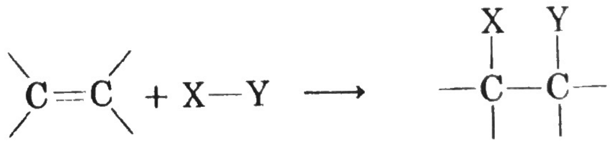
APTER 4

Alkenes and Alkynes

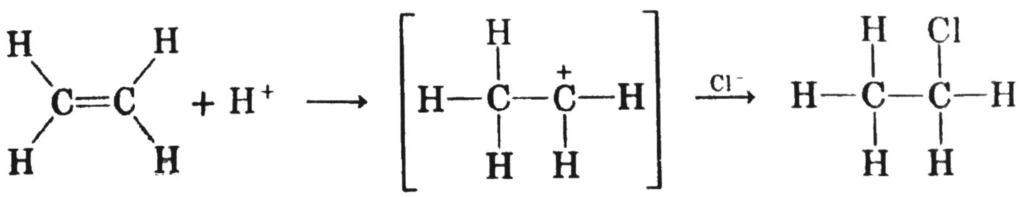
We saw in the previous chapter how organic reactions can be classified, and we developed some general ideas about how reactions can be described. In this chapter, we'll apply those general ideas to a systematic study of the alkene and alkyne families of compounds. In particular, we'll see that the most important reaction of these two functional groups is the addition of various reagents X–Y to yield saturated products:



An alkene An addition product

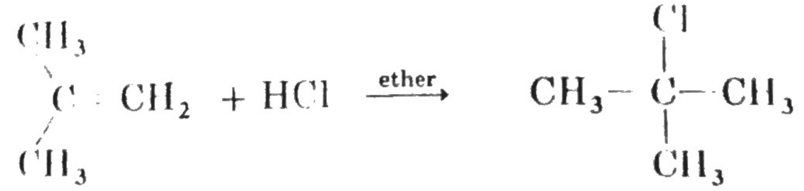
1 ADDITION OF HX TO ALKENES

We know from Section 3.8 that alkenes react with HCl to yield alkyl chloride addition products. For example, ethylene reacts with HCl to give chloroethane. The reaction takes place in two steps and involves a carbocation intermediate:

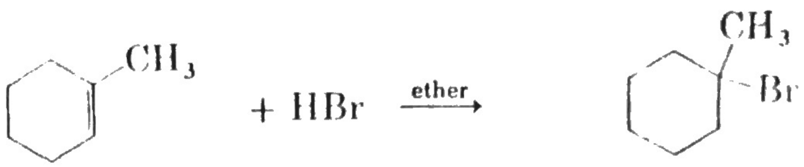


Ethylene Carbocation intermediate Chloroethane

The addition of halogen acids HX to alkenes is a general reaction that allows chemists to prepare a variety of products. Thus, HCl, HBr, and HI all add to alkenes:[1]



2-Methylpropene — 2-Chloro-2-methylpropane (94%)



1-Methylcyclohexene — 1-Bromo-1-methylcyclohexane (91%)

$$CH_3CH_2CH_2CH{=}CH_2 + HI \xrightarrow{\text{ether}} CH_3CH_2CH_2\underset{}{\overset{I}{C}}HCH_3$$

1-Pentene — 2-Iodopentane

[1] Organic reaction equations can be written in different ways to emphasize different points. For example, the reaction of ethylene with HCl might be written in the format A + B → C to emphasize that *both* reaction partners are equally important for the purposes of the discussion. The reaction solvent and notes about other reaction conditions such as temperature are usually written either above or below the reaction arrow.

solvent

$$H_2C{=}CH_2 + HCl \xrightarrow[25^\circ C]{\text{ether}} CH_3CH_2Cl$$

Alternatively, we might choose to write the same reaction in the format

$$A \xrightarrow{B} C$$

to emphasize that reagent A is the organic starting material whose chemistry is of greater interest. Reagent B is then placed above the reaction arrow, together with notes about solvent and reaction conditions. For example:

reagent

$$H_2C{=}CH_2 \xrightarrow[\text{ether, }25^\circ C]{HCl} CH_3CH_2Cl$$

solvent

Both reaction formats are frequently used in chemistry, and you sometimes have to look at the overall transformation to see what the different roles of the chemicals shown next to the reaction arrows are.

ORIENTATION OF ALKENE ADDITION REACTIONS: MARKOVNIKOV'S RULE

Look carefully at the reactions in the previous section. In every case, an unsymmetrically substituted alkene has given a *single* addition product rather than the mixture that might have been expected. For example, 2-methylpropene might have added HCl to give 1-chloro-2-methylpropane, but it didn't; it gave only 2-chloro-2-methylpropane. We say that reactions are **regiospecific** (*ree*-jee-oh-specific) when only one of the two possible directions of addition is observed.

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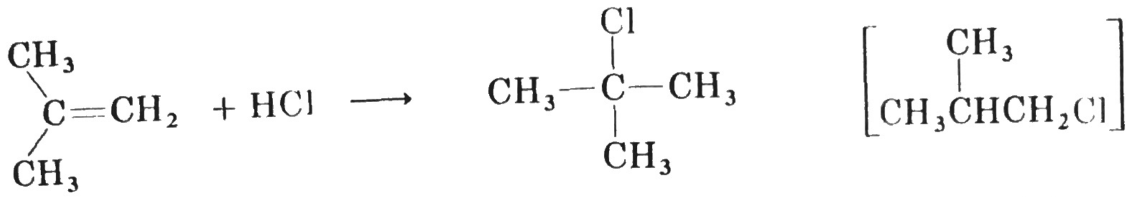
A regiospecific reaction:



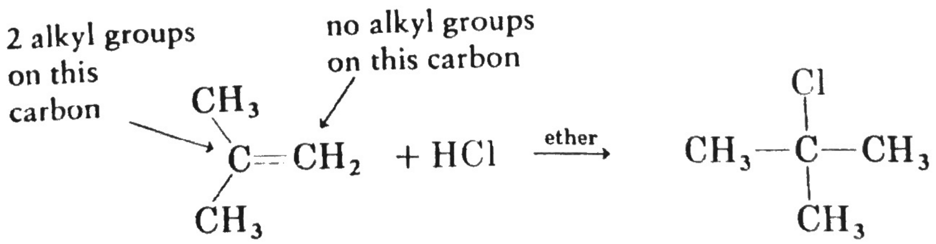
2-Methylpropene

2-Chloro-2-methylpropane (sole product)

1-Chloro-2-methylpropane (not formed)

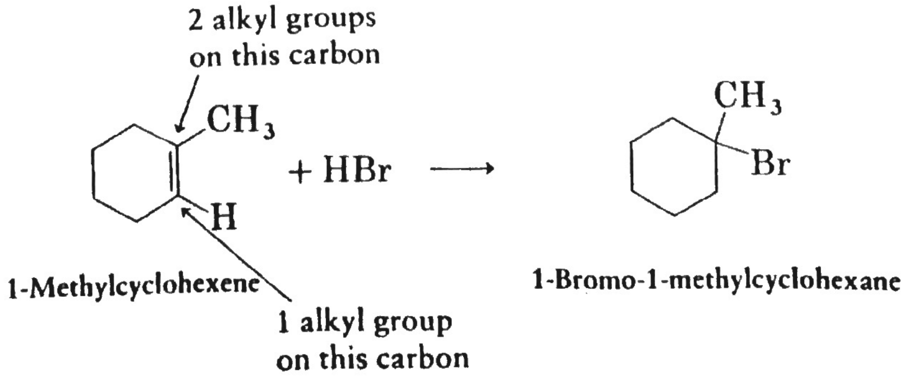
From an examination of many such reactions, the Russian chemist Vladimir Markovnikov proposed in 1905 what has come to be known as **Markovnikov's rule:** *In the addition of HX to an alkene, the H attaches to the carbon that has fewer alkyl substituents, and the X attaches to the carbon that has more alkyl substituents.*

kovnikov's rule le for licting the ntation ılkene ctrophilic lition reactions



2-Methylpropene

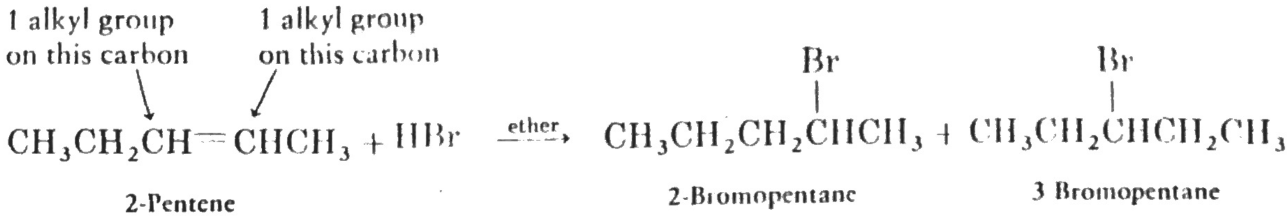
2-Chloro-2-methylpropane



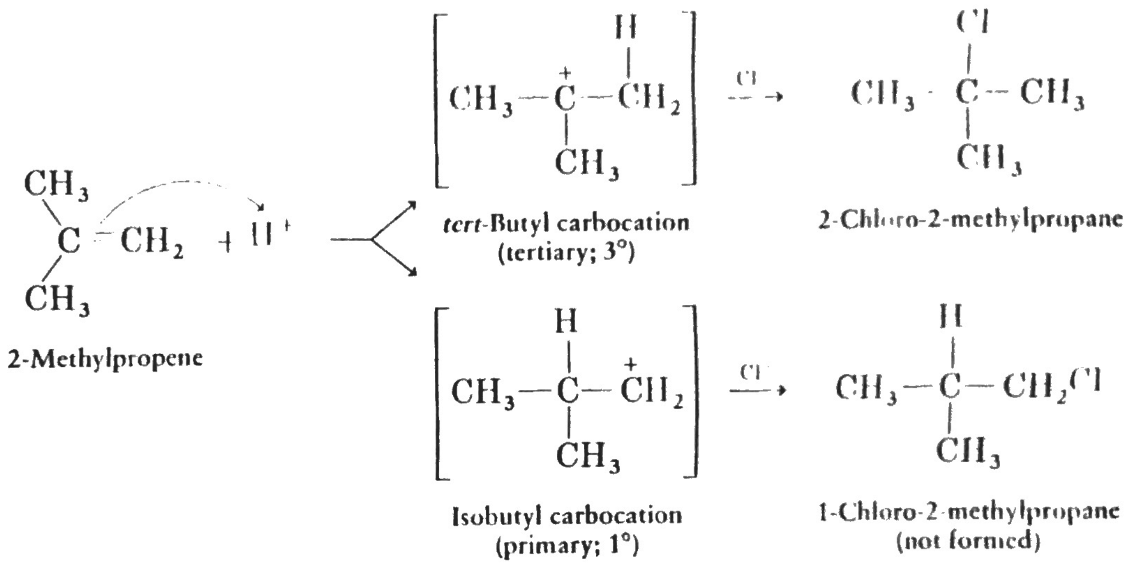
1-Methylcyclohexene

1-Bromo-1-methylcyclohexane

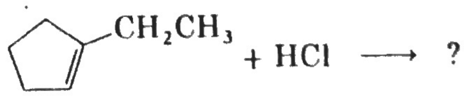
When both ends of the double bond have the same degree of substitution, however,



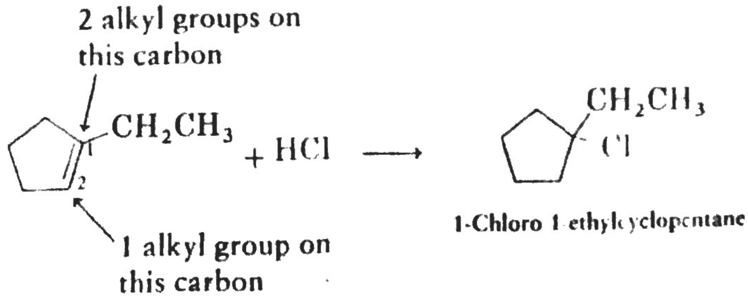
Since carbocations are involved as intermediates in these reactions (Section 3.11), another way to express Markovnikov's rule is to say that, in the addition of HX to alkenes, the more highly substituted carbocation intermediate is formed in preference to the less highly substituted one. For example, addition of H^+ to 2-methylpropene yields the intermediate tertiary carbocation rather than the primary carbocation. Why should this be?



PRACTICE PROBLEM 4.1 What product would you expect from reaction of HCl with 1-ethylcyclopentene?



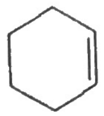
SOLUTION Markovnikov's rule predicts that the hydrogen will add to the double-bond carbon that has one alkyl group (C2 on the ring), and the chlorine will add to the double-bond carbon that has two alkyl groups (C1 on the ring). The expected product is 1-chloro-1-ethylcyclopentane.



PROBLEM 4.1 Predict the products of these reactions:

(a) $CH_3CH_2CH{=}CH_2 + HCl \longrightarrow$?

(b) $\overset{\displaystyle CH_3}{\overset{|}{CH_3C}}{=}CHCH_2CH_3 + HI \longrightarrow$?

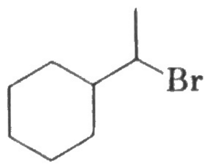
(c)  $+ HCl \longrightarrow$?

PROBLEM 4.2 What alkenes would you start with to prepare these alkyl halides?

(a) Bromocyclopentane

(b) $CH_3CH_2CHBrCH_2CH_2CH_3$

(c) 1-Iodo-1-isopropylcyclohexane

(d) 

3 CARBOCATION STRUCTURE AND STABILITY

To understand why Markovnikov's rule works, we need to learn more about the structure and stability of substituted carbocations. Regarding structure, evidence has shown that carbocations are *planar*. The positively charged carbon atom is sp^2 hybridized, and the three substituents are oriented to the corners of an equilateral triangle (Figure 4.1). Since there are only six electrons in the carbon valence shell, and since all six are used in the three sigma bonds, the p orbital extending above and below the plane is vacant.

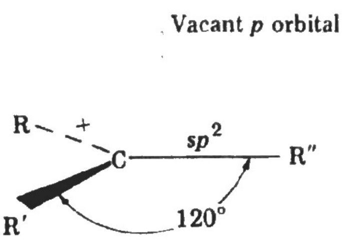
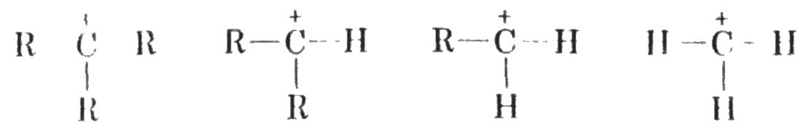


FIGURE 4.1 Carbocation structure. The carbon is sp^2 hybridized and has a vacant p orbital.

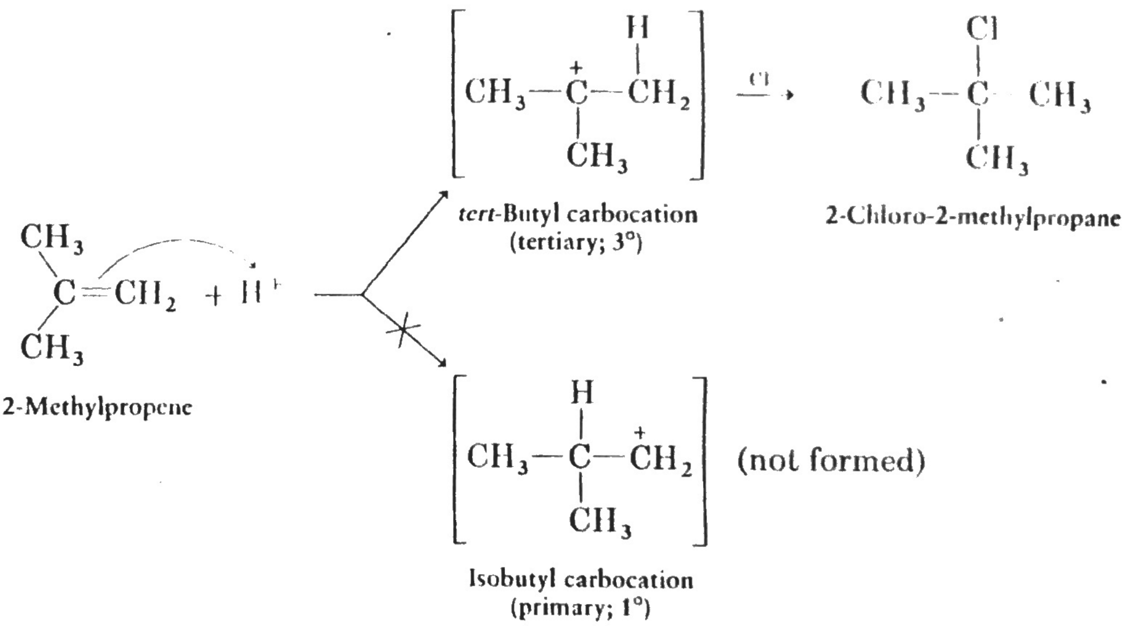
Regarding stability, measurements show that carbocation stability increases with increasing alkyl substitution. More highly substituted carbocations are more stable than less highly substituted ones because alkyl groups tend to donate electrons to the positively charged carbon atom. The more alkyl groups there are, the more electron donation there is and the more stable the carbocation.



Tertiary (3°) > Secondary (2°) > Primary (1°) > Methyl

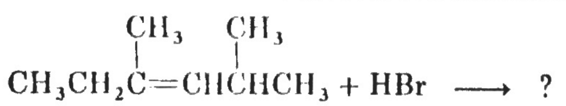
More stable ⟵ Less stable

With the above information, we can now explain Markovnikov's rule. In the reaction of 2-methylpropene with HCl, for example, the intermediate carbocation might have either *three* alkyl substituents (a tertiary cation, 3°) or *one* alkyl substituent (a primary cation, 1°). Since the tertiary cation is more stable than the primary one, it's the tertiary cation that forms as the reaction intermediate, thus leading to the observed tertiary alkyl chloride product.

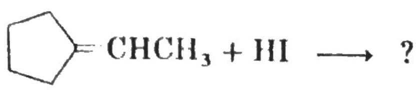


PROBLEM 4.3 Show the structures of the carbocation intermediates you would expect in these reactions:

(a)



(b)



4.4 HYDRATION OF ALKENES

Water can be added to simple alkenes like ethylene and 2-methylpropene to yield alcohols, ROH. Industrially, more than 300,000 tons of ethanol are produced each

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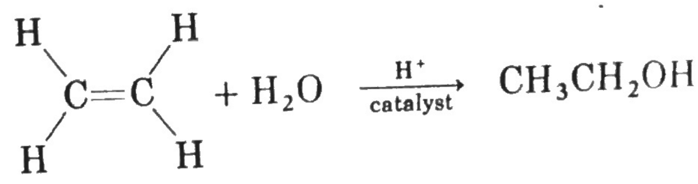
year in the United States by this **hydration** method:



Ethylene

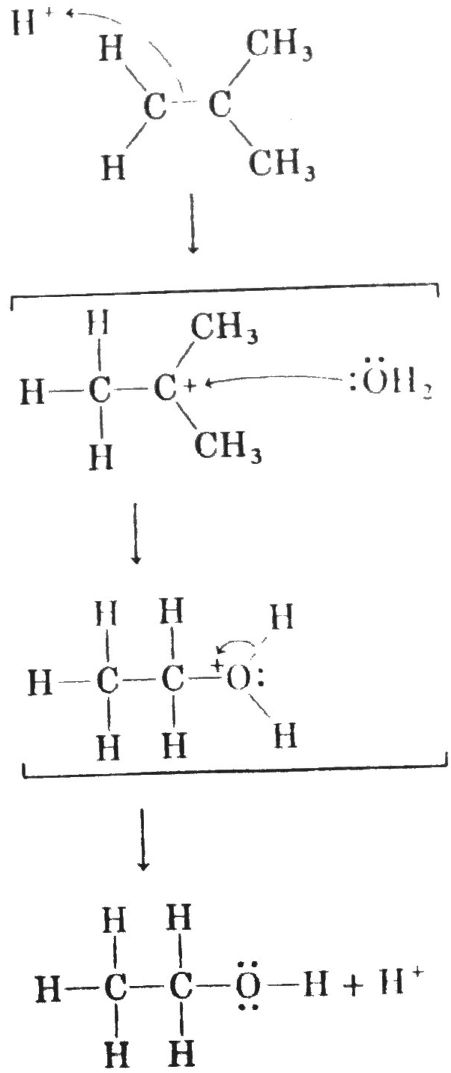
Ethanol

The hydration of an alkene takes place on reaction with aqueous acid by a mechanism similar to that of HX addition. Thus, reaction of the alkene double bond with H^+ yields a carbocation intermediate that then reacts with water as nucleophile to yield a protonated alcohol (ROH_2^+) product. Loss of H^+ from the protonated alcohol gives the neutral alcohol and regenerates the acid catalyst (Figure 4.2). The addition of water to an unsymmetrical alkene follows Markovnikov's rule, just as addition of HX does, giving the more highly substituted alcohol as product.

The alkene double bond reacts with H^+ to yield a carbocation intermediate.

Water acts as a nucleophile to donate a pair of electrons to form a carbon–oxygen bond and produce a protonated alcohol intermediate.

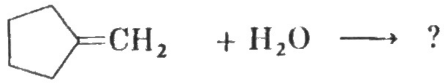
Loss of H^+ from the protonated alcohol intermediate then gives the neutral alcohol product and regenerates the acid catalyst.



... lydration of an alkene

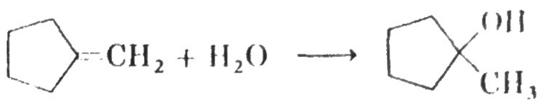
Unfortunately, the reaction conditions required for hydration are so severe that molecules are sometimes destroyed by the high temperatures and strongly acidic conditions. For example, the hydration of ethylene to produce ethanol requires a sulfuric acid catalyst and reaction temperatures of up to 250°C.

PRACTICE PROBLEM 4.2 What product would you expect from addition of water to methylenecyclopentane?



Methylenecyclopentane

SOLUTION According to Markovnikov's rule, H^+ adds to the carbon that already has more hydrogens (the CH_2 carbon), and $-OH$ adds to the carbon that has fewer hydrogens (the ring carbon). Thus, the product will be a tertiary alcohol.

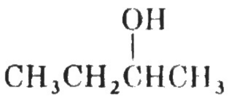


PROBLEM 4.4 What product would you expect to obtain from addition of water to these alkenes?

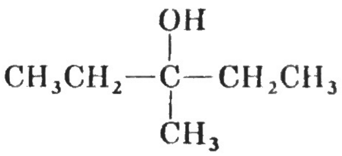
(a) $CH_3CH_2C(CH_3){=}CHCH_2CH_3$ (b) 1-Methylcyclopentene
(c) 2,5-Dimethyl-2-heptene

PROBLEM 4.5 What alkenes do you suppose these alcohols were made from?

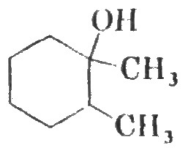
(a)



(b)

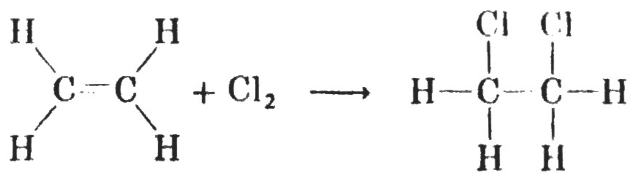


(c)



4.5 ADDITION OF HALOGENS TO ALKENES

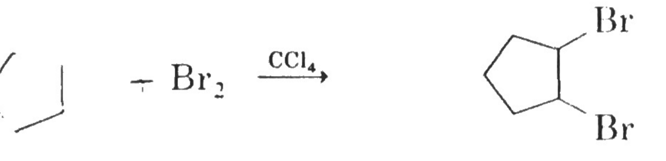
Many other reagents besides HX and H_2O add to alkenes. Bromine and chlorine are particularly effective, and their reaction with alkenes provides a general method of synthesis of 1,2-dihaloalkanes. More than 5 million tons of 1,2-dichloroethane (also called ethylene dichloride) are synthesized each year in the chemical industry by addition of Cl_2 to ethylene. The product is used both as a solvent and as starting material for the synthesis of poly(vinyl chloride), PVC.



Ethylene

1,2-Dichloroethane (ethylene dichloride)

Addition of bromine also serves as a simple and rapid laboratory test for the presence of a carbon–carbon double bond in a molecule of unknown structure. A sample of unknown structure is dissolved in tetrachloromethane, CCl_4, and several drops of bromine are added. Immediate disappearance of the reddish bromine color signals a positive test, indicating that the sample is an alkene.



Cyclopentene 1,2-Dibromocyclopentane (95%)

Bromine and chlorine react with alkenes by the pathway shown in Figure 4.3. The pi-electron pair of the alkene attacks the Br_2 molecule, displacing Br^-. The net result is that electrophilic Br^+ adds to the alkene in much the same way that H^+ does, yielding an intermediate carbocation that immediately reacts further with Br^- to give the dibromo addition product.

The electron pair from the double bond attacks the polarized bromine, forming a C–Br bond and causing the Br–Br bond to break. Bromide ion departs with both electrons from the former Br Br bond.

Bromide ion uses an electron pair to attack the carbocation intermediate, forming a C–Br bond and giving the neutral addition product.

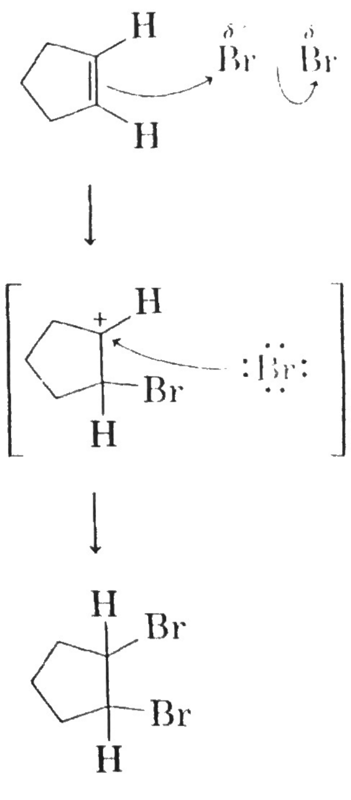


FIGURE 4.3 Addition of bromine to cyclopentene

The mechanism of halogen addition to alkenes shown in Figure 4.3 looks reasonable, but it's not completely consistent with known facts. In particular, the mechanism doesn't explain the *stereochemistry* of halogen addition. That is, the mechanism doesn't explain what product stereoisomers (Section 2.7) are formed in the reaction.

Let's look again at the reaction of Br_2 with cyclopentene and assume that Br^+ adds from the bottom face to form the cation intermediate shown in Figure 4.4. The addition could just as well occur from the top face, but we'll consider only

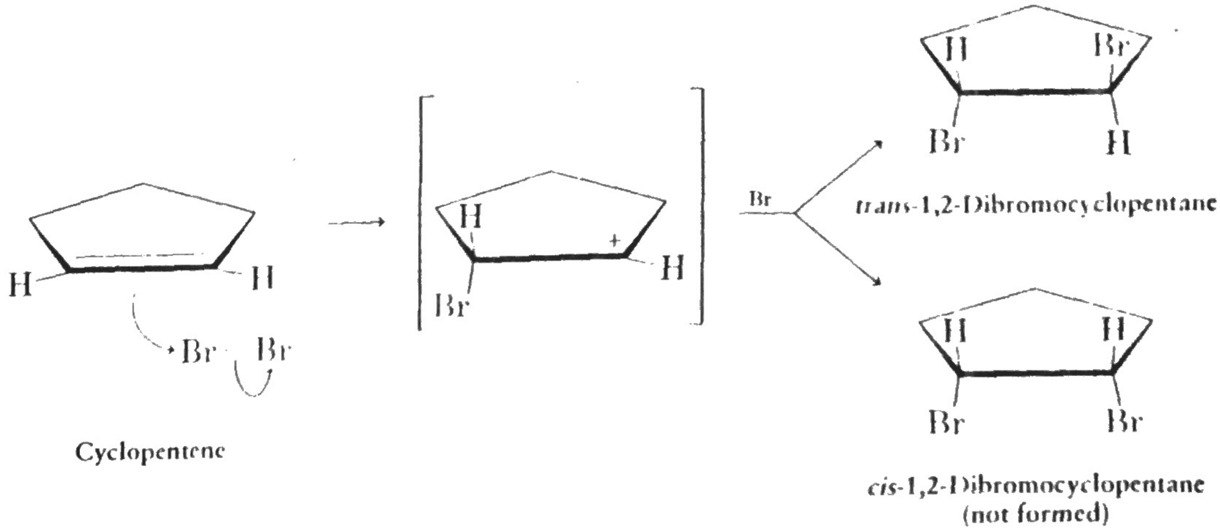


FIGURE 4.4 Stereochemistry of the addition of bromine to cyclopentene. Only the trans product is formed.

sp^2 hybridized, it could be attacked by bromide ion in the second step of the reaction from either the top or the bottom side. Thus, a mixture of products might result, in which the two bromine atoms are either on the same side of the ring (cis) or on opposite sides (trans). We find, however, that only *trans*-1,2-dibromocyclopentane is produced: The two bromine atoms add to opposite faces of the double bond, a result described by saying that the reaction occurs with **anti stereochemistry.** (*Anti* means that the two bromines that have added came from opposite sides of the molecule approximately 180° apart.)

anti stereochemistry Referring to a reaction in which both top and bottom sides of a reactant are involved

bromonium ion a species with a positively charged, divalent bromine atom

The stereochemistry of bromine addition is best explained by imagining that the reaction intermediate is not a true carbocation. Instead, the intermediate is a *bromonium ion,* formed by the overlap of the vacant carbocation *p* orbital with a lone pair of electrons on the neighboring bromine atom (Figure 4.5). (A **bromonium ion** is a species that contains a positively charged, divalent bromine, R_2Br^+.) Since the bromine atom shields one face of the molecule, reaction with bromide ion in the second step can occur only from the opposite, more accessible face to give the anti product.

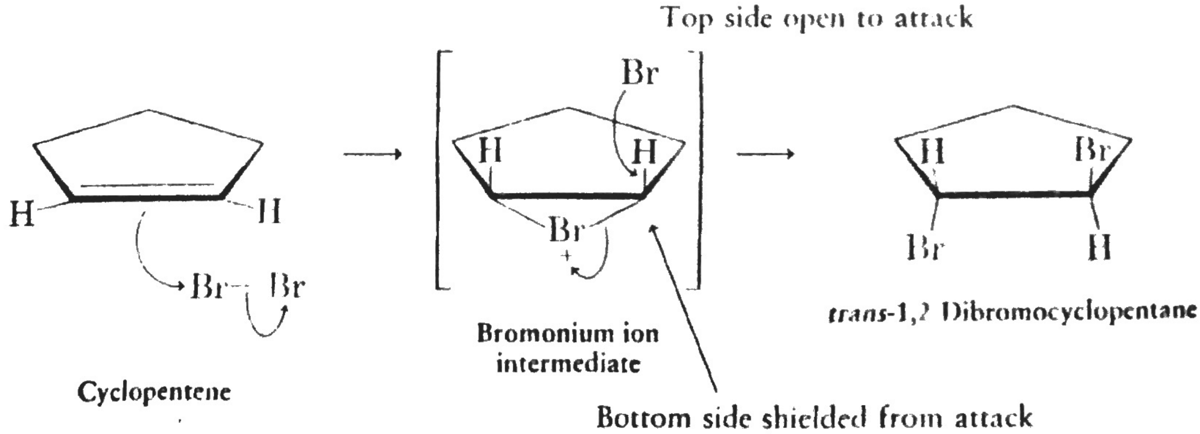


FIGURE 4.5 Formation of a bromonium-ion intermediate by addition of Br^+ to an alkene

PROBLEM 4.6 What product would you expect to obtain from addition of Br_2 to 1,2-dimethylcyclohexene? Show the stereochemistry of the product.

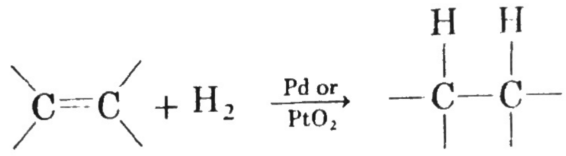
PROBLEM 4.7 Show the structure of the intermediate bromonium ion formed in Problem 4.6.

5 HYDROGENATION OF ALKENES

rogenation addition of H_2 ı molecule, ally an alkene

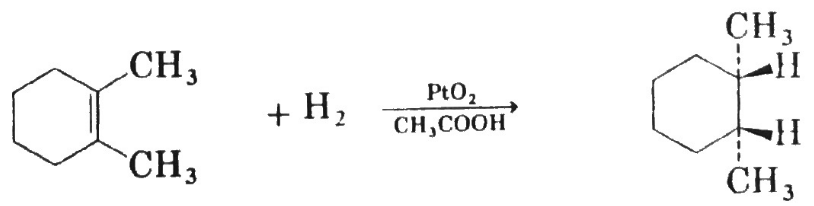
uction addition of lrogen to a lecule or the ıoval of oxygen n it

Addition of hydrogen to the double bond occurs when alkenes are exposed to an atmosphere of hydrogen gas in the presence of a catalyst. We describe the result by saying that the double bond has been **hydrogenated,** or **reduced.** (The word *reduction* in organic chemistry refers to the addition of hydrogen or removal of oxygen from a molecule.) For most alkene hydrogenations, either palladium or platinum (as PtO_2) is used as the catalyst.



1 **reochemistry** erring to a ıction in which ıly one side of a actant is involved

Catalytic hydrogenation of alkenes is unlike most other organic reactions in that it is a heterogeneous process, rather than a homogeneous one. That is, the hydrogenation reaction occurs on the surface of solid catalyst particles rather than in solution. The reaction occurs with **syn stereochemistry** (the opposite of *anti*), meaning that both hydrogens add to the double bond from the same side.



1,2-Dimethylcyclohexene

cis-1,2-Dimethylcyclohexane (82%)

In addition to its usefulness in the laboratory, alkene hydrogenation is a reaction of great commercial value. In the food industry, unsaturated vegetable oils are catalytically hydrogenated on a vast scale to produce the saturated fats used in margarine.

PROBLEM 4.8 What product would you expect to obtain from catalytic hydrogenation of these alkenes?
(a) $(CH_3)_2C{=}CHCH_2CH_3$ (b) 3,3-Dimethylcyclopentene

4.7 OXIDATION OF ALKENES

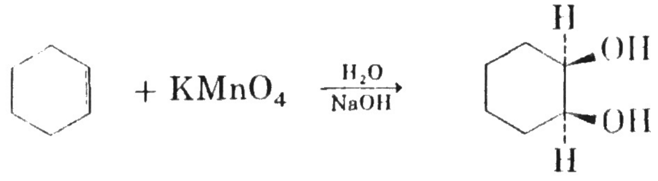
ıydroxylation

Hydroxylation of an alkene—the addition of a hydroxyl group to each of the ... be carried out by treatment of the alkene with potassium

oxidation the addition of oxygen to a molecule or the removal of hydrogen from it

diol a dialcohol

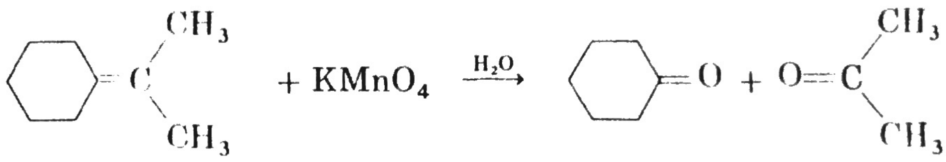
during the reaction, we call this an **oxidation.** The reaction occurs with syn stereochemistry and yields a cis 1,2-dialcohol (**diol**) product. For example, cyclohexene gives *cis*-1,2-cyclohexanediol in 37% yield.



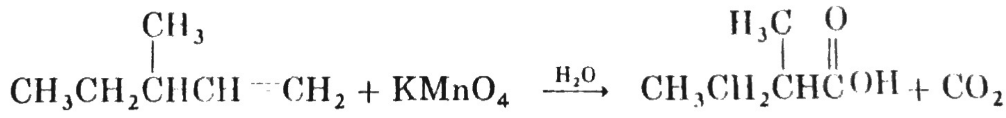
Cyclohexene

cis-1,2-Cyclohexanediol (37%)

If the reaction of the alkene with $KMnO_4$ is carried out in either neutral or acidic solution, cleavage of the double bond occurs, giving carbonyl-containing products in moderate yield. If the double bond is tetrasubstituted, the two carbonyl-containing products are ketones; if a hydrogen is present on the double bond, one of the carbonyl-containing products is a carboxylic acid; and if two hydrogens are present on one carbon, CO_2 is formed:



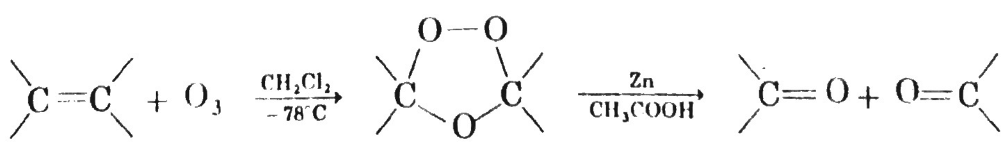
Isopropylidenecyclohexane **Cyclohexanone** **Acetone** **(two ketones)**



3-Methyl-1-pentene **2-Methylbutanoic acid (45%)**

ozonide the addition product of ozone and an alkene

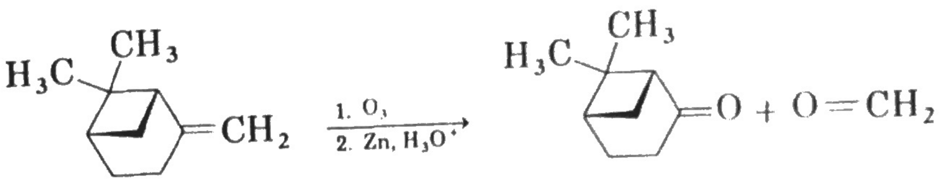
An alternative method for oxidatively cleaving carbon–carbon double bonds is to treat an alkene with ozone, O_3. Conveniently prepared by passing a stream of oxygen through a high-voltage electrical discharge, ozone adds rapidly to alkenes at low temperature to yield **ozonides.**



An ozonide

Since they're sometimes explosive, ozonides aren't usually isolated. Instead, they are treated with a reducing agent such as zinc metal in acetic acid to convert them to carbonyl compounds. The net result of the ozonolysis–zinc-reduction sequence is that the carbon–carbon double bond is cleaved, and oxygen becomes doubly bonded to each of the original alkene carbons. If a tetrasubstituted double bond is ozonized, two ketones result; if a trisubstituted double bond is ozonized, one ketone and one aldehyde result; and so on.

$$\underset{\text{4-Octene}}{CH_3CH_2CH_2CH{=}CHCH_2CH_2CH_3} \xrightarrow[\text{2. Zn, } H_3O^+]{\text{1. } O_3} \underset{\substack{\text{Butanal}\\ \text{(two aldehydes)}}}{2\ CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H}$$



β-Pinene — Nopinone — Formaldehyde (one ketone and one aldehyde)

PRACTICE PROBLEM 4.3 Predict the product of reaction of 2-pentene with aqueous acidic $KMnO_4$.

SOLUTION Reaction of acidic $KMnO_4$ with an alkene yields carbonyl-containing products in which the double bond is broken and the two fragments have C=O in place of the original alkene C=C. If a hydrogen is present on the double bond, a carboxylic acid is produced. Thus, 2-pentene gives the following reaction:

$$\underset{\text{2-Pentene}}{CH_3CH_2CH{=}CHCH_3} + KMnO_4 \xrightarrow{H_2O} \underset{\text{Propanoic acid}}{CH_3CH_2\overset{O}{\overset{\|}{C}}OH} + \underset{\text{Acetic acid}}{HO\overset{O}{\overset{\|}{C}}CH_3}$$

PRACTICE PROBLEM 4.4 What alkene gives a mixture of acetone and propanal on ozonolysis followed by reduction with zinc?

$$? \xrightarrow[\text{2. Zn, } H_3O^+]{\text{1. } O_3} CH_3\overset{O}{\overset{\|}{C}}CH_3 + CH_3CH_2\overset{O}{\overset{\|}{C}}H$$

SOLUTION To find out what starting alkene gives the ozonolysis products shown, simply remove the oxygen atoms from the two products and rejoin the carbon fragments with a double bond:

$$\underset{\text{2-Methyl-2-pentene}}{CH_3\overset{CH_3}{\overset{|}{C}}{\neq}CHCH_2CH_3} \xrightarrow[\text{2. Zn, } H_3O^+]{\text{1. } O_3} \underset{\text{Acetone}}{CH_3\overset{O}{\overset{\|}{C}}CH_3} + \underset{\text{Propanal}}{CH_3CH_2\overset{O}{\overset{\|}{C}}H}$$

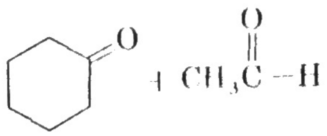
PROBLEM 4.9 Predict the product of the reaction of 1,2-dimethylcyclohexene with the following:

(a) Aqueous acidic $KMnO_4$ (b) Ozone, followed by zinc

PROBLEM 4.10 Propose structures for alkenes that yield these products on ozonolysis–reduction:

(a) $(CH_3)_2C{=}O + CH_2{=}O$ (b) 2 equiv. $CH_3CH_2CH{=}O$

(c)



4.8 ALKENE POLYMERS

polymer a large molecule built up by repetitive bonding of smaller units

monomer a small building block from which polymers are made

No other group of synthetic organic compounds has had as great an impact on our day-to-day living as the synthetic polymers. A **polymer** is a large molecule built up by repetitive bonding together of many smaller units, called **monomers**. As we'll see in later chapters, nature makes wide use of biological polymers. For example, cellulose is a polymer built of repeating sugar units; proteins are polymers built of repeating amino acid units; and nucleic acids are polymers built of repeating nucleotide units. Although synthetic polymers are chemically much simpler than biopolymers, there is an immense diversity to the structures and properties of synthetic polymers, depending on the nature of the monomers and on the reaction conditions used for polymerization.

Radical Polymerization of Alkenes

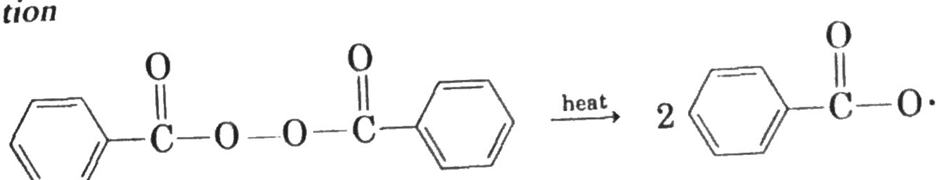
Many simple alkenes undergo rapid polymerization when treated with a small amount of a radical catalyst. For example, ethylene yields polyethylene. Ethylene polymerization is usually carried out at high pressure (1000–3000 atm) and high temperature (100–250°C) with a radical catalyst like benzoyl peroxide. The resultant polymer may have anywhere from a few hundred to a few thousand monomer units incorporated into the chain.

$$\underset{\text{Ethylene}}{H_2C{=}CH_2} \xrightarrow[\text{peroxide}]{\text{benzoyl}} \underset{\text{A segment of polyethylene}}{\wr\, CH_2CH_2{-}CH_2CH_2{-}CH_2CH_2{-}CH_2CH_2{-}CH_2CH_2 \,\wr}$$

Radical polymerizations of alkenes involve three kinds of steps: initiation steps, propagation steps, and termination steps. *Initiation* occurs when small amounts of radicals are generated by the catalyst (step 1). For example, when benzoyl peroxide is used as initiator, the oxygen–oxygen bond is broken on heating to yield benzoyloxy radicals. One of these radicals adds to the double bond of an ethylene molecule to generate a new carbon radical (step 2), and the polymerization is off and running. Note that this radical addition step results in formation of a bond between the initiator and the ethylene molecule in which one electron has been contributed by each partner. The remaining electron from the ethylene pi bond remains on carbon as the new radical site.

Initiation

Step 1



Benzoyl peroxide

Benzoyloxy radical (initiator, In·)

Step 2 $\quad In\cdot + H_2C{=}CH_2 \longrightarrow In{-}CH_2{-}CH_2\cdot$

Propagation of the reaction occurs when the carbon radical adds to another ethylene molecule (step 3). Repetition of step 3 for hundreds or thousands of times builds the polymer chain.

Propagation

Step 3 $\quad In{-}CH_2{-}CH_2\cdot + H_2C{=}CH_2 \longrightarrow In{-}CH_2{-}CH_2{-}CH_2{-}CH_2\cdot$

$$\xrightarrow[\text{times}]{\text{repeat many}} In{-}(CH_2CH_2{-})_nCH_2CH_2\cdot$$

Eventually, the polymer chain is *terminated* by reactions that consume the radical. For example, combination of two chains by chance meeting (step 4) is a possible chain-terminating reaction.

Termination

Step 4 $\quad 2\,R{-}CH_2CH_2\cdot \longrightarrow R{-}CH_2CH_2{-}CH_2CH_2{-}R$

Polymerization of Substituted Ethylenes

vinyl monomer a simple substituted ethylene used to make polymers

Many substituted ethylenes (**vinyl monomers**) undergo radical-initiated polymerization to yield polymers with substituent groups (denoted by a circled S) regularly spaced along the polymer backbone.

$$CH_2{=}\overset{|}{C}H \longrightarrow {-}(CH_2\overset{|}{C}HCH_2\overset{|}{C}HCH_2\overset{|}{C}H{-})$$

Monomer $\qquad$ Polymer

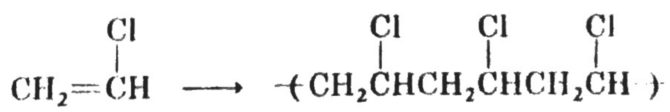
Table 4.1 shows some of the more important vinyl monomers and lists the ... different polymers that result.

TABLE 4.1 Some alkene polymers and their uses

Monomer name	*Formula*	*Trade or common names of polymer*	*Uses*
Ethylene	$H_2C{=}CH_2$	Polyethylene	Packaging, bottles, cable insulation, films and sheets
Propene (propylene)	$H_2C{=}CHCH_3$	Polypropylene	Automotive moldings, rope, carpet fibers
Chloroethylene (vinyl chloride)	$H_2C{=}CHCl$	Poly(vinyl chloride), Tedlar	Insulation, films, pipes
Styrene	$H_2C{=}CHC_6H_5$	Polystyrene, Styron	Foam and molded articles
Tetrafluoroethylene	$F_2C{=}CF_2$	Teflon	Valves and gaskets, coatings
Acrylonitrile	$H_2C{=}CHCN$	Orlon, Acrilan	Fibers
Methyl methacrylate	$H_2C{=}C(CH_3)CO_2CH_3$	Plexiglas, Lucite	Molded articles, paints
Vinyl acetate	$H_2C{=}CHOCOCH_3$	Poly(vinyl acetate)	Paints, adhesives
Vinyl alcohol	"$H_2C{=}CHOH$"	Poly(vinyl alcohol)	Fibers, adhesives

PRACTICE PROBLEM 4.5 Show the structure of poly(vinyl chloride) by drawing several repeating units. Vinyl chloride is $H_2C{=}CHCl$.

SOLUTION The general structure of poly(vinyl chloride) is

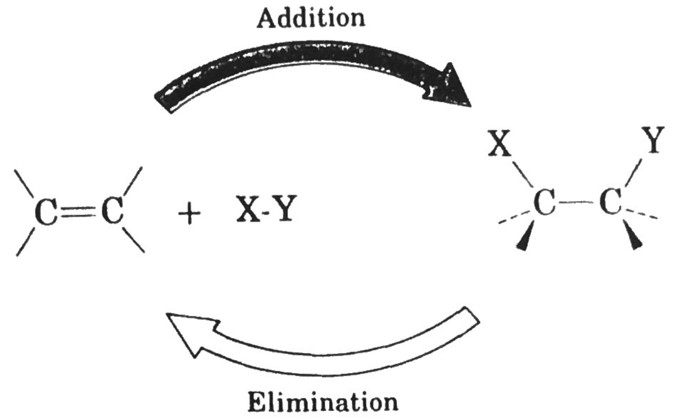


Vinyl chloride → Poly(vinyl chloride)

PROBLEM 4.11 Show the structure of polypropylene by drawing several repeating units. Propylene is $CH_3CH{=}CH_2$.

PREPARATION OF ALKENES: ELIMINATION REACTIONS

Just as addition reactions account for most of the chemistry that alkenes undergo, *elimination reactions* account for most of the ways used to prepare alkenes. Additions and eliminations are, in many respects, two sides of the same coin:



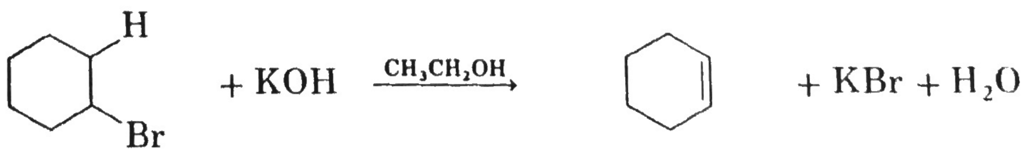
ydrohalogeon elimination of from an alkyl de to yield an ene

ıydration loss of water n an alcohol to 'd an alkene

Let's look briefly at two elimination reactions, the **dehydrohalogenation** of an alkyl halide (elimination of HX) and the **dehydration** of an alcohol (elimination of water, H_2O). We'll return for a closer look at how these reactions take place in Chapter 7.

Elimination of HX from Alkyl Halides: Dehydrohalogenation

Alkyl halides can be synthesized by addition of HX to alkenes. Conversely, alkenes can be synthesized by elimination of HX from alkyl halides. Dehydrohalogenation is usually effected by treating the alkyl halide with a strong base. Thus, bromocyclohexane yields cyclohexene when treated with potassium hydroxide in alcohol solution:



Bromocyclohexane **Cyclohexene (81%)**

Elimination reactions are somewhat more complex than addition reactions because of the regiochemistry problem: what products will result from dehydrohalogenation of unsymmetrical halides? In fact, elimination reactions almost always give mixtures of alkene products. The best we can usually do is to predict which product will be major.

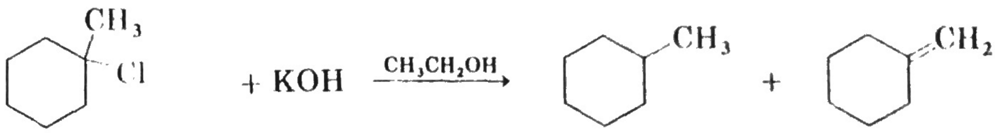
According to a rule formulated by the Russian chemist Alexander Zaitsev[2], base-induced elimination reactions generally give the more highly substituted alkene product. For example, if 2-bromobutane is treated with sodium ethoxide in ethanol, Zaitsev's rule predicts that 2-butene (disubstituted; two alkyl-group substituents on the double-bond carbons) should predominate over 1-butene (monosubstituted; one alkyl-group substituent on the double-bond carbons). This is exactly what is found.

$$CH_3CH_2CH(Br)CH_3 \xrightarrow[CH_3CH_2OH]{KOH} CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CH_2$$

2-Bromobutane — 2-Butene (81%) — 1-Butene (19%)

PRACTICE PROBLEM 4.6 What product would you expect from reaction of 1-chloro-1-methylcyclohexane with KOH?

SOLUTION Treatment of an alkyl halide with a strong base like KOH causes dehydrohalogenation and yields an alkene. To find the products in a specific case, draw the structure of the starting material and locate the hydrogen atoms on each neighboring carbon. Then generate the potential alkene products by removing HX in as many ways as possible. The major product will be the one that has the most highly substituted double bond:



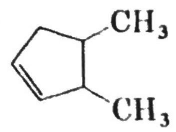
1-Chloro-1-methylcyclohexane — 1-Methylcyclohexene (major) — Methylenecyclohexane (minor)

PROBLEM 4.12 What products would you expect from the reaction of 2-bromo-2-methylbutane with KOH? Which will be major?

PROBLEM 4.13 What alkyl halide starting materials might these alkenes have come from?

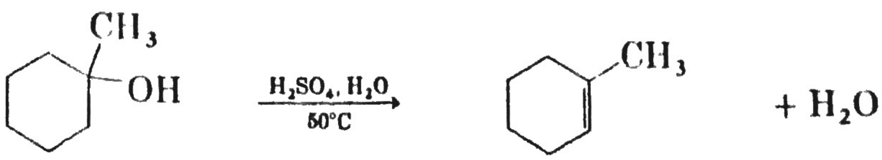
(a) $CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH{=}CH_2$

(b)



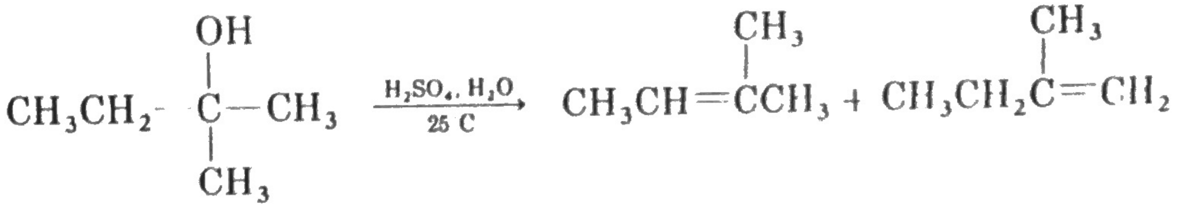
Elimination of H_2O from Alcohols: Dehydration

The dehydration of alcohols is one of the most useful methods of alkene synthesis, and many ways of carrying out the reaction have been devised. A method that works particularly well for tertiary alcohols is acid-catalyzed dehydration. For example, when 1-methylcyclohexanol is treated with aqueous sulfuric acid, dehydration occurs to yield 1-methylcyclohexene:



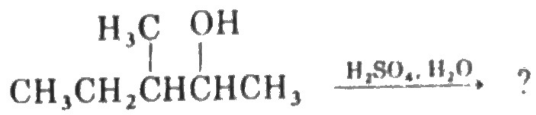
1-Methylcyclohexanol — 1-Methylcyclohexene (91%)

Acid-catalyzed dehydrations usually follow Zaitsev's rule and yield the more highly substituted alkene as major product. Thus, 2-methyl-2-butanol gives primarily 2-methyl-2-butene (trisubstituted) rather than 2-methyl-1- butene (disubstituted):

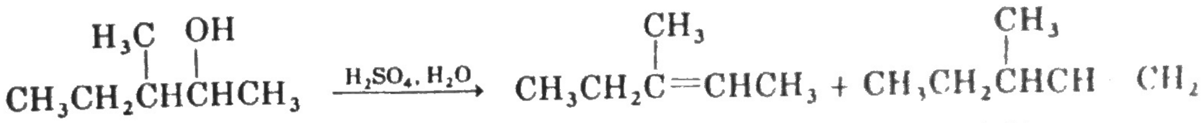


2-Methyl-2-butanol — 2-Methyl-2-butene (major) — 2-Methyl-1-butene (minor)

PRACTICE PROBLEM 4.7 Predict the major product of this reaction:



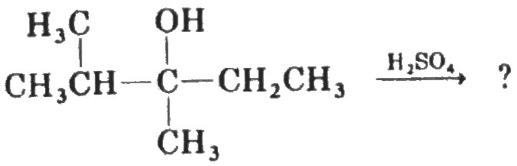
SOLUTION Treatment of an alcohol with acid leads to dehydration and formation of the more highly substituted alkene product (Zaitsev's rule). Thus, dehydration of 3-methyl-2-pentanol should yield 3-methyl-2-pentene as the major product rather than 3-methyl-1-pentene:



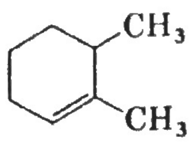
3-Methyl-2-pentanol — 3-Methyl-2-pentene (major) — 3-Methyl-1-pentene (minor)

PROBLEM 4.14 Predict the products you would expect from these reactions. Indicate the major product in each case.

(a) 2-Bromo-2-methylpentane + KOH ⟶ ?

(b) 

PROBLEM 4.15 What alcohols might these alkenes have come from?

(a)  (b) $CH_3CH_2CH{=}CHCH_2CH_2CH_3$

10 CONJUGATED DIENES

jugation
rnating single

Double bonds that alternate with single bonds are said to be conjugated. Thus, 1,3-butadiene is a conjugated diene whereas 1,4-pentadiene is a nonconjugated

conjugated diene
a diene whose two double bonds are separated by a single bond

1,3-Butadiene	1,4-Pentadiene
$H_2C{=}CH{-}CH{=}CH_2$	$H_2C{=}CH{-}CH_2{-}CH{=}CH_2$
A conjugated diene with alternating single and double bonds	A nonconjugated diene with nonalternating single and double bonds

What's so special about conjugated dienes that we need to look at them separately? The orbital view of 1,3-butadiene shown in Figure 4.6 provides a clue to the answer: *There is an electronic interaction between the two double bonds of a conjugated diene* because of *p*-orbital overlap across the central single bond. This interaction of *p* orbitals across a single bond gives conjugated dienes some unusual properties.

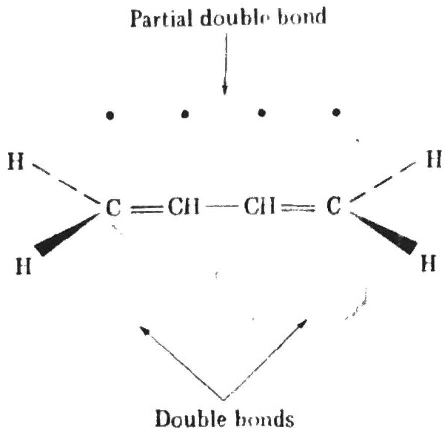


FIGURE 4.6 An orbital view of 1,3-butadiene. Each of the four carbon atoms has a *p* orbital, allowing for an electronic interaction across the C2–C3 single bond.

Although much of the chemistry of conjugated dienes and isolated alkenes is similar, there's a striking difference in their addition reactions with electrophiles like HX and X_2. When HX adds to an isolated alkene, Markovnikov's rule usually predicts the formation of a single product. When HX adds to a conjugated diene, though, mixtures of products are usually obtained. For example, reaction of HBr with 1,3-butadiene yields two products:

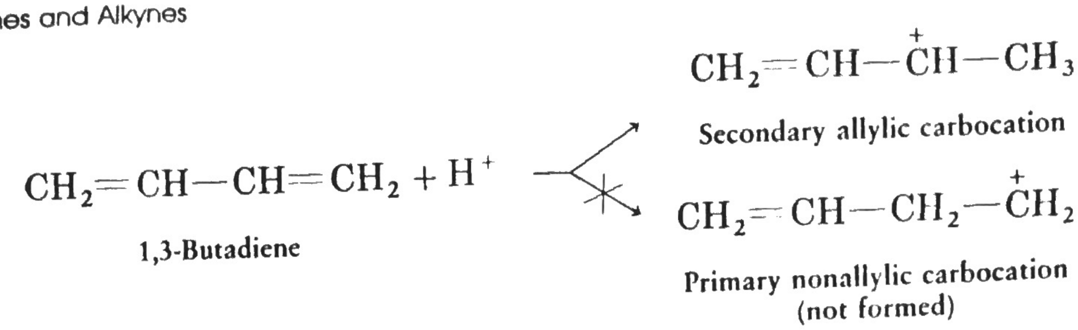
$$\underset{\text{1,3-Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} + HBr \longrightarrow \underset{\substack{\text{3-Bromo-1-butene (71\%)}\\ \text{(1,2-addition)}}}{\overset{4}{C}H_2{=}\overset{3}{C}H{-}\overset{2}{C}H(Br){-}\overset{1}{C}H_2(H)} + \underset{\substack{\text{1-Bromo-2-butene (29\%)}\\ \text{(1,4-addition)}}}{\overset{4}{C}H_2(Br){-}\overset{3}{C}H{=}\overset{2}{C}H{-}\overset{1}{C}H_2(H)}$$

1,4-addition
the addition of an electrophile to carbons 1 and 4 of a conjugated diene

3-Bromo-1-butene (a secondary bromide) is the normal product of Markovnikov addition, but 1-bromo-2-butene (a primary bromide) is unexpected. The double bond in this product has moved to a position between carbons 2 and 3, and H–Br has added to carbons 1 and 4. How can we account for the formation of this 1,4-addition product?

allylic
next to a double bond

The answer is that an *allylic carbocation* is involved as an intermediate in the reaction (allylic means next to a double bond). When H^+ adds to an electron-rich pi bond of 1,3-butadiene, two carbocation intermediates are possible: a primary nonallylic carbocation and a secondary allylic carbocation. Allylic carbocations are very stable and therefore form in preference to less stable, nonallylic carbocations.



1 STABILITY OF ALLYLIC CARBOCATIONS: RESONANCE

Why are allylic carbocations stable? To get an idea of the reason, look at the orbital picture of an allylic carbocation in Figure 4.7. The positively charged carbon atom has a vacant *p* orbital that can overlap the *p* orbitals of the neighboring double bond.

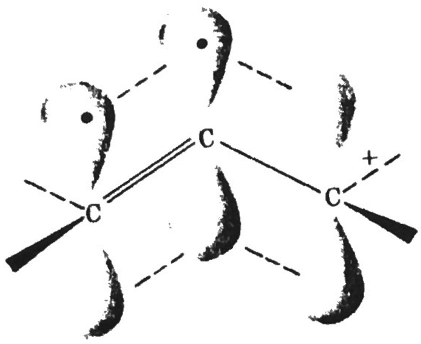
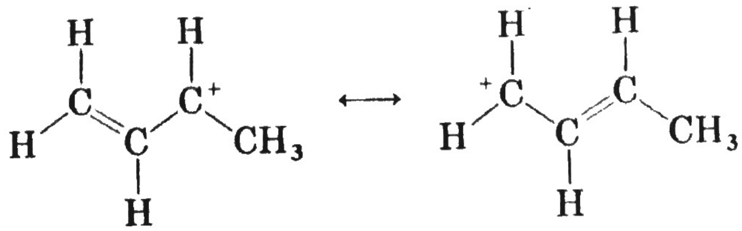


FIGURE 4.7 An orbital picture of an allylic carbocation. The vacant *p* orbital on the positively charged carbon can overlap the double-bond *p* orbitals.

From a *p*-orbital point of view, an allylic carbocation is symmetrical. All three carbon atoms are sp^2 hybridized, and each has a *p* orbital. Thus, the *p* orbital on the central carbon can overlap equally well with *p* orbitals on *either* of the two neighboring carbons. The two electrons are free to move about and spread out over the entire three-orbital array, as indicated in Figure 4.7.

One consequence of this orbital picture is that there are two ways to draw an allylic carbocation. We can draw it with the vacant orbital on the left and the double bond on the right, or we can draw it with the vacant orbital on the right and the double bond on the left. *Neither structure is completely correct: The true structure of the allylic carbocation is somewhere in between the two.*



Two resonance forms of an allylic carbocation

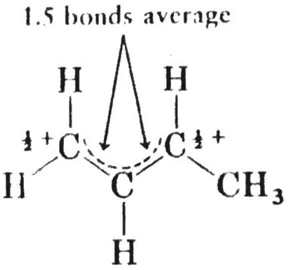
sonance forms
o representations
a molecule that
fer only in where

The two individual structures are called **resonance forms**, and their special relationship is indicated by the double-headed arrow between them. The only difference between the resonance forms is the position of the bonding electrons. The

The best way to think about resonance is to realize that a species like an allylic carbocation is no different from any other organic substance. An allylic carbocation doesn't jump back and forth between two resonance forms, spending part of its time looking like one and the rest of its time looking like the other; rather, it has a single, unchanging structure that we call a **resonance hybrid.** (A useful analogy is to think of a resonance hybrid as being like a mutt, or mixed-breed dog. Just as a dog that's a mixture of dachshund and German shepherd doesn't change back and forth from one to the other, a resonance hybrid doesn't change back and forth.)

resonance hybrid the true structure of a molecule described by different resonance forms

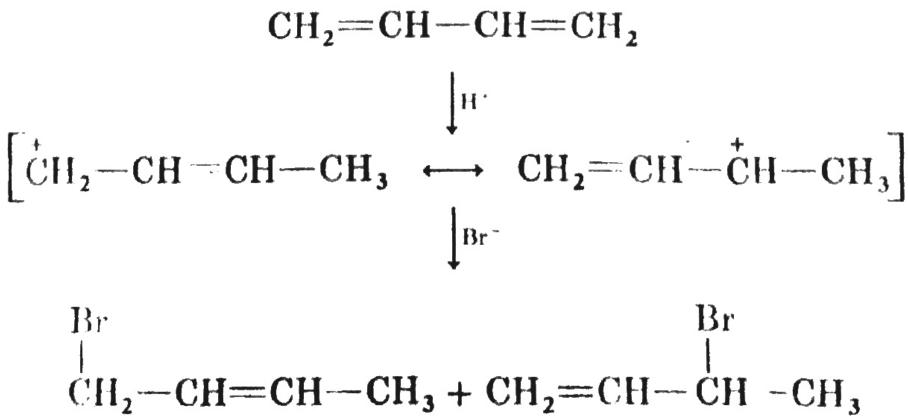
The difficulty in understanding resonance hybrids is visual, because we can't draw an accurate single picture of a resonance hybrid by using familiar kinds of structures. The line-bond structures that serve so well to represent most organic molecules just don't work well for resonance hybrids like allylic carbocations. We might try to represent the allylic carbocation by using a dotted line to indicate that the two C–C bonds are equivalent and that each is approximately $1\frac{1}{2}$ bonds, but such a drawing really doesn't help much and won't be used again in this book.



An allylic carbocation

One of the most important postulates of resonance theory is that ***the greater the number of possible resonance forms, the greater the stability of the compound.*** Since an allylic carbocation is a resonance hybrid of two line-bond structures, it's therefore more stable than a normal carbocation. This stability is due to the fact that the pi electrons can be spread out (*delocalized*) over an extended *p*-orbital network rather than centered on only one site.

In addition to affecting stability, the resonance picture of an allylic carbocation also has chemical consequences. When the allylic carbocation produced by protonation of 1,3-butadiene reacts with bromide ion to complete the addition reaction, attack can occur at either C1 or C3 because both share the positive charge. The result is a mixture of 1,2- and 1,4-addition products:

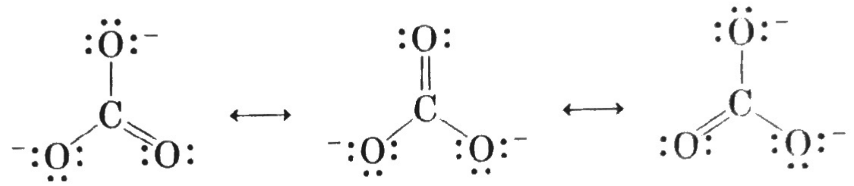


1,4-Addition **1,2-Addition**

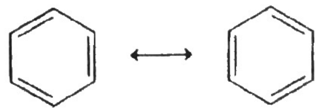
ROBLEM 4.16 1,3-Butadiene reacts with Br_2 to yield a mixture of 1,2- and 1,4-addition products. Show the structure of each.

2 DRAWING AND INTERPRETING RESONANCE FORMS

Resonance is an extremely useful concept for explaining a variety of phenomena. In inorganic chemistry, for example, the carbonate ion CO_3^{2-} is known to have identical bond lengths for its three C–O bonds. Although there is no single line-bond structure that can account for this equality of C–O bonds, resonance theory accounts for it nicely. The carbonate ion is simply a resonance hybrid of three resonance forms. The three oxygens share the pi electrons and the negative charges equally:



As an example from organic chemistry, we'll see in the next chapter that the six C–C bonds in aromatic compounds like benzene are equivalent because benzene is a resonance hybrid of two forms. Each form has alternating single and double bonds, and neither form is correct by itself. The true benzene structure is a hybrid of the two forms.



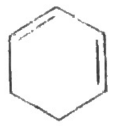
Two resonance forms of benzene

When first dealing with resonance theory, it's often useful to have a set of guidelines that describe how to draw and interpret resonance forms. The following five rules should prove helpful:

Rule 1. *Resonance forms are imaginary, not real.* The real structure is a composite hybrid of the different forms. Substances like the allylic carbocation, the carbonate ion, and benzene are no different from any other substance in having single, unchanging structures. The only difference is in the way they must be represented on paper.

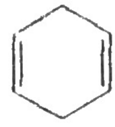
Rule 2. *Resonance forms differ from each other only in the placement of the pi electrons.* Neither the position nor the hybridization of atoms changes from one resonance form to another. In benzene, for example, the pi electrons in the double bonds move, but the six carbon atoms remain in place:

By contrast, two structures like 1,3-cyclohexadiene and 1,4-cyclohexadiene are *not* resonance structures because their hydrogen atoms don't occupy the same positions. Instead, the two dienes are constitutional isomers:



1,3-Cyclohexadiene

Constitutional isomers
not
resonance forms

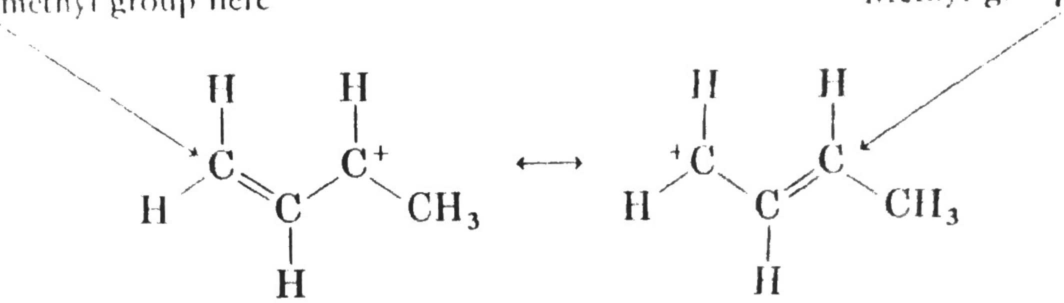


1,4-Cyclohexadiene

Rule 3. Different resonance forms of a substance don't have to be equivalent. For example, the allylic carbocation obtained by reaction of 1,3-butadiene with H^+ is unsymmetrical. One end of the delocalized pi-electron system has a methyl substituent, and the other end is unsubstituted. Even though the two resonance forms aren't equivalent, they both contribute to the overall resonance hybrid.

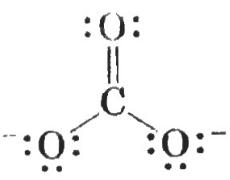
No methyl group here

Methyl group here

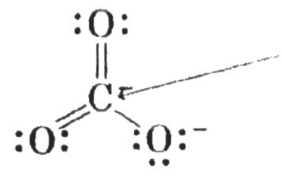


In general, when two resonance forms are not equivalent, the actual structure of the resonance hybrid is closer to the more stable form than to the less stable form. Thus, we might expect the butenyl carbocation to look a bit more like a secondary carbocation than like a primary one.

Rule 4. All resonance forms must obey normal rules of valency. Resonance forms are like any other structure: The octet rule still holds. For example, one of the following structures for the carbonate ion is not a valid resonance form because the carbon atom has five bonds and ten electrons:



Carbonate ion

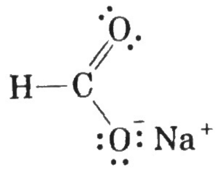


10 electrons here

Not a resonance form

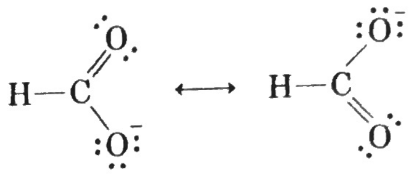
Rule 5. The resonance hybrid is more stable than any single resonance form. In other words, resonance leads to stability. The greater the number of resonance forms possible, the more stable the substance. We've already seen, for example, that an allylic carbocation is more stable than a normal carbocation. In a similar manner, we'll see in the next chapter that a benzene ring is more stable than a cyclic alkene.

RACTICE ROBLEM 4.8 Use resonance structures to explain why the two C–O bonds of sodium formate are equivalent.



Sodium formate

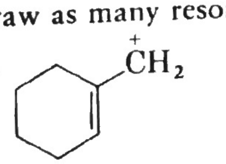
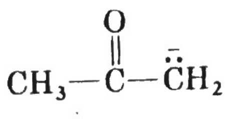
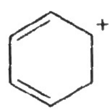
SOLUTION The formate anion is a resonance hybrid of two equivalent resonance forms. The two resonance forms can be drawn by showing the double bond either to the top oxygen or to the bottom oxygen. Only the positions of the electrons are different in the two structures.



ROBLEM 4.17 Give the structure of all possible monoadducts of HCl and 1,3-pentadiene.

PROBLEM 4.18 Look at the possible carbocation intermediates produced during addition of HCl to 1,3-pentadiene (Problem 4.17) and predict which is the most stable.

PROBLEM 4.19 Draw as many resonance structures as you can for these species:

(a)  (b)  (c) 

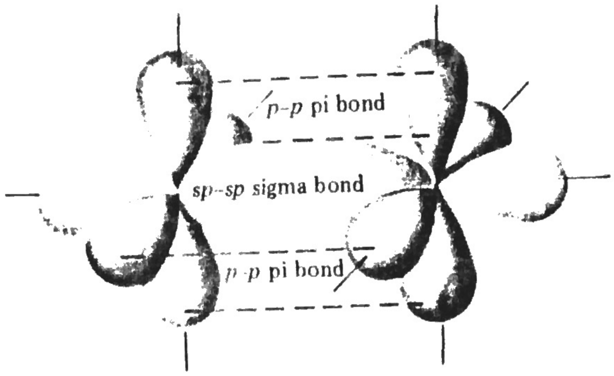
13 ALKYNES

ne /drocarbon has a ɔon–carbon ə bond

Alkynes are hydrocarbons that contain a carbon–carbon triple bond. Since two pairs of hydrogens must be removed from an alkane, C_nH_{2n+2}, to generate a triple bond, the general formula for an alkyne is C_nH_{2n-2}.

As we saw in Section 1.11, a carbon–carbon triple bond results from the overlap of two *sp*-hybridized carbon atoms. The two *sp*-hybrid orbitals of carbon lie at an angle of 180° to each other along an axis that is perpendicular to the axes of the two unhybridized $2p_y$ and $2p_z$ orbitals. When two such *sp*-hybridized carbons approach each other for bonding, the geometry is perfect for the formation of one *sp–sp* sigma bond and two *p–p* pi bonds—a net triple bond (Figure 4.8). The two remaining *sp* orbitals form bonds to other atoms at an angle of 180° from the carbon–carbon sigma bond. For example, acetylene, H–C≡C–H, is a linear molecule with H–C–C bond angles of 180°.

Alkynes follow closely the general rules of hydrocarbon nomenclature already discussed for alkanes (Section 2.3) and alkenes (Section 3.1). The suffix *-yne* is used



The carbon–carbon triple bond

FIGURE 4.8 The electronic structure of a carbon–carbon triple bond

in the base hydrocarbon name to denote an alkyne, and the position of the triple bond is indicated by its number in the chain. Numbering always begins at the chain end nearer the triple bond so that the triple bond receives as low a number as possible.

$$\begin{array}{c} \quad\quad CH_3 \\ \quad\quad | \\ \underset{7}{C}H_3\underset{6}{C}H_2\underset{5}{C}H\underset{4}{C}H_2\underset{3}{C}{\equiv}\underset{2}{C}\underset{1}{C}H_3 \end{array}$$

Begin numbering carbons at the end nearer the triple bond

5-Methyl-2-heptyne

Compounds containing both double and triple bonds are called *enynes*, not *ynenes*. Numbering of the hydrocarbon chain always starts from the end nearer the first multiple bond, but if there's a choice in numbering, double bonds receive lower numbers than triple bonds. For example:

$$\underset{1}{C}H_3\underset{2}{C}H{=}\underset{3}{C}H\underset{4}{C}H_2\underset{5}{C}H_2\underset{6}{C}{\equiv}\underset{7}{C}\underset{8}{C}H_3$$

2-Octen-6-yne (not 6-octen-2-yne)

PROBLEM 4.20 Provide IUPAC names for these compounds:

(a) $CH_3CH_2C{\equiv}CCH_2CH(CH_3)_2$ (b) $HC{\equiv}CC(CH_3)_3$
(c) $CH_3CH(CH_3)CH_2C{\equiv}CCH_3$ (d) $CH_3CH{=}CHCH_2C{\equiv}CCH_3$

4.14 REACTIONS OF ALKYNES: ADDITION OF H_2, HX, AND X_2

Based on their structural similarity, we might expect alkynes and alkenes to show chemical similarities also. As a general rule, this prediction is true: Alkynes react in much the same way that alkenes do.

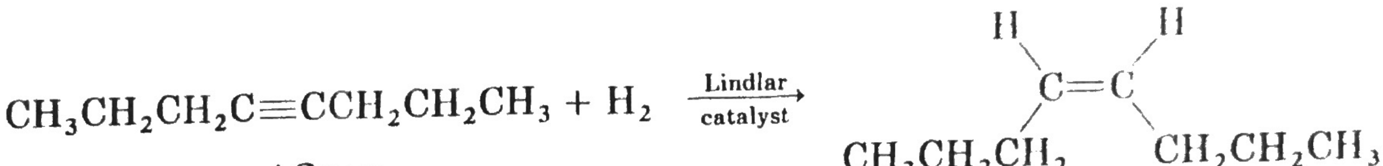
Addition of H_2 to Alkynes

Alkynes are easily converted into alkanes by reduction with two molar equivalents of hydrogen over a palladium catalyst.

$$CH_3CH_2CH_2C{\equiv}CCH_2CH_2CH_3 + 2\,H_2 \xrightarrow[\text{catalyst}]{\text{Pd}} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

4-Octyne — Octane (95%)

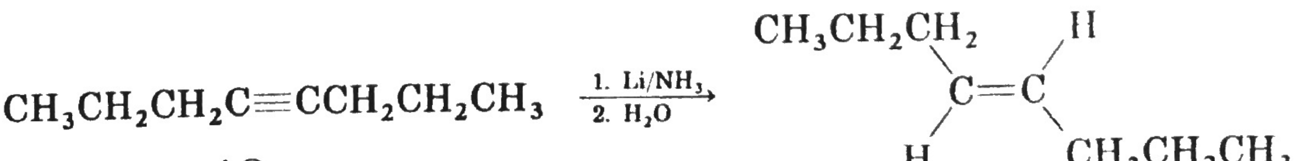
The catalytic hydrogenation of an alkyne to yield an alkane proceeds through an intermediate alkene, and the reaction can be stopped at the alkene stage if the proper catalyst is used. The catalyst most often used for this purpose is the Lindlar catalyst, a specially prepared form of palladium metal. Because hydrogenation occurs with syn stereochemistry, alkynes are catalytically reduced to give cis alkenes. For example:



4-Octyne

cis-4-Octene (92%)

Another method for the reduction of alkynes to alkenes employs lithium metal in liquid ammonia solvent. Remarkably, lithium metal dissolves in pure liquid ammonia solvent at −33°C to produce a deep blue solution. When an alkyne is added to this blue solution, reduction of the triple bond occurs. This method is complementary to the Lindlar reduction, since it yields trans alkenes rather than cis alkenes:



4-Octyne

trans-4-Octene (79%)

Addition of HX to Alkynes

Alkynes give the expected addition products with HCl, HBr, and HI. Although the ...ions can usually be stopped after addition of 1 molar equivalent of HX to yield ...ene, an excess of reagent leads to formation of the dihalide product. As ... examples indicate, the regiochemistry of addition to monosubstituted ... Markovnikov's rule: The H atom adds to the terminal carbon of ... the X atom adds to the internal, more highly substituted,

$$CH_3CH_2CH_2CH_2C{\equiv}CH + HBr \longrightarrow CH_3CH_2CH_2CH_2C(Br){=}CH_2$$

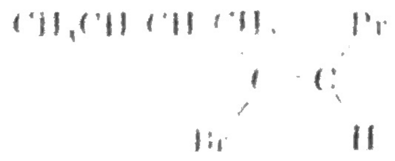
1-Hexyne 2-Bromo-1-hexene

Addition of X_2 to Alkynes

Bromine and chlorine add to alkynes to give addition products with trans stereochemistry:

$$CH_3CH_2CH_2CH_2C{\equiv}CH + Br_2 \xrightarrow{CCl_4}$$

1-Hexyne



(*E*)-1,2-Dibromo-1-hexene

PROBLEM 4.21 What products would you expect from these reactions?

(a) $CH_3CH_2CH_2C{\equiv}CH$ + 1 equiv Cl_2

(b) $CH_3CH_2CH_2C{\equiv}CCH_2CH_3$ + 1 equiv HBr

(c) $CH_3CH(CH_3)CH_2C{\equiv}CCH_2CH_3 + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar}}$?

4.15 ADDITION OF WATER TO ALKYNES

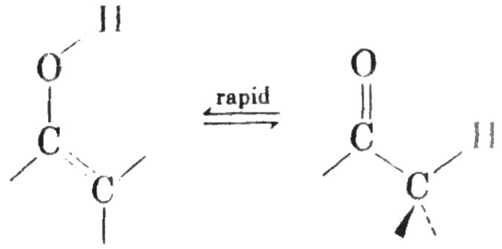
Addition of water takes place when an alkyne is treated with aqueous sulfuric acid in the presence of mercuric sulfate catalyst:

$$CH_3CH_2CH_2C{\equiv}CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} \left[CH_3CH_2CH_2C(OH){=}CH_2\right] \longrightarrow CH_3CH_2CH_2C(=O)CH_3$$

1-Pentyne An enol 2-Pentanone (78%)

tautomerism a word used to describe two rapidly interconverting constitutional isomers

Markovnikov regiochemistry is found for the hydration reaction, with the H attaching to the less substituted carbon and the OH attaching to the more substituted carbon. Interestingly, though, the expected alkenyl alcohol or ***enol*** (*ene* = alkene; *ol* = alcohol) is not isolated. Instead, this intermediate enol rearranges to a more stable isomer, a ketone ($R_2C{=}O$). It turns out that enols and ketones rapidly interconvert—a process called **tautomerism**. Tautomers, special kinds of isomers that are readily interconvertible through a rapid equilibration, will be studied in more detail in Section 11.1. With few exceptions, the tautomeric equilibrium heavily favors the ketone; enols are almost never isolated.



Enol tautomer (less favored) — Keto tautomer (more favored)

A mixture of both possible ketones results when an internal alkyne ($R-C\equiv C-R'$) is hydrated, but only a single product is formed from reaction of a terminal alkyne ($R-C\equiv CH$).

$$\underset{\text{2-Pentyne (an internal alkyne)}}{CH_3CH_2C\equiv CCH_3} + H_2O \xrightarrow[HgSO_4]{H_2SO_4} \underset{\text{3-Pentanone}}{CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3} + \underset{\text{2-Pentanone}}{CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3}$$

$$\underset{\text{1-Pentyne (a terminal alkyne)}}{CH_3CH_2CH_2C\equiv CH} + H_2O \xrightarrow[HgSO_4]{H_2SO_4} \underset{\text{2-Pentanone}}{CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3}$$

PRACTICE PROBLEM 4.9 What product would you obtain by hydration of 4-methyl-1-hexyne?

SOLUTION Addition of water to 4-methyl-1-hexyne according to Markovnikov's rule should yield a product with the OH group attached to C2 rather than to C1. This enol then isomerizes to yield a ketone:

$$\underset{\text{4-Methyl-1-hexyne}}{CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2C\equiv CH} + H_2O \xrightarrow[HgSO_4]{H_2SO_4} \left[CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2\overset{\overset{OH}{|}}{C}=CH_2\right]$$

$$\longrightarrow \underset{\text{4-Methyl-2-hexanone}}{CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2\overset{\overset{O}{\|}}{C}CH_3}$$

What product would you obtain by hydration of 4-octyne?

...alkynes would you start with to prepare these ketones by a hydration reaction?

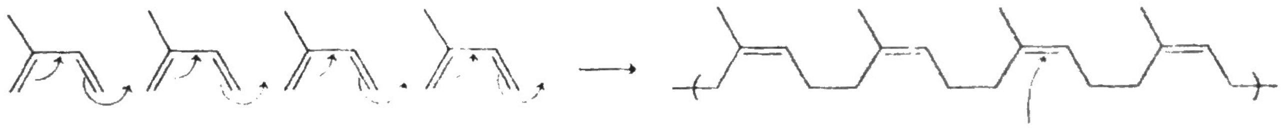
(a) $\overset{\overset{O}{\|}}{C}CH_3$ (b) $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3$

INTERLUDE

Natural Rubber

Rubber—a most unusual name for a most unusual substance—is a naturally occurring alkene polymer produced by more than 400 different plants. The major source, however, is the so-called rubber tree, *Hevea brasiliensis,* from which the crude material is harvested as it drips from a slice made through the bark. The name *rubber* was coined by Joseph Priestley, the discoverer of oxygen and early researcher of rubber chemistry, for the simple reason that one of its early uses was to rub out pencil marks on paper.

Unlike polyethylene and other simple alkene polymers, natural rubber is a polymer of a conjugated diene, isoprene, or 2-methyl-1,3-butadiene. The polymerization takes place by 1,4-addition (Section 4.10) of each isoprene monomer unit to the growing chain, leading to formation of a polymer that still contains double bonds spaced regularly at four-carbon intervals. As the following structure shows, these double bonds have *Z* stereochemistry.



Many isoprenes (1,3-butadiene)

Segment of natural rubber

Z-geometry

Crude rubber (latex) is collected from the tree as an aqueous dispersion that is washed, dried, and coagulated by warming in air to give a polymer with chains that average about 5000 monomer units in length and have molecular weights of 200,000 to 500,000. This crude coagulate is too soft and tacky to be useful until it is hardened by heating with elemental sulfur, a process called *vulcanization.* By mechanisms that are still not fully understood, vulcanization cross-links the rubber chains by forming carbon–sulfur bonds between them, thereby hardening and stiffening the polymer. The exact degree of hardening can be varied, yielding material soft enough for automobile tires or hard enough for bowling balls (*ebonite*).

The remarkable ability of rubber to stretch and then contract to its original shape is due to the irregular shapes of the polymer chains caused by the double bonds. These double bonds introduce bends and kinks into the polymer chains, thereby preventing neighboring chains from nestling together into tightly packed, semicrystalline regions. When stretched, the randomly coiled chains straighten out and orient along the direction of the pull but are kept from sliding over each other by the cross-links. When the stretch is released, the polymer reverts to its original random state (Figure 4.9).

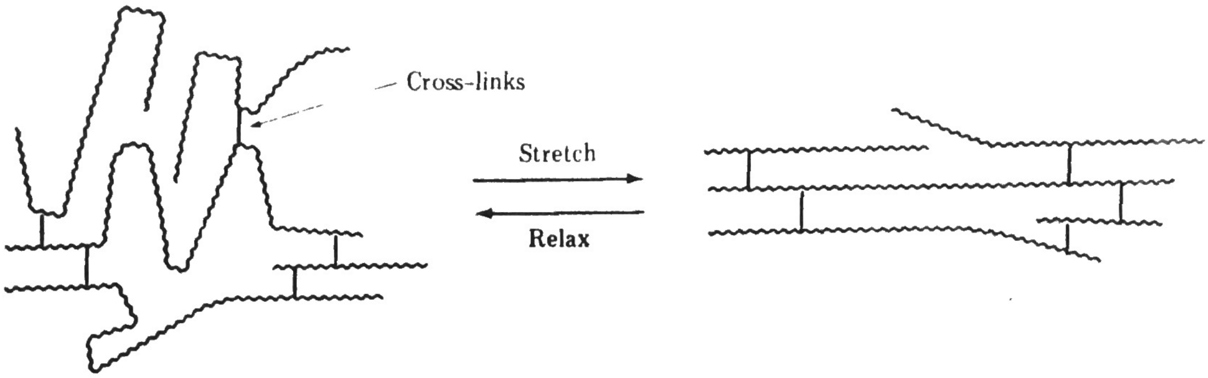


FIGURE 4.9 Unstretched and stretched sections of cross-linked rubber chains

MMARY AND KEY WORDS

The chemistry of alkenes is dominated by **addition reactions** of electrophiles. When HX reacts with an alkene, **Markovnikov's rule** predicts that the hydrogen will add to the carbon that has fewer alkyl substituents, and the X group will add to the carbon that has more alkyl substituents. For example:

$$(H_3C)_2C{=}CH_2 + HCl \longrightarrow H_3C{-}C(Cl)(CH_3){-}CH_3$$

Many other electrophiles besides HX add to alkenes. Thus, bromine and chlorine add to give **1,2-dihalide** addition products having **anti stereochemistry.** Addition of water takes place on reaction of the alkene with aqueous acid. Hydrogen can be added to alkenes by reaction in the presence of a metal catalyst such as platinum or palladium.

Oxidation of alkenes is carried out using potassium permanganate, $KMnO_4$. Under basic conditions, $KMnO_4$ reacts with alkenes to yield cis 1,2-diols. Under neutral or acidic conditions, however, $KMnO_4$ cleaves double bonds to yield carbonyl-containing products. Double-bond cleavage can also be effected by reaction of the alkene with ozone, followed by treatment with zinc in acetic acid.

Alkenes are prepared from alkyl halides and alcohols by **elimination reactions.** Treatment of an alkyl halide with strong base effects **dehydrohalogenation,** and treatment of an alcohol with acid effects **dehydration.** These elimination re-
ions usually give a mixture of alkene products in which the more highly sub-
d alkene predominates (**Zaitsev's rule**).

ugated dienes like 1,3-butadiene contain alternating single and double
gated dienes undergo **1,4-addition** of electrophiles through the forma-
ce-stabilized allylic carbocation intermediate. No single line-bond

representation can depict the true structure of an allylic carbocation. Rather, the true structure is a resonance hybrid somewhere intermediate between two contributing resonance forms. The only difference between two resonance structures is in the location of bonding electrons: The nuclei remain in the same places in both structures.

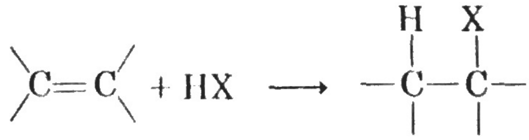
Many simple alkenes undergo **polymerization** when treated with a radical catalyst. **Polymers** are large molecules built up by the repetitive bonding together of many small monomer units.

Alkynes are hydrocarbons that contain carbon–carbon triple bonds. Much of the chemistry of alkynes is similar to that of alkenes. For example, alkynes react with one equivalent of HBr and HCl to yield vinylic halides, and with one equivalent of Br_2 and Cl_2 to yield 1,2-dihalides. Alkynes can also be hydrated by reaction with aqueous sulfuric acid in the presence of mercuric sulfate catalyst. The reaction leads initially to an intermediate enol that immediately isomerizes to a ketone. Alkynes can also be hydrogenated. Reduction over the Lindlar catalyst yields cis alkenes whereas reduction with lithium metal in liquid ammonia yields the trans alkene.

SUMMARY OF REACTIONS

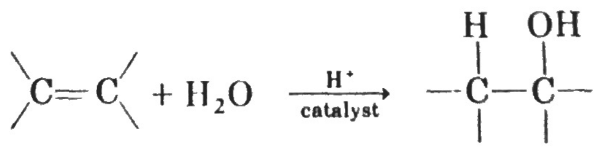
1. Addition reactions of alkenes

(a) Addition of HX, where X = Cl, Br, or I (Sections 4.1 and 4.2)



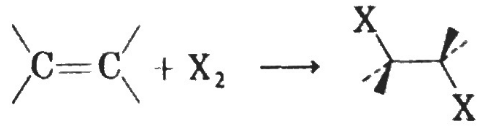
Markovnikov's rule: H adds to the less highly substituted carbon and X adds to the more highly substituted one.

(b) Addition of H_2O (Section 4.4)



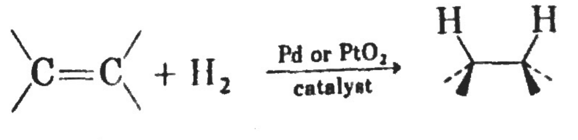
Markovnikov's rule: H adds to the less highly substituted carbon and OH adds to the more highly substituted one.

(c) Addition of X_2, where X = Cl, Br (Section 4.5)



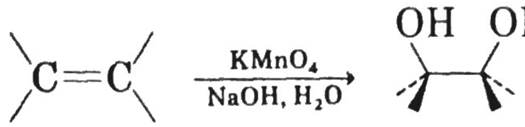
Anti addition

(d) Addition of H_2 (Hydrogenation; Section 4.6)



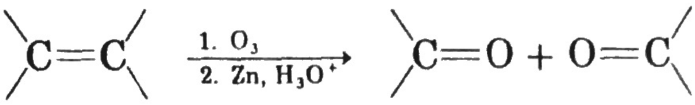
Syn addition

(e) Hydroxylation (Section 4.7)



Syn addition

2. Oxidative cleavage of alkenes with ozone (Section 4.7)

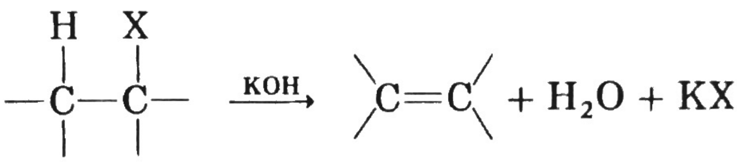


3. Radical-induced polymerization of alkenes (Section 4.8)

$$n\,H_2C{=}CH_2 \xrightarrow[\text{initiator}]{\text{radical}} -\!(CH_2CH_2)_n\!-$$

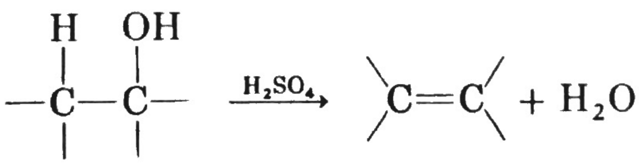
4. Synthesis of alkenes by elimination reactions

(a) Dehydrohalogenation of alkyl halides (Section 4.9)



Zaitsev's rule: Major product formed is the alkene with the more highly substituted double bond.

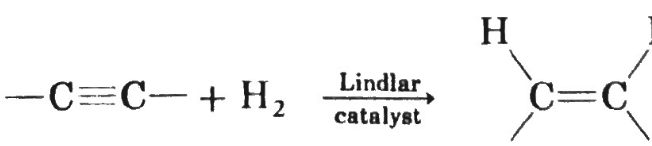
(b) Dehydration of alcohols (Section 4.9)



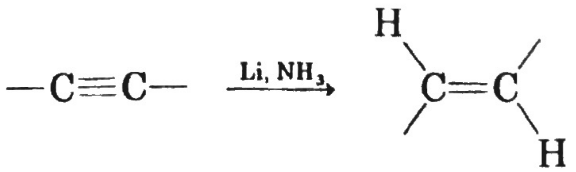
Zaitsev's rule: Major product formed is the alkene with the more highly substituted double bond.

5. Addition reactions of alkynes

(a) Addition of H_2 (hydrogenation; Section 4.14)

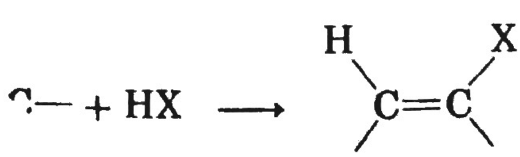


Syn addition



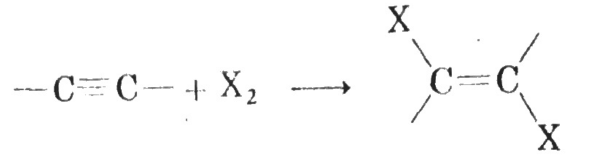
Trans addition

(b) Addition of HX, where X = Cl, Br, I (Section 4.14)

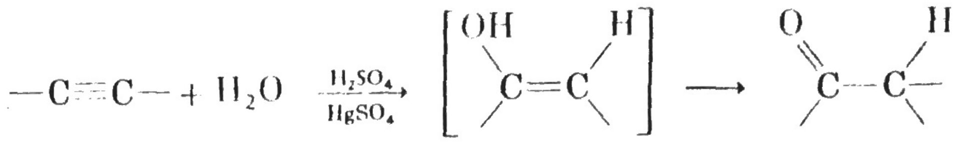


Markovnikov's rule: H adds to the less highly substituted carbon and X adds to the more highly substituted one.

(c) Addition of X_2, where X = Cl, Br (Section 4.14)

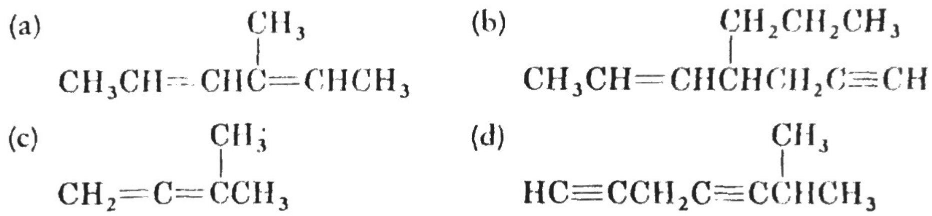


(d) Addition of H_2O to yield ketones (Section 4.15)



ADDITIONAL PROBLEMS

4.24 Provide IUPAC names for these compounds:



4.25 Draw structures corresponding to these IUPAC names:

(a) 3-Ethyl-1-heptyne (b) 3,5-Dimethyl-4-hexen-1-yne
(c) 1,5-Heptadiyne (d) 1-Methyl-1,3-cyclopentadiene

4.26 Draw three possible structures for each of these formulas:

(a) C_6H_8 (b) C_6H_8O

4.27 Name these alkynes according to IUPAC rules:

(a) $CH_3CH_2C{\equiv}CCH_2CH_2CH_3$ (b) $CH_3CH_2C{\equiv}CC(CH_3)_3$
(c) $CH_3C{\equiv}CCH_2C{\equiv}CCH_2CH_3$ (d) $H_2C{=}CHCH{=}CHC{\equiv}CH$

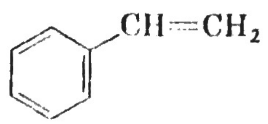
4.28 Draw structures corresponding to these IUPAC names:

(a) 3-Heptyne (b) 3,3-Dimethyl-4-octyne
(c) 3,4-Dimethylcyclodecyne (d) 2,2,5,5-Tetramethyl-3-hexyne

4.29 Draw and name all of the possible pentyne isomers, C_5H_8.

4.30 Draw and name the six possible diene isomers of formula C_5H_8. Which of the six are conjugated dienes?

4.31 Predict the products of these reactions. Indicate regiochemistry where relevant. (The aromatic ring is inert to all of the indicated reagents.)



Styrene

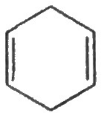
(a) Styrene + H_2 $\xrightarrow{Pd}$?

(b) Styrene + Br_2 $\longrightarrow$?

(c) Styrene + HBr $\longrightarrow$?

(d) Styrene + $KMnO_4$ $\xrightarrow{NaOH,\ H_2O}$?

4.32 Using an oxidative cleavage reaction, explain how you would distinguish between these two isomeric cyclohexadienes:


and


4.33 Formulate the reaction of cyclohexene with Br_2, showing the reaction intermediate and the final product with correct stereochemistry.

4.34 What products would you expect to obtain from reaction of 1,3-cyclohexadiene with each of the following?

(a) 1 mol Br_2 in CCl_4 (b) O_3, followed by Zn (c) 1 mol HCl
(d) 1 mol DCl (D = deuterium) (e) H_2 over a Pd catalyst

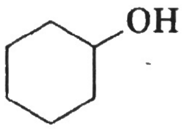
4.35 Draw the structure of a hydrocarbon that reacts with only 1 mol equiv. of hydrogen on catalytic hydrogenation and that gives only pentanal, $CH_3CH_2CH_2CH_2CHO$, on treatment with ozone. Write the reactions involved.

4.36 Give the structure of an alkene that yields the following keto aldehyde on reaction with ozone, followed by treatment with Zn/H_3O^+.

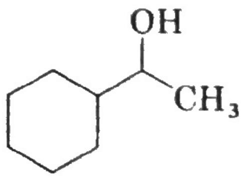
$$? \xrightarrow[2.\ Zn,\ H_3O^+]{1.\ O_3} \mathrm{H\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3}$$

4.37 What alkenes would you hydrate to obtain these alcohols?

(a) $\mathrm{CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_3}$ (b)

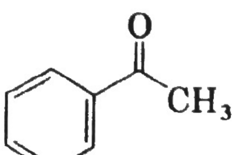


(c)



4.38 What alkynes would you hydrate to obtain these products?

(a) $\mathrm{CH_3\overset{CH_3}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}CH_3}$ (b)



4.39 Draw the structure of a hydrocarbon that reacts with 2 mol equiv. of hydrogen on catalytic hydrogenation and that gives only butanedial, $OHCCH_2CH_2CHO$, on reaction with ozone.

4.40 Predict the products of these reactions:

$CH_3CH_2CH_2CH_2C{\equiv}CH$
1-Hexyne

(a) $\xrightarrow{\text{1 equiv HBr}}$?

(b) $\xrightarrow{\text{1 equiv } Cl_2}$?

4.41 Predict the products of these reactions:

$CH_3CH_2CH_2CH_2C{\equiv}CCH_2CH_2CH_2CH_3$

5-Decyne

(a) $\xrightarrow{H_2,\ \text{Lindlar catalyst}}$

(b) $\xrightarrow{Li,\ NH_3}$

(c) $\xrightarrow{2\ \text{equiv. } Br_2}$

(d) $\xrightarrow{H_2O,\ H_2SO_4,\ HgSO_4}$

4.42 Acrylonitrile, $H_2C{=}CHC{\equiv}N$, contains a carbon–carbon double bond and a carbon–nitrogen triple bond. Sketch the orbitals involved in the bonding in acrylonitrile and indicate the hybridization of the carbons. Is acrylonitrile conjugated?

4.43 Using 1-butyne as the only organic starting material, along with any inorganic reagents needed, how would you synthesize these compounds? More than one step may be needed.

(a) Butane (b) 1,1,2,2-Tetrachlorobutane
(c) 2-Bromobutane (d) 2-Butanone ($CH_3CH_2COCH_3$)

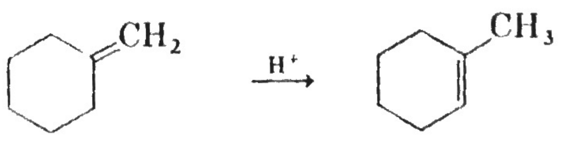
4.44 Give the structure of an alkene that provides only acetone, $(CH_3)_2C{=}O$, on reaction with ozone.

4.45 Compound A has the formula C_8H_8. It reacts rapidly with acidic $KMnO_4$ but reacts with only 1 equiv of H_2 over a palladium catalyst. On hydrogenation under conditions that reduce aromatic rings, A reacts with 4 equiv of H_2, and hydrocarbon B, C_8H_{16} is produced. The reaction of A with $KMnO_4$ gives CO_2 and a carboxylic acid C, $C_7H_6O_2$. What are the structures of A, B, and C? Write all of the reactions.

4.46 Draw a reaction energy diagram for the addition of HBr to 1-pentene. Let one curve on your diagram show the formation of 1-bromopentane product and another curve on the same diagram show the formation of 2-bromopentane product. Label the position for all reactants, intermediates, and products.

4.47 Make sketches of what you imagine the transition-state structures to look like in the reaction of HBr with 1-pentene (Problem 4.43).

4.48 Methylenecyclohexane, on treatment with strong acid, isomerizes to yield 1-methylcyclohexene:



Methylenecyclohexane 1-Methylcyclohexene

Propose a mechanism by which this reaction might occur.