Chapter 4

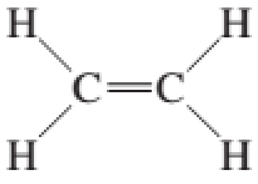
Part I

Alkenes

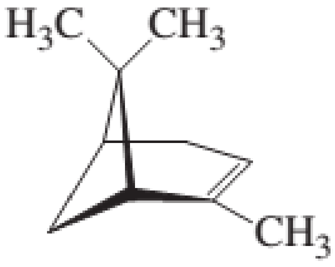
Nomenclature, Structure, Properties, and an Introduction to Synthesis

General remarks of alkenes

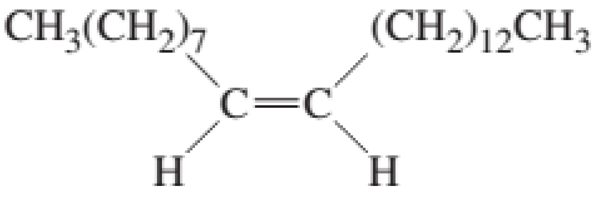
- **Alkenes** are hydrocarbons with carbon–carbon double bonds.
- Alkenes are sometimes called **olefins,** a term derived from *olefiant gas*, meaning “oil-forming gas.” This term originated with early experimentalists who noticed the oily appearance of alkene derivatives.
- Alkenes are among the most important industrial compounds, and many alkenes are also found in plants and animals.
- *Ethylene* is the largest-volume industrial organic compound, used to make polyethylene and a variety of other industrial and consumer chemicals.
- *Pinene* is a major component of *turpentine*, the paint solvent distilled from extracts of evergreen trees.
- *Muscalure* (*cis*-tricos-9-ene) is the sex attractant of the common housefly.



ethylene (ethene)



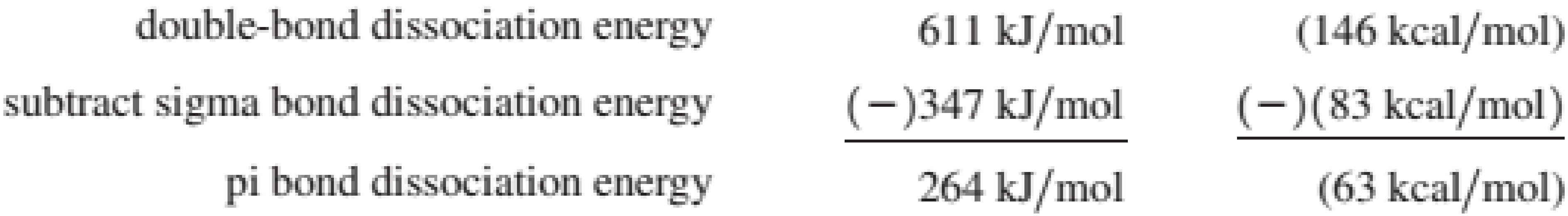
α-pinene



cis-tricos-9-ene, “muscalure”

General remarks of alkenes

- The bond energy of a carbon–carbon double bond is about 611 kJ mol (146 kcal mol), compared with the single-bond energy of about 347 kJ mol (83 kcal mol). From these energies, we can calculate the approximate energy of a pi bond:



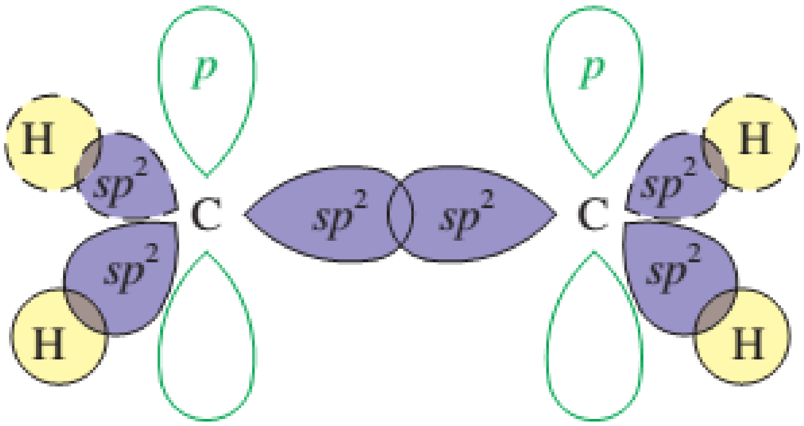
double-bond dissociation energy	611 kJ/mol	(146 kcal/mol)
subtract sigma bond dissociation energy	(−)347 kJ/mol	(−)(83 kcal/mol)
pi bond dissociation energy	264 kJ/mol	(63 kcal/mol)

- This value of **264** kJ/mol is much less than the sigma bond energy of **347** kJ mol, showing that **pi bonds should be more reactive than sigma bonds**.
- Because a carbon–carbon double bond is relatively reactive, it is considered to be a *functional group*, and alkenes are characterized by the reactions of their double bonds.

The orbital description of the alkene double bond: The sigma bond framework

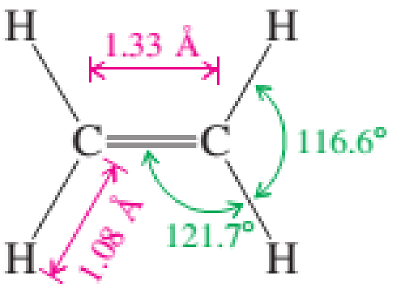
➢ In ethylene, each carbon atom is bonded to three other atoms (one carbon and two hydrogens), and there are no nonbonding electrons.

➢ Three hybrid orbitals are needed, implying hybridization. Recall that sp^2 hybridization corresponds to bond angles of about 120°, giving optimum separation of three atoms bonded to the carbon atom.

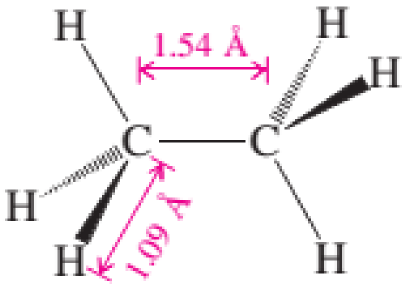


sigma bonding orbitals of ethylene

- Each of the carbon–hydrogen sigma bonds is formed by overlap of an sp^2 hybrid orbital on carbon with the 1*s* orbital of a hydrogen atom. The C- H bond length in ethylene (1.08 Å) is slightly shorter than the bond in ethane (1.09 Å) because the orbital in ethylene has more *s* character (one-third *s*) than an orbital (one fourth *s*). The *s* orbital is closer to the nucleus than the *p* orbital, contributing to shorter bonds.



ethylene

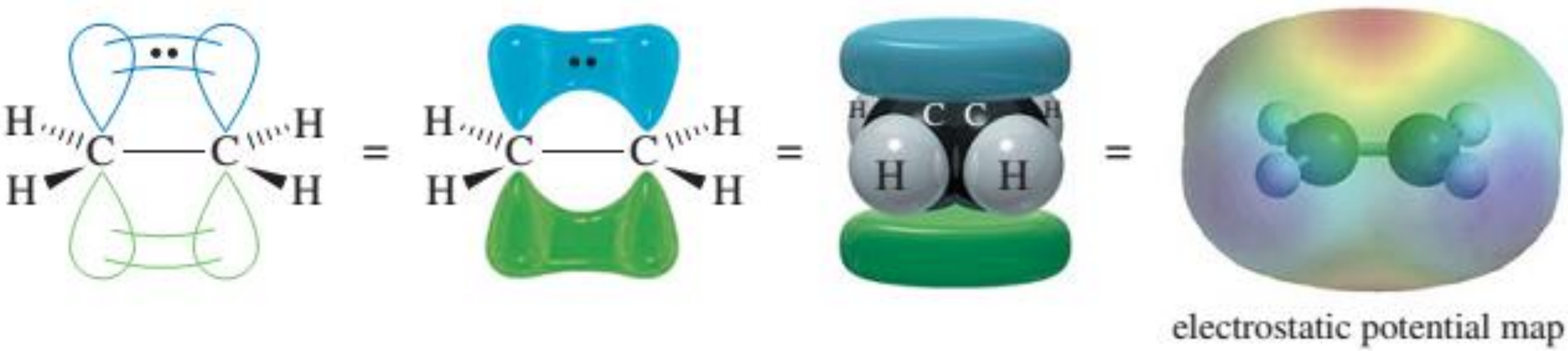


ethane

- The remaining sp^2 orbitals overlap in the region between the carbon nuclei, providing a bonding orbital. This bond is a sigma bond because its electron density is centered along the line joining the nuclei.
- The C=C bond in ethylene (1.33 Å) is much shorter than the C-C bond (1.54 Å) in ethane, partly because the sigma bond of ethylene is formed from orbitals (with more *s* character) and partly because there are two bonds drawing the atoms together. The second carbon–carbon bond is a pi bond.

The Pi bond

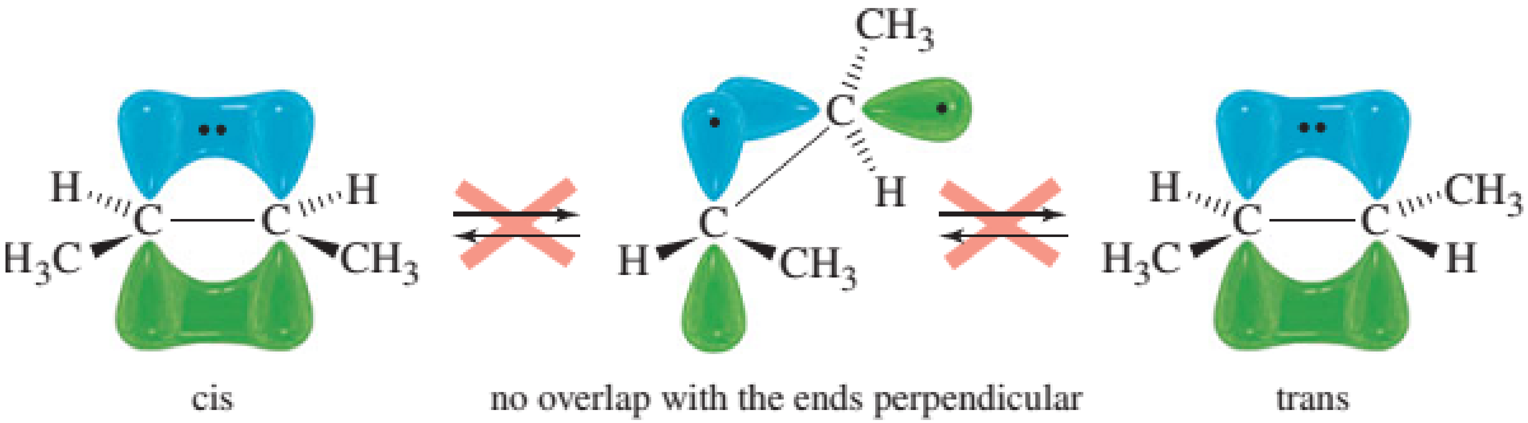
- Each carbon atom still has an un-hybridized *p* orbital, and these side-overlap to form a pi (π) -bonding molecular orbital.
- For pi overlap to occur, these *p* orbitals must be parallel, which requires that the two carbon atoms be oriented with all their bonds in a single plane.
- Half of the pi-bonding orbital is above the sigma bond, and the other half is below the sigma bond. The pi-bonding electrons give rise to regions of high electron density (red) in the electrostatic potential map of ethylene.



Parallel *p* orbitals in ethylene. The pi bond in ethylene is formed by overlap of the unhybridized *p* orbitals on the sp^2 hybrid carbon atoms. This overlap requires the two ends of the molecule to be coplanar.

The Pi bond

- Unlike single bonds, a carbon–carbon double bond does not permit rotation.
- Six atoms, including the double-bonded carbon atoms and the four atoms bonded to them, must remain in the same plane. This is the origin of cis-trans isomerism.
- If two groups are on the same side of a double bond (cis), they cannot rotate to opposite sides (trans) without breaking the pi bond.
- The figure below shows that there are two distinct isomers of but-2-ene: *cis*-but-2-ene and *trans*-but-2-ene.



Distinct isomers resulting from double bonds. The two isomers of but-2-ene cannot interconvert by rotation about the carbon–carbon double bond without breaking the pi bond.

Elements of unsaturation in hydrocarbons

- Alkenes are said to be **unsaturated** because they are capable of adding hydrogen in the presence of a catalyst. The product, an alkane, is called **saturated** because it cannot react with any more hydrogen.
- The presence of a pi bond of an alkene (or an alkyne) or the ring of a cyclic compound decreases the number of hydrogen atoms in a molecular formula. These structural features are called **elements of unsaturation** (*Degree of unsaturation* and *index of hydrogen deficiency* are equivalent terms). Each element of unsaturation corresponds to two fewer hydrogen atoms than in the "saturated" formula.

$CH_3{-}CH_2{-}CH_3$

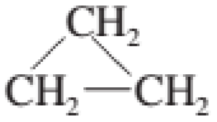
propane, C_3H_8

saturated

$CH_3{-}CH{=}CH_2$

propene, C_3H_6

one element of unsaturation



cyclopropane, C_3H_6

one element of unsaturation

$CH_3{-}C{\equiv}C{-}H$

propyne, C_3H_4

two elements of unsaturation

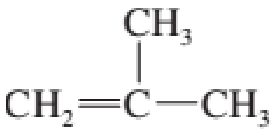
- Consider, for example, the formula C_4H_8. A saturated alkane would have a C_nH_{2n+2} formula, or C_4H_{10}. The formula is missing two hydrogen atoms, so it has one element of unsaturation, either a pi bond or a ring. There are five constitutional isomers of formula C_4H_8:

$CH_2{=}CH{-}CH_2CH_3$

but-1-ene

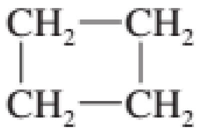
$CH_3{-}CH{=}CH{-}CH_3$

but-2-ene

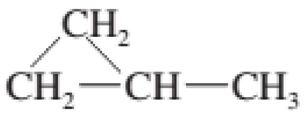


$CH_2{=}C(CH_3){-}CH_3$

isobutylene



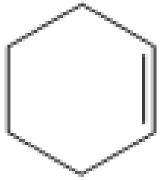
cyclobutane



methylcyclopropane

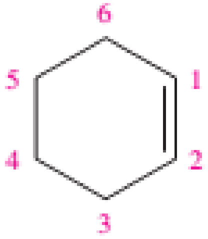
Nomenclature of alkenes

- Simple alkenes are named much like alkanes, using the root name of the longest chain containing the double bond. The ending is changed from -*ane* to -*ene*. For example, “ethane” becomes “ethene,” “propane” becomes “propene,” and “cyclohexane” becomes “cyclohexene.”

	$CH_2{=}CH_2$	$CH_2{=}CH{-}CH_3$	
IUPAC names:	ethene	propene	cyclohexene
Common names:	ethylene	propylene	

- When the chain contains more than three carbon atoms, a number is used to give the location of the double bond. The chain is numbered starting from the end closest to the double bond, and the double bond is given the *lower* number of its two double-bonded carbon atoms. Cycloalkenes are assumed to have the double bond in the number 1 position.

	$\overset{1}{CH_2}{=}\overset{2}{CH}{-}\overset{3}{CH_2}{-}\overset{4}{CH_3}$	$\overset{1}{CH_2}{=}\overset{2}{CH}{-}\overset{3}{CH_2}{-}\overset{4}{CH_2}{-}\overset{5}{CH_3}$
old IUPAC names:	1-butene	1-pentene
new IUPAC names:	but-1-ene	pent-1-ene

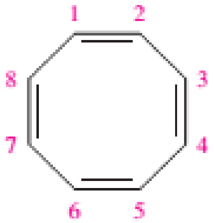


cyclohexene

Nomenclature of alkenes

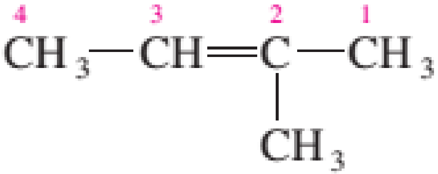
	$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_3}$	$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_2}-\overset{5}{CH_3}$
old IUPAC names:	2-butene	2-pentene
new IUPAC names:	but-2-ene	pent-2-ene

- ➢ In 1993, the IUPAC recommended a logical change in the positions of the numbers used in names. Instead of placing the numbers before the root name (1-butene), they recommended placing them immediately before the part of the name they locate (but-1-ene). The new placement is helpful for clarifying the names of compounds containing multiple functional groups.
- ➢ In this section, names using the old number placement are printed in blue, and those using the **new number** placement are printed in **green**.
- ➢ A compound with two double bonds is a **diene.** A **triene** has three double bonds, and a **tetraene** has four. Numbers are used to specify the locations of the double bonds.

	$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH}=\overset{4}{CH_2}$	$\overset{7}{CH_3}-\overset{6}{CH}=\overset{5}{CH}-\overset{4}{CH}=\overset{3}{CH}-\overset{2}{CH}=\overset{1}{CH_2}$	
old IUPAC names:	1,3-butadiene	1,3,5-heptatriene	1,3,5,7-cyclooctatetraene
new IUPAC names:	buta-1,3-diene	hepta-1,3,5-triene	cycloocta-1,3,5,7-tetraene

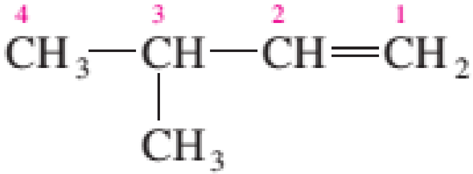
Nomenclature of alkenes

- Each alkyl group attached to the main chain is listed with a number to give its location. Note that the double bond is still given preference in numbering, however.



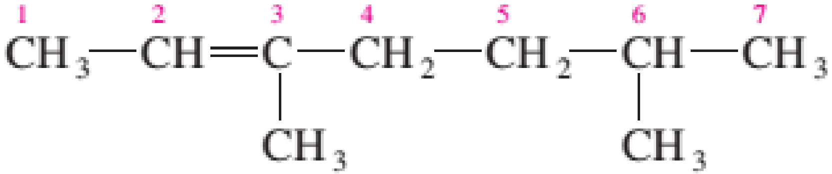
$$\overset{4}{\mathrm{CH_3}}-\overset{3}{\mathrm{CH}}=\underset{\begin{array}{c}|\\ \mathrm{CH_3}\end{array}}{\overset{2}{\mathrm{C}}}-\overset{1}{\mathrm{CH_3}}$$

2-methyl-2-butene
2-methylbut-2-ene



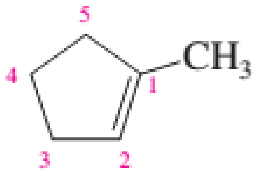
$$\overset{4}{\mathrm{CH_3}}-\underset{\begin{array}{c}|\\ \mathrm{CH_3}\end{array}}{\overset{3}{\mathrm{CH}}}-\overset{2}{\mathrm{CH}}=\overset{1}{\mathrm{CH_2}}$$

3-methyl-1-butene
3-methylbut-1-ene

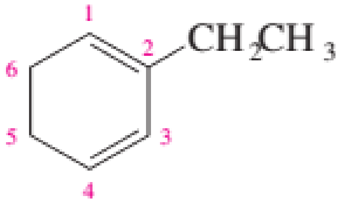


$$\overset{1}{\mathrm{CH_3}}-\overset{2}{\mathrm{CH}}=\underset{\begin{array}{c}|\\ \mathrm{CH_3}\end{array}}{\overset{3}{\mathrm{C}}}-\overset{4}{\mathrm{CH_2}}-\overset{5}{\mathrm{CH_2}}-\underset{\begin{array}{c}|\\ \mathrm{CH_3}\end{array}}{\overset{6}{\mathrm{CH}}}-\overset{7}{\mathrm{CH_3}}$$

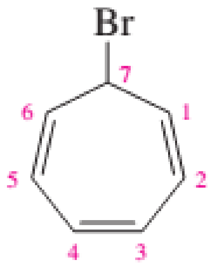
3,6-dimethyl-2-heptene
3,6-dimethylhept-2-ene



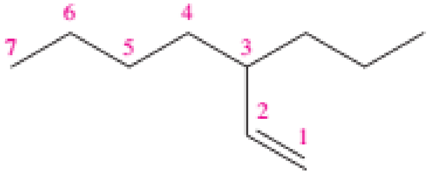
1-methylcyclopentene
1-methylcyclopentene



2-ethyl-1,3-cyclohexadiene
2-ethylcyclohexa-1,3-diene



7-bromo-1,3,5-cycloheptatriene
7-bromocyclohepta-1,3,5-triene



3-propyl-1-heptene
3-propylhept-1-ene

Alkenes as Substituents

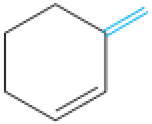
- Alkenes named as substituents are called *alkenyl groups*. They can be named systematically (ethenyl, propenyl, etc.), or by common names. Common alkenyl substituents are the vinyl, allyl, methylene, and phenyl groups. The phenyl group (Ph) is different from the others because it is aromatic and does not undergo the typical reactions of alkenes.

$\wr{=}CH_2$

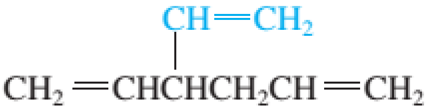
methylene group
(methylidene group)

$\wr{-}CH{=}CH_2$

vinyl group
(ethenyl group)



3-methylenecyclohexene

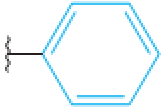


$$CH_2{=}CH\underset{}{\overset{\overset{\displaystyle CH{=}CH_2}{|}}{C}}HCH_2CH{=}CH_2$$

3-vinyl-1,5-hexadiene
3-vinylhexa-1,5-diene

$\wr{-}CH_2{-}CH{=}CH_2$

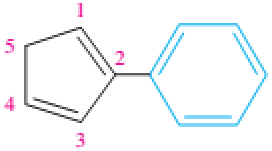
allyl group
2-propenyl group



phenyl group
(Ph)

$CH_2{=}CH{-}CH_2{-}Cl$

allyl chloride
3-chloropropene

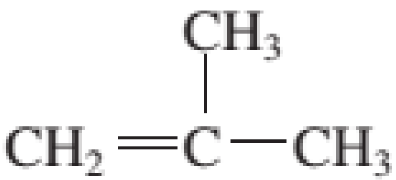


2-phenyl-1,3-cyclopentadiene
2-phenylcyclopenta-1,3-diene

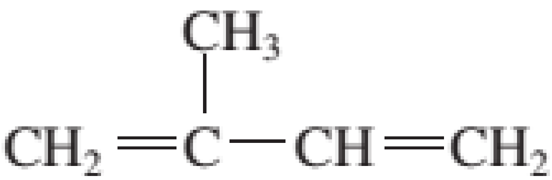
Common names

- Most alkenes are conveniently named by the IUPAC system, but common names are sometimes used for the simplest compounds.

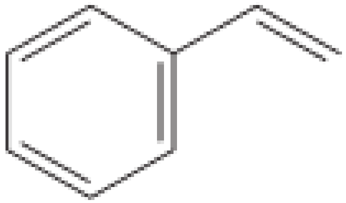
	$CH_2=CH_2$	$CH_2=CH-CH_3$
IUPAC names:	ethene	propene
common name:	ethylene	propylene


$CH_2=C(CH_3)-CH_3$

2-methylpropene
isobutylene


$CH_2=C(CH_3)-CH=CH_2$

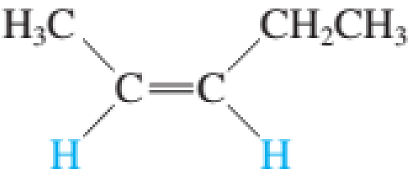
2-methylbuta-1,3-diene
isoprene

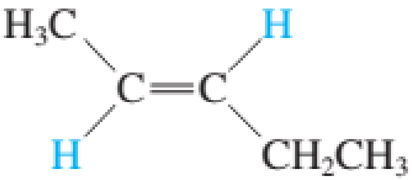


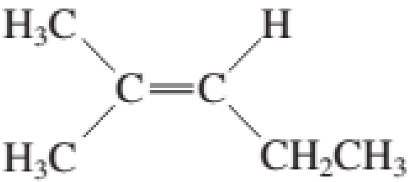
ethenylbenzene
styrene
(vinylbenzene)

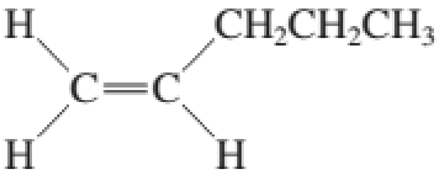
cis-trans Nomenclature

- The rigidity and lack of rotation of carbon–carbon double bonds give rise to **cis-trans isomerism,** also called **geometric isomerism.**
- If two similar groups bonded to the carbons of the double bond are on the same side of the bond, the alkene is the **cis** isomer. If the similar groups are on opposite sides of the bond, the alkene is **trans.**
- Not all alkenes are capable of showing cis-trans isomerism. If either carbon of the double bond holds two identical groups, the molecule cannot have cis and trans forms.
- Following are some cis and trans alkenes and some alkenes that cannot show cis-trans isomerism.


cis-2-pentene
cis-pent-2-ene


trans-2-pentene
trans-pent-2-ene

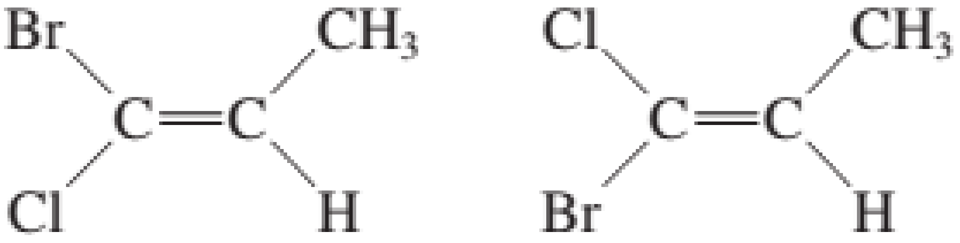

2-methyl-2-pentene
2-methylpent-2-ene


1-pentene
pent-1-ene

(neither cis nor trans)

E-Z Nomenclature

- The cis-trans nomenclature for geometric isomers sometimes gives an ambiguous name. For example, the isomers of 1-bromo-1-chloropropene are not clearly cis or trans because it is not obvious which substituents are referred to as being cis or trans.

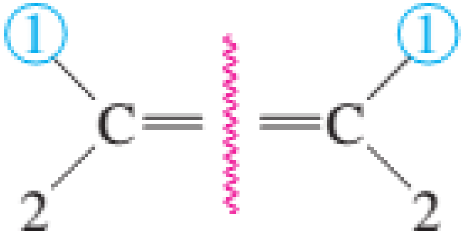


geometric isomers of 1-bromo-1-chloropropene

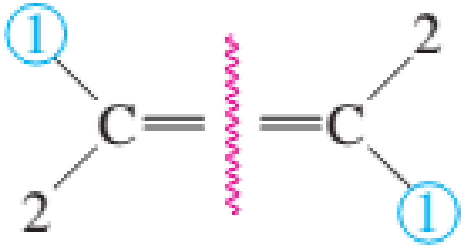
- To deal with this problem, we use the *E-Z* system of nomenclature (pun intended) for cis-trans isomers, which is patterned after the Cahn–Ingold–Prelog convention for asymmetric carbon atoms. It assigns a unique configuration of either *E* or *Z* to any double bond capable of geometric isomerism.

E-Z Nomenclature

- To name an alkene by the *E-Z* system, mentally separate the double bond into its two ends. Remember how you used the Cahn–Ingold–Prelog rules to assign relative priorities to groups on an asymmetric carbon atom so you could name it (*R*) or (*S*).
- Consider each end of the double bond separately, and use those same rules to assign first and second priorities to the two substituent groups on that end. Do the same for the other end of the double bond.
- If the two first-priority atoms are ***together (cis)*** on the same side of the double bond, you have the ***Z*** isomer, from the German word *zusammen*, "together."
- If the two first-priority atoms are on ***opposite (trans)*** sides of the double bond, you have the ***E*** isomer, from the German word *entgegen*, "opposite."



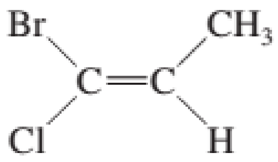
Zusammen



Entgegen

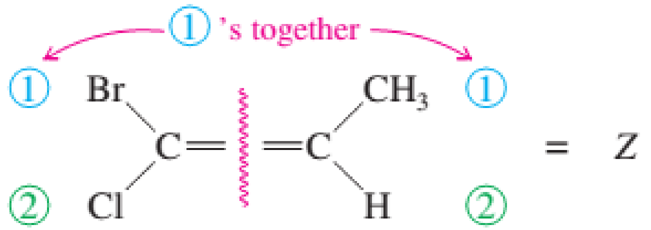
E-Z Nomenclature

For example,

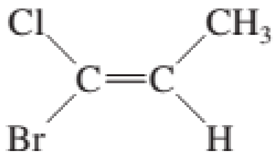


(Z)-1-bromo-1-chloropropene

becomes

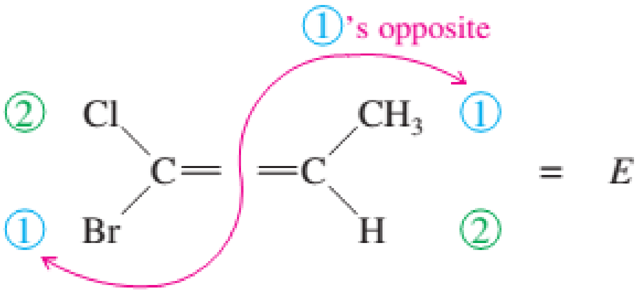


The other isomer is named similarly:

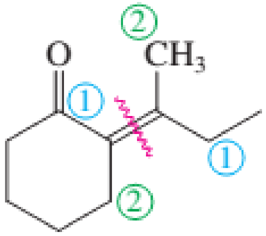


(E)-1-bromo-1-chloropropene

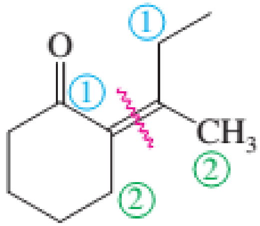
becomes



- The following example shows the use of the *E*-*Z* nomenclature with cyclic stereoisomers that are not clearly cis or trans.



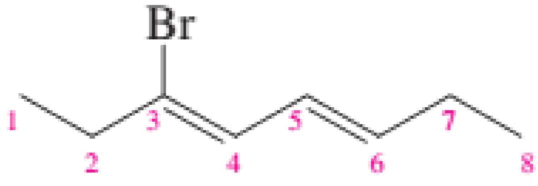
(E) isomer



(Z) isomer

E-Z Nomenclature

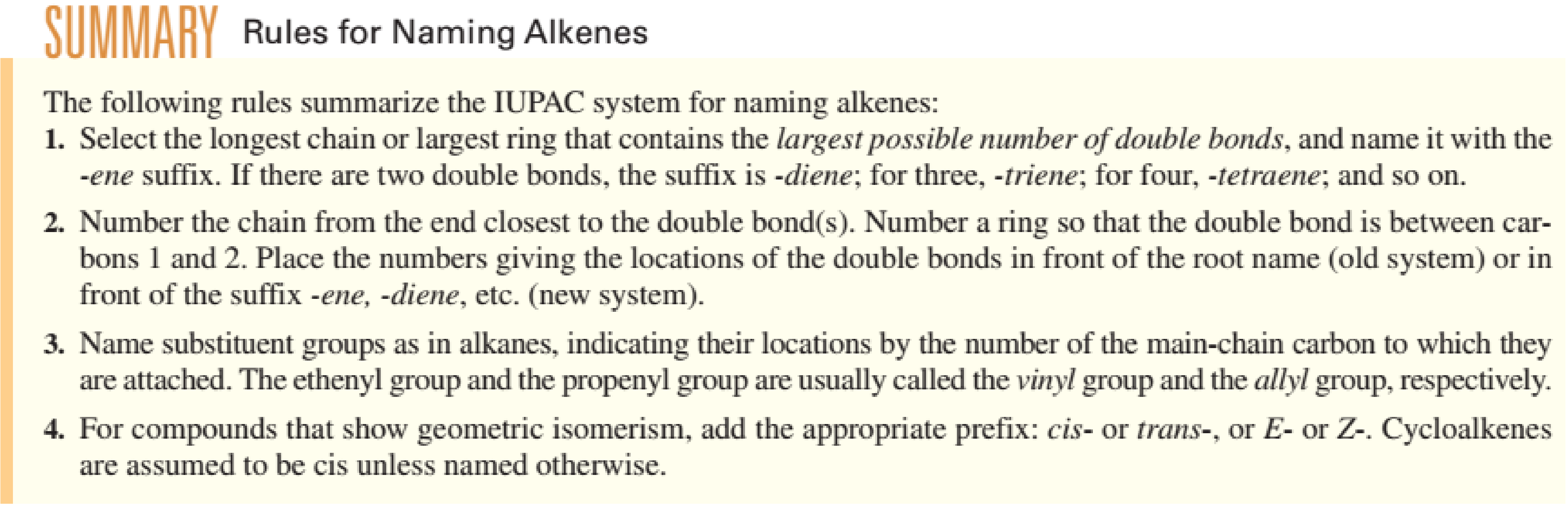
- If the alkene has more than one double bond, the stereochemistry about each double bond should be specified. The following compound is properly named (3*Z*,5*E*)-3-bromoocta-3,5-diene:



(3*Z*,5*E*)-3-bromoocta-3,5-diene

- The use of *E-Z* names (rather than cis and trans) is always an option, but it is required whenever a double bond is not clearly cis or trans. Most trisubstituted and tetrasubstituted double bonds are more clearly named *E* or *Z* rather than cis or trans.

Nomenclature of alknenes: Summary



SUMMARY Rules for Naming Alkenes

The following rules summarize the IUPAC system for naming alkenes:

1. Select the longest chain or largest ring that contains the *largest possible number of double bonds*, and name it with the *-ene* suffix. If there are two double bonds, the suffix is *-diene*; for three, *-triene*; for four, *-tetraene*; and so on.
2. Number the chain from the end closest to the double bond(s). Number a ring so that the double bond is between carbons 1 and 2. Place the numbers giving the locations of the double bonds in front of the root name (old system) or in front of the suffix *-ene, -diene*, etc. (new system).
3. Name substituent groups as in alkanes, indicating their locations by the number of the main-chain carbon to which they are attached. The ethenyl group and the propenyl group are usually called the *vinyl* group and the *allyl* group, respectively.
4. For compounds that show geometric isomerism, add the appropriate prefix: *cis*- or *trans*-, or *E*- or *Z*-. Cycloalkenes are assumed to be cis unless named otherwise.

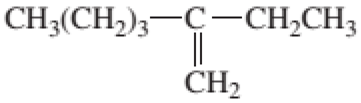
Nomenclature of alkenes

PROBLEM 7-5

Give the systematic (IUPAC) names of the following alkenes.

(a) $CH_2{=}CH-CH_2-CH(CH_3)_2$

(b)

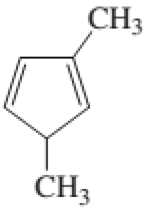


$CH_3(CH_2)_3-\underset{\underset{CH_2}{\|}}{C}-CH_2CH_3$

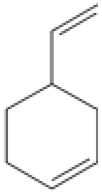
(c) $CH_2{=}CH-CH_2-CH{=}CH_2$

(d) $CH_2{=}C{=}CH-CH{=}CH_2$

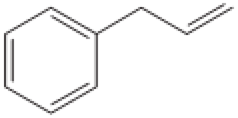
(e)



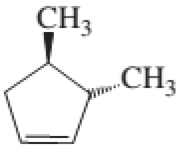
(f)



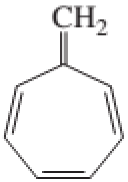
(g)



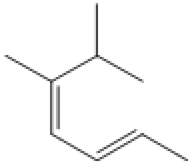
(h)



(i)



(j)



PROBLEM 7-6

1. Determine which of the following compounds show cis-trans isomerism.
2. Draw and name the cis and trans (or *Z* and *E*) isomers of those that do.

(a) hex-3-ene

(b) buta-1,3-diene

(c) hexa-2,4-diene

(d) 3-methylpent-2-ene

(e) 2,3-dimethylpent-2-ene

(f) 3,4-dibromocyclopentene

Nomenclature of alkenes

PROBLEM 7-7

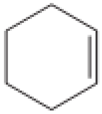
The following names are all incorrect. Draw the structure represented by the incorrect name (or a consistent structure if the name is ambiguous), and give your drawing the correct name.

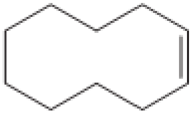
(a) *cis*-2,3-dimethyl-2-pentene
(b) 3-vinylhex-4-ene
(c) 2-methylcyclopentene
(d) 6-chlorocyclohexadiene
(e) 2,5-dimethylcyclohexene
(f) *cis*-2,5-dibromo-3-ethylpent-2-ene

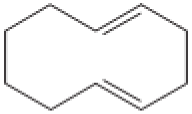
PROBLEM 7-8

Some of the following examples can show geometric isomerism, and some cannot. For the ones that can, draw all the geometric isomers, and assign complete names using the *E-Z* system.

(a) 3-bromo-2-chloropent-2-ene
(b) 3-ethylhexa-2,4-diene
(c) 3-bromo-2-methylhex-3-ene
(d) penta-1,3-diene
(e) 3-ethyl-5-methyloct-3-ene
(f) 3,7-dichloroocta-2,5-diene

(g)

cyclohexene

(h)

cyclodecene

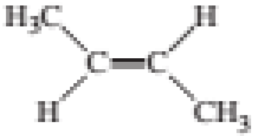
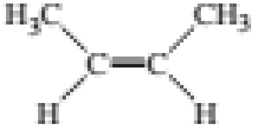
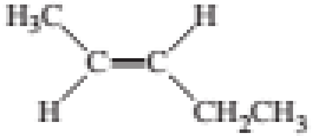
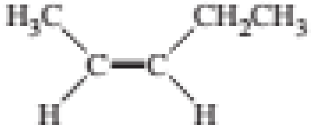
(i)

cyclodeca-1,5-diene

Physical properties

- Most physical properties of alkenes are similar to those of the corresponding alkanes. For example, the boiling points of but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene, and *n*-butane are all close to 0 °C.
- Also like the alkanes, alkenes have densities around 0.6 or 0.7 g/cm^3.
- The boiling points of alkenes increase smoothly with molecular weight.
- As with alkanes, increased branching leads to greater volatility and lower boiling points. For example, 2-methylpropene (isobutylene) has a boiling point of -7 ^oC which is lower than the boiling point of any of the unbranched butenes.

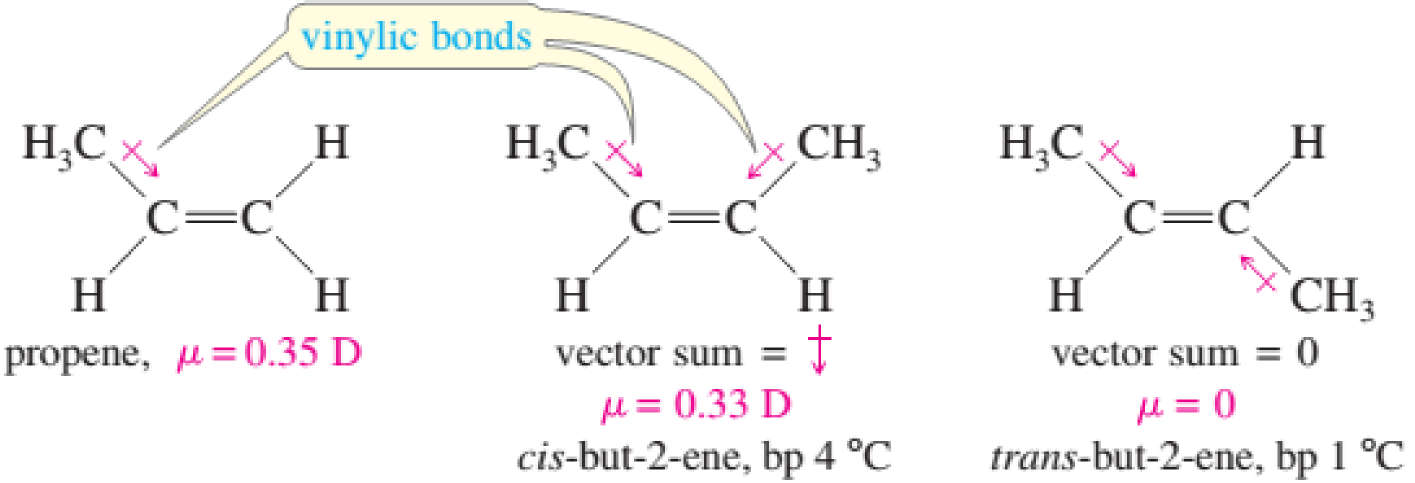
Physical properties

TABLE 7-2 Physical Properties of Some Representative Alkenes

Name	Structure	Carbons	Boiling Point (°C)	Density (g/cm^3)
ethene (ethylene)	$CH_2{=}CH_2$	2	−104	
propene (propylene)	$CH_3CH{=}CH_2$	3	−47	0.52
2-methylpropene (isobutylene)	$(CH_3)_2C{=}CH_2$	4	−7	0.59
but-1-ene	$CH_3CH_2CH{=}CH_2$	4	−6	0.59
trans-but-2-ene		4	1	0.60
cis-but-2-ene		4	4	0.62
3-methylbut-1-ene	$(CH_3)_2CH{-}CH{=}CH_2$	5	25	0.65
pent-1-ene	$CH_3CH_2CH_2{-}CH{=}CH_2$	5	30	0.64
trans-pent-2-ene		5	36	0.65
cis-pent-2-ene		5	37	0.66
2-methylbut-2-ene	$(CH_3)_2C{=}CH{-}CH_3$	5	39	0.66
hex-1-ene	$CH_3(CH_2)_3{-}CH{=}CH_2$	6	64	0.68
2,3-dimethylbut-2-ene	$(CH_3)_2C{=}C(CH_3)_2$	6	73	0.71
hept-1-ene	$CH_3(CH_2)_4{-}CH{=}CH_2$	7	93	0.70
oct-1-ene	$CH_3(CH_2)_5{-}CH{=}CH_2$	8	122	0.72
non-1-ene	$CH_3(CH_2)_6{-}CH{=}CH_2$	9	146	0.73
dec-1-ene	$CH_3(CH_2)_7{-}CH{=}CH_2$	10	171	0.74

Physical properties: Polarity

- Like alkanes, alkenes are relatively nonpolar. They are insoluble in water but soluble in nonpolar solvents such as hexane, gasoline, halogenated solvents, and ethers.
- Alkenes tend to be slightly more polar than alkanes, however, for two reasons: The more weakly held electrons in the pi bond are more polarizable (contributing to instantaneous dipole moments), and the vinylic bonds tend to be slightly polar (contributing to a permanent dipole moment).
- Alkyl groups are slightly electron-donating toward a double bond, helping to stabilize it. This donation slightly polarizes the vinylic bond, with a small partial positive charge on the alkyl group and a small negative charge on the double-bond carbon atom.
- For example, propene has a small dipole moment of 0.35 D.



propene, $\mu = 0.35$ D

vector sum = ↓
$\mu = 0.33$ D
cis-but-2-ene, bp 4 °C

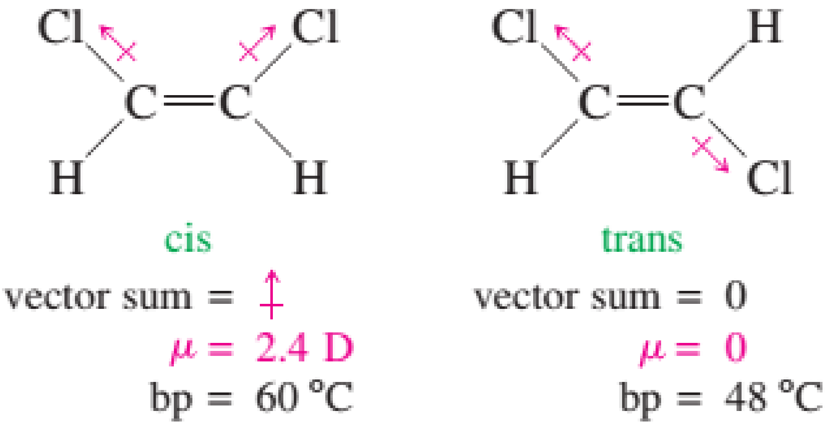
vector sum = 0
$\mu = 0$
trans-but-2-ene, bp 1 °C

Physical properties

➢ In a cis-disubstituted alkene, the vector sum of the two dipole moments is directed perpendicular to the double bond. In a trans-disubstituted alkene, the two dipole moments tend to cancel out. If an alkene is symmetrically trans disubstituted, the dipole moment is zero. For example, *cis*-but-2-ene has a nonzero dipole moment, but *trans*-but-2-ene has no measurable dipole moment.

➢ Compounds with permanent dipole moments engage in dipole–dipole attractions, while those without permanent dipole moments engage only in van der Waals attractions. *cis*-But-2-ene and *trans*-but-2-ene have similar van der Waals attractions, but only the cis isomer has dipole–dipole attractions. Because of its increased intermolecular attractions, *cis*-but-2-ene must be heated to a slightly higher temperature (4 °C versus 1 °C) before it begins to boil.

➢ The effect of bond polarity is even more apparent in the 1,2-dichloroethenes, with their strongly polar carbon–chlorine bonds. The cis isomer has a large dipole moment (2.4 D), giving it a boiling point 12 degrees higher than the trans isomer, with zero dipole moment.

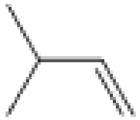


Stability of alkenes

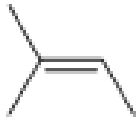
More substituted double bonds are usually more stable.

- In other words, the alkyl groups attached to the double-bonded carbons stabilize the alkene.
- Two factors are probably responsible for the stabilizing effect of alkyl groups on a double bond. Alkyl groups are electron-donating, and they contribute electron density to the pi bond. In addition, bulky substituents like alkyl groups are best situated as far apart as possible. In an alkane, they are separated by the tetrahedral bond angle, about 109.5°. A double bond increases this separation to about 120°. In general, alkyl groups are separated best by the most highly substituted double bond.
- This steric effect is illustrated in the figure in the next slide for two **double-bond isomers** (isomers that differ only in the position of the double bond). The isomer with the monosubstituted double bond separates the alkyl groups by only 109.5°, while the trisubstituted double bond separates them by about 120°.

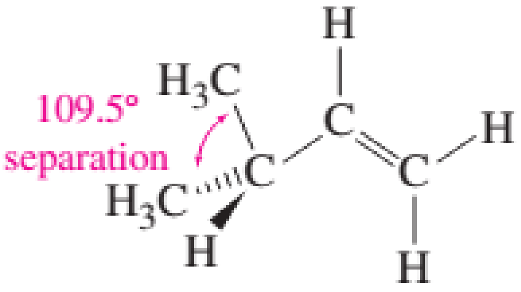
Stability of alkenes



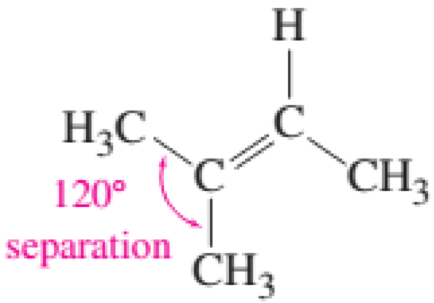
less substituted



more substituted



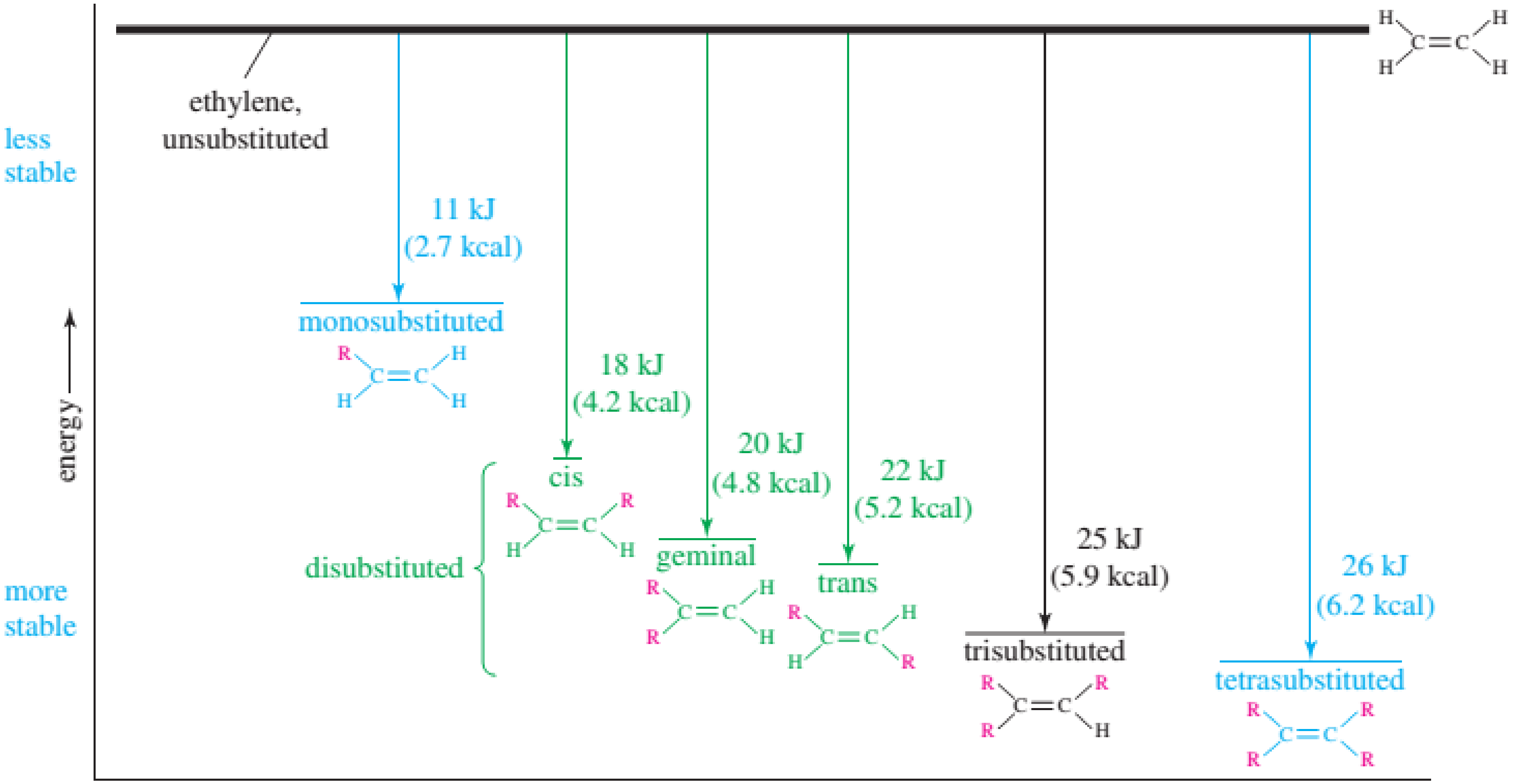
closer groups



wider separation

- ➢ Bond angles in double-bond isomers. The isomer with the more substituted double bond has a larger angular separation between the bulky alkyl groups.

Stability of alkenes



Relative energies of typical bonds compared with ethylene.

Chemical properties

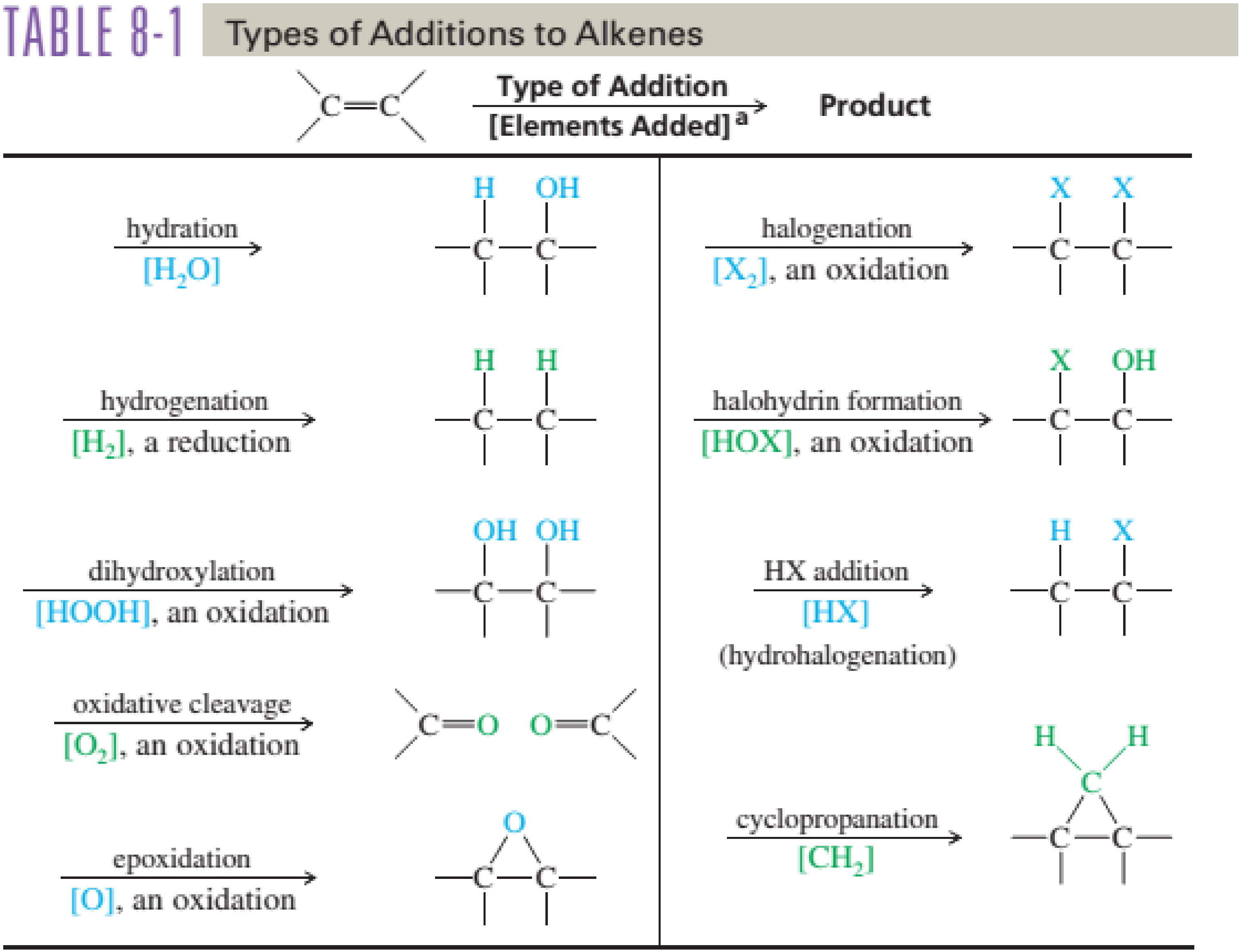


TABLE 8-1 Types of Additions to Alkenes

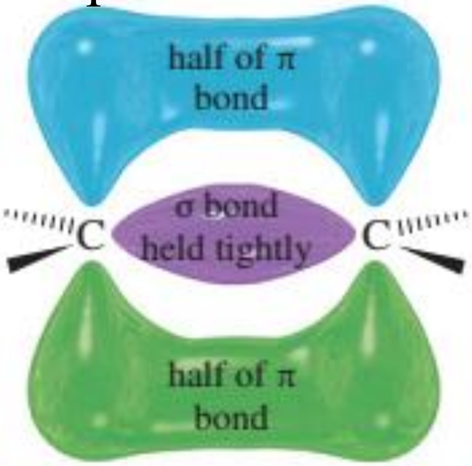
$>C=C<$ $\xrightarrow[\text{[Elements Added]}^{a}]{\text{Type of Addition}}$ **Product**

Type of Addition [Elements Added][a]	Product	Type of Addition [Elements Added][a]	Product
hydration $[H_2O]$	$-\overset{H}{\overset{\vert}{\underset{\vert}{C}}}-\overset{OH}{\overset{\vert}{\underset{\vert}{C}}}-$	halogenation $[X_2]$, an oxidation	$-\overset{X}{\overset{\vert}{\underset{\vert}{C}}}-\overset{X}{\overset{\vert}{\underset{\vert}{C}}}-$
hydrogenation $[H_2]$, a reduction	$-\overset{H}{\overset{\vert}{\underset{\vert}{C}}}-\overset{H}{\overset{\vert}{\underset{\vert}{C}}}-$	halohydrin formation [HOX], an oxidation	$-\overset{X}{\overset{\vert}{\underset{\vert}{C}}}-\overset{OH}{\overset{\vert}{\underset{\vert}{C}}}-$
dihydroxylation [HOOH], an oxidation	$-\overset{OH}{\overset{\vert}{\underset{\vert}{C}}}-\overset{OH}{\overset{\vert}{\underset{\vert}{C}}}-$	HX addition [HX] (hydrohalogenation)	$-\overset{H}{\overset{\vert}{\underset{\vert}{C}}}-\overset{X}{\overset{\vert}{\underset{\vert}{C}}}-$
oxidative cleavage $[O_2]$, an oxidation	$>C=O \quad O=C<$		
epoxidation [O], an oxidation		cyclopropanation $[CH_2]$	

[a] These are not the reagents used but simply the groups that appear in the product.

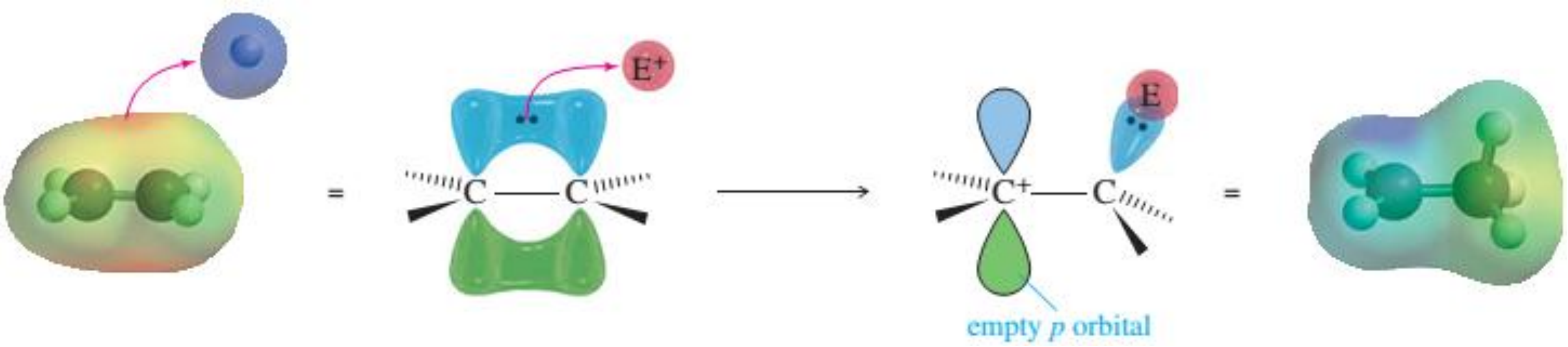
Relation between structure and chemical properties of alkenes

- The pi bond is delocalized above and below the sigma bond.
- The pi-bonding electrons are spread farther from the carbon nuclei, and they are more loosely held.
- **A strong electrophile has an affinity for these loosely held electrons.** It can pull them away to form a new bond, leaving one of the carbon atoms with only three bonds and a positive charge: a carbocation.
- Most addition reactions involve a second step in which a nucleophile attacks the carbocation (as in the second step of the reaction), forming a stable addition product.
- In effect, the **double bond** has reacted as a **nucleophile**, donating a pair of electrons to the electrophile.



Chemical properties: Electrophilic addition reaction of alkenes

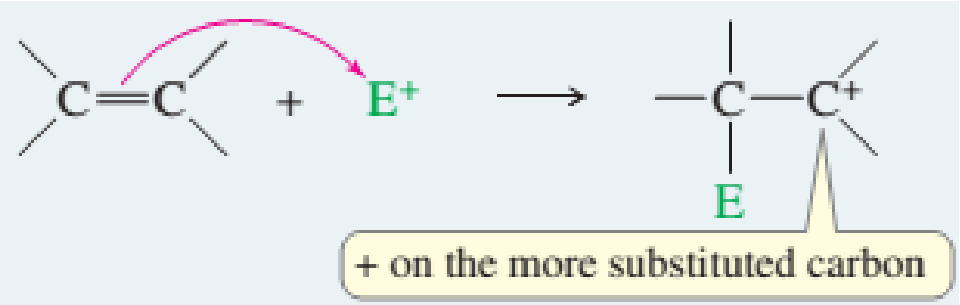
- In the product, both the electrophile and the nucleophile are bonded to the carbon atoms that were connected by the double bond.
- This type of reaction requires a strong electrophile to attract the electrons of the pi bond and generate a carbocation in the rate-limiting step. Most alkene reactions fall into this large class of **electrophilic additions** to alkenes.



Chemical properties: Electrophilic addition of H-X to alkenes

- First, a strong electrophile attracts the loosely held electrons from the pi bond of an alkene.
- The electrophile forms a sigma bond to one of the carbons of the (former) double bond, while the other carbon becomes a carbocation..

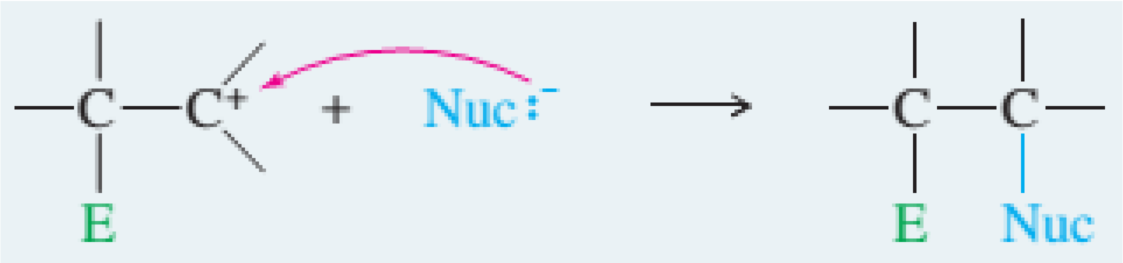
Step 1: **Attack of the pi bond on the electrophile forms a carbocation.**



+ on the more substituted carbon

- The carbocation (a strong electrophile) reacts with a nucleophile (often a weak nucleophile) to form another sigma bond

Step 2: **Attack by a nucleophile gives the addition product.**



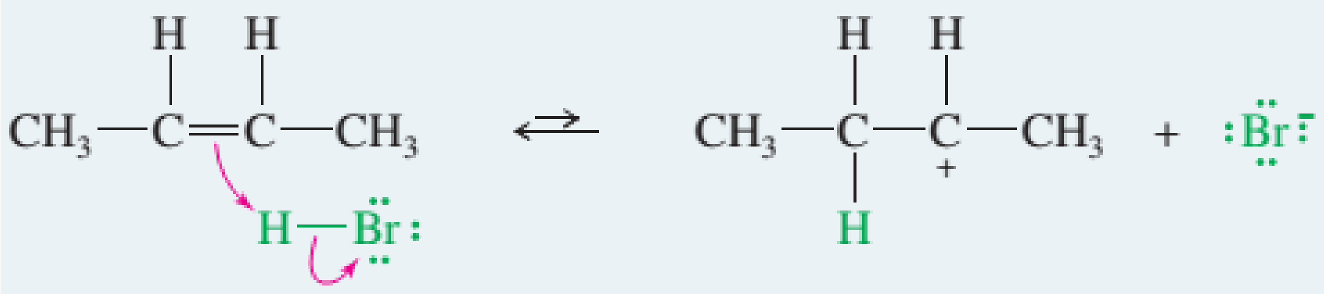
E-Nu: H-X (X: Cl, Br, I), H-OH, H-OR, X2 (X: Cl, Br, I),

Chemical properties: Electrophilic Addition of H-Br to alkenes

- Ionic addition of HBr to but-2-ene.

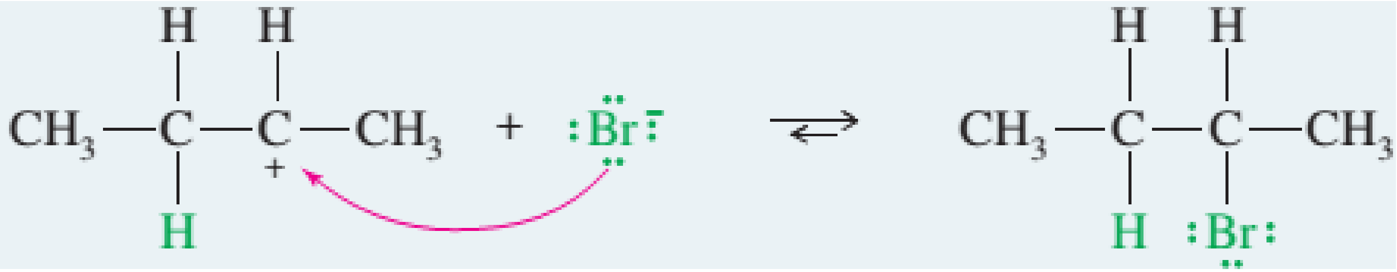
+ The proton H^+ in HBr is electrophilic; it reacts with the alkene to form a carbocation.

Step 1: **Protonation of the double bond forms a carbocation.**



+ Bromide ion reacts rapidly with the carbocation to give a stable product in which the elements of HBr have added to the ends of the double bond.

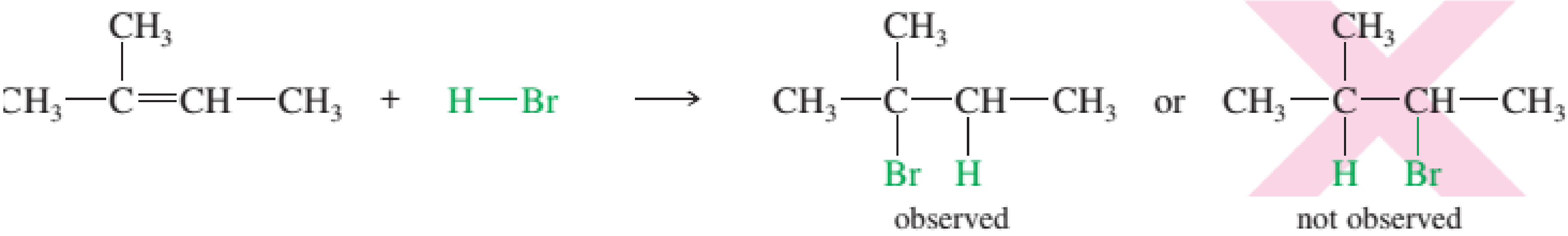
Step 2: **Bromide ion attacks the carbocation.**



PROBLEM: Explain why the charge of the carbocation always appears at the carbon of the (former) double bond that has NOT bonded to the electrophile.

Orientation of Addition: Markovnikov's Rule

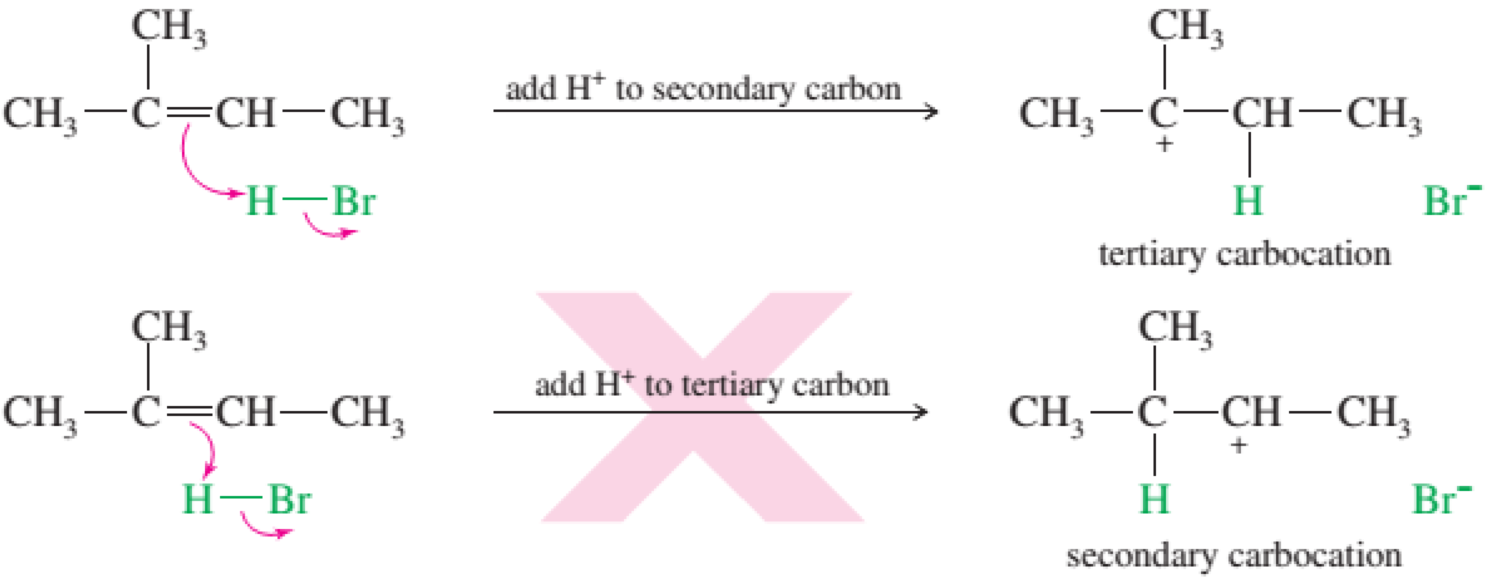
- The addition of HBr to 2-methylbut-2-ene could lead to either of two products, yet only one is observed.



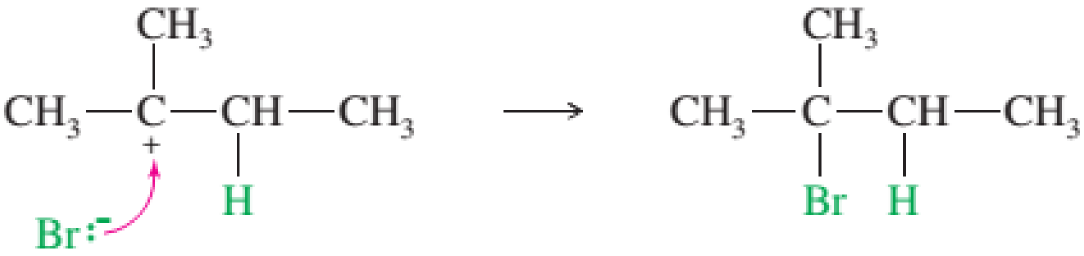
$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3 + H-Br \longrightarrow CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{H}{|}}{CH}-CH_3 \text{ or } CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{Br}{|}}{CH}-CH_3$$

Chemical properties: Electrophilic Addition of H-Br to alkenes

- When the proton adds to the secondary carbon, a tertiary carbocation results. When the proton adds to the tertiary carbon atom, a secondary carbocation results.
- The tertiary carbocation is more stable, so the first reaction is favored.

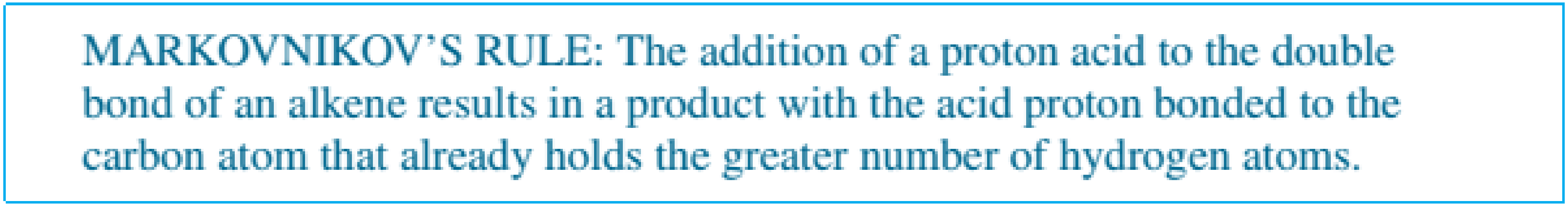


- The second half of the mechanism produces the final product of the addition of HBr to 2-methylbut-2-ene.



Markovnikov's Rule

- There are many examples of reactions where the proton adds to the less substituted carbon atom of the double bond in order to produce the more substituted carbocation. The addition of HBr (and other hydrogen halides) is said to be **regioselective** because in each case, one of the two possible orientations of addition results preferentially over the other.
- **Markovnikov's Rule** A Russian chemist, Vladimir Markovnikov, first showed the orientation of addition of HBr to alkenes in 1869. Markovnikov stated:

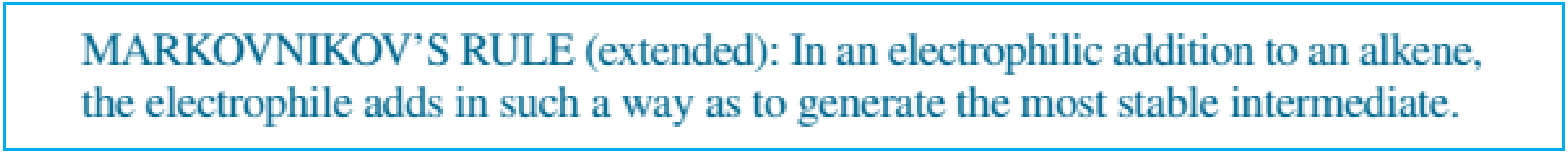


MARKOVNIKOV'S RULE: The addition of a proton acid to the double bond of an alkene results in a product with the acid proton bonded to the carbon atom that already holds the greater number of hydrogen atoms.

- This is the original statement of **Markovnikov's rule.** Reactions that follow this rule are said to follow **Markovnikov orientation** and give the **Markovnikov product.**

Extended Markovnikov's Rule

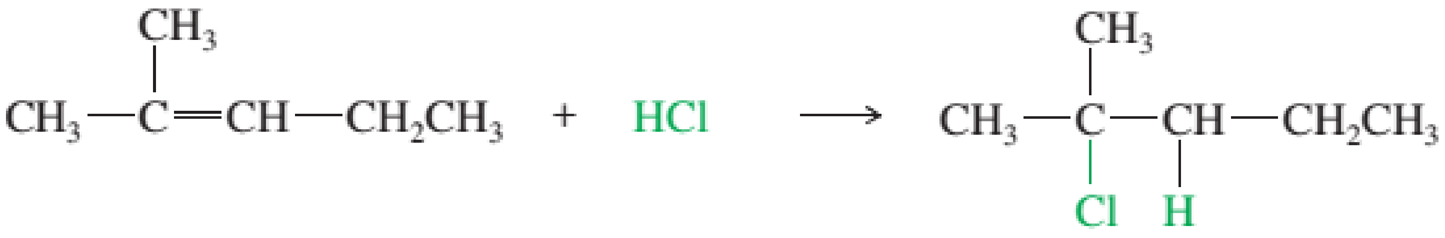
- We are often interested in adding electrophiles other than proton acids to the double bonds of alkenes. Markovnikov's rule can be extended to include a wide variety of other additions, based on the addition of the electrophile in such a way as to produce the most stable carbocation.



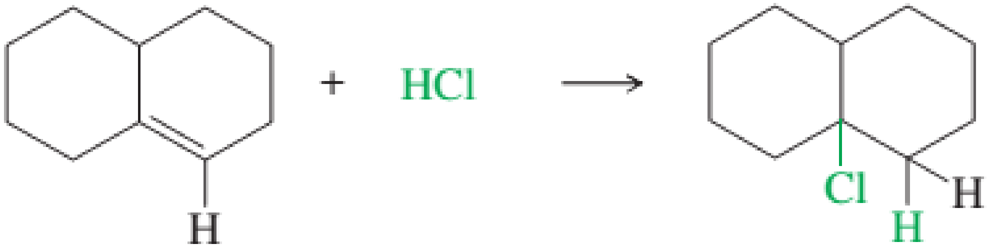
MARKOVNIKOV'S RULE (extended): In an electrophilic addition to an alkene, the electrophile adds in such a way as to generate the most stable intermediate.

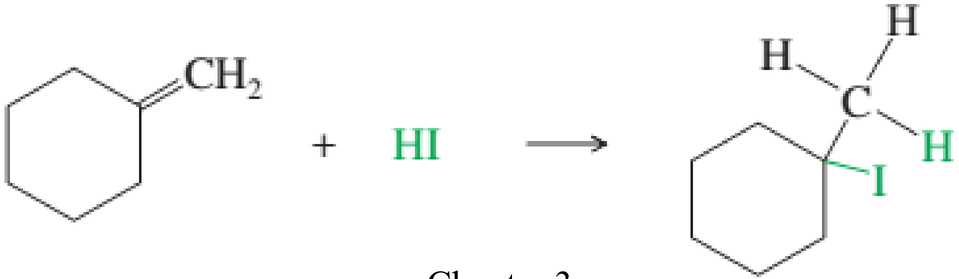
Chemical properties: Electrophilic Addition of H-X to alkenes

- Like HBr, both HCl and HI add to the double bonds of alkenes, and they also follow Markovnikov's rule;
- For example:

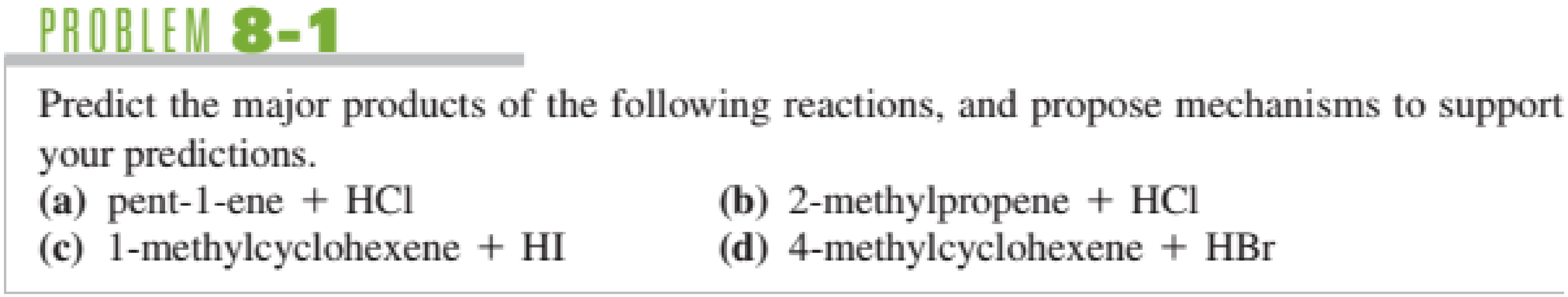


$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2CH_3 + HCl \longrightarrow CH_3-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{H}{\underset{|}{CH}}-CH_2CH_3$$





Chemical properties



PROBLEM **8-1**

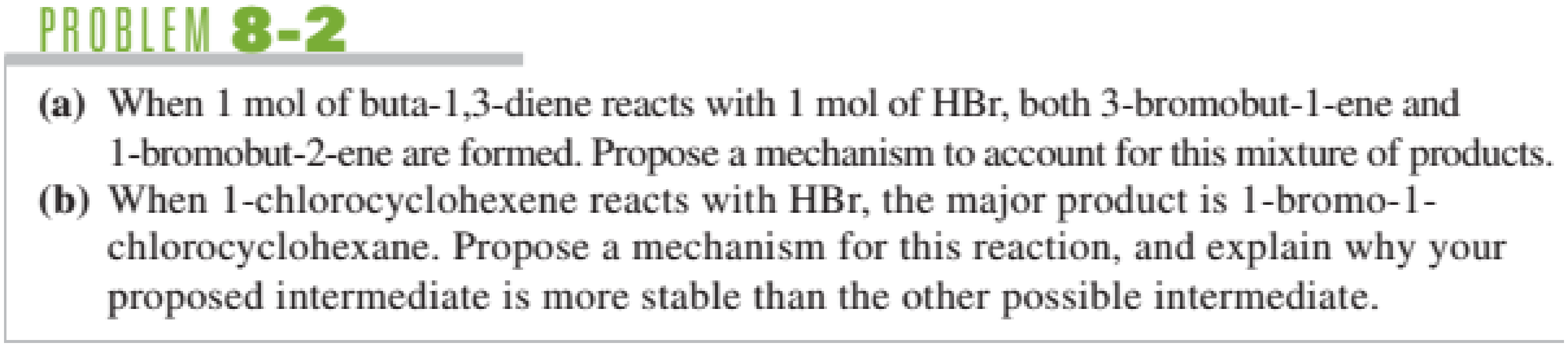
Predict the major products of the following reactions, and propose mechanisms to support your predictions.

(a) pent-1-ene + HCl

(b) 2-methylpropene + HCl

(c) 1-methylcyclohexene + HI

(d) 4-methylcyclohexene + HBr



PROBLEM **8-2**

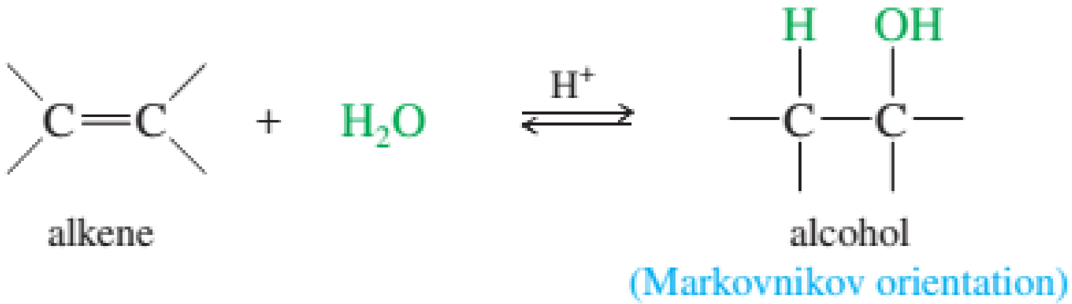
(a) When 1 mol of buta-1,3-diene reacts with 1 mol of HBr, both 3-bromobut-1-ene and 1-bromobut-2-ene are formed. Propose a mechanism to account for this mixture of products.

(b) When 1-chlorocyclohexene reacts with HBr, the major product is 1-bromo-1-chlorocyclohexane. Propose a mechanism for this reaction, and explain why your proposed intermediate is more stable than the other possible intermediate.

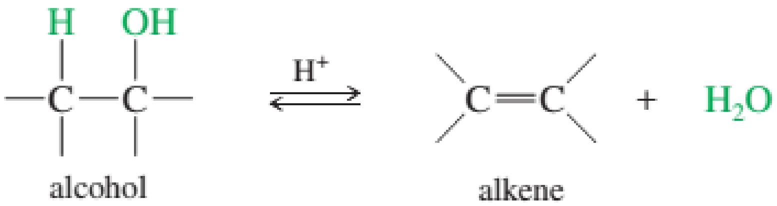
Addition of water: Hydration of alkenes

- An alkene may react with water in the presence of a strongly acidic catalyst to form an alcohol.
- Formally, this reaction is a **hydration** (the addition of water), with a hydrogen atom adding to one carbon and a hydroxyl group adding to the other.
- Hydration of an alkene is the reverse of the dehydration of alcohols.

Hydration of an alkene



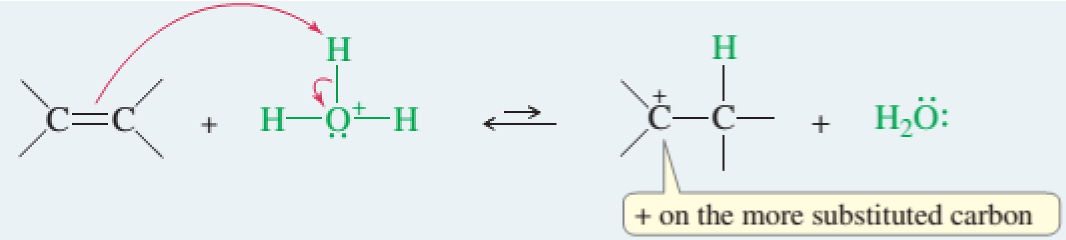
Dehydration of an alcohol



- For dehydrating alcohols, a concentrated dehydrating acid (such as or) is used to drive the equilibrium to favor the alkene. Hydration of an alkene, on the other hand, is accomplished by adding excess water to drive the equilibrium toward the alcohol.

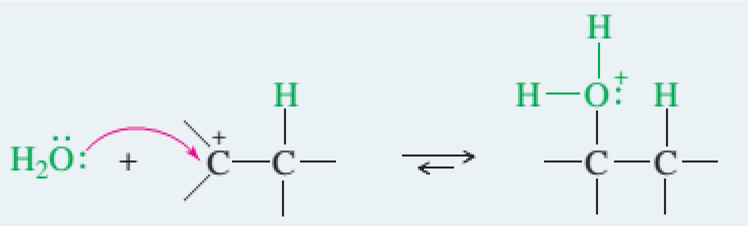
Chemical properties: Hydration of alkenes

Step 1: Protonation of the double bond forms a carbocation.

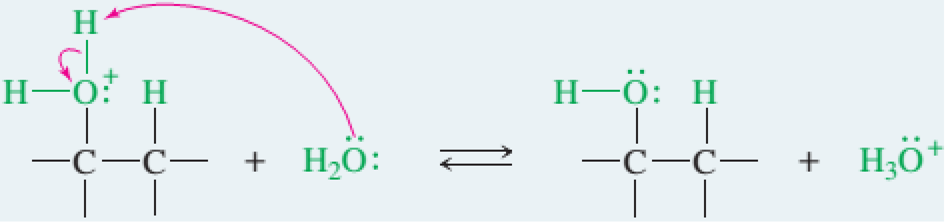


+ on the more substituted carbon

Step 2: Nucleophilic attack by water gives a protonated alcohol.



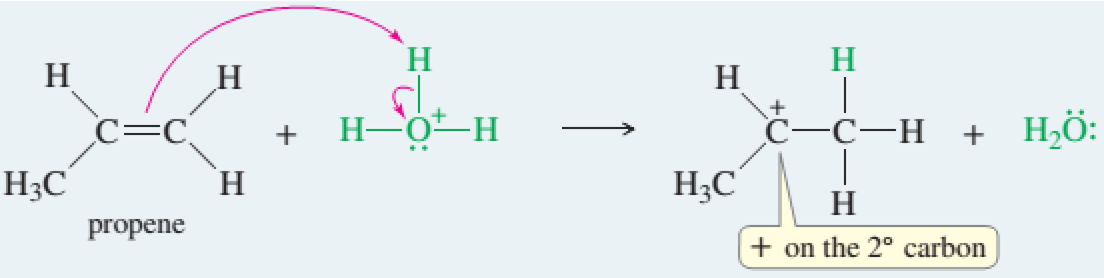
Step 3: Deprotonation gives the alcohol.



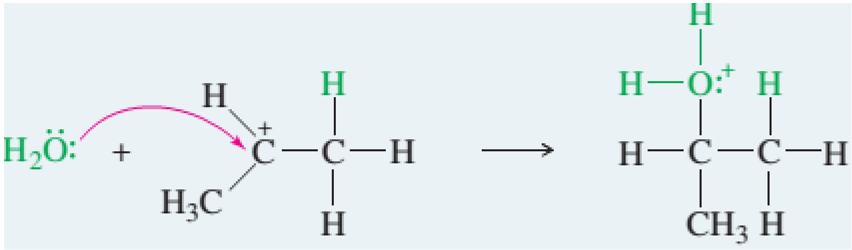
Chemical properties: Hydration of alkenes

EXAMPLE: Acid-catalyzed hydration of propene.

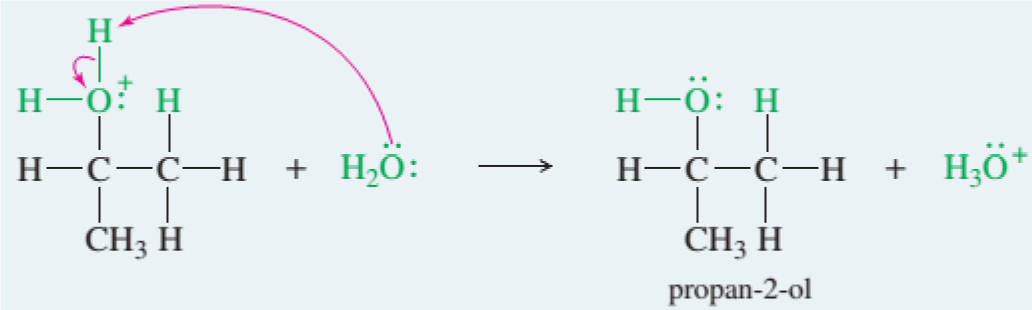
Step 1: **Protonation of the double bond forms a secondary carbocation.**



Step 2: **Nucleophilic attack by water gives a protonated alcohol.**

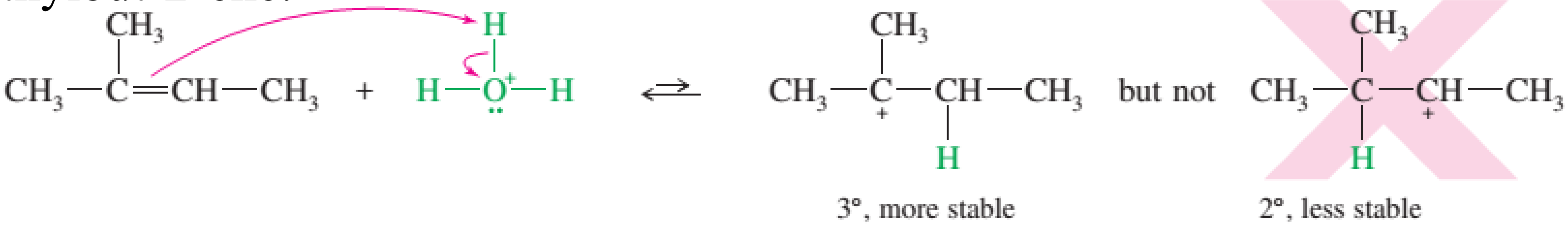


Step 3: **Deprotonation gives the alcohol.**

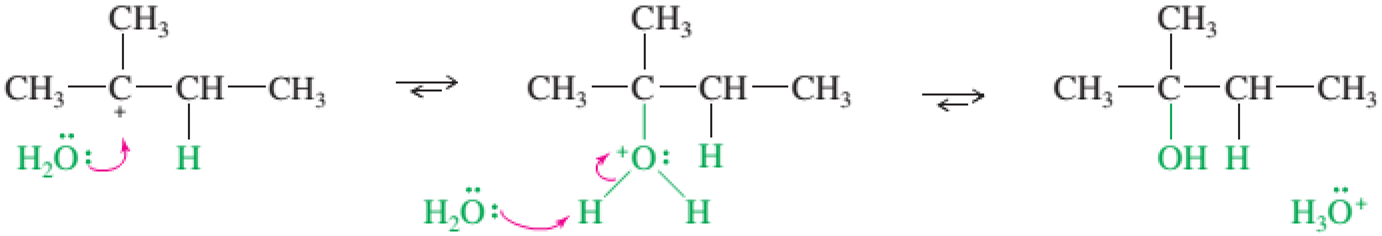


Orientation of hydration: Hydration of alkenes

- Step 1 of the hydration mechanism is similar to the first step in the addition of HBr.
- The proton adds to the *less* substituted end of the double bond to form the *more* substituted carbocation. Water attacks the carbocation to give (after loss of a proton) the alcohol with the group on the more substituted carbon. Like the addition of hydrogen halides, hydration is *regioselective*: It follows Markovnikov's rule, giving a product in which the new hydrogen has added to the less substituted end of the double bond. Consider the hydration of 2-methylbut-2-ene:



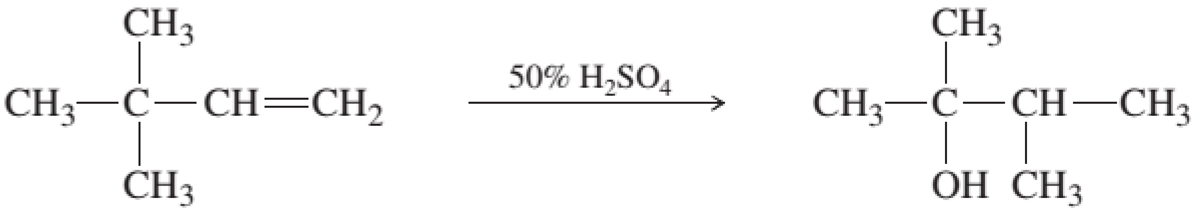
- The proton adds to the less substituted end of the double bond, so the positive charge appears at the more substituted end. Water attacks the carbocation to give the protonated alcohol.



The reaction follows Markovnikov's rule

Chemical properties

- Like other reactions that involve carbocation intermediates, hydration may take place with rearrangement. For example, when 3,3-dimethylbut-1-ene undergoes acid catalyzed hydration, the major product results from rearrangement of the carbocation intermediate.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH=CH_2 \xrightarrow{50\%\ H_2SO_4} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

3,3-dimethylbut-1-ene

2,3-dimethylbutan-2-ol
(major product)

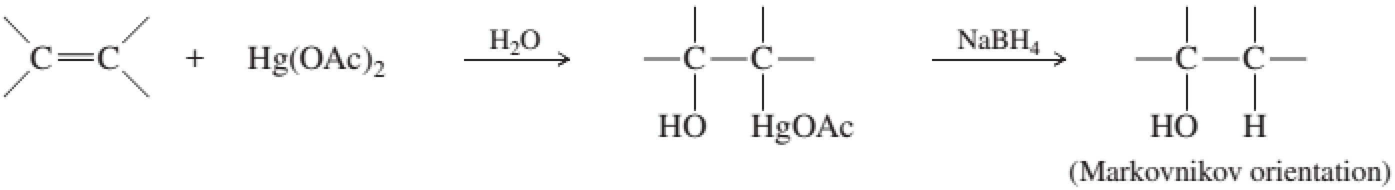
PROBLEM 8-5

Propose a mechanism to show how 3,3-dimethylbut-1-ene reacts with dilute aqueous H_2SO_4 to give 2,3-dimethylbutan-2-ol and a small amount of 3,3-dimethylbut-2-ene.

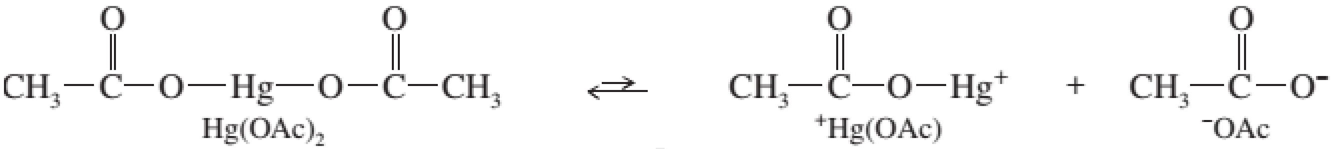
Chemical properties: Oxymercuration–demercuration

- Many alkenes do not easily undergo hydration in aqueous acid.
- Some alkenes are nearly insoluble in aqueous acid, and others undergo side reactions such as rearrangement, polymerization, or charring under these strongly acidic conditions.
- **Oxymercuration–demercuration** is another method for converting alkenes to alcohols with Markovnikov orientation. Oxymercuration–demercuration works with many alkenes that do not easily undergo direct hydration, and it takes place under milder conditions. No free carbocation is formed, so there is no opportunity for rearrangements or polymerization.

Oxymercuration–Demercuration



- The reagent for mercuration is mercuric acetate, $Hg(OCOCH_3)_2$, abbreviated $Hg(OAc)_2$. There are several theories as to how this reagent acts as an electrophile; the simplest one is that mercuric acetate dissociates slightly to form a positively charged mercury species, $^{+}Hg(OAc)$.



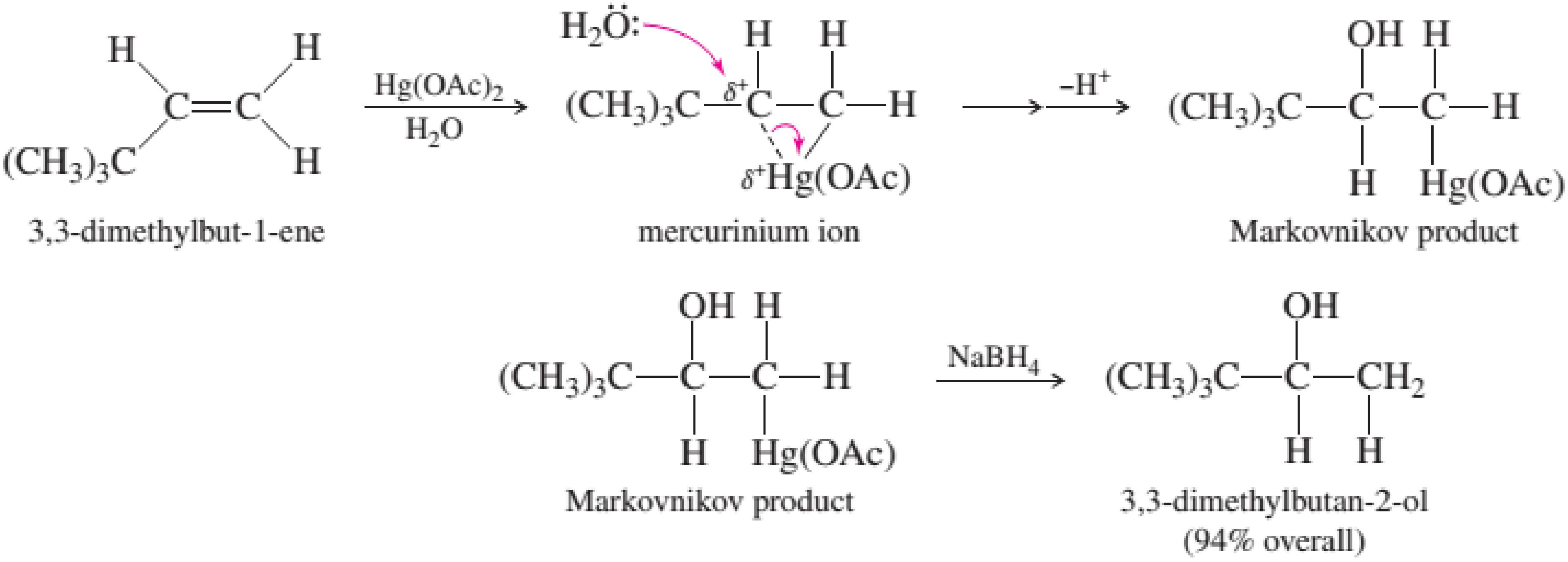
$$CH_3-\overset{O}{\overset{\|}{C}}-O-Hg-O-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-O-Hg^{+} + CH_3-\overset{O}{\overset{\|}{C}}-O^{-}$$

Oxymercuration–demercuration

- Oxymercuration–demercuration of an unsymmetrical alkene generally gives Markovnikov orientation of addition, as shown by the oxymercuration of propene in the preceding example. The mercurinium ion has a considerable amount of positive charge on both of its carbon atoms, but there is more of a positive charge on the more substituted carbon atom, where it is more stable. Attack by water occurs on this more electrophilic carbon, giving Markovnikov orientation. The electrophile, remains bonded to the less substituted end of the double bond. Reduction of the organomercurial alcohol gives the Markovnikov alcohol: propan-2-ol.
- Similarly, oxymercuration – demercuration of 3,3-dimethylbut-1-ene gives the Markovnikov product, 3,3-dimethylbutan-2-ol, in excellent yield.
- Contrast this unrearranged product with the rearranged product formed in the acid - catalyzed hydration of the same alkene.

Oxymercuration–demercuration reliably adds water across the double bond of an alkene with Markovnikov orientation and without rearrangement.

Chemical properties: Oxymercuration–demercuration



3,3-dimethylbut-1-ene

mercurinium ion

Markovnikov product

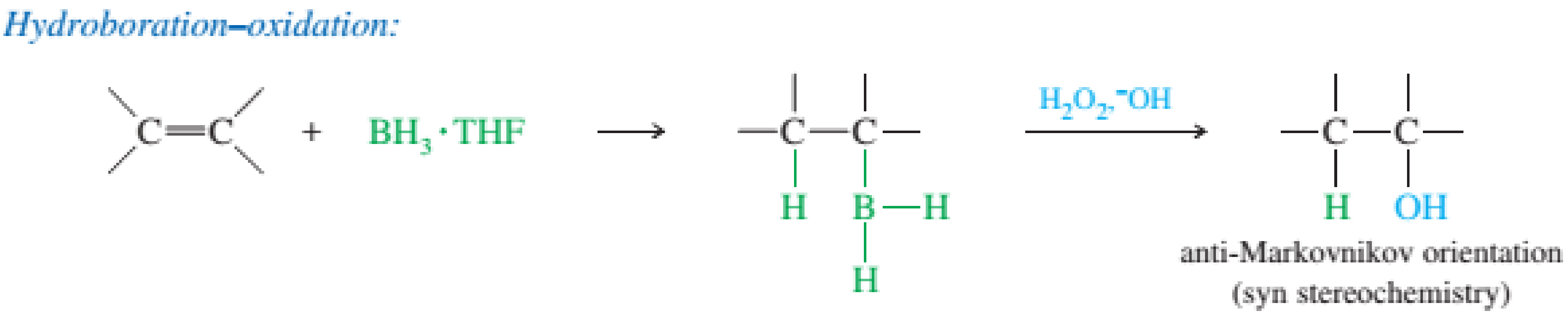
Markovnikov product

3,3-dimethylbutan-2-ol
(94% overall)

- Of the methods we have seen for Markovnikov hydration of alkenes, **oxymercuration–demercuration is most commonly used in the laboratory**. It gives better yields than direct acid-catalyzed hydration, it avoids the possibility of rearrangements, and it does not involve harsh conditions. There are also disadvantages, however. Organomercurial compounds are highly toxic. They must be used with great care and then must be disposed of properly.

Hydroboration of alkenes

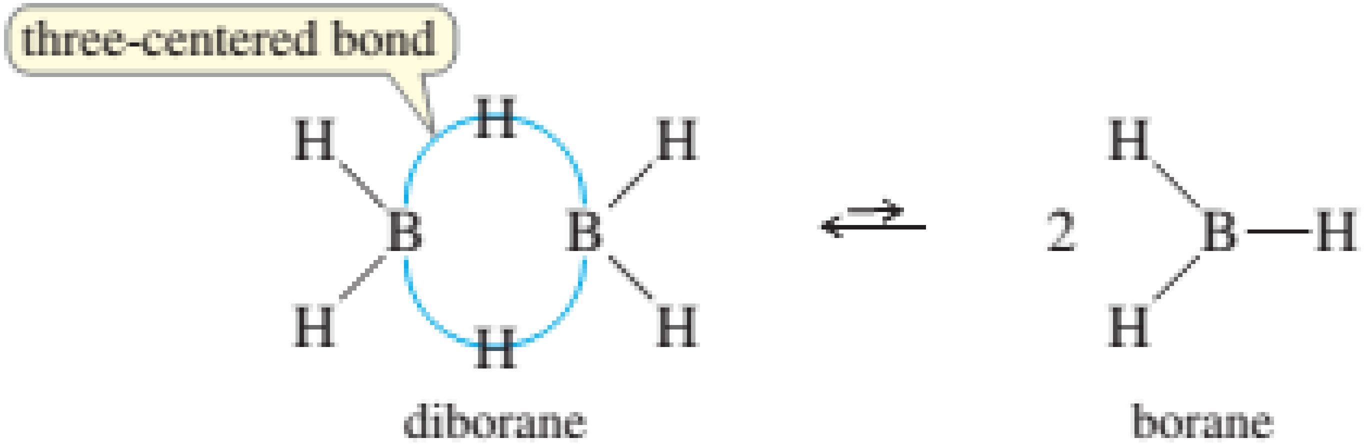
- How to convert an alkene to the anti-Markovnikov alcohol?



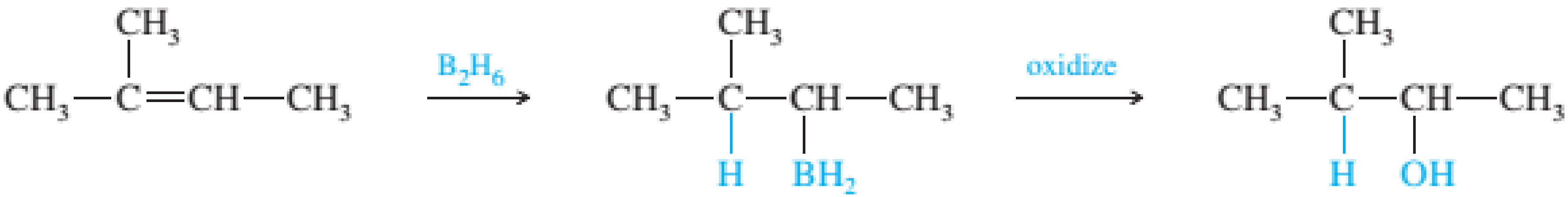
- Such an anti-Markovnikov hydration was impossible until H. C. Brown, of Purdue University, discovered that diborane adds to alkenes with anti-Markovnikov orientation to form alkylboranes, which can be oxidized to give anti-Markovnikov alcohols. This discovery led to the development of a large field of borane chemistry, for which Brown received the Nobel Prize in Chemistry in 1979.

Hydroboration of alkenes

- Diborane is a dimer composed of two molecules of borane.
- The bonding in diborane is unconventional, using three-centered (banana-shaped) bonds with protons in the middle of them.
- Diborane is in equilibrium with a small amount of borane as a strong Lewis acid with only six valence electrons.



Hydroboration of alkenes



2-methylbut-2-ene

an alkylborane

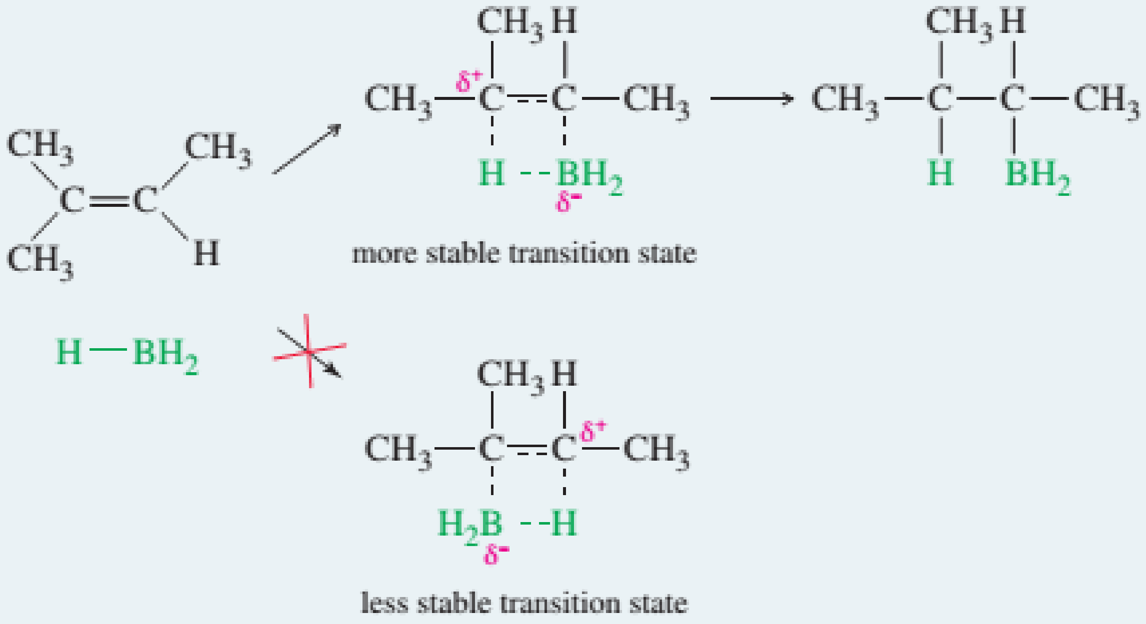
3-methylbutan-2-ol (>90%)

- ➢ Borane is an electron-deficient compound. It has only six valence electrons, so the boron atom in cannot have an octet.
- ➢ As an electron-deficient compound, it is a strong electrophile, capable of adding to a double bond.
- ➢ This **hydroboration** of the double bond occurs in one step, with the boron atom adding to the less substituted end of the double bond. In the transition state, the electrophilic boron atom withdraws electrons from the pi bond, and the carbon at the other end of the double bond acquires a partial positive charge. This partial charge is more stable on the more substituted carbon atom.
- ➢ The product shows boron bonded to the less substituted end of the double bond and hydrogen bonded to the more substituted end. Also, steric hindrance favors boron adding to the less hindered, less substituted end of the double bond.

Hydroboration of alkenes

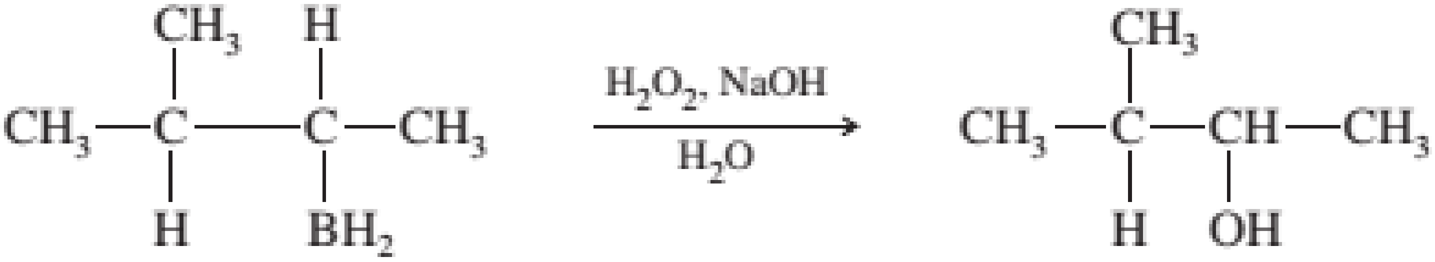
MECHANISM 8-6 Hydroboration of an Alkene

Borane adds to the double bond in a single step. Boron adds to the less hindered, less substituted carbon, and hydrogen adds to the more substituted carbon.



Hydroboration of alkenes

- The boron atom is removed by oxidation, using aqueous sodium hydroxide and hydrogen peroxide (HOOH or) to replace the boron atom with a hydroxyl group.

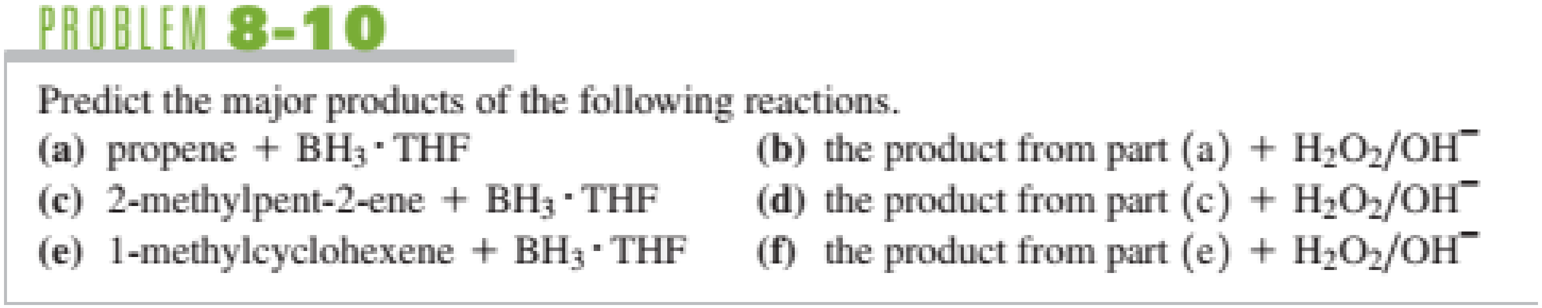


- This hydration of an alkene by hydroboration–oxidation is another example of a reaction that does not follow the original statement of Markovnikov's rule (the product is anti-Markovnikov), but still follows our understanding of the reasoning behind Markovnikov's rule. The electrophilic boron atom adds to the *less* substituted end of the double bond, placing the positive charge (and the hydrogen atom) at the more substituted end.

Hydroboration of alkenes

SOLVED PROBLEM 8-3

Show how you would convert 1-methylcyclopentanol to 2-methylcyclopentanol.



PROBLEM 8-10

Predict the major products of the following reactions.

(a) propene + $BH_3 \cdot THF$

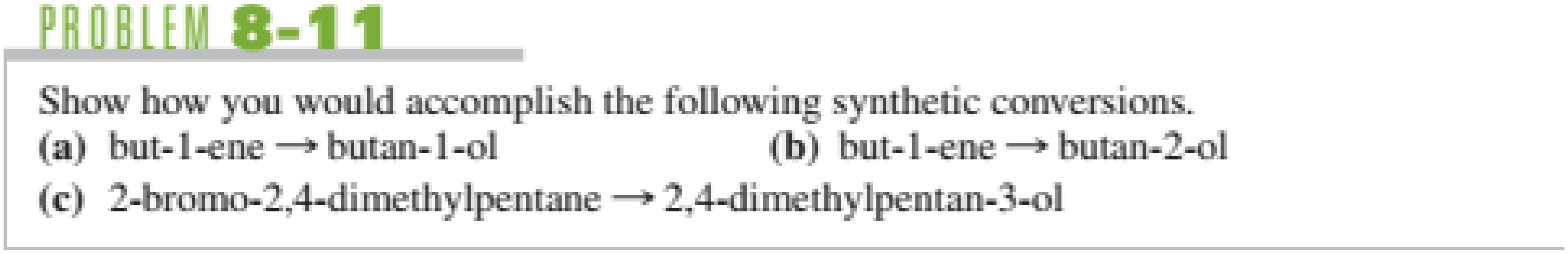
(b) the product from part (a) + H_2O_2/OH^-

(c) 2-methylpent-2-ene + $BH_3 \cdot THF$

(d) the product from part (c) + H_2O_2/OH^-

(e) 1-methylcyclohexene + $BH_3 \cdot THF$

(f) the product from part (e) + H_2O_2/OH^-



PROBLEM 8-11

Show how you would accomplish the following synthetic conversions.

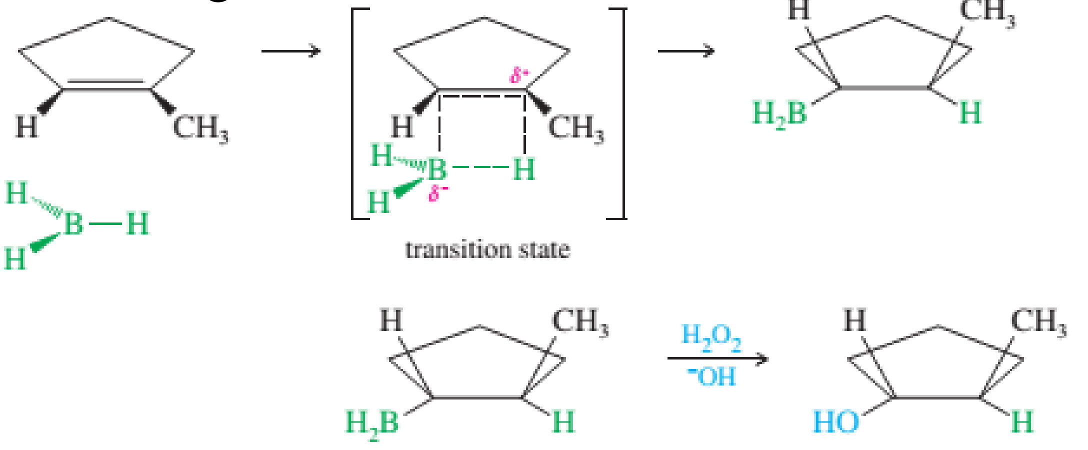
(a) but-1-ene → butan-1-ol

(b) but-1-ene → butan-2-ol

(c) 2-bromo-2,4-dimethylpentane → 2,4-dimethylpentan-3-ol

Stereochemistry of Hydroboration

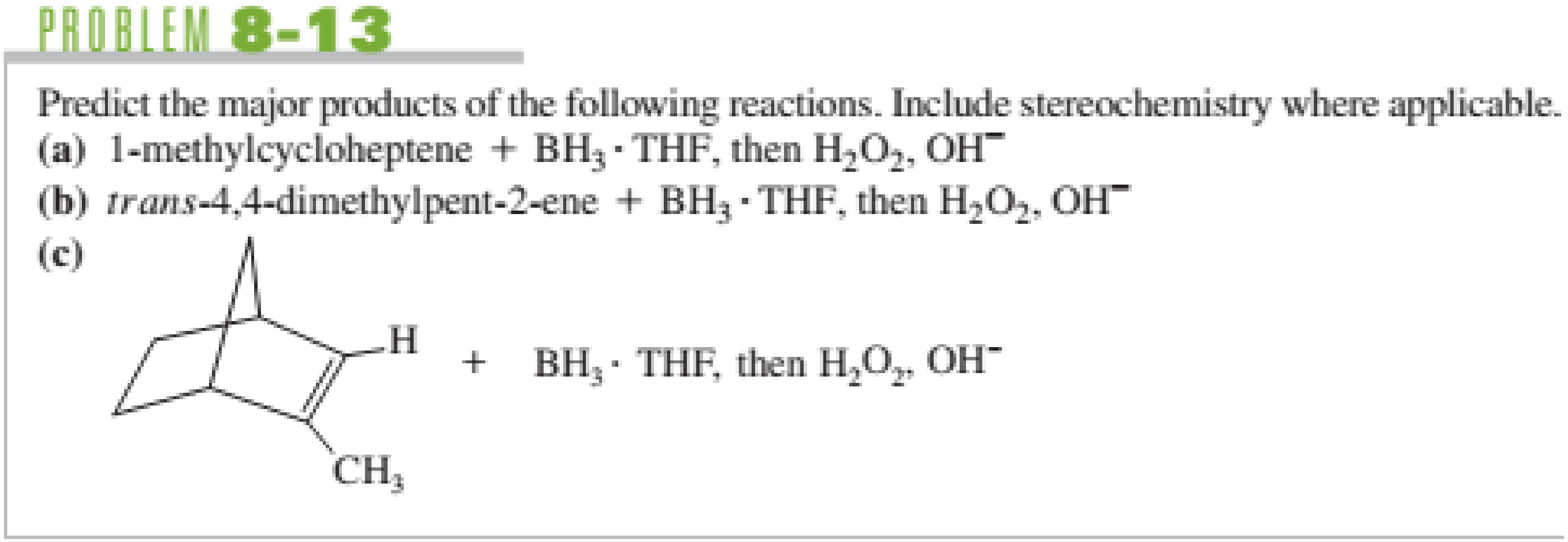
- The simultaneous addition of boron and hydrogen to the double bond leads to a **syn addition:** Boron and hydrogen add across the double bond on the *same side* of the molecule. (If they added to opposite sides of the molecule, the process would be an **anti addition.**)
- Boron and hydrogen add to the same face of the double bond (syn) to form a trialkylborane. Oxidation of the trialkylborane replaces boron with a hydroxyl group in the same stereochemical position. The product is *trans*-2-methylcyclopentanol. A racemic mixture is expected because a chiral product is formed from achiral reagents.



trans-2-methylcyclopentanol
(85% overall)
(racemic mixture of enantiomers)

- The second step (oxidation of the borane to the alcohol) takes place with retention of configuration. Hydroperoxide ion adds to the borane, causing the alkyl group to migrate from boron to oxygen. Hydrolysis of the borate ester gives the alcohol.

Hydroboration of alkenes



PROBLEM 8-13

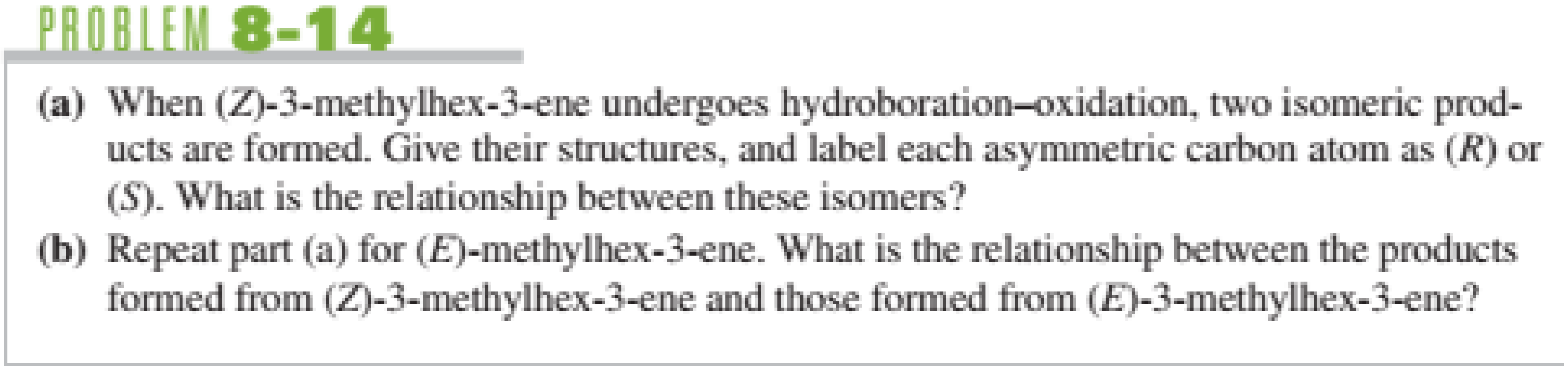
Predict the major products of the following reactions. Include stereochemistry where applicable.

(a) 1-methylcycloheptene + $BH_3 \cdot THF$, then H_2O_2, OH^-

(b) *trans*-4,4-dimethylpent-2-ene + $BH_3 \cdot THF$, then H_2O_2, OH^-

(c)

+ $BH_3 \cdot THF$, then H_2O_2, OH^-



PROBLEM 8-14

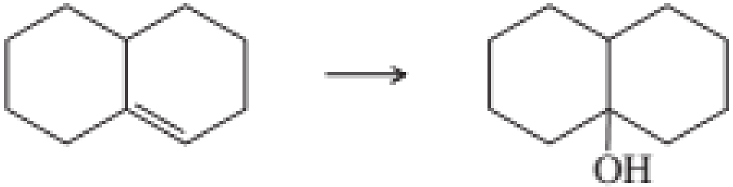
(a) When (*Z*)-3-methylhex-3-ene undergoes hydroboration–oxidation, two isomeric products are formed. Give their structures, and label each asymmetric carbon atom as (*R*) or (*S*). What is the relationship between these isomers?

(b) Repeat part (a) for (*E*)-methylhex-3-ene. What is the relationship between the products formed from (*Z*)-3-methylhex-3-ene and those formed from (*E*)-3-methylhex-3-ene?

Hydroboration of alkenes

PROBLEM 8-15

Show how you would accomplish the following transformations.

(a) 

(b) 

(c) 1-methylcycloheptanol → 2-methylcycloheptanol

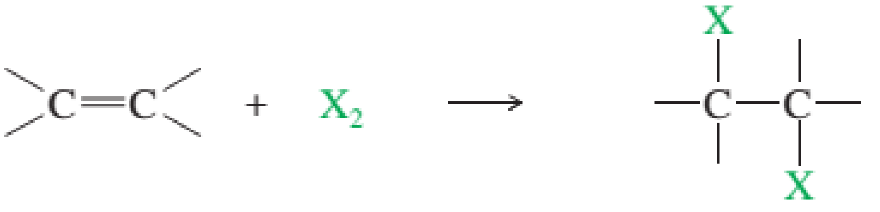
PROBLEM 8-16

(a) When HBr adds across the double bond of 1,2-dimethylcyclopentene, the product is a mixture of the cis and trans isomers. Show why this addition is not stereospecific.

(b) When 1,2-dimethylcyclopentene undergoes hydroboration–oxidation, one diastereomer of the product predominates. Show why this addition is stereospecific, and predict the stereochemistry of the major product.

Addition of halogen to alkenes

- ➢ Halogens add to alkenes to form vicinal dihalides.



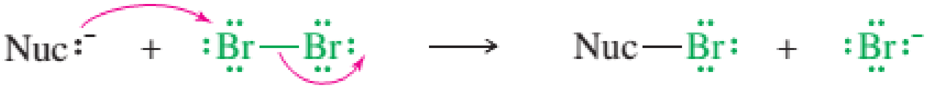
(X_2 = Cl_2, Br_2, sometimes I_2)

usually anti addition

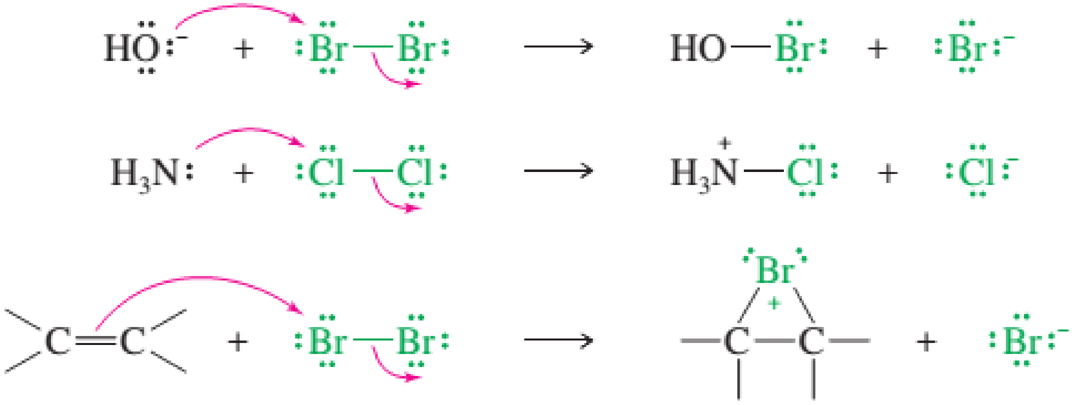
- ➢ Mechanism of halogen addition

+ A halogen molecule is electrophilic;

+ a nucleophile can react with a halogen, displacing a halide ion:



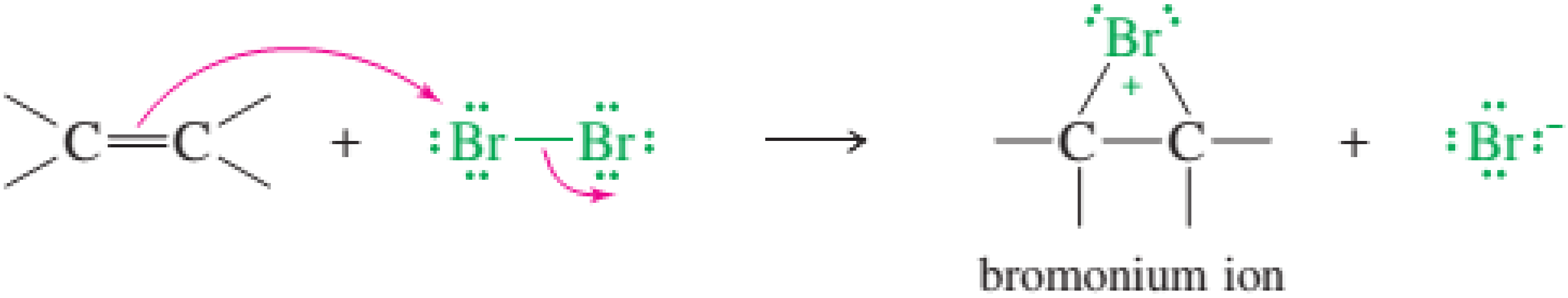
➢ The nucleophile attacks the electrophilic nucleus of one bromine atom, and the other bromine serves as the leaving group, departing as bromide ion. Many reactions fit this general pattern; for example:

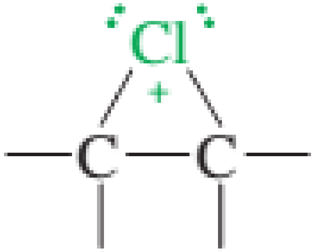


bromonium ion

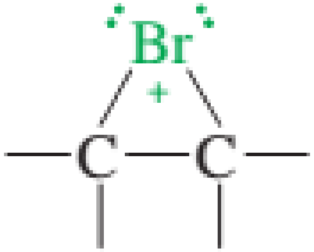
Addition of halogen to alkenes

- The pi electrons of an alkene attack the bromine molecule, expelling bromide ion.
- A **bromonium ion** results, containing a three-membered ring with a positive charge on the bromine atom.
- Similar reactions with other halogens form other **halonium ions.** The structures of a **chloronium ion,** a **bromonium ion,** and an **iodonium ion** are shown next.

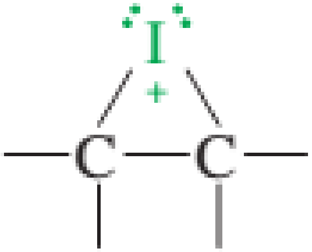




chloronium ion



bromonium ion

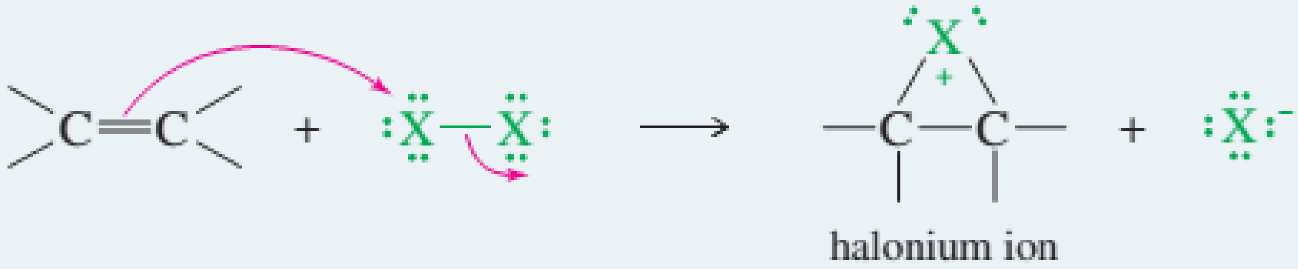


iodonium ion

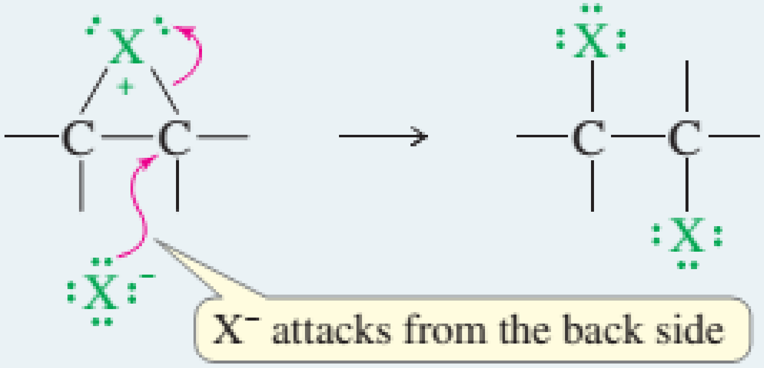
Addition of halogen to alkenes

MECHANISM 8-7 Addition of Halogens to Alkenes

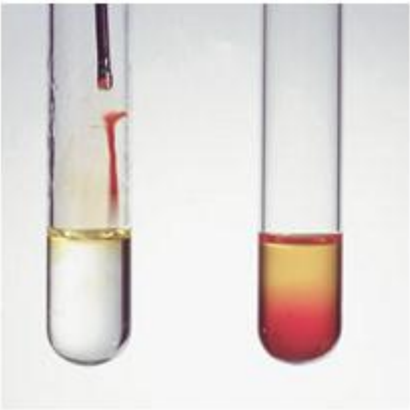
Step 1: Electrophilic attack forms a halonium ion.



Step 2: The halide ion opens the halonium ion.



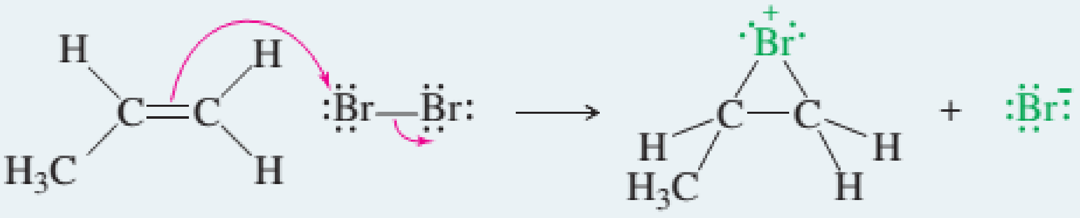
Addition of halogen to alkenes



When a solution of bromine (red-brown) is added to cyclohexene, the bromine color quickly disappears because bromine adds across the double bond. When bromine is added to cyclohexane (at right), the color persists because no reaction occurs.

EXAMPLE: Addition of Br_2 to propene.

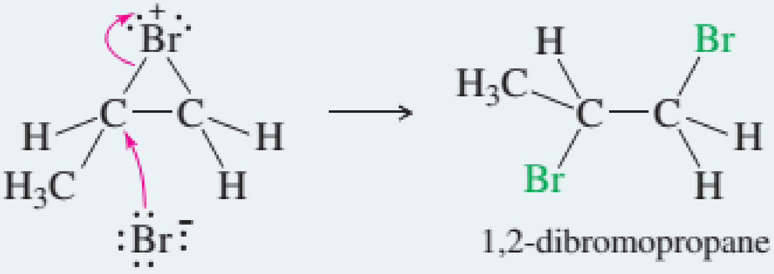
Step 1: Electrophilic attack forms a bromonium ion.



propene

bromonium ion

Step 2: Bromide ion opens the bromonium ion.



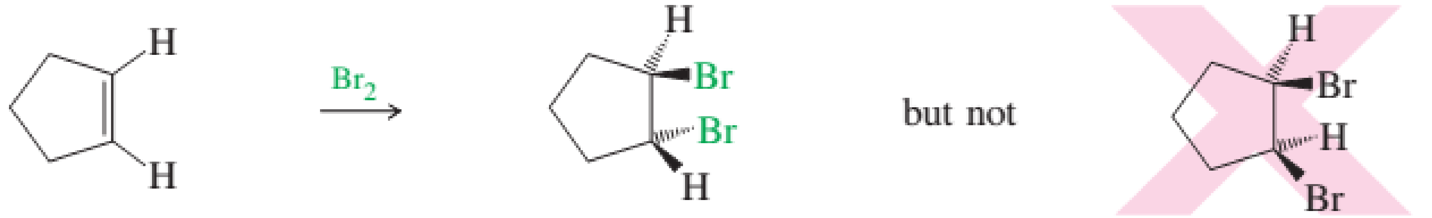
1,2-dibromopropane

Addition of halogen to alkenes

- Chlorine and bromine commonly add to alkenes by the halonium ion mechanism.
- Iodination is used less frequently because diiodide products decompose easily.
- Any solvents used must be inert to the halogens; methylene chloride (CH_2Cl_2); chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) are the most frequent choices.
- The addition of bromine has been used as a simple chemical test for the presence of olefinic double bonds. A solution of bromine in carbon tetrachloride is a clear, deep red color. When this red solution is added to an alkene, the red bromine color disappears (we say it is "decolorized"), and the solution becomes clear and colorless. (Although there are other functional groups that decolorize bromine, few do it as quickly as alkenes.)

Stereochemistry of halogen addition

- The addition of bromine to cyclopentene is a stereospecific **anti addition.**

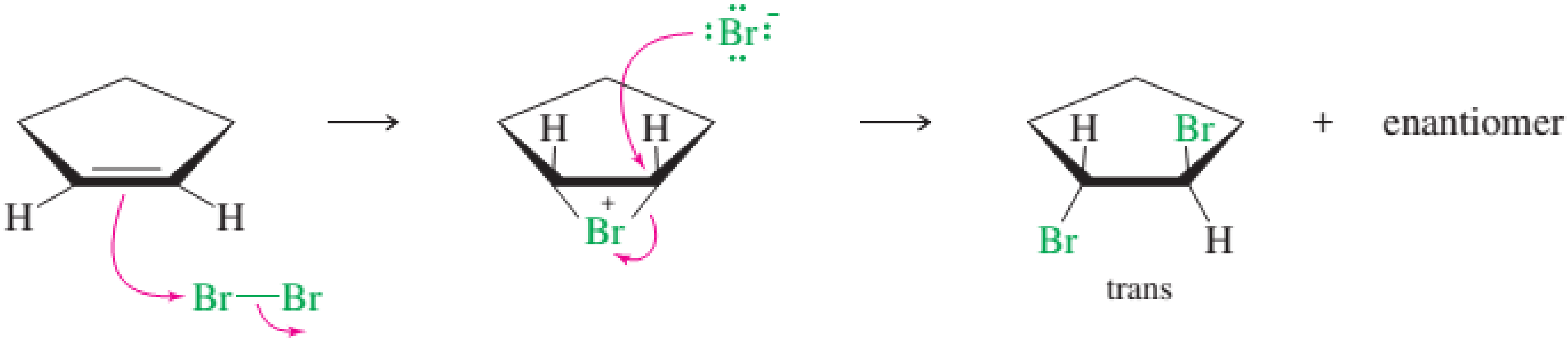


cyclopentene

trans-1,2-dibromocyclopentane (92%)
(both enantiomers)

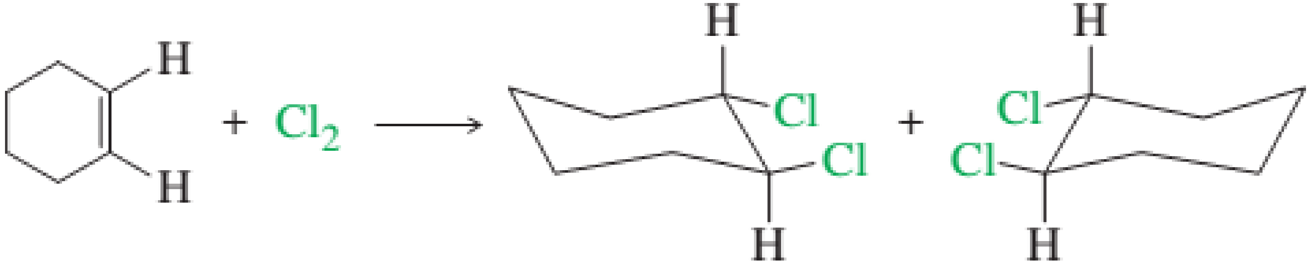
cis-1,2-dibromocyclopentane
(not formed)

- Anti stereochemistry results from the bromonium ion mechanism. When a nucleophile attacks a halonium ion, it must do so from the back side, in a manner similar to the displacement. This back-side attack assures anti stereochemistry of addition.



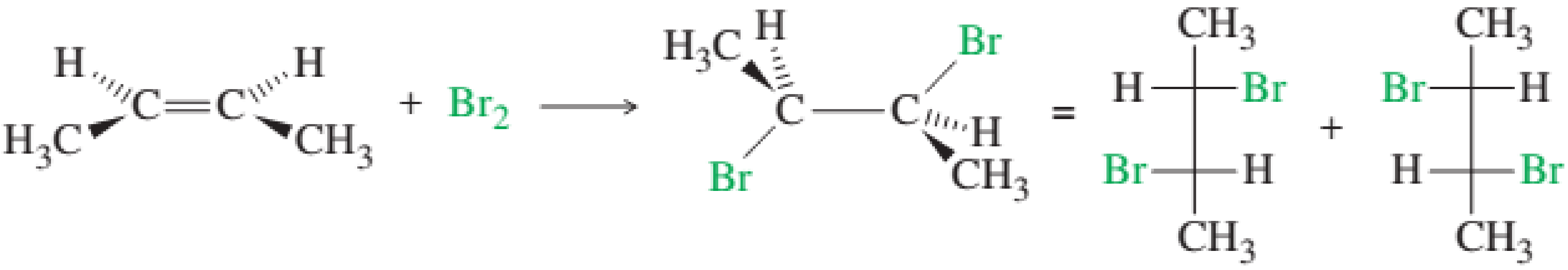
Halogen addition

- Halogen addition is another example of a stereospecific reaction, in which different stereoisomers of the starting material give different stereoisomers of the product.



cyclohexene

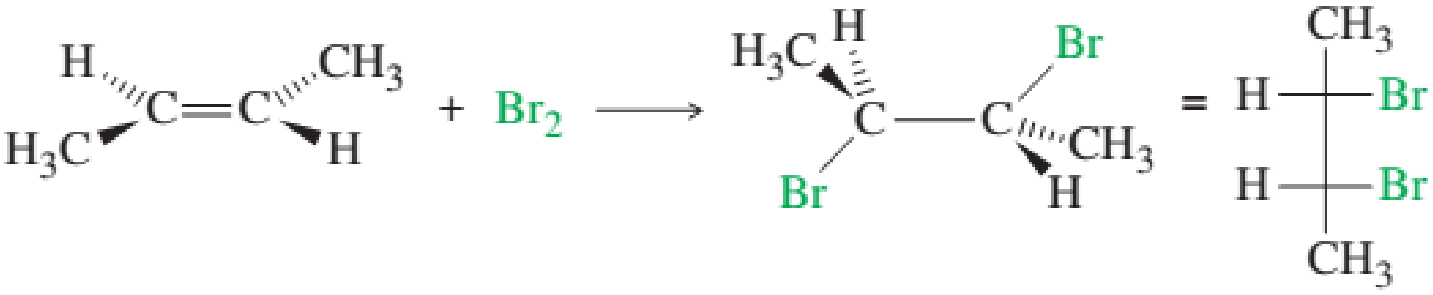
racemic *trans*-1,2-dichlorocyclohexane



cis-but-2-ene

(both enantiomers)

(±)-2,3-dibromobutane



trans-but-2-ene

meso-2,3-dibromobutane

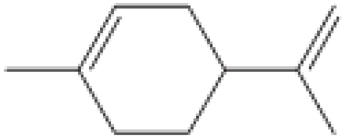
PROBLEM 8-17

Give mechanisms to account for the stereochemistry of the products observed from the addition of bromine to *cis*- and *trans*-but-2-ene (Figure 8-4). Why are two products formed from the cis isomer but only one from the trans? (Making models will be helpful.)

PROBLEM 8-18

Propose mechanisms and predict the major products of the following reactions. Include stereochemistry where appropriate.

(a) cycloheptene + Br_2 in CH_2Cl_2

(b)  + 2 Cl_2 in CCl_4

(c) (*E*)-dec-3-ene + Br_2 in CCl_4

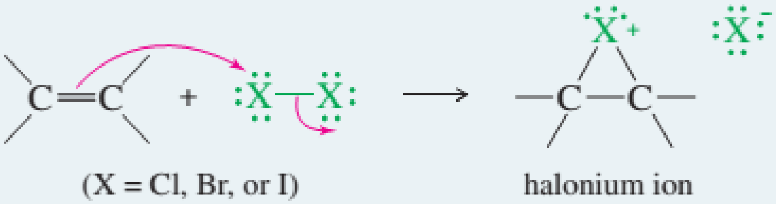
(d) (*Z*)-dec-3-ene + Br_2 in CCl_4

Formation of halohydrins

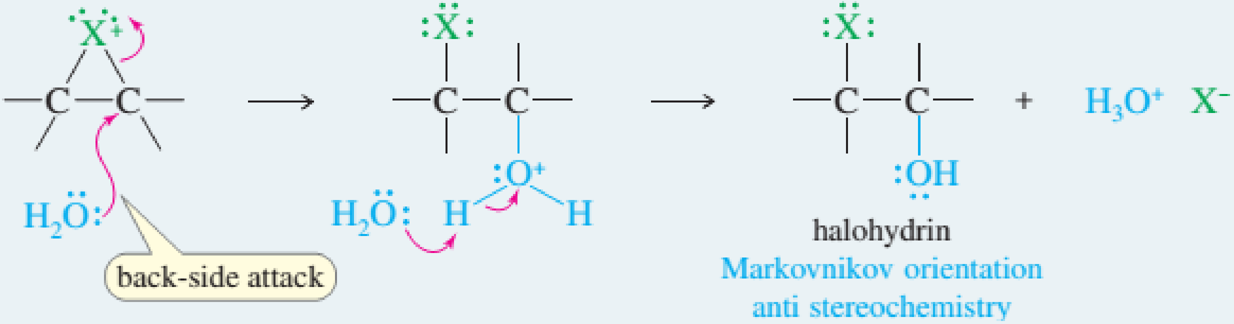
- A **halohydrin** is an alcohol with a halogen on the adjacent carbon atom. In the presence of water, halogens add to alkenes to form halohydrins.
- The electrophilic halogen adds to the alkene to give a halonium ion, which is also electrophilic. Water acts as a nucleophile to open the halonium ion and form the halohydrin.

MECHANISM 8-8 Formation of Halohydrins

Step 1: Electrophilic attack forms a halonium ion.

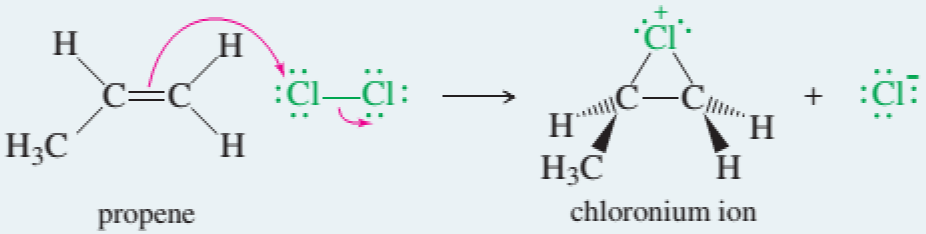


Step 2: Water opens the halonium ion; deprotonation gives the halohydrin.

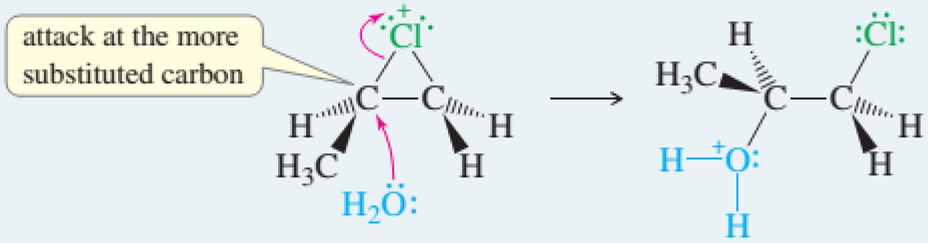


EXAMPLE: Addition of Cl_2 to propene in water.

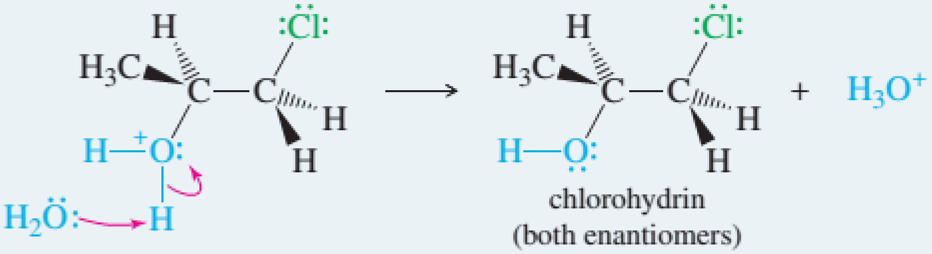
Step 1: Electrophilic attack forms a chloronium ion.



Step 2: Back-side attack by water opens the chloronium ion.

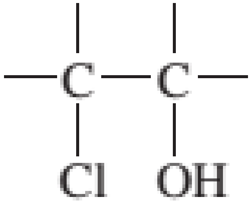

attack at the more substituted carbon

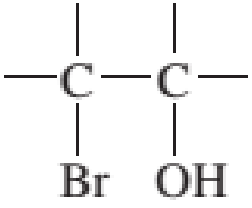
Step 3: Water removes a proton to give the chlorohydrin.

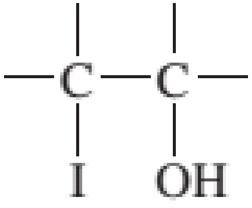


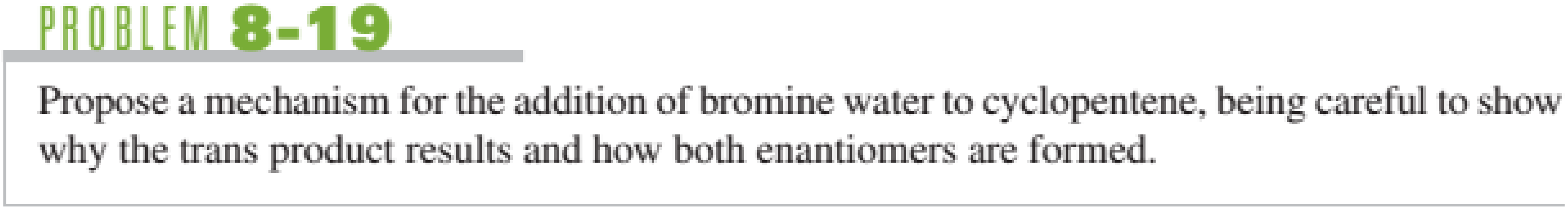
The formation of halohydrin

- When halogenation takes place with no solvent or with an inert solvent such as carbon tetrachloride or chloroform only the halide ion is available as a nucleophile to attack the halonium ion. A dihalide results.
- When an alkene reacts with a halogen in the presence of a nucleophilic solvent such as water, a solvent molecule is the most likely nucleophile to attack the halonium ion. When a water molecule attacks the halonium ion, the final product is a halohydrin, with a halogen on one carbon atom and a hydroxyl group on the adjacent carbon. The product may be a *chlorohydrin*, a *bromohydrin*, or an *iodohydrin*, depending on the halogen.


chlorohydrin


bromohydrin


iodohydrin

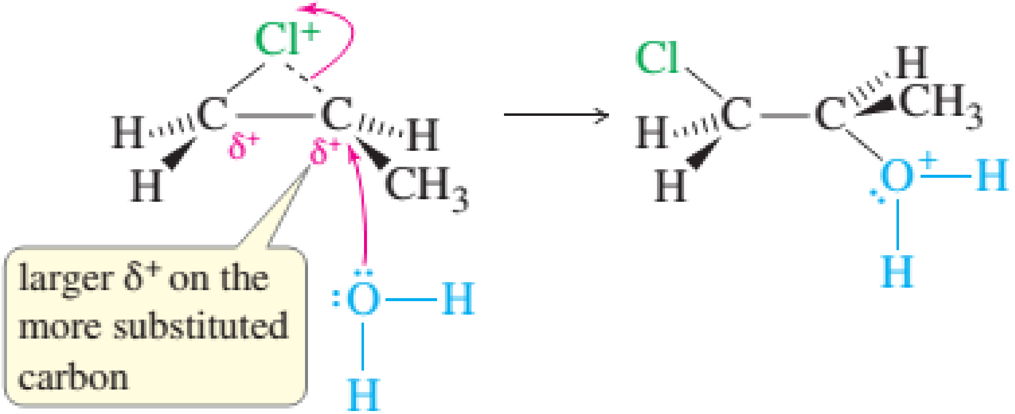


PROBLEM 8-19

Propose a mechanism for the addition of bromine water to cyclopentene, being careful to show why the trans product results and how both enantiomers are formed.

Orientation of halohydrin formation

➢ Even though a halonium ion is involved, rather than a carbocation, the extended version of Markovnikov's rule applies to halohydrin formation. When propene reacts with chlorine water, the major product has the electrophile (the chlorine atom) bonded to the less substituted carbon of the double bond. The nucleophile (the hydroxyl group) is bonded to the more substituted carbon.



$$H_2C{=}CH{-}CH_3 + Cl_2 + H_2O \longrightarrow \underset{Cl}{H_2C}{-}\underset{OH}{CH}{-}CH_3 + HCl$$

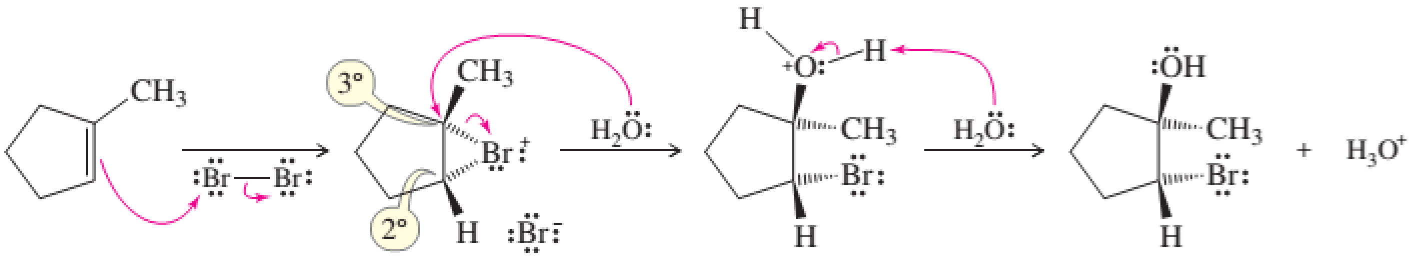
- The Markovnikov orientation observed in halohydrin formation is explained by the structure of the halonium ion intermediate.
- The two carbon atoms bonded to the halogen have partial positive charges, with a larger charge (and a weaker bond to the halogen) on the more substituted carbon atom.
- The nucleophile (water) attacks this more substituted, more electrophilic carbon atom. The result is both anti stereochemistry and Markovnikov orientation.

SOLVED PROBLEM 8-5

Propose a mechanism for the reaction of 1-methylcyclopentene with bromine water.

SOLUTION

1-Methylcyclopentene reacts with bromine to give a bromonium ion. Attack by water could occur at either the secondary carbon or the tertiary carbon of the bromonium ion. Attack actually occurs at the more substituted carbon, which bears more of the positive charge. The product is formed as a racemic mixture.



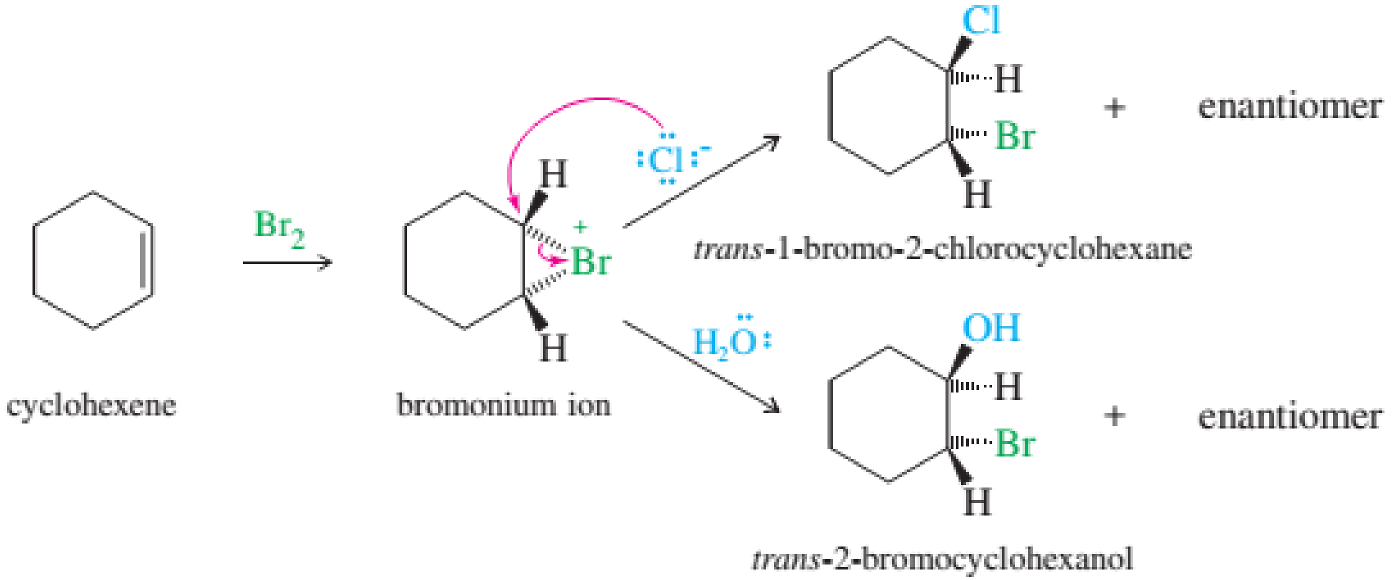
(both enantiomers)

SOLVED PROBLEM 8-6

When cyclohexene is treated with bromine in saturated aqueous sodium chloride, a mixture of *trans*-2-bromocyclohexanol and *trans*-1-bromo-2-chlorocyclohexane results. Propose a mechanism to account for these two products.

SOLUTION

Cyclohexene reacts with bromine to give a bromonium ion, which will react with any available nucleophile. The most abundant nucleophiles in saturated aqueous sodium chloride solution are water and chloride ions. Attack by water gives the bromohydrin, and attack by chloride gives the dihalide. Either of these attacks gives anti stereochemistry.



Chemical properties: Free-Radical Addition of HBr: Anti-Markovnikov Addition

- In 1933, M. S. Kharasch and F. W. Mayo found that some additions of HBr (but not HCl or HI) to alkenes gave products that were opposite to those expected from Markovnikov's rule.
- These **anti-Markovnikov** reactions were most likely when the reagents or solvents came from old supplies that had accumulated peroxides from exposure to the air.
- **Peroxides** give rise to free radicals that initiate the addition, causing it to occur by a radical mechanism.
- The oxygen–oxygen bond in peroxides is rather weak, so it can break to give two alkoxy radicals.

Free-radical addition of HBr to propene.

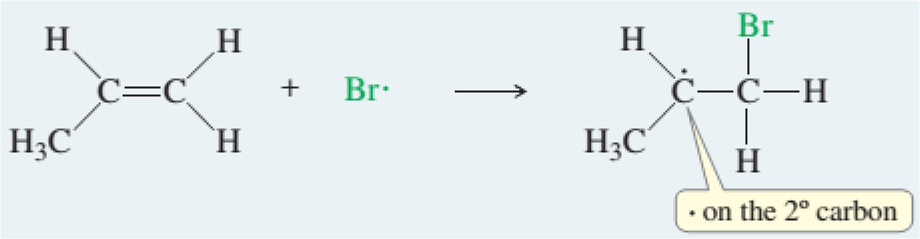
Initiation: Radicals are formed.

$$\mathrm{R{-}O{-}O{-}R} \xrightarrow{\text{heat}} \mathrm{R{-}O\cdot} + \mathrm{\cdot O{-}R}$$

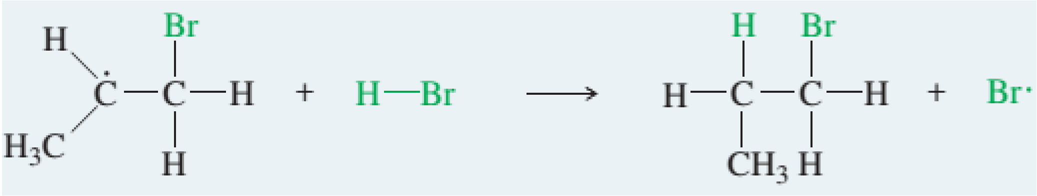
$$\mathrm{R{-}O\cdot} + \mathrm{H{-}Br} \longrightarrow \mathrm{R{-}O{-}H} + \mathrm{Br\cdot}$$

Propagation: A radical reacts to generate another radical.

Step 1: **A bromine radical adds to the double bond to generate an alkyl radical on the secondary carbon atom.**



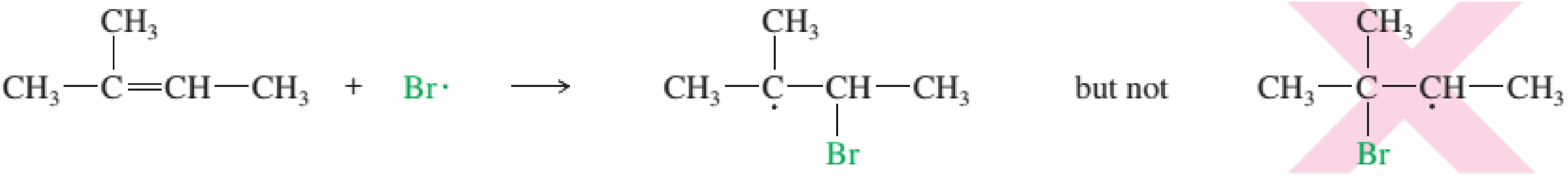
Step 2: **The alkyl radical abstracts a hydrogen atom from HBr to generate the product and a bromine radical.**



- The bromine radical generated in Step 2 goes on to react in Step 1, continuing the chain.

Radical addition of HBr to unsymmetrical alkenes: the anti-Markovnikov orientation

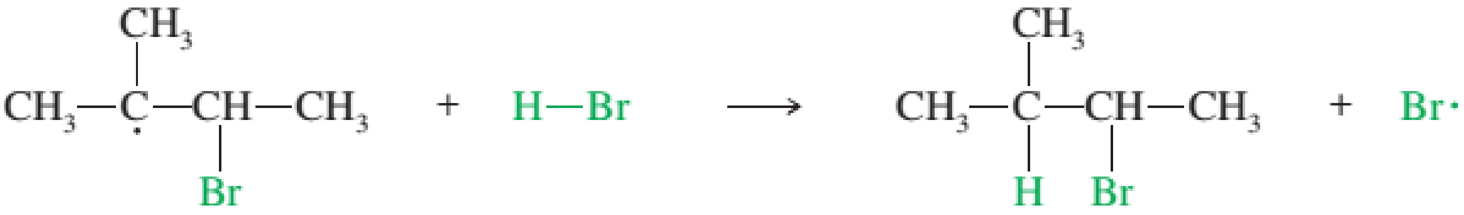
- The anti-Markovnikov orientation found in the products of the peroxide-catalyzed reaction.
- With an unsymmetrical alkene like 2-methylbut-2-ene, adding the bromine radical to the secondary end of the double bond forms a tertiary radical.



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3 + Br\cdot \longrightarrow CH_3-\underset{\cdot}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{Br}{|}}{CH}-CH_3 \quad \text{but not} \quad CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\cdot}{CH}-CH_3$$

tertiary radical (more stable) secondary radical (less stable)

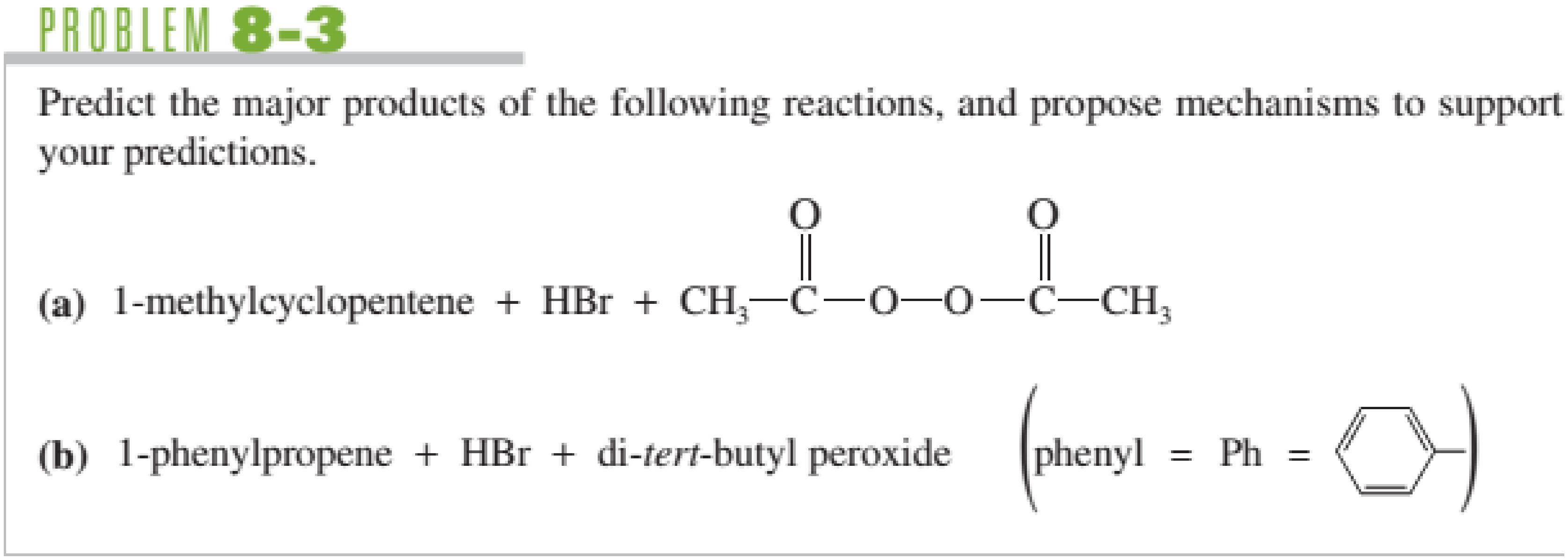
- As we saw in the protonation of an alkene, the electrophile (in this case,) adds to the less substituted end of the double bond, and the unpaired electron appears on the more substituted carbon to give the more stable free radical. This intermediate reacts with HBr to give the anti-Markovnikov product, in which H has added to the more substituted end of the double bond: the end that started with *fewer* hydrogens.



$$CH_3-\underset{\cdot}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{Br}{|}}{CH}-CH_3 + H-Br \longrightarrow CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{Br}{|}}{CH}-CH_3 + Br\cdot$$

anti-Markovnikov product

Chemical properties

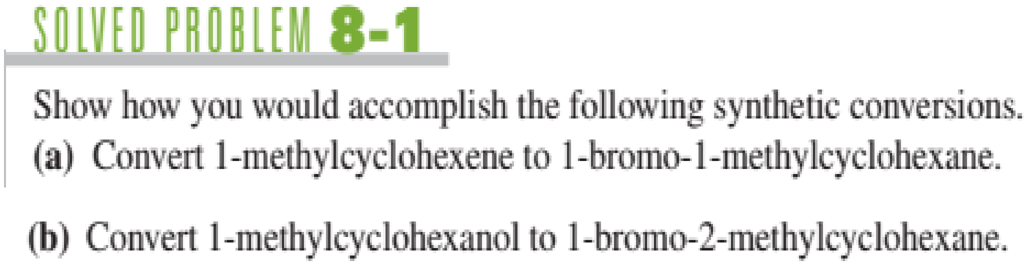


PROBLEM 8-3

Predict the major products of the following reactions, and propose mechanisms to support your predictions.

(a) 1-methylcyclopentene + HBr + $CH_3-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-CH_3$

(b) 1-phenylpropene + HBr + di-*tert*-butyl peroxide (phenyl = Ph =)



SOLVED PROBLEM 8-1

Show how you would accomplish the following synthetic conversions.

(a) Convert 1-methylcyclohexene to 1-bromo-1-methylcyclohexane.

(b) Convert 1-methylcyclohexanol to 1-bromo-2-methylcyclohexane.

Chemical properties

Note that *both* mechanisms for the addition of HBr to an alkene (with and without peroxides) follow the extended statement of Markovnikov's rule:

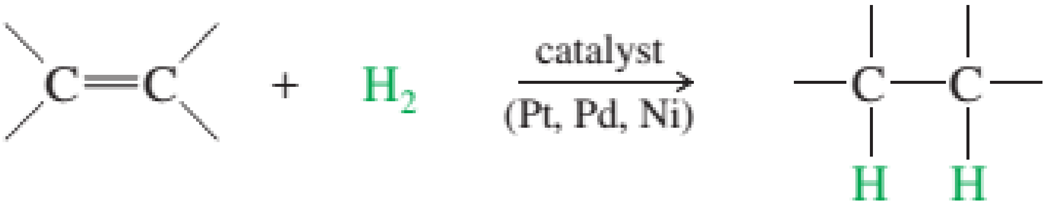
+ In both cases, the electrophile adds to the less substituted end of the double bond to give the more stable intermediate, either a carbocation or a free radical.

+ In the ionic reaction, the electrophile is an proton H^+

+ In the peroxide-catalyzed free-radical reaction, the radical $R^\cdot$ is the electrophile.

Catalytic hydrogenation of alkenes

- Hydrogenation of an alkene is formally a reduction, with adding across the double bond to give an alkane.
- The process usually requires a catalyst containing Pt, Pd, or Ni.



Example

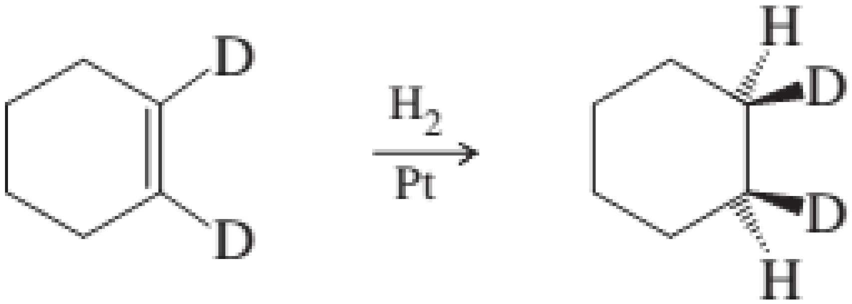
$$CH_3{-}CH{=}CH{-}CH_3 \quad + \quad H_2 \quad \xrightarrow{Pt} \quad CH_3{-}CH_2{-}CH_2{-}CH_3$$

- For most alkenes, hydrogenation takes place at room temperature, using hydrogen gas at atmospheric pressure.
- The alkene is usually dissolved in an alcohol, an alkane, or acetic acid. A small amount of platinum, palladium, or nickel catalyst is added, and the container is shaken or stirred while the reaction proceeds.
- Hydrogenation actually takes place at the surface of the metal, where the liquid solution of the alkene comes into contact with hydrogen and the catalyst.

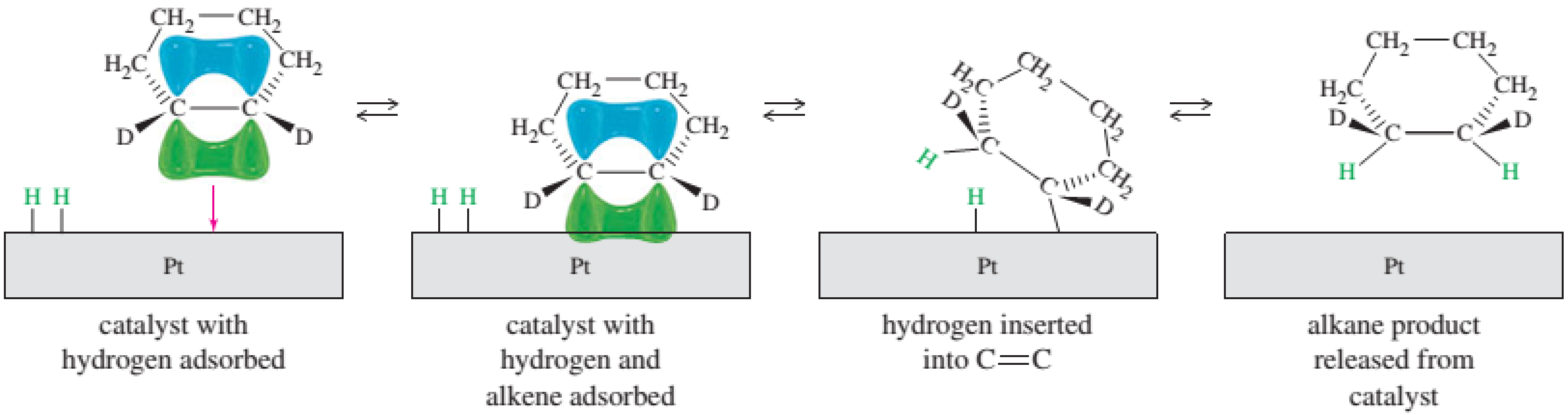
Heterogeneous catalysis

- Hydrogen gas is adsorbed onto the surface of these metal catalysts, and the catalyst weakens the bond.
- Hydrogenation is an example of **heterogeneous catalysis,** because the (solid) catalyst is in a different phase from the reactant solution.
- In contrast, **homogeneous catalysis** involves reactants and catalyst in the same phase, as in the acid-catalyzed dehydration of an alcohol.

- Because the two hydrogen atoms add from a solid surface, they add with **syn** stereochemistry. For example, when 1,2-deuteriocyclohexene is treated with hydrogen gas over a catalyst, the product is the cis isomer resulting from syn addition.

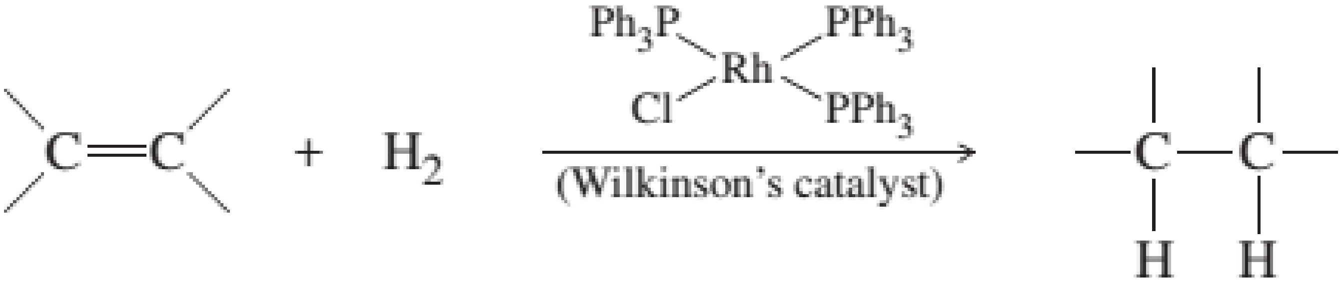


- One face of the alkene pi bond binds to the catalyst, which has hydrogen adsorbed on its surface. Hydrogen inserts into the pi bond, and the product is freed from the catalyst. Both hydrogen atoms add to the face of the double bond that is complexed with the catalyst.



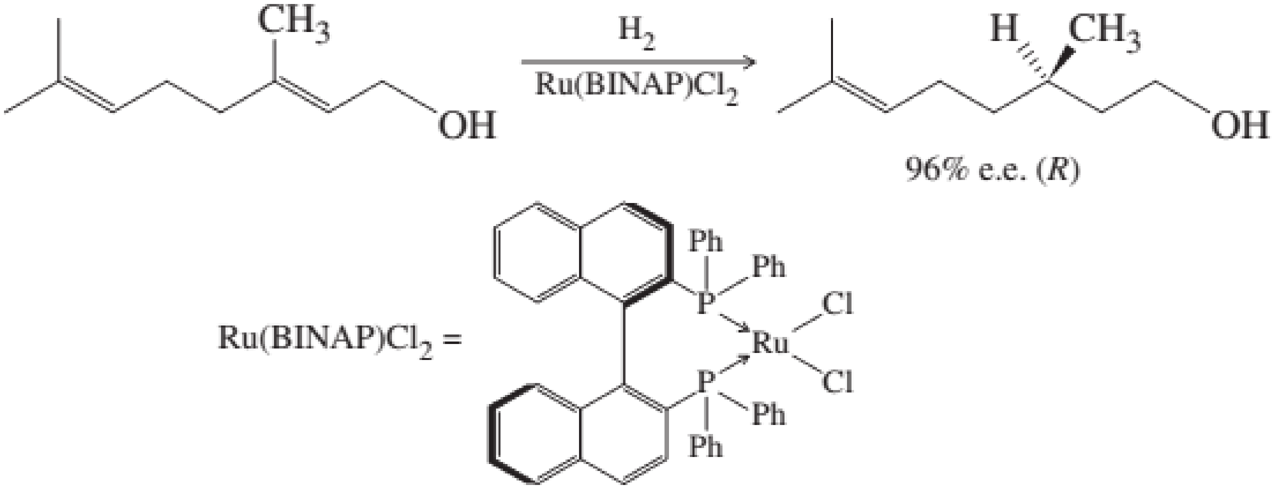
Homogeneous catalysis

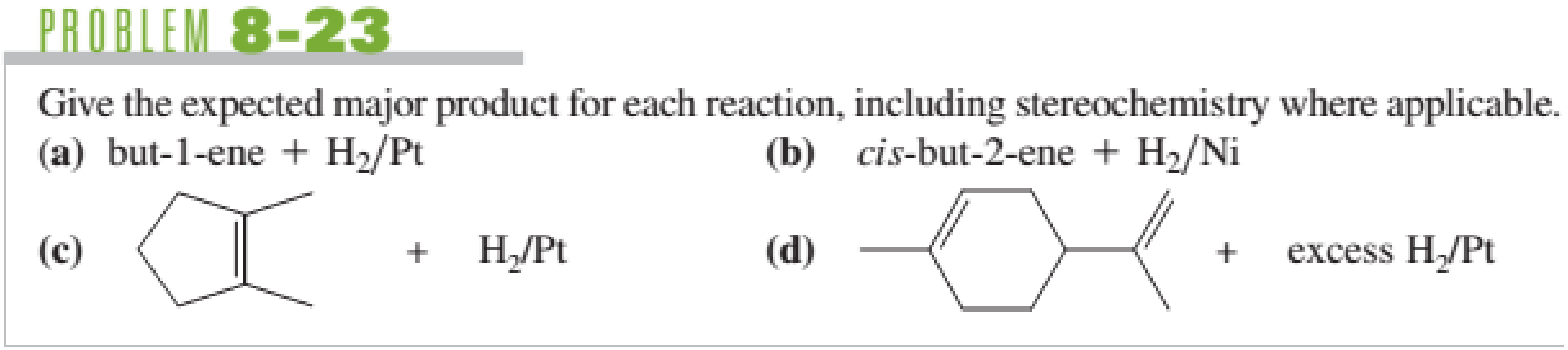
- Soluble homogeneous catalysts, such as *Wilkinson's catalyst*, also catalyze the hydrogenation of carbon–carbon double bonds.



- Wilkinson's catalyst is not chiral, but its triphenylphosphine ligands can be replaced by chiral ligands to give chiral catalysts that are capable of converting optically inactive starting materials to optically active products. Such a process is called **asymmetric induction** or **enantioselective synthesis.**
- For example, the figure below shows a chiral ruthenium complex catalyzing an enantioselective hydrogenation of a carbon–carbon double bond to give a large excess of one enantiomer. Because the catalyst is chiral, the transition states leading to the two enantiomers of product are diastereomeric. They have different energies, and the transition state leading to the (*R*) enantiomer is favored.
- Ryoji Noyori and William Knowles shared the 2001 Nobel Prize in Chemistry for their work on chirally catalyzed hydrogenation reactions.

- Enantioselective synthesis is particularly important in the pharmaceutical industry, because only one enantiomer of a chiral drug is likely to have the desired effect. For example, levodopa [(-) or *l*-dopa] is used in patients with Parkinson's disease to counteract a deficiency of dopamine, one of the neurotransmitters in the brain.
- Dopamine itself is useless as a drug because it cannot cross the "blood–brain barrier"; that is, it cannot get into the cerebrospinal fluid from the bloodstream. on the other hand, is an amino acid related to tyrosine. It crosses the blood–brain barrier into the cerebrospinal fluid, where it undergoes enzymatic conversion to dopamine. Only the enantiomer of dopa can be transformed into dopamine; the other enantiomer, is toxic to the patient.





PROBLEM 8-23

Give the expected major product for each reaction, including stereochemistry where applicable.

(a) but-1-ene + H_2/Pt

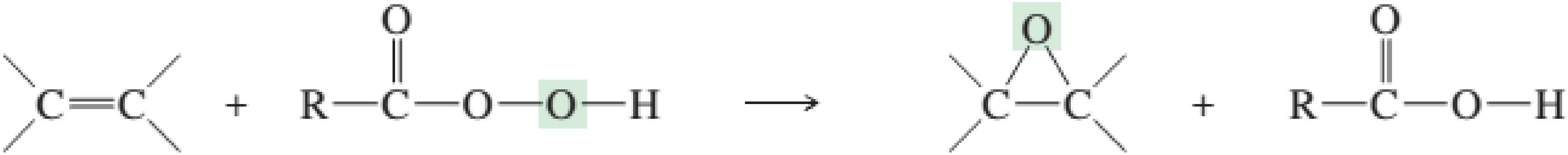
(b) *cis*-but-2-ene + H_2/Ni

(c) + H_2/Pt

(d) + excess H_2/Pt

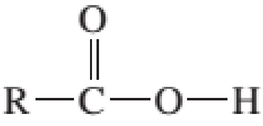
Epoxide

- An **epoxide** is a three-membered cyclic ether, also called an **oxirane.**
- An alkene is converted to an epoxide by a **peroxyacid,** a carboxylic acid that has an extra oxygen atom in a (peroxy) linkage.



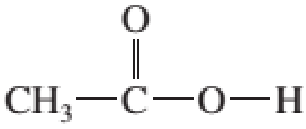
alkene peroxyacid epoxide (oxirane) acid

- Some simple peroxyacids (sometimes called *peracids*) and their corresponding carboxylic acids are shown next.



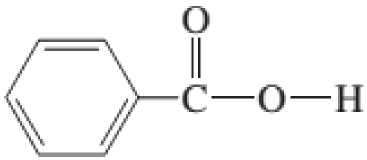
$R-\overset{O}{\overset{\|}{C}}-O-H$

a carboxylic acid

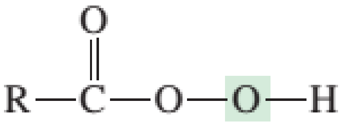


$CH_3-\overset{O}{\overset{\|}{C}}-O-H$

acetic acid

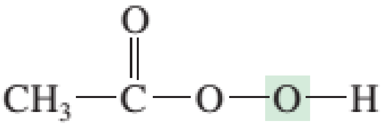


benzoic acid, $PhCO_2H$



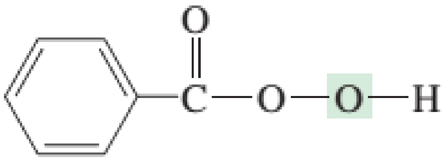
$R-\overset{O}{\overset{\|}{C}}-O-O-H$

a peroxyacid

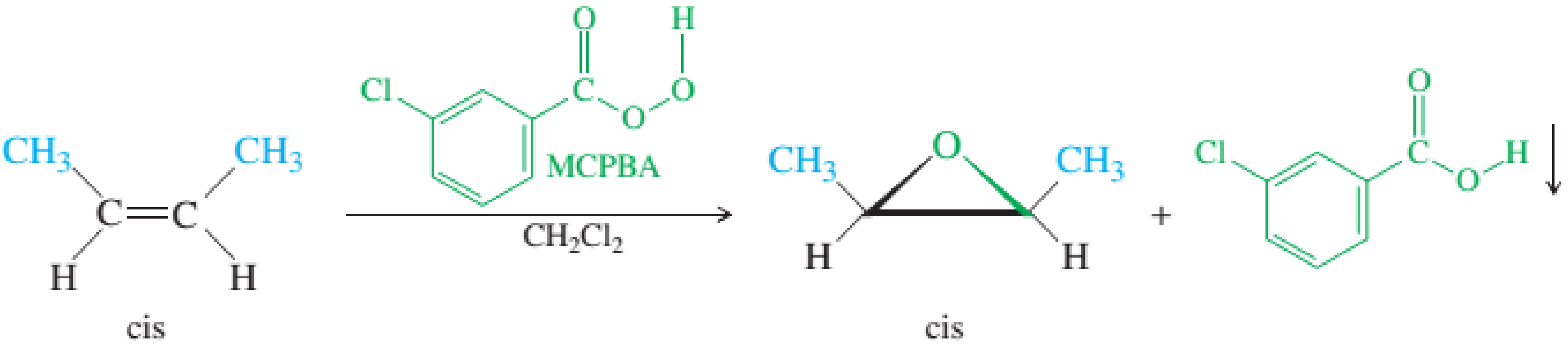


$CH_3-\overset{O}{\overset{\|}{C}}-O-O-H$

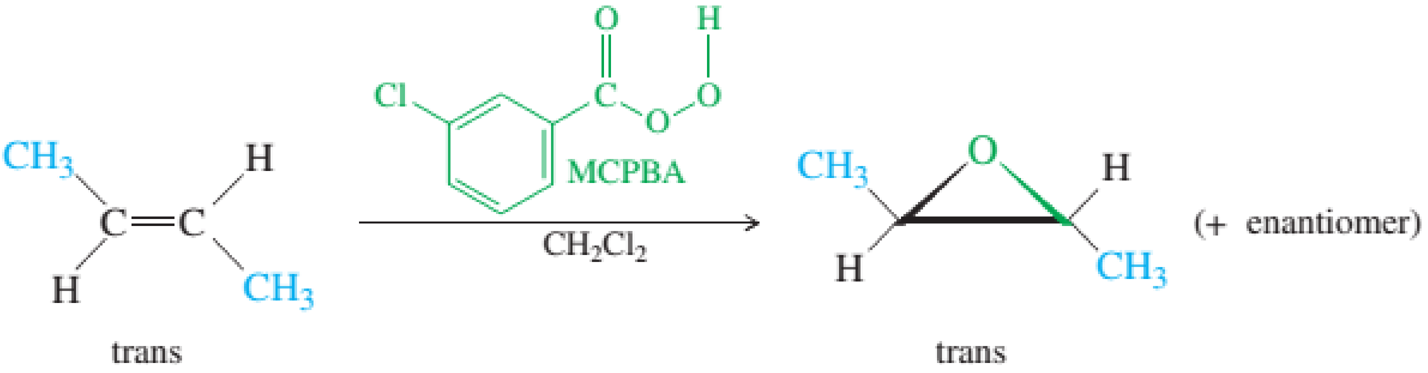
peroxyacetic acid



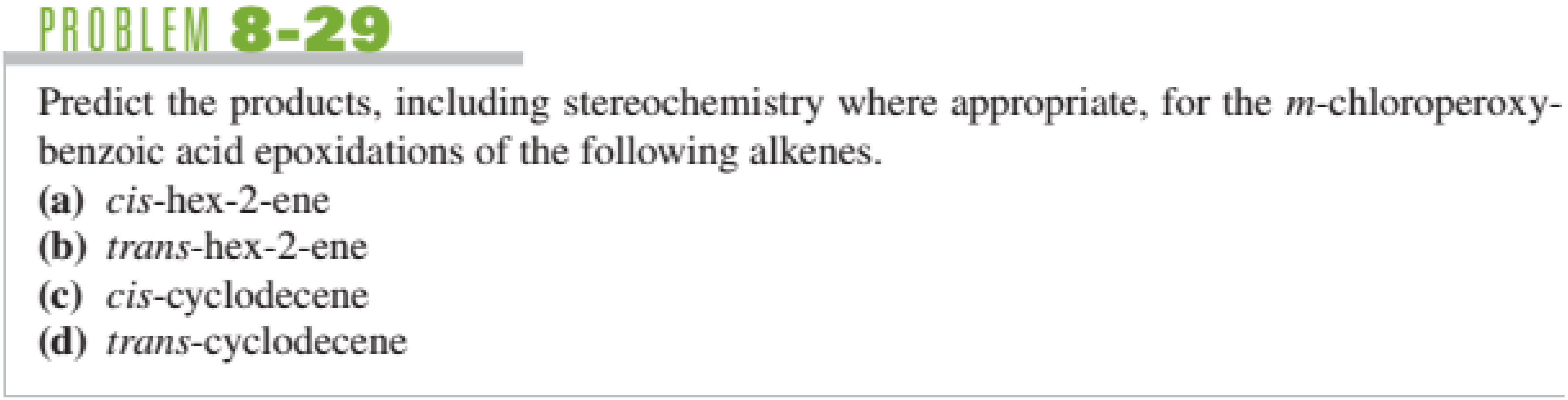
peroxybenzoic acid, $PhCO_3H$



MCPBA
CH$_2$Cl$_2$
cis
cis



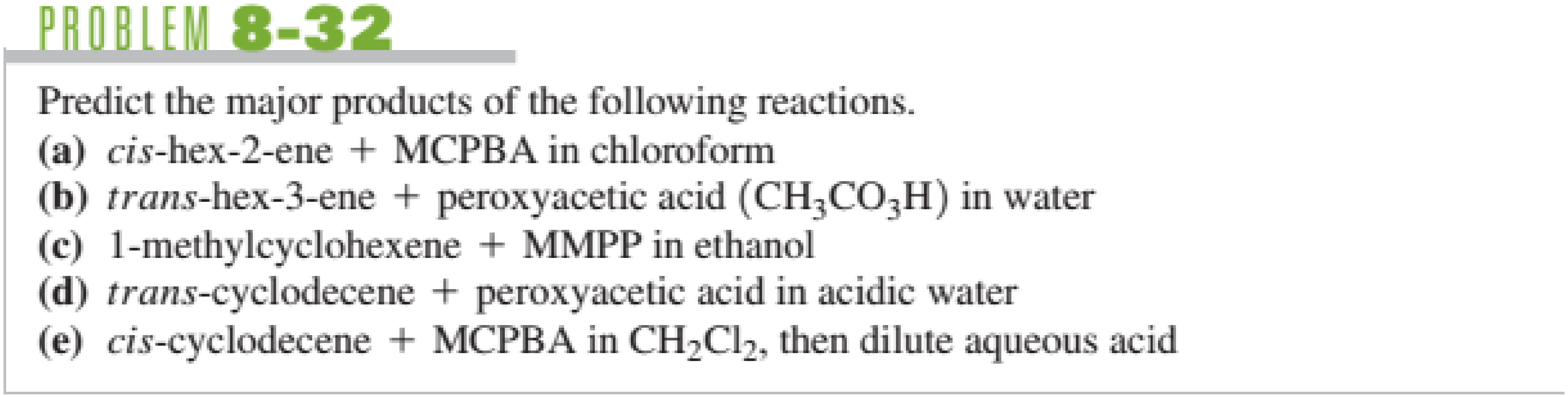
MCPBA
CH$_2$Cl$_2$
(+ enantiomer)
trans
trans



PROBLEM 8-29

Predict the products, including stereochemistry where appropriate, for the *m*-chloroperoxybenzoic acid epoxidations of the following alkenes.

(a) *cis*-hex-2-ene
(b) *trans*-hex-2-ene
(c) *cis*-cyclodecene
(d) *trans*-cyclodecene



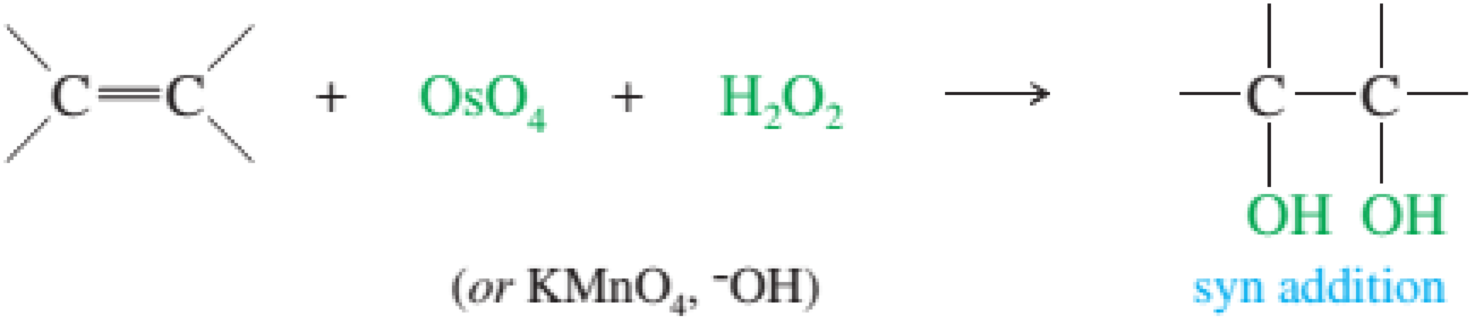
PROBLEM 8-32

Predict the major products of the following reactions.

(a) *cis*-hex-2-ene + MCPBA in chloroform
(b) *trans*-hex-3-ene + peroxyacetic acid (CH_3CO_3H) in water
(c) 1-methylcyclohexene + MMPP in ethanol
(d) *trans*-cyclodecene + peroxyacetic acid in acidic water
(e) *cis*-cyclodecene + MCPBA in CH_2Cl_2, then dilute aqueous acid

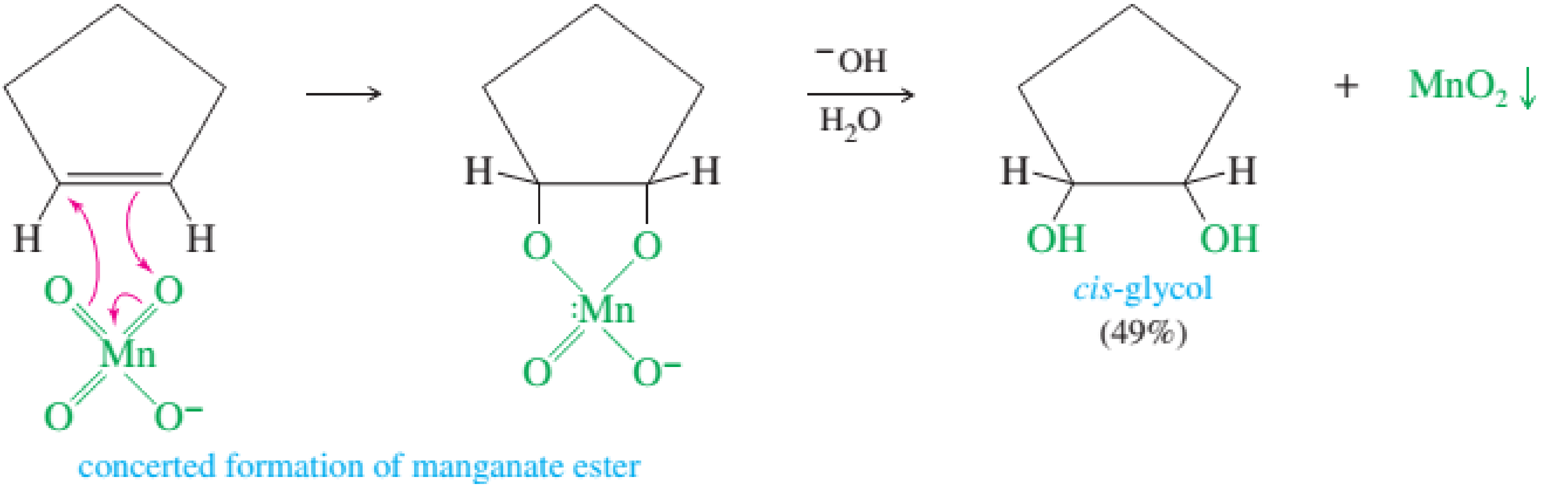
Syn-dihydroxylation of alkenes

- Converting an alkene to a glycol requires adding a hydroxyl group to each end of the double bond.
- This addition is called **dihydroxylation** of the double bond.
- Reagents are available for the dihydroxylation of alkenes with *syn* stereochemistry. The two most common reagents for this purpose are **osmium tetroxide (OsO_4)** and **potassium permanganate ($KMnO_4$)**.

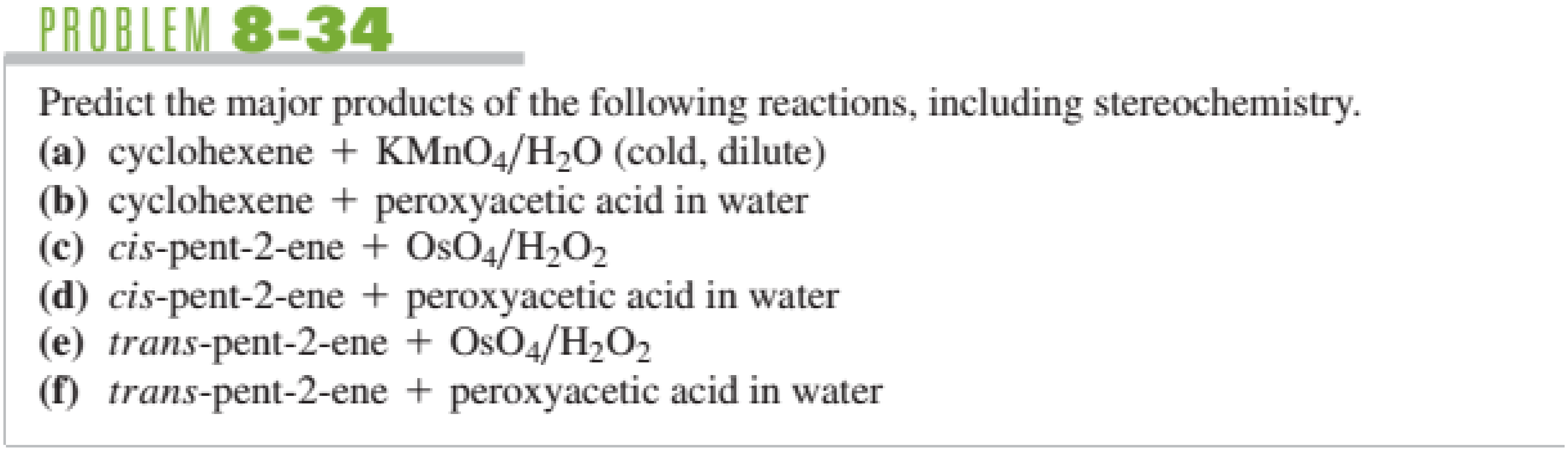


Permanganate Dihydroxylation

- Osmium tetroxide is expensive, highly toxic, and volatile.
- A cold, dilute solution of potassium permanganate also hydroxylates alkenes with syn stereochemistry, with slightly reduced yields in most cases.
- Permanganate adds to the alkene double bond to form a cyclic ester: a manganate ester in this case.
- The basic solution hydrolyzes the manganate ester, liberating the glycol and producing a brown precipitate of manganese dioxide, MnO_2.



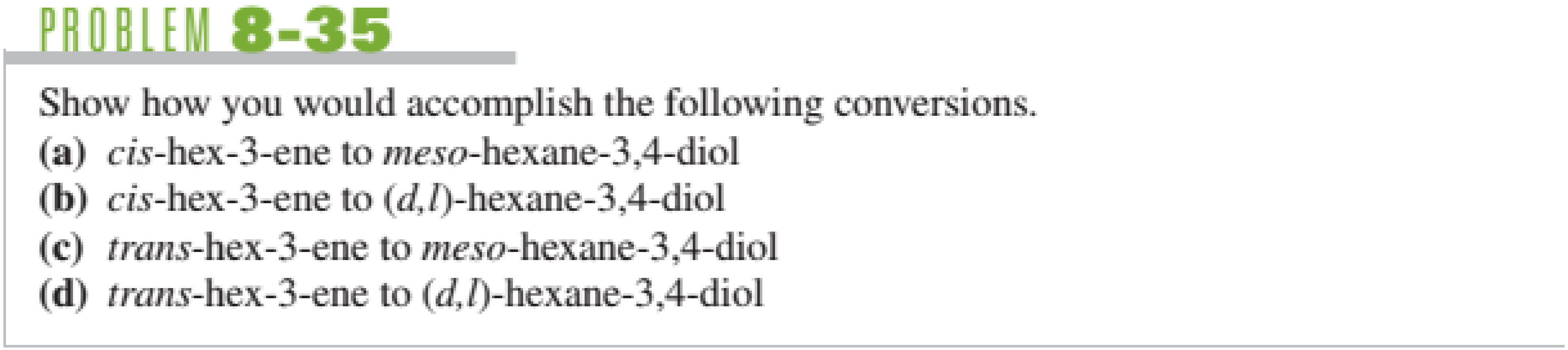
- In addition to its synthetic value, the permanganate oxidation of alkenes provides a simple chemical test for the presence of an alkene. When an alkene is added to a clear, deep purple aqueous solution of potassium permanganate, the solution loses its purple color and becomes the murky, opaque brown color of MnO_2.



PROBLEM 8-34

Predict the major products of the following reactions, including stereochemistry.

(a) cyclohexene + $KMnO_4/H_2O$ (cold, dilute)
(b) cyclohexene + peroxyacetic acid in water
(c) *cis*-pent-2-ene + OsO_4/H_2O_2
(d) *cis*-pent-2-ene + peroxyacetic acid in water
(e) *trans*-pent-2-ene + OsO_4/H_2O_2
(f) *trans*-pent-2-ene + peroxyacetic acid in water



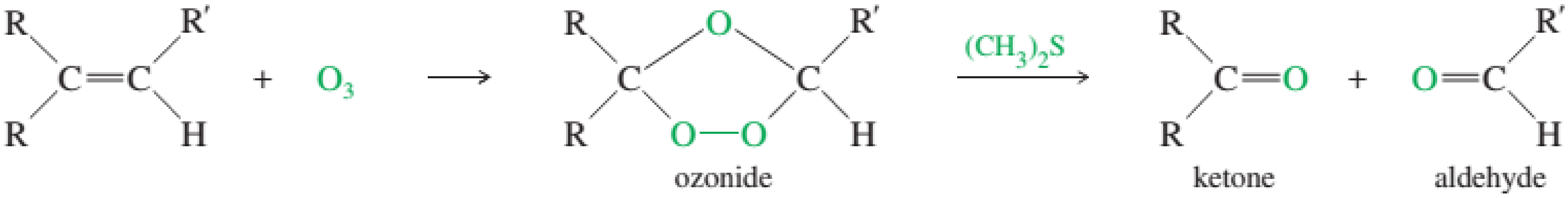
PROBLEM 8-35

Show how you would accomplish the following conversions.

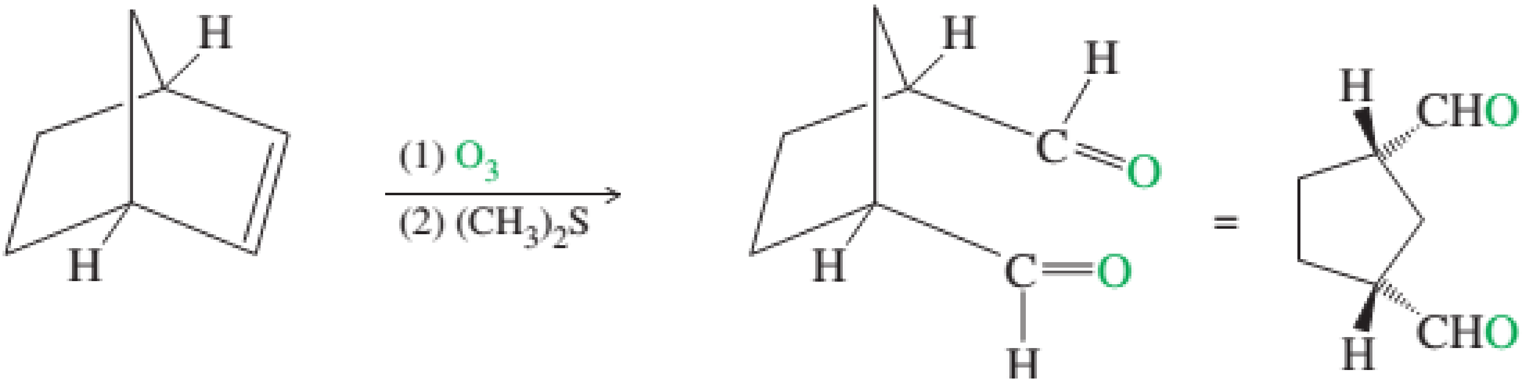
(a) *cis*-hex-3-ene to *meso*-hexane-3,4-diol
(b) *cis*-hex-3-ene to (*d,l*)-hexane-3,4-diol
(c) *trans*-hex-3-ene to *meso*-hexane-3,4-diol
(d) *trans*-hex-3-ene to (*d,l*)-hexane-3,4-diol

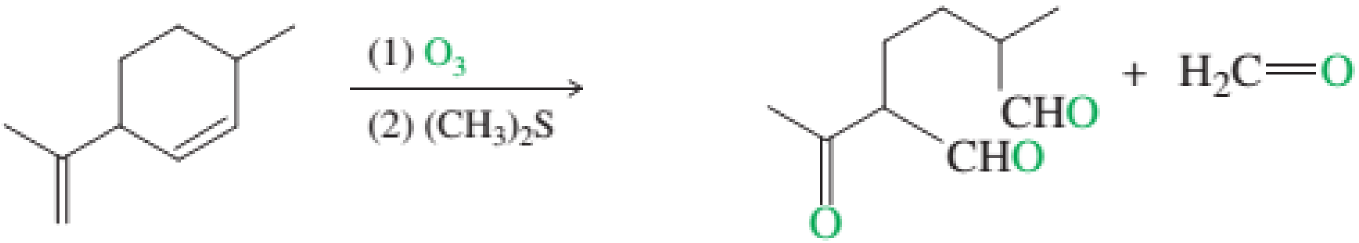
Ozonolysis

- Ozone cleaves double bonds to give ketones and aldehydes.

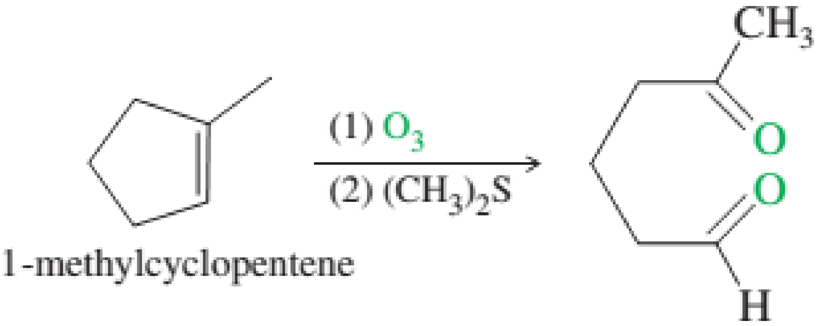


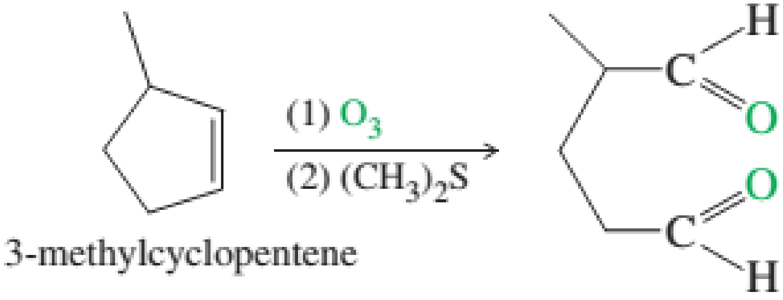

non-3-ene
(1) O_3
(2) $(CH_3)_2S$
CH_3CH_2CHO + $CH_3(CH_2)_4CHO$
(65%)


H
H
(1) O_3
(2) $(CH_3)_2S$
H
H
H
C
O
C
O
H
=
H
CHO
H
CHO


(1) O_3
(2) $(CH_3)_2S$
CHO
CHO
O
+ $H_2C{=}O$

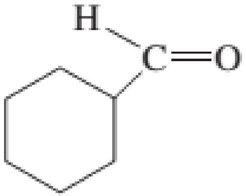
- One of the most common uses of ozonolysis has been for **determining the positions of double bonds in alkenes**.
- For example, if we were uncertain of the position of the methyl group in a methylcyclopentene, the products of ozonolysis–reduction would confirm the structure of the original alkene.



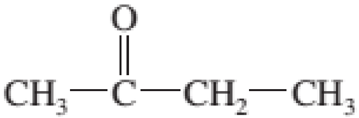


SOLVED PROBLEM 8-7

Ozonolysis–reduction of an unknown alkene gives an equimolar mixture of cyclohexanecarbaldehyde and butan-2-one. Determine the structure of the original alkene.



cyclohexanecarbaldehyde

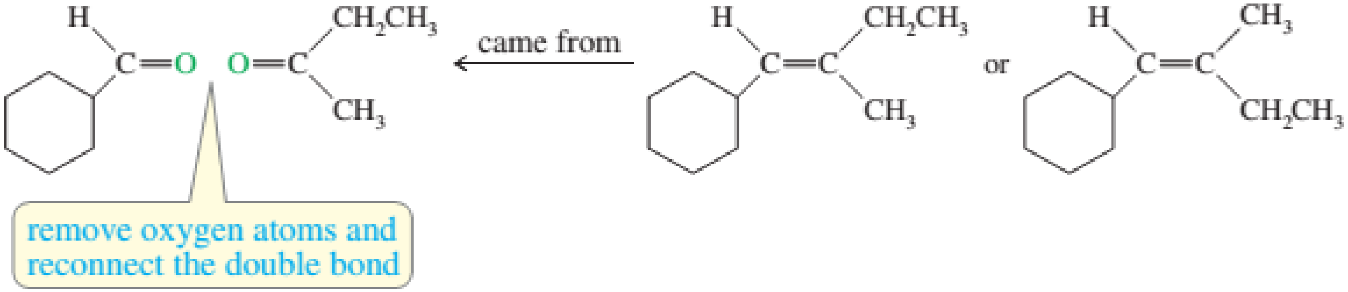


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

butan-2-one

SOLUTION

We can reconstruct the alkene by removing the two oxygen atoms of the carbonyl groups (C═O) and connecting the remaining carbon atoms with a double bond. One uncertainty remains, however: The original alkene might be either of two possible geometric isomers.

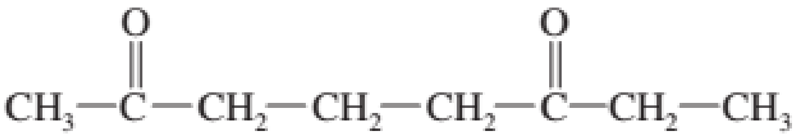


remove oxygen atoms and reconnect the double bond

PROBLEM 8-36

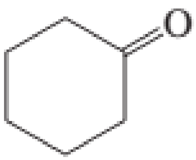
Give structures of the alkenes that would give the following products upon ozonolysis–reduction.

(a)



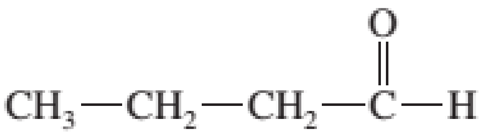
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

(b)



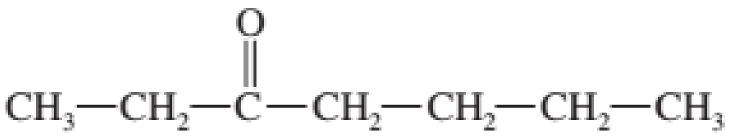
cyclohexanone

and



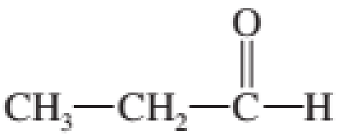
$$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H$$

(c)



$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_3$$

and

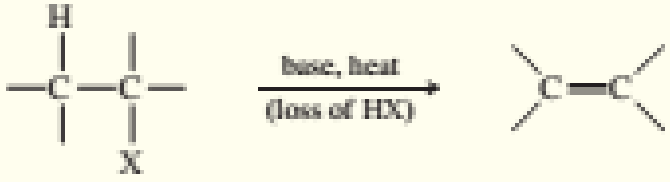


$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$$

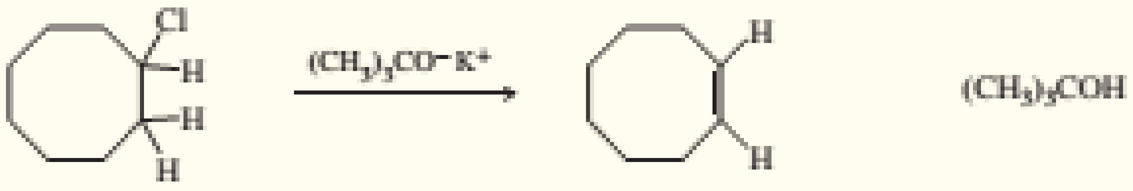
Alkene synthesis

SUMMARY Methods for Synthesis of Alkenes

1. *Dehydrohalogenation of alkyl halides* (Section 7-9)



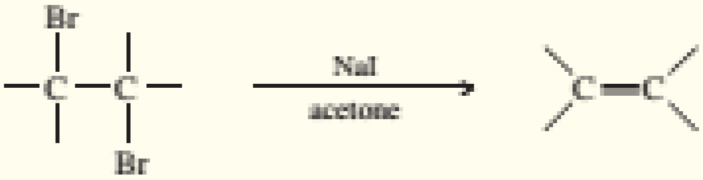
Example



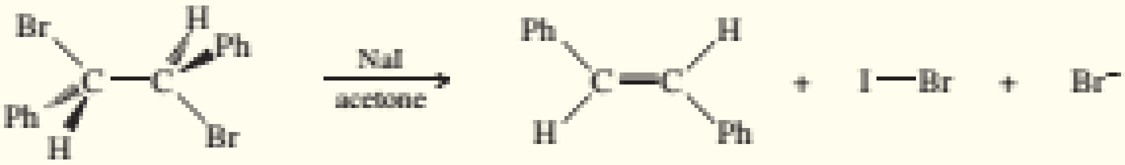
chlorocyclooctane

cyclooctene

2. *Dehalogenation of vicinal dibromides* (Section 7-9D)

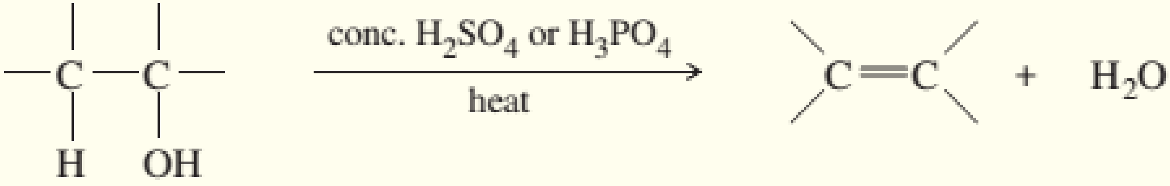


Example

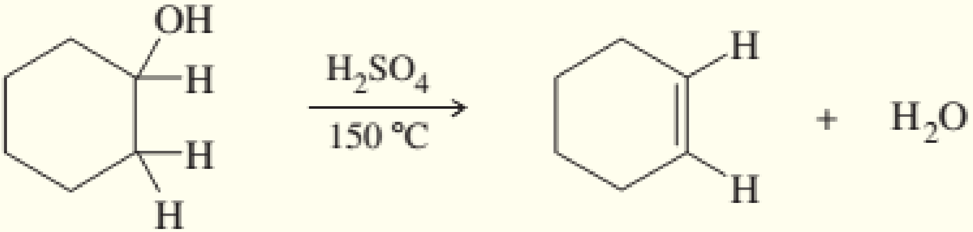


Alkene synthesis

3. *Dehydration of alcohols* (Section 7-10)

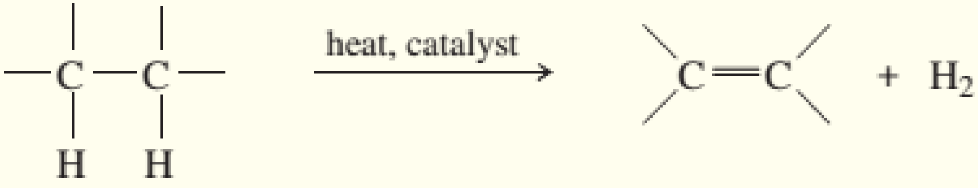


Example



cyclohexanol cyclohexene

4. *Dehydrogenation of alkanes* (Section 7-11B)



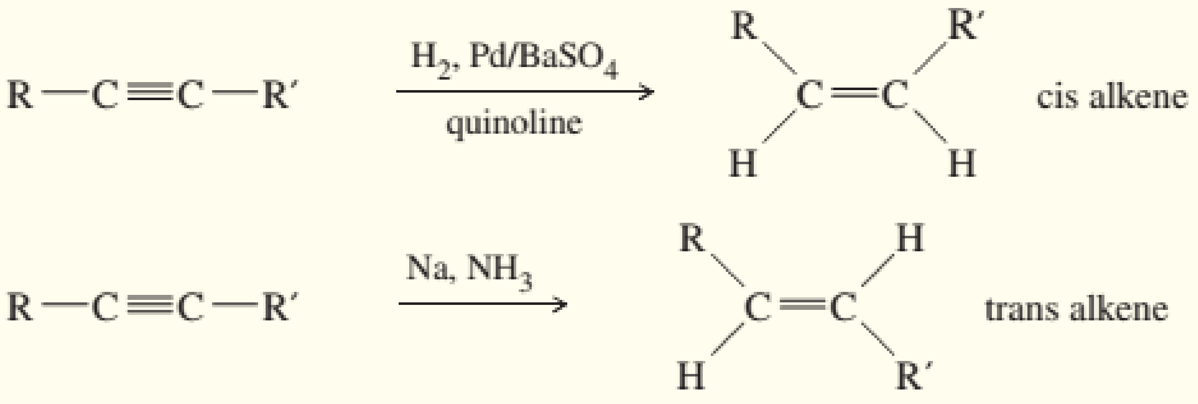
(Industrial prep, useful only for small alkenes; commonly gives mixtures.)

Example

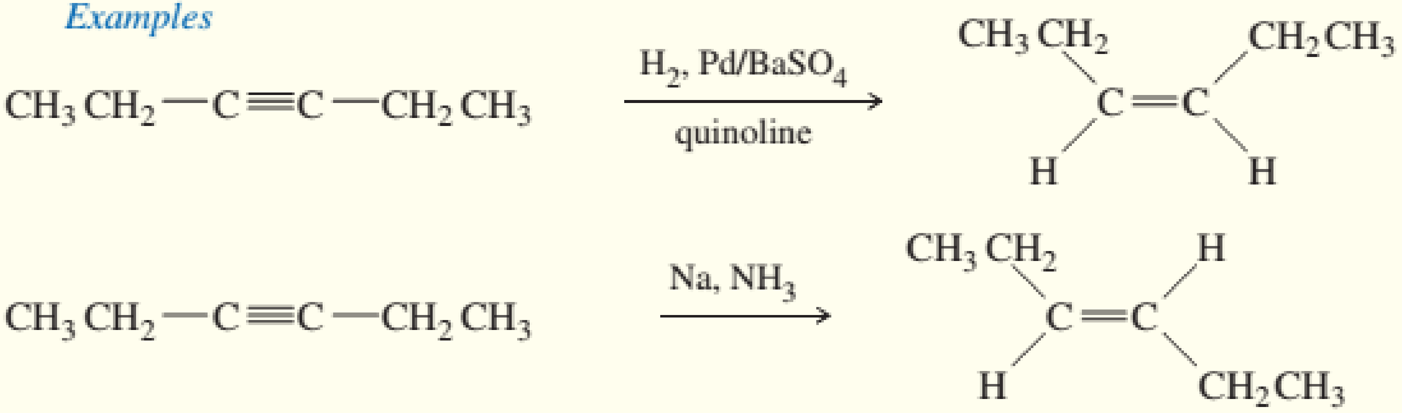
$$CH_3CH_2CH_2CH_3 \xrightarrow{\text{Pt, 500 °C}} \begin{cases} \text{but-1-ene} + \textit{cis-}\text{ and }\textit{trans-}\text{but-2-ene} + \\ \text{buta-1,3-diene} + H_2 \end{cases}$$

Alkene synthesis by the reduction of alkynes

6. *Reduction of alkynes* (Section 9-9)

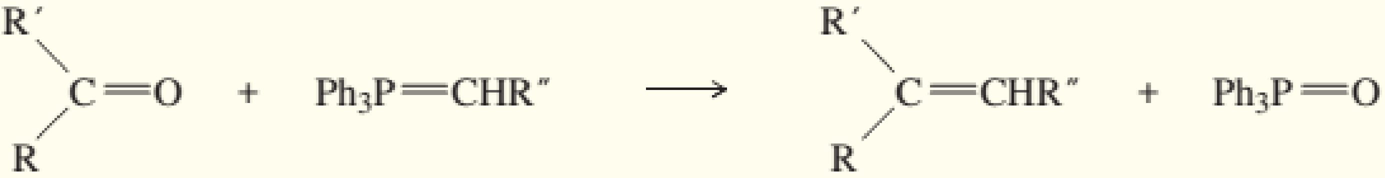


Examples

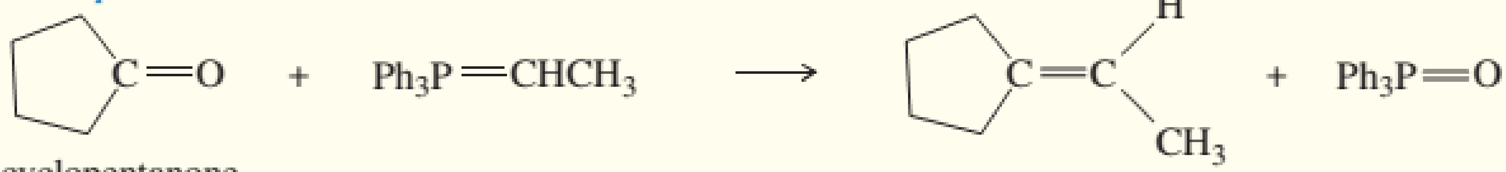


Alkene synthesis by the Wittig reaction

7. *Wittig reaction* (Section 18-12)



Example



cyclopentanone

Uses and sources of alkenes: Commercial important of alkenes

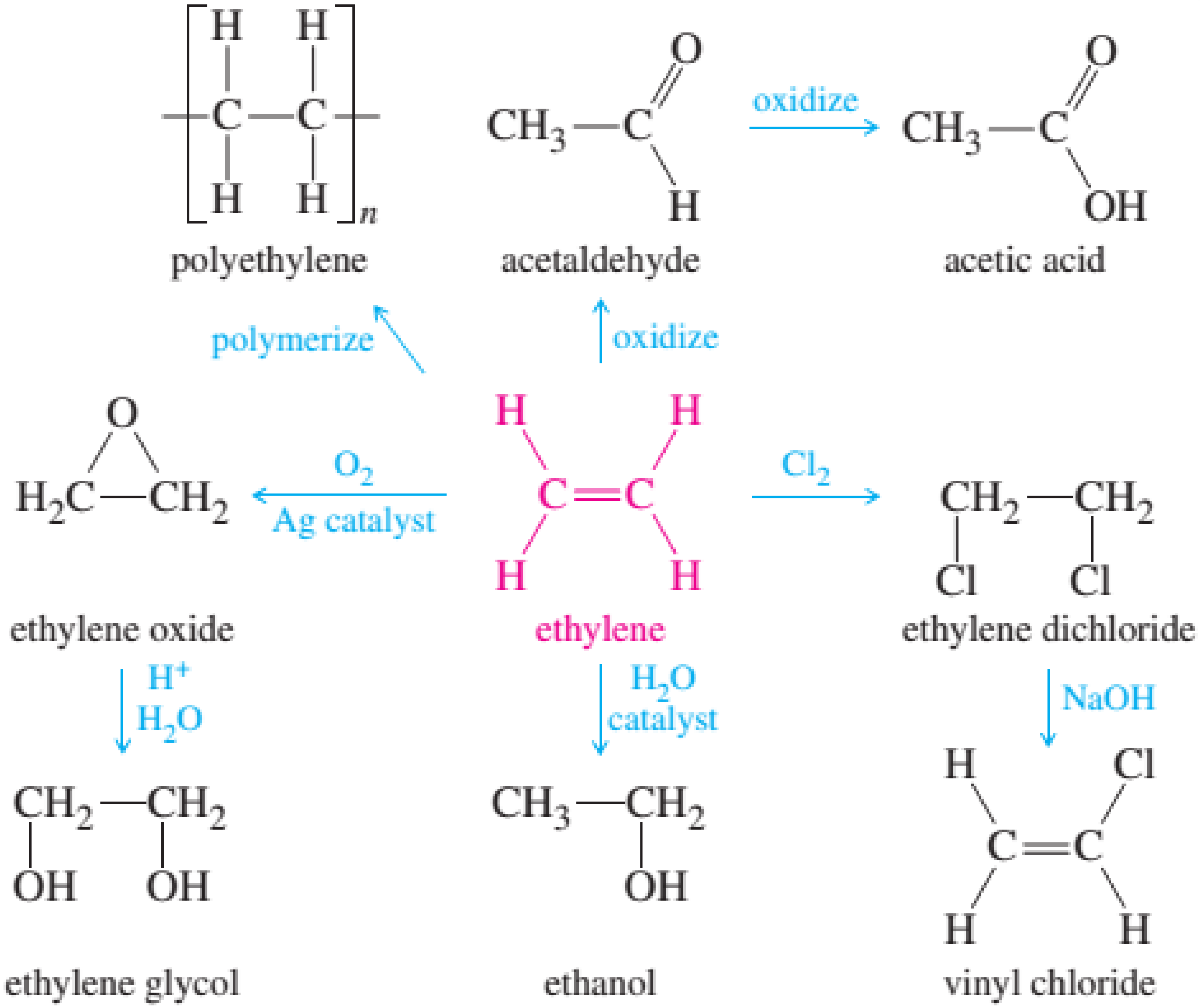
- Because the carbon–carbon double bond is readily converted to other functional groups, alkenes are important intermediates in the synthesis of polymers, drugs, pesticides, and other valuable chemicals.
- Ethylene is the organic compound produced in the largest volume, at around 160 billion pounds per year worldwide.

+ Most of this ethylene is polymerized to form about 90 billion pounds of polyethylene per year.

+ The remainder is used to synthesize a wide variety of organic chemicals including ethanol, acetic acid, ethylene glycol, and vinyl chloride.

+ Ethylene also serves as a plant hormone, accelerating the ripening of fruit. For example, tomatoes are harvested and shipped while green, then treated with ethylene to make them ripen and turn red just before they are placed on display.

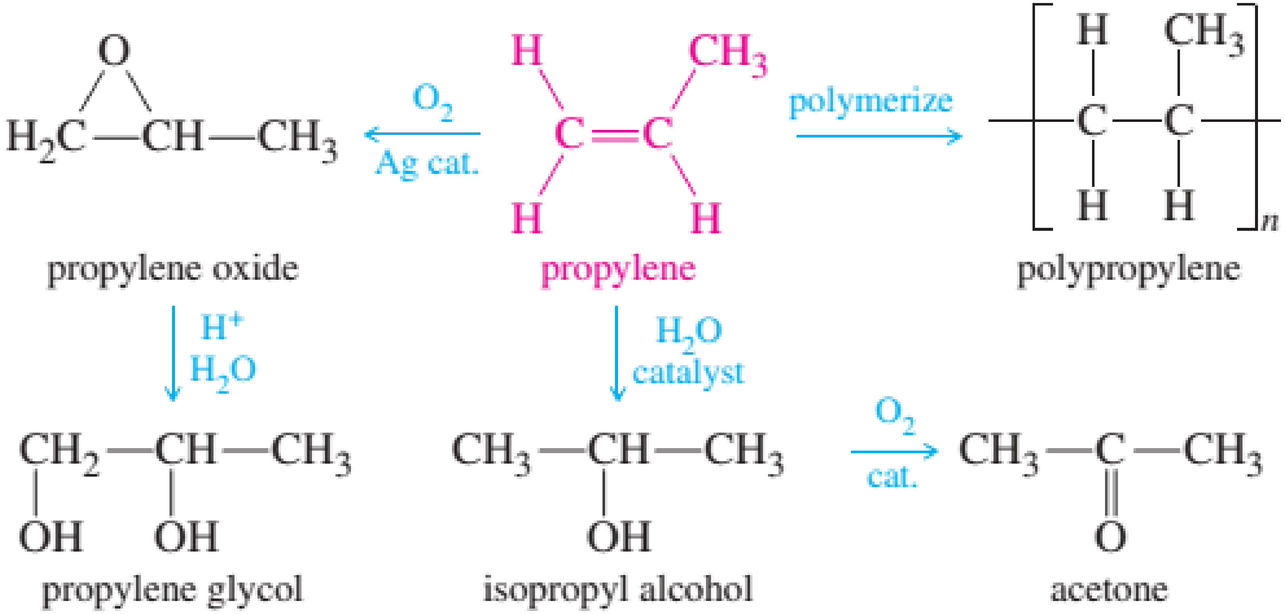
Uses and sources of alkanes



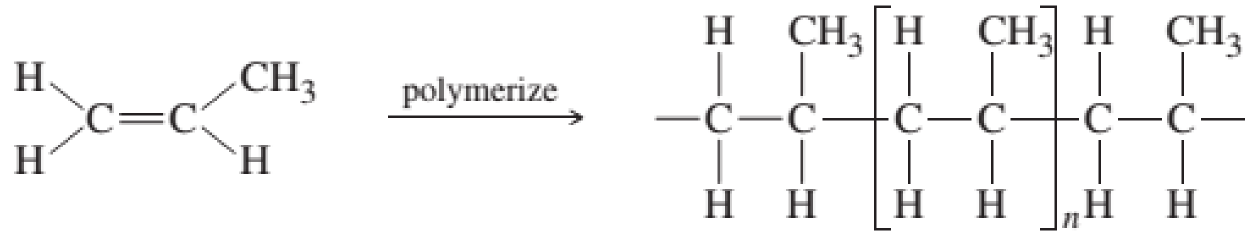
Alkene sources

- Propylene is produced at the rate of about 90 billion pounds per year worldwide, with much of that going to make about 40 billion pounds of polypropylene. The rest is used to make propylene glycol, acetone, isopropyl alcohol, and a variety of other useful organic chemicals.
- Many common polymers are made by polymerizing alkenes. These polymers are used in consumer products from shoes to plastic bags to car bumpers.
- A **polymer** (Greek, *poly*, “many,” and *meros*, “parts”) is a large molecule made up of many **monomer** (Greek, *mono*, “one”) molecules.
- An alkene monomer can **polymerize** by a chain reaction where additional alkene molecules add to the end of the growing polymer chain.

- The figure below shows some addition polymers made from simple alkenes and haloalkenes.

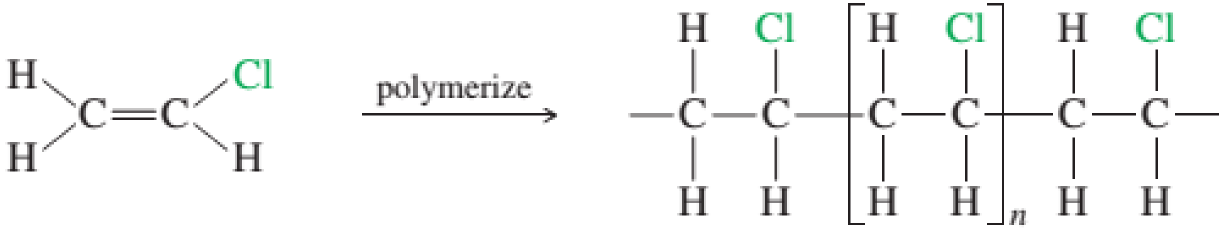


Uses of propylene. Most propylene is polymerized to make polypropylene. It is also used to make several important three-carbon compounds.



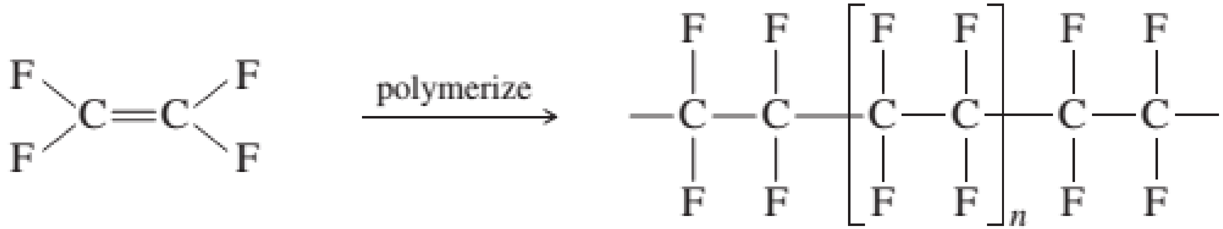
propylene (monomer)

polypropylene (polymer)



vinyl chloride

poly(vinyl chloride)
PVC, "vinyl"



tetrafluoroethylene

poly(tetrafluoroethylene)
PTFE, Teflon®

Alkenes polymerize to form addition polymers. Many common polymers are produced this way.