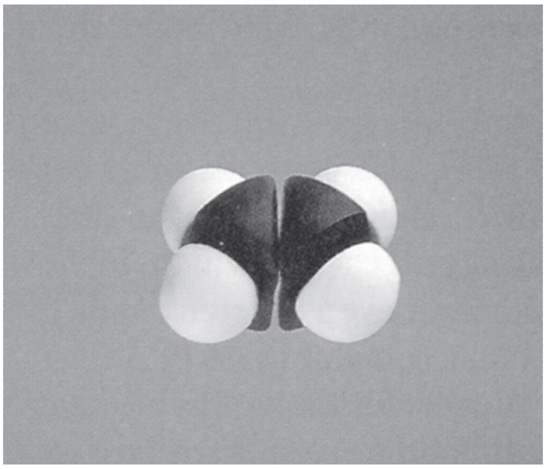
6



Alkenes

6A. Structure and Preparation
(*Elimination*)

6A.1 Classes of organic compounds having one or more functional group(s)

Functional group is the reactive center in a molecule. For example, C=C is the functional group of alkenes. The functional group determines the general properties of a class of compounds to a large extent.

6A.2 Unsaturated hydrocarbons

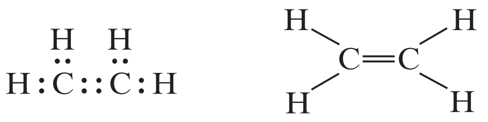
In our discussion of the alkanes we mentioned briefly another family of hydrocarbons, the **alkenes**, which contain less hydrogen, carbon for carbon, than the alkanes, and which can be converted into alkanes by addition of hydrogen. The alkenes were further described as being obtained from alkanes by loss of hydrogen in the cracking process.

Since alkenes evidently contain less than the maximum quantity of hydrogen, they are referred to as **unsaturated hydrocarbons**. This unsaturation can be satisfied by reagents other than hydrogen and gives rise to the characteristic chemical properties of alkenes.

6A.3 Structure of ethylene. The carbon–carbon double bond

The simplest member of the alkene family is **ethylene**, C_2H_4. In view of the ready conversion of ethylene into ethane, we can reasonably expect certain structural similarities between the two compounds.

To start, then, we connect the carbon atoms by a covalent bond, and then attach two hydrogen atoms to each carbon atom. At this stage we find that each carbon atom possesses only six electrons in its valence shell, instead of the required eight, and that the entire molecule needs an additional pair of electrons if it is to be neutral. We can solve both these problems by assuming that the carbon atoms can share two pairs of electrons. To describe this sharing of two pairs of electrons, we say that the carbon atoms are joined by a *double bond. The* **carbon–carbon double bond** *is the distinguishing feature of the alkene structure.*



$$\mathrm{H}:\overset{\mathrm{H}}{\ddot{\mathrm{C}}}::\overset{\mathrm{H}}{\ddot{\mathrm{C}}}:\mathrm{H}$$

Ethylene

Quantum mechanics gives a more detailed picture of ethylene and the carbon–carbon double bond. To form bonds with three other atoms, carbon makes use of three equivalent hybrid orbitals, sp^2 orbitals, formed by the mixing of *one s* and *two p* orbitals. As we have seen, sp^2 orbitals lie in one plane, that of the carbon nucleus, and are directed toward the corners of an equilateral triangle; the angle between any pair of orbitals is thus 120°. This **trigonal** arrangement (Fig. 6A.1) permits the hybrid orbitals to be as far apart as possible. Just as mutual repulsion among orbitals gives four tetrahedral bonds, so it gives three trigonal bonds.

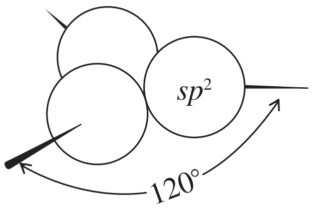


Figure 6A.1 Atomic orbitals: hybrid sp^2 orbitals. The axes are directed toward the corners of an equilateral triangle.

If we arrange the two carbons and four hydrogens of ethylene to permit maximum overlap of orbitals, we obtain the structure shown in Fig. 6A.2. Each carbon atom lies at the center of a triangle, at whose corners are located the two hydrogen atoms and the other carbon atom. Every bond angle is 120°. Although distributed differently about the carbon nucleus, these bonds individually are very similar to the bonds in ethane, being cylindrically symmetrical about a line joining the nuclei, and are given the same designation: σ *bond* (*sigma bond*).

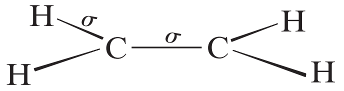


Figure 6A.2 Ethylene molecule: only σ bonds are shown.

The molecule is not yet complete, however. In forming the sp^2 orbitals, each carbon atom has used only two of its three *p* orbitals. The remaining *p* orbital consists of two equal lobes, one lying above and the other lying below the plane of the three sp^2 orbitals in Fig. 6A.3; it is occupied by a single electron. If the *p* orbital of one carbon atom overlaps the *p* orbital of the other carbon atom, the electrons pair up and an additional bond is formed.

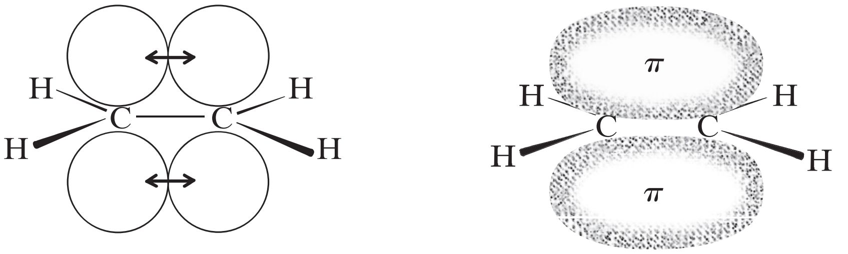


Figure 6A.3 Ethylene molecule: carbon–carbon double bond. Overlap of p orbitals gives a π bond; there is a π cloud above and below the plane.

Because it is formed by the overlap of p orbitals, and to distinguish it from the differently shaped σ bonds, this bond is called a π *bond* (*pi bond*). It consists of two parts, one electron cloud that lies above the plane of the atoms, and another electron cloud that lies below. Because of lesser overlap, the π bond is weaker than the carbon–carbon σ bond. As we can see from Fig.6A.3, this overlap can occur only when all six atoms lie in the same plane. Ethylene, then, is a *flat molecule*.

The carbon–carbon "double bond" is thus made up of a strong σ bond and a weak π bond. The total bond energy of 146 kcal is greater than that of the carbon–carbon single bond of ethane (88 kcal). Since the carbon atoms are held more tightly together, the C—C distance in ethylene is less than the C—C distance in ethane; that is to say, the carbon–carbon double bond is shorter than the carbon–carbon single bond.

The σ bond in ethylene has been estimated to have a strength of about 95 kcal: stronger than the one in ethane because it is formed by overlap of sp^2 orbitals. On this basis, we would estimate the strength of the π bond to be 51 kcal.

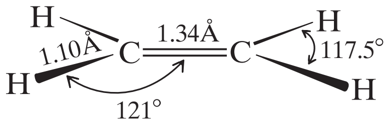


Figure 6A.4 Ethylene molecule: shape and size.

This quantum mechanical structure of ethylene is verified by direct evidence. Electron diffraction and spectroscopic studies show ethylene (Fig. 6A.4) to be a flat molecule, with bond angles very close to 120°. The C—C distance is 1.34 Å as compared with the C—C distance of 1.53 Å in ethane (see Fig. 6A.5).

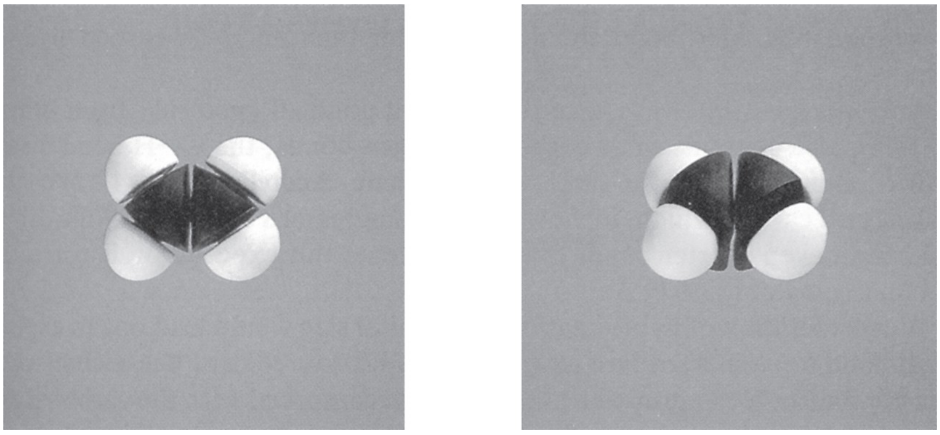
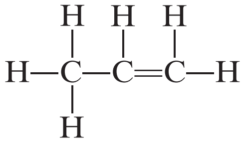


Figure 6A.5 Electronic configuration and molecular shape. Model of the ethylene molecule: two views.

In addition to these direct measurements, we shall soon see that two important aspects of alkene chemistry are consistent with the quantum mechanical picture of the double bond, and are most readily understood in terms of that picture. These are (a) the concept of *hindered rotation* and the accompanying phenomenon of *geomet-ric isomerism* and (b) the kind of reactivity characteristic of the carbon–carbon double bond.

6A.4 Propylene

The next member of the alkene family is **propylene**, C_3H_6. In view of its great similarity to ethylene, it seems reasonable to assume that this compound also contains a carbon–carbon double bond. Starting with two carbons joined by a double bond, and attaching the other atoms according to our rule of one bond per hydrogen and four bonds per carbon, we arrive at the structure



$$\begin{array}{ccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & = & C & - & H \\ & & | & & & & & & \\ & & H & & & & & & \end{array}$$

Propylene

6A.5 Hybridization and orbital size

The carbon–carbon double bond in alkenes is shorter than the carbon–carbon single bond in alkanes because four electrons bind more tightly than two. But, in addition, certain other bonds in alkenes are significantly shorter than their counterparts in alkanes: for example, the C—H distance is 1.103 Å in ethylene compared with 1.112 Å in ethane. To account for this and other differences in bond length, we must consider differences in hybridization of carbon.

The carbon–hydrogen bonds of ethylene are single bonds just as in, say, ethane, but they are formed by overlap of sp^2 orbitals of carbon, instead of sp^3 orbitals as in ethane. Now, compared with an sp^3 orbital, an sp^2 orbital has less p character and more s character. A p orbital extends some distance from the nucleus; an s orbital, on the other hand, lies close about the nucleus. As the s character of a hybrid orbital increases, the effective size of the orbital decreases and, with it, the length of the bond to a given second atom. Thus an sp^2–s carbon–hydrogen bond should be shorter than an sp^3–s carbon–hydrogen bond.

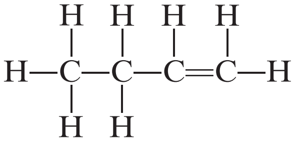
Benzene, in most ways a quite different kind of molecule from ethylene, also contains sp^2–s carbon–hydrogen bonds; the C—H bond distance is 1.10 Å, almost exactly the same as in ethylene. Acetylene contains sp-hybridized carbon which, in view of the even greater s character of the orbitals, should form even shorter bonds than in ethylene; this expectation is correct, the sp–s bond being only 1.079 Å.

A consideration of hybridization and orbital size would lead one to expect an sp^2–sp^3 bond to be shorter than an sp^3–sp^3 bond. In agreement, the carbon–carbon single bond distance in propylene is 1.501 Å, as compared with the carbon–carbon distance of 1.534 Å in ethane. The sp–sp^3 carbon–carbon single bond in methyl-acetylene is even shorter, 1.459 Å. These differences in carbon–carbon single bond lengths are greater than the corresponding differences in carbon–hydrogen bond lengths; however, another factor besides the particular hybridization of carbon may be at work here.

Consideration of hybridization and orbital size helps us to understand other properties, of molecules besides bond length: the relative acidities of certain hydrocarbons, for example, and the relative basicities of certain amines. We might reasonably expect shorter bonds to be stronger bonds, and in agreement combustion experiments shows that the C—H bond dissociation energy in ethylene (108 kcal) is larger than that in ethane (98 kcal), and the C—C (single) bond dissociation energy in propylene (92 kcal) is greater than that in ethane (88 kcal). Indeed, as will be discussed, by affecting the stability of molecules, changes in hybridization may be of more fundamental importance than has been generally recognized.

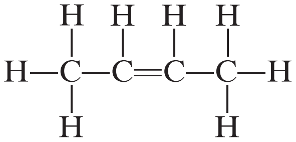
6A.6 The butylenes

Going on to the **butylenes**, C_4H_8, we find that there are a number of possible arrangements. First of all, we may have a straight-chain skeleton as in *n*-butane, or a branched-chain structure as in isobutane. Next, even when we restrict ourselves to the straight-chain skeleton, we find that there are two possible arrangements that differ in position of the double bond in the chain. So far, then, we have a total of three structures; as indicated, these are given the names *1-butene*, *2-butene*, and *isobutylene*.



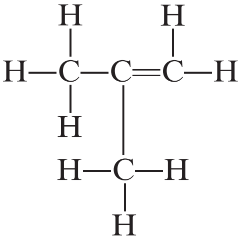
$\mathrm{H_3C{-}CH_2{-}CH{=}CH_2}$

1-Butene



$\mathrm{H_3C{-}CH{=}CH{-}CH_3}$

2-Butene



Isobutylene

How do the facts agree with the prediction of three isomeric butylenes? Experiment has shown that not three but *four* alkenes of the formula C_4H_8 exist; they have the physical properties shown in Table 6A.1.

Table 6A.1 PHYSICAL PROPERTIES OF THE BUTYLENES

Name	B.p., °C	M.p., °C	Relative density (at –20 °C)	Refractive index (at –12.7 °C)
Isobutylene	−7	−141	0.640	1.3727
1-Butene	−6	<−195	0.641	1.3711
trans-2-Butene	+1	−106	0.649	1.3778
cis-2-Butene	+4	−139	0.667	1.3868

On hydrogenation, the isomer of b.p. −7 °C yields isobutane; this butylene evidently contains a branched chain, and has therefore the structure we have designated isobutylene.

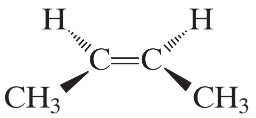
On hydrogenation, the other three isomers all yield the same compound, *n*-butane; they evidently have a straight-chain skeleton. In ways that we shall study later, it is possible to break an alkene molecule apart at the double bond, and from the fragments obtained deduce the position of the double bond in the molecule.

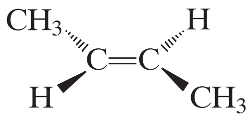
When this procedure is carried out, the isomer of b.p. -6 °C yields products indicating clearly that the double bond is at the end of the chain; this butylene has therefore the structure we have designated 1-butene. When the same procedure is carried out on the two remaining isomers, both yield the same mixture of products; these products show that the double bond is in the middle of the chain.

Judging from the products of hydrogenation and the products of cleavage, we would conclude that the butylenes of b.p. $+1$ °C and $+4$ °C *both* have the structure we have designated 2-butene. Yet the differences in boiling point, melting point, and other physical properties show clearly that they are not the same compound, that is, that they are isomers. In what way can their structures differ?

To understand the kind of isomerism that gives rise to two 2-butenes, we must examine more closely the structure of alkenes and the nature of the carbon–carbon double bond. Ethylene is a flat molecule. We have seen that this flatness is a result of the geometric arrangement of the bonding orbitals, and in particular the overlap that gives rise to the π orbital. For the same reasons, a portion of any alkene must also be flat, the two doubly bonded carbons and the four atoms attached to them lying in the same plane.

If we examine the structure of 2-butene more closely, and particularly if we use molecular models, we find that there are two quite different ways, I and II, in which the atoms can be arranged (aside from the infinite number of possibilities arising from rotation about the single bonds). In one of the structures the methyl groups lie on the same side of the molecule (I), and in the other structure they lie on opposite sides of the molecule (II).


I


II

Now the question arises: can we expect to isolate two isomeric 2-butenes corresponding to these two different structures, or are they too readily interconverted—like, say, the conformations of *n*-butane?

Conversion of I into II involves rotation about the carbon–carbon double bond. The possibility of isolating isomers depends upon the energy required for this rotation. We have seen that the formation of the π bond involves overlap of the p orbitals that lie above and below the plane of the σ orbitals. To pass from one of these 2-butenes to the other, the molecule must be twisted so that the p orbitals no longer overlap; that is, the π bond must be broken (see Fig. 6A.6).

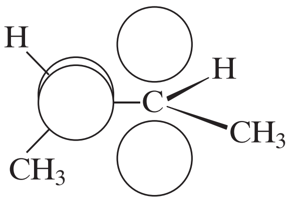


Figure 6A.6 Hindered rotation about the carbon–carbon double bond. Rotation would prevent overlap of the p orbitals and would break the π bond.

Breaking the π bond requires about 70 kcal energy; at room temperature an insignificant proportion of collisions possess this necessary energy, and hence the rate of this interconversion is extremely small. Because of this 70-kcal energy barrier, then, *there is* **hindered rotation** *about the carbon–carbon double bond.* As a result of this hindered rotation,two isomeric 2-butenes can be isolated. These are,of course, the butylenes of b.p $+1$ °C and b.p $+4$ °C.

When we take up the physical properties of the alkenes, we shall discuss one of the ways in which we can tell whether a particular substance is the *cis* or *trans* isomer, that is, one of the ways in which we *assign configuration*.

6A.7 Higher alkenes

As we can see, the butylenes contain one carbon and two hydrogens more than propylene, which in turn contains one carbon and two hydrogens more than ethylene. The alkenes, therefore, form another homologous series, the increment being the same as for the alkanes: CH_2. The general formula for this family is C_nH_{2n}.

As we ascend the series of alkenes, the number of isomeric structures for each member increases even more rapidly than in the case of the alkane series; in addition to variations in the carbon skeletons, there are variations in the position of the double bond for a given skeleton, and the possibility of geometric isomerism.

Problem 6A.1 Neglecting enantiomerism, draw structures of: (a) the six isomeric pentylenes (C_5H_{10}); (b) the four chloropropylenes (C_3H_5Cl); (c) the eleven chlorobutylenes (C_4H_7Cl). Specify as Z or E each geometric isomer.

6A.8 Names of alkenes

Common names are seldom used except for three simple alkenes: *ethylene*, *propylene*, and *isobutylene*. The various alkenes of a given carbon number, however, are sometimes referred to collectively as the *pentylenes* (*amylenes*), *hexylenes, heptylenes*, and so on. (One sometimes encounters the naming of alkenes as derivatives of ethylene: as, for example, *tetramethylethylene* for $(CH_3)_2C{=}C(CH_3)_2$.) Most alkenes are named by the IUPAC system.

The rules of the IUPAC system are:

1. Select as the parent structure the longest continuous chain *that contains the carbon–carbon double bond*; then consider the compound to have been derived from this structure by replacement of hydrogen by various alkyl groups. The parent structure is known as *ethene, propene, butene, pentene*, and so on, depending upon the number of carbon atoms; each name is derived by changing the ending *-ane* of the corresponding alkane name to **-ene**:

$H_2C{=}CH_2$

Ethene

$CH_3{-}CH{=}CH_2$

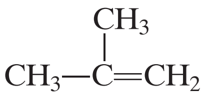
Propene

$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H{=}\overset{1}{C}H_2$

1-Butene

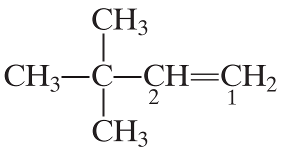
$CH_3CH{=}CHCH_3$

2-Butene
(*cis*- or *trans*-)



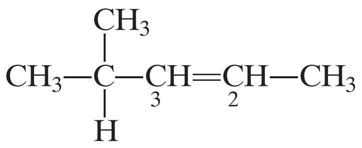
$$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2$$

2-Methylpropene



$$CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}\underset{2}{C}H{=}\underset{1}{C}H_2$$

3,3-Dimethyl-1-butene



$$CH_3{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}\underset{3}{C}H{=}\underset{2}{C}H{-}CH_3$$

4-Methyl-2-pentene
(*cis*- or *trans*-)

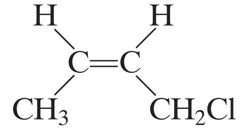
2. Indicate by a number the position of the double bond in the parent chain. Although the double bond involves two carbon atoms, designate its position by the number of the *first* doubly bonded carbon encountered when numbering from the end of the chain nearest the double bond; thus *1-butene* and *2-butene*.
3. Indicate by numbers the positions of the alkyl groups attached to the parent chain.

When a geometric isomer is to be specified, a prefix is added: ***cis***- or ***trans***-, or (***Z***)- or (***E***)-.

An alkene containing halogen is generally named as a **haloalkene**, that is, as an alkene containing halogen as a side chain.Two unsaturated groups are so commonly encountered that they are given special names: **vinyl**, $CH_2{=}CH{-}$; and **allyl**, $CH_2{=}CH{-}CH_2{-}$.

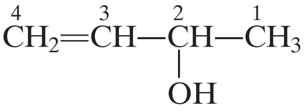
$CH_2{=}CH{-}Cl$
Chloroethene
Vinyl chloride

$CH_2{=}CH{-}CH_2Br$
3-Bromopropene
Allyl bromide


(*Z*)-1-Chloro-2-butene

An alcohol containing a double bond is named as an **alkenol**, with numbers to indicate the positions of the double bond and the hydroxyl group.

$\overset{3}{C}H_2{=}\overset{2}{C}H{-}\overset{1}{C}H_2OH$
2-Propen-1-ol
Allyl alcohol


$\overset{4}{C}H_2{=}\overset{3}{C}H{-}\underset{\displaystyle OH}{\overset{2}{C}H}{-}\overset{1}{C}H_3$
3-Buten-2-ol

Note that *-ol* takes priority over *-ene*; *-ol* appears last in the name, and, where possible, is given the lower number.

Problem 6A.2 Give the structural formula of:

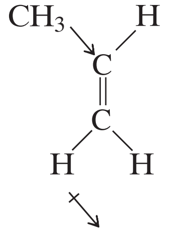
(a) 2,3-dimethyl-2-butene
(b) 3-bromo-2-methylpropene
(c) *cis*-2-methyl-3-heptene
(d) (*E*)-2-chloro-2-butene

Problem 6A.3 Referring to your answer to Problem 6A.1, give IUPAC names for: (a) the isomeric pentylenes; (b) the isomeric chloropropenes.

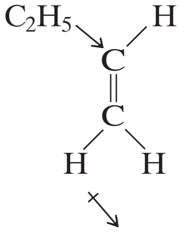
6A.9 Physical properties

As a class, the alkenes possess physical properties that are essentially the same as those of the alkanes. They are insoluble in water, but quite soluble in non-polar solvents like benzene, ether, chloroform, or ligroin. They are less dense than water. As we can see from Table 6A.2, the boiling point rises with increasing carbon num-ber; as with the alkanes, the boiling point rise is 20–30 degrees for each added car-bon, except for the very small homologs. As before, branching lowers the boiling point. A comparison of alkenes in Table 6A.2 with those of alkanes shows that the boiling point of an alkene is very nearly the same as that of the alkane with the same carbon skeleton.

Like alkanes, alkenes are at most only weakly polar. Since the loosely held π electrons of the double bond are easily pulled or pushed, dipole moments are larger than for alkanes. They are still small, however: compare the dipole moments shown for propylene and 1-butene, for example, with the moment of 1.83 D for methyl chloride. The bond joining the alkyl group to the doubly bonded carbon has a small polarity, which is believed to be in the direction shown, that is, with the alkyl group releasing electrons to the doubly bonded carbon. Since this polarity is not canceled by a corresponding polarity in the opposite direction, it gives a net dipole moment to the molecule.

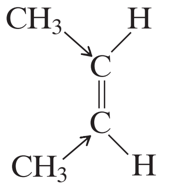


Propylene
$\mu = 0.35$ D

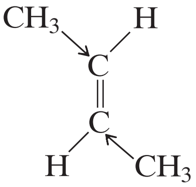


1-Butene
$\mu = 0.37$ D

cis-2-Butene, with two methyl groups on one side of the molecule and two hydrogens on the other, should have a small dipole moment. In *trans*-2-butene, on the other hand, with one methyl and one hydrogen on each side of the molecule, the bond moments should cancel out. Although the dipole moments have not been measured directly, a small difference in polarity is reflected in the higher boiling point of the *cis* isomer.



cis-2-Butene
expect small +⟶
b.p. +4 °C
m.p. −139 °C



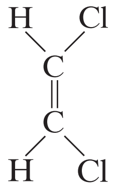
trans-2-Butene
expect $\mu = 0$
b.p. +1 °C
m.p. −106 °C

Table 6A.2 ALKENES

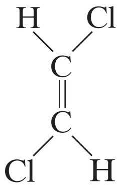
Name	Formula	M.p., °C	B.p., °C	Relative density (at 20 °C)
Ethylene	$CH_2{=}CH_2$	−169	−102	
Propylene	$CH_2{=}CHCH_3$	−185	−48	
1-Butene	$CH_2{=}CHCH_2CH_3$		−6.5	
1-Pentene	$CH_2{=}CH(CH_2)_2CH_3$		30	0.643
1-Hexene	$CH_2{=}CH(CH_2)_3CH_3$	−138	−63.5	0.675
1-Heptene	$CH_2{=}CH(CH_2)_4CH_3$	−119	93	0.698
1-Octene	$CH_2{=}CH(CH_2)_5CH_3$	−104	122.5	0.716
1-Nonene	$CH_2{=}CH(CH_2)_6CH_3$		146	0.731
1-Decene	$CH_2{=}CH(CH_2)_7CH_3$	−87	171	0.743
cis-2-Butene	*cis*-$CH_3CH{=}CHCH_3$	−139	4	
trans-2-Butene	*trans*-$CH_3CH{=}CHCH_3$	−106	1	
Isobutylene	$CH_2{=}C(CH_3)_2$	−141	−7	
cis-2-Pentene	*cis*-$CH_3CH{=}CHCH_2CH_3$	−151	37	0.655
trans-2-Pentene	*trans*-$CH_3CH{=}CHCH_2CH_3$		36	0.647
3-Methyl-1-butene	$CH_2{=}CHCH(CH_3)_2$	−135	25	0.648
2-Methyl-2-butene	$CH_3CH{=}C(CH_3)_2$	−123	39	0.660
2,3-Dimethyl-2-butene	$(CH_3)_2C{=}C(CH_3)_2$	−74	73	0.705

This same relationship exists for many pairs of geometric isomers. Because of its higher polarity the *cis* isomer is generally the higher boiling of a pair; because of its lower symmetry it fits into a crystalline lattice more poorly, and thus generally has the lower melting point.

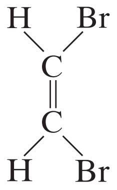
The differences in polarity, and hence the differences in melting point and boiling point, are greater for alkenes that contain elements whose electronegativities differ widely from that of carbon. For example:



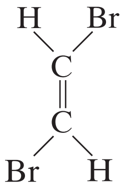
cis
$\mu = 1.85$ D
b.p. 60 °C
m.p. −80 °C



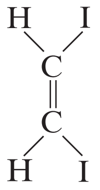
trans
$\mu = 0$
b.p. 48 °C
m.p. −50 °C



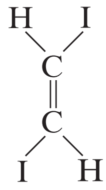
cis
$\mu = 1.35$ D
b.p. 110 °C
m.p. −53 °C



trans
$\mu = 0$
b.p. 108 °C
m.p. −6 °C



cis
$\mu = 0.75$ D
b.p. 188 °C
m.p. −14 °C



trans
$\mu = 0$
b.p. 192 °C
m.p. +72 °C

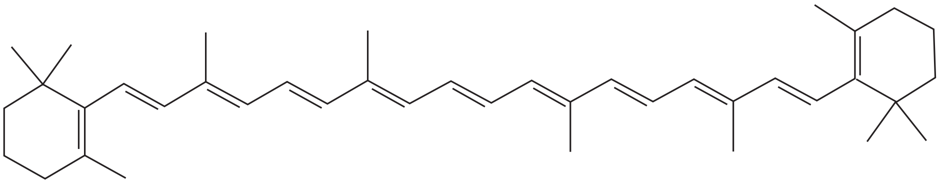
The relationship between configuration and boiling point or melting point is only a rule of thumb, to which there are many exceptions (for example, the boiling points of the diiodoethenes). Measurement of dipole moment, on the other hand, frequently enables us positively to designate a particular isomer as *cis* or *trans*.

Problem 6A.4 (a) Indicate the direction of the net dipole moment for each of the dihaloethenes. (b) Would *cis*-2,3-dichloro-2-butene have a larger or smaller dipole moment than *cis*-1,2-dichloroethene? (c) Indicate the direction of the net dipole moment of *cis*-1,2-dibromo-1,2-dichloroethene. Will it be larger or smaller than the dipole moment of *cis*-1,2-dichloroethene? Why?

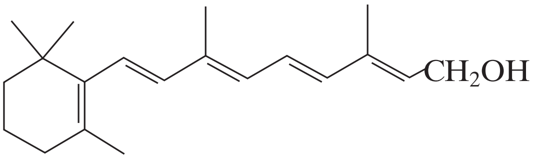
6A.10 The organic chemistry of vision

Molecular shape does much more than affect the melting point or boiling point of a compound: it plays a vital role in determining biological action. To see, in perhaps the most graphic way possible, how this happens, let us look very briefly at the chemistry of *vision*—or, rather, at just one aspect of that chemistry. Vision, in the final analysis, comes down to the *detection of light*: light strikes the eye, and the brain receives a signal that something is there. The recognition of just *what* is there—the size, shape, brightness, and distance of the object seen—is a matter of the physics of the eye and the biology of the brain. But all this depends upon one initial event: light does something in the eye—something which starts off the entire process and without which there would be no vision. That "something", it turns out, is a simple, purely chemical transformation; it is that rare occurrence in biology, an organic reaction that does not require catalysis by an enzyme. It is so direct and uncomplicated—so *elegant*—that it has been adopted as the basis of vision in every form of animal life.

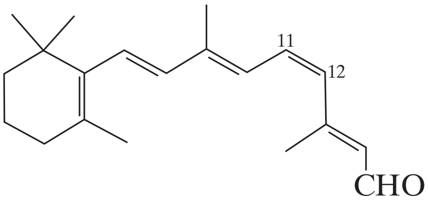
In the rod cells of the retina of a mammal there is a conjugated protein called *rhodopsin*. Part of this protein (its *prosthetic group*) is 11-*cis*-retinal: an unsaturated aldehyde derived from vitamin A, which in turn is derived from β-carotene, the pigment that makes carrots yellow. Retinal is not only bonded covalently to the protein, but is held in a lipophilic pocket.



β-Carotene

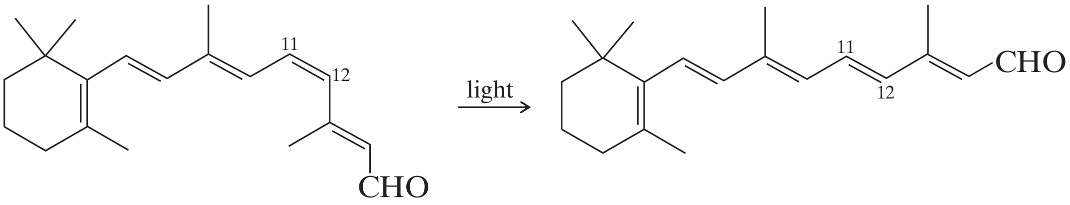


Vitamin A_1
(Retinol)



11-*cis*-Retinal

When light strikes rhodopsin it does just one thing, and then plays no further part: it transforms the 11-*cis*-retinal into 11-*trans*-retinal. *It is this transformation, this change of one geometric isomer into another, that is the beginning of the visual process*; it is the link between the impingement of light and the series of chemical reactions that generates the nerve impulses that let us *see*.



11-*cis*-Retinal 11-*trans*-Retinal

Light brings energy to the rhodopsin, energy that, in effect, opens carbon–carbon double bonds and permits the rotation that is necessary for *cis-trans* isomerization. This isomerization changes the *shape* of the retinal; the bend is removed and the molecule straightens out. With the change in shape of the retinal moiety there is a change in shape of the entire rhodopsin molecule; the protein portion must adjust its conformation to accommodate this altered guest. This, it is believed, affects the permeability of certain membranes, and permits the passage of Ca^{2+} ions that trigger off nerve impulses to the brain. The entire process is amazingly efficient: the human eye can detect the absorption of as few us *five* photons of light by five rod cells!

A great deal more then happens: a series of enzyme-catalysed reactions that supply the energy needed to convert the *trans*-retinal back into the less stable *cis* isomer, so that the process can start all over again.

What we have described is the absorption of light by the rod cells of a mammal. Animals of very different kinds—arthropods, mollusks—have very different optical systems. But, regardless of differences in anatomy, the process of seeing always begins with the same simple organic reaction: the transformation of 11-*cis*-retinal into its geometric isomer.

6A.11 Industrial source

Petroleum and natural gas provide the alkanes that are the chief primary source of organic chemicals: the chemicals on which a vast industry is built and the chemicals we use in the laboratory. Now, alkanes themselves are ill-suited for direct conversion into a variety of other compounds: they are comparatively unreactive, and the reactions they do undergo take place more or less indiscriminately over the molecule to yield complex mixtures.

But from alkanes there are obtained, by cracking in its various forms, certain more reactive substances: the *aromatic hydrocarbons* benzene, toluene, and the xylenes; and the smaller *alkenes* ethylene, propylene, and the butylenes. From these few compounds, plus methane, most aromatic and aliphatic chemicals are ultimately made. Ethylene, for example, is the organic compound consumed in the largest amount by the chemical industry—and it ranks fifth among all compounds, following only sulfuric acid, lime, ammonia, and oxygen.

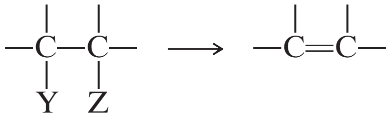
In contrast to alkanes, we shall find, alkenes are highly reactive by virtue of their functional group, the carbon–carbon double bond. (Alkanes really have *no* functional group—or, if they do, it is —H, which occurs everywhere in the molecule.) Not only do alkenes undergo a wide variety of reactions, but these reactions take place at well-defined places in the molecule: at the double bond itself, or at certain positions having a specific relationship to the double bond. The conditions under which alkenes are allowed to react on an industrial scale may, for practical, economic reasons, differ vastly from those used in the laboratory; but in the final analysis the reactions actually taking place are the same ones that we shall study in a later chapter.

To the extent that the renewable biomass some day replaces the non-renewable fossil mass as the primary source of organic chemicals, alkenes will undoubtedly continue to play a central role. Ethylene, for example, is readily formed by dehydration of ethanol, produced by fermentation of carbohydrates.

6A.12 Preparation

Alkenes containing up to four carbon atoms can be obtained in pure form from the petroleum industry. Pure samples of more complicated alkenes must be prepared by methods like those outlined below.

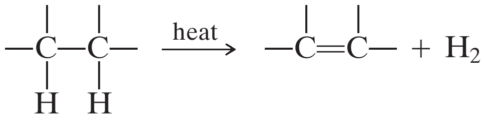
The introduction of a carbon–carbon double bond into a molecule containing only single bonds must necessarily involve the **elimination** of atoms or groups from two adjacent carbons:



$$-\overset{|}{\underset{\underset{\displaystyle Y}{|}}{C}}-\overset{|}{\underset{\underset{\displaystyle Z}{|}}{C}}- \longrightarrow -\overset{|}{C}=\overset{|}{C}-$$

Elimination

In the cracking process already discussed, for example, the atoms eliminated are both hydrogen atoms:

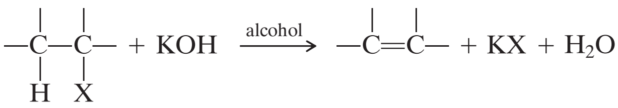


$$-\overset{|}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{|}{\underset{\underset{\displaystyle H}{|}}{C}}- \xrightarrow{\text{heat}} -\overset{|}{C}=\overset{|}{C}- + H_2$$

The elimination reactions described below not only can be used to make simple alkenes, but also—and this is much more important—provide the best general ways to introduce carbon–carbon double bonds into molecules of all kinds.

PREPARATION OF ALKENES

1. Dehydrohalogenation of alkyl halides.



$$-\overset{|}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{|}{\underset{\underset{\displaystyle X}{|}}{C}}- + KOH \xrightarrow{\text{alcohol}} -\overset{|}{C}=\overset{|}{C}- + KX + H_2O$$

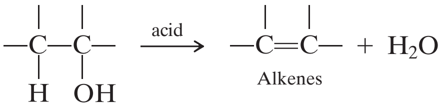
Ease of dehydrohalogenation of alkyl halides
$3° > 2° > 1°$

Examples:

$$\underset{n\text{-Butyl chloride}}{CH_3CH_2CH_2CH_2Cl} \xrightarrow{\text{KOH(alc)}} \underset{\text{1-Butene}}{CH_3CH_2CH=CH_2}$$

$$\underset{sec\text{-Butyl chloride}}{CH_3CH_2CHClCH_3} \xrightarrow{\text{KOH(alc)}} \underset{\substack{\text{2-Butene}\\ 80\%}}{CH_3CH=CHCH_3} + \underset{\substack{\text{1-Butene}\\ 20\%}}{CH_3CH_2CH=CH_2}$$

2. Dehydration of alcohols.



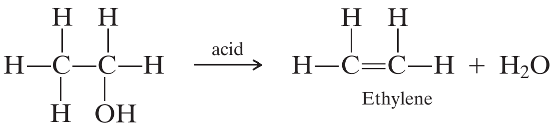
$$-\overset{|}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{|}{\underset{\underset{\displaystyle OH}{|}}{C}}- \xrightarrow{\text{acid}} -\overset{|}{C}=\overset{|}{C}- + H_2O$$

Alcohols

Alkenes

Ease of dehydration of alcohols
$3° > 2° > 1°$

Examples:



$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-H \xrightarrow{\text{acid}} H-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-H + H_2O$$

Ethyl alcohol

Ethylene

$$\underset{n\text{-Butyl alcohol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{\text{acid}} \underset{\text{1-Butene}}{CH_3CH_2CH=CH_2} + \underset{\substack{\text{2-Butene}\\ \textit{Chief product}}}{CH_3CH=CHCH_3}$$

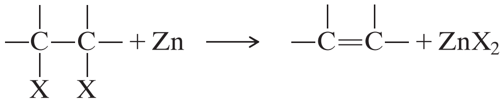
$$CH_3CH_2-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3 \xrightarrow{\text{acid}} \underset{\substack{\text{2-Butene}\\ \textit{Chief product}}}{CH_3CH=CHCH_3} + \underset{\text{1-Butene}}{CH_3CH_2CH=CH_2}$$

sec-Butyl alcohol

CONTINUED

CONTINUED

3. Dehalogenation of vicinal dihalides.

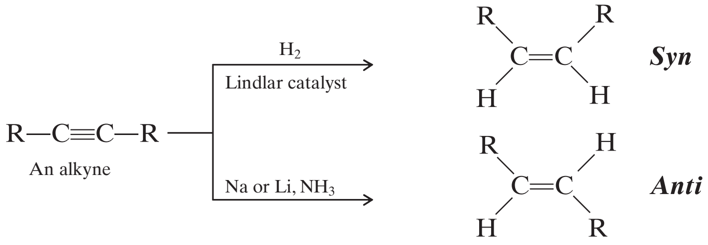


$$-\underset{X}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}- + Zn \longrightarrow -\overset{|}{C}=\overset{|}{C}- + ZnX_2$$

Example:

$$\underset{\text{2,3-Dibromobutane}}{CH_3CHBrCHBrCH_3} \xrightarrow{Zn} \underset{\text{2-Butene}}{CH_3CH{=}CHCH_3}$$

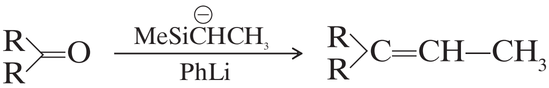
4. Reduction of alkynes.



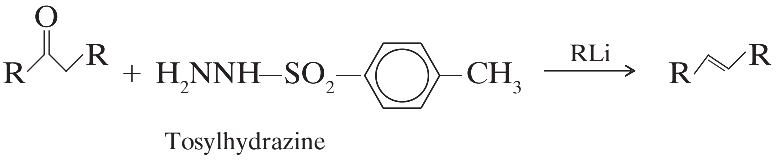
5. Conversion of aldehydes and ketones to alkenes.

(a) Wittig's reaction

(b) Peterson reaction

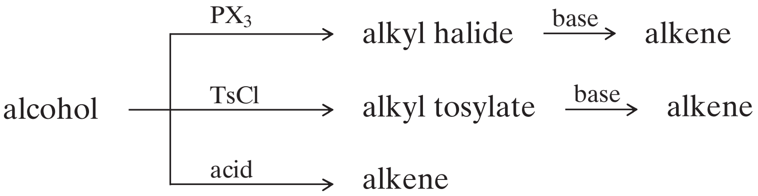


(c) Shapiro reaction



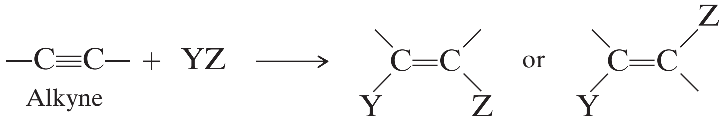
The most important of these methods of preparation—since they are the most generally applicable—are the **dehydrohalogenation of alkyl halides**, promoted by base, and the **dehydration of alcohols**, catalysed by acid. Both dehydrohalogenation and dehydration suffer from the disadvantage that, where the structure permits, hydrogen can be eliminated from the carbon on either side of the carbon bearing the —X or —OH; this frequently produces isomers.

Not surprisingly, alkyl sulfonates undergo a base-promoted elimination closely analogous to dehydrohalogenation; most of what we have to say about dehydrohalogenation applies equally well to this reaction, too. As we have seen, alkyl halides and sulfonates are nearly always prepared from the corresponding alcohols, and hence all these methods ultimately involve preparation from alcohols; however, base-promoted elimination generally leads to fewer complications and is often the preferred method despite the extra step in the sequence.



Dehalogenation of vicinal (Latin: *vicinalis*, neighboring) dihalides is severely limited by the fact that these dihalides are themselves generally prepared from the alkenes. However, it is sometimes useful to convert an alkene into a dihalide while we perform some operation on another part of the molecule, and then to regenerate the alkene by treatment with zinc; this procedure is referred to as *protecting the double bond*.

Just as a carbon–carbon double bond can be generated from a carbon–carbon single bond by elimination, so it can be generated from a carbon–carbon triple bond by *addition*.



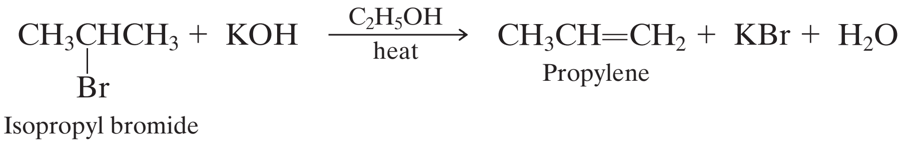
Addition to triple bond

Since such addition can often be controlled to yield either the *cis* or *trans* alkene, as desired, triply bonded compounds are important intermediates in the synthesis of stereochemically pure *cis* or *trans* alkenes.

Key intermediates in the above syntheses are alcohols and alkynes. Both these kinds of compounds, we shall find, are themselves readily prepared from smaller, simpler substances. By combining the chemistry of alkenes with the chemistry of alcohols and alkynes, we shall be able to make alkenes in a wide variety of sizes and shapes.

6A.13 Dehydrohalogenation of alkyl halides: 1,2-elimination

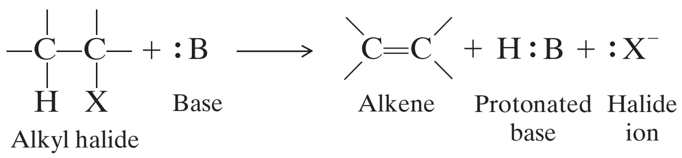
When isopropyl bromide is treated with a hot concentrated alcoholic solution of a strong base like potassium hydroxide, there is obtained propylene, potassium bromide, and water.



$$CH_3\underset{\underset{\text{Br}}{|}}{C}HCH_3 + KOH \xrightarrow[\text{heat}]{C_2H_5OH} CH_3CH{=}CH_2 + KBr + H_2O$$

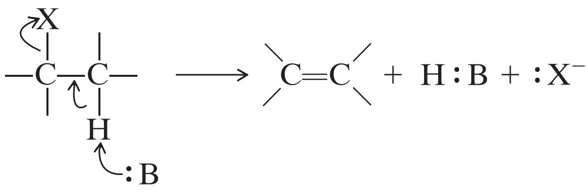
This is an example of **dehydrohalogenation:** *1,2-elimination of the elements of hydrogen halide.* Dehydrohalogenation involves loss—elimination—of the halogen atom and of a hydrogen atom from a carbon adjacent to the one losing the halogen. The reagent required is a *base*, whose function is to abstract the hydrogen as a proton.

Dehydrohalogenation: 1,2-elimination of HX

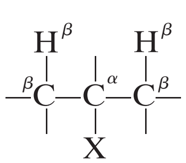


The base :B can be neutral or negatively charged: for example, H_2O or OH^-. The conjugate acid **H :B** will then be positively charged or neutral: for example, H_3O^+ or H_2O.

Now, how does such an elimination generate a double bond? Regardless of the exact mechanism, the products of reaction show that what must happen is the following. Halogen leaves the molecule as halide ion, and hence must take its electron pair along. Hydrogen is abstracted by the base as a proton, and hence must leave its electron pair behind; it is this electron pair that is available to form the second bond—the π bond—between the carbon atoms.

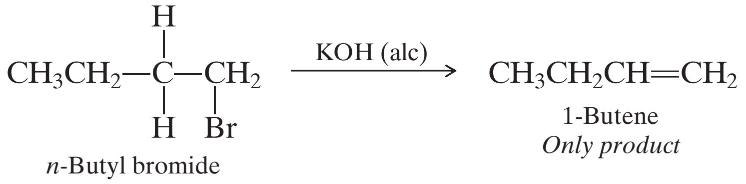


We have called this *1,2*-elimination: for the double bond to form, the hydrogen must come from a carbon that is adjacent to the carbon holding the halogen. Now, the carbon holding the halogen is commonly called the α-carbon (*alpha*-carbon).



Any carbon attached to the α-carbon is a β-carbon (*beta*-carbon), and its hydrogens are β-hydrogens. *Elimination, then, involves loss of a β-hydrogen.*

In some cases, dehydrohalogenation yields a single alkene, and in other cases yields a mixture. To predict which products can be formed in a given reaction, we have only to examine the structure of the substrate. We can expect an alkene corresponding to the loss of *any* one of the β-hydrogens—*but no other alkenes*. *n*-Butyl bromide, for example, can lose hydrogen only from C−2,

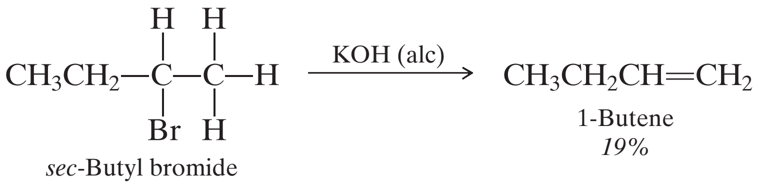


$$\mathrm{CH_3CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}\underset{\displaystyle Br}{CH_2}} \xrightarrow{\text{KOH (alc)}} \mathrm{CH_3CH_2CH{=}CH_2}$$

n-Butyl bromide

1-Butene
Only product

and hence yields only 1-butene. *sec*-Butyl bromide, on the other hand, can lose hydrogen either from C−1,

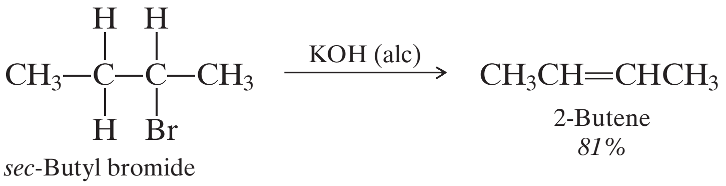


$$\mathrm{CH_3CH_2{-}\overset{\displaystyle H}{\underset{\displaystyle Br}{C}}{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H} \xrightarrow{\text{KOH (alc)}} \mathrm{CH_3CH_2CH{=}CH_2}$$

sec-Butyl bromide

1-Butene
19%

or from C–3,



$$\mathrm{CH_3{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}\overset{\displaystyle H}{\underset{\displaystyle Br}{C}}{-}CH_3} \xrightarrow{\text{KOH (alc)}} \mathrm{CH_3CH{=}CHCH_3}$$

sec-Butyl bromide

2-Butene
81%

and hence yields both 1-butene and 2-butene. Where the two alkenes can be formed, 2-butene is the chief product; this fact fits into a general pattern for dehydrohalogenation which we shall discuss later.

Problem 6A.5 Give structures of all alkenes expected from dehydrohalogenation by strong base of:

(a) 1-chloropentane
(b) 2-chloropentane
(c) 3-chloropentane
(d) 2-chloro-2-methylbutane
(e) 3-chloro-2-methylbutane
(f) 2-chloro-2,3-dimethylbutane
(g) 1-chloro-2,2-dimethylpropane

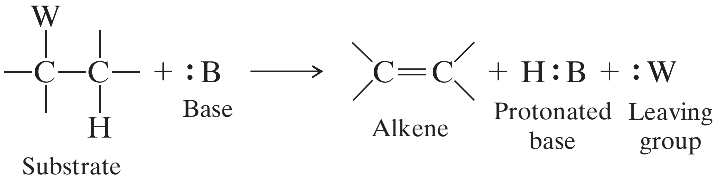
Problem 6A.6 What alkyl halide (*if any*) would yield each of the following pure alkenes upon dehydrohalogenation by strong base?

(a) isobutylene
(b) 1-pentene
(c) 2-pentene
(d) 2-methyl-1-butene
(e) 2-methyl-2-butene
(f) 3-methyl-1-butene

(What we have just discussed assumes that no rearrangement takes place, an assumption that is justified for dehydrohalogenation carried out under the usual conditions: in concentrated alcoholic solutions of strong base. We shall learn to recognize situations where rearrangements are likely, and to predict the elimination products in those cases, too.)

In studying dehydrohalogenation we shall learn a good deal about the entire class of reactions to which it belongs, and of which it is typical: **1,2-elimination**.

1,2-Elimination



Such elimination reactions are characterized by the following:

(a) The substrate contains a **leaving group**, an atom or group that leaves the molecule, taking its electron pair with it.

(b) In a position *beta* to the leaving group, the substrate contains an atom or group—nearly always **hydrogen**—that can be extracted by a base, leaving its electron pair behind.

(c) Reaction is brought about by action of a **base**.

Typically, the base is a strongly basic anion like hydroxide, or an alkoxide derived from an alcohol: ethoxide, $C_2H_5O^-$; *tert*-butoxide, $(CH_3)_3CO^-$; etc. But the solvent itself, a neutral substance like an alcohol or water, sometimes serves as the base, although a considerably weaker one.

For convenience, particularly in designating solvents or reagents, one often abbreviates the names of the simpler alkyl groups: methyl, Me; ethyl, Et; *n*-propyl, *n*-Pr; isopropyl, *i*-Pr; *tert*-butyl, *t*-Bu. Thus, methanol becomes MeOH; sodium methoxide, NaOMe; methoxide ion, MeO^-.

In elimination, a good leaving group is a weakly basic anion or molecule, just as in nucleophilic substitution—and for exactly the same reasons. As a weak base, it readily releases a proton; as a good leaving group, it readily releases carbon. In dehydrohalogenation the leaving group is the very weakly basic halide ion; it is not just accidental that alkyl halides are important substrates in both nucleophilic substitution and elimination. Nor is it just accidental that the same alternatives to alkyl halides can be used in both kinds of reaction—other substrates that can release weakly basic anions. Chief among these other substrates are the *sulfonates* that we have encountered.

(The similarity of substrates in nucleophilic substitution and in elimination, coupled with the fact that both nucleophiles and bases are electron-rich reagents—indeed, are very often the *same* reagent—can lead to problems: potentially, there is always *competition* between the two reactions.)

Now, what mechanism or mechanisms does dehydrohalogenation follow? Just by examining the structures of the reactants and products, we have arrived at certain conclusions about what happens during the reaction: bonds are being broken and bonds are being formed. But what is the *timing* of all these bond-breakings and bond-makings? As always, this question must be answered if we are to have a mechanism.

Problem 6A.7 Starting with an alcohol in each case, outline the synthesis of isobutylene by three different routes.

6A.14 Kinetics of dehydrohalogenation. Duality of mechanism

The theory of elimination reactions developed in a way remarkably similar to the way the theory of nucleophilic substitution developed. Again it was in the mid-1950s that a broad theory of the reaction was proposed, and again it was Hughes and Ingold who proposed it. Here, too, they proposed two mechanisms differing in molecularity. Much of what we shall discuss is based on work done since their initial proposals, and by other workers. This subsequent work has led to refinements in the theory, and has given us a closer look at just what is going on; but, by and large, it has fitted remarkably well into the pattern they laid out.

Let us begin our study where Hughes and Ingold did, with the *kinetics* of elimination. As ordinarily carried out, with a concentrated solution of a strong base, dehydrohalogenation *follows second-order kinetics*. That is, the rate of alkene formation depends upon the concentration of *two* substances: alkyl halide and base. This second-order reaction is observed for all classes of alkyl halides.

$$\text{rate} = k\,[\text{RX}][:\text{B}]$$

Now, if one proceeds along a series of substrates, 1° to 2° to 3°, and if one reduces the strength or concentration of the base, a second kind of behavior begins to appear: *first-order kinetics*. The rate of elimination depends only upon the concentration of alkyl halide, and is independent of the concentration of base.

$$\text{rate} = k\,[\text{RX}]$$

In general, this first-order reaction is encountered only with secondary or tertiary substrates, and in solutions where the base is either weak or in low concentration.

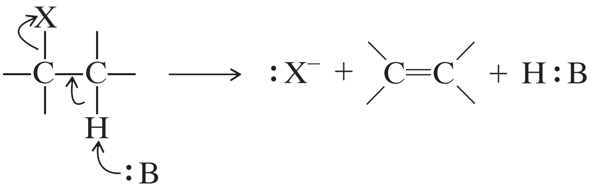
To account for the two kinds of kinetics behavior, Hughes and Ingold proposed that elimination, like nucleophilic substitution, can proceed by two different mechanisms. These mechanisms, for reasons that will emerge, they named **E2** and **E1**.

6A.15 The E2 mechanism

For the reaction that proceeds by second-order kinetics, Hughes and Ingold proposed the **E2 mechanism**. Reaction involves *a single step*: base pulls a proton away from carbon; simultaneously a halide ion departs and the double bond forms. Halogen takes its electron pair with it; hydrogen leaves its electron pair behind, to form the double bond. These are the electronic changes that we said must happen in dehydrohalogenation; what characterizes this particular mechanism is that they are all happening simultaneously, in a single step, via a single transition state.

E2

Bimolecular elimination



In this transition state, two bonds are being broken: C—H and C—X. Now, where does the energy for this bond-breaking come from? As usual, it comes *from bond-making*: formation of the bond between the proton and the base, and formation of the π bond. (Although weaker than a σ bond, the π bond does supply about 70 kcal/mol.)

Consider what happens as the base begins to pull the proton away from the molecule. The β-carbon, armed with the electron pair the departing proton is leaving behind, begins to form a bond to the α-carbon: a second bond, the π bond. As the π bond starts to form, the carbon–halogen bond starts to break: the π bond-making helps to supply energy for the carbon–halogen bond-breaking. Halogen is being *pushed out* in what, from the viewpoint of the α-carbon, is a kind of nucleophilic attack, not unlike an S_N2 reaction.

This mechanism, we said, was proposed for second-order elimination. Second-order kinetics is, of course, exactly what must be observed for a reaction proceeding by the E2 mechanism. The rate-determining step—the *only* step—involves reaction between a molecule of alkyl halide and a molecule of base, and its rate is proportional to the concentration of both reactants. This mechanism was named E2, that is, *elimination, bimolecular*, because in the rate-determining step two molecules undergo covalency changes.

$$\text{rate} = k\,[\mathrm{RX}][:\mathrm{B}]$$

E2 reaction

Second-order kinetics

6A.16 Evidence for the E2 mechanism. Kinetics and absence of rearrangements

What is the evidence for the E2 mechanism? The elimination reactions that

(a) *follow second-order kinetics*

also

(b) *are not accompanied by rearrangements;*
(c) *show a large hydrogen isotope effect*;

(d) *are not accompanied by hydrogen exchange*; and
(e) *show a large element effect.*

Facts (a) and (b) are, of, course, exactly what we would expect for the E2 mechanism. The rate-determining step (the *only* step) involves reaction between a molecule of alkyl halide and a molecule of base; the result is *second-order kinetics*. This single step simply provides *no opportunity for rearrangement*.

6A.17 Evidence for the E2 mechanism. Isotope effects

Now we come to the third piece of evidence for the E2 mechanism. These second-order eliminations (c) *show a large hydrogen isotope effect*. To understand what this means, we must first learn what an isotope effect is and what, in general, it signifies.

Different isotopes of the same element have, by definition, the same electronic configuration, and hence similar chemical properties. This similarity is the basis of the isotopic tracer technique: one isotope does pretty much what another will do, but, from its radioactivity or unusual mass, can be traced through a chemical sequence.

Yet different isotopes have, also by definition, different masses, and because of this their chemical properties are *not identical*: the same reactions can occur but at somewhat different rates (or, for reversible reactions, with different positions of equilibrium). *A difference in rate* (*or position of equilibrium*) *due to a difference in the isotope present in the reaction system is called an* **isotope effect**.

Theoretical considerations, which we cannot go into, supported by much experimental evidence, lead to the conclusion: *if a particular atom is less tightly bound in the transition state of a reaction than in the reactant, the reaction involving the heavier isotope of that atom will go more slowly*. The hydrogen isotopes have the greatest proportional differences in mass: deuterium (D) is twice as heavy as protium (H), and tritium (T) is three times as heavy. As a result, hydrogen isotope effects are the biggest, the easiest to measure, and—because of the special importance of hydrogen in organic chemistry—the most often studied. (If you doubt the importance of hydrogen, look at the structure of almost any compound in this book.)

One kind of reaction in which an atom is less tightly bound in the transition state than in the reactant is a reaction in which a bond to that atom is being broken. Isotope effects due to the breaking of a bond to the isotopic atom are called *primary isotope effects*. They are in general the biggest effects observed for a particular set of isotopes.

In this book we shall be concerned with **primary hydrogen isotope effects**, which amount to this: *a bond to protium* (*H*) *is broken faster than a bond to deuterium* (*D*). For many reactions of this kind, in which hydrogen is abstracted as an atom, positive ion, or negative ion, deuterium isotope effects (k^{H}/k^{D}) as large as 5 to 8 (at room temperature) have been observed; that is to say, the reaction is 5 to 8 times as fast for ordinary hydrogen as for deuterium. (Tritium isotope effects, k^{H}/k^{T}, are about twice as large as deuterium isotope effects.)

(1) $$\sim\!\mathrm{C{-}H} + \mathrm{Z} \xrightarrow{k^{H}} [\sim\!\mathrm{C}\cdots\mathrm{H}\cdots\mathrm{Z}] \longrightarrow \sim\!\mathrm{C} + \mathrm{H{-}Z}$$

(2) $$\sim\!\mathrm{C{-}D} + \mathrm{Z} \xrightarrow{k^{D}} [\sim\!\mathrm{C}\cdots\mathrm{D}\cdots\mathrm{Z}] \longrightarrow \sim\!\mathrm{C} + \mathrm{D{-}Z}$$

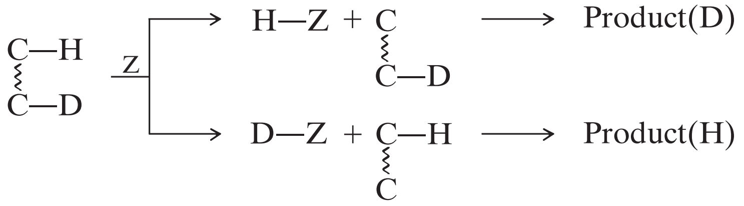
These differences in rate can be measured in a variety of ways. In some cases, the rates of the two individual reactions (1) and (2) can be measured directly and the rate constants k^{H} and k^{D} compared. Often, however, it is more feasible to use our familiar method of competition in either of two ways.

In *intermolecular* competition, a mixture of labeled and unlabeled reactants compete for a limited amount of reagent; reactions (1) and (2) thus go on in the same mixture, and we measure the relative amounts of H—Z and D—Z produced. (Sometimes, larger amounts of the reagent Z are used, and the relative amounts of the two reactants—ordinary and labeled—left *unconsumed* are measured; the less reactive will have been used up more slowly and will predominate. The relative rates of reaction can be calculated without much difficulty.)

In *intramolecular* competition, a single reactant is used which contains several equivalent positions, some labeled and some not:

(3)

(4)



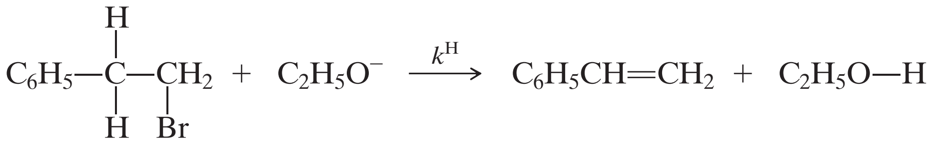
One can then measure either the relative amounts of H—Z and D—Z, or the relative amounts of the D-containing product formed by reaction (3) and the H-containing product formed by reaction (4).

Problem 6A.8 (a) When excess toluene-*α-d* ($C_6H_5CH_2D$) was photochemically monochlorinated at 80 °C with 0.1 mol of chlorine, there were obtained 0.0212 mol DCl and 0.0868 mol HCl. What is the value of the isotope effect k^H/k^D (*per hydrogen atom*, of course)? (b) What relative amounts of DCl and HCl would you expect to get from $C_6H_5CHD_2$?

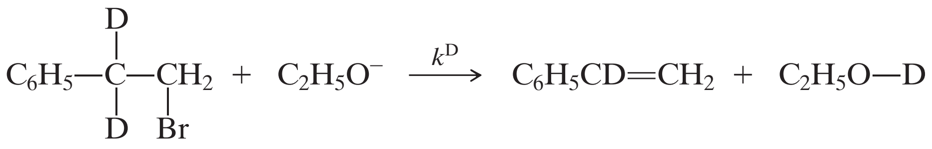
The presence—or *absence*—of an isotope effect for a particular reaction can be of enormous significance to the organic chemist. As our first example of how this concept can be used, let us return to our original topic, the evidence supporting the E2 mechanism.

Let us consider the substituted alkyl halide 2-phenylethyl bromide, $C_6H_5CH_2CH_2Br$. The *phenyl* group, —C_6H_5, is derived from the aromatic compound *benzene*, C_6H_6. (Phenyl is often represented by —Ph.) For the present we need only know that the —C_6H_5 group itself is inert toward the reagents that bring about elimination, and can be considered as just another substituent.

The labeled 2-phenylethyl bromide $C_6H_5CD_2CH_2Br$ was prepared. This compound, we see, contains deuterium at both *β*-positions, the positions from which hydrogen must be lost in elimination. The rate constant (k^D) for its dehydrobromination by sodium ethoxide was measured, and compared with the rate constant (k^H) for reaction of ordinary (unlabeled) 2-phenylethyl bromide under the same conditions. It was found that $k^H/k^D = 7$, that is, the compound containing protium reacts *seven times as fast* as the compound containing deuterium. An isotope effect of this size, we saw, is what we would expect for the breaking of a carbon–hydrogen bond.



$$C_6H_5\text{—}\underset{H}{\overset{H}{C}}\text{—}\underset{Br}{CH_2} + C_2H_5O^- \xrightarrow{k^H} C_6H_5CH{=}CH_2 + C_2H_5O\text{—}H$$



$$C_6H_5CD_2CH_2Br + C_2H_5O^- \xrightarrow{k^D} C_6H_5CD{=}CH_2 + C_2H_5O{-}D$$

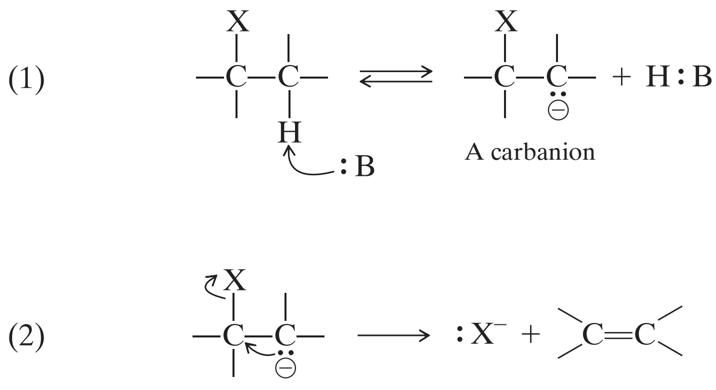
$$k^H/k^D = 7$$

Now, what is significant about the existence of an isotope effect here? Not that it shows the breaking of a β-carbon–hydrogen bond; we already know that, just from the products of reaction. What is significant is that it shows the breaking of a β-carbon–hydrogen bond in a *rate-determining step*.

This fact is, of course, consistent with the E2 mechanism: a β-carbon–hydrogen bond is broken in the only—and, hence, rate-determining—step.

6A.18 Evidence for the E2 mechanism. Absence of hydrogen exchange

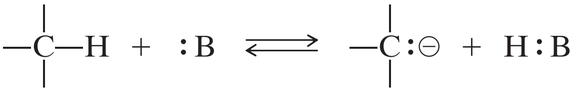
Facts (a), (b), and (c) are, then, consistent with the E2 mechanism. But there is another reasonable possibility that we must consider: the *carbanion mechanism*. Such a mechanism involves two steps. In step (1) the substrate loses a proton to the base to form a negatively charged particle, a carbanion. In step (2) this carbanion loses halide ion to yield the alkene.



Elimination via carbanion
Seldom observed

Step (1) is an acid–base reaction in the Lowry–Brønsted sense, with the substrate acting as an acid. *Since the acidic proton is attached to carbon, the substrate is called a* **carbon acid**. Like most carbon acids, it is extremely weak.

The products of step (1) are the conjugate acid of the base—water, say, from the base, hydroxide ion—and the conjugate base of the carbon acid, a carbanion. *A* **carbanion** *is the conjugate base of a carbon acid.*



A carbon acid — Base — A carbanion: *conjugate base of carbon acid* — Conjugate acid

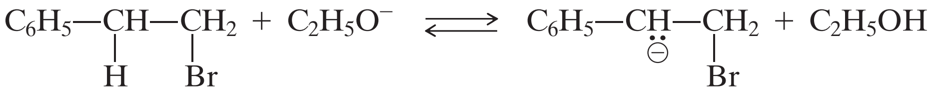
(Elimination via carbanions is often called ElcB, *elimination, unimolecular*, of the *conjugate base*.)

The carbanion mechanism, like the E2, is consistent with facts (a), (b), and (c). In attempts to distinguish between these two possibilities, experiments have been carried out using deuterium as a label: this time, not to test for isotope effects, but simply as a tracer, to test for *hydrogen exchange*. Let us see how this approach works.

Consider the dehydrohalogenation of 2-phenylethyl bromide, $C_6H_5CH_2CH_2Br$. (This substrate was selected because, for reasons that we shall see that the phenyl group,

$$\underset{\text{2-Phenylethyl bromide}}{C_6H_5CH_2CH_2Br} \xrightarrow[C_2H_5OH]{C_2H_5ONa} \underset{\text{Phenylethylene}}{C_6H_5CH{=}CH_2}$$

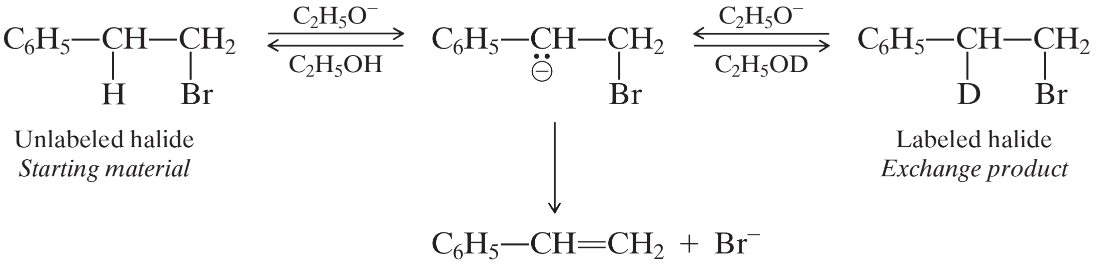
C_6H_5, should strongly favor formation of carbanions.) Dehydrohalogenation was brought about by the strong base sodium ethoxide, C_2H_5ONa, in ethanol solution. Formation of carbanions would involve conversion of the base, ethoxide ion, into its conjugate acid, ethanol, which is the solvent.



$$C_6H_5-\underset{\underset{H}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2} + C_2H_5O^- \rightleftharpoons C_6H_5-\underset{\overset{\bullet\bullet}{\ominus}}{CH}-\underset{\underset{Br}{|}}{CH_2} + C_2H_5OH$$

2-Phenylethyl bromide *Acid* Ethoxide ion *Base* Carbanion *Base* Ethanol *Acid*

Now, in the actual experiment, the substrate was ordinary (unlabeled) 2-phenylethyl bromide, and the solvent was *labeled* ethanol, C_2H_5OD. Consider what would happen if carbanions were formed—and formed reversibly. Most of them would regain hydrogen many times to regenerate starting material before eventually losing halide ion to yield alkene. And they would regain this hydrogen *from the solvent*, the conjugate acid of the base and, in fact, the only acid around of appreciable acidity. But nearly all the molecules of solvent are C_2H_5OD, not C_2H_5OH; and so, in this reversal, the carbanion would be almost certain to gain a *deuteron*, not a proton.



$$C_6H_5-\underset{\underset{H}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2} \underset{C_2H_5OH}{\overset{C_2H_5O^-}{\rightleftharpoons}} C_6H_5-\underset{\overset{\bullet\bullet}{\ominus}}{CH}-\underset{\underset{Br}{|}}{CH_2} \underset{C_2H_5OD}{\overset{C_2H_5O^-}{\leftrightharpoons}} C_6H_5-\underset{\underset{D}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2}$$

$$\downarrow$$

$$C_6H_5-CH{=}CH_2 + Br^-$$

Unlabeled halide
Starting material

Labeled halide
Exchange product

Elimination product

Reaction was allowed to run until about half the substrate had been converted into alkene. Reaction was then interrupted, and unconsumed 2-phenylethyl bromide was recovered. Mass spectrometric analysis showed that it contained *no deuterium*. Similar experiments with other systems have given similar results. Typical second-order elimination reactions (d) *are not accompanied by hydrogen exchange*.

Fact (d) thus rules out the mechanism in which carbanions are formed reversibly. It is, of course, consistent with the E2 mechanism, which provides no opportunity for hydrogen exchange.

6A.19 Evidence for the E2 mechanism. The element effect

These second-order eliminations (e) *show a large element effect.*

Let us look at the two steps of the carbanion mechanism again. The absence of hydrogen exchange discussed in the preceding section does not completely rule out such a mechanism. It simply shows that *if* carbanions are formed, they are formed *irreversibly*: that they lose halide ions much faster than they regain protons. That is, k_2 would have to be much larger than k_{-1}.

Now, if this were so, step (1) would be rate-determining, and the rate of step (2) would have no effect on the overall rate of reaction—just as in an S_N1 or E1 reaction. Depending upon conditions, step (2) might go faster or slower, but it really would not matter; step (1) would be the bottleneck and its rate would determine how fast elimination occurs.

Now, is this true? How can we tell whether or not the rate at which halide ion is lost affects the rate of elimination? We might consider looking for an isotope effect, as was done in studying the cleavage of the carbon–hydrogen bond. But here that would be a more difficult job. We are not dealing with loss of hydrogen, whose isotopes differ twofold and threefold in mass. We are dealing with loss of heavier elements like chlorine, whose isotopes differ by only a few percent, with correspondingly small differences in the ease with which bonds are broken.

It has been pointed out by Joseph Bunnett that evidence on this point has existed for many years in what he has named the *element effect.*

Heterolytic bond dissociation energies show that the strength of carbon–halogen bonds follows the sequence

Heterolytic bond dissociation energy R—F > R—Cl > R—Br > R—I

In both S_N2 and S_N1 reactions the carbon–halogen bond is broken in the rate-determining step. And, as expected, reactivity in nucleophilic substitution follows the sequence,

Reactivity toward S_N2 or S_N1 R—I > R—Br > R—Cl > R—F

with the rate of reaction reflecting the ease of breaking the carbon–halogen bond. The differences in rate here are quite large: alkyl bromides, for example, react 25 to 50 times as fast as the corresponding alkyl chlorides. These element effects are, in fact, much larger than the isotope effects observed for the breaking of bonds to protium and deuterium—as, indeed, they *should* be, in view of the much greater differences in bond strength.

Now, in these elimination reactions the reactivity of alkyl halides follows the same sequence as for substitution,

Reactivity toward E2 R—I > R—Br > R—Cl > R—F and with element effects of just about the same size: alkyl bromides react 40 to 60 times as fast as the chlorides, and—to take the full range of reactivity—alkyl iodides react more than 25000 times as fast as the fluorides. Clearly, the rate of breaking the carbon–halogen bond *does* affect the overall rate of elimination.

Thus, only the E2 mechanism fits all the facts, and is generally accepted as the principal pathway followed by 1,2-elimination.

6A.20 The E2 reaction: orientation and reactivity

So far we have been concerned with the evidence that second-order dehydrohalogenation proceeds by the E2 mechanism. Now let us look at some other characteristics of this reaction.

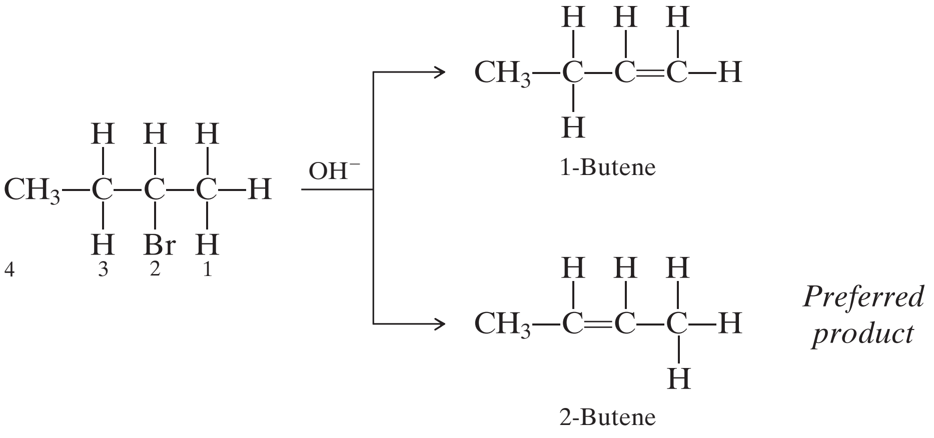
Dehydrohalogenation, we have seen, often yields a mixture of isomeric alkenes. In such a case, which isomer, if any, will predominate? Study of many reactions has shown that one isomer generally does predominate, and that it is possible to predict which isomer this will be—that is, to predict the *orientation* of elimination—on the basis of molecular structure.

$$CH_3CH_2CHBrCH_3 \xrightarrow{\text{KOH (alc)}} \underset{81\%}{CH_3CH{=}CHCH_3} + \underset{19\%}{CH_3CH_2CH{=}CH_2}$$

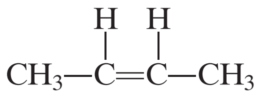
$$CH_3CH_2CH_2CHBrCH_3 \xrightarrow{\text{KOH (alc)}} \underset{71\%}{CH_3CH_2CH{=}CHCH_3} + \underset{29\%}{CH_3CH_2CH_2CH{=}CH_2}$$

$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}BrCH_3 \xrightarrow{\text{KOH (alc)}} \underset{71\%}{CH_3CH{=}\overset{\overset{CH_3}{|}}{C}CH_3} + \underset{29\%}{CH_3CH_2\overset{\overset{CH_3}{|}}{C}{=}CH_2}$$

Take, for example, *sec*-butyl bromide. Attack by base at any one of three β-hydrogens (those on C–1) can lead to the formation of 1-butene; attack at either of two β-hydrogens (on C–3) can lead to the formation of 2-butene. We see that 2-butene is the preferred product *despite* a probability factor of 3:2 working against its formation.



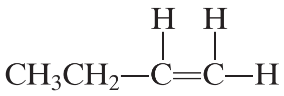
If we focus our attention, not on the hydrogen being lost, but on the alkene being formed, we see the following. The preferred product, 2-butene, is a *di*substituted alkene, whereas 1-butene is a *mono*substituted alkene; that is, in 2-butene there are two alkyl groups (two CH_3 groups) attached to the doubly bonded carbons, and in 1-butene there is only one alkyl group (C_2H_5).



$CH_3-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_3$

Disubstituted alkene

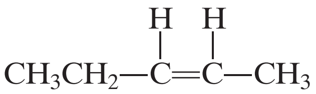
preferred over



$CH_3CH_2-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H$

Monosubstituted alkene

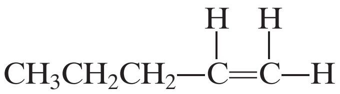
In the other examples we see that a disubstituted alkene is preferred over a monosubstituted alkene, and a trisubstituted alkene is preferred over a disubstituted alkene.



$CH_3CH_2-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_3$

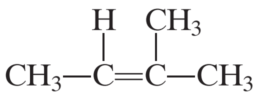
Disubstituted alkene

preferred over



$CH_3CH_2CH_2-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H$

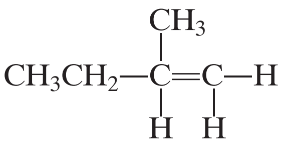
Monosubstituted alkene



$CH_3-\overset{H}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3$

Trisubstituted alkene

preferred over



$CH_3CH_2-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}=\underset{H}{\underset{|}{C}}-H$

Disubstituted alkene

These form part of a pattern first observed by the Russian chemist Alexander Saytzeff, who in 1875 formulated a "rule" which can be summarized as: *in dehydrohalogenation the preferred product is the alkene that has the greater number of alkyl groups attached to the doubly bonded carbon atoms.*

Now, dehydrohalogenation is an irreversible reaction, so that once again orientation is determined by the relative rates of competing reactions. More 2-butene than 1-butene is obtained from *sec*-butyl bromide because 2-butene is formed faster than 1-butene. The alkene with the greater number of alkyl groups is the preferred product because it is formed faster than alternative alkenes. What the Saytzeff rule gives us, then, is a sequence showing the relative rates of formation of alkenes.

Ease of formation of alkenes

$$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2,\ RCH{=}CHR > RCH{=}CH_2$$

We shall find evidence that the stability of alkenes follows exactly the same sequence.

Stability of alkenes

$$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2,\ RCH{=}CHR > RCH{=}CH_2 > CH_2{=}CH_2$$

On this basis we can recast **Saytzeff's rule** to read: **in dehydrohalogenation, the more stable the alkenes, the faster it is formed**. Predominant formation of the more stable isomer is called **Saytzeff orientation**.

In this form the rule is more generally useful, since it applies to cases where alkene stability is determined by structural features other than alkyl substituents. Furthermore, this formulation leads directly to the factor actually at work.

Consider the transition state for the E2 reaction. Bonds to hydrogen and the leaving group are partly broken, and the double bond is partly formed. The transition state has thus acquired considerable *alkene character*. Factors that stabilize the alkene—alkyl groups in these cases—also stabilize the incipient alkene in the transition state. E_{act} is lowered, and the alkene is formed faster. Once again, as in the formation of free radicals and of carbocations, the product character of the transition state is a major factor in determining its stability, and hence the rate of reaction.

Transition state:
partly formed double bond

But the alkene character of the transition state is not the only factor at work in elimination and, as a result, orientation is not always Saytzeff. This is particularly true when substrates other than alkyl halides and alkyl sulfonates are involved. We shall look at another kind of orientation, *Hofmann*, and at the factors that lie behind it, too. We shall see that orientation in elimination is the net result of the working of several factors—often opposing each other—and that the Saytzeff orientation generally observed for elimination from alkyl halides and sulfonates simply reflects a transition state where one factor, alkene stability, is dominant.

Alkene stability not only determines *orientation* of dehydrohalogenation, but also is an important factor in determining the *reactivity* of an alkyl halide toward elimination, as shown below, for example, for reaction with sodium ethoxide in ethanol at 55 °C. We see that, even after we have allowed for the number of β-hydrogens, the relative rate *per hydrogen* increases as the alkene becomes more highly substituted.

Substrate	⟶	*Product*	*Relative rates*	*Relative rates per H*
CH_3CH_2Br	⟶	$CH_2{=}CH_2$	1.0	1.0
$CH_3CH_2CH_2Br$	⟶	$CH_3CH{=}CH_2$	3.3	5.0
$CH_3CHBrCH_3$	⟶	$CH_3CH{=}CH_2$	9.4	4.7
$(CH_3)_3CBr$	⟶	$(CH_3)_2C{=}CH_2$	120	40

As one proceeds along a series of alkyl halides from 1° to 2° to 3°, the structure by definition becomes more branched at the carbon carrying the halogen. This increased branching has two results: it provides a greater number of β-hydrogens for attack by base, and hence a more favorable probability factor toward elimination; and it leads to a more highly branched, more stable alkene, and hence a more stable transition state and lower E_{act}. As a result of this combination of factors, **in E2 dehydrohalogenation the order of reactivity of alkyl halides is**

Reactivity of RX toward E2 $3^\circ > 2^\circ > 1^\circ$

We can, however, look deeper than this in analyzing the structures of substrates. A substrate may be of the same class as another and yet yield a more highly branched alkene; and, in general, we expect it to be more reactive. This is usually true even though the number of β-hydrogens is smaller; where the two factors oppose each other, alkene stability tends to outweigh the probability factor.

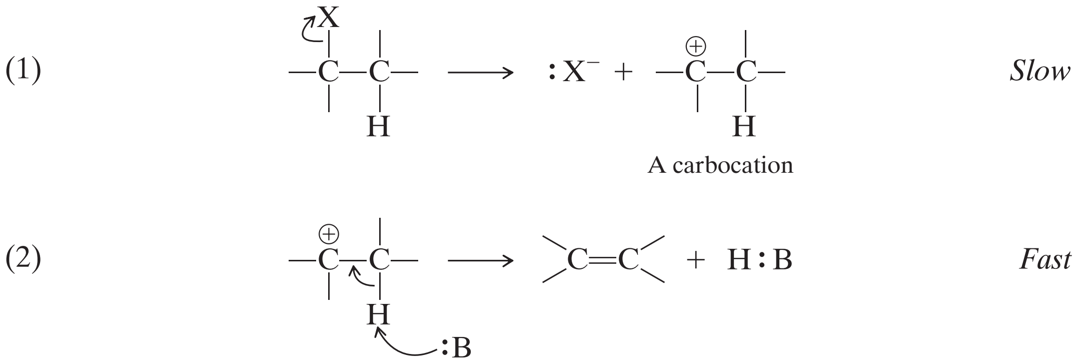
Problem 6A.9 Predict the major product of each dehydrohalogenation in Problem 6A.5

Problem 6A.10 Predict the order of reactivity toward E2 dehydrohalogenation of the following compounds: ethyl bromide, *n*-propyl bromide, isobutyl bromide, neopentyl bromide. Explain your answer in detail.

6A.21 The E1 mechanism

For the reaction proceeding by first-order kinetics, Hughes and Ingold proposed the **E1 mechanism**. In this mechanism the electronic changes—the bond-breaking and bond-making—are the same as in E2; here, however, they are taking place, not simultaneously, but one after the other. Where E2 involves a single step, E1 involves two steps. In step (1) the substrate undergoes slow heterolysis to form halide ion and a carbocation. In step (2) the carbocation rapidly loses a proton to the base and forms the alkene.

E1
Unimolecular *elimination*



We recognize step (1) as identical to the first step in S_N1. In the second step of S_N1 the carbocation combines with a nucleophile to yield the substitution product; in step (2) of E1 the carbocation reacts with the base to yield the elimination product.

Here, as always, the reactions of a carbocation have a common end: *they provide a pair of electrons to complete the octet of the electron-deficient carbon*. In S_N1 these electrons are an unshared pair on the nucleophile; in E1 they are the pair originally shared by the proton, and made available—through π bond formation—by departure of the proton.

On the basis of step (2), we can add another reaction to our list. **A carbocation may:**

(a) combine with a nucleophile;
(b) rearrange to a more stable carbocation;
(c) eliminate a proton to form an alkene.

This list will continue to grow.

The E1 reaction follows first-order kinetics just as an S_N1 reaction does, and for exactly the same reason. The overall rate of reaction is determined only by the slow first step. Except for the many necessary solvent molecules, this *rate-determining* step involves only substrate, and its rate depends only on the concentration of substrate. The rate of an E1 reaction is independent of base concentration because the reaction *whose rate we are measuring* does not involve base. Again it is the rate of formation of carbocations that determines how fast a reaction goes. Once formed, the carbocations rapidly react to yield product—in this case, the alkene.

$$\text{rate} = k[\text{RX}] \qquad \textbf{E1 reaction}$$

First-order kinetics

This mechanism was named E1, that is, *elimination, unimolecular*, because in the rate-determining step only one molecule, substrate, undergoes covalency change.

6A.22 Evidence for the E1 mechanism

What is the evidence for the E1 mechanism? The elimination reactions that

(a) *follow first-order kinetics*

also

(b) *are not accompanied by a primary hydrogen isotope effect*;

(c) show the same *effect of structure on reactivity* as S_N1 reactions do; and

(d) where the structure permits, are *accompanied by rearrangement.*

Let us examine each piece of evidence.

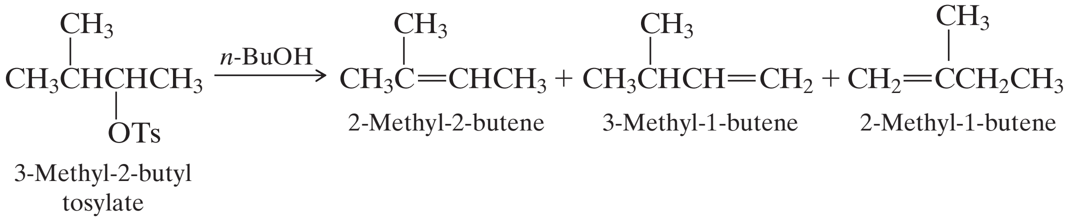
These first-order reactions (b) *are not accompanied by a primary hydrogen isotope effect.* Such an isotope effect would be expected in elimination only if the β-carbon–hydrogen bond is broken *in the rate-determining step*. It is expected in E2, with its single step; and a large, primary isotope effect is in fact observed in second-order eliminations. It is *not* expected in E1, where the proton is lost in the second, fast step. And it is a fact that a primary isotope effect is not observed in first-order eliminations.

Next, first-order eliminations (c) show the same *effect of structure on reactivity* as S_N1 reactions do. To understand this evidence, we need only recall that E1 involves *exactly the same first step* as S_N1. Since this first step is rate-determining, it follows that the order of reactivity of alkyl halides in E1 must be the same as in S_N1. Experiment has shown that this is so.

Reactivity in E1 $3° > 2° > 1°$

In E1, as in S_N1, reactivity is determined by the rate of formation of the carbocation; and this depends upon the stability of the carbocation.

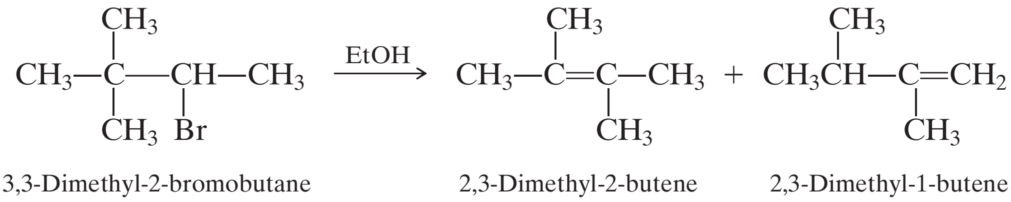
Where the structure permits, these first-order eliminations (d) *are accompanied by rearrangement.* Again we turn to the fact that the first step is the same as in S_N1. Since this first step yields carbocations, it follows that E1 should be susceptible to rearrangements, and of exactly the same kind as those characteristic of S_N1. This, too, is confirmed by experiment. The double bond appears in places remote from the carbon that held the leaving group:



$$\mathrm{CH_3\overset{CH_3}{C}H\underset{OTs}{C}HCH_3} \xrightarrow{n\text{-BuOH}} \mathrm{CH_3\overset{CH_3}{C}{=}CHCH_3 + CH_3\overset{CH_3}{C}HCH{=}CH_2 + CH_2{=}\overset{CH_3}{C}CH_2CH_3}$$

3-Methyl-2-butyl tosylate; 2-Methyl-2-butene; 3-Methyl-1-butene; 2-Methyl-1-butene

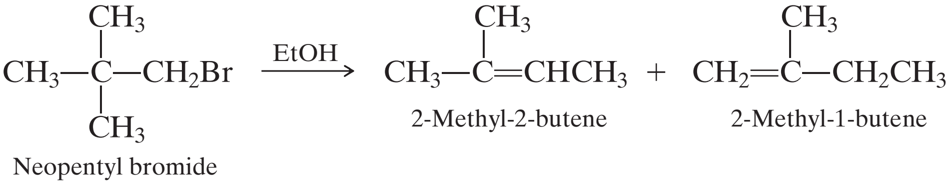
Sometimes the carbon skeleton is changed:



$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{Br}{C}H{-}CH_3} \xrightarrow{\mathrm{EtOH}} \mathrm{CH_3{-}\overset{CH_3}{C}{=}\underset{CH_3}{C}{-}CH_3 + CH_3\overset{CH_3}{C}H{-}\underset{CH_3}{C}{=}CH_2}$$

3,3-Dimethyl-2-bromobutane; 2,3-Dimethyl-2-butene; 2,3-Dimethyl-1-butene

Alkenes are even obtained from substrates that do not contain β-hydrogen:

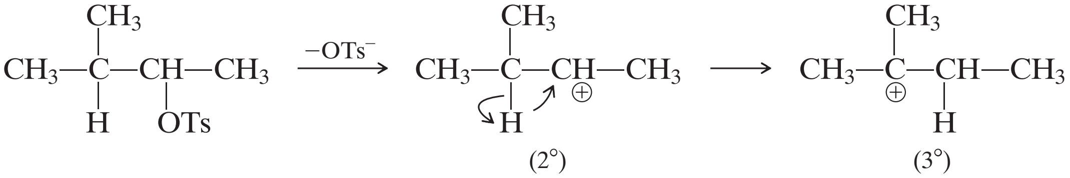


$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2Br} \xrightarrow{\mathrm{EtOH}} \mathrm{CH_3{-}\overset{CH_3}{C}{=}CHCH_3 + CH_2{=}\overset{CH_3}{C}{-}CH_2CH_3}$$

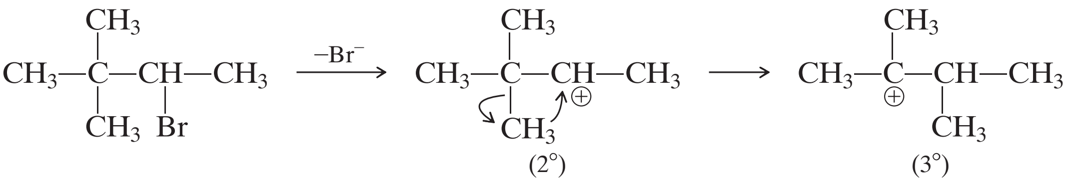
Neopentyl bromide; 2-Methyl-2-butene; 2-Methyl-1-butene

In each case it is evident that if, indeed, the alkene is formed from a carbocation, *it is not the same carbocation that was initially formed from the substrate.* And, of course, it is not.

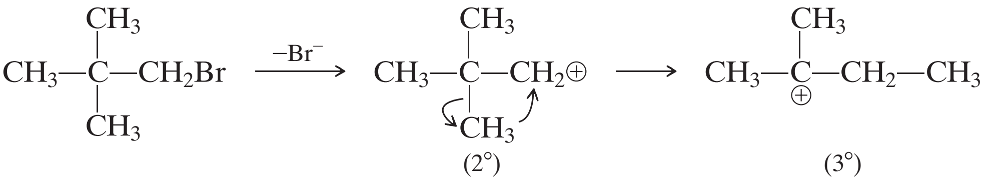
In each of these examples the initially formed carbocation can rearrange by a 1,2-shift to form a more stable carbocation. And—as we saw for S_N1 reactions—when this can happen, it *does*.



$$\mathrm{CH_3{-}\underset{H}{\overset{CH_3}{C}}{-}\underset{OTs}{C}H{-}CH_3} \xrightarrow{-\mathrm{OTs}^-} \underset{(2°)}{\mathrm{CH_3{-}\underset{H}{\overset{CH_3}{C}}{-}\overset{\oplus}{C}H{-}CH_3}} \longrightarrow \underset{(3°)}{\mathrm{CH_3{-}\underset{\oplus}{\overset{CH_3}{C}}{-}\underset{H}{C}H{-}CH_3}}$$

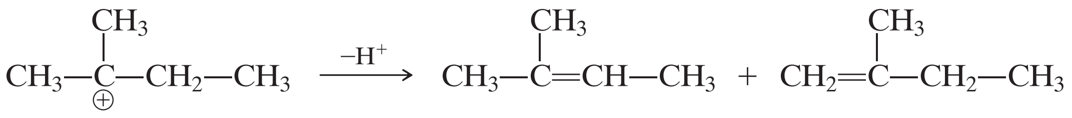


$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\underset{Br}{C}H{-}CH_3} \xrightarrow{-\mathrm{Br}^-} \underset{(2°)}{\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\overset{\oplus}{C}H{-}CH_3}} \longrightarrow \underset{(3°)}{\mathrm{CH_3{-}\underset{\oplus}{\overset{CH_3}{C}}{-}\underset{CH_3}{C}H{-}CH_3}}$$



$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2Br} \xrightarrow{-\mathrm{Br}^-} \underset{(2°)}{\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2\oplus}} \longrightarrow \underset{(3°)}{\mathrm{CH_3{-}\underset{\oplus}{\overset{CH_3}{C}}{-}CH_2{-}CH_3}}$$

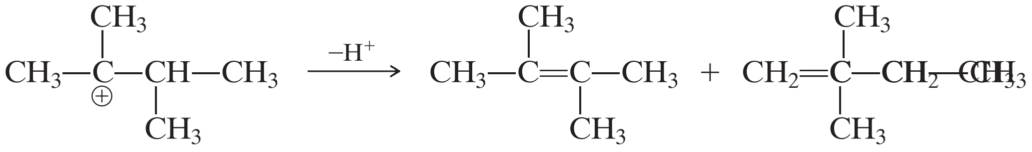
It is this new carbocation that loses the proton—in a perfectly straightforward way from the β-position—to yield the “unexpected” alkenes.



$$CH_3{-}\underset{\oplus}{\overset{CH_3}{C}}{-}CH_2{-}CH_3 \xrightarrow{-H^+} CH_3{-}\overset{CH_3}{C}{=}CH{-}CH_3 + CH_2{=}\overset{CH_3}{C}{-}CH_2{-}CH_3$$

Rearranged cation

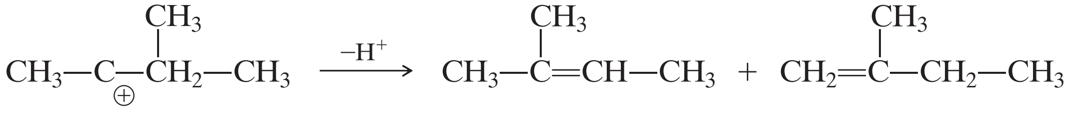
Chief product



$$CH_3{-}\underset{\oplus}{\overset{CH_3}{C}}{-}\underset{CH_3}{CH}{-}CH_3 \xrightarrow{-H^+} CH_3{-}\overset{CH_3}{C}{=}\underset{CH_3}{C}{-}CH_3 + CH_2{=}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}CH_3$$

Rearranged cation

Chief product



$$CH_3{-}\underset{\oplus}{C}{-}\overset{CH_3}{CH_2}{-}CH_3 \xrightarrow{-H^+} CH_3{-}\overset{CH_3}{C}{=}CH{-}CH_3 + CH_2{=}\overset{CH_3}{C}{-}CH_2{-}CH_3$$

Rearranged cation

Chief product

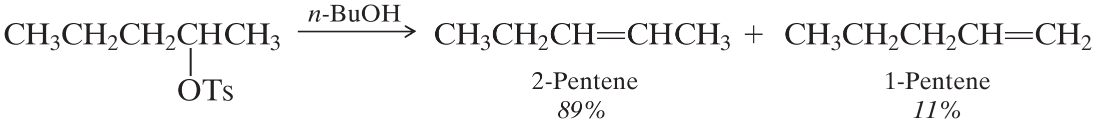
We can begin to see the pattern of rearrangements that runs through reactions of many different types, the pattern first glimpsed by Meerwein in 1922, and which led him to conceive of the carbocation as a reactive intermediate.

Problem 6A.11 When heated with catalytic amounts of strong acids like H_2SO_4 or $HClO_4$, alcohols are converted into alkenes. The order of reactivity of alcohols is *tert*-butyl > isopropyl > ethyl. The alcohol 3,3-dimethyl-2-butanol gives 2,3-dimethyl-2-butene together with a smaller amount of 2,3-dimethyl-l-butene.

Assuming that these observations represent typical behavior (they *do*), write all steps in a possible mechanism for *dehydration of alcohols*.

6A.23 The E1 reaction: orientation

Elimination by E1 shows strong Saytzeff orientation. That is to say, when more than one alkene can be formed, the more highly branched—the *more stable*—alkene is the preferred product. Thus a disubstituted alkene is preferred over a monosubstituted,



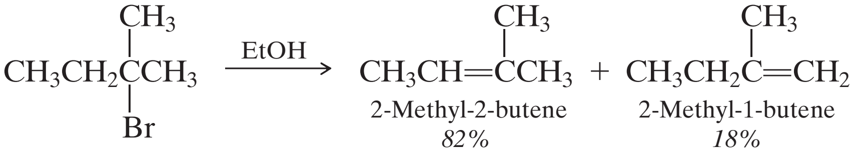
$$CH_3CH_2CH_2\underset{OTs}{CH}CH_3 \xrightarrow{n\text{-BuOH}} CH_3CH_2CH{=}CHCH_3 + CH_3CH_2CH_2CH{=}CH_2$$

2-Pentene *89%*

1-Pentene *11%*

2-Pentyl tosylate

and a trisubstituted over a disubstituted.



$$CH_3CH_2\underset{Br}{\overset{CH_3}{C}}CH_3 \xrightarrow{EtOH} CH_3CH{=}\overset{CH_3}{C}CH_3 + CH_3CH_2\overset{CH_3}{C}{=}CH_2$$

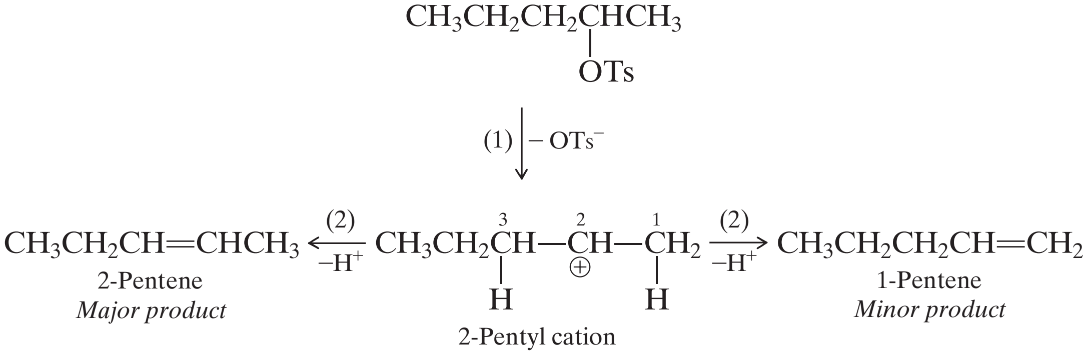
2-Methyl-2-butene *82%*

2-Methyl-1-butene *18%*

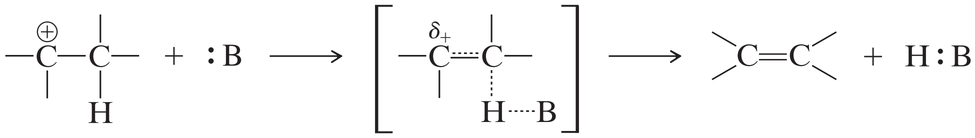
tert-Pentyl bromide

How do we account for this kind of orientation? In other reactions that we have taken up so far, orientation and reactivity have gone hand-in-hand. Both are determined by relative rates of reaction, and *in the same step*: abstraction of a hydrogen by a chlorine atom, say, or the formation of a double bond by concerted loss of a proton and the leaving group.

But here, in E1, we find a difference. Orientation and reactivity are still determined by relative rates of reaction—but of *different steps*. How fast the substrate reacts is determined by the rate of step (1). But which alkene is produced is clearly determined by which β-proton is lost faster from the carbocation in step (2). The 2-pentyl cation, for example, can lose either a proton from C–3 to form 2-pentene or a proton from C–1 to form 1-pentene. There is a competition, and more 2-pentene is obtained because 2-pentene is formed faster.



Let us examine the transition state, then, for this product-determining step. The carbon-hydrogen bond is partly broken, and the double bond is partly formed.



Transition state:
partly formed double bond

The transition state has acquired *alkene character*. As in E2, factors that stabilize the alkene also stabilize the incipient alkene in the transition state. E_{act} is lowered, and the alkene is formed faster.

When rearrangement occurs in E1, we still predict orientation by Saytzeff's rule. But now we must consider the loss of β-protons from the rearranged cations as well as from the cations initially formed.

Problem 6A.12 When 2-methyl-3-pentyl tosylate was heated in *n*-butyl alcohol with no added base, the following alkenes were obtained in the proportions indicated: 2-methyl-2-pentene (80%), 4-methyl-2-pentene (11%), 2-methyl-1-pentene (9%). How do you account for (a) the formation of each of these products, (b) their relative proportions, and (c) the fact that the 4-methyl-2-pentene was entirely the *trans* isomer?

6A.24 Stereochemistry of elimination from alicyclic compounds

So far, we have been concerned with the stereoisomerism of these cyclic compounds, and the relative stabilities of various isomers and conformations. Now let us apply what we have learned, and see how the cyclic nature of these molecules can sometimes determine *the way they react.* That is to say, let us see how the factors we have discussed can affect the relative stabilities of transition states.

As our example, let us return to the stereochemistry of E2 elimination. This reaction, we saw, is stereoselective, and typically involves *anti*-elimination: in the transition state the hydrogen and the leaving group are located in the *anti* relationship, as contrasted to the *gauche* or *eclipsed* (Fig. 6A.7).

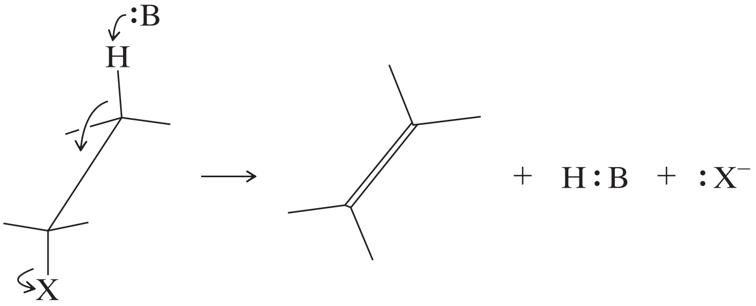


Figure 6A.7 The E2 reaction of alkyl halides: *anti*-elimination. Hydrogen and the leaving group —X, are as far apart as possible, in the *anti* relationship.

Just how strong the preference for *anti*-elimination from halides can be is best shown by study of cyclic compounds. In cyclohexane rings, 1,2-substituents can take up the *anti* conformation only by occupying axial positions; this, in turn, is possible only if they are *trans* to each other (see Fig. 6A.8).

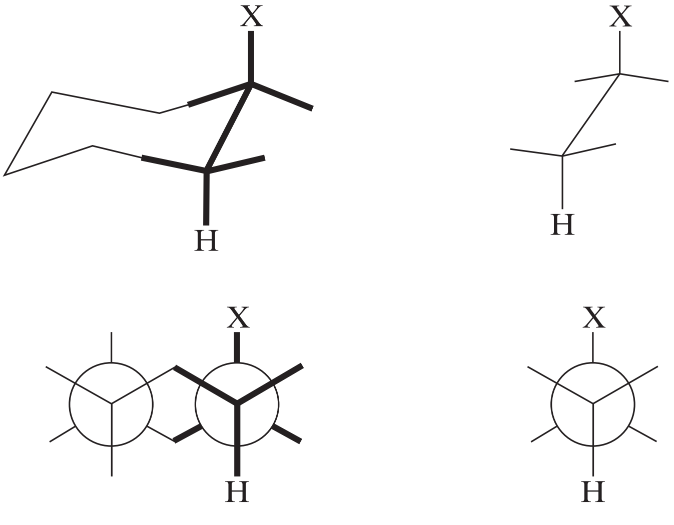
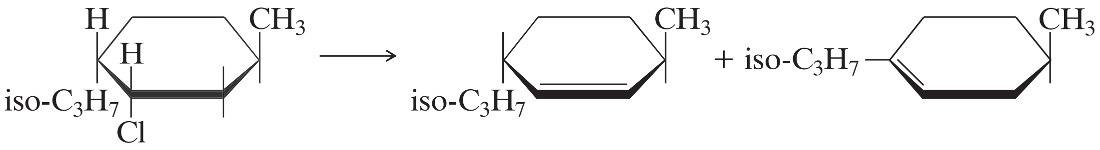
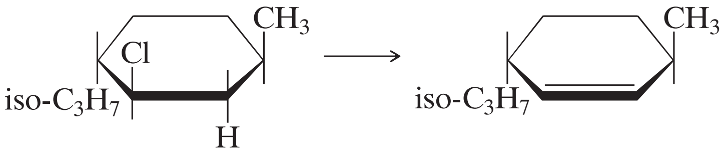


Figure 6A.8 Only *trans*-1,2-substituents can assume the *anti* relationship.

To take a specific example: E2 elimination converts *neomenthyl chloride* into a mixture of 75% 3-menthene and 25% 2-menthene. This is about what we might expect, the more stable—because more highly substituted—3-menthene being the preferred product. But, in marked contrast, E2 elimination converts the diastereomeric *menthyl chloride* exclusively into the less stable 2-menthene.



Neomenthyl chloride 2-Menthene *25%* 3-Menthene *75%*



Menthyl chloride 2-Menthene *Only product*

How are we to account for these differences in behavior? In neomenthyl chloride there is a hydrogen on either side of the chlorine which is *trans* to the chlorine, and which can take up a conformation *anti* to it. Either hydrogen *can* be eliminated, and the ratio of products is determined in the usual way, by the relative stabilities of the alkenes being formed. In menthyl chloride, on the other hand, only one hydrogen is *trans* to the chlorine, and it is the only one that is eliminated, despite the fact that this yields the less stable alkene.

It is clear that E2 reactions can also proceed by *syn*-elimination: in the transition state the hydrogen and leaving group are in the *eclipsed* (or *gauche*) relationship. Although uncommon for alkyl halides, *syn*-elimination is often observed for quaternary ammonium salts and sometimes for alkyl sulfonates. On electronic grounds, the most stable transition states seem to be those in which the hydrogen and leaving group are *periplanar* (in the same plane) to permit overlap of incipient *p* orbitals in the partially formed double bond. Of the two periplanar eliminations, the *anti* is probably easier than the *syn*—other things being equal. But various factors may throw the stereochemistry one way or the other. Conformational effects enter in, and the degree of carbanion character; the stereochemistry is affected by the strength of the base and by its bulk and the bulk of the leaving group. Ring systems present special situations: it is difficult for *cis*-1,2-substituents to become *syn* periplanar in cyclohexanes, but easy in cyclopentanes.

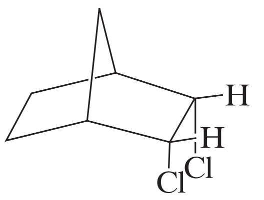
Problem 6A.13 Of the various isomeric 1,2,3,4,5,6-hexachlorocyclohexanes, one isomer undergoes dehydrohalogenation by base much more slowly than the others. Which isomer is probably the unreactive one, and why is it unreactive?

Problem 6A.14 The behavior of menthyl chloride described above is that observed in reaction with sodium ethoxide in ethanol. By contrast, when menthyl chloride is heated in ethanol in the absence of added base, it yields both 3-menthene (68%) and 2-menthene (32%). How do you account for this difference in behavior?

Problem 6A.15 Using models, suggest explanations for the following.

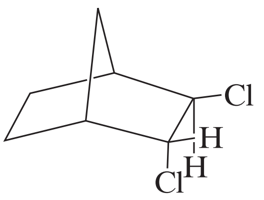
(a) Attached to a doubly bonded carbon, phenyl greatly stabilizes an alkene, and hence exerts a powerful effect on the orientation of elimination. On E2 elimination with *t*-BuOK/*t*-BuOH, both *cis*- and *trans*-2-phenylcyclopentyl tosylates give 1-phenylcyclopentene as the only alkene; the *cis* isomer reacts nine times as fast as the *trans*.

(b) On E2 elimination with *n*-$C_5H_{11}ONa$/*n*-$C_5H_{11}OH$ to give 2-chloronorbornene, II reacts about 100 times as fast as its diastereomer, I.



I

endo-*cis*-2,3-Dichloronorbornane



II

trans-2,3-Dichloronorbornane

6A.25 Elimination: E2 *vs.* E1

How can we tell which mechanism, E2 or E1, is likely to operate under a particular set of conditions?

First, let us look at the effect of the nature of the alkyl group of the substrate. As one proceeds along the sequence 1°, 2°, 3°, reactivity by both mechanisms increases, although for different reasons. Reactivity by E2 increases chiefly because of the greater stability of the more highly branched alkenes being formed. Reactivity by E1 increases because of the greater stability of the carbocations being formed in the rate-determining step. Thus, except that it is very difficult for primary substrates even to form carbocations, we can expect no abrupt shift in mechanism due simply to changes in the alkyl group.

But if we turn to the role played by the other reagent, the base, we find a striking difference between the two mechanisms: in E2, base takes part in the rate-determining step; in E1, it does not. (We have already encountered an analogous competition between a bimolecular (S_N2) and a unimolecular (S_N1) mechanism, and what follows will come as no surprise to us.)

The rate of E2 depends upon the *concentration* of the base; the rate of E1 does not. The rate of E2 depends upon the *nature* of the base; a stronger base pulls a proton away from the substrate faster. The rate of E1 is independent of the nature of the base; stronger or weaker, the base waits until the carbocation is formed.

For a given substrate, then, the more concentrated the base, or the stronger the base, the more E2 is favored over E1. Under the conditions typically used to bring about dehydrohalogenation—a concentrated solution of a strong base—the E2 mechanism is the path taken by elimination. In general, the E1 mechanism is encountered only with secondary or tertiary substrates, and in solutions where the base is either in low concentration or weak—typically, where the base is the solvent.

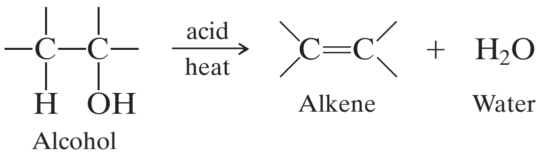
Problem 6A.16 Dehydrohalogenation of isopropyl bromide, which requires several hours of refluxing in alcoholic KOH, is brought about in less than a minute at room temperature by *t*-BuO — K^+ in DMSO. Suggest a possible explanation for this.

6A.26 Dehydration of alcohols

So far, we have been dealing with the kind of 1,2-elimination that is promoted by *base*. Now let us turn to 1,2-elimination that is catalysed by *acid*: the *dehydration of alcohols*. Despite the drastic change in reaction conditions, we shall find, dehydration is fundamentally not very different from the elimination we have already discussed.

An alcohol is converted into an alkene by **dehydration**; *elimination of a molecule of water*.

Dehydration: 1,2-elimination H_2O



Dehydration requires the presence of an acid and the application of heat. It is generally carried out in either of two ways: (a) by heating the alcohol with sulfuric or phosphoric acid; or (b) by passing the alcohol vapor over a catalyst, commonly alumina (Al_2O_3), at high temperatures. (The alumina functions as an acid: either as a Lewis acid or, through —OH groups on its surface, as a Lowry–Brønsted acid.)

The various classes of alcohols differ widely in ease of dehydration, the order of reactivity being

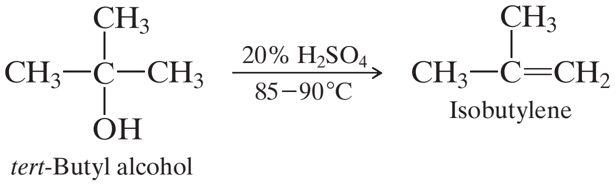
Ease of dehydration of alcohols $3° > 2° > 1°$

The following examples show how these differences in reactivity affect the experimental conditions of the dehydration. (Certain tertiary alcohols are so prone to dehydration that they can be distilled only if precautions are taken to protect the system from the acid fumes present in the ordinary laboratory.)

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[170\ °C]{95\%\ H_2SO_4} \underset{\text{Ethylene}}{CH_2{=}CH_2}$$

$$\underset{n\text{-Butyl alcohol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[140\ °C]{75\%\ H_2SO_4} \underset{\substack{\text{2-Butene}\\ \textit{Chief product}}}{CH_3CH{=}CHCH_3}$$

$$\underset{sec\text{-Butyl alcohol}}{CH_3CH_2CHOHCH_3} \xrightarrow[100\ °C]{60\%\ H_2SO_4} \underset{\substack{\text{2-Butene}\\ \textit{Chief product}}}{CH_3CH{=}CHCH_3}$$



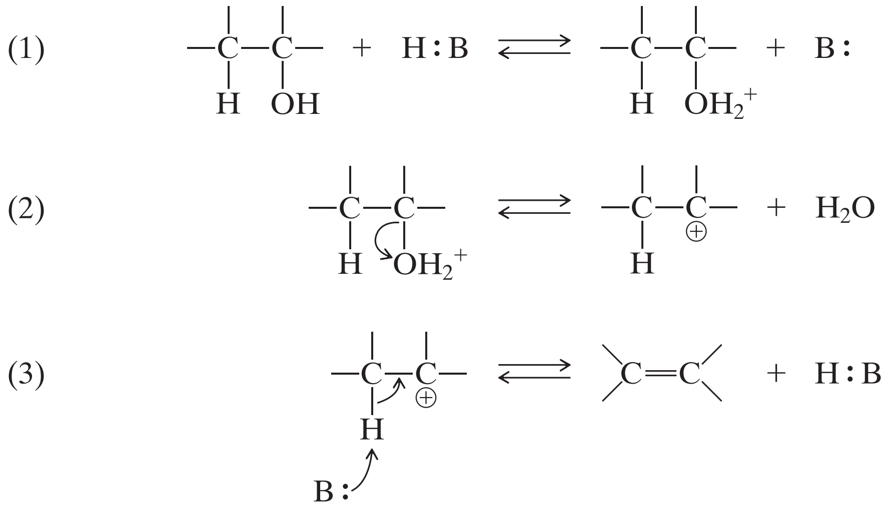
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3 \xrightarrow[85-90°C]{20\%\ H_2SO_4} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$$

tert-Butyl alcohol

Isobutylene

For dehydration of secondary and tertiary alcohols the following mechanism is generally accepted. Step (1) is a fast acid-base reaction between the alcohol and the catalyzing acid which gives the protonated alcohol and the conjugate base of the acid. In step (2) the protonated alcohol undergoes heterolysis to form the carbocation and water. In step (3) the carbocation loses a proton to the base to yield alkene.

Dehydration



In steps (2) and (3) of this mechanism we recognize a kind of E1 elimination with the protonated alcohol as substrate. Step (1) is simply the fast, reversible prelude that produces the actual substrate.

Let us look at the facts about dehydration and see how they are accounted for by this mechanism.

Dehydration is acid-catalysed. Acid is needed to convert the alcohol into the protonated alcohol, which can then undergo heterolysis to lose the weakly basic water molecule. In the absence of acid, heterolysis would require loss of the strongly basic hydroxide ion: a process which, as we have seen, is so difficult that it seldom if ever happens. Acid transforms the very poor leaving group, —OH, into the very good leaving group, $—OH_2^+$.

We spoke of dehydrohalogenation as being base-*promoted*: base is consumed by the reaction, and must be present in molar amounts. We speak of dehydration as being acid-*catalysed*; acid is not consumed and, for the more reactive alcohols, need be present in only trace amounts. This fact is consistent with the mechanism: the acid used in step (1) is regenerated in step (3). Take, for example, dehydration in aqueous sulfuric acid. The acid H : B is the hydronium ion, H_3O^+ ; the conjugate base :B is water. In step (1) H_3O^+ loses a proton to form H_2O; in step (3) H_2O is the base that takes a proton from the carbocation and, in doing this, is reconverted into H_3O^+.

We notice here the fundamental similarity of dehydration to dehydrohalogenation. Once the alcohol has been protonated—and this requires an acidic medium—a base plays its customary essential role in the elimination process by abstracting a proton.

Problem 6A.17 In the dehydration of *tert*-butyl alcohol by the addition of a drop of concentrated sulfuric acid to the dry alcohol, what is the principal base :B of our mechanism? What is the acid H : B? Write equations to show exactly what happens.

Dehydration is reversible. Unlike base-promoted 1,2-elimination, this elimination is reversible. As we shall soon see, acid catalyses the hydration of alkenes to give alcohols. In agreement with this fact, each step of the mechanism is shown as reversible. Under the conditions of dehydration the alkene, being quite volatile, is generally driven from the reaction mixture, and thus equilibrium (3) is shifted to the right. As a consequence the entire reaction sequence is forced toward elimination.

Now, according to the **principle of microscopic reversibility**, a reaction and its reverse follow exactly the same path but in opposite directions. (The lowest pass across a mountain ridge from one side is also the lowest from the other side.) On this basis, dehydration of alcohols must involve exactly the same steps—but in reverse—that are involved in hydration of alkenes. Any evidence, therefore, that is gathered about the mechanism of hydration adds to our understanding of the mechanism of dehydration.

Problem 6A.18 In light of what you have learned so far, write a detailed mechanism for the hydration of alkenes, that is, the acid-catalysed addition of water to alkenes to give alcohols.

The **order of reactivity of alcohols** toward dehydration, we have seen, is

Ease of dehydration of alcohols $3^\circ > 2^\circ > 1^\circ$

There is evidence (some of it from the study of hydration) that the rate of dehydration depends upon both step (2), formation of the carbocation, and step (3), its loss of a proton. Tertiary alcohols undergo dehydration the most rapidly of the alcohols, because they form the most stable carbocations and then, once formed, these cations yield the most stable alkenes.

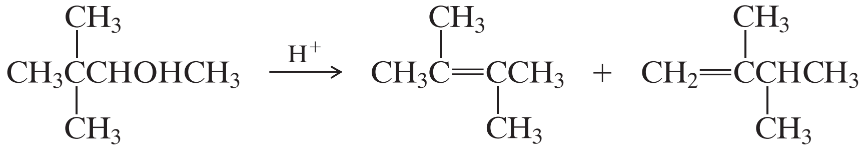
Strictly speaking, then, dehydration is not an E1 reaction of the protonated alcohol. In a true E1 elimination, the rate of reaction depends only upon the heterolysis step, since every carbocation formed goes rapidly on to product; that is, loss of a proton is much faster than regeneration of substrate. Here that is not the case: carbocations are formed reversibly from the protonated alcohol, and every so often one loses a proton to yield alkene.

Problem 6A.19 *tert*-Butyl alcohol was heated with sulfuric acid in water that was enriched with the isotope ^{18}O. At intervals samples were withdrawn and analysed for isobutylene and for labeled alcohol, $t\text{-Bu}^{18}OH$. The kinetics showed that formation of the labeled alcohol (that is, isotopic exchange) was 20 to 30 times as fast as alkene formation. How do you interpret these findings, and what is their significance?

Where the structure of the alkyl group permits, **rearrangement takes place**. This follows the pattern we observed for E1 dehydrohalogenation. For example:

$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2OH \xrightarrow{H^+} CH_3CH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}CH_3 + CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2$$

2-Methyl-1-butanol — 2-Methyl-2-butene *Chief product* — 2-Methyl-1-butene



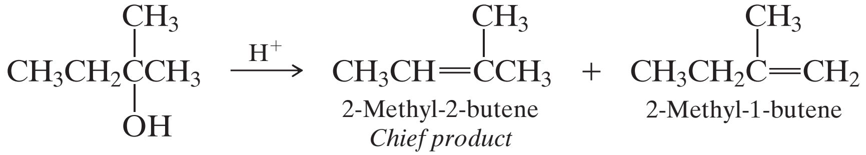
$$CH_3\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CHOHCH_3 \xrightarrow{H^+} CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}{=}\underset{\underset{\displaystyle CH_3}{|}}{C}CH_3 + CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_3$$

3,3-Dimethyl-2-butanol — 2,3-Dimethyl-2-butene *Chief product* — 2,3-Dimethyl-1-butene

In each case we can account for the products on the usual basis: the initially formed carbocation rearranges to a more stable carbocation. The alkenes obtained are those formed by loss of a proton from this rearranged carbocation as well as from the original one.

Problem 6A.20 As was done on previous pages, account in detail for all the alkenes formed in the examples shown above.

Orientation is strongly Saytzeff. Where more than one alkene can be formed, the preferred product is the more stable one. For example:



$$CH_3CH_2\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CH_3 \xrightarrow{H^+} CH_3CH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}CH_3 + CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2$$

tert-Pentyl alcohol — 2-Methyl-2-butene *Chief product* — 2-Methyl-1-butene

(In addition, look again at the examples of rearrangement given above.) This is, of course, exactly what we would expect for loss of a proton from a carbocation.

Another factor comes in here. Since dehydration is reversible, the composition of the product does not necessarily reflect which alkene is formed faster but—depending upon how nearly reaction approaches equilibrium—which alkene is more stable. As we have seen, however, the more stable alkene generally is formed faster. On either basis, orientation is consistent with the mechanism, and the predictions we make about orientation are likely to be good ones.

Secondary and tertiary alcohols, we have said, react by this carbocation mechanism. Primary alcohols pose a special problem. As we have seen, primary carbocations are extremely difficult to form. Yet dehydration of primary alcohols typically gives the rearrangements so characteristic of carbocation reactions. For example:

$$\underset{n\text{-Butyl alcohol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{heat}]{H^+} \underset{\substack{\text{2-Butene} \\ \textit{Chief product}}}{CH_3CH{=}CHCH_3}$$

There are several possible explanations. It may be that, in the concentrated acid used to dehydrate primary alcohols, a primary cation *is* generated—heavily encumbered, but capable of rearrangement. It may be that for these substrates dehydration is an E2 reaction of the protonated alcohol. In that case, the rearranged alkenes result, not from the rearrangement of a primary cation, but from the *reversibility* of dehydration.

In dehydration we see once again the vital role played by protonation of the —OH group: to transform a very poor leaving group into a very good leaving group. In the reaction of alcohols with hydrogen halides, this transformation makes nucleophilic substitution possible; here, it makes elimination possible.

In dehydration the protonated alcohol reacts, in most cases, by the carbocation route, as in E1; alkyl halides, on the other hand, mostly undergo E2. We encountered the same situation in nucleophilic substitution, and the explanation here is essentially the same. To undergo dehydration an alcohol must be protonated, and therefore an acidic medium is required. For E2 elimination we need a fairly strong base to attack the substrate without waiting for it to dissociate into carbocations. But a strong base and an acidic medium are, of course, incompatible: any base much stronger than the alcohol itself would become protonated at the expense of the alcohol. Forced, then, to take place in the absence of strong base, dehydration generally follows the carbocation route. Since alcohols are the usual precursors of alkyl halides and sulfonates, all the eliminations in this chapter are, in a sense, illustrations of the same thing: transformation of —OH into a better leaving group. Conversion into an alkyl halide or sulfonate accomplishes this. So does protonation; it is simpler, but it exacts a price—we are limited in our choice of that key reagent, the base.

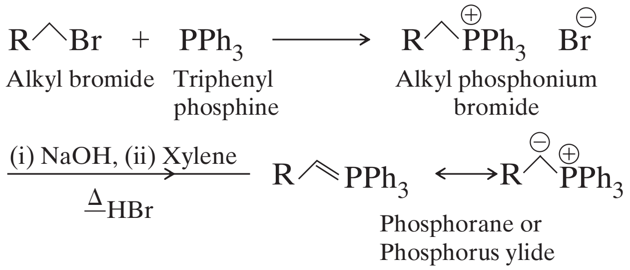
6A.27 Conversion of aldehydes and ketones to alkenes

A direct conversion of C=O group of aldehydes and ketones to C=C can be brought about by Wittig, Peterson or Shapiro reaction. Whereas, Wittig and Peterson reactions are similar as both of them involve ylides and the product contains more carbon atoms than the starting carbonyl compound, Shapiro reaction procedes through a hydrazone derivative and the product alkene contains same number of carbon atoms as the starting carbonyl compound.

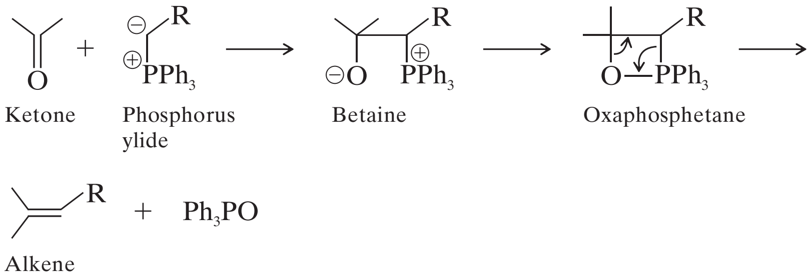
Wittig reaction

Direct conversion of C=O of aldehydes and ketones into C=C using a phosphorane or phosphorus ylide is called Wittig reaction.

The phosphorane or phosphorus ylide is prepared by alkylation of triphenyl phosphine with alkyl halides having atleast one α-H atom. The resulting phosphonium halide on treatment with an alkali in an inert solvent like xylene forms phosphorane or the phosphorus ylide.



The phosphorus ylide reacts with a carbonyl group to form a oxaphosphetane via a betaine. The oxaphosphetane undergoes a cycloelimination reaction to give the desired alkene and Ph_3PO.

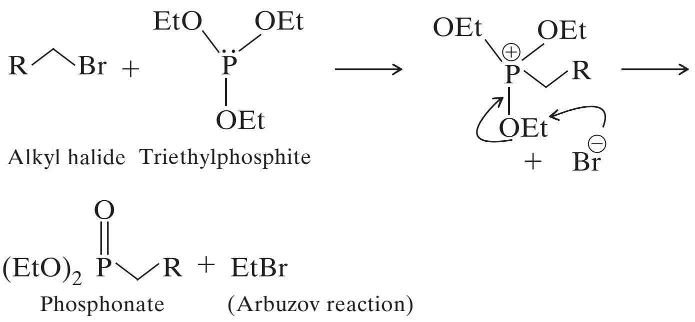


Formation of oxaphosphetane and its decomposition to an alkene takes place under quite mild conditions for which this olefination method tolerates the presence many functional groups like $-NR_2$, -COOR, -OH, acetals etc. The driving force of such facile cycloelimination of oxaphosphetane is the high affinity of phosphorus for oxygen to form Ph_3PO.

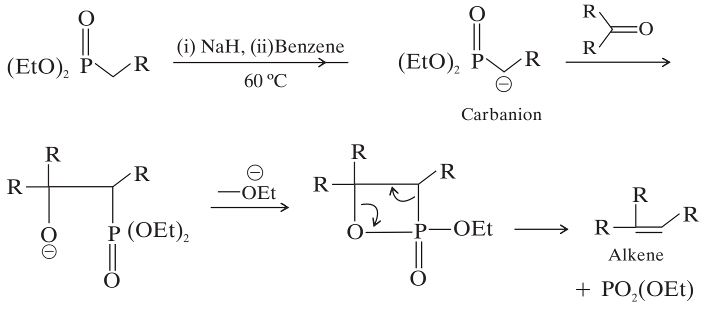
Though the cycloelimination of oxaphosphetane is a highly stereoselective reaction, formation of the betaine is not. So, the reaction on the whole is not highly stereoselective. However, as a general rule, stabilized ylides (where R group is Ar, COR or C=C etc.) react with aldehydes to form mainly the E-isomer of the alkene, while unstabilized ylides form mainly the Z-isomer.

In Wittig reaction one of the difficulties is to purify the product alkene. Removal of Ph_3PO poses a real problem.

This difficulty has been overcome by Horner – Wordsworth - Emmons modification of Wittig reaction. In this modification instead of a phosphorane, a phosphonate is used. Phosphonates are easily prepared from triethyl phosphite and alkyl halides. This reaction is known as Arbuzov reaction.



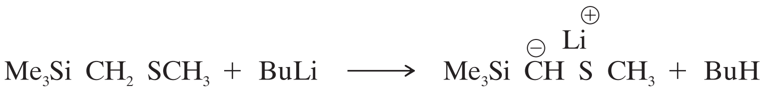
The phosphonate on warming with a strong base like sodiumhydride in an inert solvent like benzene gives a stabilized carbanion. This carbanion reacts with the carbonyl group to form a oxaphosphetane which rapidly decomposes to give the alkene.



(Wittig-Horner reaction)

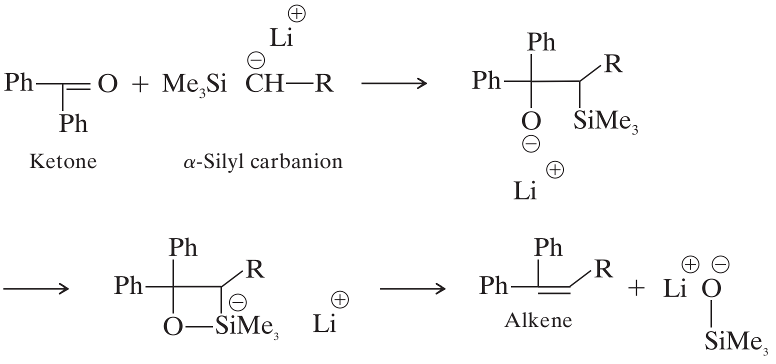
Peterson reaction

α - Silyl carbanions can be prepared readily, since silicon can stabilize α-carbanion by resonance. eg.



$$Me_3Si\ CH_2\ SCH_3 + BuLi \longrightarrow Me_3Si\ \overset{\ominus\ \overset{\oplus}{Li}}{CH}\ S\ CH_3 + BuH$$

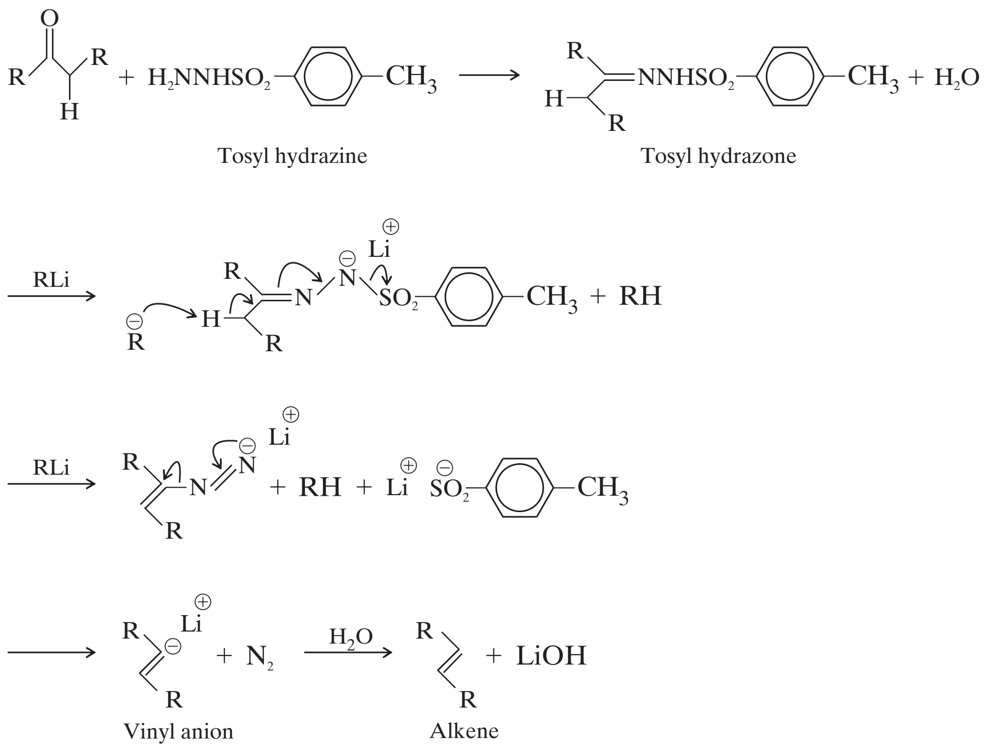
α - Silyl carbanions attack the C=O group of aldehydes and ketones to form β-hydroxy silanes which are unstable and spontaneously eliminate a silyloxy group to form an alkene.



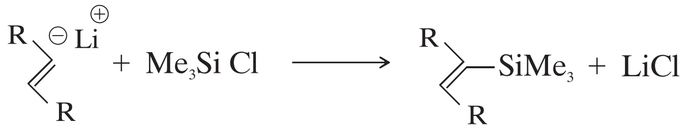
The reaction is comparable to Wittig reaction. However, since α-silylcarbanions are more reactive than phosphorus ylides, Peterson reaction may be applied to olefinate easily enolizable carbonyl compounds. (where Wittig reaction fails).

Shapiro reaction

It is a method of converting a ketone to the corresponding alkene. The ketone must have at least one α-H atom. The reaction is carried out by converting the ketone to its tosylhydrazone followed by treatment of the hydrazone with a strong base. The reaction takes place through a vinyl anion intermediate as follows.



Evolution of N_2 gas during the reaction supports the above proposed mechanism. Formation of vinyl anion can also be confirmed by trapping it as a trimethyl silyl derivative.



6A.28 Reactions of the carbon–carbon double bond of alkenes

The characteristic feature of the alkene structure, we have said, is the carbon–carbon double bond. It is thus the *functional group* of alkenes and, as the functional group, it determines the characteristic reactions that alkenes undergo.

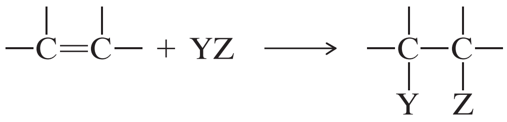
These reactions are of two kinds. (a) First, there are those that take place at the double bond itself and, in doing this, destroy the double bond. These reactions we shall take up in the present chapter. (Addition reactions).

(b) Next, there are the reactions that take place, not at the double bond, but at certain positions having special relationships to the double bond. Outwardly the double bond is not involved; it is found intact in the product. Yet it plays an essential, though hidden, part in the reaction: it determines how fast reaction takes place and by which mechanism—even whether it takes place at all. (Reactions at allylic position).

6A.29 Addition reactions: electrophilic additions

What kind of reactions can we expect of the carbon–carbon double bond? The double bond consists of a strong σ bond and a weak π bond; we might expect, therefore, that reaction would involve breaking of this weaker bond. This expectation is correct; the typical reactions of the double bond are of the sort where the π bond is broken and two strong σ bonds are formed in its place.

Addition



$$-\overset{|}{C}=\overset{|}{C}- + YZ \longrightarrow -\underset{\underset{Y}{|}}{\overset{|}{C}}-\underset{\underset{Z}{|}}{\overset{|}{C}}-$$

A reaction in which two molecules combine to yield a single molecule of product is called an **addition reaction**. The reagent is simply *added to* the substrate, in contrast to a substitution reaction where part of the reagent is *substituted* for a part of the substrate. Addition reactions are necessarily limited to compounds that contain atoms sharing more than one pair of electrons, that is, to compounds that contain multiply bonded atoms. Formally, addition is the opposite of elimination; just as elimination generates a multiple bond, so addition destroys it.

What kind of reagent can we expect to add to the carbon–carbon double bond? In our structure of the bond there is a cloud of π electrons above and below the plane of the atoms (see Fig. 6A.9). These π electrons are less involved than the σ electrons in holding together the carbon nuclei. As a result, they are themselves held less tightly. These loosely held π electrons are particularly available to a reagent that is seeking electrons. It is not surprising, then, that in many of its reactions the carbon–carbon double bond serves as a **source of electrons**: that is, it acts as a **base**. The compounds with which it reacts are those that are deficient in electrons, that is, are *acids*. *These acidic reagents that are seeking a pair of electrons are called* **electrophilic reagents** (Greek: electron-loving). *The typical reaction of an alkene is* **electrophilic addition (AdE)**, or, in other words, addition of acidic reagents.

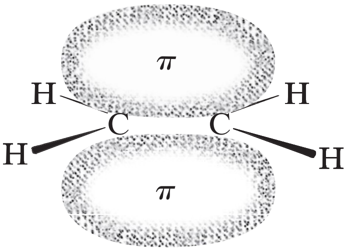


Figure 6A.9 Carbon–carbon double bond: the π bond is a source of electrons.

Reagents of another kind, *free radicals*, seek electrons—or, rather, seek *an* electron. And so we find that alkenes also undergo **free-radical addition**.

Most alkenes contain not only the carbon–carbon double bond but also alkyl groups, which have essentially the alkane structure. Besides the addition reactions characteristic of the carbon–carbon double bond, therefore, alkenes may undergo the free-radical substitution characteristic of alkanes. The most important of these addition and substitution reactions are summarized below, and will be discussed in detail in following sections: in this chapter and later chapters.

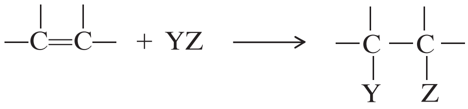
There are reagents that can add either as acids or as free radicals, and with strikingly different results; there are reagents that are capable both of adding to the double bond and of bringing about substitution. We shall see how, by our choice of conditions, we can lead these reagents along the particular reaction path—electrophilic or free radical, addition or substitution—we want them to follow.

The alkyl groups attached to the doubly bonded carbons modify the reactions of the double bond; the double bond modifies the reactions of the alkyl groups. We shall see what these modifications are and, where possible, how they can be accounted for.

We shall take up the stereochemistry of these addition reactions, both for the practical reason of knowing what we are likely to obtain in a synthesis, and for what it can tell us about how these reactions take place.

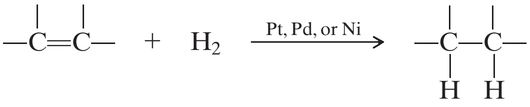
REACTIONS OF ALKENES

Addition Reactions



$$-\overset{|}{C}=\overset{|}{C}- \; + \; YZ \longrightarrow -\underset{\underset{Y}{|}}{\overset{|}{C}}-\underset{\underset{Z}{|}}{\overset{|}{C}}-$$

1. Addition of hydrogen. Catalytic hydrogenation.

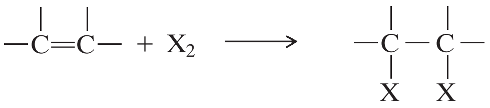


$$-\overset{|}{C}=\overset{|}{C}- \; + \; H_2 \xrightarrow{\text{Pt, Pd, or Ni}} -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}-$$

Example:

$$\underset{\substack{\text{Propene}\\\text{(Propylene)}}}{CH_3CH{=}CH_2} \xrightarrow{H_2,\,Ni} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

2. Addition of halogens.

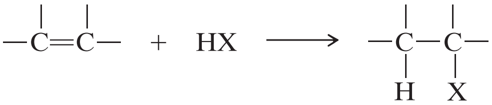


$$-\overset{|}{C}=\overset{|}{C}- \; + \; X_2 \longrightarrow -\underset{\underset{X}{|}}{\overset{|}{C}}-\underset{\underset{X}{|}}{\overset{|}{C}}- \qquad X_2 = Cl_2, Br_2$$

Example:

$$\underset{\substack{\text{Propene}\\\text{(Propylene)}}}{CH_3CH{=}CH_2} \xrightarrow{Br_2 \text{ in } CCl_4} \underset{\substack{\text{1,2-Dibromopropane}\\\text{(Propylene bromide)}}}{CH_3CH_2BrCH_2Br}$$

3. Addition of hydrogen halides.



$$-\overset{|}{C}=\overset{|}{C}- \; + \; HX \longrightarrow -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{X}{|}}{\overset{|}{C}}- \qquad HX = HCl, HBr, HI$$

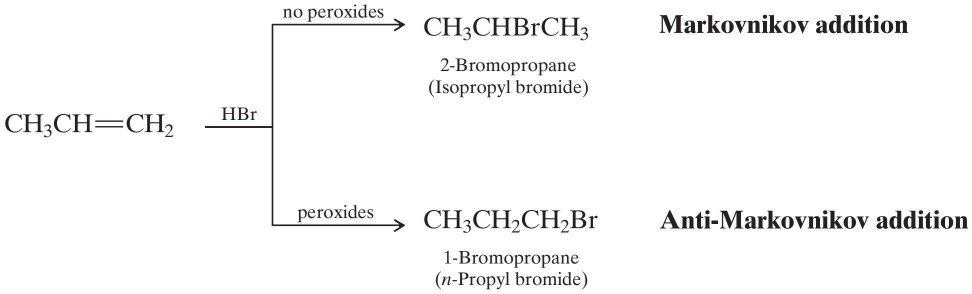
CONTINUED

CONTINUED

Examples:

$$CH_3CH{=}CH_2 \xrightarrow{HI} CH_3CHICH_3$$

Propene — 2-Iodopropane (Isopropyl iodide)



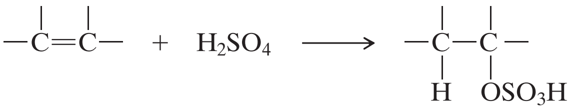
$$CH_3CH{=}CH_2 \xrightarrow{HBr,\ \text{no peroxides}} CH_3CHBrCH_3$$

2-Bromopropane (Isopropyl bromide) **Markovnikov addition**

$$CH_3CH{=}CH_2 \xrightarrow{HBr,\ \text{peroxides}} CH_3CH_2CH_2Br$$

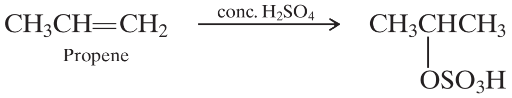
1-Bromopropane (*n*-Propyl bromide) **Anti-Markovnikov addition**

4. Addition of sulfuric acid.



$$-\overset{|}{C}{=}\overset{|}{C}- + H_2SO_4 \longrightarrow -\underset{H}{\overset{|}{C}}-\underset{OSO_3H}{\overset{|}{C}}-$$

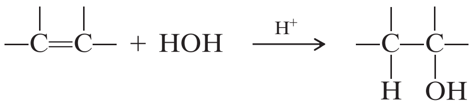
Example:



$$\underset{\text{Propene}}{CH_3CH{=}CH_2} \xrightarrow{\text{conc. } H_2SO_4} CH_3\underset{OSO_3H}{CH}CH_3$$

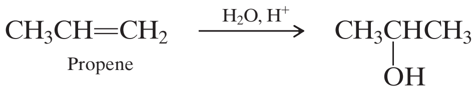
Isopropyl hydrogen sulfate

5. Addition of water. Hydration.



$$-\overset{|}{C}{=}\overset{|}{C}- + HOH \xrightarrow{H^+} -\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-$$

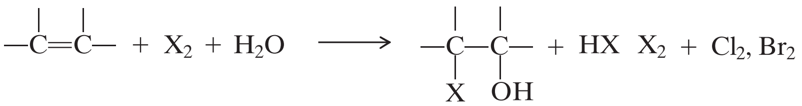
Example:



$$\underset{\text{Propene}}{CH_3CH{=}CH_2} \xrightarrow{H_2O,\ H^+} CH_3\underset{OH}{CH}CH_3$$

Isopropyl alcohol (2-Propanol)

6. Halohydrin formation.



$$-\overset{|}{C}{=}\overset{|}{C}- + X_2 + H_2O \longrightarrow -\underset{X}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- + HX \quad X_2 + Cl_2, Br_2$$

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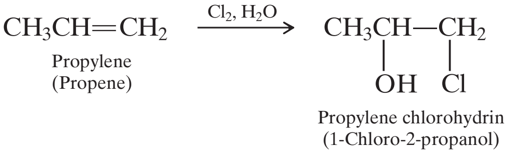
Example:



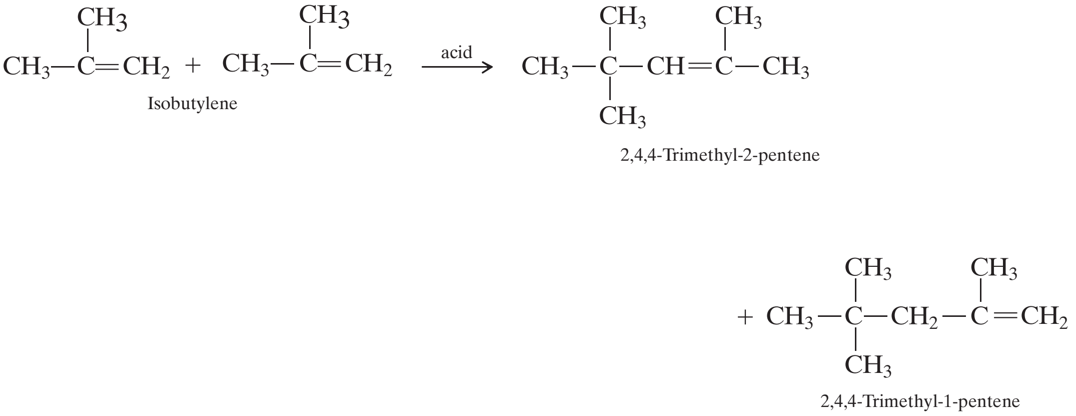
$$CH_3CH{=}CH_2 \xrightarrow{Cl_2,\ H_2O} CH_3\underset{OH}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$$

Propylene (Propene)

Propylene chlorohydrin (1-Chloro-2-propanol)

7. Dimerization.

Example:



$$CH_3-\overset{CH_3}{\overset{|}{C}}{=}CH_2 + CH_3-\overset{CH_3}{\overset{|}{C}}{=}CH_2 \xrightarrow{acid} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH{=}\overset{CH_3}{\overset{|}{C}}-CH_3$$

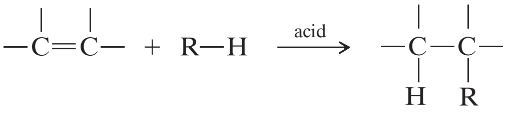
$$+\ CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\overset{|}{C}}{=}CH_2$$

Isobutylene

2,4,4-Trimethyl-2-pentene

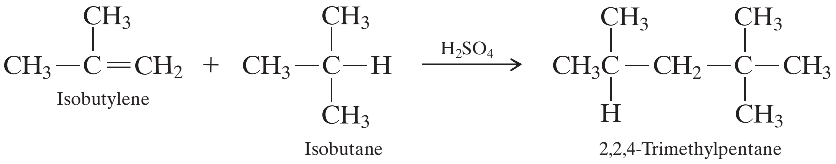
2,4,4-Trimethyl-1-pentene

8. Alkylation.



$$-\overset{|}{C}{=}\overset{|}{C}- + R-H \xrightarrow{acid} -\underset{H}{\overset{|}{C}}-\underset{R}{\overset{|}{C}}-$$

Example:



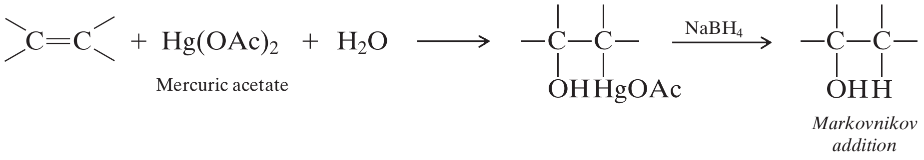
$$CH_3-\overset{CH_3}{\overset{|}{C}}{=}CH_2 + CH_3-\overset{CH_3}{\underset{CH_3}{C}}-H \xrightarrow{H_2SO_4} CH_3\overset{CH_3}{\underset{H}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

Isobutylene

Isobutane

2,2,4-Trimethylpentane

9. Oxymercuration–demercuration.



$$\gt C{=}C\lt\ + Hg(OAc)_2 + H_2O \longrightarrow -\underset{OH}{\overset{|}{C}}-\underset{HgOAc}{\overset{|}{C}}- \xrightarrow{NaBH_4} -\underset{OH}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}-$$

Mercuric acetate

Markovnikov addition

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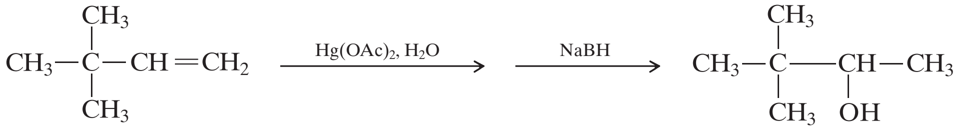
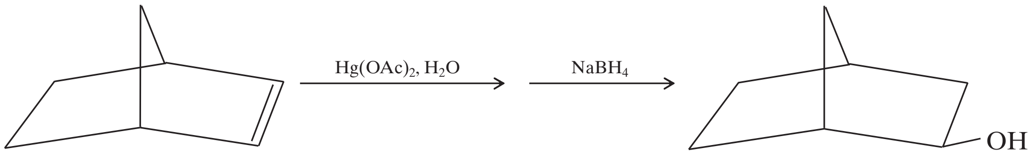
Examples:



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2 \xrightarrow{\text{Hg(OAc)}_2,\ H_2O} \xrightarrow{\text{NaBH}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_3$$

3,3-Dimethyl-1-butene

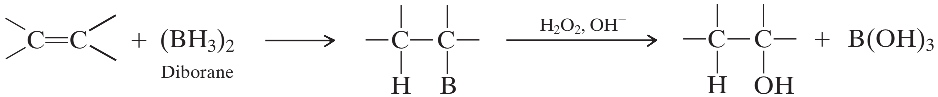
3,3-Dimethyl-2-butanol
No rearrangement



Norbornene

exo-Norborneol

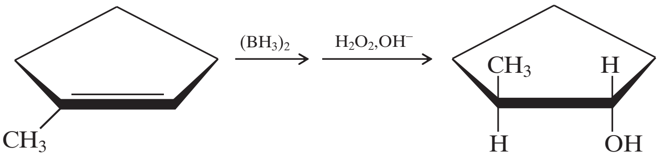
10. Hydroboration–oxidation.



Diborane

Alkylborane

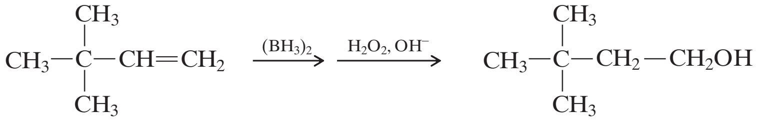
Anti-Markovnikov orientation



syn-Addition

1-Methylcyclopentene

trans-2-Methyl-1-cyclopentanol



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2 \xrightarrow{(BH_3)_2} \xrightarrow{H_2O_2,\ OH^-} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2OH$$

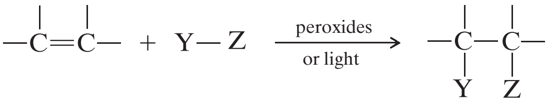
No rearrangement

3,3-Dimethyl-1-butene

3,3-Dimethyl-1-butanol

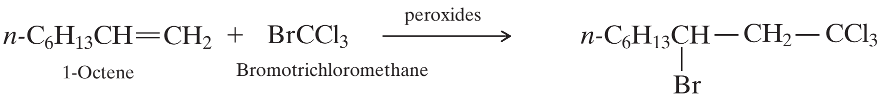
Examples:

11. Addition of free radicals.



$$-\overset{|}{C}=\overset{|}{C}- \ + \ Y-Z \xrightarrow[\text{or light}]{\text{peroxides}} -\underset{Y}{\overset{|}{C}}-\underset{Z}{\overset{|}{C}}-$$

Examples:



$$n\text{-}C_6H_{13}CH=CH_2 + BrCCl_3 \xrightarrow{\text{peroxides}} n\text{-}C_6H_{13}\underset{Br}{CH}-CH_2-CCl_3$$

1-Octene

Bromotrichloromethane

3-Bromo-1,1,1-trichlorononane

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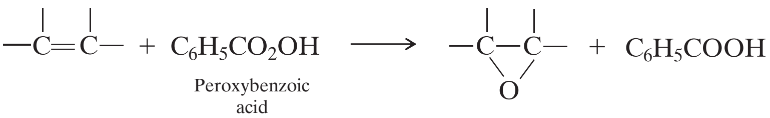
12. Polymerization.

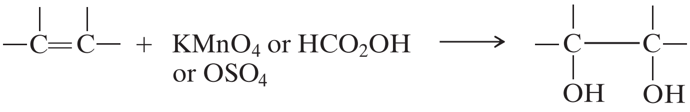
13. Addition of carbenes.

14. Epoxidation.



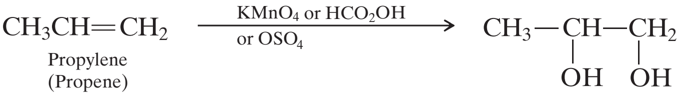
$$-\overset{|}{C}=\overset{|}{C}- \; + \; \underset{\text{Peroxybenzoic acid}}{C_6H_5CO_2OH} \longrightarrow -\overset{|}{C}-\overset{|}{C}- \; + \; C_6H_5COOH$$

15. Hydroxylation. Glycol formation.



$$-\overset{|}{C}=\overset{|}{C}- \; + \; \text{KMnO}_4 \text{ or } HCO_2OH \text{ or } OSO_4 \longrightarrow -\overset{|}{\underset{OH}{C}}-\overset{|}{\underset{OH}{C}}-$$

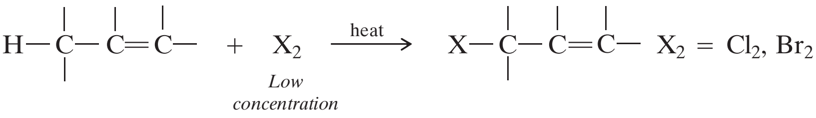
Example:



$$\underset{\text{Propylene (Propene)}}{CH_3CH=CH_2} \xrightarrow[\text{or } OSO_4]{\text{KMnO}_4 \text{ or } HCO_2OH} \underset{\text{1,2-Propanediol}}{CH_3-\underset{OH}{CH}-\underset{OH}{CH_2}}$$

Substitution Reactions

16. Halogenation. Allylic substitution.



$$H-\overset{|}{\underset{|}{C}}-\overset{|}{C}=\overset{|}{C}- \; + \; \underset{\textit{Low concentration}}{X_2} \xrightarrow{\text{heat}} X-\overset{|}{\underset{|}{C}}-\overset{|}{C}=\overset{|}{C}- \quad X_2 = Cl_2, Br_2$$

Examples:

$$\underset{\text{Propylene (Propene)}}{CH_3CH=CH_2} \xrightarrow{Cl_2,\,600\,^\circ C} \underset{\text{Allyl chloride (3-Chloro-1-propene)}}{Cl-CH_2\,CH=CH_2}$$

Cyclohexene 3-Bromocyclohexene

N-Bromosuccinimide

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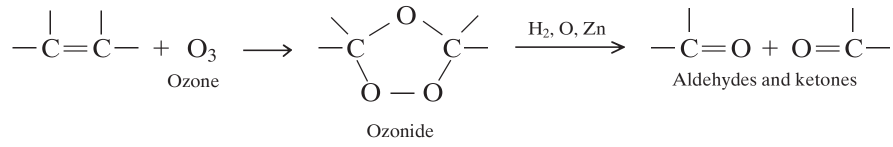
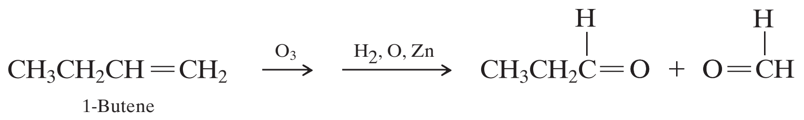
Cleavage Reactions

17. Ozonolysis.



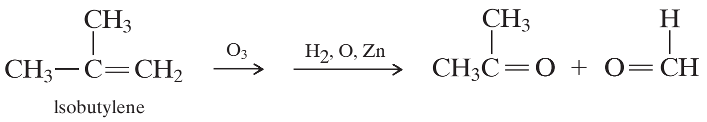
Used to determine structure

Examples:



$$CH_3CH_2CH{=}CH_2 \xrightarrow{O_3} \xrightarrow{H_2,\,O,\,Zn} CH_3CH_2\overset{\overset{H}{|}}{C}{=}O + O{=}\overset{\overset{H}{|}}{C}H$$

1-Butene



$$CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 \xrightarrow{O_3} \xrightarrow{H_2,\,O,\,Zn} CH_3\overset{\overset{CH_3}{|}}{C}{=}O + O{=}\overset{\overset{H}{|}}{C}H$$

Isobutylene

■

6A.30 Hydrogenation. Heat of hydrogenation

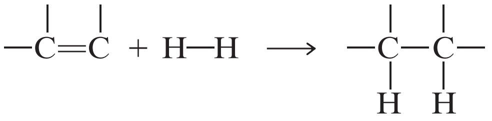
We have already encountered hydrogenation as the most useful method for preparing alkanes. It is not limited to the synthesis of alkanes, but is a general method for the conversion of a carbon–carbon double bond into a carbon–carbon single bond in almost any kind of compound we encounter. Using the same apparatus, the same catalyst, and very nearly the same conditions, we can convert an alkene into an alkane, an unsaturated alcohol into a saturated alcohol, or an unsaturated ester into a saturated ester. By varying the catalyst and conditions, we can *selectively* hydrogenate one multiple bond but not another in the same molecule: a carbon–carbon double bond but not a carbon–oxygen double bond; a triple bond but not a double bond; even one carbon–carbon double bond but not another. We can even, as we shall see, convert an optically inactive unsaturated compound into an optically active product!

Hydrogenation is of two general kinds: (a) *heterogeneous* (two-phase) and (b) *homogeneous* (one-phase). In both cases a catalyst brings about addition of molecular hydrogen, H_2, to the double bond.

Heterogeneous hydrogenation is the classical method, and is still widely used. The catalyst is a finely divided metal, usually platinum, palladium, or nickel. A solution of the alkene is shaken under a slight pressure of hydrogen gas in the presence of a small amount of the catalyst. Reaction takes place rapidly and smoothly and, when it is complete, the solution of the saturated product is simply filtered from the insoluble catalyst.

The much newer **homogeneous hydrogenation** offers a flexibility not possible with the old-style catalysts. Through modifications in the catalysts, hydrogenation can be carried out with unprecedented selectivity. The catalysts are organic complexes of transition metals like rhodium or iridium: *Wilkinson's catalyst*, for example. They are soluble in organic solvents, and hydrogenation thus takes place in a single phase, the solution. An inconvenience of the method has been the difficulty of separating the catalyst from the product once reaction is over. Methods are being worked out, however, to avoid this problem: the catalyst is attached—built-in chemically—to a solid soluble polymer (giant molecule), thus permitting easy filtration at the end of the reaction. Homogeneous hydrogenation thus becomes heterogeneous; but the mode of action seems to remain the same. We shall discuss these catalysts in some detail: their structure, how they work, and in particular how they permit stereochemical control of hydrogenation and many other reactions.

Since the reaction is generally quantitative, and since the volume of hydrogen consumed can be easily measured, hydrogenation is frequently used as an analytical tool; it can, for example, tell us the number of double bonds in a compound.



$$-\overset{|}{C}=\overset{|}{C} + \mathrm{H{-}H} \longrightarrow -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}- \qquad \Delta H = \textbf{heat of hydrogenation}$$

Hydrogenation is exothermic: the two σ bonds (C—H) being formed are, together, stronger than the σ bond (H—H) and π bond being broken. *The quantity of heat evolved when one mole of an unsaturated compound is hydrogenated is called the* **heat of hydrogenation**; it is simply ΔH of the reaction, but the minus sign is not included. The heat of hydrogenation of nearly every alkene is fairly close to a value of 30 kcal for each double bond in the compound. Heats of hydrogenation of a few alkenes are listed in Table 6A.3.

Although hydrogenation is an exothermic reaction, it proceeds at a negligible rate in the absence of a catalyst, even at elevated temperatures. The uncatalysed reaction must have, therefore, a very large energy of activation. The function of the catalyst is to lower the energy of activation (E_{act}) so that the reaction can proceed rapidly at room temperature. The catalyst does not, of course, affect the net energy change of the overall reaction; it simply lowers the energy hill between the reactants and products (see Fig. 6A.10).

A catalyst lowers E_{act}, by permitting reaction to take place in a different way, that is, by a different mechanism. In this case, the reactants are adsorbed on the enormous surface of a finely divided solid metal, or bonded temporarily to a soluble metal ion. Reaction under these conditions is very different from the reaction that would have to take place otherwise. It is believed, for example, that the surface of a solid catalyst breaks the π bond of the alkene prior to reaction with hydrogen. In homogeneous hydrogenation, the complex metal ion breaks the hydrogen–hydrogen bond and transfers the hydrogens, one at a time, to the double bond.

Lowering the energy hill, as we can see, decreases the energy of activation of the reverse reaction as well, and thus increases the rate of *de*hydrogenation. We might expect, therefore, that the solid catalysts platinum, palladium, and nickel, under the proper conditions, should serve as dehydrogenation catalysts; this is indeed the case. We are familiar with the fact that, although a catalyst speeds up a reaction, it does not shift the position of equilibrium; this is, of course, because it speeds up *both* the forward and reverse reactions.

Table 6A.3 Heats of Hydrogenation of Alkenes

Alkene	Heat of hydrogenation, kcal/mol
Ethylene	32.8
Propylene	30.1
1-Butene	30.3
1-Pentene	30.1
1-Heptene	30.1
3-Methyl-1-butene	30.3
3,3-Dimethyl-1-butene	30.3
4,4-Dimethyl-1-pentene	29.5
cis-2-Butene	28.6
trans-2-Butene	27.6
Isobutylene	28.4
cis-2-Pentene	28.6
trans-2-Pentene	27.6
2-Methyl-1-butene	28.5
2,3-Dimethyl-1-butene	28.0
2-Methyl-2-butene	26.9
2,3-Dimethyl-2-butene	26.6

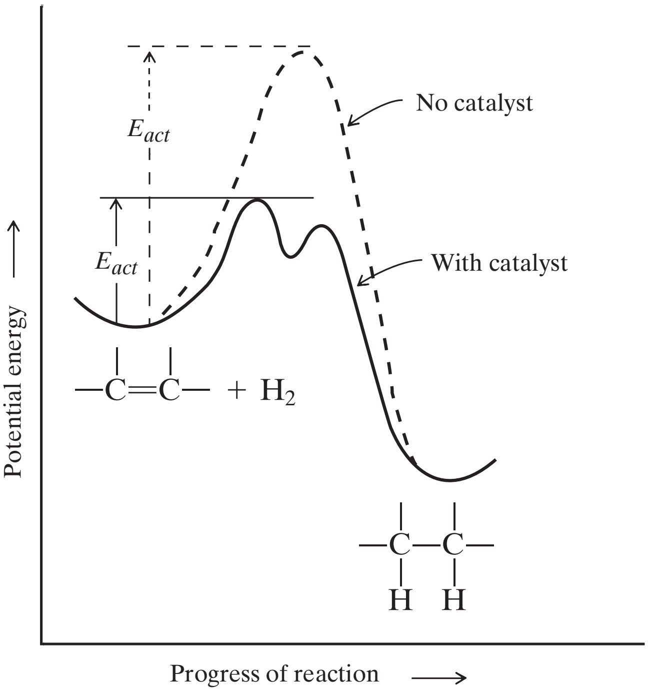
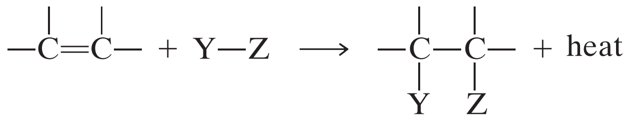


Figure 6A.10 Potential energy changes during progress of reaction: effect of the catalyst.

Like hydrogenation, the addition of other reagents to the double bond is generally exothermic. The energy consumed by the breaking of the Y—Z and π bonds is almost always less than that liberated by formation of the C—Y and C—Z bonds.



$$-\overset{|}{C}=\overset{|}{C}- + Y{-}Z \longrightarrow -\underset{Y}{\overset{|}{\underset{|}{C}}}-\underset{Z}{\overset{|}{\underset{|}{C}}}- + \text{heat}$$

6A.31 Heat of hydrogenation and stability of alkenes

Heats of hydrogenation can often give us valuable information about the relative stabilities of unsaturated compounds. For example, of the isomeric 2-butenes, the *cis* isomer has a heat of hydrogenation of 28.6 kcal, the *trans* isomer one of 27.6 kcal. Both reactions consume one mole of hydrogen and yield the same product, *n*-butane. Therefore, if the *trans* isomer *evolves* 1 kcal less energy than the *cis* isomer, it can only mean that it *contains* 1 kcal less energy; in other words, the *trans* isomer is *more stable* by 1 kcal than the *cis* isomer (see Fig. 6A.11). In a similar way, *trans*-2-pentene (heat of hydrogenation = 27.6 kcal) must be more stable by 1.0 kcal than *cis*-2-pentene (heat of hydrogenation = 28.6 kcal).

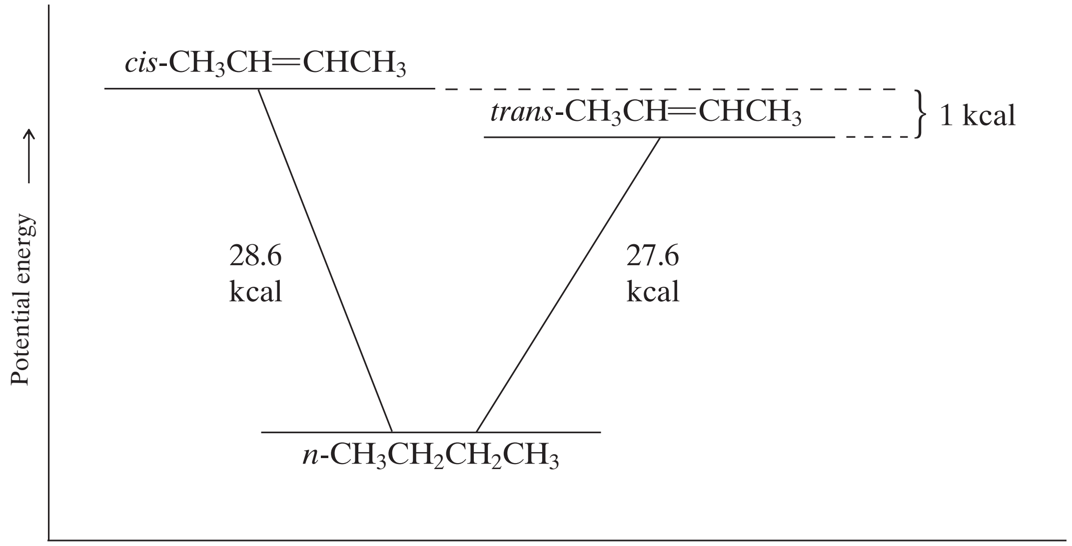


Figure 6A.11 Heats of hydrogenation and stability: *cis*- and *trans*-2-butene.

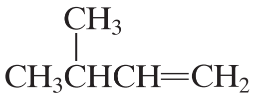
Of simple dialkylethylenes, it is usually the *trans* isomer that is the more stable. The two larger substituents are located farther apart than in the *cis* isomer; there is less crowding, and less van der Waals strain.

Heats of hydrogenation show that the stability of an alkene also depends upon the position of the double bond. The following examples are typical:

$CH_3CH_2CH{=}CH_2$	$CH_3CH{=}CHCH_3$
30.3 kcal	*cis* 28.6; *trans* 27.6

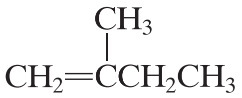
$CH_3CH_2CH_2CH{=}CH_2$ 30.1 kcal

$CH_3CH_2CH{=}CHCH_3$ *cis* 28.6; *trans* 27.6



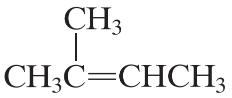
$$CH_3\overset{\overset{\large CH_3}{|}}{C}HCH{=}CH_2$$

30.3 kcal



$$CH_2{=}\overset{\overset{\large CH_3}{|}}{C}CH_2CH_3$$

28.5



$$CH_3\overset{\overset{\large CH_3}{|}}{C}{=}CHCH_3$$

26.9

Each set of isomeric alkenes yields the same alkane. The differences in heat of hydrogenation must therefore be due to differences in stability. In each case, **the greater the number of alkyl groups attached to the doubly bonded carbon atoms, the more stable the alkene**.

Stability of alkenes

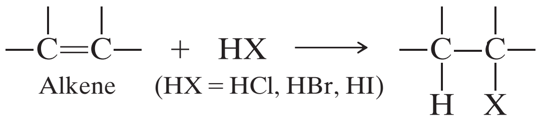
$$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2,$$
$$RCH{=}CHR > RCH{=}CH_2 > CH_2{=}CH_2$$

We have already seen the important role that stability of alkenes plays in orientation and reactivity in elimination reactions.

Problem 6A.21 (a) Write a balanced equation for combustion of 1-butene. (b) How does this equation compare with the corresponding one for *cis*-2-butene? For *trans*-2-butene? (c) The following heats of combustion have been measured for these three butenes: 648.1, 647.1, 649.8 kcal. Which heat of combustion do you think applies to each butene? (d) Assign the following heats of combustion to 1-pentene, and *cis*- and *trans*-2-pentene: 804.3, 806.9, 805.3 kcal.

6A.32 Addition of hydrogen halides. Markovnikov's rule. Regioselective reactions

An alkene is converted by hydrogen chloride, hydrogen bromide, or hydrogen iodide into the corresponding alkyl halide.



$$-\overset{|}{C}{=}\overset{|}{C}- \; + \; HX \longrightarrow -\underset{\underset{\large H}{|}}{\overset{|}{C}}-\underset{\underset{\large X}{|}}{\overset{|}{C}}-$$

Alkene (HX = HCl, HBr, HI) Alkyl halide

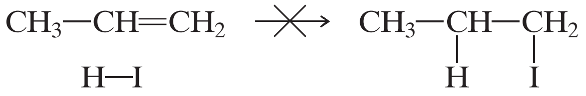
The reaction is frequently carried out by passing the dry gaseous hydrogen halide directly into the alkene. sometimes the moderately polar solvent, acetic acid, which will dissolve both the polar hydrogen halide and the non-polar alkene, is used. The familiar aqueous solutions of the hydrogen halides are not generally used; in part, this is to avoid the addition of water to the alkene.

Problem 6A.22 (a) What is the acid in an aqueous solution of HBr? In dry HBr? (b) Which is the stronger acid? (c) Which can better transfer a hydrogen ion to an alkene?

In this way, ethylene is converted into ethyl halide, the hydrogen becoming attached to one doubly bonded carbon and the halogen to the other.

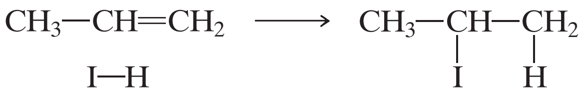
$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + HI \longrightarrow \underset{\text{Ethyl iodide}}{CH_3CH_2I}$$

Propylene could yield either of two products, the *n*-propyl halide or the isopropyl halide, depending upon the orientation of addition, that is, depending upon which carbon atoms the hydrogen and halogen become attached to. Actually, only the isopropyl halide is formed.



$$\underset{H-I}{CH_3-CH{=}CH_2} \;\not\longrightarrow\; CH_3-\underset{H}{\underset{|}{CH}}-\underset{I}{\underset{|}{CH_2}}$$

n-Propyl iodide

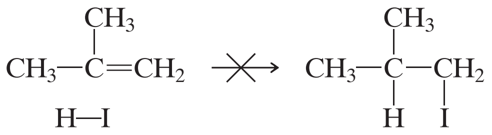


$$\underset{I-H}{CH_3-CH{=}CH_2} \longrightarrow CH_3-\underset{I}{\underset{|}{CH}}-\underset{H}{\underset{|}{CH_2}}$$

Actual product

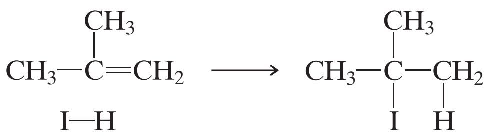
Isopropyl iodide

In the same way, isobutylene could yield either of two products, isobutyl halide or *tert*-butyl halide; here the orientation of addition is such that only the *tert*-butyl halide is formed.



$$\underset{H-I}{CH_3-\overset{CH_3}{\overset{|}{C}}{=}CH_2} \;\not\longrightarrow\; CH_3-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{I}{\underset{|}{CH_2}}$$

Isobutyl iodide



$$\underset{I-H}{CH_3-\overset{CH_3}{\overset{|}{C}}{=}CH_2} \longrightarrow CH_3-\underset{I}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{H}{\underset{|}{CH_2}}$$

Actual product

tert-Butyl iodide

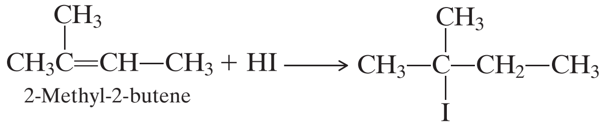
Thus, in the addition of a reagent YZ to an alkene, orientation depends upon which doubly bonded carbon accepts Y and which accepts Z.

On examination of a large number of such additions, the Russian chemist Vladimir Markovnikov observed that, where two isomeric products are possible, one of them usually predominates. He pointed out in 1869 that the orientation of addition follows a pattern which we can summarize as: *in the addition of an acid to the carbon–carbon double bond of an alkene, the hydrogen of the acid attaches itself to the carbon that already holds the greater number of hydrogens.* This statement is generally known as **Markovnikov's rule**. Thus: "Unto everyone that hath shall be given", or "Them as has, gits".

Thus, in the addition to propylene we see that the hydrogen goes to the carbon bearing two hydrogen atoms rather than to the carbon bearing one. In the addition to isobutylene, the hydrogen goes to the carbon bearing two hydrogens rather than to the carbon bearing none.

Using Markovnikov's rule, we can correctly predict the principal product of many reactions. For example:

$$\underset{\text{1-Butene}}{CH_3CH_2CH{=}CH_2} + HI \longrightarrow \underset{\substack{\textit{sec}\text{-Butyl iodide} \\ \text{(2-Iodobutane)}}}{CH_3CH_2CHICH_3}$$



$$\underset{\text{2-Methyl-2-butene}}{CH_3\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_3} + HI \longrightarrow CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{I}{|}}{C}}{-}CH_2{-}CH_3$$

tert-Pentyl iodide
(2-Iodo-2-methylbutane)

$$\underset{\text{2-Butene}}{CH_3CH{=}CHCH_3} + HI \longrightarrow \underset{\substack{\textit{sec}\text{-Butyl iodide} \\ \text{(2-Iodobutane)}}}{CH_3CHICH_2CH_3}$$

$$\underset{\substack{\text{Vinyl chloride} \\ \text{(Chloroethene)}}}{CH_2{=}CHCl} + Hl \longrightarrow \underset{\text{1-Chloro-1-iodoethane}}{CH_3CHICl}$$

$$\underset{\text{2-Pentene}}{CH_3CH_2CH{=}CHCH_3} + HI \longrightarrow \underset{\text{3-Iodopentane}}{CH_3CH_2CHICH_2CH_3} + \underset{\text{2-Iodopentane}}{CH_3CH_2CH_2CHICH_3}$$

In 2-pentene each of the doubly bonded carbons holds one hydrogen, so that according to the rule we should expect neither product to predominate. Here again the prediction is essentially correct, roughly equal quantities of the two isomers actually being obtained.

The examples have involved the addition of hydrogen iodide; exactly similar results are obtained in the addition of hydrogen chloride and, except for special conditions indicated in the following section, of hydrogen bromide.

Reactions that, from the standpoint of orientation, give exclusively or nearly exclusively one of several possible isomeric products are called **regioselective**. (From the Latin *regio*, direction, and pronounced "reejio".)

Problem 6A.23 Saytzeff actually stated his rule for orientation of elimination in terms, not of alkyl groups on the alkene being formed, but, like Markovnikov, of numbers of hydrogens on carbon atoms of the substrate. Suggest a wording for this original Saytzeff rule.

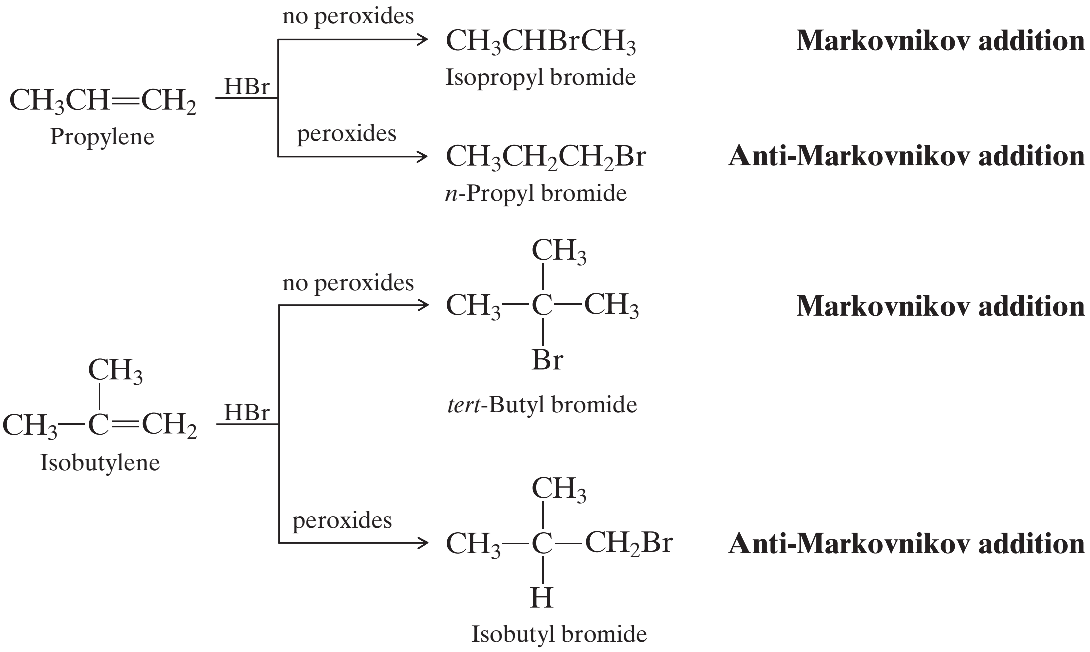
6A.33 Addition of hydrogen bromide. Peroxide effect

Addition of hydrogen chloride and hydrogen iodide to alkenes follows Markovnikov's rule. Until 1933 the situation with respect to hydrogen bromide was exceedingly confused. It had been reported by some workers that addition of hydrogen bromide to a particular alkene yields a product in agreement with Markovnikov's rule; by others, a product in contradiction to Markovnikov's rule; and by still others, a mixture of both products. It had been variously reported that the product obtained depended upon the presence or absence of water, or of light, or of certain metallic halides; it had been reported that the product obtained depended upon the solvent used, or upon the nature of the surface of the reaction vessel.

In 1933, M. S. Kharasch and F. R. Mayo brought order to this chemical chaos by discovering that the orientation of addition of hydrogen bromide to the carbon–carbon double bond is determined solely by the presence or absence of **peroxides**.

Organic peroxides are compounds containing the —O—O— linkage. They are encountered, generally in only very small amounts, as impurities in many organic compounds, where they have been slowly formed by the action of oxygen. Certain peroxides are deliberately synthesized, and used as reagents: *tert*-butyl peroxide or benzoyl peroxide $(C_6H_5COO)_2$ for example.

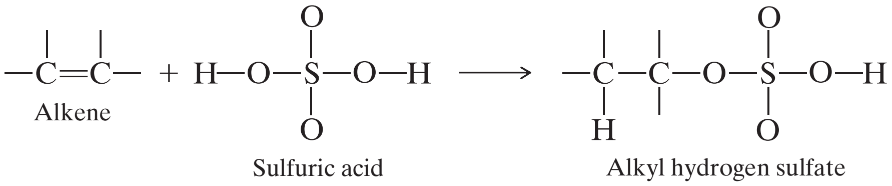
Kharasch and Mayo found that if one carefully excludes peroxides from the reaction system, or if one adds certain **inhibitors**—*hydroquinone*, for example, or *diphenylamine*—the addition of HBr to alkenes follows Markovnikov's rule. On the other hand, if one does not exclude peroxides, or if one deliberately puts peroxides into the reaction system, HBr adds to alkenes in exactly the reverse direction.



This reversal of the orientation of addition caused by the presence of peroxides is known as the **peroxide effect**. Of the reactions we are studying, *only* the addition of hydrogen bromide shows the peroxide effect. The presence or absence of peroxides has no effect on the orientation of addition of hydrogen chloride, hydrogen iodide, sulfuric acid, water, etc. As we shall see, both Markovnikov's rule and the peroxide effect can readily be accounted for in ways that are quite consistent with the chemistry we have learned so far.

6A.34 Addition of sulfuric acid

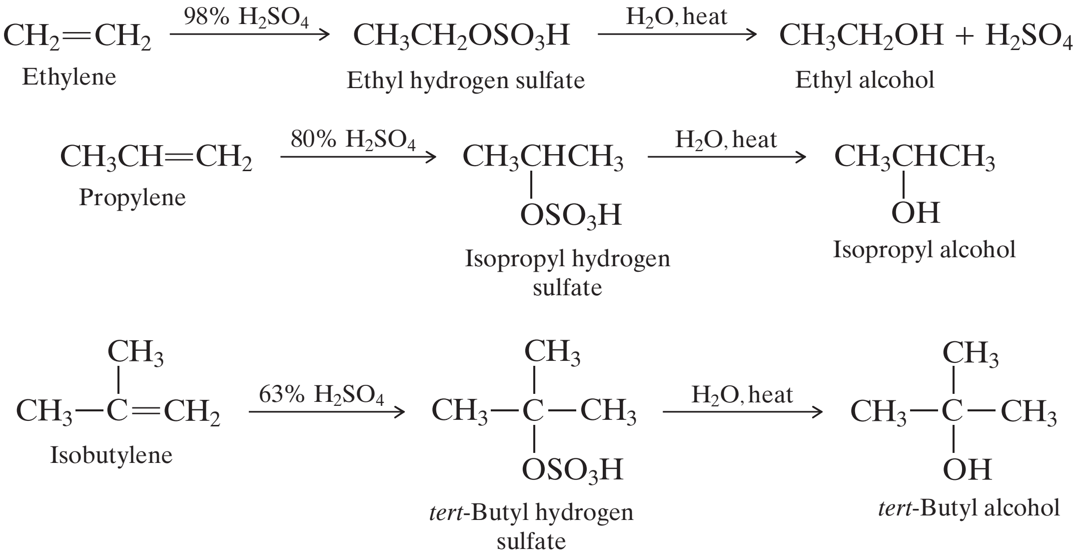
Alkenes react with cold concentrated sulfuric acid to form compounds of the general formula $ROSO_3H$, known as **alkyl hydrogen sulfates**. These products are formed by addition of hydrogen to one carbon of the double bond and bisulfate ion to the other.



$$-\overset{|}{C}=\overset{|}{C}- + H-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{S}}-O-H \longrightarrow -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{S}}-O-H$$

Like alkyl sulfonates, these compounds are *esters*: esters of sulfuric acid, just as alkyl sulfonates are esters of sulfonic acids.

Reaction is carried out simply by bringing the reactants into contact: a gaseous alkene is bubbled into the acid, and a liquid alkene is stirred or shaken with the acid. Since alkyl hydrogen sulfates are soluble in sulfuric acid, a clear solution results. The alkyl hydrogen sulfates are deliquescent solids, and are difficult to isolate. As the examples below show, the concentration of sulfuric acid required for reaction depends upon the particular alkene involved; we shall account for this later.



$$CH_2{=}CH_2 \xrightarrow{98\%\ H_2SO_4} CH_3CH_2OSO_3H \xrightarrow{H_2O,\ heat} CH_3CH_2OH + H_2SO_4$$

$$CH_3CH{=}CH_2 \xrightarrow{80\%\ H_2SO_4} CH_3\underset{\underset{OSO_3H}{|}}{C}HCH_3 \xrightarrow{H_2O,\ heat} CH_3\underset{\underset{OH}{|}}{C}HCH_3$$

$$CH_3-\overset{\overset{CH_3}{|}}{C}{=}CH_2 \xrightarrow{63\%\ H_2SO_4} CH_3-\underset{\underset{OSO_3H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow{H_2O,\ heat} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

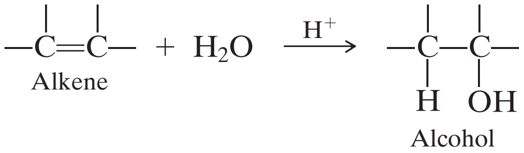
If the sulfuric acid solution of the alkyl hydrogen sulfate is diluted with water and heated, there is obtained an alcohol bearing the same alkyl group as the original alkyl hydrogen sulfate. The ester has been cleaved by water to form the alcohol and sulfuric acid, and is said to have been *hydrolysed*. This sequence of reactions affords a route to the alcohols, and it is for this purpose that addition of sulfuric acid to alkenes is generally carried out. This is an excellent method for the large-scale manufacture of alcohols, since alkenes are readily obtained by the cracking of petroleum. As the examples show, *the addition of sulfuric acid follows Markovnikov's rule*. Consequently, certain alcohols cannot be obtained by this method. For example, isopropyl alcohol can be made, but not *n*-propyl alcohol; *tert*-butyl alcohol, but not isobutyl alcohol.

The fact that alkenes dissolve in cold concentrated sulfuric acid to form the alkyl hydrogen sulfates is made use of in the purification of certain other kinds of compounds. Alkanes or alkyl halides, for example, which are insoluble in sulfuric acid, can be freed from alkene impurities by washing with sulfuric acid. A gaseous alkane is bubbled through several bottles of sulfuric acid, and a liquid alkane is shaken with sulfuric acid in a separatory funnel.

> **Problem 6A.24** (a) To what class of reactions does the hydrolysis of alkyl hydrogen sulfates probably belong? Explain. (b) Suggest a mechanism or mechanisms for hydrolysis of ethyl hydrogen sulfate; (c) for hydrolysis of *tert*-butyl hydrogen sulfate.

6A.35 Addition of water. Hydration

Water adds to the more reactive alkenes in the presence of acids to yield alcohols. Since this addition, too, follows Markovnikov's rule, the alcohols are the same



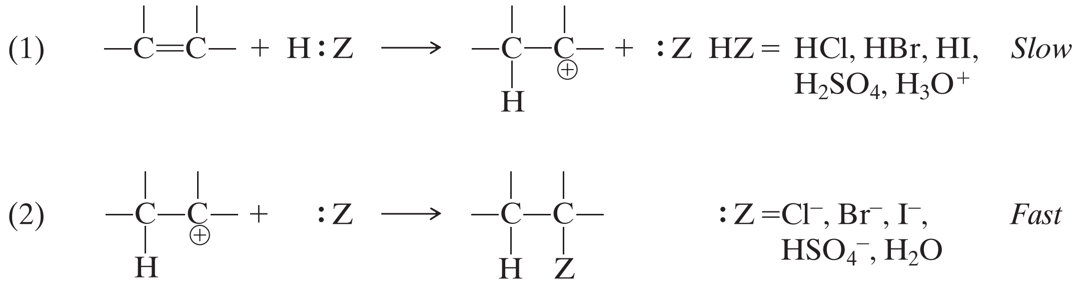
$$\underset{\text{Alkene}}{-\overset{|}{C}=\overset{|}{C}-} + H_2O \xrightarrow{H^+} \underset{\text{Alcohol}}{-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-}$$

as those obtained by the two-step synthesis just described. Hydration of alkenes, directly or via the alkyl hydrogen sulfates, is the principal industrial source of those lower alcohols whose formation is consistent with Markovnikov's rule.

6A.36 Mechanism of electrophilic addition reactions

Before we take up other reactions of alkenes, let us examine the mechanism of the reactions we have discussed so far. After we have done this, we shall return to our systematic consideration of alkene reactions, prepared to understand them better in terms of these earlier reactions.

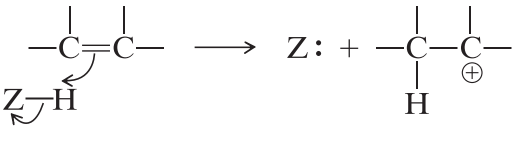
Addition of the acidic reagent, HZ, involves two steps:



$$(1)\quad -\overset{|}{C}=\overset{|}{C}- + H{:}Z \longrightarrow -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{\oplus}{\overset{|}{C}}- + {:}Z \qquad HZ = \text{HCl, HBr, HI, } H_2SO_4, H_3O^+ \qquad \textit{Slow}$$

$$(2)\quad -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{\oplus}{\overset{|}{C}}- + {:}Z \longrightarrow -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{Z}{\overset{|}{\underset{|}{C}}}- \qquad {:}Z = Cl^-, Br^-, I^-, HSO_4^-, H_2O \qquad \textit{Fast}$$

Step (1) is the transfer of hydrogen ion from: Z to the alkene to form a carbocation: a transfer of a proton from one base to another.



$$-\overset{|}{C}=\overset{|}{C}- \;\; Z{-}H \longrightarrow Z{:} + -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{\oplus}{\overset{|}{C}}-$$

Electrophilic addition

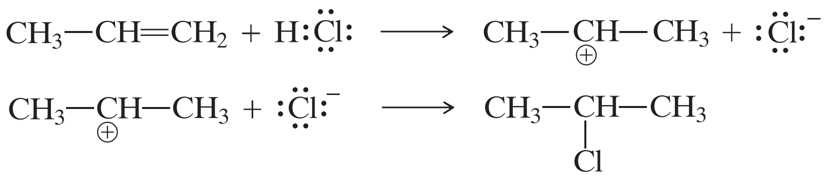
Step (2) is the combining of the carbocation with the base: Z.

The reagent H : Z can be neutral or positively charged: for example, HCl or H_3O^+. The base: Z will then be negatively charged or neutral: for example, Cl^- or H_2O.

Let us see what happens in step (1), focusing our attention on HZ and the two doubly bonded carbons of the alkene. Hydrogen is transferred as a proton—that is, *without its electrons*, which are left behind on the base: Z. To form the bond to hydrogen, carbon uses the π electrons formerly shared with the other carbon. This leaves this other carbon with only a sextet of electrons; it thus becomes the electron-deficient carbon of a carbocation.

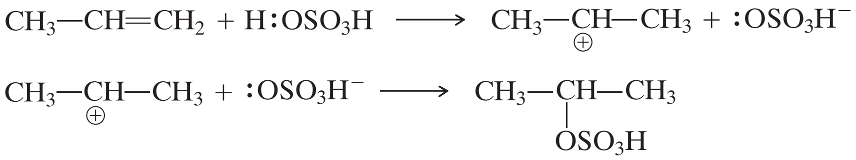
Step (1) is the slow, difficult step, and its rate largely or entirely controls the overall rate of addition. This step involves attack by an acidic, electron-seeking reagent—that is, an *electrophilic* reagent—and hence the reaction is an example of **electrophilic addition**. The electrophile is not necessarily a Lowry–Brønsted acid transferring a proton, as shown here, but, as we shall see, can be almost any kind of electron-deficient molecule (Lewis acid).

The general mechanism can be illustrated by specific examples: addition of hydrogen chloride,



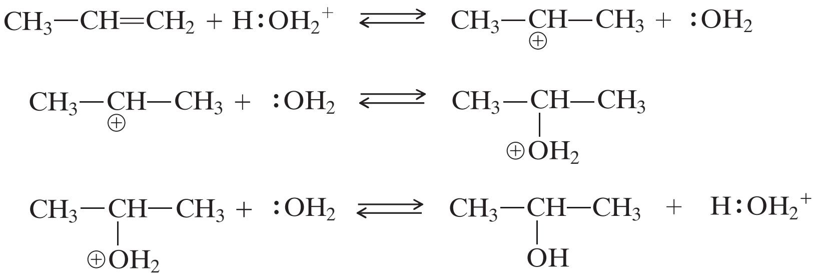
$$
\begin{aligned}
&(1) \quad CH_3{-}CH{=}CH_2 + H{:}\ddot{\underset{..}{Cl}}{:} \longrightarrow CH_3{-}\underset{\oplus}{C}H{-}CH_3 + {:}\ddot{\underset{..}{Cl}}{:}^- \\
&(2) \quad CH_3{-}\underset{\oplus}{C}H{-}CH_3 + {:}\ddot{\underset{..}{Cl}}{:}^- \longrightarrow CH_3{-}\underset{\substack{|\\ Cl}}{C}H{-}CH_3
\end{aligned}
$$

of sulfuric acid,



$$
\begin{aligned}
&(1) \quad CH_3{-}CH{=}CH_2 + H{:}OSO_3H \longrightarrow CH_3{-}\underset{\oplus}{C}H{-}CH_3 + {:}OSO_3H^- \\
&(2) \quad CH_3{-}\underset{\oplus}{C}H{-}CH_3 + {:}OSO_3H^- \longrightarrow CH_3{-}\underset{\substack{|\\ OSO_3H}}{C}H{-}CH_3
\end{aligned}
$$

and of water.



$$
\begin{aligned}
&(1) \quad CH_3{-}CH{=}CH_2 + H{:}OH_2^+ \rightleftharpoons CH_3{-}\underset{\oplus}{C}H{-}CH_3 + {:}OH_2 \\
&(2a) \quad CH_3{-}\underset{\oplus}{C}H{-}CH_3 + {:}OH_2 \rightleftharpoons CH_3{-}\underset{\substack{|\\ \oplus OH_2}}{C}H{-}CH_3 \\
&(2b) \quad CH_3{-}\underset{\substack{|\\ \oplus OH_2}}{C}H{-}CH_3 + {:}OH_2 \rightleftharpoons CH_3{-}\underset{\substack{|\\ OH}}{C}H{-}CH_3 + H{:}OH_2^+
\end{aligned}
$$

We notice that the carbocation combines with water to form not the alcohol but the protonated alcohol; in a subsequent reaction this protonated alcohol releases a hydrogen ion to another base to form the alcohol. This sequence of reactions, we can see, is just the reverse of that proposed for the dehydration of alcohols. In dehydration, the equilibria are shifted in favor of the alkene chiefly by the removal of the alkene from the reaction mixture by distillation: in hydration, the equilibria are shifted in favor of the alcohol partly by the high concentration of water.

Now, what is the evidence for this mechanism? It includes the following:

(a) The *rate of reaction* depends upon the concentration of both the alkene and the reagent HZ.
(b) *Reaction requires an acidic reagent.*
(c) Where the structure permits, *reaction is accompanied by rearrangements.*

In addition, the mechanism is consistent with:

(d) the *orientation* of addition; and
(e) the *relative reactivities* of alkenes.

Let us examine this evidence.

First, (a) the *rate of reaction* depends upon concentration of both the alkene and the reagent HZ. This fact is, of course, consistent with a mechanism that starts with reaction between these two reagents.

Next, (b) *reaction requires an acidic reagent*. According to the mechanism, the first step in all these reactions is the transfer of a proton to the alkene. This agrees with the fact that all these reagents except water are strong acids in the Lowry–Brønsted sense; that is, they can readily transfer protons. The exception, water, requires the presence of added strong acid for reaction to occur. An alkene is a *weak* base, and accepts protons to a significant degree only from strong acids.

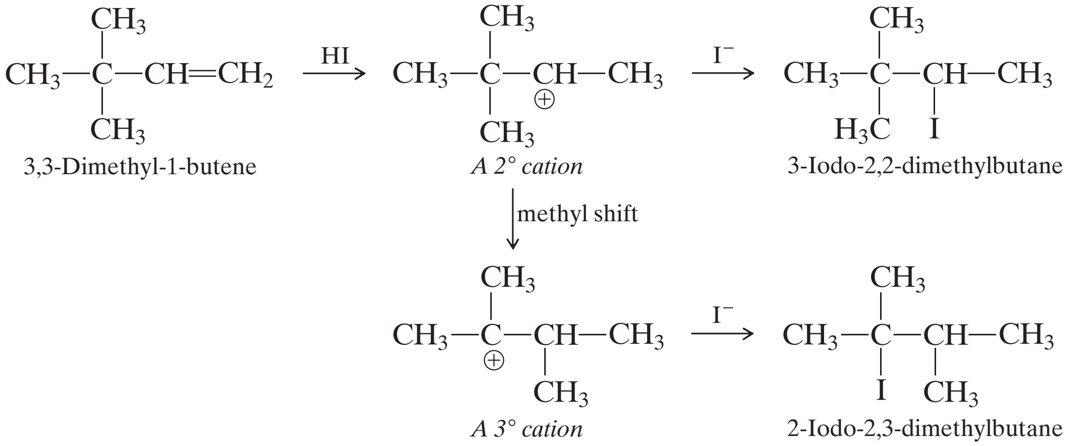
Problem 6A.25 Addition of D_2O to 2-methyl-2-butene (in the presence of D^+) was found (as we might expect) to yield the alcohol $(CH_3)_2C(OD)CHDCH_3$. When reaction was half over, it was interrupted and the unconsumed alkene was isolated; mass spectrometric analysis showed that it contained almost no deuterium. What, specifically, does this show about the mechanism?

6A.37 Electrophilic 1,2-shift during electrophilic additions

Where the structure permits, (c) *reaction is accompanied by rearrangements*. The product sometimes contains the group Z attached to a carbon that was not doubly bonded in the substrate; sometimes the product even has a carbon skeleton different from that of the substrate.

These "unexpected" products, it turns out, are readily accounted for by rearrangements of the carbocations proposed as intermediates. These rearrangements follow exactly the same pattern that we have come to expect from our study of carbocations in S_N1 substitution and in E1 elimination.

For example, addition of hydrogen iodide to 3,3-dimethyl-1-butene yields not only the expected 3-iodo-2,2-dimethylbutane, but also 2-iodo-2,3-dimethylbutane:



Since a 1,2-shift of a methyl group can convert the initially formed secondary cation into a more stable tertiary cation, such a rearrangement does occur, and much of the product is derived from this new ion.

The change in carbon skeleton accompanying this last example of *addition* is identical to that accompanying two reactions of 3,3-dimethyl-2-butanol: dehydration, an *elimination* reaction; and conversion into the chloride, a *substitution* reaction. This is a particularly dramatic example of the kind of evidence that gave rise to the idea that these apparently unrelated reactions proceed through the same intermediate: the carbocation.

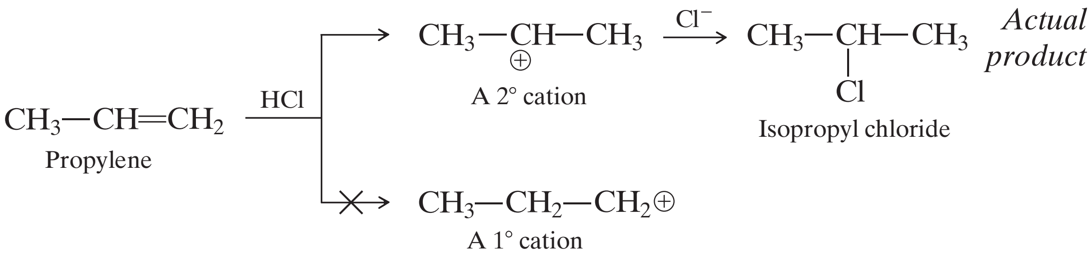
Of all the evidence supporting the mechanism we have given for electrophilic addition, the strongest single piece is the occurrence of rearrangements, since this bears directly on the heart of the mechanism: the formation of the carbocation.

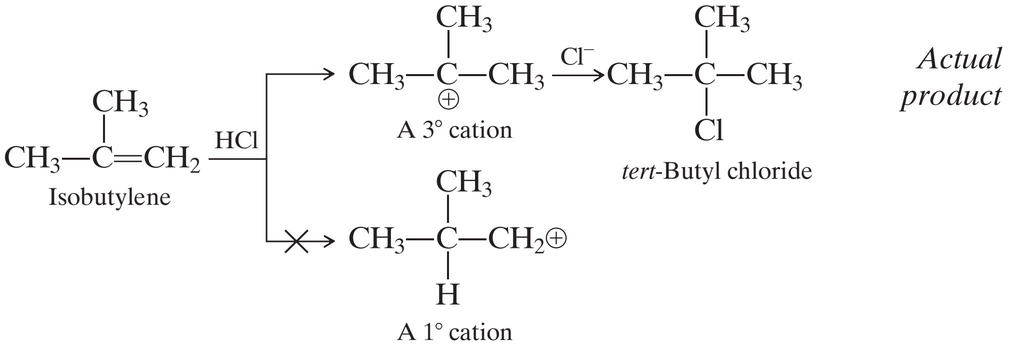
Problem 6A.26 Addition of HCl to 3-methyl-1-butene yields a mixture of two alkyl chlorides. What are they likely to be, and how is each formed? Give detailed equations.

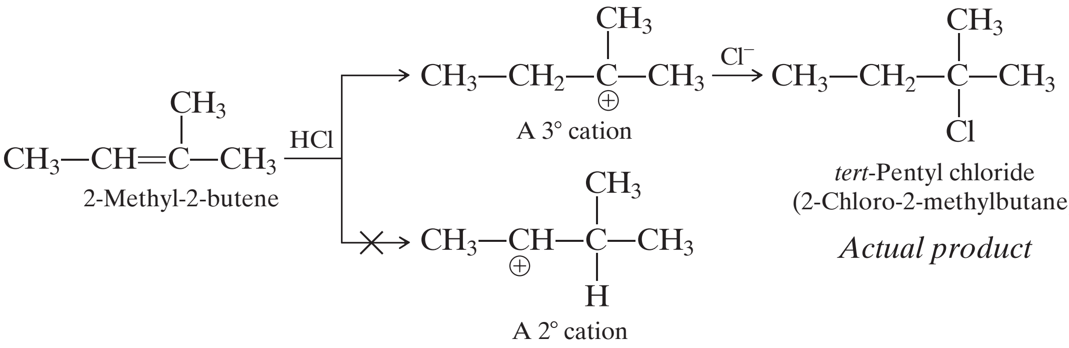
6A.38 Reactivity and regioselectivity in electrophilic additions

The mechanism is consistent with (d) the *orientation* of addition of acidic reagents, and (e) the effect of structure on the *relative reactivities* of alkenes.

Addition of hydrogen chloride to three typical alkenes is outlined below, with the two steps of the mechanism shown. In accord with Markovnikov's rule, propylene yields isopropyl chloride, isobutylene yields *tert*-butyl chloride, and 2-methyl-2-butene yields *tert*-pentyl chloride.







According to the mechanism, hydrogen from the reagent adds to one or the other of the two doubly bonded carbons to give one or the other of two possible carbocations. For example, if hydrogen goes to C–2 of propylene, there is formed the *n*-propyl cation; if it goes to C–l, there is formed the isopropyl cation. Once formed, the carbocation rapidly reacts to yield product. Which halide is obtained, then, depends upon which carbocation is formed in the first step. The fact that propylene yields isopropyl chloride rather than *n*-propyl chloride shows that the isopropyl cation is formed rather than—that is, *faster than*—the *n*-propyl cation. Thus, orientation in electrophilic addition is determined by the relative rates of two competing reactions: *formation of one carbocation or the other*.

In each of the examples given above, the product obtained shows that in the initial step a secondary cation is formed faster than a primary, or a tertiary faster than a primary, or a tertiary faster than a secondary. Examination of the orientation in many cases shows that this is a general rule: in electrophilic addition the rate of formation of carbocations follows the sequence

Rate of formation of carbocations $3° > 2° > 1° > CH_3^+$

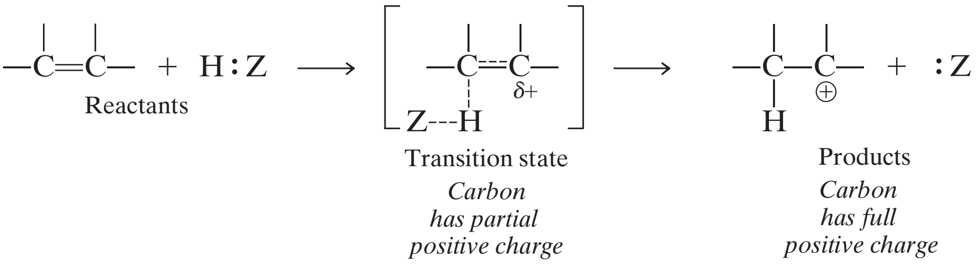
In listing carbocations in order of their rate of formation from alkenes, we find that, once again, we have listed them in order of their stability.

Stability of carbocations $3° > 2° > 1° > CH_3^+$

We can now reword **Markovnikov's rule** as: **electrophilic addition to a carbon–carbon double bond involves the intermediate formation of the more stable carbocation**.

As with Saytzeff's rule, this rewording gives a rule that not only is more generally applicable, but leads us to the factor actually at work.

How can we account for the fact that the rate of formation of a carbocation in electrophilic addition depends upon its stability? Once more we must compare the structure of the reactants with the structure of the transition state. In the reactants, hydrogen is attached to: Z, and the doubly bonded carbons are held to each other not only by a σ bond but also by a π bond. In the products, hydrogen is attached to one of the carbons; the π bond is broken, and the other carbon is left with only a sextet of electrons and hence a positive charge. In the transition state, the bond between hydrogen and: Z is partly broken, and the bond between hydrogen and carbon is partly formed. The π bond is partly broken, and *carbon has partly gained the positive charge it will carry in the carbocation.*



$$-C{=}C- + H{:}Z \longrightarrow \left[\begin{array}{c} -C{=}\!{=}C- \\ \overset{\delta+}{} \\ Z\text{---}H \end{array}\right] \longrightarrow \underset{H}{-C}-\overset{}{\underset{\oplus}{C}}- + :Z$$

Electron-releasing groups tend to disperse the partial positive charge developing on carbon, and in this way stabilize the transition state. Stabilization of the transition state lowers E_{act} and permits a faster reaction (see Fig. 6A.12). To the extent that the π bond is broken, the organic group possesses the character of the carboca-tion it is to become. As before, the same factor, electron release, that stabilizes the carbocation also stabilizes the *incipient* carbocation in the transition state. Once again, we find, *the more stable the carbocation, the faster it is formed.*

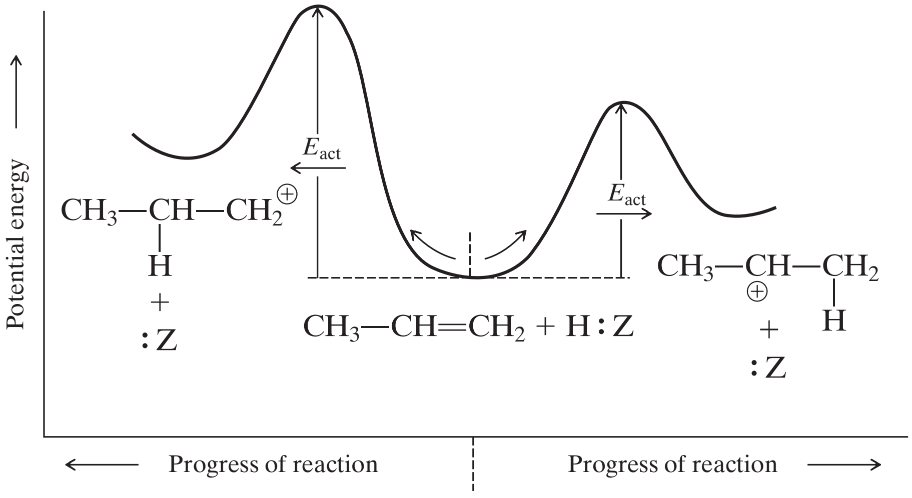
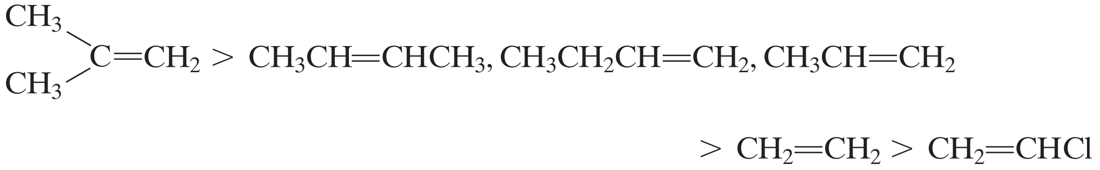


Figure 6A.12 Molecular structure and orientation of reaction. The stability of the transition state parallels the stability of the carbocation: the more stable carbocation is formed faster.

Thus, the rate of addition of a hydrogen ion to a double bond depends upon the stability of the carbocation being formed. As we might expect, this factor determines not only the **orientation** of addition to a single alkene, but also the **relative reactivities** of different alkenes.

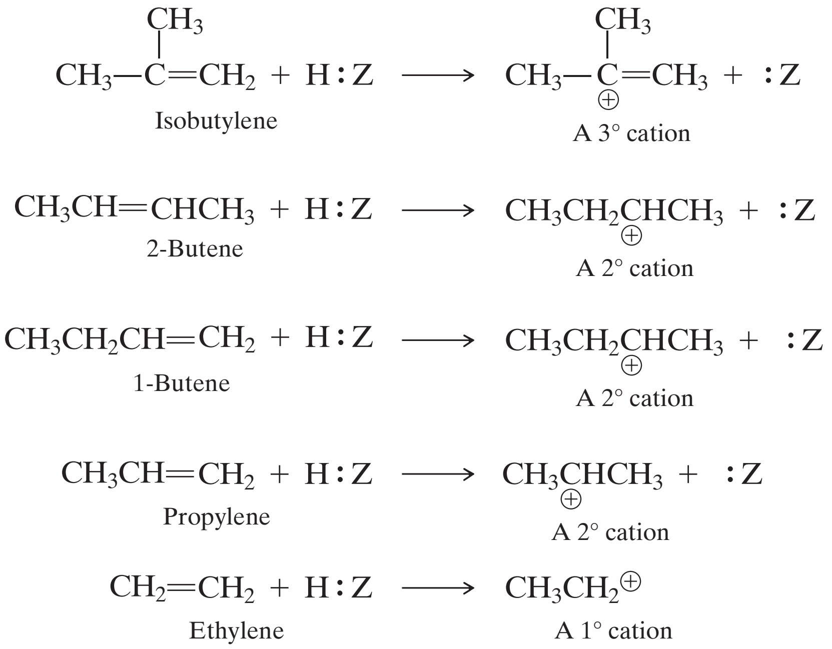
Alkenes generally show the following order of reactivity toward addition of acids:

Reactivity of alkenes toward acids



$$(CH_3)_2C{=}CH_2 > CH_3CH{=}CHCH_3,\ CH_3CH_2CH{=}CH_2,\ CH_3CH{=}CH_2 > CH_2{=}CH_2 > CH_2{=}CHCl$$

Isobutylene, which forms a tertiary cation, reacts faster than 2-butene, which forms a secondary cation. 1-Butene, 2-butene, and propylene, which form secondary cations, react faster than ethylene, which forms a primary cation.



$$\underset{\text{Isobutylene}}{CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2} + H{:}Z \longrightarrow \underset{\text{A 3° cation}}{CH_3{-}\underset{\oplus}{\overset{\displaystyle CH_3}{\overset{|}{C}}}{=}CH_3} + {:}Z$$

$$\underset{\text{2-Butene}}{CH_3CH{=}CHCH_3} + H{:}Z \longrightarrow \underset{\text{A 2° cation}}{CH_3CH_2\underset{\oplus}{C}HCH_3} + {:}Z$$

$$\underset{\text{1-Butene}}{CH_3CH_2CH{=}CH_2} + H{:}Z \longrightarrow \underset{\text{A 2° cation}}{CH_3CH_2\underset{\oplus}{C}HCH_3} + {:}Z$$

$$\underset{\text{Propylene}}{CH_3CH{=}CH_2} + H{:}Z \longrightarrow \underset{\text{A 2° cation}}{CH_3\underset{\oplus}{C}HCH_3} + {:}Z$$

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + H{:}Z \longrightarrow \underset{\text{A 1° cation}}{CH_3CH_2^{\oplus}}$$

As substituents, halogens tend to attract electrons. Just as electron release by alkyl groups disperses the positive charge and stabilizes a carbocation, so electron withdrawal by halogens intensifies the positive charge and destabilizes the carbocation. We saw that this electron withdrawal slows down the formation of carbocations in heterolysis, in the same way, it slows down formation of carbocations in electrophilic addition. Vinyl chloride, $CH_2{=}CHCl$, for example is *less* reactive than ethylene.

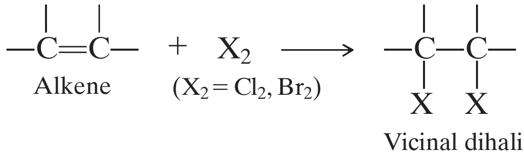
When we said that the carbocation is the heart of the mechanism of electrophilic addition, we meant not just that it is an intermediate; we meant that, as in other carbocation reactions we have studied, it is the *rate of formation of the carbocation* that determines the course of reaction.

We can begin to see what a powerful weapon we have for attacking the problems that arise in connection with a wide variety of reactions that involve carbocations. We know that the more stable the carbocation, the faster it is formed; that its stability depends upon dispersal of charge; and that dispersal of charge is determined by the electronic effect of the attached groups. We have already found that this same approach enables us to deal with such seemingly different matters as (a) the relative reactivities of substrates in S_N1 substitution; (b) the relative ease of dehydration of alcohols; (c) the relative reactivities of alkenes toward addition of acids; (d) the orientation of addition of acids to alkenes; and (e) the pattern of rearrangements that can occur in all these reactions.

Problem 6A.27 We have seen that dehydration of alcohols is reversible; its reverse is, of course, hydration of alkenes. On the basis of what you have just learned, show how dehydration of 1-butanol could give rise to 2-butene without involving rearrangement of—or even formation of—a *n*-butyl cation.

6A.39 Addition of halogens

Alkenes are readily converted by chlorine or bromine into saturated compounds that contain two atoms of halogen attached to adjacent carbons; iodine generally fails to react.



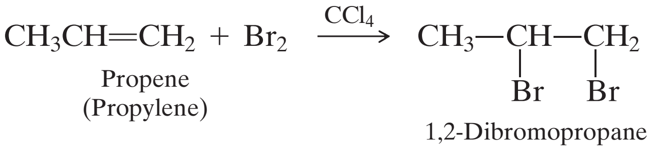
$$-\overset{|}{C}=\overset{|}{C}- \;+\; X_2 \longrightarrow -\underset{X}{\underset{|}{\overset{|}{C}}}-\underset{X}{\underset{|}{\overset{|}{C}}}-$$

Alkene (X$_2$ = Cl$_2$, Br$_2$)

Vicinal dihalide

The reaction is carried out simply by mixing together the two reactants, usually in an inert solvent like carbon tetrachloride. The addition proceeds rapidly at room temperature or below, and does not require exposure to ultraviolet light; in fact, we deliberately avoid higher temperatures and undue exposure to light, as well as the presence of excess halogen, since under those conditions substitution might become an important side reaction.

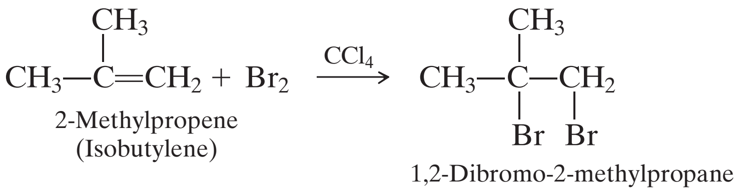
This reaction is by far the best method of preparing **vicinal dihalides**. For example:



$$CH_3CH{=}CH_2 + Br_2 \xrightarrow{CCl_4} CH_3-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}$$

Propene (Propylene)

1,2-Dibromopropane



$$CH_3-\overset{CH_3}{\overset{|}{C}}{=}CH_2 + Br_2 \xrightarrow{CCl_4} CH_3-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{Br}{\underset{|}{CH_2}}$$

2-Methylpropene (Isobutylene)

1,2-Dibromo-2-methylpropane

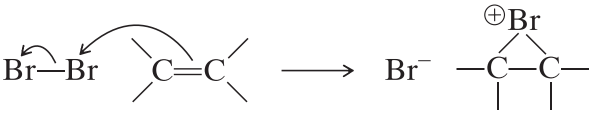
Addition of bromine is extremely useful for detection of the carbon–carbon double bond. A solution of bromine in carbon tetrachloride is red; the dihalide, like the alkene, is colorless. Rapid decolorization of a bromine solution is characteristic of compounds containing the carbon–carbon double bond.

6A.40 Mechanism of addition of halogens (stereoselectivity of the reaction)

The addition of halogens to alkenes, like the addition of protic acids, is believed to be electrophilic addition, and to involve two steps. Again, the first step involves the formation of a cation. But this cation, in most cases, is not a carbocation, but something new to us: a *halonium ion*. Let us see what a halonium ion is, and what evidence there is for its formation.

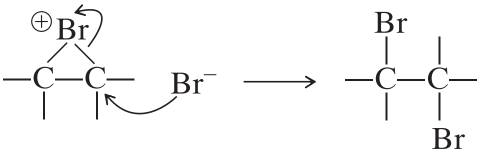
Let us use addition of bromine as our example. In step (1) bromine is transferred from a bromine molecule to the alkene: not to just one of the doubly bonded carbons, but to both, forming a cyclic **bromonium ion**.

(1)



A bromonium ion

(2)



Step (1) does indeed represent electrophilic addition. Bromine is transferred as *positive* bromine: that is, without a pair of electrons, which are left behind on the newly formed bromide ion. In step (2) this bromide ion, or more probably another just like it, reacts with the bromonium ion to yield the product, the dibromide.

What is being proposed here is *not* a π-complex in which the (acidic) bromine molecule is held by the (basic) π cloud of the alkene. Bromine is bonded by two π bonds—one to each carbon—to form a ring. A π-complex of molecular Br_2 and alkene may, however, be a reversibly formed precursor of the bromonium ion.

The transfer of a proton from a strong acid to an alkene, while new to us, does fit into a familiar framework of acid–base reactions. But how are we to understand the transfer of positive bromine from a bromine molecule? To begin with, it *is* an acid–base reaction—although not in the Lowry–Brønsted sense. Just as alkenes are bases, so halogens are acids, of the Lewis type.

We can understand this reaction better if we change our viewpoint. From the standpoint of a halogen molecule, the reaction with an alkene is nucleophilic substitution. Acting as a nucleophile, the alkene attaches itself to one of the bromines and pushes the other bromine out as bromide ion. Bromide ion is the leaving group; and, as we have seen, bromide ion is a very *good* leaving group.

What are the facts upon which this mechanism is based? They are:

(a) the *effect of the structure of the alkene on reactivity*;
(b) the *effect of added nucleophiles* on the products obtained;
(c) the fact that halogens add with *complete stereoselectivity* and in the *anti* sense;

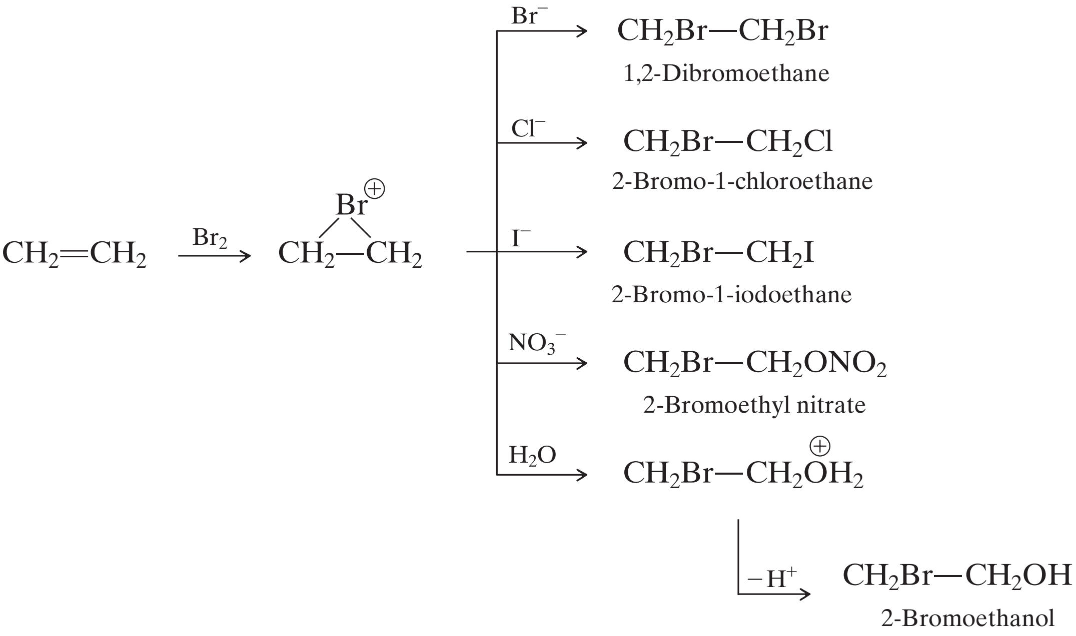
(d) the *direct observation of halonium ions* under superacid conditions; and
(e) the role played by halonium ions in *neighboring group effects*.

We shall examine each of these pieces of evidence: (a) and (b) now, and (c) and (d) in later chapters.

First, there is (a) the *effect of the structure of the alkene on reactivity*. Alkenes show the same order of reactivity toward halogens as toward the acids already studied: electron-releasing substituents activate an alkene, and electron-withdrawing substituents deactivate. This fact supports the idea that addition is indeed electrophilic—that the alkene is acting as an electron source, and that halogen acts as an acid.

Next, there is (b) the e*ffect of added nucleophiles* on the products obtained. If a halonium ion is the intermediate, and capable of reacting with halide ion, then we might expect it to react with almost any negative ion or basic molecule we care to provide. The bromonium ion formed in the reaction between ethylene and bromine, for example, should be able to react not only with bromide ion but also—if these are present—with fluoride ion, iodide ion, nitrate ion, or water.

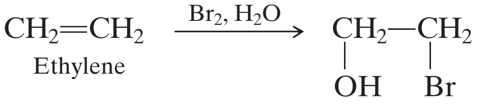
The facts are in complete agreement with this expectation. When ethylene is bubbled into an aqueous solution of bromine and sodium chloride, there is formed not only the dibromo compound but also the bromochloro compound and the bromoalcohol. Aqueous sodium chloride *alone* is completely inert toward ethylene; chloride ion or water can react only after the halonium ion has been formed by the action of bromine. In a similar way bromine and aqueous sodium iodide or sodium nitrate convert ethylene into the bromoiodo compound or the bromonitrate, as well as the dibromo compound and the bromoalcohol. Bromine in water with no added ion yields the dibromo compound and the bromoalcohol.



Now, this elegant work certainly shows that ethylene reacts with bromine to form *something* that can react with these other nucleophiles—but it need not be a bromonium ion. On this evidence alone the intermediate cation could be the simple open carbocation $BrCH_2CH_2^+$. As we shall see, it was the *stereochemistry* of the reaction that led to the concept of an intermediate bromonium ion, a concept that has since been supported by actual observation of such ions.

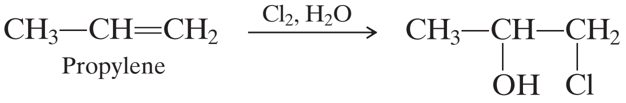
6A.41 Halohydrin formation: addition of the elements of hypohalous acids

As we have seen, addition of chlorine or bromine in the presence of water can yield compounds containing halogen and hydroxyl on adjacent carbon atoms. These compounds are thus chloroalcohols or bromoalcohols. They are commonly referred to as **halohydrins**: *chlorohydrins* or *bromohydrins*. Under proper conditions they can be made the major products. For example:



$$\underset{\text{Ethylene}}{CH_2{=}CH_2} \xrightarrow{Br_2,\ H_2O} \underset{OH}{\underset{|}{CH_2}}{-}\underset{Br}{\underset{|}{CH_2}}$$

2-Bromoethanol
(Ethylene bromohydrin)

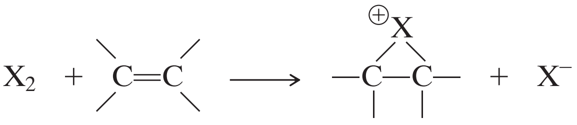


$$\underset{\text{Propylene}}{CH_3{-}CH{=}CH_2} \xrightarrow{Cl_2,\ H_2O} CH_3{-}\underset{OH}{\underset{|}{CH}}{-}\underset{Cl}{\underset{|}{CH_2}}$$

1-Chloro-2-propanol
(Propylene chlorohydrin)

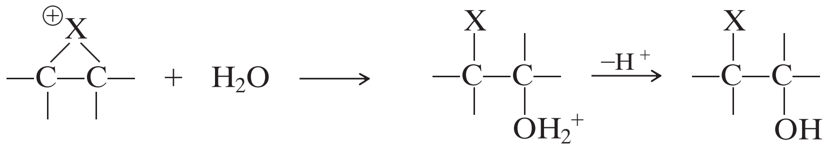
There is evidence, of a kind we are not prepared to go into here, that these compounds are not formed by addition of preformed hypohalous acid, HOX, but by reaction of the alkene with, successively, halogen and water.

(1)



A halonium ion

(2)



A halohydrin

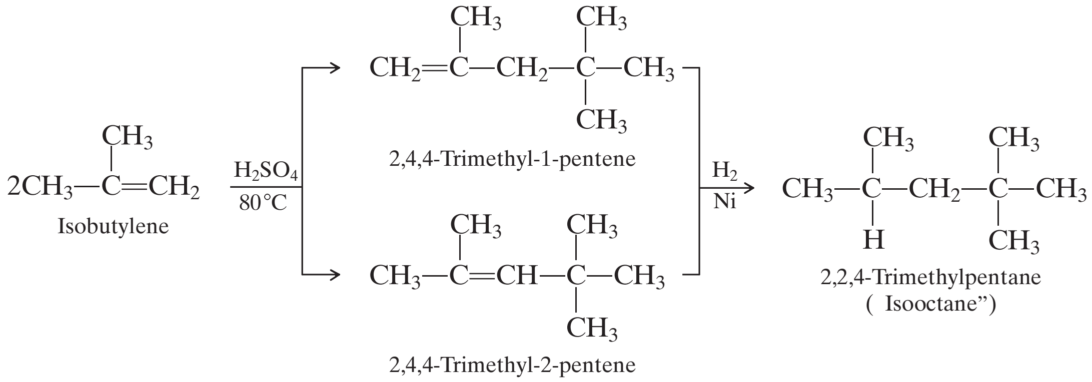
Halogen adds (step 1) to form the halonium ion; this then reacts, in part, not with bromide ion, but with water (step 2) to yield the protonated alcohol. Whatever the mechanism, the result is addition of the elements of hypohalous acid (HO— and —X), and the reaction is often referred to in that way.

Propylene, we see above, gives the chlorohydrin in which chlorine is attached to the terminal carbon. This is typical behavior for an unsymmetrical alkene; orientation follows Markovnikov's rule, with positive halogen going to the same carbon that the hydrogen of a protic reagent would.

Now, this orientation would be perfectly understandable if the intermediate were an open carbocation: the initial addition of halogen yields the more stable carbocation—secondary, in the case of propylene. But the stereochemistry indicates that the intermediate is *not* an open carbocation, but a cyclic halonium ion.

6A.42 Addition of alkenes. Dimerization

Under proper conditions, isobutylene is converted by sulfuric or phosphoric acid into a mixture of two alkenes of molecular formula C_8H_{16}. Hydrogenation of either of these alkenes produces the same alkane, 2,2,4-trimethylpentane. The two alkenes are isomers, then, and differ only in position of the double bond. (*Problem*: Could they, instead, be geometric isomers?) When studied by the methods discussed at the end of this chapter, these two alkenes are found to have the structures shown:

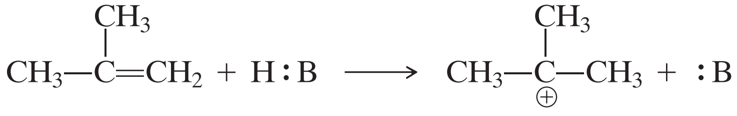


Since the alkenes produced contain exactly twice the number of carbon and hydrogen atoms as the original isobutylene, they are known as **dimers** (*di* = two, *mer* = part) of isobutylene, and the reaction is called **dimerization**. Other alkenes undergo analogous dimerizations.

Let us see if we can devise an acceptable mechanism for this dimerization. There are a great many isomeric octenes; if our mechanism should lead us to just the two that are actually formed, this in itself would provide considerable support for the mechanism.

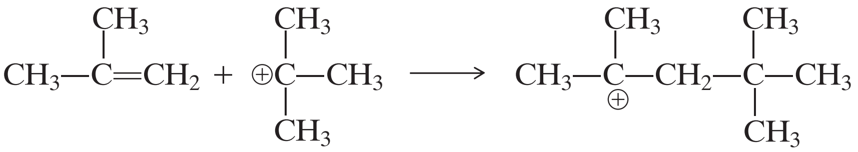
Since the reaction is catalysed by acid, let us write as step (1) addition of a hydrogen ion to isobutylene to form the carbocation; the tertiary cation would, of course, be the preferred ion.

(1)



$$CH_3\text{—}\overset{\displaystyle CH_3}{\overset{|}{C}}\text{=}CH_2 + H\!:\!B \longrightarrow CH_3\text{—}\underset{\oplus}{\overset{\displaystyle CH_3}{\overset{|}{C}}}\text{—}CH_3 + \,:\!B$$

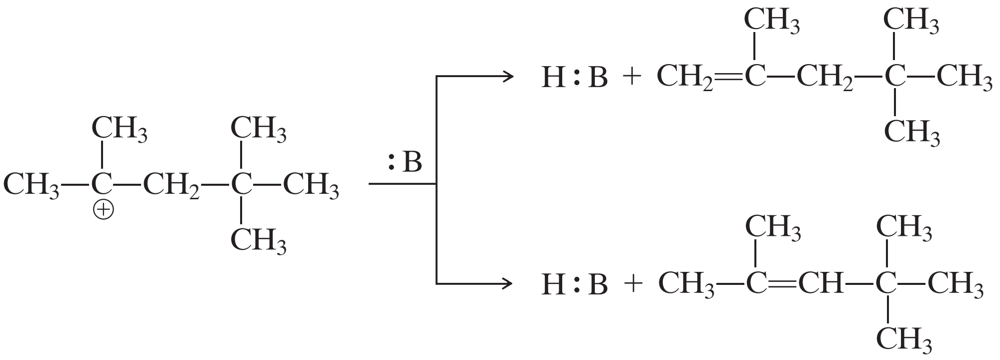
A carbocation undergoes reactions that provide electrons to complete the octet of the positively charged carbon atom. A carbon–carbon double bond is an excellent electron source, and a carbocation might well go there in its quest for electrons. Let us write as step (2), then, addition of the *tert*-butyl cation to isobutylene; again, the orientation of addition is such as to yield the more stable tertiary cation.

(2) 

$$CH_3-\overset{CH_3}{C}=CH_2 + \oplus\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{\oplus}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

Step (2) brings about the union of two isobutylene units, which is, of course, necessary to account for the products.

What is this new carbocation likely to do? We might expect that it could add to another molecule of alkene and thus make an even larger molecule; under certain conditions this does indeed happen. Under the present conditions, however, we know that this reaction stops at eight-carbon compounds, and that these compounds are alkenes. Evidently, the carbocation undergoes a reaction familiar to us: loss of a hydrogen ion (step 3). Since the hydrogen ion can be lost from a carbon on either side of the positively charged carbon, two products should be possible.

(3) 

$$CH_3-\underset{\oplus}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{:B} \begin{cases} H:B + CH_2=\overset{CH_3}{C}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \\ H:B + CH_3-\overset{CH_3}{C}=CH-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \end{cases}$$

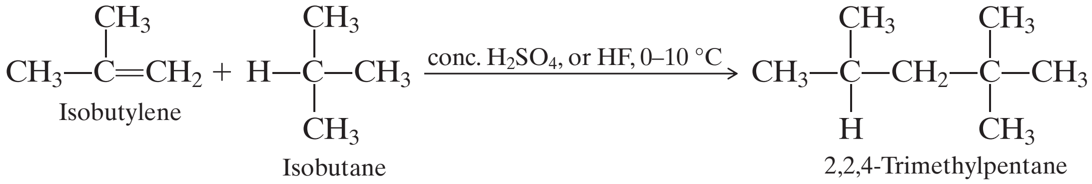
We find that the products expected on the basis of our mechanism are just the ones that are actually obtained. The fact that we can make this prediction simply on the basis of the fundamental properties of carbocations as we understand them is, of course, powerful support for the entire carbocation theory.

We have studied this dimerization, not for its great industrial importance—"isooctane" is made by a new, cheaper process—but for what it reveals about carbo-cations and alkenes. The attachment of carbocations (or carbocation-like species) to π-electron systems is a fundamental reaction type that is encountered both in ordinary organic chemistry and—in a modified form—in biogenesis, the sequence of reactions by which a compound is formed in living systems, plant or animal.

6A.43 Addition of alkanes. Alkylation

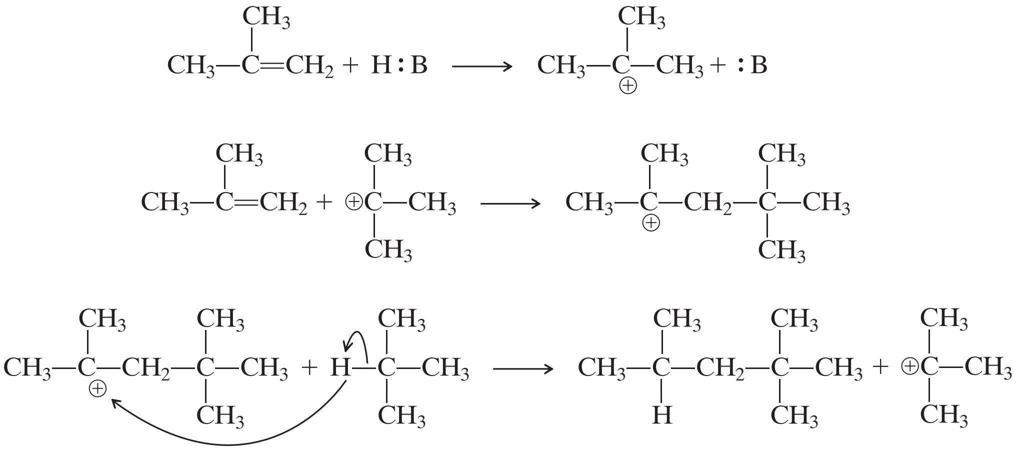
Now let us look at the industrial method that *is* used today to make the large amounts of 2,2,4-trimethylpentane ("isooctane") that are consumed as high-test gasoline. In doing this we shall learn still more about the fundamental properties of carbocations—and something rather surprising about alkanes.

When isobutylene and isobutane are allowed to react in the presence of an acidic catalyst, they form directly 2,2,4-trimethylpentane. This reaction is, in effect, addition of an alkane to an alkene.



$$\underset{\text{Isobutylene}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2} + \underset{\text{Isobutane}}{H-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3} \xrightarrow{\text{conc. } H_2SO_4\text{, or HF, 0–10 °C}} \underset{\text{2,2,4-Trimethylpentane}}{CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3}$$

The commonly accepted mechanism of this **alkylation** is based on the study of many related reactions and involves in step (3) a reaction of carbocations that we have not previously encountered.



$$(1)\quad CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 + H:B \longrightarrow CH_3-\underset{\oplus}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 + :B$$

$$(2)\quad CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 + \oplus\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 \longrightarrow CH_3-\underset{\oplus}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

$$(3)\quad CH_3-\underset{\oplus}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 + H-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 \longrightarrow CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 + \oplus\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

then (2), (3), (2), (3), etc.

The first two steps are identical with those of the dimerization reaction. In step (3) a carbocation abstracts a hydrogen atom *with its pair of electrons* (a **hydride ion**, essentially) from a molecule of alkane. This abstraction of hydride ion yields an alkane of eight carbons, and a new carbocation to continue the chain. As we might expect, abstraction occurs in the way that yields the *tert*-butyl cation rather than the less stable (1°) isobutyl cation.

This is not our first encounter with the transfer of hydride ion to an electron-deficient carbon; we saw much the same thing in the 1,2-shifts accompanying the rearrangement of carbocations. There, transfer was *intramolecular* (within a molecule); here, it is *intermolecular* (between molecules). This reaction shows us what an extremely strong acid a carbocation is. At the same time, it illustrates something we hinted at earlier: that the "inertness" of alkanes is greatly exaggerated. With a strong enough acid as reagent, an alkane reacts quite readily, and in a heterolytic fashion, too.

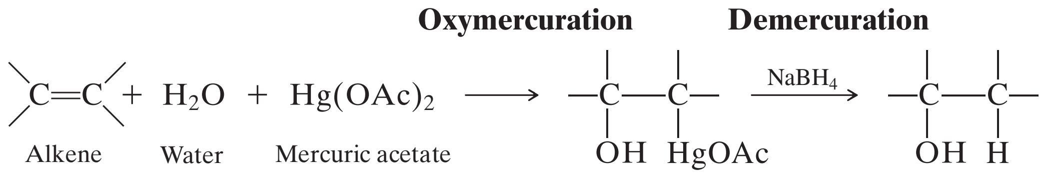
Now let us bring our list of carbocation reactions up to date. **A carbocation may:**

(a) combine with a negative ion or other basic molecule;
(b) rearrange to a more stable carbocation;
(c) eliminate a proton to form an alkene;
(d) add to an alkene to form a larger carbocation;
(e) abstract a hydride ion from an alkane.

A carbocation formed by (b) or (d) can subsequently undergo any of the reactions.

6A.44 Oxymercuration–demercuration

Alkenes react with mercuric acetate in the presence of water to give hydroxymercurial compounds which on reduction yield alcohols.

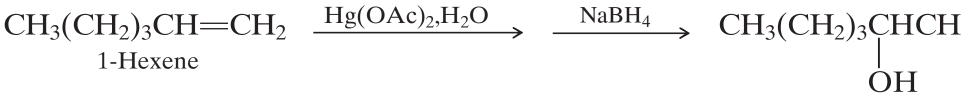


$$—OAc = CH_3COO—$$

The first stage, *oxymercuration*, involves addition to the carbon–carbon double bond of —OH and —HgOAc. Then, in *demercuration*, the —HgOAc is replaced by —H. The reaction sequence amounts to hydration of the alkene, but is much more widely applicable than direct hydration.

The two-stage process of oxymercuration–demercuration is fast and convenient, takes place under mild conditions, and gives excellent yields—often over 90%. The alkene is added at room temperature to an aqueous solution of mercuric acetate diluted with the solvent tetrahydrofuran. Reaction is generally complete within minutes. The organomercurial compound is not isolated but is simply reduced *in situ* by sodium borohydride, $NaBH_4$. (The mercury is recovered as a ball of elemental mercury.)

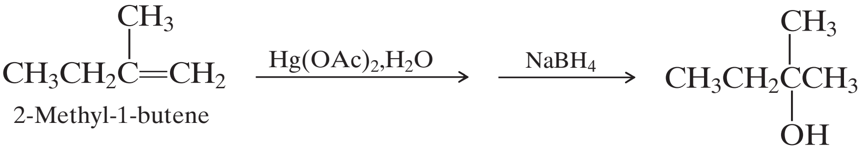
Oxymercuration–demercuration is highly regioselective, and gives alcohols corresponding to *Markovnikov* addition of water to the carbon–carbon double bond. For example:



$$\underset{\text{1-Hexene}}{CH_3(CH_2)_3CH{=}CH_2} \xrightarrow{Hg(OAc)_2,H_2O} \xrightarrow{NaBH_4} \underset{\text{2-Hexanol}}{CH_3(CH_2)_3\underset{|\atop OH}{C}HCH}$$

1-Hexene

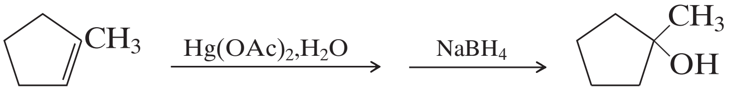
2-Hexanol



$$CH_3CH_2\overset{CH_3\atop |}{C}{=}CH_2 \xrightarrow{Hg(OAc)_2,H_2O} \xrightarrow{NaBH_4} CH_3CH_2\overset{CH_3\atop |}{\underset{|\atop OH}{C}}CH_3$$

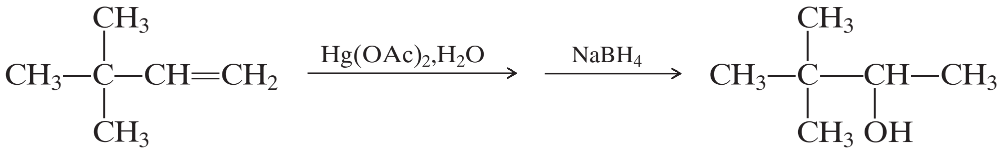
2-Methyl-1-butene

tert-Pentyl alcohol



1-Methylcyclopentene

1-Methylcyclopentanol

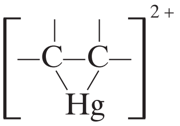


$$CH_3{-}\overset{CH_3\atop |}{\underset{|\atop CH_3}{C}}{-}CH{=}CH_2 \xrightarrow{Hg(OAc)_2,H_2O} \xrightarrow{NaBH_4} CH_3{-}\overset{CH_3\atop |}{\underset{|\atop CH_3}{C}}{-}\underset{|\atop OH}{CH}{-}CH_3$$

3,3-Dimethyl-1-butene

3,3-Dimethyl-2-butanol

Oxymercuration involves electrophilic addition to the carbon–carbon double bond, with the mercuric ion acting as electrophile. The absence of rearrangement argues against an open carbocation as intermediate. Instead, it has been proposed, there is formed a cyclic *mercurinium ion*, analogous to the bromonium and chloronium ions involved in the addition of halogens. In 1971, Olah reported spectroscopic evidence for the preparation of stable solutions of such mercurinium ions, and they have since been observed in the gas phase.



The mercurinium ion is attacked by the nucleophilic solvent—water, in the present case—to yield the addition product.

As in halohydrin formation, the Markovnikov orientation is just what we would expect if the intermediate were an open carbocation, with the mercuric ion adding in such a way as to form the more stable cation.

Rearrangements can occur, but are not common. The reaction of 3,3,-dimethyl-1-butene shown above illustrates the absence of the rearrangements that are typical of intermediate carbocations.

Mercuration can be carried out in different solvents to yield products other than alcohols. This use of *solvomercuration* as a general synthetic tool is due largely to H. C. Brown.

Problem 6A.28 (a) Predict the product of the reaction of propylene with mercuric acetate in methanol solution, followed by reduction with $NaBH_4$. (b) This is an example of an important method of synthesis of an entire class of compounds. What compounds are these? (c) What advantage does it have over an alternative method that you have already learned?

6A.45 Hydroboration–oxidation

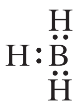
With the reagent *diborane*, $(BH_3)_2$, alkenes undergo *hydroboration* to yield alkylboranes, R_3B, which on oxidation give alcohols. For example:

$$\underset{\text{Diborane}}{(BH_3)_2} \xrightarrow{H_2C{=}CH_2} CH_3CH_2BH_2 \xrightarrow{H_2C{=}CH_2} (CH_3CH_2)_2BH \xrightarrow{H_2C{=}CH_2} \underset{\text{Triethylboron}}{(CH_3CH_2)_3B}$$

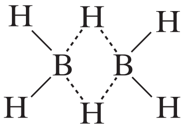
$$\underset{\text{Triethylboron}}{(CH_3CH_2)_3B} + \underset{\substack{\text{Hydrogen}\\ \text{peroxide}}}{3H_2O_2} \xrightarrow{OH^-} \underset{\text{Ethyl alcohol}}{3CH_3CH_2OH} + \underset{\text{Boric acid}}{B(OH)_3}$$

The reaction procedure is simple and convenient, the yields are exceedingly high, and, as we shall see, the products are ones difficult to obtain from alkenes in any other way.

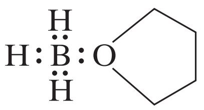
Diborane is the dimer of the hypothetical BH_3 (*borane*) and, in the reactions that concern us, acts much as though it were BH_3. Indeed, in tetrahydrofuran, one of the solvents used for hydroboration, the reagent exists as the monomer, in the form of an acid–base complex with the solvent.



Borane



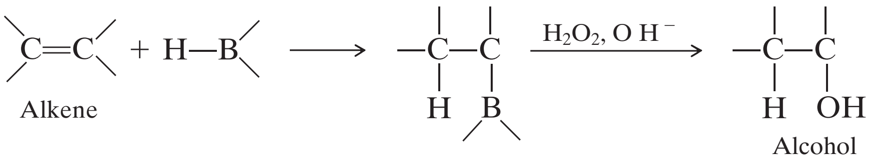
Diborane



Borane–tetrahydrofuran complex

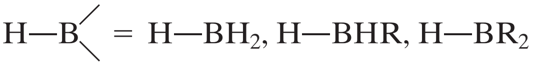
Hydroboration involves addition of BH_3 (or, in following stages, BH_2R and BHR_2) to the double bond, with hydrogen becoming attached to one doubly bonded carbon, and boron to the other. The alkylborane can then undergo oxidation, in which the boron is replaced by —OH.

Hydroboration **Oxidation**



Alkene

Alcohol



$$\text{H—B}\langle = \text{H—BH}_2, \text{H—BHR}, \text{H—BR}_2$$

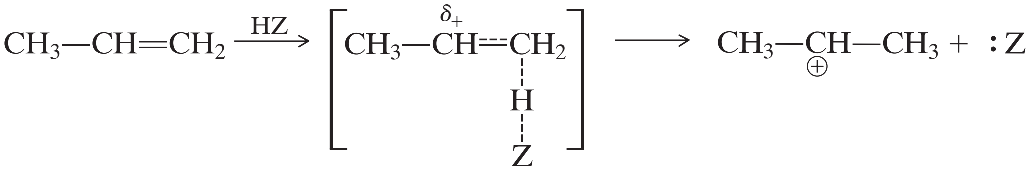
Thus, the two-stage reaction process of hydroboration–oxidation permits, in effect, the addition to the carbon–carbon double bond of the elements of H—OH.

Reaction is carried out in an ether, commonly tetrahydrofuran or “diglyme” (*di*ethylene *gly*col *me*thyl ether, $CH_3OCH_2CH_2OCH_2CH_2OCH_3$). Diborane is commercially available in tetrahydrofuran solution. The alkylboranes are not isolated, but are simply treated *in situ* with alkaline hydrogen peroxide.

6A.46 Mechanism of hydroboration (regio- and stereoselectivity of the reaction)

Much of the usefulness of hydroboration-oxidation lies in the “unusual” orientation of the hydration. The —OH takes the position occupied by boron in the intermediate alkylborane, and hence the final product reflects the orientation of the hydroboration step. But is this orientation really “unusual”?

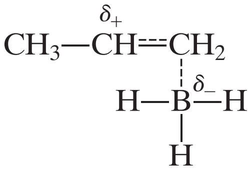
The orientation appears to be unusual because hydrogen adds to the opposite end of the double bond from where it adds in ordinary electrophilic addition. But the fundamental idea in electrophilic addition is that the *electrophilic* part of the reagent—the *acidic* part—becomes attached, using the π electrons, in such a way that the carbon being deprived of the π electrons is the one best able to stand the



$$CH_3\text{—}CH\text{=}CH_2 \xrightarrow{HZ} \left[CH_3\text{—}\overset{\delta_+}{CH}\text{=}\underset{\substack{\vdots \\ H \\ \vdots \\ Z}}{CH_2} \right] \longrightarrow CH_3\text{—}\underset{\oplus}{CH}\text{—}CH_3 + :Z$$

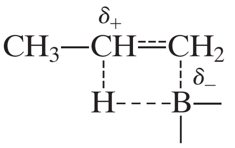
deprivation. In the addition of HZ to propylene, for example, the proton attaches itself to C–1; in that way the positive charge develops on C–2, where it can be dispersed by the methyl group. A secondary carbocation is formed instead of a primary.

Now, what is the center of acidity in BH_3? Clearly, *boron*, with only six electrons. It is not at all surprising that boron should seek out the π electrons of the double bond and begin to attach itself to carbon. In doing this, it attaches itself in such a way that the positive charge can develop on the carbon best able to accommodate it. Thus:



$$CH_3-\overset{\delta_+}{CH}=CH_2\cdots\overset{\delta_-}{B}H_3$$

Unlike ordinary electrophilic addition, however, the reaction does not proceed to give a carbocation. As the transition state is approached, the carbon that is losing the π electrons becomes itself increasingly acidic: electron-deficient boron is acidic but so, too, is electron-deficient carbon. Not too far away is a hydrogen atom held to boron by a pair of electrons. Carbon begins to take that hydrogen, with its electron pair; boron, as it gains the π electrons, is increasingly willing to release that hydrogen. Boron and hydrogen both add to the doubly bonded carbons in the same transition state:



$$\begin{array}{ccc} CH_3- & \overset{\delta_+}{CH} & = CH_2 \\ & \vdots & \vdots\ \delta_- \\ & H & \text{- - -}B- \end{array}$$

Transition state for hydroboration

In view of the basic nature of alkenes and the acidic nature of BH_3, the principal driving force of the reaction is almost certainly *attachment of boron to carbon*. In the transition state attachment of boron to C–1 has proceeded to a greater extent than attachment of hydrogen to C–2. Thus loss of (π) electrons by C–2 to the C(1)—B bond exceeds its gain of electrons from hydrogen, and so C–2, the carbon that can best accommodate the charge, has become positive.

On theoretical grounds it has been postulated that the step we have described must follow a preliminary step in which boron attaches itself to both carbon atoms, or perhaps to the π electrons.

Thus orientation of addition in hydroboration is controlled in fundamentally the same way as in two-step electrophilic addition. Hydrogen becomes attached to opposite ends of the double bond in the two reactions because it adds without electrons in one case (as a *proton*, an acid), and with electrons in the other case (as a *hydride ion*, a base).

Because of the Lowry–Brønsted treatment of acids and bases, we tend to think of hydrogen chiefly in its proton character. Actually, its hydride character has considerably more *reality*. Solid lithium hydride, for example, has an ionic crystalline lattice made up of Li^+ and H^-; by contrast, a naked unsolvated proton is not encountered by the organic chemist.

We are already familiar with the facile transfer of hydride from carbon to carbon: within a single molecule (hydride shift in rearrangements), and between molecules. Later on we shall encounter a set of remarkably versatile reducing agents (hydrides like *lithium aluminum hydride,* $LiAlH_4$, and *sodium borohydride,* $NaBH_4$) that function by transfer of hydride ion to organic molecules.

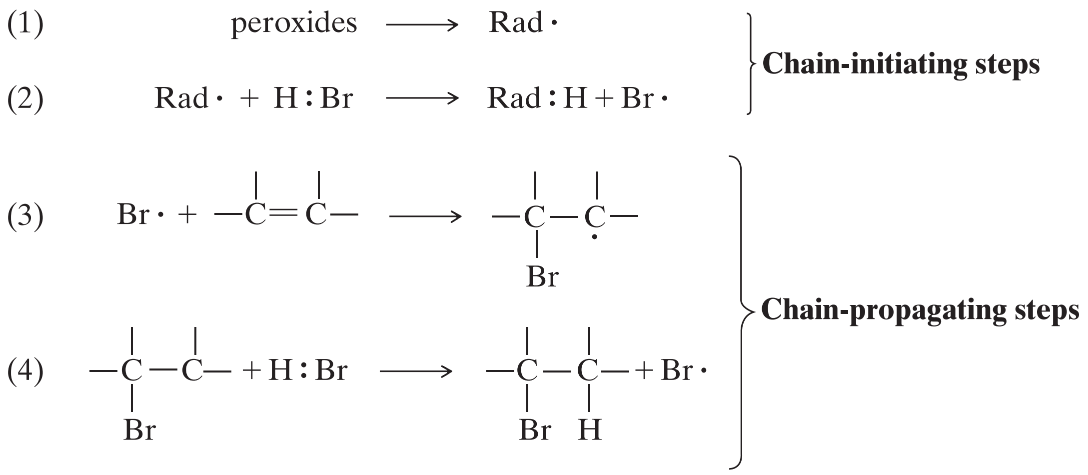
The orientation of hydroboration is affected, not just by the polar factor we have just described, but also by a steric factor: attachment of the boron moiety of the reagent (not just —BH_2, remember, but the larger —BHR and —BR_2) takes place more readily to the less crowded carbon of the double bond. Since this in general would lead to the same orientation as would the polar factor alone, it is not easy to tell which factor is in control. We can, however, expect this much: the bulkier the substituents on the alkene, the more important the steric factor; the more strongly electron-releasing or electron-withdrawing the substituents, the more important the polar factor.

6A.47 Free-radical addition. Mechanism of the peroxide-initiated addition of HBr

In the absence of peroxides, hydrogen bromide adds to alkenes in agreement with Markovnikov's rule; in the presence of peroxides, the direction of addition is exactly reversed.

To account for this *peroxide effect*, Kharasch and Mayo proposed that addition can take place by two entirely different mechanisms: Markovnikov addition by the electrophilic mechanism that we have just discussed, and anti-Markovnikov addition by a free-radical mechanism. Peroxides initiate the free-radical reaction; in their absence, addition follows the usual electrophilic path.

The essence of the mechanism is that hydrogen and bromine add to the double bond homolytically rather than heterolytically; the intermediate is a *free radical* rather than a carbocation. Like halogenation of alkanes, this is a chain reaction, this time involving addition rather than substitution.



$$\text{(1)}\quad \text{peroxides} \longrightarrow \text{Rad}\cdot$$

$$\text{(2)}\quad \text{Rad}\cdot + \text{H:Br} \longrightarrow \text{Rad:H} + \text{Br}\cdot$$

Chain-initiating steps

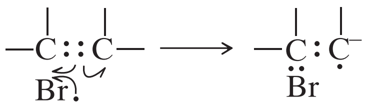
$$\text{(3)}\quad \text{Br}\cdot + -\overset{|}{C}=\overset{|}{C}- \longrightarrow -\underset{\text{Br}}{\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{\cdot}{C}}-$$

$$\text{(4)}\quad -\underset{\text{Br}}{\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{\cdot}{C}}- + \text{H:Br} \longrightarrow -\underset{\text{Br}}{\overset{|}{\underset{|}{C}}}-\underset{\text{H}}{\overset{|}{\underset{|}{C}}}- + \text{Br}\cdot$$

Chain-propagating steps

then (3), (4), (3), (4), etc.

Decomposition of the peroxide (step 1) to yield free radicals is a well-known reaction. The free radical thus formed abstracts hydrogen from hydrogen bromide (step 2) to form a bromine atom. In step (3) this bromine atom attaches itself to one of the doubly bonded carbons; in doing this, it uses its odd electron and *one* of the π electrons. The other carbon is left with an odd electron, and the alkene is thus converted into a free radical.



Free-radical addition

This free radical, like the free radical initially generated from the peroxide, abstracts hydrogen from hydrogen bromide (step 4). Addition is now complete, and a new bromine atom has been generated to continue the chain. As in halogenation of alkanes, every so often a reactive particle combines with another one, or is captured by the wall of the reaction vessel, and a chain is terminated.

The mechanism is well supported by the facts. The fact that a very few molecules of peroxide can change the orientation of addition of many molecules of hydrogen bromide strongly indicates a chain reaction. So, too, does the fact that a very few molecules of inhibitor can prevent this change in orientation. It is not surprising to find that these same compounds are efficient inhibitors of many other chain reactions. Although their exact mode of action is not understood, it seems clear that they break the chain, presumably by forming unreactive radicals.

We must not confuse the effects of peroxides, which may have been formed by the action of oxygen, with the effects of oxygen itself. Peroxides *initiate* free-radical reactions; oxygen *inhibits* free-radical reactions.

The mechanism involves addition of a bromine atom to the double bond. It is supported, therefore, by the fact that anti-Markovnikov addition is caused not only by the presence of peroxides but also by irradiation with light of a wavelength known to dissociate hydrogen bromide into hydrogen and bromine atoms.

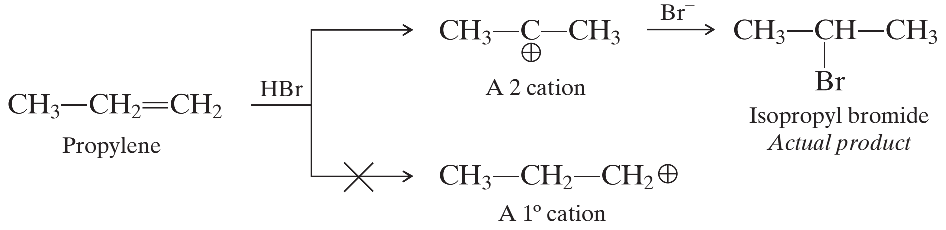
The light-catalysed addition of hydrogen bromide to several alkenes was studied by means of ESR (electron spin resonance) spectroscopy, which not only can detect the presence of free radicals at extremely low concentrations, but also can tell something about their structure. Organic free radicals were shown to be present at appreciable concentration, in agreement with the mechanism.

6A.48 Regioselectivity of free-radical addition

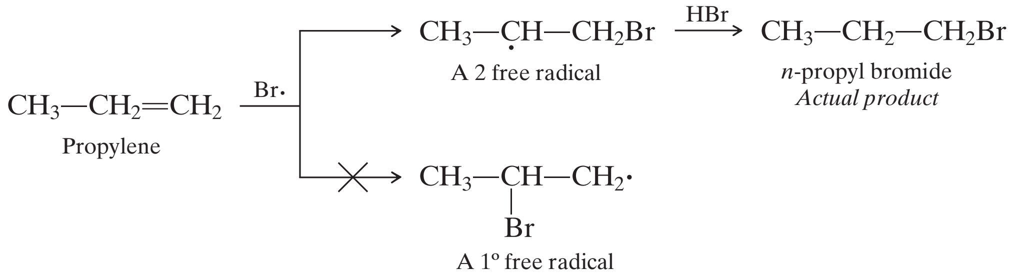
Now, how do we account for the fact that free-radical addition of hydrogen bromide occurs with orientation opposite to that of electrophilic addition? Let us compare the two kinds of addition to propylene.

Electrophilic addition yields isopropyl bromide because the isopropyl cation is formed faster than the *n*-propyl cation. This we have already accounted for: the isopropyl cation is the more stable cation, and the same factors that stabilize it stabilize the transition state leading to its formation.

Electrophilic addition: *Markovnikov orientation*



Free-radical addition: *Anti-Markovnikov orientation*

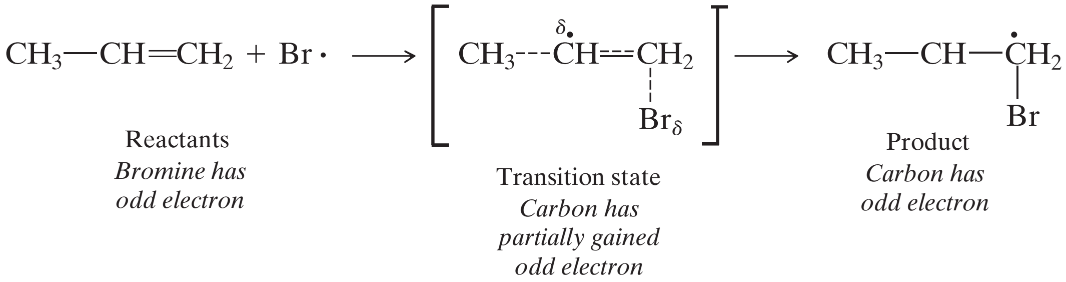


Free-radical addition yields *n*-propyl bromide because the secondary free radical is formed faster than the primary. Now, why does this happen? Study of the addition of many different free radicals to many different alkenes indicates that three factors can be involved:

(a) the stability of the free radical being formed;
(b) polar factors; and
(c) steric factors.

Let us look at each of these, using free-radical addition of HBr as our example. As always in dealing with relative rates, we must consider the transition state for the reaction, and see how its stability might be affected by each of these factors.

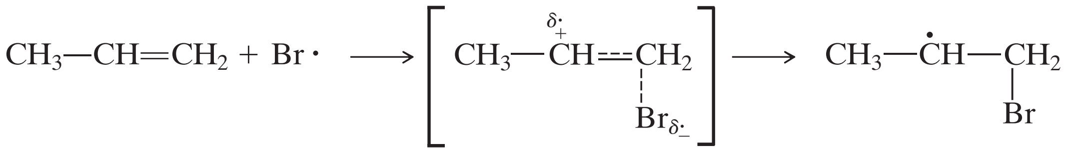
Let us begin with the **stability of the free radical being formed**. This is a factor with which we are already familiar. In the transition state, the bond between bromine and one of the carbons is partly formed. The π bond is partly broken and the other carbon has partly gained the odd electron it will carry in the intermediate



free radical. To some degree, the organic group possesses the character of the free radical it is to become. Factors that stabilize the free radical also stabilize the incipient free radical in the transition state. Thus, in our example, the secondary free radical is formed faster than the primary because it is more stable. That is one interpretation, then, and the most obvious: rate of reaction depends upon the free-radical character of the transition state.

A great many observations in other areas of free-radical chemistry have made it clear that reactions of free radicals can be affected—and sometimes even controlled—by **polar factors**. Although free radicals are neutral, they have certain tendencies to gain or lose electrons, and hence they partake of the character of electrophilic or nucle-ophilic reagents. The transition states for their reactions can be polar, with the radical moiety acquiring a partial negative or positive charge at the expense of the substrate.

Now, because of its electronegativity we would expect the bromine atom to be *electrophilic*. In the transition state, bromine holds more than its share of electrons, at the expense of the alkene. The transition state is thus a polar one, and the substrate moiety has not only free-radical character but also carbocation character.



$$CH_3{-}CH{=}CH_2 + Br\cdot \longrightarrow \left[CH_3{-}\overset{\overset{\delta\cdot}{+}}{C}H{=\!=}\underset{\underset{Br_{\underset{-}{\delta\cdot}}}{\vdots}}{C}H_2 \right] \longrightarrow CH_3{-}\overset{\bullet}{C}H{-}\underset{\underset{Br}{|}}{C}H_2$$

Transition state
Bromine has negative charge;
carbon has positive charge

The stability of the transition state, and hence the rate of reaction, depends upon the ability of the substrate not only to accommodate the odd electron, but also to accommodate the partial positive charge.

The polar factor will thus favor the orientation that places the charge on the carbon that can best accommodate it. In our example, addition of Br· to C–1 is favored, since in this way positive charge develops on C–2 rather than C–1; and secondary carbocation character is more stabilizing than primary.

Finally, there is the **steric factor**. Addition of a free radical to the terminal carbon, C–1, is less hindered than addition to C–2; the transition state is less crowded, and therefore more stable.

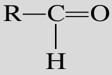
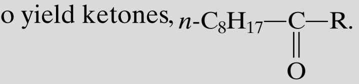
In the particular reaction we are studying here, free-radical addition of hydrogen bromide, all three factors would be expected to favor formation of the same intermediate and hence bring about the same orientation. The question is: what is the relative importance of each? Which, if any, is the controlling factor?

This is a difficult question to answer. There is little doubt that each factor exists and, in the proper system, can be dominant. Free-radical addition to conjugated dienes and styrenes is clearly controlled by the stability of the radical being formed. Orientation of addition of very bulky radicals like $\cdot CBr_3$ is very probably determined by steric factors. Addition of powerfully electrophilic radicals like $\cdot CF_3$ is subject to marked polar effects—particularly if the alkene, too, contains substituents with strongly electron-withdrawing or electron-releasing tendencies.

But each of these examples is an extreme case: a very stable radical is being formed; a very bulky or a very electrophilic radical is the reagent. What does this tell us about the addition of the bromine atom—only moderately electrophilic and not very big—to a simple alkene, with formation of the only moderately stable secondary radical? Probably, just this: that all three factors may well be at work.

Orientation in both electrophilic and free-radical addition of hydrogen bromide is determined by preferential formation of the more highly substituted particle, whether *carbocation or free radical. Orientation is reversed simply because the hydrogen adds first in the electrophilic reaction, and bromine adds first in the radical reaction.*

Problem 6A.29 In the presence of a trace of peroxide or under the influence of ultraviolet light, 1-octene reacts:

(a) with $CHCl_3$ to form 1,1,1-trichlorononane;
(b) with $CHBr_3$ to form 1,1,3-tribromononane;
(c) with $CBrCl_3$ to form 1,1,1-trichloro-3-bromononane;
(d) with H—S—CH_2COOH (thioglycolic acid) to yield n-C_8H_{17}—S—CH_2COOH;
(e) with aldehydes,  $\underset{\displaystyle H}{R\text{—}\overset{}{C}\text{=}O}$, to yield ketones,  $n\text{-}C_8H_{17}\text{—}\underset{\displaystyle \overset{\|}{O}}{C}\text{—}R$.

Show all steps of a likely mechanism for these reactions.

Problem 6A.30 From the addition of CCl_4 to alkenes, $RCHPCH_2$, there is obtained not only $RCHClCH_2CCl_3$, but also  $RCHClCH_2\text{—}\underset{\displaystyle H}{C}HCH_2CCl_3$. *Using only the kinds of reactions you have already encountered*, suggest a mechanism for the formation of this second product.

Problem 6A.31 In the dark at room temperature, a solution of chlorine in tetrachloroethylene can be kept for long periods with no sign of reaction. When irradiated with ultraviolet light, however, the chlorine is rapidly consumed, with the formation of hexachloroethane; many molecules of product are formed for each photon of light absorbed; this reaction is slowed down markedly when oxygen is bubbled through the solution.

(a) How do you account for the absence of reaction in the dark? (b) Outline all steps in the most likely mechanism for the photochemical reaction. Show how it accounts for the facts, including the effect of oxygen.

6A.49 Free-radical polymerization of alkenes

When ethylene is heated under pressure with oxygen, there is obtained a compound of high molecular weight (about 20 000), which is essentially an alkane with a very long chain. This compound is made up of many ethylene units and

$$nCH_2{=}CH_2 \xrightarrow{O_2,\text{ heat, pressure}} \sim\!CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2\!\sim$$

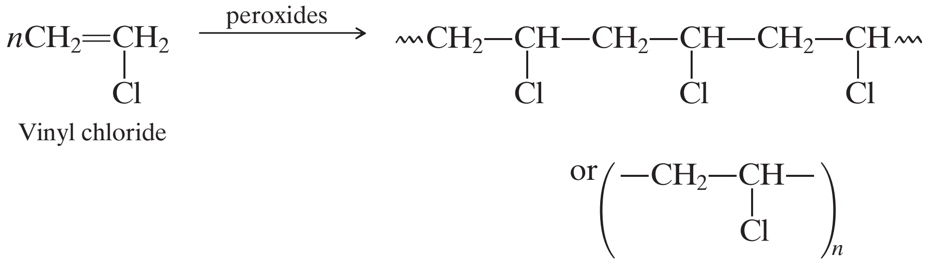
$$\text{or } (\text{—}CH_2CH_2\text{—})_n$$

Polyethylene

hence is called *polyethylene*. It is familiar to most of us as the plastic material of packaging films.

The formation of polyethylene is a simple example of the process called **polymerization**: the *joining together of many small molecules to form very large molecules*. The compound composed of these very large molecules is called a **polymer** (Greek: *poly* + *meros*, many parts). The simple compounds from which polymers are made are called **monomers** (*mono*, one).

Polymerization of substituted ethylenes yields compounds whose structures contain the long chain of polyethylene, with substituents attached at more or less regular intervals. For example, vinyl chloride yields *poly*(*vinyl chloride*), used to make phonograph records, plastic pipe, and—when plasticized with high-boiling esters—raincoats, shower curtains, and coatings for metals and upholstery fabrics.



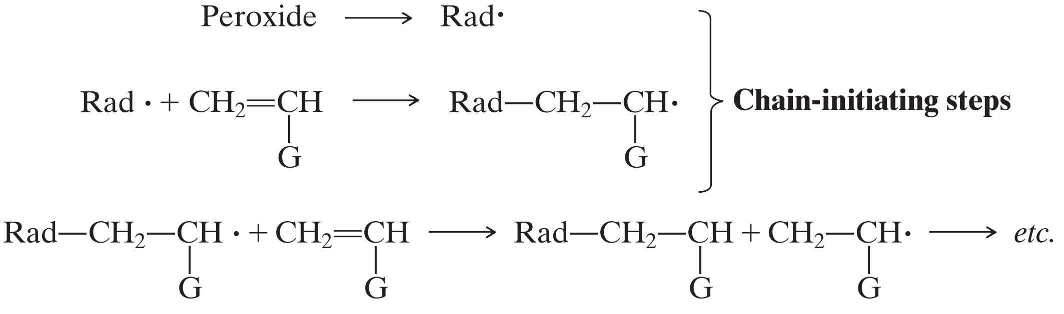
$$n\mathrm{CH_2{=}}\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{CH_2}} \xrightarrow{\text{peroxides}} \sim\mathrm{CH_2{-}}\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{CH}}\mathrm{{-}CH_2{-}}\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{CH}}\mathrm{{-}CH_2{-}}\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{CH}}\sim \quad \text{or} \left(\mathrm{{-}CH_2{-}}\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{CH}}\mathrm{{-}}\right)_n$$

Vinyl chloride

Poly(vinyl chloride)

Many other groups (e.g., $—COOCH_3$, $— CH_3$, $—C_6H_5$) may be attached to the doubly bonded carbons. These substituted ethylenes polymerize more or less readily, and yield plastics of widely differing physical properties and uses, but the polymerization process and the structure of the polymer are basically the same as for ethylene or vinyl chloride.

Polymerization requires the presence of a small amount of an **initiator**. Among the commonest of these initiators are peroxides, which function by breaking down to form a free radical. This radical adds to a molecule of alkene, and in doing so generates another free radical. This radical adds to another molecule of alkene to generate a still larger radical, which in turn adds to another molecule of alkene, and so on. Eventually the chain is terminated by steps, such as union of two radicals, that consume but do not generate radicals.



$$\text{Peroxide} \longrightarrow \text{Rad}\cdot$$

$$\text{Rad}\cdot + \mathrm{CH_2{=}}\underset{\substack{|\\ \mathrm{G}}}{\mathrm{CH}} \longrightarrow \text{Rad}\mathrm{{-}CH_2{-}}\underset{\substack{|\\ \mathrm{G}}}{\mathrm{CH}}\cdot$$

Chain-initiating steps

$$\text{Rad}\mathrm{{-}CH_2{-}}\underset{\substack{|\\ \mathrm{G}}}{\mathrm{CH}}\cdot + \mathrm{CH_2{=}}\underset{\substack{|\\ \mathrm{G}}}{\mathrm{CH}} \longrightarrow \text{Rad}\mathrm{{-}CH_2{-}}\underset{\substack{|\\ \mathrm{G}}}{\mathrm{CH}} + \mathrm{CH_2{-}}\underset{\substack{|\\ \mathrm{G}}}{\mathrm{CH}}\cdot \longrightarrow \textit{etc.}$$

Chain-propagating step

This kind of polymerization, each step of which consumes a reactive particle and produces another, similar particle, is an example of *chain-reaction polymerization*. We shall encounter chain-reaction polymerization that takes place, not by way of free radicals, but by way of organic ions, or within the coordination sphere of a transition metal complex. We shall also encounter *step-reaction polymerization*, which involves a series of reactions each of which is essentially independent of the others.

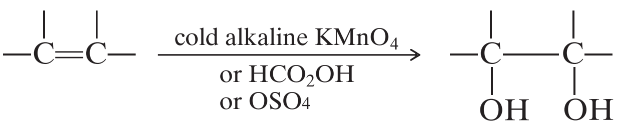
Problem 6A.32 Give the structure of the monomer from which each of the following polymers would most likely be made:

(a) Orlon (fibers, fabrics), $\sim\sim\mathrm{CH_2CH(CN)CH_2CH(CN)}\sim\sim$;
(b) Saran (packaging film, seat covers), $\sim\sim\mathrm{CH_2CCl_2CH_2CCl_2}\sim\sim$;
(c) Teflon (chemically resistant articles), $\sim\sim\mathrm{CF_2CF_2CF_2CF_2}\sim\sim$.

Problem 6A.33 Can you suggest a reason why polymerization should take place in a way ("head-to-tail") that yields a polymer with regularly alternating groups?

6A.50 Hydroxylation. Formation of 1,2-diols

Certain oxidizing agents convert alkenes into **1,2-diols**: dihydroxy alcohols containing the two —OH groups on adjacent carbons. (They are also known as *glycols*.) The reaction amounts to addition of two hydroxyl groups to the double bond.



$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow[\text{or } HCO_2OH \text{ or } OSO_4]{\text{cold alkaline } KMnO_4} -\underset{OH}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-$$

A 1,2-diol

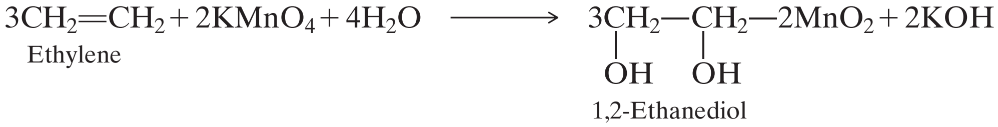
Of the numerous oxidizing agents that bring about hydroxylation, three of the most commonly used are (a) cold alkaline potassium *permanganate* ($KMnO_4$), and (b) *peroxy acids*, such as peroxyformic acid (HCO_2OH). (c) OSO_4 in pyridine.

Since permanganate is one of the most important oxidizing agents in organic chemistry, we should perhaps become familiar now with certain of its general characteristics. It is a powerful oxidizing agent, and conditions must be carefully selected—acidity or alkalinity, temperature, quantity of the reagent used—to avoid over-oxidation, that is, taking reaction past the oxidation stage we want. A major problem has been that of solubility: one must get the water-soluble permanganate into contact with the very often water-insoluble substrate. Yet many solvents commonly used to bring polar and non-polar reagents together—alcohols, for example—are themselves oxidized by permanganate. In recent years, this problem has been solved in part by use of phase-transfer catalysts. Quaternary ammonium ions can carry permanganate ions from an aqueous layer into a non-aqueous layer (benzene, say, or dichloromethane) where the substrate awaits. Crown ethers can complex potassium ions and thus make solid $KMnO_4$ soluble in benzene; the resulting "purple benzene" is an excellent oxidizing agent.

Hydroxylation with permanganate carried out by stirring together at room temperature the alkene and the aqueous permanganate solution: either neutral—the reaction produces OH^- —or, better, slightly alkaline. Higher yields are sometimes, obtained by use of "purple benzene" solutions. *Mild conditions* are the key consideration. Heat and the addition of acid are avoided, since these more vigorous conditions promote further oxidation of the diol, with cleavage of the carbon–carbon double bond.

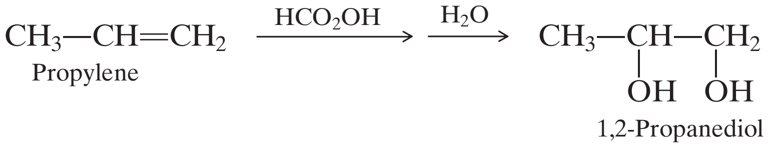
Hydroxylation with peroxyformic acid is carried out by allowing the alkene to stand with a mixture of hydrogen peroxide and formic acid, HCOOH, for a few hours, and then heating the product with water to hydrolyse certain intermediate compounds.

For example:



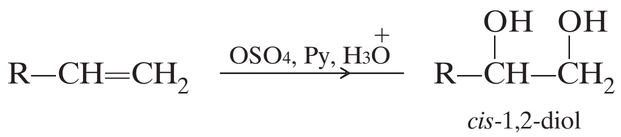
$$\underset{\text{Ethylene}}{3CH_2{=}CH_2} + 2KMnO_4 + 4H_2O \longrightarrow 3\underset{\mathrm{OH}}{\underset{|}{CH_2}}-\underset{\mathrm{OH}}{\underset{|}{CH_2}}-2MnO_2 + 2KOH$$

1,2-Ethanediol



$$\underset{\text{Propylene}}{CH_3-CH{=}CH_2} \xrightarrow{HCO_2OH} \xrightarrow{H_2O} CH_3-\underset{\mathrm{OH}}{\underset{|}{CH}}-\underset{\mathrm{OH}}{\underset{|}{CH_2}}$$

1,2-Propanediol



$$R-CH{=}CH_2 \xrightarrow{OSO_4,\ Py,\ H_3\overset{+}{O}} R-\overset{\mathrm{OH}}{\overset{|}{CH}}-\overset{\mathrm{OH}}{\overset{|}{CH_2}}$$

cis-1,2-diol

Hydroxylation of alkenes is the most important method for the synthesis of 1,2-diols, with the special feature of permitting *stereochemical control* by the choice of reagent.

Oxidation by permanganate is the basis of a very useful analytical test known as the Baeyer test. *Hydroxylation by osmolysis and Prevost oxidation.*

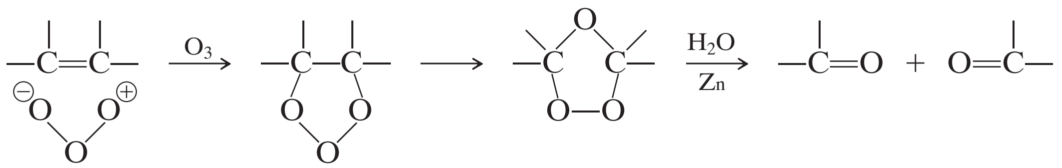
6A.51 Cleavage: determination of structure by degradation. Ozonolysis (1,3-dipolar cycloaddition)

So far we have discussed the addition reactions of alkenes; we shall take up their substitution reactions. But there is a third general kind of alkene reaction, **cleavage:** a reaction in which the double bond is completely broken and the alkene molecule converted into two smaller molecules.

The classical reagent for cleaving the carbon–carbon double bond is ozone. **Ozonolysis** (cleavage by ozone) is carried out in two stages: first, addition of ozone to the double bond to form an *ozonide*; and second, hydrolysis of the ozonide to yield the cleavage products.

Ozone gas is passed into a solution of the alkene in some inert solvent like carbon tetrachloride; evaporation of the solvent leaves the ozonide as a viscous oil. This unstable, explosive compound is not purified, but is treated directly with water, generally in the presence of a reducing agent.

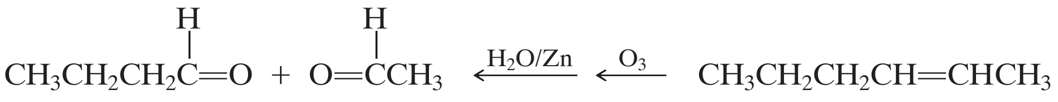
In the cleavage products a doubly bonded oxygen is found attached to each of the originally doubly bonded carbons:



Alkene Molozonide Ozonide Cleavage products (Aldehydes and ketones)

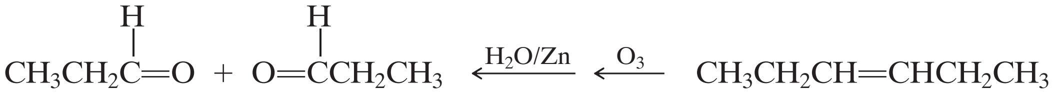
These compounds containing the C=O group are aldehydes and ketones, which we have already encountered as products of oxidation of alcohols. The function of the reducing agent, which is frequently zinc dust, is to prevent formation of hydrogen peroxide, which would otherwise react with the aldehydes and ketones. (Aldehydes, RCHO, are often converted into acids, RCOOH, for ease of isolation.)

Knowing the number and arrangement of carbon atoms in these aldehydes and ketones, we can work back to the structure of the original alkene. For example, for three of the isomeric hexylenes:



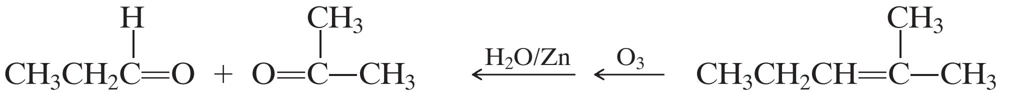
$$CH_3CH_2CH_2\overset{H}{C}{=}O + O{=}\overset{H}{C}CH_3 \xleftarrow{H_2O/Zn} \xleftarrow{O_3} CH_3CH_2CH_2CH{=}CHCH_3$$

Aldehydes 2-Hexene



$$CH_3CH_2\overset{H}{C}{=}O + O{=}\overset{H}{C}CH_2CH_3 \xleftarrow{H_2O/Zn} \xleftarrow{O_3} CH_3CH_2CH{=}CHCH_2CH_3$$

Aldehydes 3-Hexene

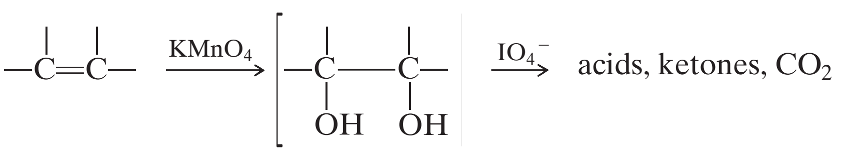


$$CH_3CH_2\overset{H}{C}{=}O + O{=}\overset{CH_3}{C}{-}CH_3 \xleftarrow{H_2O/Zn} \xleftarrow{O_3} CH_3CH_2CH{=}\overset{CH_3}{C}{-}CH_3$$

Aldehydes Ketone 2-Methyl-2-pentene

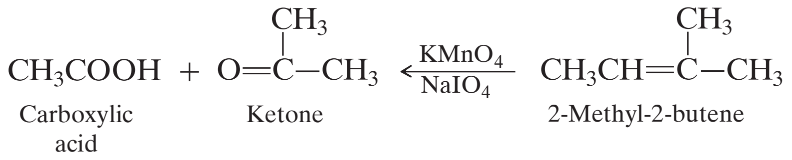
One general approach to the determination of the structure of an unknown compound is **degradation**, the breaking down of the unknown compound into a number of smaller, more easily identifiable fragments. Ozonolysis is a typical means of degradation.

Another method of degradation that gives essentially the same information is oxidation by sodium periodate ($NaIO_4$) in the presence of *catalytic amounts* of permanganate. Periodate, we shall find, is much used for cleavage of 1,2-diols. The permanganate hydroxylates the double bond to give the 1,2-diol, and is itself reduced to the manganate state. The periodate then (a) cleaves the 1,2-diol and (b) oxidizes manganate back up to permanganate, and the reaction continues.



$$-\overset{|}{C}{=}\overset{|}{C}- \xrightarrow{KMnO_4} \left[-\underset{OH}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \right] \xrightarrow{IO_4^-} \text{acids, ketones, } CO_2$$

Carboxylic acids, RCOOH, are generally obtained instead of aldehydes, RCHO. A terminal $=CH_2$ group is oxidized to CO_2. For example:



$$CH_3COOH + O{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_3 \xleftarrow[NaIO_4]{KMnO_4} CH_3CH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_3$$

Carboxylic acid Ketone 2-Methyl-2-butene

$$CH_3CH_2CH_2COOH + CO_2 \xleftarrow[NaIO_4]{KMnO_4} CH_3CH_2CH_2CH{=}CH_2$$

Carboxylic acid Carbon dioxide 1-Pentene

Problem 6A.34 What products would you expect from each of the dimers of iso-butylene upon cleavage by: (a) ozonolysis; (b) $NaIO_4/KMnO_4$?

EXERCISE

1. Give the structural formula of:

(a) 3,6-dimethyl-1-octene
(b) 3-chloropropene
(c) 2,4,4-trimethyl-2-pentene
(d) *trans*-3,4-dimethyl-3-hexene
(e) (*Z*)-3-chloro-4-methyl-3-hexene
(f) (*E*)-1-deuterio-2-chloropropene
(g) (*R*)-3-bromo-1-butene
(h) (*S*)-*trans*-4-methyl-2-hexene

2. Draw out the structural formula and give the IUPAC name of:

(a) isobutylene
(b) *cis*-$CH_3CH_2CH{=}CHCH_2CH_3$
(c) $(CH_3)_3CCH{=}CH_2$
(d) *trans*-$(CH_3)_2CHCH{=}CHCH(CH_3)_2$
(e) $(CH_3)_2CHCH_2CH{=}C(CH_3)_2$
(f) $(CH_3CH_2)_2C{=}CH_2$

3. Indicate which of the following compounds show geometric (*cis-trans*) isomerism, draw the isomeric structures, and specify each as *Z* or *E*.

(a) 1-butene
(b) 2-butene
(c) 1,1-dichloroethene
(d) 1,2-dichloroethene
(e) 2-methyl-2-butene
(f) 1-pentene
(g) 2-pentene
(h) 1-chloropropene
(i) 1-chloro-2-methyl-2-butene
(j) 4-ethyl-3-methyl-3-hexene
(k) 2,4-hexadiene
($CH_3CH{=}CHCH{=}CHCH_3$)

4. In which of the following will *cis*-3-hexene differ from *trans*-3-hexene?

(a) b.p.
(b) m.p.
(c) adsorption on alumina
(d) infrared spectrum
(e) dipole moment
(f) refractive index
(g) rate of hydrogenation
(h) product of hydrogenation
(i) solubility in ethyl alcohol
(j) density
(k) retention time in gas chromatography

(1) Which *one* of the above would absolutely prove the configuration of each isomer?

5. Write balanced equations for preparation of propylene from:

(a) $CH_3CH_2CH_2OH$ (*n*-propyl alcohol)
(b) $CH_3CHOHCH_3$ (isopropyl alcohol)
(c) isopropyl chloride
(d) *n*-propyl tosylate (use Ts for tosyl)
(e) 1,2-dibromopropane
(f) the alkyne, $CH_3C{\equiv}CH$

6. Give structures of the products expected from dehydrohalogenation of:

(a) 1-bromohexane
(b) 2-bromohexane
(c) 1-bromo-2-methylpentane
(d) 2-bromo-2-methylpentane
(e) 3-bromo-2-methylpentane
(f) 4-bromo-2-methylpentane
(g) 1-bromo-4-methylpentane
(h) 3-bromo-2,3-dimethylpentane

7. In those cases in Problem 6 where more than one product can be formed, predict the *major* product.

8. Which alcohol of each pair would you expect to be more easily dehydrated?

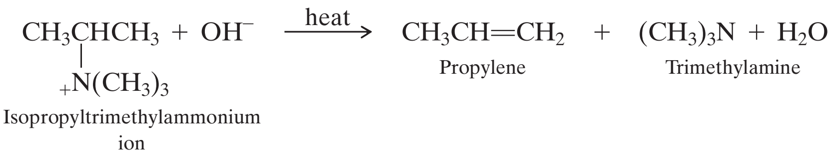
(a) $CH_3CH_2CH_2CH_2CH_2OH$ or $CH_3CH_2CH_2CHOHCH_3$
(b) $(CH_3)_2C(OH)CH_2CH_3$ or $(CH_3)_2CHCHOHCH_3$
(c) $(CH_3)_2CHC(OH)(CH_3)_2$ or $(CH_3)_2CHCH(CH_3)CH_2OH$

9. Arrange the compounds of each set in order of reactivity toward dehydrohalogenation by strong base:

(a) 2-bromo-2-methylbutane, 1-bromopentane, 2-bromopentane, 3-bromopentane
(b) 1-bromo-3-methylbutane, 2-bromo-2-methylbutane, 3-bromo-2-methylbutane
(c) 1-bromobutane, 1-bromo-2,2-dimethylpropane, 1-bromo-2-methylbutane, 1-bromo-3-methylbutane

10. When neopentyl alcohol, $(CH_3)_3CCH_2OH$, is heated with acid, it is slowly converted into an 85:15 mixture of two alkenes of formula C_5H_{10}. What are these alkenes, and how are they formed? Which one would you think is the major product, and why?

11. On treatment with strong base, quaternary ammonium ions, R_4N^+, undergo elimination. For example:



$$\underset{\substack{|\\ {}_{+}N(CH_3)_3}}{CH_3CHCH_3} + OH^- \xrightarrow{heat} CH_3CH{=}CH_2 + (CH_3)_3N + H_2O$$

Isopropyltrimethylammonium ion

Propylene

Trimethylamine

The corresponding ammonium ions RNH_3+ do not, although the basicity of NH_3 is not very different from that of $(CH_3)_3N$. How do you account for this difference in behavior?

12. When 3,3-dimethyl-1-butene is treated with hydrogen chloride there is obtained a mixture of 3-chloro-2,2-dimethylbutane and 2-chloro-2,3-dimethylbutane. What does the formation of the second product suggest to you? Propose a likely mechanism for this reaction, which is an example of *electrophilic addition*, the most important class of reactions undergone by alkenes.

13. Outline all steps in a possible laboratory synthesis of each of the following compounds from alcohols of four carbons or fewer.

(a) isobutylene
(b) 1-butene
(c) *tert*-butyl *n*-propyl ether
(d) *sec*-butyl isobutyl ether

14. Give structures and names of the products (if any) expected from reaction of isobutylene with:

(a) H_2,Ni
(b) Cl_2
(c) Br_2
(d) I_2
(e) HBr
(f) HBr (peroxides)
(g) HI
(h) HI (peroxides)
(i) H_2SO_4
(j) H_2O, H^+
(k) Br_2,H_2O
(l) Br_2 + NaCl(aq)
(m) $H_2SO_4(\longrightarrow C_8H_{16})$
(n) isobutane + HF
(o) cold alkaline $KMnO_4$
(p) hot $KMnO_4$
(q) HCO_2OH
(r) O_3; then Zn, H_2O
(s) $Hg(OAc)_2$,H_2O; $NaBH_4$
(t) $(BH_3)_2$;H_2O_2,OH^-

15. Which alkene of each pair would you expect to be more reactive toward addition of H_2SO_4?

(a) ethylene or propylene
(b) ethylene or vinyl bromide
(c) propylene or 2-butene
(d) 2-butene or isobutylene
(e) vinyl chloride or 1,2-dichloroethene
(f) 1-pentene or 2-methyl-1-butene
(g) ethylene or $CH_2{=}CHCOOH$
(h) propylene or 3,3,3-trifluoropropene

16. Give structures and names of the principal products expected from addition of HI to:

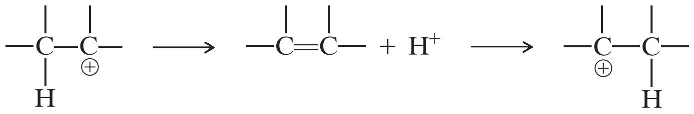
(a) 2-butene
(b) 2-pentene
(c) 2-methyl-1-butene
(d) 2-methyl-2-butene
(e) 3-methyl-1-butene (two products)
(f) vinyl bromide
(g) 2,3-dimethyl-1-butene
(h) 2,2,4-trimethyl-2-pentene

17. Consider the possible synthesis of the eight isomeric pentyl alcohols by oxymercuration–demercuration and hydroboration–oxidation. For each alcohol show the alkene or alkenes (if any) from which it could be made in pure form, and the synthesis method that would be used in each case.

18. Account for the fact that addition of $CBrCl_3$ in the presence of peroxides takes place faster to 2-ethyl-1-hexene than to 1-octene.

19. (a) In methyl alcohol solution (CH_3OH), bromine adds to ethylene to yield not only ethylene bromide but also $Br{-}CH_2CH_2{-}OCH_3$. How can you account for this? Write equations for all steps. (b) Predict the products formed under the same conditions from propylene.

20. As an alternative to the one-step 1,2-hydride shift, one might instead propose—in view of the reactions we have studied in this chapter—that carbocations rearrange by a two-step mechanism, involving the intermediate formation of an alkene:

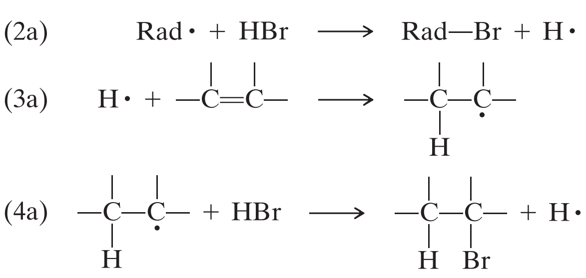


When (by a reaction we have not yet taken up) the isobutyl cation was generated in D_2O containing D_3O^+, there was obtained *tert*-butyl alcohol containing *no* deuterium attached to carbon. How does this experiment permit one to rule out the two-step mechanism?

21. Identify the acids and bases (Lewis or Lowry–Brønsted) in each of the following reactions:

(a) $Li^+H^- + H_2O \longrightarrow H_2 + Li^+OH^-$
(b) $(C_2H_5)_3B + NH_3 \longrightarrow (C_2H_5)_3{:}\overset{-}{B}\overset{+}{N}H_3$
(c) $(BH_3)_2 + 2(CH_3)_3N \longrightarrow 2H_3{:}\overset{-}{B}\overset{+}{N}(CH_3)_3$
(d) $2Li^+H^- + (BH_3)_2 \longrightarrow 2Li^+BH_4^-$

22. A mechanism was presented for free-radical addition of hydrogen bromide. Equally consistent with the evidence given there is the following alternative mechanism:



(2a) $\text{Rad}\cdot + HBr \longrightarrow \text{Rad}{-}Br + H\cdot$

then (3a), (4a), (3a), (4a), etc.

(a) In steps (2a) and (4a) an alkyl radical abstracts bromine instead of hydrogen from hydrogen bromide. On the basis of homolytic bond dissociation energies, is this mechanism more or less likely? Explain.

(b) The ESR study showed that the intermediate free radical from a given alkene is the *same* whether HBr or DBr (deuterium bromide) is being added to the double bond. Explain how this evidence permits a definite choice between mechanism (2a)–(4a) and mechanism (2)–(4).

23. (a) Write all steps in the free-radical addition of HBr to propylene, (b) Write all steps that would be involved in the free-radical addition of HCl to propylene.

(c) List ΔH for each reaction in (a) and (b). Assume the following homolytic bond dissociation energies: π bond, 51 kcal; 1° R—Br, 69 kcal; 1° R—Cl, 82 kcal; 2° R—H, 95 kcal.

(d) Suggest a possible reason why the peroxide effect is observed for HBr but not for HCl.

24. When isobutylene and chlorine are allowed to react in the dark at 0 °C in the absence of peroxides, the principal product is not the addition product but methallyl chloride (3-chloro-2-methyl-1-propene). Bubbling oxygen through the reaction mixture produces no change.

This reaction was carried out with labeled isobutylene ([1-^{14}C]2-methyl-1-propene, $(CH_3)_2C{=}^{14}CH_2$), and the methallyl chloride contained was collected, purified, and subjected to ozonolysis. Formaldehyde ($H_2C{=}O$) and chloroacetone ($ClCH_2COCH_3$) were obtained; all (97% or more) of the radioactivity was present in the chloroacetone.

(a) Give the structure, including the position of the isotopic label, of the methallyl chloride obtained, (b) Judging from the evidence, is the reaction ionic or free-radical? (c) Using only steps with which you are already familiar, outline a mechanism that accounts for the formation of this product, (d) Can you suggest one reason why isobutylene is more prone than 1- or 2-butene to undergo this particular reaction? (e) Under similar conditions, and in the presence of oxygen, 3,3-dimethyl-1- butene yields mostly the addition product, but also a small yield of 4-chloro-2,3-dimethyl-1-butene. In light of your answer to (c) how do you account for the formation of this minor product?

25. When treated with bromine and water, allyl bromide gives chiefly (80%) the primary alcohol, $CH_2BrCHBrCH_2OH$, in contrast to propylene, which gives the secondary alcohol, $CH_3CHOHCH_2Br$. In light of the discussion, can you suggest an explanation for this difference in orientation?

26. When ethylene is alkylated by isobutane in the presence of acid, there is obtained, not neohexane, $(CH_3)_3CCH_2CH_3$, but chiefly 2,3-dimethylbutane. Account in detail for the formation of this product.

27. Like other oxygen-containing compounds, *n*-butyl *tert*-butyl ether dissolves in cold concentrated H_2SO_4. On standing, however, an acid-insoluble layer, made up of high-boiling hydrocarbon material, slowly separates from the solution. What is this material likely to be, and how is it formed?

28. (a) Hydration of either 2-methyl-1-butene or 2-methyl-2-butene yields the same alcohol. Which alcohol would you expect this to be? Showing all steps in the reactions, explain your answer.

(b) Each of these alkenes *separately* was allowed to react with aqueous HNO_3. When hydration was about half over, reaction was interrupted and unconsumed alkene was recovered. In each case, *only* the original alkene was recovered; there was *none* of its isomer present.

How do you interpret this finding? What is its fundamental significance to the mechanism of electrophilic addition?

29. Give the structure of the alkene that yields on ozonolysis:

(a) $CH_3CH_2CH_2CHO$ and HCHO

(b) 

$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}CHO$ and CH_3CHO

(c) Only $CH_3{-}CO{-}CH_3$

(d) CH_3CHO and HCHO and $OHC{-}CH_2{-}CHO$

(e) Only $OHC{-}CH_2CH_2CH_2{-}CHO$ (*Think hard.*)

(f) What would each of these alkenes yield upon cleavage by $NaIO_4/KMnO_4$?

30. Describe simple chemical tests that would distinguish between:

(a) isobutane and isobutylene
(b) 2-hexene and *tert*-butyl bromide
(c) 2-chloropentane and *n*-heptane
(d) *tert*-pentyl alcohol and 2,2-dimethylhexane
(e) diisopropyl ether and diallyl ether
(f) *n*-propyl alcohol and allyl alcohol ($CH_2{=}CHCH_2OH$)
(g) *sec*-butyl alcohol and *n*-heptane
(h) 1-octene and *n*-pentyl alcohol
(i) allyl bromide and 1-hexene
(j) divinyl ether and diethyl ether
(k) *tert*-butyl alcohol, *tert*-butyl chloride, and 2-hexene
(l) 2-chloroethanol, 1,2-dichloroethane, and 1,2-ethanediol
(m) *n*-pentyl alcohol, *n*-pentane, 1-pentene, and *n*-pentyl bromide

Tell exactly what you would *do* and *see*. (Qualitative elemental analysis is a simple chemical test; degradation is not.)

31. Assign structures to the compounds A through J.

(a) ethylene + $Cl_2(aq) \longrightarrow$ A (C_2H_5OCl)
A + $NaHCO_3(aq) \longrightarrow$ B ($C_2H_6O_2$)
(b) ethylene + $Cl_2(aq) \longrightarrow$ A (C_2H_5OCl)
A + $HNO_3 \longrightarrow$ C ($C_2H_3O_2Cl$)
C + $H_2O \longrightarrow$ D
(c) allyl alcohol + $Br_2/CCl_4 \longrightarrow$ E ($C_3H_6OBr_2$)
E + $HNO_3 \longrightarrow$ F ($C_3H_4O_2Br_2$)
F + Zn $\longrightarrow$ G ($C_3H_4O_2$)
(d) $CH_2{=}CH_2 + Cl_2/H_2O \longrightarrow$ A (C_2H_5OCl)
A + H_2SO_4 + heat $\longrightarrow$ H ($C_4H_8O_2Cl_2$)
H + alc. KOH $\longrightarrow$ I (C_4H_6O)
(e) $CH_2{=}CHCH_2CH_2CH_2OH + Hg(OAc)_2 + H_2O$, then $NaBH_4 \longrightarrow$ J ($C_5H_{10}O$)

32. A hydrocarbon, K, adds one mole of hydrogen in the presence of a platinum catalyst to form *n*-hexane. When K is oxidized vigorously with $KMnO_4$ a single carboxylic acid, containing three carbon atoms, is isolated. Give the structure and name of K. Show your reasoning, including equations for all reactions.

33. Give the structure of the alkene you would start with, and the reagents and any special conditions necessary to convert it into each of these products:

(a) *tert*-butyl alcohol
(b) isopropyl iodide
(c) isobutyl bromide
(d) 1-chloro-2-methyl-2-butanol
(e) 2-methylpentane
(f) 2,3-dimethyl-2,3-butanediol

34. Starting with alcohols of four carbons or fewer, outline all steps in a possible synthesis of each of the following:

(a) 1,2-dichloropropane
(b) 1,2-dichlorobutane
(c) 1,2-propanediol
(d) 1-bromo-2-methyl-2-propanal
(e) isobutane
(f) ethyl isopropyl ether
(g) ethyl isopropyl ether by a second method

6B. Dienes
(*Conjugation and Resonance*)

6B.1 The carbon–carbon double bond as a substituent

We saw the double bond as a place in the alkene molecule where reaction can occur: electrophilic or free-radical addition. But that is only part of the story. Besides providing a site for addition, the double bond exerts powerful effects on certain reactions taking place elsewhere on the molecule. Although suffering no permanent change itself, the double bond plays an essential role in determining the course of reaction. It is this part of alkene chemistry that we shall take up in this chapter: the carbon–carbon double bond, not as a functional group, but *as a substituent*.

Now, at this point in our study we have discussed several families of compounds: alkanes, alkyl halides (and related compounds), alcohols, ethers, and alkenes. We have seen some of the chemical properties that are associated with the functional group of each of these families: C—H of alkanes, —X and —OH of alkyl halides and alcohols, the carbon–carbon double bond of alkenes. This approach has led us to several of the major types of organic reactions: free-radical substitution, nucleophilic substitution, elimination, and addition. We have discussed the effects exerted on these reactions by substituents—alkyl groups, mostly: their polar effects, steric effects, and (until now unspecified) effects on the stability of free radicals and alkenes. We have looked at the inductive effect of halogens.

In this chapter we shall return to these families of compounds and these reaction types, and look at the effects exerted by a different kind of substituent: the carbon–carbon double bond. A double bond, we shall find, exerts its effect differently from an alkyl group, and, as a result, its effects are often more powerful. Most of these effects stem from the structural feature called *conjugation*: the location of the π orbital in such a way that it can overlap other orbitals in the molecule. And to implement our discussion of conjugation we shall make use of the structural theory called *resonance*.

6B.2 Free-radical halogenation of alkenes: substitution *vs.* addition

Let us look at the structure of the simple alkene, propylene. It contains a carbon–carbon double bond, where the same addition reactions that are characteristic of ethylene take place. With hydrogen chloride, for example, propylene

$$CH_2{=}CH{-}CH_3$$

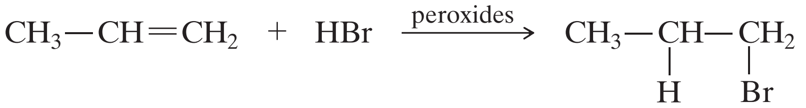
Propylene

undergoes electrophilic addition; with hydrogen bromide in the presence of peroxides, it undergoes free-radical addition.

$$CH_3{-}CH{=}CH_2 + HCl \longrightarrow CH_3{-}\underset{Cl}{\underset{|}{CH}}{-}\underset{H}{\underset{|}{CH_2}}$$

More readily than for ethylene

Isopropyl chloride
Only product



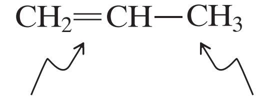
$$CH_3-CH=CH_2 \ + \ HBr \xrightarrow{\text{peroxides}} CH_3-\underset{H}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}$$

More readily than for ethylene

n-Propyl bromide
Only product

But propylene also contains a methyl group, and this modifies the reactions taking place at the double bond. Because of the methyl group, the electrophilic addition takes place faster than with ethylene itself, and gives exclusively isopropyl chloride. And because of the methyl group, the free-radical addition takes place faster than with ethylene, and gives exclusively *n*-propyl bromide. Thus, as a substituent, the methyl group affects the reactivity of the carbon–carbon double bond and determines the orientation of attack.

Now let us change our point of view and consider the methyl group, not as a substituent, but as the site of reaction. What kind of reactions can we expect to take place here? The methyl group has an alkane-like structure, and hence we might expect it to undergo alkane-like reactions: free-radical substitution of a halogen, for example.



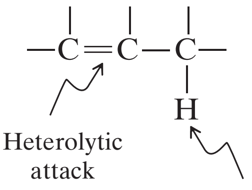
$CH_2=CH-CH_3$

Alkene-like:
site of addition

Alkane-like:
site of substitution

Let us consider, then, the reaction of propylene with halogens. But the propy-lene molecule presents *two* sites where halogen can attack, the double bond and the methyl group. Can we direct the attack to just one of these sites? The answer is yes, *by our choice of reaction conditions.*

We know that alkanes undergo substitution by halogen at high temperatures or under the influence of ultraviolet light, and generally in the gas phase: conditions that favor formation of free radicals. We know that alkenes undergo addition of halogen at low temperatures and in the absence of light, and generally in the liquid phase: conditions that favor heterolytic reactions, or at least do not aid formation of radicals.

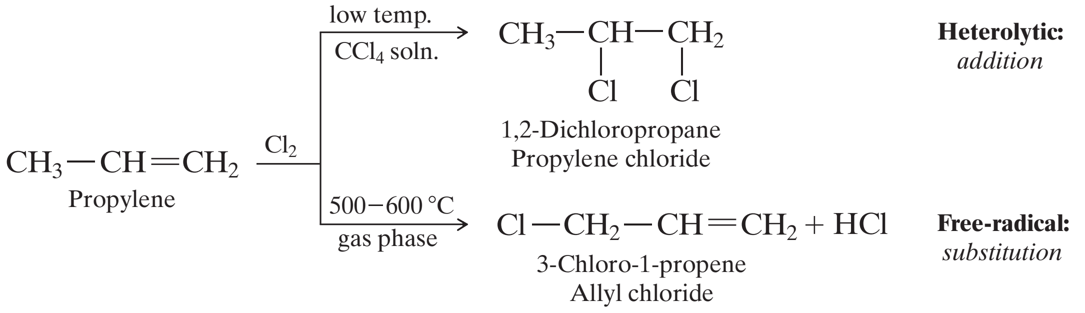


Heterolytic
attack
Addition

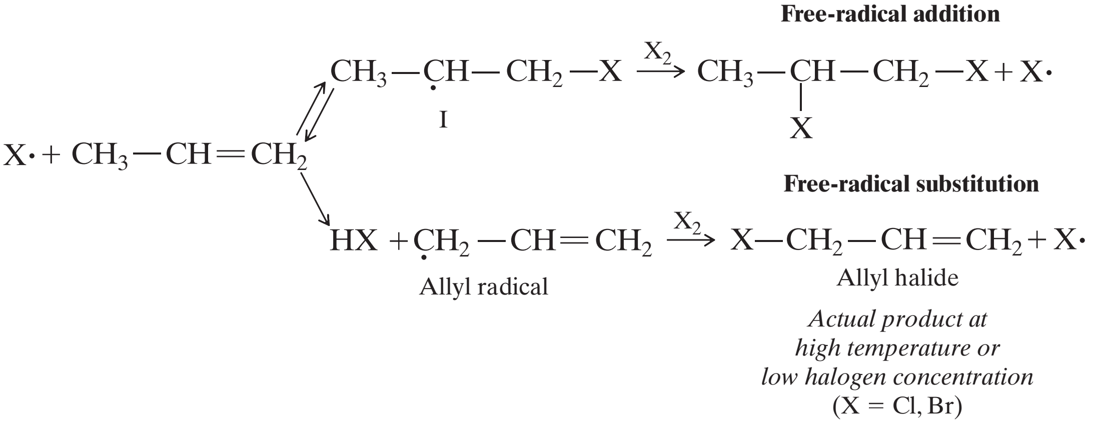
Free-radical
attack
Substitution

If we wish to direct the attack of halogen to the alkyl portion of an alkene molecule, then, we choose conditions that are favorable for the free-radical reaction and unfavorable for the heterolytic reaction. Chemists of the Shell Development

Company found that, at a temperature of 500–600 °C, a mixture of gaseous propylene and chlorine yields chiefly the substitution product, 3-chloro-1-propene, known as *allyl chloride* ($CH_2{=}CH{-}CH_2{-}$ = **allyl**). Bromine behaves similarly.



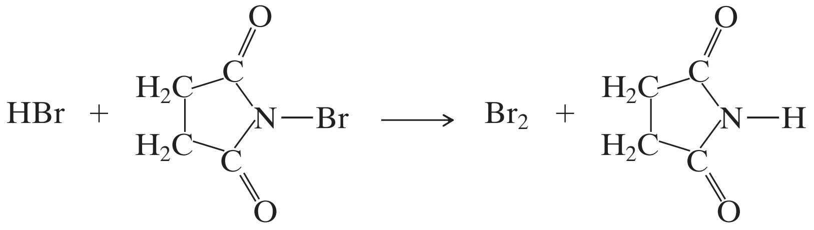
We might wonder why a halogen atom does not add to a double bond, instead of abstracting a hydrogen atom. H. C. Brown has suggested that the halogen atom *does* add but, at high temperatures, is expelled before the second step of free-radical addition can occur.



Consistent with Brown's explanation is the finding that *low concentration* of halogen can be used instead of high temperature to favor substitution over (free-radical) addition. Addition of the halogen atom gives radical I, which falls apart (to regenerate the starting material) if the temperature is high or if it does not soon encounter a halogen molecule to complete the addition. The allyl radical, on the other hand, once formed, has little option but to wait for a halogen molecule, whatever the temperature or however low the halogen concentration.

Problem 6B.1 (a) What would the allyl radical have to do to return to the starting material? (b) From bond dissociation energies, calculate the minimum E_{act} for this reaction.

The compound ***N*-bromosuccinimide (NBS)** is a reagent used *for the specific purpose of brominating alkenes at the allylic position*; NBS functions simply by providing a constant, low concentration of bromine. As each molecule of HBr is formed by the halogenation, NBS converts it into a molecule of Br_2.

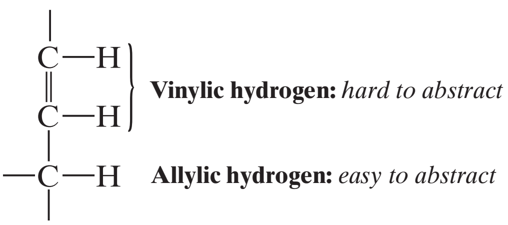


N-Bromosuccinimide (NBS) Succinimide

6B.3 Free-radical substitution in alkenes: orientation and reactivity

The alkyl groups of alkenes, then, undergo substitution by halogen in exactly the same manner as alkanes do. But attached to these alkyl groups there is a substituent, the double bond. Just as the alkyl groups affect the reactivity of the double bond, so the double bond affects the reactivity of the alkyl groups. Let us see what this effect is, and how it arises.

Halogenation of many alkenes has shown that: (a) hydrogens attached to doubly bonded carbons undergo very little substitution; and (b) hydrogens attached to carbons adjacent to doubly bonded carbons are particularly reactive toward substitution. Examination of reactions which involve attack not only by halogen atoms but by other free radicals as well has shown that this is a general rule: hydrogens attached to doubly bonded carbons, known as **vinylic** hydrogens, are harder to abstract than ordinary primary hydrogens; hydrogens attached to a carbon atom next to a double bond, known as **allylic** hydrogens, are even easier to abstract than tertiary hydrogens.



We can now expand the reactivity sequence.

Ease of abstraction of hydrogen atoms

$$\text{allylic} > 3^\circ > 2^\circ > 1^\circ > CH_4 > \text{vinylic}$$

Substitution in alkenes proceeds by the same mechanism as substitution in alkanes. For example:

$$\underset{\text{Ethylene}}{CH_2{=}CH{-}H} \xrightarrow{Cl\cdot} \underset{\text{Vinyl radical}}{CH_2{=}CH\cdot} \xrightarrow{Cl_2} \underset{\text{Vinyl chloride}}{CH_2{=}CH{-}Cl}$$

$$\underset{\text{Propylene}}{CH_2{=}CH{-}CH_2{-}H} \xrightarrow{Cl\cdot} \underset{\text{Allyl radical}}{CH_2{=}CH{-}CH_2\cdot} \xrightarrow{Cl_2} \underset{\text{Allyl chloride}}{CH_2{=}CH{-}CH_2Cl}$$

Evidently the vinyl radical is formed very slowly and the allyl radical is formed very rapidly. We can now expand the sequence.

Ease of formation of free radicals allyl $>$ 3° $>$ 2° $>$ 1° $>$ $CH_3\cdot$ $>$ vinyl

Are these findings in accord with our rule that *the more stable the radical, the more rapidly it is formed*? Is the slowly formed vinyl radical relatively unstable, and the rapidly formed allyl radical relatively stable?

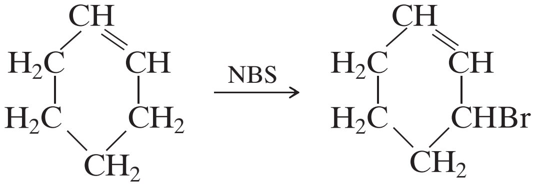
The bond dissociation energies show that 108 kcal of energy is needed to form vinyl radicals from a mole of ethylene, as compared with 98 kcal for formation of ethyl radicals from ethane. Relative to the hydrocarbon from which each is formed, then, the vinyl radical contains more energy and is less stable than a methyl radical.

On the other hand, bond dissociation energies show that only 88 kcal is needed for formation of allyl radicals from propylene, as compared with 92 kcal for formation of *tert*-butyl radicals. Relative to the hydrocarbon from which each is formed, the allyl radical contains less energy and is more stable than the *tert*-butyl radical.

We can now expand the sequence; relative to the hydrocarbon from which each is formed, the order of stability of free radicals is:

Stability of free radicals allyl $>$ 3° $>$ 2° $>$ 1° $>$ $CH_3\cdot$ $>$ vinyl

In some way, then, the double bond affects the stability of certain free radicals; it exerts a similar effect on the incipient radicals of the transition state, and thus affects the rate of their formation. Through these effects on rate of reaction, the double bond helps to determine both the *orientation* of free-radical substitution in an alkene, and the *relative reactivities* of different alkenes. Thus, the cyclic alkene cyclohexene is brominated almost exclusively at the allylic positions,



Cyclohexene 3-Bromocyclohexene

and reacts much faster than the saturated hydrocarbon cyclohexane despite a probability factor of 12:4 favoring attack on the saturated compound. (*Problem*: Why 12:4?)

As we know, free radicals are formed, not only by abstraction of hydrogen atoms, but also by addition to a double bond. Here too, we shall find, a double bond—a *second* double bond, not the one undergoing addition—can, through its effect on the stability of the incipient free radical, help to determine orientation and reactivity.

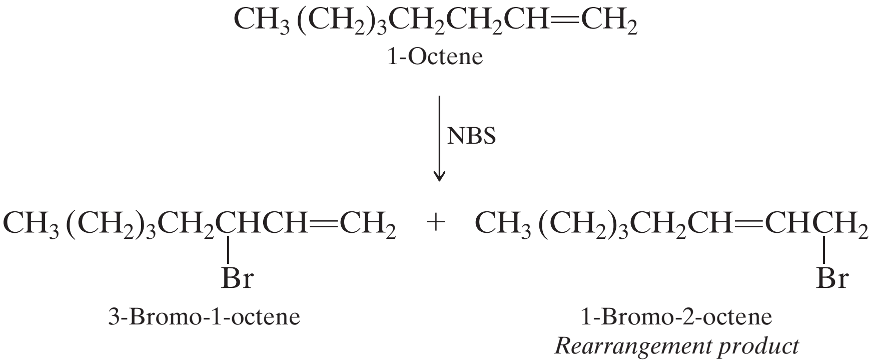
We have already seen a possible explanation for the low stability of vinylic radicals. Bonding of a vinylic hydrogen to carbon results from overlap with an *sp*^{2} orbital of carbon rather than the *sp*^{3} orbital of saturated carbon; this carbon–hydrogen bond is therefore shorter and stronger, and more energy must be supplied to break it. Relative to the hydrocarbon from which it is made, then, a vinylic radical is relatively unstable.

The high stability of allylic radicals is, as we shall see, readily accounted for by the structural theory: specifically, by the concept of resonance. But before we turn to resonance, let us look at some other characteristics of allylic radicals which, like their stability, are unusual.

6B.4 Free-radical substitution in alkenes: allylic rearrangement

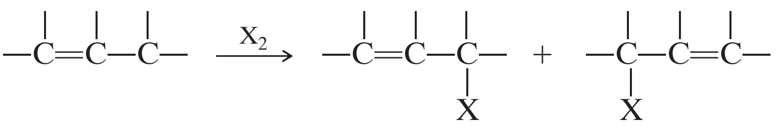
Since we shall use the allyl radical as our introduction to both the concept of conjugation and the theory of resonance, let us examine its structure in detail. Besides the fact that (a) *the allyl radical is especially stable*, there are other facts that must be accounted for by a satisfactory structure. Let us see what these facts are.

(b) *Free-radical substitution at allylic positions can lead to allylic rearrangement.* When 1-octene, for example, is treated with *N*-bromosuccinimide, there is obtained not only the expected 3-bromo-1-octene, but also—and in larger amounts—1-bromo-2-octene (both *Z* and *E*). It is an allylic hydrogen on C–3 that is abstracted,



$$\underset{\text{1-Octene}}{CH_3(CH_2)_3CH_2CH_2CH{=}CH_2} \xrightarrow{\text{NBS}} \underset{\text{3-Bromo-1-octene}}{CH_3(CH_2)_3CH_2\underset{Br}{C}HCH{=}CH_2} + \underset{\substack{\text{1-Bromo-2-octene}\\ \textit{Rearrangement product}}}{CH_3(CH_2)_3CH_2CH{=}CH\underset{Br}{C}H_2}$$

but in much of the product bromine appears on C–1. Whenever the structure permits, such allylic rearrangement occurs, and according to a well-defined pattern:



$$-\overset{|}{C}{=}\overset{|}{C}-\overset{|}{C}- \xrightarrow{X_2} -\overset{|}{C}{=}\overset{|}{C}-\underset{X}{\overset{|}{C}}- + -\underset{X}{\overset{|}{C}}-\overset{|}{C}{=}\overset{|}{C}-$$

As we see, the allylic radical reacts to give two different products: one in which halogen has become attached to the carbon that lost the hydrogen; and the other in which halogen has become attached to the carbon at the other end of the three-carbon unit—the allylic system—that we represent as C=C—C·.

Examination of the structures involved shows us that such rearrangement involves no migration of atoms or groups; only the double bond appears in a different position from the one it occupied in the reactant.

Problem 6B.2 Free-radical chlorination with *tert*-butyl hypochlorite shows a strong preference for allylic substitution rather than addition. Whether one starts with 1-butene or 2-butene (*cis* or *trans*), such chlorination yields a mixture of the same chloroalkenes (neglecting stereoisomerism). What are these chloroalkenes likely to be, and how are they formed?

6B.5 The theory of resonance

It will be helpful first to list some of the general principles of the concept of resonance, and then to discuss these principles in terms of a specific example, the structure of the allyl radical.

(a) *Whenever a molecule can he represented by two or more structures that differ only in the arrangement of electrons—that is, by structures that have the same arrangement of atomic nuclei—there is* **resonance**. The molecule is a **hybrid** of all these structures, and cannot be represented satisfactorily by any one of them. Each of these structures is said to **contribute** to the hybrid.

(b) *When these contributing structures are of about the same stability (that is, have about the same energy content), then* **resonance is important**. The contribution of each structure to the hybrid depends upon the relative stability of that structure: the more stable structures make the larger contribution.

(c) *The resonance hybrid is more stable than any of the contributing structures*. This increase in stability is called the **resonance energy**. The more nearly equal in stability the contributing structures, the greater the resonance energy.

There can be resonance only between structures that contain the *same number of odd electrons*. We need concern ourselves about this restriction only in dealing with *di*radicals: molecules that contain *two* unpaired electrons. There cannot be resonance between a diradical structure and a structure with all electrons paired.

6B.6 The allyl radical as a resonance hybrid

In the language of the resonance theory, then, the allyl radical is a resonance hybrid of the two structures, I and II.

$$\underset{\text{I}}{CH_2{=}CH{-}CH_2\cdot} \qquad \underset{\text{II}}{\cdot CH_2{-}CH{=}CH_2}$$

This simply means that the allyl radical does not correspond to either I or II, but rather to a structure intermediate between I and II. Furthermore, since I and II are exactly equivalent, and hence have exactly the same stability, the resonance hybrid is equally related to I and to II; that is, I and II are said to make *equal contributions to the hybrid*.

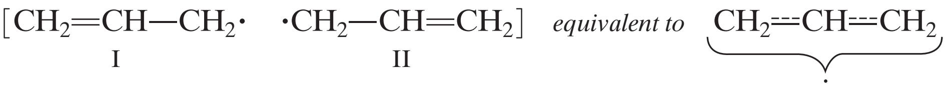
This does *not* mean that the allyl radical consists of molecules half of which correspond to I and half to II, nor does it mean that an individual molecule changes back and forth between I and II. All molecules are the same; each one has a structure intermediate between I and II.

An analogy to biological hybrids that was suggested by Professor G. W. Wheland is helpful. When we refer to a mule as a hybrid of a horse and a donkey, we do not mean that some mules are horses and some mules are donkeys; nor do we mean that an individual mule is a horse part of the time and a donkey part of the time. We mean simply that a mule is an animal that is related to both a horse and a donkey, and that can be conveniently defined in terms of those familiar animals.

An analogy used by Professor John D. Roberts is even more apt. A medieval European traveler returns home from a journey to India, and describes a rhinoceros as a sort of cross between a dragon and a unicorn—a quite satisfactory description of a real animal in terms of two familiar but entirely imaginary animals.

It must be understood that our drawing of two structures to represent the allyl radical does not imply that either of these structures (or the molecules each would singly represent) has any existence. The two pictures are necessary because of the limitations of our rather crude methods of representing molecules. We draw two pictures because no *single* one would suffice. It is not surprising that certain molecules cannot be represented by one structure of the sort we have employed; on the contrary, the surprising fact is that the crude dot-and-dash representation used by organic chemists has worked out to the extent that it has.

The resonance theory further tells us that the allyl radical does not contain one carbon–carbon single bond and one carbon–carbon double bond (as in I or II), but rather contains two *identical* bonds, each one intermediate between a single and a double bond. This new type of bond—this **hybrid bond**—has been described as a *one-and-a-half bond*. It is said to possess one-half single-bond character and one-half double-bond character.

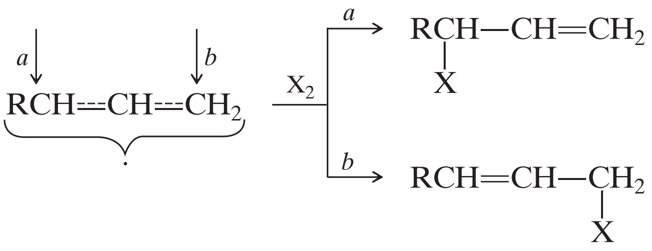


$$\Big[\underset{\text{I}}{CH_2{=}CH{-}CH_2\cdot} \quad \underset{\text{II}}{\cdot CH_2{-}CH{=}CH_2}\Big] \quad \textit{equivalent to} \quad \underset{\text{III}}{\underbrace{CH_2\text{---}CH\text{---}CH_2}_{\cdot}}$$

The odd electron is not localized on one carbon or the other but is *delocalized*, being equally distributed over both terminal carbons. We might represent this symmetrical hybrid molecule as in III, where the broken lines represent half bonds.

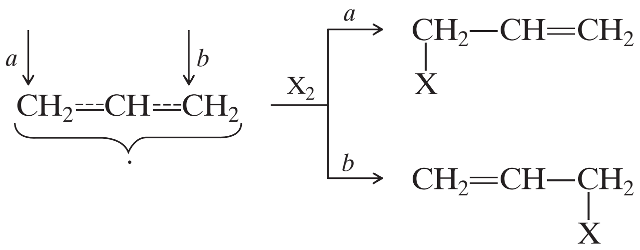
What we have arrived at is, of course, exactly the kind of highly symmetrical structure indicated by the ESR spectrum of the allyl radical.

Allylic rearrangement is a natural consequence of the hybrid character of an allylic radical. The terminal carbons of the three-carbon allylic system are exactly



$$\underbrace{\overset{a\downarrow}{RCH}\text{---}CH\text{---}\overset{\downarrow b}{CH_2}}_{\cdot} \xrightarrow{X_2} \begin{cases} \xrightarrow{a} RCH(X){-}CH{=}CH_2 \\ \xrightarrow{b} RCH{=}CH{-}CH_2X \end{cases}$$

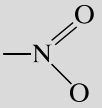
equivalent in the allyl radical itself, and very similar in an unsymmetrically substituted allylic radical. When halogen reacts with such a radical, it can become attached to either of these terminal carbons. Where the structure permits, as in 1-octene for example, this attachment to either end is shown by the formation of two different products. In the case of the unsubstituted allyl radical itself, the same product is



obtained whichever end receives the halogen, and so no rearrangement is *seen*; but there can be little doubt that here, too, both carbons are subject to attack.

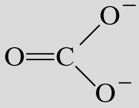
Problem 6B.3 Actually, one *could* detect “rearrangement”—that is, attachment to either end of the allyl radical—in the chlorination of propylene. Tell how.

Problem 6B.4 The nitro group, —NO_2, is usually represented as



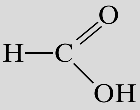
Actual measurement shows that the two nitrogen–oxygen bonds of a nitro compound have exactly the same length. In nitromethane, CH_3NO_2, for example, the two nitrogen–oxygen bond lengths are each 1.21 Å, as compared with a usual length of 1.36 Å for a nitrogen–oxygen single bond and 1.18 Å for a nitrogen–oxygen double bond. What is a better representation of the —NO_2 group?

Problem 6B.5 The carbonate ion, CO_3^{2-}, might be represented as



Actual measurement shows that all the carbon–oxygen bonds in $CaCO_3$ have the same length, 1.31 Å, as compared with a usual length of about 1.36 Å for a carbon–oxygen single bond and about 1.23 Å for a carbon–oxygen double bond. What is a better representation of the CO_3^{2-} ion?

Problem 6B.6 How do you account for the following facts: formic acid, HCOOH, contains one carbon–oxygen bond of 1.36 Å and another of 1.23 Å, yet sodium formate, $HCOO^- Na^+$, contains two equal carbon–oxygen bonds, each of 1.27 Å.



Formic acid

6B.7 Stability of the allyl radical

A further, most important outcome of the resonance theory is this: *as a resonance hybrid, the allyl radical is more stable (that is, contains less energy) than either of the contributing structures*. This additional stability possessed by the molecule is referred to *as resonance energy*. Since these particular contributing structures are exactly equivalent and hence of the same stability, we expect stabilization due to resonance to be large.

Just *how* large is the resonance energy of the allyl radical? To know the exact value, we would have to compare the actual, hybrid allyl radical with a *non-existent* radical of structure I or II—something we cannot do, experimentally. We can, however, estimate the resonance energy by comparing two reactions: dissociation of propane to form a *n*-propyl radical, and dissociation of propylene to form an allyl radical.

$$\underset{\text{Propane}}{CH_3CH_2CH_3} \longrightarrow \underset{n\text{-Propyl radical}}{CH_3CH_2CH_2\cdot} + H\cdot \qquad \Delta H = +98\ \text{kcal}$$

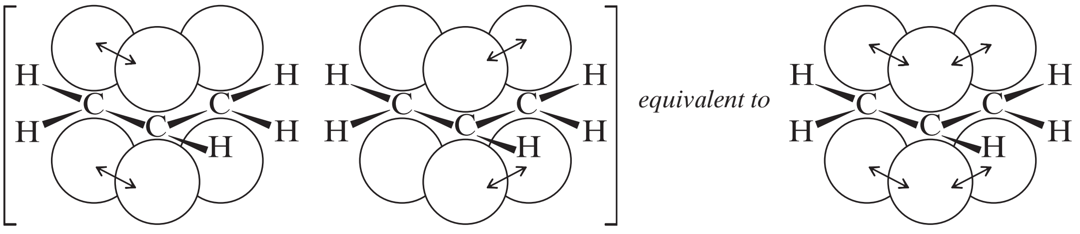
$$\underset{\text{Propylene}}{CH_2{=}CH{-}CH_3} \longrightarrow \underset{\text{Allyl radical}}{CH_2{=}CH{-}CH_2\cdot} + H\cdot \qquad \Delta H = +88$$

Propane, the *n*-propyl radical, and propylene are each fairly satisfactorily represented by a single structure; the allyl radical, on the other hand, is a resonance hybrid. We see that the energy difference between propylene and the allyl radical is 10 kcal/mol less (98—88) than the energy difference between propane and the *n*-propyl radical; we attribute the lower dissociation energy entirely to resonance stabilization of the allyl radical, and estimate the resonance energy to be 10 kcal/mol.

6B.8 Orbital picture of the allyl radical

To get a clearer picture of what a resonance hybrid is—and, especially, to understand how resonance stabilization arises—let us consider the bond orbitals in the allyl radical.

Since each carbon is bonded to three other atoms, it uses sp^2 orbitals. Overlap of these orbitals with each other and with the *s* orbitals of five hydrogen atoms gives the molecular skeleton shown in Fig. 6B.1, with all bond angles 120°. In addition,



$$[CH_2{=}CH{-}CH_2\cdot \qquad \cdot CH_2{-}CH{=}CH_2] \quad \textit{equivalent to} \quad \underbrace{CH_2 \overset{\cdots}{\text{—}} CH \overset{\cdots}{\text{—}} CH_2}_{\cdot}$$

Figure 6B.1 Allyl radical. The *p* porbital of the middle carbon overlaps *p* orbitals on both sides to permit delocalization of electrons.

each carbon atom has a *p* orbital which, as we know, consists of two equal lobes, one lying above and the other lying below the plane of the σ bonds; it is occupied by a single electron.

As in the case of ethylene, the *p* orbital of one carbon can overlap the *p* orbital of an adjacent carbon atom, permitting the electrons to pair and a bond to be formed. In this way we would arrive at either of the contributing structures, I or II, with the odd electron occupying the *p* orbital of the remaining carbon atom. But the overlap is not limited to a pair of *p* orbitals as it was in ethylene; the *p* orbital of the middle carbon atom overlaps equally well the *p* orbitals of *both* the carbon atoms to which it is bonded. The result is two continuous π electron clouds, one lying above and one lying below the plane of the atoms.

Since no more than two electrons may occupy the same orbital (Pauli exclusion principle), these π clouds are actually made up of *two* orbitals. One of these, containing two π electrons, encompasses all three carbon atoms; the other, containing the third (odd) π electron, is divided equally between the terminal carbons.

The overlap of the *p* orbitals in both directions, and the resulting participation of each electron in two bonds, is equivalent to our earlier description of the allyl radical as a resonance hybrid of two structures. These two methods of representation, the drawing of several resonance structures and the drawing of an electron cloud, are merely our crude attempts to convey by means of pictures the idea that *a given pair of electrons may serve to bind together more than two nuclei*. It is this ability of π electrons to participate in several bonds, this **delocalization of electrons**, that results in stronger bonds and a more stable molecule. For this reason the term *delocalization energy* is frequently used instead of *resonance energy*.

The covalent bond owes its strength to the fact that an electron is attracted more strongly by two nuclei than by one. In the same way an electron is more strongly attracted by three nuclei than by two.

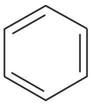
We saw earlier that the methyl radical may not be quite flat: that hybridization of carbon may be intermediate between sp^2 and sp^3. For the allyl radical, on the other hand—and for many other free radicals—flatness is clearly required to permit the overlap of *p* orbitals that leads to stabilization of the radical.

In terms of the conventional valence-bond structures we employ, it is difficult to visualize a single structure that is intermediate between the two structures, I and II. The orbital approach, on the other hand, gives us a rather clear picture of the allyl radical: the density of electrons holding the central carbon to each of the others is intermediate between that of a single bond and that of a double bond.

For generations, chemists have used the word *conjugated* to describe molecules containing alternating single and double (or triple) bonds: 1,3-butadiene, for example, or (and especially) benzene. A special name was given to compounds with this structural feature since it was observed that they had certain special properties in common.

$CH_2{=}CH{-}CH{=}CH_2$

1,3-Butadiene



Benzene

With the advent of the theory of resonance in the 1930s, the special properties of these conjugated molecules were attributed to interaction of the π orbitals of two or more double bonds: overlap much like what we have just described for the "double bond" of an allyl radical with the p orbital containing the odd electron. The meaning of the word *conjugation* became broadened to include the juxtaposition of a double bond and any π or p orbital—juxtaposition that permits overlap. And with *hyperconjugation*, the concept has been further broadened to include a similar juxtaposition of bonds of any kind—σ as well as π or p— juxtaposition, again, that permits sideways overlap.

The allyl radical is, then, a conjugated molecule. We interpret its special properties, as we shall do for other conjugated molecules, by the use of the theory of resonance. We can expect the carbon–carbon double bond to play a special role as a substituent whenever its location in a molecule creates a conjugated system: a system that, according to our interpretation, must exist as a resonance hybrid.

Problem 6B.7 In the reaction in which the 1-chloro-2-butene obtained from *cis*-2-butene is exclusively the *cis* isomer, and the 1-chloro-2-butene obtained from *trans*-2-butene is exclusively the *trans* isomer. What does this show about the intermediate allylic radicals? How do you account for this on the basis of their structure?

6B.9 Using the resonance theory

The great usefulness, and hence the great value, of the resonance theory lies in the fact that it retains the simple though crude type of structural representation which we have used so far in this book. Particularly helpful is the fact that the stability of a structure can often be roughly estimated from its **reasonableness**. If only one reasonable structure can be drawn for a molecule, the chances are good that this one structure adequately describes the molecule.

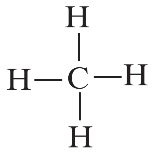
The criterion of reasonableness is not so vague as it might appear. The fact that a particular structure seems reasonable to us means that we have previously encountered a compound whose properties are pretty well accounted for by a structure of that type; the structure must, therefore, represent a fairly stable kind of arrangement of atoms and electrons. For example, each of the contributing structures for the allyl radical appears quite reasonable because we have encountered compounds, alkenes and free radicals, that possess the features of this structure.

There are a number of other criteria that we can use to estimate relative stabilities, and hence relative importance, of contributing structures. One of these has to do with (a) *electronegativity and location of charge.*

For example, a convenient way of indicating the polarity (*ionic character*) of the hydrogen–chlorine bond is to represent HCl as a hybrid of structures I and II. We judge that II is appreciably stable and hence makes significant contribution, because in it a negative charge is located on a highly electronegative atom, chlorine.

$$\underset{\text{I}}{\mathrm{H{-}Cl}} \qquad \underset{\text{II}}{\mathrm{H^{+}Cl^{-}}}$$

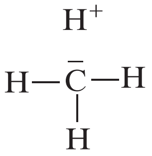
On the other hand, we consider methane to be represented adequately by the single structure III.



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

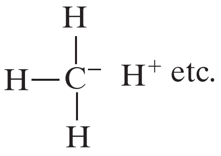
III

Although it is possible to draw additional, ionic structures like IV and V, we judge these to be unstable since in them a negative charge is located on an atom of low electronegativity, carbon. We expect IV and V to make negligible contribution to the hybrid and hence we ignore them.



$$\begin{array}{c} H^+ \\ \\ H-\bar{C}-H \\ | \\ H \end{array}$$

IV



$$\begin{array}{c} H \\ | \\ H-C^- \\ | \\ H \end{array} \quad H^+ \text{ etc.}$$

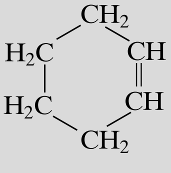
V

In later sections we shall use certain other criteria to help us estimate stabilities of possible contributing structures: (b) *number of bonds*; (c) *dispersal of charge*; (d) *complete vs. incomplete octet*; (e) *separation of charge*.

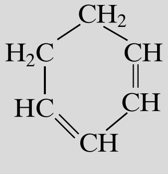
Finally, we shall find certain cases where the overwhelming weight of evidence—bond lengths, dipole moments, reactivity—indicates that an accurate description of a given molecule requires contribution from structures of a sort that may appear quite unreasonable to us; this simply reminds us that, after all, we know very little about the structure of molecules, and must be prepared to change our ideas of what is reasonable to conform with evidence provided by experimental facts.

In the next section, we shall encounter contributing structures that are very strange looking indeed.

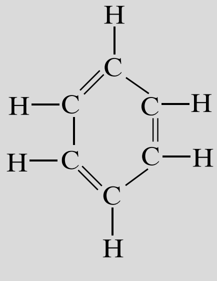
Problem 6B.8 *Benzene*, C_6H_6, is a flat molecule with all bond angles 120° and all carbon–carbon bonds 1.39 Å long. Its heat of hydrogenation (absorption of three moles of hydrogen) is 49.8 kcal/mol, as compared with values of 28.6 for cyclohexene (one mole of hydrogen) and 55.4 for 1,3-cyclohexadiene (two moles of hydrogen). (a) Is benzene adequately represented by the Kekulé formula shown? (b) Suggest a better structure for benzene in both valence-bond and orbital terms.



Cyclohexene



1,3-Cyclohexadiene



Benzene
(Kekulé formula)

6B.10 Resonance stabilization of alkyl radicals. Hyperconjugation

At this point let us look at an extension of the resonance theory which, although it does not involve a double bond, does nevertheless involve a kind of conjugation.

The relative stabilities of tertiary, secondary, and primary alkyl radicals are accounted for on exactly the same basis as the stability of the allyl radical: *delocalization of electrons,* this time through overlap between the *p* orbital occupied by the odd electron and a σ orbital of the alkyl group (Fig. 6B.2). Through this overlap, individual electrons can, to an extent, help bind together three nuclei, two carbons and one hydrogen. This kind of delocalization, involving σ bond orbitals, is called **hyperconjugation**.

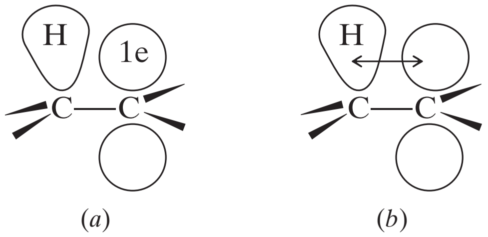
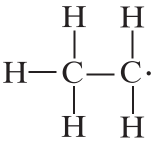


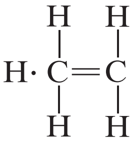
Figure 6B.2 Hyperconjugation in an alkyl free radical, (*a*) Separate σ and *p* orbitals. (*b*) Overlapping orbitals.

In resonance language, we would say that the ethyl radical, for example, is a hybrid of not only the usual structure, I, but also three additional structures, II, III, and IV, in which a double bond joins the two carbons, and the odd electron is held by a hydrogen atom.



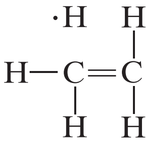
$$\begin{array}{ccccc} & & \mathrm{H} & & \mathrm{H} \\ & & | & & | \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C}\cdot \\ & & | & & | \\ & & \mathrm{H} & & \mathrm{H} \end{array}$$

I



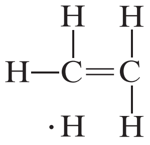
$$\begin{array}{cccc} & \mathrm{H} & & \mathrm{H} \\ & | & & | \\ \mathrm{H}\cdot & \mathrm{C} & = & \mathrm{C} \\ & | & & | \\ & \mathrm{H} & & \mathrm{H} \end{array}$$

II



$$\begin{array}{ccccc} & & \cdot\mathrm{H} & & \mathrm{H} \\ & & & & | \\ \mathrm{H} & - & \mathrm{C} & = & \mathrm{C} \\ & & | & & | \\ & & \mathrm{H} & & \mathrm{H} \end{array}$$

III



$$\begin{array}{ccccc} & & \mathrm{H} & & \mathrm{H} \\ & & | & & | \\ \mathrm{H} & - & \mathrm{C} & = & \mathrm{C} \\ & & & & | \\ & & \cdot\mathrm{H} & & \mathrm{H} \end{array}$$

IV

Individually, each of these "no-bond" resonance structures appears strange but, taken together, they mean that the carbon–hydrogen bond is something less than a single bond, that the carbon–carbon bond has some double-bond character, and that the odd electron is partly accommodated by hydrogen atoms. Contribution from these unstable structures is not nearly so important as from, say, the equivalent structures for the allyl radical, and the resulting stabilization is not nearly so large. It is believed, however, to stabilize the ethyl radical to the extent of 6 kcal relative to the methyl radical (104–98) for which such resonance is not possible.

If we extend this idea to the isopropyl radical, we find that instead of three hyperconjugation structures we now have six. (*Draw them.*) The larger number of contributing structures means more extensive delocalization of the odd electron, and hence greater stabilization of the radical. In agreement with this expectation, we find that the bond dissociation energy of the isopropyl–hydrogen bond is only 95 kcal, indicating a resonance energy of 9 kcal/mol (104–95).

For the *tert*-butyl radical there should be nine such hyperconjugation structures. (*Draw them.*) Here we find a bond dissociation energy of 92 kcal, indicating a resonance stabilization of 12 kcal/mol (104–92).

In summary, the relative stabilities of the free radicals we have studied are determined by delocalization of electrons. Delocalization takes place through overlap of the p orbital occupied by the odd electron: overlap with the π cloud of a double bond in the allyl radical, or overlap with σ bonds in alkyl radicals.

First advanced in 1939 by R. S. Mulliken, the idea of hyperconjugation, in some of its applications at least, has aroused considerable controversy. A great deal of research has been done—and is still going on—in an effort to evaluate the importance of hyperconjugative effects. (Mulliken received the Nobel Prize for his work.)

Problem 6B.9 It has been postulated that the relative stabilities of alkyl cations are determined not only by inductive effects but also by resonance stabilization. How might you account for the following order of stability of cations?

tert-butyl > isopropyl > ethyl > methyl

6B.11 The allyl cation as a resonance hybrid

Let us turn to heterolytic chemistry, and see how this is affected by the presence of a double bond in the substrate molecule. Since carbocations are key intermediates in much of heterolytic chemistry, let us begin by examining the structure of the *allyl cation*:

$$\mathrm{CH_2{=}CH{-}CH_2{}^+}$$

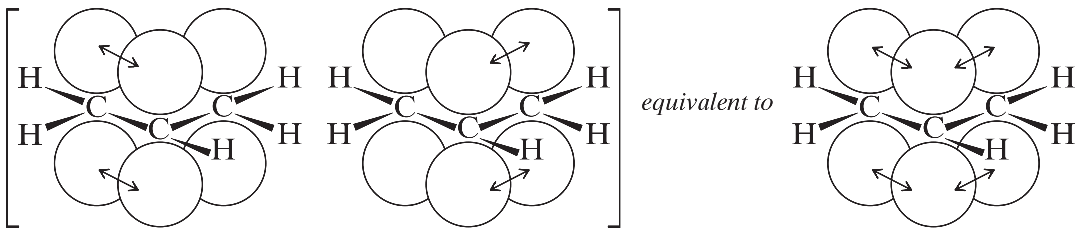
Allyl cation
Classical structure

Before we look at the facts, let us see what predictions we might make about this carbocation, using our newly acquired theory of resonance. We begin, as usual, by examining the structure of the molecule. We have drawn the allyl cation as I, but we could just as well have drawn its structure as II. The structures I and II, we now immediately recognize, meet the conditions for resonance: *structures that differ only in the arrangement of electrons*.

$$[\underset{\mathrm{I}}{\mathrm{CH_2{=}CH{-}CH_2{}^+}} \quad \underset{\mathrm{II}}{\mathrm{{}^+CH_2{-}CH{=}CH_2}}] \quad \textit{equivalent to} \quad \underset{\mathrm{III}}{\underbrace{\mathrm{CH_2{=}CH{=}CH_2}}_{\oplus}}$$

According to the resonance theory, neither I nor II adequately represents the cation; it is, instead, a *hybrid* of I and II, and has a structure we might represent as III. Since I and II are exactly equivalent, and hence of exactly the same stability, they make equal contributions to the hybrid. Like the allyl radical, the allyl cation does not contain one carbon–carbon single bond and one carbon–carbon double bond; it contains two identical bonds, each one intermediate between a single and double bond. The positive charge is not located on either terminal carbon atom, but is spread over both.

As was true with the allyl radical, we can get a clearer picture of this molecule by examining the bond orbitals involved. In either of the contributing structures, there is an empty *p* orbital on the electron-deficient carbon. Overlap of this empty *p* orbital with the π cloud of the double bond results in delocalization of the π electrons: each of these two electrons helps to hold together all three carbon nuclei (Fig. 6B.3).



$$[CH_2{=}CH{-}CH_2^+ \qquad {}^+CH_2{-}CH{=}CH_2] \quad \text{equivalent to} \quad \underbrace{CH_2{\overset{...}{=}}CH{\overset{...}{=}}CH_2}_{\oplus}$$

Figure 6B.3 Allyl cation. The *p* orbital of the middle carbon overlaps *p* orbitals on both sides to permit delocalization of electrons.

Now, on the basis of the structure we have arrived at, what predictions can we make about the properties of the allyl cation? First, since I and II are exactly equivalent, we expect resonance to be *important,* and *to give rise to considerable stabilization of the molecule*.

This prediction is borne out by the facts. The heterolytic bond dissociation energy for allyl chloride is 173 kcal, 12 kcal less than for *n*-propyl chloride, and about the same as for isopropyl chloride (170 kcal). Thus, although structure I or II is, formally, that of a primary cation, the allyl cation is about as stable as a secondary cation. We can now expand the sequence.

Stability of carbocations

$$3^\circ > \overset{\text{allyl}}{2^\circ} > 1^\circ > CH_3^+$$

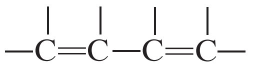
Next, we expect the allyl cation *to be symmetrical about the central carbon*. Again the facts show that this is so. The allyl cation and symmetrically substituted allylic cations have been prepared under strongly acidic conditions and studied spec-troscopically. The infrared spectrum for such a cation is particularly revealing. There are not two absorption bands for carbon–carbon stretching, one for C—C and one for C=C; instead, there is just *one*. This band appears at a frequency intermediate between those characteristic of C—C and of C=C, indicating two equivalent C=C bonds. The intensity of this band—it is the most intense infrared band observed for organic compounds—indicates a system with positive charge located on both terminal carbons.

6B.12 Dienes: structure and properties

So far in this chapter, we have discussed the effect of the double bond, acting as a substituent, on certain reactions taking place elsewhere in the molecule: free-radical substitution and nucleophilic substitution. Now let us look at its effect on alkene chemistry. That is, let us look at the effect of a double bond on the chemistry of *another* double bond in the same molecule: on its formation and on the reactions it undergoes.

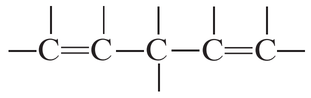
To do this we shall study chiefly **dienes**, alkenes that contain two carbon–carbons double bonds. What we shall say applies equally well to compounds with more than two double bonds. The double bond in a diene has essentially the same properties as a double bond in the alkenes we have already studied. But in certain of the dienes, these properties are *modified* by the presence of the second double bond; we shall focus our attention on these modifications.

Dienes are divided into three classes according to the arrangement of the double bonds. Double bonds that alternate with single bonds are **conjugated**. Double bonds that are separated by more than one single bond are **isolated**. Double bonds that share a carbon are *cumulated*, and the compounds are called **allenes**. For example:



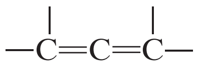
$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-$

Conjugated
double bonds



$-\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}-\overset{|}{C}=\overset{|}{C}-$

Isolated
double bonds



$-\overset{|}{C}=C=\overset{|}{C}-$

Cumulated
double bonds

$CH_2{=}CH{-}CH{=}CH_2$
1,3-Butadiene
A conjugated diene

$CH_2{=}CH{-}CH_2{-}CH{=}CH_2$
1,4-Pentadiene

$CH_3CH{=}C{=}CH_2$
1,2-Butadiene
An allene

The chemical properties of a diene depend upon this arrangement of its double bonds. Isolated double bonds exert little effect on each other, and hence each reacts as though it were the only double bond in the molecule. Except for the consumption of larger amounts of reagents, then, the chemical properties of the non-conjugated dienes are identical with those of the simple alkenes. Allenes are of increasing interest to organic chemists, but we shall have time to do very little with them.

We shall concentrate our attention on conjugated dienes. They differ from simple alkenes in four ways: (a) they are *more stable*; (b) they are the *preferred products of elimination*; (c) they undergo *1,4-addition*, both electrophilic and free-radical; and (d) toward free-radical addition, they are *more reactive*.

6B.13 Stability of conjugated dienes

We find that the heats of hydrogenation of alkenes having similar structures are remarkably constant. For monosubstituted alkenes ($RCH{=}CH_2$) the values are very close to 30 kcal/mol; for disubstituted alkenes ($R_2C{=}CH_2$ or $RCH{=}CHR$), 28 kcal/mol; and for trisubstituted alkenes ($R_2C{=}CHR$), 27 kcal/mol. For a compound containing more than one double bond we might expect a heat of hydrogenation that is the sum of the heats of hydrogenation of the individual double bonds.

For non-conjugated dienes this additive relationship is found to hold. As shown in Table 6B.1, 1,4-pentadiene and 1,5-hexadiene, for example, have heats of hydrogenation very close to 2×30 kcal, or 60 kcal/mol.

For conjugated dienes, however, the measured values are slightly lower than expected. For 1,3-butadiene we might expect 2×30, or 60 kcal: the actual value, 57 kcal, is 3 kcal lower. In the same way the values for 1,3-pentadiene and 2,3-dimethyl-1,3-butadiene are also below the expected values by 2–4 kcal.

Table 6B.1 HEATS OF HYDROGENATION OF DIENES

Diene	ΔH of hydrogenation, kcal/mol
1,4-Pentadiene	60.8
1,5-Hexadiene	60.5
1,3-Butadiene	57.1
1,3-Pentadiene	54.1
2-Methyl-1,3-butadiene (Isoprene)	53.4
2,3-Dimethyl-1,3-butadiene	53.9
1,2-Propadiene (Allene)	71.3

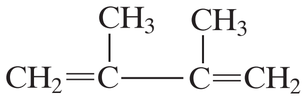
Heats of hydrogenation

$CH_2{=}CH{-}CH{=}CH_2$

Expected: 30 + 30 = 60 kcal
Observed: 57

$CH_3{-}CH{=}CH{-}CH{=}CH_2$

Expected: 28 + 30 = 58 kcal
Observed: 54



$$\begin{array}{ccc} & CH_3 & CH_3 \\ & | & | \\ CH_2{=} & C{-}{-}{-} & C{=}CH_2 \end{array}$$

Expected: 28 + 28 = 56 kcal
Observed: 54

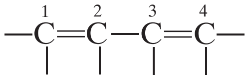
What do these heats of hydrogenation tell us about the conjugated dienes? Let us compare, for example, 1,3-pentadiene (heat of hydrogenation, 54 kcal) and 1,4-pentadiene (heat of hydrogenation, 61 kcal). They both consume two moles of hydrogen and yield the same product, *n*-pentane. If 1,3-pentadiene *evolves* less energy than 1,4-pentadiene, it can only mean that it *contains* less energy; that is to say, the conjugated 1,3-pentadiene is more stable than the nonconjugated 1,4-pentadiene.

In the next two sections we shall see the factors that have been invoked to account for the relative stabilities of conjugated dienes, and of simple alkenes as well.

Problem 6B.10 (a) Predict the heat of hydrogenation of *allene*, $CH_2{=}C{=}CH_2$. (b) The actual value is 71 kcal. What can you say about the stability of a *cumulated* diene?

6B.14 Resonance in conjugated dienes

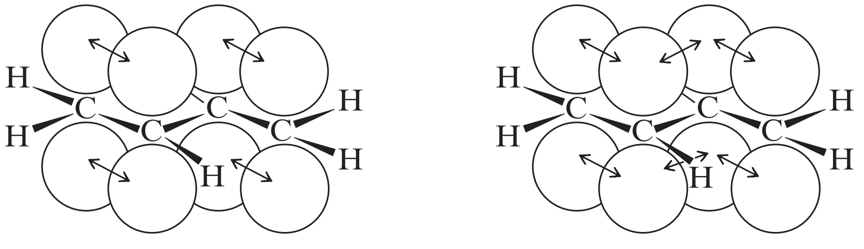
Let us focus our attention on the four key carbon atoms of any conjugated diene system. We ordinarily write the C(1)–C(2) and C(3)–C(4) bonds as double, and the C(2)–C(3) bond as single:



$$\begin{array}{c} \overset{1}{\underset{|}{C}}{=}\overset{2}{\underset{|}{C}}{-}\overset{3}{\underset{|}{C}}{=}\overset{4}{\underset{|}{C}} \end{array}$$

This would correspond to an orbital picture of the molecule (see Fig. 6B.4*a*, on the next page) in which π bonds are formed by overlap of the *p* orbitals of C–1 and C–2, and overlap of the *p* orbitals of C–3 and C–4.

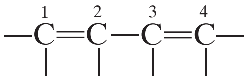
In the allyl radical and cation we saw that resonance resulted from the overlap of the *p* orbital of a carbon atom with *p* orbitals on *both* sides. We might expect that, in the same way, there could be a certain amount of overlap between the *p* orbitals of C–2 and C–3, as shown in Fig. 6B.4*b* the resulting delocalization of the π electrons makes the molecule more stable: each pair of electrons attracts—and is attracted by—not just two carbon nuclei, but *four*.



(*a*) (*b*)

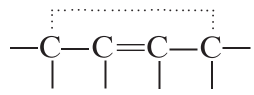
Figure 6B.4 Conjugated diene. (*a*) Overlap of *p* orbitals to form two double bonds. (*b*) Overlap of *p* orbitals to form conjugated system: delocalization of π electrons.

Using the language of conventional valence-bond structures, we say that a conjugated diene is a resonance hybrid of I and II. The dotted line in II represents a *formal bond*, and simply means that an electron on C–1 and an electron on C–4 have opposite spins, that is to say, are *paired*.



$$-\underset{|}{\overset{1}{C}}=\underset{|}{\overset{2}{C}}-\underset{|}{\overset{3}{C}}=\underset{|}{\overset{4}{C}}-$$

I



$$-\underset{|}{C}-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}-$$

II

To the extent that II contributes to the structure, it gives a certain double-bond character to the C(2)–C(3) bond and a certain single-bond character to the C(1)–C(2) and C(3)–C(4) bonds; most important, it makes the molecule more stable than we would expect I (the most stable contributing structure) to be.

Formation of a bond releases energy and stabilizes a system; all other things being equal, the more bonds, the more stable a structure. Consideration of *number of bonds* is one of the criteria that can be used to estimate relative stability and hence relative importance of a contributing structure. On this basis we would expect II with 10 bonds (the formal bond does not count) to be less stable than I with 11 bonds. The resonance energy for such a hybrid of non-equivalent structures should be less than for a hybrid made up of equivalent structures. The structure of a conjugated diene should resemble I more than II, since the more stable structure I makes the larger contribution to the hybrid.

Consistent with partial double-bond character, the C(2)–C(3) bond in 1,3-butadiene is 1.48 Å long, as compared with 1.53 Å for a pure single bond. The resonance energy of a conjugated diene is only 2–4 kcal/mol, compared with 10 kcal/mol for the allyl radical.

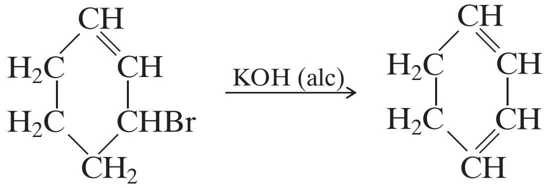
It has been argued, most notably by M. J. S. Dewar of the University of Florida, that there is no need to invoke hyperconjugation in molecules like these, and that the changes in C—C bond length—like the changes in C—H bond length—are due simply to changes in hybridization of carbon. These shorter bonds are stronger, and the molecules are more stable.

In a similar way, the unusual stability of conjugated dienes is attributed, not to delocalization of the π electrons, but to the fact that sp^2–sp^2 hybridization makes the C(2)–C(3) bond short (1.48 Å) and strong.

There is little doubt that both factors, delocalization of π electrons and change in σ bonds, are at work. The question is: what is the relative importance of each? The answer may well turn out to be: *both* are important.

6B.15 Ease of formation of conjugated dienes: orientation of elimination

The greater stability of conjugated dienes is reflected in their greater ease of formation. Where possible, they are the preferred diene products of elimination reactions. For example:



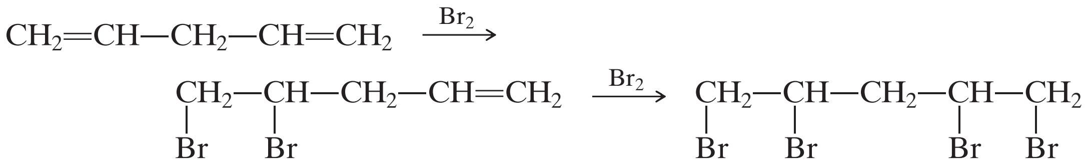
3-Bromocyclohexene 1,3-Cyclohexadiene

The most important diene, **1,3-butadiene** (used to make rubber substitutes), is obtained industrially in very large amounts by the cracking of hydrocarbons.

Problem 6B.11 Predict the major product of dehydrohalogenation of 4-bromo-1-hexene.

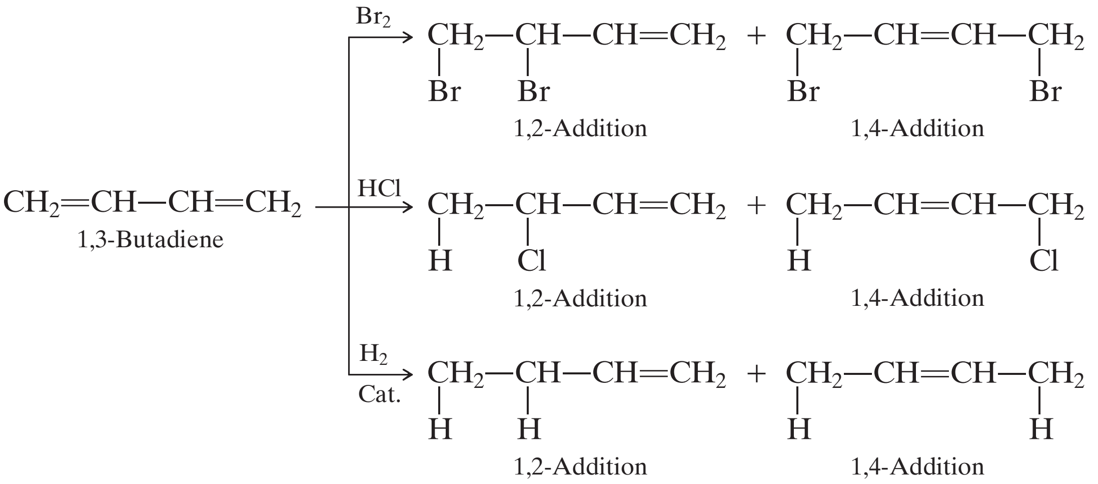
6B.16 Electrophilic addition to conjugated dienes. 1,4-Addition

When 1,4-pentadiene is treated with bromine under conditions (what are they?) that favor formation of the *dihalide*, there is obtained the expected product, 4,5-dibromo-1-pentene. Addition of more bromine yields the 1,2,4,5-tetrabromopentane. This is typical of the behavior of dienes containing isolated double bonds: the double bonds react independently, as though they were in different molecules.



$$CH_2{=}CH{-}CH_2{-}CH{=}CH_2 \xrightarrow{Br_2} \underset{Br}{CH_2}{-}\underset{Br}{CH}{-}CH_2{-}CH{=}CH_2 \xrightarrow{Br_2} \underset{Br}{CH_2}{-}\underset{Br}{CH}{-}CH_2{-}\underset{Br}{CH}{-}\underset{Br}{CH_2}$$

When 1,3-butadiene is treated with bromine under similar conditions, there is obtained not only the expected 3,4-dibromo-1-butene, but also 1,4-dibromo-2-butene. Treatment with HCl yields not only 3-chloro-1-butene, but also 1-chloro-2-butene. Hydrogenation yields not only 1-butene but also 2-butene.

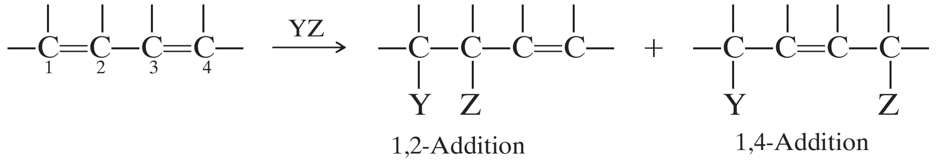


$$\underset{\text{1,3-Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} \xrightarrow{Br_2} \underset{\text{1,2-Addition}}{\underset{Br}{CH_2}{-}\underset{Br}{CH}{-}CH{=}CH_2} + \underset{\text{1,4-Addition}}{\underset{Br}{CH_2}{-}CH{=}CH{-}\underset{Br}{CH_2}}$$

$$\xrightarrow{HCl} \underset{\text{1,2-Addition}}{\underset{H}{CH_2}{-}\underset{Cl}{CH}{-}CH{=}CH_2} + \underset{\text{1,4-Addition}}{\underset{H}{CH_2}{-}CH{=}CH{-}\underset{Cl}{CH_2}}$$

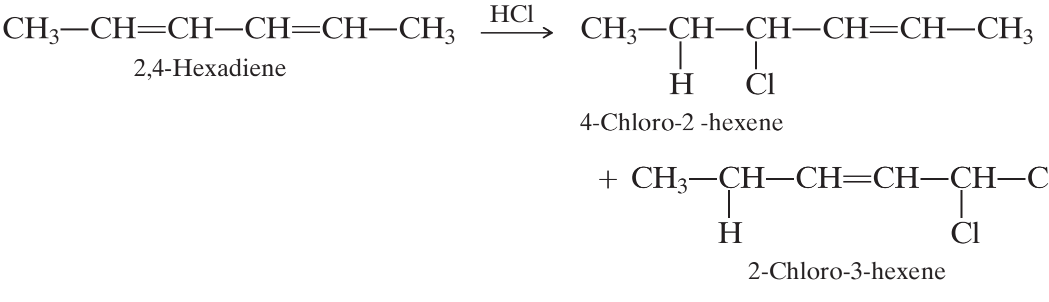
$$\xrightarrow[\text{Cat.}]{H_2} \underset{\text{1,2-Addition}}{\underset{H}{CH_2}{-}\underset{H}{CH}{-}CH{=}CH_2} + \underset{\text{1,4-Addition}}{\underset{H}{CH_2}{-}CH{=}CH{-}\underset{H}{CH_2}}$$

Study of many conjugated dienes and many reagents shows that such behavior is typical: *in* **additions to conjugated dienes**, *a reagent may attach itself not only to a pair of adjacent carbons* (**1,2-addition**), *but also to the carbons at the two ends of the conjugated system* (**1,4-addition**). Very often the 1,4-addition product is the major one.



$$-\underset{1}{C}{=}\underset{2}{C}{-}\underset{3}{C}{=}\underset{4}{C}- \xrightarrow{YZ} \underset{\text{1,2-Addition}}{-\underset{Y}{C}{-}\underset{Z}{C}{-}C{=}C-} + \underset{\text{1,4-Addition}}{-\underset{Y}{C}{-}C{=}C{-}\underset{Z}{C}-}$$

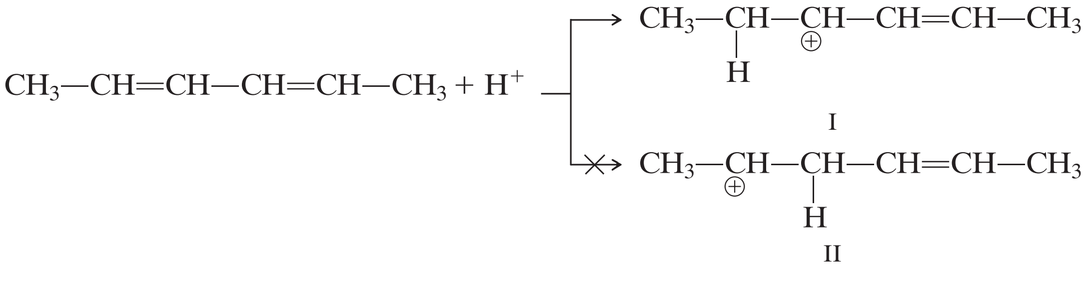
How can we account for the products that are obtained and, particularly, for the occurrence of 1,4-addition? We have seen that electrophilic addition is a two-step process, and that the first step takes place in the way that yields the more stable carbocation. Let us apply this principle to the addition, for example, of HCl to 2,4-hexadiene, which yields 4-chloro-2-hexene and 2-chloro-3-hexene:



$$\underset{\text{2,4-Hexadiene}}{CH_3{-}CH{=}CH{-}CH{=}CH{-}CH_3} \xrightarrow{HCl} \underset{\text{4-Chloro-2 -hexene}}{CH_3{-}\underset{H}{CH}{-}\underset{Cl}{CH}{-}CH{=}CH{-}CH_3}$$

$$+ \underset{\text{2-Chloro-3-hexene}}{CH_3{-}\underset{H}{CH}{-}CH{=}CH{-}\underset{Cl}{CH}{-}CH_3}$$

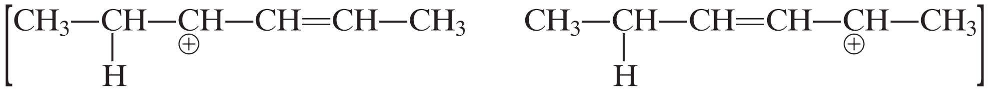
These products show, first of all, that hydrogen adds to C–2 to yield carbocation I, rather than to C–3 to yield carbocation II:



$$CH_3{-}CH{=}CH{-}CH{=}CH{-}CH_3 + H^+ \longrightarrow \underset{\text{I}}{CH_3{-}\underset{H}{CH}{-}\underset{\oplus}{CH}{-}CH{=}CH{-}CH_3}$$

$$\not\longrightarrow \underset{\text{II}}{CH_3{-}\underset{\oplus}{CH}{-}\underset{H}{CH}{-}CH{=}CH{-}CH_3}$$

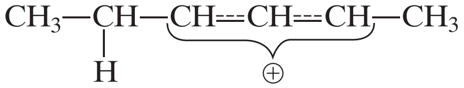
Since both I and II are secondary cations, how can we account for this preference? The answer is found, of course, in the structure of I: it is not simply a secondary cation, but is an *allylic* cation as well, since the carbon bearing the positive charge is attached to a doubly bonded carbon. It is, then, a resonance hybrid:



$$\left[\mathrm{CH_3{-}\underset{H}{C}H{-}\underset{\oplus}{C}H{-}CH{=}CH{-}CH_3} \qquad \mathrm{CH_3{-}\underset{H}{C}H{-}CH{=}CH{-}\underset{\oplus}{C}H{-}CH_3}\right]$$

I III

equivalent to

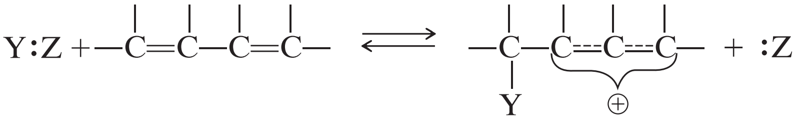


$$\mathrm{CH_3{-}\underset{H}{C}H{-}\underbrace{CH{=}CH{=}CH}_{\oplus}{-}CH_3}$$

IV

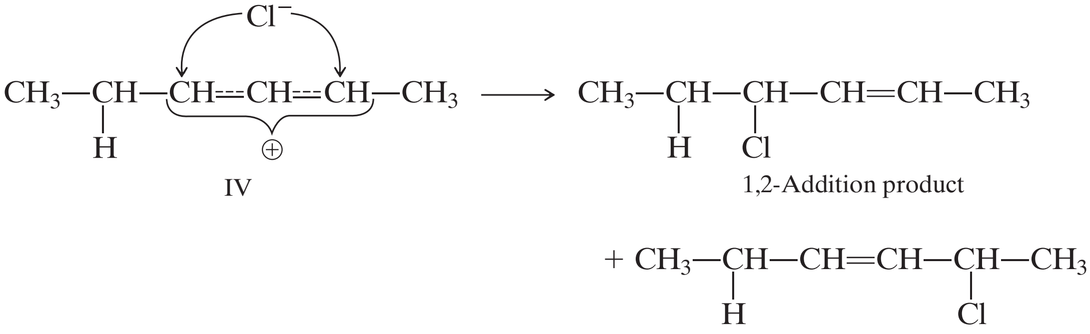
As a cation that is both secondary and allylic, I is more stable than II, and is the preferred cationic intermediate.

The products obtained from addition to conjugated dienes are always consistent with the formation of the most stable intermediate carbocation: an allylic cation. This requires the first step to be *addition to one of the ends* of the conjugated system. Now, in the second step cation IV combines with chloride ion to form the product. The chloride ion can attach itself to either end of the allylic system and thus yield the 1,2- or 1,4-product.



$$\mathrm{Y{:}Z} + \mathrm{{-}\overset{|}{C}{=}\overset{|}{C}{-}\overset{|}{C}{=}\overset{|}{C}{-}} \rightleftharpoons \mathrm{{-}\underset{Y}{\overset{|}{C}}{-}\underbrace{\overset{|}{C}{=}\overset{|}{C}{=}\overset{|}{C}}_{\oplus}{-}} + \mathrm{{:}Z}$$

Adds to end of conjugated system An allylic cation



$$\mathrm{CH_3{-}\underset{H}{C}H{-}\underbrace{CH{=}CH{=}CH}_{\oplus}{-}CH_3} \xrightarrow{\mathrm{Cl^-}} \mathrm{CH_3{-}\underset{H}{C}H{-}\underset{Cl}{C}H{-}CH{=}CH{-}CH_3}$$

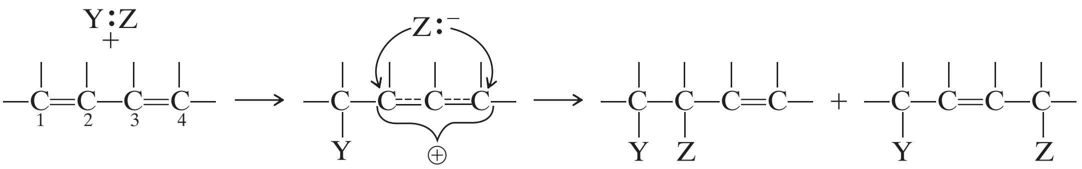
$$+\ \mathrm{CH_3{-}\underset{H}{C}H{-}CH{=}CH{-}\underset{Cl}{C}H{-}CH_3}$$

IV

1,2-Addition product

1,4-Addition product

Like allylic rearrangement, we see, the occurrence of 1,4-addition is a natural consequence of the hybrid nature of the intermediate allylic cation.



$$\underset{1\ \ 2\ \ 3\ \ 4}{\mathrm{{-}\overset{|}{C}{=}\overset{|}{C}{-}\overset{|}{C}{=}\overset{|}{C}{-}}} \xrightarrow{\mathrm{Y{:}Z}} \mathrm{{-}\underset{Y}{\overset{|}{C}}{-}\underbrace{\overset{|}{C}{=}\overset{|}{C}{=}\overset{|}{C}}_{\oplus}{-}} \xrightarrow{\mathrm{Z{:}^-}} \mathrm{{-}\underset{Y}{\overset{|}{C}}{-}\underset{Z}{\overset{|}{C}}{-}\overset{|}{C}{=}\overset{|}{C}{-}} + \mathrm{{-}\underset{Y}{\overset{|}{C}}{-}\overset{|}{C}{=}\overset{|}{C}{-}\underset{Z}{\overset{|}{C}}{-}}$$

Addition to end of conjugated system Allylic cation 1,2-Addition 1,4-Addition

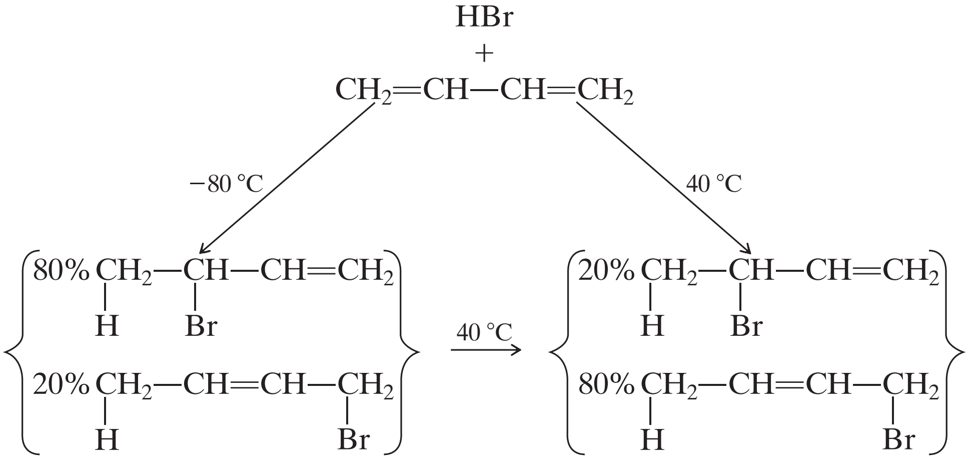
Thus the hybrid nature of the allylic cation governs both steps of electrophilic addition to conjugated dienes: the first, through stabilization of the cation; the second, by permitting attachment to either of two carbon atoms.

Problem 6B.12 Account for the fact that 2-methyl-1,3-butadiene reacts (a) with HCl to yield only 3-chloro-3-methyl-1-butene and 1-chloro-3-methyl-2-butene; (b) with bromine to yield only 3,4-dibromo-3-methyl-1-butene and 1,4-dibromo-2-methyl-2-butene.

6B.17 1,2- *vs.* 1,4-Addition. Rate *vs.* equilibrium (kinetically and thermodynamically controlled reactions)

A very important principle emerges when we look at the relative amounts of 1,2- and 1,4-addition products obtained.

Addition of HBr to 1,3-butadiene yields both the 1,2- and the 1,4-products; the *proportions* in which they are obtained are markedly affected by the temperature at which the reaction is carried out. Reaction at a low temperature (−80 °C) yields a mixture containing 20% of the 1,4-product and 80% of the 1,2-product. Reaction at a higher temperature (40 °C) yields a mixture of quite different composition, 80% 1,4- and 20% 1,2-product. At intermediate temperatures, mixtures of intermediate compositions are obtained. Although each isomer is quite stable at low temperatures, prolonged heating of either the 1,4- or the 1,2-compound yields the same mixture. How are these observations to be interpreted?



The fact that either compound is converted into the same mixture by heating indicates that this mixture is the result of equilibrium between the two compounds. The fact that the 1,4-compound predominates in the equilibrium mixture indicates that it is the more stable of the two.

The fact that more 1,2- than 1,4-product is obtained at –80 °C indicates that the 1,2-product is formed *faster* than the 1,4-product; since each compound remains unchanged at –80 °C, the proportions in which they are isolated show the proportions in which they were initially formed. As the reaction temperature is raised, the proportions in which the products are initially formed may remain the same, but there is faster conversion of the initially formed products into the equilibrium mixture.

The proportions of products actually isolated from the low-temperature addition are determined by the **rates** of addition, whereas for the high-temperature addition they are determined by the **equilibrium** between the two isomers.

Let us examine the matter of 1,2- and 1,4-additipn more closely by drawing a potential energy curve for the reactions involved (Fig. 6B.5). The carbocation initially formed reacts to yield the 1,2-product faster than the 1,4-product; consequently, the energy of activation leading to the 1,2-product must be less than that leading to the 1,4-product. We represent this by the lower hill leading from the cation to the 1,2-product. More collisions have enough energy to climb the low hill than the high hill, so that the 1,2-compound is formed faster than the 1,4-compound. The 1,4-product, however, is more stable than the 1,2-product, and hence we must place its valley at a lower level than that of the 1,2-product.

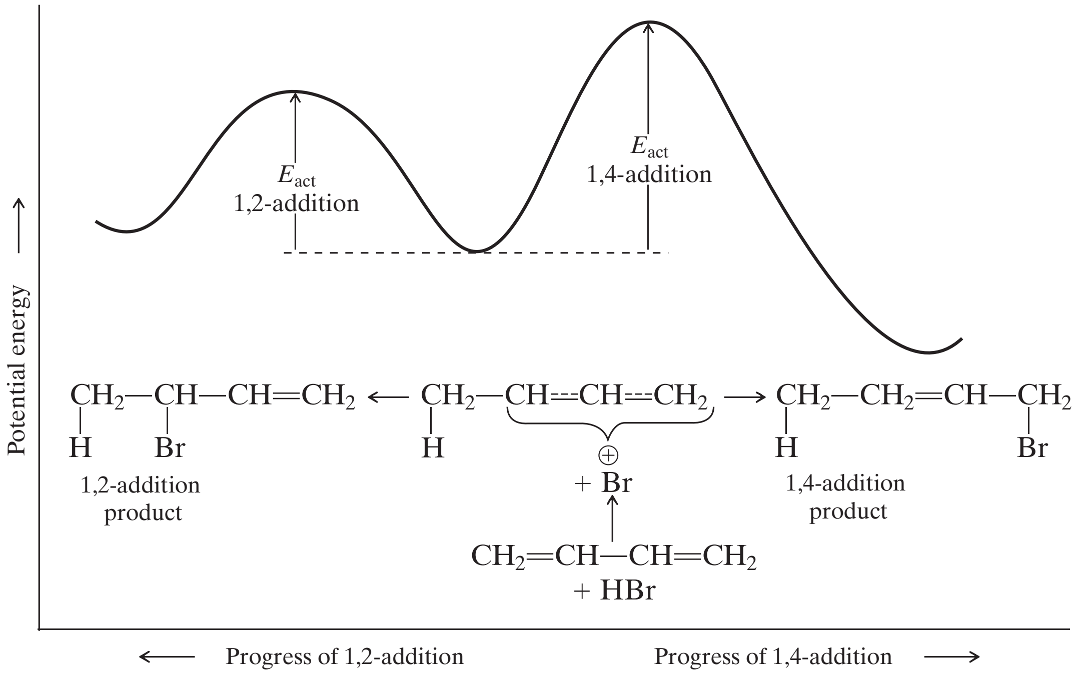
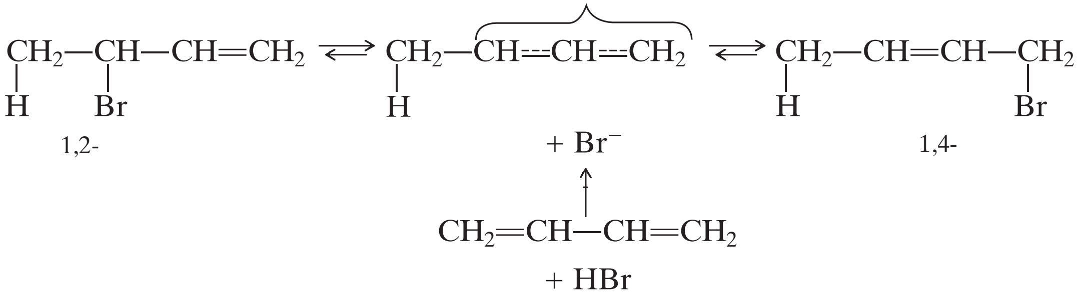


Figure 6B.5 Potential energy changes during progress of reaction: 1,2- *vs.* 1,4-addition.

As we know, allylic halides readily undergo heterolysis, that is, ionization. Now ionization of either bromo compound yields the same carbocation; the most likely—and simplest—way in which the 1,2- and 1,4-products reach equilibrium is through this cation.



Ionization of the bromides involves climbing the potential hills back toward this carbocation. But there is a higher hill separating the cation from the 1,4-product than from the 1,2-product; consequently, the 1,4-product will ionize more slowly than the 1,2-product. Equilibrium is reached when the rates of the opposing reactions are equal. The 1,2-product is formed rapidly, but ionizes rapidly. The 1,4-product is formed slowly, but ionizes even more slowly; once formed, the 1,4-product tends to persist. At temperatures high enough for equilibrium to be reached—that is, high enough for significantly fast ionization—the more stable 1,4-product predominates.

We have not tried to account for the fact that the 1,2-product is formed faster than the 1,4-product, or for the fact that the 1,4-product is more stable than the 1,2-product (although we notice that this is consistent with our generalization that disubstituted alkenes are more stable than monosubstituted alkenes). We have accepted these facts and have simply tried to show what they mean in terms of energy considerations. Similar relationships have been observed for other dienes and reagents. The 1,2-adduct is the kinetically controlled product and the 1,4-adduct is the thermodynamically controlled one.

These facts illustrate two important points. First, we must be cautious when we interpret product composition in terms of rates of reaction; we must be sure that one product is not converted into the other *after* its formation. Second, the more stable product is by no means *always* formed faster. *On the basis of much evidence*, we have concluded that *generally* the more stable a carbocation or free-radical, the faster it is formed; a consideration of the transition states for the various reactions has shown that this is reasonable. *We must not, however, extend this principle to other reactions unless the evidence warrants it.*

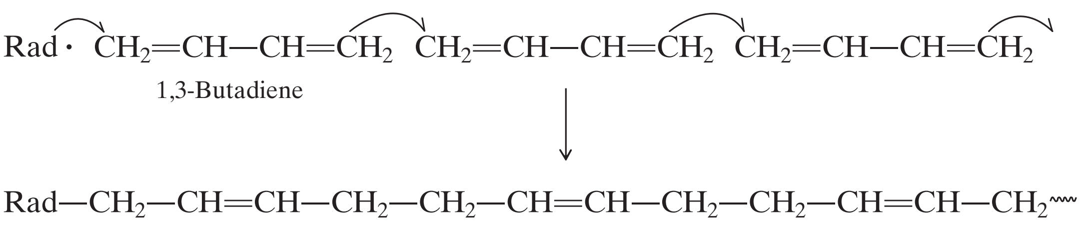
Problem 6B.13 When 1,3-butadiene is treated with $BrCCl_3$ in the presence of a peroxide, there are obtained both $Cl_3CCH_2CHBrCH{=}CH_2$ and $Cl_3CCH_2CH{=}CHCH_2Br$. Account in detail for the formation of these two products.

6B.18 Free-radical polymerization of dienes. Rubber and rubber substitutes

Like substituted ethylenes, conjugated dienes, too, undergo free-radical polymerization. From 1,3-butadiene, for example, there is obtained a polymer whose

$$\underset{\text{1,3-Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} \qquad \underset{\text{Polybutadiene}}{[-CH_2{-}CH{=}CH{-}CH_2-]_n}$$

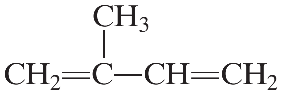
structure indicates that 1,4-addition occurs predominantly:



$$\text{Rad}\cdot\ \ CH_2{=}CH{-}CH{=}CH_2\ \ CH_2{=}CH{-}CH{=}CH_2\ \ CH_2{=}CH{-}CH{=}CH_2$$
$$\downarrow$$
$$\text{Rad}{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2\sim$$

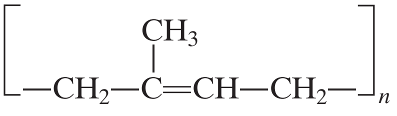
Such a polymer differs from the polymers of simple alkenes in one very important way: each unit still contains one double bond.

Natural rubber has a structure that strongly resembles these synthetic polydienes. We could consider it to be a polymer of the conjugated diene 2-methyl-1,3-butadiene, **isoprene**.



$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{=}CH_2$$

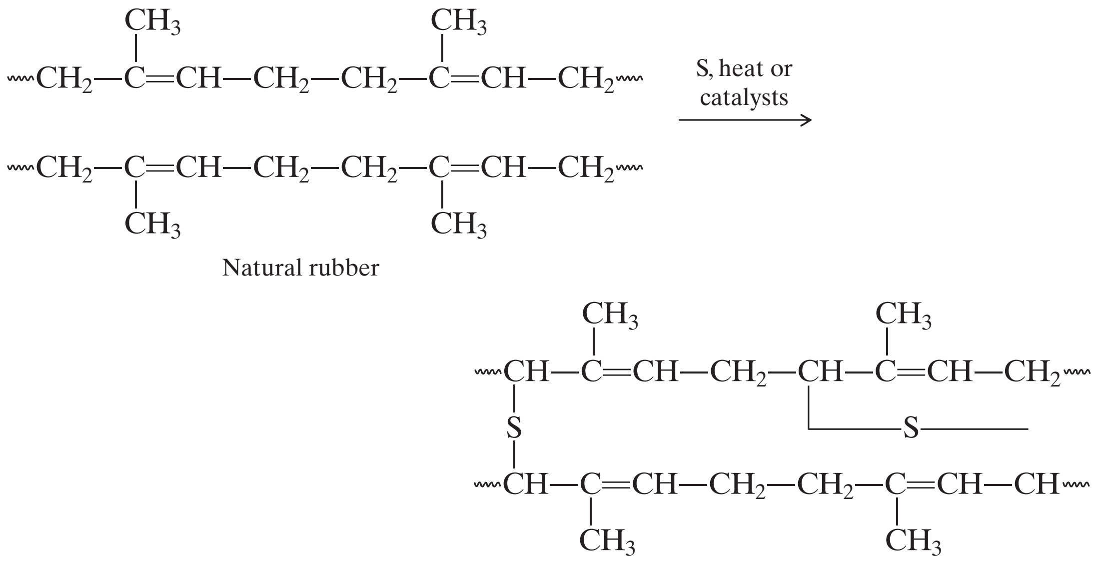
Isoprene



$$\left[{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_2{-}\right]_n$$

cis-Polyisoprene
Natural rubber

The double bonds in the rubber molecule are highly important, since—apparently by providing reactive allylic hydrogens—they permit *vulcanization*, the formation of sulfur bridges between different chains. These *cross-links* make the rubber harder and stronger, and do away with the tackiness of the untreated rubber.



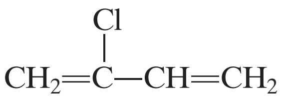
$$\begin{array}{l}\sim CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_2{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_2\sim \\ \sim CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_2\sim\end{array} \xrightarrow[\text{catalysts}]{\text{S, heat or}}$$

Natural rubber

$$\begin{array}{l}\sim CH{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_2{-}CH{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_2\sim \\ \quad | \qquad\qquad\qquad\qquad\qquad\; \llcorner\!\!-\!\!-S\!\!-\!\!-\!\!-\\ \quad S \\ \quad | \\ \sim CH{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH\sim\end{array}$$

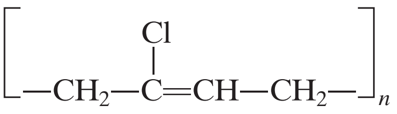
Vulcanized rubber

Polymerization of dienes to form substitutes for rubber was the forerunner of the enormous present-day plastics industry. *Polychloroprene* (Neoprene, Duprene) was the first commercially successful rubber substitute in the United States.



$$CH_2{=}\overset{\displaystyle Cl}{\overset{|}{C}}{-}CH{=}CH_2$$

Chloroprene



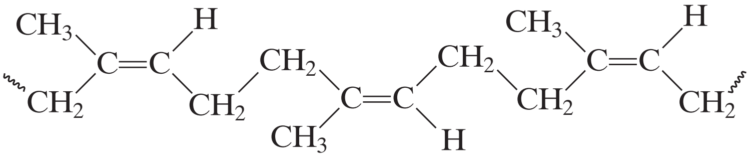
$$\left[{-}CH_2{-}\overset{\displaystyle Cl}{\overset{|}{C}}{=}CH{-}CH_2{-}\right]_n$$

Polychloroprene

The properties of rubber substitutes—like those of other polymers—are determined, in part, by the nature of the substituent groups. Polychloroprene, for example, is inferior to natural rubber in some properties, but superior in its resistance to oil, gasoline, and other organic solvents.

Polymers of isoprene, too, can be made artificially: they contain the same unsaturated chain and the same substituent (the —CH_3 group) as natural rubber.

But polyisoprene made by the free-radical process we have been talking about was—in the properties that really matter—a far cry from natural rubber. It differed in *stereochemistry*: natural rubber has the *cis* configuration at (nearly) every double bond; the artificial material was a mixture of *cis* and *trans*. Not until 1955 could a true synthetic *rubber* be made; what was needed was an entirely new kind of catalyst and an entirely new mechanism of polymerization. With these, it became possible to carry out a stereoselective polymerization of isoprene to a material virtually identical with natural rubber: *cis*-1,4-polyisoprene.



Natural rubber
All-cis configuration

EXERCISE

1. Draw the structure of 6-methyl-2-heptene. Label each set of hydrogen atoms to show their relative reactivities toward chlorine atoms, using (1) for the most reactive, (2) for the next, etc.

2. (a) Draw structures of all isomeric dienes of formula C_6H_{10}, omitting cumulated dienes. (b) Name each one. (c) Indicate which ones are conjugated, (d) Indicate which ones can show geometric isomerism, and draw the isomeric structures, (e) Draw structures of the ozonolysis products expected from each, (f) Which isomers (other than *cis-trans* pairs) could not be distinguished on the basis of (e)?

3. Give structures and names of the organic products expected from the reaction (if any) of 1,3-butadiene with:

(a) 1 mol H_2, Ni
(b) 2 mol H_2, Ni
(c) 1 mol Br_2
(d) 2 mol Br_2
(e) 1 mol HCl
(f) 2 mol HCl
(g) O_3, then H_2O
(h) hot $KMnO_4/NaIO_4$

4. Answer Problem 3 for 1,4-pentadiene instead of 1,3-butadiene.

5. Give structures and names of the products from dehydrohalogenation by strong base of each of the following halides. Where more than one product is expected, indicate which will be the major product.

(a) 1-chlorobutane; 2-chlorobutane
(b) 1-chlorobutane; 4-chloro-1-butene
(c) 2-bromo-2-methylbutane; 2-bromo-3-methylbutane
(d) 1-bromo-2-methylbutane; 1-bromo-3-methylbutane
(e) 1-chloro-2,3-dimethylbutane; 2-chloro-2,3-dimethylbutane
(f) 4-chloro-1-butene; 5-chloro-1-pentene

6. Which alkyl halide of each set in Problem 5 would you expect to undergo dehydro halogenation faster?

7. Give structures of the chief product or products expected from addition of one mole of HCl to each of the following compounds:

(a) 1,3-butadiene; 1-butene
(b) 1,3-butadiene; 1,4-pentadiene
(c) 1,3-butadiene; 2-methyl-1,3-butadiene
(d) 1,3-butadiene; 1,3-pentadiene

8. Answer Problem 7 for the addition of $BrCCl_3$ in the presence of peroxides instead of addition of HCl.

9. Arrange the compounds of each set in order of reactivity toward S_N1 substitution. (If you expect two of them to be of about the same reactivity, say so.)

(a) 1-chloropropene, 3-chloropropene, *n*-propyl chloride
(b) 2-bromobutane, 3-bromo-1-butene, 2-bromo-1-butene
(c) 4-bromo-2-pentene, 4-bromo-2-methyl-2-pentene, 4-bromo-3-methyl-2-pentene
(d) 2-buten-1-yl tosylate, 2-penten-4-yl tosylate, 4-methyl-2-penten-4-yl tosylate
(e) *sec*-butyl tosylate, *sec*-butyl triflate, *sec*-butyl chloride, sec-butyl bromide

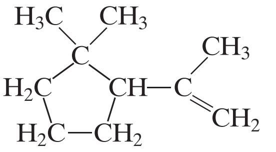
10. (a) Make a model of *allene*, $CH_2{=}C{=}CH_2$, a cumulated diene. What is the spatial relationship between the pair of hydrogens at one end of the molecule and the pair of hydrogens at the other end? (b) Substituted allenes of the type $RCH{=}C{=}CHR$ have been obtained in optically active form. Is this consistent with the shape of the molecule in (a)? Where are the chiral centers in the substituted allene? (c) Work out the electronic configuration of allene. (*Hint*: How many atoms are attached to the middle carbon? To each of the end carbons?) Does this lead to the same shape of molecule that you worked out in (a) and (b)?

11. When allowed to react with aqueous HBr, 3-buten-2-ol ($CH_3CHOHCH{=}CH_2$) yields not only 3-bromo-1-butene ($CH_3CHBrCH{=}CH_2$) but also 1-bromo-2-butene ($CH_3CH{=}CHCH_2Br$). (a) How do you account for these results? (b) Predict the product of the reaction between HBr and 2-buten-1-ol ($CH_3CH{=}CHCH_2OH$).

12. Treatment of $CF_3(C_6H_5)O{=}CF_2$ with EtONa/EtOH yields chiefly $CF_3(C_6H_5)C{=}CF(OEt)$. Similar treatment of $CF_2Cl(C_6H_5)C{=}CF_2$ yields $EtOCF_2(C_6H_5)C{=}CF_2$. The rates of the two reactions are almost identical. It has been suggested that both reactions proceed by the same mechanism.

Show all steps in a mechanism that is consistent with the nature of these reactants, and that accounts for the similarity in rate despite the difference in final product.

13. Treatment with phosphoric acid converts 2,7-dimethyl-2,6-octadiene into I.



I

1,1-Dimethyl-2-isopropenylcyclopentane

Using reaction steps already familiar to you, suggest a mechanism for this reaction.

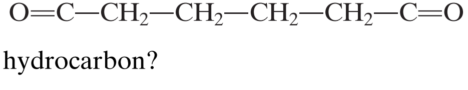
14. Describe simple chemical tests that would distinguish between:

(a) 1,3-pentadiene and *n*-pentane
(b) allyl bromide and 2,3-dimethyl-1,3-butadiene
(c) 1-chloro-2-butene and 2-chloro-2-butene
Tell exactly what you would *do* and *see*.

15. When 1,4-hexadien-3-ol is dissolved in H_2SO_4, it is converted completely into 3,5-hexadien-2-ol. How do you account for this?

16. Addition of one mole of bromine to 1,3,5-hexatriene yields only 5,6-dibromo-l,3-hexadiene and l,6-dibromo-2,4-hexadiene. (a) Are these products consistent with the formation of the most stable intermediate carbocation? (b) What other product or products would also be consistent? (c) Actually, which factor appears to be in control, rate or position of equilibrium?

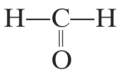
17. A hydrocarbon of formula C_6H_{10} absorbs only *one* mole of H_2, upon catalytic hydrogenation. Upon ozonolysis the hydrocarbon yields



$$O{=}\overset{H}{\overset{|}{C}}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\overset{H}{\overset{|}{C}}{=}O$$

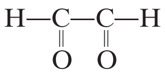
What is the structure of the hydrocarbon?

18. A hydrocarbon was found to have a molecular weight of 80–85. A 10.02-mg sample took up 8.40 mL of H_2 gas measured at 0 °C and 760 mm pressure. Ozonolysis yielded only



$H{-}\underset{\underset{O}{\|}}{C}{-}H$

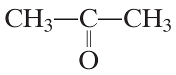
and



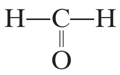
$H{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}H$

What was the hydrocarbon?

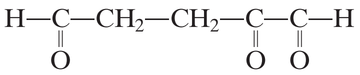
19. *Myrcene*, $C_{10}H_{16}$, a terpene isolated from oil of bay, absorbs three moles of hydrogen to form $C_{10}H_{22}$. Upon ozonolysis myrcene yields:



$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3$



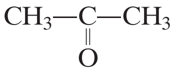
$H{-}\underset{\underset{O}{\|}}{C}{-}H$



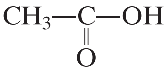
$H{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}H$

(a) What structures are consistent with these facts?
(b) On the basis of the isoprene rule, what is the most likely structure for myrcene?

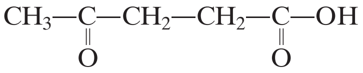
20. *Dihydromyrcene*, $C_{10}H_{18}$, formed from myrcene (Problem 19), absorbs two moles of hydrogen to form $C_{10}H_{22}$. Upon cleavage by $KMnO_4$, dihydromyrcene yields:



$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3$



$CH_3{-}\underset{\underset{O}{\|}}{C}{-}OH$



$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}OH$

(a) Keeping in mind the isoprene rule, what is the most likely structure for dihydromyrcene?
(b) Is it surprising that a compound of this structure is formed by reduction of myrcene?