system, mentally separate the double bond into its two ends. Remember how you used the Cahn–Ingold–Prelog rules (page 181) to assign relative priorities to groups on an asymmetric carbon atom so you could name it (*R*) or (*S*). Consider each end of the double bond separately, and use those same rules to assign first and second priorities to the two substituent groups on that end. Do the same for the other end of the double bond. If the two first-priority atoms are *together (cis)* on the same side of the double bond, you have the ***Z*** isomer, from the German word *zusammen*, "together." If the two first-priority atoms are on *opposite (trans)* sides of the double bond, you have the ***E*** isomer, from the German word *entgegen*, "opposite."



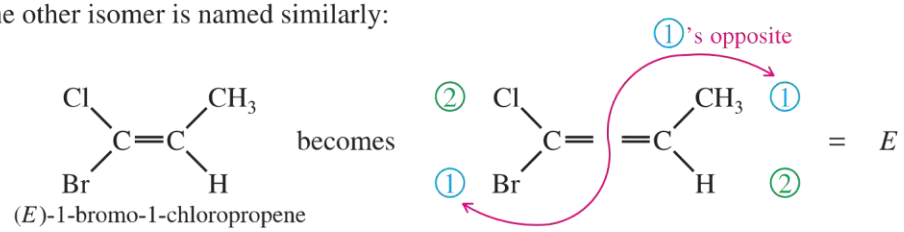
Zusammen Entgegen

For example,



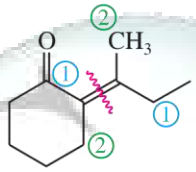
(*Z*)-1-bromo-1-chloropropene

The other isomer is named similarly:

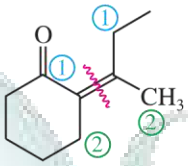


(*E*)-1-bromo-1-chloropropene

The following example shows the use of the *E*-*Z* nomenclature with cyclic stereoisomers that are not clearly cis or trans.

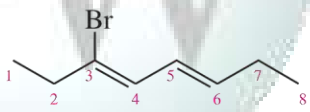


(*E*) isomer



(*Z*) isomer

If the alkene has more than one double bond, the stereochemistry about each double bond should be specified. The following compound is properly named (3*Z*,5*E*)-3-bromoocta-3,5-diene:



(3*Z*,5*E*)-3-bromoocta-3,5-diene

The use of *E*-*Z* names (rather than cis and trans) is always an option, but it is required whenever a double bond is not clearly cis or trans. Most trisubstituted and tetrasubstituted double bonds are more clearly named *E* or *Z* rather than cis or trans.

SUMMARY Rules for Naming Alkenes

The following rules summarize the IUPAC system for naming alkenes:

1. Select the longest chain or largest ring that contains the *largest possible number of double bonds*, and name it with the *-ene* suffix. If there are two double bonds, the suffix is *-diene*; for three, *-triene*; for four, *-tetraene*; and so on.
2. Number the chain from the end closest to the double bond(s). Number a ring so that the double bond is between carbons 1 and 2. Place the numbers giving the locations of the double bonds in front of the root name (old system) or in front of the suffix *-ene, -diene*, etc. (new system).
3. Name substituent groups as in alkanes, indicating their locations by the number of the main-chain carbon to which they are attached. The ethenyl group and the propenyl group are usually called the *vinyl* group and the *allyl* group, respectively.
4. For compounds that show geometric isomerism, add the appropriate prefix: *cis-* or *trans-*, or *E-* or *Z-*. Cycloalkenes are assumed to be cis unless named otherwise.

PROBLEM 7-5

Give the systematic (IUPAC) names of the following alkenes.

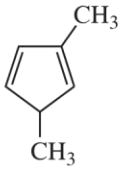
(a) $CH_2{=}CH{-}CH_2{-}CH(CH_3)_2$

(b) $CH_3(CH_2)_3{-}C(=CH_2){-}CH_2CH_3$

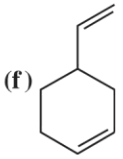
(c) $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$

(d) $CH_2{=}C{=}CH{-}CH{=}CH_2$

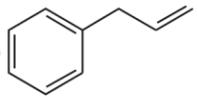
(e)



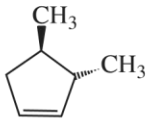
(f)



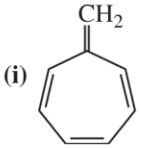
(g)



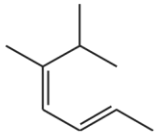
(h)



(i)



(j)



Problem-solving Hint

To see whether a compound can have cis and trans isomers, draw the structure, then draw it again with the groups on one end of the double bond reversed. See if you can describe a difference between the two.

PROBLEM 7-6

1. Determine which of the following compounds show cis-trans isomerism.
2. Draw and name the cis and trans (or *Z* and *E*) isomers of those that do.

(a) hex-3-ene **(b)** buta-1,3-diene **(c)** hexa-2,4-diene
(d) 3-methylpent-2-ene **(e)** 2,3-dimethylpent-2-ene **(f)** 3,4-dibromocyclopentene

PROBLEM 7-7

The following names are all incorrect. Draw the structure represented by the incorrect name (or a consistent structure if the name is ambiguous), and give your drawing the correct name.

(a) *cis*-2,3-dimethyl-2-pentene **(b)** 3-vinylhex-4-ene
(c) 2-methylcyclopentene **(d)** 6-chlorocyclohexadiene
(e) 2,5-dimethylcyclohexene **(f)** *cis*-2,5-dibromo-3-ethylpent-2-ene

PROBLEM 7-8

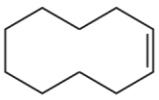
Some of the following examples can show geometric isomerism, and some cannot. For the ones that can, draw all the geometric isomers, and assign complete names using the *E*-*Z* system.

(a) 3-bromo-2-chloropent-2-ene **(b)** 3-ethylhexa-2,4-diene
(c) 3-bromo-2-methylhex-3-ene **(d)** penta-1,3-diene
(e) 3-ethyl-5-methyloct-3-ene **(f)** 3,7-dichloroocta-2,5-diene

(g)

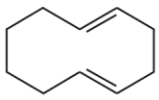
cyclohexene

(h)



cyclodecene

(i)



cyclodeca-1,5-diene

USE THE STRATEGY

PROBLEM 2 ♦

What is the molecular formula for each of the following?

a. a 4-carbon hydrocarbon with two π bonds and no rings
b. a 10-carbon hydrocarbon with one π bond and 2 rings

LEARN THE STRATEGY

PROBLEM 3 SOLVED

Determine the degree of unsaturation for a hydrocarbon with a molecular formula of $C_{10}H_{16}$.

SOLUTION For a 10-carbon hydrocarbon with no π bonds and no rings, $C_nH_{2n+2} = C_{10}H_{22}$. A 10-carbon compound with molecular formula $C_{10}H_{16}$ has six fewer hydrogens, so the degree of unsaturation is $6/2 = 3$.

USE THE STRATEGY

PROBLEM 4 ♦

Determine the degree of unsaturation for hydrocarbons with the following molecular formulas:

a. $C_{20}H_{34}$ **b.** C_8H_{16} **c.** $C_{12}H_{20}$ **d.** $C_{40}H_{56}$

PROBLEM 5

Determine the degree of unsaturation and then draw possible structures for noncyclic compounds with the following molecular formulas:

a. C_3H_6 **b.** C_3H_4 **c.** C_4H_6

PROBLEM 6 ♦

Several studies have shown that β-carotene, a precursor of vitamin A, may play a role in preventing cancer. β-Carotene has a molecular formula of $C_{40}H_{56}$, and it contains two rings and no triple bonds. How many double bonds does it have?

β-Carotene is an orange colored compound found in carrots, apricots, and flamingo feathers (Sections 13.21 and 16.13).

5.2 THE NOMENCLATURE OF ALKENES

We saw that the IUPAC system uses a suffix to denote certain functional groups (Sections 3.6 and 3.7). The double bond is the functional group of an alkene; its presence is denoted by the suffix "ene." Therefore, the systematic (IUPAC) name of an alkene is obtained by replacing the "ane" ending of the corresponding alkane with "ene." For example, a two-carbon alkene is called ethene, and a three-carbon alkene is called propene. Ethene also is frequently called by its common name: ethylene.

	$H_2C{=}CH_2$	$CH_3CH{=}CH_2$		
systematic name:	Ethene	Propene	Cyclopentene	Cyclohexene
common name:	Ethylene	Propylene		

Most alkene names need a number to indicate the position of the double bond. (The four names above do not because there is no ambiguity.) The IUPAC rules you learned in Sections 3.3 and 3.6 apply to alkenes as well:

LEARN THE STRATEGY

1. The longest continuous chain that contains the functional group (in this case, the carbon–carbon double bond) is numbered in the direction that gives the functional group suffix the lowest possible number. For example, 1-butene signifies that the double bond is between the first and second carbons of butene; 2-hexene signifies that the double bond is between the second and third carbons of hexene.

Number the longest continuous chain containing the functional group in the direction that gives the functional group suffix the lowest possible number.

$^{4}CH_3{}^{3}CH_2{}^{2}CH{=}{}^{1}CH_2$ 1-butene

$^{1}CH_3{}^{2}CH{=}{}^{3}CHCH_3$ 2-butene

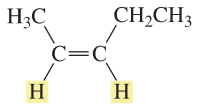
$^{1}CH_3{}^{2}CH{=}{}^{3}CH{}^{4}CH_2{}^{5}CH_2{}^{6}CH_3$ 2-hexene

$^{6}CH_3{}^{5}CH_2{}^{4}CH_2{}^{3}CH_2{}^{2}C(=CH_2)CH_2CH_2CH_3$ (1-CH_2) 2-propyl-1-hexene

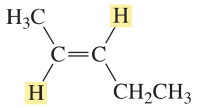
the longest continuous chain has 8 carbons, but the longest continuous chain containing the functional group has 6 carbons, so the parent name of the compound is hexene

Notice that 1-butene does not have a common name. You might be tempted to call it "butylene," which is analogous to "propylene" for propene. Butylene, however, is not an appropriate name because it could signify either 1-butene or 2-butene, and a name must be unambiguous.

Recall that the stereoisomers of an alkene are named using a *cis* or *trans* (or *E* or *Z*) prefix (Sections 4.1 and 4.2).

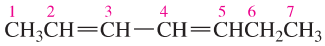


***cis*-2-pentene**
or
(*Z*)-2-pentene



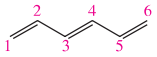
***trans*-2-pentene**
or
(*E*)-2-pentene

2. For a compound with two or more double bonds, the "ne" ending of the corresponding alkane is replaced with "diene," "triene," "tetraene," and so on, depending on the number of double bonds in the parent hydrocarbon.



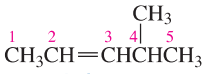
2,4-heptadiene

1,3-pentadiene

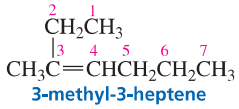


(3*E*)-1,3,5-hexatriene

3. The name of a substituent is stated before the name of the longest continuous chain that contains the functional group, together with a number to designate the carbon to which the substituent is attached. Notice that *if a compound's name contains both a functional group suffix and a substituent, the chain is numbered so that the functional group suffix gets the lowest possible number.*

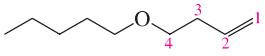


4-methyl-2-pentene

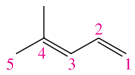


3-methyl-3-heptene

When there are both a functional group and a substituent, the functional group suffix gets the lowest possible number.

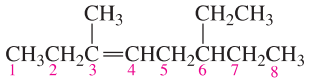


4-pentoxy-1-butene

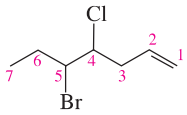


4-methyl-1,3-pentadiene

4. If a chain has more than one substituent, the substituents are stated in alphabetical order, using the same rules for alphabetizing discussed in Section 3.2. Then the appropriate number is assigned to each substituent.



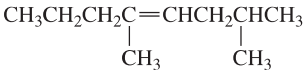
6-ethyl-3-methyl-3-octene



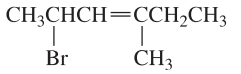
5-bromo-4-chloro-1-heptene

Substituents are stated in alphabetical order.

5. If counting in either direction results in the same number for the functional group suffix, the correct name is the one containing the lowest substituent number. For example, the compound shown below on the left is a 4-octene whether the longest continuous chain is numbered from left to right or from right to left. If you number from left to right, then the substituents are at positions 4 and 7, but if you number from right to left, they are at positions 2 and 5. Of those four substituent numbers, 2 is the lowest, so the compound is named 2,5-dimethyl-4-octene.



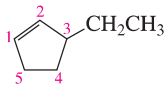
2,5-dimethyl-4-octene
not
4,7-dimethyl-4-octene
because 2 < 4



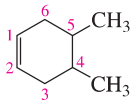
2-bromo-4-methyl-3-hexene
not
5-bromo-3-methyl-3-hexene
because 2 < 3

A substituent receives the lowest possible number only when there is no functional group suffix or the same number for the functional group suffix is obtained in both directions.

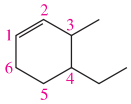
6. A number is not needed to denote the position of the double bond in a cyclic alkene because the ring is always numbered so that the double bond is between carbons 1 and 2. To assign numbers to any substituents, count around the ring in the direction (clockwise or counterclockwise) that puts the lowest number into the name.



3-ethylcyclopentene

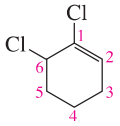


4,5-dimethylcyclohexene

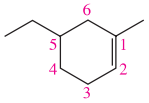


4-ethyl-3-methylcyclohexene

Notice that 1,6-dichlorocyclohexene is *not* called 2,3-dichlorocyclohexene because the former has the lowest substituent number (1), even though it does not have the lowest sum of substituent numbers (1 + 6 = 7 versus 2 + 3 = 5).

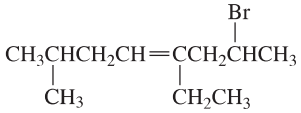


1,6-dichlorocyclohexene
not
2,3-dichlorocyclohexene
because 1 < 2

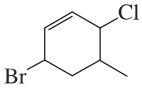


5-ethyl-1-methylcyclohexene
not
4-ethyl-2-methylcyclohexene
because 1 < 2

7. If counting in either direction leads to the same number for the alkene functional group suffix and the same lowest number or numbers for one or more of the substituents, then ignore those substituents and choose the direction that gives the lowest number to one of the remaining substituents.



2-bromo-4-ethyl-7-methyl-4-octene
not
7-bromo-5-ethyl-2-methyl-4-octene
because 4 < 5



6-bromo-3-chloro-4-methylcyclohexene
not
3-bromo-6-chloro-5-methylcyclohexene
because 4 < 5

Remember that the name of a substituent is stated *before* the name of the parent hydrocarbon and that a functional group suffix is stated *after* the name of the parent hydrocarbon.

USE THE STRATEGY

PROBLEM 7 ♦

What is each compound's systematic name?

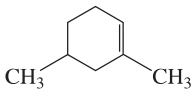
a. $CH_3CHCH{=}CHCH_3$ (CH_3 on the first carbon)

b. $CH_3CH_2C{=}CCHCH_3$ (CH_3 and Cl on the first carbon)

c.

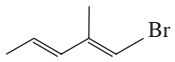
d. $BrCH_2CH_2CH{=}CCH_3$ (CH_2CH_3 on the third carbon)

e.

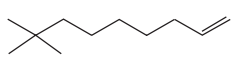


f. $CH_3CH{=}CHCH_2OCH_2CH_2CH_2CH_3$

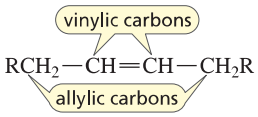
g.



h.



The sp^2 carbons of an alkene are called **vinylic carbons.** An sp^3 carbon that is adjacent to a vinylic carbon is called an **allylic carbon.** A hydrogen bonded to a vinylic carbon is called a **vinylic hydrogen,** and a hydrogen bonded to an allylic carbon is called an **allylic hydrogen.**



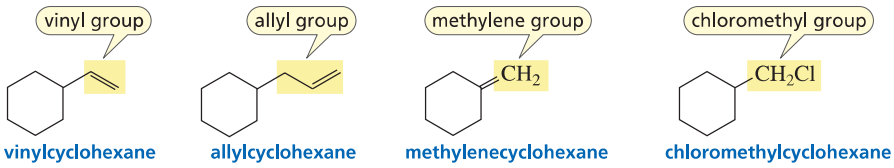
PROBLEM 8 ♦

a. How many vinylic hydrogens does cyclopentene have?
b. How many allylic hydrogens does it have?

Two groups containing a carbon–carbon double bond are used in common names—the **vinyl group** and the **allyl group.** The vinyl group is the smallest possible group that contains a vinylic carbon, and the allyl group is the smallest possible group that contains an allylic carbon. When "vinyl" or "allyl" is used in a name, the substituent must be attached to the vinylic or allylic carbon, respectively.

	$CH_2{=}CH-$	$CH_2{=}CHCH_2-$
	vinyl group	**allyl group**
	$CH_2{=}CHCl$	$CH_2{=}CHCH_2Br$
common name:	vinyl chloride	allyl bromide
systematic name:	chloroethene	3-bromopropene

Notice how these groups and some others can be used as substituent names in systematic nomenclature.



PROBLEM 9 ♦

Draw the structure for each of the following:

a. 3,3-dimethylcyclopentene
b. 6-bromo-2,3-dimethyl-2-hexene
c. ethyl vinyl ether
d. allyl alcohol

5.3 THE STRUCTURE OF ALKENES

Alkenes have structures similar to that of ethene, the smallest alkene, whose structure was described in Section 1.8. Each double bonded carbon of an alkene has three sp^2 orbitals. Each of these orbitals overlaps an orbital of another atom to form a σ bond, one of which is one of the bonds in the double bond. Thus, the σ bond of the double bond is formed by the overlap of an sp^2 orbital of one carbon with an sp^2 orbital of the other carbon. The other bond of the double bond is a π bond formed from side-to-side overlap of the remaining p orbital on each of the sp^2 carbons.