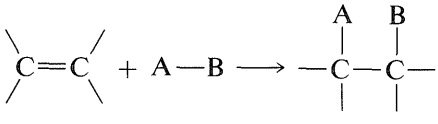
10

ALKENES AND ALKYNES I. IONIC AND RADICAL ADDITION REACTIONS

Carbon–carbon double and triple bonds undergo a wide variety of addition reactions in which *one* of the multiple bonds is broken and two new bonds to carbon are formed:



The importance of such reactions to synthetic organic chemistry is paramount. It is our intention in this and the following chapter to show the great diversity, utility, and specificity of addition reactions of alkenes and alkynes.

We will begin with a brief discussion of the physical and spectroscopic properties of alkenes and alkynes. But the major emphasis in the chapter is on two main types of reactions, ionic addition and radical-chain addition. For ionic additions we will make extensive use of the classification of reagents as electrophiles and nucleophiles, as described in Chapter 8.

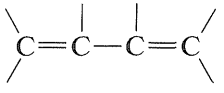
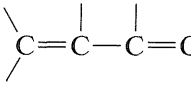
10-1 PHYSICAL AND SPECTROSCOPIC PROPERTIES OF ALKENES AND ALKYNES

10-1A Physical Properties

In general, the physical properties of alkenes are similar to those of alkanes. The data of Table 10-1 allow comparison of the boiling points, melting points, and densities of several alkenes with the corresponding alkanes that have the same carbon skeleton. Like the continuous-chain alkanes, the 1-alkenes form a homologous series of compounds that show regular changes in physical properties with increasing chain length.

The boiling points, melting points, and densities of the simple alkynes (also included in Table 10-1) are somewhat higher than those of the corresponding alkanes or alkenes, and these properties also show regular changes as the chain length is increased.

10-1B Spectroscopic Properties of Alkenes

The *infrared spectra of alkenes* are sufficiently different from those of alkanes in most instances to make it possible to recognize when a double bond is present. For example, in the infrared spectrum of 1-butene (Figure 10-1) the absorption band near 1650 cm^{-1} is characteristic of the stretching vibration of the double bond. In general, the intensity and position of this band depends on the structure of the alkene; it varies with the degree of branching at the double bond, with the presence of a second unsaturated group in conjugation with the first (i.e.,  or ), and with the symmetry of the substitution of the double bond (see Section 9-7B). However, in many cases the absorption bands caused by the various modes of vibration of the alkenic C—H bonds frequently are more useful for detecting a double bond and identifying its type than is the absorption band caused by C=C stretch. With 1-butene, absorptions arising from the C—H vibrations of the terminal $=CH_2$ group occur near 3100 cm^{-1}, 1420 cm^{-1}, and 915 cm^{-1}, and those of the —CH= grouping near 3020 cm^{-1}, 1420 cm^{-1}, and 1000 cm^{-1}. In general, absorption bands at these frequencies are from the grouping $-CH=CH_2$. The bands near 1420 cm^{-1} are due to in-plane bending, whereas those at 915 cm^{-1} to 1000 cm^{-1} arise from out-of-plane bending. The other intense absorptions, near 1460 cm^{-1} and 3000 cm^{-1}, are due to C—H vibrations of the CH_3CH_2— group (see Section 9-7D). These illustrate a further point—namely, the positions of the infrared absorptions of alkyl C—H bonds are significantly different from those of alkenic C—H bonds.

The double bonds of an alkene with no alkenic hydrogens are difficult to detect by infrared spectroscopy and in such cases Raman spectroscopy is helpful (see Section 9-8).

Table 10-1
Comparison of Physical Properties of Alkanes, Alkenes, and Alkynes

Hydrocarbon	Formula	Bp, °C	Mp, °C	Density, d_4^{20}
ethane	$CH_3—CH_3$	−88.6	−183[a]	
ethene	$CH_2=CH_2$	−105	−169	
ethyne	$CH\equiv CH$	−83	−81	
propane	$CH_3—CH_2—CH_3$	−42.1	−187[a]	0.501[b]
propene	$CH_3—CH=CH_2$	−47.8	−185[a]	0.514[b]
propyne	$CH_3—C\equiv CH$	−23.2	−102.7	0.706[b]
butane	$CH_3—CH_2—CH_2—CH_3$	−0.5	−138	0.579[b]
1-butene	$CH_3—CH_2—CH=CH_2$	−6.3	−185[a]	0.595[b]
cis-2-butene	$CH_3—CH=CH—CH_3$	3.7	−139	0.621[b]
trans-2-butene	$CH_3—CH=CH—CH_3$	0.9	−106	0.604[b]
1-butyne	$CH_3—CH_2—C\equiv CH$	8.1	−126	0.65[b]
2-butyne	$CH_3—C\equiv C—CH_3$	27.0	−32	0.691
pentane	$CH_3—CH_2—CH_2—CH_2—CH_3$	36.1	−129	0.626
1-pentene	$CH_3—CH_2—CH_2—CH=CH_2$	30.0	−165	0.641
cis-2-pentene	$CH_3—CH_2—CH=CH—CH_3$	37.9	−151	0.656
trans-2-pentene	$CH_3—CH_2—CH=CH—CH_3$	36.4	−140	0.648
1-pentyne	$CH_3—CH_2—CH_2—C\equiv CH$	40.2	−106	0.690
2-pentyne	$CH_3—CH_2—C\equiv C—CH_3$	56.1	−109	0.711
hexane	$CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$	68.7	−95	0.659
1-hexene	$CH_3—CH_2—CH_2—CH_2—CH=CH_2$	63.5	−140	0.674
cis-2-hexene	$CH_3—CH_2—CH_2—CH=CH—CH_3$	68.8	−141	0.687
trans-2-hexene	$CH_3—CH_2—CH_2—CH=CH—CH_3$	67.9	−133	0.678
cis-3-hexene	$CH_3—CH_2—CH=CH—CH_2—CH_3$	66.4	−138	0.680
trans-3-hexene	$CH_3—CH_2—CH=CH—CH_2—CH_3$	67.1	−113	0.677
1-hexyne	$CH_3—CH_2—CH_2—CH_2—C\equiv CH$	71	−132	0.716
2-hexyne	$CH_3—CH_2—CH_2—C\equiv C—CH_3$	84.0	−88	0.732
3-hexyne	$CH_3—CH_2—C\equiv C—CH_2—CH_3$	81.8	−105	0.724

[a]At the triple point (i.e., the temperature at which the solid, liquid, and vapor all are in equilibrium).
[b]Under pressure.

The infrared absorption of 1-butene that occurs at 1830 cm^{-1} (Figure 10-1) falls in the region where stretching vibrations of alkene bonds usually are not observed. However, this band actually arises from an **overtone** (harmonic) of the $=CH_2$ out-of-plane bending at 915 cm^{-1}. Such overtone absorptions come at exactly *twice* the frequency of the fundamental frequency, and whenever an absorption like this is observed that does not seem to fit with the normal fundamental vibrations, the possibility of its being an overtone should be checked.

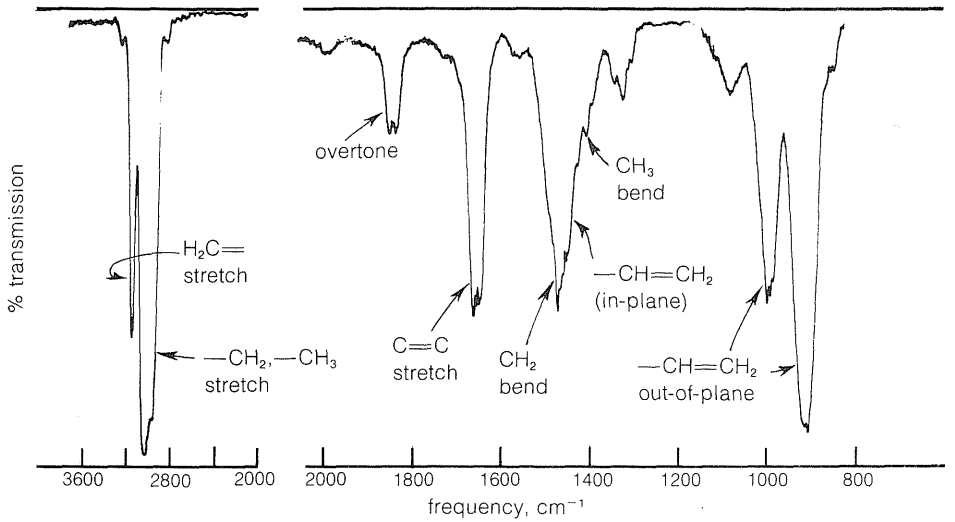


Figure 10-1 Infrared spectrum of 1-butene showing the vibrational assignments made to the various absorptions

Exercise 10-1 Deduce possible structures of the substances whose infrared spectra are shown in Figure 10-2. Assign as many of the bands as you can to *specific* stretching and bending vibrations by comparison with Figure 10-1. Be sure your structural assignments fit with the spectrum—that is, think twice about assigning a structure that has $-CH_2-$ groups if there are no $-CH_2-$ bands in the spectrum, or that has no $-CH_3$ groups when there appear to be strong $-CH_3$ absorptions.

With regard to *electronic spectra,* a π electron of a simple alkene can be excited to a higher energy (π^*) state by light of wavelength 180 nm to 100 nm. However, many other substances absorb in this region of the spectrum, including air, the quartz sample cell, and most solvents that might be used to dissolve the sample, and as a result the spectra of simple alkenes are not obtained easily with the usual ultraviolet spectrometers. When the double bond is conjugated as in $\diagdown\!\!\diagup C=C-C=C\diagdown\!\!\diagup$ or $\diagdown\!\!\diagup C=C-C=O$, then the wavelengths of maximum absorption shift to longer wavelengths and such absorptions are determined more easily and accurately (also see Section 9-9B).

In proton *nmr spectra,* the chemical shifts of alkenic hydrogens are toward lower fields than those of alkane hydrogens and normally fall in the range 4.6–5.3 ppm relative to TMS (see Section 9-10E and Table 9-4). Spin-spin couplings of alkenic hydrogens are discussed in Section 9-10G and 9-10J.

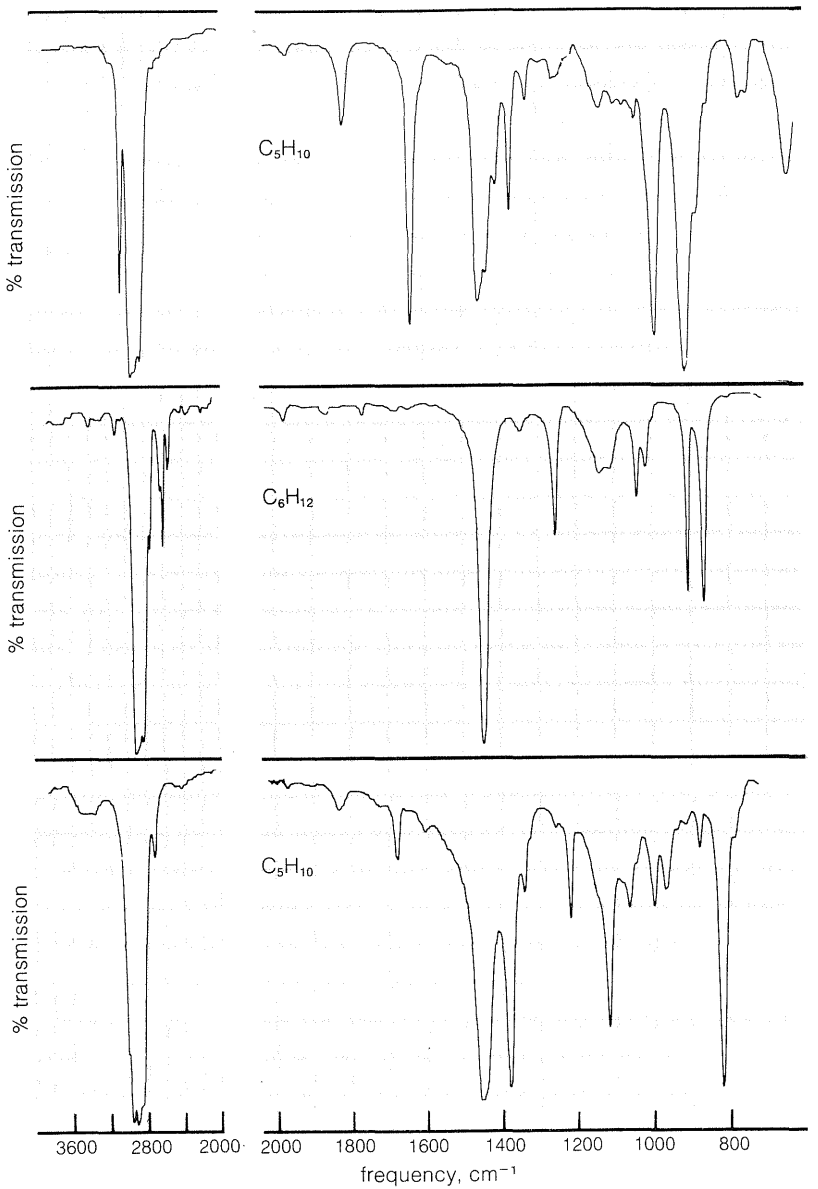


Figure 10-2 Infrared spectra for Exercise 10-1

Exercise 10-2 Deduce the structures of the substances whose proton nmr spectra are shown in Figure 10-3. Analyze the spectra in as much detail as you can in terms of chemical shifts and spin-spin splitting.

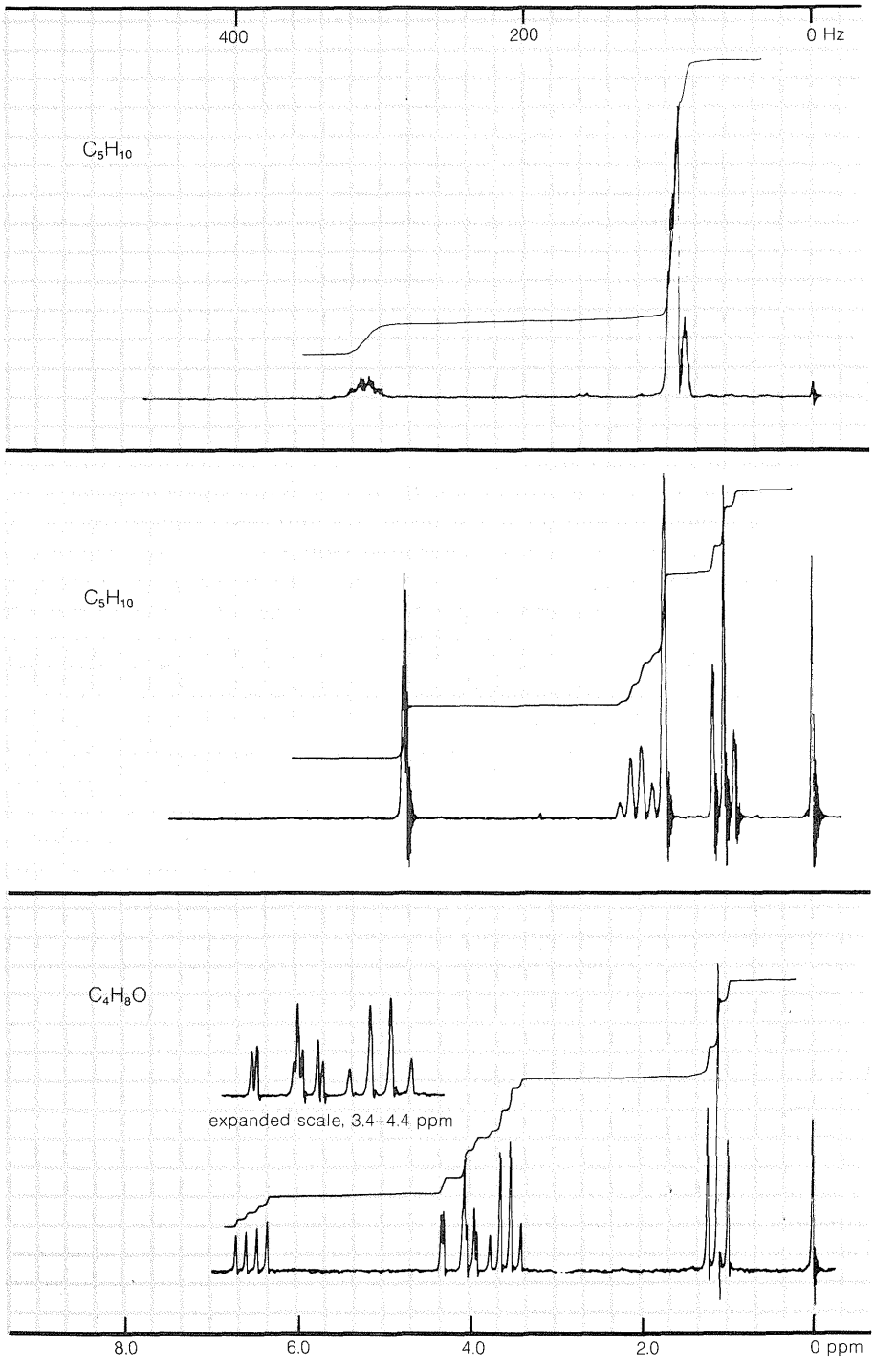


Figure 10-3 Proton nmr spectra at 60 MHz with TMS as the standard at 0 ppm. See Exercise 10-2.

10-1C Spectroscopic Properties of Alkynes

The *infrared spectrum* of a monosubstituted alkyne such as ethynylbenzene, $C_6H_5C{\equiv}CH$ (Figure 10-4), has a strong band near 3300 cm^{-1}, which is characteristic of the carbon–hydrogen stretching vibration in the grouping $\equiv C{-}H$. At a lower frequency (longer wavelength) around 2100 cm^{-1}, there is a band associated with the stretching vibration of the triple bond (also see Figure 9-36). Therefore the presence of the grouping $-C{\equiv}CH$ in a molecule may be detected readily by infrared spectroscopy. However, the triple bond of a disubstituted alkyne, $R{-}C{\equiv}C{-}R$, is detected less easily because there is no $\equiv C{-}H$ absorption near 3300 cm^{-1}, and furthermore the $C{\equiv}C$ absorption sometimes is of such low intensity that it may be indiscernible. Raman spectroscopy (Section 9-8) or chemical methods must then be used to confirm the presence of a triple bond.

Alkynes, like alkenes, undergo *electronic absorption* strongly only at wavelengths in the relatively inaccessible region below 200 nm. However, when the triple bond is conjugated with one or more unsaturated groups, radiation of longer wavelength is absorbed. To illustrate, ethyne absorbs at 150 nm and 173 nm, whereas 1-buten-3-yne ($CH_2{=}CH{-}C{\equiv}CH$) absorbs at 219 nm and 227.5 nm. The effects of such conjugation on spectra is discussed in more detail in Section 9-9B.

The proton *nuclear magnetic resonance* spectrum of ethynylbenzene is shown in Figure 10-5. The peaks near 435 Hz and 185 Hz correspond to resonances of the phenyl and $\equiv C{-}H$ protons, respectively. The difference

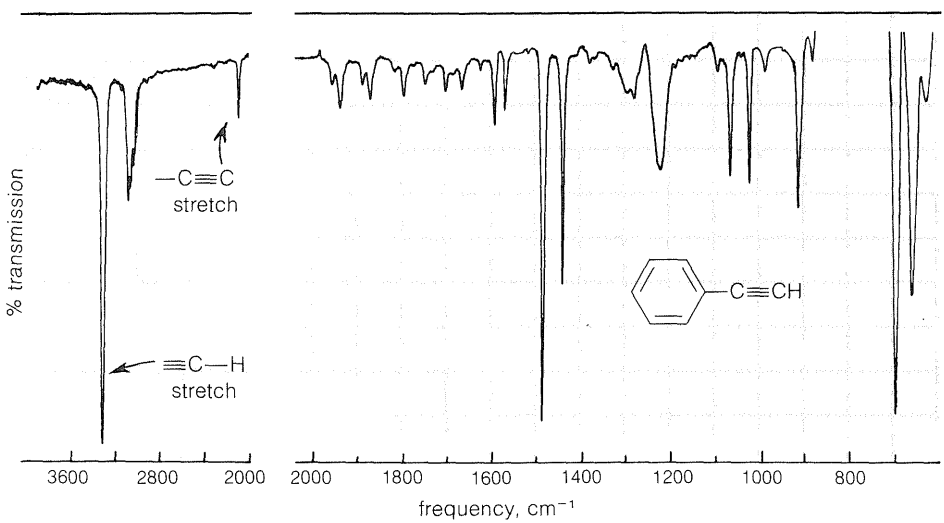


Figure 10-4 Infrared spectrum of ethynylbenzene in carbon tetrachloride solution

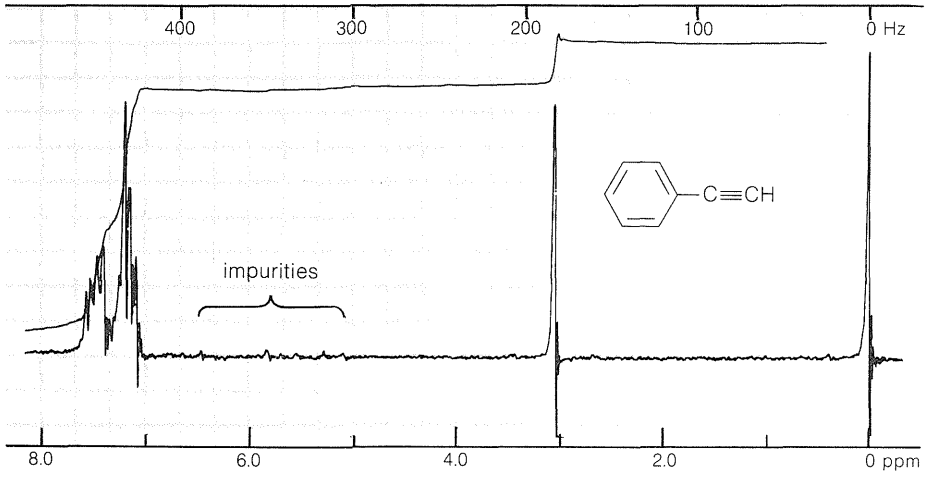


Figure 10-5 The proton nmr spectrum and integral of ethynylbenzene at 60 MHz relative to TMS as 0.00. This spectrum also illustrates the use of nmr for detection of small amounts of impurities. The almost imperceptible peaks around 6 ppm are in the correct locations for alkene hydrogens. The integral indicates that the ratio of alkene to ethyne hydrogens is on the order of 1 : 15. The substance most likely to give rise to the peaks is ethenylbenzene (styrene, $C_6H_5CH{=}CH_2$) and, if so, it is present to the extent of about 2%.

in chemical shift between the two types of protons is considerably larger than between alkenic and aromatic protons (compare Figure 10-5 with Figure 9-37) and, in general, alkynic protons come into resonance at higher magnetic fields (i.e., they are subject to more diamagnetic shielding, Section 9-10E) than alkenic or aromatic protons. In fact, the ≡C—H protons of alkynes have chemical shifts approaching those of alkyl protons. (Also see Figure 9-36.)

The *mass spectra* of alkenes and alkynes usually give distinct molecular ions; however, the fragmentation is often complex and not easily interpreted.

Exercise 10-3 Sketch the principal features you would expect for the infrared and proton nmr spectra of each of the following substances. (It will be helpful to review Sections 9-7 and 9-10.)

a. $CH_3C{\equiv}CCH_3$

b. $CH_3C{\equiv}CH$ (expect a four-bond coupling of about 3 Hz)

c. $CH_3CH_2C{\equiv}CCH_2CH_3$

d. $HC{\equiv}C{-}CH{=}CH{-}C{\equiv}CH$ (cis and trans)

Exercise 10-4 Deduce the structure of a compound with the following spectral properties:

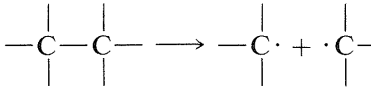
Mass spectrum	Infrared	Nmr
m/e 82 (highest mass number)	3320 cm^{-1} (s)	δ 0.93, area 3, triplet
m/e 39 (base peak)	2950 cm^{-1} (s)	1.18–1.65, 4, complex
	2120 cm^{-1} (m)	1.73, 1, closely spaced triplet
	1460 cm^{-1} (s)	
	1375 cm^{-1} (w)	2.16, 2, complex
	640 cm^{-1} (s)	

No electronic absorption was evident at wavelengths longer than 200 nm.

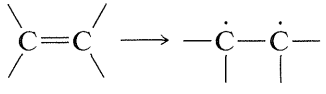
10-2 THE REACTIVITY OF MULTIPLE CARBON–CARBON BONDS

In the early days of organic chemistry, alkenes were described as "unsaturated" because, in contrast to the "saturated" alkanes, they were found to react readily with substances such as halogens, hydrogen halides, oxidizing agents, and so on. Therefore, the "chemical affinity" of alkenes was regarded as unsatisfied or "unsaturated." (Also see Section 1-1I.)

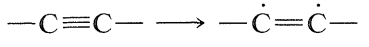
One reason alkenes and alkynes react more readily than alkanes is because the carbon–carbon bonds of a multiple bond are individually weaker than normal carbon–carbon single bonds. Consider the bond energies involved. According to Table 4-3, the strengths of carbon–carbon single, double, and triple bonds are 83, 146, and 200 kcal, respectively. From these values we can calculate that cleavage of one-half of a carbon–carbon double bond should require 63 kcal and cleavage of one-third of a carbon–carbon triple bond should require 54 kcal:



$\Delta H^0 = 83$ kcal



$\Delta H^0 = 146 - 83 = 63$ kcal



$\Delta H^0 = 200 - 146 = 54$ kcal

As a result, addition reactions to multiple bonds are expected to be about 20–30 kcal more exothermic than the corresponding cleavage reactions

of carbon–carbon single bonds, as estimated here for reaction with bromine:

$$CH_3{-}CH_3 + Br_2 \longrightarrow 2CH_3Br \qquad \Delta H^0 = -7 \text{ kcal}$$
$$CH_2{=}CH_2 + Br_2 \longrightarrow Br{-}CH_2{-}CH_2{-}Br \qquad \Delta H^0 = -27 \text{ kcal}$$
$$HC{\equiv}CH + Br_2 \longrightarrow BrCH{=}CHBr \qquad \Delta H^0 = -36 \text{ kcal}$$

The substantial difference in the heats of reaction of ethane, ethene, and ethyne with bromine is reflected in a very important practical consideration in handling ethyne (acetylene), namely its thermodynamic stability relative to solid carbon and hydrogen gas. Unlike ethane, both ethene and ethyne can be shown from bond energies to be unstable with respect to formation of solid carbon and gaseous hydrogen:

$$HC{\equiv}CH(g) \longrightarrow 2C(s) + H_2(g) \qquad \Delta H^0 = -54 \text{ kcal}$$
$$H_2C{=}CH_2(g) \longrightarrow 2C(s) + 2H_2(g) \qquad \Delta H^0 = -13 \text{ kcal}$$
$$H_2C{-}CH_3(g) \longrightarrow 2C(s) + 3H_2(g) \qquad \Delta H^0 = +20 \text{ kcal}$$

Although this does not seem to offer particular problems with ethene, an explosive decomposition of ethyne to carbon and hydrogen may occur if the gas is compressed to 10–20 kg cm^{-2}. Even liquid ethyne (bp −83°) must be handled with care. Ethyne is not used commercially under pressure unless it is mixed with an inert gas and handled in rugged equipment. Ethyne burns with pure oxygen to give a very hot flame that is widely used for welding. For this purpose, the gas is dissolved under about 15 kg cm^{-2} in 2-propanone (acetone, $CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_3$, bp 56.5°) and contained in cylinders packed with diatomaceous earth.

Why is ethyne so much less stable than ethene or ethane? First, C–C bonds are not as strong as C–H bonds. Therefore a gain in stability usually is to be expected when C–H bonds are made at the expense of C–C bonds; ethene and ethane each have more C–H bonds than ethyne has. Second, ethyne has six electrons held between the two carbons and these electrons experience considerable mutual interelectronic repulsion. This accounts for the fact that the *average* C—C bond strength for the triple bond of an alkyne is 200/3 = 67 kcal, compared to 146/2 = 73 for the double bond of an alkene and 83 kcal for a normal single bond of an alkane.

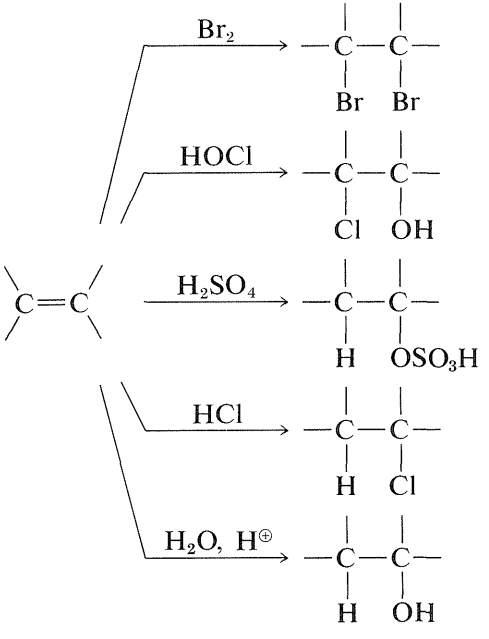
10-3 ELECTROPHILIC ADDITIONS TO ALKENES

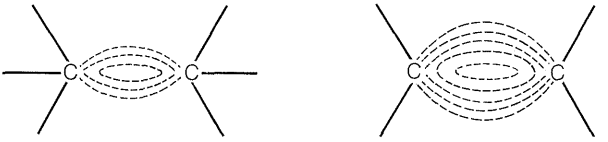
The reactions of alkanes discussed in Chapter 4 are *homolytic* processes, which means that the bonds are made and broken through radical or atomic intermediates. In contrast, the S_N and E reactions of alkyl halides, considered

in Chapter 8, involve heterolytic bond cleavage and ionic reagents or products. An especially important factor contributing to the differences between the reactions of the alkanes and alkyl halides is the slight ionic character of C–H bonds compared to C–halide bonds (see Section 1-3). The alkenes are like the alkanes in being nonpolar compounds (Section 4-1) and it may come as a surprise that many important reactions of alkenes are heterolytic reactions. Why should this be so? No doubt because the electrons in the alkene double bonds are more exposed and accessible than the electrons in an alkane C–C bond.

This is evident from the atomic-orbital models of ethene described in Section 6-4C. The electrons of the double bond are pushed outward by their mutual repulsions, and their average positions are considerably farther from the bond axis than the electron positions of a single bond (Figure 10-6). In such circumstances, electrophilic reagents, which act to acquire electrons in chemical reactions (Section 8-1), are expected to be particularly reactive. This is actually the case. Furthermore, reagents that are primarily nucleophilic (electron-donating) are notoriously poor for initiating reactions at carbon–carbon double bonds. Exceptions occur when the double bonds carry substituents with a sufficiently high degree of electron-attracting power to reduce the electron density in the double bond enough to permit attack by a nucleophilic agent.

Examples of electrophilic reagents that normally add to carbon–carbon double bonds of alkenes to give saturated compounds include halogens (Cl_2, Br_2, and I_2), hydrogen halides (HCl and HBr), hypohalous acids (HOCl and HOBr), water, and sulfuric acid:





region of high electron density
single bond

relatively diffuse region of high electron density
double bond

Figure 10-6 Schematic representations of average densities of electrons in carbon–carbon single and double bonds

The mechanisms of these reactions have much in common and have been studied extensively from this point of view. They also have very considerable synthetic utility. The addition of water to alkenes (hydration) is particularly important for the preparation of a number of commercially important alcohols. Thus ethanol and 2-propanol (isopropyl alcohol) are made on a very large scale by the hydration of the corresponding alkenes (ethene and propene) using sulfuric or phosphoric acids as catalysts. The nature of this type of reaction will be described later.

$$CH_2{=}CH_2 + H_2O \xrightarrow{H_3PO_4} \underset{\text{ethanol}}{CH_3CH_2OH}$$

$$CH_3CH{=}CH_2 \xrightarrow{H_2SO_4} \left[CH_3\underset{\displaystyle OSO_3H}{\underset{|}{C}}H{-}CH_3 \right] \xrightarrow{H_2O} CH_3{-}\underset{\displaystyle OH}{\underset{|}{C}}H{-}CH_3$$

2-propanol

Exercise 10-5 Use the bond energies (Table 4-3) to calculate ΔH^0 for the addition of Br_2, Cl_2, I_2, HOCl, HCl, HBr, HI, and H_2O to ethene in the gas phase. The addition of HCl, HBr, and HI is energetically unfavorable in dilute water solution. Why should this be so?

10-3A The Stepwise Ionic Mechanism. Halogen Addition

We shall give particular attention here to the addition of bromine to alkenes because this reaction is carried out very conveniently in the laboratory and illustrates a number of important points about electrophilic addition reactions. Much of what follows applies to addition of the other halogens, except fluorine.

A significant observation concerning bromine addition is that it and many of the other reactions listed on page 360 proceed in the dark and are *not* influenced by radical inhibitors. This is evidence against a radical-chain mechanism of the type involved in the halogenation of alkanes (Section 4-4D). However, it does not preclude the operation of radical-addition reactions under other conditions, and, as we shall see later in this chapter, bromine, chlorine, and many other reagents that commonly add to alkenes by ionic mechanisms also can add by radical mechanisms.

One alternative to a radical-chain reaction for bromine addition to an alkene would be the simple four-center, one-step process shown in Figure 10-7.

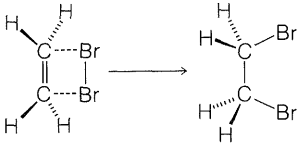


Figure 10-7 Representation of a one-step suprafacial mechanism for addition of bromine to ethene. Gas-phase additions appear to proceed in this manner.

The mechanism of Figure 10-7 cannot be correct for bromine addition to alkenes in solution for two important reasons. First, notice that this mechanism requires that the two C–Br bonds be formed on the *same* side of the double bond, and hence produce *suprafacial addition.* However, there is much evidence to show that bromine and many other reagents add to alkenes to form *antarafacial addition* products (Figure 10-8).

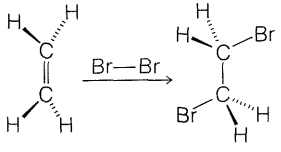
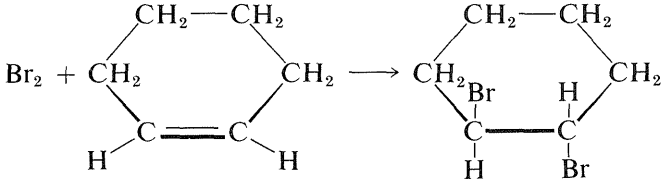


Figure 10-8 Antarafacial addition of bromine to ethene; usually observed in solution

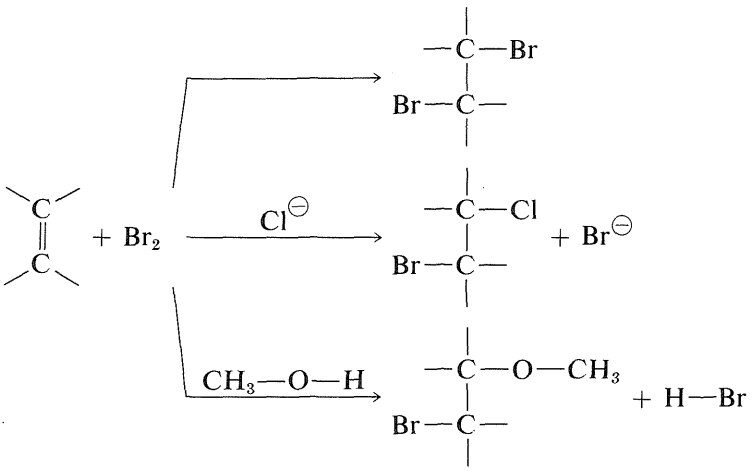
Cyclohexene adds bromine to give *trans*-1,2-dibromocyclohexane:



trans-1,2-dibromocyclohexane

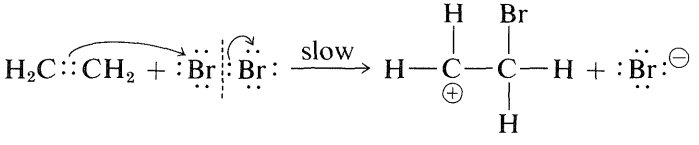
The cis isomer is not formed at all. To give the trans isomer, the two new C–Br bonds have to be formed on *opposite sides* of the double bond by antarafacial addition. But this is impossible by a one-step mechanism because the Br–Br bond would have to stretch too far to permit the formation of both C–Br bonds at the same time.

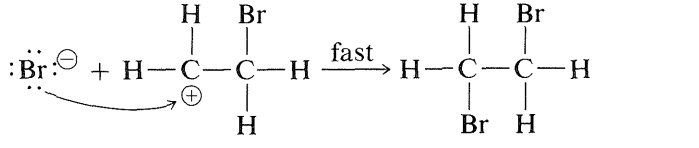
The second piece of evidence against the mechanism of Figure 10-7 is that bromine addition reactions carried out in the presence of more than one nucleophilic reagent usually give mixtures of products. Thus the addition of bromine to an alkene in methanol solution containing lithium chloride leads not only to the expected dibromoalkane, but also to products resulting from attack by chloride ions and by the solvent:



The intervention of extraneous nucleophiles suggests a *stepwise* mechanism in which the nucleophiles compete for a reactive intermediate formed in one of the steps.

A somewhat oversimplified two-step mechanism that accounts for most of the foregoing facts is illustrated for the addition of bromine to ethene. [In the formulation shown below, the curved arrows are not considered to have real mechanistic significance, but are used primarily to show which atoms can be regarded as nucleophilic (donate electrons) and which as electrophilic (accept electrons). The arrowheads always should be drawn to point to the atoms that are formulated as accepting a pair of electrons.]

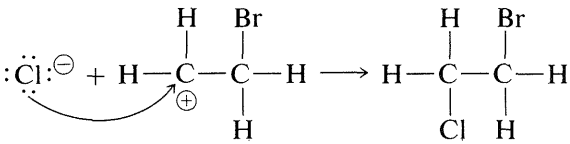




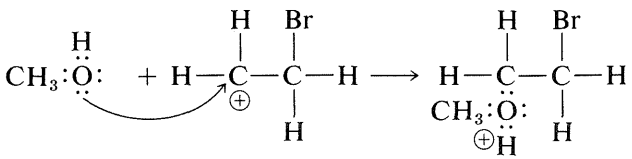
1,2-dibromoethane
(ethylene dibromide)

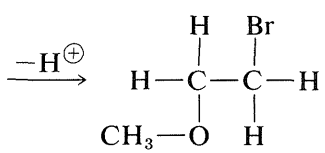
The first step (which involves electrophilic attack by bromine on the double bond) produces a bromide ion and a carbocation, as shown in Equation 10-1.[1]

As we know from our study of S_N1 reactions (Section 8-4), carbocations react readily with nucleophilic reagents. Therefore in the second step of the bromine-addition mechanism, shown in Equation 10-2, the bromoethyl cation is expected to combine rapidly with bromide ion to give the dibromo compound. However, if other nucleophiles, such as $Cl^{\ominus}$ or CH_3OH, are present in solution, they should be able to compete with bromide ion for the cation, as in Equations 10-3 and 10-4, and mixtures of products will result:



(10-3)





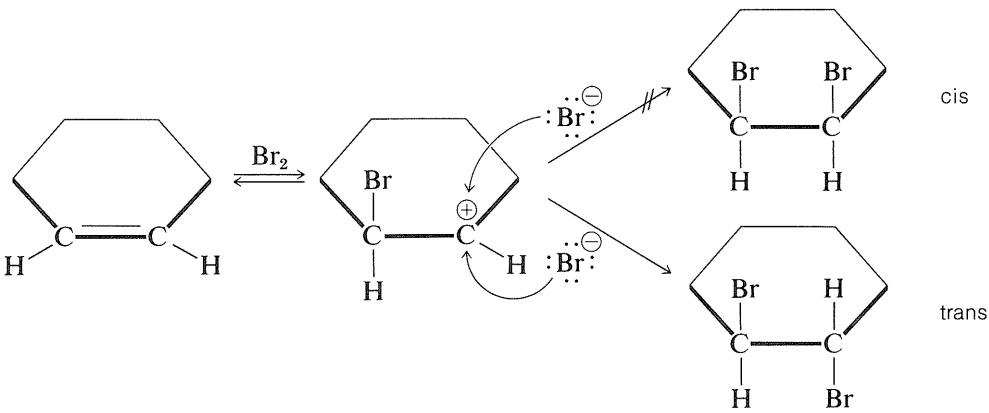
(10-4)

To account for the observation that all of these reactions result in antarafacial addition, we must conclude that the first and second steps take place from *opposite sides of the double bond.*

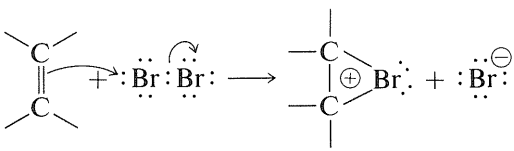
[1]An alternative to Equation 10-1 would be to have Br_2 ionize to $Br^{\oplus}$ and $Br^{\ominus}$, with a subsequent attack of $Br^{\oplus}$ on the double bond to produce the carbocation. The fact is that energy required for such an ionization of Br_2 is prohibitively large even in water solution ($\Delta H^0 \geq 80$ kcal). One might well wonder why Equation 10-1 could possibly be more favorable. The calculated ΔH^0 for $CH_2{=}CH_2 + Br_2 \longrightarrow \cdot CH_2{-}CH_2Br + Br\cdot$ is +41 kcal, which is only slightly more favorable than the ΔH^0 for $Br_2 \longrightarrow 2Br\cdot$ of 46.4 kcal. However, available thermochemical data suggest that the ease of transferring an electron from $\cdot CH_2CH_2Br$ to $Br\cdot$ to give $^{\oplus}CH_2CH_2Br + :Br^{\ominus}$ is about 80 kcal more favorable than $2Br\cdot \longrightarrow Br^{\oplus} + :Br^{\ominus}$. Thus the overall ΔH^0 of Equation 10-1 is likely to be about 85 kcal more favorable than $Br_2 \longrightarrow Br^{\oplus} + :Br^{\ominus}$.

10-3B Why Antarafacial Addition?

The simple carbocation intermediate of Equation 10-1 does not account for formation of the antarafacial-addition product. The results with S_N1 reactions (Section 8-6) and the atomic-orbital representation (see Section 6-4E) predict that the bonds to the positively charged carbon atom of a carbocation should lie in a plane. Therefore, in the second step of addition of bromine to cycloalkenes, bromide ion could attack either side of the planar positive carbon to give a mixture of *cis*- and *trans*-1,2-dibromocyclohexanes. Nonetheless, antarafacial addition occurs exclusively:



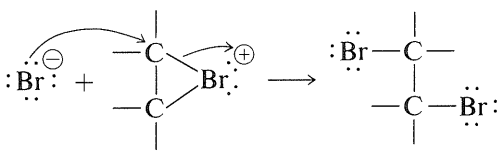
To account for the stereospecificity of bromine addition to alkenes, it has been suggested that in the initial electrophilic attack of bromine a cyclic intermediate is formed that has bromine bonded to *both* carbons of the double bond. Such a "bridged" ion is called a **bromonium ion** because the bromine formally carries the positive charge:



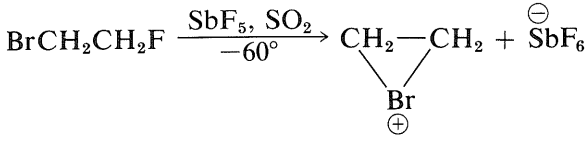
bromonium ion

(10-5)

An S_N2-type of attack of bromide ion, or other nucleophile, at carbon on the side *opposite* to the bridging group then results in formation of the antarafacial-addition product:



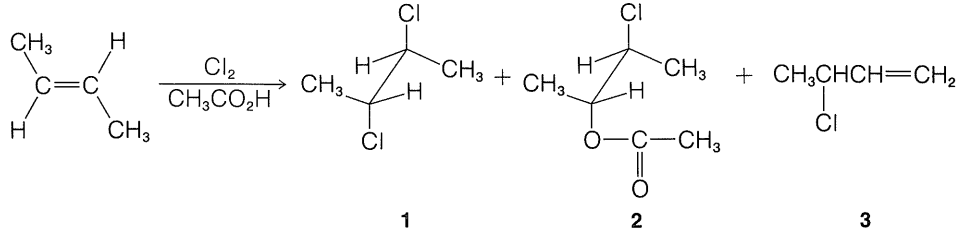
We may seem to have contradicted ourselves because Equation 10-1 shows a carbocation to be formed in bromine addition, but Equation 10-5 suggests a bromonium ion. Actually, the formulation of intermediates in alkene addition reactions as "open" ions or as cyclic ions is a controversial matter, even after many years of study. Unfortunately, it is not possible to determine the structure of the intermediate ions by any direct physical method because, under the conditions of the reaction, the ions are so reactive that they form products more rapidly than they can be observed. However, it is possible to generate stable bromonium ions, as well as the corresponding chloronium and iodonium ions. The technique is to use low temperatures in the absence of any strong nucleophiles and to start with a 1,2-dihaloalkane and antimony pentafluoride in liquid sulfur dioxide:



ethenebromonium ion

The $C_2H_4Br^{\oplus}$ ions produced in this way are relatively stable and have been shown by nmr to have the cyclic halonium ion structure.

Exercise 10-6 Addition of chlorine to *trans*-2-butene in ethanoic acid (acetic acid, CH_3CO_2H) as solvent gives 74% *meso*-2,3-dichlorobutane, **1**, 24% 2-chloro-1-methylpropyl ethanoate, **2**, and 2% 3-chloro-1-butene, **3**. (*Note:* **2** is formed as a D,L pair, although only one enantiomer is shown here.)



1 **2** **3**

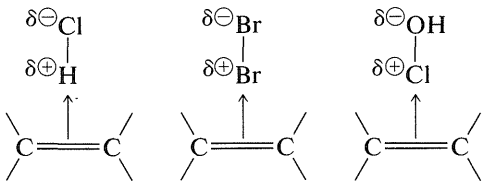
Write a mechanism to show how all three products could be obtained from a common chloronium ion intermediate. Draw structures for the products expected from addition of chlorine to *cis*-2-butene in ethanoic acid. Show the configurations. If necessary, review Section 5-5 before working this problem.

Exercise 10-7 In the formation of ethenebromonium ion from 1-bromo-2-fluoroethane and SbF_5 in SO_2, is the SbF_5 playing the role of an acid, a base, an electrophile, or a nucleophile? How strong a nucleophile do you judge $SbF_6^{\ominus}$ to be? Explain.

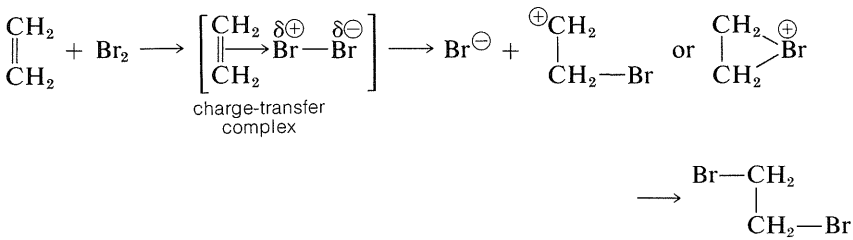
10-3C Complexes of Electrophilic Agents with Double Bonds

There is a further aspect of polar additions to alkenes that we should consider, namely, that electrophilic reagents form loose complexes with the π electrons of the double bonds of alkenes *prior* to reaction by addition. Complexes of this type are called **charge-transfer complexes** (or **π complexes**). Formation of a complex between iodine and cyclohexene is demonstrated by the fact that iodine dissolves in cyclohexene to give a *brown* solution, whereas its solutions in cyclohexane are *violet*. The brown solution of iodine in cyclohexene slowly fades as addition occurs to give colorless *trans*-1,2-diiodocyclohexane.

Precise Lewis structures cannot be written for charge-transfer complexes, but they commonly are represented as



with the arrow denoting that electrons of the double bond are associated with the electrophile. These complexes probably represent the first stage in the formation of addition products by a sequence such as the following for bromine addition:



10-3D Addition of Proton Acids

We have seen that electrophiles can react with alkenes to form carbon–halogen bonds by donating positive halogen, $Br^{\oplus}$, $Cl^{\oplus}$, or $I^{\oplus}$. Likewise, carbon–hydrogen bonds can be formed by appropriately strong proton donors, which, of course, are typically strong proton acids. These acids are more effective in the absence of large amounts of water because water can compete with the alkene as a proton acceptor (also see Section 10-3E). Hydrogen chloride addition to ethene occurs by way of a proton-transfer step to give the ethyl cation and a

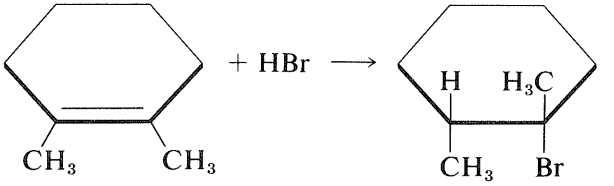
chloride ion (Equation 10-6) followed by a step in which the nucleophilic chloride ion combines with the ethyl cation (Equation 10-7):

$$CH_2{=}CH_2 + H{-}Cl \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} CH_2{-}\overset{H}{\overset{|}{C}}H_2 + Cl^{\ominus} \qquad (10\text{-}6)$$

$$CH_3\overset{\oplus}{C}H_2 + Cl^{\ominus} \xrightarrow{\text{fast}} CH_3CH_2Cl \qquad (10\text{-}7)$$

All of the hydrogen halides (HF, HCl, HBr, and HI) will add to alkenes. Addition of hydrogen fluoride, while facile, is easily reversible. However, a solution of 70% anhydrous hydrogen fluoride and 30% of the weak organic base, pyridine, which is about 1/10,000 times as strong as ammonia, works better, and with cyclohexene gives fluorocyclohexane. With hydrogen iodide, care must be taken to prevent I_2 addition products resulting from iodine formed by oxidation reactions such as $4HI + O_2 \longrightarrow 2I_2 + 2H_2O$. With hydrogen bromide, radical-chain addition may intervene unless the reaction conditions are controlled carefully (this will be discussed in Section 10-7).

The stereochemistry of addition depends largely on the structure of the alkene, but for simple alkenes and cycloalkenes, addition occurs predominantly in an antarafacial manner. For example, hydrogen bromide reacts with 1,2-dimethylcyclohexene to give the antarafacial addition product:



1,2-dimethylcyclohexene

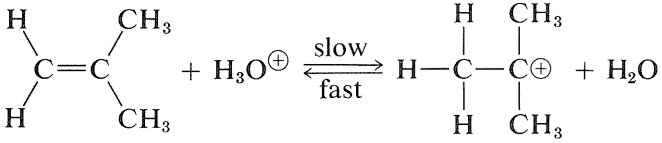
trans-1-bromo-1,2-dimethylcyclohexane

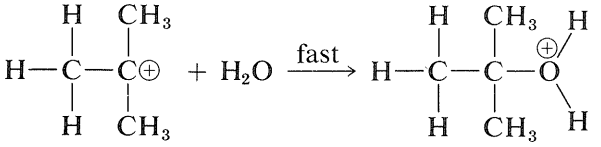
10-3E Hydration

We mentioned previously that the hydration of alkenes requires a strong acid as a catalyst, because water itself is too weak an acid to initiate the proton-transfer step. However, if a small amount of a strong acid such as sulfuric acid is present, hydronium ions, $H_3O^{\oplus}$, are formed in sufficient amount to protonate reasonably reactive alkenes, although by no means as effectively as does concentrated sulfuric acid. The carbocation formed then is attacked rapidly by a

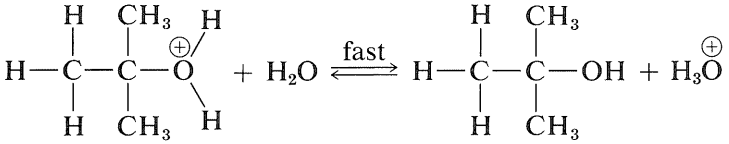
nucleophilic water molecule to give the alcohol as its conjugate acid,[2] which regenerates hydronium ion by transferring a proton to water. The reaction sequence follows for 2-methylpropene:

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^{\oplus} + HSO_4^{\ominus}$$





conjugate acid of
2-methyl-2-propanol

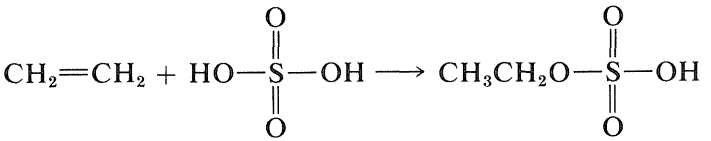


In this sequence, the acid acts as a *catalyst* because the hydronium ion used in the proton addition step is regenerated in the final step.

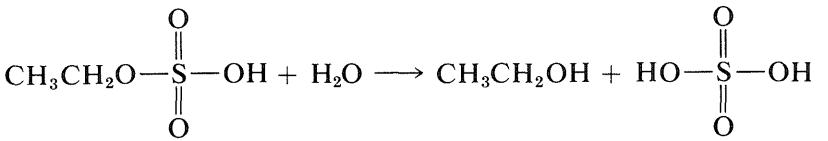
Sulfuric acid (or phosphoric acid) is preferred as an acid catalyst for addition of water to alkenes because the conjugate base, $HSO_4^{\ominus}$ (or $H_2PO_4^{\ominus}$), is a poor nucleophile and does not interfere in the reaction. However, if the water concentration is kept low by using concentrated acid, addition occurs to give sulfate (or phosphate) esters. The esters formed with sulfuric acid are either alkyl acid sulfates R—OSO_3H or dialkyl sulfates $(RO)_2SO_2$. In fact, this is one of the major routes used in the commercial production of ethanol and

[2]The terms **conjugate acid** and **conjugate base** are very convenient to designate substances that are difficult to name simply as acids, bases, or salts. The conjugate acid of a compound X is $XH^{\oplus}$ and the conjugate base of HY is $Y^{\ominus}$. Thus $H_3O^{\oplus}$ is the conjugate acid of water, while $OH^{\ominus}$ is its conjugate base. Water itself is then both the conjugate base of $H_3O^{\oplus}$ and the conjugate acid of $OH^{\ominus}$.

2-propanol. Ethene and sulfuric acid give ethyl hydrogen sulfate, which reacts readily with water in a second step to give ethanol:



ethene sulfuric acid ethyl hydrogen sulfate



ethyl hydrogen sulfate ethanol sulfuric acid

Exercise 10-8 Show the steps involved in the formation of ethyl hydrogen sulfate from ethene and sulfuric acid. Show how diethyl sulfate, $(CH_3CH_2O)_2SO_2$, could be formed from the same reagents.

10-3F Aqueous versus Nonaqueous Acids. Acid Strengths

One of the more confusing features of organic chemistry is the multitude of conditions that are used to carry out a given kind of reaction, such as the electrophilic addition of proton acids to different alkenes. Strong acids, weak acids, water, no water—Why can't there be a standard procedure? The problem is that alkenes have very different tendencies to accept protons. In the vapor phase, ΔH^0 for addition of a proton to ethene is about 35 kcal more positive than for 2-methylpropene, and although the difference should be smaller in solution, it still would be large. Therefore we can anticipate (and we find) that a much more powerful proton donor is needed to initiate addition of an acid to ethene than to 2-methylpropene. But why not use in all cases a strong enough acid to protonate *any* alkene one might want to have a proton acid add to? Two reasons: First, strong acids can induce undesirable side reactions, so that one usually will try not to use a stronger acid than necessary; second, very strong acid may even prevent the desired reaction from occurring!

In elementary chemistry, we usually deal with acids in more or less dilute aqueous solution and we think of sulfuric, hydrochloric, and nitric acids as being similarly strong because each is essentially completely dissociated in dilute water solution:

$$HCl + H_2O \rightleftharpoons H_3O^{\oplus} + Cl^{\ominus}$$

This does not mean they actually are equally strong acids. It means only that each of the acids is sufficiently strong to donate all of its protons to water. We can say that water has a "leveling effect" on acid strengths because as long as

an acid can donate its protons to water, the solution has but one acid "strength" that is determined by the $H_3O^{\oplus}$ concentration, because $H_3O^{\oplus}$ is where the protons are.

Now, if we use poorer proton acceptors as solvent we find the proton-donating powers of various "strong" acids begin to spread out immensely. Furthermore, new things begin to happen. For example, ethene is not hydrated appreciably by dilute aqueous acid; it just is too hard to transfer a proton from hydronium ion to ethene. So we use concentrated sulfuric acid, which is strong enough to add a proton to ethene. But now we don't get hydration, because any water that is present in concentrated sulfuric acid is virtually all converted to $H_3O^{\oplus}$, which is non-nucleophilic!

$$H_2SO_4 + H_2O \longrightarrow H_3O^{\oplus} + HSO_4^{\ominus}$$

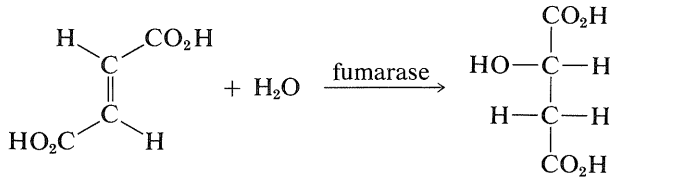
However, formation of $H_3O^{\oplus}$ leads to formation of $HSO_4^{\ominus}$, which has enough nucleophilic character to react with the $CH_3CH_2^{\oplus}$ to give ethyl hydrogen sulfate and this is formed instead of the conjugate acid of ethanol (Section 10-3 E). The epitome of the use of stronger acid and weaker nucleophile is with liquid SO_2 (bp $-10°$) as the solvent and $HSbF_6$ as the acid. This solvent is a very poor proton acceptor (which means that its conjugate acid is a very good proton donor) and $SbF_6^{\ominus}$ is an extremely poor nucleophile. If we add ethene to such a solution, a stable solution of $CH_3CH_2^{\oplus}SbF_6^{\ominus}$ is formed. The reason is that there is no better proton acceptor present than $CH_2{=}CH_2$ and no nucleophile good enough to combine with the cation.

Exercise 10-9* Suppose we were gradually to add water to a solution of $CH_3CH_2^{\oplus}$-$SbF_6^{\ominus}$ and excess $HSbF_6$ in SO_2. What changes would you expect to take place? Write equations for the reactions you expect to occur.

Exercise 10-10* Assess the possibility of adding ammonia, NH_3, to 2-methylpropene with the aid of sulfuric acid as a catalyst.

10-3G A Biological Hydration Reaction

The conversion of fumaric acid to malic acid is an important biological hydration reaction. It is one of a cycle of reactions (Krebs citric acid cycle) involved in the metabolic combustion of fuels (amino acids and carbohydrates) to CO_2 and H_2O in a living cell.



trans-butenedioic acid (fumaric acid)

2-hydroxybutanedioic acid (L-malic acid)

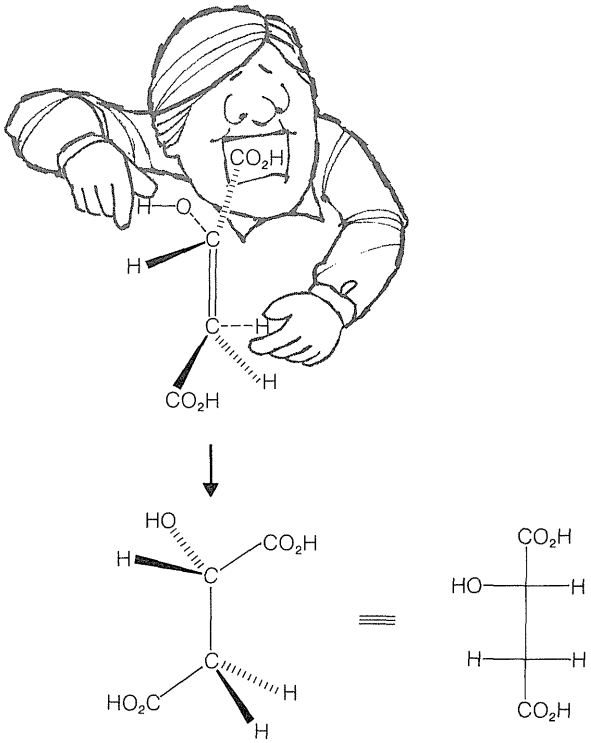
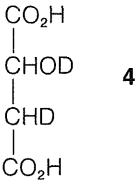


Figure 10-9 Representation of the course of enzyme-induced hydration of fumaric acid (*trans*-butenedioic acid) to give L-malic acid (L-2-hydroxybutanedioic acid). If the enzyme complexes with *either* —CO_2H (carboxyl) group of fumaric acid, and then adds OH from *its right* hand and H from *its left,* the proper stereoisomer (L) is produced by antarafacial addition to the double bond. At least three *particular* points of contact must occur between enzyme and substrate to provide the observed stereospecificity of the addition. Thus, if the enzyme functions equally well with the alkenic hydrogen or the carboxyl toward its mouth (as shown in the drawing) the reaction still will give antarafacial addition, but D,L-malic acid will be the product.

The reaction is remarkable for a number of reasons. It is readily reversible and is catalyzed by an enzyme (fumarase) at nearly neutral conditions (pH ≅ 7). Without the enzyme, no hydration occurs under these conditions. Also, the enzymatic hydration is a completely stereospecific antarafacial addition and creates L-malic acid. The enzyme operates on fumaric acid in such a way that the proton adds on one side and the hydroxyl group adds on the other side of the double bond of fumaric acid. This is shown schematically in Figure 10-9.

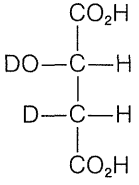
Exercise 10-11* Show by projection formulas the stereochemical course you would expect for the *acid-catalyzed* addition of D_2O to fumaric acid to give the deuterated

malic acid **4**. Be sure you consider the stereochemistry of the C—D bond relative to the C–O bond. Indicate your reasoning.



4

Exercise 10-12* The hydration of fumaric acid catalyzed by *fumarase* in D_2O leads to malic acid with only *one* C–D bond, which is selectively removed when malic acid is enzymatically reconverted to fumaric acid. The configuration of deuteriomalic acid prepared in this way has been shown to correspond to the following projection formula:

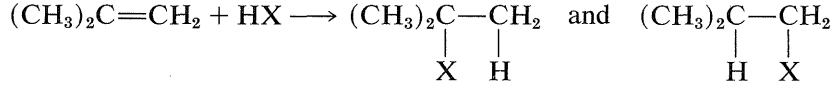


Deduce the stereochemistry of both the forward and backward reactions (hydration and dehydration) from this information.

10-4 ORIENTATION IN ADDITION TO ALKENES

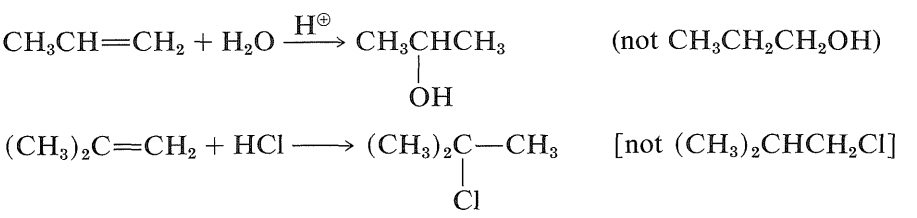
10-4A Addition of HX

Addition of an unsymmetrical substance such as HX to an unsymmetrical alkene theoretically can give two products,

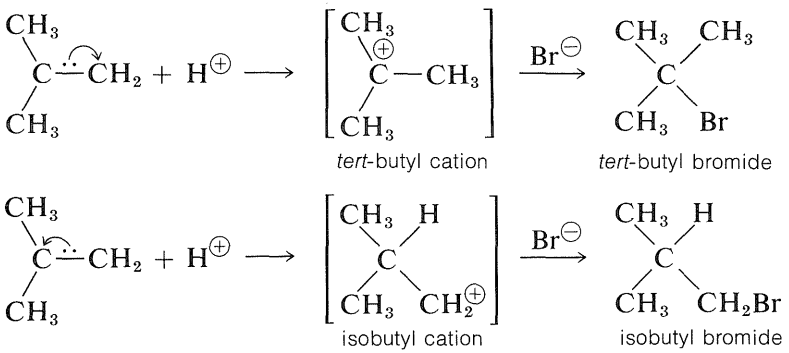


but both seldom are formed in equal amounts; in fact, one isomer usually is formed to the exclusion of the other. For example, the hydration of propene

gives 2-propanol (not 1-propanol), and hydrogen chloride adds to 2-methylpropene to give *tert*-butyl chloride (not isobutyl chloride):



To understand the reason for the pronounced selectivity in the orientation of addition of electrophiles, it will help to consider one example, hydrogen bromide addition to 2-methylpropene. Two different carbocation intermediates could be formed by attachment of a proton to one or the other of the double-bond carbons:



Subsequent reactions of the cations with bromide ion give *tert*-butyl bromide and isobutyl bromide. In the usual way of running these additions, the product is very pure *tert*-butyl bromide.

How could we have predicted which product would be favored? The first step is to decide whether the prediction is to be based on (1) which of the two products is the *more stable,* or (2) which of the two products is formed *more rapidly.* If we make a decision on the basis of product stabilities, we take into account ΔH^0 values, entropy effects, and so on, to estimate the equilibrium constants K_{eq} for the reactants and each product. When the ratio of the products is determined by the ratio of their equilibrium constants, we say the overall reaction is subject to **equilibrium** (or **thermodynamic**) **control.** Equilibrium control requires that the reaction be *reversible.*

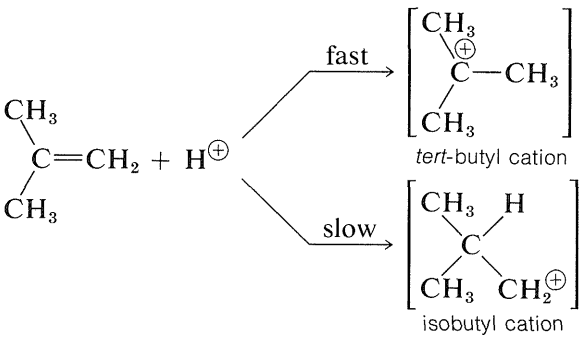
When a reaction is carried out under conditions in which it is *not reversible,* the ratio of the products is determined by the relative rates of formation of the various products. Such reactions are said to be under **kinetic control.**

The products obtained in a reaction subject to kinetic control are not necessarily the same as those obtained under equilibrium control. Indeed, the equilibrium constant for interconversion of *tert*-butyl bromide and isobutyl

bromide at 25° is 4.5, and if the addition of hydrogen bromide to 2-methylpropene were under equilibrium control, the products would be formed in this ratio:

$$K_{eq} = \frac{[\textit{tert}\text{-butyl bromide}]}{[\text{isobutyl bromide}]} = 4.5$$

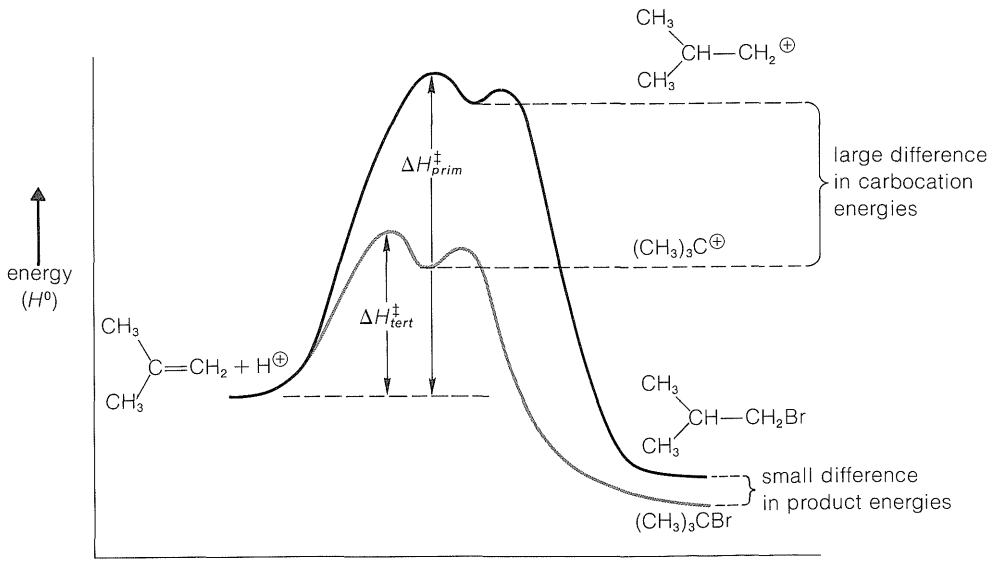
But the addition product is 99+% *tert*-butyl bromide so the reaction clearly is kinetically controlled, *tert*-butyl bromide being formed considerably faster than isobutyl bromide. *The slow, or rate-determining, step in this reaction is the formation of the intermediate cation rather than the reaction of the cation with bromide ion.* So to account for the formation of *tert*-butyl bromide we have to consider why the *tert*-butyl cation is formed more rapidly than the isobutyl cation:



As we have seen in Section 8-7B, alkyl groups are more electron donating than hydrogen. This means that the more alkyl groups there are on the positive carbon of the cation, the more stable and the more easily formed the cation will be. The reason is that electron-donating groups can partially compensate for the electron deficiency of the positive carbon. As a result, we can predict that the *tert*-butyl cation with three alkyl groups attached to the positive center will be formed more readily than the primary isobutyl cation with one alkyl group attached to the positive center.

Thus the problem of predicting which of the two possible products will be favored in the addition of unsymmetrical reagents to alkenes under kinetic control reduces to predicting which of two possible carbocation intermediates will be formed most readily. With simple alkenes, we shall expect the preference of formation of the carbocations to be in the order *tertiary* > *secondary* > *primary*.

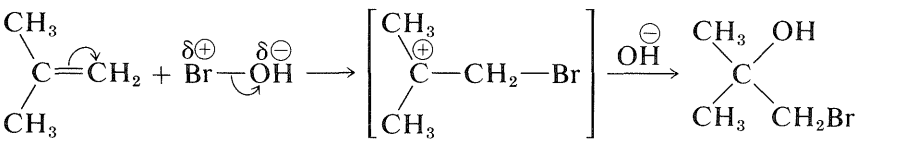
The reaction scheme can be represented conveniently in the form of an energy diagram (Figure 10-10). The activation energy, $\Delta H^{\ddagger}_{tert}$ for the formation of the *tert*-butyl cation is less than $\Delta H^{\ddagger}_{prim}$ for the formation of the isobutyl cation because the tertiary ion is much more stable (relative to the reactants) than the primary ion, and therefore is formed at the faster rate. The second step, to form the product from the intermediate cation, is very rapid


energy
(H^0)
CH_3
CH_3
CH_3

Exercise 10-15 Arrange ethene, propene, and 2-methylpropene in order of expected ease of hydration with aqueous acid. Show your reasoning.

10-4B Addition of Other Reagents to Unsymmetrical Alkenes. The Electronegativity Chart

We can extend Markownikoff's rule to cover additions of substances of the general type X—Y to unsymmetrically substituted alkenes when a clear-cut decision is possible as to whether X or Y is the more electrophilic atom of X—Y. If the polarization of the X—Y bond is such that X is positive, $^{\delta\oplus}X—Y^{\delta\ominus}$, then X will be expected to add as $X^{\oplus}$ to the alkene to form the more stable carbocation. This step will determine the direction of addition. For example, if we know that the O–Br bond of HOBr is polarized as $HO^{\delta\ominus}—Br^{\delta\oplus}$, then we can predict that addition of HOBr to 2-methylpropene will give 1-bromo-2-methyl-2-propanol:



1-bromo-2-methyl-2-propanol

The polarization of X—Y bonds may be predicted by considering the electron-attracting powers, or electronegativities, of the various elements and groups. The general problem of assigning electronegativities to the various elements has been considered in detail by Pauling. In the **Pauling electronegativity chart** (Figure 10-11), the elements of each horizontal row in the periodic table are arranged in order of increasing electronegativity from left to right. In a given horizontal row of the periodic table, electronegativity *increases* with increasing atomic number. However, electronegativity *decreases* with increasing atomic number in a given vertical column of the periodic table.

Pauling's value for the electronegativity of carbon makes it slightly more electron-attracting than hydrogen. However, we expect that the electron-attracting power of a carbon atom (or of other elements) will depend also on the electronegativities of the groups to which it is attached. In fact, many experimental observations indicate that carbon in methyl or other alkyl groups is significantly *less* electron-attracting than hydrogen. Conversely, the CF_3— group is, as expected, far *more* electron-attracting than hydrogen.

The direction of polarization of bonds between various elements may be predicted from Figure 10-11. For example, an O–Cl bond should be polarized so the oxygen is negative; a C–N bond should be polarized so the nitrogen is negative:

$O^{\delta\ominus}$-------$Cl^{\delta\oplus}$ $C^{\delta\oplus}$-------$N^{\delta\ominus}$

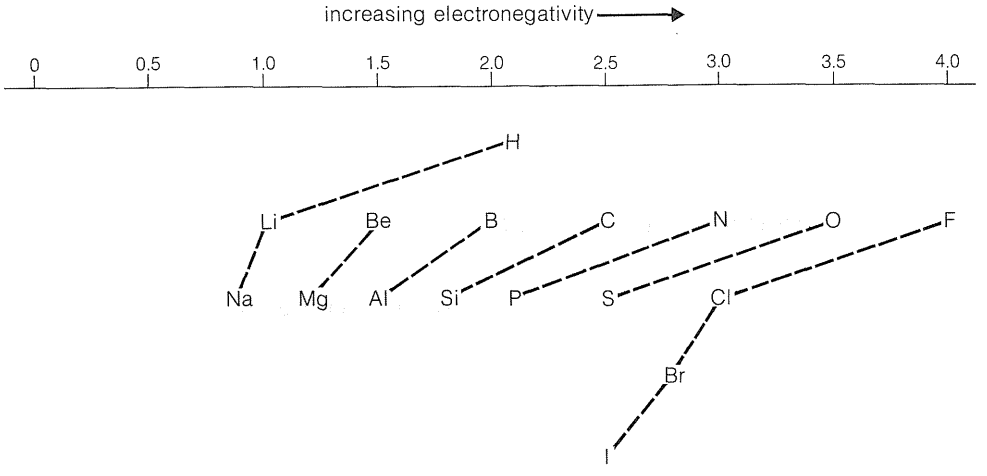
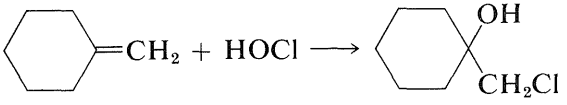


Figure 10-11 Pauling electronegativities of elements. The dashed lines connect elements in particular vertical columns of the periodic table.

We then can predict that, in the addition of HOCl to an alkene, the chlorine will add preferentially to form the more stable of two possible carbon cations. Generally, this means that chlorine will bond to the carbon carrying the greater number of hydrogens:



A number of reagents that are useful sources of electrophilic halogen are included in Table 10-2. Some of these reagents, notably those with *O*–halogen or *N*–halogen bonds, actually are sources of hypohalous acids, HOX, and function to introduce halogen and hydroxyl groups at carbon. There are very few good fluorinating agents whereby the fluorine is added as $F^{\oplus}$.

Exercise 10-16 Use the electronegativity chart of Figure 10-11 and Table 10-2 to predict the products of the following additions under conditions of kinetic control. Indicate the configuration of the products where possible.

a. 2-methyl-2-butene with ICl, and with INO_2

b. a carbon–nitrogen double bond with water

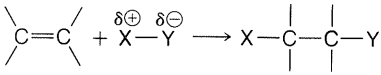
c. *N*-bromosuccinimide and cyclohexene in aqueous medium

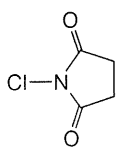
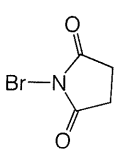
d. 2-methylpropene with HOF

e. 2-methylpropene with *N*-bromosuccinimide and 70% hydrogen fluoride in pyridine (Notice that the pyridine serves only to moderate the activity of the hydrogen fluoride.)

Table 10-2

Reagents that add to Alkenes by Electrophilic Attack:

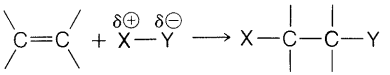


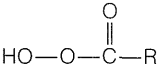
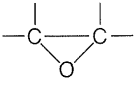
Reagent ($\delta\oplus$ X—Y $\delta\ominus$)		Adduct	
Name	Structure	Name	Structure
sulfuric acid	H—OSO_3H	sulfate ester	H—C—C—OSO_3H
hydrogen fluoride[a]	H—F	fluoroalkane	H—C—C—F
hydrogen chloride	H—Cl	chloroalkane	H—C—C—Cl
hydrogen bromide	H—Br	bromoalkane	H—C—C—Br
water[b]	H—OH	alcohol	H—C—C—OH
alcohol[b]	H—OR	ether	H—C—C—OR
carboxylic acid[b]	H—OCR (O double-bonded)	carboxylic ester	H—C—C—OCR (O double-bonded)
trifluoromethyl hypofluorite	F—O—CF_3	2-fluoroalkyl trifluoromethyl ether	F—C—C—OCF_3
chlorine	Cl—Cl	dichloroalkane	Cl—C—C—Cl
hypochlorous acid	Cl—OH	chloroalcohol	Cl—C—C—OH
tert-butyl hypochlorite[c]	Cl—$OC(CH_3)_3$	chloroalcohol	Cl—C—C—OH
N-chlorosuccinimide[c]		chloroalcohol	Cl—C—C—OH
N-chlorosuccinimide and hydrogen fluoride[a]		chlorofluoroalkane	Cl—C—C—F
bromine	Br—Br	dibromoalkane	Br—C—C—Br
bromine chloride	Br—Cl	bromochloroalkane	Br—C—C—Cl
cyanogen bromide	Br—CN	bromonitrile	Br—C—C—CN
bromine azide	Br—N_3	bromoalkyl azide	Br—C—C—N_3
hypobromous acid	Br—OH	bromoalcohol	Br—C—C—OH
N-bromosuccinimide[c]		bromoalcohol	Br—C—C—OH
N-bromosuccinimide and hydrogen fluoride[a]		bromofluoroalkane	Br—C—C—F
iodine	I—I	diiodoalkane	I—C—C—I
iodine chloride	I—Cl	chloroiodoalkane	I—C—C—Cl
hypoiodous acid	I—OH	iodoalcohol	I—C—C—OH

(Table 10-2 continued on following page.)

Table 10-2 (continued)

Reagents that add to Alkenes by Electrophilic Attack:



Reagent (X—Y)		Adduct	
Name	Structure	Name	Structure
N-iodosuccinimide and hydrogen fluoride[a]		iodofluoroalkane	I—C—C—F
sulfenyl chlorides	RS—Cl	chlorothioether	RS—C—C—Cl
nitrosyl chloride	O=N—Cl	chloronitrosoalkane	O=N—C—C—Cl
nitryl iodide	O_2N—I	nitroiodoalkane	O_2N—C—C—I
mercuric salts[d]	XHg—X	alkylmercuric compound	XHg—C—C—X
thallium salts	XTl—X	alkylthallium compound	XTl—C—C—X
alkanes[e]	R—H	alkane	R—C—C—H
boranes[f]	R_2B—H	trialkylborane	R_2B—C—C—H
peroxyacids[g]		oxirane	

[a]A 70% solution of anhydrous hydrogen fluoride in pyridine (a rather weak nitrogen base).

[b]Weak acids require a strong acid catalyst to initiate electrophilic attack.

[c]In aqueous solution; serves as source of HOX, X = Br or Cl.

[d]See Section 10-5A. [e]See Section 10-9. [f]See Section 11-6. [g]See Section 11-7D.

10-4C Additions to Substituted Alkenes

For alkenes that have halogen or similar substituents at the doubly bonded carbons, the same principles apply as with the simple alkenes. That is, under kinetic control the preferred product will be the one derived from the more stable of the two possible intermediate carbon cations. Consider a compound of the type Y—CH=CH_2. If Y is *more* electron-attracting than hydrogen, then hydrogen halide should add in such a way as to put the proton of HX on the YCH= end and X on the =CH_2 end. The reason is that the positive car-

bon is expected to be more favorably located if it is not attached directly to an electron-attracting substituent:

$$Y{-}CH{=}CH_2 + H^{\oplus} \rightleftharpoons Y{-}\underset{\text{Y is more electron-attracting than hydrogen}}{\overset{H}{\overset{|}{C}}H{-}\overset{\oplus}{C}H_2} \xrightarrow{X^{\ominus}} Y{-}CH_2{-}CH_2{-}X$$

The addition goes as predicted, *provided that the atom directly attached to the carbon of the double bond carries no unshared (nonbonding) electron pairs.* For example,

$$CF_3{-}CH{=}CH_2 + HCl \longrightarrow CF_3{-}CH_2{-}CH_2{-}Cl$$

Such substituents are relatively uncommon, and most of the reported H—X additions have been carried out with Y groups having unshared electron pairs on an atom connected directly to a carbon of the double bond:

$$\ddot{Y}{-}CH{=}CH_2 \qquad Y = R{:}\ddot{O}{-},\ {:}\ddot{F}{-},\ {:}\ddot{Cl}{-},\ \text{etc.}$$

These substituents usually are strongly electronegative relative to hydrogen, and this often causes diminished reactivity of the double bond toward electrophiles. Nonetheless, *the preferred orientation of HX addition situates the positive charge of the intermediate carbocation next to the substituent:*

$$\ddot{Y}{-}CH{=}CH_2 \xrightarrow{H^{\oplus}} \left[\ddot{Y}{-}\overset{\oplus}{C}H{-}CH_3 \longleftrightarrow \overset{\oplus}{\ddot{Y}}{=}CH{-}CH_3\right] \xrightarrow{X^{\ominus}} Y{-}\overset{X}{\overset{|}{\underset{H}{\underset{|}{C}}}}{-}CH_3$$

The electron-attracting power of the substituent is more than counterbalanced by stabilization of the intermediate cation by the ability of the substituents to delocalize their *unshared* electrons to the adjacent positive carbon (see Section 6-6).

Exercise 10-17 Make atomic-orbital models of the 1- and 2-fluoroethyl carbocations ($CH_3CHF^{\oplus}$ and $FCH_2CH_2^{\oplus}$). Predict which should be formed more rapidly by the addition of $H^{\oplus}$ to fluoroethene. Give your reasoning.

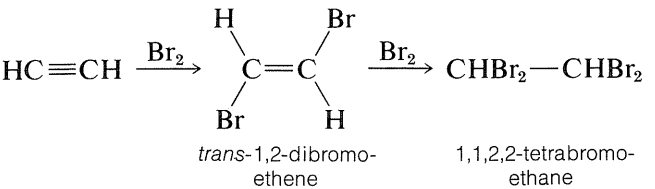
Exercise 10-18 Predict the predominant product from addition of hydrogen chloride to each of the following alkenes. Give your reasoning.

a. $CH_2{=}CCl_2$ **c.** $CF_3{-}CH{=}CH{-}CH_3$

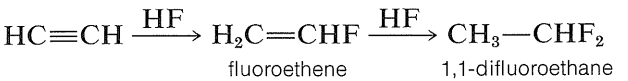
b. $(CH_3)_2C{=}CCl_2$ **d.** $CH_3OCH{=}CHF$

10-5 ELECTROPHILIC ADDITION REACTIONS OF ALKYNES

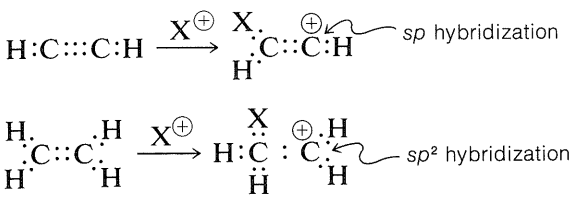
The alkynes behave in many ways as if they were doubly unsaturated alkenes. For example, bromine adds to ethyne in two stages—first to give *trans*-1,2-dibromoethene by antarafacial addition, and finally to give 1,1,2,2,-tetrabromoethane:



Likewise, anhydrous hydrogen fluoride adds first to give fluoroethene and ultimately to give 1,1-difluoroethane:



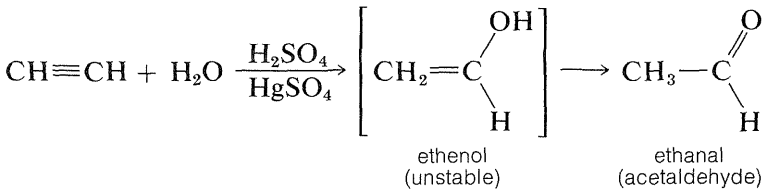
However, there is an interesting contrast in reactivity. Alkynes are substantially *less* reactive than corresponding alkenes toward many electrophiles. This is perhaps surprising because the electrons of a triple bond, like those of a double bond, are highly exposed, which suggests that the reactivity (nucleophilicity) of a triple bond should be high. Evidently this is not the case. A simple but reasonable explanation is that the carbocation formed from the alkyne is less stable than that from the alkene because it cannot achieve the sp^2 hybrid-orbital configuration expected to be the most stable arrangement for a carbocation (see Section 6-4E):



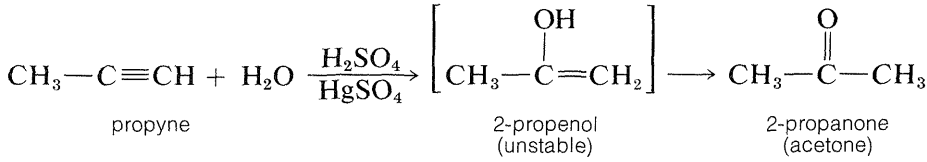
Exercise 10-19 The ethenyl carbocation, $CH_2{=}CH^{\oplus}$, apparently is formed much more easily by addition of a proton from HCl to ethyne than it is by S_N1 reactions of ethenyl chloride. Deduce from bond energies why this should be so.

10-5A Hydration of Alkynes

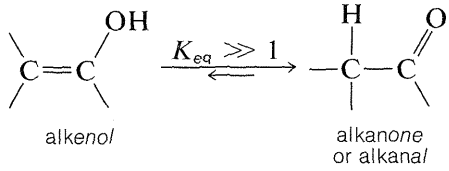
Alkynes, unlike alkenes, are not hydrated readily in aqueous acid unless a mercuric salt is present as a catalyst. Also, the products that are isolated are either aldehydes or ketones instead of alcohols. Even though the addition of one molecule of water to ethyne probably gives ethenol (vinyl alcohol) *initially*, this compound is unstable relative to its structural isomer (ethanal) and rapidly rearranges:



Similarly, addition of water to propyne leads to 2-propanone by way of its unstable isomer, 2-propenol:

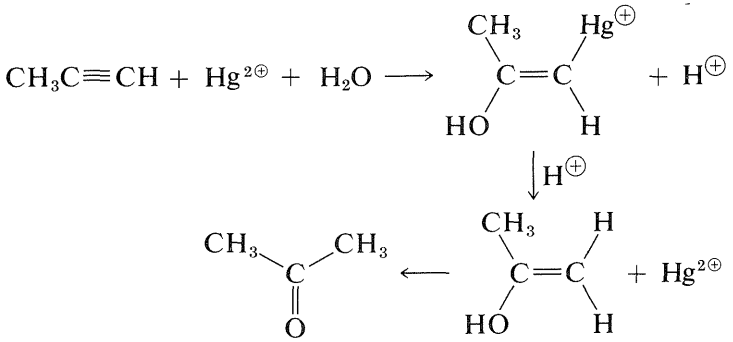


In general, the position of equilibrium for interconversion of a carbonyl compound with the corresponding alkenol (or *enol*), having the hydroxyl group attached to the double bond, lies far on the side of the carbonyl compound:



Because mercuric salts catalyze the hydration of alkynes, they probably are acting as electrophiles. Mercuric salts are known to add to both alkenes

and alkynes, and if the reaction mixture is acidic, the carbon–mercury bond is cleaved to form a carbon–hydrogen bond. The overall sequence in propyne hydration may be written as follows:



Exercise 10-20 Show how the rearrangement of ethenol to ethanal could take place in aqueous solution with water behaving as both a proton acceptor (base) and a proton donor (acid).

Exercise 10-21 Predict the predominant products in each of the following reactions. Show the expected configurations of the intermediates and products.

a. 2-butyne with mercuric ethanoate, $Hg(O\overset{O}{\overset{\|}{C}}CH_3)_2$, in ethanoic acid

b. ethenylbenzene with aqueous sulfuric acid containing mercuric sulfate, $HgSO_4$

c. ethyne with mercuric chloride in methanol

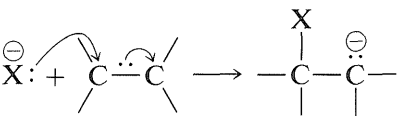
(*Note:* A mercuric salt of structure HgX_2 is a potential source of an electrophile, $HgX^{\oplus}$. *Mercuric sulfate probably is a source of the electrophilic cation,* $HgOSO_3H^{\oplus}$, *in* aqueous sulfuric acid.)

10-6 NUCLEOPHILIC ADDITION REACTIONS

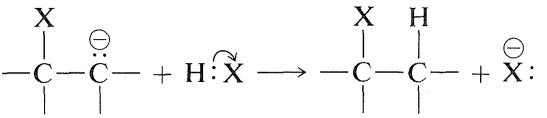
When a stepwise ionic addition reaction involves *nucleophilic* attack at carbon as a first step, it is described as a **nucleophilic addition.** Reactions of this type often are catalyzed by bases, which generate the required nucleophile. For example, consider the addition of some weakly acidic reagent HX to an alkene. In the presence of a strong base ($^{\ominus}OH$), HX could give up its proton to form the conjugate base $X^{\ominus}$, which is expected to be a much better nucleophile than HX:

$$H{:}X + {}^{\ominus}OH \rightleftharpoons H_2O + {:}X^{\ominus}$$

What can follow with an alkene is an *ionic chain reaction* with the following two propagating steps. First, the nucleophile attacks at carbon to form a carbon anion (carbanion) intermediate (Equation 10-8). Second, electrophilic transfer of a proton from HX to the carbanion forms the adduct and regenerates the nucleophile (Equation 10-9). The overall reaction is the addition of HX to the double bond:

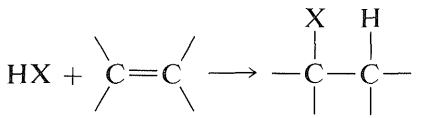


(10-8)

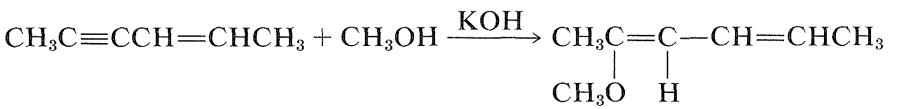


(10-9)

net reaction:



The HX reagent can be water, an alcohol (ROH), a thiol (RSH), an amine (RNH_2), or hydrogen cyanide (HCN) or other carbon acids (i.e., compounds with acidic C–H bonds). However, nucleophilic addition of these reagents to simple alkenes *rarely* is encountered. To have nucleophilic addition the double bond must be substituted with strongly electron-withdrawing groups such as carbonyl-containing groups, NO_2, C≡N, or positively charged ammonium or sulfonium groups. However, alkynes generally are more reactive toward nucleophiles than they are toward electrophiles. For example, with a base catalyst, 2-hexen-4-yne adds methanol across the triple bond, leaving the double bond untouched:



(Nonetheless, the double bond seems to be necessary because a corresponding addition is not observed for 2-butyne, $CH_3C{\equiv}CCH_3$.)

Exercise 10-22 Show the steps involved in the base-initiated addition of methanol to 2-hexen-4-yne (review Section 6-6).

Exercise 10-23 Sodium chloride in the presence of $OH^{\ominus}$ with 2-hexen-4-yne does not yield $CH_3CCl{=}CH{-}CH{=}CHCH_3$. Explain.

Many nucleophilic addition reactions have considerable synthetic value, particularly those involving addition of carbon acids, such as HCN, because they provide ways of forming carbon–carbon bonds. More of their utility will be discussed in Chapters 14, 17, and 18.

10-7 RADICAL-CHAIN ADDITION REACTIONS TO ALKENES

The early literature concerning the addition of hydrogen bromide to unsymmetrical alkenes at best is confused. Sometimes the same alkene was reported to give addition both according to, and in opposition to, the principles discussed for electrophilic ionic addition (Section 10-4). Much of the uncertainty on the addition of hydrogen bromide was removed by the classical researches of M. S. Kharasch and F. R. Mayo (1933) who showed that there must be two reaction mechanisms, each giving a different product. Kharasch and Mayo found, in the presence of radical inhibitors, hydrogen bromide adds to propene in a rather slow reaction to give pure 2-bromopropane:

$$CH_3CH{=}CH_2 + HBr \xrightarrow[\text{inhibitors}]{\text{slow, radical}} CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$$

With light, peroxides, radical initiators, and in the absence of radical inhibitors a rapid radical-chain addition of hydrogen bromide occurs to yield 80% or more of 1-bromopropane:

$$CH_3CH{=}CH_2 + HBr \xrightarrow[\text{peroxides}]{\text{fast}} CH_3CH_2CH_2Br$$

Similar effects have been noted occasionally with hydrogen chloride, but never with hydrogen iodide or hydrogen fluoride. A few substances apparently add to alkenes only by radical mechanisms, and always add in the opposite way to that expected for electrophilic ionic addition.

The ionic addition of hydrogen bromide was discussed in Section 10-4 and will not be considered further at this point. Two questions with regard to the so-called *abnormal addition* will be given special attention. Why does the radical mechanism give a product of different structure than the ionic addition? Why does the radical addition occur readily with hydrogen bromide but rarely with the other hydrogen halides? (See Exercise 10-25.)

The abnormal addition of hydrogen bromide is catalyzed strongly by peroxides, which have the structure R—O—O—R and decompose thermally to give RO· radicals (see Section 4-5B):

$$R{-}\ddot{O}{:}\ddot{O}{-}R \longrightarrow 2R{-}\ddot{O}\cdot \qquad \Delta H^0 = +35 \text{ kcal}$$

The RO· radicals can react with hydrogen bromide in two ways, to abstract either hydrogen atoms or bromine atoms:

$$\mathrm{RO\cdot + HBr} \begin{cases} \longrightarrow \mathrm{ROH + Br\cdot} & \Delta H^0 = -23 \text{ kcal} \\ \longrightarrow \mathrm{ROBr + H\cdot} & \Delta H^0 = +39 \text{ kcal} \end{cases}$$

Clearly, the formation of ROH and a bromine atom is energetically more favorable. The overall process of decomposition of peroxide and attack on hydrogen bromide, which results in the formation of a bromine atom, can initiate a radical-chain addition of hydrogen bromide to an alkene.

chain propagation

$$\mathrm{CH_3CH{=}CH_2 + Br\cdot \longrightarrow CH_3\dot{C}H{-}CH_2Br} \qquad \Delta H^0 = -5 \text{ kcal}$$

$$\mathrm{CH_3\dot{C}H{-}CH_2Br + HBr \longrightarrow CH_3CH_2CH_2Br + Br\cdot} \qquad \Delta H^0 = -11 \text{ kcal}$$

chain termination: $\mathrm{R'\cdot + R'\cdot \longrightarrow R'{-}R'}$ $\mathrm{R'\cdot}$ = atom or radical

The two chain-propagating steps, taken together, are exothermic by 16 kcal and have a fairly reasonable energy balance between the separate steps. The reaction chains apparently are rather long, because the addition is strongly inhibited by radical traps and only traces of peroxide catalyst are needed.

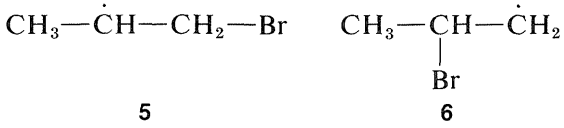
Exercise 10-24 Write two different radical mechanisms for peroxide-initiated addition of hydrogen chloride to alkenes and consider the energetic feasibility for each.

Exercise 10-25 Calculate the ΔH^0 values for initiation and chain-propagation steps of radical addition of hydrogen fluoride, hydrogen chloride, and hydrogen iodide to an alkene. Would you expect these reagents to add easily to double bonds by such a mechanism?

10-7A Orientation of Addition

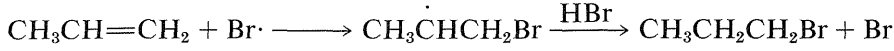
The direction of addition of hydrogen bromide to propene clearly depends on which end of the double bond the bromine atom attacks. The important question is which of the two possible carbon radicals that may be formed is the

more stable, the 1-bromo-2-propyl radical, **5**, or the 2-bromo-1-propyl radical, **6**:



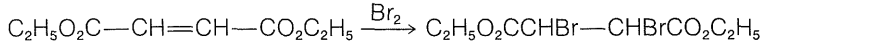
5 **6**

From C–H bond-dissociation energies of alkanes (see Table 4-6), the ease of formation and stabilities of the carbon radicals is seen to follow the sequence *tertiary* > *secondary* > *primary*. By analogy, the *secondary* 1-bromo-2-propyl radical, **5**, is expected to be more stable and more easily formed than the *primary* 2-bromo-1-propyl radical, **6**. The product of radical addition should be, and indeed is, 1-bromopropane:



Other reagents, such as the halogens, also can add to alkenes and alkynes by both radical-chain and ionic mechanisms. Radical addition usually is initiated by light, whereas ionic addition is favored by low temperatures and no light. Nevertheless, it often is difficult to keep both mechanisms from operating at the same time. This is important even when the alkene is symmetrical because, although the adduct will then have the same structural formula regardless of mechanism, the stereochemical configurations may differ. Electrophilic addition of halogens generally is a stereospecific antarafacial addition, but radical-chain additions are less stereospecific (see Exercise 10-26).

Exercise 10-26 **a.** Bromine adds to diethyl fumarate (diethyl *trans*-butenedioate) to give the meso adduct **7**, and to diethyl maleate (diethyl *cis*-butenedioate) to give the D,L adduct **8**, provided that the reaction mixtures are kept at 25° or less and are carefully protected from light. Deduce whether the stereochemistry of the reaction is suprafacial or antarafacial under these conditions.



diethyl fumarate (trans) ⟶ meso adduct **7**

diethyl maleate (cis) ⟶ D,L adduct **8**

b.* Diethyl maleate rearranges rapidly to diethyl fumarate on irradiation with ultraviolet light, provided that a trace of bromine is present. Irradiation of *equimolar* amounts of bromine and diethyl maleate leads to a mixture of D,L and meso adducts. Under these conditions the fumarate ester gives only the meso adduct. Show the steps involved in these transformations and explain clearly why the light-induced addition to the cis ester is not stereospecific.

There are many reagents that add to alkenes only by radical-chain mechanisms. A number of these are listed in Table 10-3. They have in common a relatively weak bond, X—Y, that can be cleaved homolytically either by light or by chemical initiators such as peroxides. In the propagation steps, the radical that attacks the double bond does so to produce the more stable carbon radical. For addition to simple alkenes and alkynes, the more stable carbon radical is the one with the fewest hydrogens or the most alkyl groups at the radical center.

initiation: $X\text{—}Y \xrightarrow{In\cdot} In\text{:}Y + X\cdot$ (In· is an initiator radical; with ROOR as initiator, In· is RO·)

propagation

$$\text{>C=CH}_2 + X\cdot \longrightarrow \text{—}\dot{C}\text{—CH}_2\text{—X}$$

$$X\text{—}Y + \text{—}\dot{C}\text{—CH}_2\text{—X} \longrightarrow \text{—}\overset{Y}{\underset{|}{C}}\text{—CH}_2\text{—X} + X\cdot$$

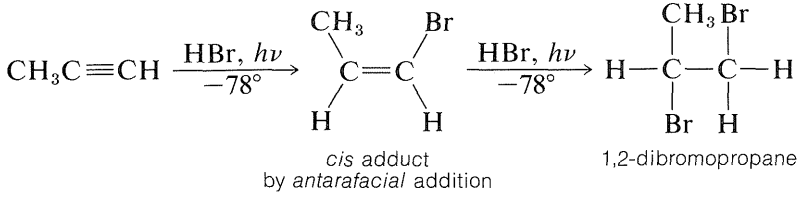
Table 10-3

Reagents that add to Alkenes and Alkynes by Radical-Chain Mechanisms

$$\text{>C=C<} + X\text{—}Y \longrightarrow X\text{—}\overset{|}{\underset{|}{C}}\text{—}\overset{|}{\underset{|}{C}}\text{—}Y$$

Reagent (X—Y)		Adduct	
Name	Structure	Name	Structure
hydrogen bromide	H—Br	bromoalkane	H—C—C—Br
bromine	Br—Br	dibromoalkane	Br—C—C—Br
polyhalomethanes	Cl—CCl_3	polyhaloalkanes	Cl—C—C—CCl_3
	Br—CCl_3		Br—C—C—CCl_3
	I—CF_3		I—C—C—CF_3
sulfonyl halides	Cl—SO_2R	halosulfones	Cl—C—C—SO_2R
alcohols			
methanol	H—CH_2OH	primary alcohol	H—C—C—CH_2OH
primary	H—CHROH	secondary alcohol	H—C—C—CHROH
secondary	H—CR_2OH	tertiary alcohol	H—C—C—CR_2OH
carboxylic acids	H—CR_2CO_2H	carboxylic acids	H—C—C—CR_2CO_2H
aldehydes	H—C(=O)R	ketones	H—C—C—C(=O)R
thiols	H—SR	thioethers	H—C—C—SR
amines	H—NR_2	alkylamines	H—C—C—NR_2
silanes	H—SiR_3	alkylsilanes	H—C—C—SiR_3
phosphines	H—PR_2	alkylphosphines	H—C—C—PR_2

The principles of radical addition reactions of alkenes appear to apply equally to alkynes, although there are fewer documented examples of radical additions to triple bonds. Two molecules of hydrogen bromide can add to propyne first to give *cis*-1-bromopropene (by antarafacial addition) and then 1,2-dibromopropane:



cis adduct by *antarafacial* addition

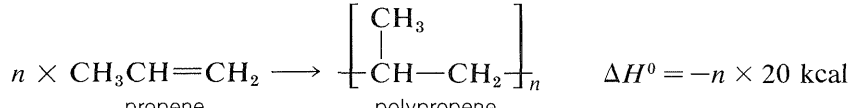
1,2-dibromopropane

Exercise 10-27 A radical of structure $CH_3\dot{C}{=}CHBr$ is involved in the light-induced addition of HBr to propyne (see above). What geometry would you expect it to have? Draw an atomic-orbital picture of the radical with particular attention to the hybridization of the orbitals at the radical center.

Exercise 10-28 Bromotrichloromethane, $BrCCl_3$, adds to 1-octene by a radical-chain mechanism on heating in the presence of a peroxide catalyst. Use the bond-energy tables to devise a feasible mechanism for this reaction and work out the most likely structure for the product. Show your reasoning. Show the most likely product of addition of $BrCCl_3$ to 1-octyne. [*Note:* Radical-chain reactions involve abstraction of atoms, not abstraction of groups.]

10-8 POLYMERIZATION OF ALKENES

One of the most important technical reactions of alkenes is their conversion to higher-molecular-weight compounds or **polymers** (Table 10-4). A polymer is defined as a *long-chain molecule with recurring structural units*. Thus polymerization of propene gives a long-chain hydrocarbon with recurring $-\overset{CH_3}{\overset{|}{C}}H-CH_2-$ units:



propene (propylene)

polypropene (polypropylene)

Table 10-4
Alkene Monomers and Their Polymers

Monomer	Formula	Type of addition polymerization	Polymer or Trade Name	Uses
ethene	$CH_2{=}CH_2$	radical (high pressure), coordination	polyethene	film, containers, piping
chloroethene (vinyl chloride)	$CH_2{=}CHCl$	radical	polyvinyl chloride (PVC)	film, insulation, piping, leatherette
fluoroethene	$CH_2{=}CHF$	radical	Tedlar	coatings
chlorotrifluoroethene	$CF_2{=}CFCl$	radical	Kel-F	gaskets, insulation
tetrafluoroethene	$CF_2{=}CF_2$	radical	Teflon	gaskets, valves, insulation, coatings
propene	$CH_3CH{=}CH_2$	coordination	polypropene, Herculon	fibers, molded articles
2-methylpropene	$(CH_3)_2C{=}CH_2$	cationic	Vistanex, Oppanol, butyl rubber	pressure-sensitive adhesives
styrene	$C_6H_5CH{=}CH_2$	radical	polystyrene	molded articles
propenenitrile (acrylonitrile)	$CH_2{=}CHCN$	radical	Orlon, Acrilan	acrylic fibers
methyl 2-methyl-propenoate (methyl methacrylate)	$CH_2{=}C(CH_3)CO_2CH_3$	radical anionic	Lucite, Plexiglas	coatings, molded articles

Most technically important polymerizations of alkenes occur by chain mechanisms and may be classed as anion, cation, or radical reactions, depending upon the character of the chain-carrying species. In each case, the key steps involve successive additions to molecules of the alkene, the differences being in the number of electrons that are supplied by the attacking agent for formation of the new carbon–carbon bond. For simplicity, these steps will be illustrated by using ethene, even though it does not polymerize very easily by any of them:

$$R{-}CH_2{-}\overset{\ominus}{C}H_2{:} + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2{-}CH_2{-}\overset{\ominus}{C}H_2{:}, \text{ etc.}$$

$$R{-}CH_2{-}\overset{\oplus}{C}H_2 + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2{-}CH_2{-}\overset{\oplus}{C}H_2, \text{ etc.}$$

$$R{-}CH_2{-}CH_2{\cdot} + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2{-}CH_2{-}CH_2{\cdot}, \text{ etc.}$$

10-8A Anionic Polymerization

Initiation of alkene polymerization by the anion-chain mechanism may be formulated as involving an attack by a nucleophilic reagent $Y{:}^{\ominus}$ on one end of the double bond and formation of a carbanion:

$$\overset{\ominus}{Y}{:} + CH_2{=}CH_2 \longrightarrow \underset{\text{carbanion}}{Y{:}CH_2{-}\overset{\ominus}{C}H_2{:}}$$

Attack by the carbanion on another alkene molecule would give a four-carbon carbanion, and subsequent additions to further alkene molecules would lead to a high-molecular-weight anion:

$$Y{:}CH{-}\overset{\ominus}{C}H_2{:} + CH_2{=}CH_2 \longrightarrow Y{:}CH_2{-}CH_2{-}CH_2{-}\overset{\ominus}{C}H_2{:}$$

$$\xrightarrow{n \times CH_2{=}CH_2} Y{:}CH_2{-}CH_2{-}(CH_2{-}CH_2)_n{-}CH_2{-}\overset{\ominus}{C}H_2{:}$$

The growing chain can be terminated by any reaction (such as the addition of a proton) that would destroy the carbanion on the end of the chain:

$$Y{:}CH_2{-}CH_2{-}(CH_2{-}CH_2)_n{-}CH_2{-}\overset{\ominus}{C}H_2{:}$$

$$\xrightarrow{H^{\oplus}} Y{:}CH_2{-}CH_2{-}(CH_2{-}CH_2)_n{-}CH_2{-}CH_2{-}H$$

Anionic polymerization of alkenes is quite difficult to achieve because few anions (or nucleophiles) are able to add readily to alkene double bonds (see Section 10-6). Anionic polymerization occurs readily only with alkenes sub-

stituted with sufficiently powerful electron-attracting groups to expedite nucleophilic attack. By this reasoning, alkynes should polymerize more readily than alkenes under anionic conditions, but there appear to be no technically important alkyne polymerizations in operation by this or any other mechanism. Perhaps this is because the resultant polymer would be highly conjugated, and therefore highly reactive, and may not survive the experimental conditions:

$$n \times \underset{\text{ethyne}}{HC{\equiv}CH} \longrightarrow \underset{\text{polyethyne (expected to be unstable)}}{YHC{=}CH{+}CH{=}CH{\rightarrow}_{\overline{n}}CH{=}CH_2}$$

Exercise 10-29 Propenenitrile (acrylonitrile, $CH_2{=}CHCN$) will polymerize readily at −50° in a polar solvent [e.g., dimethylmethanamide, $HCON(CH_3)_2$] under the influence of sodium cyanide, NaCN. Show the initiation and propagation steps of this reaction, and predict the structure of the polymer. Why is a polar solvent necessary? Why does this polymerization proceed but not that of propene under the same conditions?

10-8B Cationic Polymerization

Polymerization of an alkene by acidic reagents can be formulated by a mechanism similar to the addition of hydrogen halides to alkene linkages. First, a proton from a suitable acid adds to an alkene to yield a carbocation. Then, in the absence of any other reasonably strong nucleophilic reagent, another alkene molecule donates an electron pair and forms a longer-chain cation. Continuation of this process can lead to a high-molecular-weight cation. Termination can occur by loss of a proton. The following equations represent the overall reaction sequence:

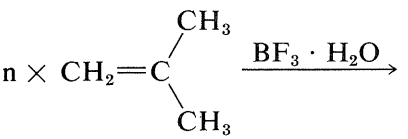
$$H^{\oplus} + \overset{\curvearrowleft}{CH_2}{=}CH_2 \rightleftharpoons CH_3{-}\overset{\oplus}{C}H_2 \xrightarrow{CH_2{=}CH_2} CH_3{-}CH_2{-}CH_2{-}\overset{\oplus}{C}H_2$$

$$\xrightarrow{n \times CH_2{=}CH_2} CH_3{-}CH_2{+}CH_2{-}CH_2{\rightarrow}_{\overline{n}}CH_2{-}\overset{\oplus}{C}H_2$$

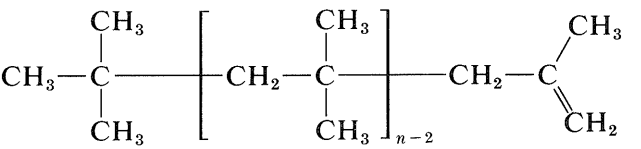
$$\xrightarrow{-H^{\oplus}} CH_3{-}CH_2{+}CH_2{-}CH_2{\rightarrow}_{\overline{n}}CH{=}CH_2$$

Ethene does not polymerize by the cationic mechanism because it does not have sufficiently effective electron-donating groups to permit easy formation of the intermediate growing-chain cation. 2-Methylpropene has electron-donating alkyl groups and polymerizes much more easily than ethene by this type of mechanism. The usual catalysts for cationic polymerization of 2-methylpropene are sulfuric acid, hydrogen fluoride, or a complex of boron

trifluoride and water. Under nearly anhydrous conditions a very long chain polymer called polyisobutylene is formed.



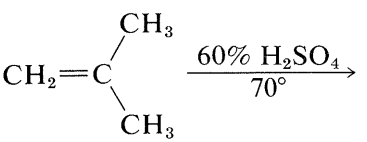
2-methylpropene
(isobutylene)

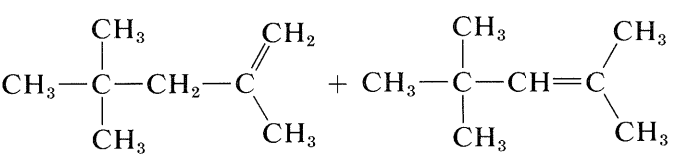


poly-2-methylpropene
(polyisobutylene)

Polyisobutylene fractions of particular molecular weights are very tacky and are used as adhesives for pressure-sealing tapes.

In the presence of 60% sulfuric acid, 2-methylpropene is *not* converted to a long-chain polymer, but to a mixture of eight-carbon alkenes. The mechanism is like that of the polymerization of 2-methylpropene under nearly anhydrous conditions, except that chain termination occurs after only one 2-methylpropene molecule has been added:



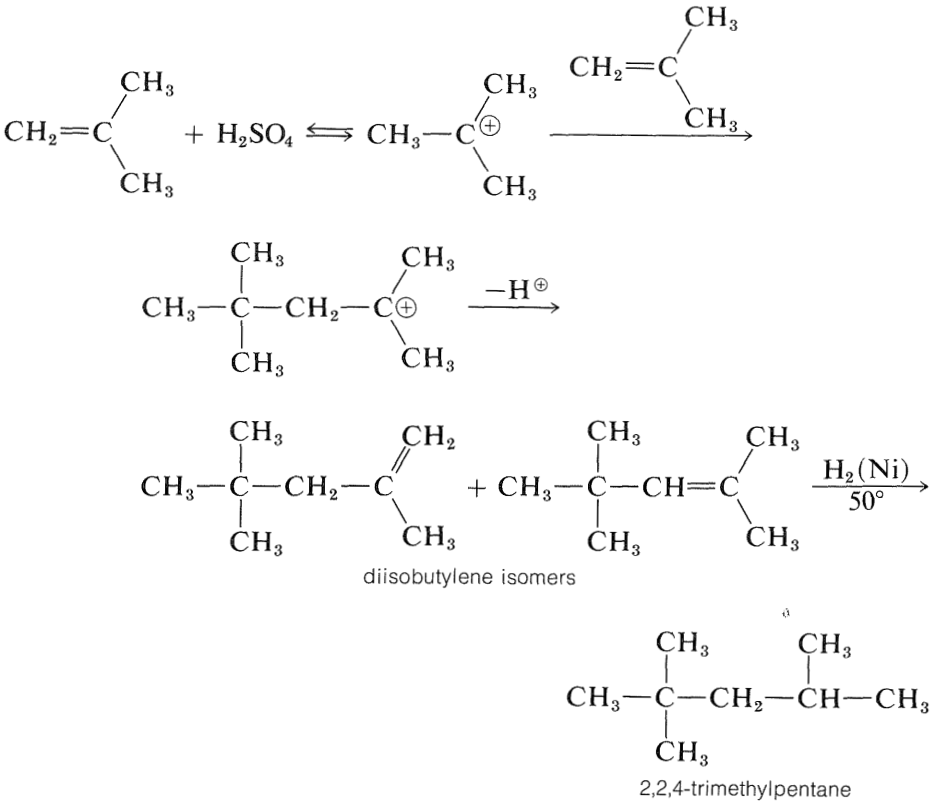


"diisobutylene"

The short chain length is due to the *high water concentration;* the intermediate carbocation loses a proton to water *before* it can react with another alkene molecule.

The proton can be lost in two different ways, and a mixture of alkene isomers is obtained. The alkene mixture is known as "diisobutylene" and has a number of commercial uses. Hydrogenation yields 2,2,4-trimethylpentane

(often erroneously called "isooctane"), which is used as the standard "100 antiknock rating" fuel for internal-combustion gasoline engines:



10-8C Radical Polymerization

Ethene can be polymerized with peroxide catalysts under high pressure (1000 atm or more, literally in a cannon barrel) at temperatures in excess of 100°. The initiation step involves formation of radicals, and chain propagation entails stepwise addition of radicals to ethene molecules.

initiation: $R{:}\ddot{O}{:}\ddot{O}{:}R \longrightarrow 2R{:}\ddot{O}\cdot$

propagation:

$$R{:}\ddot{O}\cdot + CH_2{=}CH_2 \longrightarrow R{:}\ddot{O}{:}CH_2{-}CH_2\cdot$$

$$R{:}\ddot{O}{:}CH_2{-}CH_2\cdot + n \times CH_2{=}CH_2 \longrightarrow RO{-}(CH_2{-}CH_2)_n{-}CH_2{-}CH_2\cdot$$

Chain termination can occur by any reaction resulting in combination or disproportionation of free radicals.

termination:

$$2RO\text{-}(\text{-}CH_2\text{—}CH_2\text{-})_n CH_2\text{—}CH_2\cdot \longrightarrow [RO\text{-}(\text{-}CH_2\text{—}CH_2\text{-})_n CH_2\text{—}CH_2\text{-}]_2$$

combination

$$2RO\text{-}(\text{-}CH_2\text{—}CH_2\text{-})_n CH_2\text{—}CH_2\cdot \xrightarrow{H\cdot \text{ transfer}}$$

$$RO\text{-}(\text{-}CH_2\text{—}CH_2\text{-})_n CH{=}CH_2 + RO\text{-}(\text{-}CH_2\text{—}CH_2\text{-})_n CH_2\text{—}CH_3$$

disproportionation

The polyethene produced in this way has from 100 to 1000 ethene units in the hydrocarbon chain. The polymer possesses a number of desirable properties as a plastic and is used widely for electrical insulation, packaging films, piping, and a variety of molded articles. Propene and 2-methylpropene do not polymerize satisfactorily by radical mechanisms.

Exercise 10-30 Write a reasonable mechanism for termination of ethene polymerization by disproportionation. Calculate ΔH^0 values for termination of the chain reaction by combination and disproportionation. Which is the more favorable process?

10-8D Coordination Polymerization

A relatively low-pressure, low-temperature ethene polymerization has been achieved with an aluminum–molybdenum oxide catalyst, which requires occasional activation with hydrogen (Phillips Petroleum process). Ethene also polymerizes quite rapidly at atmospheric pressure and room temperature in an alkane solvent containing a suspension of the insoluble reaction product from triethylaluminum and titanium tetrachloride (Ziegler process). Both the Phillips and Ziegler processes produce very high-molecular-weight polyethene with exceptional physical properties. The unusual characteristics of these reactions indicate that no simple anion, cation, or radical mechanism can be involved. It is believed that the catalysts act by coordinating with the alkene molecules in somewhat the same way that hydrogenation catalysts combine with alkenes (Section 11-2A).

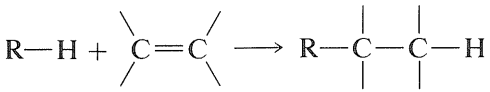
Polymerization of propene by the Ziegler process gives a very useful plastic material. It can be made into durable fibers or molded into a variety of shapes. Copolymers (polymers with more than one kind of monomer unit in the polymer chains) of ethene and propene made by the Ziegler process have highly desirable rubberlike properties and are potentially the cheapest useful elastomers

(elastic polymers). A Nobel Prize was shared in 1963 by K. Ziegler and G. Natta for their work on alkene polymerization.

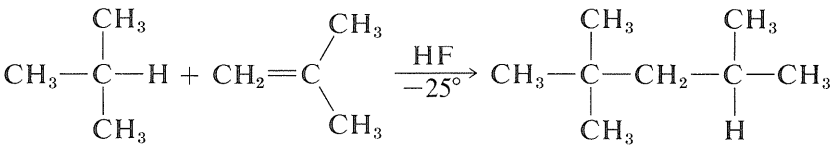
The properties and uses of polymers are discussed in greater detail in Chapters 13 and 29. The most important alkene monomers used in addition polymerization are listed in Table 10-4 along with some names and uses of the corresponding polymers.

10-9 ALKYLATION OF ALKENES

Addition of a saturated hydrocarbon (R—H) to an alkene to yield a saturated hydrocarbon of higher molecular weight is known as **alkylation:**

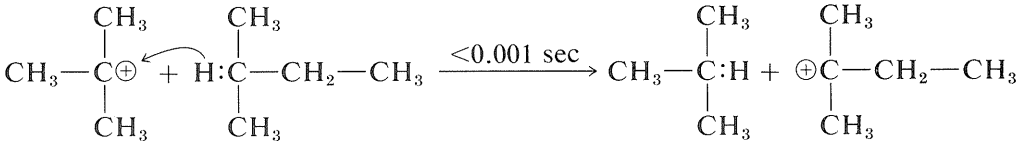


Such reactions are used by the petroleum industry to produce medium-molecular-weight hydrocarbons from smaller molecules. A particularly important example is afforded by the addition of 2-methylpropane to 2-methylpropene in the presence of sulfuric acid or anhydrous hydrogen fluoride to yield 2,2,4-trimethylpentane:



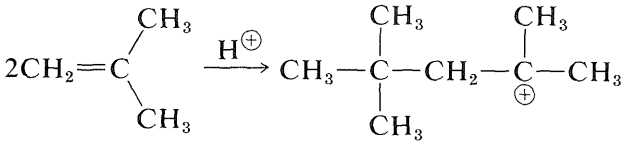
The overall reaction appears to be different from any so far discussed, because it involves addition of a nonpolar reagent (RH) to an alkene bond.

The key to the mechanism of hydrocarbon alkylation was provided by the discovery by P. D. Bartlett, in 1940, that a carbocation can react rapidly with a hydrocarbon having a tertiary hydrogen to yield a new carbocation and a new hydrocarbon. Some of these "hydrogen-transfer" reactions are extraordinarily fast and may be complete in seconds or less. The hydrogen is transferred with *both* bonding electrons (H:$^{\ominus}$). For example,

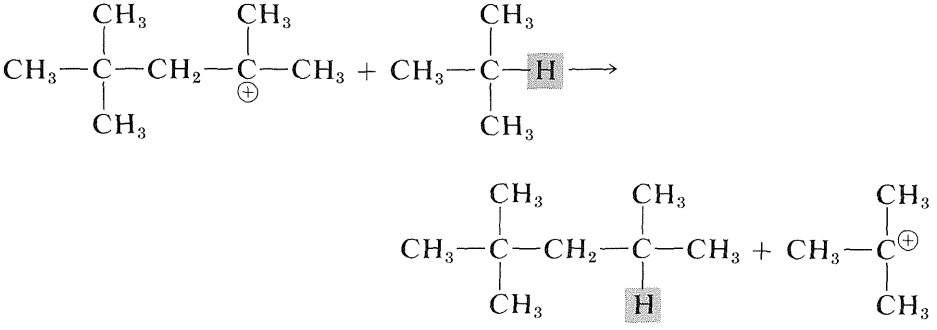


With the knowledge that the hydrogen transfer is fast, the alkylation of 2-methylpropene with 2-methylpropane can be formulated as involving first

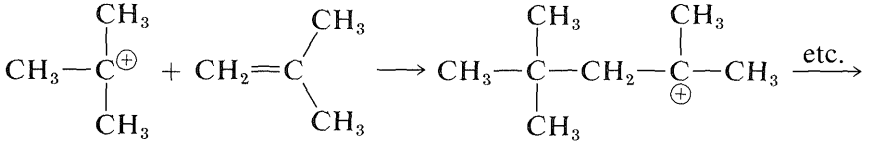
polymerization of two 2-methylpropene molecules under the influence of the sulfuric acid catalyst to give the same octyl cation as was postulated for the dimerization of 2-methylpropene:



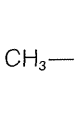
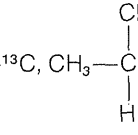
The octyl cation then can undergo a hydrogen-transfer reaction with 2-methylpropane to furnish 2,2,4-trimethylpentane and a *tert*-butyl cation:



Attack by the *tert*-butyl cation on another molecule of 2-methylpropene produces an eight-carbon tertiary cation, which then proceeds to another molecule of "alkylate":



This is an important example of a *cationic chain* reaction.

Exercise 10-31 It has been reported that a mixture of 2-methylpropane-2-D,  and 2-methylpropane-1-^{13}C,  (^{13}C is the stable carbon isotope of mass 13) is converted only very slowly by sulfuric acid to a mixture containing the two starting materials, ordinary 2-methylpropane and 2-methylpropane-1-^{13}C-2-D.

The reaction is speeded up greatly by addition of small amounts of 2-methylpropene. Explain. Would you expect any significant formation of D_2SO_4 when the reaction is carried out in the presence of 2-methylpropene? Why?

Additional Reading

M. L. Poutsma, "Chlorination of Unsaturated Compounds in Non-Polar Media," *Science* **157,** 997 (1967).

C. Walling and E. S. Huyser, "Free-Radical Additions to Olefins to Form Carbon–Carbon Bonds," *Organic Reactions* **3,** 91 (1963).

F. N. Stacey and J. F. Harris, Jr., "Formation of Carbon–Hetero Atom Bonds by Free-Radical Chain Additions to Carbon–Carbon Multiple Bonds," *Organic Reactions* **3,** 150 (1963).

H. Saltzman, "Arthur Lapworth: The Genesis of Reaction Mechanism," *J. Chem. Educ.* **49,** 750 (1972).

N. Isenberg and M. Grdinic, "A Modern Look at Markovnikov's Rule and the Peroxide Effect," *J. Chem. Educ.* **46,** 601 (1969).

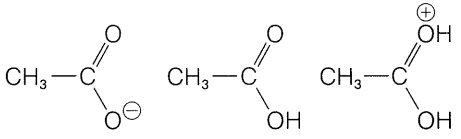
W. R. Dolbier, Jr., "Electrophilic Additions to Alkenes (Research Summary)," *J. Chem. Educ.* **46,** 343 (1969).

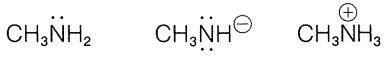
Supplementary Exercises

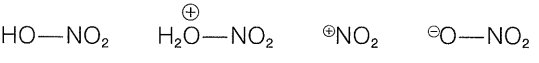
10-32 For each of the following groups of substances designate which is the strongest electrophile and which is the strongest nucleophile. Give your reasoning.

a. H_2O $H_3O^{\oplus}$ $HO^{\ominus}$

b. I_2 $I^{\ominus}$ $H_2\overset{\oplus}{O}I$

c. 

d. 

e. 

f. HF, HF + SbF_5, $SbF_6^{\ominus}$, $F^{\ominus}$

g. FSO_3H, $ClSO_3H$, $HOSO_3^{\ominus}$

10-33 Identify the nucleophile and the electrophile in each of the following reactions:

a. $H_2C{=}\overset{\oplus}{O}H + H_2O \rightleftharpoons H_2C(OH)\overset{\oplus}{O}(H)H$

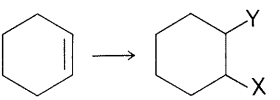
b. $H_2C{=}CH_2 + Br_2 \rightleftharpoons H_2C(Br)\overset{\oplus}{C}H_2 + Br^{\ominus}$

c. $H_2C{=}CH_2 + :CH_2 \rightleftharpoons$

d. $CH_2{=}CHCN + NH_2^{\ominus} \rightleftharpoons NH_2{-}CH_2{-}\overset{\ominus}{C}HCN$

10-34 Indicate what reagents and conditions would convert cyclohexene to the following derivatives:

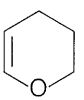
	X	Y
a.	Cl	H
b.	OH	H
c.	Cl	OH
d.	$-OCCH_3$ (O)	H
e.	F	Br



10-35 Use the electronegativity chart (Figure 10-11) to predict how the indicated bond would be expected to be polarized for each of the following compounds:

a. $H_3C{-}H$
b. $H_3Si{-}H$
c. $CH_3{-}Li$
d. $CH_3{-}MgCH_3$
e. $CH_3S{-}Cl$
f. $H_2N{-}SCH_3$
g. $H_2N{-}OH$
h. $H_2N{-}Br$
i. $H_2P{-}Cl$
j. $(CH_3)_3Si{-}Cl$

10-36 Draw structures for the major products of each of the following reactions. Indicate the stereochemistry of the product, where possible. (D is deuterium, the hydrogen isotope of mass 2.)

a.  $+ Br_2 \xrightarrow{CCl_4}$

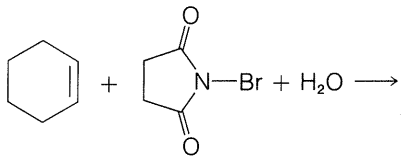
b. $CH_3CH{=}CH_2 + HF \longrightarrow$

c. *cis*-1-phenylpropene $+ DBr \xrightarrow{CH_2Cl_2}$

d. $C_6H_5C{\equiv}CCH_3 + HCl + CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH$ (solvent) $\longrightarrow$

e. $CH_3C{\equiv}CH \xrightarrow{1.\ HgCl_2} \xrightarrow{2.\ DCl}$

f. $C_6H_5CH{=}CH_2 + CH_3SCl \longrightarrow$

g.  $+ H_2O \longrightarrow$

10-37 Why is molecular fluorine generally unsatisfactory as a reagent to convert alkenes to 1,2-difluoroalkanes?

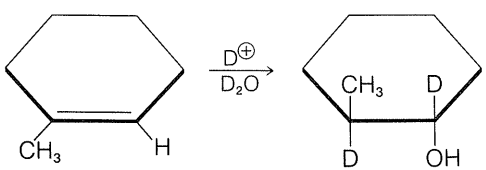
10-38 Why does the addition of chlorine to 2-pentene in methanol give a mixture of the following products?
2,3-dichloropentane (16%)
2-chloro-3-methoxypentane (35%)
3-chloro-2-methoxypentane (49%)

10-39 Suggest a mechanism to account for the following reaction:

$$CH_2{=}CH(CH_2)_2CH_2OH \xrightarrow[CCl_4]{I_2} ICH_2{-}CH\begin{array}{l}CH_2{-}CH_2\\ \quad\ \ |\\ \quad\ \ O{-}CH_2\end{array}$$

10-40 In Section 1-1I, the addition of bromine to tetrachloroethene was reported to be catalyzed by aluminum bromide. What is the function of aluminum bromide in this addition?

10-41 Evaluate (show your reasoning) the possibility that the following reaction will give the indicated product:



If you do not think the indicated product would be important, write the structure(s) of the product(s) you think would be more likely to be found.

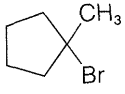
10-42 2-Methylpropene reacts with ethene and hydrogen chloride under polar conditions to yield 1-chloro-3,3-dimethylbutane. Show a mechanism for this reaction that is consistent with the reactants, conditions, and product. Give your reasoning.

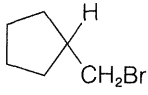
10-43 2-Methylpropane (containing traces of 2-methylpropene) is converted by a *large excess* of deuteriosulfuric acid (D_2SO_4) rather rapidly to 2-methylpropane with only nine deuteriums.

a. Write a polar mechanism for this hydrogen-exchange reaction that is in harmony with the known chemical properties of sulfuric acid and that predicts exchange of no more than nine of the ten hydrogens of 2-methylpropane.

b. Explain how 2-methylpropane-D_9 can be formed more rapidly than 2-methylpropane-D_n with $n < 9$ in the early stages of the reaction.

10-44 Suggest how each of the following compounds may be prepared. Assume any necessary starting hydrocarbons are available. Specify the reaction conditions as closely as possible and indicate when isomer separations may be necessary.

a. 

b. 

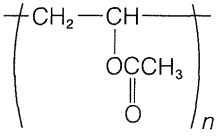
c. 1,1,1-trichloro-3-bromohexane

d. $C_6H_5CCH_2CH_3$ (O)

e. $C_6H_5CHCH_3$ (OH)

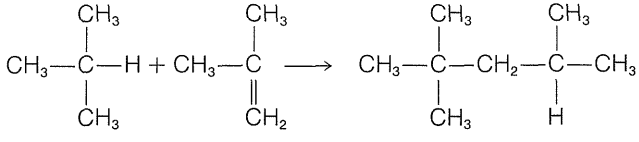
f. $Cl_2CHCHCl_2$

g. $CH_2{=}CH{-}O{-}C{-}CH_3$ (O) (ethenyl ethanoate)

h. 

10-45 Calculate ΔH^0 values for the following reactions in the gas phase per mole of the principal reactants, using the bond-energy table (Table 4-3).

a. $n \times CH_2{=}CH_2 \longrightarrow \text{-}(CH_2{-}CH_2)\text{-}_n$

b. 

10-46 Use bond energies (Table 4-3) to investigate the possibility of adding water to propene, using peroxide (ROOR) catalysts. It has been reported that γ rays, such as from a cobalt-60 source, decompose water into H· and HO·. Could such radiation initiate a *chain*-addition reaction of water to propene? How about a nonchain mechanism (i.e., one γ-ray photon per molecule of reacting propene)? In a nonchain mechanism, would you expect to get 1-propanol or 2-propanol? What other products may be obtained in a nonchain reaction? Give your reasoning in detail.

10-47 Use bond energies (Table 4-3) to investigate the energetic feasibility of adding ammonia (NH_3) to an alkene by a radical-chain mechanism with the aid of a peroxide (ROOR) catalyst. What product would you expect to obtain from propene and ammonia by a radical mechanism of addition?

10-48 Draw an energy diagram similar to Figure 10-10 for the progress of a two-step reaction $A + BC \rightleftharpoons A{-}B{-}C \xrightarrow{D} A{-}B + C{-}D$ in which the first step is a rapidly established equilibrium and the second step is the slow or rate-determining step. Label the diagram to show what part represents the transition state, reaction intermediate, overall energy of activation ($\Delta H^{\ddagger}$), and overall standard enthalpy change (ΔH^{0}) for the process $A + BC + D \longrightarrow AB + CD$. Assume that the overall equilibrium constant, $K_{eq} > 1$.

10-49 Complete the following equations showing the structures of the expected products under the reaction conditions:

a. $CH_2{=}CHCN + (C_2H_5)_3SiH \xrightarrow{ROOR}$

b. $+ HOCH_2CH_2SH \xrightarrow{ROOR}$

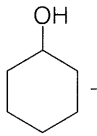
c. $+ HSCH_2CO_2H \xrightarrow{ROOR}$

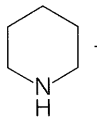
d. 1-octene $+ Cl_3SiH \xrightarrow{ROOR}$

e. $(CH_3)_2C{=}CH_2 + CCl_4 \xrightarrow{ROOR}$

f. $HC{\equiv}CCH_2O\overset{\overset{O}{\|}}{C}CH_3 + BrCCl_3 \xrightarrow{ROOR}$

g. $CH_3C{\equiv}CH + CF_3I \xrightarrow{h\nu}$

h. 1-hexene +  $\xrightarrow{ROOR}$

i. 1-hexene +  $\xrightarrow{ROOR}$

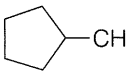
j. 1-hexene $+ CH_3CO_2H \xrightarrow{ROOR}$

10-50 This problem illustrates one of the complications that can arise in radical-addition reactions.

Cyclohexene reacts with bromotrichloromethane at 40° in the presence of small quantities of peroxides to give a mixture of products: 2-bromo-1-trichloromethylcyclohexane (67%) and 3-bromocyclohexene (33%). Account for the formation of both of these products under the reaction conditions.

10-51 Describe how you would prepare each of the following compounds from the indicated starting materials. Assume that any other necessary inorganic or organic reagents are available. Specify the reagents and reaction conditions as closely as possible.

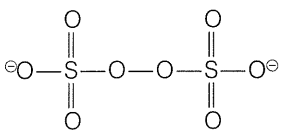
a. $HO_2CCH_2CH_2CH_2CH_2CO_2H$ (hexanedioic acid) from CH_3CO_2H (ethanoic acid) and $HC{\equiv}CH$ (ethyne) by a radical-chain addition

b.  from methylenecyclopentane

c. $CH_3(CH_2)_7\overset{\overset{O}{\|}}{C}CH_3$ (2-decanone) from 1-octene

d. 2-decanone from 1-decyne

10-52* The molecular weight of a polymer obtained by radical-addition polymerization can be reduced by addition of a thiol, RSH. For example, when propenoic acid (acrylic acid) is polymerized in the presence of potassium peroxodisulfate, $K_2S_2O_8$, adding mercaptoethanoic acid, $HSCH_2CO_2H$, causes the average molecular weight of the polymer molecule to become much smaller. Draw the structure of the polymer and explain how the thiol compound functions to reduce the molecular weight. Would an alcohol do as well? Show how the potassium peroxodisulfate could function as an initiator. Would you expect it to decompose more rapidly in alkaline or strongly acid solution? Explain.

 peroxodisulfate

10-53 a. 1-Bromocyclopentene adds hydrogen bromide on irradiation with ultraviolet light to give 94% *cis*-1,2-dibromocyclopentane and 6% of the trans isomer. Explain why 1,1-dibromocyclopentane is not obtained and why the cis isomer predominates.

b. From your answer to the questions in Part a, predict the structure and stereochemistry of the major products in the following reactions:

(i) $CH_3{-}C{\equiv}C{-}CH_3 + 2HBr \xrightarrow{\text{peroxides}}$

(ii) $CH_3C{\equiv}CBr + HBr \xrightarrow{\text{ultraviolet light}}$

(iii) *cis*-$CH_3CH{=}CHCH_3 + DBr \xrightarrow{\text{peroxides}}$

(iv) $HC{\equiv}CH + DCl \xrightarrow{HgCl_2}$ (monoaddition product of DCl)