Chapter 6

Alkenes II. Reactions of the Carbon–Carbon Double Bond

Electrophilic and Free-Radical Addition

6.1 The functional group

The characteristic feature of the alkene structure is the carbon–carbon double bond. The characteristic reactions of an alkene are those that take place at the double bond. *The atom or group of atoms that defines the structure of a particular family of organic compounds and, at the same time, determines their properties is called the* **functional group**.

In alkyl halides the functional group is the halogen atom, and in alcohols the —OH group; in alkenes it is the carbon–carbon double bond. We must not forget that an alkyl halide, alcohol, or alkene has alkyl groups attached to these functional groups; under the proper conditions, the alkyl portions of these molecules undergo the reactions typical of alkanes. However, the reactions that are *characteristic* of each of these compounds are those that occur at the halogen atom or the hydroxyl group or the carbon–carbon double bond.

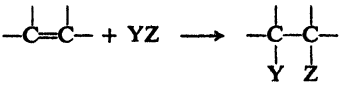
A large part of organic chemistry is therefore the chemistry of the various functional groups. We shall learn to associate a particular set of properties with a particular group wherever we may find it. When we encounter a complicated molecule, which contains a number of different functional groups, we may expect the properties of this molecule to be roughly a composite of the properties of the various functional groups. The properties of a particular group may be modified, of course, by the presence of another group and it is important for us to understand these modifications, but our point of departure is the chemistry of individual functional groups.

6.2 Reactions of the carbon–carbon double bond: addition

Alkene chemistry is the chemistry of the carbon–carbon double bond.

What kind of reaction may we expect of the double bond? The double bond consists of a strong σ bond and a weak π bond; we might expect, therefore, that

reaction would involve the breaking of this weaker bond. This expectation is correct; the typical reactions of the double bond are of the sort,



Addition

where the π bond is broken and two strong σ bonds are formed in its place.

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 organic molecule, in contrast to a substitution reaction where part of the reagent is *substituted for* a portion of the organic molecule. 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.

What kind of reagent may 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. 6.1). These π electrons are less involved than the

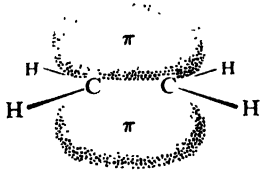


Figure 6.1. Carbon–carbon double bond: π bond is source of electrons.

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**, or, in other words, addition of acidic reagents.

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.

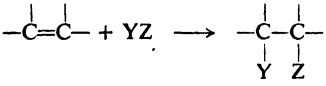
There are reagents that can add either as acids or as free radicals, and with strikingly different results; there are reagents that are capable both of adding to the double bond and of bringing about substitution. We shall see how, by our choice of conditions, we can lead these reagents along the particular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

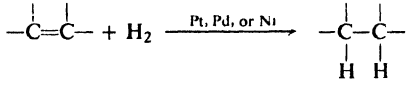
We shall be concerned with seeing what these modifications are and, where possible, how they can be accounted for.

REACTIONS OF ALKENES

Addition Reactions



1. Addition of hydrogen. Catalytic hydrogenation. Discussed in Sec. 6.3.



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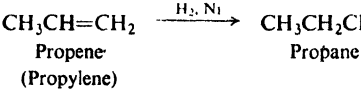
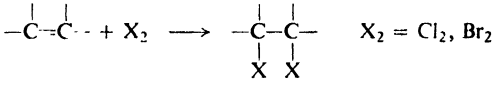


2. Addition of halogens. Discussed in Secs. 6.5, 6.13, and 7.11–7.12.



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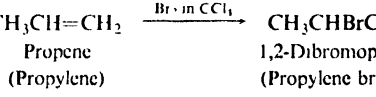
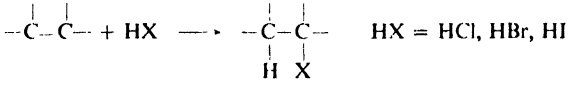


3. Addition of hydrogen halides. Discussed in Secs. 6.6–6.7 and 6.17.



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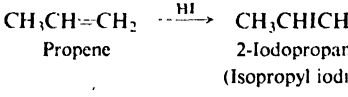
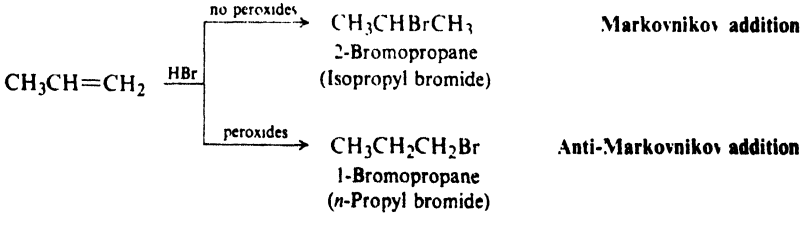
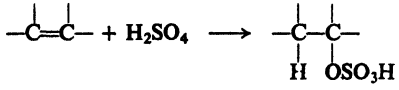




4. Addition of sulfuric acid. Discussed in Sec. 6.8.



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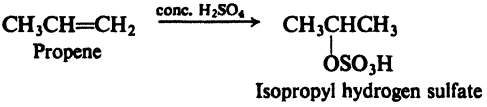
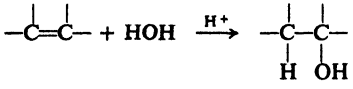


Propene

Isopropyl hydrogen sulfate

5. Addition of water. Hydration. Discussed in Sec. 6.9.



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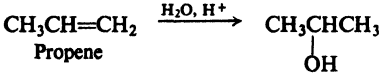
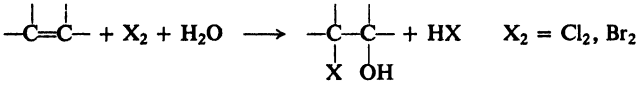


Propene

Isopropyl alcohol
(2-Propanol)

6. Halohydrin formation. Discussed in Sec. 6.14.



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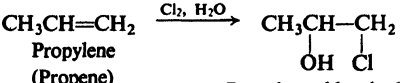
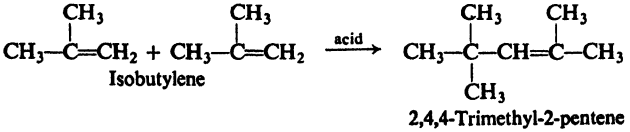


Propylene
(Propene)

Propylene chlorohydrin
(1-Chloro-2-propanol)

7. Dimerization. Discussed in Sec. 6.15.

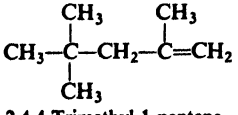
Example:



Isobutylene

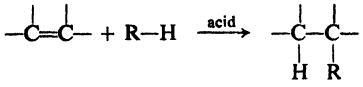
2,4,4-Trimethyl-2-pentene

and



2,4,4-Trimethyl-1-pentene

8. Alkylation. Discussed in Sec. 6.16.



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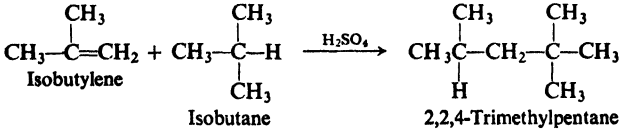
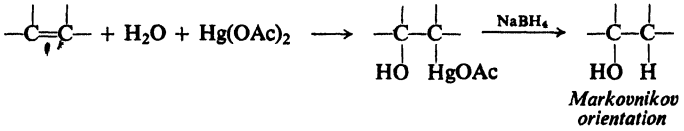
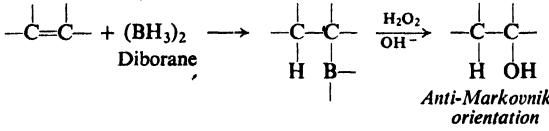


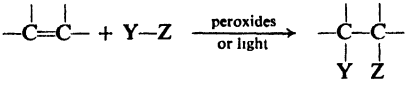
9. Oxymercuration-demercuration. Discussed in Sec. 15.8.



10. Hydroboration-oxidation. Discussed in Secs. 15.9–15.11.



11. Addition of free radicals. Discussed in Secs. 6.17 and 6.18.



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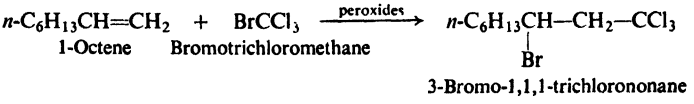
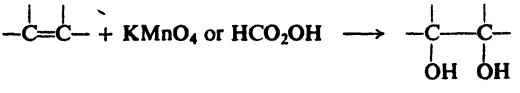


12. Polymerization. Discussed in Secs. 6.19 and 32.3–32.6.

13. Addition of carbenes. Discussed in Secs. 9.15–9.16.

14. Hydroxylation. Glycol formation. Discussed in Secs. 6.20 and 17.12.



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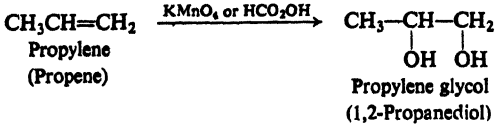
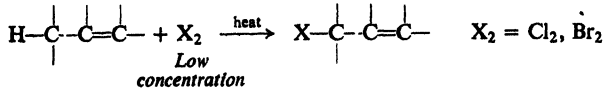


Propylene (Propene)

Propylene glycol (1,2-Propanediol)

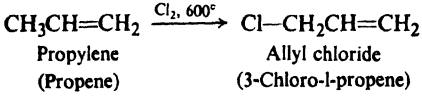
Substitution Reactions

15. Halogenation. Allylic substitution. Discussed in Sec. 6.21.



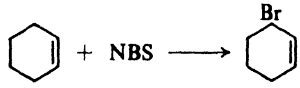
Low concentration

Examples:



Propylene (Propene)

Allyl chloride (3-Chloro-1-propene)



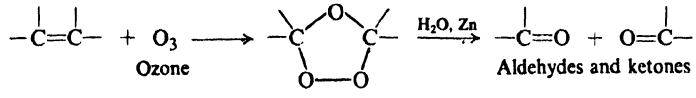
Cyclohexene

3-Bromocyclohexene

N-Bromosuccinimide

Cleavage Reactions

16. Ozonolysis. Discussed in Sec. 6.29.



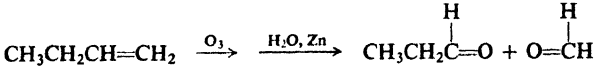
Ozone

Ozonide

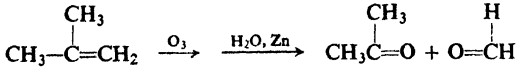
Aldehydes and ketones

Used to determine structure

Examples:



1-Butene

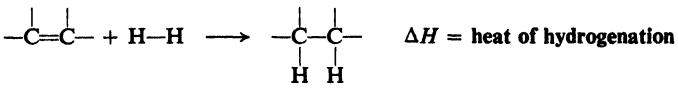


Isobutylene

6.3 Hydrogenation. Heat of hydrogenation

We have already encountered hydrogenation as the most useful method for preparing alkanes (Sec. 3.15). 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: 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. 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.



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 an approximate value of 30 kcal for each double bond in the compound (see Table 6.1).

Table 6.1 HEATS OF HYDROGENATION OF ALKENES

Alkene	Heat of hydrogenation, kcal/mole
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

Although hydrogenation is an exothermic reaction, it proceeds at a negligible rate in the absence of a catalyst, even at elevated temperatures. The uncatalyzed 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. 6.2).

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 the finely divided metal, where reaction actually occurs. Reaction between the adsorbed molecules is very different from the reaction that would have to take place otherwise; it is believed, for example, that the catalytic surface breaks the π bond of the alkene prior to reaction with hydrogen.

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 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

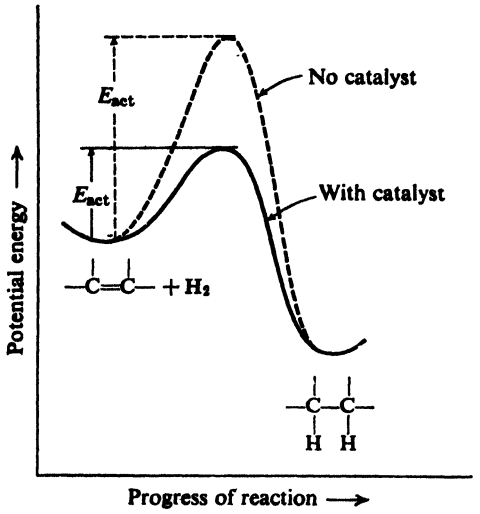


Figure 6.2. Potential energy changes during progress of reaction: effect of catalyst.

not shift the position of equilibrium; this is, of course, because it speeds up both the forward and reverse reactions (See Sec. 30.7).

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.

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

6.4 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. 6.3). 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).

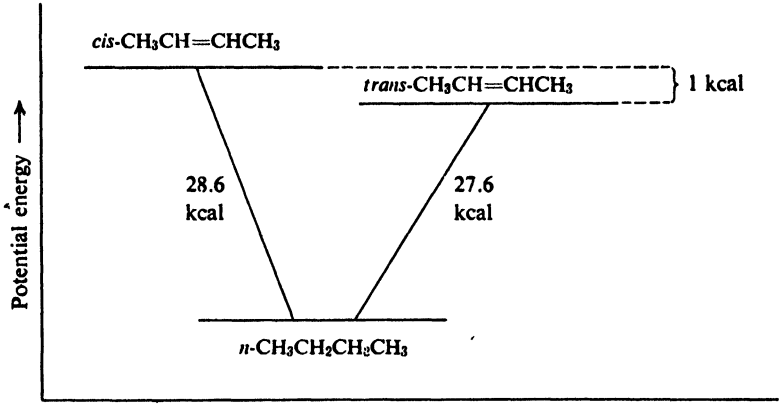


Figure 6.3. Heats of hydrogenation and stability: *cis*- and *trans*-2-butene.

Of simple disubstituted ethylenes, 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 (Sec. 3.5).

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

$CH_3CH_2CH{=}CH_2$ 30.3 kcal

$CH_3CH{=}CHCH_3$ *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

$CH_3CH(CH_3)CH{=}CH_2$ 30.3 kcal

$CH_2{=}C(CH_3)CH_2CH_3$ 28.5

$CH_3C(CH_3){=}CHCH_3$ 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

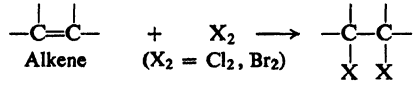
$$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2, RCH{=}CHR > RCH{=}CH_2 > CH_2{=}CH_2$$

We have seen (Secs. 5.14, 5.23) that the stability of alkenes determines orientation in dehydrohalogenation and dehydration.

Problem 6.1 (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.

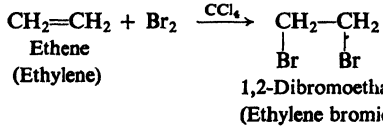
6.5 Addition of halogens

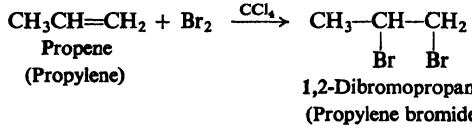
Alkenes are readily converted by chlorine or bromine into saturated compounds that contain two atoms of halogen attached to adjacent carbons; iodine generally fails to react.

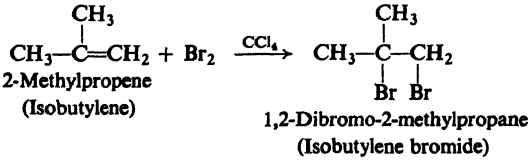


The reaction is carried out simply by mixing together the two reactants, usually in an inert solvent like carbon tetrachloride. The addition proceeds rapidly at room temperature or below, and does not require exposure to ultraviolet light; in fact, we deliberately avoid higher temperatures and undue 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:







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. (However, see Sec. 6.30.)

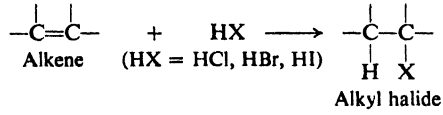
A common method of naming alkene derivatives is illustrated here. As we see, the product of the reaction between ethylene and bromine has the IUPAC name of 1,2-dibromoethane. It is also frequently called *ethylene bromide*, the word *ethylene* forming part of the name even though the compound is actually

saturated. This is an old-fashioned name, and is meant to indicate the product of the reaction between ethylene and bromine, just as, for example, *sodium bromide* would indicate the product of the reaction between sodium and bromine. It should not be confused with the different compound, 1,2-dibromoethene, BrCH=CHBr. In a similar way, we have *propylene bromide*, *isobutylene bromide*, and so on.

We shall shortly encounter other saturated compounds that are named in a similar way, as, for example, *ethylene bromohydrin* and *ethylene glycol*. These names have in common the use of two words, the first of which is the name of the alkene; in this way they can be recognized as applying to compounds no longer containing the double bond.

6.6 Addition of hydrogen halides. Markovnikov's rule

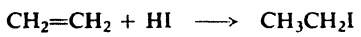
An alkene is converted by hydrogen chloride, hydrogen bromide, or hydrogen iodide into the corresponding alkyl halide.



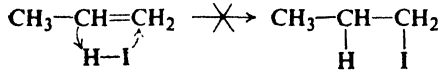
The reaction is frequently carried out by passing the dry gaseous hydrogen halide directly into the alkene. Sometimes the moderately polar solvent, acetic acid, which will dissolve both the polar hydrogen halide and the non-polar alkene, is used. The familiar aqueous solutions of the hydrogen halides are not generally used; in part, this is to avoid the addition of water to the alkene (Sec. 6.9).

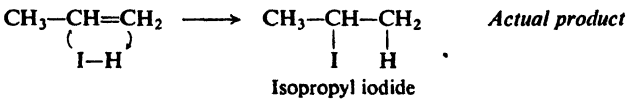
Problem 6.2 (a) What is the acid in an aqueous solution of HBr? In dry HBr? (b) Which is the stronger acid? (c) Which can better transfer a hydrogen ion to an alkene?

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

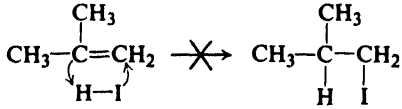


Propylene could yield either of two products, the *n*-propyl halide or the isopropyl halide, depending upon the orientation of addition, that is, depending upon which carbon atoms the hydrogen and halogen become attached to. Actually, it is found that the isopropyl halide greatly predominates.

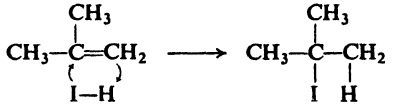




In the same way, isobutylene could yield either of two products, isobutyl halide or *tert*-butyl halide; here the orientation of addition is such that the *tert*-butyl halide greatly predominates.



Isobutyl iodide



Actual product

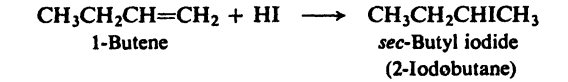
tert-Butyl iodide

Orientation in alkane substitutions (Sec. 3.21) depends upon which hydrogen is replaced; orientation in alkene additions depends upon which doubly-bonded carbon accepts Y and which accepts Z of a reagent YZ.

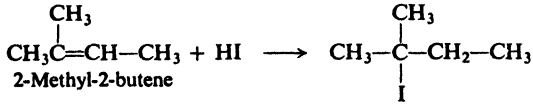
Examination of a large number of such additions showed the Russian chemist Vladimir Markovnikov (of the University of Kazan) that where two isomeric products are possible, one product usually predominates. He pointed out in 1869 that the orientation of addition follows a pattern which we can summarize as: *In the ionic addition of an acid to the carbon–carbon double bond of an alkene, the hydrogen of the acid attaches itself to the carbon atom 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.

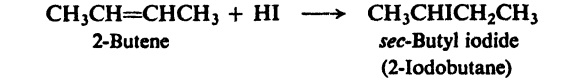
Using Markovnikov's rule, we can correctly predict the principal product of many reactions. For example:



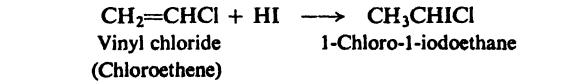
1-Butene — *sec*-Butyl iodide (2-Iodobutane)



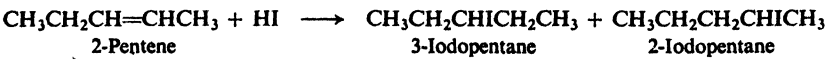
2-Methyl-2-butene — *tert*-Pentyl iodide (2-Iodo-2-methylbutane)



2-Butene — *sec*-Butyl iodide (2-Iodobutane)



Vinyl chloride (Chloroethene) — 1-Chloro-1-iodoethane



2-Pentene — 3-Iodopentane + 2-Iodopentane

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 **regiospecific.** (From the Latin *regio*, direction, and pronounced "reejio.")

Addition of hydrogen halides to alkenes can be used to make alkyl halides. The fact that addition occurs with a specific orientation, as summarized by Markovnikov's rule, rather than at random, is an advantage since a fairly pure product can generally be obtained. At the same time, the synthesis is, of course, limited to those products that are formed in agreement with Markovnikov's rule; for example, we can make isopropyl iodide in this way, but not *n*-propyl iodide. (As we shall see later, there are other, more important ways to prepare alkyl halides.)

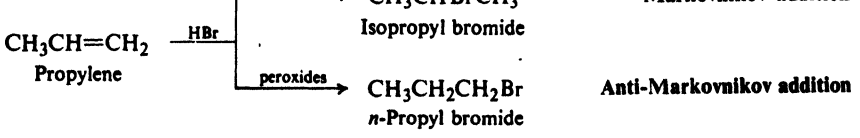
6.7 Addition of hydrogen bromide. Peroxide effect

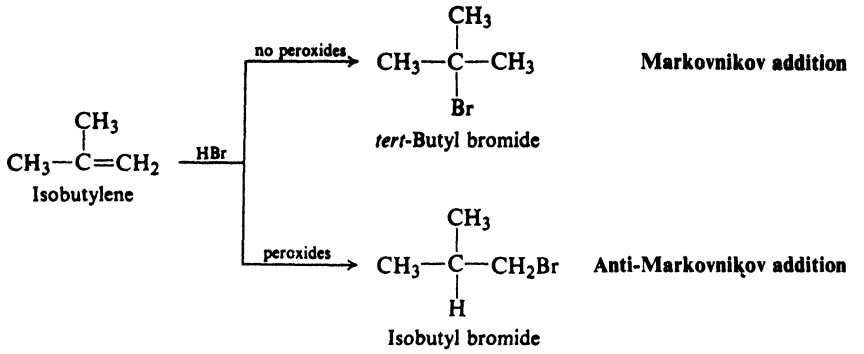
Addition of hydrogen chloride and hydrogen iodide to alkenes follows Markovnikov's rule. Until 1933 the situation with respect to hydrogen bromide was exceedingly confused. It had been reported by some workers that addition of hydrogen bromide to a particular alkene yields a product in agreement with 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. W. Mayo at the University of Chicago 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.

Kharasch and Mayo found that if one carefully excludes peroxides from the reaction system, or if one adds certain **inhibitors**—*hydroquinone* (p. 878), for example, or *diphenylamine* (p. 728)—the addition of HBr to alkenes follows Markovnikov's rule. On the other hand, if one does not exclude peroxides, or if one



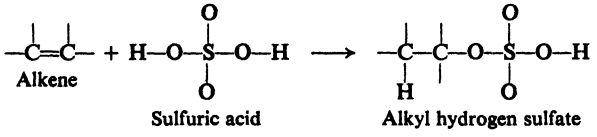


deliberately puts peroxides into the reaction system, HBr adds to alkenes in exactly the reverse direction.

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 (Secs. 6.11 and 6.17), 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.

6.8 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 ion to one side of the double bond and bisulfate



ion to the other. It is important to notice that carbon is bonded to oxygen and not to sulfur.

Reaction is carried out simply by bringing the reactants into contact: a gaseous alkene is bubbled through 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 later account for this in a reasonable way (Sec. 6.11).

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 alkyl hydrogen sulfate has been cleaved by water to form the alcohol and sulfuric acid, and is said to have been *hydrolyzed.* 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

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} \xrightarrow{98\%\ H_2SO_4} \underset{\text{Ethyl hydrogen sulfate}}{CH_3CH_2OSO_3H} \xrightarrow{H_2O,\ \text{heat}} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + H_2SO_4$$

$$\underset{\text{Propylene}}{CH_3CH{=}CH_2} \xrightarrow{80\%\ H_2SO_4} \underset{\text{Isopropyl hydrogen sulfate}}{CH_3CH(OSO_3H)CH_3} \xrightarrow{H_2O,\ \text{heat}} \underset{\text{Isopropyl alcohol}}{CH_3CH(OH)CH_3}$$

$$\underset{\text{Isobutylene}}{CH_3C(CH_3){=}CH_2} \xrightarrow{63\%\ H_2SO_4} \underset{\textit{tert}\text{-Butyl hydrogen sulfate}}{CH_3C(OSO_3H)(CH_3)CH_3} \xrightarrow{H_2O,\ \text{heat}} \underset{\textit{tert}\text{-Butyl alcohol}}{CH_3C(OH)(CH_3)CH_3}$$

obtained by the cracking of petroleum. Because the addition of sulfuric acid follows Markovnikov's rule, 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.

6.9 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

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

the same as those obtained by the two-step synthesis just described; this direct hydration is, of course, the simpler and cheaper of the two processes. Hydration of alkenes is the principal industrial source of those lower alcohols whose formation is consistent with Markovnikov's rule.

$$\underset{\text{Isobutylene}}{CH_3C(CH_3){=}CH_2} \xrightarrow{H_2O,\ H^+} \underset{\textit{tert}\text{-Butyl alcohol}}{CH_3C(OH)(CH_3)CH_3}$$

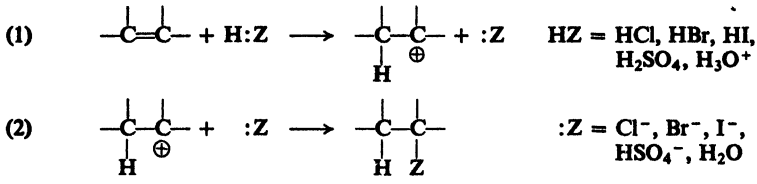
6.10 Electrophilic addition: mechanism

Before we consider other reactions of alkenes, it will be helpful to examine the mechanism of some of the reactions we have already discussed. 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.

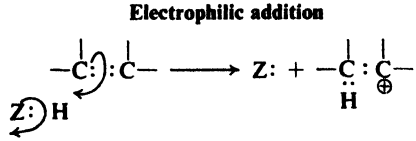
We shall take up first the addition of those reagents which contain ionizable hydrogen: the hydrogen halides, sulfuric acid, and water. The generally accepted mechanism will be outlined, and then we shall see how this mechanism accounts for certain facts. Like dehydration of alcohols, addition is pictured as involving carbonium ions. We shall notice certain resemblances between these two kinds of reaction; these resemblances are evidence that a common intermediate is involved.

Addition of the acidic reagent, HZ, is believed to proceed by two steps:

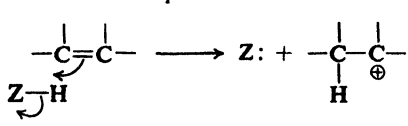


Step (1) involves transfer of hydrogen ion from :Z to the alkene to form a carbonium ion; this is a transfer of a proton from one base to another.

Electrophilic addition



represented as



Step (2) is the union of the carbonium ion with the base :Z.

Step (1) is the 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 called **electrophilic addition**. The electrophile need not necessarily be a Lowry–Bronsted acid transferring a proton, as shown here, but, as we shall see, can be almost any kind of electron-deficient molecule (Lewis acid).

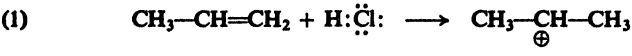
On the basis of step (2), we can add another reaction to our list of Sec. 5.22.

A carbonium ion may:

(c) combine with a negative ion or other basic molecule to form a halide, a bisulfate, an alcohol, etc.

This reaction, like the earlier ones, provides the electron-deficient carbon with a pair of electrons.

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



(2) $CH_3-\underset{\oplus}{CH}-CH_3 + :\ddot{\underset{\cdot\cdot}{Cl}}:^- \longrightarrow CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3$

of sulfuric acid,

(1) $CH_3-CH=CH_2 + H:OSO_3H \longrightarrow CH_3-\underset{\oplus}{CH}-CH_3 + :OSO_3H^-$

(2) $CH_3-\underset{\oplus}{CH}-CH_3 + :OSO_3H^- \longrightarrow CH_3-\underset{OSO_3H}{\underset{|}{CH}}-CH_3$

and of water.

(1) $CH_3-CH=CH_2 + H:OH_2^+ \rightleftharpoons CH_3-\underset{\oplus}{CH}-CH_3 + :OH_2$

(2a) $CH_3-\underset{\oplus}{CH}-CH_3 + :OH_2 \rightleftharpoons CH_3-\underset{\oplus OH_2}{\underset{|}{CH}}-CH_3$

(2b) $CH_3-\underset{\oplus OH_2}{\underset{|}{CH}}-CH_3 + :OH_2 \rightleftharpoons CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 + H:OH_2^+$

We notice that the carbonium ion 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 (Sec. 5.20). 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.

Let us see how this mechanism accounts for some of the facts.

First, the mechanism is consistent with (a) *the acidic nature of the reagents.* According to the mechanism, the first step in all these reactions is the transfer of a hydrogen ion to the alkene. This agrees with the fact that all these reagents except water are strong acids in the classical sense; that is, they can readily supply hydrogen ions. The exception, water, requires the presence of a strong acid for reaction to occur.

Next, the mechanism is consistent with (b) *the basic nature of alkenes.* The mechanism pictures the alkene as a base, supplying electrons to an attacking acid. This agrees with the structure of the carbon–carbon double bond: basicity is due to the loosely held, mobile π electrons.

In the following sections we shall see that the mechanism is also consistent with (c) *the orientation of addition,* (d) *the relative reactivities of alkenes,* and (e) *the occurrence of rearrangements.*

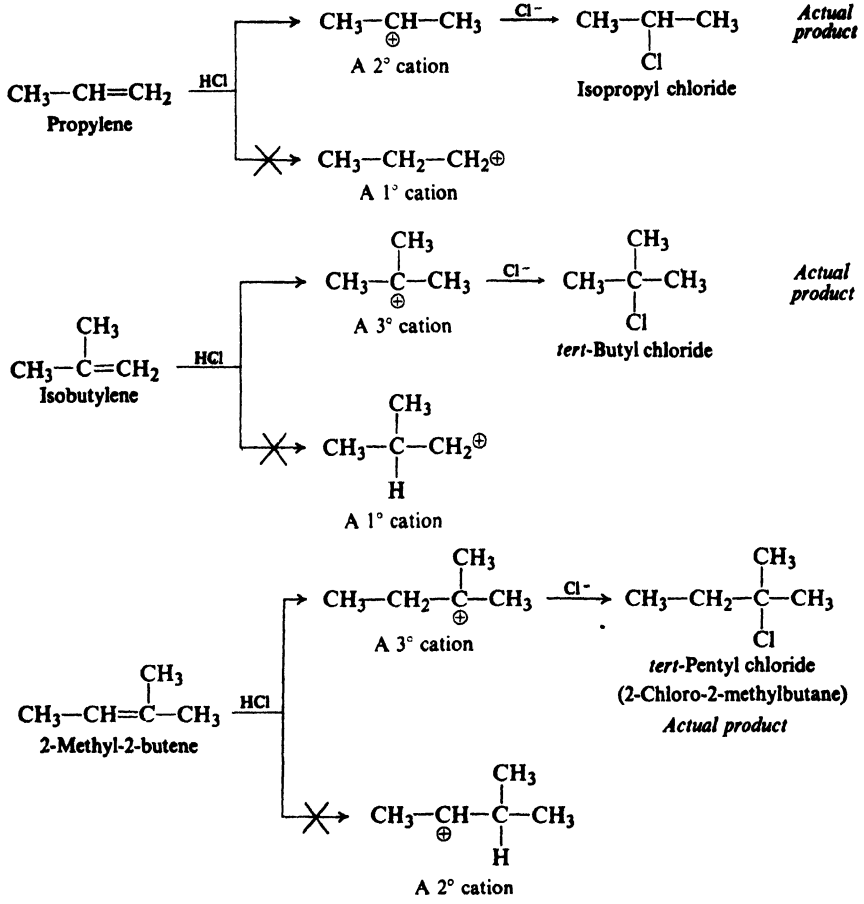
Problem 6.3 Addition of D_2O to 2-methyl-2-butene (in the presence of D^+) was found (as we might expect) to yield the alcohol $(CH_3)_2C(OD)CHDCH_3$. When the reaction was about half over, it was interrupted and the unconsumed alkene was isolated; mass spectrometric analysis showed that it contained almost no deuterium. This fact is considered to be evidence that formation of the carbonium ion is rate-determining: that as soon as a carbonium ion is formed, it rapidly reacts with water to yield the alcohol. Show how this conclusion is justified. (*Hint:* What results would

you expect if the carbonium ions were formed rapidly and reversibly, and only every so often combined with water?)

6.11 Electrophilic addition: orientation and reactivity

The mechanism is consistent with the orientation of addition of acidic reagents, and with the effect of structure on relative reactivities.

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.



Which alkyl halide is obtained depends upon which intermediate carbonium ion is formed. This in turn depends upon the alkene and upon which carbon of the double bond hydrogen goes to. Propylene, for example, could yield an *n*-propyl cation if hydrogen went to C–2 or an isopropyl cation if hydrogen went to C–1.

Orientation is thus determined by the relative rates of two competing reactions: formation of one carbonium ion or another. The fact that propylene is converted

into the isopropyl cation instead of the *n*-propyl cation means that the isopropyl cation is formed *faster* than the *n*-propyl cation.

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 many cases of addition of acids to alkenes shows that this is a general rule: orientation is governed by the ease of formation of carbonium ions, which follows the sequence $3° > 2° > 1°$.

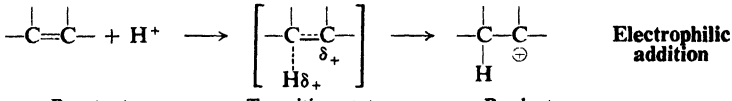
In listing carbonium ions in order of their ease of formation from alkenes, we find that once more (compare Sec. 5.21) we have listed them in order of their stability (Sec. 5.18).

Stability of carbonium ions $3° > 2° > 1° > CH_3^+$

We can now replace Markovnikov's rule by a more general rule: **electrophilic addition to a carbon–carbon double bond involves the intermediate formation of the more stable carbonium ion.**

Is it reasonable that the more stable carbonium ion should be formed more easily? We answered this question in Sec. 5.21 by considering the transition state leading to a carbonium ion; let us do the same here.

In addition reactions, the carbonium ion is formed by attachment of hydrogen ion to one of the doubly-bonded carbons. In the reactant the positive charge is entirely on the hydrogen ion; in the product it is on the carbon atom. In the transition state, the C—H bond must be partly formed, and the double bond partly broken. As a result the positive charge is divided between hydrogen and carbon.



Reactants	Transition state	Product
Hydrogen has full positive charge	*Carbon and hydrogen have partial positive charges*	*Carbon has full positive charge*

Electron-releasing groups tend to disperse the partial positive charge (δ_+) 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. 6.4). As before, the electron release that stabilizes the carbonium ion also stabilizes the *incipient* carbonium ion in the transition state. The more stable carbonium ion is formed faster.

Thus, the rate of addition of a hydrogen ion to a double bond depends upon the stability of the carbonium ion being formed. As we might expect, this factor determines not only the **orientation** of addition to a simple 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

$$\begin{matrix} CH_3 \\ \diagdown \\ \quad C{=}CH_2 \\ \diagup \\ CH_3 \end{matrix} > CH_3CH{=}CHCH_3, CH_3CH_2CH{=}CH_2, CH_3CH{=}CH_2 > CH_2{=}CH_2 > CH_2{=}CHCl$$

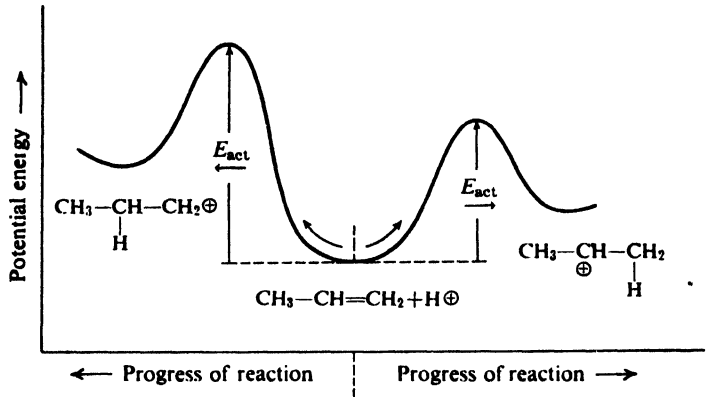


Figure 6.4. Molecular structure and orientation of reaction. Stability of transition state parallels stability of carbonium ion: more stable carbonium ion formed faster.

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.

$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + H^+ \longrightarrow CH_3-\overset{CH_3}{\overset{|}{\underset{\oplus}{C}}}-CH_3$$
Isobutylene — A 3° cation

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

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

$$CH_3CH=CH_2 + H^+ \longrightarrow CH_3\underset{\oplus}{C}HCH_3$$
Propylene — 2° cation

$$CH_2=CH_2 + H^+ \longrightarrow CH_3CH_2\oplus$$
Ethylene — A 1° cation

Halogens, like other elements in the upper right-hand corner of the Periodic Table, tend to attract electrons. Just as electron release by alkyl groups disperses the positive charge and stabilizes a carbonium ion, so electron withdrawal by halogens intensifies the positive charge and destabilizes the carbonium ion. It is not surprising that vinyl chloride, CH_2=CHCl, is *less* reactive than ethylene.

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 carbonium ions. We know that the more stable the carbonium ion, the faster it is formed; that its stability depends upon dispersal of the charge; and that dispersal

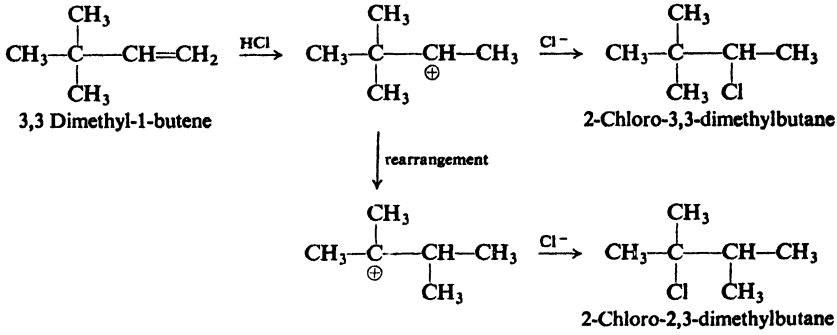
of charge is determined by the electronic effects of the attached groups. We have already found that this same approach enables us to deal with such seemingly different facts as (a) the relative ease of dehydration of alcohols; (b) the relative reactivities of alkenes toward addition of acids; and (c) the orientation of addition of acids to alkenes.

6.12 Electrophilic addition: rearrangement

The mechanism of electrophilic addition is consistent with the occurrence of rearrangements.

If carbonium ions are intermediates in electrophilic addition, then we should expect the reaction to be accompanied by the kind of rearrangement that we said earlier is highly characteristic of carbonium ions (Sec. 5.22). Rearrangements are not only observed, but they occur according to just the pattern that would be predicted.

For example, addition of hydrogen chloride to 3,3-dimethyl-1-butene yields not only 2-chloro-3,3-dimethylbutane, but also 2-chloro-2,3-dimethylbutane:



Since a 1,2-shift of a methyl group can convert the initially formed secondary cation into the more stable tertiary cation, such a rearrangement does occur, and much of the product is derived from this new ion. (If we compare this change in carbon skeleton with the one accompanying dehydration of 3,3-dimethyl-2-butanol (p. 171), we can begin to see how the idea arose that these apparently unrelated reactions proceed through the same intermediate.)

Problem 6.4 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.

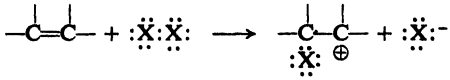
Problem 6.5 The reaction of aqueous HCl with 3,3-dimethyl-2-butanol yields 2,3-dimethyl-2-chlorobutane. ***Using only reaction steps that you have already encountered,*** propose a detailed mechanism for this reaction. (Check your answer in Sec. 16.5.)

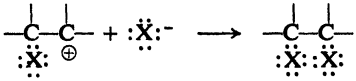
6.13 Mechanism of addition of halogens

Electrophilic addition of acids to alkenes involves two steps, the first being attachment of hydrogen ion to form the carbonium ion. What is the mechanism of the addition of chlorine and bromine?

From the structure of the double bond we might expect that here again it is an electron source, a base, and hence that the halogen acts as an electrophilic reagent, an acid. This idea is supported by the fact that alkenes usually 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 an alkene.

The commonly accepted mechanism for addition of halogens to alkenes has two steps, and is quite analogous to the mechanism for addition of hydrogen-containing acids (protic acids). In step (1) halogen adds as a positive halogen ion

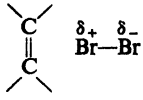
(1) 

(2) 

to the double bond to form a carbonium ion. In step (2) the carbonium ion combines with a negative halide ion. (The mechanism is somewhat simplified for our present purpose, and will be modified in Sec. 7.12.)

It seems reasonable that an alkene should abstract hydrogen ion from the very polar hydrogen halide molecule. Is it reasonable that an alkene should abstract a positive halogen ion from the non-polar halogen molecule? Let us look at this problem more closely.

It is true that a halogen molecule is non-polar, since the two identical atoms share electrons equally. This is certainly not true, however, for a halogen molecule while it is under the influence of the powerful electric field of a nearby carbon–carbon double bond. The dense electron cloud of the double bond tends to repel the similarly charged electron cloud of the halogen molecule; this repulsion makes the halogen atom that is nearer the double bond relatively positive and its partner



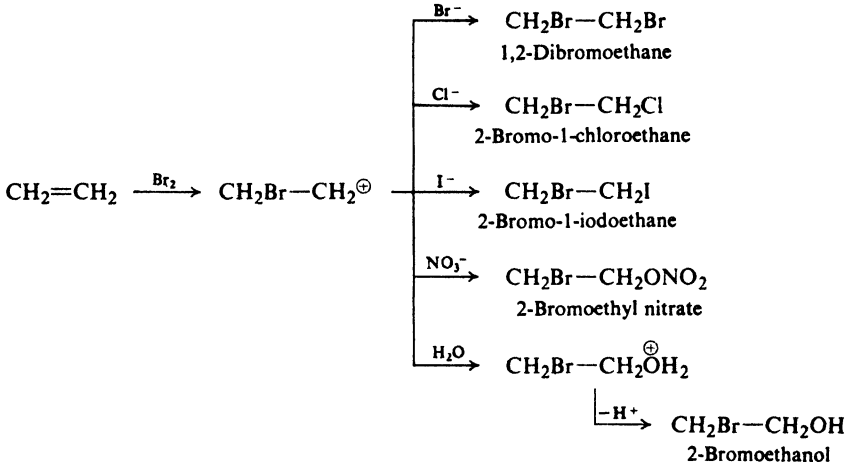
Polarization of Br_2 by a double bond

relatively negative. *The distortion of the electron distribution in one molecule caused by another molecule is called* **polarization**. Here, we would say that the alkene has *polarized* the halogen molecule.

The more positive halogen of this polarized molecule is then abstracted by the alkene to form a carbonium ion, leaving a negative halide ion. This halide ion, or more probably another just like it, finally collides with the carbonium ion to yield the product, a dihalide.

Let us look at some of the evidence for this mechanism. If a carbonium ion is the intermediate, we might expect it to react with almost any negative ion or basic molecule that we care to provide. For example, the carbonium ion formed in the reaction between ethylene and bromine should be able to react not only with bromide ion but also—if these are present—with chloride 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 carbonium 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 into the dibromo compound and the bromoalcohol:

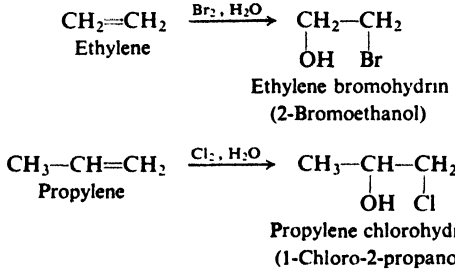


Bromine in water with no added ions yields the dibromo compound and the bromoalcohol.

In addition to the elegant work just described, the stereochemistry of the reaction provides powerful support for a two-step addition of halogen. At the same time, as we shall see in Sec. 7.12, it requires a modification in the mechanism.

6.14 Halohydrin formation

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

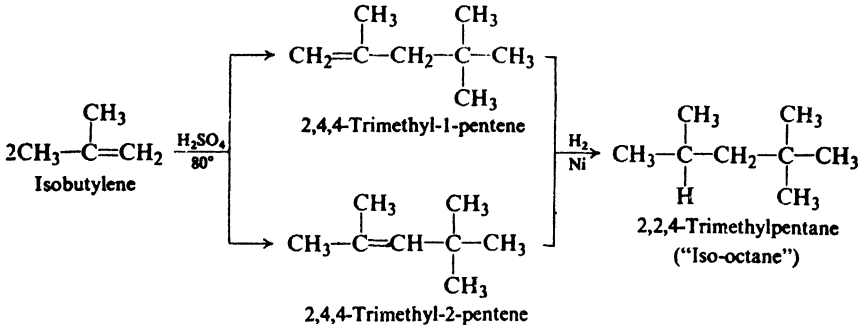


There is evidence, of a kind we are not prepared to go into here, that these compounds are formed by reaction of halogen and water (as shown in Sec. 6.13) rather than by addition of preformed hypohalous acid, HOX. Whatever the mechanism, the result is addition of the elements of hypohalous acid (HO— and —X), and the reaction is often referred to in that way.

We notice that in propylene chlorohydrin chlorine is attached to the terminal carbon. This orientation is, we say, quite understandable in light of the mechanism and what we know about formation of carbonium ions: the initial addition of chlorine occurs in the way that yields the more stable secondary cation. However, we shall have to modify (Sec. 17.15) this interpretation of the orientation to fit the modified mechanism of Sec. 7.12.

6.15 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 (Sec. 3.30). The two alkenes are isomers, then, and differ only in position of the double bond. *{Problem:* Could they, instead, be *cis–trans* isomers?) When studied by the methods discussed at the end of this chapter (Sec. 6.29), these two alkenes are found to have the structures shown:



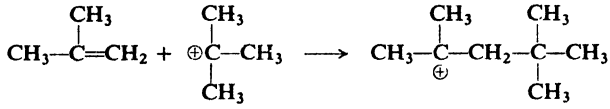
Since the alkenes produced contain exactly twice the number of carbon and hydrogen atoms as the original isobutylene, they are known as **dimers** (*di* = two, *mer* = part) of isobutylene, and the reaction is called **dimerization**. Other alkenes undergo analogous dimerizations.

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

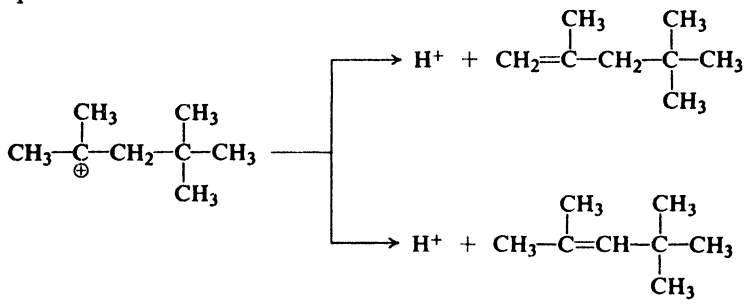
(1) $$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 + H^+ \longrightarrow CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_3 \quad (\oplus)$$

A carbonium ion undergoes reactions that provide electrons to complete the octet of the positively charged carbon atom. But a carbon–carbon double bond is an excellent electron source, and a carbonium ion 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. Step (2) brings about the union of two isobutylene units, which is, of course, necessary to account for the products.

What is this new carbonium ion 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 carbonium ion 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.



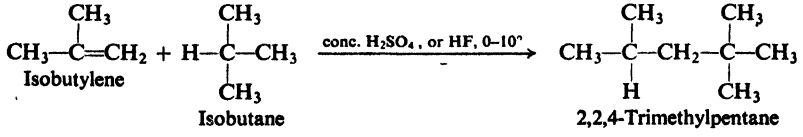
We find that the products expected on the basis of our mechanism are just the ones that are actually obtained. The fact that we can make this prediction simply on the basis of the fundamental properties of carbonium ions as we understand them is, of course, powerful support for the entire carbonium ion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

From what we have seen here, we can add one more reaction to those undergone by carbonium ions. **A carbonium ion may:**

(d) add to an alkene to form a larger carbonium ion.

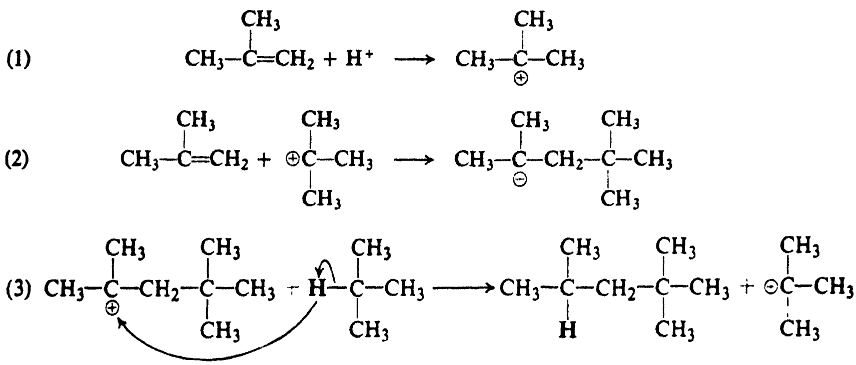
6.16 Addition of alkanes. Alkylation

The large amounts of 2,2,4-trimethylpentane consumed as high-test gasoline are not made today by the dimerization reaction just described, but in another, cheaper way. Isobutylene and isobutane are allowed to react in the presence of an



acidic catalyst, to form directly 2,2,4-trimethylpentane, or "iso-octane." This reaction is, in effect, addition of an alkane to an alkene.

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



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

The first two steps are identical with those of the dimerization reaction. In step (3) a carbonium ion 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 carbonium ion 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 carbonium ions (Sec. 5.22). There, transfer was *intramolecular* (within a molecule); here, it is *intermolecular* (between molecules). We shall find hydride transfer playing an important part in the chemistry of carbonyl compounds (Chap. 19).

Let us now bring our list of carbonium ion reactions up to date. **A carbonium ion may:**

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

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

As we see, all reactions of a carbonium ion have a common end: *they provide a pair of electrons to complete the octet of the positively charged carbon.*

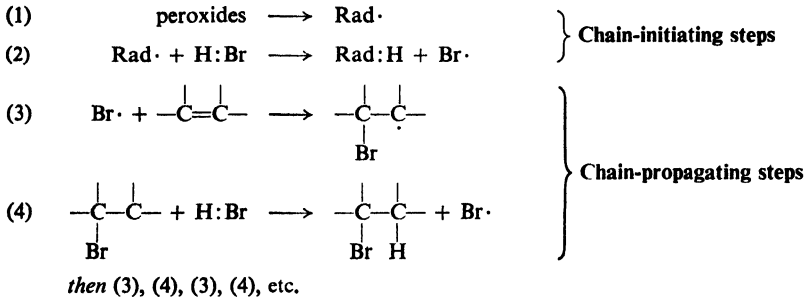
Problem 6.6 When ethylene is alkylated by isobutane in the presence of acid, there is obtained, not neohexane, $(CH_3)_3CCH_2CH_3$, but chiefly 2,3-dimethylbutane. Account in detail for the formation of this product.

6.17 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 (see Sec. 6.7).

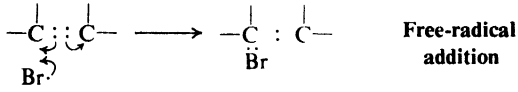
To account for this *peroxide effect*, Kharasch and Mayo proposed that addition can take place by two entirely different mechanisms: Markovnikov addition by the ionic mechanism that we have just discussed, and anti-Markovnikov addition by a free-radical mechanism. Peroxides initiate the free-radical reaction; in their absence (or if an inhibitor, p. 189, is added), addition follows the usual ionic path.

The essence of the mechanism is that hydrogen and bromine add to the double bond as *atoms* rather than as ions; the intermediate is a *free radical* rather than a



carbonium ion. Like halogenation of alkanes, this is a chain reaction, this time involving addition rather than substitution.

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. The bromine atom adds to the double bond (step 3), and, in doing so, converts the alkene into a free radical.



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.

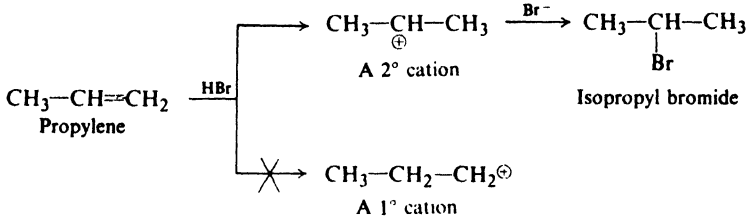
We must not confuse the effects of peroxides, which may have been formed by the action of oxygen, with the effects of oxygen itself. Peroxides *initiate* free-radical reactions; oxygen *inhibits* free-radical reactions (see Sec. 2.14).

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.

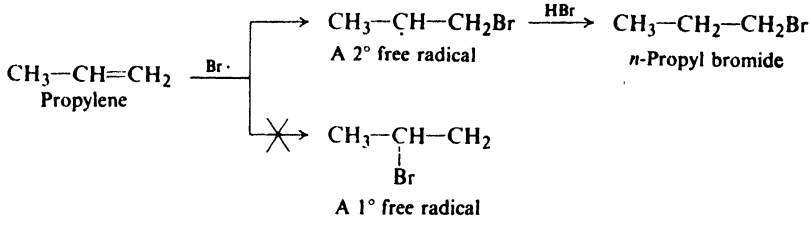
Recently, the light-catalyzed addition of hydrogen bromide to several alkenes was studied by means of esr (electron spin resonance) spectroscopy, which not only can detect the presence of free radicals at extremely low concentrations, but also can tell something about their structure (see Sec. 13.14). Organic free radicals were shown to be present at appreciable concentration, in agreement with the mechanism.

Is it reasonable that free-radical addition of hydrogen bromide should occur with orientation opposite to that of ionic addition? Let us compare the two kinds of addition to propylene.

Ionic addition: *Markovnikov orientation*



Free-radical addition: *Anti-Markovnikov orientation*



Ionic addition yields isopropyl bromide because a secondary cation is formed faster than a primary. Free-radical addition yields *n*-propyl bromide because a secondary free radical is formed faster than a primary. Examination of many cases of anti-Markovnikov addition shows that orientation is governed by the ease of formation of free radicals, which follows the sequence 3° > 2° > 1°.

In listing free radicals in order of their ease of formation from alkenes, we find that once more (compare Sec. 3.25) we have listed them in order of their stability (Sec. 3.24):

Stability of free radicals $3° > 2° > 1° > CH_3\cdot$

Free-radical addition to a carbon–carbon double bond involves the intermediate formation of the more stable free radical.

Thus we find the chemistry of free radicals and the chemistry of carbonium ions following much the same pattern: the more stable particle is formed more easily, whether by abstraction or dissociation, or by addition to a double bond. Even the order of stability of the two kinds of particle is the same: $3° > 2° > 1° > CH_3$. In this particular case orientation is reversed simply because the hydrogen adds first in the ionic reaction, and bromine adds first in the radical reaction.

6.18 Other free-radical additions

In the years since the discovery of the peroxide effect, dozens of reagents besides HBr have been found (mostly by Kharasch) to add to alkenes in the presence of peroxides or light. Exactly analogous free-radical mechanisms are generally accepted for these reactions, too.

For the addition of carbon tetrachloride to an alkene, for example,

$$RCH{=}CH_2 + CCl_4 \xrightarrow{\text{peroxides}} \underset{\displaystyle Cl}{\overset{|}{RCH}}{-}CH_2{-}CCl_3$$

the following mechanism has been proposed:

(1) $$\text{peroxide} \longrightarrow \text{Rad}\cdot$$

(2) $$\text{Rad} + Cl{:}CCl_3 \longrightarrow \text{Rad}{:}Cl + CCl_3$$

(3) $$CCl_3 + RCH{=}CH_2 \longrightarrow \underset{\displaystyle \cdot}{RCH}{-}CH_2{-}CCl_3$$

(4) $$\underset{\displaystyle \cdot}{RCH}{-}CH_2{-}CCl_3 + Cl{:}CCl_3 \longrightarrow \underset{\displaystyle Cl}{\overset{|}{RCH}}{-}CH_2{-}CCl_3 + \cdot CCl_3$$

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

In the next section, we shall encounter another example of free-radical addition—*polymerization*—which has played a key part in the creation of this age of plastics.

Problem 6.7 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 $n\text{-}C_8H_{17}{-}S{-}CH_2COOH$;
(e) with aldehydes, $\underset{\displaystyle H}{\overset{|}{R{-}C}}{=}O$, to yield ketones, $n\text{-}C_8H_{17}{-}\underset{\displaystyle O}{\overset{\|}{C}}{-}R$.

Show all steps of a likely mechanism for these reactions.

Problem 6.8 From the addition of CCl_4 to alkenes, $RCH{=}CH_2$, there is obtained not only $RCHClCH_2CCl_3$, but also $RCHClCH_2{-}\underset{\displaystyle R}{\overset{|}{C}}HCH_2CCl_3$. *Using only the kinds of reactions you have already encountered,* suggest a mechanism for the formation of this second product.

Problem 6.9 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.

Free-radical addition is probably even commoner than has been suspected. Recent work indicates that free-radical chains do not always require light or decomposition of highly unstable compounds like peroxides for their initiation. Sometimes a change from a polar solvent—which can stabilize a polar transition state—to a non-polar solvent causes a change from a heterolytic reaction to a homolytic one (Sec. 1.14). In some cases, it may even be that chains are started by *concerted homolysis*, in which cleavage of comparatively stable molecules (halogens, for example) is aided by the simultaneous breaking and making of other bonds. In the absence of the clue usually given by the method of initiation, the free-radical nature of such reactions is harder to detect; one depends upon inhibition by oxygen, detailed analysis of reaction kinetics, or a change in orientation or stereochemistry.

6.19 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

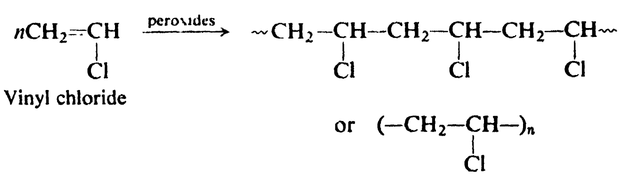
$$n\mathrm{CH_2{=}CH_2} \xrightarrow{\mathrm{O_2,\ heat,\ pressure}} \sim\mathrm{CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2}\sim \quad \text{or} \quad (\mathrm{{-}CH_2CH_2{-}})_n$$

Polyethylene

hence is called *polyethylene* (**poly** = many). 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 make 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



Vinyl chloride

Poly(vinyl chloride)

make phonograph records, plastic pipe, and—when plasticized with high-boiling esters—raincoats, shower curtains, and coatings for metals and upholstery fabrics.

Many other groups (e.g., $-COOCH_3$, $-CN$, $-C_6H_5$) 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.

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

$$\text{Rad}\cdot + CH_2{=}CH(R) \longrightarrow \text{Rad}CH_2{-}CH(R)\cdot \quad \left.\right\} \text{Chain-initiating steps}$$

$$\text{Rad}CH_2{-}CH(R)\cdot + CH_2{=}CH(R) \longrightarrow \text{Rad}CH_2{-}CH(R){-}CH_2{-}CH(R)\cdot \longrightarrow \textit{etc.}\ \textbf{Chain-propagating step}$$

This kind of polymerization, each step of which consumes a reactive particle and produces another, similar particle, is an example of *chain-reaction polymerization.* In Chap. 32, we shall encounter chain-reaction polymerization that takes place, not by way of free radicals, but by way of organic ions. We shall also encounter *step-reaction polymerization,* which involves a series of reactions each of which is essentially independent of the others.

Problem 6.10 Give the structure of the monomer from which each of the following polymers would most likely be made:

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

Problem 6.11 Can you suggest a reason why polymerization should take place in a way ("head-to-tail") that yields a polymer with regularly alternating groups?

6.20 Hydroxylation. Glycol formation

Certain oxidizing agents convert alkenes into compounds known as **glycols.** Glycols are simply dihydroxy alcohols; their formation amounts to the addition of two hydroxyl groups to the double bond.

$$-\overset{|}{C}{=}\overset{|}{C}- \xrightarrow[\text{or } HCO_3OH]{\text{cold alkaline } KMnO_4} -\overset{|}{\underset{OH}{C}}-\overset{|}{\underset{OH}{C}}-$$

A glycol

Of the numerous oxidizing agents that cause hydroxylation, two of the most commonly used are (a) cold alkaline $KMnO_4$, and (b) peroxyformic acid, HCO_2OH.

Hydroxylation with permanganate is 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. Heat and the addition of acid are avoided, since these more vigorous conditions promote further oxidation of the glycol, with cleavage of the carbon–carbon double bond (Sec. 6.29).

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 hydrolyze certain intermediate compounds.

A glycol is frequently named by adding the word *glycol* to the name of the alkene from which it is formed. For example:

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

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

Hydroxylation of alkenes is the most important method for the synthesis of glycols. Moreover, oxidation by permanganate is the basis of a very useful analytical test known as the **Baeyer test** (Sec. 6.30).

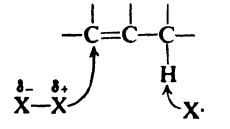
(We shall discuss the stereochemistry and mechanism of glycol formation in Sec. 17.12.)

6.21 Substitution by halogen. Allylic hydrogen

So far in our discussion of alkenes, we have concentrated on the carbon–carbon double bond, and on the addition reactions that take place there. Now let us turn to the alkyl groups that are present in most alkene molecules.

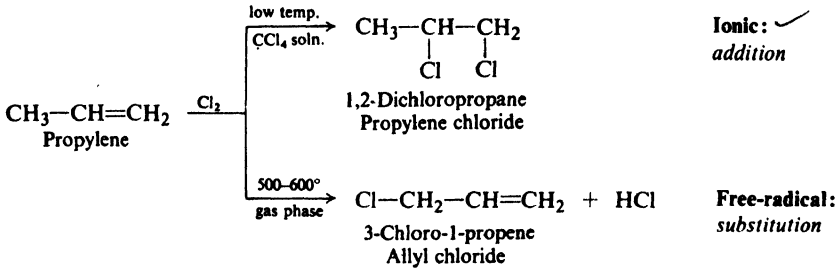
Since these alkyl groups have the alkane structure, they should undergo alkane reactions, for example, substitution by halogen. But an alkene molecule presents *two* sites where halogen can attack, the double bond and the alkyl groups. Can we direct the attack to just one of these sites? The answer is yes, *by our choice of experimental 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 ionic reactions, or at least do not aid formation of radicals.

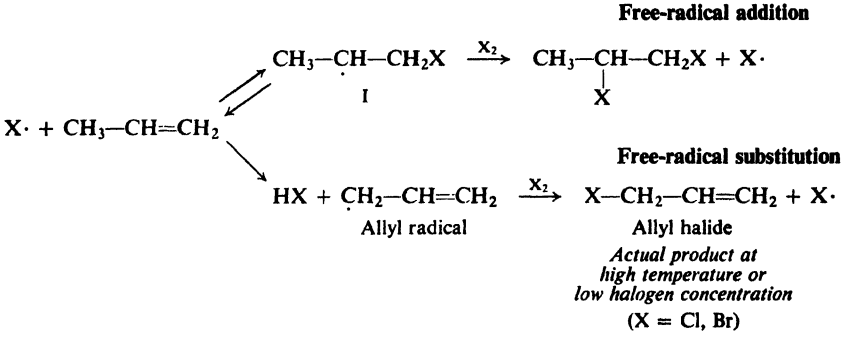


Ionic attack *Addition* — Free-radical attack *Substitution*

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 ionic reaction. Chemists of the Shell Development Company found that, at a temperature of 500–600°, 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.



In view of Secs. 6.17–6.18, we might wonder why a halogen atom does not add to a double bond, instead of abstracting a hydrogen atom. H. C. Brown (of Purdue University) has suggested that the halogen atom *does* add but, at high temperatures, is expelled before the second step of free-radical addition can occur.

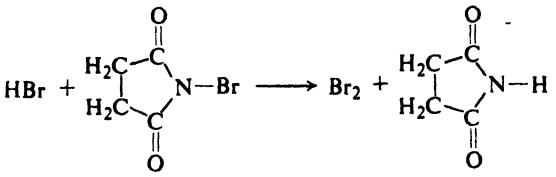


Consistent with Brown's explanation is the finding that *low concentration* of halogen can be used instead of high temperature to favor substitution over (free-radical) addition. Addition of the halogen atom gives radical I, which falls apart (to regenerate the starting material) if the temperature is 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 6.12 (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.

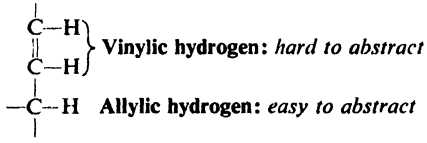


N-Bromosuccinimide (NBS) Succinimide

6.22 Orientation and reactivity in substitution

Thus alkenes undergo substitution by halogen in exactly the same way as do alkanes. Furthermore, just as the alkyl groups affect the reactivity of the double bond toward addition, so the double bond affects the reactivity of the alkyl groups toward substitution.

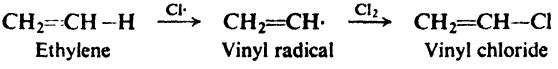
Halogenation of many alkenes has shown that: (a) hydrogens attached to doubly-bonded carbons undergo very little substitution; and (b) hydrogens attached to carbons adjacent to doubly-bonded carbons are particularly reactive toward substitution. Examination of reactions which involve attack not only 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 adjacent to a double bond, known as **allylic** hydrogens, are even easier to abstract than tertiary hydrogens.

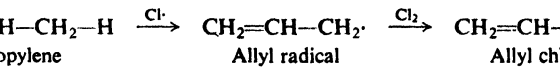


We can now expand the reactivity sequence of Sec. 3.23.

Ease of abstraction of hydrogen atoms allylic > 3° > 2° > 1° > CH_4, vinylic

Substitution in alkenes seems to proceed by the same mechanism as substitution in alkanes. For example:





Evidently the vinyl radical is formed very slowly and the allyl radical is formed very rapidly. We can now expand the sequence of Sec. 3.25.

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 in Table 1.2 (p. 21) show that 104 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 primary radical, and about the same as 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 91 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 of Sec. 3.24; 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. We have already seen (Sec. 5.4) a possible explanation for the unusually strong bond to vinylic hydrogen. The high stability of the allyl radical is readily accounted for by the structural theory: specifically, by the concept of *resonance.*

6.23 Resonance theory

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 be 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.

6.24 Resonance structure of the allyl radical

In the language of the resonance theory, then, the allyl radical is a resonance hybrid of the two structures, I and II.

$$\underset{\text{I}}{CH_2{=}CH{-}CH_2\cdot} \qquad \underset{\text{II}}{CH_2{-}CH{=}CH_2}$$

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 of the University of Chicago 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 of the California Institute of Technology 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.

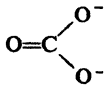
$$\underset{\text{I}\quad\text{II}}{[CH_2{=}CH{-}CH_2\cdot \quad \cdot CH_2{-}CH{=}CH_2]} \textit{ equivalent to } \underbrace{CH_2{=}CH{-}CH_2}_{\text{III}}$$

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.

Problem 6.13 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 A, as compared with a usual length of 1.36 A for a nitrogen-oxygen single bond and 1.18 A for a nitrogen-oxygen double bond. What is a better representation of the $-NO_2$ group?

Problem 6.14 The carbonate ion, CO_3^{--}, might be represented as



Actual measurement shows that all the carbon-oxygen bonds in $CaCO_3$ have the same length, 1.31 A, as compared with a usual length of about 1.36 A for a carbon-oxygen single bond and about 1.23 A for a carbon-oxygen double bond. What is a better representation of the CO_3^{--} ion?

6.25 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* (i.e., *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.

$$\underset{\text{Propane}}{CH_3CH_2CH_3} \longrightarrow \underset{n\text{-Propyl radical}}{CH_3CH_2CH_2\cdot} + H\cdot \qquad \Delta H = +98 \text{ kcal}$$

$$\underset{\text{Propylene}}{CH_2{=}CH{-}CH_3} \longrightarrow \underset{\text{Allyl radical}}{CH_2{=}CH{-}CH_2\cdot} + H\cdot \qquad \Delta H = +85$$

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/mole 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/mole.

6.26 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 (as in ethylene, Sec. 5.2). Overlap of these orbitals with each other and with the *s* orbitals of five hydrogen atoms gives the molecular skeleton shown in Fig. 6.5, with all bond angles 120°. In addition, 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.

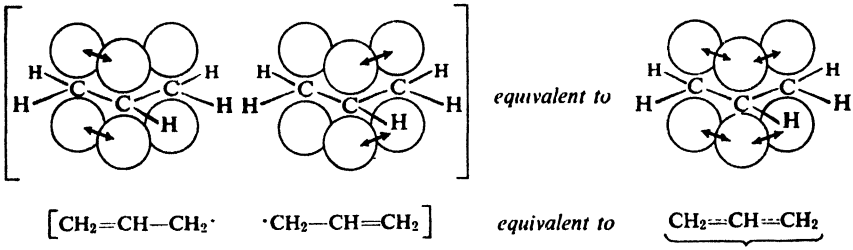


Figure 6.5. Allyl radical. The *p* orbital of the middle carbon overlaps *p* orbitals on both sides to permit delocalization of electrons.

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 (See 29.5). 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 (Sec. 2.21) 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.

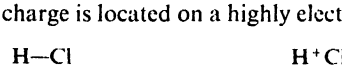
6.27 Using the resonance theory

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.

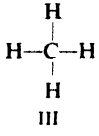
There are a number of other criteria that we can use to estimate relative stabilities, and hence relative importance, of contributing structures. One of these has to do with (a) *electronegativity and location of charge*.

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.



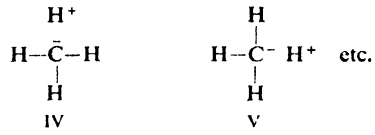
I II

On the other hand, we consider methane to be represented adequately by the single structure III.



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



IV V

electronegativity, carbon. We expect IV and V to make negligible contribution to the hybrid and hence we ignore them.

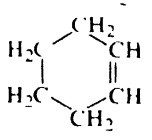
In later sections we shall use certain other criteria to help us estimate stabilities of possible contributing structures: (b) *number of bonds* (Sec. 8.17); (c) *dispersal of charge* (Sec. 11.19); (d) *complete vs. incomplete octet* (Sec. 11.20); (e) *separation of charge* (Sec. 18.12).

Finally, we shall find certain cases where the overwhelming weight of evidence —bond lengths, dipole moments, reactivity-- indicate that an accurate description of a given molecule requires contribution from structures of a sort that may appear quite unreasonable to us (Secs. 6.28 and 8.18); 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.

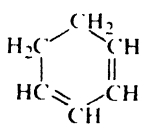
In the next section, we shall encounter contributing structures that are very strange looking indeed.

Problem 6.15 The ionization potential of the allyl radical is 188 kcal/mole. (a) How does the allyl cation compare in stability with the simple alkyl cations of Sec. 5.18? (b) Is the cation adequately represented by the structure CH_2–$CHCH_2^+$? Describe its structure in both valence-bond and orbital terms. (Check your answer in Sec. 8.21.)

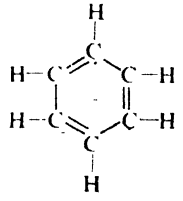
Problem 6.16 *Benzene*, C_6H_6, is a flat molecule with all bond angles 120° and all carbon carbon bonds 1.39 A long. Its heat of hydrogenation (absorption of three moles of hydrogen) is 49.8 kcal/mole, as compared with values of 28.6 for cyclohexene (one mole of hydrogen) and 55.4 for 1,3-cyclohexadiene (two moles of hydrogen). (a) Is benzene adequately represented by the Kekulé formula shown? (b) Suggest a



Cyclohexene



1,3-Cyclohexadiene



Benzene
(Kekulé formula)

better structure for benzene in both valence-bond and orbital terms. (Check your answer in Secs. 10.7–10.8.)

6.28 Resonance stabilization of alkyl radicals. Hyperconjugation

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. 6.6). Through this

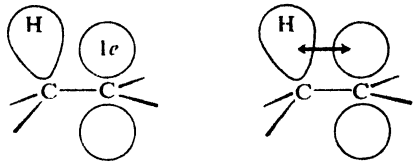
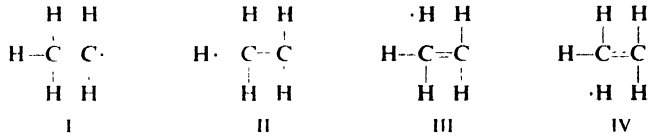


Figure 6.6. Hyperconjugation in an alkyl free radical. (a) Separate σ and *p* orbitals. (b) Overlapping orbitals.

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**.

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.

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, Sec. 3.24), 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/mole (104 − 95).

For the *tert*-butyl radical there should be nine such hyperconjugation structures. (*Draw them.*) Here we find a bond dissociation energy of 91 kcal, indicating a resonance stabilization of 13 kcal/mole (104 − 91).

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.

Problem 6.17 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

6.29 Ozonolysis. Determination of structure by degradation

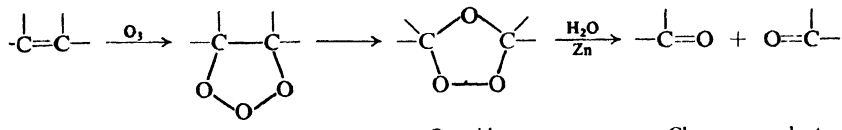
Along with addition and substitution we may consider a third general kind of alkene reaction, **cleavage**: a reaction in which the double bond is completely broken and the alkene molecule converted into two smaller molecules.

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:

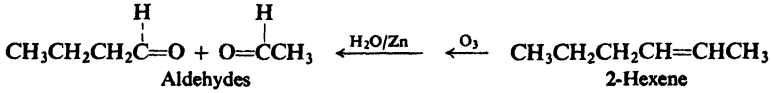
Ozonolysis



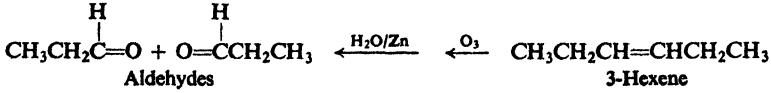
Alkene — Molozonide — Ozonide — Cleavage products (Aldehydes and ketones)

These compounds containing the C=O group are called *aldehydes* and *ketones*; at this point we need only know that they are compounds that can readily be identified (Sec. 19.17). 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.)

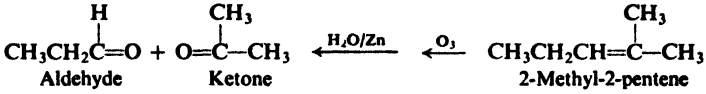
Knowing the number and arrangement of carbon atoms in these aldehydes and ketones, we can work back to the structure of the original alkene. For example, for three of the isomeric hexylenes:



Aldehydes — 2-Hexene

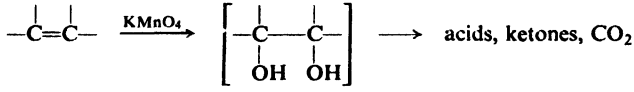


Aldehydes — 3-Hexene

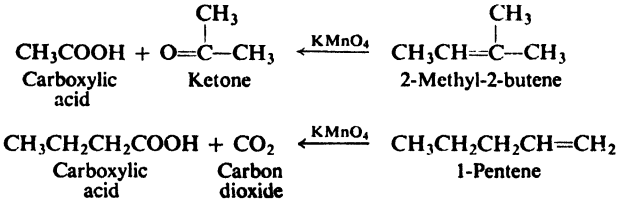


One general approach to the determination of the structure of an unknown compound is **degradation**, the breaking down of the unknown compound into a number of smaller, more easily identifiable fragments. Ozonolysis is a typical means of degradation.

Another method of degradation that gives essentially the same information—although somewhat less reliable—is vigorous oxidation by permanganate, which is believed to involve formation and cleavage of intermediate glycols (Sec. 6.20).



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



Problem 6.18 What products would you expect from each of the dimers of isobutylene (Sec. 6.15) upon cleavage by: (a) ozonolysis, (b) $KMnO_4$?

6.30 Analysis of alkenes

The functional group of an alkene is the carbon–carbon double bond. To characterize an unknown compound as an alkene, therefore, we must show that it undergoes the reactions typical of the carbon–carbon double bond. Since there are so many of these reactions, we might at first assume that this is an easy job. But let us look at the problem more closely.

First of all, which of the many reactions of alkenes do we select? Addition of hydrogen bromide, for example? Hydrogenation? Let us imagine ourselves in the laboratory, working with gases and liquids and solids, with flasks and test tubes and bottles.

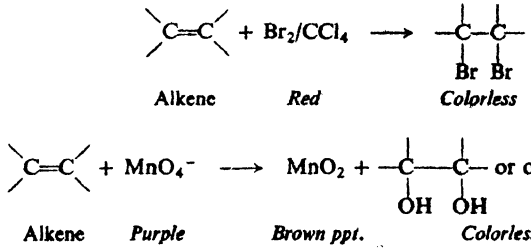
We could pass dry hydrogen bromide from a tank through a test tube of an unknown liquid. But what would we see? How could we tell whether or not a reaction takes place? A colorless gas bubbles through a colorless liquid; a different colorless liquid may or may not be formed.

We could attempt to hydrogenate the unknown compound. Here, we might say, we could certainly tell whether or not reaction takes place: a drop in the hydrogen pressure would show us that addition had occurred. This is true, and hydrogenation can be a useful analytical tool. But a catalyst must be prepared,

and a fairly elaborate piece of apparatus must be used; the whole operation might take hours.

Whenever possible, *we select for a characterization test a reaction that is rapidly and conveniently carried out, and that gives rise to an easily observed change.* We select a test that requires a few minutes and a few test tubes, a test in which a color appears or disappears, or bubbles of gas are evolved, or a precipitate forms or dissolves.

Experience has shown that an alkene is best characterized, then, by its property of decolorizing both a solution of bromine in carbon tetrachloride (Sec. 6.5) and a cold, dilute, neutral permanganate solution (the Baeyer test, Sec. 6.20). Both tests are easily carried out; in one, a red color disappears, and in the other, a purple color disappears and is replaced by brown manganese dioxide.



Granting that we have selected the best tests for the characterization of alkenes, let us go on to another question. We add bromine in carbon tetrachloride to an unknown organic compound, let us say, and the red color disappears. What does this tell us? Only that our unknown is a compound that reacts with bromine. It *may* be an alkene. But it is not enough merely to know that a particular kind of compound reacts with a given reagent; we must also know what *other* kinds of compounds also react with the reagent. In this case, the unknown may equally well be an alkyne. (It may also be any of a number of compounds that undergo rapid *substitution* by bromine; in that case, however, hydrogen bromide would be evolved and could be detected by the cloud it forms when we blow our breath over the test tube.)

In the same way, decolorization of permanganate does not prove that a compound is an alkene, but only that it contains some functional group that can be oxidized by permanganate. The compound *may* be an alkene; but it may instead be an alkyne, an aldehyde, or any of a number of easily oxidized compounds. It may even be a compound that is contaminated with an *impurity* that is oxidized; alcohols, for example, are not oxidized under these conditions, but often contain impurities that *are*. We can usually rule out this by making sure that more than a drop or two of the reagent is decolorized.

By itself, a single characterization test seldom proves that an unknown is one particular kind of compound. It may limit the number of possibilities, so that a final decision can then be made on the basis of additional tests. Or, conversely, if certain possibilities have already been eliminated, a single test may permit a final choice to be made. Thus, the bromine or permanganate test would be sufficient to differentiate an alkene from an alkane, or an alkene from an alkyl halide, or an alkene from an alcohol.

The tests most used in characterizing alkenes, then, are the following: (a) rapid decolorization of bromine in carbon tetrachloride without evolution of HBr, a test also given by alkynes; (b) decolorization of cold, dilute, neutral, aqueous permanganate solution (the Baeyer test), a test also given by alkynes and aldehydes. Also helpful is the solubility of alkenes in cold concentrated sulfuric acid, a test also given by a great many other compounds, including all those containing oxygen (they form soluble oxonium salts) and compounds that are readily sulfonated (Secs. 12.11 and 17.8). Alkanes or alkyl halides are not soluble in cold concentrated sulfuric acid.

Of the compounds we have dealt with so far, alcohols also dissolve in sulfuric acid. Alcohols can be distinguished from alkenes, however, by the fact that alcohols give a negative test with bromine in carbon tetrachloride and a negative Baeyer test—so long as we are not misled by impurities. Primary and secondary alcohols *are* oxidized by chromic anhydride, CrO_3, in aqueous sulfuric acid: within *two seconds*, the clear orange solution turns blue-green and becomes opaque.

$$\underset{\substack{1^\circ \text{ or } 2^\circ \\ \textit{Clear, orange}}}{ROH} + HCrO_4^- \longrightarrow \textit{Opaque, blue-green}$$

Tertiary alcohols do not give this test; nor do alkenes.

Problem 6.19 Describe simple chemical tests (if any) that would distinguish between: (a) an alkene and an alkane; (b) an alkene and an alkyl halide; (c) an alkene and a secondary alcohol; (d) an alkene, an alkane, an alkyl halide, and a secondary alcohol. Tell exactly what you would *do* and *see*.

Problem 6.20 Assuming the choice to be limited to alkane, alkene, alkyl halide, secondary alcohol, and tertiary alcohol, characterize compounds A, B, C, D, and E on the basis of the following information:

Compound	Qual. elem. anal.	H_2SO_4	Br_2/CCl_4	$KMnO_4$	CrO_3
A	-----	Insoluble	–	–	–
B	-----	Soluble	–	–	+
C	Cl	Insoluble	–	–	–
D	----	Soluble	+	+	–
E	----	Soluble	–	–	–

Once characterized as an alkene, an unknown may then be identified as a previously reported alkene on the basis of its physical properties, including its infrared spectrum and molecular weight. Proof of structure of a new compound is best accomplished by degradation: cleavage by ozone or permanganate, followed by identification of the fragments formed (Sec. 6.29).

(Spectroscopic analysis of alkenes will be discussed in Secs. 13.15–13.16.)

PROBLEMS

1. Draw a structural formula and give (when you can) an alternative name for:

(a) ethylene bromide
(b) ethyl bromide
(c) bromoethylene
(d) ethylene glycol
(e) propylene glycol
(f) propylene bromohydrin
(g) vinyl bromide
(h) allyl chloride

2. 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

3. 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

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

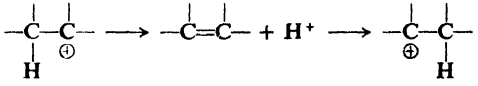
(a) 2-butene
(b) 2-pentene
(c) 2-methyl-1-butene
(d) 2-methyl-2-butene
(e) 3-methyl-1-butene (2 products)
(f) vinyl bromide
(g) 2,3-dimethyl-1-butene
(h) 2,4,4-trimethyl-2-pentene

5. 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.

6. 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.

7. 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.

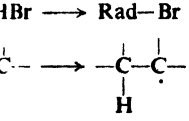
8. As an alternative to the one-step 1,2-hydride shift described in Sec. 5.22, one might instead propose—in view of the reactions we have studied in this chapter—that carbonium ions rearrange by a two-step mechanism, involving the intermediate formation of an alkene:

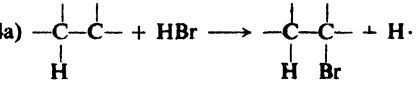


When (by a reaction we have not yet taken up) the isobutyl cation was generated in D_2O containing D_3O^+, there was obtained *tert*-butyl alcohol containing *no* deuterium attached to carbon. How does this experiment permit one to rule out the two-step mechanism?

9. In Sec. 6.17 a mechanism was presented for free-radical addition of hydrogen bromide. Equally consistent with the evidence given there is the following alternative mechanism:

(2a) Rad· + HBr $\longrightarrow$ Rad—Br + H·

(3a) 

(4a)  + H·

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 bond dissociation energies (Table 1.2, p. 21), is this mechanism more or less likely than (2)-(4) on p. 203? Explain.

(b) The esr study (p. 204) 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).

10. (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 bond dissociation energies: π bond, 68 kcal; 1° R—Br, 69 kcal; 1° R—Cl, 82 kcal; 2° R—H, 95 kcal.

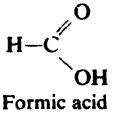
(d) Suggest a possible reason why the peroxide effect is observed for HBr but not for HCl.

11. When isobutylene and chlorine are allowed to react in the dark at 0° 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?

12. How do you account for the following facts: formic acid, HCOOH, contains one carbon-oxygen bond of 1.36 A and another of 1.23 A, yet sodium formate, $HCOO^-Na^+$, contains two equal carbon-oxygen bonds, each of 1.27 A. (Check your answer in Sec. 18.13.)



Formic acid

13. (a) When 1-octene is allowed to react with N-bromosuccinimide, there is obtained not only 3-bromo-1-octene but also 1-bromo-2-octene. How can you account for this? (b) Propylene, $CH_3CH{=}{}^{14}CH_2$, labeled with carbon-14 (a radioactive isotope) is converted into allyl bromide by free-radical bromination. What would you predict about the position of the tagged atom (^{14}C) in the product?

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

(a) $CH_3CH_2CH_2CHO$ and HCHO

(b) $CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CHO$ and CH_3CHO

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

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

(e) What would each of these alkenes yield upon cleavage by $KMnO_4$?

15. Describe simple chemical tests that would distinguish between:

(a) 2-chloropentane and *n*-heptane
(b) 2-hexene and *tert*-butyl bromide
(c) isobutane and isobutylene
(d) allyl bromide and 1-hexene
(e) *sec*-butyl alcohol and *n*-heptane
(f) 1-octene and *n*-pentyl alcohol
(g) *tert*-pentyl alcohol and 2,2-dimethylhexane
(h) *n*-propyl alcohol and allyl alcohol ($CH_2{=}CHCH_2OH$)

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

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

17. Outline all steps in a possible laboratory synthesis of each of the following compounds, using only the organic source given, plus any necessary solvents and inorganic reagents. (See general instructions about synthesis below.)

(a) ethylene from ethane
(b) propylene from propane
(c) ethyl iodide from ethane
(d) 2-bromopropane from propane (*Note:* simple monobromination of propane yields, of course, a mixture of 1-bromopropane and 2-bromopropane, and is therefore not satisfactory for this synthesis. The mixture might, however, be used as an *intermediate.*)
(e) 1,2-dibromopropane from propane
(f) 1,2-dibromobutane from 1-bromobutane
(g) 2-iodobutane from 1-chlorobutane
(h) 2-methylpentane from propylene
(i) 3-methylheptane from *n*-butyl bromide
(j) 1,2-dibromo-2-methylpropane from isobutane
(k) 2-iodobutane from *n*-butyl alcohol
(l) *n*-propyl bromide from isopropyl bromide
(m) propylene chlorohydrin from *n*-propyl iodide
(n) isohexane from $(CH_3)_2C(OH)CH_2CH_2CH_3$
(o) 2,2-dimethylbutane from 3-chloro-2,2-dimethylbutane

About Synthesis

Each synthesis should be the one that gives a reasonably pure product in reasonably good yield.

It is not necessary to complete and balance each equation. Simply draw the structure of the organic compounds, and write on the arrow the necessary reagents and any critical conditions. For example:

$$CH_3CH_2OH \xrightarrow{H^+,\ heat} CH_2{=}CH_2 \xrightarrow{H_2,\ Ni} CH_3CH_3$$

At this stage you may be asked to make a particular compound by a method that would never actually be used for that compound: for example, the synthesis of ethane just above. But if you can work out a way to make ethane from ethyl alcohol, then, when the need arises, you will also know how to make a complicated alkane from a complicated alcohol, and, in fact, how to replace an —OH group by —H in just about any compound you encounter. Furthermore, you will have gained practice in putting together what you have learned about several different kinds of compounds.

Chapter 7 Stereochemistry II. Preparation and Reactions of Stereoisomers

7.1 Stereoisomerism

Stereoisomers, we have learned, are isomers that differ only in the way their atoms are oriented in space. So far, our study has been limited to finding out what the various kinds of stereoisomers are, how to predict their existence, how to name them, and, in a general way, how their properties compare.

In Chap. 4, we learned that stereoisomers exist of the kind called *enantiomers* (mirror-image isomers), that they can be optically active, and that both their existence and their optical activity are the result of the *chirality* of certain molecules, that is, of the non superimposability of such molecules on their mirror images. We learned how to predict, from a simple examination of molecular structure, whether or not a particular compound can display this kind of isomerism. We learned how to specify the configuration of a particular enantiomer by use of the letters R and S.

We learned about *diastereomers*: stereoisomers that are *not* mirror images. Some of these (Secs. 4.17 and 4.18) were of the kind that contained more than one chiral center. Others (Sec. 5.6) were the kind, *geometric isomers*, that owe their existence to hindered rotation about double bonds.

In Secs. 4.20 and 5.6, we learned that stereoisomers can be classified not only as to whether or not they are mirror images, but also—and quite independently of the other classification—as to how they are interconverted. Altogether, we have: (a) *configurational isomers*, interconverted by inversion (turning-inside-out) at a chiral center; (b) *geometric isomers*, interconverted—in principle—by rotation about a double bond; and (c) *conformational isomers*, interconverted by rotations about single bonds.

The operation required—rotation—is the same for interconversion of geometric and conformational isomers, and it has been suggested that they be called collectively *rotational* (or *torsional*) *isomers*. Geometric isomers are thus double-bond rotational isomers, and conformational isomers are single-bond rotational isomers.

On the other hand, from the very practical standpoint of *isolability*, geometric isomers are more akin to configurational isomers: interconversion requires bond breaking—a π bond in the case of geometric isomers—and hence is always a difficult process. Conformational isomers are interconverted by the (usually) easy process of rotation about single bonds.

For convenience, we laid down (Sec. 4.20) the following "ground rule" for discussions and problems in this book: unless specifically indicated otherwise, *the terms "stereoisomers," "enantiomers," and "diastereomers" will refer only to configurational isomers, including geometric isomers*, and will exclude conformational isomers. The latter will be referred to as "conformational isomers," "conformers," "conformational enantiomers," and "conformational diastereomers."

7.2 Reactions involving stereoisomers

Now let us go on from the *existence* of stereoisomers, and look at their *involvement* in chemical reactions: reactions in which stereoisomers are *formed*, and reactions in which stereoisomers are *consumed*; reactions in which the reagent is of the ordinary (i.e., optically inactive) kind and those in which the reagent is optically active.

We shall take up:

(a) the conversion of an achiral molecule into a chiral molecule, with the generation of a chiral center;

(b) reactions of chiral molecules in which bonds to the chiral center are not broken, and see how such reactions can be used to relate the configuration of one compound to that of another;

(c) reactions of the kind in (b) in which a second chiral center is generated;

(d) reactions of chiral compounds with optically active reagents.

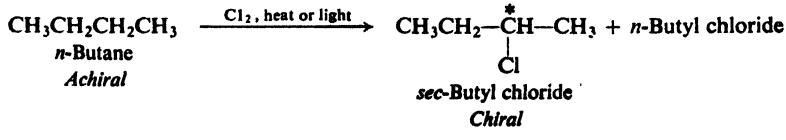
Then we shall examine the stereochemistry of several reactions we have already studied—free-radical halogenation of alkanes, and electrophilic addition of halogens to alkenes—and see how stereochemistry can be used to get information about reaction mechanisms. In doing this, we shall take up:

(e) a reaction of a chiral compound in which a bond to a chiral center is broken;

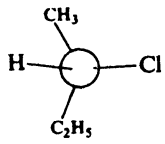
(f) a reaction of an achiral compound in which two chiral centers are generated at the same time.

7.3 Generation of a chiral center. Synthesis and optical activity

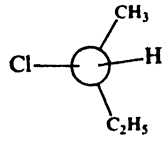
One of the products of chlorination of *n*-butane is the chiral compound, *sec*-butyl chloride. It can exist as two enantiomers, I and II, which are specified



(Sec. 4.16) as S and R, respectively.



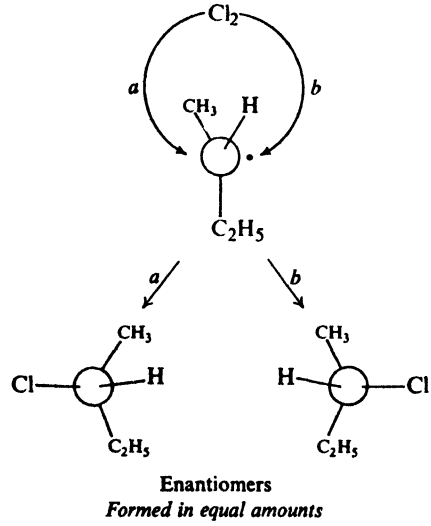
I
S-(+)-*sec*-butyl chloride



II
R-(−)-*sec*-butyl chloride

Each enantiomer should, of course, be optically active. Now, if we were to put the *sec*-butyl chloride actually prepared by the chlorination of *n*-butane into a polarimeter, would it rotate the plane of polarized light? The answer is *no*, because prepared as described it would consist of the racemic modification. The next question is: *why is the racemic modification formed?*

In the first step of the reaction, a chlorine atom abstracts hydrogen to yield hydrogen chloride and a *sec*-butyl free radical. The carbon that carries the odd electron in the free radical is sp^2-hybridized (*trigonal*, Sec. 2.21), and hence a part of the molecule is *flat*, the trigonal carbon and the three atoms attached to it lying in the same plane. In the second step, the free radical abstracts chlorine from a chlorine molecule to yield *sec*-butyl chloride. But chlorine may become attached to either face of the flat radical, and, depending upon which face, yield either of two products: R or S (see Fig. 7.1). Since the chance of attachment to one face is exactly the same as for attachment to the other face, the enantiomers are obtained in exactly equal amounts. The product is the racemic modification.



Enantiomers
Formed in equal amounts

Figure 7.1. Generation of a chiral center. Chlorine becomes attached to either face of flat free radical, via (*a*) or (*b*), to give enantiomers, and in equal amounts.

If we were to apply the approach just illustrated to the synthesis of any compound whatsoever—and on the basis of any mechanism, correct or incorrect—we would arrive at the same conclusion: as long as neither the starting material nor the reagent (nor the environment) is optically active, we should obtain an optically

inactive product. At some stage of the reaction sequence, there will be two alternative paths, one of which yields one enantiomer and the other the opposite enantiomer. The two paths will always be equivalent, and selection between them *random*. The facts agree with these predictions. **Synthesis of chiral compounds from achiral reactants always yields the racemic modification.** This is simply one aspect of the more general rule: **optically inactive reactants yield optically inactive products.**

Problem 7.1 Show in detail why racemic *sec*-butyl chloride would be obtained if: (a) the *sec*-butyl radical were not flat, but pyramidal; (b) chlorination did not involve a free *sec*-butyl radical at all, but proceeded by a mechanism in which a chlorine atom displaced a hydrogen atom, taking the position on the carbon atom formerly occupied by that hydrogen.

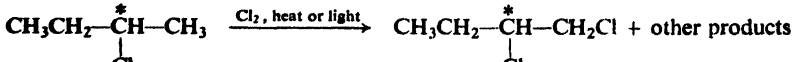
To purify the *sec*-butyl chloride obtained by chlorination of *n*-butane, we would carry out a fractional distillation. But since the enantiomeric *sec*-butyl chlorides have exactly the same boiling point, they cannot be separated, and are collected in the same distillation fraction. If recrystallization is attempted, there can again be no separation since their solubilities in every (optically inactive) solvent are identical. It is easy to see, then, that whenever a racemic modification is *formed* in a reaction, we will *isolate* (by ordinary methods) a racemic modification.

If an ordinary chemical synthesis yields a racemic modification, and if this cannot be separated by our usual methods of distillation, crystallization, etc., how do we know that the product obtained *is* a racemic modification? It is optically inactive; how do we know that it is actually made up of a mixture of two optically active substances? The separation of enantiomers (called *resolution*) can be accomplished by special methods; these involve the use of optically active reagents, and will be discussed later (Sec. 7.9).

Problem 7.2 Isopentane is allowed to undergo free-radical chlorination, and the reaction mixture is separated by careful fractional distillation. (a) How many fractions of formula $C_5H_{11}Cl$ would you expect to collect? (b) Draw structural formulas, stereochemical where pertinent, for the compounds making up each fraction. Specify each enantiomer as R or S. (c) Which if any, of the fractions, as collected, would show optical activity? (d) Account in detail—just as was done in the preceding section—for the optical activity or inactivity of each fraction.

7.4 Reactions of chiral molecules. Bond breaking

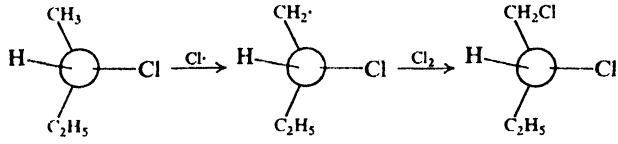
Having made a chiral compound, *sec*-butyl chloride, let us see what happens when it, in turn, undergoes free-radical chlorination. A number of isomeric dichlorobutanes are formed, corresponding to attack at various positions in the molecule. (*Problem:* What are these isomers?)



sec-Butyl chloride 1,2-Dichlorobutane

Let us take, say, (S)-*sec*-butyl chloride (which, we saw in Sec. 7.3, happens to rotate light to the right), and consider only the part of the reaction that yields 1,2-dichlorobutane. Let us make a model (I) of the starting molecule, using a

single ball for $-C_2H_5$ but a separate ball for each atom in $-CH_3$. Following the familiar steps of the mechanism, we remove an —H from $-CH_3$ and replace it with a —Cl. Since we break no bond to the chiral center in either step, the model we arrive at necessarily has configuration II, in which the spatial arrangement



I (S)-*sec*-Butyl chloride II (R)-1,2-Dichlorobutane

about the chiral center is unchanged—or, as we say, *configuration is retained*—with $-CH_2Cl$ now occupying the same relative position that was previously occupied by $-CH_3$. It is an axiom of stereochemistry that molecules, too, behave in just this way, and that *a reaction that does not involve the breaking of a bond to a chiral center proceeds with retention of configuration about that chiral center.*

(If a bond to a chiral center *is* broken in a reaction, we can make no general statement about stereochemistry, except that configuration *can* be—and more than likely *will* be—changed. As discussed in Sec. 7.10, just what happens depends on the mechanism of the particular reaction.)

Problem 7.3 We carry out free-radical chlorination of (S)-*sec*-butyl chloride, and by fractional distillation isolate the various isomeric products. (a) Draw stereochemical formulas of the 1,2-, 2,2-, and 1,3-dichlorobutanes obtained in this way. Give each enantiomer its proper R or S specification. (b) Which of these fractions, as isolated, will be optically active, and which will be optically inactive?

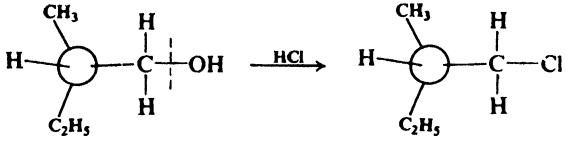
Now, let us see how the axiom about bond breaking is applied in relating the configuration of one chiral compound to that of another.

7.5 Reactions of chiral molecules. Relating configurations

We learned (Sec. 4.14) that the configuration of a particular enantiomer can be determined directly by a special kind of x-ray diffraction, which was first applied in 1949 by Bijvoet to (+)-tartaric acid. But the procedure is difficult and time-consuming, and can be applied only to certain compounds. In spite of this limitation, however, the configurations of hundreds of other compounds are now known, since they had already been related by chemical methods to (+)-tartaric acid. Most of these relationships were established by application of the axiom given above; that is, *the configurational relationship between two optically active compounds can be determined by converting one into the other by reactions that do not involve breaking of a bond to a chiral center.*

Let us take as an example (−)-2-methyl-1-butanol (the enantiomer found in fusel oil) and accept, for the moment, that it has configuration III, which we would specify S. We treat this alcohol with hydrogen chloride and obtain the alkyl chloride, 1-chloro-2-methylbutane. Without knowing the mechanism of this reaction, we can see that the carbon–oxygen bond is the one that is broken. *No bond to the chiral center is broken,* and therefore configuration is retained, with

$-CH_2Cl$ occupying the same relative position in the product that was occupied by $-CH_2OH$ in the reactant. We put the chloride into a tube, place this tube in a polarimeter, and find that the plane of polarized light is rotated to the right;

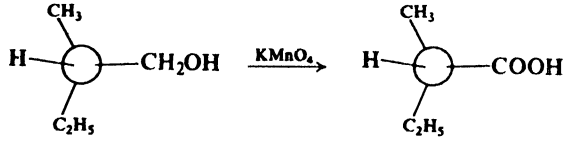


III IV

S-(−)-2-Methyl-1-butanol S-(+)-1-Chloro-2-methylbutane

that is, the product is (+)-1-chloro-2-methylbutane. Since (−)-2-methyl-1-butanol has configuration III, (+)-1-chloro-2-methylbutane must have configuration IV.

Or, we oxidize (−)-2-methyl-1-butanol with potassium permanganate, obtain the acid 2-methylbutanoic acid, and find that this rotates light to the right. Again, no bond to the chiral center is broken, and we assign configuration V to (+)-2-methylbutanoic acid.



III V

(S)-(−)-2-Methyl-1-butanol (S)-(+)-2-Methylbutanoic acid

We can nearly always tell whether or not a bond to a chiral center is broken by simple inspection of the formulas of the reactant and product, as we have done in these cases, and without a knowledge of the reaction mechanism. We must be aware of the possibility, however, that a bond may break and re-form during the course of a reaction without this being evident on the surface. This kind of thing does not happen at random, but in certain specific situations which an organic chemist learns to recognize. Indeed, stereochemistry plays a leading role in this learning process: one of the best ways to detect hidden bond-breaking is so to design the experiment that if such breaking occurs, it must involve a chiral center.

But how do we know in the first place that (−)-2-methyl-1-butanol has configuration III? Its configuration was related in this same manner to that of another compound, and that one to the configuration of still another, and so on, going back ultimately to (+)-tartaric acid and Bijvoet's x-ray analysis.

We say that the (−)-2-methyl-1-butanol, the (+)-chloride, and the (+)-acid have *similar* (or the *same*) configurations. The enantiomers of these compounds, the (+)-alcohol, (−)-chloride, and (−)-acid, form another set of compounds with similar configurations. The (−)-alcohol and, for example, the (−)-chloride are said to have *opposite* configurations. As we shall find, we are usually more interested in knowing whether two compounds have similar or opposite configurations than in knowing what the actual configuration of either compound actually is. That is to say, we are more interested in *relative* configurations than in *absolute* configurations.

In this set of compounds with similar configurations, we notice that two are dextrorotatory and the third is levorotatory. The sign of rotation is important as a means of keeping track of a particular isomer—just as we might use boiling point or refractive index to tell us whether we have *cis*- or *trans*-2-butene, *now that their configurations have been assigned*—but the fact that two compounds happen to have the same sign or opposite sign of rotation means little; they may or may not have similar configurations.

The three compounds all happen to be specified as S, but this is simply because $-CH_2Cl$ and $-COOH$ happen to have the same relative priority as $-CH_2OH$. If we were to replace the chlorine with deuterium (*Problem:* How could this be done?), the product would be specified R, yet obviously it would have the same configuration as the alcohol, halide, and acid. Indeed, looking back to *sec*-butyl chloride and 1,2-dichlorobutane, we see that the similar configurations I and II *are* specified differently, one S and the other R; here, a group ($-CH_3$) that has a lower priority than $-C_2H_5$ is converted into a group ($-CH_2Cl$) that has a higher priority. We cannot tell whether two compounds have the same or opposite configuration by simply looking at the letters used to specify their configurations; we must work out and compare the absolute configurations indicated by those letters.

Problem 7.4 Which of the following reactions could safely be used to relate configurations?

(a) $(+)\text{-}C_6H_5CH(OH)CH_3 + PBr_3 \longrightarrow C_6H_5CHBrCH_3$

(b) $(+)\text{-}CH_3CH_2CHClCH_3 + C_6H_6 + AlCl_3 \longrightarrow C_6H_5CH(CH_3)CH_2CH_3$

(c) $(-)\text{-}C_6H_5CH(OC_2H_5)CH_2OH + HBr \longrightarrow C_6H_5CH(OC_2H_5)CH_2Br$

(d) $(+)\text{-}CH_3CH(OH)CH_2Br + NaCN \longrightarrow CH_3CH(OH)CH_2CN$

(e) $(+)\text{-}CH_3CH_2C(=O)\text{-}{}^{18}OCH(CH_3)C_2H_5 + OH^- \longrightarrow CH_3CH_2COO^- + CH_3CH_2CH^{18}OHCH_3$

(f) $(-)\text{-}CH_3CH_2CHBrCH_3 + C_2H_5O^-Na^+ \longrightarrow C_2H_5\text{-}O\text{-}CH(CH_3)CH_2CH_3$

(g) $(+)\text{-}CH_3CH_2CHOHCH_3 \xrightarrow{Na} CH_3CH_2CH(ONa)CH_3 \xrightarrow{C_2H_5Br} C_2H_5\text{-}O\text{-}CH(CH_3)CH_2CH_3$

Problem 7.5 What general conclusion must you draw from each of the following observations? (a) After standing in an aqueous acidic solution, optically active $CH_3CH_2CHOHCH_3$ is found to have lost its optical activity. (b) After standing in solution with potassium iodide, optically active $n\text{-}C_6H_{13}CHICH_3$ is found to have lost its optical activity. (c) Can you suggest experiments to test your conclusions? (See Sec. 3.29.)

7.6 Optical purity

Reactions in which bonds to chiral centers are not broken can be used to get one more highly important kind of information: the specific rotations of optically pure compounds. For example, the 2-methyl-1-butanol obtained from fusel oil (which happens to have specific rotation $-5.756°$) is *optically pure*—like most chiral compounds from biological sources—that is, it consists entirely of the one enantiomer, and contains none of its mirror image. When this material is treated with hydrogen chloride, the 1-chloro-2-methylbutane obtained is found to have specific rotation of $+1.64°$. Since no bond to the chiral center is broken, every

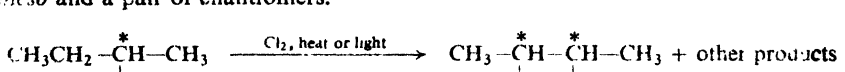
molecule of alcohol with configuration III is converted into a molecule of chloride with configuration IV; since the alcohol was optically pure, the chloride of specific rotation +1.64° is also optically pure. Once this *maximum rotation* has been established, anyone can determine the optical purity of a sample of 1-chloro-2-methylbutane in a few moments by simply measuring its specific rotation.

If a sample of the chloride has a rotation of +0.82°, that is, 50% of the maximum, we say that it is *50% optically pure*. We consider the components of the mixture to be (+)-isomer and (±)-isomer (not (+)-isomer and (−)-isomer). (*Problem:* What are the percentages of (+)-isomer and (−)-isomer in this sample?)

Problem 7.6 **Predict the specific rotation of the chloride obtained by treatment with hydrogen chloride of 2-methyl-1-butanol of specific rotation +3.12°.**

7.7 Reactions of chiral molecules. Generation of a second chiral center

Let us return to the reaction we used as our example in Sec. 7.4, free-radical chlorination of *sec*-butyl chloride, but this time focus our attention on one of the other products, one in which a second chiral center is generated: 2,3-dichlorobutane. This compound, we have seen (Sec. 4.18), exists as three stereoisomers, *meso* and a pair of enantiomers.



sec-Butyl chloride 2,3-Dichlorobutane

Let us suppose that we take optically active *sec*-butyl chloride (the (S)-isomer, say), carry out the chlorination, and by fractional distillation separate the 2,3-dichlorobutanes from all the other products (the 1,2-isomer, 2,2-isomer, etc.). Which stereoisomers can we expect to have?

Figure 7.2 shows the course of reaction. Three important points are illustrated which apply in all cases where a second chiral center is generated. First, since no bonds to the original chiral center, C-2, are broken, its configuration is retained in all the products. Second, there are two possible configurations about the new chiral center, C-3, and both of these appear; in this particular case, they result from attacks (*a*) and (*b*) on opposite sides of the flat portion of the free radical, giving the diastereomeric S,S and R,S (or *meso*) products. Third, the diastereomeric products will be formed in unequal amounts; in this case because attack (*a*) and attack (*b*) are not equally likely.

In Sec. 7.3 we saw that generation of the first chiral center in a compound yields equal amounts of enantiomers, that is, yields an optically inactive racemic modification. Now we see that generation of a new chiral center in a compound that is already optically active yields an optically active product containing unequal amounts of diastereomers.

Suppose (as is actually the case) that the products from (S)-*sec*-butyl chloride show an S,S:*meso* ratio of 29:71. What would we get from chlorination of (R)-*sec*-butyl chloride? We would get (R,R-) and *meso*-products, and the R,R:*meso* ratio would be exactly 29:71. Whatever factor favors *meso*-product over (S,S)-product will favor *meso*-product over (R,R)-product, and to exactly the same extent.

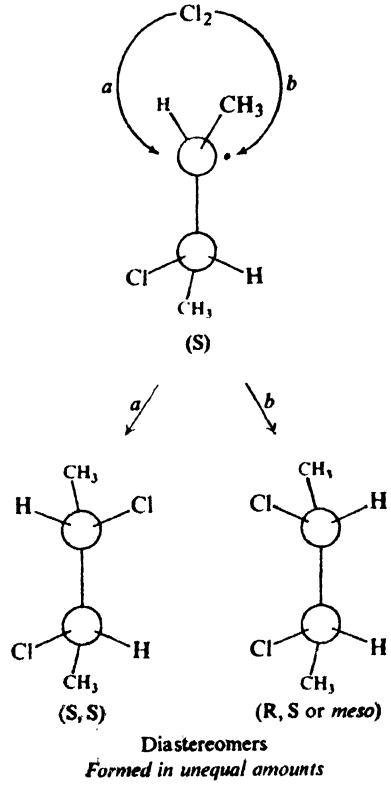


Figure 7.2. Generation of a second chiral center. Configuration at original chiral center unchanged. Chlorine becomes attached via (*a*) or (*b*) to give diastereomers, and in unequal amounts.

Finally, what can we expect to get from optically inactive, racemic *sec*-butyl chloride? The (S)-isomer that is present would yield (S,S)- and *meso*-products in the ratio of 29:71; the (R)-isomer would yield (R,R)- and *meso*-products, and in the ratio of 29:71. Since there are exactly equal quantities of (S)- and (R)-reactants, the two sets of products would exactly balance each other, and we would obtain racemic and *meso* products in the ratio of 29:71. Optically inactive reactants yield optically inactive products.

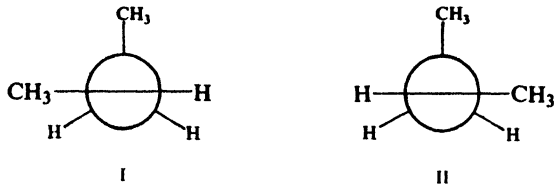
One point requires further discussion. Why are the diastereomeric products formed in unequal amounts? It is because the intermediate 3-chloro-2-butyl radical in Fig. 7.2 already contains a chiral center. The free radical is chiral, and lacks the symmetry that is necessary for attack at the two faces to be equally likely. (Make a model of the radical and assure yourself that this is so.)

In the following section, this point is discussed in more detail.

7.8 Formation of enantiomers and diastereomers: a closer look

To understand better how formation of diastereomers differs from formation of enantiomers, let us contrast the reaction of the chiral 3-chloro-2-butyl radical shown in Fig. 7.2 with the reaction of the achiral *sec*-butyl radical.

In Sec. 7.3, we said that attachment of chlorine to either face of the *sec*-butyl radical is equally likely. This is in effect true, but deserves closer examination. Consider any conformation of the free radical: I, for example. It is clear that attack by chlorine from the top of I and attack from the bottom are *not*



I II

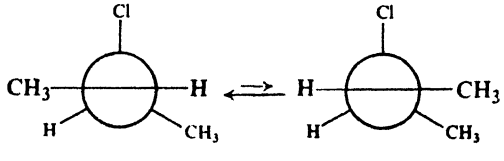
sec-Butyl radical
Achiral

equally likely. But a rotation of 180° about the single bond converts I into II; these are two conformations of the same free radical, and are, of course, in equilibrium with each other. They are mirror images, and hence of equal energy and equal abundance; any preferred attack from, say, the bottom of I to give the (R)-product will be exactly counterbalanced by attack from the bottom of II to give the (S)-product.

The "randomness of attack" that yields the racemic modification from achiral reactants is not necessarily due to the symmetry of any individual reactant molecule, but rather to the random distribution of such molecules between mirror-image conformations (or to random selection between mirror-image transition states).

Now, let us turn to reaction of the chiral 3-chloro-2-butyl radical (Fig. 7.2). Here, the free radical we are concerned with already contains a chiral center, about which it has the (S)-configuration; attack is *not* random on such a radical because mirror-image conformations are not present—they could only come from (R) free radicals, and there are none of those radicals present.

Preferred attack from, say, the bottom of conformation III—a likely preference since this would keep the two chlorine atoms as far apart as possible in the transition state—would yield *meso*-2,3-dichlorobutane. A rotation of 180° about the single bond would convert III into IV. Attack from the bottom of IV would



III IV

3-Chloro-2-butyl radical
Chiral

yield the (S,S)-isomer. But III and IV are not mirror images, are not of equal energy, and are not of equal abundance. In particular, because of lesser crowding between the methyl groups, we would expect III to be more stable and hence more abundant than IV, and the *meso* product to predominate over the (S,S)-isomer (as it actually does).

We might have made a different guess about the preferred direction of attack, and even a different estimate about relative stabilities of conformations, but we would still arrive at the same basic conclusion: except by sheer coincidence, the two diastereomers would not be formed in equal amounts.

In this discussion, we have assumed that the relative rates of competing reactions depend on relative populations of the conformations of the reactants. This assumption is correct here, if, as seems likely, reaction of the free radicals with chlorine is easier and faster than the rotation that interconverts conformations.

If, on the other hand, reaction with chlorine were a relatively difficult reaction and much slower than interconversion of conformations, then relative rates would be determined by relative stabilities of the transition states. We would still draw the same general conclusions. In the reaction of the achiral *sec*-butyl radical, the transition states are mirror images and therefore of the same stability, and the rates of formation of the two products would be exactly the same. In the reaction of the chiral 3-chloro-2-butyl radical, the transition states are not mirror-images and therefore not of the same stability, and rates of formation of the two products would be different. (In the latter case, we would even make the same prediction, that the *meso* product would predominate, since the same relationship between methyl groups that would make conformation III more stable would also make the transition state resembling conformation III more stable.)

Problem 7.7 Answer the following questions about the formation of 2,3-dichlorobutane from (R)-*sec*-butyl chloride. (a) Draw conformations (V and VI) of the intermediate radicals that correspond to III and IV above. (b) What is the relationship between V and VI? (c) How will the V:VI ratio compare with the III:IV ratio? (d) Assuming the same preferred direction of attack by chlorine as on III and IV, which stereoisomeric product would be formed from V? From VI? (e) Which product would you expect to predominate? (f) In view of the ratio of products actually obtained from (S)-*sec*-butyl chloride, what ratio of products must be obtained from (R)-*sec*-butyl chloride?

Problem 7.8 Each of the following reactions is carried out, and the products are separated by careful fractional distillation or recrystallization. For each reaction tell how many fractions will be collected. Draw stereochemical formulas of the compound or compounds making up each fraction, and give each its R/S specification. Tell whether each fraction, as collected, will show optical activity or optical inactivity.

(a) monochlorination of (R)-*sec*-butyl chloride at 300°;
(b) monochlorination of racemic *sec*-butyl chloride at 300°;
(c) monochlorination of racemic 1-chloro-2-methylbutane at 300°;
(d) addition of bromine to (S)-3-bromo-1-butene.

7.9 Reactions of chiral molecules with optically active reagents. Resolution

So far in this chapter we have discussed the reactions of chiral compounds only with optically inactive reagents. Now let us turn to reactions with optically *active* reagents, and examine one of their most useful applications: **resolution of a racemic modification**, that is, *the separation of a racemic modification into enantiomers*.

We know (Sec. 7.3) that when optically inactive reactants form a chiral compound, the product is the racemic modification. We know that the enantiomers making up a racemic modification have identical physical properties (except for direction of rotation of polarized light), and hence cannot be separated by the usual methods of fractional distillation or fractional crystallization. Yet throughout this book are frequent references to experiments carried out using

optically active compounds like (+)-*sec*-butyl alcohol, (−)-2-bromooctane, (−)-α-phenylethyl chloride, (+)-α-phenylpropionamide. How are such optically active compounds obtained?

Some optically active compounds are obtained from natural sources, since living organisms usually produce only one enantiomer of a pair. Thus only (−)-2-methyl-1-butanol is formed in the yeast fermentation of starches, and only (+)-lactic acid, $CH_3CHOHCOOH$, in the contraction of muscles; only (−)-malic acid, $HOOCCH_2CHOHCOOH$, is obtained from fruit juices, only (−)-quinine from the bark of the cinchona tree. Indeed, we deal with optically active substances to an extent that we may not realize. We eat optically active bread and optically active meat, live in houses, wear clothes, and read books made of optically active cellulose. The proteins that make up our muscles and other tissues, the glycogen in our liver and in our blood, the enzymes and hormones that enable us to grow, and that regulate our bodily processes—all these are optically active. Naturally occurring compounds are optically active because the enzymes that bring about their formation—and often the raw materials from which they are made—are themselves optically active. As to the origin of the optically active enzymes, we can only speculate.

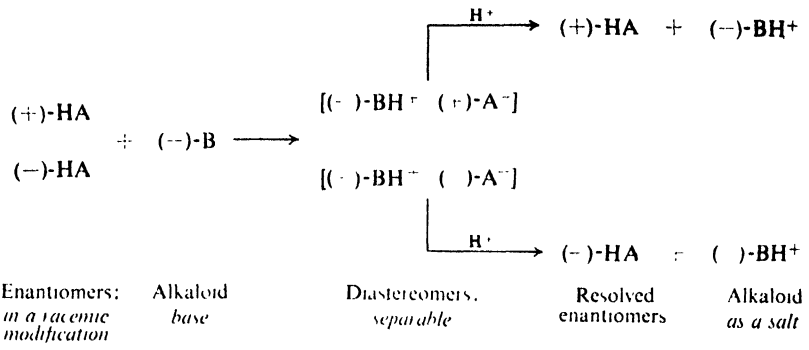
Amino acids, the units from which proteins are made, have been reported present in meteorites, but in such tiny amounts that the speculation has been made that "what appears to be the pitter-patter of heavenly feet is probably instead the print of an earthly thumb." Part of the evidence that the amino acids found in a meteorite by Cyril Ponnamperuma (of NASA) are really extraterrestrial in origin is that they are optically *inactive*—not optically active as earthly contaminants from biological sources would be.

From these naturally occurring compounds, other optically active compounds can be made. We have already seen, for example, how (−)-2-methyl-1-butanol can be converted without loss of configuration into the corresponding chloride or acid (Sec. 7.5); these optically active compounds can, in turn, be converted into many others.

Most optically active compounds are obtained by the resolution of a racemic modification, that is, by a separation of a racemic modification into enantiomers. Most such resolutions are accomplished through the use of reagents that are themselves optically active; these reagents are generally obtained from natural sources.

The majority of resolutions that have been carried out depend upon the reaction of organic bases with organic acids to yield salts. Let us suppose, for example, that we have prepared the racemic acid, (±)-HA. Now, there are isolated from various plants very complicated bases called *alkaloids* (that is, *alkali-like*), among which are cocaine, morphine, strychnine, and quinine. Most alkaloids are produced by plants in only one of two possible enantiomeric forms, and hence they are optically active. Let us take one of these optically active bases, say a levorotatory one, (−)-B, and mix it with our racemic acid (±)-HA. The acid is present in two configurations, but the base is present in only one configuration; there will result, therefore, crystals of two different salts, $[(-)\text{-}BH^+ (+)\text{-}A^-]$ and $[(-)\text{-}BH^+\text{-}(-)\text{-}A^-]$.

What is the relationship between these two salts? They are not superimposable, since the acid portions are not superimposable. They are not mirror images, since the base portions are not mirror images. The salts are stereoisomers that are not enantiomers, and therefore are *diastereomers*.



These diastereomeric salts have, of course, different physical properties, including solubility in a given solvent. They can therefore be separated by fractional crystallization. Once the two salts are separated, optically active acid can be recovered from each salt by addition of strong mineral acid, which displaces the weaker organic acid. If the salt has been carefully purified by repeated crystallizations to remove all traces of its diastereomer, then the acid obtained from it is *optically pure*. Among the alkaloids commonly used for this purpose are (−)-brucine, (−)-quinine, (−)-strychnine, and (+)-cinchonine.

Resolution of organic bases is carried out by reversing the process just described: using naturally occurring optically active acids, (−)-malic acid, for example. Resolution of alcohols, which we shall find to be of special importance in synthesis, poses a special problem: since alcohols are neither appreciably basic nor acidic, they cannot be resolved by direct formation of salts. Yet they can be resolved by a rather ingenious adaptation of the method we have just described: one attaches to them an acidic "handle," which permits the formation of salts, and then when it is no longer needed can be removed.

Compounds other than organic bases, acids, or alcohols can also be resolved. Although the particular chemistry may differ from the salt formation just described, the principle remains the same: **a racemic modification is converted by an optically active reagent into a mixture of diastereomers which can then be separated.**

7.10 Reactions of chiral molecules. Mechanism of free-radical chlorination

So far, we have discussed only reactions of chiral molecules in which bonds to the chiral center are not broken. What is the stereochemistry of reactions in which the bonds to the chiral center *are* broken? The answer is: *it depends.* It depends on the *mechanism* of the reaction that is taking place; because of this, stereochemistry can often give us information about a reaction that we cannot get in any other way.

For example, stereochemistry played an important part in establishing the mechanism that was the basis of our entire discussion of the halogenation of alkanes (Chap. 3). The chain-propagating steps of this mechanism are:

(2a) $$X\cdot + RH \longrightarrow HX + R\cdot$$

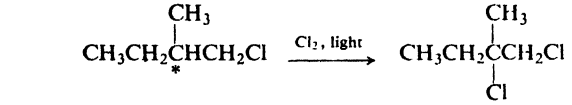
(3a) $$R\cdot + X_2 \longrightarrow RX + X\cdot$$

Until 1940 the existing evidence was just as consistent with the following alternative steps:

(2b) $$X\cdot + RH \longrightarrow RX + H\cdot$$

(3b) $$H\cdot + X_2 \longrightarrow HX + X\cdot$$

To differentiate between these alternative mechanisms, H. C. Brown, M. S. Kharasch, and T. H. Chao, working at the University of Chicago, carried out the photochemical halogenation of optically active S-(+)-1-chloro-2-methylbutane. A number of isomeric products were, of course, formed, corresponding to attack at various positions in the molecule. (*Problem:* What were these products?) They focused their attention on just *one* of these products: 1,2-dichloro-2-methylbutane, resulting from substitution at the chiral center (C–2).



(S)-(+)-1-Chloro-2-methylbutane (±)-1,2-Dichloro-2-methylbutane
Optically active *Optically inactive*

They had planned the experiment on the following basis. The two mechanisms differed as to whether or not a free alkyl radical is an intermediate. The most likely structure for such a radical, they thought, was *flat*—as, it turns out, it very probably is—and the radical would lose the original chirality. Attachment of chlorine to either face would be equally likely, so that an optically inactive, racemic product would be formed. That is to say, the reaction would take place *with racemization* (see Fig. 7.3).

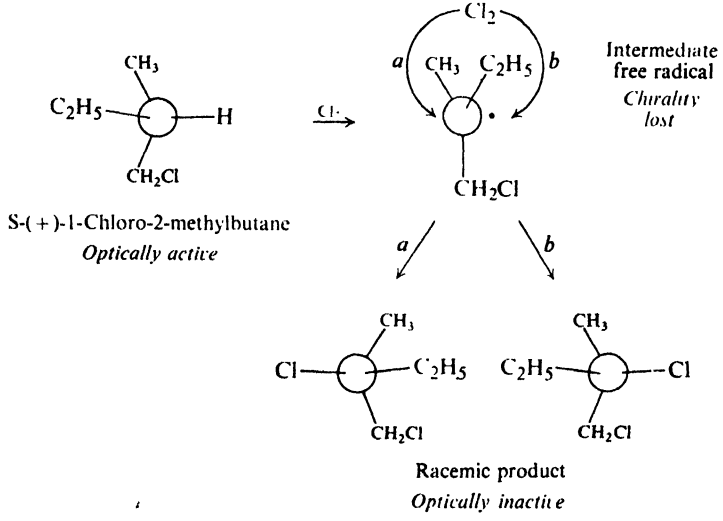


Figure 7.3. Racemization through free-radical formation. Chlorine becomes attached to either face of free radical, via (*a*) or (*b*), to give enantiomers, and in equal amounts.

For the alternative mechanism, in which chlorine would become attached to the molecule while the hydrogen was being displaced, they could make no prediction, except that formation of an optically inactive product would be highly unlikely: there was certainly no reason to expect that *back-side* attack (on the face opposite the hydrogen) would take place to exactly the same extent as *front-side* attack. (In ionic displacements, attack is generally back-side.)

By careful fractional distillation they separated the 1,2-dichloro-2-methylbutane from the reaction mixture, and found it to be *optically inactive*. From this they concluded that the mechanism involving free alkyl radicals, (2a), (3a), is the correct one. This mechanism is accepted without question today, and the work of Brown, Kharasch, and Chao is frequently referred to as evidence of the stereochemical behavior of free radicals, with the original significance of the work exactly reversed.

We can begin to see how stereochemistry provides the organic chemist with one of his most powerful tools for finding out what is going on in a chemical reaction.

Problem 7.9 This work does *not* prove that free radicals are flat. Racemization is consistent with what other structure for free radicals? Explain. (*Hint:* See Sec. 2.21.)

Problem 7.10 Altogether, the free-radical chlorination of (S)-(+)-1-chloro-2-methylbutane gave six fractions of formula $C_5H_{10}Cl_2$. Four fractions were found to be optically active, and two fractions optically inactive. Draw structural formulas for the compounds making up each fraction. Account in detail for optical activity or inactivity in each case.

7.11 Stereoselective and stereospecific reactions. *syn-* and *anti*-Addition

As our second example of the application of stereochemistry to the study of reaction mechanisms, let us take another familiar reaction: addition of halogens to alkenes. In this section we shall look at the stereochemical facts and, in the next, see how these facts can be interpreted.

Addition of bromine to 2-butene yields 2,3-dibromobutane. Two chiral centers are generated in the reaction, and the product, we know, can exist as a *meso* compound and a pair of enantiomers.

$$\underset{\text{2-Butene}}{CH_3CH{=}CHCH_3} + Br_2 \longrightarrow \underset{\text{2,3-Dibromobutane}}{CH_3{-}\overset{*}{C}H(Br){-}\overset{*}{C}H(Br){-}CH_3}$$

The reactant, too, exists as diastereomers: a pair of geometric isomers. If we start with, say, *cis*-2-butene, which of the stereoisomeric products do we get? A mixture of all of them? No. *cis*-2-Butene yields *only* racemic 2,3-dibromobutane; none of the *meso* compound is obtained. *A reaction that yields predominantly one stereoisomer (or one pair of enantiomers) of several diastereomeric possibilities is called a* **stereoselective reaction.**

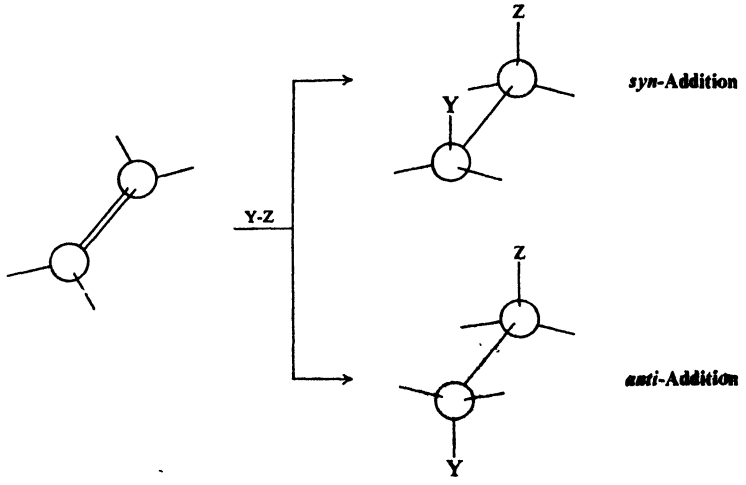
Now, suppose we start with *trans*-2-butene. Does this, too, yield the racemic dibromide? No. *trans*-2-Butene yields *only meso*-2,3-dibromobutane. *A reaction in which stereochemically different reactants give stereochemically different products is called a* **stereospecific reaction.**

Addition of bromine to alkenes is both stereoselective and stereospecific. We say it is *completely* stereoselective since, from a given alkene, we obtain *only* one diastereomer (or one pair of enantiomers). We say it is stereospecific, since just which stereoisomer we obtain depends upon which stereoisomeric alkene we start with.

In the above definition, *stereochemically different* means, in practice, *diastereomerically different*. The term *stereospecific* is not applied to reactions, like those in Secs. 7.4 and 7.5, in which enantiomerically different reactants give enantiomerically different products.

All stereospecific reactions are necessarily stereoselective, but the reverse is not true. There are reactions from which one particular stereoisomer is the predominant product *regardless* of the stereochemistry of the reactant; there are reactions in which the reactant cannot exist as stereoisomers, but from which one particular stereoisomer is the predominant product. Such reactions are stereoselective but not stereospecific.

To describe stereospecificity in addition reactions, the concepts of *syn*-addition and *anti*-addition are used. These terms are not the names of specific mechanisms. They simply indicate the stereochemical facts: that the product obtained is the one to be expected if the two portions of the reagent were to add to the same face of the alkene (*syn*) or to opposite faces (*anti*).



Addition of bromine to the 2-butenes involves *anti*-addition. If we start (Fig. 7.4) with *cis*-2-butene, we can attach the bromine atoms to opposite faces of the alkene either as in (*a*) or in (*b*) and thus obtain the enantiomers. Since, whatever the mechanism, (*a*) and (*b*) should be equally likely, we obtain the racemic modification.

Starting with *trans*-2-butene (Fig. 7.5), we can again attach the bromine atoms to opposite faces of the alkene in two ways but, whichever way we choose, we obtain the *meso*-dibromide.

anti-Addition is the general rule for the reaction of bromine or chlorine with simple alkenes. We shall encounter other examples of stereospecific additions, both *anti* and *syn*. We shall find that other reactions besides addition can be

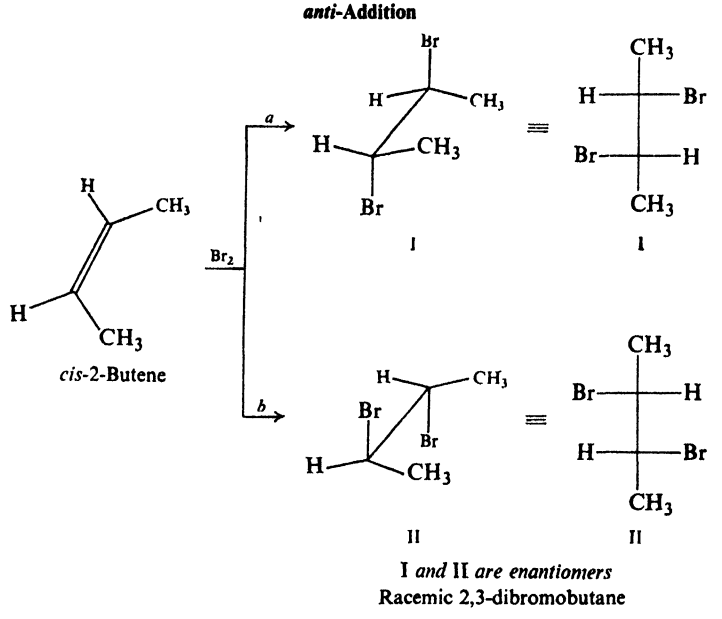


Figure 7.4. *anti*-Addition to *cis*-2-butene. Attachment as in (*a*) or (*b*) equally likely: gives racemic modification.

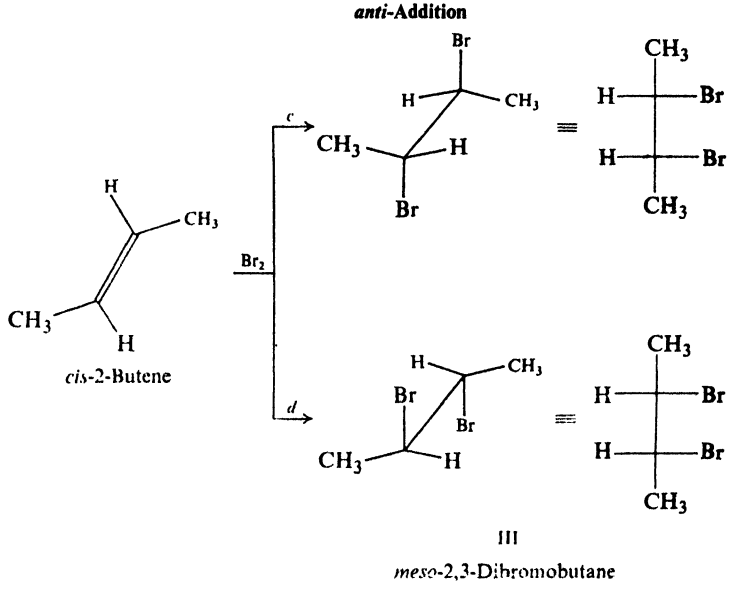


Figure 7.5. *anti*-Addition to *trans*-2-butene. Attachment as in (*c*) or (*d*) gives *meso* product.

stereospecific—and also that some can be non-stereospecific. Whatever the stereochemistry of a reaction, it must, of course, be accounted for by a satisfactory mechanism.

Problem 7.11 On treatment with permanganate, *cis*-2-butene yields a glycol of m.p. 34°, and *trans*-2-butene yields a glycol of m.p. 19°. Both glycols are optically inactive. Handling as described in Sec. 7.9 converts the glycol of m.p. 19° (but not the one of m.p. 32°) into two optically active fractions of equal but opposite rotation.

(a) What is the configuration of the glycol of m.p. 19°? Of m.p. 32°?

(b) Assuming these results are typical (they are), *what is the stereochemistry of hydroxylation with permanganate?*

(c) Treatment of the same alkenes with peroxy acids gives the opposite results: the glycol of m.p. 19° from *cis*-2-butene, and the glycol of m.p. 32° from *trans*-2-butene. *What is the stereochemistry of hydroxylation with peroxy acids?*

7.12 Mechanism of halogen addition

We saw earlier (Sec. 6.13) that addition of halogens to alkenes is believed to proceed by two steps: first, addition of a positive halogen ion to form an organic

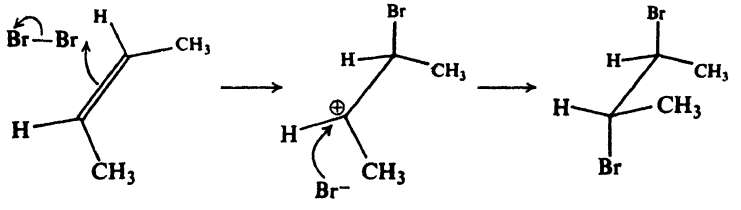
(1) $\text{>C=C<} + \text{X–X} \longrightarrow \text{–C(X)–C(}\oplus\text{)–} + \text{X}^-$

(2) $\text{–C(X)–C(}\oplus\text{)–} + \text{X}^- \longrightarrow \text{–C(X)–C(X)–}$

cation; then combination of this cation with a negative halide ion. We saw some of the facts that provide evidence for this mechanism.

In the last section, we learned another fact: halogens add to simple alkenes with *complete* stereospecificity, and in the *anti* sense. Let us reexamine the mechanism in the light of this stereochemistry, and focus our attention on the nature of the intermediate cation. This intermediate we represented simply as the carbonium ion. A part of a carbonium ion, we remember (Sec. 5.16), is *flat*: the carbon that carries the positive charge is sp^2-hybridized, and this trigonal carbon and the three atoms attached to it lie in the same plane.

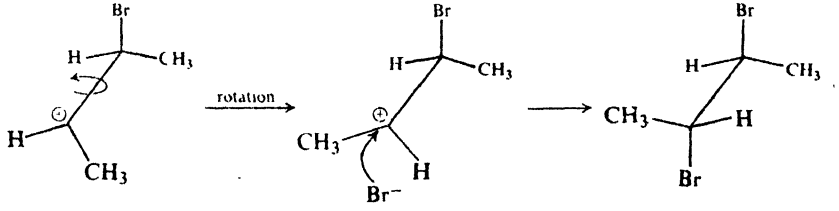
Now, is the observed stereochemistry consistent with a mechanism involving such an intermediate? Let us use addition of bromine to *cis*-2-butene as an example. A positive bromine ion is transferred to, say, the top face of the alkene to



cis-2-Butene Cation I (S,S)-2,3-Dibromobutane

form the carbonium ion I. Then, a bromide ion attacks the *bottom* face of the positively charged carbon to complete the *anti* addition; attack at this face is preferred, we might say, because it permits the two bromines to be as far apart as possible in the transition state. (We obtain the racemic product: the S,S-dibromide as shown, the R,R-dibromide through attachment of positive bromine to the near end of the alkene molecule.)

But this picture of the reaction is not satisfactory, and for two reasons. First, to account for the *complete* stereospecificity of addition, we must assume that attack at the bottom face of the cation is not just preferred, but is the *only* line of attack: conceivable, but—especially in view of other reactions of carbonium ions (Sec. 14.13)—not likely. Then, even if we accept this exclusively bottom-side attack, we are faced with a second problem. Rotation about the carbon–carbon bond would convert cation I into cation II; bottom-side attack on cation II would



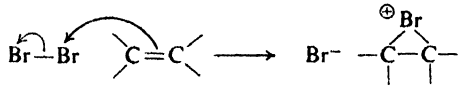
Cation I Cation II *meso*-2,3-Dibromobutane

yield not the racemic dibromide but the *meso* dibromide—in effect *syn*-addition, and contrary to fact.

To accommodate the stereochemical facts, then, we would have to make two assumptions about halogen addition: after the carbonium ion is formed, it is attacked by bromide ion (a) before rotation about the single bond can occur, and (b) exclusively from the side away from the halogen already in the cation. Neither of these assumptions is very likely; together, they make the idea of a simple carbonium ion intermediate hard to accept.

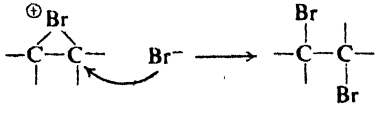
In 1937, to account better for the observed stereochemistry, I. Roberts and G. E. Kimball at Columbia University proposed the following mechanism. In step (1) of the addition of bromine, for example, positive bromine attaches itself

(1)



A bromonium ion

(2)



not to just one of the doubly-bonded carbon atoms, but to both, forming a cyclic **bromonium ion**. In step (2), bromide ion attacks this bromonium ion to yield the dibromide.

Now, how does the bromonium ion mechanism account for *anti*-addition? Using models, let us first consider addition of bromine to *cis*-2-butene (Fig. 7.6).

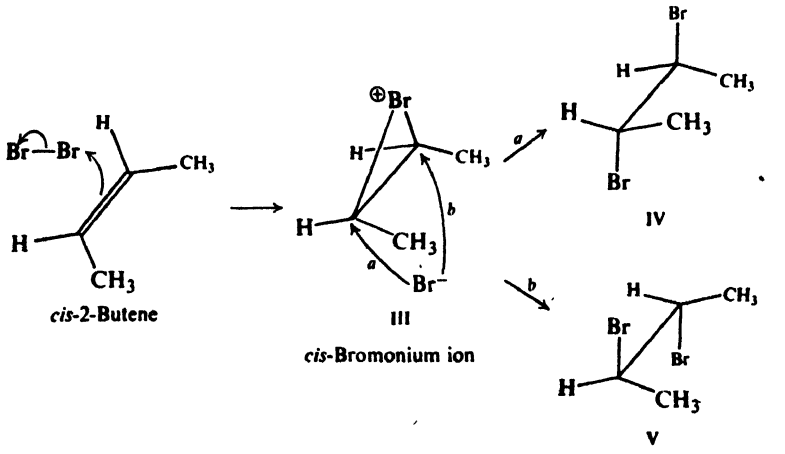


Figure 7.6. Addition of bromine to *cis*-2-butene via cyclic bromonium ion. Opposite-side attacks (*a*) and (*b*) equally likely, give enantiomers in equal amounts.

In the first step, positive bromine becomes attached to either the top or bottom face of the alkene. Let us see what we would get if bromine becomes attached to the top face. When this happens, the carbon atoms of the double bond tend to become tetrahedral, and the hydrogens and methyls are displaced downward. The methyl groups are, however, still located across from each other, as they were in the alkene. In this way, bromonium ion III is formed.

Now bromonium ion III is attacked by bromide ion. A new carbon–bromine bond is formed, and an old carbon–bromine bond is broken. This attack occurs on the bottom face of III, so that the bond being formed is on the opposite of carbon from the bond being broken. Attack can occur by path (*a*) to yield structure IV or by path (*b*) to yield structure V. We recognize IV and V as enantiomers. Since attack by either (*a*) or (*b*) is equally likely, the enantiomers are formed in equal amounts, and thus we obtain the racemic modification. The same results are obtained if positive bromine initially becomes attached to the bottom face of *cis*-2-butene. (Show with models that this is so.)

Next, let us carry through the same operation on *trans*-2-butene (Fig. 7.7). This time, bromonium ion VI is formed. Attack on it by path (*c*) yields VII, attack by (*d*) yields VIII. If we simply rotate either VII or VIII about the carbon–carbon bond, we readily recognize the symmetry of the compound. It is *meso*-2,3-dibromo-butane; VII and VIII are identical. The same results are obtained if

positive bromine is initially attached to the bottom face of *trans*-2-butene. (Show with models that this is so.)

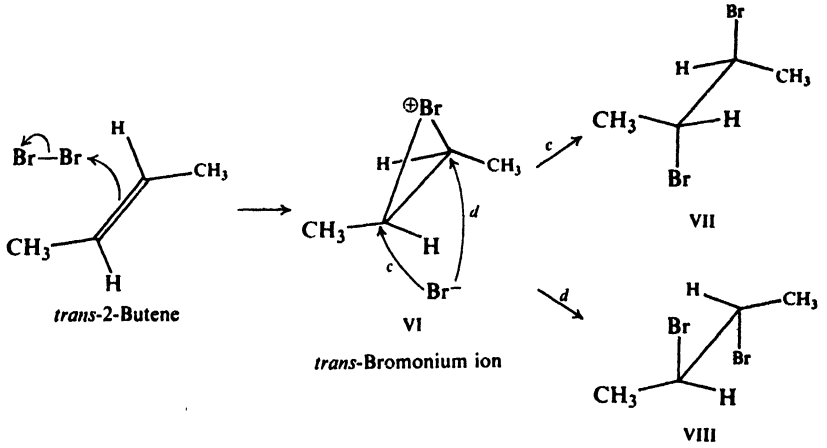


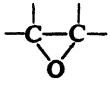
Figure 7.7. Addition of bromine to *trans*-2-butene via cyclic bromonium ion. Opposite-side attacks (*c*) and (*d*) give same product.

Problem 7.12 (a) What is the relationship between the bromonium ions formed by attachment of positive bromine to the top and bottom faces of *trans*-2-butene? In what proportions are they formed? (b) Answer the same questions for *cis*-2-butene. (c) For *trans*-2-pentene. (d) For *cis*-2-pentene.

Problem 7.13 (a) Predict the products of addition of bromine to *trans*-2-pentene. Is attack by bromide ion by the two paths equally likely? Account for the fact that inactive material is actually obtained. (b) Do the same for *cis*-2-pentene.

The concept of a halonium ion solves both of the problems associated with an open carbonium ion: a halogen bridge prevents rotation about the carbon–carbon bond, and at the same time restricts bromide ion attack exclusively to the opposite face of the cation. This opposite-side approach, we shall find (Sec. 14.10), is *typical* of attack by bases (nucleophiles) on tetrahedral carbon.

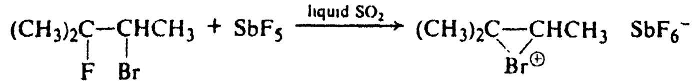
That such cyclic intermediates *can* give rise to *anti*-addition is demonstrated by hydroxylation with peroxy acids (Problem 7.11, p. 242): there, analogous intermediates—perfectly respectable compounds called *epoxides* (Chap. 17)—can actually be isolated and studied.



An epoxide

Cyclic halonium ions were first proposed, then, simply as the most reasonable explanation for the observed stereochemistry. Since that time, however,

more positive evidence has been discovered. In 1967, Olah (p. 160) prepared cations whose nmr spectra indicate that they are indeed cyclic halonium ions. For example:



The idea of a bromonium or chloronium ion may appear strange to us, in contrast to the already familiar oxonium and ammonium ions. The tendency for halogen to share two pairs of electrons and acquire a positive charge, we might say, should be weak because of the high electronegativity of halogens. But the evidence—here, and in other connections (Sec. 11.21 and Sec. 25.6)—shows that this tendency is *appreciable*. In halogen addition we are concerned with this question: which is more stable, an open carbonium ion in which carbon has only a sextet of electrons, or a halonium ion in which each atom (except hydrogen, of course) has a complete octet? It is not a matter of which atom, halogen or carbon, can better accommodate a positive charge; it is a matter of completeness or incompleteness of octets.

In halonium ion formation we see one more example of what underlies all carbonium ion behavior: *the need to get a pair of electrons to complete the octet of the positively charged carbon.*

There are exceptions to the rule of *anti*-addition of halogens, but exceptions that are quite understandable. If the alkene contains substituents that can strongly stabilize the open carbonium ion—as, for example, in a *benzyl* cation (Sec. 12.19)—then addition proceeds with little or no stereospecificity. Carbon is getting the electrons it needs, but in a different way.

Problem 7.14 Olah treated compounds of the formula $(CH_3)_2CXCF(CH_3)_2$ with SbF_5. He observed the formation of halonium ions when X = Cl, Br, or I, but an open carbonium ion when X = F. How do you account for the difference in behavior of the difluoro compound? (*Hint:* See Sec. 1.15.)

PROBLEMS

1. Each of the following reactions is carried out, and the products are separated by careful fractional distillation or recrystallization. For each reaction tell how many fractions will be collected. Draw stereochemical formulas of the compound or compounds making up each fraction, and give each its R/S specification. Tell whether each fraction, as collected, will show optical activity or optical inactivity.

(a) *n*-pentane + Cl_2 (300°) $\longrightarrow$ $C_5H_{11}Cl$;
(b) 1-chloropentane + Cl_2 (300°) $\longrightarrow$ $C_5H_{10}Cl_2$;
(c) (S)-2-chloropentane + Cl_2 (300°) $\longrightarrow$ $C_5H_{10}Cl_2$;
(d) (R)-2-chloro-2,3-dimethylpentane + Cl_2 (300°) $\longrightarrow$ $C_7H_{14}Cl_2$;
(e) *meso*-$HOCH_2CHOHCHOHCH_2OH$ + HNO_3 $\longrightarrow$ $HOCH_2CHOHCHOHCOOH$;
(f) (R)-*sec*-butyl chloride + KOH (alc);
(g) (S)-3-chloro-1-butene + HCl;
(h) racemic $C_6H_5COCHOHC_6H_5$ + H_2, catalyst $\longrightarrow$ $C_6H_5CHOHCHOHC_6H_5$.

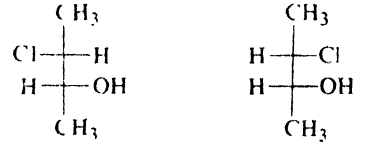
2. In Problem 7.11 we saw that *hydroxylation with permanganate is syn*, and *hydroxylation with peroxy acids is anti*. Keeping in mind that reaction of epoxides (Sec. 17.12) is acid-catalyzed, give a detailed mechanism for hydroxylation with peroxy acids. (Check your answer in Sec. 17.12.)

3. Give the absolute configuration and R/S specification of compounds A

(a) (R)-$HOCH_2CHOHCH{=}CH_2$ + cold alkaline $KMnO_4$ ⟶ A (optically acti
B (optically inactive);
(b) (S)-1-chloro-2-methylbutane + Li, then + CuI ⟶ C;
(c) C + (S)-1-chloro-2-methylbutane ⟶ D;
(d) (R,R)-$HOCH_2CHOHCHOHCH_2OH$ + HBr ⟶ E ($HOCH_2CHOHCHOHCH_2Br$);
(e) (R)-3-methyl-2-ethyl-1-pentene + H_2/Ni ⟶ F (optically active) + G (optically inactive).

4. An excess of the racemic acid $CH_3CHClCOOH$ is allowed to react with (S)-2-methyl-1-butanol to form the ester, $CH_3CHClC(=O)OCH_2CH(CH_3)CH_2CH_3$, and the reaction mixture is carefully distilled. Three fractions are obtained, each of which is optically active. Draw stereochemical formulas of the compound or compounds making up each fraction.

5. Addition of chlorine water to 2-butene yields not only 2,3-dichlorobutane but the chlorohydrin, 3-chloro-2-butanol. *cis*-2-Butene gives only the *threo* chlorohydrin, and *trans*-2-butene gives only the *erythro* chlorohydrin. What is the stereochemistry of chlorohydrin formation, and how do you account for it?



3-Chloro-2-butanol

6. (a) How do you account for the fact that when allyl bromide is treated with dilute H_2SO_4, there is obtained not only 1-bromo-2-propanol, but also 2-bromo-1-propanol? (b) In contrast, allyl chloride yields only one product, 1-chloro-2-propanol. How do you account for this difference between the chloride and the bromide?

7. (a) Alfred Hassner (University of Colorado) has found iodine azide, IN_3, to add to terminal alkenes with the orientation shown, and with complete stereospecificity

$$RCH{=}CH_2 + IN_3 \longrightarrow RCH(N_3)CH_2I$$

(*anti*) to the 2-butenes. Suggest a mechanism for this reaction.

(b) In polar solvents like nitromethane, BrN_3 adds with the same orientation and stereospecificity as IN_3. In non-polar solvents like *n*-pentene, however, orientation is reversed, and addition is non-stereospecific. In solvents of intermediate polarity like methylene chloride, mixtures of products are obtained; light or peroxides favor formation of $RCHBrCH_2N_3$; oxygen favors formation of $RCH(N_3)CH_2Br$. Account in detail for these observations.

carbon–carbon double bond of ethylene (163 kcal) or the carbon–carbon single bond of ethane (88 kcal), and therefore is shorter than either.

Again, the quantum mechanical structure is verified by direct evidence. Electron diffraction, x-ray diffraction, and spectroscopy show acetylene (Fig. 8.4)

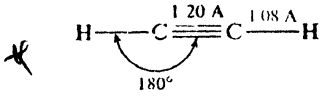


Figure 8.4. Acetylene molecule: shape and size.

to be a linear molecule. The C–C distance is 1.21 A, as compared with 1.34 A in ethylene and 1.53 A in ethane. As in the case of the double bond, the structure of the triple bond is verified—although this time in a negative way—by the evidence of isomer number. As we can readily see from models, the linearity of the bonding should not permit geometric isomerism; no such isomers have ever been found.

The C–H distance in acetylene is 1.08 A, even shorter than in ethylene (1.103 A); because of their greater *s* character, *sp* orbitals are smaller than sp^2 orbitals, and *sp*-hybridized carbon forms shorter bonds than sp^2-hybridized carbon. The C–H bond dissociation energy in acetylene is not known, but we would expect it to be even greater than in ethylene. Oddly enough, the same *sp* hybridization that almost certainly makes cleavage of the C–H bond to form free radicals (*homolysis*) more difficult, makes cleavage to form ions (*heterolysis*) easier, as we shall see (Sec. 8.10).

$$HC{\equiv}C{:}H \longrightarrow HC{\equiv}C\cdot + H\cdot$$

Homolysis: *one electron to each fragment*

$$HC{\equiv}C{:}H \longrightarrow HC{\equiv}C{:}^{-} + H^{+}$$

Heterolysis: *both electrons to one fragment*

Problem 8.1 Compare the electronic configurations of CO_2, which is a linear molecule (check your answer to Problem 1.6, p. 25), and H_2O, which has a bond angle of 105°.

8.3 Higher alkynes. Nomenclature

Like the alkanes and alkenes, the alkynes form a homologous series, the increment again being $-CH_2-$.

The alkynes are named according to two systems. In one, they are considered to be derived from acetylene by replacement of one or both hydrogen atoms by alkyl groups.

$H-C{\equiv}C-C_2H_5$	$CH_3-C{\equiv}C-CH_3$	$CH_3-C{\equiv}C-CH(CH_3)_2$
Ethylacetylene	Dimethylacetylene	Methylisopropylacetylene
1-Butyne	2-Butyne	4-Methyl-2-pentyne

For more complicated alkynes the **IUPAC** names are used. The rules are exactly the same as for the naming of alkenes, except that the ending **-yne** replaces

-ene. The parent structure is the longest continuous chain that contains the triple bond, and the positions both of substituents and of the triple bond are indicated by numbers. The triple bond is given the number of the *first* triply-bonded carbon encountered, starting from the end of the chain nearest the triple bond.

8.4 Physical properties of alkynes

Being compounds of low polarity, the alkynes have physical properties that are essentially the same as those of the alkanes and alkenes. They are insoluble in water but quite soluble in the usual organic solvents of low polarity: ligroin, ether, benzene, carbon tetrachloride. They are less dense than water. Their boiling points (Table 8.1) show the usual increase with increasing carbon number,

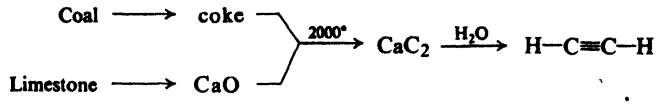
Table 8.1 ALKYNES

Name	Formula	M.p., °C	B.p., °C	Density (at 20°)
Acetylene	$HC{\equiv}CH$	− 82	− 75	
Propyne	$HC{\equiv}CCH_3$	−101.5	− 23	
1-Butyne	$HC{\equiv}CCH_2CH_3$	−122	9	
1-Pentyne	$HC{\equiv}C(CH_2)_2CH_3$	−98	40	0.695
1-Hexyne	$HC{\equiv}C(CH_2)_3CH_3$	−14	72	.719
1-Heptyne	$HC{\equiv}C(CH_2)_4CH_3$	−80	100	.733
1-Octyne	$HC{\equiv}C(CH_2)_5CH_3$	−70	126	.747
1-Nonyne	$HC{\equiv}C(CH_2)_6CH_3$	−65	151	.763
1-Decyne	$HC{\equiv}C(CH_2)_7CH_3$	−36	182	.770
2-Butyne	$CH_3C{\equiv}CCH_3$	− 24	27	.694
2-Pentyne	$CH_3C{\equiv}CCH_2CH_3$	−101	55	.714
3-Methyl-1-butyne	$HC{\equiv}CCH(CH_3)_2$		29	.665
2-Hexyne	$CH_3C{\equiv}C(CH_2)_2CH_3$	− 92	84	.730
3-Hexyne	$CH_3CH_2C{\equiv}CCH_2CH_3$	− 51	81	.725
3,3-Dimethyl-1-butyne	$HC{\equiv}CC(CH_3)_3$	− 81	38	.669
4-Octyne	$CH_3(CH_2)_2C{\equiv}C(CH_2)_2CH_3$		131	.748
5-Decyne	$CH_3(CH_2)_3C{\equiv}C(CH_2)_3CH_3$		175	.769

and the usual effects of chain-branching; they are very nearly the same as the boiling points of alkanes or alkenes with the same carbon skeletons.

8.5 Industrial source of acetylene

The alkyne of chief industrial importance is the simplest member of the family, **acetylene.** It can be prepared by the action of water on calcium carbide, CaC_2, which itself is prepared by the reaction between calcium oxide and coke at the very high temperatures of the electric furnace. The calcium oxide and coke are in turn obtained from limestone and coal, respectively. Acetylene is thus obtained by a few steps from three abundant, cheap raw materials: water, coal, limestone.



An alternative synthesis, based on petroleum, is displacing the carbide process. This involves the controlled, high-temperature partial oxidation of methane.

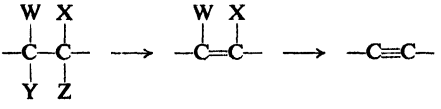
$$6CH_4 + O_2 \xrightarrow{1500°} 2HC{\equiv}CH + 2CO + 10H_2$$

(The economic feasibility of this process is partly due to use of side-products: carbon monoxide and hydrogen for production of alcohols, and some hydrogen as fuel to maintain the oxidation temperature.)

Enormous quantities of acetylene are consumed each year. Dissolved under pressure in acetone contained in tanks, it is sold to be used as fuel for the oxyacetylene torch. It is the organic starting material for the large-scale synthesis of important organic compounds, including acetic acid and a number of unsaturated compounds that are used to make plastics and synthetic rubber. Many of the synthetic uses of acetylene have grown out of work done in Germany before and during World War II by W. Reppe (at the I. G. Farbenindustrie). Aimed at replacing petroleum (scarce in Germany) by the more abundant coal as the primary organic source, this work has revolutionized the industrial chemistry of acetylene.

8.6 Preparation of alkynes

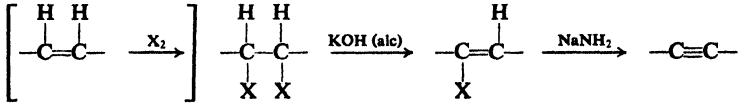
A carbon–carbon triple bond is formed in the same way as a double bond: elimination of atoms or groups from two adjacent carbons. The groups eliminated



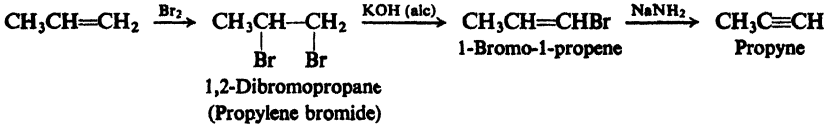
and the reagents used are essentially the same as in the preparations of alkenes.

PREPARATION OF ALKYNES

1. Dehydrohalogenation of alkyl dihalides. Discussed in Sec. 8.6.



Example:



2. Reaction of sodium acetylides with primary alkyl halides. Discussed in Sec. 8.12.

$$-C{\equiv}CH \xrightarrow[\text{or Na metal}]{NaNH_2} -C{\equiv}C{:}^{-}Na^{+} + RX \longrightarrow -C{\equiv}C-R + NaX$$

(R *must be 1°*)

Examples:

$$HC{\equiv}C{:}^{-}Na^{+} + CH_3CH_2CH_2CH_2Br \longrightarrow HC{\equiv}CCH_2CH_2CH_2CH_3$$

Sodium acetylide — *n*-Butyl bromide — 1-Hexyne (*n*-Butylacetylene)

$$CH_3(CH_2)_4C{\equiv}C{:}^{-}Na^{+} + CH_3(CH_2)_3CH_2Cl \longrightarrow CH_3(CH_2)_4C{\equiv}C(CH_2)_4CH_3$$

Sodium *n*-pentylacetylide — *n*-Pentyl chloride — 6-Dodecyne

3. Dehalogenation of tetrahalides. Discussed in Sec. 8.6.

$$-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}- + 2Zn \longrightarrow -C{\equiv}C- + 2ZnX_2$$

Example:

$$CH_3-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{CH}} \xrightarrow{Zn} CH_3-C{\equiv}CH$$

Propyne

Dehydrohalogenation of vicinal dihalides is particularly useful since the dihalides themselves are readily obtained from the corresponding alkenes by addition of halogen. This amounts to conversion—by several steps—of a double bond into a triple bond.

Dehydrohalogenation can generally be carried out in two stages as shown.

$$-\overset{H}{\underset{X}{C}}-\overset{H}{\underset{X}{C}}- \xrightarrow{KOH\ (alc)} -\overset{H}{\underset{X}{C}}{=}C- \xrightarrow{NaNH_2} -C{\equiv}C-$$

A vinyl halide
Very unreactive

Carried through only the first stage, it is a valuable method for preparing unsaturated halides. The halides thus obtained, with halogen attached directly to doubly-bonded carbon, are called **vinyl halides**, and are very unreactive (Sec. 25.5). Under mild conditions, therefore, dehydrohalogenation stops at the vinyl halide stage; more vigorous conditions—use of a stronger base—are required for alkyne formation.

Reaction of sodium acetylides with alkyl halides permits conversion of smaller alkynes into larger ones. Practically, the reaction is limited to the use of primary halides because of the great tendency for secondary and tertiary halides to undergo a side reaction, elimination; this point will be discussed further (Sec. 8.12) after we have learned something about the nature of acetylides.

Dehalogenation of tetrahalides is severely limited by the fact that these halides are themselves generally prepared from the alkynes. As is the case with the double

bond and a dihalide, the triple bond may be protected by conversion into a tetrahalide with subsequent regeneration of the triple bond by treatment with zinc.

8.7 Reactions of alkynes

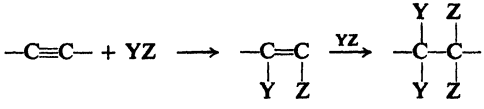
Just as alkene chemistry is the chemistry of the carbon–carbon double bond, so alkyne chemistry is the chemistry of the carbon–carbon triple bond. Like alkenes, alkynes undergo electrophilic addition, and for the same reason: availability of the loosely held π electrons. For reasons that are not understood, the carbon–carbon triple bond is *less* reactive than the carbon–carbon double bond toward electrophilic reagents.

Reasonably enough, the triple bond is *more* reactive than the double bond toward reagents that are themselves electron-rich. Thus alkynes undergo a set of reactions, *nucleophilic addition*, that are virtually unknown for simple alkenes. Although time does not permit us to go into these particular reactions here, we shall take up nucleophilic addition later in connection with other kinds of compounds (Chaps. 19 and 27).

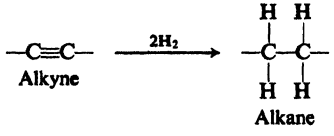
Besides addition, alkynes undergo certain reactions that are due to the acidity of a hydrogen atom held by triply-bonded carbon.

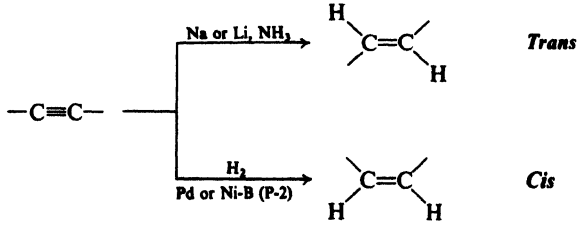
REACTIONS OF ALKYNES

Addition Reactions

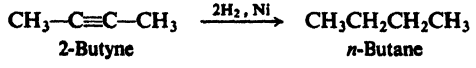


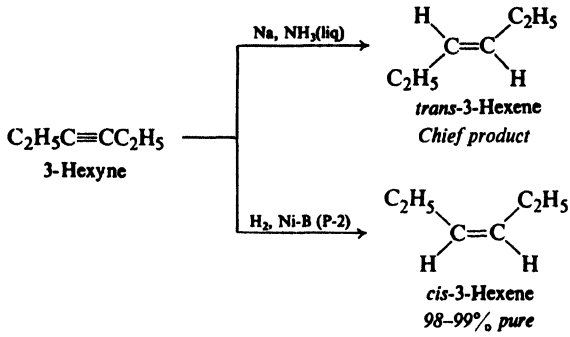
1. Addition of hydrogen. Discussed in Sec. 8.9.



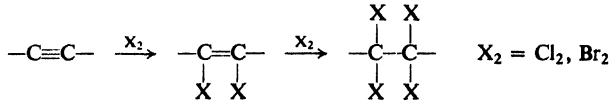


Examples:

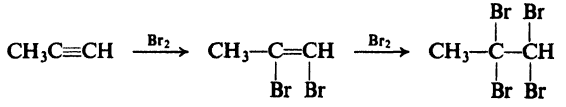




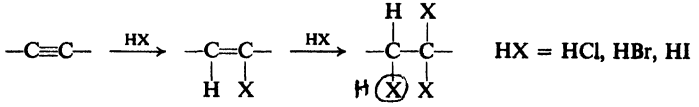
2. Addition of halogens. Discussed in Sec. 8.8.



Example:



3. Addition of hydrogen halides. Discussed in Sec. 8.8.



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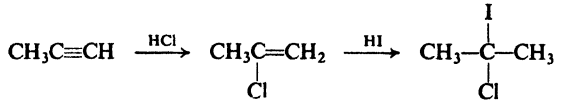
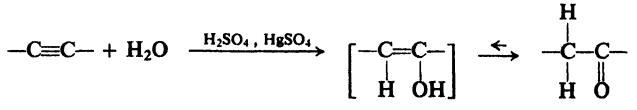
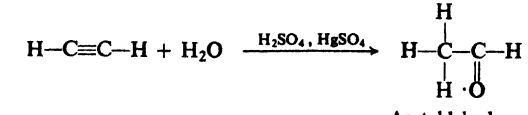
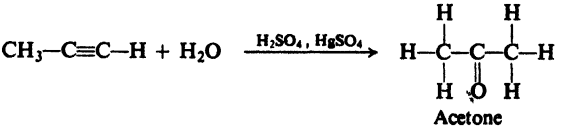


4. Addition of water. Hydration. Discussed in Sec. 8.13.



Examples:





Reactions as Acids

$$-C{\equiv}C-H + \text{base} \longrightarrow -C{\equiv}C:^-$$

5. Formation of heavy metal acetylides. Discussed in Sec. 8.11.

$$-C{\equiv}C-H + M^+ \longrightarrow -C{\equiv}C-M + H^+$$

Examples:

$$H-C{\equiv}C-H + 2Ag^+ \xrightarrow{\text{alcohol}} \underset{\text{Silver acetylide}}{Ag-C{\equiv}C-Ag} + 2H^+$$

Identification of terminal alkynes

$$CH_3C{\equiv}C-H + Cu(NH_3)_2^+ \longrightarrow \underset{\substack{\text{Cuprous}\\ \text{methylacetylide}}}{CH_3C{\equiv}C-Cu} + NH_4^+ + NH_3$$

6. Formation of alkali metal acetylides. Discussed in Sec. 8.10.

Examples:

$$H-C{\equiv}C-H + Na \xrightarrow{\text{liq } NH_3} \underset{\text{Sodium acetylide}}{H-C{\equiv}C:^-Na^+} + \tfrac{1}{2}H_2$$

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C{\equiv}C-H + NaNH_2 \xrightarrow{\text{ether}} \underset{\text{Sodium isopropylacetylide}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C{\equiv}C:^-Na^+} + NH_3$$

8.8 Addition reactions of alkynes

Addition of hydrogen, halogens, and hydrogen halides to alkynes is very much like addition to alkenes, except that here *two* molecules of reagent can be consumed for each triple bond. As shown, it is generally possible, by proper selection of conditions, to limit reaction to the first stage of addition, formation of alkenes. In some cases at least, this is made simpler because of the way that the atoms introduced in the first stage affect the second stage.

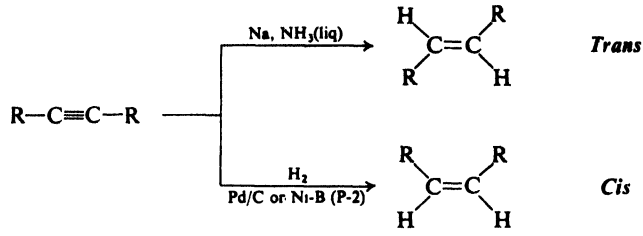
Problem 8.2 (a) Write the equation for the two-stage addition of bromine to 2-butyne. (b) How will the first two bromine atoms affect the reactivity of the double bond? (c) How will this influence the competition for halogen between 2-butyne and 2,3-dibromo-2-butene? (d) In what proportions would you mix the reagents to help limit reaction to the first stage? (e) Would you bubble 2-butyne into a solution of Br_2 in CCl_4, or drip the bromine solution into a solution of 2-butyne?

8.9 Reduction to alkenes

Reduction of an alkyne to the double-bond stage can—unless the triple bond is at the end of a chain—yield either a *cis*-alkene or a *trans*-alkene. Just which isomer predominates depends upon the choice of reducing agent.

Predominantly *trans*-alkene is obtained by reduction of alkynes with sodium or lithium in liquid ammonia. Almost entirely *cis*-alkene (as high as 98%) is obtained by hydrogenation of alkynes with several different catalysts: a specially

prepared palladium called *Lindlar's catalyst*; or a nickel boride called *P-2 catalyst* reported by H. C. Brown (see p. 507) and his son, C. A. Brown.



Each of these reactions is, then, highly stereoselective. The stereoselectivity in the *cis*-reduction of alkynes is attributed, in a general way, to the attachment of two hydrogens to the same side of an alkyne sitting on the catalyst surface; presumably this same stereochemistry holds for the hydrogenation of terminal alkynes, RC≡CH, which cannot yield *cis*- and *trans*-alkenes.

The mechanism that gives rise to *trans*-reduction is not understood.

Problem 8.3 Most methods of making alkenes (Secs. 5.14 and 5.23) yield predominantly the more stable isomer, usually the *trans*. Outline all steps in the conversion of a mixture of 75% *trans*-2-pentene and 25% *cis*-2-pentene into essentially pure *cis*-2-pentene.

8.10 Acidity of alkynes. Very weak acids

In our earlier consideration of acids (in the Lowry-Brønsted sense, Sec. 1.22), we took *acidity* to be a measure of the tendency of a compound to lose a hydrogen ion. Appreciable acidity is generally shown by compounds in which hydrogen is attached to a rather electronegative atom (e.g., N, O, S, X). The bond holding the hydrogen is polar, and the relatively positive hydrogen can separate as the positive ion; considered from another viewpoint, an electronegative element can better accommodate the pair of electrons left behind. In view of the electronegativity series, F > O > N > C, it is not surprising to find that HF is a fairly strong acid, H_2O a comparatively weak one, NH_3 still weaker, and CH_4 so weak that we would not ordinarily consider it an acid at all.

In organic chemistry we are frequently concerned with the acidities of compounds that do not turn litmus red or taste sour, yet have a tendency—even though small—to lose a hydrogen ion.

A triply-bonded carbon acts as though it were an entirely different element—a more electronegative one—from a carbon having only single or double bonds. As a result, hydrogen attached to triply-bonded carbon, as in acetylene or any alkyne with the triple bond at the end of the chain (RC≡C—H), shows appreciable acidity. For example, sodium reacts with acetylene to liberate hydrogen gas and form the compound *sodium acetylide*.

$$HC{\equiv}C{-}H + Na \longrightarrow \underset{\text{Sodium acetylide}}{HC{\equiv}C{:}^{-}Na^{+}} + \tfrac{1}{2}H_2$$

Just how strong an acid is acetylene? Let us compare it with two familiar compounds, ammonia and water.

Sodium metal reacts with ammonia to form sodamide, $NaNH_2$, which is the salt of the weak acid, $H—NH_2$.

$$NH_3 + Na \longrightarrow \underset{\text{Sodamide}}{Na^+NH_2^-} + \tfrac{1}{2}H_2$$

Addition of acetylene to sodamide dissolved in ether yields ammonia and sodium acetylide.

$$\underset{\text{Stronger acid}}{HC{\equiv}C—H} + \underset{\text{Stronger base}}{Na^+NH_2^-} \rightleftharpoons \underset{\text{Weaker acid}}{H—NH_2} + \underset{\text{Weaker base}}{HC{\equiv}C^-Na^+}$$

The weaker acid, $H—NH_2$, is displaced from its salt by the stronger acid, $HC{\equiv}C—H$. In other language, the stronger base, NH_2^-, pulls the hydrogen ion away from the weaker base, $HC{\equiv}C^-$; if NH_2^- holds the hydrogen ion more tightly than $HC{\equiv}C^-$, then $H—NH_2$ must necessarily be a weaker acid than $HC{\equiv}C—H$.

Addition of water to sodium acetylide forms sodium hydroxide and regenerates

$$\underset{\text{Stronger acid}}{H—OH} + \underset{\text{Stronger base}}{HC{\equiv}C^-Na^+} \rightleftharpoons \underset{\text{Weaker acid}}{HC{\equiv}C—H} + \underset{\text{Weaker base}}{Na^+OH^-}$$

acetylene. The weaker acid, $HC{\equiv}C—H$, is displaced from its salt by the stronger acid, H—OH.

Thus we see that acetylene is a stronger acid than ammonia, but a weaker acid than water.

Acidity $H_2O > HC{\equiv}CH > NH_3$

Other alkynes that have a hydrogen attached to triply-bonded carbon show comparable acidity.

The method we have just described for comparing acidities of acetylene, ammonia, and water is a general one, and has been used to determine relative acidities of a number of extremely weak acids. *One compound is shown to be a stronger acid than another by its ability to displace the second compound from salts.*

$$\underset{\text{Stronger acid}}{A—H} + B^-M^+ \longrightarrow \underset{\text{Weaker acid}}{B—H} + A^-M^+$$

How can we account for the fact that hydrogen attached to triply-bonded carbon is especially acidic? How can we account for the fact that acetylene is a stronger acid than, say, ethane? A possible explanation can be found in the electronic configurations of the anions.

If acetylene is a stronger acid than ethane, then the acetylide ion must be a weaker base than the ethide ion, $C_2H_5^-$. In the acetylide anion the unshared

pair of electrons occupies an *sp* orbital; in the ethide anion the unshared pair of electrons occupies an sp^3 orbital. The availability of this pair for sharing with acids determines the basicity of the anion. Now, compared with an sp^3 orbital,

$$\underset{\substack{\text{Acetylene}\\\text{Stronger acid}}}{HC{\equiv}C{:}H} \rightleftharpoons \underset{\substack{\text{Acetylide ion}\\\text{Weaker base}}}{H^+ + HC{\equiv}C{:}^-}$$

$$\underset{\substack{\text{Ethane}\\\text{Weaker acid}}}{CH_3CH_2{:}H} \longleftarrow \underset{\substack{\text{Ethide ion}\\\text{Stronger base}}}{H^+ + CH_3CH_2{:}^-}$$

an *sp* orbital has less *p* character and more *s* character (Sec. 5.4). An electron in a *p* orbital is at some distance from the nucleus and is held relatively loosely; an electron in an *s* orbital, on the other hand, is close to the nucleus and is held more tightly. The acetylide ion is the weaker base since its pair of electrons is held more tightly, in an *sp* orbital.

Problem 8.4 When 1-hexyne was added to a solution of *n*-propylmagnesium bromide, a gas was evolved. The density of the gas showed that it had a molecular weight of 44. When it was bubbled through aqueous $KMnO_4$ or Br_2 in CCl_4, there was no visible change. (a) What was the gas? (b) Write an equation to account for its formation. (c) How could you have predicted such a reaction?

Problem 8.5 What do you suppose the structure of calcium carbide is? Can you suggest another name for it? What is the nature of its reaction with water?

8.11 Formation of heavy metal acetylides

The acidic acetylenes react with certain heavy metal ions, chiefly Ag^+ and Cu^+, to form insoluble acetylides. Formation of a precipitate upon addition of an alkyne to a solution of $AgNO_3$ in alcohol, for example, is an indication of hydrogen attached to triply-bonded carbon. This reaction can be used to differentiate *terminal* alkynes (those with the triple bond at the *end* of the chain) from *non-terminal* alkynes.

$$\underset{\substack{\text{1-Butyne}\\\textit{A terminal alkyne}}}{CH_3CH_2C{\equiv}C{-}H} \xrightarrow{Ag^+} \underset{\text{Precipitate}}{CH_3CH_2C{\equiv}C{-}Ag} \left[\xrightarrow{HNO_3} \underset{\text{1-Butyne}}{CH_3CH_2C{\equiv}C{-}H} + Ag^+\right]$$

$$\underset{\substack{\text{2-Butyne}\\\textit{A non-terminal alkyne}}}{CH_3{-}C{\equiv}C{-}CH_3} \xrightarrow{Ag^+} \text{no reaction}$$

If allowed to dry, these heavy metal acetylides are likely to explode. They should be destroyed while still wet by warming with nitric acid; the strong mineral acid regenerates the weak acid, acetylene.

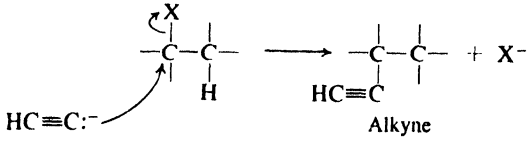
8.12 Reaction of sodium acetylides with alkyl halides. Substitution *vs.* elimination

Sodium acetylides are used in the synthesis of higher alkynes. For example:

$$HC{\equiv}C{:}^{-}Na^{+} + C_2H_5{:}\ddot{X}{:} \longrightarrow \underset{\text{1-Butyne}}{HC{\equiv}C{-}C_2H_5} + Na^{+}{:}\ddot{X}{:}^{-}$$

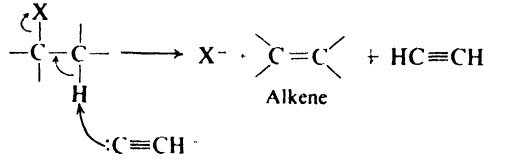
$$C_2H_5C{\equiv}C{:}^{-}Na^{+} + CH_3{:}\ddot{X}{:} \longrightarrow \underset{\text{2-Pentyne}}{C_2H_5C{\equiv}C{-}CH_3} + Na^{+}{:}\ddot{X}{:}^{-}$$

This reaction involves substitution of acetylide ion for halide ion. It results from attack by the acetylide ion on carbon..



Attack on C: *substitution*

Since sodium acetylide is the salt of the extremely weak acid, acetylene, the acetylide ion is an extremely strong base, stronger in fact than hydroxide ion. In our discussion of the synthesis of alkenes from alkyl halides (Sec. 5.13), we saw that the basic hydroxide ion causes elimination by abstracting a hydrogen ion. It is not surprising that the even more basic acetylide ion can also cause elimination.



Attack on H: *elimination*

The acetylide ion, then, can react with an alkyl halide in two ways: by attack at carbon to give **substitution**, or by attack at hydrogen to give **elimination**. We have seen that the order of reactivity of alkyl halides toward elimination (Sec. 5.14) is 3° > 2° > 1°. In substitution (of the present kind), we shall find (Sec. 14.11) the order of reactivity is just the opposite: 1° > 2° > 3°. It is to be expected, then, that: *where substitution and elimination are competing reactions, the proportion of elimination increases as the structure of an alkyl halide is changed from primary to*

$$RX = \underset{\text{Substitution increases}}{\overset{\text{Elimination increases}}{1^\circ \quad 2^\circ \quad 3^\circ}}$$

Elimination (E2) *vs.* Substitution (S_N2)

secondary to tertiary. Many tertiary halides—fastest at elimination and slowest at substitution—yield exclusively alkenes under these conditions.

When the attacking reagent is a *strong* base like hydroxide or acetylide, that is, when the reagent has a strong affinity for hydrogen ion, elimination is particularly important. Practically speaking, *only primary halides give good yields of*

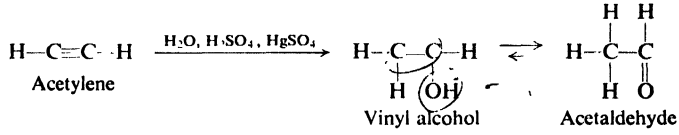
the substitution product, the alkyne. With secondary and tertiary halides, elimination predominates to such an extent that the method is essentially useless. We shall encounter this competition between substitution and elimination again and again in our study of organic chemistry.

Reflecting their ability to form carbon–carbon bonds (Sec. 3.17), copper acetylides, too, are used to couple with organic halides, particularly with the ordinarily unreactive *vinyl* and *aryl* halides (Chap. 25).

8.13 Hydration of alkynes. Tautomerism

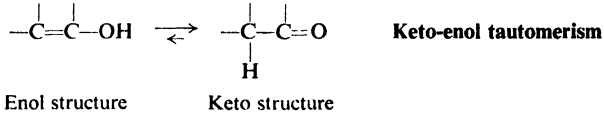
Addition of water to acetylene to form *acetaldehyde*, which can then be oxidized to *acetic acid*, is an extremely important industrial process.

From the structure of acetaldehyde, it at first appears that this reaction follows a different pattern from the others, in which two groups attach themselves to the two triply-bonded carbons. Actually, however, the product can be accounted for in a rather simple way.



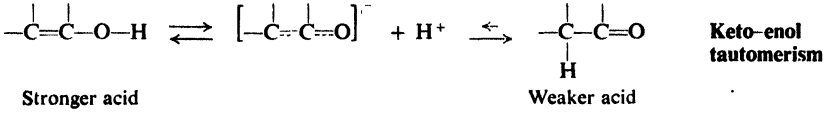
If hydration of acetylene followed the same pattern as hydration of alkenes, we would expect addition of H— and —OH to the triple bond to yield the structure that we would call *vinyl alcohol.* But all attempts to prepare vinyl alcohol result—like hydration of acetylene—in the formation of acetaldehyde.

A structure with —OH attached to doubly-bonded carbon is called an **enol** (*-ene* for the carbon-carbon double bond, *-ol* for *alcohol*). It is almost always true that when we try to make a compound with the enol structure, we obtain instead a compound with the **keto** structure (one that contains a C=O group).



There is an equilibrium between the two structures, but it generally lies very much in favor of the keto form. Thus, vinyl alcohol is formed initially by hydration of acetylene, but it is rapidly converted into an equilibrium mixture that is almost all acetaldehyde.

Rearrangements of this enol–keto kind take place particularly easily because of the polarity of the —O—H bond. A hydrogen ion separates readily from oxygen to form a hybrid anion; but when a hydrogen ion (most likely a *different* one) returns, it may attach itself either to oxygen or to carbon of the anion. When it returns to oxygen, it may readily come off again; but when it attaches itself to



carbon, it tends to stay there. We recognize this reaction as another example of the conversion of a stronger acid into a weaker acid (Sec. 8.10).

Compounds whose structures differ markedly in arrangement of atoms, but which exist in equilibrium, are called **tautomers.** The most common kind of **tautomerism** involves structures that differ in the point of attachment of *hydrogen.* In these cases, as in **keto–enol tautomerism,** the tautomeric equilibrium generally favors the structure in which hydrogen is bonded to carbon rather than to a more electronegative atom; that is, equilibrium favors the weaker acid.

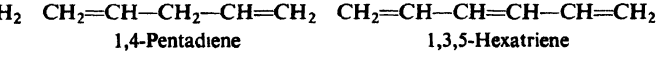
Problem 8.6 Hydration of propyne yields the ketone *acetone,* CH_3COCH_3, rather than the aldehyde CH_3CH_2CHO. What does this suggest about the orientation of the initial addition?

DIENES

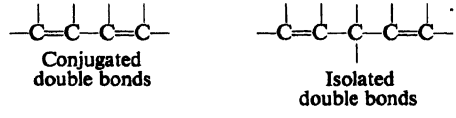
8.14 Structure and nomenclature of dienes

Dienes are simply alkenes that contain two carbon–carbon double bonds. They therefore have essentially the same properties as the alkenes we have already studied. For certain of the dienes, these alkene properties are *modified* in important ways; we shall focus our attention on these modifications. Although we shall consider chiefly *di*enes in this section, what we shall say applies equally well to compounds with more than two double bonds.

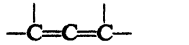
Dienes are named by the IUPAC system in the same way as alkenes, except that the ending **-diene** is used, with *two* numbers to indicate the positions of the *two* double bonds. This system is easily extended to compounds containing any number of double bonds.



Dienes are divided into two important classes according to the arrangement of the double bonds. Double bonds that alternate with single bonds are said to be **conjugated**; double bonds that are separated by more than one single bond are said to be **isolated.**



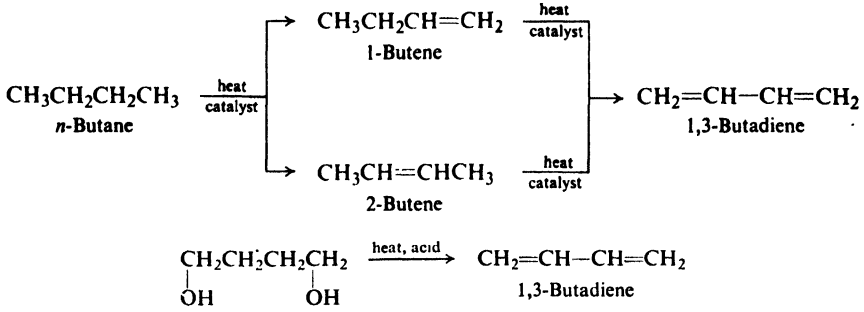
A third class of dienes, of increasing interest to organic chemists, contain *cumulated* double bonds; these compounds are known as **allenes:**



8.15 Preparation and properties of dienes

Dienes are usually prepared by adaptations of the methods used to make simple alkenes. For example, the most important diene, **1,3-butadiene** (used to

make synthetic rubber, Sec. 8.25), has been made in this country by a cracking process, and in Germany by dehydration of an alcohol containing two —OH groups:



The chemical properties of a diene depend upon the 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.

Conjugated dienes differ from simple alkenes in three ways: (a) they are *more stable*, (b) they undergo *1,4-addition*, and (c) toward free radical addition, they are *more reactive*.

8.16 Stability of conjugated dienes

If we look closely at Table 6.1 (p. 183), 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/mole; for disubstituted alkenes (R_2C CH_2 or RCH CHR), 28 kcal/mole; and for trisubstituted alkenes (R_2C CHR), 27 kcal/mole. 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 8.2, 1,4-pentadiene and 1,5-hexadiene, for example, have heats of hydrogenation very close to 2 × 30 kcal, or 60 kcal/mole.

Table 8.2 HEATS OF HYDROGENATION OF DIENES

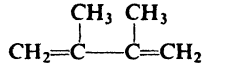
Diene	ΔH of Hydrogenation, kcal/mole
1,4-Pentadiene	60.8
1,5-Hexadiene	60.5
1,3-Butadiene	57.1
1,3-Pentadiene	54.1
2-Methyl-1,3-butadiene (Isoprene)	53.4
2,3-Dimethyl-1,3-butadiene	53.9
1,2-Propadiene (Allene)	71.3

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.

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


Expected: 28 + 28 = 56 kcal
Observed: 54

What do these heats of hydrogenation tell us about the conjugated dienes? Using the approach of Sec. 6.4, 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 non-conjugated 1,4-pentadiene.

In the next three sections we shall see how two different factors have been invoked to account for the relative stabilities of conjugated dienes, and of simple alkenes as well: (a) delocalization of π electrons, and (b) strengthening of σ bonds through changes in hybridization of carbon.

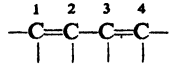
Unusual stability of conjugated dienes is also strongly indicated by the fact that, where possible, they are the preferred diene products of elimination reactions (Sec. 5.14).

Problem 8.7 Predict the major product of dehydrohalogenation of 4-bromo-1-hexene.

Problem 8.8 (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?

8.17 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:



This would correspond to an orbital picture of the molecule (see Fig. 8.5*a*), 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 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. 8.5*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*.

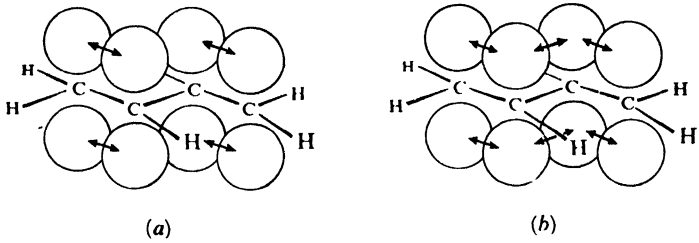


Figure 8.5. Conjugated diene. (*a*) Overlap of p orbitals to form two double bonds. (*b*) Overlap of p orbitals to form conjugated system: delocalization of π electrons.

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*.

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 (Sec. 6.27) 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 A long, as compared with 1.53 A for a pure single bond. The resonance energy of a conjugated diene is only 2–4 kcal/mole, compared with 10 kcal/mole for the allyl radical. (However, for an alternative interpretation, see Sec. 8.19.)

8.18 Resonance in alkenes. Hyperconjugation

Heats of hydrogenation showed us (Sec. 6.4) that alkenes are stabilized not only by conjugation but also by the presence of alkyl groups: *the greater the number of alkyl groups attached to the doubly-bonded carbon atoms, the more stable the alkene.* To take the simplest example, the heat of hydrogenation of propylene is 2.7 kcal lower than that of ethylene, indicating that (relative to the corresponding alkane) propylene is 2.7 kcal more stable than ethylene.

Stabilization by alkyl groups has been attributed to the same fundamental factor as stabilization by a second double bond: *delocalization of electrons*, this time through overlap between a p orbital and a σ orbital of the alkyl group.

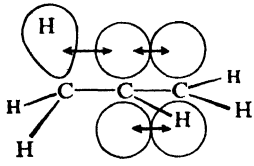
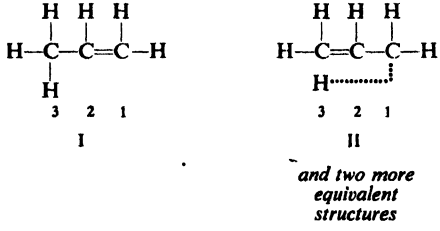


Figure 8.6. Hyperconjugation in an alkene: overlap between p and π orbitals.

Through this overlap, individual electrons can, to an extent, help bind together four nuclei. Delocalization of this kind, involving σ bond orbitals, we recognize as *hyperconjugation* (Sec. 6.28).

Translated into resonance terminology, such hyperconjugation is represented by contribution from structures like II. (As before, the dotted line in II represents



a formal bond, indicating that electrons on the two atoms are paired.) Considered by itself, a structure like II is indeed strange, since there is no real bond joining the hydrogen to carbon. This is, however, simply a rough way of indicating that the carbon–hydrogen bond is something *less* than a single bond, that the C_2—C_3 bond has some double-bond character, and that the C_1—C_2 bond has some single-bond character.

Consistent with partial double-bond character, the carbon–carbon "single" bond in propylene is 1.50 A long, as compared to 1.53 A for a pure single bond.

The greater the number of alkyl groups attached to the doubly-bonded carbons, the greater the number of contributing structures like II, the greater the delocalization of electrons, and the more stable the alkene.

Hyperconjugation of the kind described above is called *sacrificial hyperconjugation*, since there is one less real bond in structures like II than in I. In contrast, the kind of

hyperconjugation we encountered in connection with free radicals and carbonium ions involves no "sacrifice" of a bond and is called *isovalent hyperconjugation.*

8.19 Stability of dienes and alkenes: an alternative interpretation

We have seen that the carbon–hydrogen bond length decreases as we proceed along the series ethane, ethylene, acetylene, and we attributed this to changes in hybridization of carbon (see Table 8.3). As the *p* character of the bonding orbital

Table 8.3 CARBON–HYDROGEN SINGLE BOND LENGTHS AND HYBRIDIZATION

Compound	Length, A	Hybridization
CH_3—CH_3	1.112	sp^3–s
CH_2=CH_2	1.103	sp^2–s
HC≡CH	1.079	sp–s

decreases, the orbital size decreases, and the bond becomes shorter (Sec. 5.4).

The carbon–carbon single-bond length also decreases along an analogous series, ethane, propylene, propyne (Table 8.4). We notice that these differences

Table 8.4 CARBON CARBON SINGLE BOND LENGTHS AND HYBRIDIZATION

Compound	Length, A	Hybridization
CH_3—CH_3	1.53	sp^3 sp^3
CH_2=CH—CH_3	1.50	sp^2–sp^3
HC≡C—CH_3	1.46	sp–sp^3

are bigger than for carbon–hydrogen bonds. Here, the bond-shortening has been attributed to hyperconjugation, as discussed in Sec. 8.18.

It has been argued, most notably by M. J. S. Dewar of the University of Texas, 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.

Furthermore, Dewar has proposed that such shortening of bonds is accompanied by a proportional increase in bond energies (E); that is, shortening a bond makes the molecule more stable. Change in hybridization affects bond lengths more—and hence affects molecular stability more—when carbon–carbon bonds are involved than when carbon–hydrogen bonds are involved. An alkyl substituent stabilizes an alkene, relative to the corresponding alkane, because sp^2 hybridization strengthens a carbon–carbon bond more than a carbon–hydrogen bond.

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 A) and strong.

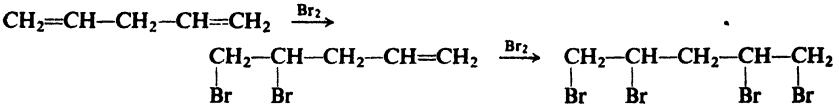
There is little doubt that both factors, delocalization of π electrons and change in σ bonds, are at work. The question is: what is the relative importance of each? The answer may well turn out to be: ***both*** are important.

In the case of molecules like the allyl radical, where clearly no single structure is acceptable, Dewar has not questioned the importance of π-electron delocalization,

although he considers σ-bond stability to play a larger part than has been recognized. He also accepts a more important role for isovalent hyperconjugation—in free radicals and carbonium ions—than for the sacrificial hyperconjugation we have so far discussed.

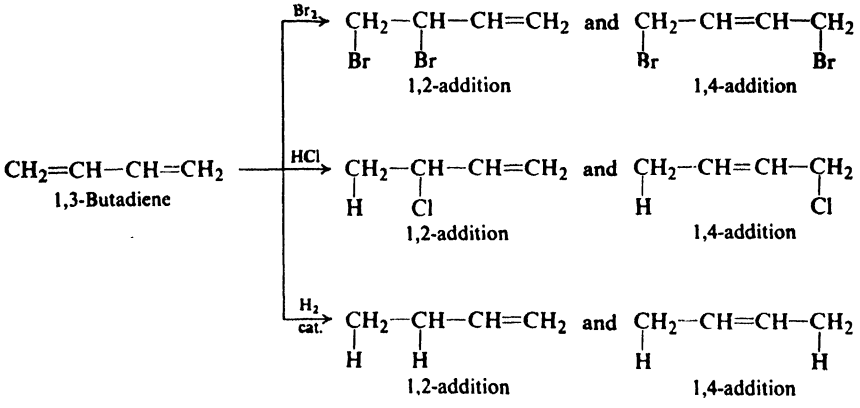
8.20 Electrophilic addition to conjugated dienes. 1,4-Addition

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-tetrabromo-

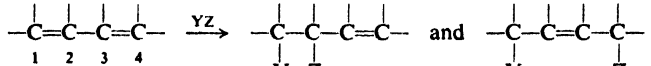


pentane. This is typical of the behavior of dienes containing isolated double bonds: the double bonds react independently, as though they were in different molecules.

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.



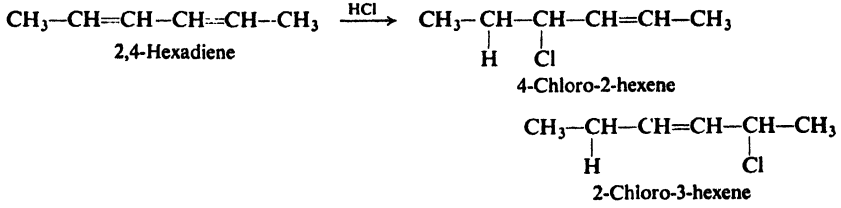
Study of many conjugated dienes and many reagents shows that such behavior is typical: *in* **additions to conjugated dienes**, *a reagent may attach itself not only to a pair of adjacent carbons* (**1,2-addition**), *but also to the carbons at the two ends of the conjugated system* (**1,4-addition**). Very often the 1,4-addition product is the major one.



8.21 Allyl cations. Delocalization in carbonium ions

How can we account for the products obtained? We have seen (Secs. 6.10 and 6.11) that electrophilic addition is a two-step process, and that the first step

takes place in the way that yields the more stable carbonium ion. 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:

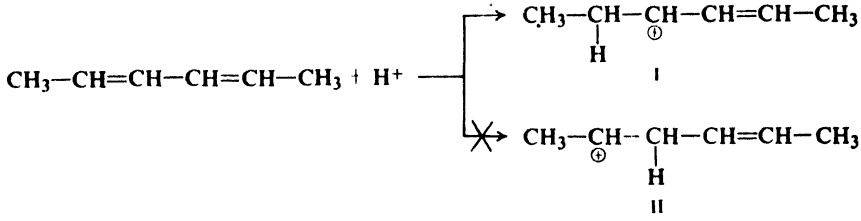


2,4-Hexadiene

4-Chloro-2-hexene

2-Chloro-3-hexene

These products show that hydrogen adds to C–2 to yield carbonium ion I, rather than to C–3 to yield carbonium ion II:



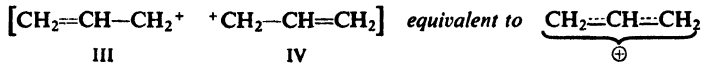
Since both I and II are secondary cations, how can we account for the preference? I is not simply a secondary cation, but is an *allyl* cation as well, since the carbon bearing the positive charge is attached to a doubly-bonded carbon.

Let us look more closely at such cations, using the parent allyl cation, $CH_2{=}CH{-}CH_2^+$, as our example. Bond dissociation energies showed us that allyl radicals are unusually stable, and we attributed this stability to resonance between equivalent structures (Secs. 6.24–6.25). The ionization potential (188 kcal) of the allyl radical enables us to calculate that the allyl cation, too, is unusually stable. Even though we have just drawn its structure as that of a primary cation, it is 24 kcal more stable than the ethyl cation, and just about as stable as the isopropyl cation. We can now expand the sequence of Sec. 5.18.

Stability of carbonium ions

$$3^\circ > \overset{\text{allyl}}{2^\circ} > 1^\circ > CH_3^+$$

Like the allyl radical, the allyl cation is a resonance hybrid of two **exactly** equivalent structures:



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 them helps to hold together all three carbon nuclei (Fig. 8.7). We see how *flatness* is required to permit

the overlap that provides electrons to the electron-deficient carbon and stabilizes the cation.

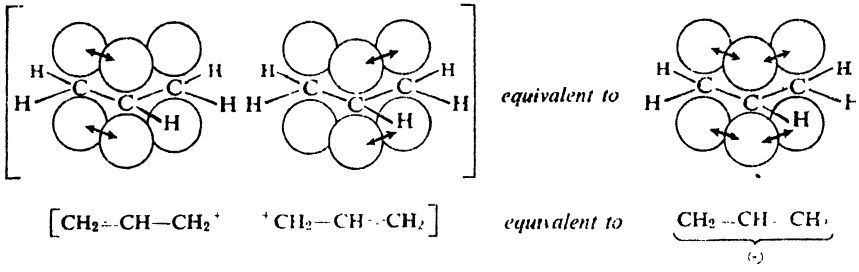
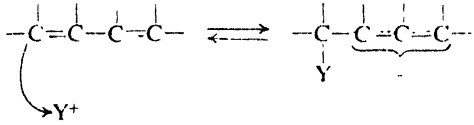


Figure 8.7 Allyl cation. The *p* orbital of the middle carbon overlaps *p* orbitals on both sides to permit delocalization of electrons.

The relative stabilities of simple alkyl cations has also been attributed to delocalization, this time by overlap of the *p* orbital with π bonds, that is, through *hyperconjugation* (Sec. 6.28).

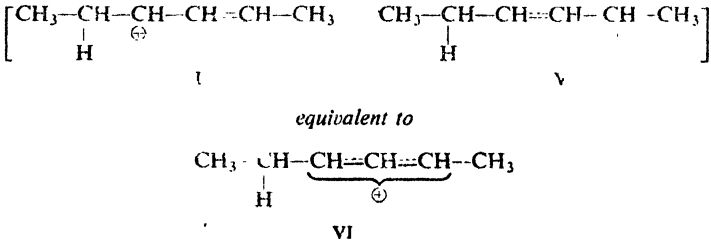
Problem 8.9 Draw resonance structures to show how the order of stability of alkyl cations could be accounted for on the basis of hyperconjugation.

The products obtained from addition to conjugated dienes are always consistent with the formation of the most stable intermediate carbonium ion: an allyl cation. This requires the first step to be *addition to one of the ends* of the conjugated system.



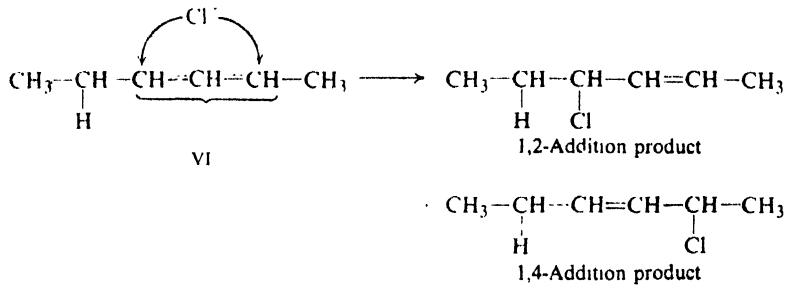
Adds to end of conjugated system An allyl carbonium ion

The first step of addition to 2,4-hexadiene yields, then, not cation I, but the hybrid cation VI in which the charge is spread over two carbons:

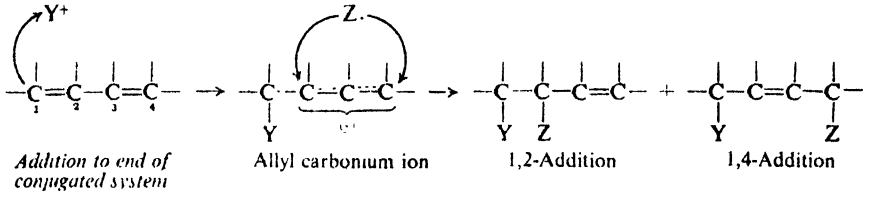


VI

In the second step, the negative chloride ion can attach itself to either of these carbons and thus yield the 1,2- or 1,4-product.



We have not shown *why* 1,4-addition occurs; we have simply shown that it is not unreasonable that it *does* happen. In summary:



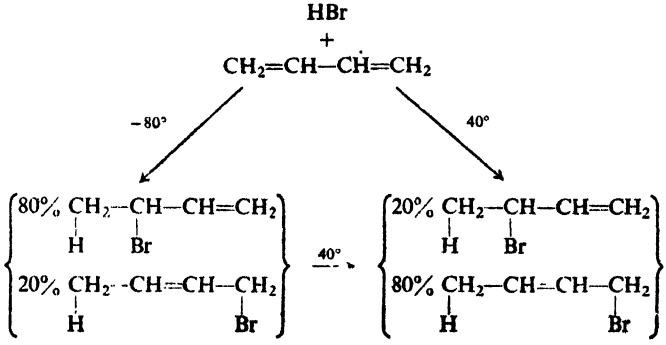
Thus the hybrid nature of the allyl cation governs both steps of electrophilic addition to conjugated dienes: the first, through stabilization; the second, by permitting attachment to either of two carbon atoms.

Problem 8.10 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.

8.22 1,2- *vs.* 1,4-Addition. Rate *vs.* equilibrium

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°) yields a mixture containing 20% of the 1,4-product and 80% of the 1,2-product. Reaction at a higher temperature (40°) 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° indicates that the 1,2-product is formed *faster* than the 1,4-product; since each compound remains unchanged at −80°, 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-addition more closely by drawing a potential energy curve for the reactions involved (Fig. 8.8). The carbonium ion 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

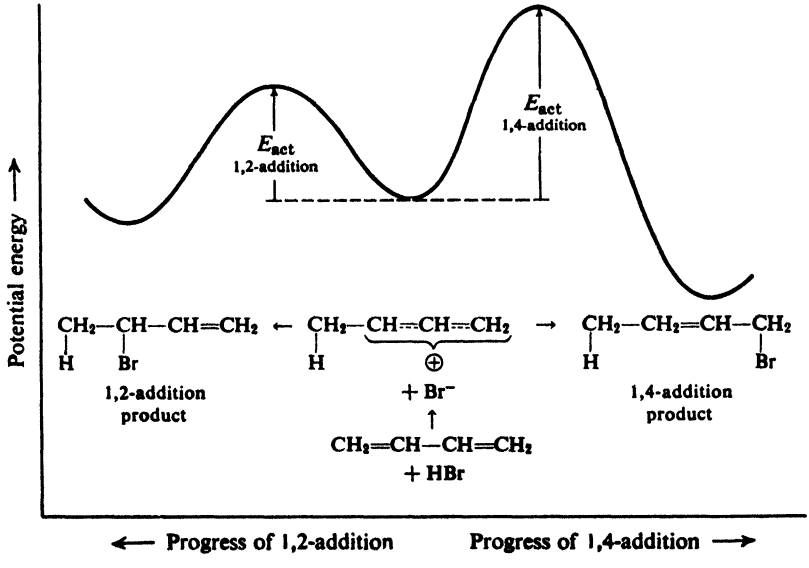
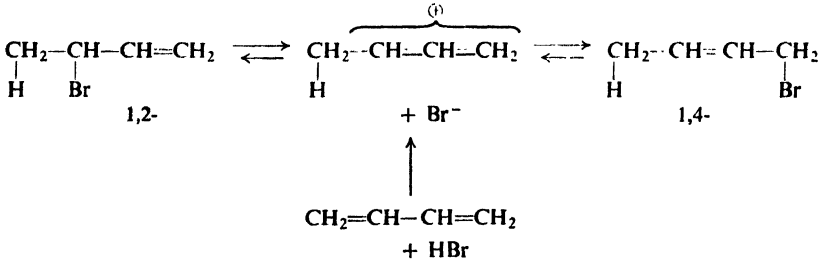


Figure 8.8. Potential energy changes during progress of reaction: 1,2- vs. 1,4-addition.

that leading to the 1,4-product. We represent this by the lower hill leading from the ion 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.

We shall see later (Sec. 14.12) that alkyl halides, and particularly allyl halides, can undergo ionization. Now ionization of either bromo compound yields the same carbonium ion; the most likely—and simplest—way in which the 1,2- and 1,4-products reach equilibrium is through this ion.



Ionization of the bromides involves climbing the potential hills back toward this carbonium ion. But there is a higher hill separating the ion 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.

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 carbonium ion or free radical, the faster it is formed; a consideration of the transition states for the various reactions has shown (Secs. 3.26, 5.21, and 6.11) that this is reasonable. ***We must not, however, extend this principle to other reactions unless the evidence warrants it.***

Problem 8.11 Addition of one mole of bromine to 1,3,5-hexatriene yields only 5,6-dibromo-1,3-hexadiene and 1,6-dibromo-2,4-hexadiene. (a) Are these products

consistent with the formation of the most stable intermediate carbonium ion? (b) What other product or products would also be consistent? (c) Actually, which factor appears to be in control, rate or position of equilibrium?

8.23 Free-radical addition to conjugated dienes: orientation

Like other alkenes, conjugated dienes undergo addition not only by electrophilic reagents but also by free radicals. In free-radical addition, conjugated dienes show two special features: they undergo **1,4-addition** as well as 1,2-addition, and they are **much more reactive** than ordinary alkenes. We can account for both features—*orientation* and *reactivity*—by examining the structure of the intermediate free radical.

Let us take, as an example, addition of $BrCCl_3$ to 1,3-butadiene in the presence of a peroxide. As we have seen (Sec. 6.18), the peroxide decomposes (step 1) to yield a free radical, which abstracts bromine from $BrCCl_3$ (step 2) to generate a CCl_3 radical.

(1) $$\text{Peroxide} \longrightarrow \text{Rad}\cdot$$

(2) $$\text{Rad}\cdot + BrCCl_3 \longrightarrow \text{Rad—Br} + \cdot CCl_3$$

The $\cdot CCl_3$ radical thus formed adds to the butadiene (step 3). Addition to one of the *ends* of the conjugated system is the preferred reaction, since this yields a resonance-stabilized allyl free radical.

(3) $$\overset{\cdot CCl_3}{\underset{1}{CH_2}}=\underset{2}{CH}-\underset{3}{CH}=\underset{4}{CH_2} \longrightarrow \left[Cl_3C-CH_2-CH-CH=CH_2 \;\leftrightarrow\; Cl_3C-CH_2-CH=CH-CH_2\right]$$

Addition to end of conjugated system

equivalent to

$$Cl_3C-CH_2-\underbrace{CH=CH=CH_2}$$

Allylic free radical

The allyl free radical then abstracts bromine from a molecule of $BrCCl_3$ (step 4) to complete the addition, and in doing so forms a new $\cdot CCl_3$ radical which can carry on the chain. In step (4) bromine can become attached to either C-2 or C-4 to yield either the 1,2- or 1,4-product.

(4) $$Cl_3C-CH_2-\underbrace{CH=CH=CH_2} \xrightarrow{BrCCl_3} Cl_3C-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH=CH_2$$

Allylic free radical

1,2-Addition product

and $Cl_3C-CH_2-CH=CH-CH_2-Br$

1,4-Addition product

8.24 Free-radical addition to conjugated dienes: reactivity

If $BrCCl_3$ is allowed to react with a 50:50 mixture of 1,3-butadiene and a simple alkene like 1-octene, addition occurs almost exclusively to the 1,3-butadiene. Evidently the $\cdot CCl_3$ radical adds much more rapidly to the conjugated diene than

to the simple alkene. Similar results have been observed in a great many radical additions.

How can we account for the unusual reactivity of conjugated dienes? In our discussion of halogenation of the simple alkenes (Sec. 3.27), we found that not only orientation but also relative reactivity was related to the stability of the free radical formed in the first step. On this basis alone, we might expect addition to a conjugated diene, which yields a stable allyl free radical, to occur faster than addition to a simple alkene.

On the other hand, we have just seen (Sec. 8.16) that conjugated dienes are more stable than simple alkenes. On this basis alone, we might expect addition to conjugated dienes to occur more slowly than to simple alkenes.

The relative rates of the two reactions depend chiefly upon the E_{act}'s. Stabilization of the incipient allyl free radical lowers the energy level of the transition state; stabilization of the diene lowers the energy of the reactants. Whether the net E_{act} is larger or smaller than for addition to a simple alkene depends upon *which* is stabilized *more* (see Fig. 8.9).

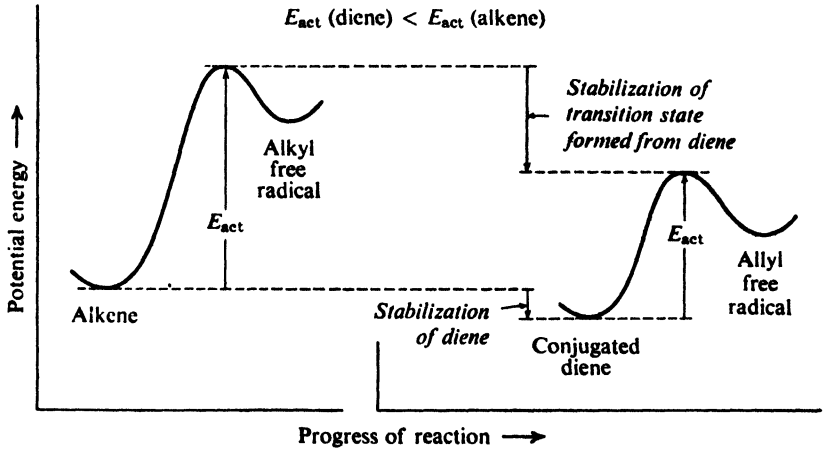


Figure 8.9. Molecular structure and rate of reaction. Transition state from diene stabilized more than diene itself: E_{act} is lowered. (Plots aligned with each other for easy comparison.)

The fact is that conjugated dienes are more reactive than simple alkenes. In the present case, then—and in most cases involving alkenes and free radicals, or alkenes and carbonium ions—the factors stabilizing the transition state are more important than the factors stabilizing the reactant. However, this is *not always* true. (It does not seem to be true, for example, in electrophilic addition to conjugated dienes.)

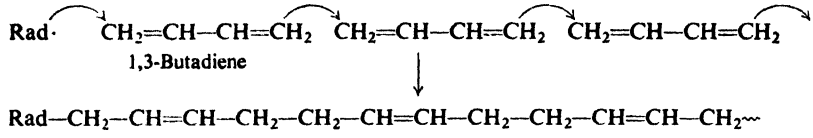
8.25 Free-radical polymerization of dienes. Rubber and rubber substitutes

Like substituted ethylenes, conjugated dienes, too, undergo free-radical polymerization. From 1,3-butadiene, for example, there is obtained a polymer

$CH_2{=}CH{-}CH{=}CH_2$ 1,3-Butadiene

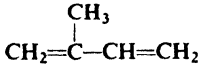
$[{-}CH_2{-}CH{=}CH{-}CH_2{-}]_n$ Polybutadiene

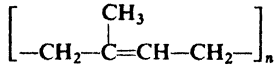
whose structure indicates that 1,4-addition occurs predominantly:



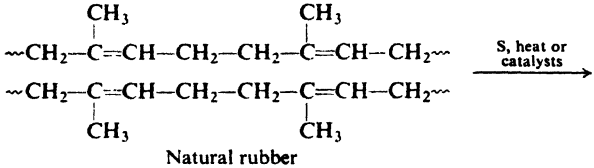
Such a polymer differs from the polymers of simple alkenes in one very important way: each unit still contains one double bond.

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**.

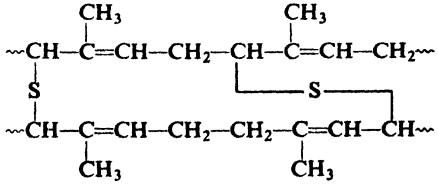

Isoprene


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.

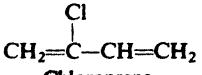


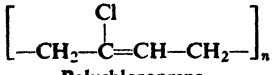
Natural rubber



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.

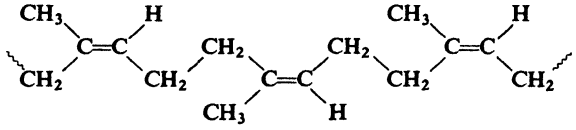

Chloroprene


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.

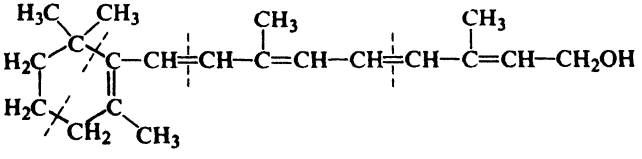
Polymers of isoprene, too, can be made artificially: they contain the same unsaturated chain and the same substituent (the $-CH_3$ group) as natural rubber. But polyisoprene made by the free-radical process we have been talking about was—in the properties that really matter—a far cry from natural rubber. 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 (Sec. 32.6). 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.



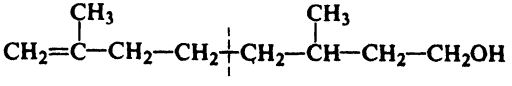
Natural rubber
All cis-configurations

8.26 Isoprene and the isoprene rule

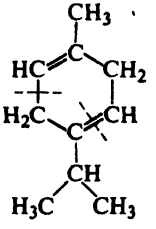
The isoprene unit is one of nature's favorite building blocks. It occurs not only in rubber, but in a wide variety of compounds isolated from plant and animal sources. For example, nearly all the *terpenes* (found in the essential oils of many plants) have carbon skeletons made up of isoprene units joined in a regular, head-to-tail way. Recognition of this fact—the so-called **isoprene rule**—has been of great help in working out structures of terpenes.



Vitamin A

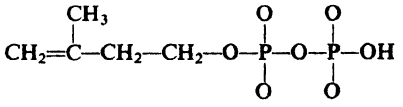


Citronellol: *a terpene*
(found in oil of geranium)



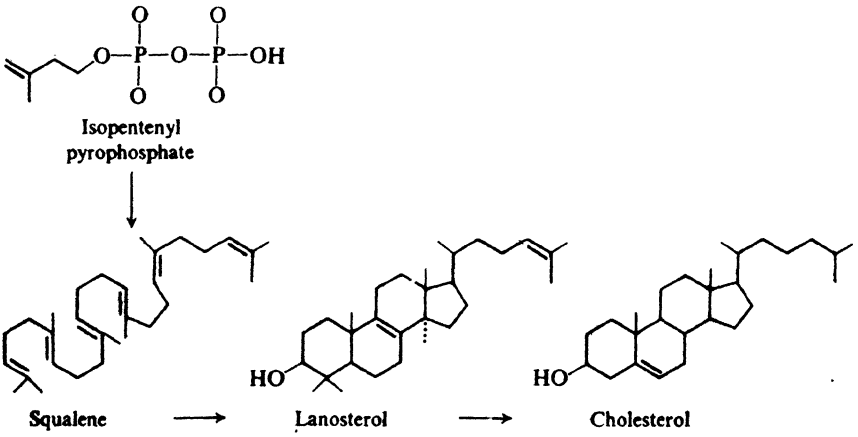
γ-Terpinene: *a terpene*
(found in coriander oil)

A fascinating area of research linking organic chemistry and biology is the study of the *biogenesis* of natural products: the detailed sequence of reactions by which a compound is formed in living systems, plant or animal. All the isoprene units in nature, it appears, originate from the same compound, "isopentenyl" pyrophosphate.



Isopentyl pyrophosphate

Work done since about 1950 has shown how compounds as seemingly different from rubber as *cholesterol* (p. 507) are built up, step by step, from isoprene units.



Isopentenyl pyrophosphate

Squalene → Lanosterol → Cholesterol

Problem 8.12 (a) Mark off the isoprene units making up the squalene molecule. (b) There is one deviation from the head-to-tail sequence. Where is it? Does its particular location suggest anything to you—in general terms—about the biogenesis of this molecule? (c) What skeletal changes, if any, accompany the conversion of squalene into lanosterol? Of lanosterol into cholesterol?

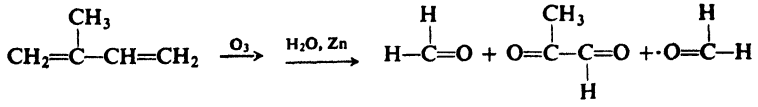
8.27 Analysis of alkynes and dienes

Alkynes and dienes respond to characterization tests in the same way as alkenes: they decolorize bromine in carbon tetrachloride without evolution of hydrogen bromide, and they decolorize cold, neutral, dilute permanganate; they are not oxidized by chromic anhydride. They are, however, more unsaturated than alkenes. This property can be detected by determination of their molecular formulas (C_nH_{2n-2}) and by a quantitative hydrogenation (two moles of hydrogen are taken up per mole of hydrocarbon).

Proof of structure is best accomplished by the same degradative methods that are used in studying alkenes. Upon ozonolysis alkynes yield carboxylic acids, whereas alkenes yield aldehydes and ketones. For example:

$$\underset{\text{2-Pentyne}}{CH_3CH_2C{\equiv}CCH_3} \xrightarrow{O_3} \xrightarrow{H_2O} \underset{\text{Carboxylic acids}}{CH_3CH_2COOH + HOOCCH_3}$$

Ozonolysis of dienes yields aldehydes and ketones, including double-ended ones containing two C=O groups per molecule. For example:



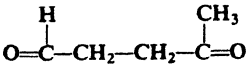
A terminal alkyne (RC≡CH) is characterized, and differentiated from isomers, by its conversion into insoluble silver and cuprous acetylides (Sec. 8.11).

(Spectroscopic analysis of alkynes and dienes is discussed in Secs. 13.15–13.16.)

Problem 8.13 Contrast the ozonolysis products of the following isomers: (a) 1-pentyne, (b) 2-pentyne, (c) 3-methyl-1 butyne, (d) 1,3-pentadiene, (e) 1,4-pentadiene, (f) isoprene (2-methyl-1,3-butadiene).

Problem 8.14 Predict the ozonolysis products from polybutadiene, $(C_4H_6)_n$: (a) if 1,2-addition is involved in the polymerization; (b) if 1,4-addition is involved.

Problem 8.15 Ozonolysis of natural rubber yields chiefly (90%) the compound



What does this tell us about the structure of rubber?

PROBLEMS

1. (a) Draw structures of the seven isomeric alkynes of formula C_6H_{10}. (b) Give the IUPAC and derived name of each. (c) Indicate which ones will react with Ag^+ or $Cu(NH_3)_2^+$. (d) Draw structures of the ozonolysis products expected from each.

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. Write equations for all steps in the manufacture of acetylene starting from limestone and coal.

4. Outline all steps in the synthesis of propyne from each of the following compounds, using any needed organic or inorganic reagents. Follow the other directions given on page 224.

(a) 1,2-dibromopropane
(b) propylene
(c) isopropyl bromide
(d) propane
(e) *n*-propyl alcohol
(f) 1,1-dichloropropane
(g) acetylene
(h) 1,1,2,2-tetrabromopropane

5. Outline all steps in the synthesis from acetylene of each of the following compounds, using any needed organic or inorganic reagents.

(a) ethylene
(b) ethane
(c) ethylidene bromide (1,1-dibromoethane)
(d) vinyl chloride
(e) 1,2-dichloroethane
(f) acetaldehyde
(g) propyne
(h) 1-butyne
(i) 2-butyne
(j) *cis*-2-butene
(k) *trans*-2-butene
(l) 1-pentyne
(m) 2-pentyne
(n) 3-hexyne

6. Give structures and names of the organic products expected from the reaction (if any) of 1-butyne with:

(a) 1 mole H_2, Ni
(b) 2 moles H_2, Ni
(c) 1 mole Br_2
(d) 2 moles Br_2
(e) 1 mole HCl
(f) 2 moles HCl
(g) H_2O, H^+, Hg^{++}
(h) Ag^+
(i) product (h) + HNO_3
(j) $NaNH_2$
(k) product (j) + C_2H_5Br
(l) product (j) + *tert*-butyl chloride
(m) C_2H_5MgBr
(n) product (m) + H_2O
(o) O_3, then H_2O
(p) hot $KMnO_4$

7. Answer Problem 6 for 1,3-butadiene instead of 1-butyne.

8. Answer Problem 6 for 1,4-pentadiene instead of 1-butyne.

9. Give structures and names of the products from dehydrohalogenation 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; 3-bromo-2-methylbutane
(d) 1-bromo-2-methylbutane; 4-bromo-2-methylbutane
(e) 1-chloro-2,3-dimethylbutane; 2-chloro-2,3-dimethylbutane
(f) 4-chloro-1-butene; 5-chloro-1-pentene

10. Which alkyl halide of each pair in Problem 9 would you expect to undergo dehydrohalogenation faster?

11. 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

12. Answer Problem 11 for the addition of $BrCCl_3$ in the presence of peroxides (Sec. 6.18) instead of addition of HCl.

13. Which compound of each pair in Problem 12 would you expect to be more reactive toward addition of $BrCCl_3$?

14. (a) The heat of hydrogenation of acetylene (converted into ethane) is 75.0 kcal/mole. Calculate ΔH for hydrogenation of acetylene to ethylene. (b) How does the stability of an alkyne relative to an alkene compare with the stability of an alkene relative to an alkane? (c) Solely on the basis of your answer to (b), would you expect acetylene to be more or less reactive than ethylene toward addition of a free methyl radical, $CH_3\cdot$? (d) Draw the structure of the free radical expected from addition of $CH_3\cdot$ to acetylene: from addition of $CH_3\cdot$ to ethylene. Judging only from the relative stabilities of the radicals being formed, would you expect $CH_3\cdot$ to add to acetylene faster or slower than to ethylene? (e) $CH_3\cdot$ has been found to add more slowly to acetylene than to ethylene. Which factor—reactant stability or radical stability—is more important here?

15. (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)?

16. A useful method of preparing 1-alkenes involves reaction of Grignard reagents with the unusually reactive halide, allyl bromide:

$$RMgX + BrCH_2CH{=}CH_2 \longrightarrow R{-}CH_2CH{=}CH_2$$

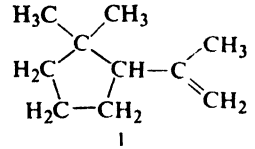
When 1-hexene (b.p. 63.5°) is prepared in this way, it is contaminated with *n*-hexane (b.p. 69°) and 1,5-hexadiene (b.p. 60°); these are difficult to remove because of the closeness of boiling points. The mixture is treated with bromine and the product distilled. There are obtained three fractions: b.p. 68–69°; b.p. 77–78° at 15 mm pressure; and a high-boiling residue.

(a) What does each of these fractions contain? (b) What would you do next to get pure 1-hexene? (c) Show how this procedure could be applied to the separation of *n*-pentane (b.p. 36°) and 1-pentene (b.p. 30°); 1-decene (b.p. 171°) and 5-decyne (b.p. 175°).

17. Outline all steps in a possible laboratory synthesis of each of the following, using alcohols of four carbons or fewer as your only organic source, and any necessary inorganic reagents. (*Remember:* Work backwards.)

(a) *meso*-3,4-dibromohexane;
(b) (2R,3R;2S,3S)-2,3-heptanediol, a racemic modification.

18. 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.

19. *Gutta percha* is a non-elastic naturally-occurring polymer used in covering golf balls and underwater cables. It has the same formula, $(C_5H_8)_n$, and yields the same hydrogenation product and the same ozonolysis product (Problem 8.15, page 279) as natural rubber. Using structural formulas, show the most likely structural difference between gutta percha and rubber.

20. Describe simple chemical tests that would distinguish between:

(a) 2-pentyne and *n*-pentane
(b) 1-pentyne and 1-pentene
(c) 1-pentyne and 2-pentyne
(d) 1,3-pentadiene and *n*-pentane
(e) 1,3-pentadiene and 1-pentyne
(f) 2-hexyne and isopropyl alcohol
(g) allyl bromide and 2,3-dimethyl-1,3-butadiene

Tell exactly what you would *do* and *see*.

21. Describe chemical methods (not necessarily simple tests) that would distinguish between:

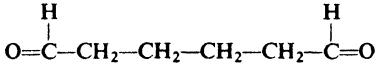
(a) 2-pentyne and 2-pentene
(b) 1,4-pentadiene and 2-pentene
(c) 1,4-pentadiene and 2-pentyne
(d) 1,4-pentadiene and 1,3-pentadiene

22. On the basis of physical properties, an unknown compound is believed to be one of the following:

n-pentane (b.p. 36°)
2-pentene (b.p. 36°)
1-chloropropene (b.p. 37°)
trimethylethylene (b.p. 39°)
1-pentyne (b.p. 40°)
methylene chloride (b.p. 40°)
3,3-dimethyl-1-butene (b.p. 41°)
1,3-pentadiene (b.p. 42°)

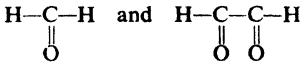
Describe how you would go about finding out which of the possibilities the unknown actually is. Where possible, use simple chemical tests; where necessary, use more elaborate chemical methods like quantitative hydrogenation and cleavage. Tell exactly what you would *do* and *see*.

23. A hydrocarbon of formula C_6H_{10} absorbs only *one* mole of H_2 upon catalytic hydrogenation. Upon ozonolysis the hydrocarbon yields



What is the structure of the hydrocarbon? (Check your answer in Sec. 9.17.)

24. A hydrocarbon was found to have a molecular weight of 80–85. A 10.02-mg sample took up 8.40 cc of H_2 gas measured at 0° and 760 mm pressure. Ozonolysis yielded only

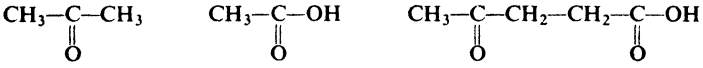


What was the hydrocarbon?

25. *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:

(a) What structures are consistent with these facts?
(b) On the basis of the isoprene rule (Sec. 8.26), what is the most likely structure for myrcene?

26. *Dihydromyrcene*, $C_{10}H_{18}$, formed from myrcene (Problem 25), absorbs two moles of hydrogen to form $C_{10}H_{22}$. Upon cleavage by $KMnO_4$, dihydromyrcene yields:



(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?

27. At the beginning of the biogenesis of squalene (Sec. 8.26) isopentenyl pyrophosphate, $CH_2{=}C(CH_3)CH_2CH_2OPP$, is enzymatically isomerized to dimethylallyl pyrophosphate, $(CH_3)_2C{=}CHCH_2OPP$. These two compounds then react together to yield *geranyl pyrophosphate*, $(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCH_2OPP$. (a) Assuming that the weakly basic pyrophosphate anion is, like the protonated hydroxyl group, a good leaving group,

$$R{-}OPP \longrightarrow R^{\oplus} + OPP^{-}$$

can you suggest a series of familiar steps by which geranyl pyrophosphate might be formed? (b) Geranyl pyrophosphate then reacts with another molecule of isopentenyl pyrophosphate to form *farnesyl pyrophosphate*. What is the structure of farnesyl pyrophosphate? (c) What is the relationship between farnesyl pyrophosphate and squalene? (d) An enzyme system from the rubber plant catalyzes the conversion of isopentenyl pyrophosphate into rubber; dimethylallyl pyrophosphate appears to act as an initiator for the process. Can you suggest a "mechanism" for the formation of natural rubber?

Chapter 9

Alicyclic Hydrocarbons

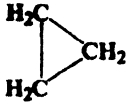
9.1 Open-chain and cyclic compounds

In the compounds that we have studied in previous chapters, the carbon atoms are attached to one another to form *chains*; these are called **open-chain** compounds. In many compounds, however, the carbon atoms are arranged to form *rings*; these are called **cyclic** compounds.

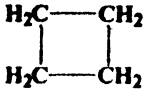
In this chapter we shall take up the *alicyclic* hydrocarbons (*aliphatic cyclic* hydrocarbons). Much of the chemistry of cycloalkanes and cycloalkenes we already know, since it is essentially the chemistry of open-chain alkanes and alkenes. But the cyclic nature of some of these compounds confers very special properties on them. It is because of these special properties that, during the past fifteen years, alicyclic chemistry has become what Professor Lloyd Ferguson, of the California State College at Los Angeles, has called "the playground for organic chemists." It is on some of these special properties that we shall focus our attention.

9.2 Nomenclature

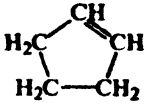
Cyclic aliphatic hydrocarbons are named by prefixing **cyclo-** to the name of the corresponding open-chain hydrocarbon having the same number of carbon atoms as the ring. For example:



Cyclopropane



Cyclobutane



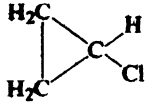
Cyclopentene

Substituents on the ring are named, and their positions are indicated by numbers,

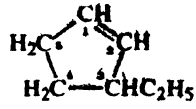
Table 9.1 CYCLIC ALIPHATIC HYDROCARBONS

Name	M.p., °C	B.p., °C	Density (at 20°C)
Cyclopropane	−127	− 33	
Cyclobutane	− 80	13	
Cyclopentane	− 94	49	0.746
Cyclohexane	6.5	81	.778
Cycloheptane	− 12	118	.810
Cyclooctane	14	149	.830
Methylcyclopentane	−142	72	.749
cis-1,2-Dimethylcyclopentane	− 62	99	.772
trans-1,2-Dimethylcyclopentane	−120	92	.750
Methylcyclohexane	−126	100	.769
Cyclopentene	− 93	46	.774
1,3-Cyclopentadiene	− 85	42	.798
Cyclohexene	−104	83	.810
1,3-Cyclohexadiene	− 98	80.5	.840
1,4-Cyclohexadiene	− 49	87	.847

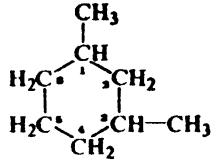
the lowest combination of numbers being used. In simple cycloalkenes and cycloalkynes the doubly- and triply-bonded carbons are considered to occupy positions 1 and 2. For example:



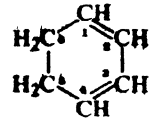
Chlorocyclopropane



3-Ethylcyclopentene



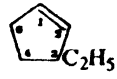
1,3-Dimethylcyclohexane



1,3-Cyclohexadiene

For convenience, aliphatic rings are often represented by simple geometric figures: a triangle for cyclopropane, a square for cyclobutane, a pentagon for cyclopentane, a hexagon for cyclohexane, and so on. It is understood that two hydrogens are located at each corner of the figure unless some other group is indicated. For example:

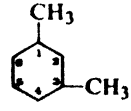
Cyclopentane



3-Ethylcyclopentene

1,3-Cyclopentadiene

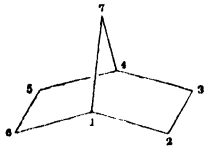
Cyclohexane



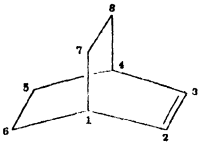
1,3-Dimethylcyclohexane

1,3-Cyclohexadiene

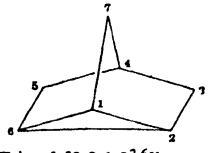
Polycyclic compounds contain two or more rings that share two or more carbon atoms. We can illustrate the naming system with *norbornane*, whose systematic name is bicyclo[2.2.1]heptane: (a) *heptane*, since it contains a total of *seven* carbon atoms; (b) *bicyclo*, since it contains *two* rings, that is, breaking two carbon–



Bicyclo[2.2.1]heptane
Norbornane



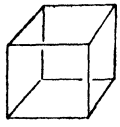
Bicyclo[2.2.2]octa-2-ene



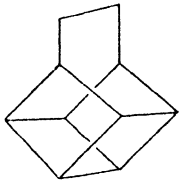
Tricyclo[2.2.1.$0^{2,6}$]heptane
Nortricyclene

carbon bonds converts it into an open-chain compound; (c) [2.2.1], since the number of carbons between bridgeheads (shared carbons) is *two* (C–2 and C–3), *two* (C–5 and C–6), and *one* (C–7).

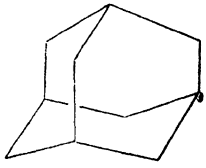
Polycyclic compounds in a variety of strange and wonderful shapes have been made, and their properties have revealed unexpected facets of organic chemistry. Underlying much of this research there has always been the challenge: ***can such a compound be made?***



Cubane

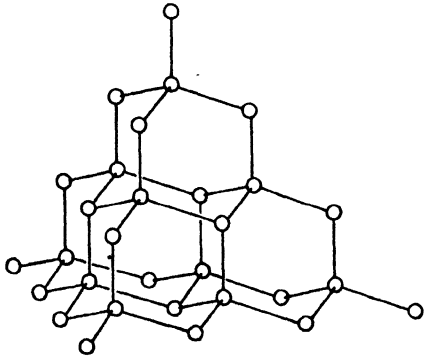


Basketane



Adamantane

The ultimate polycyclic aliphatic system is *diamond* which is, of course, not a hydrocarbon at all, but one of the allotropic forms of elemental carbon. In diamond each



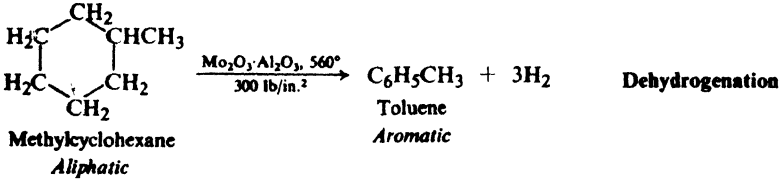
Diamond

carbon atom is attached to four others by tetrahedral bonds of the usual single bond length, 1.54 A. (Note the cyclohexane chairs, Sec. 9.11.)

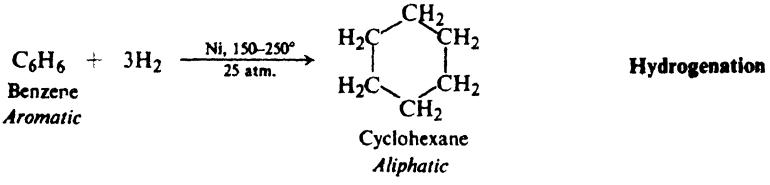
9.3 Industrial source

We have already mentioned (Sec. 3.13) that petroleum from certain areas (in particular California) is rich in cycloalkanes, known to the petroleum industry as *naphthenes*. Among these are cyclohexane, methylcyclohexane, methylcyclopentane, and 1,2-dimethylcyclopentane.

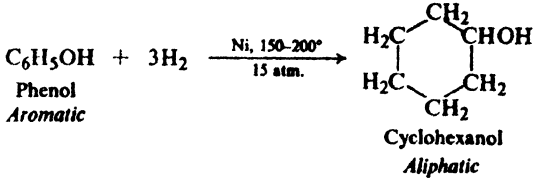
These cycloalkanes are converted by *catalytic reforming* into aromatic hydrocarbons, and thus provide one of the major sources of these important compounds (Sec. 12.4). For example:



Just as elimination of hydrogen from cyclic aliphatic compounds yields aromatic compounds, so addition of hydrogen to aromatic compounds yields cyclic aliphatic compounds, specifically cyclohexane derivatives. An important example of this is the hydrogenation of benzene to yield pure cyclohexane.



As we might expect, hydrogenation of substituted benzenes yields substituted cyclohexanes. For example:



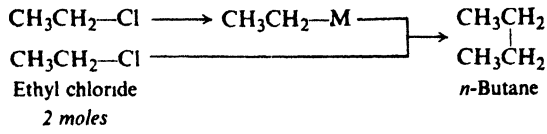
From cyclohexanol many other cyclic compounds containing a six-membered ring can be made.

9.4 Preparation

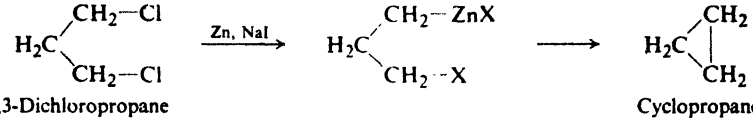
Preparation of alicyclic hydrocarbons from other aliphatic compounds generally involves two stages: (a) conversion of some open-chain compound or

compounds into a compound that contains a ring, a process called *cyclization*; (b) conversion of the cyclic compound thus obtained into the kind of compound that we want: for example, conversion of a cyclic alcohol into a cyclic alkene, or of a cyclic alkene into a cyclic alkane.

Very often, cyclic compounds are made by the *adapting* of a standard method of preparation to the job of closing a ring. For example, we have seen (Sec. 3.17) that the alkyl groups of two alkyl halides can be coupled together through conversion of one halide into an organometallic compound (a lithium dialkylcopper):



The same method applied to a *di*halide can bring about coupling between two alkyl groups *that are part of the same molecule*:



In this case zinc happens to do a good job. Although this particular method works well only for the preparation of cyclopropane, it illustrates an important principle: the carrying out of what is normally an *intermolecular* (between-molecules) reaction under such circumstances that it becomes an *intramolecular* (within-a-molecule) reaction. As we can see, it involves tying together the ends of a difunctional molecule.

Alicyclic hydrocarbons are prepared from other cyclic compounds (e.g., halides or alcohols) by exactly the same methods that are used for preparing open-chain hydrocarbons from other open-chain compounds.

Problem 9.1 Starting with cyclohexanol (Sec. 9.3), how would you prepare: (a) cyclohexene, (b) 3-bromocyclohexene, (c) 1,3-cyclohexadiene?

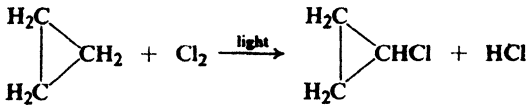
Problem 9.2 Bromocyclobutane can be obtained from open-chain compounds. How would you prepare cyclobutane from it?

The most important route to rings of many different sizes is through the important class of reactions called **cycloadditions**: *reactions in which molecules are added together to form rings.* We shall see one example of cycloaddition in Secs. 9.15–9.16, and others later on.

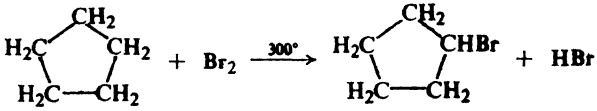
9.5 Reactions

With certain very important and interesting exceptions, alicyclic hydrocarbons undergo the same reactions as their open-chain analogs.

Cycloalkanes undergo chiefly free-radical substitution (compare Sec. 3.19). For example:

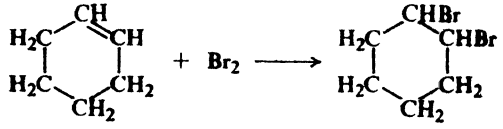


Cyclopropane Chlorocyclopropane

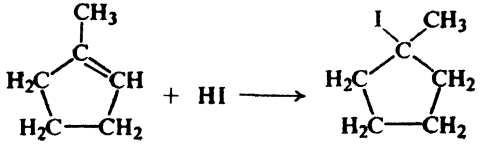


Cyclopentane Bromocyclopentane

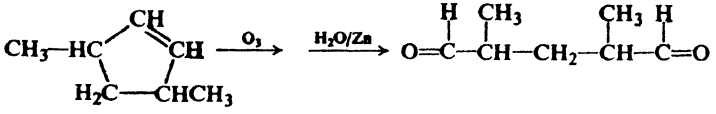
Cycloalkenes undergo chiefly addition reactions, both electrophilic and free radical (compare Sec. 6.2); like other alkenes, they can also undergo cleavage and allylic substitution. For example:



Cyclohexene 1,2-Dibromocyclohexane



1-Methylcyclopentene 1-Iodo-1-methylcyclopentane



3,5-Dimethylcyclopentene A dialdehyde

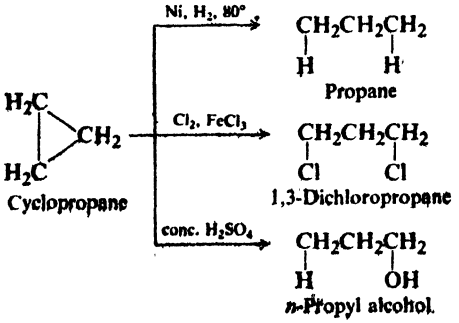
The two smallest cycloalkanes, cyclopropane and cyclobutane, show certain chemical properties that are entirely different from those of the other members of their family. Some of these exceptional properties fit into a pattern and, as we shall see, can be understood in a general way.

The chemistry of bicyclic compounds is even more remarkable, and is right now one of the most intensively studied areas of organic chemistry (Sec. 28.13).

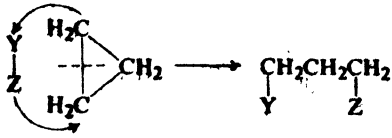
9.6 Reactions of small-ring compounds. Cyclopropane and cyclobutane

Besides the free-radical substitution reactions that are characteristic of cycloalkanes and of alkanes in general, cyclopropane and cyclobutane undergo certain

addition reactions. These addition reactions destroy the cyclopropane and cyclobutane ring systems, and yield open-chain products. For example:



In each of these reactions a carbon–carbon bond is broken, and the two atoms of the reagent appear at the ends of the propane chain:



In general, cyclopropane undergoes addition less readily than propylene: chlorination, for example, requires a Lewis acid catalyst to polarize the chlorine molecule (compare Sec. 11.11). Yet the reaction with sulfuric acid and other aqueous protic acids takes place considerably faster for cyclopropane than for propylene. (Odder still, treatment with bromine and $FeBr_3$ yields a grand mixture of bromopropanes.)

Cyclobutane does not undergo most of the ring-opening reactions of cyclopropane; it is hydrogenated, but only under more vigorous conditions than those required for cyclopropane. Thus cyclobutane undergoes addition less readily than cyclopropane and, with some exceptions, cyclopropane less readily than an alkene. The remarkable thing is that these cycloalkanes undergo addition at all.

9.7 Baeyer strain theory

In 1885 Adolf von Baeyer (of the University of Munich) proposed a theory to account for certain aspects of the chemistry of cyclic compounds. The part of his theory dealing with the ring-opening tendencies of cyclopropane and cyclobutane is generally accepted today, although it is dressed in more modern language. Other parts of his theory have been shown to be based on false assumptions, and have been discarded.

Baeyer's argument was essentially the following. In general, when carbon is bonded to four other atoms, the angle between any pair of bonds is the tetrahedral angle 109.5°. But the ring of cyclopropane is a triangle with three angles of 60°, and the ring of cyclobutane is a square with four angles of 90°. In cyclopropane or cyclobutane, therefore, one pair of bonds to each carbon cannot assume the tetrahedral angle, but must be compressed to 60° or 90° to fit the geometry of the ring.

These deviations of bond angles from the "normal" tetrahedral value cause the molecules to be *strained*, and hence to be unstable compared with molecules in which the bond angles are tetrahedral. Cyclopropane and cyclobutane undergo ring-opening reactions since these relieve the strain and yield the more stable open-chain compounds. Because the deviation of the bond angles in cyclopropane ($109.5° - 60° = 49.5°$) is greater than in cyclobutane ($109.5° - 90° = 19.5°$), cyclopropane is more highly strained, more unstable, and more prone to undergo ring-opening reactions than is cyclobutane.

The angles of a regular pentagon (108°) are very close to the tetrahedral angle (109.5°), and hence cyclopentane should be virtually free of angle strain. The angles of a regular hexagon (120°) are somewhat larger than the tetrahedral angle, and hence, Baeyer proposed (incorrectly), there should be a certain amount of strain in cyclohexane. Further, he suggested (incorrectly) that as one proceed d to cycloheptane, cyclooctane, etc., the deviation of the bond angles from 109.5° would become progressively larger, and the molecules would become progressively more strained.

Thus Baeyer considered that rings smaller or larger than cyclopentane or cyclohexane were unstable; it was because of this instability that the three- and four-membered rings underwent ring-opening reactions; it was because of this instability that great difficulty had been encountered in the synthesis of the larger rings. How does Baeyer's strain theory agree with the facts?

9.8 Heats of combustion and relative stabilities of the cycloalkanes

We recall (Sec. 2.6) that the heat of combustion is the quantity of heat evolved when one mole of a compound is burned to carbon dioxide and water. Like heats of hydrogenation (Secs. 6.4 and 8.16), heats of combustion can often furnish valuable information about the relative stabilities of organic compounds. Let us see if the heats of combustion of the various cycloalkanes support Baeyer's proposal that rings smaller or larger than cyclopentane and cyclohexane are unstable.

Examination of the data for a great many compounds has shown that the heat of combustion of an aliphatic hydrocarbon agrees rather closely with that calculated by assuming a certain characteristic contribution from each structural unit. For open-chain alkanes each methylene group, $—CH_2—$, contributes very close to 157.4 kcal/mole to the heat of combustion. Table 9.2 lists the heats of combustion that have been measured for some of the cycloalkanes.

Table 9.2 HEATS OF COMBUSTION OF CYCLOALKANES

Ring size	Heat of combustion per CH_2, kcal/mole	Ring size	Heat of combustion per CH_2, kcal/mole
3	166.6	10	158.6
4	164.0	11	158.4
5	158.7	12	157.6
6	157.4	13	157.8
7	158.3	14	157.4
8	158.6	15	157.5
9	158.8	17	157.2
	Open-chain 157.4		

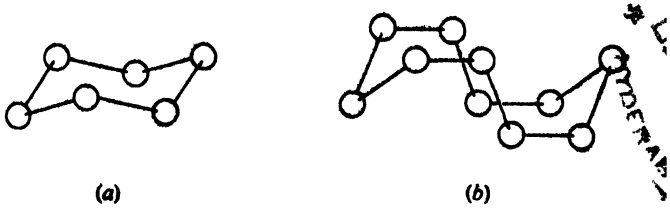
We notice that for cyclopropane the heat of combustion per $-CH_2-$ group is 9 kcal higher than the open-chain value of 157.4; for cyclobutane it is 7 kcal higher than the open-chain value. Whatever the compound in which it occurs, a $-CH_2-$ group yields the same products on combustion: carbon dioxide and water.

$$-CH_2- + \tfrac{3}{2}O_2 \longrightarrow CO_2 + H_2O + \text{heat}$$

If cyclopropane and cyclobutane evolve more energy per $-CH_2-$ group than an open-chain compound, it can mean only that they *contain* more energy per $-CH_2-$ group. In agreement with the Baeyer angle-strain theory, then, cyclopropane and cyclobutane are less stable than open-chain compounds; it is reasonable to suppose that their tendency to undergo ring-opening reactions is related to this instability.

According to Baeyer, rings larger than cyclopentane and cyclohexane also should be unstable, and hence also should have high heats of combustion; furthermore relative instability—and, with it, heat of combustion—should increase steadily with ring size. However, we see from Table 9.2 that almost exactly the opposite is true. For none of the rings larger than four carbons does the heat of combustion per $-CH_2-$ deviate much from the open-chain value of 157.4. Indeed, one of the biggest deviations is for Baeyer's "most stable" compound, cyclopentane: 1.3 kcal per $-CH_2-$, or 6.5 kcal for the molecule. Rings containing seven to eleven carbons have about the same value as cyclopentane, and when we reach rings of twelve carbons or more, heats of combustion are indistinguishable from the open-chain values. Contrary to Baeyer's theory, then, none of these rings is appreciably less stable than open-chain compounds, and the larger ones are completely free of strain. Furthermore, once they have been synthesized, these large-ring cycloalkanes show little tendency to undergo the ring-opening reactions characteristic of cyclopropane and cyclobutane.

What is wrong with Baeyer's theory that it does not apply to rings larger than four members? Simply this: the angles that Baeyer used for each ring were based on the assumption that the rings were *flat*. For example, the angles of a regular (flat) hexagon are 120°, the angles for a regular decagon are 144°. But the cyclohexane ring is not a regular hexagon, and the cyclodecane ring is not a regular decagon. These rings are not flat, but are puckered (see Fig. 9.1) so that each bond angle of carbon can be 109.5°.



(*a*) (*b*)

Figure 9.1. Puckered rings. (*a*) Cyclohexane. (*b*) Cyclodecane.

A three-membered ring must be planar, since three points (the three carbon nuclei) define a plane. A four-membered ring need not be planar, but puckering

here would increase (angle) strain. A five-membered ring need not be planar, but in this case a planar arrangement would permit the bond angles to have nearly the tetrahedral value. All rings larger than this are puckered. (Actually, as we shall see, cyclobutane and cyclopentane are puckered, too, but this is *in spite of* increased angle strain.)

If large rings are stable, why are they difficult to synthesize? Here we encounter Baeyer's second false assumption. The fact that a compound is difficult to synthesize does not necessarily mean that it is unstable. The closing of a ring requires that two ends of a chain be brought close enough to each other for a bond to form. The larger the ring one wishes to synthesize, the longer must be the chain from which it is made, and the less is the likelihood of the two ends of the chain approaching each other. Under these conditions the end of one chain is more likely to encounter the end of a *different* chain, and thus yield an entirely different product (see Fig. 9.2).

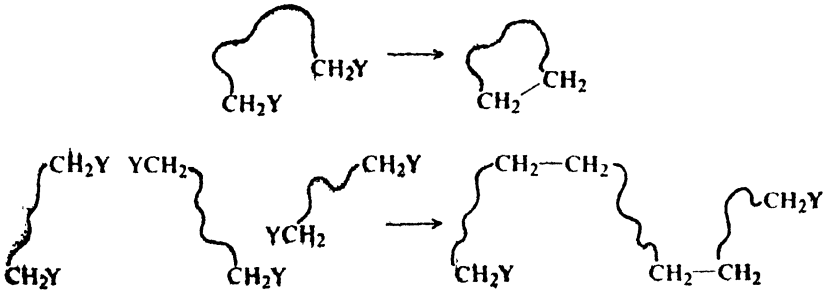


Figure 9.2. Ring closure (upper) *vs.* chain lengthening (lower).

The methods that are used successfully to make large rings take this fact into consideration. Reactions are carried out in highly dilute solutions where collisions between two different chains are unlikely; under these conditions the ring-closing reaction, although slow, is the principal one. Five- and six-membered rings are the kind most commonly encountered in organic chemistry because they are large enough to be free of angle strain, and small enough that ring closure is likely.

9.9 Orbital picture of angle strain

What is the meaning of Baeyer's angle strain in terms of the modern picture of the covalent bond?

We have seen (Sec. 1.8) that, for a bond to form, two atoms must be located so that an orbital of one overlaps an orbital of the other. For a given pair of atoms, the greater the overlap of atomic orbitals, the stronger the bond. When carbon is bonded to four other atoms, its bonding orbitals (sp^3 orbitals) are directed to the corners of a tetrahedron; the angle between any pair of orbitals is thus 109.5°. Formation of a bond with another carbon atom involves overlap of one of these sp^3 orbitals with a similar sp^3 orbital of the other carbon atom.

This overlap is most effective, and hence the bond is strongest, when the two atoms are located so that an sp^3 orbital of each atom points toward the other atom. This means that when carbon is bonded to two other carbon atoms the C—C—C bond angle should be 109.5°.

In cyclopropane, however, the C—C—C bond angle cannot be 109.5°, but instead must be 60°. As a result, the carbon atoms cannot be located to permit

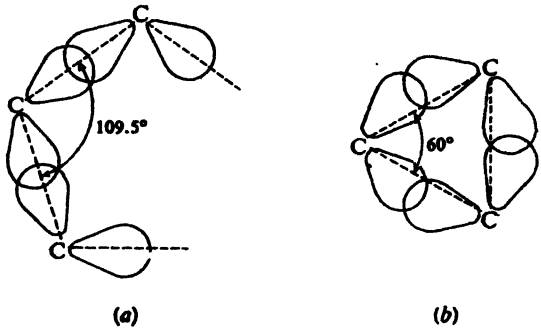


Figure 9.3. Angle strain. (*a*) Maximum overlap permitted for open-chain or large-ring compounds. (*b*) Poor overlap for cyclopropane ring. Bent bonds have much *p* character.

their sp^3 orbitals to point toward each other (see Fig. 9.3). There is less overlap and the bond is weaker than the usual carbon–carbon bond.

The decrease in stability of a cyclic compound attributed to *angle strain* is due to poor overlap of atomic orbitals in the formation of the carbon–carbon bonds.

On the basis of quantum mechanical calculations, C. A. Coulson and W. A. Moffitt (of Oxford University) proposed *bent bonds* between carbon atoms of cyclopropane rings; this idea is supported by electron density maps based on X-ray studies. Carbon uses sp^2 orbitals for carbon–hydrogen bonds (which are short and strong), and orbitals with much *p* character (sp^4 to sp^5) for the carbon–carbon bonds. The high *p* character of these carbon–carbon bonds, and their location—largely outside the ring—seems to underlie much of the unusual chemistry of these rings. The carbon–carbon bond orbitals can overlap orbitals on adjacent atoms; the resulting delocalization is responsible for the effects of cyclopropyl as a substituent. The carbon–carbon bond orbitals provide a site for the attack by acids that is the first step of ring-opening. (Indeed, "edge-protonated" cyclopropanes seem to be key intermediates in many reactions that do not, on the surface, seem to involve cyclopropane rings.)

Ring-opening is *due to* the weakness of the carbon–carbon bonds, but the *way in which it happens* reflects the unusual nature of the bonds; all this stems ultimately from the geometry of the rings and angle strain.

9.10 Factors affecting stability of conformations

To go more deeply into the chemistry of cyclic compounds, we must use conformational analysis (Sec. 4.20). As preparation for that, let us review the factors that determine the stability of a conformation.

Any atom tends to have bond angles that match those of its bonding orbitals: tetrahedral (109.5°) for sp^3-hybridized carbon, for example. Any deviations from the "normal" bond angles are accompanied by **angle strain** (Secs. 9.8–9.9).

Any pair of tetrahedral carbons attached to each other tend to have their bonds staggered. That is to say, any ethane-like portion of a molecule tends, like ethane, to take up a staggered conformation. Any deviations from the staggered arrangement are accompanied by **torsional strain** (Sec. 3.3).

Any two atoms (or groups) that are not bonded to each other can interact in several ways, depending on their size and polarity, and how closely they are brought together. These non-bonded interactions can be either repulsive or attractive, and the result can be either destabilization or stabilization of the conformation.

Non-bonded atoms (or groups) that just touch each other—that is, that are about as far apart as the sum of their van der Waals radii—attract each other. If brought any closer together, they repel each other: such crowding together is accompanied by **van der Waals strain (steric strain)** (Secs. 1.19, 3.5).

Non-bonded atoms (or groups) tend to take positions that result in the most favorable **dipole–dipole interactions**: that is, positions that minimize dipole–dipole repulsions or maximize dipole–dipole attractions. (A particularly powerful attraction results from the special kind of dipole–dipole interaction called the **hydrogen bond** (Sec. 1.19).

All these factors, working together or opposing each other, determine the net stability of a conformation. To figure out what the most stable conformation of a particular molecule should be, one ideally should consider all possible combinations of bond angles, angles of rotation, and even bond lengths, and see which combination results in the lowest energy content. A start in this direction—feasible only by use of computers—has been made, most notably by Professor James F. Hendrickson (of Brandeis University).

Both calculations and experimental measurements show that the final result is a compromise, and that few molecules have the idealized conformations that we assign them and, for convenience, usually work with. For example, probably no tetravalent carbon compound—except one with four identical substituents—has *exactly* tetrahedral bond angles: a molecule accepts a certain amount of angle strain to relieve van der Waals strain or dipole–dipole interaction. In the *gauche* conformer of *n*-butane (Sec. 3.5), the dihedral angle between the methyl groups is not 60°, but almost certainly larger: the molecule accepts some torsional strain to ease van der Waals strain between the methyl groups.

9.11 Conformations of cycloalkanes

Let us look more closely at the matter of puckered rings, starting with cyclohexane, the most important of the cycloalkanes. Let us make a model of the molecule, and examine the conformations that are free of angle strain.

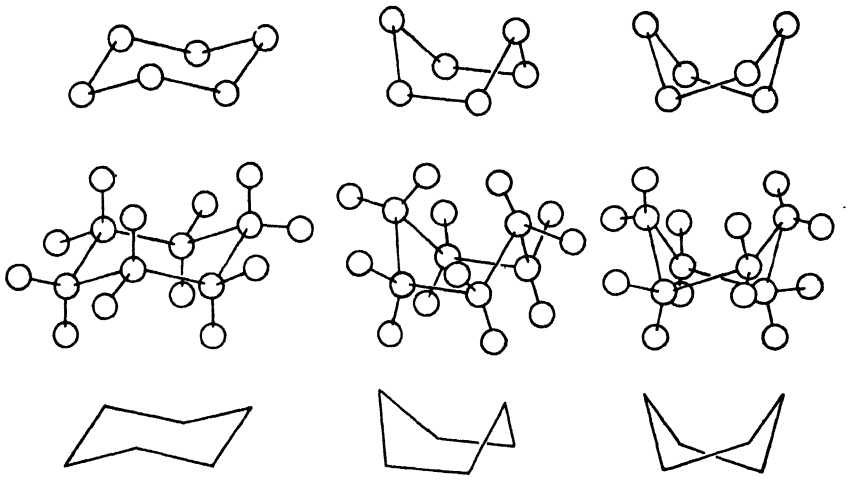
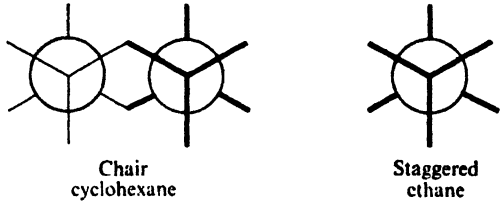


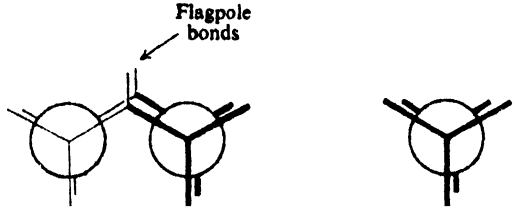
Figure 9.4. Conformations of cyclohexane that are free of angle strain.

First, there is the **chair form** (Fig. 9.4). If we sight along each of the carbon–carbon bonds in turn, we see in every case perfectly staggered bonds:



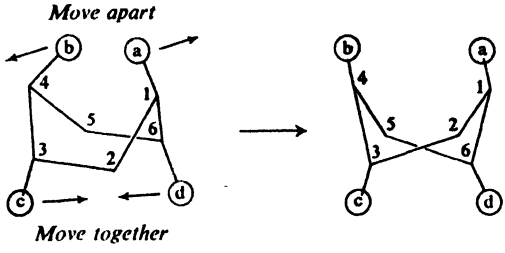
The conformation is thus not only free of angle strain but free of torsional strain as well. It lies at an energy minimum, and is therefore a conformational isomer. *The chair form is the most stable conformation of cyclohexane, and, indeed, of nearly every derivative of cyclohexane.*

Next, let us flip the "left" end of the molecule up (Fig. 9.4) to make the *boat conformation*. (Like all the transformations we shall carry out in this section, this involves only rotations about single bonds; what we are making are indeed conformations.) This is not a very happy arrangement. Sighting along either of two carbon–carbon bonds, we see sets of exactly eclipsed bonds,



and hence we expect considerable torsional strain: as much as in *two* ethane molecules. In addition, there is van der Waals strain due to crowding between the "flagpole" hydrogens, which lie only 1.83 A apart, considerably closer than the sum of their van der Waals radii (2.5 A). The boat conformation is a good deal less stable (6.9 kcal/mole, it has been calculated) than the chair conformation. It is believed to lie, not at an energy minimum, but at an energy maximum; it is thus not a conformer, but a transition state between two conformers.

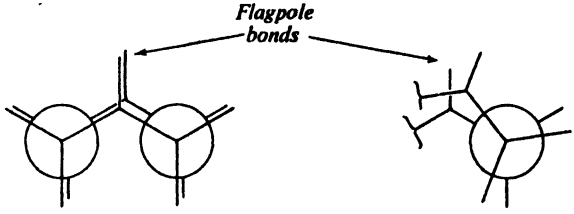
Now, what are these two conformers that lie—energetically speaking—on either side of the boat conformation? To see what they are, let us hold a model of the boat conformation with the flagpole hydrogens (H_a and H_b) pointing up, and look down through the ring. We grasp C-2 and C-3 in the right hand and C-5



Boat Twist-boat

Cyclohexane

and C-6 in the left hand, and *twist* the molecule so that, say, C-3 and C-6 go *down*, and C-2 and C-5 come *up*. As we do this, H_a and H_b move diagonally apart, and we see (below the ring) a pair of hydrogens, H_c and H_d (on C-3 and C-6, respectively), begin to approach each other. (If this motion is continued, we make a new boat conformation with H_c and H_d becoming the flagpole hydrogens.) When the H_a—H_b distance is equal to the H_c—H_d distance, we stop and examine the molecule. We have minimized the flagpole–flagpole interactions, and at the same time have partly relieved the torsional strain at the C_2—C_3 and C_5—C_6 bonds.



Boat cyclohexane Twist-boat cyclohexane

This new configuration is the **twist-boat form.** It is a conformer, lying at an energy minimum 5.5 kcal above the chair conformation. The twist-boat conformer is separated from another, enantiomeric twist-boat conformer by an energy barrier 1.6 kcal high, at the top of which is the boat conformation.

Between the chair form and the twist-boat form lies the highest barrier of all: a transition state conformation (the *half-chair*) which, with angle strain and torsional strain, lies about 11 kcal above the chair form.

The overall relationships are summarized in Fig. 9.5. Equilibrium exists between the chair and twist-boat forms, with the more stable chair form being favored—10,000 to 1 at room temperature.

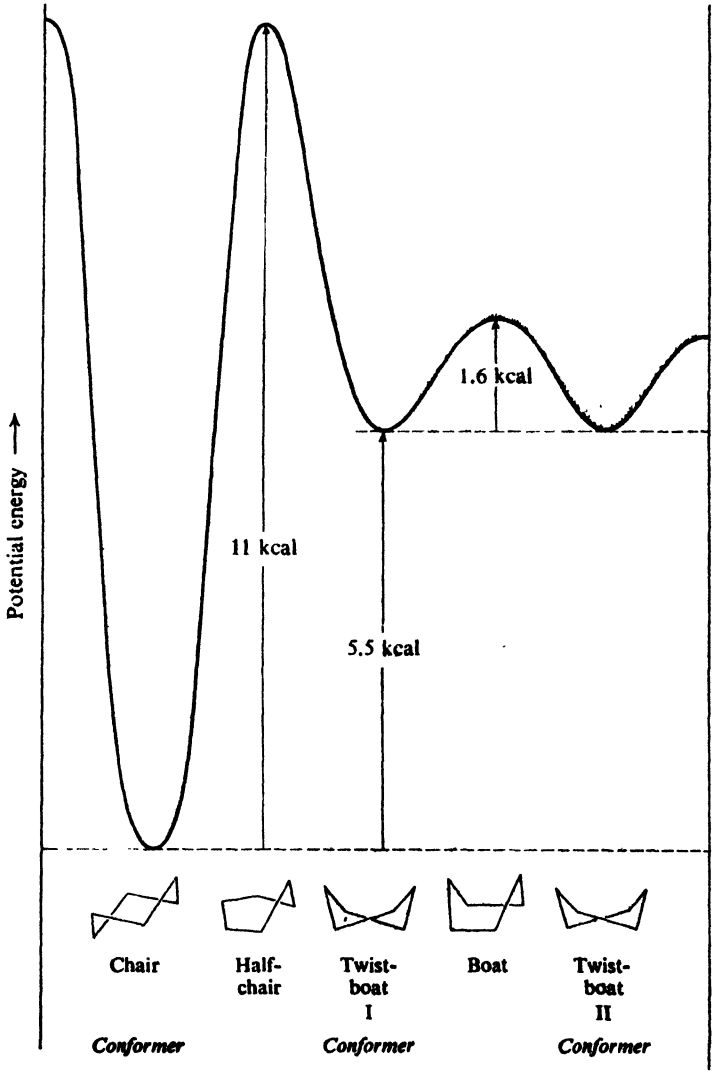


Figure 9.5. Potential energy relationships among conformations of cyclohexane.

If chair cyclohexane is, conformationally speaking, the perfect specimen of a cycloalkane, planar cyclopentane (Fig. 9.6) must certainly be the poorest: there is

exact bond eclipsing between every pair of carbons. To (partially) relieve this torsional strain, cyclopentane takes on a slightly puckered conformation, even at the cost of a little angle strain. (See also Problem 10, p. 316.)

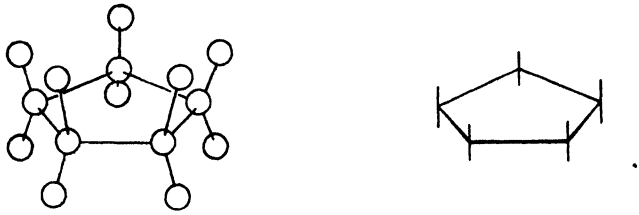


Figure 9.6. Planar cyclopentane: much torsional strain. Molecule actually puckered.

Evidence of many kinds strongly indicates that cyclobutane is not planar, but rapidly changes between equivalent, slightly folded conformations (Fig. 9.7). Here, too, torsional strain is partially relieved at the cost of a little angle strain.

Figure 9.7. Cyclobutane: rapid transformation between equivalent nonplanar "folded" conformations.

Rings containing seven to twelve carbon atoms are also subject to torsional strain, and hence these compounds, too, are less stable than cyclohexane; scale models also reveal serious crowding of hydrogens inside these rings. Only quite large ring systems seem to be as stable as cyclohexane.

9.12 Equatorial and axial bonds in cyclohexane

Let us return to the model of the chair conformation of cyclohexane (see Fig. 9.8). Although the cyclohexane ring is not flat, we can consider that the carbon atoms lie roughly in a plane. If we look at the molecule in this way, we see that the hydrogen atoms occupy two kinds of position: six hydrogens lie in the plane,

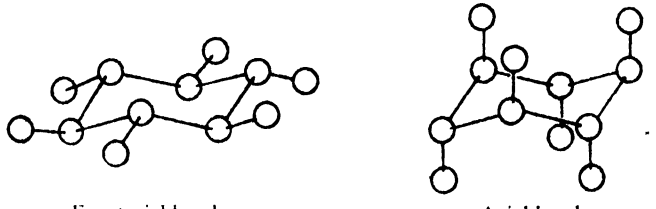


Figure 9.8. Equatorial and axial bonds in cyclohexane.

while six hydrogens lie above or below the plane. The bonds holding the hydrogens that are in the plane of the ring lie in a belt about the "equator" of the ring, and are called **equatorial bonds**. The bonds holding the hydrogen atoms that are above and below the plane are pointed along an axis perpendicular to the plane and are called **axial bonds**. In the chair conformation each carbon atom has one equatorial bond and one axial bond.

Cyclohexane itself, in which only hydrogens are attached to the carbon atoms, is not only free of angle strain and torsional strain, but free of van der Waals strain as well. Hydrogens on adjacent carbons are the same distance apart (2.3 A) as in (staggered) ethane and, if anything, feel mild van der Waals attraction for each other. We notice that the three axial hydrogens on the same side of the molecule are thrown rather closely together, despite the fact that they are attached to alternate carbon atoms; as it happens, however, they are the same favorable distance apart (2.3 A) as the other hydrogens are.

If, now, a hydrogen is replaced by a larger atom or group, crowding occurs. The most severe crowding is among atoms held by the three axial bonds on the same side of the molecule; the resulting interaction is called **1,3-diaxial interaction**. Except for hydrogen, *a given atom or group has more room in an equatorial position than in an axial position.*

As a simple example of the importance of 1,3-diaxial interactions, let us consider methylcyclohexane. In estimating relative stabilities of various conformations of this compound, we must focus our attention on methyl, since it is the largest substituent on the ring and hence the one most subject to crowding. There are two

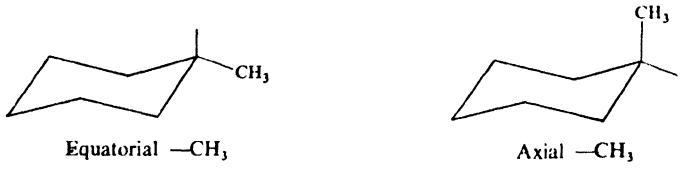


Figure 9.9. Chair conformations of methylcyclohexane.

possible chair conformations (see Fig. 9.9), one with $-CH_3$ in an equatorial position, the other with $-CH_3$ in an axial position. As shown in Fig. 9.10, the two axial hydrogens (on C-3 and C-5) approach the axial $-CH_3$ (on C-1) more closely than any hydrogens approach the equatorial $-CH_3$. We would expect

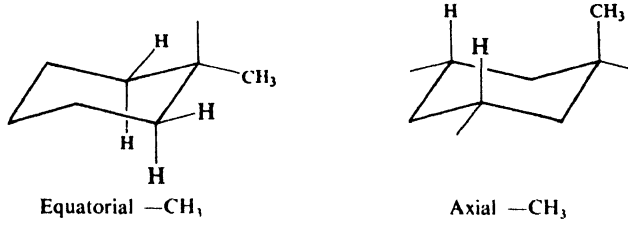


Figure 9.10. 1,3-Diaxial interaction in methylcyclohexane. Axial $-CH_3$ more crowded than equatorial $-CH_3$.

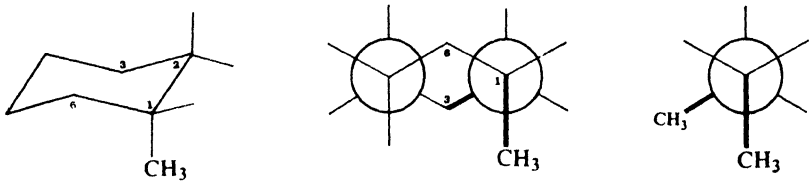
the equatorial conformation to be the more stable, and it is, by about 1.8 kcal. Most molecules (about 95% at room temperature) exist in the conformation with methyl in the uncrowded equatorial position.

In an equatorial position, we see, $-CH_3$ points *away from* its nearest neighbors: the two hydrogens—one axial, and one equatorial—on the adjacent carbons. This is not true of $-CH_3$ in an axial position, since it is held by a bond that is *parallel to* the bonds holding its nearest neighbors: the two axial hydrogens.

Conformational analysis can account not only for the fact that one conformation is more stable than another, but often—with a fair degree of accuracy—for just *how much* more stable it is. We have attributed the 1.8-kcal energy difference between the two conformations of methylcyclohexane to 1,3-diaxial interactions between a methyl group and *two* hydrogens. If, on that basis, we assign a value of 0.9 kcal/mole to each 1,3-diaxial methyl–hydrogen interaction, we shall find that we can account amazingly well for the energy differences between conformations of a variety of cyclohexanes containing more than one methyl group.

We notice that 0.9 kcal is nearly the same value that we earlier (Sec. 3.5) assigned to a *gauche* interaction in *n*-butane; examination of models shows that this is not just accidental.

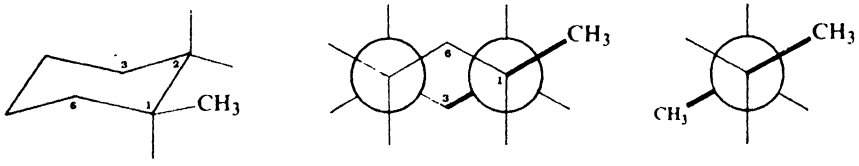
Let us make a model of the conformation of methylcyclohexane with axial methyl. If we hold it so that we can sight along the C_1—C_2 bond, we see something like this, represented by a Newman projection:



Axial $-CH_3$ *Gauche* *n*-Butane

The methyl group and C-3 of the ring have the same relative locations as the two methyl groups in the *gauche* conformation of *n*-butane (Sec. 3.5). If we now sight along the C_1—C_6 bond, we see a similar arrangement but with C-5 taking the place of C-3.

Next, let us make a model of the conformation with equatorial methyl. This time, if we sight along the C_1—C_2 bond, we see this:



Equatorial CH_3 *Anti* *n*-Butane

Here, methyl and C-3 of the ring have the same relative locations as the two methyl groups in the *anti* conformation of *n*-butane. And if we sight along the C_1—C_6 bond, we see methyl and C-5 in the *anti* relationship.

Thus, for each 1,3-diaxial methyl-hydrogen interaction there is a "butane-*gauche*" interaction between the methyl group and a carbon atom of the ring. Of the two approaches, however, looking for 1,3-diaxial interactions is much the easier and has the advantage, when we study substituents other than methyl, of focusing our attention on the sizes of the groups being crowded together.

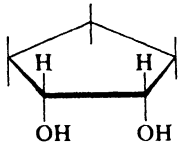
In general, then, it has been found that (a) chair conformations are more stable than twist conformations, and (b) the most stable chair conformations are those in which the largest groups are in equatorial positions. There are exceptions to both these generalizations (which we shall encounter later in problems), but the exceptions are understandable ones.

Problem 9.3 For other alkylcyclohexanes the difference in energy between equatorial and axial conformations has been found to be: ethyl, 1.9 kcal/mole; isopropyl, 2.1 kcal/mole; and *tert*-butyl, more than 5 kcal/mole. Using models, can you account for the big increase at *tert*-butyl? (*Hint:* Don't forget freedom of rotation about *all* the single bonds.)

9.13 Stereoisomerism of cyclic compounds: *cis*- and *trans*-isomers

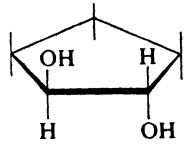
Let us turn for the moment from conformational analysis, and look at configurational isomerism in cyclic compounds.

We shall begin with the glycol of cyclopentene, 1,2-cyclopentanediol. Using models, we find that we can arrange the atoms of this molecule as in I, in which both hydroxyls lie below (or above) the plane of the ring, and as in II, in which one hydroxyl lies above and the other lies below the plane of the ring.



I

cis-1,2-Cyclopentanediol



II

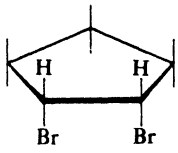
trans-1,2-Cyclopentanediol

I and II cannot be superimposed, and hence are isomers. They differ only in the way their atoms are oriented in space, and hence are stereoisomers. No amount of rotation about bonds can interconvert I and II, and hence they are not conformational isomers. They are configurational isomers; they are interconverted only by breaking of bonds, and hence are isolable. They are not mirror images, and hence are diastereomers; they should, therefore, have different physical properties, as the two glycols actually have. Configuration I is designated the *cis*-configuration, and II is designated the *trans*-configuration. (Compare *cis*- and *trans*-alkenes, Sec. 5.6.)

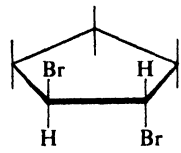
Problem 9.4 You have two bottles labeled "1,2-Cyclopentanediol," one containing a compound of m.p. 30°, the other a compound of m.p. 55°; both compounds are optically inactive. How could you decide, beyond any doubt, which bottle should be labeled "*cis*" and which "*trans*"?

Problem 9.5 (a) Starting from cyclopentanol, outline a synthesis of stereochemically pure *cis*-1,2-cyclopentanediol. (b) Of stereochemically pure *trans*-1,2-cyclopentanediol.

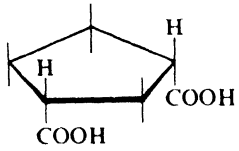
Stereoisomerism of this same sort should be possible for compounds other than glycols, and for rings other than cyclopentane. Some examples of isomers that have been isolated are:



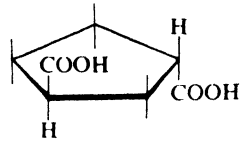
cis-1,2-Dibromocyclopentane



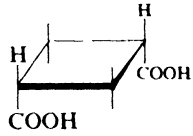
trans-1,2-Dibromocyclopentane



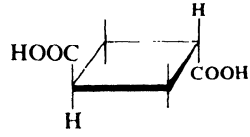
cis-1,3-Cyclopentanedicarboxylic acid



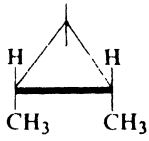
trans-1,3-Cyclopentanedicarboxylic acid



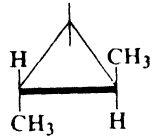
cis-1,3-Cyclobutanedicarboxylic acid



trans-1,3-Cyclobutanedicarboxylic acid

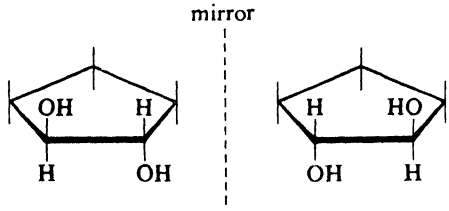


cis-1,2-Dimethylcyclopropane



trans-1,2-Dimethylcyclopropane

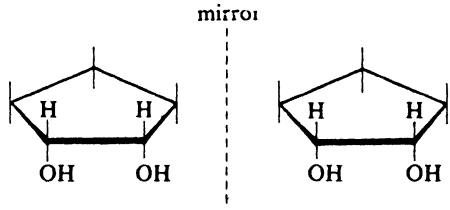
If we examine models of *cis*- and *trans*-1,2-cyclopentanediol more closely, we find that each compound contains two chiral centers. We know (Sec. 4.18) that compounds containing more than one chiral center are often –but not always —chiral. Are these glycols chiral? As always, to test for possible chirality, we construct a model of the molecule and a model of its mirror image, and see if the two are superimposable. When we do this for the *trans*-glycol, we find that the models



Not superimposable
Enantiomers: resolvable
trans-1,2-Cyclopentanediol

are not superimposable. The *trans* glycol is chiral, and the two models we have constructed therefore correspond to enantiomers. Next, we find that the models are not interconvertible by rotation about single bonds. They therefore represent, not conformational isomers, but configurational isomers; they should be capable of isolation—*resolution*—and, when isolated, each should be optically active.

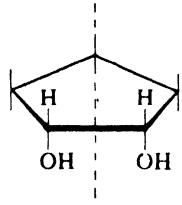
Next let us look at *cis*-1,2-cyclopentanediol. This, too, contains two chiral centers; is it also chiral? This time we find that a model of the molecule and a model of its mirror image *are* superimposable. In spite of its chiral centers, *cis*-1,2-



Superimposable
A meso compound
cis-1,2-Cyclopentanediol

cyclopentanediol is not chiral; it cannot exist in two enantiomeric forms, and cannot be optically active. It is a *meso* compound.

We might have recognized *cis*-1,2-cyclopentanediol as a *meso* structure on sight from the fact that one half of the molecule is the mirror image of the other half (Sec. 4.18):



A meso compound
cis-1,2-Cyclopentanediol

Thus, of the two 1,2-cyclopentanediols obtainable from cyclopentene, only one is separable into enantiomers, that is, is *resolvable*; this must necessarily be the *trans*-glycol. The other glycol is a single, inactive, nonresolvable compound, and it must have the *cis* configuration.

What is the relationship between the *meso cis*-glycol and either of the enantiomeric *trans*-glycols? They are *diastereomers*, since they are stereoisomers that are not enantiomers.

Problem 9.6 Five of the eight structures shown at the top of p. 302 are achiral. Which are these?

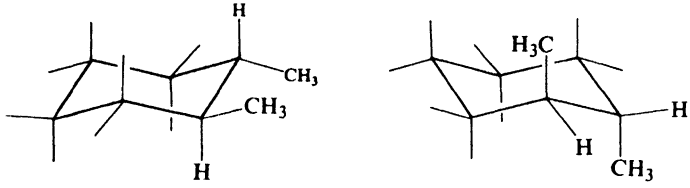
9.14 Stereoisomerism of cyclic compounds. Conformational analysis

So far, we have described the relative positions of groups in *cis*- and *trans*-isomers in terms of flat rings: both groups are below (or above) the plane of the

ring, one group is above and the other is below the plane of the ring. In view of what we have said about puckering, however, we realize that this is a highly simplified picture even for four- and five-membered rings, and for six-membered rings is quite inaccurate.

Let us apply the methods of conformational analysis to the stereochemistry of cyclohexane derivatives; and, since we are already somewhat familiar with interactions of the methyl group let us use the dimethylcyclohexanes as our examples.

If we consider only the more stable, chair conformations, we find that a particular molecule of *trans*-1,2-dimethylcyclohexane, to take our first example, can exist in two conformations (see Fig. 9.11). In one, both $-CH_3$ groups are in

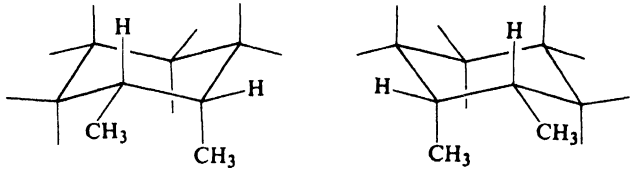


Diequatorial Diaxial

Figure 9.11. Chair conformations of *trans*-1,2-dimethylcyclohexane.

equatorial positions, and in the other, both $-CH_3$ groups are in axial positions. Thus, we see, the two $-CH_3$ groups of the *trans*-isomer are not necessarily on opposite sides of the ring; in fact, because of lesser crowding between $-CH_3$ groups and axial hydrogens of the ring (less 1,3-diaxial interaction), the more stable conformation is the diequatorial one.

A molecule of *cis*-1,2-dimethylcyclohexane can also exist in two conformations (see Fig. 9.12). In this case, the two are of equal stability (they are mirror images) since in each there is one equatorial and one axial $-CH_3$ group.



Equatorial-axial Axial-equatorial

Figure 9.12. *Chair conformations of cis-1,2-dimethylcyclohexane.*

In the most stable conformation of *trans*-1,2-dimethylcyclohexane, both $-CH_3$ groups occupy uncrowded equatorial positions. In either conformation of the *cis*-1,2-dimethylcyclohexane, only one $-CH_3$ group can occupy an equatorial position. It is not surprising to find that *trans*-1,2-dimethylcyclohexane is more stable than *cis*-1,2-dimethylcyclohexane.

It is interesting to note that in the most stable conformation (diequatorial) of the *trans*-isomer, the $-CH_3$ groups are exactly the same distance apart as they are in either conformation of the *cis*-isomer. Clearly, it is not repulsion between

the $-CH_3$ groups—as one might incorrectly infer from planar representations—that causes the difference in stability between the *trans*- and *cis*-isomers: the cause is 1,3-diaxial interactions (Sec. 9.12).

Now, just *how much* more stable is the *trans*-isomer? In the *cis*-1,2-dimethylcyclohexane there is one axial methyl group, which means *two* 1,3-diaxial methyl–hydrogen interactions: one with each of two hydrogen atoms. (Or, what is equivalent (Sec. 9.12), there are two butane-*gauche* interactions between the methyl groups and carbon atoms of the ring.) In addition, there is one butane-*gauche* interaction between the two methyl groups. On the basis of 0.9 kcal for each 1,3-diaxial methyl–hydrogen interaction or butane-*gauche* interaction, we calculate a total of 2.7 kcal of van der Waals strain for the *cis*-1,2-dimethylcyclohexane. In the (diequatorial) *trans*-isomer there are no 1,3-diaxial methyl–hydrogen interactions, but there is one butane-*gauche* interaction between the methyl groups; this confers 0.9 kcal of van der Waals strain on the molecule. We subtract 0.9 kcal from 2.7 kcal and conclude that the *trans*-isomer should be more stable than the *cis*-isomer by 1.8 kcal/mole, in excellent agreement with the measured value of 1.87 kcal.

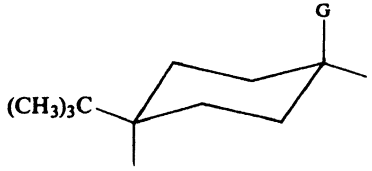
Problem 9.7 Compare stabilities of the possible chair conformations of: (a) *cis*-1,2-dimethylcyclohexane; (b) *trans*-1,2-dimethylcyclohexane; (c) *cis*-1,3-dimethylcyclohexane; (d) *trans*-1,3-dimethylcyclohexane; (e) *cis*-1,4-dimethylcyclohexane; (f) *trans*-1,4-dimethylcyclohexane. (g) On the basis of 0.9 kcal/mole per 1,3-diaxial methyl–hydrogen interaction, predict (where you can) the potential energy difference between the members of each pair of conformations.

Problem 9.8 On theoretical grounds, K. S. Pitzer (then at the University of California) calculated that the energy difference between the conformations of *cis*-1,3-dimethylcyclohexane should be about 5.4 kcal, much larger than that between the chair conformations of *trans*-1,2-dimethylcyclohexane or of *trans*-1,4-dimethylcyclohexane. (a) What special factor must Pitzer have recognized in the *cis*-1,3-isomer? (b) Using the 0.9 kcal value where it applies, what value must you assign to the factor you invoked in (a), if you are to arrive at the energy difference of 5.4 kcal for the *cis*-1,3-conformations? (c) The potential energy difference between *cis*- and *trans*-1,1,3,5-tetramethylcyclohexane was then measured by Norman L. Allinger (at Wayne State University) as 3.7 kcal/mole. This measurement was carried out because of its direct bearing on the matter of *cis*-1,3-dimethylcyclohexane. What is the connection between this measurement and parts (a) and (b)? Does Allinger's measurement support Pitzer's calculation?

Problem 9.9 Predict the relative stabilities of the *cis*- and *trans*-isomers of: (a) 1,3-dimethylcyclohexane; (b) 1,4-dimethylcyclohexane. (c) On the basis of 0.9 kcal/mole per 1,3-diaxial methyl–hydrogen interaction or butane-*gauche* interaction, and assuming that each stereoisomer exists exclusively in its more stable conformation, predict the potential energy difference between members of each pair of stereoisomers.

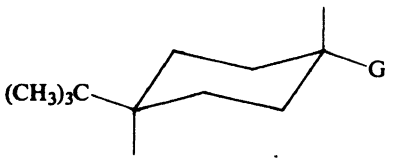
Conformational analysis of cyclohexane derivatives containing several *different* substituents follows along the same lines as that of the dimethylcyclohexanes. We need to keep in mind that, of two groups, the larger one will tend to call the tune. Because of its very large 1,3-diaxial interactions (Problem 9.3, p. 301), the bulky *tert*-butyl group is particularly prone to occupy an equatorial position. If—as is usually the case—other substituents are considerably smaller than *tert*-butyl, the molecule is virtually locked in a single conformation: the one with an

equatorial *tert*-butyl group. Consider cyclohexanes I and II containing a 4-*tert*-butyl group *cis* or *trans* to another substituent —G. In each diastereomer, *tert*-butyl holds —G exclusively in the axial or in the equatorial position, yet, because



I

A *cis*-4-*tert*-butyl substituted cyclohexane



II

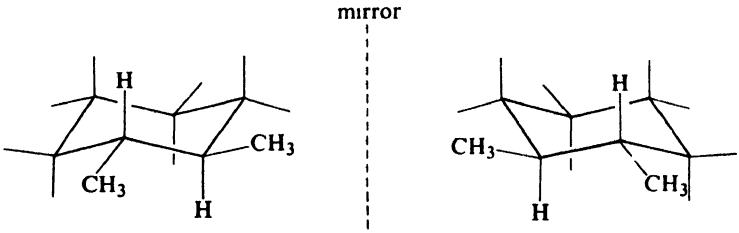
A *trans*-4-*tert*-butyl substituted cyclohexane

of its distance, exerts little electronic effect on —G. Following a suggestion by Professor Saul Winstein (of the University of California, Los Angeles), *tert*-butyl has been widely used as a holding group, to permit the study of physical and chemical properties associated with a purely axial or purely equatorial substituent.

Problem 9.10 Use the energy differences given in Problem 9.3 (p. 301) to calculate values for the various alkyl–hydrogen 1,3-diaxial interactions, and from these calculate the difference in energy between the two conformations of:

(a) *cis*-4-*tert*-butylmethylcyclohexane;
(b) *trans*-4-*tert*-butylmethylcyclohexane;
(c) *trans*-3-*cis*-4-dimethyl-*tert*-butylcyclohexane.

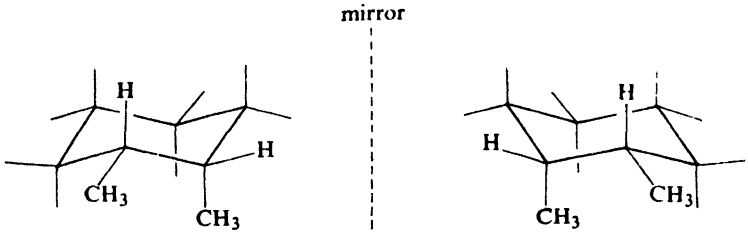
Now, what can we say about the possible chirality of the 1,2-dimethylcyclohexanes? Let us make a model of *trans*-1,2-dimethylcyclohexane—in the more stable diequatorial conformation, say—and a model of its mirror image. We find



Not superimposable; not interconvertible
trans-1,2-Dimethylcyclohexane
A resolvable racemic modification

they are not superimposable, and therefore are enantiomers. We find that they are not interconvertible, and hence are configurational isomers. (When we flip one of these into the opposite chair conformation, it is converted, not into its mirror image, but into a diaxial conformation.) Thus, *trans*-1,2-dimethylcyclohexane should, in principle, be resolvable into (configurational) enantiomers, each of which should be optically active.

Next, let us make a model of *cis*-1,2-dimethylcyclohexane and a model of its mirror image. We find they are not superimposable, and hence are enantiomers.



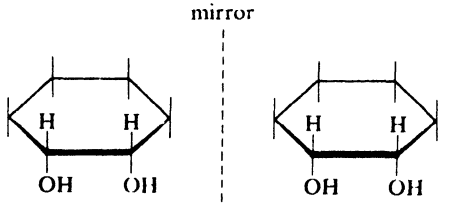
Not superimposable; but interconvertible
cis-1,2-Dimethylcyclohexane
A non-resolvable racemic modification

In contrast to what we have said for the *trans*-compound, however, we find that these models *are* interconvertible by flipping one chair conformation into the other. These are conformational enantiomers and hence, except possibly at low temperatures, should interconvert too rapidly for resolution and measurement of optical activity.

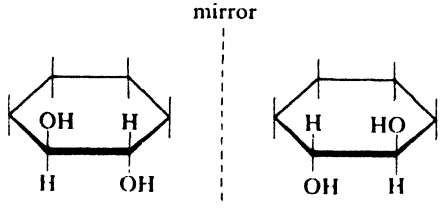
Thus, just as with the *cis*- and *trans*-1,2-cyclopentanediols (Sec. 9.13), we could assign configurations to the *cis*- and *trans*-1,2-dimethylcyclohexanes by finding out which of the two is resolvable. The *cis*-1,2-dimethylcyclohexane is not literally a *meso* compound, but it is a non-resolvable racemic modification, which for most practical purposes amounts to the same thing.

To summarize, then, 1,2-dimethylcyclohexane exists as a pair of (configurational) diastereomers: the *cis*- and *trans*-isomers. The *cis*-isomer exists as a pair of conformational enantiomers. The *trans*-isomer exists as a pair of configurational enantiomers, each of which in turn exists as two conformational diastereomers (axial–axial and equatorial–equatorial).

Because of the ready interconvertibility of chair conformations, it is possible to use planar drawings to predict the configurational stereoisomerism of cyclo-



Superimposable
cis-1,2-Cyclohexanediol



Not superimposable
trans-1,2-Cyclohexanediol

hexane derivatives. To understand the true geometry of such molecules, however, and with it the matter of stability, one must use models and formulas like those in Figs. 9.11 and 9.12.

Problem 9.11 Which of the following compounds are resolvable, and which are non-resolvable? Which are truly *meso* compounds? Use models as well as drawings.

(a) *cis*-1,2-cyclohexanediol
(b) *trans*-1,2-cyclohexanediol
(c) *cis*-1,3-cyclohexanediol
(d) *trans*-1,3-cyclohexanediol
(e) *cis*-1,4-cyclohexanediol
(f) *trans*-1,4-cyclohexanediol

Problem 9.12 Tell which, if any, of the compounds of Problem 9.11 exist as:

(a) a single conformation;
(b) a pair of conformational enantiomers;
(c) a pair of conformational diastereomers;
(d) a pair of (configurational) enantiomers, each of which exists as a single conformation;
(e) a pair of (configurational) enantiomers, each of which exists as a pair of conformational diastereomers;
(f) none of the above answers. (Give the correct answer.)

Problem 9.13 Draw structural formulas for all stereoisomers of the following. Label any *meso* compounds and indicate pairs of enantiomers. Do any (like *cis*-1,2-dimethylcyclohexane) exist as a non-resolvable racemic modification?

(a) *cis*-2-chlorocyclohexanol
(b) *trans*-2-chlorocyclohexanol
(c) *cis*-3-chlorocyclopentanol
(d) *trans*-3-chlorocyclopentanol
(e) *cis*-4-chlorocyclohexanol
(f) *trans*-4-chlorocyclohexanol

9.15 Carbenes. Methylene

The difference between successive members of a homologous series, we have seen, is the CH_2 unit, or *methylene*. But methylene is more than just a building block for the mental construction of compounds; it is an actual molecule, and its chemistry and the chemistry of its derivatives, the **carbenes**, has become one of the most exciting and productive fields of organic research.

Methylene is formed by the photolysis of either *diazomethane*, CH_2N_2, or *ketene*, $CH_2{-}C{=}O$. (Notice that the two starting materials and the two other

$$\underset{\text{Diazomethane}}{CH_2{-}\overset{+}{N}{=}\overset{-}{N}} \xrightarrow{\text{ultraviolet light}} \underset{\text{Methylene}}{CH_2} + N_2$$

$$\underset{\text{Ketene}}{CH_2{=}C{=}O} \xrightarrow{\text{ultraviolet light}} \underset{\text{Methylene}}{CH_2} + CO$$

products, nitrogen and carbon monoxide, are pairs of *isoelectronic* molecules, that is, molecules containing the same number of valence electrons.)

Methylene as a highly reactive molecule was first proposed in the 1930s to account for the fact that something formed by the above reactions was capable of removing certain metal mirrors (compare Problem 16, p. 72). Its existence was definitely established in 1959 by spectroscopic studies.

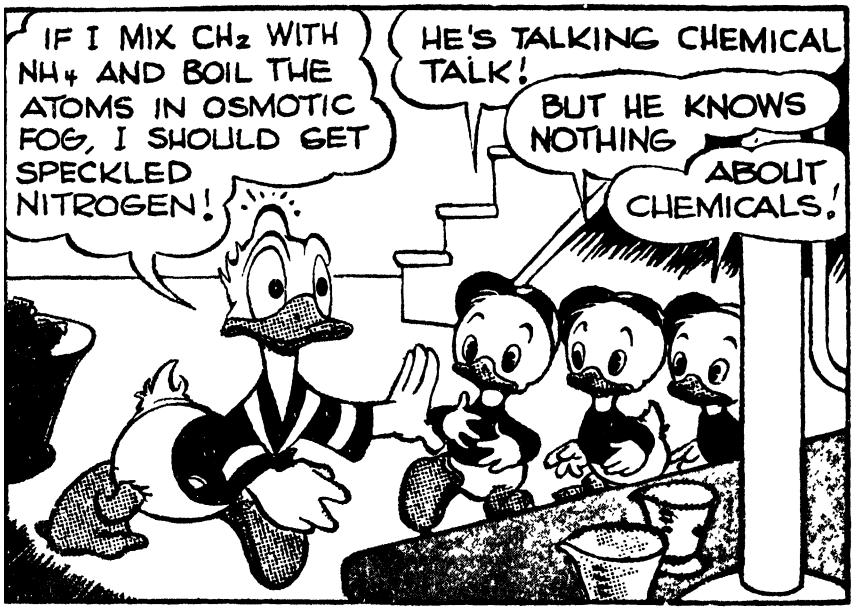
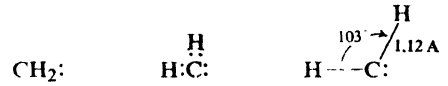


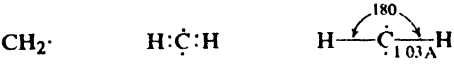
Figure 9.13. Evidence of early (1944) research on methylene, CH_2, by D. Duck. (As unearthed by Professors P. P. Gaspar and G. S. Hammond of the California Institute of Technology.)

These studies revealed that methylene not only exists but exists in two different forms (different spin states), generally referred to by their spectroscopic designations: *singlet* methylene, in which the unshared electrons are paired:



Singlet methylene
Unshared electrons paired

and *triplet* methylene, in which the unshared electrons are *not* paired.



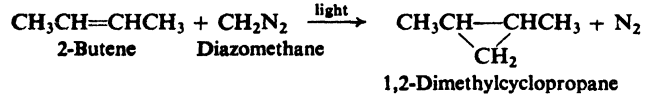
Triplet methylene
Unshared electrons not paired
a diradical

Triplet methylene is thus a free radical: in fact, it is a *di*radical. As a result of the difference in electronic configuration, the two kinds of molecules differ in shape and in chemical properties. Singlet methylene is the less stable form, and is often the form first generated, in the initial photolysis.

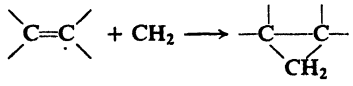
The exact chemical properties observed depend upon which form of methylene

is reacting, and this in turn depends upon the experimental conditions. In the liquid phase, the first-formed singlet methylene reacts rapidly with the abundant solvent molecules before it loses energy. In the gas phase—especially in the presence of an inert gas like nitrogen or argon—singlet methylene loses energy through collisions and is converted into triplet methylene, which then reacts.

When methylene is generated in the presence of alkenes, there are obtained cyclopropanes. For example:



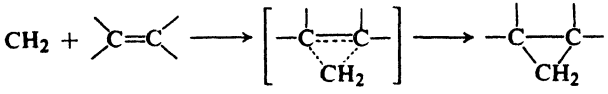
This is an example of the most important reaction of methylene and other carbenes: *addition to the carbon–carbon double bond.* Its most striking feature is that it can occur with two different kinds of stereochemistry.



For example, photolysis of diazomethane in liquid *cis*-2-butene gives only *cis*-1,2-dimethylcyclopropane, and in liquid *trans*-2-butene gives only *trans*-1,2-dimethylcyclopropane. Addition here is stereospecific and *syn*. Photolysis of diazomethane in gaseous 2-butene—either *cis* or *trans*—gives *both cis*- and *trans*-1,2-dimethylcyclopropanes. Addition here is non-stereospecific.

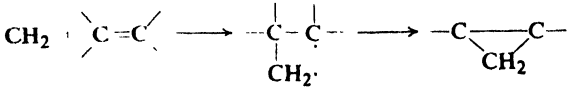
There seems to be little doubt that the following interpretation, due to P. S. Skell of Pennsylvania State University, is the correct one.

It is **singlet** methylene that undergoes the *stereospecific addition*. Although neutral, singlet methylene is electron-deficient and hence electrophilic; like other



electrophiles, it can find electrons at the carbon–carbon double bond. The stereochemistry strongly indicates simultaneous attachment to both doubly-bonded carbon atoms. (However, on both theoretical and experimental grounds, the transition state is believed to be unsymmetrical: attachment to one carbon has proceeded further than attachment to the other, with the development of considerable positive charge on the second carbon.)

It is **triplet** methylene that undergoes the *non-stereospecific addition*. Triplet



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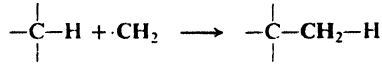
methylene is a diradical, and it adds by a free-radical-like two-step mechanism: actually, addition followed by combination. The intermediate diradical I lasts long enough for rotation to occur about the central carbon–carbon bond, and

both *cis* and *trans* products are formed. (*Problem:* Using the approach of Sec. 7.12, assure yourself that this is so.)

Besides addition, methylene undergoes another reaction which, quite literally, belongs in a class by itself: *insertion.*



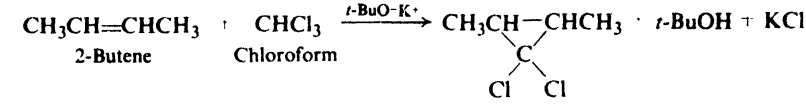
Insertion

Methylene can *insert itself* into every carbon-hydrogen bond of most kinds of molecules. We cannot take time to say more here about this remarkable reaction, except that when addition is the desired reaction, insertion becomes an annoying side-reaction.

Problem 9.14 In the gas phase, with low alkene concentration and in the presence of an inert gas, addition of methylene to the 2-butenes is, we have seen, nonstereospecific. If, however, there is present in this system a little oxygen, addition becomes completely stereospecific (*syn*). Account in detail for the effect of oxygen. (*Hint:* See Sec. 2.14.)

9.16 Substituted carbenes. α-Elimination

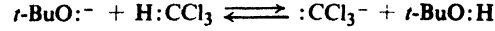
A more generally useful way of making cyclopropanes is illustrated by the reaction of 2-butene with chloroform in the presence of potassium *tert*-butoxide (*t*-Bu = *tert*-butyl):

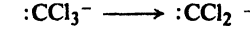


2-Butene Chloroform 3,3-Dichloro-1,2-dimethylcyclopropane

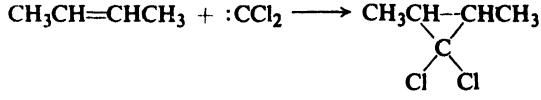
The dichlorocyclopropanes obtained can be reduced to hydrocarbons or hydrolyzed to *ketones*, the starting point for many syntheses (Chap. 19).

Here, too, reaction involves a divalent carbon compound, a derivative of methylene: *dichlorocarbene*, $:CCl_2$. It is generated in two steps, initiated by attack on chloroform by the very strong base, *tert*-butoxide ion, and then adds to the alkene.

(1) 

(2) 

Dichlorocarbene

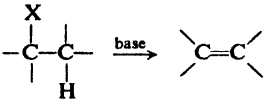
(3) 

It is believed that, because of the presence of the halogen atoms, the singlet form, with the electrons paired, is the more stable form of dichlorocarbene, and is the one adding to the double bond. (Stabilization by the halogen atoms is presumably one reason why dihalocarbenes do not generally undergo the insertion reaction that is so characteristic of unsubstituted singlet methylene.)

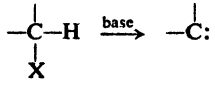
The addition of dihalocarbenes, like that of singlet methylene, is *stereospecific* and *syn*.

Problem 9.15 (a) Addition of $:CCl_2$ to cyclopentene yields a single compound. What is it? (b) Addition of :CBrCl to cyclopentene yields a mixture of stereoisomers. In light of (a), how do you account for this? What are the isomers likely to be? (*Hint:* Use models.)

In dehydrohalogenation of alkyl halides (Sec. 5.13), we have already encountered a reaction in which hydrogen ion and halide ion are eliminated from a molecule by the action of base; there —H and —X were lost from adjacent carbons, and so the process is called *β-elimination*. In the generation of the methylene shown here, both —H and —X are eliminated from the same carbon, and the process is called *α-elimination*. (Later on, in Sec. 24.12, we shall see some of the evidence for the mechanism of α-elimination shown above.)



Beta-elimination

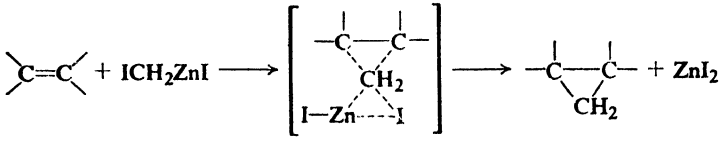


Alpha-elimination

Problem 9.16 (a) Why does $CHCl_3$ not undergo β-elimination through the action of base? (b) What factor would you expect to make α-elimination from $CHCl_3$ easier than from, say, CH_3Cl?

There are many ways of generating what appear to be carbenes. But in some cases at least, it seems clear that no *free* carbene is actually an intermediate; instead, a *carbenoid* (carbene-like) reagent transfers a carbene unit directly to a double bond. For example, in the extremely useful Simmons-Smith reaction

$$CH_2I_2 + Zn(Cu) \longrightarrow ICH_2ZnI$$



(H. E. Simmons and R. D. Smith of the du Pont Company) the carbenoid is an organozinc compound which delivers methylene stereospecifically (and without competing insertion) to the double bond.

9.17 Analysis of alicyclic hydrocarbons

A cyclopropane readily dissolves in concentrated sulfuric acid, and in this resembles an alkene or alkyne. It can be differentiated from these unsaturated hydrocarbons, however, by the fact that it is not oxidized by cold, dilute, neutral permanganate.

Other alicyclic hydrocarbons have the same kind of properties as their open-chain counterparts, and they are characterized in the same way: cycloalkanes by their general inertness, and cycloalkenes and cycloalkynes by their response to

tests for unsaturation (bromine in carbon tetrachloride, and aqueous permanganate). That one is dealing with cyclic hydrocarbons is shown by molecular formulas and by degradation products.

The properties of cyclohexane, for example, show clearly that it is an alkane. However, combustion analysis and molecular weight determination show its molecular formula to be C_6H_{12}. Only a cyclic structure (although not necessarily a six-membered ring) is consistent with both sets of data.

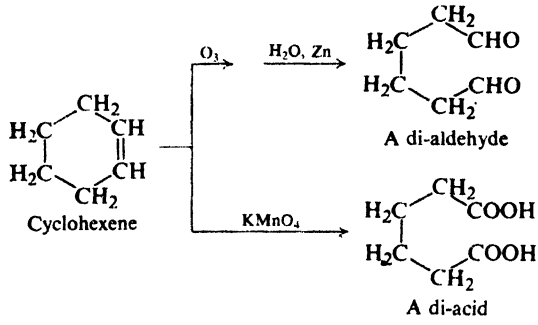
Similarly, the absorption of only one mole of hydrogen shows that cyclohexane contains only one carbon–carbon double bond; yet its molecular formula is C_6H_{10}, which in an open-chain compound would correspond to two carbon–carbon double bonds or one triple bond. Again, only a cyclic structure fits the facts.

Problem 9.17 Compare the molecular formulas of: (a) *n*-hexane and cyclohexane; (b) *n*-pentane and cyclopentane; (c) 1-hexene and cyclohexene; (d) dodecane, *n*-hexylcyclohexane, and cyclohexylcyclohexane. (e) In general, how can you deduce the number of rings in a compound from its molecular formula and degree of unsaturation?

Problem 9.18 What is the molecular formula of: (a) cyclohexane; (b) methylcyclopentane; (c) 1,2-dimethylcyclobutane? (d) Does the molecular formula give any information about the *size* of ring in a compound?

Problem 9.19 The yellow plant pigments α-, β-, and γ-*carotene*, and the red pigment of tomatoes, *lycopene*, are converted into Vitamin A in the liver. All four have the molecular formula $C_{40}H_{56}$. Upon catalytic hydrogenation, α- and β-carotene yield $C_{40}H_{78}$, γ-carotene yields $C_{40}H_{80}$, and lycopene yields $C_{40}H_{82}$. How many rings, if any, are there in each compound?

Cleavage products of cycloalkenes and cycloalkynes also reveal the cyclic structure. Ozonolysis of cyclohexene, for example, does not break the molecule into two aldehydes of lower carbon number, but simply into a single six-carbon compound containing *two* aldehyde groups.



Problem 9.20 Predict the ozonolysis products of: (a) cyclohexene; (b) 1-methylcyclopentene; (c) 3-methylcyclopentene; (d) 1,3-cyclohexadiene; (e) 1,4-cyclohexadiene.

Problem 9.21 Both cyclohexene and 1,7-octadiene yield the di-aldehyde $OHC(CH_2)_4CHO$ upon ozonolysis. What other facts would enable you to distinguish between the two compounds?

(Analysis of cyclic aliphatic hydrocarbons by spectroscopy will be discussed in Secs. 13.15–13.16.)

PROBLEMS

1. Draw structural formulas of:

(a) methylcyclopentane
(b) 1-methylcyclohexene
(c) 3-methylcyclopentene
(d) *trans*-1,3-dichlorocyclobutane
(e) *cis*-2-bromo-1-methylcyclopentane
(f) cyclohexylcyclohexane
(g) cyclopentylacetylene
(h) 1,1-dimethyl-4-chlorocycloheptane
(i) bicyclo[2.2.1]hepta-2,5-diene
(j) 1-chlorobicyclo[2.2.2]octane

2. Give structures and names of the principal organic products expected from each of the following reactions:

(a) cyclopropane + Cl_2, $FeCl_3$
(b) cyclopropane + Cl_2 (300°)
(c) cyclopropane + conc. H_2SO_4
(d) cyclopentane + Cl_2, $FeCl_3$
(e) cyclopentane + Cl_2 (300°)
(f) cyclopentane + conc. H_2SO_4
(g) cyclopentene + Br_2/CCl_4
(h) cyclopentene + Br_2 (300°)
(i) 1-methylcyclohexene + HCl
(j) 1-methylcyclohexene + Br_2(aq)
(k) 1-methylcyclohexene + HBr (peroxides)
(l) 1,3-cyclohexadiene + HCl
(m) cyclopentanol + H_2SO_4 (heat)
(n) bromocyclohexane + KOH(alc)
(o) cyclopentene + cold $KMnO_4$
(p) cyclopentene + HCO_2OH
(q) cyclopentene + hot $KMnO_4$
(r) chlorocyclopentane + $(C_2H_5)_2CuLi$
(s) 1-methylcyclopentene + cold conc. H_2SO_4
(t) 3-methylcyclopentene + O_3, then H_2O/Zn
(u) cyclohexene + $H_2SO_4 \longrightarrow C_{12}H_{20}$
(v) cyclopentene + $CHCl_3$ + *t*-BuOK
(w) cyclopentene + CH_2I_2 + Zn(Cu)

3. Outline all steps in the laboratory synthesis of each of the following from cyclohexanol.

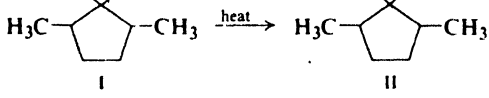
(a) cyclohexene
(b) cyclohexane
(c) *trans*-1,2-dibromocyclohexane
(d) *cis*-1,2-cyclohexanediol
(e) *trans*-1,2-cyclohexanediol
(f) $OHC(CH_2)_4CHO$
(g) adipic acid, $HOOC(CH_2)_4COOH$
(h) bromocyclohexane
(i) 2-chlorocyclohexanol
(j) 3-bromocyclohexene
(k) 1,3-cyclohexadiene
(l) cyclohexylcyclohexane
(m) *norcarane*, bicyclo[4.1.0]heptane

4. Give structure of all isomers of the following. For cyclohexane derivatives, planar formulas (p. 307) will be sufficient here. Label pairs of enantiomers, and *meso* compounds.

(a) dichlorocyclopropanes
(b) dichlorocyclobutanes
(c) dichlorocyclopentanes
(d) dichlorocyclohexanes
(e) chloro-1,1-dimethylcyclohexanes
(f) 1,3,5-trichlorocyclohexanes

(g) There are a number of stereoisomeric 1,2,3,4,5,6-hexachlorocyclohexanes. Without attempting to draw all of them, give the structure of the most stable isomer, and show its preferred conformation.

5. (a) 2,5-Dimethyl-1,1-cyclopentanedicarboxylic acid (I) can be prepared as two optically inactive substances (A and B) of different m.p. Draw their structures. (b) Upon heating, A yields two 2,5-dimethylcyclopentanecarboxylic acids (II), and B yields only one. Assign structures to A and B.



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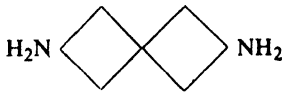
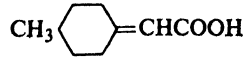
6. (a) The following compounds can be resolved into optically active enantiomers.



3,3'-Diaminospiro[3.3]heptane



4-Methylcyclohexylideneacetic acid

Using models and then drawing three-dimensional formulas, account for this. Label the chiral center in each compound.

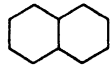
(b) Addition of bromine to optically active 4-methylcyclohexylideneacetic acid yields two optically active dibromides. Assuming a particular configuration for the starting material, draw stereochemical formulas for the products.

7. (a) *trans*-1,2-Dimethylcyclohexane exists about 99% in the diequatorial conformation. *trans*-1,2-Dibromocyclohexane (or *trans*-1,2-dichlorocyclohexane), on the other hand, exists about equally in the diequatorial and diaxial conformations; furthermore, the fraction of the diaxial conformation decreases with increasing polarity of the solvent. How do you account for the contrast between the dimethyl and dibromo (or dichloro) compounds? (*Hint:* See Problem 11, p. 141.)

(b) If *trans*-3-*cis*-4-dibromo-*tert*-butylcyclohexane is subjected to prolonged heating, t is converted into an equilibrium mixture (about 50:50) of itself and a diastereomer. What is the diastereomer likely to be? How do you account for the approximately equal stability of these two diastereomers? (Here, and in (c), consider the more stable conformation of each diastereomer to be the one with an equatorial *tert*-butyl group.)

(c) There are two more diastereomeric 3,4-dibromo-*tert*-butylcyclohexanes. What are they? How do you account for the fact that neither is present to an appreciable extent in the equilibrium mixture?

8. The compound *decalin*, $C_{10}H_{18}$, consists of two fused cyclohexane rings:

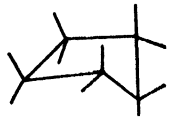


Decalin

(a) Using models, show how there can be two isomeric decalins, *cis* and *trans*. (b) How many different conformations free of angle strain are possible for *cis*-decalin? For *trans*-decalin? (c) Which is the most stable conformation of *cis*-decalin? Of *trans*-decalin? (*Hint*: Consider each ring in turn. What are the largest substituents on each ring?) (d) Account for the fact that *trans*-decalin is more stable than *cis*-decalin. (e) The difference in stability between *cis*- and *trans*-decalin is about 2 kcal/mole; conversion of one into the other takes place only under very vigorous conditions. The chair and twist-boat forms of cyclohexane, on the other hand, differ in stability by about 6 kcal/mole, yet are readily interconverted at room temperature. How do you account for the contrast? Draw energy curves to illustrate your answer.

9. Allinger (p. 305) found the energy difference between *cis*- and *trans*-1,3-di-*tert*-butylcyclohexane to be 5.9 kcal/mole, and considers that this value represents the energy difference between the chair and twist-boat forms of cyclohexane. Defend Allinger's position.

10. It has been suggested that in certain substituted cyclopentanes the ring exists preferentially in the "envelope" form:

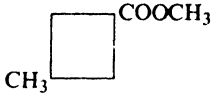


Using models, suggest a possible explanation for each of the following facts:

(a) The attachment of a methyl group to the badly strained cyclopentane ring raises the heat of combustion very little more than attachment of a methyl group to the unstrained cyclohexane ring. (*Hint:* Where is the methyl group located in the "envelope" form?)

(b) Of the 1,2-dimethylcyclopentanes, the *trans*-isomer is more stable than the *cis*. Of the 1,3-dimethylcyclopentanes, on the other hand, the *cis*-isomer is more stable than the *trans*.

(*c*) The *cis*-isomer of methyl 3-methylcyclobutanecarboxylate



is more stable than the *trans*-isomer

11. Each of the following reactions is carried out, and the products are separated by careful distillation, recrystallization, or chromatography. For each reaction tell how many fractions will be collected. Draw a stereochemical formula of the compound or compounds making up each fraction. Tell whether each fraction, as collected, will be optically active or optically inactive.

(a) (R)-3-hydroxycyclohexene + $KMnO_4 \longrightarrow C_6H_{12}O_3$;
(b) (R)-3-hydroxycyclohexene + $HCO_2OH \longrightarrow C_6H_{12}O_3$;
(c) (S,S)-1,2-dichlorocyclopropane + Cl_2 (300°) $\longrightarrow C_3H_3Cl_3$;
(d) *racemic* 4-methylcyclohexene + Br_2/CCl_4.

12. Outline all steps in a possible laboratory synthesis of each of the following, using alcohols of four carbons or fewer as your only organic source, and any necessary inorganic reagents. (*Remember:* Work backwards.)

(a) *cis*-1,2-di(*n*-propyl)cyclopropane;
(b) racemic *trans*-1-methyl-2-ethyl-3,3-dichlorocyclopropane.

13. Describe simple chemical tests that would distinguish between:

(a) cyclopropane and propane
(b) cyclopropane and propylene
(c) 1,2-dimethylcyclopropane and cyclopentane
(d) cyclobutane and 1-butene
(e) cyclopentane and 1-pentene
(f) cyclopentane and cyclopentene
(g) cyclohexanol and *n*-butylcyclohexane
(h) 1,2-dimethylcyclopentene and cyclopentanol
(i) cyclohexane, cyclohexene, cyclohexanol, and bromocyclohexane

14. How many rings does each of the following contain?

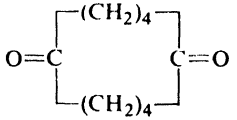
(a) *Camphane*, $C_{10}H_{18}$, a terpene related to camphor, takes up no hydrogen. (*b*) *Cholestane*, $C_{27}H_{48}$, a steroid of the same ring structure as cholesterol, cortisone, and the sex hormones, takes up no hydrogen. (c) *β-Phellandrene*, $C_{10}H_{16}$, a terpene, reacts with bromine to form $C_{10}H_{16}Br_4$. (d) *Ergocalciferol* (so-called "Vitamin D_2"), $C_{28}H_{44}O$, an alcohol, gives $C_{28}H_{52}O$ upon catalytic hydrogenation. (e) How many double bonds does ergocalciferol contain?

15. On the basis of the results of catalytic hydrogenation, how many rings does each of the following aromatic hydrocarbons contain?

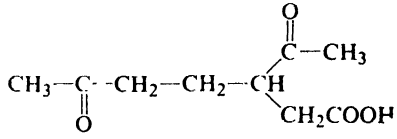
(a) *benzene* (C_6H_6) $\longrightarrow C_6H_{12}$
(b) *naphthalene* ($C_{10}H_8$) $\longrightarrow C_{10}H_{18}$
(c) *toluene* (C_7H_8) $\longrightarrow C_7H_{14}$
(d) *anthracene* ($C_{14}H_{10}$) $\longrightarrow C_{14}H_{24}$
(e) *phenanthrene* ($C_{14}H_{10}$) $\longrightarrow C_{14}H_{24}$
(f) 3,4-*benzpyrene* ($C_{20}H_{12}$) $\longrightarrow C_{20}H_{32}$
(g) *chrysene* ($C_{18}H_{12}$) $\longrightarrow C_{18}H_{30}$

(Check your answers by use of the index.)

16. (a) A hydrocarbon of formula $C_{10}H_{16}$ absorbs only one mole of H_2 upon hydrogenation. How many rings does it contain? (b) Upon ozonolysis it yields 1,6-cyclodecanedione (III). What is the hydrocarbon?



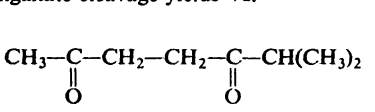
III



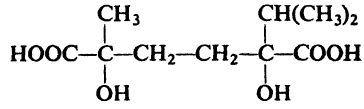
IV

17. *Limonene*, $C_{10}H_{16}$, a terpene found in orange, lemon, and grapefruit peel, absorbs only two moles of hydrogen, forming *p-menthane*, $C_{10}H_{20}$. Oxidation by permanganate converts limonene into IV. (a) How many rings, if any, are there in limonene? (b) What structures are consistent with the oxidation product? (c) On the basis of the isoprene rule (Sec. 8.26), which structure is most likely for limonene? For *p*-menthane? (d) Addition of one mole of H_2O converts limonene into *α-terpineol*. What are the most likely structures for α-terpineol? (e) Addition of two moles of H_2O to limonene yields *terpin hydrate*. What is the most likely structure for terpin hydrate?

18. *α-Terpinene*, $C_{10}H_{16}$, a terpene found in coriander oil, absorbs only two moles of hydrogen, forming *p-menthane*, $C_{10}H_{20}$. Ozonolysis of α-terpinene yields V; permanganate cleavage yields VI.



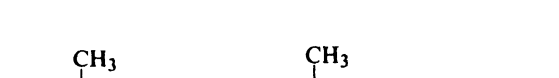
V



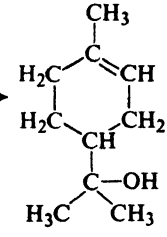
VI

(a) How many rings, if any, are there in α-terpinene? (b) On the basis of the cleavage products, V and VI, and the isoprene rule, what is the most likely structure for α-terpinene? (c) How do you account for the presence of the —OH groups in VI?

19. Using only chemistry that you have already encountered, can you suggest a mechanism for the conversion of *nerol* ($C_{10}H_{18}O$) into α-terpineol ($C_{10}H_{18}O$) in the presence of dilute H_2SO_4?



Nerol (found in bergamot)



α-Terpineol

Chapter 10 Benzene & Aromatic Character

10.1 Aliphatic and aromatic compounds

Chemists have found it useful to divide all organic compounds into two broad classes: **aliphatic** compounds and **aromatic** compounds. The original meanings of the words "aliphatic" (*fatty*) and "aromatic" (*fragrant*) no longer have any significance.

Aliphatic compounds are open-chain compounds and those cyclic compounds that resemble the open-chain compounds. The families we have studied so far—alkanes, alkenes, alkynes, and their cyclic analogs—are all members of the aliphatic class.

Aromatic compounds *are benzene and compounds that resemble benzene in chemical behavior.* Aromatic properties are those properties of benzene that distinguish it from aliphatic hydrocarbons. Some compounds that possess aromatic properties have structures that seem to differ considerably from the structure of benzene: actually, however, there is a basic similarity in electronic configuration (Sec. 10.10).

Aliphatic hydrocarbons, as we have seen, undergo chiefly addition and free-radical substitution; addition occurs at multiple bonds, and free-radical substitution occurs at other points along the aliphatic chain. In contrast, we shall find that *aromatic hydrocarbons are characterized by a tendency to undergo ionic substitution.* We shall find this contrast maintained in other families of compounds (i.e., acids, amines, aldehydes, etc.); the hydrocarbon parts of their molecules undergo reactions characteristic of either aliphatic or aromatic hydrocarbons.

It is important not to attach undue weight to the division between aliphatic and aromatic compounds. Although extremely useful, it is often less important than some other classification. For example, the similarities between aliphatic and aromatic acids, or between aliphatic and aromatic amines, are more important than the differences.

10.2 Structure of benzene

It is obvious from our definition of aromatic compounds that any study of their chemistry must begin with a study of benzene. Benzene has been known since 1825; its chemical and physical properties are perhaps better known than those of any other single organic compound. In spite of this, no satisfactory structure for benzene had been advanced until about 1931, and it was ten to fifteen years before this structure was generally used by organic chemists.

The difficulty was not the complexity of the benzene molecule, but rather the limitations of the structural theory as it had so far developed. Since an understanding of the structure of benzene is important both in our study of aromatic compounds and in extending our knowledge of the structural theory, we shall examine in some detail the facts upon which this structure of benzene is built.

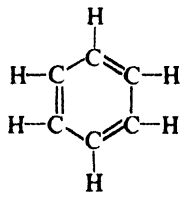
10.3 Molecular formula. Isomer number. Kekulé structure

(*a*) *Benzene has the molecular formula* C_6H_6. From its elemental composition and molecular weight, benzene was known to contain six carbon atoms and six hydrogen atoms. The question was: how are these atoms arranged?

In 1858, August Kekulé (of the University of Bonn) had proposed that carbon atoms can join to one another to form *chains*. Then, in 1865, he offered an answer to the question of benzene: these carbon chains can sometimes be closed, to form *rings*.

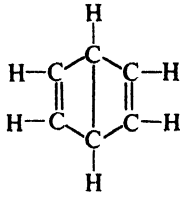
> "I was sitting writing at my textbook, but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire, and dozed. Again the atoms were gamboling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of this kind, could now distinguish larger structures of manifold conformations; long rows, sometimes more closely fitted together; all twisting and turning in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I woke;... I spent the rest of the night working out the consequences of the hypothesis. Let us learn to dream, gentlemen, and then perhaps we shall learn the truth."—August Kekulé, 1865.

Kekulé's structure of benzene was one that we would represent today as I.



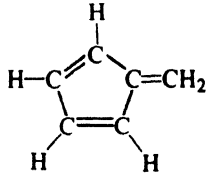
I

Kekulé formula

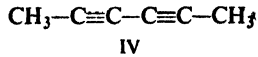


II

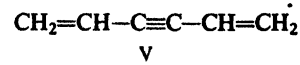
"Dewar" formula



III



IV



V

Other structures are, of course, consistent with the formula C_6H_6: for example, II–V. Of all these, Kekulé's structure was accepted as the most nearly satisfactory;

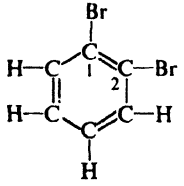
the evidence was of a kind with which we are already familiar: **isomer number** (Sec. 4.2).

(*b*) *Benzene yields only one monosubstitution product*, C_6H_5Y. Only one bromobenzene, C_6H_5Br, is obtained when one hydrogen atom is replaced by bromine; similarly, only one chlorobenzene, C_6H_5Cl, or one nitrobenzene, $C_6H_5NO_2$, etc., has ever been made. This fact places a severe limitation on the structure of benzene: each hydrogen must be exactly equivalent to every other hydrogen, since the replacement of any one of them yields the same product.

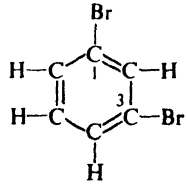
Structure V, for example, must now be rejected, since it would yield two isomeric monobromo derivatives, the 1-bromo and the 2-bromo compounds; all hydrogens are not equivalent in V. Similar reasoning shows us that II and III are likewise unsatisfactory. (How many monosubstitution products would each of these yield?) I and IV, among others, are still possibilities, however.

(*c*) *Benzene yields three isomeric disubstitution products*, $C_6H_4Y_2$ or C_6H_4YZ. Three and only three isomeric dibromobenzenes, $C_6H_4Br_2$, three chloronitrobenzenes, $C_6H_4ClNO_2$, etc., have ever been made. This fact further limits our choice of a structure; for example, IV must now be rejected. (How many disubstitution products would IV yield?)

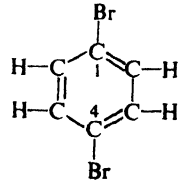
At first glance, structure I seems to be consistent with this new fact; that is, we can expect three isomeric dibromo derivatives, the 1,2- the 1,3-, and the 1,4-dibromo compounds shown:



1,2-Dibromobenzene

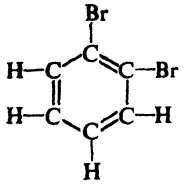


1,3-Dibromobenzene

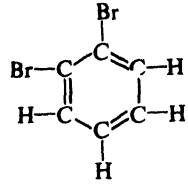


1,4-Dibromobenzene

Closer examination of structure I shows, however, that *two* 1,2-dibromo isomers (VI and VII), differing in the positions of bromine relative to the double bonds, should be possible:

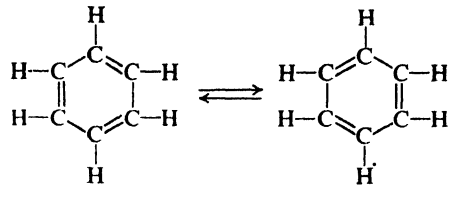


VI

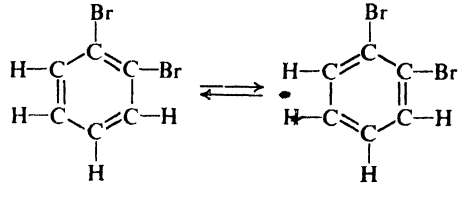


VII

But Kekulé visualized the benzene molecule as a dynamic thing: ". . . the form whirled mockingly before my eyes . . ." He described it in terms of two structures, VIII and IX, between which the benzene molecule alternates. As a consequence, the two 1,2-dibromobenzenes (VI and VII) would be in rapid equilibrium and hence could not be separated.



VIII IX



VI VII

Later, when the idea of tautomerism (Sec. 8.13) became defined, it was assumed that Kekulé's "alternation" essentially amounted to tautomerism.

On the other hand, it is believed by some that Kekule had intuitively anticipated by some 75 years our present concept of delocalized electrons, and drew two pictures (VIII and IX)—as we shall do, too—as a crude representation of something that neither picture alone satisfactorily represents. Rightly or wrongly, the term "Kekulé structure" has come to mean a (hypothetical) molecule with alternating single and double bonds—just as the term "Dewar benzene" has come to mean a structure (II) that James Dewar devised in 1867 as an example of what benzene was *not*.

10.4 Stability of the benzene ring. Reactions of benzene

Kekulé's structure, then, accounts satisfactorily for facts (*a*), (*b*), and (*c*) in Sec. 10.3. But there are a number of facts that are still not accounted for by this structure; most of these unexplained facts seem related to unusual stability of the benzene ring. The most striking evidence of this stability is found in the chemical reactions of benzene.

(*d*) *Benzene undergoes substitution rather than addition.* Kekulé's structure of benzene is one that we would call "cyclohexatriene." We would expect this cyclohexatriene, like the very similar compounds, cyclohexadiene and cyclohexene, to undergo readily the addition reactions characteristic of the alkene structure. As the examples in Table 10.1 show, this is not the case; under conditions that cause an alkene to undergo rapid addition, benzene reacts either not at all or very slowly.

Table 10.1 CYCLOHEXENE *vs.* BENZENE

Reagent	Cyclohexene gives	Benzene gives
$KMnO_4$ (cold, dilute, aqueous)	Rapid oxidation	No reaction
Br_2/CCl_4 (in the dark)	Rapid addition	No reaction
HI	Rapid addition	No reaction
H_2 + Ni	Rapid hydrogenation at 25°, 20 lb/in.^{2}	Slow hydrogenation at 100–200°, 1500 lb/in.^{2}

In place of addition reactions, benzene readily undergoes a new set of reactions, all involving **substitution.** The most important are shown below.

REACTIONS OF BENZENE

1. Nitration. Discussed in Sec. 11.8.

$$C_6H_6 + HONO_2 \xrightarrow{H_2SO_4} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O$$

2. Sulfonation. Discussed in Sec. 11.11.

$$C_6H_6 + HOSO_3H \xrightarrow{SO_3} \underset{\text{Benzenesulfonic acid}}{C_6H_5SO_3H} + H_2O$$

3. Halogenation. Discussed in Sec. 11.10.

$$C_6H_6 + Cl_2 \xrightarrow{Fe} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + HCl$$

$$C_6H_6 + Br_2 \xrightarrow{Fe} \underset{\text{Bromobenzene}}{C_6H_5Br} + HBr$$

4. Friedel-Crafts alkylation. Discussed in Secs. 11.9 and 12.6.

$$C_6H_6 + RCl \xrightarrow{AlCl_3} \underset{\text{An alkylbenzene}}{C_6H_5R} + HCl$$

5. Friedel-Crafts acylation. Discussed in Sec. 19.6.

$$\underset{\text{An acyl chloride}}{C_6H_6 + RCOCl} \xrightarrow{AlCl_3} \underset{\text{A ketone}}{C_6H_5COR} + HCl$$

In each of these reactions an atom or group has been substituted for one of the hydrogen atoms of benzene. The product can itself undergo further substitution of the same kind; the fact that it has retained the characteristic properties of benzene indicates that it has retained the characteristic structure of benzene.

It would appear that benzene resists addition, in which the benzene ring system would be destroyed, whereas it readily undergoes substitution, in which the ring system is preserved.

10.5 Stability of the benzene ring. Heats of hydrogenation and combustion

Besides the above qualitative indications that the benzene ring is more stable than we would expect cyclohexatriene to be, there exist quantitative data which show *how much* more stable.

(*e*) *Heats of hydrogenation and combustion of benzene are lower than expected.* We recall (Sec. 6.3) that heat of hydrogenation is the quantity of heat evolved when one mole of an unsaturated compound is hydrogenated. In most cases the value is about 28–30 kcal for each double bond the compound contains. It is not surprising, then, that cyclohexene has a heat of hydrogenation of 28.6 kcal and cyclohexadiene has one about twice that (55.4 kcal.)

We might reasonably expect cyclohexatriene to have a heat of hydrogenation about three times as large as cyclohexene, that is, about 85.8 kcal. Actually, the value for benzene (49.8 kcal) is *36 kcal less* than this expected amount.

This can be more easily visualized, perhaps, by means of an energy diagram (Fig. 10.1), in which the height of a horizontal line represents the potential energy content of a molecule. The broken lines represent the expected values, based upon three equal steps of 28.6 kcal. The final product, cyclohexane, is the same in all three cases.

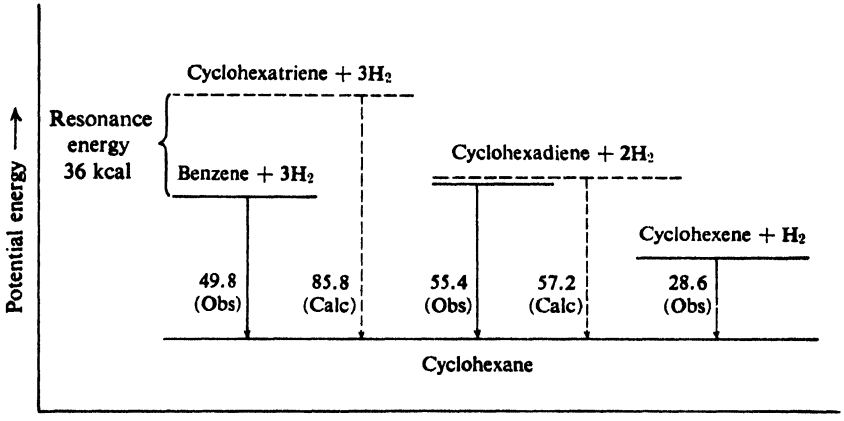


Figure 10.1. Heats of hydrogenation and stability: benzene, cyclohexadiene, and cyclohexene.

The fact that benzene *evolves* 36 kcal less energy than predicted can only mean that benzene *contains* 36 kcal less energy than predicted; in other words, benzene is more stable by 36 kcal than we would have expected cyclohexatriene to be. The heat of combustion of benzene is also lower than that expected, and by about the same amount.

Problem 10.1 From Fig. 10.1 determine the ΔH of the following reactions: (a) benzene + H_2 ⟶ 1,3-cyclohexadiene; (b) 1,3-cyclohexadiene + H_2 ⟶ cyclohexene.

Problem 10.2 For a large number of organic compounds, the heat of combustion actually measured agrees rather closely with that calculated by assuming a certain characteristic contribution from each kind of bond, e.g., 54.0 kcal for each C—H bond, 49.3 kcal for each C—C bond, and 117.4 kcal for each C=C bond (*cis*-1,2-disubstituted). (a) On this basis, what is the calculated heat of combustion for cyclohexatriene? (b) How does this compare with the measured value of 789.1 kcal for benzene?

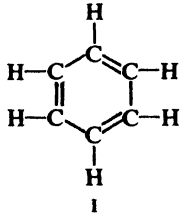
10.6 Carbon–carbon bond lengths in benzene

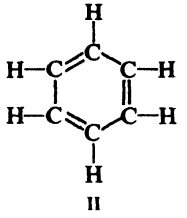
(*f*) *All carbon–carbon bonds in benzene are equal and are intermediate in length between single and double bonds.* Carbon–carbon double bonds in a wide variety of compounds are found to be about 1.34 A long. Carbon–carbon single bonds, in which the nuclei are held together by only one pair of electrons, are considerably longer: 1.53 A in ethane, for example, 1.50 A in propylene, 1.48 A in 1,3-butadiene.

If benzene actually possessed three single and three double bonds, as in a Kekulé structure, we would expect to find three short bonds (1.34 A) and three long bonds (1.48 A, probably, as in 1,3-butadiene). Actually, x-ray diffraction studies show that the six carbon–carbon bonds in benzene are equal and have a length of 1.39 A, and are thus intermediate between single and double bonds.

10.7 Resonance structure of benzene

The Kekulé structure of benzene, while admittedly unsatisfactory, was generally used by chemists as late as 1945. The currently accepted structure did not arise from the discovery of new facts about benzene, but is the result of an extension or modification of the structural theory; this extension is the concept of *resonance* (Sec. 6.23).


I


II

or

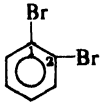

I

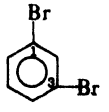

II

The Kekulé structures I and II, we now immediately recognize, meet the conditions for resonance: *structures that differ only in the arrangement of electrons*. Benzene is a *hybrid* of I and II. Since I and II are exactly equivalent, and hence of exactly the same stability, they make equal contributions to the hybrid. And, also since I and II are exactly equivalent, stabilization due to resonance should be large.

The puzzling aspects of benzene's properties now fall into place. The six bond lengths are identical because the six bonds are identical: they are one-and-a-half bonds and their length, 1.39 A, is intermediate between the lengths of single and double bonds.

When it is realized that all carbon–carbon bonds in benzene are equivalent, there is no longer any difficulty in accounting for the number of isomeric disubstitution products. It is clear that there should be just three, in agreement with experiment:


1,2-Dibromobenzene


1,3-Dibromobenzene


1,4-Dibromobenzene

Finally, the "unusual" stability of benzene is not unusual at all: it is what one would expect of a hybrid of equivalent structures. The 36 kcal of energy that benzene does not contain—compared with cyclohexatriene—is resonance energy. It is the 36 kcal of resonance energy that is responsible for the new set of properties we call *aromatic properties*.

Addition reactions convert an alkene into a more stable saturated compound. Hydrogenation of cyclohexene, for example, is accompanied by the evolution of 28.6 kcal; the product lies 28.6 kcal lower than the reactants on the energy scale (Fig. 10.1).

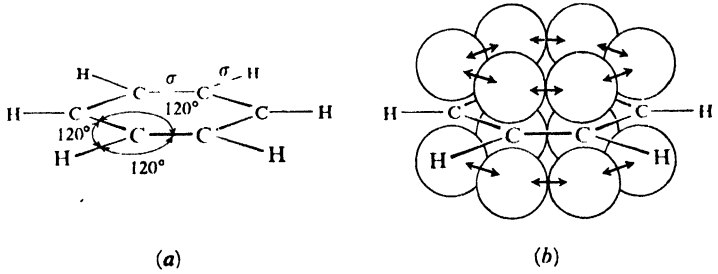
But addition would convert benzene into a *less* stable product by destroying the resonance-stabilized benzene ring system; for example, according to Fig. 10.1 the first stage of hydrogenation of benzene requires 5.6 kcal to convert benzene into the less stable cyclohexadiene. As a consequence, it is easier for reactions of benzene to take an entirely different course, one in which the ring system is retained: *substitution*.

(This is not quite all of the story in so far as stability goes. As we shall see in Sec. 10.10, an additional factor besides resonance is necessary to make benzene what it is.)

10.8 Orbital picture of benzene

A more detailed picture of the benzene molecule is obtained from a consideration of the bond orbitals in this molecule.

Since each carbon is bonded to three other atoms, it uses sp^2 orbitals (as in ethylene, Sec. 5.2). These lie in the same plane, that of the carbon nucleus, and are directed toward the corners of an equilateral triangle. If we arrange the six carbons and six hydrogens of benzene to permit maximum overlap of these orbitals, we obtain the structure shown in Fig. 10.2*a*.



(*a*) (*b*)

Figure 10.2. Benzene molecule. (*a*) Only σ bonds shown. (*b*) p orbitals overlap to form π bonds.

Benzene is a *flat molecule*, with every carbon and every hydrogen lying in the same plane. It is a very *symmetrical molecule*, too, with each carbon atom lying at the angle of a regular hexagon; every bond angle is 120°. Each bond orbital is cylindrically symmetrical about the line joining the atomic nuclei and hence, as before, these bonds are designated as σ bonds.

The molecule is not yet complete, however. There are still six electrons to be accounted for. In addition to the three orbitals already used, each carbon atom has a fourth orbital, a p orbital. As we know, this p orbital consists of two equal lobes, one lying above and the other lying below the plane of the other three orbitals, that is, above and below the plane of the ring; 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 an additional π

bond to be formed (see Fig. 10.2*b*). But the overlap here is not limited to a pair of *p* orbitals as it was in ethylene; the *p* orbital of any one carbon atom overlaps equally well the *p* orbitals of *both* carbon atoms to which it is bonded. The result (see Fig. 10.3) is two continuous doughnut-shaped electron clouds, one lying above and the other below the plane of the atoms.

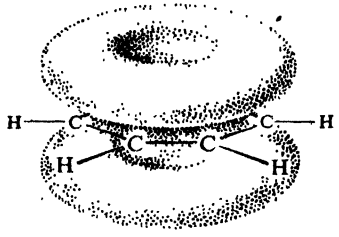


Figure 10.3. Benzene molecule. π clouds above and below plane of ring.

As with the allyl radical, it is the overlap of the *p* orbitals in both directions, and the resulting participation of each electron in several bonds that corresponds to our description of the molecule as a resonance hybrid of two structures. Again it is the *delocalization* of the π electrons—their participation in several bonds—that makes the molecule more stable.

To accommodate six π electrons, there must be *three* orbitals (Sec. 29.5). Their sum is, however, the symmetrical π clouds we have described.

The orbital approach reveals the importance of the planarity of the benzene ring. The ring is flat because the trigonal (sp^2) bond angles of carbon just fit the 120° angles of a regular hexagon; it is this flatness that permits the overlap of the *p* orbitals in both directions, with the resulting delocalization and stabilization.

The facts are consistent with the orbital picture of the benzene molecule. X-ray and electron diffraction show benzene (Fig. 10.4) to be a completely flat,

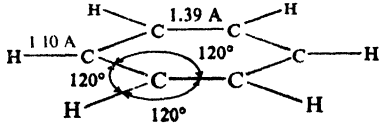


Figure 10.4. Benzene molecule: shape and size.

symmetrical molecule with all carbon-carbon bonds equal, and all bond angles 120°.

As we shall see, the chemical properties of benzene are just what we would expect of this structure. Despite delocalization, the π electrons are nevertheless more loosely held than the σ electrons. The π electrons are thus particularly available to a reagent that is seeking electrons: *the typical reactions of the benzene ring are those in which it serves as a source of electrons for electrophilic (acidic) reagents.* Because of the resonance stabilization of the benzene ring, *these reactions lead to substitution*, in which the aromatic character of the benzene ring is preserved.

Problem 10.3 The carbon-hydrogen bond dissociation energy for benzene (112 kcal) is considerably larger than for cyclohexane. On the basis of the orbital picture of benzene, what is one factor that may be responsible for this? What piece of physical evidence tends to support your answer? (*Hint:* Look at Fig. 10.4 and see Sec. 5.4.)

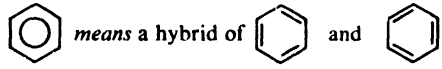
Problem 10.4 The molecules of *pyridine*, C_5H_5N, are flat, with all bond angles about 120°. All carbon–carbon bonds are 1.39 A long and the two carbon–nitrogen bonds are 1.36 A long. The measured heat of combustion is 23 kcal lower than that calculated by the method of Problem 10.2 on page 323. Pyridine undergoes such substitution reactions as nitration and sulfonation (Sec. 10.4). (a) Is pyridine adequately represented by formula I? (b) Account for the properties of pyridine by both valence-bond and orbital structures. (Check your answer in Sec. 31.6.)

I

Problem 10.5 The compound *borazole*, $B_3N_3H_6$, is shown by electron diffraction to have a flat cyclic structure with alternating boron and nitrogen atoms, and all boron–nitrogen bond lengths the same. (a) How would you represent borazole by valence-bond structures? (b) In terms of orbitals? (c) How many π electrons are there, and which atoms have they "come from"?

10.9 Representation of the benzene ring

For convenience we shall represent the benzene ring by a regular hexagon containing a circle (I); it is understood that a hydrogen atom is attached to each angle of the hexagon unless another atom or group is indicated.



I II III

I represents a resonance hybrid of the Kekulé structures II and III. The straight lines stand for the σ bonds joining carbon atoms. The circle stands for the cloud of six delocalized π electrons. (From another viewpoint, the straight lines stand for single bonds, and the circle stands for the extra *half-bonds*.)

I is a particularly useful representation of the benzene ring, since it emphasizes the equivalence of the various carbon–carbon bonds. The presence of the circle distinguishes the benzene ring from the cyclohexane ring, which is often represented today by a plain hexagon.

There is no complete agreement among chemists about how to represent the benzene ring. The student should expect to encounter it most often as one of the Kekulé formulas. The representation adopted in this book has certain advantages, and its use seems to be gaining ground. It is interesting that very much the same representation was advanced as long ago as 1899 by Johannes Thiele (of the University of Munich), who used a broken circle to stand for partial bonds ("partial valences").

10.10 Aromatic character. The Hückel $4n + 2$ rule

We have defined aromatic compounds as those that resemble benzene. But just which properties of benzene must a compound possess before we speak of it as being aromatic? Besides the compounds that contain benzene rings, there are many other substances that are called aromatic; yet some of these superficially bear little resemblance to benzene.

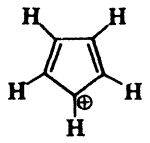
What properties do all aromatic compounds have in common?

From the experimental standpoint, aromatic compounds are compounds whose molecular formulas would lead us to expect a high degree of unsaturation, and yet which are resistant to the addition reactions generally characteristic of unsaturated compounds. Instead of addition reactions, we often find that these aromatic compounds undergo electrophilic substitution reactions like those of benzene. Along with this resistance toward addition—and presumably the cause of it—we find evidence of unusual stability: low heats of hydrogenation and low heats of combustion. Aromatic compounds are cyclic—generally containing five-, six-, or seven-membered rings—and when examined by physical methods, they are found to have flat (or nearly flat) molecules. Their protons show the same sort of *chemical shift* in nmr spectra (Sec. 13.8) as the protons of benzene and its derivatives.

From a theoretical standpoint, to be aromatic a compound must have a molecule that contains *cyclic clouds of delocalized π electrons above and below the plane of the molecule*; furthermore, the π clouds must contain a total of $(4n + 2)$ π electrons. That is to say, for the particular degree of stability that characterizes an aromatic compound, delocalization alone is not enough. There must be a particular number of π electrons: 2, or 6, or 10, etc. This requirement, called the $4n + 2$ *rule* or *Hückel rule* (after Erich Hückel, of the Institut für theoretische Physik, Stuttgart), is based on quantum mechanics, and has to do with the filling up of the various orbitals that make up the π cloud (Sec. 29.6). The Hückel rule is strongly supported by the facts.

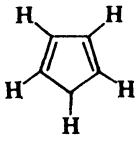
Let us look at some of the evidence supporting the Hückel rule. Benzene has six π electrons, the *aromatic sextet*; six is, of course, a Hückel number, corresponding to $n = 1$. Besides benzene and its relatives (naphthalene, anthracene, phenanthrene, Chap. 30), we shall encounter a number of heterocyclic compounds (Chap. 31) that are clearly aromatic; these aromatic heterocycles, we shall see, are just the ones that can provide an aromatic sextet.

Or, as further examples, consider these six compounds, for each of which just one contributing structure is shown:



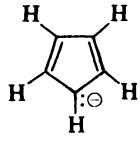
Cyclopentadienyl cation

Four π electrons



Cyclopentadienyl radical

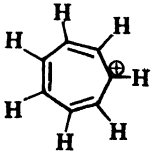
Five π electrons



Cyclopentadienyl anion

Six π electrons

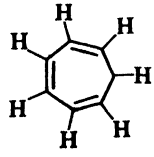
Aromatic



Cycloheptatrienyl cation (Tropylium ion)

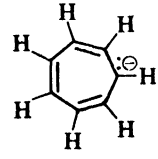
Six π electrons

Aromatic



Cycloheptatrienyl radical

Seven π electrons

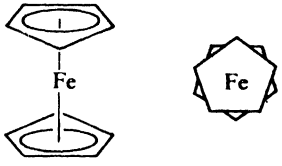


Cycloheptatrienyl anion

Eight π electrons

Each molecule is a hybrid of either five or seven equivalent structures, with the charge or odd electron on each carbon. Yet, of the six compounds, only *two* give evidence of *unusually* high stability: the cyclopentadienyl anion and the cycloheptatrienyl cation (*tropylium ion*).

For a hydrocarbon, cyclopentadiene is an unusually strong acid ($K_a = 10^{-15}$), indicating that loss of a hydrogen ion gives a particularly stable anion. (It is, for example, a much stronger acid than cycloheptatriene, $K_a = 10^{-45}$, despite the fact that the latter gives an anion that is stabilized by seven contributing structures.) Dicyclopentadienyliron (*ferrocene*), $[(C_5H_5)^-]_2Fe^{++}$, is a stable molecule that has been shown to be a "sandwich" of an iron atom between two flat five-membered rings. All carbon-carbon bonds are 1.4 A long. The rings of ferrocene undergo two typically aromatic substitution reactions: sulfonation and the Friedel-Crafts reaction.



Ferrocene

Of the cycloheptatrienyl derivatives, on the other hand, it is the cation that is unusual. Tropylium bromide, C_7H_7Br, melts above 200°, is soluble in water but insoluble in non-polar solvents, and gives an immediate precipitate of AgBr when treated with silver nitrate. This is strange behavior for an organic bromide, and strongly suggests that, even in the solid, we are dealing with an ionic compound, R^+Br^-, the cation of which is actually a *stable* carbonium ion.

Consider the electronic configuration of the cyclopentadienyl anion (Fig. 10.5). Each carbon, trigonally hybridized, is held by a σ bond to two other carbons

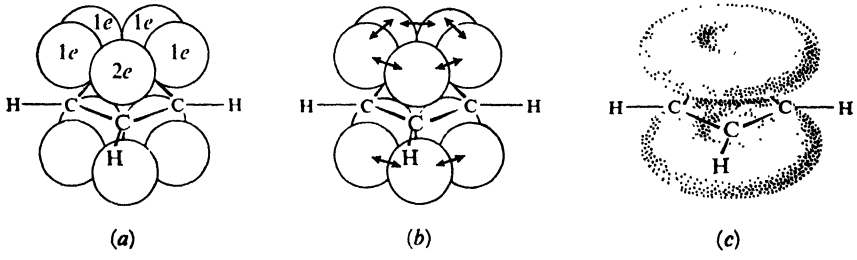


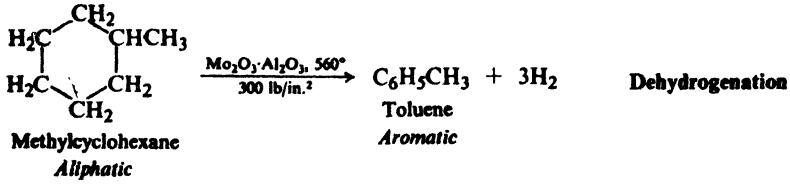
Figure 10.5. Cyclopentadienyl anion. (*a*) Two electrons in *p* orbital of one carbon; one electron in *p* orbital of each of the other carbons. (*b*) Overlap of *p* orbitals to form π bonds. (*c*) π clouds above and below plane of ring; total of six π electrons, the aromatic sextet.

and one hydrogen. The ring is a regular pentagon, whose angles (108°) are not a bad fit for the 120° trigonal angle; any instability due to imperfect overlap (angle strain) is more than made up for by the delocalization that is to follow. Four carbons have one electron each in *p* orbitals; the fifth carbon (the "one" that lost the proton, but actually, of course, indistinguishable from the others) has two

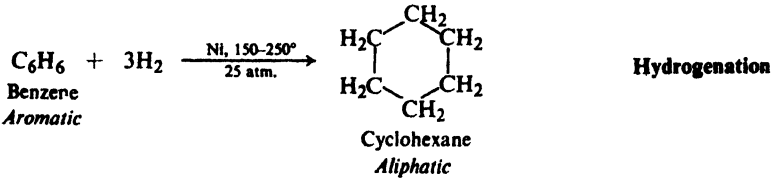
9.3 Industrial source

We have already mentioned (Sec. 3.13) that petroleum from certain areas (in particular California) is rich in cycloalkanes, known to the petroleum industry as *naphthenes*. Among these are cyclohexane, methylcyclohexane, methylcyclopentane, and 1,2-dimethylcyclopentane.

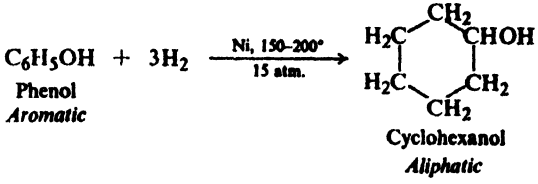
These cycloalkanes are converted by *catalytic reforming* into aromatic hydrocarbons, and thus provide one of the major sources of these important compounds (Sec. 12.4). For example:



Just as elimination of hydrogen from cyclic aliphatic compounds yields aromatic compounds, so addition of hydrogen to aromatic compounds yields cyclic aliphatic compounds, specifically cyclohexane derivatives. An important example of this is the hydrogenation of benzene to yield pure cyclohexane.



As we might expect, hydrogenation of substituted benzenes yields substituted cyclohexanes. For example:



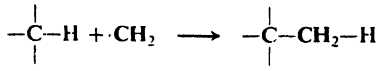
From cyclohexanol many other cyclic compounds containing a six-membered ring can be made.

9.4 Preparation

Preparation of alicyclic hydrocarbons from other aliphatic compounds generally involves two stages: (a) conversion of some open-chain compound or

both *cis* and *trans* products are formed. (*Problem:* Using the approach of Sec. 7.12, assure yourself that this is so.)

Besides addition, methylene undergoes another reaction which, quite literally, belongs in a class by itself: *insertion*.



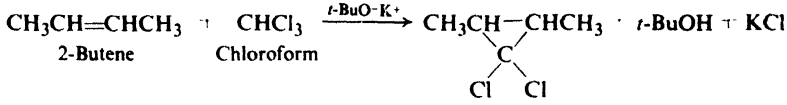
Insertion

Methylene can *insert itself* into every carbon–hydrogen bond of most kinds of molecules. We cannot take time to say more here about this remarkable reaction, except that when addition is the desired reaction, insertion becomes an annoying side-reaction.

Problem 9.14 In the gas phase, with low alkene concentration and in the presence of an inert gas, addition of methylene to the 2-butenes is, we have seen, nonstereospecific. If, however, there is present in this system a little oxygen, addition becomes completely stereospecific (*syn*). Account in detail for the effect of oxygen. (*Hint:* See Sec. 2.14.)

9.16 Substituted carbenes. α-Elimination

A more generally useful way of making cyclopropanes is illustrated by the reaction of 2-butene with chloroform in the presence of potassium *tert*-butoxide (*t*-Bu = *tert*-butyl):



2-Butene Chloroform 3,3-Dichloro-1,2-dimethylcyclopropane

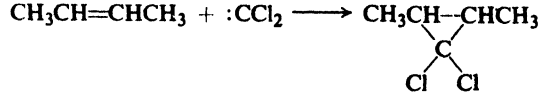
The dichlorocyclopropanes obtained can be reduced to hydrocarbons or hydrolyzed to *ketones*, the starting point for many syntheses (Chap. 19).

Here, too, reaction involves a divalent carbon compound, a derivative of methylene: *dichlorocarbene*, $:CCl_2$. It is generated in two steps, initiated by attack on chloroform by the very strong base, *tert*-butoxide ion, and then adds to the alkene.

(1) $$t\text{-BuO}:^- + H:CCl_3 \rightleftharpoons :CCl_3^- + t\text{-BuO}:H$$

(2) $$:CCl_3^- \longrightarrow :CCl_2 + Cl^-$$

Dichlorocarbene

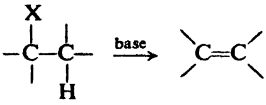
(3) 

It is believed that, because of the presence of the halogen atoms, the singlet form, with the electrons paired, is the more stable form of dichlorocarbene, and is the one adding to the double bond. (Stabilization by the halogen atoms is presumably one reason why dihalocarbenes do not generally undergo the insertion reaction that is so characteristic of unsubstituted singlet methylene.)

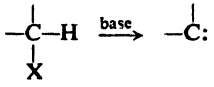
The addition of dihalocarbenes, like that of singlet methylene, is *stereospecific* and *syn*.

Problem 9.15 (a) Addition of $:CCl_2$ to cyclopentene yields a single compound. What is it? (b) Addition of :CBrCl to cyclopentene yields a mixture of stereoisomers. In light of (a), how do you account for this? What are the isomers likely to be? (*Hint:* Use models.)

In dehydrohalogenation of alkyl halides (Sec. 5.13), we have already encountered a reaction in which hydrogen ion and halide ion are eliminated from a molecule by the action of base; there —H and —X were lost from adjacent carbons, and so the process is called *β-elimination*. In the generation of the methylene shown here, both —H and —X are eliminated from the same carbon, and the process is called *α-elimination*. (Later on, in Sec. 24.12, we shall see some of the evidence for the mechanism of α-elimination shown above.)



Beta-elimination

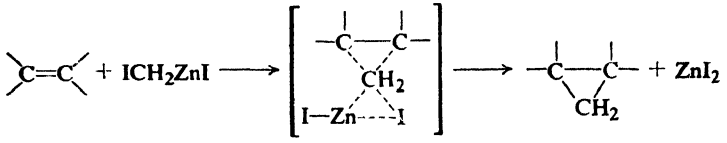


Alpha-elimination

Problem 9.16 (a) Why does $CHCl_3$ not undergo β-elimination through the action of base? (b) What factor would you expect to make α-elimination from $CHCl_3$ easier than from, say, CH_3Cl?

There are many ways of generating what appear to be carbenes. But in some cases at least, it seems clear that no *free* carbene is actually an intermediate; instead, a *carbenoid* (carbene-like) reagent transfers a carbene unit directly to a double bond. For example, in the extremely useful Simmons-Smith reaction

$$CH_2I_2 + Zn(Cu) \longrightarrow ICH_2ZnI$$



(H. E. Simmons and R. D. Smith of the du Pont Company) the carbenoid is an organozinc compound which delivers methylene stereospecifically (and without competing insertion) to the double bond.

9.17 Analysis of alicyclic hydrocarbons

A cyclopropane readily dissolves in concentrated sulfuric acid, and in this resembles an alkene or alkyne. It can be differentiated from these unsaturated hydrocarbons, however, by the fact that it is not oxidized by cold, dilute, neutral permanganate.

Other alicyclic hydrocarbons have the same kind of properties as their open-chain counterparts, and they are characterized in the same way: cycloalkanes by their general inertness, and cycloalkenes and cycloalkynes by their response to

tests for unsaturation (bromine in carbon tetrachloride, and aqueous permanganate). That one is dealing with cyclic hydrocarbons is shown by molecular formulas and by degradation products.

The properties of cyclohexane, for example, show clearly that it is an alkane. However, combustion analysis and molecular weight determination show its molecular formula to be C_6H_{12}. Only a cyclic structure (although not necessarily a six-membered ring) is consistent with both sets of data.

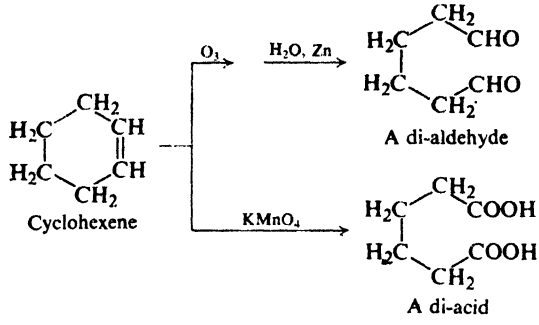
Similarly, the absorption of only one mole of hydrogen shows that cyclohexane contains only one carbon–carbon double bond; yet its molecular formula is C_6H_{10}, which in an open-chain compound would correspond to two carbon–carbon double bonds or one triple bond. Again, only a cyclic structure fits the facts.

Problem 9.17 Compare the molecular formulas of: (a) *n*-hexane and cyclohexane; (b) *n*-pentane and cyclopentane; (c) 1-hexene and cyclohexene; (d) dodecane, *n*-hexylcyclohexane, and cyclohexylcyclohexane. (e) In general, how can you deduce the number of rings in a compound from its molecular formula and degree of unsaturation?

Problem 9.18 What is the molecular formula of: (a) cyclohexane; (b) methylcyclopentane; (c) 1,2-dimethylcyclobutane? (d) Does the molecular formula give any information about the *size* of ring in a compound?

Problem 9.19 The yellow plant pigments *α*-, *β*-, and *γ-carotene*, and the red pigment of tomatoes, *lycopene*, are converted into Vitamin A in the liver. All four have the molecular formula $C_{40}H_{56}$. Upon catalytic hydrogenation, *α*- and *β*-carotene yield $C_{40}H_{78}$, *γ*-carotene yields $C_{40}H_{80}$, and lycopene yields $C_{40}H_{82}$. How many rings, if any, are there in each compound?

Cleavage products of cycloalkenes and cycloalkynes also reveal the cyclic structure. Ozonolysis of cyclohexene, for example, does not break the molecule into two aldehydes of lower carbon number, but simply into a single six-carbon compound containing *two* aldehyde groups.



Problem 9.20 Predict the ozonolysis products of: (a) cyclohexene; (b) 1-methylcyclopentene; (c) 3-methylcyclopentene; (d) 1,3-cyclohexadiene; (e) 1,4-cyclohexadiene.

Problem 9.21 Both cyclohexene and 1,7-octadiene yield the di-aldehyde $OHC(CH_2)_4CHO$ upon ozonolysis. What other facts would enable you to distinguish between the two compounds?

(Analysis of cyclic aliphatic hydrocarbons by spectroscopy will be discussed in Secs. 13.15–13.16.)

PROBLEMS

1. Draw structural formulas of:

(a) methylcyclopentane
(b) 1-methylcyclohexene
(c) 3-methylcyclopentene
(d) *trans*-1,3-dichlorocyclobutane
(e) *cis*-2-bromo-1-methylcyclopentane
(f) cyclohexylcyclohexane
(g) cyclopentylacetylene
(h) 1,1-dimethyl-4-chlorocycloheptane
(i) bicyclo[2.2.1]hepta-2,5-diene
(j) 1-chlorobicyclo[2.2.2]octane

2. Give structures and names of the principal organic products expected from each of the following reactions:

(a) cyclopropane + Cl_2, $FeCl_3$
(b) cyclopropane + Cl_2 (300°)
(c) cyclopropane + conc. H_2SO_4
(d) cyclopentane + Cl_2, $FeCl_3$
(e) cyclopentane + Cl_2 (300°)
(f) cyclopentane + conc. H_2SO_4
(g) cyclopentene + Br_2/CCl_4
(h) cyclopentene + Br_2 (300°)
(i) 1-methylcyclohexene + HCl
(j) 1-methylcyclohexene + Br_2(aq)
(k) 1-methylcyclohexene + HBr (peroxides)
(l) 1,3-cyclohexadiene + HCl
(m) cyclopentanol + H_2SO_4 (heat)
(n) bromocyclohexane + KOH(alc)
(o) cyclopentene + cold $KMnO_4$
(p) cyclopentene + HCO_2OH
(q) cyclopentene + hot $KMnO_4$
(r) chlorocyclopentane + $(C_2H_5)_2CuLi$
(s) 1-methylcyclopentene + cold conc. H_2SO_4
(t) 3-methylcyclopentene + O_3, then H_2O/Zn
(u) cyclohexene + $H_2SO_4 \longrightarrow C_{12}H_{20}$
(v) cyclopentene + $CHCl_3$ + *t*-BuOK
(w) cyclopentene + CH_2I_2 + Zn(Cu)

3. Outline all steps in the laboratory synthesis of each of the following from cyclohexanol.

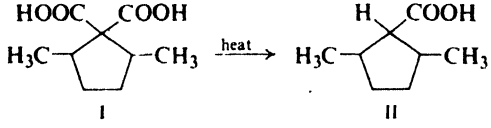
(a) cyclohexene
(b) cyclohexane
(c) *trans*-1,2-dibromocyclohexane
(d) *cis*-1,2-cyclohexanediol
(e) *trans*-1,2-cyclohexanediol
(f) $OHC(CH_2)_4CHO$
(g) adipic acid, $HOOC(CH_2)_4COOH$
(h) bromocyclohexane
(i) 2-chlorocyclohexanol
(j) 3-bromocyclohexene
(k) 1,3-cyclohexadiene
(l) cyclohexylcyclohexane
(m) *norcarane*, bicyclo[4.1.0]heptane

4. Give structure of all isomers of the following. For cyclohexane derivatives, planar formulas (p. 307) will be sufficient here. Label pairs of enantiomers, and *meso* compounds.

(a) dichlorocyclopropanes
(b) dichlorocyclobutanes
(c) dichlorocyclopentanes
(d) dichlorocyclohexanes
(e) chloro-1,1-dimethylcyclohexanes
(f) 1,3,5-trichlorocyclohexanes

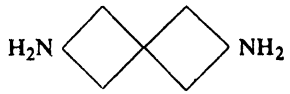
(g) There are a number of stereoisomeric 1,2,3,4,5,6-hexachlorocyclohexanes. Without attempting to draw all of them, give the structure of the most stable isomer, and show its preferred conformation.

5. (a) 2,5-Dimethyl-1,1-cyclopentanedicarboxylic acid (I) can be prepared as two optically inactive substances (A and B) of different m.p. Draw their structures. (b) Upon heating, A yields two 2,5-dimethylcyclopentanecarboxylic acids (II), and B yields only one. Assign structures to A and B.

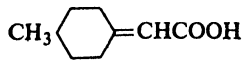


I II

6. (a) The following compounds can be resolved into optically active enantiomers.



3,3'-Diaminospiro[3.3]heptane



4-Methylcyclohexylideneacetic acid

Using models and then drawing three-dimensional formulas, account for this. Label the chiral center in each compound.

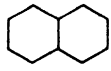
(b) Addition of bromine to optically active 4-methylcyclohexylideneacetic acid yields two optically active dibromides. Assuming a particular configuration for the starting material, draw stereochemical formulas for the products.

7. (a) *trans*-1,2-Dimethylcyclohexane exists about 99% in the diequatorial conformation. *trans*-1,2-Dibromocyclohexane (or *trans*-1,2-dichlorocyclohexane), on the other hand, exists about equally in the diequatorial and diaxial conformations; furthermore, the fraction of the diaxial conformation decreases with increasing polarity of the solvent. How do you account for the contrast between the dimethyl and dibromo (or dichloro) compounds? (*Hint:* See Problem 11, p. 141.)

(b) If *trans*-3-*cis*-4-dibromo-*tert*-butylcyclohexane is subjected to prolonged heating, t is converted into an equilibrium mixture (about 50:50) of itself and a diastereomer. What is the diastereomer likely to be? How do you account for the approximately equal stability of these two diastereomers? (Here, and in (c), consider the more stable conformation of each diastereomer to be the one with an equatorial *tert*-butyl group.)

(c) There are two more diastereomeric 3,4-dibromo-*tert*-butylcyclohexanes. What are they? How do you account for the fact that neither is present to an appreciable extent in the equilibrium mixture?

8. The compound *decalin*, $C_{10}H_{18}$, consists of two fused cyclohexane rings:

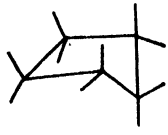


Decalin

(a) Using models, show how there can be two isomeric decalins, *cis* and *trans*. (b) How many different conformations free of angle strain are possible for *cis*-decalin? For *trans*-decalin? (c) Which is the most stable conformation of *cis*-decalin? Of *trans*-decalin? (*Hint*: Consider each ring in turn. What are the largest substituents on each ring?) (d) Account for the fact that *trans*-decalin is more stable than *cis*-decalin. (e) The difference in stability between *cis*- and *trans*-decalin is about 2 kcal/mole; conversion of one into the other takes place only under very vigorous conditions. The chair and twist-boat forms of cyclohexane, on the other hand, differ in stability by about 6 kcal/mole, yet are readily interconverted at room temperature. How do you account for the contrast? Draw energy curves to illustrate your answer.

9. Allinger (p. 305) found the energy difference between *cis*- and *trans*-1,3-di-*tert*-butylcyclohexane to be 5.9 kcal/mole, and considers that this value represents the energy difference between the chair and twist-boat forms of cyclohexane. Defend Allinger's position.

10. It has been suggested that in certain substituted cyclopentanes the ring exists preferentially in the "envelope" form:

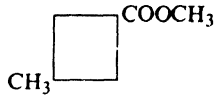


Using models, suggest a possible explanation for each of the following facts:

(a) The attachment of a methyl group to the badly strained cyclopentane ring raises the heat of combustion very little more than attachment of a methyl group to the unstrained cyclohexane ring. (*Hint:* Where is the methyl group located in the "envelope" form?)

(b) Of the 1,2-dimethylcyclopentanes, the *trans*-isomer is more stable than the *cis*. Of the 1,3-dimethylcyclopentanes, on the other hand, the *cis*-isomer is more stable than the *trans*.

(c) The *cis*-isomer of methyl 3-methylcyclobutanecarboxylate



is more stable than the *trans*-isomer

11. Each of the following reactions is carried out, and the products are separated by careful distillation, recrystallization, or chromatography. For each reaction tell how many fractions will be collected. Draw a stereochemical formula of the compound or compounds making up each fraction. Tell whether each fraction, as collected, will be optically active or optically inactive.

(a) (R)-3-hydroxycyclohexene + $KMnO_4 \longrightarrow C_6H_{12}O_3$;
(b) (R)-3-hydroxycyclohexene + $HCO_2OH \longrightarrow C_6H_{12}O_3$;
(c) (S,S)-1,2-dichlorocyclopropane + Cl_2 (300°) $\longrightarrow C_3H_3Cl_3$;
(d) *racemic* 4-methylcyclohexene + Br_2/CCl_4.

12. Outline all steps in a possible laboratory synthesis of each of the following, using alcohols of four carbons or fewer as your only organic source, and any necessary inorganic reagents. (*Remember:* Work backwards.)

(a) *cis*-1,2-di(*n*-propyl)cyclopropane;
(b) racemic *trans*-1-methyl-2-ethyl-3,3-dichlorocyclopropane.

13. Describe simple chemical tests that would distinguish between:

(a) cyclopropane and propane
(b) cyclopropane and propylene
(c) 1,2-dimethylcyclopropane and cyclopentane
(d) cyclobutane and 1-butene
(e) cyclopentane and 1-pentene
(f) cyclopentane and cyclopentene
(g) cyclohexanol and *n*-butylcyclohexane
(h) 1,2-dimethylcyclopentene and cyclopentanol
(i) cyclohexane, cyclohexene, cyclohexanol, and bromocyclohexane

14. How many rings does each of the following contain?

(a) *Camphane*, $C_{10}H_{18}$, a terpene related to camphor, takes up no hydrogen. (*b*) *Cholestane*, $C_{27}H_{48}$, a steroid of the same ring structure as cholesterol, cortisone, and the sex hormones, takes up no hydrogen. (c) *β-Phellandrene*, $C_{10}H_{16}$, a terpene, reacts with bromine to form $C_{10}H_{16}Br_4$. (d) *Ergocalciferol* (so-called "Vitamin D_2"), $C_{28}H_{44}O$, an alcohol, gives $C_{28}H_{52}O$ upon catalytic hydrogenation. (e) How many double bonds does ergocalciferol contain?

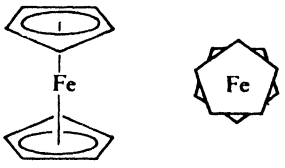
15. On the basis of the results of catalytic hydrogenation, how many rings does each of the following aromatic hydrocarbons contain?

(a) *benzene* (C_6H_6) $\longrightarrow C_6H_{12}$
(b) *naphthalene* ($C_{10}H_8$) $\longrightarrow C_{10}H_{18}$
(c) *toluene* (C_7H_8) $\longrightarrow C_7H_{14}$
(d) *anthracene* ($C_{14}H_{10}$) $\longrightarrow C_{14}H_{24}$
(e) *phenanthrene* ($C_{14}H_{10}$) $\longrightarrow C_{14}H_{24}$
(f) 3,4-*benzpyrene* ($C_{20}H_{12}$) $\longrightarrow C_{20}H_{32}$
(g) *chrysene* ($C_{18}H_{12}$) $\longrightarrow C_{18}H_{30}$

(Check your answers by use of the index.)

Each molecule is a hybrid of either five or seven equivalent structures, with the charge or odd electron on each carbon. Yet, of the six compounds, only *two* give evidence of *unusually* high stability: the cyclopentadienyl anion and the cycloheptatrienyl cation (*tropylium ion*).

For a hydrocarbon, cyclopentadiene is an unusually strong acid ($K_a = 10^{-15}$), indicating that loss of a hydrogen ion gives a particularly stable anion. (It is, for example, a much stronger acid than cycloheptatriene, $K_a = 10^{-45}$, despite the fact that the latter gives an anion that is stabilized by seven contributing structures.) Dicyclopentadienyliron (*ferrocene*), $[(C_5H_5)^-]_2Fe^{++}$, is a stable molecule that has been shown to be a "sandwich" of an iron atom between two flat five-membered rings. All carbon–carbon bonds are 1.4 A long. The rings of ferrocene undergo two typically aromatic substitution reactions: sulfonation and the Friedel-Crafts reaction.



Ferrocene

Of the cycloheptatrienyl derivatives, on the other hand, it is the cation that is unusual. Tropylium bromide, C_7H_7Br, melts above 200°, is soluble in water but insoluble in non-polar solvents, and gives an immediate precipitate of AgBr when treated with silver nitrate. This is strange behavior for an organic bromide, and strongly suggests that, even in the solid, we are dealing with an ionic compound, R^+Br^-, the cation of which is actually a *stable* carbonium ion.

Consider the electronic configuration of the cyclopentadienyl anion (Fig. 10.5). Each carbon, trigonally hybridized, is held by a σ bond to two other carbons

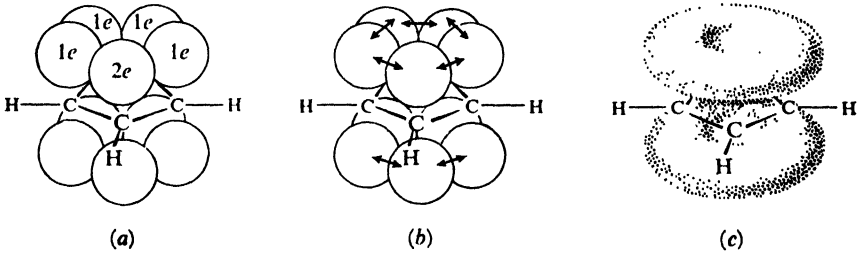


Figure 10.5. Cyclopentadienyl anion. (*a*) Two electrons in *p* orbital of one carbon; one electron in *p* orbital of each of the other carbons. (*b*) Overlap of *p* orbitals to form π bonds. (*c*) π clouds above and below plane of ring; total of six π electrons, the aromatic sextet.

and one hydrogen. The ring is a regular pentagon, whose angles (108°) are not a bad fit for the 120° trigonal angle; any instability due to imperfect overlap (angle strain) is more than made up for by the delocalization that is to follow. Four carbons have one electron each in *p* orbitals; the fifth carbon (the "one" that lost the proton, but actually, of course, indistinguishable from the others) has two

electrons. Overlap of the *p* orbitals gives rise to π clouds containing a total of six electrons, the aromatic sextet.

In a similar way, we arrive at the configuration of the tropylium ion. It is a regular heptagon (angles 128.5°). Six carbons contribute one *p* electron each, and the seventh contributes only an empty *p* orbital. Result: the aromatic sextet.

The ions are conveniently represented as:

Cyclopentadienyl anion

Cycloheptatrienyl cation

(Tropylium ion)

Six is the Hückel number most often encountered, and for good reason. To provide *p* orbitals, the atoms of the aromatic ring must be trigonally (sp^2) hybridized, which means, ideally, bond angles of 120°. To permit the overlap of the *p* orbitals that gives rise to the π cloud, the aromatic compound must be flat, or nearly so. The number of trigonally hybridized atoms that will fit a flat ring without undue angle strain (i.e., with reasonably good overlap for π bond formation) is five, six, or seven. Six is the Hückel number of π electrons that can be provided—as we have just seen—by these numbers of atoms. (It is surely no coincidence that benzene, our model for aromatic character, is the "perfect" specimen: six carbons to provide six π electrons and to make a hexagon whose angles exactly match the trigonal angle.)

Now, what evidence is there that other Hückel numbers—2, 10, 14, etc.—are also "magic" numbers? We cannot expect aromatic character necessarily to appear here in the form of highly stable compounds comparable to benzene and its derivatives. The rings will be too small or too large to accommodate trigonally hybridized atoms very well, so that any stabilization due to aromaticity may be largely offset by angle strain or poor overlap of *p* orbitals, or both.

We must look for stability on a *comparative* basis—as was done above with the cyclopentadienyl and cycloheptatrienyl derivatives—and may find evidence of aromaticity only in the fact that one molecular species is *less unstable* than its relatives. The net effect of a great deal of elegant work is strongly to support the $4n + 2$ rule. The question now seems rather to be: over how unfavorable a combination of angle strain and multiple charge can aromaticity manifest itself?

Problem 10.6 Ronald Breslow (of Columbia University) found that treatment of 3-chlorocyclopropene with $SbCl_5$ yields a stable crystalline solid, I, of formula

3-Chlorocyclopropene

$C_3H_3SbCl_6$, insoluble in non-polar solvents but soluble in polar solvents like nitromethane, acetonitrile, or sulfur dioxide. The nmr spectrum of I shows three exactly equivalent protons. 3-Chlorocyclopropene reacts with $AgBF_4$ to give AgCl and a solution with an nmr spectrum identical to that of I. Treatment of I with chloride ion regenerates 3-chlorocyclopropene.

Conversion of I into $C_3H_3^+$ by electron impact (Sec. 5.16) requires 235 kcal/mole, as compared with 255 kcal/mole for conversion of allyl chloride into $C_3H_5^+$.

(a) Give in detail the most likely structure of I, and show how this structure accounts for the various observations. (b) Of what theoretical significance are these findings?

Problem 10.7 1,3,5,7-*Cyclooctatetraene*, C_8H_8, has a heat of combustion (compare Problem 10.2, p. 322) of 1095 kcal; it rapidly decolorizes cold aqueous $KMnO_4$ and reacts with Br_2/CCl_4 to yield $C_8H_8Br_8$. (a) How should its structure be represented? (b) Upon what theoretical grounds might one have predicted its structure and properties? (c) Treatment of cyclooctatetraene with potassium metal has been found to yield a stable compound $2K^+C_8H_8^{--}$. Of what significance is the formation of this salt? (d) Using models, suggest a possible shape (or shapes) for cyclooctatetraene. What shape would you predict for the $C_8H_8^{--}$ anion?

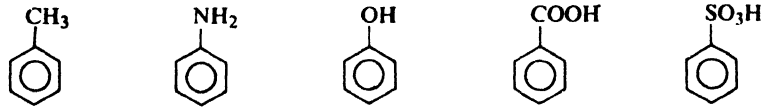
10.11 Nomenclature of benzene derivatives

In later chapters we shall consider in detail the chemistry of many of the derivatives of benzene. Nevertheless, for our present discussion of the reactions of the benzene ring it will be helpful for us to learn to name some of the more important of these derivatives.

For many of these derivatives we simply prefix the name of the substituent group to the word *-benzene*, as, for example, in *chlorobenzene*, *bromobenzene*, *iodobenzene*, or *nitrobenzene*. Other derivatives have special names which may

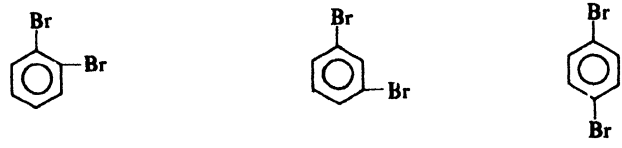
Chlorobenzene Bromobenzene Iodobenzene Nitrobenzene

show no resemblance to the name of the attached substituent group. For example, methylbenzene is always known as *toluene*, aminobenzene as *aniline*, hydroxybenzene as *phenol*, and so on. The most important of these special compounds are:



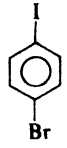
Toluene Aniline Phenol Benzoic acid Benzenesulfonic acid

If several groups are attached to the benzene ring, we must not only tell what they are, but also indicate their relative positions. The three possible isomers of a disubstituted benzene are differentiated by the use of the names ***ortho***, ***meta***, and ***para***. For example:

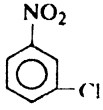


o-Dibromobenzene *ortho* *m*-Dibromobenzene *meta* *p*-Dibromobenzene *para*

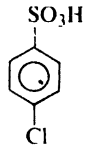
If the two groups are different, and neither is a group that gives a special name to the molecule, we simply name the two groups successively and end the word with *-benzene*, as, for example, *chloronitrobenzene*, *bromoiodobenzene*, etc. If one of the two groups is the kind that gives a special name to the molecule, then the compound is named as a derivative of that special compound, as, for example, *nitrotoluene*, *bromophenol*, etc.



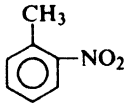
p-Bromoiodobenzene



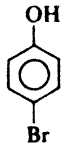
m-Chloronitrobenzene



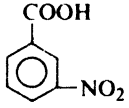
p-Chlorobenzenesulfonic acid



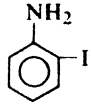
o-Nitrotoluene



p-Bromophenol

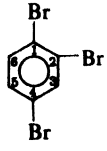


m-Nitrobenzoic acid

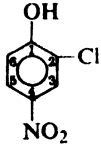


o-Iodoaniline

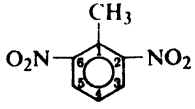
If more than two groups are attached to the benzene ring, numbers are used to indicate their relative positions. For example:



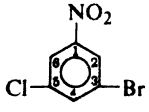
1,2,4-Tribromobenzene



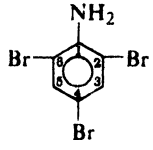
2-Chloro-4-nitrophenol



2,6-Dinitrotoluene



3-Bromo-5-chloronitrobenzene



2,4,6-Tribromoaniline

If all the groups are the same, each is given a number, the sequence being the one that gives the lowest combination of numbers; if the groups are different, then the last-named group is understood to be in position 1 and the other numbers conform to that, as, for example, in *3-bromo-5-chloronitrobenzene*. If one of the groups that gives a special name is present, then the compound is named as having the special group in position 1; thus in *2,6-dinitrotoluene* the methyl group is considered to be at the 1-position.

Problem 10.8 You have three bottles containing the three isomeric dibromobenzenes; they have the melting points +87°, +6°, and −7°. By a great deal of work,

you prepare six dibromonitrobenzenes ($C_6H_3Br_2NO_2$) and find that, of the six, *one* is related to (derived from or convertible into) the dibromobenzene of m.p. +87°, *two* to the isomer of m.p. +6°, and *three* to the isomer of m.p. −7°.

Label each bottle with the correct name of *ortho*, *meta*, or *para*.

(This work was actually carried out by Wilhelm Körner, of the University of Milan, and was the first example of the **Körner method of absolute orientation.**)

10.12 Quantitative elemental analysis: nitrogen and sulfur

This chapter has dealt with the structure of benzene and with some of its reactions. It is well to remind ourselves again that all this discussion has meaning only because it is based upon solid facts. As we saw earlier (Sec. 2.24), we can discuss the structure and reactions of a compound only when we know its molecular formula and the molecular formulas of its products.

To know a molecular formula we must know what elements are present in the compound, and in what proportions. In Sec. 2.25 we saw how various elements can be detected in an organic compound, and in Sec. 2.26 how the percentage of carbon, hydrogen, and halogen can be measured.

Quantitative analysis for nitrogen is carried out either (a) by the *Dumas method* or (b) by the *Kjeldahl method.* The Kjeldahl method is somewhat more convenient, particularly if many analyses must be carried out; however, it cannot be used for all kinds of nitrogen compounds.

In the Dumas method, the organic compound is passed through a tube containing, first, hot copper oxide and, next, hot copper metal gauze. The copper oxide oxidizes the compound (as in the carbon–hydrogen combustion, Sec. 2.26), converting combined nitrogen into molecular nitrogen. The copper gauze reduces any nitrogen oxides that may be formed, also to molecular nitrogen. The nitrogen gas is collected and its volume is measured. For example, an 8.32-mg sample of *aniline* yields 1.11 cc of nitrogen at 21° and 743 mm pressure (corrected for the vapor pressure of water). We calculate the volume at standard temperature and pressure,

$$\text{vol. } N_2 \text{ at S.T.P.} = 1.11 \times \frac{273}{273 + 21} \times \frac{743}{760} = 1.01 \text{ cc}$$

and, from it, the weight of nitrogen,

$$\text{wt. N} = \frac{1.01}{22400} \times (2 \times 14.01) = 0.00126 \text{ g } \textit{or } 1.26 \text{ mg}$$

and, finally, the percentage of nitrogen in the sample

$$\% \text{ N} = \frac{1.26}{8.32} \times 100 = 15.2\%$$

Problem 10.9 Why is the nitrogen in the Dumas analysis collected over 50% aqueous KOH rather than, say, pure water, aqueous NaCl, or mercury?

In the Kjeldahl method, the organic compound is digested with concentrated sulfuric acid, which converts combined nitrogen into ammonium sulfate. The solution is then made alkaline. The ammonia thus liberated is distilled, and its amount is determined by titration with standard acid. For example, the ammonia

formed from a 3.51-mg sample of aniline neutralizes 3.69 ml of 0.0103 N acid. For every milliequivalent of acid there is a milliequivalent of ammonia, and a

$$\text{milligram-atoms N} = \text{millieqivalents } NH_3 = \text{milliequivalents acid} = 3.69 \times 0.0103 = 0.0380$$

milligram-atom of nitrogen. From this, the weight and, finally, the percentage of nitrogen in the compound can be calculated.

$$\text{wt. N} = \text{milligram-atoms N} \times 14.01 = 0.0380 \times 14.01 = 0.53 \text{ mg}$$

$$\%\text{N} = \frac{0.53}{3.51} \times 100 = 15.1\%$$

Sulfur in an organic compound is converted into sulfate ion by the methods used in halogen analysis (Sec. 2.26): treatment with sodium peroxide or with nitric acid (*Carius method*). This is then converted into barium sulfate, which is weighed.

Problem 10.10 A Dumas nitrogen analysis of a 5.72-mg sample of *p-phenylenediamine* gave 1.31 cc of nitrogen at 20° and 746 mm. The gas was collected over saturated aqueous KOH solution (the vapor pressure of water, 6 mm). Calculate the percentage of nitrogen in the compound.

Problem 10.11 A Kjeldahl nitrogen analysis of a 3.88-mg sample of *ethanolamine* required 5.73 ml of 0.0110 N hydrochloric acid for titration of the ammonia produced. Calculate the percentage of nitrogen in the compound.

Problem 10.12 A Carius sulfur analysis of a 4.81-mg sample of *p-toluenesulfonic acid* gave 6.48 mg of $BaSO_4$. Calculate the percentage of sulfur in the compound.

Problem 10.13 How does each of the above answers compare with the theoretical value calculated from the formula of the compound? (Each compound is listed in the index.)

PROBLEMS

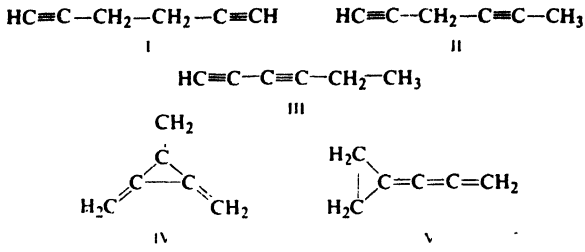
1. Draw structures of:

(a) *p*-dinitrobenzene
(b) *m*-bromonitrobenzene
(c) *o*-chlorobenzoic acid
(d) *m*-nitrotoluene
(e) *p*-bromoaniline
(f) *m*-iodophenol
(g) mesitylene (1,3,5-trimethylbenzene)
(h) 3,5-dinitrobenzenesulfonic acid
(i) 4-chloro-2,3-dinitrotoluene
(j) 2-amino-5-bromo-3-nitrobenzoic acid
(k) *p*-hydroxybenzoic acid
(l) 2,4,6-trinitrophenol (picric acid)

2. Give structures and names of all the possible isomeric:

(a) xylenes (dimethylbenzenes)
(b) aminobenzoic acids ($H_2NC_6H_4COOH$)
(c) trimethylbenzenes
(d) dibromonitrobenzenes
(e) bromochlorotoluenes
(f) trinitrotoluenes

3. (a) How many isomeric monosubstitution products are theoretically possible from each of the following structures of formula C_6H_6? (b) How many disubstitution products? (c) Which structures, if any, would be acceptable for benzene on the basis of isomer number?



4. Give structures and names of all theoretically possible products of the ring mononitration of:

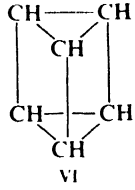
(a) *o*-dichlorobenzene
(b) *m*-dichlorobenzene
(c) *p*-dichlorobenzene
(d) *o*-bromochlorobenzene
(e) *m*-bromochlorobenzene
(f) *p*-bromochlorobenzene
(g) *o*-chloronitrobenzene
(h) *m*-chloronitrobenzene
(i) *p*-chloronitrobenzene
(j) 1,3,5-trimethylbenzene
(k) 4-bromo-1,2-dimethylbenzene
(l) *p*-ethyltoluene

5. Give structures and names of all benzene derivatives that *theoretically* can have the indicated number of isomeric ring-substituted derivatives.

(a) C_8H_{10}: one monobromo derivative
(b) C_8H_{10}: two monobromo derivatives
(c) C_8H_{10}: three monobromo derivatives
(d) C_9H_{12}: one mononitro derivative
(e) C_9H_{12}: two mononitro derivatives
(f) C_9H_{12}: three mononitro derivatives
(g) C_9H_{12}: four mononitro derivatives

6. There are three known tribromobenzenes, of m.p. 44°, 87°, and 120°. Could these isomers be assigned structures by use of the Körner method (Problem 10.8, p. 332)? Justify your answer.

7. For a time the prism formula VI, proposed in 1869 by Albert Ladenburg of Germany, was considered as a possible structure for benzene, on the grounds that it would yield one monosubstitution product and three isomeric disubstitution products.



(a) Draw Ladenburg structures of three possible isomeric dibromobenzenes.
(b) On the basis of the Körner method of absolute orientation, label each Ladenburg structure in (a) as *ortho*, *meta*, or *para*.
(c) In light of Chap. 4, can the Ladenburg formula actually pass the test of isomer number?
(Derivatives of Ladenburg "benzene," called *prismanes*, have actually been made.)

8. In 1874 Griess (p. 1077) reported that he had decarboxylated the six known diaminobenzoic acids, $C_6H_3(NH_2)_2COOH$, to the diaminobenzenes. Three acids gave a diamine of m.p. 63°, two acids gave a diamine of m.p. 104°, and one acid gave a diamine of m.p. 142°. Draw the structural formulas for the three isomeric diaminobenzenes and label each with its melting point.

9. For which of the following might you expect aromaticity (geometry permitting)?

(a) The annulenes containing up to 20 carbons. (*Annulenes* are monocyclic compounds of the general formula $[-CH{=}CH-]_n$.)

(b) The monocyclic polyenes C_9H_{10}, $C_9H_9^+$, $C_9H_9^-$.

10. The properties of *pyrrole*, commonly represented by VII,

VII

show that it is aromatic. Account for its aromaticity on the basis of orbital theory. (*Hint:* See Sec. 10.10. Check your answer in Sec. 31.2.)

11. When benzene is treated with chlorine under the influence of ultraviolet light, a solid material of m.wt. 291 is formed. Quantitative analysis gives an empirical formula of CHCl. (a) What is the molecular formula of the product? (b) What is a possible structural formula? (c) What kind of reaction has taken place? (d) Is the product aromatic? (e) Actually, the product can be separated into six isomeric compounds, one of which is used as an insecticide (Gammexane or Lindane). How do these isomers differ from each other? (f) Are more than six isomers possible?

12. Can you account for the following order of acidity. (*Hint:* See Sec. 8.10.)

acetylene > benzene > *n*-pentane