

## Chapter 8

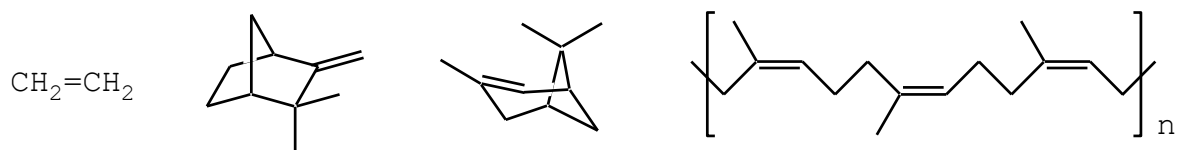
### Alkenes

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After a thorough exploration of alkyl halides in Chapters 6 and 7, this chapter examines the chemistry of our second functional group: the carbon-carbon  $\pi$  bond of **alkenes** (sometimes called **olefins**). Whereas alkyl halides initiate reaction in three different ways ( $S_N2$ , E2,  $S_N1/E1$ ), alkenes generally begin reaction according to one basic pattern. Of course, this mechanistic pattern features nucleophiles and electrophiles.

#### 8.1 Notable Alkenes

Unlike alkyl halides, which are scarce in nature, alkenes are very common. Ethene is a gaseous plant hormone that ripens fruit. Camphene and  $\alpha$ -pinene are components of several essential oils found in plants.



ethene

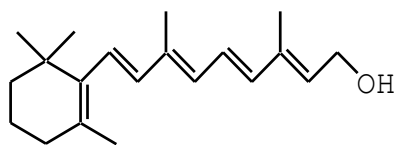
camphene

α-pinene

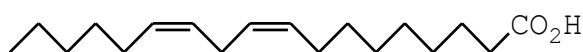
natural rubber

(4*Z*,6*E*)-4,6-heptadecadiene

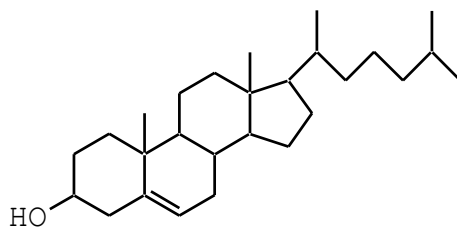
(Z)-9-tricosene



vitamin A



linoleic acid

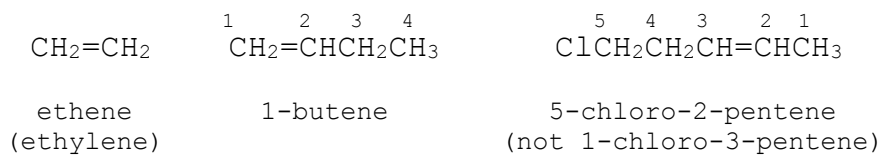


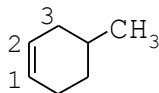
cholesterol

Natural rubber features thousands of double bonds in a macromolecule. Silk moths and house flies use (4*Z*,6*E*)-4,6-heptadecadiene and (Z)-9-tricosene, respectively, as sex attractants. Several vitamins, including vitamin A, feature an alkene functional group. Linoleic acid is one of the so-called unsaturated fatty acids that compose unsaturated fats. Alkene steroids include the notorious cholesterol.

## 8.2 Nomenclature of Alkenes

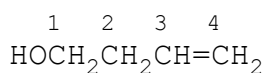
In the IUPAC system the name of an alkene is derived from the corresponding alkane, with the *-ane* suffix becoming *-ene*. For example:



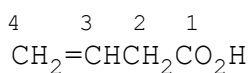


4-methylcyclohexene  
(not 1-methyl-3-cyclohexene)

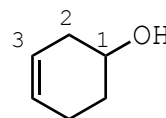
If necessary, a number is used to designate the *first* of the two doubly bonded carbons, as in 1-butene above. The longest chain or ring containing the double bond is normally numbered to give the lower possible number to the double bond, as in 5-chloro-2-pentene and 4-methylcyclohexene above. Yet, a functional group of higher priority than an alkene, such as an alcohol or carbonyl, demands priority in numbering:



3-buten-1-ol  
(not 1-buten-4-ol)



3-butenic acid

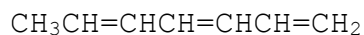


3-cyclohexenol  
(not 4-hydroxycyclohexene)

Dienes and trienes have two and three carbon-carbon double bonds, respectively:



1,3-butadiene

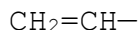


1,3,5-heptatriene

Common names are sometimes used for common alkenyl groups:



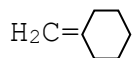
methylene



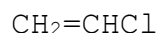
vinyl  
ethenyl



allyl  
2-propenyl



methylenecyclohexane



vinyl chloride  
chloroethene

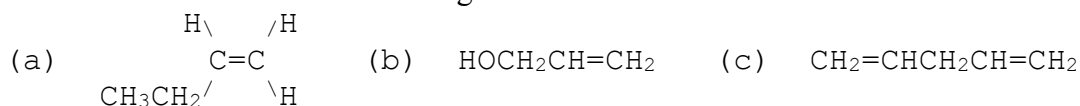


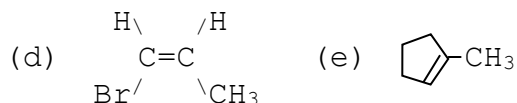
allyl alcohol  
2-propen-1-ol

The nomenclature of *E* and *Z* (i.e., trans and cis) alkene stereoisomers was discussed in Section 3.5.

### Puzzle 8.1

Give IUPAC names to the following molecules:





## Puzzle 8.2

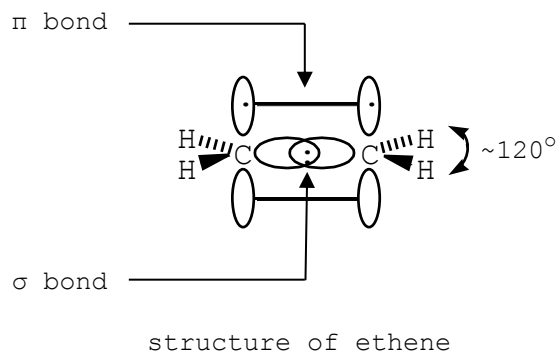
- (a) Draw the structures of vinyl bromide, allyl bromide, and 4-bromo-1-butene.  
 (b) Which has the highest boiling point? Explain.

## 8.3 Structural Features of Alkenes

Before exploring the physical and chemical properties of alkenes, we should examine the molecular structure that determines those properties.

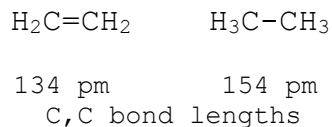
## 8.3A Geometry

A normal double bond comprises one  $\sigma$  and one  $\pi$  bond (Section 1.2C), and the carbon-carbon double bond of an alkene is no exception. Its  $\sigma$  bond arises from the head-on overlap of two orbitals, and its  $\pi$  bond results from the sideways overlap of parallel  $p$  orbitals:



Three repelling electron pairs (i.e., three  $\sigma$  bonds) surround each doubly bonded carbon. So both carbons are hybridized approximately  $sp^2$ , and the bond angles at these carbons are about  $120^\circ$  (the non-equivalence of repelling electron pairs slightly distorts the hybridization and bond angles). The doubly bonded carbons and their five  $\sigma$  bonds lie in a single plane. Perpendicular to this plane are the two unhybridized, parallel  $p$  orbitals, overlapping in the  $\pi$  bond.

The double bond between the carbons is shorter than a single bond between two carbons:



In contrast to the two orbitals overlapping in a single bond, four overlapping orbitals shorten the double bond (Section 1.7A).

## Puzzle 8.3

Which should be longer, the C-H bond of ethene or the C-H bond of ethane? Explain. Hint: see Section 1.7A.

## Puzzle 8.4

Resonance involving two double bonds stabilizes (4*Z*,6*E*)-4,6-heptadecadiene, the sex attractant for the silk moth (Section 8.1).

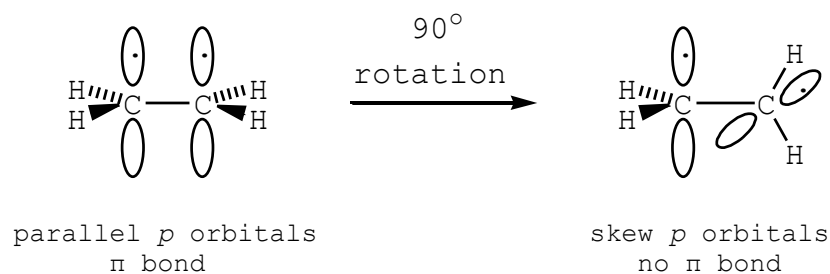
- Draw a minor resonance form for this molecule.
- Compare the lengths of the C(4)-C(5) bond in this molecule and the carbon-carbon bond in ethene. Explain.
- Compare the lengths of the C(5)-C(6) bond in this molecule and the carbon-carbon bond in ethane. Explain.

## 8.3B Bond Strength

A carbon-carbon double bond is not only shorter than the analogous single bond but also stronger. The bond strength of the double bond in ethene is 682 kJ/mol, whereas that of the carbon-carbon single bond in ethane is 368 kJ/mol. The stronger double bond naturally results from two bonds with four electrons binding the carbon atoms more strongly than does one bond with two electrons.

Which bond in the double bond is stronger, the  $\sigma$  or  $\pi$  bond? We can estimate the bond strength of the  $\sigma$  bond to be about 368 kJ/mol, as it is in ethane. This leaves  $682 - 368 = 314$  kJ/mol as the approximate bond strength of the  $\pi$  bond in the double bond. Thus, the  $\pi$  bond is weaker than a  $\sigma$  bond in the same double bond. Evidently, the sideways overlap of the parallel  $p$  orbitals of the  $\pi$  bond is not as great as the head-on overlap of the  $sp^2$  orbitals. This relative weakness of the  $\pi$  bond contributes to its serving as a reactive functional group.

Can alkenes readily rotate around their double bond, as alkanes rotate around their single bonds? To do so the  $p$  orbitals on the carbons must rotate from their parallel orientation with maximum overlap to a skew orientation with no overlap:



In effect the  $\pi$  bond must be broken to rotate around an alkene double bond. This requires about 314 kJ/mol, the bond strength of the  $\pi$  bond. In contrast, rotation around most single bonds demands only 13 kJ/mol (Section 2.6A). Molecules ordinarily have enough kinetic energy to easily rotate around single bonds, but they lack the energy to rotate around double bonds. Consequently, the *E* and *Z* (i.e., trans and cis) forms of an alkene are true, hard-to-interconvert stereoisomers and not easily interconverted conformations (Section 3.5).

## Puzzle 8.5

Which of the following can exist as *E* and *Z* stereoisomers?

- (a) 1-butene (b) 2-butene (c) 2-methyl-2-butene (d) cyclopentene

## 8.4 Physical Properties of Alkenes

Simple alkenes, without other functional groups, resemble alkanes in having no appreciably polar bonds. (A bond between an  $sp^3$  carbon and the slightly more electronegative  $sp^2$  carbon is only slightly polar.) Consequently, like alkanes simple alkenes are essentially nonpolar molecules.

So, it is not surprising that an alkene has about the same boiling point as its corresponding alkane. For example, (*Z*)-2-butene and butane have boiling points of 4°C and 0°C, respectively. These two nonpolar hydrocarbons have only dispersion forces as intermolecular forces, and their dispersion forces are about equally strong because of similar size.

How should the boiling point of (*E*)-2-butene compare with that of its *Z* stereoisomer? Because the two stereoisomers are diastereomers, not enantiomers, they should have similar but probably not identical boiling points. In fact, the *E* stereoisomer has a boiling point of 1°C, only 3° less than that of its diastereomer.

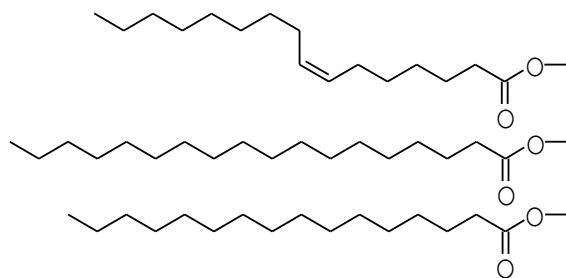
What is the best kind of solvent for simple alkenes? Their nonpolarity makes them good solutes in nonpolar solvents, such as hexane, and poor solutes in very polar water.

## Puzzle 8.6

Which has the higher boiling point, 1-butene or 1-chlorobutane? Explain.

## Puzzle 8.7

A molecule of fat is a triple ester with three long hydrocarbon chains. A monounsaturated fat has one alkene double bond on one of the hydrocarbon chains. For example:



The saturated (without double bonds) chains prefer an anti staggered conformation (Section 2.6C), which the unsaturated chain cannot adopt because of its *Z* double bond.

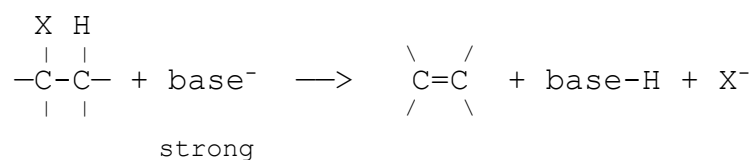
- (a) Which has a more regular crystal lattice, an unsaturated fat (with at least one *Z* double bond in its chains) or a saturated fat?
- (b) Which has a higher melting point, an unsaturated fat or a saturated fat? Assume chains of similar length. Explain.
- (c) Would a soft margarine contain fats with more *Z* double bonds than a hard margarine would?

Explain.

---

## 8.5 Syntheses of Alkenes

Alkenes can be synthesized by several methods. One synthesis, already learned in Chapter 7, is the important E2 elimination reaction of an alkyl halide with a strong base:



Other synthetic methods to be discussed later include hydrogenation reactions of alkynes (Section 9.5E), elimination reactions of alcohols (Section 10.5C), and Wittig reactions (Section 19.6).

Puzzle 8.8

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Outline a synthesis of cyclopentene by an elimination reaction.

Puzzle 8.9

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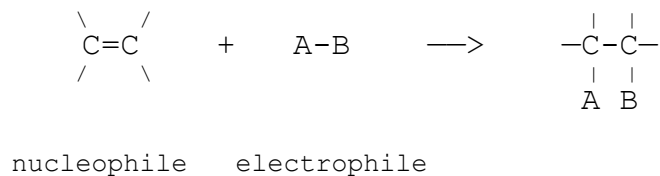
How could cholesterol (Section 8.1) be synthesized efficiently from some alkyl halide-alcohol?

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## 8.6 General Nature of Alkene Reactions

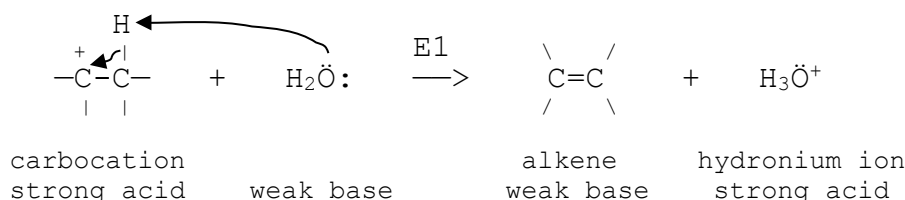
Let us use the principles of nucleophiles and electrophiles to predict how alkenes react. Of course, the first task is to decide whether an alkene is a nucleophile or electrophile. It has four electrons in the relatively concentrated region of its double bond, so it is electron-rich. Also, the electron pair of the  $\pi$  bond protrudes from the doubly bonded carbons (Section 8.3A) and so is accessible to another reactant. Furthermore, the  $\pi$  bond is a weak bond relative to a  $\sigma$  bond (Section 8.3B) and so is relatively easy to break. For these reasons a simple alkene is a nucleophile.

Therefore, we expect alkenes to react with electrophiles, and they do by the following general pattern:



This kind of reaction, typical of alkenes, is called **addition** because the alkene adds atoms or groups without losing any. In contrast, substitution reactions, such as  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$ , both add to a molecule and subtract a leaving group. Elimination reactions (e.g., E1 and E2), by removing atoms or groups without adding any, reverse the stoichiometry of addition reactions.

How strong of a nucleophile is an alkene? First, consider its basicity. An alkene is a weak base, as we already know from the behavior of its conjugate acid, a carbocation, in the second step of an E1 reaction (Section 7.3):



Even a weak base, such as water, can remove a proton from a carbocation. Therefore, the carbocation is a strong acid, and an alkene, its conjugate base, must be weak.

Softness is the other characteristic of nucleophiles to be considered, especially for weak bases, such as alkenes (Section 4.10). The atoms of a carbon-carbon double bond have no formal nor even partial charges. The lack of charge density makes alkenes soft nucleophiles. Consequently, although alkenes are weak bases, they can react as surprisingly strong nucleophiles with soft electrophiles, such as bromine (Br<sub>2</sub>) or chlorine (Cl<sub>2</sub>), as we will see in Section 8.10A.

### Puzzle 8.10

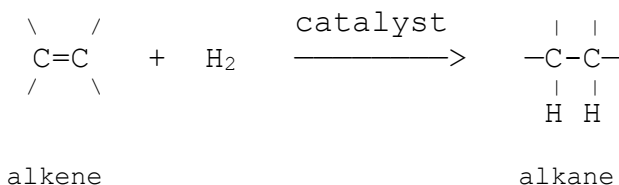
- (a) Which is the stronger base, ethene or (*Z*)-2-butene? Hint: this is an unusual puzzle where comparing conjugate acids is easier than comparing the bases.  
 (b) Which alkene is the stronger nucleophile? Explain.

## 8.7 Addition Reactions of Alkenes with Hydrogen

Our first addition reaction is important industrially, for example, in the processing of vegetable oils (Section 14.8A). Also it provides useful information about alkenes' structures.

### 8.7A Catalytic Hydrogenation

The atoms of molecular hydrogen, H<sub>2</sub>, add to an alkene double bond to make an alkane in a process called **hydrogenation**.

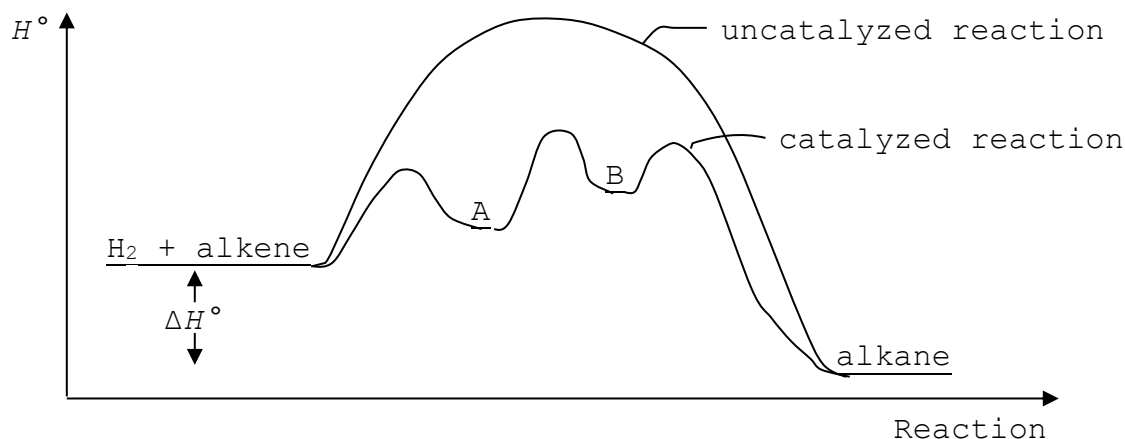


This shows a reduction of the doubly bonded carbons, because they each acquire a bond to a slightly less electronegative hydrogen (Section 8.12). Because alkanes are generally unreactive, this reaction removes any vestige of a functional group from a simple alkene. In contrast, almost all other reactions convert one functional group to another.

Note the presence of a catalyst. Without a metal catalyst the reactants can remain together



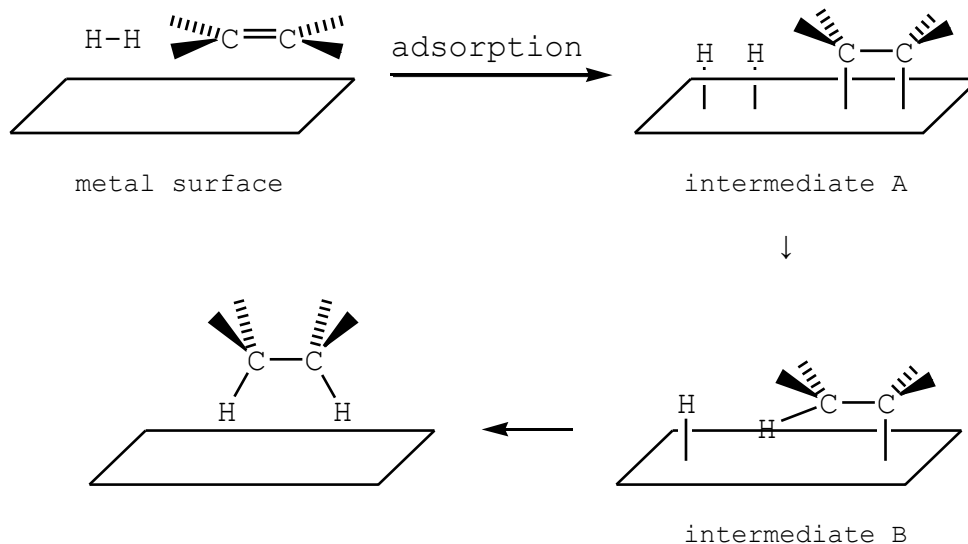
unreacted for years. With the catalyst the reaction proceeds well, often at room temperature. Similar to the example in Section 5.4B, the following energy-reaction diagrams shows how the catalyst accelerates the reaction by lowering the activation barrier:



energy-reaction diagrams: uncatalyzed and catalyzed hydrogenation reactions

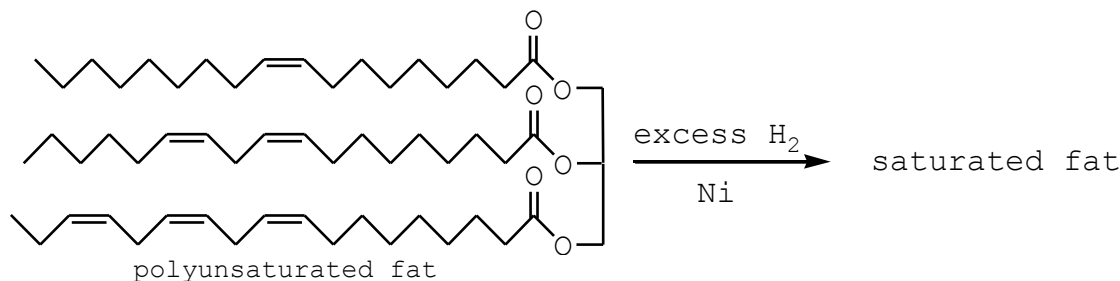
With or without a catalyst, the reaction has the same favorable, negative  $\Delta H^\circ$ . This is not surprising because the reaction forms two strong carbon-hydrogen  $\sigma$  bonds at the expense of breaking a strong hydrogen-hydrogen bond and a weaker carbon-carbon  $\pi$  bond (Section 8.3B). Yet, even with a favorable equilibrium, the uncatalyzed reaction has unfavorable kinetics because of its high activation barrier. The catalyst changes the mechanism from a one-step mechanism with a high activation energy to a three-step mechanism with a much smaller activation energy. Note the three transition states and two intermediates, A and B, for the catalyzed reaction.

Two types of catalysis aid hydrogenation of an alkene. The most common type is **heterogeneous**, where the catalyst is insoluble in the solvent for the alkene and hydrogen. The usual heterogeneous catalysts are finely divided metals from the same column of Group VIII of the periodic table: platinum, palladium and nickel. The mechanism of heterogeneous catalysis is not fully understood but is believed to involve steps approximated below:



approximate mechanism for heterogeneous catalysis of alkene hydrogenation

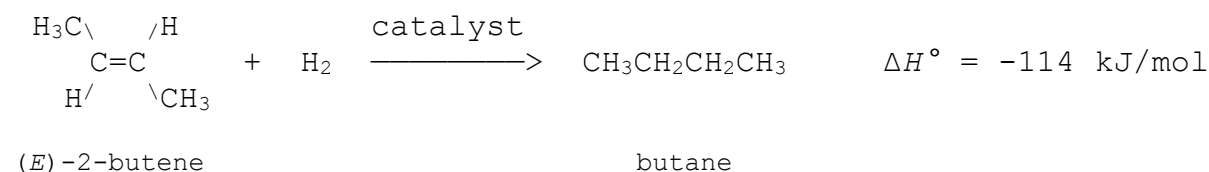
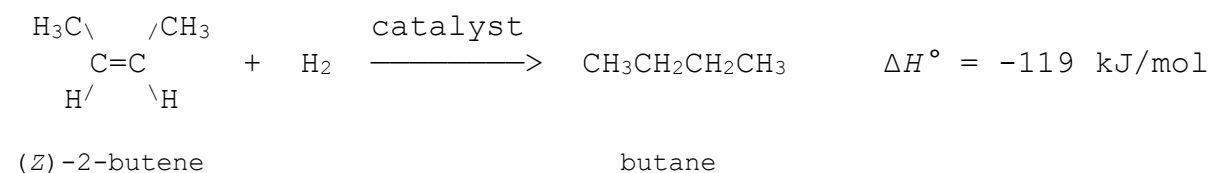




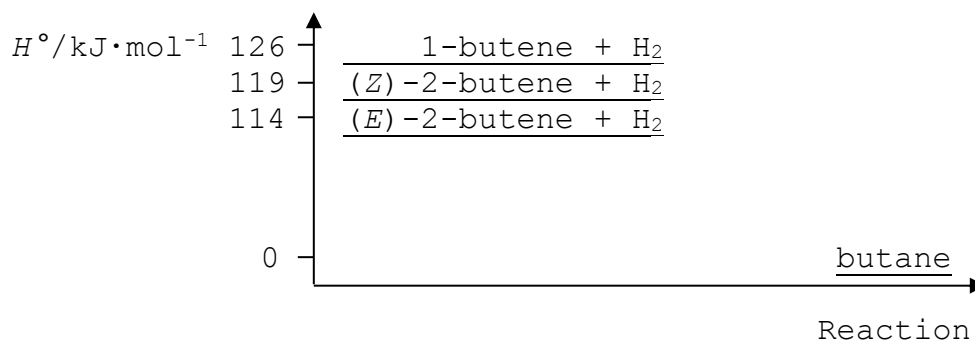
Draw the structure of the saturated fat produced.

### 8.7B Stabilities of Alkenes

Let us see how hydrogenation can reveal the relative stabilities of alkene stereoisomers and constitutional isomers. First compare the catalytic hydrogenations of the *Z* and *E* stereoisomers of 2-butene:



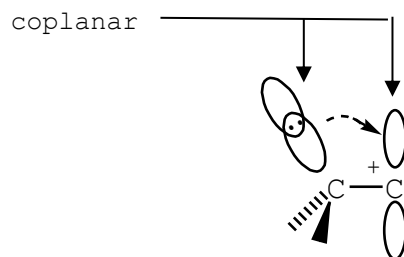
Both stereoisomers yield the same alkane product, but the hydrogenation of the *Z* stereoisomer is more exothermic by  $-114 - (-119) = 5 \text{ kJ/mol}$ . This small difference cannot result from different enthalpies of product or hydrogen reactant because these are identical for both reactions. The two stereoisomers themselves must have different enthalpies. Evidently, the *Z* stereoisomer has more enthalpy because it gives off more heat, as illustrated in these partial energy-reaction diagrams (missing activation barriers):



partial energy-reaction diagrams for hydrogenation of three  $\text{C}_4\text{H}_8$  alkenes

The *Z* stereoisomer is less stable because its two methyl substituents are on the same side of the

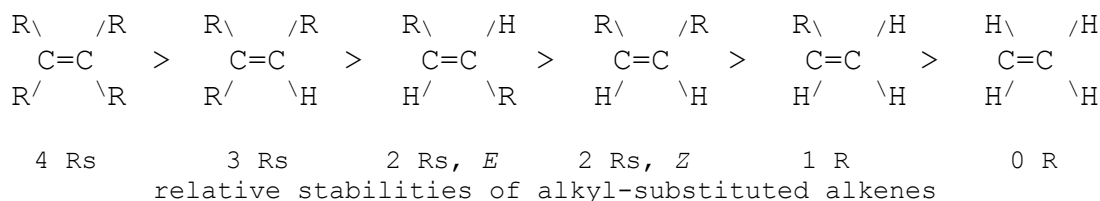




hyperconjugation of alkyl group stabilizing carbocation

In both cases, when a  $\sigma$  bond of the alkyl group is coplanar with a  $p$  orbital, it acts like a pseudo  $p$  orbital and stabilizes the adjacent  $p$  orbital by delocalizing electrons. Hydrogens bonded to the carbon-carbon double bond cannot engage in this hyperconjugation.

To summarize the relative stabilities of alkyl-substituted alkenes:



### Puzzle 8.13

By the number of  $\sigma$  and  $\pi$  bonds among reactants and products, rationalize the exothermic nature of an alkene hydrogenation reaction.

### Puzzle 8.14

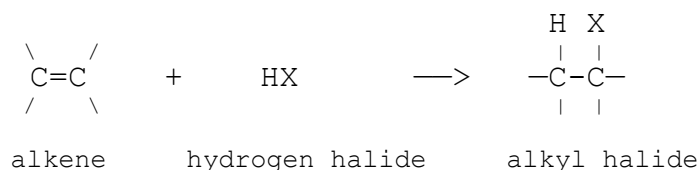
Consider 3-methyl-1-pentene, 2-ethyl-1-butene, and both stereoisomers of 3-methyl-2-pentene. Rank them by stability and then by enthalpy.

## 8.8 Addition Reactions of Alkenes with Acids

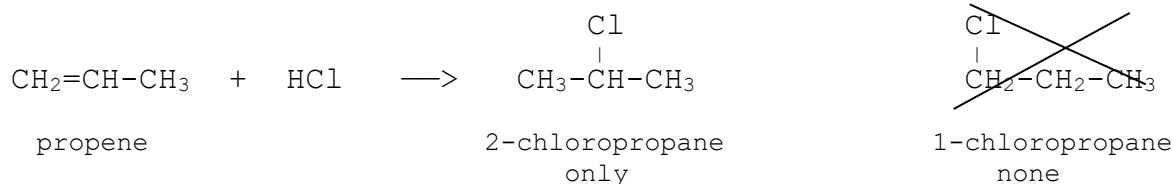
In Section 8.6 we reasoned that, as a weak base, an alkene can react with strong acids. Let us see how the strongly acidic hydrogen halides and aqueous sulfuric acid can add to alkenes.

### 8.8A Reactions with Hydrogen Halides

As a strong acid and electrophile, a hydrogen halide adds to an alkene:

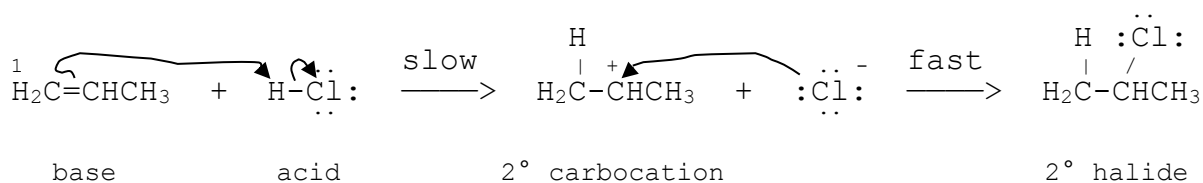


For example:



Note that this addition of hydrogen chloride yields only 2-chloropropane and none of the other possible isomer, 1-chloropropane. This kind of preference for one direction of reaction over another is called **regioselectivity**. Just as stereoselectivity leads to the predominance of one *stereoisomer* product over another, so regioselectivity results in the predominance of one *constitutional isomer* product over another.

A two-step mechanism explains this regioselectivity:

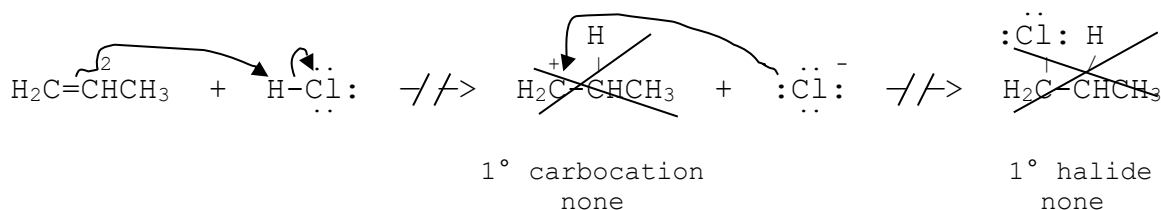


The two electron arrows of the first step obey the four rules for electron arrows (Section 5.1). The first arrow begins at the nucleophilic  $\pi$  bond. This  $\pi$  bond opens to the left so that C(1) carries the electron pair. The first arrow ends at the electrophilic hydrogen of the acid. The second arrow begins at a bonding electron pair near the end of the first arrow and ends at an atom.

During the first step, C(2) of the alkene becomes a secondary carbocation. This is the slow, rate-limiting step just as  $\text{S}_{\text{N}}1$  and  $\text{E}1$  reactions produce carbocations in their slow steps (Sections 6.5B and 7.2B). Unlike most acid-base reactions, which are fast (Section 5.4A), this step is a relatively slow acid-base reaction for reasons beyond the scope of this book.

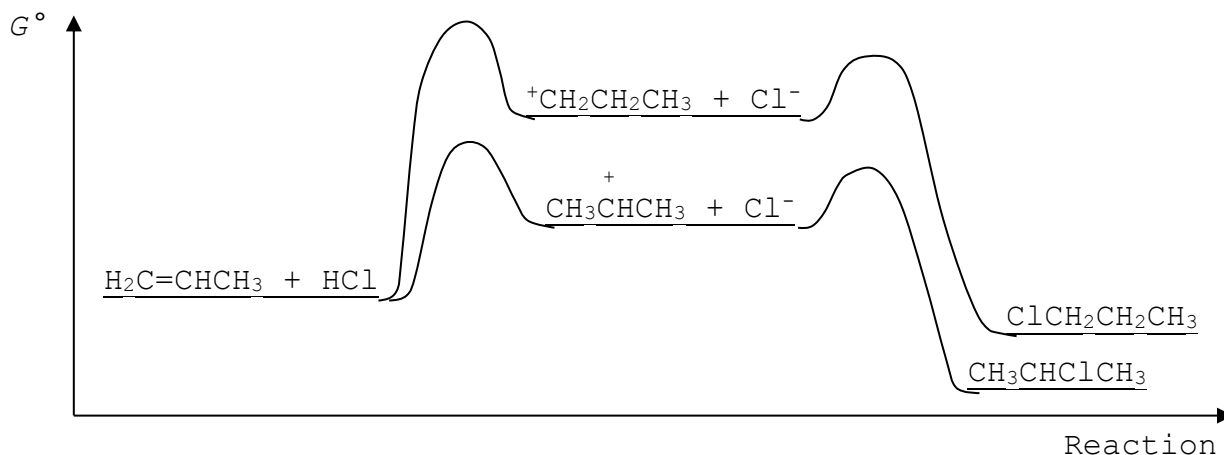
The second step quickly adds the nucleophilic chloride ion to the very electrophilic carbocation. This step is just like the second step of an  $\text{S}_{\text{N}}1$  reaction (Section 6.5C). From the secondary carbocation comes a secondary halide.

A different mechanism would lead to the unobtained primary halide, 1-chloropropane:



This time C(2) would carry the nucleophilic electron pair to the proton to form a primary carbocation. Yet, a primary carbocation is much less stable than the alternative secondary carbocation above, and is practically impossible to form because of meager hyperconjugation (Section 6.5B). Therefore, the actual addition reaction generates neither the primary carbocation nor the subsequent primary halide product.

The energy-reaction diagrams for the two, alternative reactions clarify the comparison:



energy-reaction diagrams for competing reactions of propene with HCl

Here we observe the two steps of each mechanism, the higher energy of the first transition state compared with the second (the basis for the first step being rate-limiting), and the impracticably high energy of the primary carbocation.

Most other additions of strong acids to alkenes follow the same pattern of forming the more stable carbocation intermediate. In the nineteenth century Vladimir Markovnikov (Russia, 1838-1904) discovered this pattern, although he knew nothing of the mechanism or carbocations. He stated the pattern in a different but equivalent way, called **Markovnikov's rule**: when an acid adds to an alkene, the hydrogen adds to the doubly bonded carbon with more hydrogens already attached. (If both doubly bonded carbons have the same number of hydrogens, both possible isomer products result.)

The reaction of propene above obeys Markovnikov's rule in that the hydrogen attaches to the doubly bonded carbon with more (two) hydrogens. This is equivalent to saying that the more stable carbocation is formed at the doubly bonded carbon with more (one) alkyl substituents, as we have already observed. (A free-radical addition of hydrogen bromide, which neither follows Markovnikov's rule nor forms a carbocation, is discussed in Section 23.3C.)

Other hydrogen halides add likewise to alkenes. Their order of reactivity matches their order of acidity:



relative reactivity and acidity of hydrogen halides

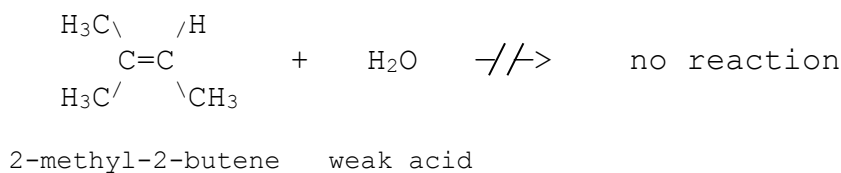
A stronger acid reacts faster in the mechanism's first step, the rate-limiting, acid-base reaction.

Puzzle 8.15

Draw the mechanism for the addition of hydrogen bromide to 2-methyl-2-butene.

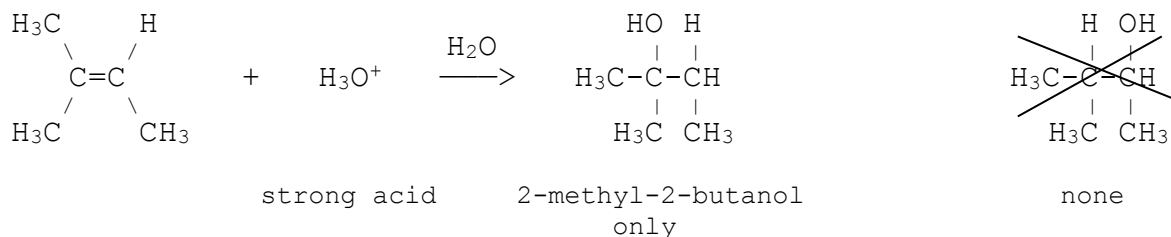
## 8.8B Reaction with Aqueous Acid

Let us try **hydrating**, that is, adding water to, an alkene with water alone:



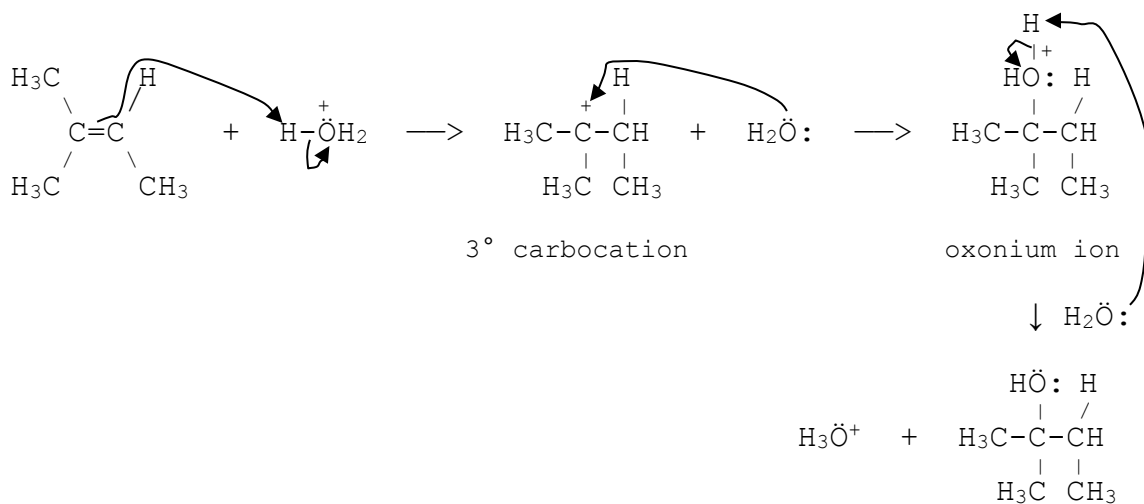
No reaction ensues because water is a weak acid, which cannot react with an alkene, a weak base (Section 8.6).

So let us try the more acidic conjugate acid of water, hydronium ion:



This reaction succeeds because a strong acid, hydronium ion, is used instead of water. Hydrations of alkenes yield very useful alcohols.

The mechanism explains the regioselective formation of only one alcohol isomer:

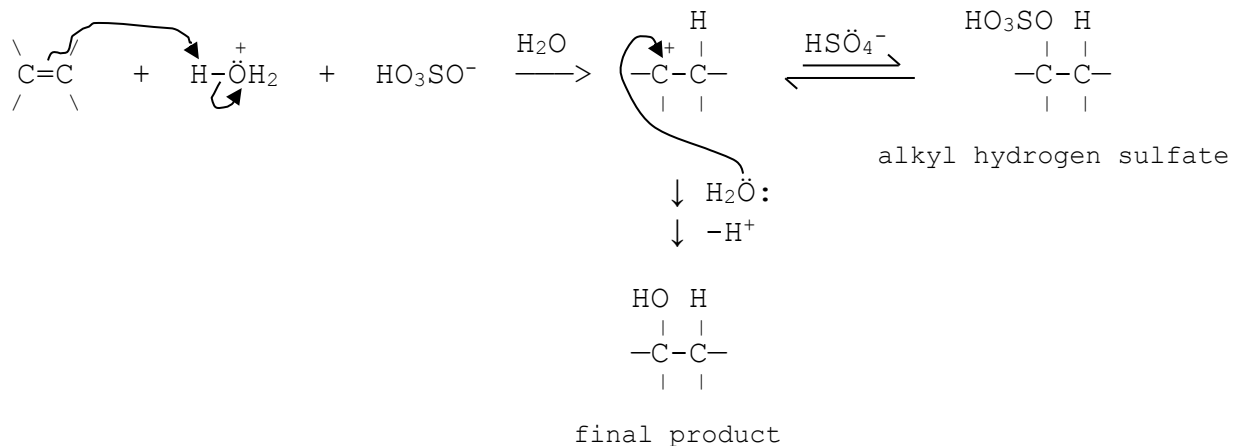


Note three similarities with the previous addition of hydrogen halides (Section 8.8A). In the first step the nucleophilic  $\pi$  bond opens to bond to the acid electrophile and form a carbocation. By opening to the right, the  $\pi$  bond forms the more stable carbocation, tertiary instead of secondary. Because the proton adds to the doubly bonded carbon with more (1) hydrogens, this addition of aqueous acid obeys Markovnikov's rule (Section 8.8A). The third similarity is the second step, where the nucleophilic conjugate base of the original acid adds to the carbocation. Although water is a weak nucleophile, it readily reacts with the carbocation, a very strong electrophile.

This hydration does differ from the two-step addition of hydrogen halides in the third mechanistic step. A base, probably water, neutralizes the oxonium ion intermediate by plucking a proton from its oxygen. This step is just like the third step of  $\text{S}_{\text{N}}1$  solvolysis (Section 6.5C). Because it is regenerated and not consumed in the overall reaction, a proton truly catalyzes the reaction.



The best source of hydronium ions for this reaction is aqueous sulfuric acid. As strong acids, aqueous hydrogen halides also provide hydronium ions, but they introduce halide nucleophiles, which form stable alkyl halide byproducts in competition with the desired alcohols (Section 8.8A). In contrast, aqueous sulfuric acid yields an *unstable* byproduct:



The unstable alkyl hydrogen sulfate, which might temporarily form, usually returns to the carbocation, which then proceeds to the desired alcohol product.

This is our third way to make an alcohol. The first two methods used an alkyl halide with hydroxide ion in an  $\text{S}_{\text{N}}2$  reaction (Section 6.3A) and with water in an  $\text{S}_{\text{N}}1$  reaction (Section 6.5C).

#### Puzzle 8.16

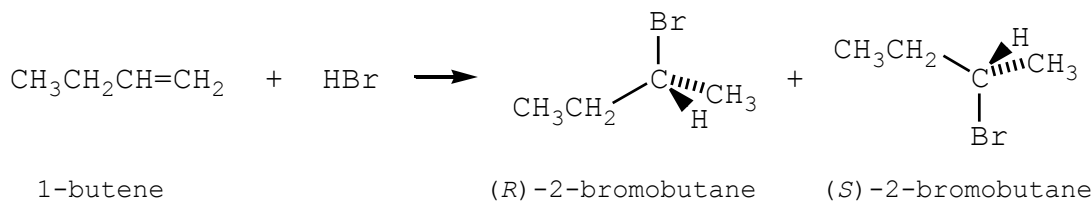
- How many constitutional isomers are produced from the addition reaction of 2-pentene with aqueous sulfuric acid.
- Draw the mechanism.

#### Puzzle 8.17

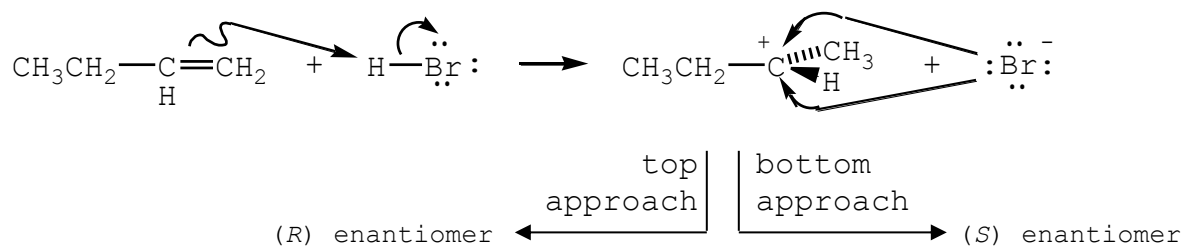
A couple of decades ago methyl *tert*-butyl ether,  $\text{H}_3\text{COC}(\text{CH}_3)_3$ , replaced a toxic lead compound as an octane booster in gasoline. By adding oxygen, it also helped gasoline burn more cleanly. It can be made from 2-methylpropene, methanol, and sulfuric acid. Draw the mechanism for this synthesis, analogous to hydration of an alkene with aqueous acid.

### 8.8C Stereochemistry of Reactions with Acids

How stereoselective are the additions of hydrogen halides and of aqueous acid to alkenes? Let us find out by noting the products of a hydrogen bromide addition that generates a chiral atom:



Both enantiomers of 2-bromobutane form, so this addition, like most other additions of hydrogen halides, is not very stereoselective. The carbocation intermediate explains this lack of selectivity:



As in  $\text{S}_{\text{N}}1$  (Section 6.5C) and  $\text{E}1$  reactions (Section 7.6B), either side of a carbocation reacts with a nucleophile. Note again that the more stable, secondary carbocation forms, instead of the alternative primary carbocation.

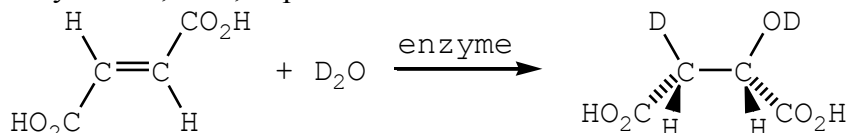
Likewise, carbocations prevent hydrations with aqueous acid from being very stereoselective.

### Puzzle 8.18

Determine the organic products, including stereoisomers, for the addition reaction of 1-butene and aqueous sulfuric acid.

### Puzzle 8.19

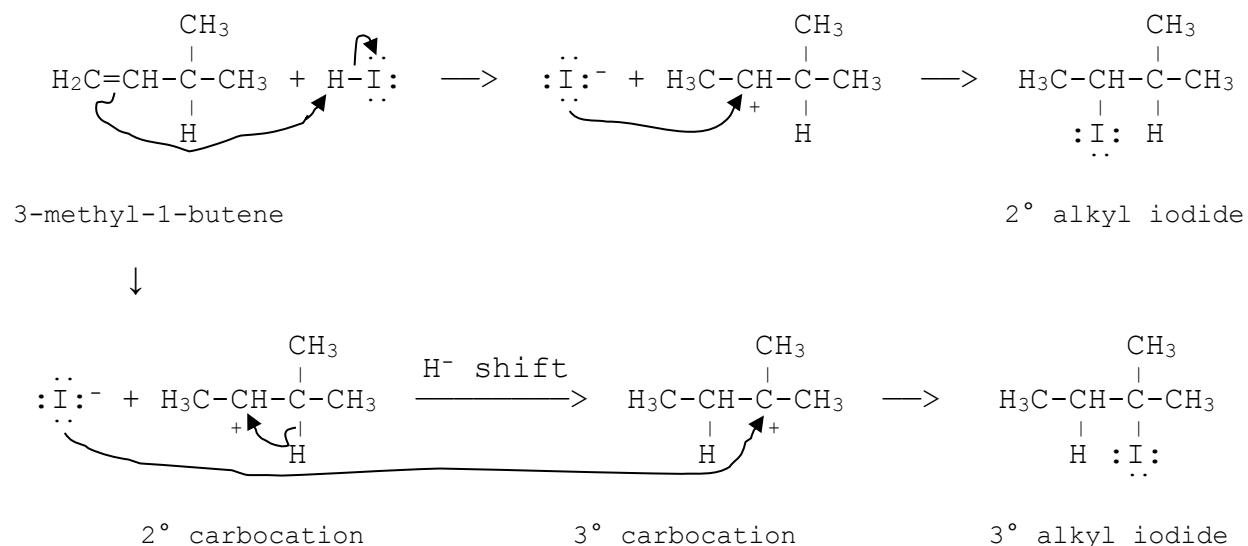
During one step of the TCA cycle, a metabolic pathway of respiration, an enzyme catalyzes the hydration of an alkene double bond in fumaric acid. To learn the stereochemistry of this hydration, one may use "heavy" water,  $\text{D}_2\text{O}$ , in place of  $\text{H}_2\text{O}$ :



- Assign *R/S* labels to the two chiral atoms of the product.
- Unlike acid-catalyzed hydrations this hydration is stereoselective. Is this addition to the double bond syn or anti? A model might help.

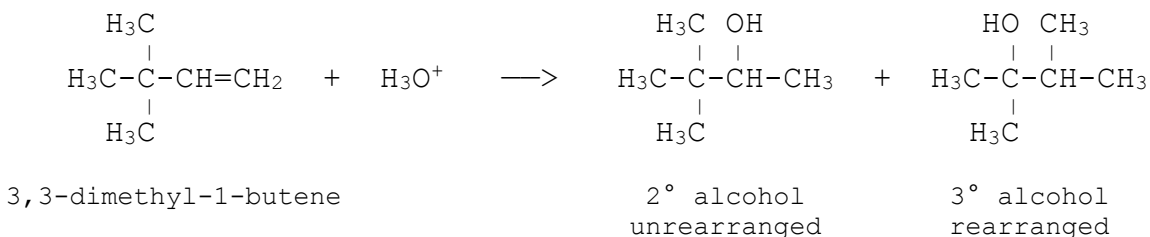
## 8.8D Carbocation Rearrangements in Reactions with Acids

The formation of a carbocation in these addition reactions has another important ramification: the possibility of carbocation rearrangements.

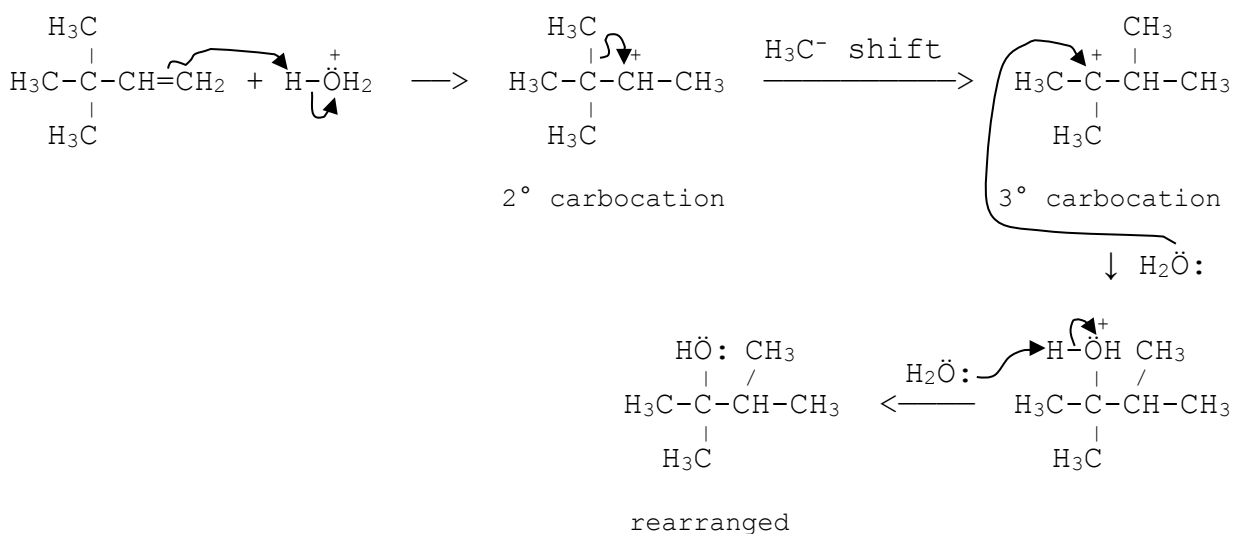


Both a secondary and a tertiary alkyl iodide are formed. A hydride shift leads the rearrangement from a secondary to a tertiary carbocation. A tertiary iodide isomer results. Thus, carbocation rearrangements sometimes occur with additions of hydrogen halides, as they do with  $\text{S}_{\text{N}}1$  (Section 6.5D) and  $\text{E}1$  reactions (Section 7.7). Note that the  $\pi$  bond of the alkene opens to the left to yield a more stable, secondary carbocation instead of a primary carbocation.

Of course, hydrations with aqueous acid, which involve a carbocation, also allow carbocation rearrangements. This example yields both an unrearranged and a rearranged alcohol:



The mechanism of the rearrangement shows a methyl shift converting a secondary carbocation to the more stable tertiary carbocation.



## Puzzle 8.20

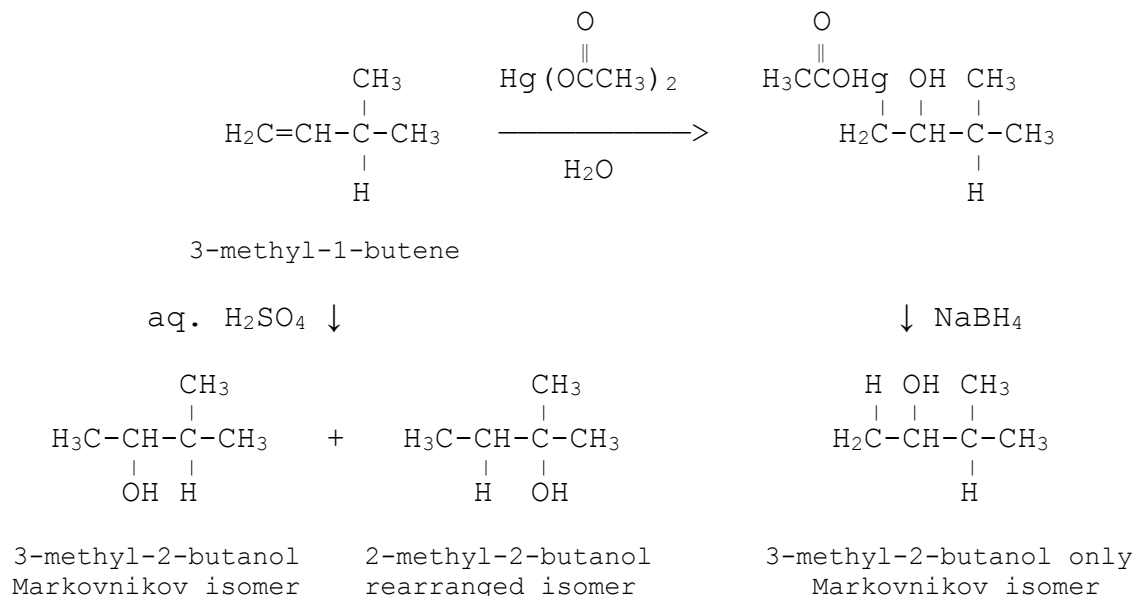
Consider the addition reactions of 3-methylcyclohexene with hydrogen chloride.

- Determine the organic products. Ignore stereoisomers.
- Draw the mechanism for the reaction that includes carbocation rearrangement.

## 8.9 Addition Reaction of Alkenes with Mercuric Ethanoate

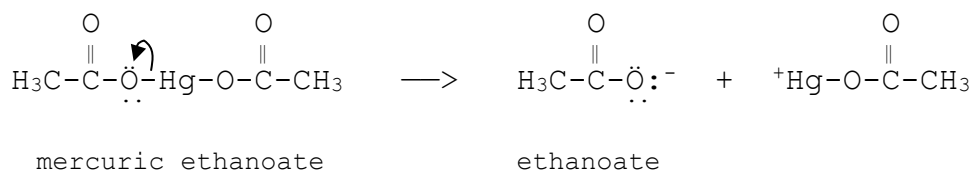
Not only do hydrations of some alkenes with aqueous acid yield rearranged isomer products (Section 8.8D), but they can lead to polymerizations (Section 24.4C). A second way to hydrate an alkene avoids these two complications and often yields more of the desired alcohol. This method uses mercuric ethanoate (i.e., mercuric acetate,  $\text{Hg}(\text{O}_2\text{CCH}_3)_2$ ) in a sequence of two reactions.

Consider alternative hydrations of 3-methyl-1-butene:



The first reaction with the mercuric ethanoate yields an alcohol with an organomercury group. In the next reaction sodium borohydride,  $\text{NaBH}_4$ , substitutes a hydrogen for the mercury ethanoate. Overall, the elements of water have been added to the alkene double bond. Furthermore, this hydration regioselectively gives only the Markovnikov isomer, 3-methyl-2-butanol. In other words, the hydrogen adds to the doubly bonded carbon with more hydrogens. This product matches a major product from hydration in aqueous sulfuric acid, also shown above. Yet, this hydration in aqueous acid also produces the isomer 2-methyl-2-butanol by a carbocation rearrangement.

To add to the alkene the mercuric ethanoate first dissociates into  $^+\text{HgO}_2\text{CCH}_3$ .



With its large, unfilled orbitals and positive charge, mercury in this cation is a strong, soft electrophile that readily adds to the soft alkene. Subsequent mechanistic details are uncertain and will not be discussed in this text.

### Puzzle 8.21

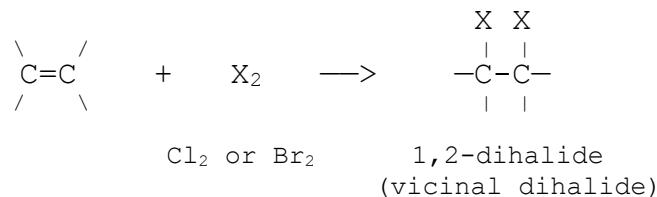
- Draw the organic products from the addition reaction of 3-methylcyclohexene and aqueous sulfuric acid.
- Draw the organic products from the treatment of 3-methyl-1-butene with mercuric ethanoate and then with sodium borohydride.

## 8.10 Addition Reactions of Alkenes with Halogens

Not all electrophiles that react with alkenes are strong. A soft, though weak, electrophile may also add to the soft alkene nucleophile.

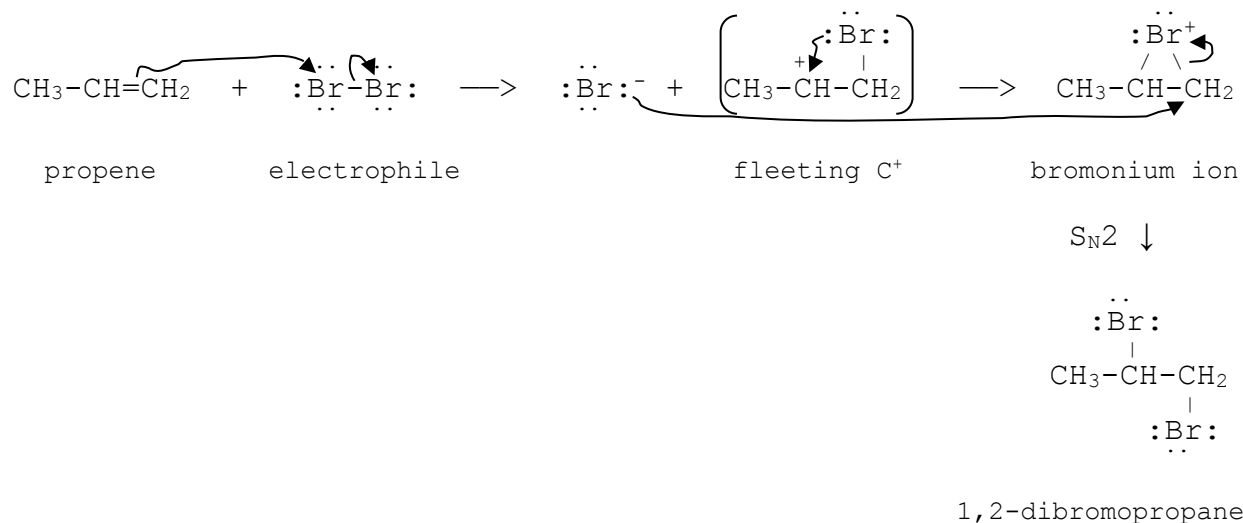
## 8.10A The Mechanism of Reactions with Halogens

Both molecular chlorine and bromine add to alkenes:



Note that a molecule with only one functional group yields a product with two functional groups. The numbers in 1,2-dihalide are not IUPAC numbers, but indicate that the two halogens are on adjacent carbons somewhere along a carbon chain. Such atoms or groups on adjacent atoms are also called **vicinal**. Molecular fluorine (F<sub>2</sub>) and iodine (I<sub>2</sub>) do not reliably give dihalides. The very reactive fluorine molecule is hard to control, whereas iodine leads to unstable diiodides, which often revert to alkenes.

The mechanism is both old and new:



Once again, the  $\pi$  bond of the alkene furnishes the nucleophilic electron pair. Bromine, however, is a surprising electrophile. By itself it has neither a formal nor a partial positive charge. Also a full octet of electrons surrounds each atom. What makes this an electrophile? It has a good leaving group: bromide ion is a weak base. A second feature is its softness. The lack of positive charge confers zero charge density and great softness to bromine (Section 4.8). Thus, although a weak electrophile, bromine reacts readily with an alkene, a soft nucleophile (Section 8.6). Likewise, chlorine is a good electrophile for alkenes because of its softness.

The brominated carbocation above is bracketed as a so-called **fleeting intermediate**. Such a halogenated carbocation from a simple alkene is even more transitory than an ordinary

carbocation. So, depictions of mechanisms usually omit it and skip to the bridged **bromonium ion**, which is more stable than the carbocation. Why is the bromonium ion more stable? Unlike the carbocation the bromonium ion has complete octets and an additional, stabilizing covalent bond.

Although the bromonium ion is more stable than the carbocation, it is destabilized by two other factors: the strain of the three-membered ring, and the positive charge on an electronegative bromine. So, this bridged ion is a strong electrophile and readily reacts in the next step with the bromide ion nucleophile, which simultaneously relieves the ring strain and neutralizes the positive charge.

---

Puzzle 8.22

Draw the mechanism for the reaction of chlorine and 1-butene.

---

Puzzle 8.23

A qualitative analysis test for alkenes involves treating a solution of the sample with a brown dichloromethane solution of bromine. Organic compounds are generally colorless unless they have many double bonds alternating with single bonds (e.g., vitamin A of Section 8.1 is yellow).

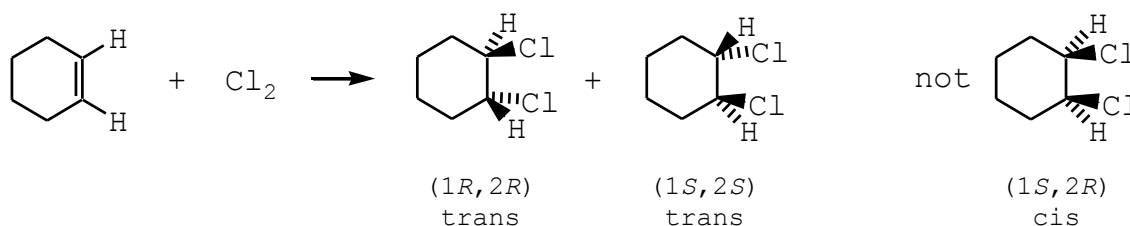
(a) Describe the color changes when a solution of cyclohexene is treated with a dichloromethane solution of bromine.

(b) By high-resolution mass spectrometry (Section 2.4A), an unknown compound is found to have the molecular formula  $C_5H_{10}$ . What can you conclude about its identity if its solution gains and retains a brown color when treated with a dichloromethane solution of bromine?

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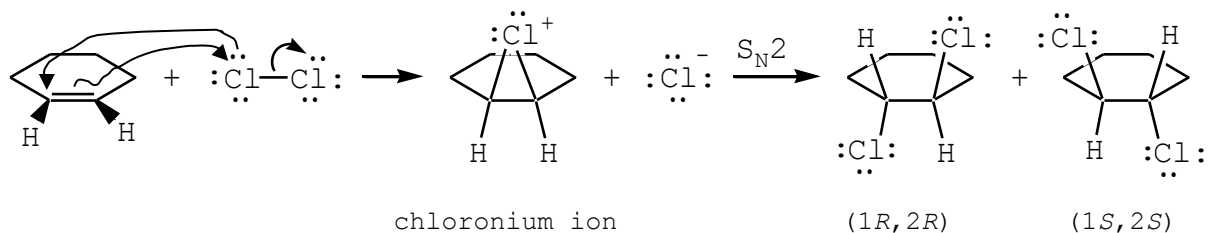
### 8.10B Stereochemistry of Reactions with Halogens

Is the addition of a halogen to an alkene stereoselective? Let us examine the result of adding chlorine to a cycloalkene, whose cyclic structure clarifies the stereochemistry:

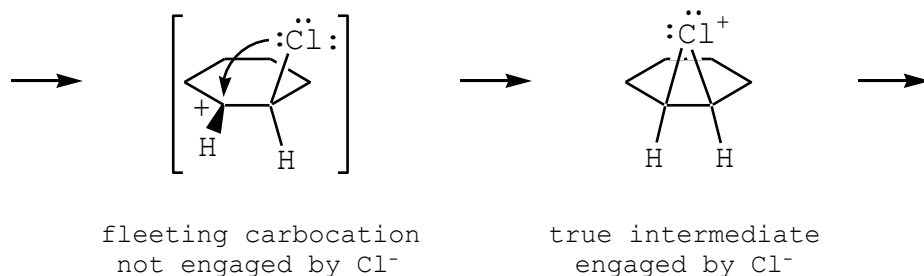


The reaction yields only the two trans, not the cis, stereoisomers in a racemic mixture. Indeed, optically inactive reactants, such as those here, must yield an optically inactive product mixture (Section 3.1C). Because not all possible stereoisomers (namely the cis) are actually produced, the addition is stereoselective, as are other additions of halogens to simple alkenes. These additions are **anti**, because the two chlorine atoms are added to opposite faces of the double bond. This contrasts with the syn hydrogenations of alkenes (Section 8.7A).

The mechanism must explain this stereoselectivity:



The anti addition results from an  $\text{S}_{\text{N}}2$  back approach by chloride ion nucleophile on the bridged **chloronium ion**. This inverts the configuration at the reacting  $\alpha$  carbon. In fact, the stereoselectivity of the reaction strongly supports the bridged chloronium ion, not a carbocation, as the true intermediate.



If the carbocation lingered before closing into the bridged ion, then the chloride ion could engage it on either side of the ring and the cis stereoisomer would also form. True carbocations are not very stereoselective, as we have seen in  $\text{S}_{\text{N}}1$  (Section 6.5C) and  $\text{E}1$  reactions (Section 7.6B), and additions of acids to alkenes (Section 8.8C).

### Puzzle 8.24

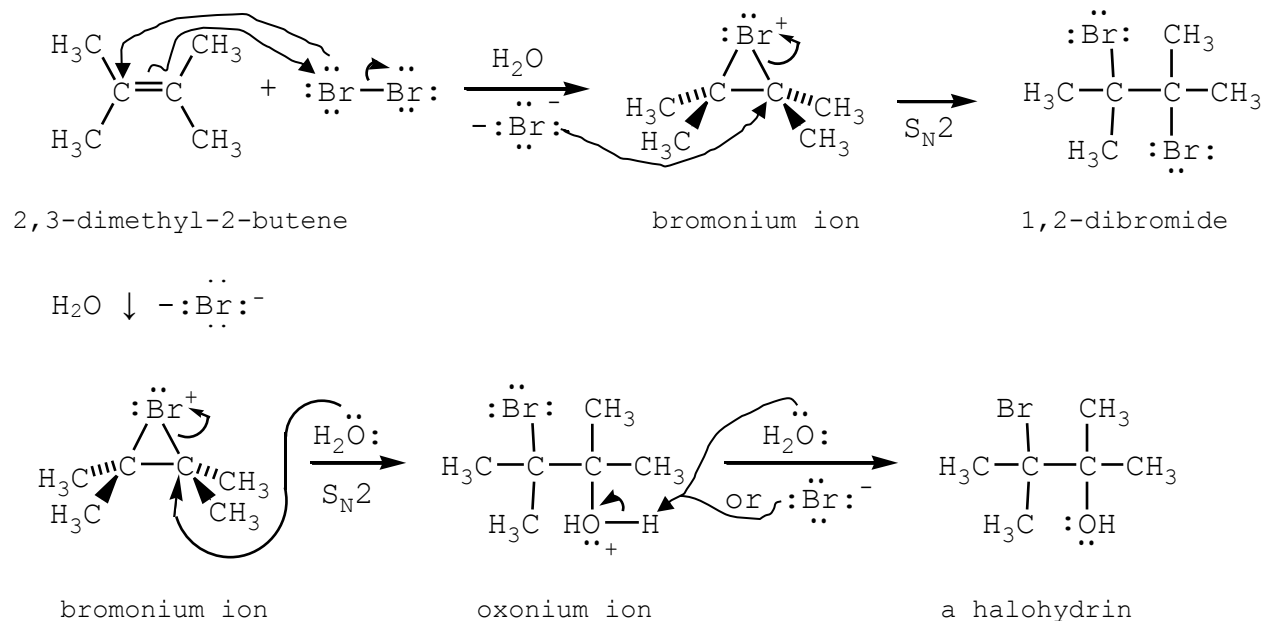
With the help of mechanisms draw the organic products, including stereoisomers, of the following reactions:



### 8.10C Reactions with Halogens in Water

If the reaction mixture includes an extra nucleophile beside the alkene and halide ion, another product may arise. For example, the addition of a halogen may occur in nucleophilic aqueous solvent, instead of the usual non-nucleophilic solvent (e.g., dichloromethane):





Two different nucleophiles can seek the **bromonium** ion intermediate. If bromide ion reacts, we get the usual 1,2-dibromide. On the other hand, if the nucleophilic solvent water reacts, a new product forms: a **halohydrin**. Halohydrin is a non-IUPAC, generic name for a compound with a halogen atom and a hydroxy group on adjacent carbons. It can be used to make an oxirane (Section 8.12B).

The bromide ion is a good, strong  $\text{S}_{\text{N}}2$  nucleophile, but water is a weak nucleophile, unsuited for normal  $\text{S}_{\text{N}}2$  reactions (Section 6.4C). So, how can water serve as an  $\text{S}_{\text{N}}2$  nucleophile here? The bromonium ion is not a normal  $\text{S}_{\text{N}}2$  electrophile. With both ring strain and a positive charge, the bromonium ion is a strong electrophile, much stronger than a simple alkyl halide. So, it can react even with a weak nucleophile, such as water. In addition, as the solvent, a water molecule is probably in the right place at the right time for reaction.

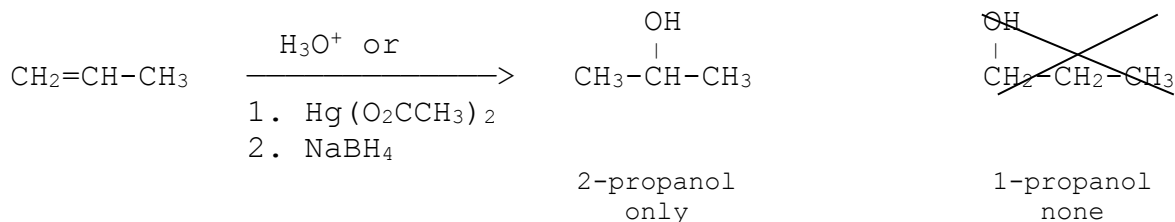
This  $\text{S}_{\text{N}}2$  behavior of water illustrates an important point: rules in organic chemistry have exceptions that are usually reasonable. In fact, rationalizing an exception is often a fascinating challenge.

### Puzzle 8.25

Predict the organic products from the reaction of (*Z*)-2-pentene with chlorine in water. Consider constitutional isomers but ignore stereoisomers.

## 8.11 Addition Reactions of Alkenes with Borane

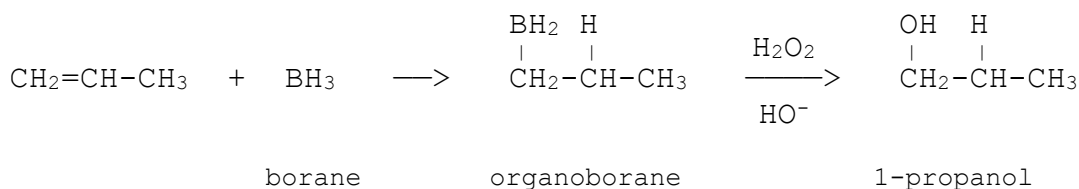
We have already found two ways of making alcohols from alkenes: using aqueous sulfuric acid (Section 8.8B) and using mercuric ethanoate with sodium borohydride (Section 8.9). Could either method yield 1-propanol from an alkene? No, because they both make the wrong isomer alcohol from propene:



Only Markovnikov addition occurs to form 2-propanol. So, a different kind of hydration is needed.

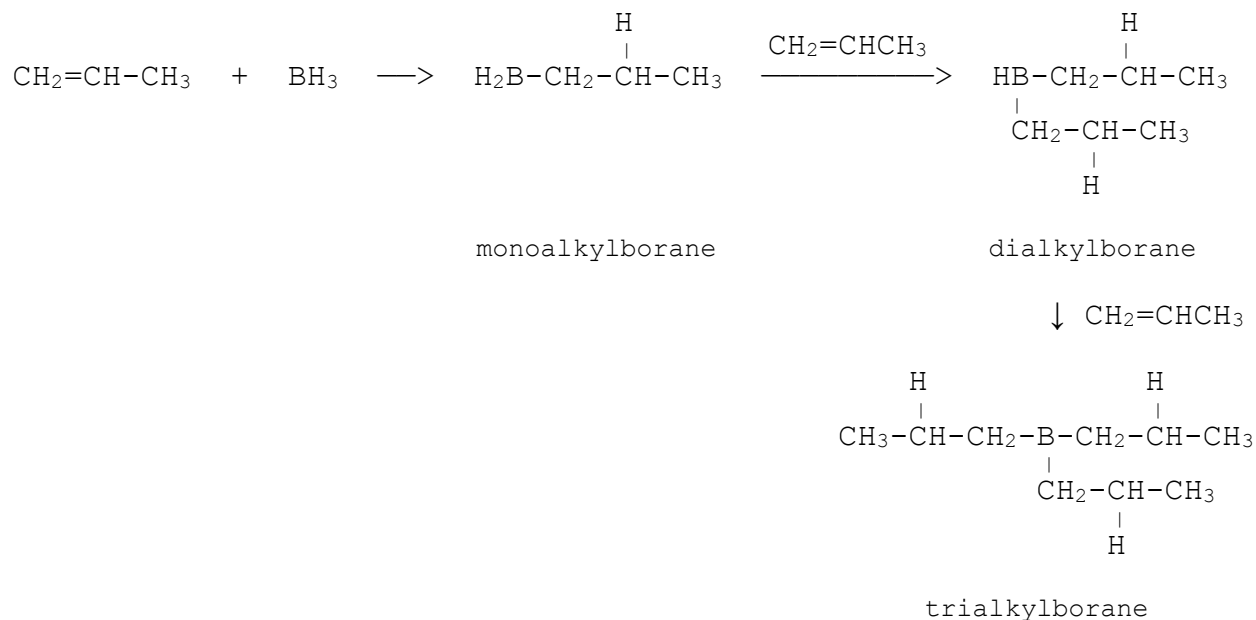
### 8.11A A Different Kind of Hydration

Since the 1950's Herbert C. Brown (USA, 1912- ) has developed many synthetic uses for borane,  $\text{BH}_3$ , and its derivatives. (Unstable when pure, borane is obtained in solution or from the dimer,  $\text{H}_3\text{BBH}_3$ .) For example, he discovered a method for hydrating alkenes in the anti-Markovnikov direction.



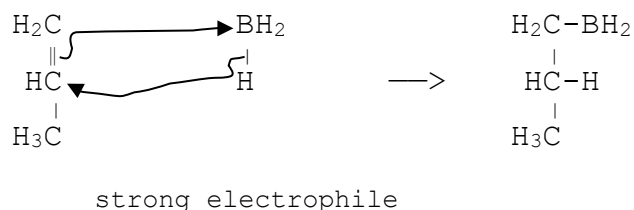
This is a two-part synthesis. First borane adds to the alkene to make the **organoborane**. Only then is this initial product reacted with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and hydroxide ion.

Actually each molecule of borane adds to three molecules of alkene in succession.



The initial monoalkylborane adds two more alkenes to make a trialkylborane. For convenience, however, only one alkyl group is often shown attached to the boron.

The mechanism for the hydroboration is novel for us:



This one-step, concerted mechanism has a cyclic electron flow. To react with the nucleophilic alkene, borane must be an electrophile. Indeed, it is a strong electrophile because only six valence electrons, not an octet, surround the boron. It temporarily fulfills its octet by receiving an electron pair with the nucleophile. The nucleophilic  $\pi$  bond here opens upward to bond to the boron. Simultaneously, a hydride ion shifts from the boron to the lower carbon. This addition is anti-Markovnikov in the sense that the hydrogen adds to the carbon with *fewer* hydrogens. The main reason for this regioselectivity is steric hindrance: the borane electrophile prefers to attach to the more sterically open, less substituted carbon of the double bond. Consequently, the hydrogen bonds to the more substituted carbon.

The synthesis' second reaction with hydrogen peroxide and hydroxide ion has a complex, unusual mechanism. Although using nucleophiles and electrophiles, this multistep mechanism will not be examined here.

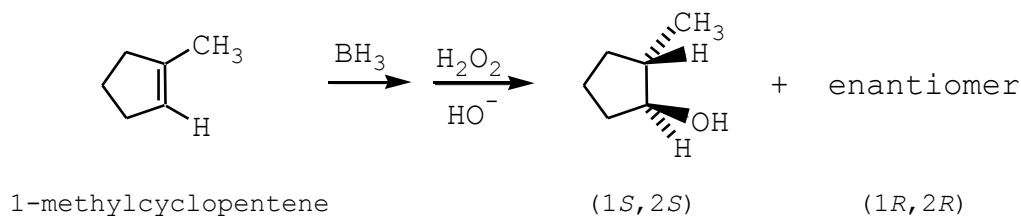
### Puzzle 8.26

Show a synthetic route from 2-methyl-2-butene to each of the following alcohols:

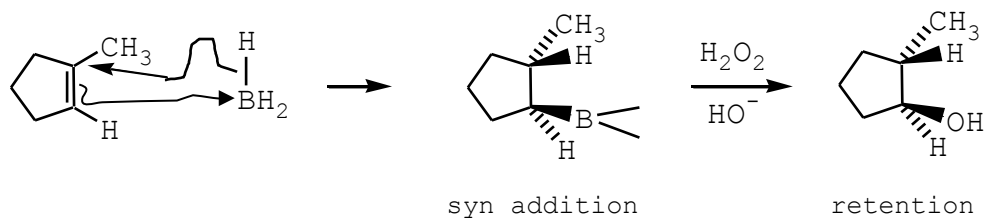
(a) 3-methyl-2-butanol (b) 2-methyl-2-butanol

### 8.11B Stereochemistry of Reaction with Borane

To appreciate the stereochemistry of borane hydration, we examine the reaction with a cyclic alkene:



This reaction is stereoselective because none of the possible (1*S*,2*R*) and (1*R*,2*S*) stereoisomers form. Because the hydrogen and hydroxy group add to the same side of the double bond, this is a syn addition. The concerted, cyclic mechanism of the hydroboration reaction begins to explain this strictly syn addition:



The boron and the hydride simultaneously add to the same side of the ring in *syn* fashion. Then the hydrogen peroxide oxidizes the organoborane to the alcohol with *retention* of configuration. Although we have not seen the mechanism for this last reaction, evidently it cannot be  $S_N2$ , which *inverts* the configuration.

Table 8.1 compares our three methods of hydrating an alkene: by aqueous acid, by mercuric ethanoate, and by hydroboration. Their contrasting properties make these reactions good alternatives for the synthesis of alcohols from alkenes.

Table 8.1 Comparison of Three Methods of Alkene Hydration

	By $H_3O^+$	By $Hg(O_2CCH_3)_2$	By $BH_3$
<b>Markovnikov addition</b>	Yes	Yes	No
<b>Stereoselective</b>	No	No	Yes, syn addition
<b>Carbocation rearrangement</b>	Yes	No	No

### Puzzle 8.27

Draw the two organoborane stereoisomers and the two final alcohol stereoisomers produced in the reaction:



## 8.12 Oxidation Reactions of Alkenes

Oxidation and reduction reactions are discussed in general chemistry, usually with oxidation numbers. Now let us redefine them for organic chemistry, not in terms of oxidation numbers, which get cumbersome with larger molecules, but more simply in terms of bonds added and lost. Carbon in an organic molecule is oxidized when it *adds* a bond to a *more electronegative* atom, such as oxygen, nitrogen, or a halogen, or when it *loses* a bond to a slightly *less electronegative* hydrogen. In contrast, carbon is reduced when it adds a bond to hydrogen or loses a bond to oxygen, nitrogen, or halogen. These definitions agree with more general definitions involving gain and loss of electrons. For example, if carbon adds a bond to a more electronegative atom, it loses electron density to this atom and is therefore oxidized.

Table 8.2 classifies the previously discussed addition reactions of alkenes as oxidations, reductions, or neither. We have seen one reduction (hydrogenation) and one oxidation (halogenation) of alkenes. Hydration and additions of hydrogen halides are neither oxidations nor reductions overall because one carbon is oxidized with OH or X and one carbon is reduced with H.

Table 8.2 Reactions of Alkenes as Oxidations or Reductions

	Product	Effect on C=C	Overall reaction
<b>Hydrogenation</b>	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \end{array}$	2 Cs reduced (reductant = H <sub>2</sub> )	reduction
<b>Halogenation</b>	$\begin{array}{c} \text{X} \quad \text{X} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \end{array}$	2 Cs oxidized (oxidant = X <sub>2</sub> )	oxidation
<b>Addition of HX</b>	$\begin{array}{c} \text{H} \quad \text{X} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \end{array}$	1 C reduced, 1 C oxidized	neither oxidation nor reduction
<b>Hydration</b>	$\begin{array}{c} \text{H} \quad \text{OH} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \end{array}$	1 C reduced, 1 C oxidized	neither oxidation nor reduction

Three more oxidation reactions of alkenes will be explored next. All three are more important for their abilities to add oxygen bonds to both doubly bonded carbons than for their unusual, somewhat obscure mechanisms.

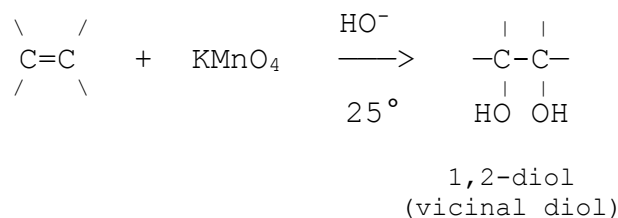
## Puzzle 8.28

In the following reactions, decide which carbons and which organic molecules are being oxidized or reduced, if any.

- (a)  $\text{CH}_3\text{CH}_2\text{Cl} + \text{HO}^- \longrightarrow \text{CH}_3\text{CH}_2\text{OH}$   
 (b)  $\text{CH}_3\text{CH}_2\text{Cl} + \text{HO}^- \longrightarrow \text{CH}_2=\text{CH}_2$   
 (c)  $\text{CH}_2=\text{CH}_2 + \text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{CH}_2\text{ClCH}_2\text{OH}$   
 (d)  $\text{HC}\equiv\text{CH} + \text{Na} + \text{NH}_3 \longrightarrow \text{H}_2\text{C}=\text{CH}_2$   
 (e)  $\text{CH}_3\text{CH}=\text{O} + \text{KMnO}_4 \longrightarrow \text{CH}_3\text{CO}_2\text{H}$   
 (f)  $\text{CH}_3\text{CH}=\text{O} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CH}(\text{OH})_2$   
 (g)  $\text{CH}_3\text{CH}=\text{O} + \text{NaBH}_4 \longrightarrow \text{CH}_3\text{CH}_2\text{OH}$

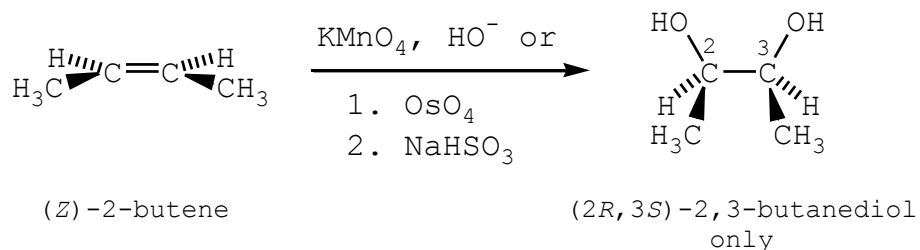
## 8.12A Oxidation Reaction with Potassium Permanganate

Potassium permanganate,  $\text{KMnO}_4$ , is an important, strong oxidizing agent in both inorganic and organic chemistry. A cold, basic solution of permanganate moderately oxidizes an alkene to a **1,2-diol**:

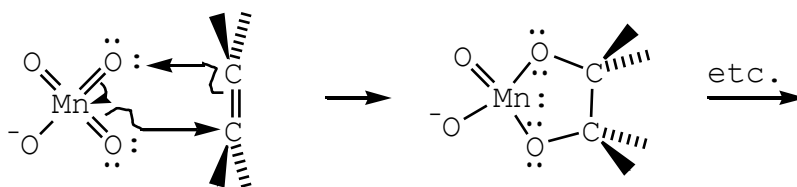


The numbers in 1,2-diol are not IUPAC numbers, but indicate that its two functional groups are on adjacent carbons of the double alcohol. Like a 1,2-dihalide, a 1,2-diol can also be called vicinal (Section 8.10A), and a common name is glycol. This is an oxidation because bonds to oxygen replace the  $\pi$  bond of the double bond. Osmium tetroxide,  $\text{OsO}_4$ , also oxidizes an alkene to a 1,2-diol.

An alkene stereoisomer shows us the stereoselectivity of the oxidation:



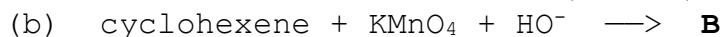
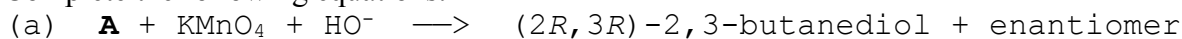
No other stereoisomer results, so this is a fully stereoselective reaction. Indeed, the addition is syn because both hydroxy groups attach to the same face of the double bond. The mechanism is uncertain but probably involves a cyclic intermediate:



The nucleophilic alkene pushes electrons toward the electron-poor, electrophilic Mn(VII) in a high oxidation state.

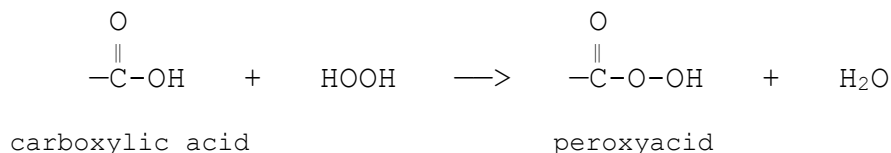
## Puzzle 8.29

Complete the following equations:

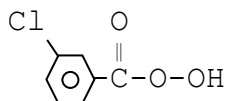


## 8.12B Oxidation Reaction with Peroxyacids

A **peroxyacid** is a special kind of **peroxide**. A peroxide, such as hydrogen peroxide (HOOH), contains a relatively weak, reactive oxygen-oxygen bond. The bond energy of this bond in HOOH is only 214 kJ/mol (Table 1.6, Section 1.8). A peroxyacid results from the oxidation of a carboxylic acid with hydrogen peroxide:

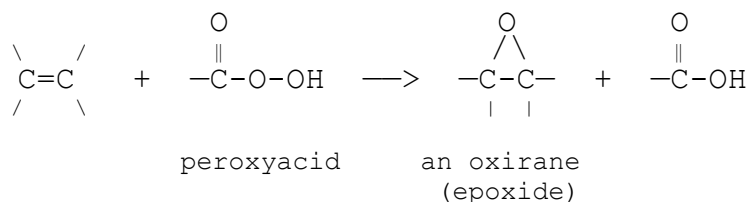


Note the oxygen-oxygen bond in the peroxyacid, which makes it an oxidizing agent, unlike carboxylic acids. A commonly used peroxyacid is *m*-chloroperoxybenzoic acid:



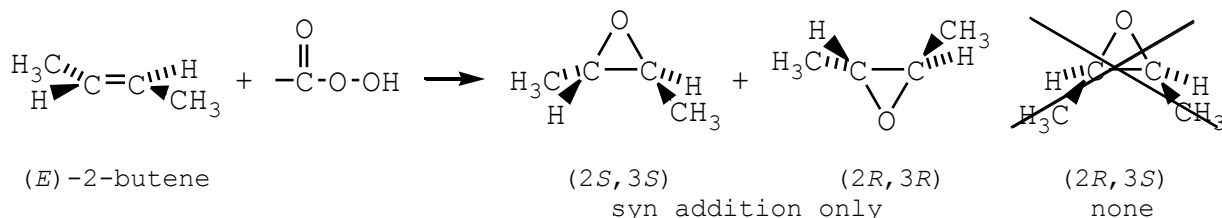
*m*-chloroperoxybenzoic acid, a common peroxyacid

Like basic permanganate a peroxyacid breaks the  $\pi$  bond of the alkene double bond and replaces it with bonds to oxygen:



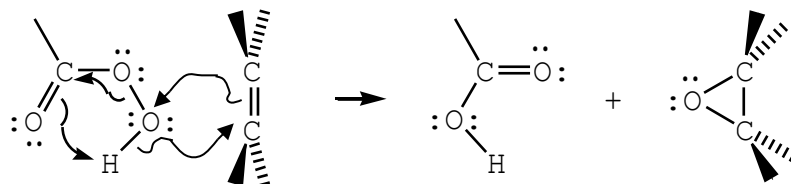
An **oxirane** (also called **epoxide**) results. One oxygen is shared by two carbons in a cyclic ether. We will learn reactions of this interesting kind of molecule in Section 10.8B.

To establish the reaction's stereoselectivity, we react a stereoisomeric alkene:



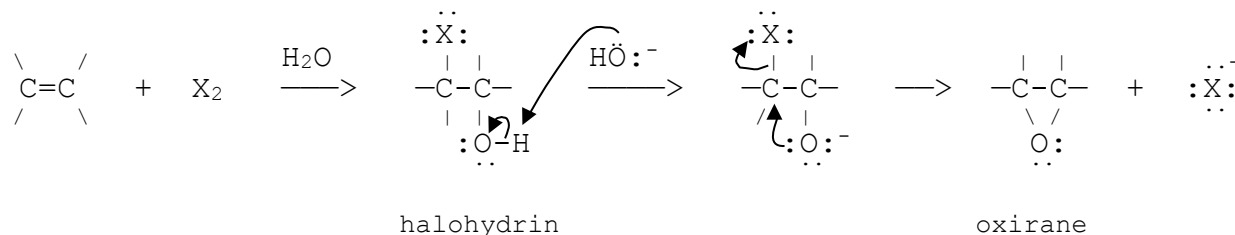
The optically inactive achiral reactants produce an optically inactive racemic mixture of enantiomers. Because one pair of enantiomers is produced without the (2*R*,3*S*) diastereomer, the reaction is stereoselective. The oxygen adds to the same face of the double bond, so this is a syn addition.

A complex, cyclic, one-step mechanism explains the stereoselectivity:



As usual, the alkene is the nucleophile, whereas the peroxyacid is the electrophile, typical of oxidizing agents.

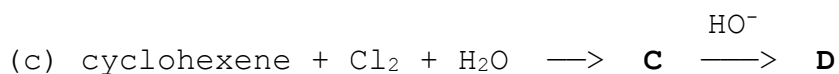
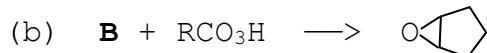
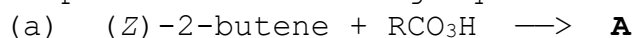
A second way of synthesizing oxiranes from alkenes uses a halohydrin (Section 8.10C):



Hydroxide ion transforms the halohydrin into a nucleophilic alkoxide ion, which pursues the nearby electrophilic alkyl halide in an intramolecular  $S_N2$ -like reaction. (This is not strictly an  $S_N2$  reaction because it is monomolecular, not bimolecular.) Although less direct than peroxyacid oxidation, this synthesis nicely illustrates how an  $S_N2$ -like reaction with a nucleophile and electrophile on the same molecule creates a ring.

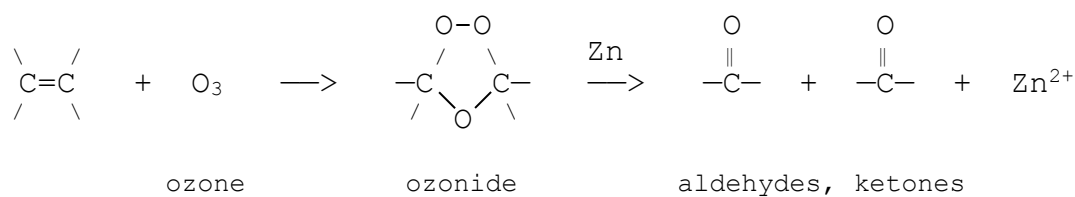
### Puzzle 8.30

Complete the following equations:



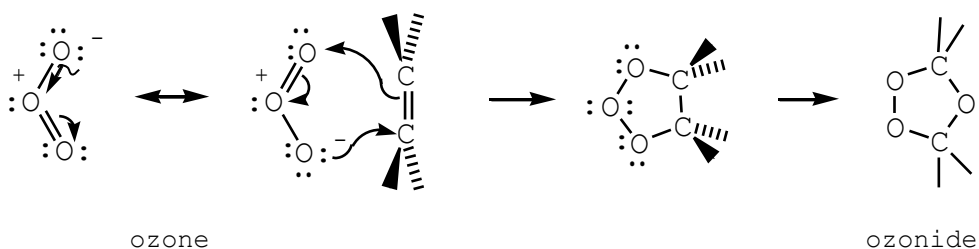
### 8.12C Oxidation Reaction with Ozone

The oxidation of an alkene can be taken a step further with ozone,  $\text{O}_3$ , a very strong oxidizing agent. While breaking only the  $\pi$  bond of the double bond, basic permanganate (Section 8.12A) or a peroxyacid (Section 8.12B) adds one oxygen bond to each doubly bonded carbon. While breaking *both* bonds of the double bond, ozone adds *two* oxygen bonds to each doubly bonded carbon:



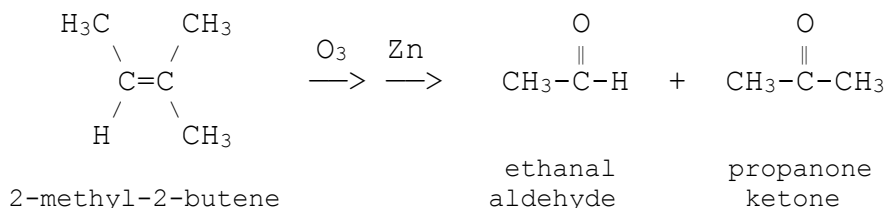


In this **ozonolysis** the alkene is broken into two smaller, carbonyl molecules. In the first reaction, which forms a cyclic **ozonide**, the alkene nucleophile pushes electrons toward the electrophilic middle oxygen of ozone, positively charged in both major resonance forms:



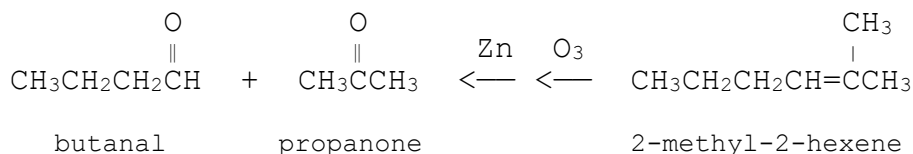
This part of the mechanism resembles the formation of the cyclic intermediate of permanganate oxidation (Section 8.12A). The mechanisms of the cyclic intermediate's rearrangement to the ozonide and of the subsequent ring opening to the aldehydes or ketones are uncertain and will not be considered.

Whether aldehydes or ketones form from the ozonide depends on the arrangement of alkyl groups on the alkene. A doubly bonded carbon with two alkyl substituents yields a ketone. Yet, if the doubly bonded carbon bears a hydrogen, an aldehyde forms:



The products can be visualized by mentally replacing the alkene double bond with two double bonds to oxygens. By breaking both bonds of the alkene double bond, ozone achieves an unusual feat: cleavage of a carbon-carbon  $\sigma$  bond. In contrast, carbon-carbon  $\pi$  bonds are relatively vulnerable to cleavage as we have seen throughout this chapter. Even ozone, however, cannot cleave an ordinary carbon-carbon single bond. It is the nucleophilicity of an alkene double bond that permits reaction.

This kind of a reaction where a large molecule is broken into smaller molecules is called a **degradation** reaction. Such reactions are most useful in the identification of large alkenes. The smaller degraded products are easier to identify and so can allow mental reconstruction of the original alkene. For example, if ozonolysis of an alkene forms butanal and propanone, the original alkene must be 2-methyl-2-hexene:



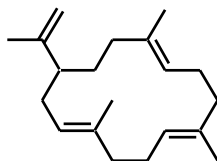
Puzzle 8.31

Complete the following equations with organic structures:

- (a) ethene  $\xrightarrow{\text{O}_3} \xrightarrow{\text{Zn}}$  **A**
- (b) 2,3-dimethyl-2-butene  $\xrightarrow{\text{O}_3} \xrightarrow{\text{Zn}}$  **B**
- (c) cyclohexene  $\xrightarrow{\text{O}_3} \xrightarrow{\text{Zn}}$  **C**
- (d) 1,4-cyclohexadiene  $\xrightarrow{\text{excess O}_3} \xrightarrow{\text{excess Zn}}$  **D**
- (e) 3-methyl-3-hexene  $\xrightarrow{\text{O}_3} \xrightarrow{\text{Zn}}$  **E + F**
- (f) **G** ( $\text{C}_6\text{H}_{10}$ )  $\xrightarrow{\text{O}_3} \xrightarrow{\text{Zn}}$   $\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CH}$
- (g) **H** ( $\text{C}_{12}\text{H}_{20}$ )  $\xrightarrow{\text{excess O}_3} \xrightarrow{\text{excess Zn}}$   $\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CH}$

## Puzzle 8.32

To mark a trail for other termites, some termites emit neocembrene:



Which organic chemicals result from degradation of neocembrene with ozone and zinc?

## Chapter Summary

- Alkenes are named by the IUPAC system, but common names, such as methylene, vinyl, and allyl, are often used for certain alkenyl groups.
- An alkene's double bond connects two  $sp^2$  carbons with one  $\sigma$  and one  $\pi$  bond.
- The alkene double bond is both shorter and stronger than a carbon-carbon single bond. Within the double bond the  $\pi$  bond is weaker than the  $\sigma$  bond.
- Because the  $\pi$  bond resists rotation around the double bond, some alkenes have *E* and *Z* diastereomers.
- Simple alkenes are practically nonpolar, with boiling points similar to alkanes of similar size. Simple alkenes do not dissolve in water.
- As a weak base and soft nucleophile, an alkene uses its nucleophilic  $\pi$  bond to react with strong or soft electrophiles in an addition reaction.
- Hydrogenation reactions of alkenes, that is, the addition of molecular hydrogen, require a catalyst for useful reaction rates.
- Heats of hydrogenation indicate that *E* stereoisomers of alkenes are a little more stable than their *Z* counterparts, which have steric repulsion. Heats of hydrogenation also indicate that alkene isomers with more alkyl substituents on the double bond are more stable than isomers with fewer alkyl substituents.
- Alkenes add hydrogen halides to form alkyl halides regioselectively, according to

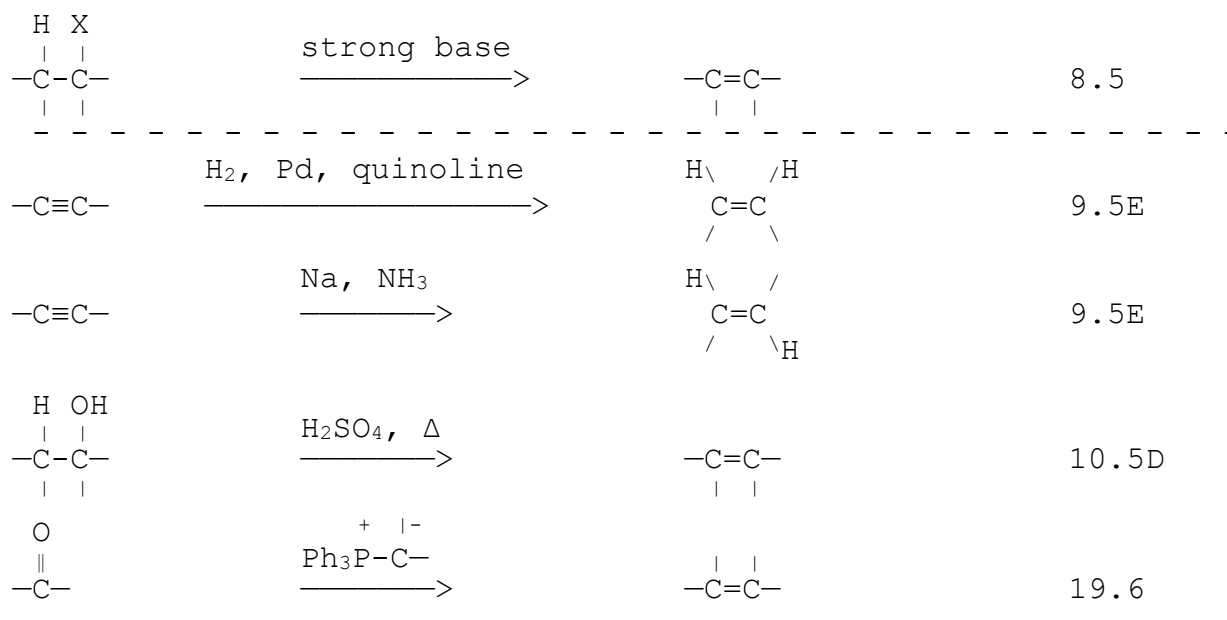
Markovnikov's rule: an acid adds to an alkene so that the hydrogen adds to the doubly bonded carbon with more hydrogens.

10. A hydrogen halide adds by a two-step mechanism, where the first, rate-limiting step yields a carbocation, which then adds the halide ion.
  11. Aqueous sulfuric acid or mercuric ethanoate followed by sodium borohydride hydrates (i.e., adds water to) an alkene to form an alcohol.
  12. Aqueous acid hydration follows Markovnikov's rule in a mechanism very like that of hydrogen halide addition.
  13. With their carbocation intermediates, both hydrogen halide additions and aqueous acid hydrations are not stereoselective and allow carbocation rearrangements.
  14. Mercuric ethanoate and sodium borohydride hydrate an alkene in the Markovnikov direction without carbocation rearrangement.
  15. The weak but soft electrophiles, chlorine and bromine, add to alkenes to yield 1,2-dihalides in a stereoselective, anti fashion.
  16. A halogen addition to an alkene yields a bridged halonium cation intermediate, which then reacts with a halide ion.
  17. Halogen additions performed in water lead to halohydrins, as well as dihalides. Halohydrins result from nucleophilic water encountering the halonium ion.
  18. The addition of borane with subsequent hydrogen peroxide oxidation hydrates an alkene to an alcohol.
  19. In contrast to aqueous acid and mercuric ethanoate hydrations, a borane hydration yields the alcohol isomer in the anti-Markovnikov direction and by stereoselective syn addition.
  20. The oxidation of a carbon in an organic compound adds a bond to an electronegative atom or removes a bond to hydrogen. A reduction adds a bond to hydrogen or removes a bond to an electronegative atom.
  21. Cold, basic potassium permanganate or osmium tetroxide followed by sodium hydrogen sulfite oxidizes an alkene to a 1,2-diol in a stereoselective syn addition.
  22. A peroxyacid oxidizes an alkene to an oxirane in a stereoselective syn addition. Oxiranes may also be synthesized from halohydrins with hydroxide ion.
  23. Ozone, followed by zinc, oxidizes an alkene to aldehydes or ketones by breaking both bonds of the double bond. This oxidation is a degradation reaction that aids the identification of large alkenes.
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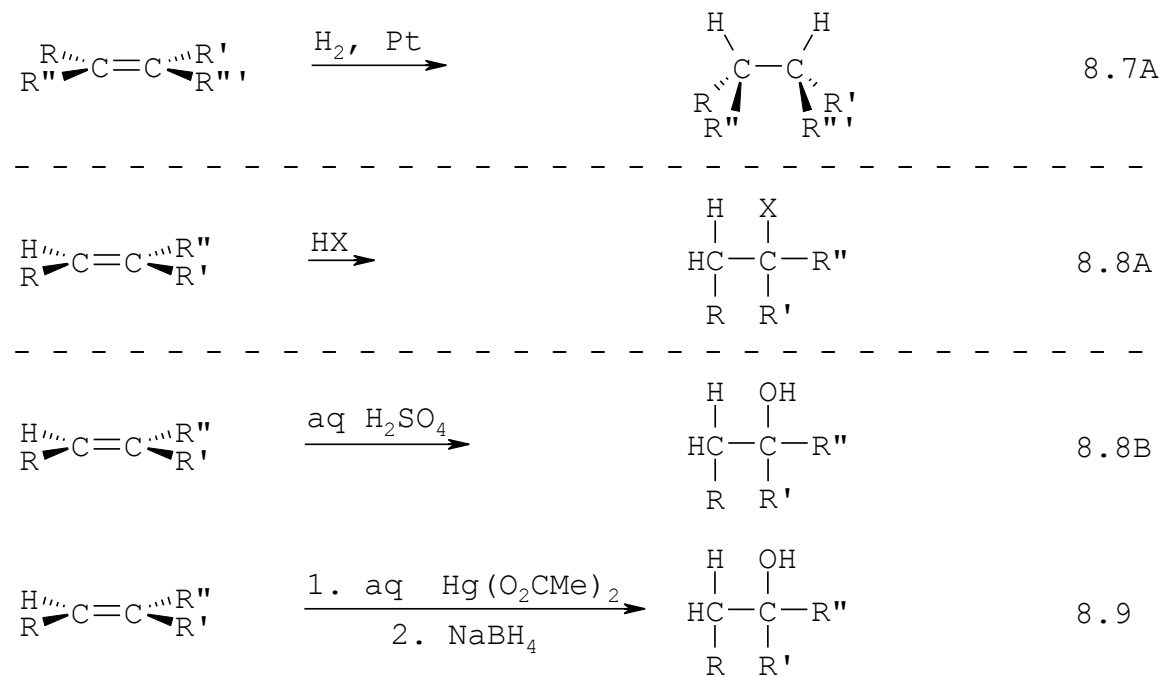
## Reaction Summary

Reactants	Product	Section
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## Syntheses of alkenes



## Reactions of alkenes



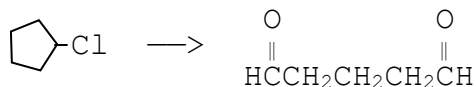
Reactants	Product	Section	
<b>Reactions of alkenes (continued)</b>			
$\begin{array}{c} \text{H} \diagup \text{C} = \text{C} \diagdown \\ \text{R} \quad \quad \text{R}' \end{array}$	$\xrightarrow[2. \text{ HOOH, HO}^-]{1. \text{ BH}_3}$	$\begin{array}{c} \text{HO} \quad \text{H} \\   \quad   \\ \text{C} - \text{C} \\   \quad   \\ \text{H} \quad \text{R}' \\ \text{R} \quad \text{R}' \end{array}$	8.11A
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$\begin{array}{c} \text{H} \diagup \text{C} = \text{C} \diagdown \\ \text{R} \quad \quad \text{R}'' \end{array}$	$\xrightarrow[\text{X} = \text{Cl or Br}]{\text{X}_2}$	$\begin{array}{c} \text{X} \quad \text{R}' \\   \quad   \\ \text{C} - \text{C} \\   \quad   \\ \text{H} \quad \text{R}'' \\ \text{R} \quad \text{X} \end{array}$	8.10A
$\begin{array}{c} \text{H} \diagup \text{C} = \text{C} \diagdown \\ \text{R} \quad \quad \text{R}' \end{array}$	$\xrightarrow[\text{H}_2\text{O}]{\text{X}_2}$	$\begin{array}{c} \text{X} \quad \text{R}' \\   \quad   \\ \text{C} - \text{C} \\   \quad   \\ \text{H} \quad \text{OH} \\ \text{R} \quad \text{R}'' \end{array}$	8.10C
-----			
$\begin{array}{c} \text{H} \diagup \text{C} = \text{C} \diagdown \\ \text{R} \quad \quad \text{R}'' \end{array}$	$\xrightarrow[\text{HO}^-]{\text{KMnO}_4}$	$\begin{array}{c} \text{HO} \quad \text{OH} \\   \quad   \\ \text{C} - \text{C} \\   \quad   \\ \text{H} \quad \text{R}' \\ \text{R} \quad \text{R}'' \end{array}$	8.12A
$\begin{array}{c} \text{H} \diagup \text{C} = \text{C} \diagdown \\ \text{R} \quad \quad \text{R}'' \end{array}$	$\xrightarrow[2. \text{ NaHSO}_3]{1. \text{ OsO}_4}$	$\begin{array}{c} \text{HO} \quad \text{OH} \\   \quad   \\ \text{C} - \text{C} \\   \quad   \\ \text{H} \quad \text{R}' \\ \text{R} \quad \text{R}'' \end{array}$	8.12A
$\begin{array}{c} \text{H} \diagup \text{C} = \text{C} \diagdown \\ \text{R} \quad \quad \text{R}'' \end{array}$	$\xrightarrow[-\text{C(=O)OOH}]{\text{O}}$	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} - \text{C} \\   \quad   \\ \text{H} \quad \text{R}' \\ \text{R} \quad \text{R}'' \end{array}$	8.12B
$\begin{array}{c} \text{H} \diagup \text{C} = \text{C} \diagdown \\ \text{R} \quad \quad \text{R}'' \end{array}$	$\xrightarrow[2. \text{ Zn}]{1. \text{ O}_3}$	$\begin{array}{c} \text{H} \diagup \text{C} = \text{O}, \text{O} = \text{C} \diagdown \\ \text{R} \quad \quad \text{R}' \end{array}$	8.12C
$\begin{array}{c} \text{H} \diagup \text{C} = \text{C} \diagdown \\ \text{R} \quad \quad \text{R}'' \end{array}$	$\xrightarrow[\text{peroxide}]{\text{HBr}}$	$\begin{array}{c} \text{Br} \quad \text{H} \\   \quad   \\ \text{HC} - \text{C} - \text{R}'' \\   \quad   \\ \text{R} \quad \text{R}' \end{array}$	23.3C

### Additional Puzzles

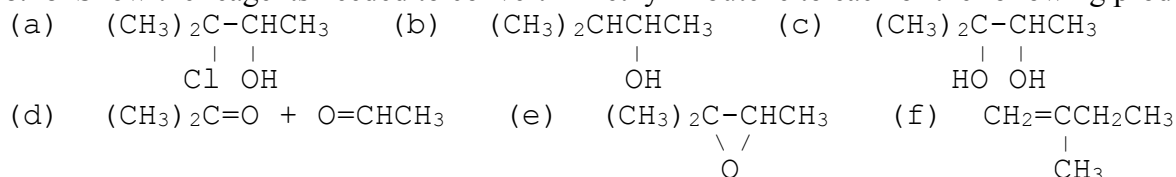
8.33 Correct the mistake in each name and draw structures with the corrected names:

- (a) butene (b) 1-bromo-4-hexene (c) 1-ethyl-2-cyclopentene (d) 1-hydroxy-2-propene  
 (e) 5-cycloheptenol

- 8.34 (a) Rank propene and 2-propen-1-ol by boiling point. Explain.  
(b) Rank propene and 2-propen-1-ol by solubility in water. Explain.
- 8.35 Show the reagents needed to make the following alkenes from alkyl halides in good yield:  
(a) 1-butene (b) 2-butene (c) 1-methylcyclopentene (d) 3-methylcyclopentene
- 8.36 Why should a heterogeneous catalyst for an alkene hydrogenation be finely divided?
- 8.37 (a) Draw all compounds that yield 2-methylbutane upon reaction with one equivalent of molecular hydrogen in the presence of platinum.  
(b) Which of these compounds would yield the most energy during reaction?  
(c) Which of the compounds would yield the least energy during reaction?
- 8.38 (a) Find an alkene that reacts with hydrogen iodide to give two constitutional isomer products without a carbocation rearrangement.  
(b) Does this example violate Markovnikov's rule?
- 8.39 Draw the mechanisms for the reactions of aqueous (as opposed to the usual anhydrous) hydrogen chloride with 2-methyl-2-butene. Two organic products form.
- 8.40 (a) Which isomer product results from the addition reaction of 1,1,1-trifluoro-2-butene with aqueous sulfuric acid? Explain with the structures of the two possible intermediates.  
(b) Does this reaction violate Markovnikov's rule?
- 8.41 (a) Draw the stereoisomers produced from the addition reaction of (*S*)-1,5-dimethylcyclohexene in aqueous sulfuric acid.  
(b) What is the relationship of the stereoisomers?
- 8.42 Draw the mechanisms for the reactions of hydrogen bromide with 3,3-dimethyl-1-butene, yielding two constitutional isomers.
- 8.43 Bromine reacts with 4-penten-1-ol to form a cyclic compound with molecular formula,  $C_5H_9BrO$ . Draw a mechanism for this reaction.
- 8.44 (a) Draw the stereoisomer products of the reaction of 1-methylcyclopentene with chlorine.  
(b) What is the relationship of these stereoisomers?
- 8.45 (a) Find a *single* alkene that can be converted to either 1-methylcyclohexanol or cyclohexylmethanol.  
(b) Show the reagents for each conversion.
- 8.46 (a) Which alkene could yield a mixture of 3-methyl-3-pentanol and 3-methyl-2-pentanol as main products of one hydration reaction?  
(b) Draw the mechanism leading to the first product.
- 8.47 Show the reactants and organic products for all reactions in the synthesis:



8.48 Show the reagents needed to convert 2-methyl-2-butene to each of the following products:

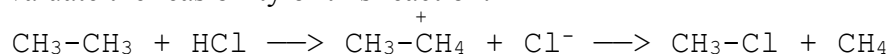


8.49 Draw the organic products from the reaction of propene with the following reagents. If there is no product, say so.

- (a) aqueous  $\text{H}_2\text{SO}_4$  (b)  $\text{Br}_2, \text{H}_2\text{O}$  (c)  $\text{CH}_3\text{CO}_3\text{H}$  (d)  $\text{HO}^-$   
 (e)  $\text{Hg}(\text{O}_2\text{CCH}_3)_2, \text{H}_2\text{O}$ ; then  $\text{NaBH}_4$  (f) cold basic  $\text{KMnO}_4$  (g)  $\text{H}_2$  (h)  $\text{Br}_2$  (i)  $\text{Br}^-$   
 (j)  $\text{BH}_3$ ; then  $\text{HOOH}, \text{HO}^-$  (k)  $\text{HCl}$  (l)  $\text{O}_3$ ; then  $\text{Zn}$  (m)  $\text{H}_2, \text{Ni}$  (n)  $\text{H}_2\text{O}$

8.50 Under what circumstances should it be possible to oxidize propane to propene? Hint: consider the reverse reaction.

8.51 Evaluate the feasibility of this reaction:



8.52 Bromine reacts with ethene in methanol to yield both a dibromide and a brominated ether. Draw the mechanism leading to the brominated ether.

8.53 Draw the stereoisomers from the reaction of (*Z*)-3-hexene with the following reagents. Identify any achiral products, enantiomeric pairs, and diastereomeric pairs.

- (a)  $\text{Br}_2$  (b)  $\text{KMnO}_4, \text{HO}^-$  (c)  $\text{CH}_3\text{CO}_3\text{H}$

8.54 Draw the stereoisomers from the reaction of (*E*)-3-hexene with the following reagents. Among the stereoisomer products find any achiral products, enantiomeric pairs, and diastereomeric pairs.

- (a)  $\text{Br}_2$  (b)  $\text{KMnO}_4, \text{HO}^-$  (c)  $\text{CH}_3\text{CO}_3\text{H}$

8.55 When a  $\text{C}_6\text{H}_8$  compound was treated with ozone followed by zinc, propanedial ( $\text{O}=\text{CHCH}_2\text{CH}=\text{O}$ ) was the only organic product. Determine the original compound.

8.56 When a  $\text{C}_9\text{H}_{14}$  compound was treated with ozone followed by zinc, 1,5-cyclononadione was the only organic product. Determine the original compound.

8.57 The complete combustion of cyclohexane in air produces 3919 kJ/mol (Section 2.7B). The complete combustion of 1-hexene in air produces 4002 kJ/mol.

- (a) Write the balanced chemical equation for each combustion.  
 (b) Which has more enthalpy, cyclohexane or 1-hexene? Explain the difference in terms of bonding.

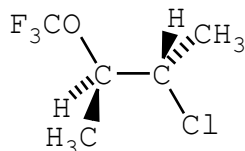
8.58 The complete combustion of cyclopropane in air produces 2091 kJ/mol (Section 2.7B). The complete combustion of propene in air produces 2058 kJ/mol.

- (a) Write the balanced chemical equation for each combustion.  
(b) Which has more enthalpy, cyclopropane or propene? Explain the difference.

8.59 Consider 1-butene and the two stereoisomers of 2-butene as fuels.

- (a) Rank them by the amount of heat produced per *mole* during complete combustion in air. Explain.  
(b) Rank them by the amount of heat produced per *gram* during complete combustion in air. Explain.

8.60 (*Z*)-2-butene reacts with  $F_3COCl$  to form this product:



Is this a syn or anti addition?

8.61 Recently it was discovered that ozone is actually formed in the human body, where it seems to play a role in forming plaques in diseased arteries. One reaction apparently involved in forming plaques is the ozonolysis of cholesterol. Draw the product of this reaction of cholesterol, shown in Section 8.1.