INTERCHAPTER G

Unsaturated Hydrocarbons

The flame from an acetylene torch. Acetylene, which is used extensively in welding, is an example of an unsaturated hydrocarbon.

In this Interchapter, we shall continue our introduction to organic chemistry by discussing unsaturated hydrocarbons. We shall see that unsaturated hydrocarbons contain double or triple bonds and are more reactive than saturated hydrocarbons.

G-1. Hydrocarbons That Contain Double Bonds Are Called Alkenes

All the hydrocarbons that we discussed in Interchapter F are saturated hydrocarbons; that is, each carbon atom is bonded to four other atoms. There is another class of hydrocarbons called **unsaturated hydrocarbons,** in which not all the carbon atoms are bonded to four other atoms. These molecules necessarily contain double or triple bonds. The double bonds and triple bonds serve as **functional groups**. A functional group is a specifically bonded group of atoms in a molecule that confers characteristic reactive properties on the molecule. As we shall see, atoms with double and triple bonds tend to react similarly due to the presence of these functional groups. Unsaturated hydrocarbons that contain one or more double bonds are called **alkenes.** The systematic name of the simplest alkene, $C_2H_4(g)$, is ethene, although it is generally referred to by its common name, ethylene, as we shall do here.

Ethylene is a colorless gas with a sweet odor and taste. It is highly flammable, and mixtures of ethylene and oxygen are highly explosive. Ethylene ranks third in U.S. annual production; some 25 million metric tons of ethylene are produced annually in the United States (Appendix H). This amounts to 85 kg (190 pounds) for every man, woman, and child in the United States. Ethylene is the starting material for about 40% of all organic substances produced commercially. It is used to make polyethylene, vinyl chloride, and polyvinyl chloride (PVC), vinyl acetate and polyvinyl acetate, styrene, polyesters, refrigerants, and anesthetics. Ethylene acts as a hormone in plants and is used commercially to accelerate the ripening of fruit (Figure G.1).

We learned in Section 9-10 that the bonding in ethylene can be described by sp^2 orbitals on each carbon atom (Figure 9.32, page 291). The double bond consists of a σ bond and a π bond (Figure 9.34, page 292). The σ bond results from the combination of two sp^2 orbitals, one from each carbon atom; and the π bond results from the combination of two p orbitals, also one from each carbon atom. The π orbital maintains the σ-bond framework in a planar shape and prevents rotation about the double bond. Consequently, all six atoms in an ethene (ethylene) molecule lie in one plane, and there are *cis* and *trans* isomers of 1,2-dichloroethene (see Section 9-11).

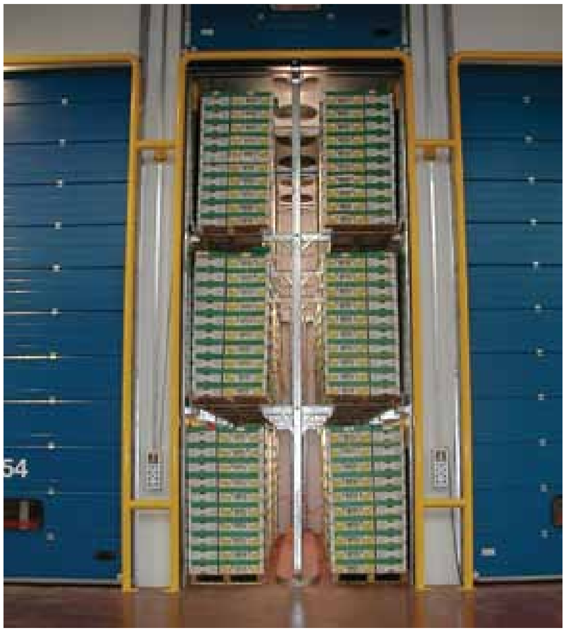
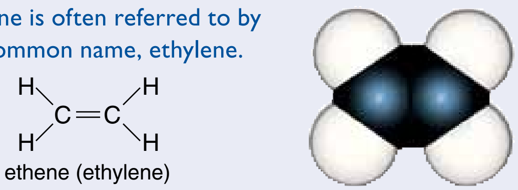
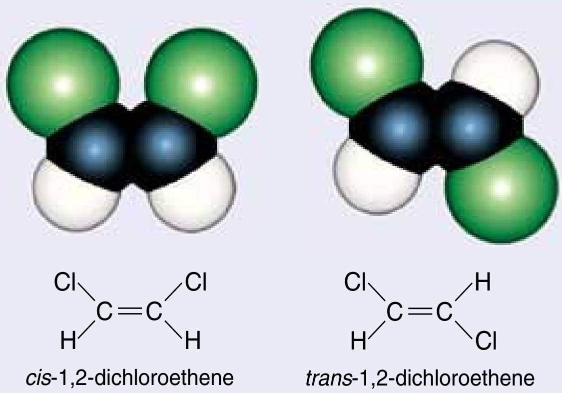
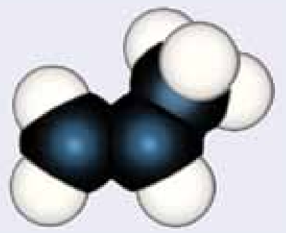


Figure G.1 Fruit being gassed with ethylene. Ethylene is a natural plant hormone that is used commercially to accelerate ripening. Fruit is often picked green, which prevents bruising during transport, and then gassed with ethylene to promote ripening before being placed on the supermarket shelf.

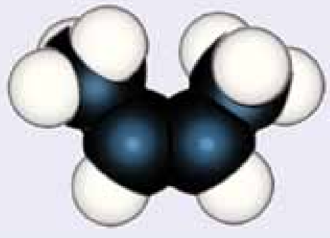
Ethene is often referred to by its common name, ethylene.



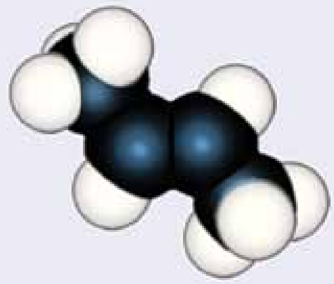




propene

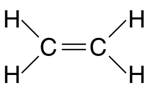


cis-2-butene

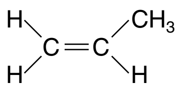


trans-2-butene

The IUPAC (International Union of Pure and Applied Chemistry) nomenclature for alkenes uses the longest chain of consecutive carbon atoms *containing the double bond* to denote the parent compound. The parent compound is named by replacing the *-ane* ending of the corresponding alkane with *-ene* and using a number to designate the carbon atom preceding the double bond. Thus, we have



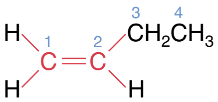
ethene (ethylene)



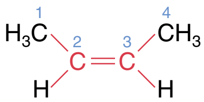
propene

In both cases the location of the double bond is between the number 1 and 2 carbons in the chain (giving precedence to the double bond) and so no number is required in the name; it would be incorrect (or at least unconventional) to write “1-propene.”

In contrast, there are two possible positions for the double bond in butene, so we have

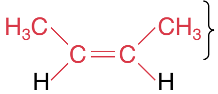


1-butene



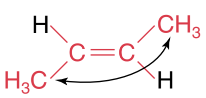
2-butene

The planar C=C portion of each of these molecules is colored red. Note that for 2-butene it is possible to draw two distinct structures due to *cis-trans* isomerism. The *cis-trans* isomers of 2-butene are



cis-2-butene
(m.p. –139°C)

cis isomer: longest carbon chain is on the same side of the double bond

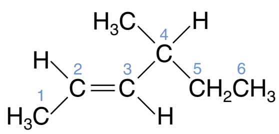


trans-2-butene
(m.p. –106°C)

trans isomer: longest carbon chain runs across the double bond

The name 2-butene is ambiguous because of *cis-trans* isomerism, and so we must include a *cis* or *trans* prefix before the number designating the location of the double bond in the name in order to distinguish between the two cases. Recall that the *cis* prefix denotes that the longest carbon chain is located on the same side of the double bond (*cis* means *same*) and the *trans* prefix denotes that the longest carbon chain is located on opposite sides of the double bond (*trans* means *across*). The longest carbon chains are shown in red above. The distinction between the *cis* and *trans* isomers of 2-butene is readily apparent from their space-filling structures in the margin. These two isomers have different physical and chemical properties. For example, the melting point of *cis*-2-butene is –139°C and that of *trans*-2-butene is –106°C.

Let’s name the compound whose Lewis formula is



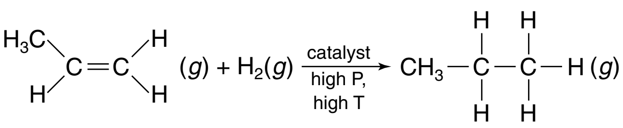
The longest chain containing the double bond consists of six carbon atoms, so the parent compound is a hexene. In particular, it is a 2-hexene because the double bond occurs after the second carbon atom in the chain. The configuration of the molecule is *trans* because the carbon atoms in the longest chain lie on opposite sides of the double bond. In addition, there is a methyl group attached to the fourth carbon atom, so the name of the compound is 4-methyl-*trans*-2-hexene.

Recall from Section 9-11 that a nice application of *cis-trans* isomerism is the conversion of the 11-*cis*-retinal portion of rhodopsin to 11-*trans*-retinal when a photon of light registers in the retina of the eye. This transition is sketched in Figure 9.36, page 294.

G-2. Alkenes Undergo Addition Reactions as Well as Combustion Reactions and Substitution Reactions

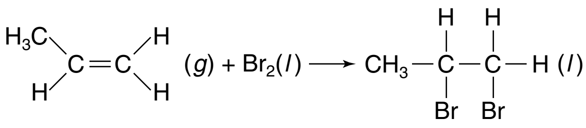
Alkenes are more reactive than alkanes because the carbon-carbon double bond provides a reactive center in the molecule. In a sense, the double bond has "extra" electrons available for reaction. So, besides the combustion and substitution reactions that alkanes undergo, alkenes undergo **addition reactions.** Examples of addition reactions are

1. Addition of hydrogen, called **hydrogenation:**



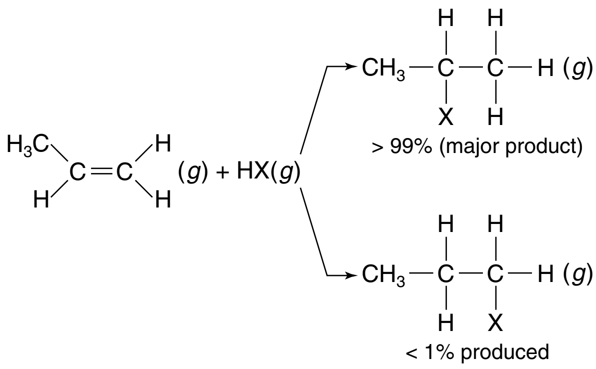
This reaction requires a catalyst and high pressure and temperature. Usually, powdered nickel or platinum is used as the catalyst. "Hydrogenated vegetable oils" are made by hydrogenating the double bonds in the molecules that constitute vegetable oils. This hydrogenation makes vegetable oils solid at room temperature.

2. Addition of chlorine or bromine:



This reaction can be carried out either with pure chlorine or bromine or by dissolving the halogen in some solvent, such as carbon tetrachloride. The addition reaction with bromine is a useful qualitative test for the presence of double bonds. A solution of bromine in carbon tetrachloride is red, whereas alkenes and bromoalkanes are usually colorless. As the bromine adds to the double bond, the red color disappears, a result providing a simple test for the presence of double bonds (Figure G.2).

3. Addition of a hydrogen halide, HX, where X is a halogen:



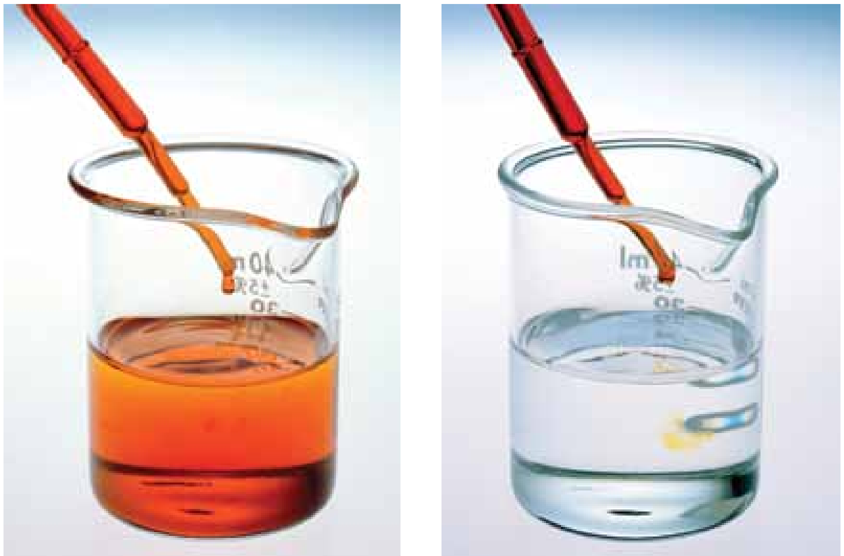
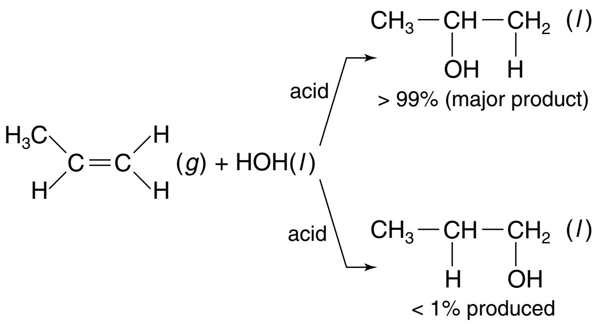


Figure G.2 A solution of bromine in carbon tetrachloride is red. Solutions of alkenes and bromoalkanes are usually colorless. As the bromine adds to the double bond, the red color disappears, a result providing a simple test for the presence of double bonds.

Although two different products might seem possible in this reaction, only one is found in any significant amount. There is a simple rule for determining which product is produced: **Markovnikov's rule** states that when HX adds to an alkene, the hydrogen atom attaches to the carbon atom in the double bond that is already directly bonded to the larger number of hydrogen atoms. More succinctly, the hydrogen-rich carbon atom gets hydrogen-richer.

4. Addition of water. In the presence of acid, which catalyzes the reaction, water adds to the more reactive alkenes:



Note that the addition of water to an alkene obeys Markovnikov's rule. Simply picture the water as H–OH. The product of this reaction is an alcohol; we shall study alcohols in Interchapter P.

G-3. Hydrocarbons That Contain a Triple Bond Are Called Alkynes

Alkynes are hydrocarbons that contain at least one carbon–carbon triple bond. The simplest alkyne is $C_2H_2(g)$. Its IUPAC name, ethyne, is formed by replacing the *-ane* ending of the corresponding alkane with the ending *-yne,* which is characteristic of alkynes. Ethyne is generally referred to by its common name, acetylene, as we shall do here.

We learned in Section 9-12 that acetylene is a linear molecule whose bonding can be described in terms of *sp* hybrid orbitals and two π-bonding orbitals on the carbon atoms (Figures 9.37 and 9.38). Acetylene is a colorless gas, which is produced primarily from petroleum. It is used in oxyacetylene torches, which produce relatively high temperatures. Acetylene also is used as the starting material for a number of plastics.

Acetylene can also be produced by the reaction of calcium carbide and water described by

$$CaC_2(s) + 2\,H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$$

This reaction is sometimes used by spelunkers as a light source in caves (Figure G.3). Acetylene is

Ethyne is generally referred to by its common name, acetylene.

$H{-}C{\equiv}C{-}H$
ethyne (acetylene)

(a) (b)

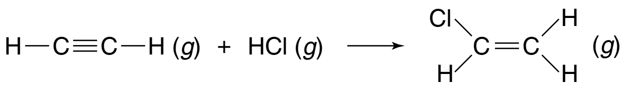
Figure G.3 (a) Chip Clark, spelunker, with a calcium carbide lamp on his helmet. (b) The reaction of calcium carbide with water yields ethyne (acetylene) gas and calcium hydroxide. The acetylene gas burns in air and is used to provide light in lamps on hats used by spelunkers.

produced by allowing $H_2O(l)$ to drop slowly onto $CaC_2(s)$ in a canister. The $C_2H_2(g)$ pressure builds up, leaks out of the canister through a nozzle, and is burned in air according to

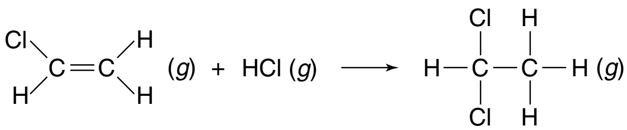
$$2\,C_2H_2(g) + 5\,O_2(air) \rightarrow 4\,CO_2(g) + 2\,H_2O(g)$$

Besides the combustion reaction that all hydrocarbons undergo, acetylene and other alkynes undergo the same type of addition reactions as alkenes do. For example, let's consider the product when $HCl(g)$ reacts with $C_2H_2(g)$.

The reaction can be broken down into two steps. The first step is



The second step is



Note that we have used Markovnikov's rule to predict the product in the second step. The major product is 1,1-dichloroethane.

TERMS YOU SHOULD KNOW

unsaturated hydrocarbon *G1*
functional group *G1*
alkene *G1*
addition reaction *G3*
hydrogenation *G3*
Markovnikov's rule *G4*
alkyne *G4*

QUESTIONS

G-1. What is meant by an "unsaturated" hydrocarbon? What exactly is unsaturated?

G-2. What is the difference between a substitution reaction and an addition reaction?

G-3. What is a hydrogenation reaction? What conditions are required for this reaction to occur?

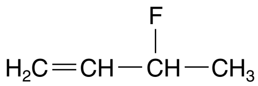
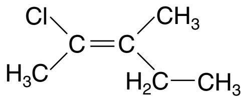
G-4. State Markovnikov's rule.

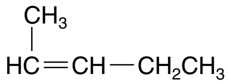
G-5. What is the difference between an alkene and an alkyne?

G-6. Can the addition reaction of two $Cl_2(g)$ molecules to an alkyne form *cis-trans* isomers? If so, give an example of such a compound. If not, explain why not.

G-7. Explain why there is no molecule named 3-butene.

G-8. Assign IUPAC names to the following alkenes:

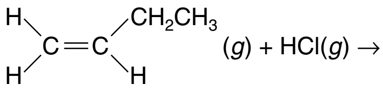
(a)  (b) 

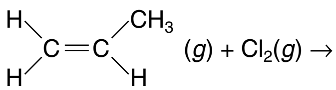
(c) 

G-9. Write the Lewis formula for and assign an IUPAC name to the product when each of the following compounds reacts with bromine:

(a) 1-butene (b) 2-butene

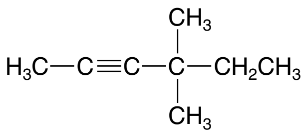
G-10. Complete the following equations and name the products:

(a) 

(b) 

G-11. Assign IUPAC names to the following alkynes:

(a) $CH_3—C\equiv CH$ (b) $CH_3—C\equiv C—CH_3$

(c) 

G-12. Complete and balance the following equations (assume complete saturation of the triple bonds):

(a) $CH_3C\equiv CH(g) + HCl(g) \rightarrow$

(b) $CH_3C\equiv CH(g) + Br_2(l) \rightarrow$

(c) $CH_3C\equiv CCH_3(g) + H_2(g) \xrightarrow{Ni(s)}$

G-13. Write the structural formula for and assign an IUPAC name to the product when each of the following compounds reacts with 1-butene:

(a) Cl_2 (addition) (b) HCl
(c) H_2O (acid catalyst) (d) H_2 (platinum catalyst)