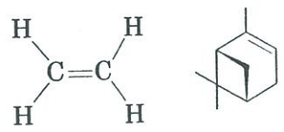
CHAPTER 3

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

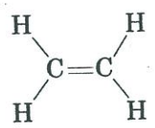
α-Pinene

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.

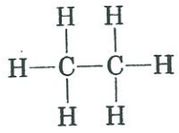
3.1 NAMING ALKENES

unsaturated
containing one or
more double or
triple 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.



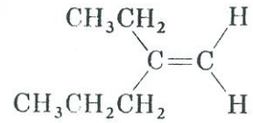
Ethylene, C_2H_4
(...hydrogens: *unsaturated*)



Ethane, C_2H_6
(more hydrogens: *saturated*)

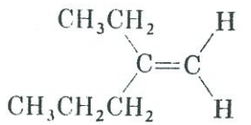
Alkenes are named according to a series of rules similar to those used for naming alkanes, with the suffix *-ene* used in place of *-ane* to identify the family. There are three steps:

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*.



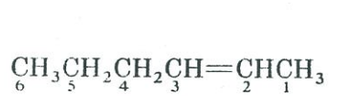
Named as a *pentene*

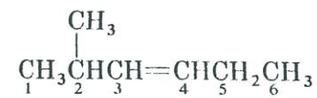
NOT



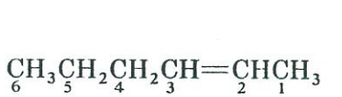
as a hexene, because the double bond is not contained in the six-carbon chain.

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:

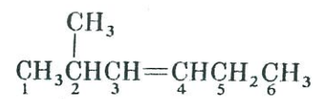




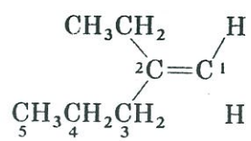
Step 3. Write the full name, numbering the substituents according to their position in the chain and listing them alphabetically. Indicate the position of the double bond by giving the number of the *first* alkene carbon. If more than one double bond is present, give the position of each and use one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



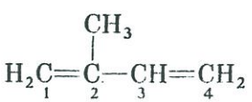
2-Hexene



2-Methyl-3-hexene



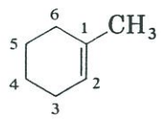
2-Ethyl-1-pentene



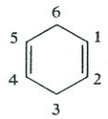
2-Methyl-1,3-butadiene

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

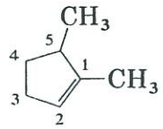
and C2 and the first substituent has as low a number as possible:



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
$CH_3C(CH_3){=}CH_2$	2-Methylpropene	Isobutylene
$H_2C{=}C(CH_3){-}CH{=}CH_2$	2-Methyl-1,3-butadiene	Isoprene

PRACTICE PROBLEM 3.1 What is the IUPAC name of this alkene:

$$CH_3C(CH_3)(CH_3)CH_2CH_2CH{=}C(CH_3)CH_3$$

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).

$$\overset{7}{C}H_3\overset{6}{C}(CH_3)(CH_3)\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H{=}\overset{2}{C}(CH_3)\overset{1}{C}H_3$$

The full name is 2,6,6-trimethyl-2-heptene.

PROBLEM 3.1 Give IUPAC names for these compounds:

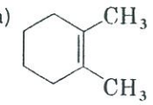
(a) $H_2C{=}CHCH_2CH(CH_3)CH_3$

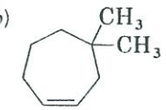
(b) $CH_3CH_2CH{=}CHCH_2CH_2CH_3$

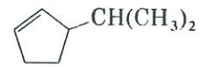
(c) $H_2C{=}CHCH_2CH_2CH{=}CHCH_3$

(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).

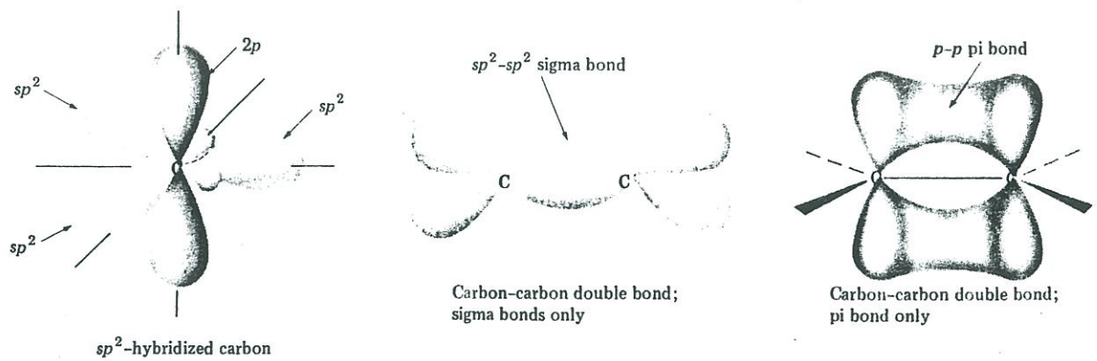


FIGURE 3.1 An orbital picture of the carbon–carbon double bond

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