CHAPTER

4

The Spectra fiber in the bulletproof vests used by police and military is made of ultra high molecular weight polyethylene, a simple alkene polymer.

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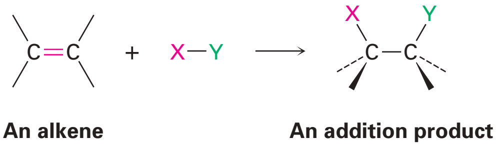
Reactions of Alkenes and Alkynes

Much of the background needed to understand organic reactions has been covered, and it's now time to begin a systematic description of the major functional groups. We'll start in this chapter with a study of the alkene and alkyne families of compounds, and we'll see that the most important reaction of these two functional groups is the addition to the C=C and C≡C multiple bonds of various reagents X–Y to yield saturated products. In fact, all the reactions we'll discuss in this chapter follow the same pattern.



WHY THIS CHAPTER?

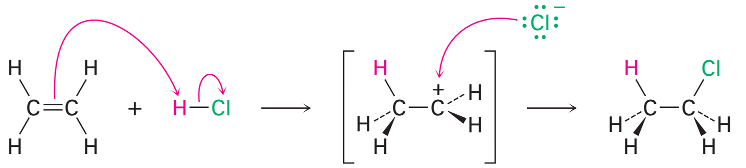
Both in this chapter on alkenes and in future chapters on other functional groups, we'll discuss a variety of reactions but will focus on the general principles and patterns of reactivity that tie organic chemistry together. There are no shortcuts; you have to know the reactions to understand organic chemistry.

OWL

Online homework for this chapter can be assigned in OWL, an online homework assessment tool.

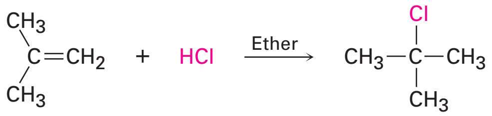
4.1 Addition of HX to Alkenes: Markovnikov's Rule

We saw in Section 3.7 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.

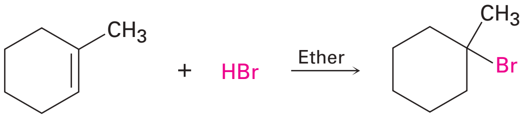


Ethylene **Carbocation intermediate** **Chloroethane**

The addition of halogen acids, HX, to alkenes is a general reaction that allows chemists to prepare a variety of halo-substituted alkane products. Thus, HCl, HBr, and HI all add to alkenes.



2-Methylpropene **2-Chloro-2-methylpropane**

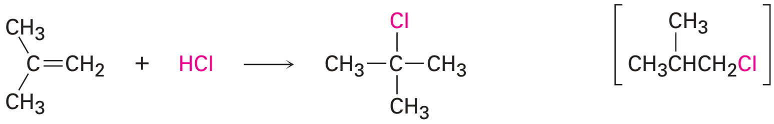


1-Methylcyclohexene **1-Bromo-1-methylcyclohexane**

Pent-1-ene **2-Iodopentane**

Look carefully at the three reactions just shown. In each 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 reacted with HCl to give 1-chloro-2-methylpropane in addition to 2-chloro-2-methylpropane, but it didn't. We say that such reactions are **regiospecific** (**ree**-jee-oh-specific) when only one of the two possible orientations of addition occurs.

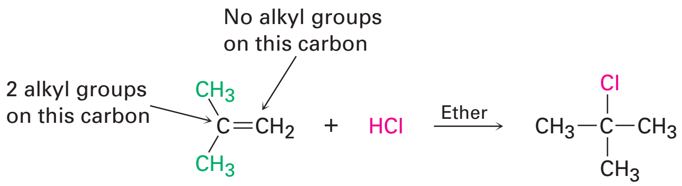
A regiospecific reaction:



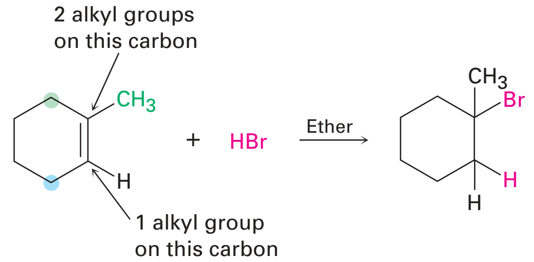
2-Methylpropene **2-Chloro-2-methylpropane** (sole product) **1-Chloro-2-methylpropane** (*NOT formed*)

After looking at the results of many such reactions, the Russian chemist Vladimir Markovnikov proposed in 1869 what has become known as **Markovnikov's rule**:

MARKOVNIKOV'S RULE In the addition of HX to an alkene, the H attaches to the carbon with fewer alkyl substituents and the X attaches to the carbon with more alkyl substituents.

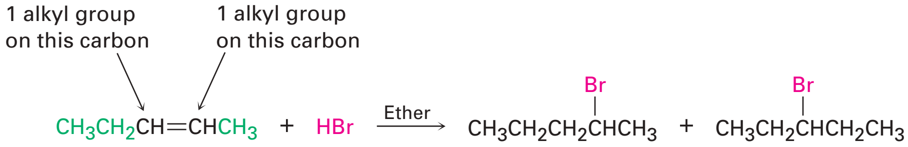


2-Methylpropene **2-Chloro-2-methylpropane**



1-Methylcyclohexene **1-Bromo-1-methylcyclohexane**

When both double-bond carbon atoms have the same degree of substitution, a mixture of addition products results.



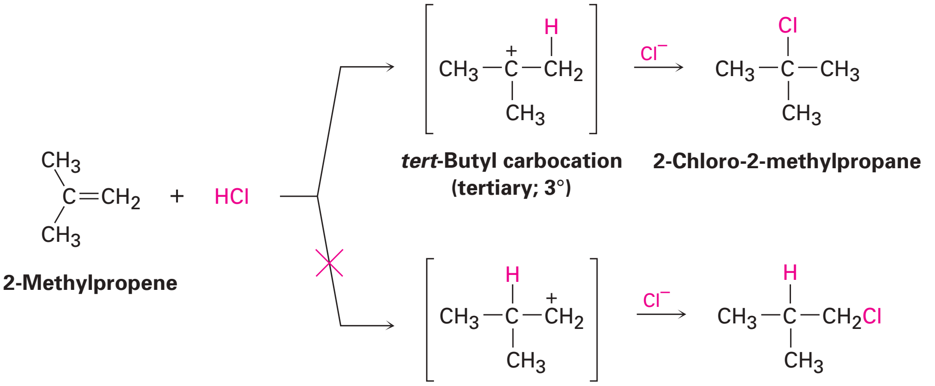
$$CH_3CH_2CH{=}CHCH_3 + HBr \xrightarrow{\text{Ether}} CH_3CH_2CH_2\overset{\displaystyle Br}{\overset{|}{C}}HCH_3 + CH_3CH_2\overset{\displaystyle Br}{\overset{|}{C}}HCH_2CH_3$$

Pent-2-ene **2-Bromopentane** **3-Bromopentane**

Because carbocations are involved as intermediates in these reactions (Section 3.8), Markovnikov's rule can be restated.

MARKOVNIKOV'S RULE (RESTATED) In the addition of HX to an alkene, the more highly substituted carbocation is formed as the intermediate rather than the less highly substituted one.

For example, addition of H^+ to 2-methylpropene yields the intermediate *tertiary* carbocation rather than the alternative primary carbocation. Why should this be?



2-Methylpropene

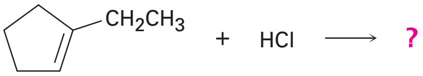
***tert*-Butyl carbocation (tertiary; 3°)** **2-Chloro-2-methylpropane**

Isobutyl carbocation (primary; 1°) **1-Chloro-2-methylpropane *(NOT formed)***

Worked Example 4.1

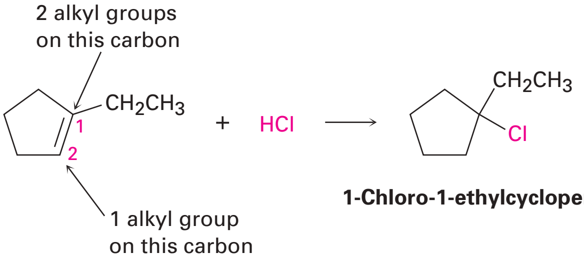
Predicting the Product of an Alkene Addition Reaction

What product would you expect from the reaction of HCl with 1-ethylcyclopentene?



Strategy When solving a problem that asks you to predict a reaction product, begin by looking at the functional group(s) in the reactants and deciding what kind of reaction is likely to occur. In the present instance, the reactant is an alkene that will probably undergo an electrophilic addition reaction with HCl. Next, recall what you know about electrophilic addition reactions, and use your knowledge to predict the product. You know that electrophilic addition reactions follow Markovnikov's rule, so H^+ will add to the double-bond carbon that has one alkyl group (C2 on the ring) and Cl will add to the double-bond carbon that has two alkyl groups (C1 on the ring).

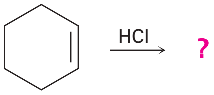
Solution The expected product is 1-chloro-1-ethylcyclopentane.



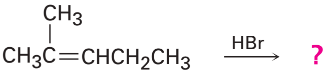
1-Chloro-1-ethylcyclopentane

Problem 4.1 Predict the products of the following reactions:

(a)

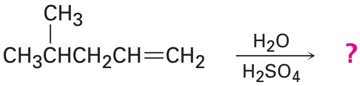


(b)



$CH_3\overset{\overset{CH_3}{|}}{C}{=}CHCH_2CH_3 \xrightarrow{HBr}$?

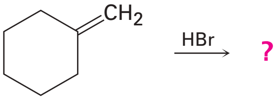
(c)



$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH{=}CH_2 \xrightarrow[H_2SO_4]{H_2O}$?

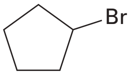
(Addition of H_2O occurs.)

(d)

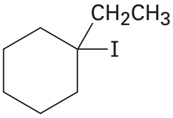


Problem 4.2 What alkenes would you start with to prepare the following alkyl halides?

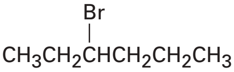
(a)



(b)

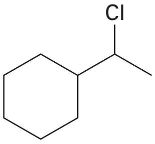


(c)



$CH_3CH_2\overset{\overset{Br}{|}}{C}HCH_2CH_2CH_3$

(d)



4.2 Carbocation Structure and Stability

To understand why Markovnikov's rule works, we need to learn more about the structure and stability of substituted carbocations. With respect to structure, experimental evidence shows that carbocations are *planar*. The positively charged carbon atom is sp^2-hybridized, and the three substituents bonded to it are oriented to the corners of an equilateral triangle, as indicated in Figure 4.1. Because there are only six valence electrons on carbon and all six are used in the three σ bonds, the p orbital extending above and below the plane is unoccupied.

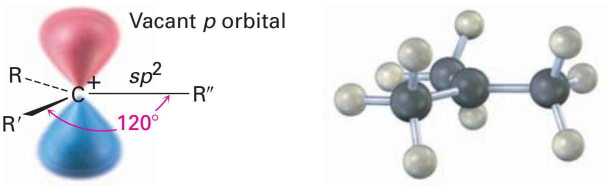
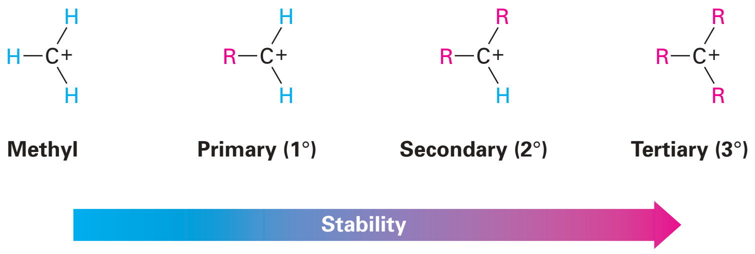
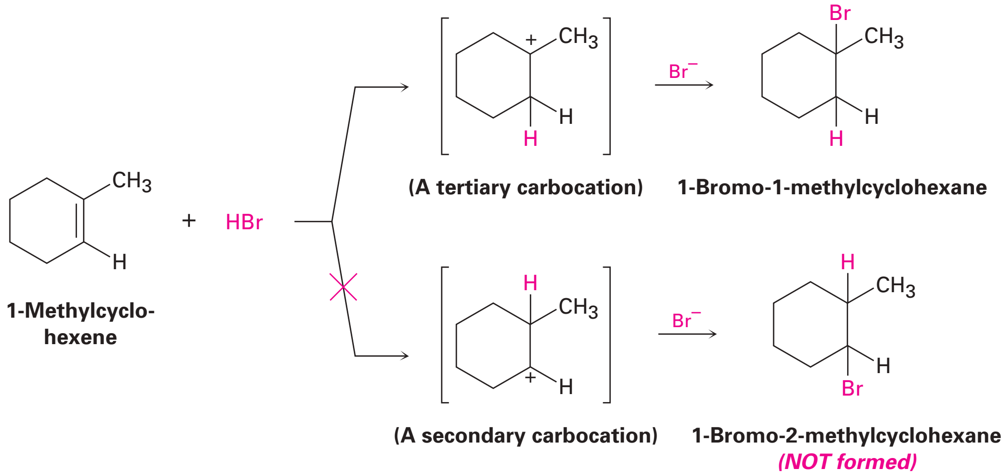


Figure 4.1 The structure of a carbocation. The trivalent carbon is sp^2-hybridized and has an unoccupied p orbital perpendicular to the plane of the carbon and three attached groups.

With respect to stability, experimental evidence shows that carbocation stability increases with increasing 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.

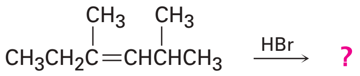


With this knowledge, we can now explain Markovnikov's rule. In the reaction of 1-methylcyclohexene with HBr, for instance, the intermediate carbocation might have either three alkyl substituents (a tertiary cation, 3°) or two alkyl substituents (a secondary cation, 2°). Because the tertiary cation is more stable than the secondary one, it's the tertiary cation that forms as the reaction intermediate, thus leading to the observed tertiary alkyl bromide product.



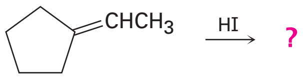
Problem 4.3 Show the structures of the carbocation intermediates you would expect in the following reactions:

(a)



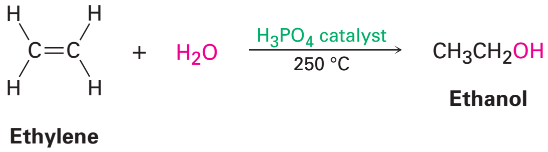
$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}{=}CH\overset{CH_3}{\overset{|}{C}}HCH_3 \xrightarrow{HBr} ?$$

(b)



4.3 Addition of Water to Alkenes

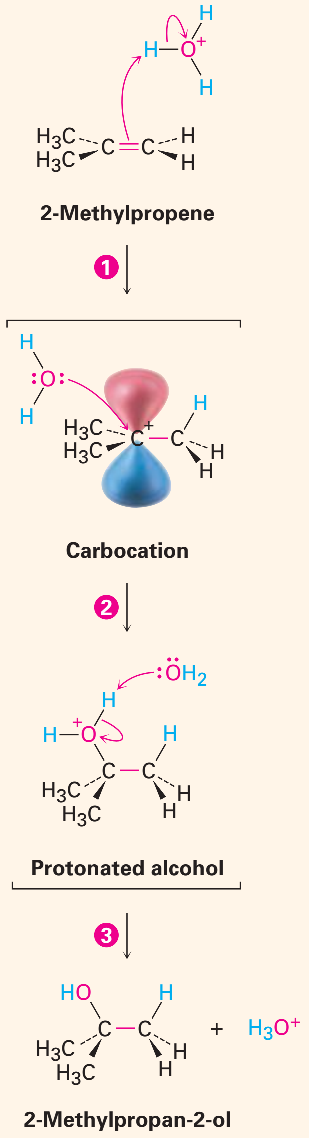
Just as HCl and HBr add to alkenes to yield alkyl halides, H_2O adds to alkenes to yield alcohols, ROH, a process called *hydration.* Industrially, more than 300,000 tons of ethanol are produced each year in the United States by this method.



Hydration takes place on treatment of the alkene with water and a strong acid catalyst by a mechanism similar to that of HX addition. Thus, protonation of the alkene double bond yields a carbocation intermediate, which reacts with water as nucleophile to yield a protonated alcohol (ROH_2^+). Loss of H^+ from this protonated alcohol then 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.

MECHANISM

Figure 4.2 Mechanism of the acid-catalyzed hydration of an alkene to yield an alcohol. Protonation of the alkene gives a carbocation intermediate, which reacts with water.



① A hydrogen atom on the electrophile H_3O^+ is attacked by π electrons from the nucleophilic double bond, forming a new C–H bond. This leaves the other carbon atom with a + charge and a vacant *p* orbital. Simultaneously, two electrons from the H–O bond move onto oxygen, giving neutral water.

② The nucleophile H_2O donates an electron pair to the positively charged carbon atom, forming a C–O bond and leaving a positive charge on oxygen in the protonated alcohol addition product.

③ Water acts as a base to remove H^+, regenerating H_3O^+ and yielding the neutral alcohol addition product.

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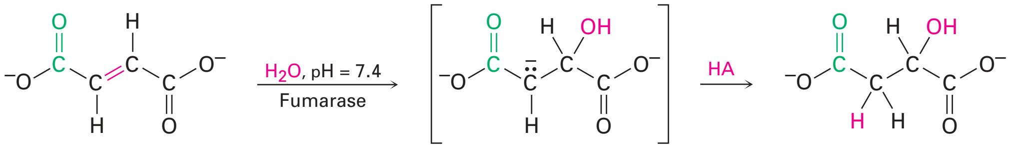
Unfortunately, the reaction conditions required for hydration are severe: the hydration of ethylene to produce ethanol, for instance, requires a phosphoric acid catalyst and reaction temperatures of up to 250 °C. As a result, sensitive molecules are sometimes destroyed. To get around this difficulty, chemists have devised several alternative methods of alkene hydration that take place under nonacidic conditions at room temperature, but we'll not discuss them here.

Hydration of carbon–carbon double bonds also occurs in various biological pathways, although not by the carbocation mechanism. Instead, biological hydrations usually require that the double bond be adjacent to a carbonyl group (C═O) for reaction to proceed. Fumarate, for instance, is hydrated to give malate as one step in the citric acid cycle of food metabolism. We'll see the function of the nearby carbonyl group in Section 9.10 but might note for now that the reaction occurs through a mechanism that involves formation of an anion intermediate followed by protonation by an acid HA.

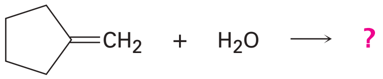


Fumarate **Anion intermediate** **Malate**

Worked Example 4.2

Predicting the Product of an Alkene Hydration Reaction

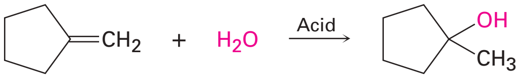
What product would you expect from acid-catalyzed addition of water to methylenecyclopentane?



Methylenecyclopentane

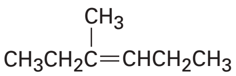
Strategy According to Markovnikov's rule, H^+ adds to the carbon that already has more hydrogens (the $=CH_2$ carbon) and OH adds to the carbon that has fewer hydrogens (the ring carbon). Thus, the product will be a tertiary alcohol.

Solution



Problem 4.4 What product would you expect to obtain from the acid-catalyzed addition of water to the following alkenes?

(a)



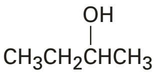
$$\mathrm{CH_3CH_2\overset{\overset{CH_3}{|}}{C}{=}CHCH_2CH_3}$$

(b) 1-Methylcyclopentene

(c) 2,5-Dimethylhept-2-ene

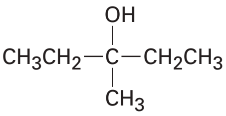
Problem 4.5 What alkenes might the following alcohols be made from?

(a)



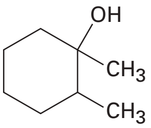
$$\mathrm{CH_3CH_2\overset{\overset{OH}{|}}{C}HCH_3}$$

(b)



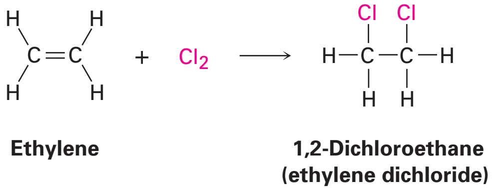
$$\mathrm{CH_3CH_2{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}{-}CH_2CH_3}$$

(c)

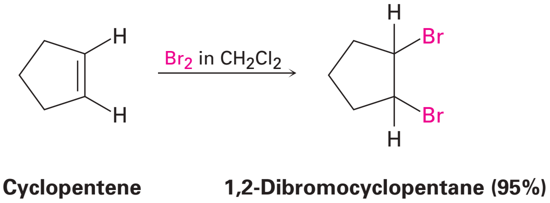


4.4 Addition of Halogens to Alkenes

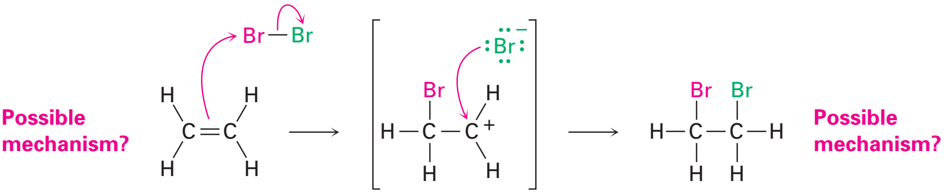
Many other substances besides HX and H_2O add to alkenes. Bromine and chlorine, for instance, add readily to yield 1,2-dihaloalkanes, a process called *halogenation*. More than 10 million tons of 1,2-dichloroethane (also called ethylene dichloride) are synthesized each year in the United States by addition of Cl_2 to ethylene. The product is used both as a solvent and as a starting material for the synthesis of poly(vinyl chloride), PVC.



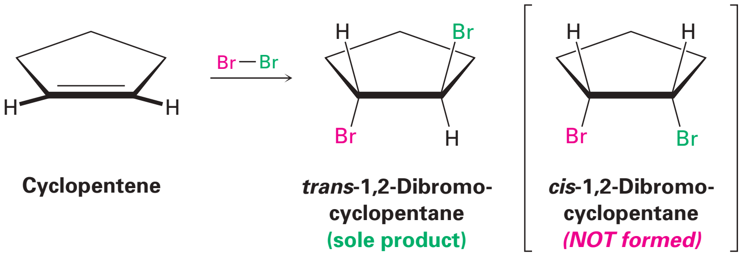
Addition of Br_2 also acts as a simple and rapid laboratory test for unsaturation. A sample of unknown structure is dissolved in dichloromethane, CH_2Cl_2, and several drops of Br_2 are added. Immediate disappearance of the reddish Br_2 color signals a positive test and indicates that the sample molecule contains a double bond.



Based on what we've seen thus far, a possible mechanism for the reaction of bromine (or chlorine) with an alkene might involve electrophilic addition of Br^+ to the alkene, giving a carbocation that could undergo further reaction with Br^- to yield the dibromo addition product.



Although this mechanism looks reasonable, it's not consistent with known facts because it doesn't explain the stereochemical (Section 2.8), or three-dimensional, aspects of halogen addition. That is, the mechanism doesn't explain what product stereoisomers are formed. When the halogenation reaction is carried out on a cycloalkene, such as cyclopentene, only *trans*-1,2-dibromocyclopentane is formed rather than the mixture of cis and trans products that might have been expected if a planar carbocation intermediate were involved. We say that the reaction occurs with **anti stereochemistry**, meaning that the two bromine atoms come from opposite faces of the double bond approximately 180° apart.



The stereochemical result is best explained by imagining that the reaction intermediate is not a true carbocation but is instead a *bromonium ion,* R_2Br^+, formed in a single step by addition of Br^+ to the double bond. Since the bromine atom effectively "shields" one side of the molecule, reaction with Br^- ion in the second step occurs from the opposite, more accessible side to give the anti product (Figure 4.3).

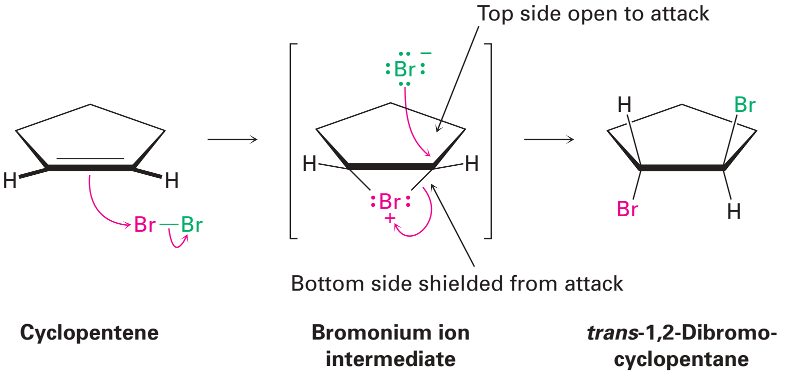
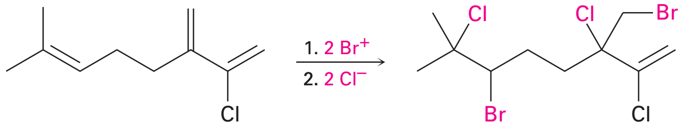


Figure 4.3 Mechanism of the addition of Br_2 to an alkene. A bromonium ion intermediate is formed, shielding one face of the double bond and resulting in trans stereochemistry for the addition product.

The addition of halogens to carbon–carbon double bonds also occurs in nature just as it does in the laboratory but is limited primarily to marine organisms, which live in a halide-rich environment. The biological halogenation reactions are carried out by enzymes called *haloperoxidases,* which use H_2O_2 to oxidize Br^- or Cl^- ions to a biological equivalent of Br^+ or Cl^+. Electrophilic addition to the double bond of a substrate molecule then yields a bromonium or chloronium ion intermediate just as in the laboratory, and reaction with another halide ion completes the process. Halomon, for example, an anticancer pentahalide isolated from red alga, is thought to arise by a route that involves twofold addition of BrCl through the corresponding bromonium ions.



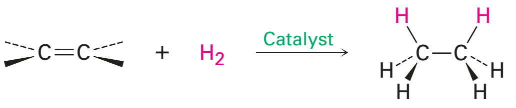
Halomon

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

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

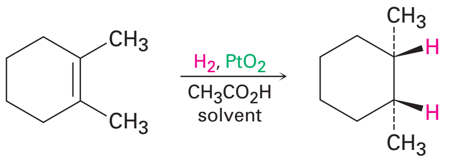
4.5 Reduction of Alkenes: Hydrogenation

Addition of H_2 to the C=C bond occurs when an alkene is exposed to an atmosphere of hydrogen gas in the presence of a metal catalyst to yield an alkane.



An alkene **An alkane**

We describe the result by saying that the double bond is **hydrogenated**, or *reduced*. (The word **reduction** in organic chemistry usually refers to the addition of hydrogen or removal of oxygen from a molecule.) For most alkene hydrogenations, either palladium metal or platinum (as PtO_2) is used as the catalyst.



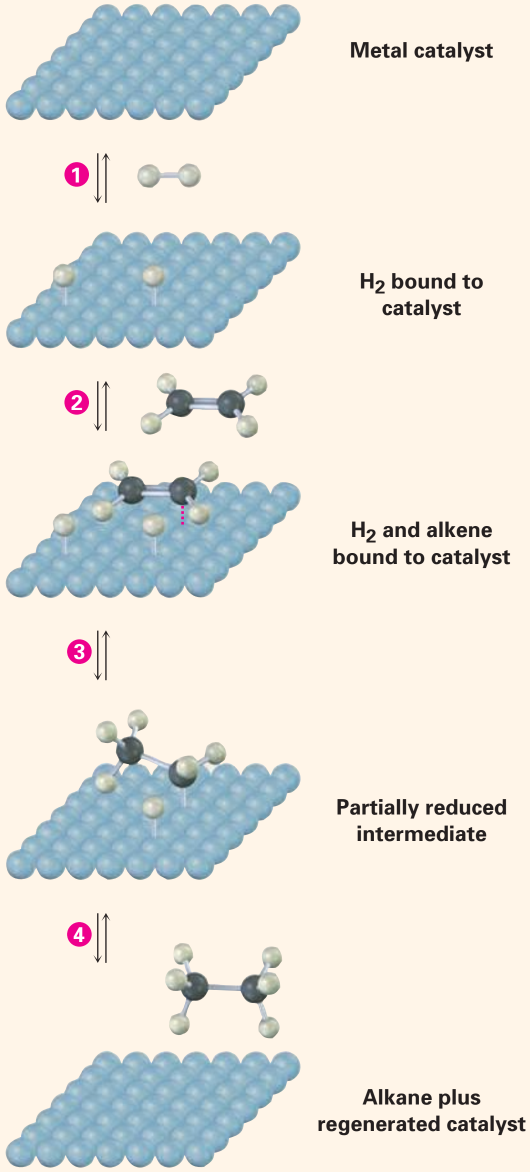
1,2-Dimethylcyclohexene ***cis*-1,2-Dimethylcyclohexane (82%)**

Catalytic hydrogenation of alkenes, unlike most other organic reactions, 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. Following initial adsorption of H_2 onto the catalyst surface, complexation between catalyst and alkene then occurs as a vacant orbital on the metal interacts with the filled alkene π orbital. Next, hydrogen is inserted into the double bond, and the saturated product diffuses away from the catalyst (Figure

4.4). The reaction occurs with **syn stereochemistry** (the opposite of *anti*), meaning that both hydrogens add to the double bond from the same side.

MECHANISM

Figure 4.4 Mechanism of alkene hydrogenation. The reaction takes place with syn stereochemistry on the surface of insoluble catalyst particles.



① Molecular hydrogen adsorbs to the catalyst surface and dissociates into hydrogen atoms.

② The alkene adsorbs to the catalyst surface, using its π bond to complex to the metal atoms.

③ A hydrogen atom is transferred from the metal to one of the alkene carbon atoms, forming a partially reduced intermediate with a C–H bond and carbon–metal σ bond.

④ A second hydrogen is transferred from the metal to the second carbon, giving the alkane product and regenerating the catalyst. Because both hydrogens are transferred to the same face of the alkene, the reduction has syn stereochemistry.

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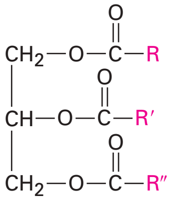
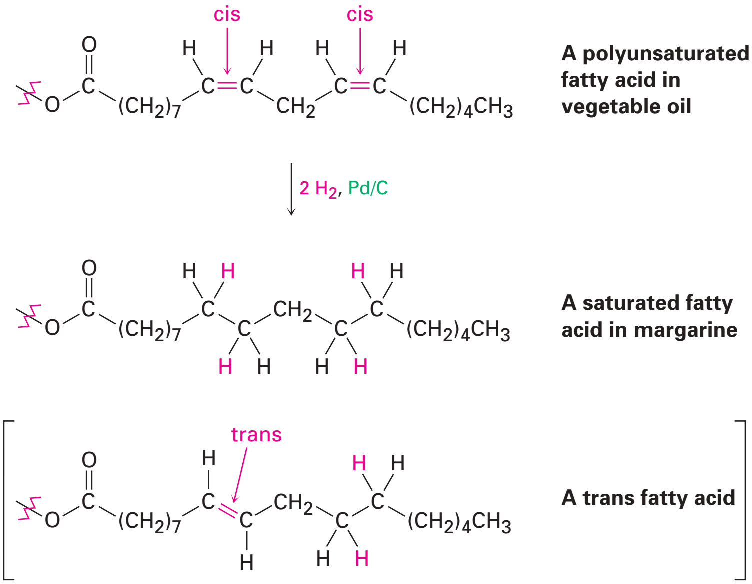
In addition to its usefulness in the laboratory, catalytic hydrogenation is also important in the food industry, where unsaturated vegetable oils are reduced to produce the saturated fats used in margarine and cooking products. As we'll see in Section 16.1, vegetable oils are triesters of glycerol, $HOCH_2CH(OH)CH_2OH$, with three long-chain carboxylic acids called *fatty acids*. The fatty acids are generally polyunsaturated, and their double bonds have cis stereochemistry. Complete hydrogenation yields the corresponding saturated fatty acids, but incomplete hydrogenation often results in partial cis–trans isomerization of a remaining double bond. When eaten and digested, the free trans fatty acids are released, raising blood cholesterol levels and contributing to potential coronary problems.

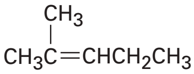


A vegetable oil



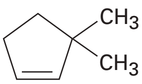
Problem 4.8 What product would you expect to obtain from catalytic hydrogenation of the following alkenes?

(a)



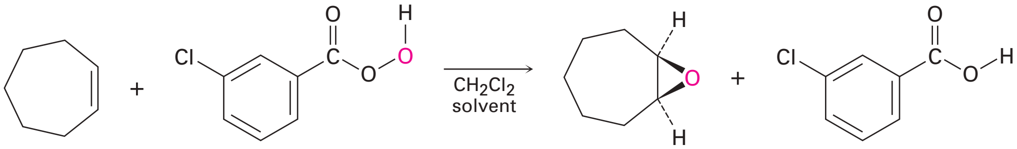
$$CH_3\overset{CH_3}{\overset{|}{C}}=CHCH_2CH_3$$

(b)



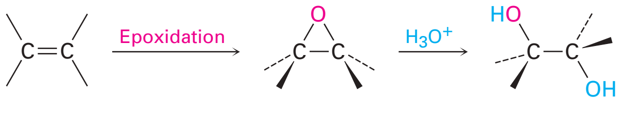
4.6 Oxidation of Alkenes: Epoxidation, Hydroxylation, and Cleavage

Just as the word *reduction* usually refers to the addition of *hydrogen* to a molecule, the word **oxidation** usually means the addition of *oxygen.* For example, alkenes are oxidized to give *epoxides* on treatment with a peroxyacid, RCO_3H, such as *meta*-chloroperoxybenzoic acid. An **epoxide**, also called an *oxirane,* is a cyclic ether with an oxygen atom in a three-membered ring.



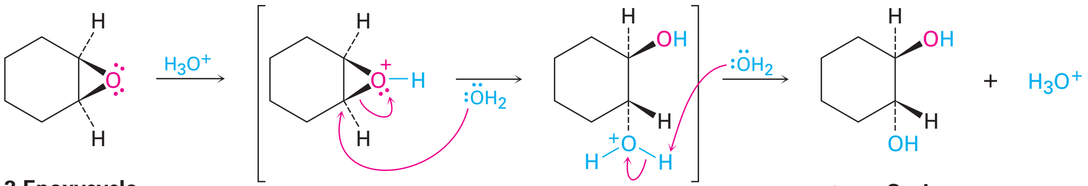
Cycloheptene **meta-Chloroperoxybenzoic acid** **1,2-Epoxycycloheptane** **meta-Chlorobenzoic acid**

Epoxides undergo an acid-catalyzed ring-opening reaction with water (a *hydrolysis*) to give the corresponding dialcohol, or *diol,* also called a *glycol.* The net result of the two-step alkene epoxidation/hydrolysis is thus a **hydroxylation**—the addition of an −OH group to each of the two double-bond carbons. In fact, more than 3 million tons of ethylene glycol, $HOCH_2CH_2OH$, most of it used for automobile antifreeze, are produced each year in the United States by epoxidation of ethylene followed by hydrolysis.



An alkene **An epoxide** **A 1,2-diol**

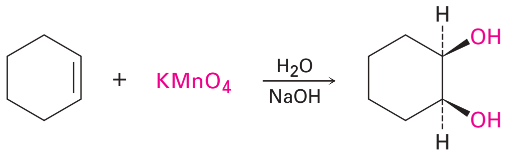
Acid-catalyzed epoxide opening takes place by protonation of the epoxide to increase its reactivity, followed by nucleophilic addition of water. This nucleophilic addition is analogous to the final step of alkene bromination that we saw in Section 4.4, in which a cyclic bromonium ion was opened by a reaction with bromide ion. As a result, a *trans*-1,2-diol results when an epoxycycloalkane is opened by aqueous acid, just as a *trans*-1,2-dibromide results when a cycloalkene is brominated.



1,2-Epoxycyclohexane

***trans*-Cyclohexane-1,2-diol (86%)**

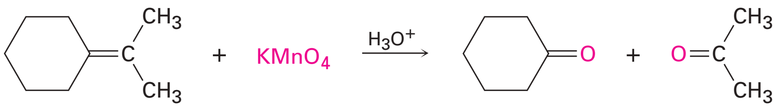
The hydroxylation of an alkene can also be carried out in a single step by reaction of the alkene with potassium permanganate, $KMnO_4$, in basic solution. For example, cyclohexene gives *cis*-cyclohexane-1,2-diol.



Cyclohexene

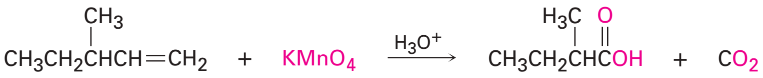
***cis*-Cyclohexane-1,2-diol (37%)**

When oxidation of the alkene is carried out with $KMnO_4$ in acidic rather than basic solution, *cleavage* of the double bond occurs and carbonyl-containing products are obtained. 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)



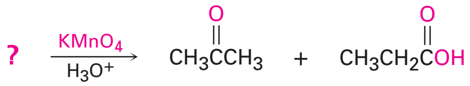
$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH{=}CH_2 + KMnO_4 \xrightarrow{H_3O^+} CH_3CH_2\overset{H_3C}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}OH + CO_2$$

3-Methylpent-1-ene **2-Methylbutanoic acid (45%)**

Worked Example 4.3

Predicting the Structure of a Reactant Given the Products

What alkene gives a mixture of acetone and propanoic acid on reaction with acidic $KMnO_4$?

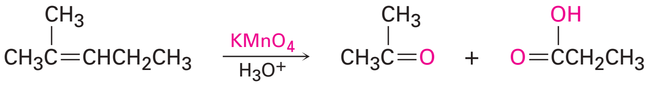


$$? \xrightarrow[H_3O^+]{KMnO_4} CH_3\overset{O}{\overset{\|}{C}}CH_3 + CH_3CH_2\overset{O}{\overset{\|}{C}}OH$$

Acetone **Propanoic acid**

Strategy When solving a problem that asks how to prepare a given product, *always work backward*. Look at the product, identify the functional group(s) it contains, and ask yourself, "How can I prepare that functional group?" In the present instance, the products are a ketone and a carboxylic acid, which can be prepared by reaction of an alkene with acidic $KMnO_4$. To find the starting alkene that gives the cleavage products shown, remove the oxygen atoms from the two products, join the fragments with a double bond, and replace the −OH by −H.

Solution



$$CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_2CH_3 \xrightarrow[H_3O^+]{KMnO_4} CH_3\overset{CH_3}{\overset{|}{C}}{=}O + O{=}\overset{OH}{\overset{|}{C}}CH_2CH_3$$

2-Methylpent-2-ene **Acetone** **Propanoic acid**

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

(a) $KMnO_4$, H_3O^+ **(b)** $KMnO_4$, OH^-, H_2O

Problem 4.10 Propose structures for alkenes that yield the following products on treatment with acidic $KMnO_4$:

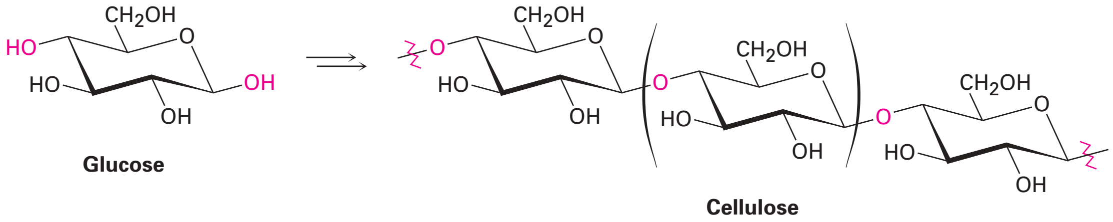
(a) $(CH_3)_2C{=}O + CO_2$ **(b)** 2 equiv $CH_3CH_2CO_2H$

4.7 Addition of Radicals to Alkenes: Polymers

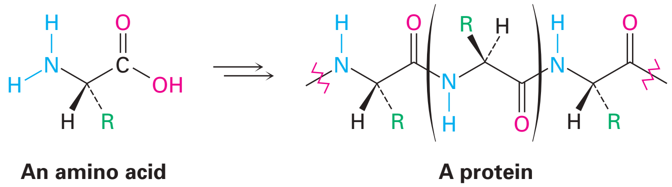
No other group of synthetic chemicals has had as great an impact on our day-to-day lives as *polymers*. From carpeting to clothing to foam coffee cups, we are literally surrounded by polymers.

A **polymer** is a large—sometimes *very* large—molecule built up by repetitive bonding together of many smaller molecules, called **monomers**. Nature makes wide use of biological polymers. Cellulose, for example, is a polymer built of repeating sugar monomers; proteins are polymers built of repeating amino acid monomers; and nucleic acids are polymers built of repeating nucleotide monomers.

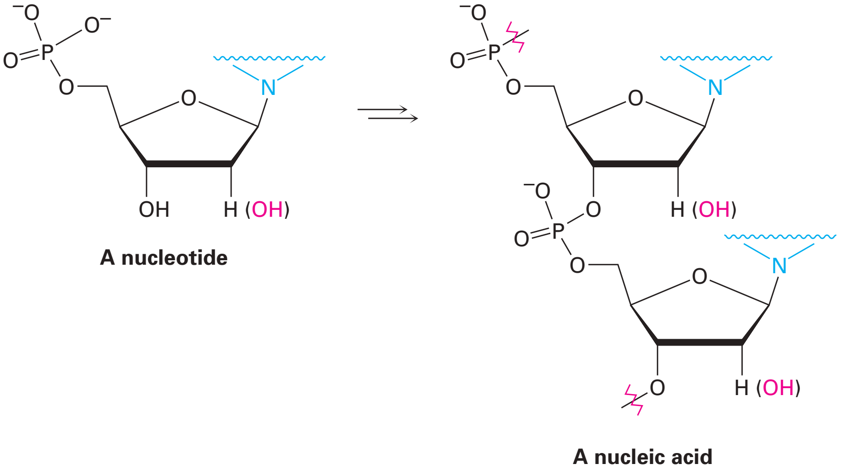
Cellulose—a glucose polymer



Protein—an amino acid polymer



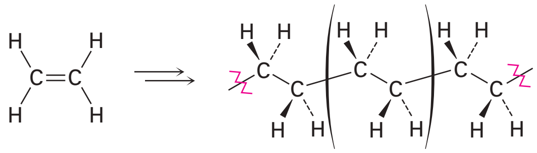
Nucleic acid—a nucleotide polymer



The simplest synthetic polymers are those that result when an alkene is treated with a small amount of a suitable polymerization catalyst. Ethylene, for example, yields polyethylene, an enormous alkane that may have up to

200,000 monomer units incorporated into a gigantic hydrocarbon chain. Approximately 19 million tons per year of polyethylene are manufactured in the United States alone.

Polyethylene—a synthetic alkene polymer

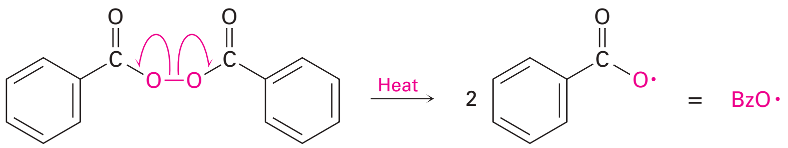


Ethylene **Polyethylene**

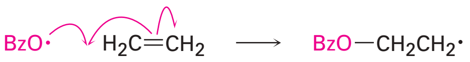
Historically, ethylene polymerization was carried out at high pressure (1000–3000 atm) and high temperature (100–250 °C) in the presence of a radical catalyst such as benzoyl peroxide, although other catalysts and reaction conditions are now more often used.

Radical polymerization of an alkene involves three kinds of steps: *initiation, propagation,* and *termination.* The key step is the addition of a radical to the ethylene double bond in a process similar to what takes place in the addition of an electrophile to an alkene (Section 3.7). In writing the mechanism, a curved half-arrow, or "fishhook," is used to show the movement of a single electron, as opposed to the full curved arrow used to show the movement of an electron pair in a polar reaction.

STEP 1 **Initiation:** The polymerization reaction is initiated when a few radicals are generated on heating a small amount of benzoyl peroxide catalyst to break the weak O–O bond. A benzoyloxy radical then adds to the C=C bond of ethylene to generate a carbon radical. One electron from the carbon–carbon double bond pairs up with the odd electron on the benzoyloxy radical to form a C–O bond, and the other electron remains on carbon.

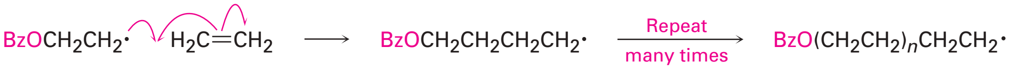


Benzoyl peroxide **Benzoyloxy radical**



$$\mathrm{BzO}\cdot \quad H_2C{=}CH_2 \longrightarrow \mathrm{BzO{-}CH_2CH_2}\cdot$$

STEP 2 **Propagation:** Polymerization occurs when the carbon radical formed in the initiation step adds to another ethylene molecule to yield another radical. Repetition of the process for hundreds or thousands of times builds the polymer chain.

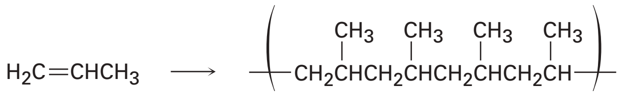


$$\mathrm{BzOCH_2CH_2}\cdot \quad H_2C{=}CH_2 \longrightarrow \mathrm{BzOCH_2CH_2CH_2CH_2}\cdot \xrightarrow[\text{many times}]{\text{Repeat}} \mathrm{BzO(CH_2CH_2)_{\mathit{n}}CH_2CH_2}\cdot$$

STEP 3 **Termination:** The polymerization process is eventually ended by a reaction that consumes the radical. Combination of two growing chains is one possible chain-terminating reaction.

$$2\ \mathrm{R{-}CH_2CH_2\cdot} \longrightarrow \mathrm{R{-}CH_2CH_2CH_2CH_2{-}R}$$

Ethylene is not unique in its ability to form a polymer. Many substituted ethylenes, called *vinyl monomers,* undergo polymerization, yielding polymers with substituent groups regularly spaced along the polymer chain. Propylene, for example, yields polypropylene.

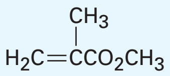


$$\mathrm{H_2C{=}CHCH_3} \longrightarrow \left(\mathrm{CH_2\overset{CH_3}{\overset{|}{C}H}CH_2\overset{CH_3}{\overset{|}{C}H}CH_2\overset{CH_3}{\overset{|}{C}H}CH_2\overset{CH_3}{\overset{|}{C}H}}\right)$$

Propylene **Polypropylene**

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

Table 4.1 Some Alkene Polymers and Their Uses

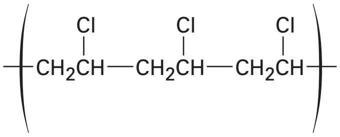
Monomer	Formula	Trade or common name of polymer	Uses
Ethylene	$H_2C{=}CH_2$	Polyethylene	Packaging, bottles
Propene (propylene)	$H_2C{=}CHCH_3$	Polypropylene	Moldings, rope, carpets
Chloroethylene (vinyl chloride)	$H_2C{=}CHCl$	Poly(vinyl chloride) Tedlar	Insulation, films, pipes
Styrene	$H_2C{=}CHC_6H_5$	Polystyrene	Foam, moldings
Tetrafluoroethylene	$F_2C{=}CF_2$	Teflon	Gaskets, nonstick coatings
Acrylonitrile	$H_2C{=}CHCN$	Orlon, Acrilan	Fibers
Methyl methacrylate	 $H_2C{=}\overset{CH_3}{\overset{\vert}{C}}CO_2CH_3$	Plexiglas, Lucite	Paint, sheets, moldings
Vinyl acetate	$H_2C{=}CHOCOCH_3$	Poly(vinyl acetate)	Paint, adhesives, foams

Worked Example 4.4 Predicting the Structure of a Polymer

Show the structure of poly(vinyl chloride), a polymer made from $H_2C{=}CHCl$, by drawing several repeating units.

Strategy Imagine breaking the carbon–carbon double bond in the monomer unit, and then form single bonds by connecting numerous units together.

Solution The general structure of poly(vinyl chloride) is

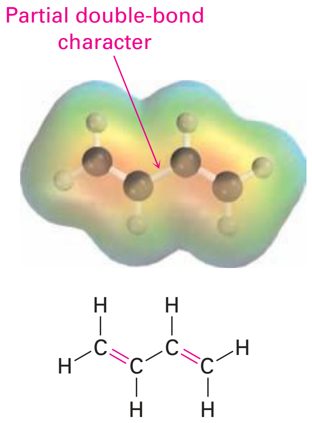


$$\left(\mathrm{CH_2\overset{Cl}{\overset{|}{C}H}{-}CH_2\overset{Cl}{\overset{|}{C}H}{-}CH_2\overset{Cl}{\overset{|}{C}H}}\right)$$

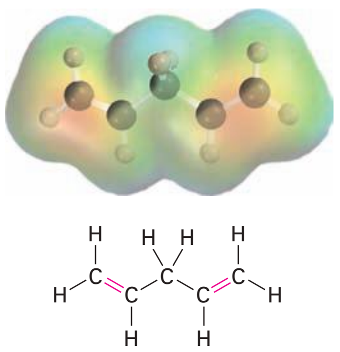
Problem 4.11 Show the structure of Teflon by drawing several repeating units. The monomer unit is tetrafluoroethylene, $F_2C{=}CF_2$.

4.8 Conjugated Dienes

The unsaturated compounds we've looked at thus far have had only one double bond, but many compounds have numerous sites of unsaturation. If the different unsaturations are well separated in a molecule, they react independently, but if they're close together, they may interact with one another. In particular, compounds that have alternating single and double bonds—so-called **conjugated** compounds—have some distinctive characteristics. The conjugated diene buta-1,3-diene, for instance, behaves quite differently from the nonconjugated penta-1,4-diene in some respects.



Buta-1,3-diene (conjugated)



Penta-1,4-diene (nonconjugated)

What's so special about conjugated dienes that we need to look at them separately? The orbital view of buta-1,3-diene shown in Figure 4.5 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.

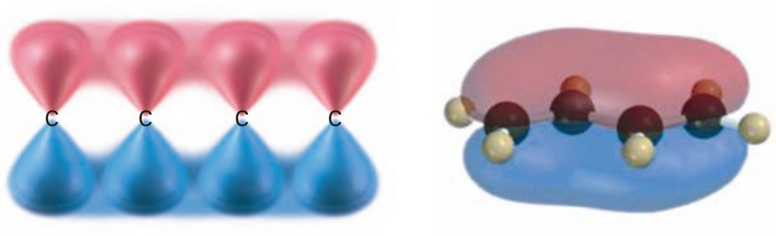
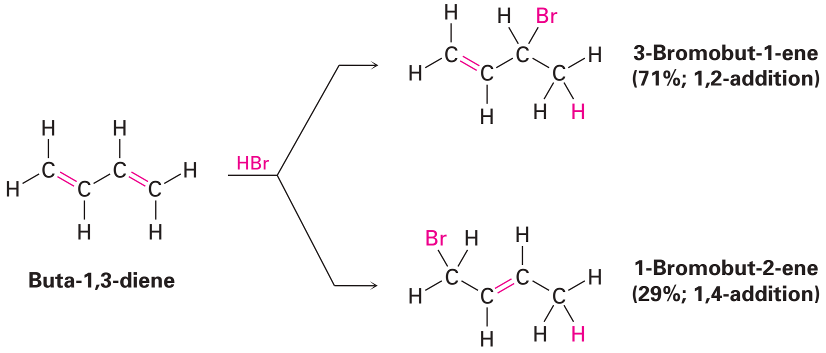
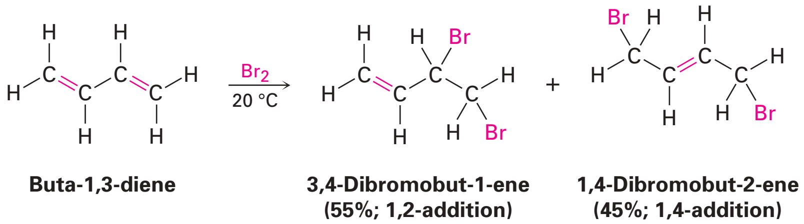


Figure 4.5 An orbital view of buta-1,3-diene. Each of the four carbon atoms has a *p* orbital, allowing for an electronic interaction across the C2–C3 single bond.

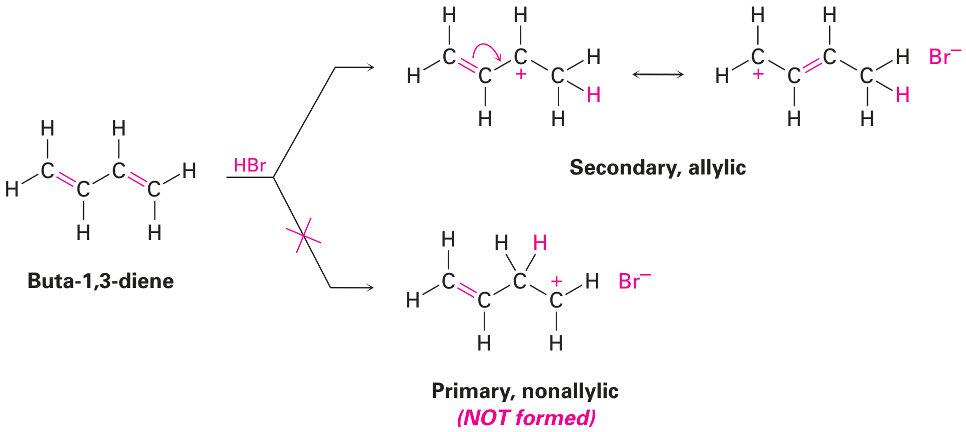
Although much of the chemistry of conjugated dienes is similar to that of isolated alkenes, there is a striking difference in their electrophilic addition reactions with HX and X_2. When HX adds to an isolated alkene, Markovnikov's rule usually predicts the formation of a single product, but when HX adds to a conjugated diene, mixtures of products are often obtained. Reaction of HBr with buta-1,3-diene, for instance, yields two products.



3-Bromobut-1-ene is the typical Markovnikov product of **1,2-addition**, but 1-bromobut-2-ene appears unusual. The double bond in this product has moved to a position between C2 and C3, and HBr has added to C1 and C4, a result described as **1,4-addition**. In the same way, Br_2 adds to buta-1,3-diene to give a mixture of 3,4-dibromobut-1-ene and 1,4-dibromobut-2-ene.



How can we account for the formation of the 1,4-addition product? The answer is that an *allylic carbocation* is involved as an intermediate in the reaction, where the word **allylic** means “next to a double bond.” When H^+ adds to an electron-rich π bond of buta-1,3-diene, two carbocation intermediates are possible—a primary nonallylic carbocation and a secondary allylic carbocation. Allylic carbocations are more stable and therefore form faster than less stable, nonallylic carbocations.



4.9 Stability of Allylic Carbocations: Resonance

Why are allylic carbocations particularly stable? To see the answer, look at the orbital picture of an allylic carbocation in Figure 4.6. From an electronic viewpoint, 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, and the two *p* electrons are free to move about the entire three-orbital array.

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

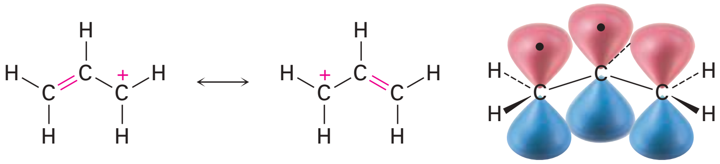


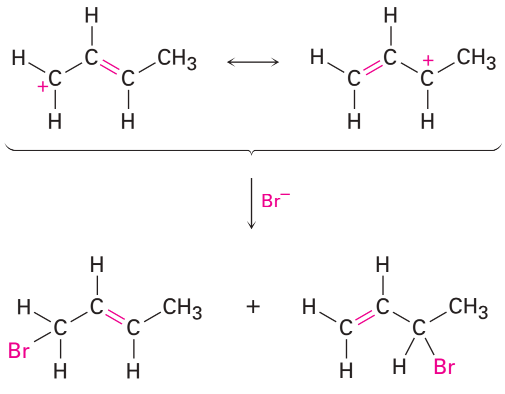
Figure 4.6 An orbital picture of an allylic carbocation. The vacant *p* orbital on the positively charged carbon can overlap the double-bond *p* orbitals. As a result, there are two ways to draw the structure.

The two individual structures of an allylic carbocation are called **resonance forms**, and their special relationship is indicated by a double-headed arrow placed between them. The only difference between the resonance forms is the position of the bonding electrons. The atoms themselves remain in exactly the same place in both resonance forms, the connections between atoms are the same, and the three-dimensional shapes of the resonance forms are the same.

A good way to think about resonance is to realize that a species like an allylic carbocation is no different from any other. 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, an allylic carbocation has a single, unchanging structure called a **resonance hybrid** that is a blend of the two individual forms and has characteristics of both. The only "problem" with the allylic carbocation is visual rather than chemical because we can't draw it using a single line-bond structure. Simple line-bond structures just don't work well for resonance hybrids. The difficulty, however, is with the *representation* of the structure, not with the structure itself.

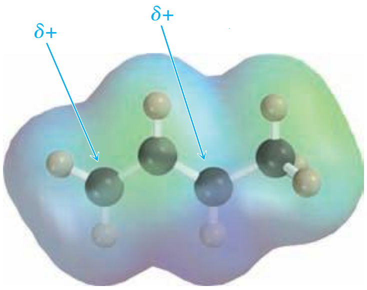
One of the most important consequences of resonance is that the resonance hybrid is more stable than any individual resonance form. In other words, *resonance leads to stability*. Generally speaking, the larger the number of resonance forms, the more stable a substance is because electrons are spread out over a larger part of the molecule and are closer to more nuclei. Because an allylic carbocation is a resonance hybrid of two forms, it is more stable than a typical nonallylic carbocation, which has only one form.

In addition to its effect on stability, the resonance picture of an allylic carbocation has chemical consequences. When the allylic carbocation produced by protonation of buta-1,3-diene reacts with Br^- ion to complete the addition, reaction 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
(29%)

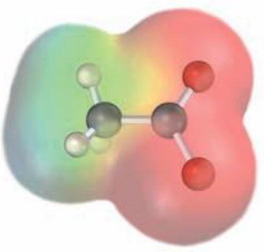
1,2-Addition
(71%)

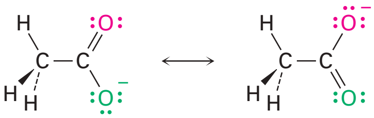


Problem 4.12 Buta-1,3-diene reacts with Br_2 to yield a mixture of 1,2- and 1,4-addition products. Show the structures of both.

4.10 Drawing and Interpreting Resonance Forms

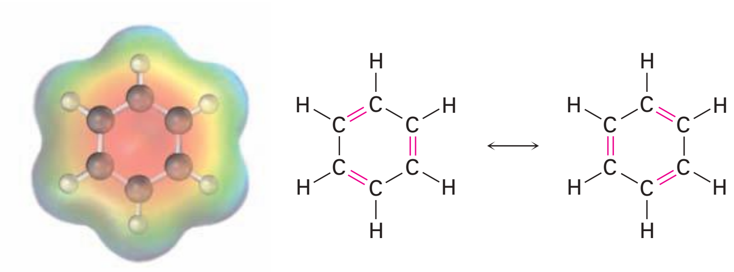
Resonance is an extremely useful concept for explaining a variety of chemical phenomena. In the acetate ion, for instance, the lengths of the two C–O bonds are identical. Although there is no single line-bond structure that can account for this equivalence of C–O bonds, resonance theory accounts for it nicely. The acetate ion is simply a resonance hybrid of two resonance forms, with both oxygens sharing the π electrons and the negative charge equally.





Acetate ion—two resonance forms

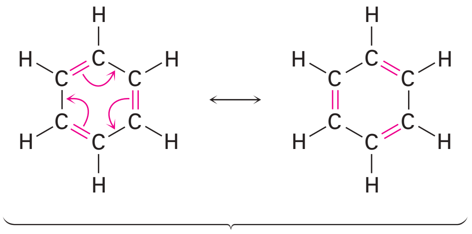
As another example, we'll see in the next chapter that the six carbon–carbon bonds in aromatic compounds like benzene are equivalent because benzene is a resonance hybrid of two forms. Each form has alternating single and double bonds, and neither form is correct by itself; the true benzene structure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



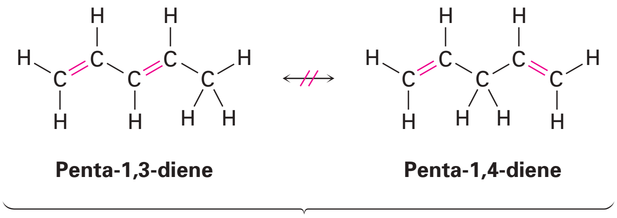
Benzene (two resonance forms)

When first dealing with resonance theory, it's useful to have a set of guidelines for drawing and interpreting resonance forms.

- **Individual resonance forms are imaginary, not real**. The real structure is a composite, or hybrid, of the different forms. Substances like the allylic carbocation, the acetate ion, and benzene are no different from any other: they have single, unchanging structures. The only difference between these and other substances is in the way they must be represented on paper.
- **Resonance forms differ only in the placement of their π or nonbonding electrons**. Neither the position nor the hybridization of any atom changes from one resonance form to another. In benzene, for example, the π electrons in the double bonds move, but the six carbon and six hydrogen atoms remain in the same place. By contrast, two structures such as penta-1,3-diene and penta-1,4-diene are *not* resonance structures because their hydrogen atoms don't occupy the same positions. Instead, the two dienes are constitutional isomers.



Benzene—two resonance forms

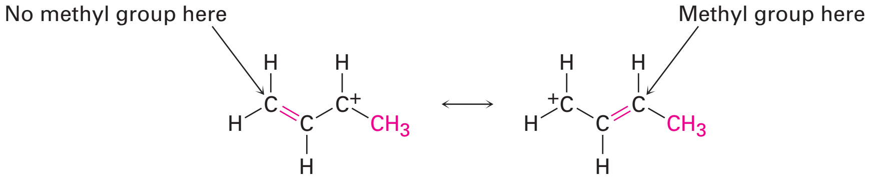


Penta-1,3-diene

Penta-1,4-diene

Constitutional isomers

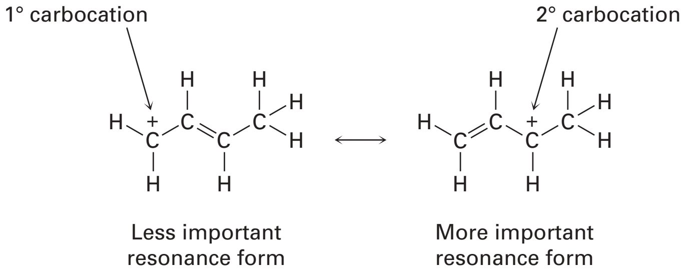
- **Different resonance forms of a substance don't have to be equivalent**. For example, the allylic carbocation obtained by reaction of buta-1,3-diene with H^+ is unsymmetrical. One end of the π electron system has a methyl substituent, and the other end is unsubstituted. Even though the two resonance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



No methyl group here

Methyl group here

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.



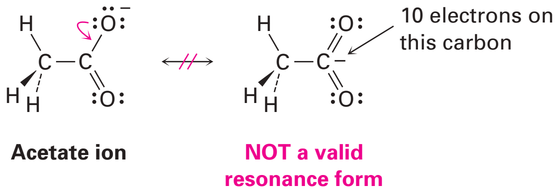
1° carbocation

2° carbocation

Less important resonance form

More important resonance form

- **Resonance forms must be valid electron-dot structures and obey normal rules of valency**. A resonance form is like any other structure: the octet rule still applies. For example, one of the following structures for the acetate ion is not a valid resonance form because the carbon atom has five bonds and ten valence electrons.



10 electrons on this carbon

Acetate ion

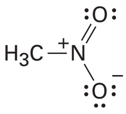
NOT a valid resonance form

- **Resonance leads to stability**. The greater the number of resonance forms, the more stable the substance. We've already seen, for example, that an allylic carbocation is more stable than a nonallylic one. In the same way, we'll see in the next chapter that a benzene ring is more stable than a cyclic alkene.

Worked Example 4.5

Using Resonance Structures

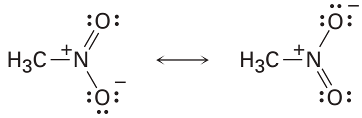
Use resonance structures to explain why the two N–O bonds of nitromethane are equivalent.



Nitromethane

Strategy Resonance forms differ only in the placement of π (multiple-bond) and nonbonding electrons. Nitromethane has two equivalent resonance forms, which 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 forms.

Solution



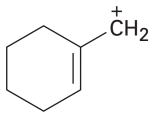
Nitromethane

Problem 4.13 Give the structure of all possible monoadducts of HCl and penta-1,3-diene, $CH_3CH{=}CH{-}CH{=}CH_2$.

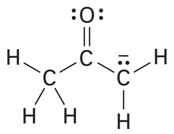
Problem 4.14 Look at the possible carbocation intermediates produced during addition of HCl to penta-1,3-diene (Problem 4.13), and predict which is the most stable.

Problem 4.15 Draw resonance structures for the following species:

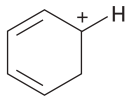
(a)



(b)



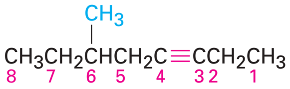
(c)



4.11 Alkynes and Their Reactions

Just as an alkene is a hydrocarbon that contains a carbon–carbon *double* bond, an alkyne is a hydrocarbon that contains a carbon–carbon *triple* bond. As we saw in Section 1.8, a C≡C bond results from the overlap of two *sp*-hybridized carbon atoms and consists of one *sp*–*sp* σ bond and two *p*–*p* π bonds. Because four hydrogens must be removed from an alkane, C_nH_{2n+2}, to produce a triple bond, the general formula for an alkyne is C_nH_{2n-2}. Alkynes occur much less commonly than alkenes, so we'll look at them only briefly.

As we saw in Section 3.1, alkynes are named using the suffix *-yne,* and the position of the triple bond is indicated by its number in the chain. Numbering begins at the chain end nearer the triple bond so that the triple bond receives as low a number as possible, and the number is placed immediately before the *-yne* suffix in the post-1993 naming system.



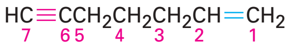
$$\underset{8\ \ 7\ \ 6\ \ 5\ \ 4\ \ 3\ 2\ \ 1}{CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2C\equiv CCH_2CH_3}$$

Begin numbering at the end nearer the triple bond.

6-Methyloct-3-yne

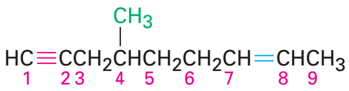
(Old name: 6-Methyl-3-octyne)

Compounds containing both double and triple bonds are called *enynes* (not ynenes). Numbering of the hydrocarbon chain starts from the end nearer the first multiple bond, whether double or triple. If there is a choice in numbering, double bonds receive lower numbers than triple bonds. For example,


$HC{\equiv}CCH_2CH_2CH_2CH{=}CH_2$

Hept-1-en-6-yne

(Old name: 1-Hepten-6-yne)

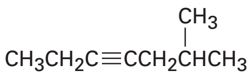

$HC{\equiv}CCH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH_2CH{=}CHCH_3$

4-Methylnon-7-en-1-yne

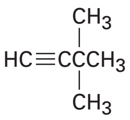
(Old name: 4-Methyl-7-nonen-1-yne)

Problem 4.16 Give IUPAC names for the following compounds:

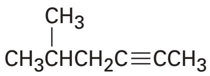
(a)


$CH_3CH_2C{\equiv}CCH_2\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_3$

(b)


$HC{\equiv}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}CH_3$

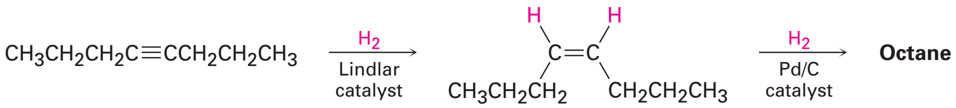
(c)


$CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2C{\equiv}CCH_3$

(d) $CH_3CH{=}CHCH_2C{\equiv}CCH_3$

Alkyne Reactions: Addition of H_2

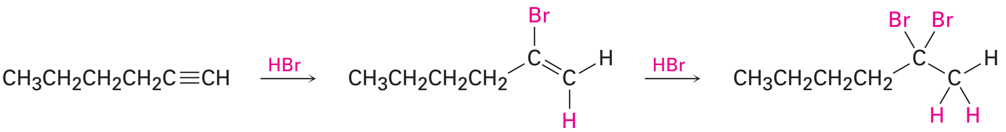
Alkynes are converted into alkanes by reduction with 2 molar equivalents of H_2 over a palladium catalyst. The reaction proceeds through an alkene intermediate, and the reaction can be stopped at the alkene stage if the right catalyst is used. The catalyst most often used for this purpose is the Lindlar catalyst, a specially prepared form of palladium metal. Because hydrogenation occurs with syn stereochemistry, alkynes give cis alkenes when reduced. For example,



Oct-4-yne **cis-Oct-4-ene**

Alkyne Reactions: Addition of HX

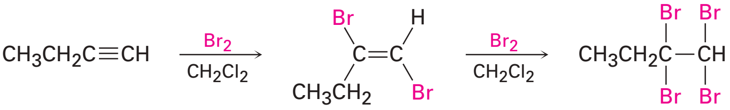
Alkynes give electrophilic addition products on reaction with HCl, HBr, and HI just as alkenes do. Although the reaction can usually be stopped after addition of 1 molar equivalent of HX to yield a *vinylic* halide (**vinylic** means "on the C=C double bond"), an excess of HX leads to formation of a dihalide product. As the following example indicates, the regioselectivity of addition to a monosubstituted alkyne usually follows Markovnikov's rule. The H atom adds to the terminal carbon of the triple bond, and the X atom adds to the internal, more highly substituted carbon.



Hex-1-yne **2-Bromohex-1-ene** **2,2-Dibromohexane**

Alkyne Reactions: Addition of X_2

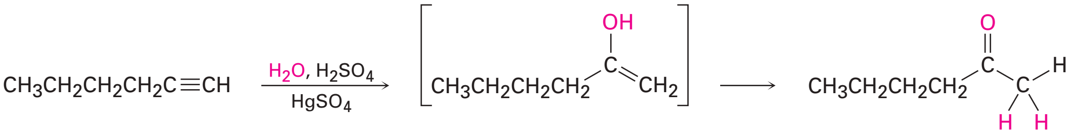
Bromine and chlorine add to alkynes to give dihalide addition products with anti stereochemistry. Either 1 or 2 molar equivalents can be added.



But-1-yne **(*E*)-1,2-Dibromobut-1-ene** **1,1,2,2-Tetrabromobutane**

Alkyne Reactions: Addition of H_2O

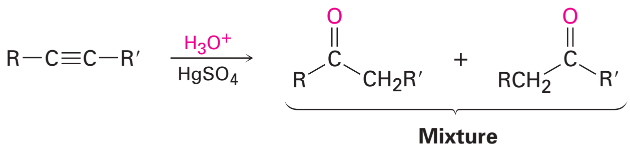
Addition of water takes place when an alkyne is treated with aqueous sulfuric acid in the presence of mercuric sulfate catalyst. Markovnikov regioselectivity is found for the hydration reaction, with the H attaching to the less substituted carbon and the OH attaching to the more substituted carbon. Interestingly, though, the product is not the expected vinylic alcohol, or *enol* (*ene* = alkene; *ol* = alcohol). Instead, the enol rearranges to a more stable ketone isomer ($R_2C{=}O$). It turns out that enols and ketones rapidly interconvert—a process we'll discuss in more detail in Section 11.1. With few exceptions, the keto–enol equilibrium heavily favors the ketone. Enols are rarely isolated.



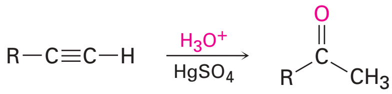
Hex-1-yne **An enol** **Hexan-2-one (78%)**

A mixture of both possible ketones results when an internal alkyne (R—C≡C—R′) is hydrated, but only a single product is formed from reaction of a terminal alkyne (R—C≡C—H).

An internal alkyne



A terminal alkyne



A methyl ketone

Alkyne Reactions: Formation of Acetylide Anions

The most striking difference between the chemistry of alkenes and alkynes is that terminal alkynes (R—C≡C—H) are weakly acidic, with $pK_a \approx 25$ (Section 1.10). Alkenes, by contrast, are far less acidic ($pK_a \approx 44$). When a terminal alkyne is treated with a strong base such as sodium amide, $NaNH_2$, the terminal hydrogen is removed and an **acetylide anion** is formed.

$$R{-}C{\equiv}C{-}H \xrightarrow{:\overset{-\,\cdot\cdot}{N}H_2\ Na^+} R{-}C{\equiv}C{:}^-\ \ Na^+ \ + \ :NH_3$$

A terminal alkyne **An acetylide anion**

The presence of an unshared electron pair on the negatively charged alkyne carbon makes acetylide anions both basic and nucleophilic. As a result, acetylide anions react with alkyl halides such as bromomethane to substitute for the halogen and yield a new alkyne product. We won't study the mechanism of this substitution reaction until Chapter 7 but will note for now that it is a very useful method for preparing larger alkynes from smaller precursors. Terminal alkynes can be prepared by reaction of acetylene itself, and internal alkynes can be prepared by further reaction of a terminal alkyne.

$$H{-}C{\equiv}C{-}H \xrightarrow{NaNH_2} \left[H{-}C{\equiv}C{:}^-\ \ Na^+\right] \xrightarrow{RCH_2Br} H{-}C{\equiv}C{-}CH_2R$$

Acetylene **A terminal alkyne**

$$R{-}C{\equiv}C{-}H \xrightarrow{NaNH_2} \left[R{-}C{\equiv}C{:}^-\ \ Na^+\right] \xrightarrow{R'CH_2Br} R{-}C{\equiv}C{-}CH_2R'$$

A terminal alkyne **An internal alkyne**

The one limitation to the reaction of an acetylide anion with an alkyl halide is that only primary alkyl halides, RCH_2X, can be used, for reasons that will be discussed in Chapter 7.

Worked Example 4.6

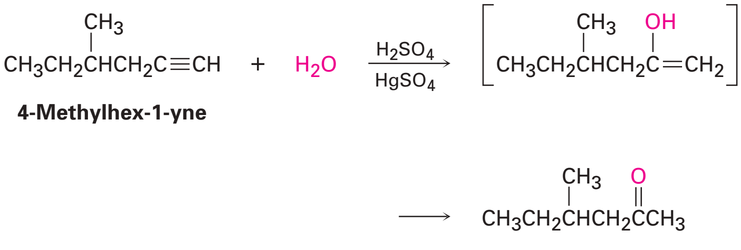
Predicting the Product of an Alkyne Hydration Reaction

What product would you obtain by hydration of 4-methylhex-1-yne?

Strategy

Ask yourself what you know about alkyne addition reactions. Addition of water to 4-methylhex-1-yne according to Markovnikov's rule will yield a product with the OH group attached to C2 rather than C1. This initially formed enol will then isomerize to yield a ketone.

Solution



$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2C\equiv CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} \left[CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2\overset{OH}{\overset{|}{C}}=CH_2 \right] \longrightarrow CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}CH_3$$

4-Methylhex-1-yne

4-Methylhexan-2-one

Worked Example 4.7

Synthesizing an Alkyne

What alkyne and what alkyl halide would you use to prepare pent-1-yne?

Strategy

As always when synthesizing a compound, work the problem backward. Draw the structure of the target molecule, and identify the alkyl group(s) attached to the triple-bonded carbons. In the present case, one of the alkyne carbons has a propyl group attached to it and the other has a hydrogen attached. Thus, pent-1-yne could be prepared by treatment of acetylene with $NaNH_2$ to yield sodium acetylide, followed by reaction with 1-bromopropane.

Solution

$$H{-}C\equiv C{-}H + :\ddot{N}H_2^-\ Na^+ \longrightarrow H{-}C\equiv C:^-\ Na^+ + :NH_3$$

Acetylene **Sodium acetylide**

$$H{-}C\equiv C:^-\ Na^+ + CH_3CH_2CH_2Br \longrightarrow H{-}C\equiv C{-}CH_2CH_2CH_3$$

1-Bromopropane **Pent-1-yne**

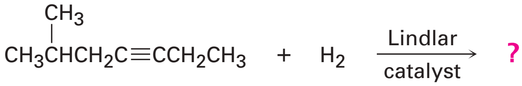
This propyl group comes from 1-bromopropane.

Problem 4.17 What products would you expect from the following reactions?

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

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

(c)

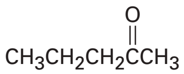


$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2C\equiv CCH_2CH_3 + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar}} ?$$

Problem 4.18 What product would you obtain by hydration of oct-4-yne?

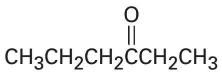
Problem 4.19 What alkynes would you start with to prepare the following ketones by a hydration reaction?

(a)



$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$

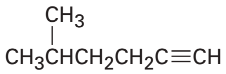
(b)



$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3$

Problem 4.20 Show the alkyne and alkyl halide from which the following products can be obtained. Where two routes look feasible, list both.

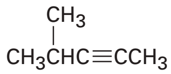
(a)



$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2C{\equiv}CH$

(b) $CH_3CH_2CH_2C{\equiv}CCH_3$

(c)



$CH_3\overset{\overset{CH_3}{|}}{C}HC{\equiv}CCH_3$

INTERLUDE

Natural Rubber

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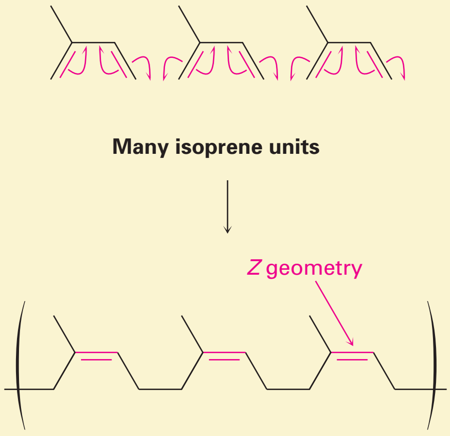
Crude rubber is harvested from the rubber tree, *Hevea brasiliensis.*

R*ubber*—an unusual name for an unusual substance—is a naturally occurring alkene polymer produced by more than 400 different plants. The major source 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 rubber's 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-methylbuta-1,3-diene. The polymerization takes place by 1,4-addition (Section 4.8) of isoprene monomers 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* configuration.



continued

INTERLUDE

Crude rubber, called *latex,* is collected from the tree as an aqueous dispersion that is washed, dried, and coagulated by warming in air. The resultant polymer has chains that average about 5000 monomer units in length and have molecular weights of 200,000 to 500,000 amu. 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 together 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. When stretched, the randomly coiled chains straighten out and orient along the direction of the pull but are kept from sliding over one another by the cross-links. When the stretch is released, the polymer reverts to its original random state.

Summary and Key Words

acetylide anion 139
1,2-addition 131
1,4-addition 131
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conjugation 130
epoxide 124
hydrogenation 122
hydroxylation 125
Markovnikov's rule 113
monomer 127
oxidation 124
polymer 127
reduction 122
regiospecific 113
resonance form 132
resonance hybrid 132
syn stereochemistry 123
vinylic 137

With the background needed to understand organic reactions now covered, this chapter has begun the systematic description of major functional groups. The chemistry of alkenes is dominated by addition reactions of electrophiles. When HX reacts with an alkene, **Markovnikov's rule** predicts that the H will add to the carbon that has fewer alkyl substituents and the X group will add to the carbon that has more alkyl substituents. Many electrophiles besides HX add to alkenes. Thus, Br_2 and Cl_2 add to give 1,2-dihalide addition products having **anti stereochemistry**. Addition of H_2O (*hydration*) takes place on reaction of the alkene with aqueous acid, and addition of H_2 (**hydrogenation**) occurs in the presence of a metal catalyst such as platinum or palladium. **Oxidation** of alkenes is often 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, $KMnO_4$ cleaves double bonds to yield carbonyl-containing products. Alkenes can also be converted into **epoxides** by reaction with a peroxy acid (RCO_3H), and epoxides can be hydrolyzed by aqueous acid to yield trans 1,2-diols.

Conjugated dienes, such as buta-1,3-diene, contain alternating single and double bonds. Conjugated dienes undergo **1,4-addition** of electrophiles through the formation of a resonance-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** intermediate between two contributing resonance forms. The only difference between two **resonance forms** is in the location of double-bond and lone-pair electrons. The atoms remain in the same places in both structures.

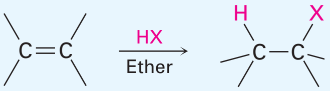
Many simple alkenes undergo **polymerization** when treated with a radical catalyst. **Polymers** are large molecules built up by the repetitive bonding together of many small **monomer** units.

Alkynes are hydrocarbons that contain a carbon–carbon triple bond. Much of the chemistry of alkynes is similar to that of alkenes. For example, alkynes react with 1 equivalent of HBr and HCl to yield **vinylic** halides, and with 1 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 to an intermediate enol that immediately isomerizes to a ketone. Alkynes can be hydrogenated with the Lindlar catalyst to yield a cis alkene. Terminal alkynes are weakly acidic and can be converted into **acetylide anions** by treatment with a strong base. Reaction of the acetylide anion with a primary alkyl halide then gives an internal alkyne.

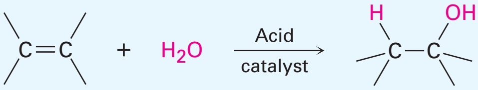
Summary of Reactions

Note: No stereochemistry is implied unless specifically stated or indicated with wedged, solid, and dashed lines.

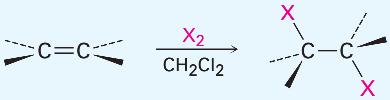
1. Reactions of alkenes
   (a) Addition of HX, where X = Cl, Br, or I (Sections 4.1–4.2)



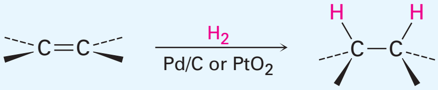
   (b) Addition of H_2O (Section 4.3)



   (c) Addition of X_2, where X = Cl, Br (Section 4.4)

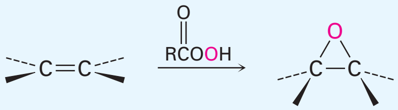


   (d) Addition of H_2 (Section 4.5)

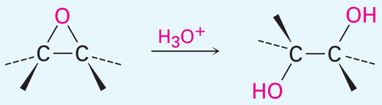


continued

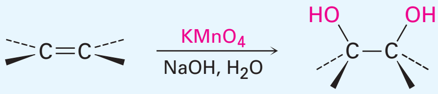
(e) Epoxidation (Section 4.6)



(f) Hydroxylation by acid-catalyzed epoxide hydrolysis (Section 4.6)

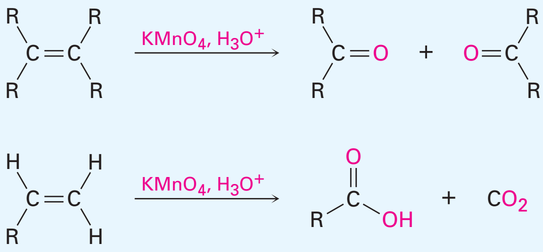


(g) Hydroxylation with $KMnO_4$ (Section 4.6)

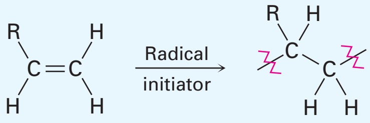


Syn addition

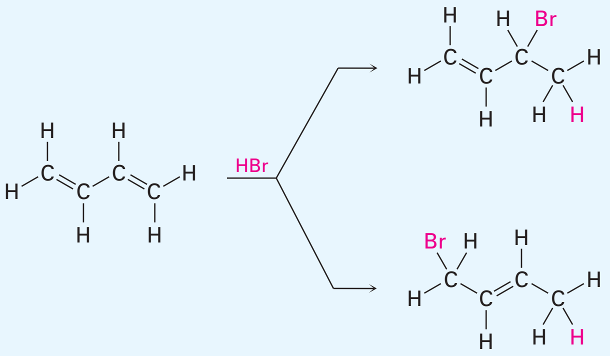
(h) Oxidative cleavage of alkenes with acidic $KMnO_4$ (Section 4.6)



(i) Polymerization of alkenes (Section 4.7)

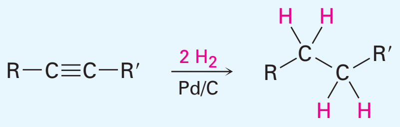


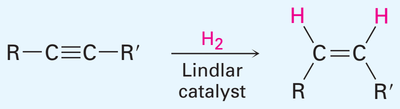
2. Addition reaction of conjugated dienes (Section 4.8)



3. Reactions of alkynes (Section 4.11)

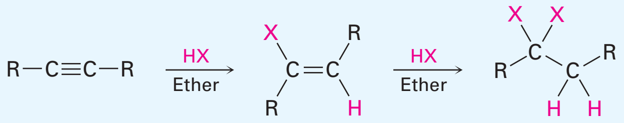
(a) Addition of H_2



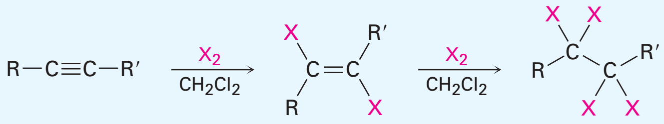


A cis alkene

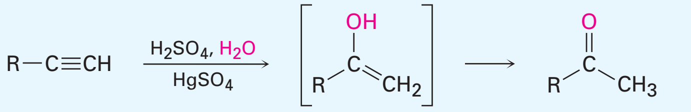
(b) Addition of HX, where X = Cl, Br, or I



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



(d) Addition of H_2O



An enol **A methyl ketone**

(e) Acetylide anion formation

$$R{-}C{\equiv}C{-}H \xrightarrow[NH_3]{NaNH_2} R{-}C{\equiv}C{:}^- \ Na^+ \quad + \quad NH_3$$

(f) Reaction of acetylide anions with alkyl halides

$$HC{\equiv}CH \xrightarrow{NaNH_2} HC{\equiv}C^- \ Na^+ \xrightarrow{RCH_2Br} HC{\equiv}CCH_2R$$

Acetylene **A terminal alkyne**

$$RC{\equiv}CH \xrightarrow{NaNH_2} RC{\equiv}C^- \ Na^+ \xrightarrow{R'CH_2Br} RC{\equiv}CCH_2R'$$

A terminal alkyne **An internal alkyne**

Exercises

Visualizing Chemistry

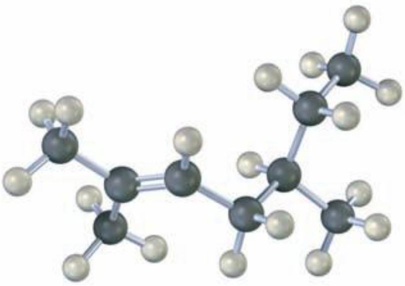
(Problems 4.1–4.20 appear within the chapter.)

OWL

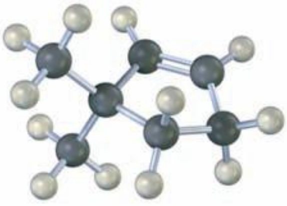
Interactive versions of these problems are assignable in OWL.

4.21 Name the following alkenes, and predict the products of their reaction with (i) $KMnO_4$ in aqueous acid and (ii) $KMnO_4$ in aqueous NaOH:

(a)

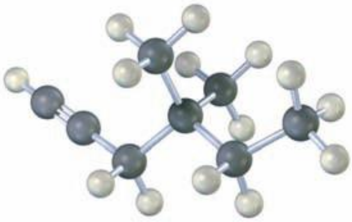


(b)

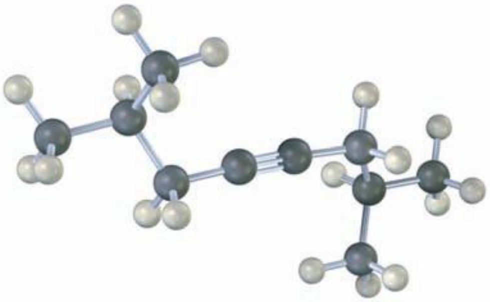


4.22 Name the following alkynes, and predict the products of their reaction with (i) H_2 in the presence of a Lindlar catalyst and (ii) H_3O^+ in the presence of $HgSO_4$:

(a)

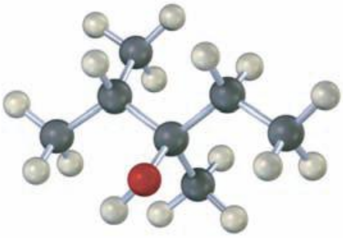


(b)

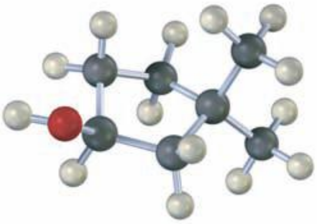


4.23 What alkenes would give the following alcohols on hydration? (Red = O).

(a)

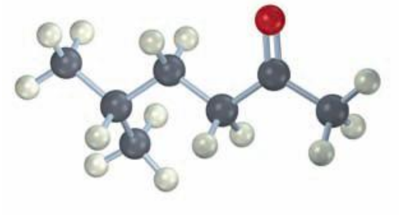


(b)

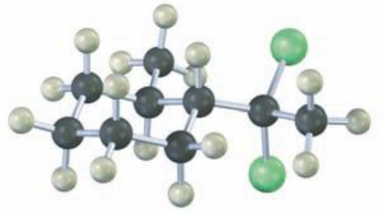


4.24 From what alkyne might each of the following substances have been made? (Red = O, yellow-green = Cl).

(a)

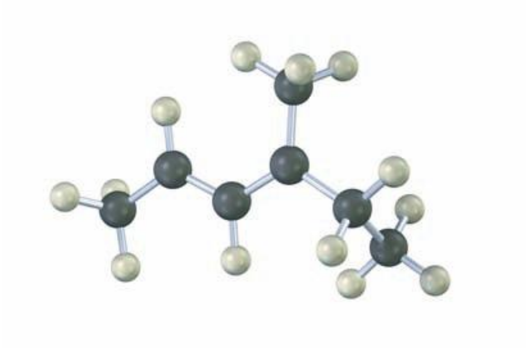


(b)



4.25 From what alkene was the following 1,2-diol made, and what method was used, epoxide hydrolysis or $KMnO_4$ in basic solution? (Red = O).

4.26 The following model is that of an allylic carbocation intermediate formed by protonation of a conjugated diene with HBr. Show the structure of the diene and the structures of the final reaction products.

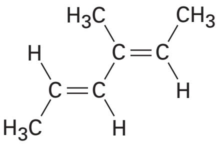


Additional Problems

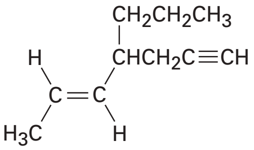
NAMING ALKENES AND ALKYNES

4.27 Give IUPAC names for the following compounds:

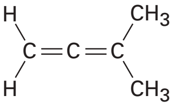
(a)



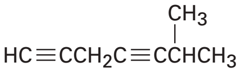
(b)



(c)



(d)



$HC{\equiv}CCH_2C{\equiv}C\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_3$

4.28 Draw structures corresponding to the following IUPAC names:
(a) 3-Ethylhept-1-yne **(b)** 3,5-Dimethylhex-4-en-1-yne
(c) Hepta-1,5-diyne **(d)** 1-Methylcyclopenta-1,3-diene

4.29 The following two hydrocarbons have been isolated from plants in the sunflower family. Name them according to IUPAC rules.
(a) $CH_3CH{=}CHC{\equiv}CC{\equiv}CCH{=}CHCH{=}CHCH{=}CH_2$ (all trans)
(b) $CH_3C{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}CCH{=}CH_2$

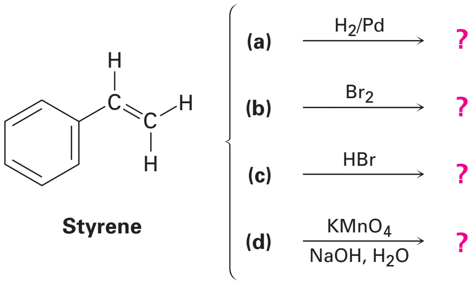
4.30 Draw and name all the possible pentyne isomers, C_5H_8.

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

4.32 Draw three possible structures for each of the following formulas:
(a) C_6H_8 **(b)** C_6H_8O

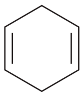
PREDICT THE PRODUCTS

4.33 Predict the products of the following reactions. Indicate regioselectivity where relevant. (The aromatic ring is inert to all the indicated reagents.)

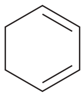


Styrene

4.34 Using an oxidative cleavage reaction, explain how you would distinguish between the following two isomeric cyclohexadienes:



and



4.35 Formulate the reaction of cyclohexene with (i) Br_2 and (ii) *meta*-chloroperoxybenzoic acid followed by H_3O^+. Show the reaction intermediates and the final products with correct cis or trans stereochemistry.

4.36 What products would you expect to obtain from reaction of cyclohexa-1,3-diene with each of the following?

(a) 1 mol Br_2 in CH_2Cl_2 **(b)** 1 mol HCl
(c) 1 mol DCl (D = deuterium, ^2H) **(d)** 2 mol H_2 over a Pd catalyst

4.37 Predict the products of the following reactions on hex-1-yne:

(a) $\xrightarrow{\text{1 equiv HBr}}$? **(b)** $\xrightarrow{\text{1 equiv } Cl_2}$? **(c)** $\xrightarrow{H_2\text{, Lindlar catalyst}}$?

4.38 Predict the products of the following reactions on dec-5-yne:

(a) $\xrightarrow{H_2\text{, Lindlar catalyst}}$? **(b)** $\xrightarrow{\text{2 equiv } Br_2}$? **(c)** $\xrightarrow{H_2O,\ H_2SO_4,\ HgSO_4}$?

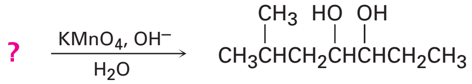
4.39 Suggest structures for alkenes that give the following reaction products. There may be more than one answer for some cases.

(a) ? $\xrightarrow{H_2\text{/Pd catalyst}}$ 2-Methylhexane

(b) ? $\xrightarrow{Br_2 \text{ in } CH_2Cl_2}$ 2,3-Dibromo-5-methylhexane

(c) ? $\xrightarrow{HBr}$ 2-Bromo-3-methylheptane

(d)

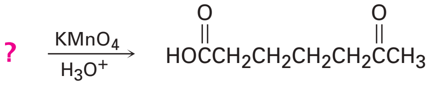


$$? \xrightarrow[H_2O]{KMnO_4,\ OH^-} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2\overset{HO}{\overset{|}{C}}H\overset{OH}{\overset{|}{C}}HCH_2CH_3$$

Predict the Reactants

4.40 Draw the structure of a hydrocarbon that reacts with only 1 equivalent of H_2 on catalytic hydrogenation and gives only pentanoic acid, $CH_3CH_2CH_2CH_2CO_2H$, on treatment with acidic $KMnO_4$. Write the reactions involved.

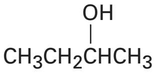
4.41 Give the structure of an alkene that yields the following keto acid on reaction with $KMnO_4$ in aqueous acid:



$$? \xrightarrow[H_3O^+]{KMnO_4} HO\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$$

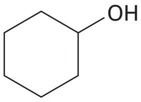
4.42 What alkenes would you hydrate to obtain the following alcohols?

(a)

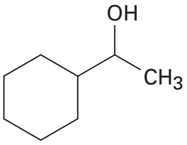


$CH_3CH_2\overset{\overset{OH}{|}}{C}HCH_3$

(b)

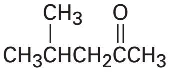


(c)



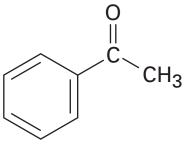
4.43 What alkynes would you hydrate to obtain the following ketones?

(a)

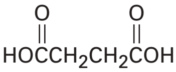


$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2\overset{\overset{O}{\|}}{C}CH_3$

(b)



4.44 Draw the structure of a hydrocarbon that reacts with 2 equivalents of H_2 on catalytic hydrogenation and gives only succinic acid on reaction with acidic $KMnO_4$.



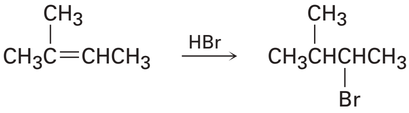
$HO\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{O}{\|}}{C}OH$

Succinic acid

SYNTHESIS

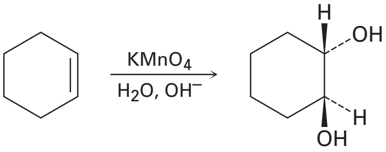
4.45 In planning the synthesis of a compound, it's as important to know what *not* to do as to know what to do. What is wrong with each of the following reactions?

(a)

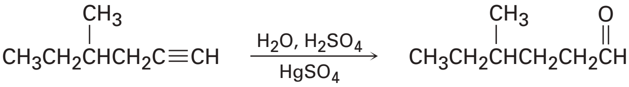


$CH_3\overset{\overset{CH_3}{|}}{C}{=}CHCH_3 \xrightarrow{HBr} CH_3\overset{\overset{CH_3}{|}}{C}H\underset{\underset{Br}{|}}{C}HCH_3$

(b)



(c)



$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2C{\equiv}CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{O}{\|}}{C}H$

4.46 How would you prepare *cis*-but-2-ene starting from propyne, an alkyl halide, and any other reagents needed? (This problem can't be worked in a single step. You'll have to carry out more than one reaction.)

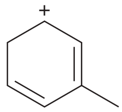
4.47 Using but-1-yne as the only organic starting material, along with any inorganic reagents needed, how would you synthesize the following compounds? (More than one step may be needed.)

(a) Butane **(b)** 1,1,2,2-Tetrachlorobutane
(c) 2-Bromobutane **(d)** Butan-2-one ($CH_3CH_2COCH_3$)

RESONANCE

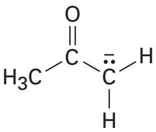
4.48 Draw the indicated number of additional resonance structures for each of the following substances:

(a)



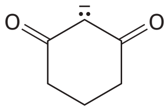
(two)

(b)



(one)

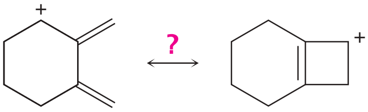
(c)



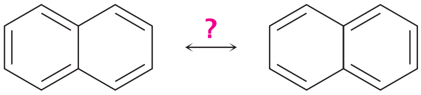
(two)

4.49 One of the following pairs of structures represents resonance forms, and one does not. Explain which is which.

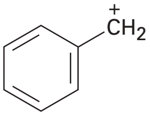
(a)



(b)

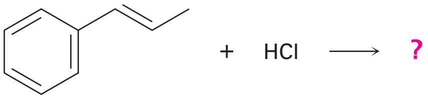


4.50 Draw three additional resonance structures for the benzyl cation.



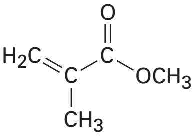
Benzyl cation

4.51 In light of your answer to Problem 4.50, what product would you expect from the following reaction? Explain.



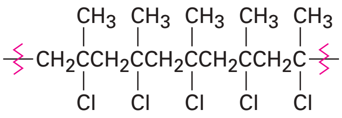
POLYMERS

4.52 Plexiglas, a clear plastic used to make many molded articles, is made by polymerization of methyl methacrylate. Draw a representative segment of Plexiglas.



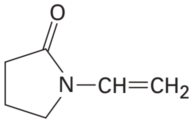
Methyl methacrylate

4.53 What monomer unit might be used to prepare the following polymer?



$$\text{-CH}_2\underset{\text{Cl}}{\overset{\text{CH}_3}{\text{C}}}\text{CH}_2\underset{\text{Cl}}{\overset{\text{CH}_3}{\text{C}}}\text{CH}_2\underset{\text{Cl}}{\overset{\text{CH}_3}{\text{C}}}\text{CH}_2\underset{\text{Cl}}{\overset{\text{CH}_3}{\text{C}}}\text{CH}_2\underset{\text{Cl}}{\overset{\text{CH}_3}{\text{C}}}\text{-}$$

4.54 Poly(vinyl pyrrolidone), prepared by from *N*-vinylpyrrolidone, is used both in cosmetics and as a synthetic blood substitute. Draw a representative segment of the polymer.



***N*-Vinylpyrrolidone**

GENERAL PROBLEMS

4.55 Reaction of 2-methylpropene with CH_3OH in the presence of H_2SO_4 catalyst yields methyl *tert*-butyl ether, $CH_3OC(CH_3)_3$, by a mechanism analogous to that of acid-catalyzed alkene hydration. Write the mechanism.

4.56 Compound **A** has the formula C_8H_8. It reacts rapidly with acidic $KMnO_4$ but reacts with only 1 equivalent of H_2 over a palladium catalyst. On hydrogenation under conditions that reduce aromatic rings, A reacts with 4 equivalents 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 the reactions.

4.57 Compound A, C_9H_{12}, absorbs 3 equivalents of H_2 on catalytic reduction over a palladium catalyst to give **B**, C_9H_{18}. On reaction with $KMnO_4$, compound **A** gives, among other things, a ketone that was identified as cyclohexanone. On treatment with $NaNH_2$ in NH_3, followed by addition of iodomethane, compound **A** gives a new hydrocarbon **C**, $C_{10}H_{14}$. What are the structures of **A**, **B**, and **C**?

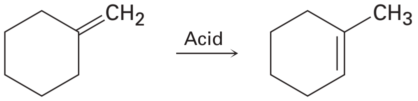
4.58 The sex attractant of the common housefly is a hydrocarbon named *muscalure,* $C_{23}H_{46}$. On treatment of muscalure with aqueous acidic $KMnO_4$, two products are obtained, $CH_3(CH_2)_{12}CO_2H$ and $CH_3(CH_2)_7CO_2H$. Propose a structure for muscalure.

4.59 How would you synthesize muscalure (Problem 4.58) starting from acetylene and any alkyl halides needed? (The double bond in muscalure is cis.)

4.60 Draw an energy diagram for the addition of HBr to pent-1-ene. 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 positions for all reactants, intermediates, and products.

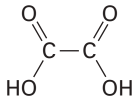
4.61 Make sketches of what you imagine the transition-state structures to look like in the reaction of HBr with pent-1-ene (Problem 4.60).

4.62 Methylenecyclohexane, on treatment with strong acid, isomerizes to yield 1-methylcyclohexene. Propose a mechanism by which the reaction might occur.

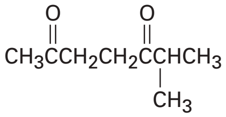


Methylenecyclohexane **1-Methylcyclohexene**

4.63 α-Terpinene, $C_{10}H_{16}$, is a pleasant-smelling hydrocarbon that has been isolated from oil of marjoram. On hydrogenation over a palladium catalyst, α-terpinene reacts with 2 mol equiv of hydrogen to yield a new hydrocarbon, $C_{10}H_{20}$. On reaction with acidic $KMnO_4$, α-terpinene yields oxalic acid and 6-methylheptane-2,5-dione. Propose a structure for α-terpinene.



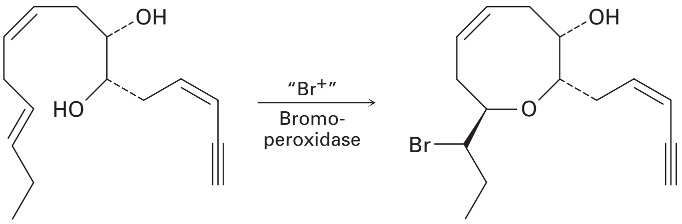
Oxalic acid



$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{|}{C}H}CH_3$$

6-Methylheptane-2,5-dione

4.64 Prelaureatin, a substance isolated from marine algae, is thought to arise from laurediol by the following route. Propose a mechanism.

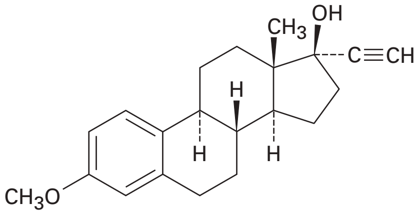


Laurediol **Prelaureatin**

4.65 Hydroxylation of *cis*-but-2-ene with basic $KMnO_4$ yields a different product than hydroxylation of *trans*-but-2-ene. Draw the structure, show the stereochemistry of each product, and explain the result. We'll explore the stereochemistry of the products in more detail in Chapter 6.

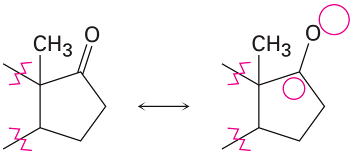
In the Medicine Cabinet

4.66 The oral contraceptive agent Mestranol is synthesized by addition of acetylide ion to a carbonyl group.



Mestranol

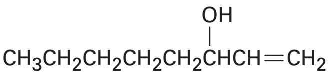
(a) To understand the acetylide-addition reaction, first draw a resonance structure of the C=O double bond based on electronegativity values, indicating where the + and − charges belong in the circles on the following abbreviated structure:



(b) Then draw a two-step mechanism for the addition of acetylide ion to this resonance structure and subsequent protonation of the intermediate with acid.

IN THE FIELD

4.67 Oct-1-en-3-ol, a potent mosquito attractant commonly used in mosquito traps, can be prepared in two steps from hexanal, $CH_3CH_2CH_2CH_2CH_2CHO$. The first step is an acetylide-addition reaction like that described in Problem 4.66. What is the structure of the product from the first step, and how can it be converted into oct-1-en-3-ol?



$$CH_3CH_2CH_2CH_2CH_2\overset{\displaystyle OH}{\overset{|}{C}}HCH{=}CH_2$$

Oct-1-en-3-ol

4.68 As we saw in the *Interlude* at the end of this chapter, natural rubber is a polymer of 2-methylbuta-1,3-diene that contains *Z* double bonds. Synthetic rubber, by contrast, is similar to natural rubber but contains *E* double bonds. Draw the structure of a representative section of synthetic rubber.