Reactions of Alkenes

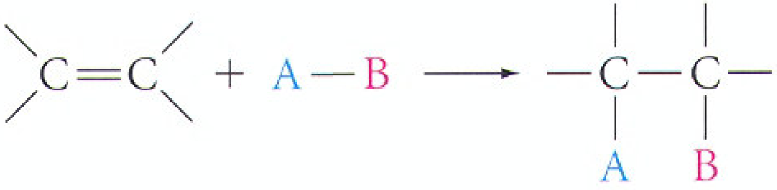
3.6 Addition & Substitution Reactions Compared

We saw in Chapter 2 that, aside from combustion, the most common reaction of alkanes is **substitution** (for example, halogenation). This reaction type can be expressed by a general equation.

$$R\text{—}H + A\text{—}B \longrightarrow R\text{—}A + H\text{—}B \qquad (3.3)$$

where R—H stands for an alkane and A—B may stand for the halogen molecule.

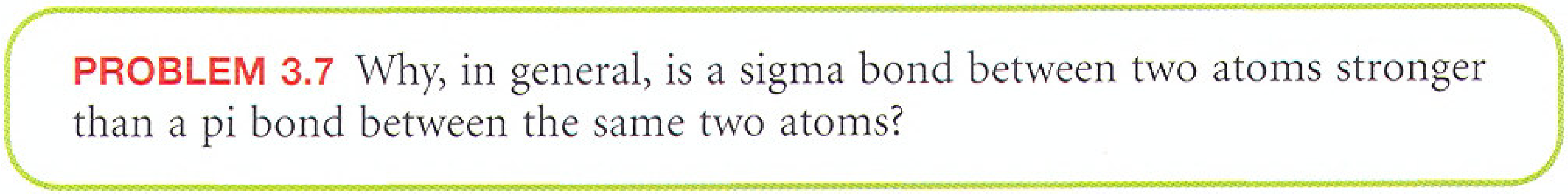
With alkenes, on the other hand, the most common reaction is **addition:**



(3.4)

Generally the reaction is exothermic because one π and one σ bond are converted to two σ bonds

Question & Answer



PROBLEM 3.7 Why, in general, is a sigma bond between two atoms stronger than a pi bond between the same two atoms?

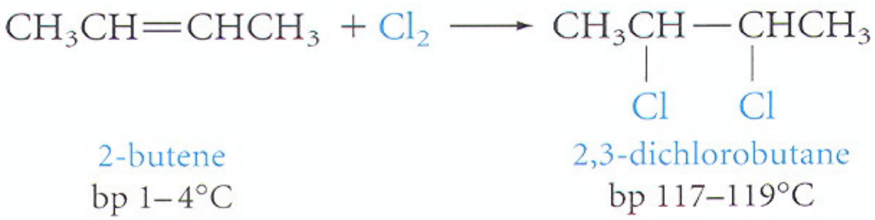
The electron pair in a σ bond lies directly between the nuclei it joins. In a π bond, the electron pair is further from the two nuclei that it joins. Therefore more energy is required to break a σ bond than a π bond.

3.7 Polar Addition Reactions

Several reagents add to double bonds by a two-step polar process. In this section, we will describe examples of this reaction type, after which we will consider details of the reaction mechanism.

3.7.a Addition of Halogens

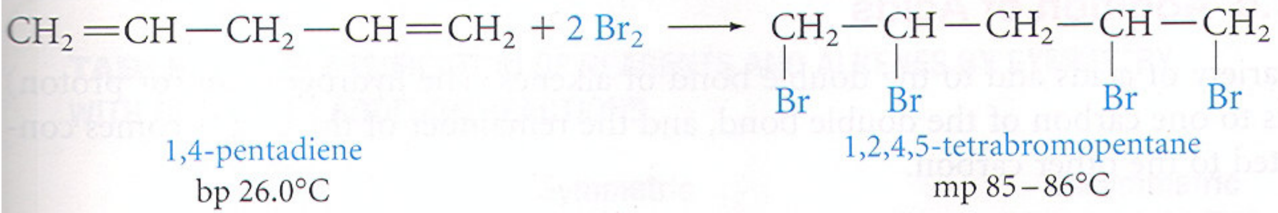
Alkenes readily add chlorine or bromine.



$$\mathrm{CH_3CH{=}CHCH_3} + \mathrm{Cl_2} \longrightarrow \mathrm{CH_3}\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}\mathrm{CH_3} \qquad (3.5)$$

2-butene
bp 1–4°C

2,3-dichlorobutane
bp 117–119°C



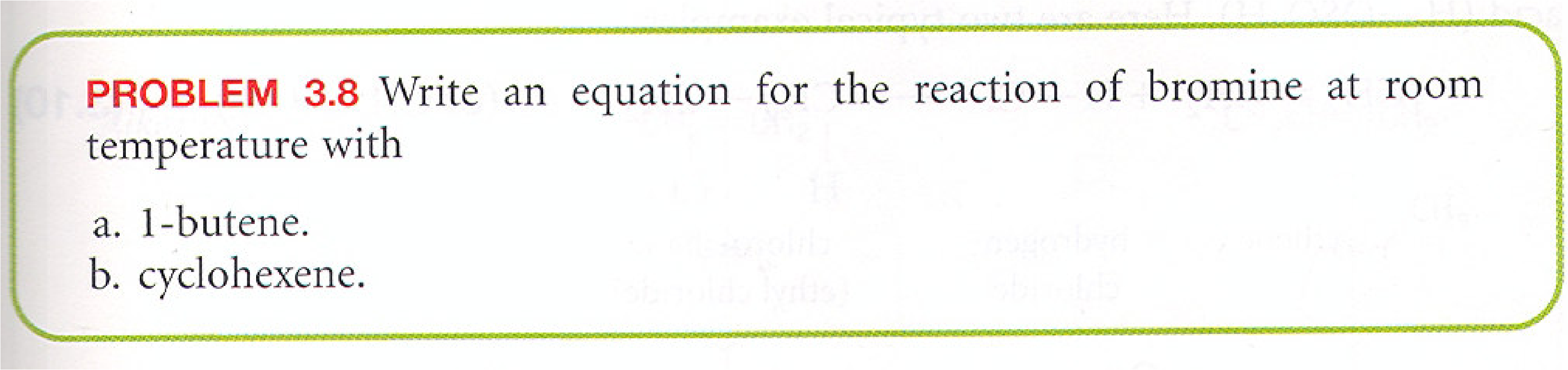
$$\mathrm{CH_2{=}CH{-}CH_2{-}CH{=}CH_2} + 2\,\mathrm{Br_2} \longrightarrow \underset{\mathrm{Br}}{\underset{|}{\mathrm{CH_2}}}-\underset{\mathrm{Br}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{Br}}{\underset{|}{\mathrm{CH}}}-\underset{\mathrm{Br}}{\underset{|}{\mathrm{CH_2}}} \qquad (3.6)$$

1,4-pentadiene
bp 26.0°C

1,2,4,5-tetrabromopentane
mp 85–86°C

Usually the halogen is dissolved in some inert solvent such as tri- or tetrachloromethane, and then this solution is added dropwise to the alkene. Reaction is nearly instantaneous, even at room temperature or below. No light or heat is required, as in the case of substitution reactions.

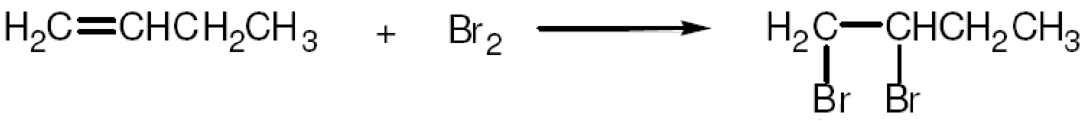
Q&A



PROBLEM 3.8 Write an equation for the reaction of bromine at room temperature with

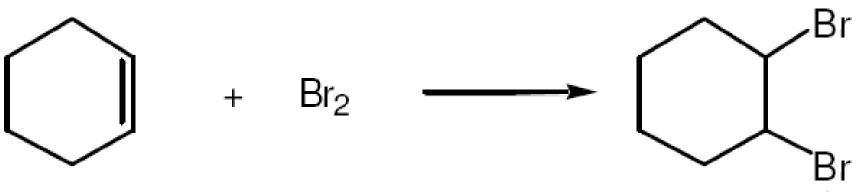
a. 1-butene.
b. cyclohexene.

a. One bromine atom adds to each doubly bonded carbon, and the double bond in the starting material becomes a single bond in the product:



$$H_2C{=}CHCH_2CH_3 + Br_2 \longrightarrow H_2\underset{Br}{\underset{|}{C}}{-}\underset{Br}{\underset{|}{C}}HCH_2CH_3$$

b.



Br_2/CCl_4 Unsaturation Test

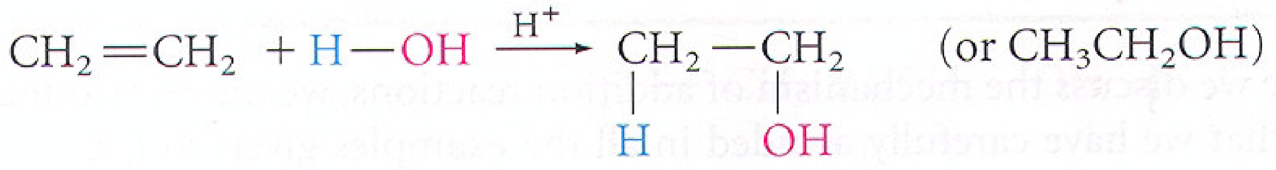
The addition of brom
saturation in an organic co
reddish-brown, and the u
both colorless. As the bro
bromine color disappears.
with bromine under these

test for the presence of un-
tetrachloromethane are dark
bromine adduct are usually
unsaturated compound, the
is saturated, it will not react
persist.

Bromine solution (red-brown) is added to a saturated hydrocarbon (left) and an unsaturated hydrocarbon (right).

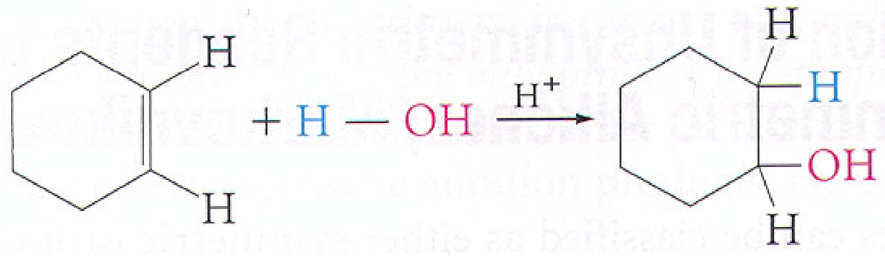
3.7.b Addition of Water (Hydration)

If an acid catalyst is present, water adds to alkenes. It adds as H—OH, and the products are alcohols.



$$CH_2{=}CH_2 + H{-}OH \xrightarrow{H^+} \underset{H}{\underset{|}{CH_2}}{-}\underset{OH}{\underset{|}{CH_2}} \qquad (\text{or } CH_3CH_2OH) \qquad \textbf{(3.7)}$$

ethanol



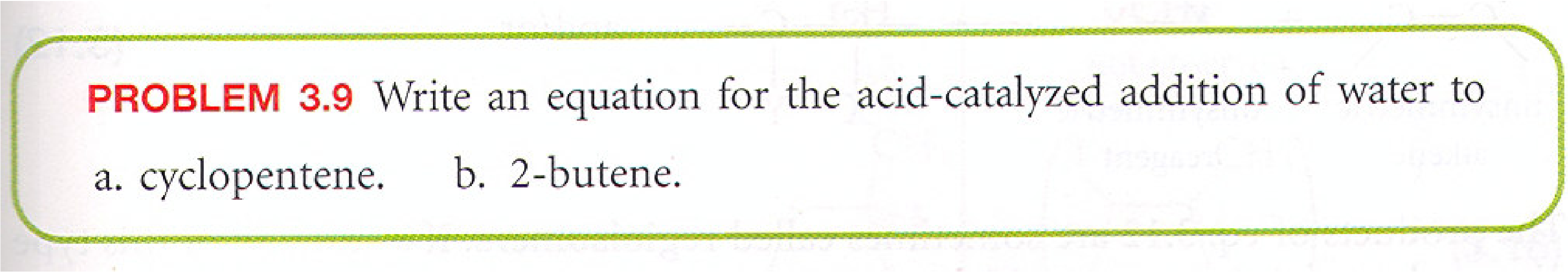
(3.8)

cyclohexene
bp 83.0°C

cyclohexanol
bp 161.1°C

An acid catalyst is required in this case, because the neutral water molecule is not acidic enough to provide protons to start the reaction. The stepwise mechanism for this reaction is given later in eq. 3.20. Hydration is used industrially and occasionally in the laboratory to synthesize alcohols from alkenes.

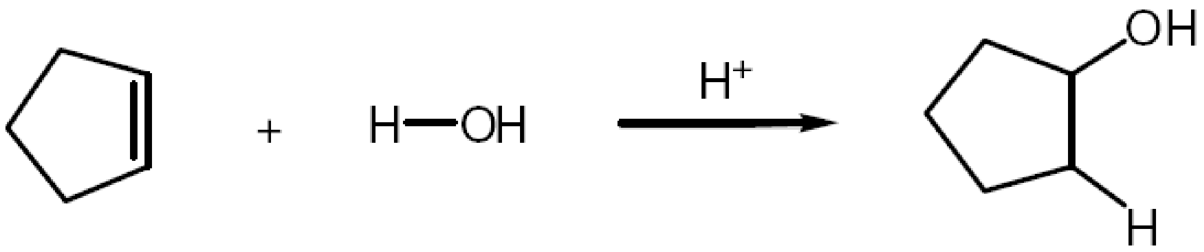
Q&A



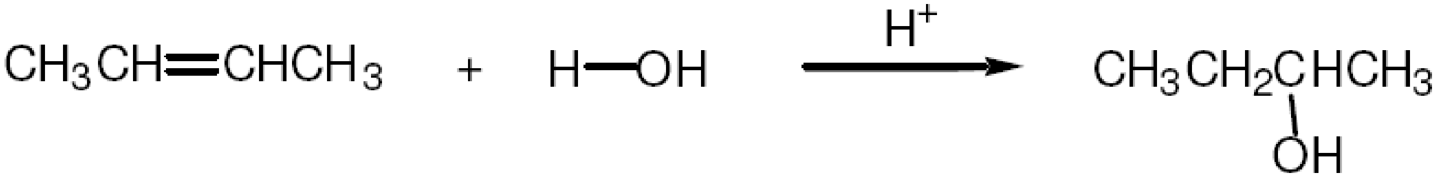
PROBLEM 3.9 Write an equation for the acid-catalyzed addition of water to

a. cyclopentene. b. 2-butene.

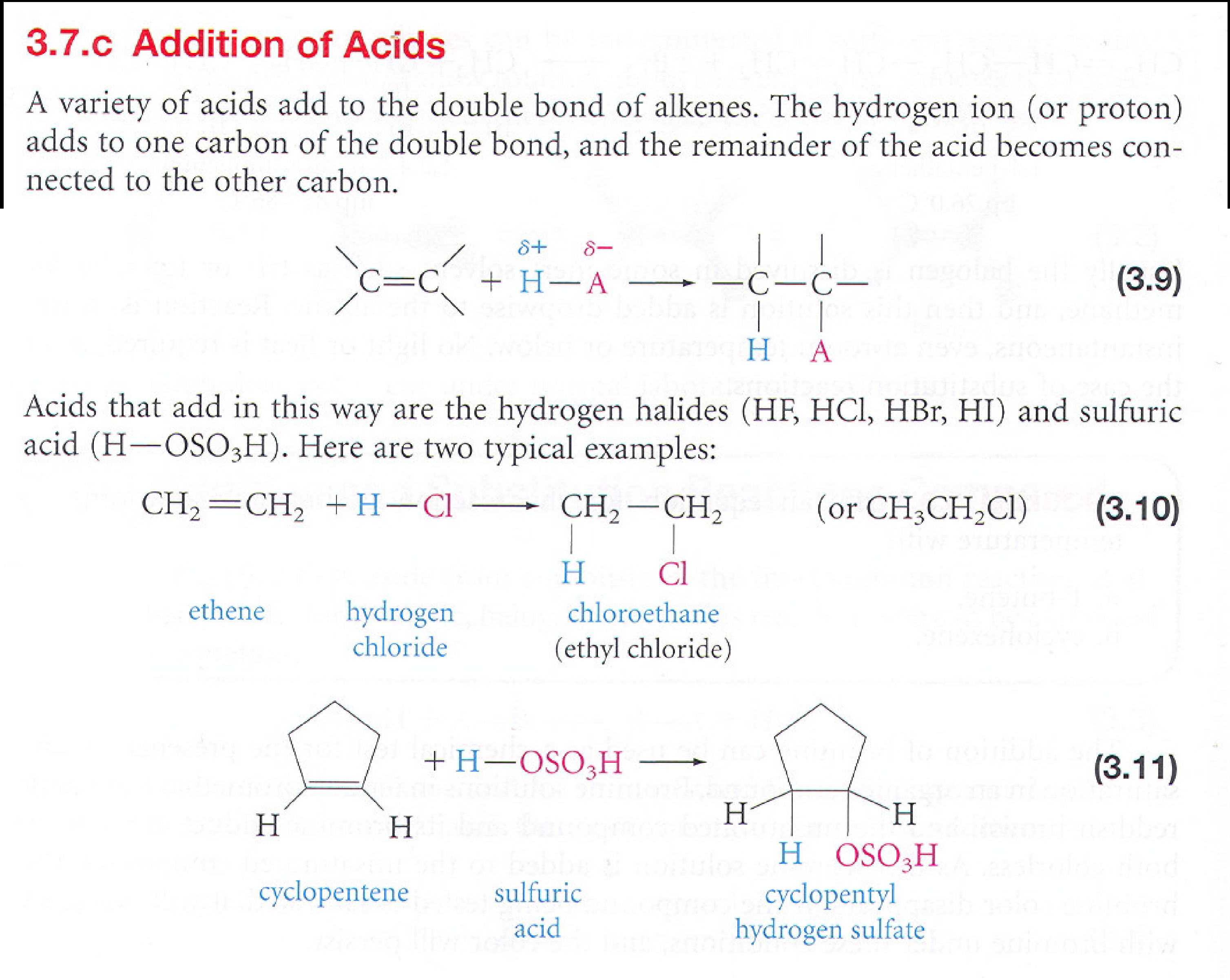
a.



b.



$$CH_3CH{=}CHCH_3 + H{-}OH \xrightarrow{H^+} CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$



3.7.c Addition of Acids

A variety of acids add to the double bond of alkenes. The hydrogen ion (or proton) adds to one carbon of the double bond, and the remainder of the acid becomes connected to the other carbon.

$$\mathrm{>C{=}C<} + \overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{A}} \longrightarrow -\underset{\mathrm{H}}{\overset{|}{\underset{|}{\mathrm{C}}}}-\underset{\mathrm{A}}{\overset{|}{\underset{|}{\mathrm{C}}}}- \qquad (3.9)$$

Acids that add in this way are the hydrogen halides (HF, HCl, HBr, HI) and sulfuric acid ($H{-}OSO_3H$). Here are two typical examples:

$$\mathrm{CH_2{=}CH_2} + \mathrm{H{-}Cl} \longrightarrow \underset{\mathrm{H}}{\underset{|}{\mathrm{CH_2}}}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH_2}}} \quad (\text{or } \mathrm{CH_3CH_2Cl}) \qquad (3.10)$$

ethene

hydrogen chloride

chloroethane (ethyl chloride)

$$+ \mathrm{H{-}OSO_3H} \longrightarrow \qquad (3.11)$$

cyclopentene

sulfuric acid

cyclopentyl hydrogen sulfate

Q&A

PROBLEM 3.10 Write an equation for each of the following reactions:

a. 2-butene + HI

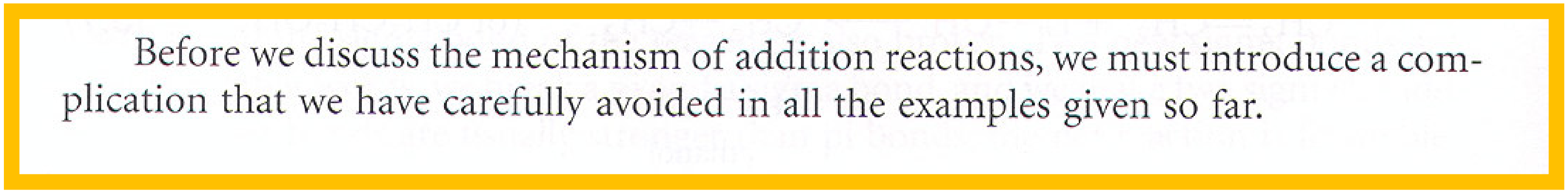
b. cyclohexene + HBr

a.

$$CH_3CH{=}CHCH_3 + H{-}I \longrightarrow CH_3CH_2\underset{\displaystyle I}{\underset{|}{C}}HCH_3$$

b.

[redacted]



Before we discuss the mechanism of addition reactions, we must introduce a complication that we have carefully avoided in all the examples given so far.

Markovnikov's Rule

3.8 Addition of Unsymmetric Reagents to Unsymmetric Alkenes

Symmetry

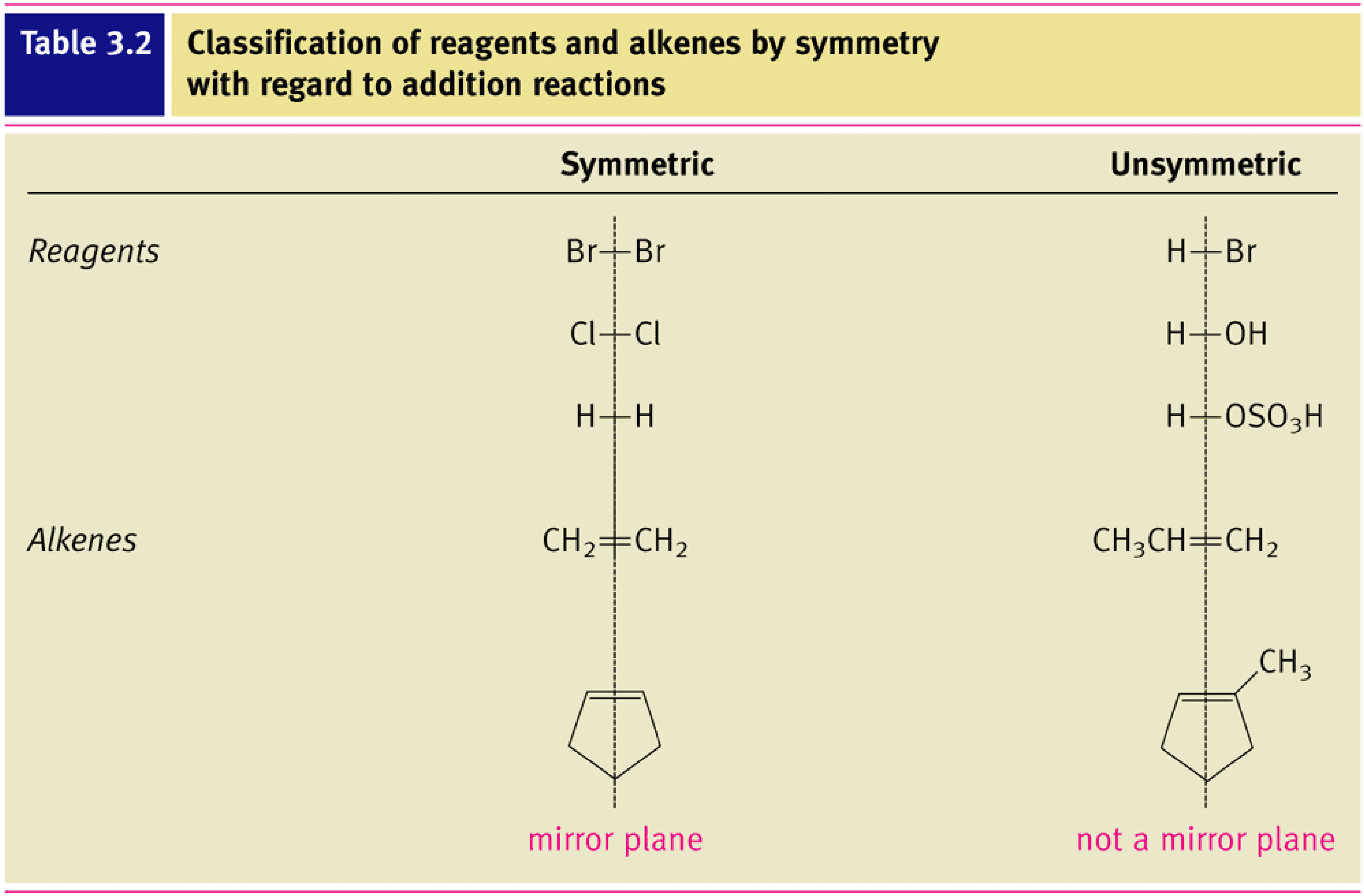
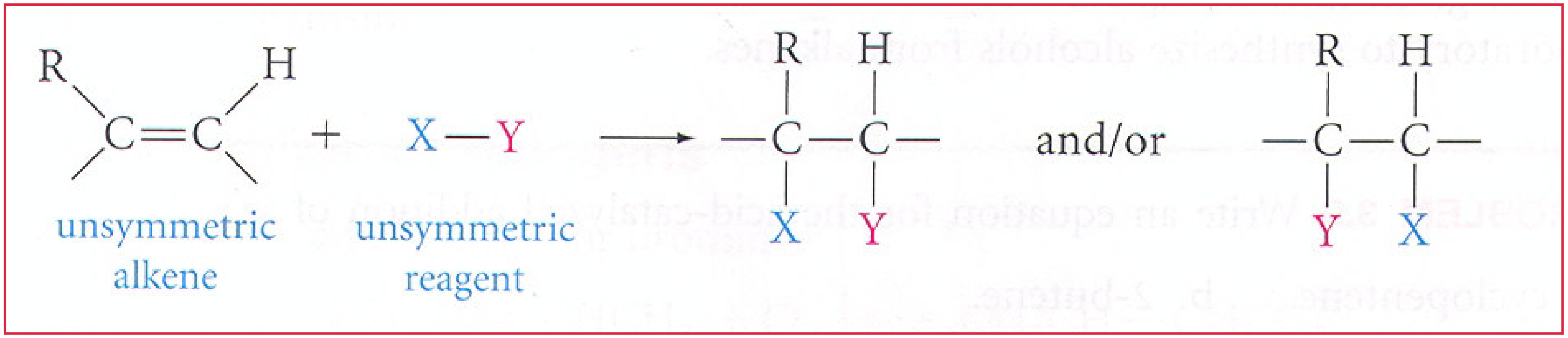


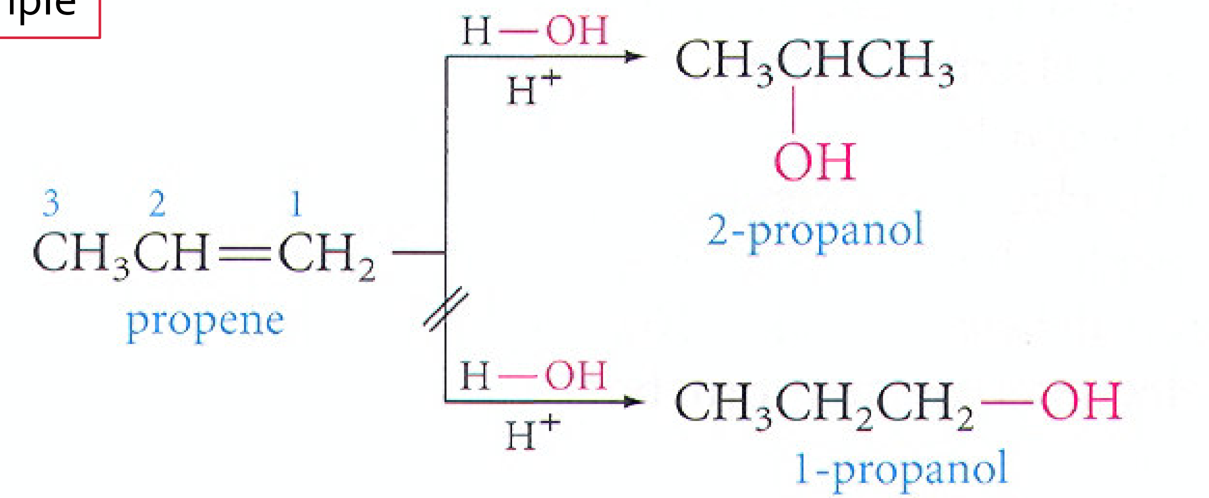
Table 3.2 **Classification of reagents and alkenes by symmetry with regard to addition reactions**

	Symmetric	**Unsymmetric**
Reagents	Br—Br	H—Br
	Cl—Cl	H—OH
	H—H	H—OSO_3H
Alkenes	$CH_2{=}CH_2$	$CH_3CH{=}CH_2$
		CH_3
	mirror plane	not a mirror plane

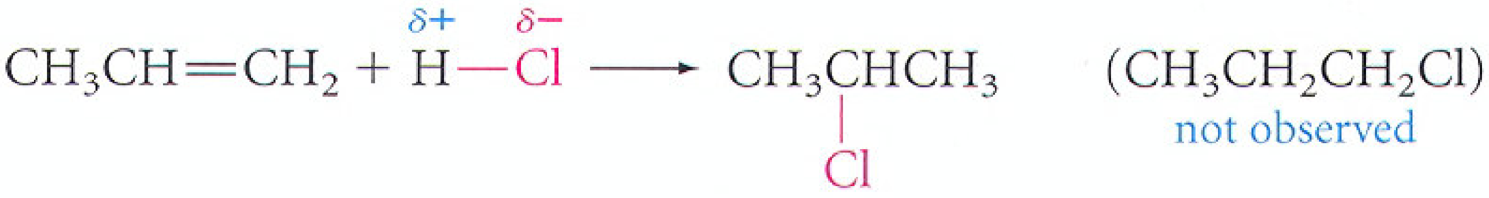
[redacted] if *both* the reagent *and* the alkene are *unsymmetric,* two products are, in principle, possible.



Specific Example

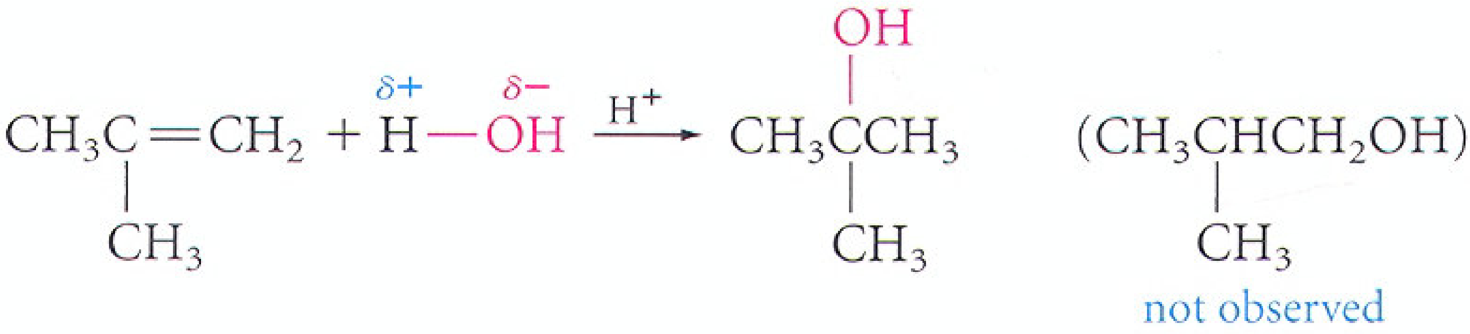


Exapmles



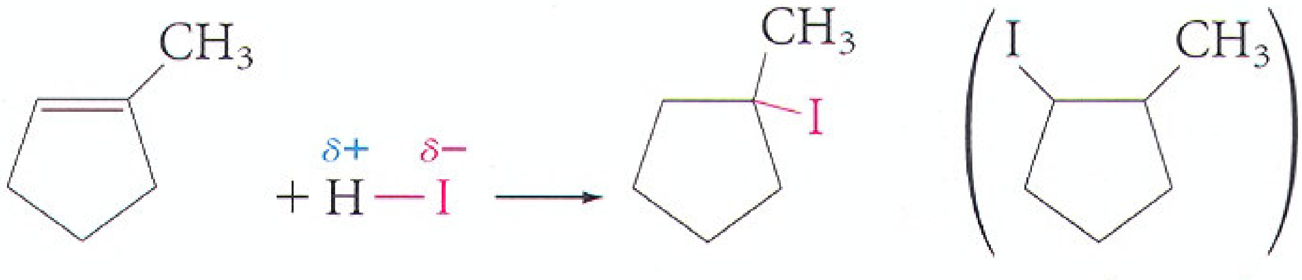
$$CH_3CH{=}CH_2 + \overset{\delta+}{H}-\overset{\delta-}{Cl} \longrightarrow CH_3\underset{\mid \atop Cl}{C}HCH_3 \qquad (CH_3CH_2CH_2Cl)$$

not observed



$$CH_3\underset{\mid \atop CH_3}{C}{=}CH_2 + \overset{\delta+}{H}-\overset{\delta-}{OH} \xrightarrow{H^+} CH_3\overset{OH \atop \mid}{\underset{\mid \atop CH_3}{C}}CH_3 \qquad (CH_3\underset{\mid \atop CH_3}{C}HCH_2OH)$$

not observed

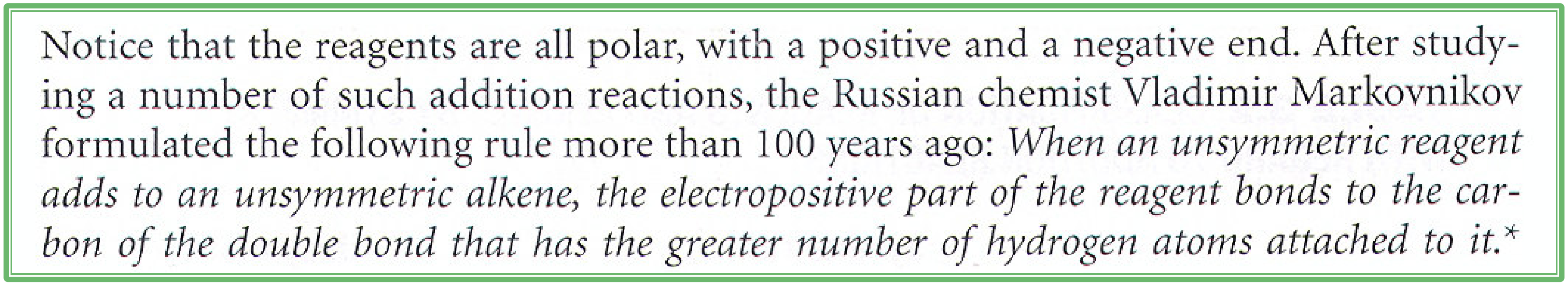


not observed

The Addition is Regiospecific

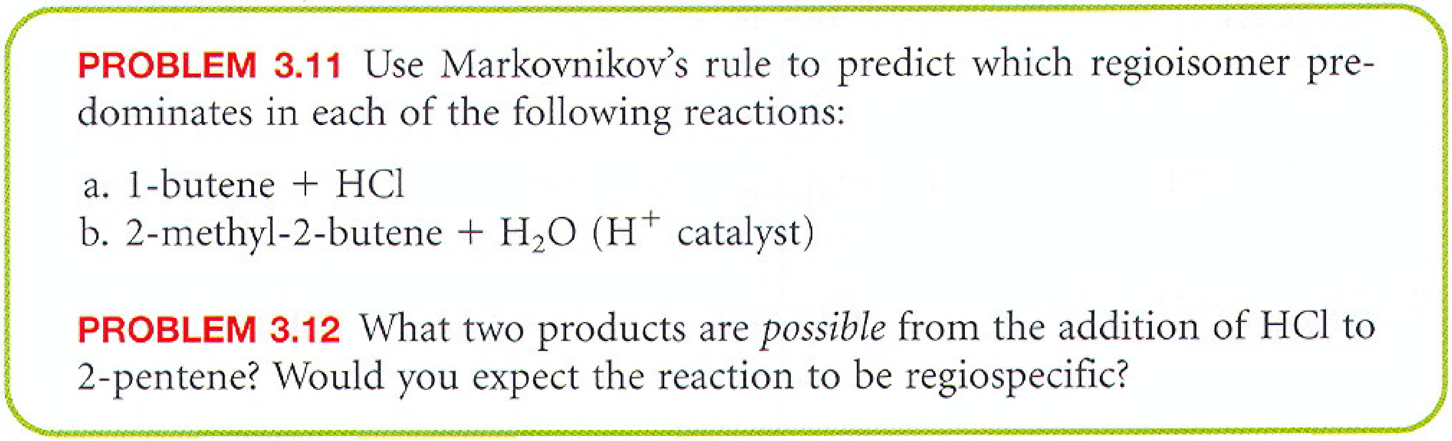
- Regiospecific addition
  - Only one product (regioisomer) is observed.

Markovnikov's Rule



Notice that the reagents are all polar, with a positive and a negative end. After studying a number of such addition reactions, the Russian chemist Vladimir Markovnikov formulated the following rule more than 100 years ago: *When an unsymmetric reagent adds to an unsymmetric alkene, the electropositive part of the reagent bonds to the carbon of the double bond that has the greater number of hydrogen atoms attached to it.*[*]

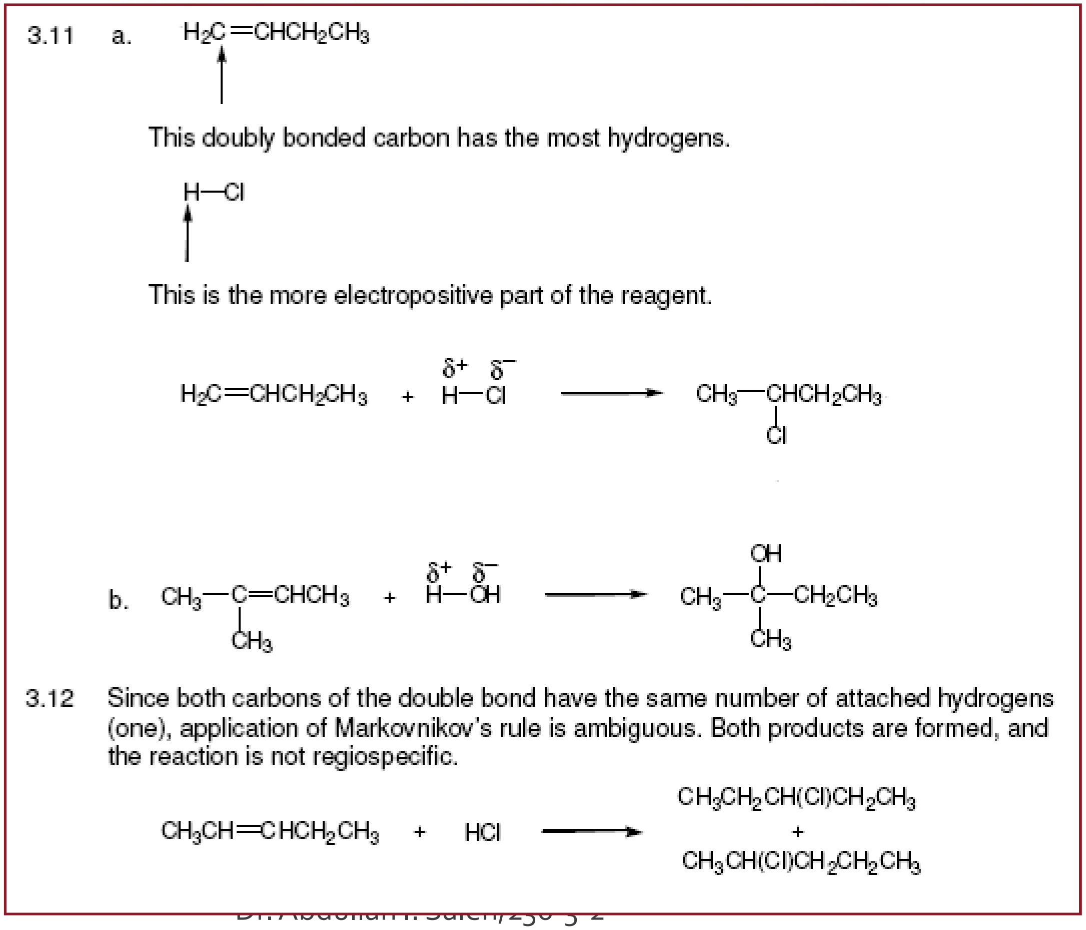
Q&A



PROBLEM 3.11 Use Markovnikov's rule to predict which regioisomer predominates in each of the following reactions:

a. 1-butene + HCl
b. 2-methyl-2-butene + H_2O (H^+ catalyst)

PROBLEM 3.12 What two products are *possible* from the addition of HCl to 2-pentene? Would you expect the reaction to be regiospecific?



3.11 a. $H_2C{=}CHCH_2CH_3$

This doubly bonded carbon has the most hydrogens.

$H{-}Cl$

This is the more electropositive part of the reagent.

$$H_2C{=}CHCH_2CH_3 + \overset{\delta+}{H}{-}\overset{\delta-}{Cl} \longrightarrow CH_3{-}\underset{Cl}{\underset{|}{C}H}CH_2CH_3$$

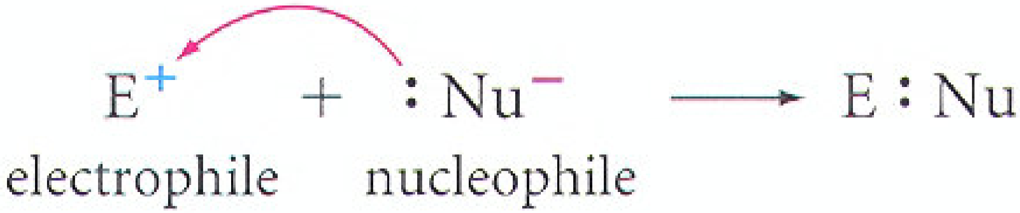
b. $$CH_3{-}\underset{CH_3}{\underset{|}{C}}{=}CHCH_3 + \overset{\delta+}{H}{-}\overset{\delta-}{OH} \longrightarrow CH_3{-}\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}CH_2CH_3$$

3.12 Since both carbons of the double bond have the same number of attached hydrogens (one), application of Markovnikov's rule is ambiguous. Both products are formed, and the reaction is not regiospecific.

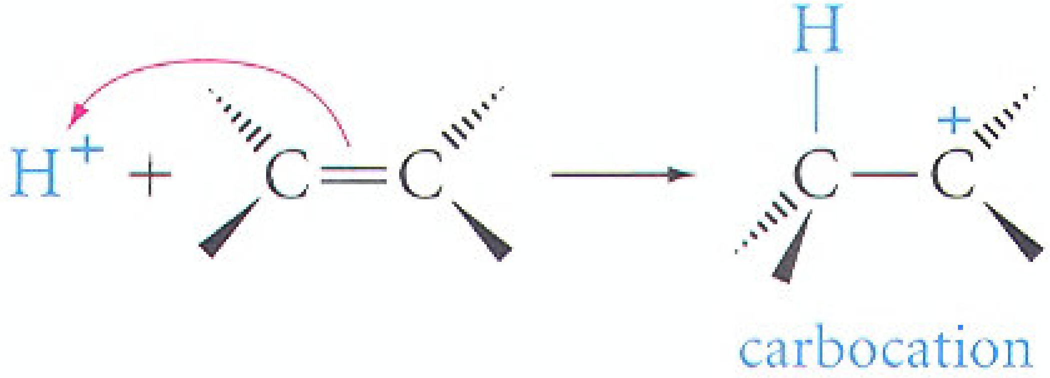
$$CH_3CH{=}CHCH_2CH_3 + HCl \longrightarrow \begin{matrix} CH_3CH_2CH(Cl)CH_2CH_3 \\ + \\ CH_3CH(Cl)CH_2CH_2CH_3 \end{matrix}$$

3.9 Mechanism of Electrophilic Addition to Alkenes

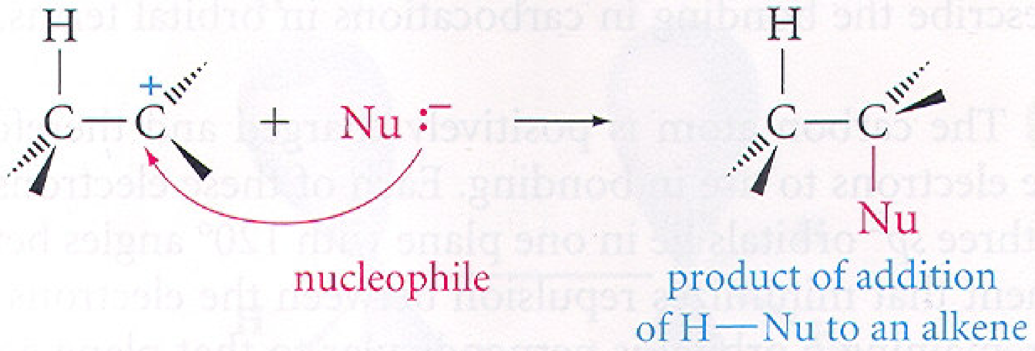
Electrophiles are electron-poor reactants; they seek electrons. **Nucleophiles** are electron-rich reactants; they form bonds by donating electrons to electrophiles.



$$E^{+} + :Nu^{-} \longrightarrow E:Nu \qquad (3.17)$$

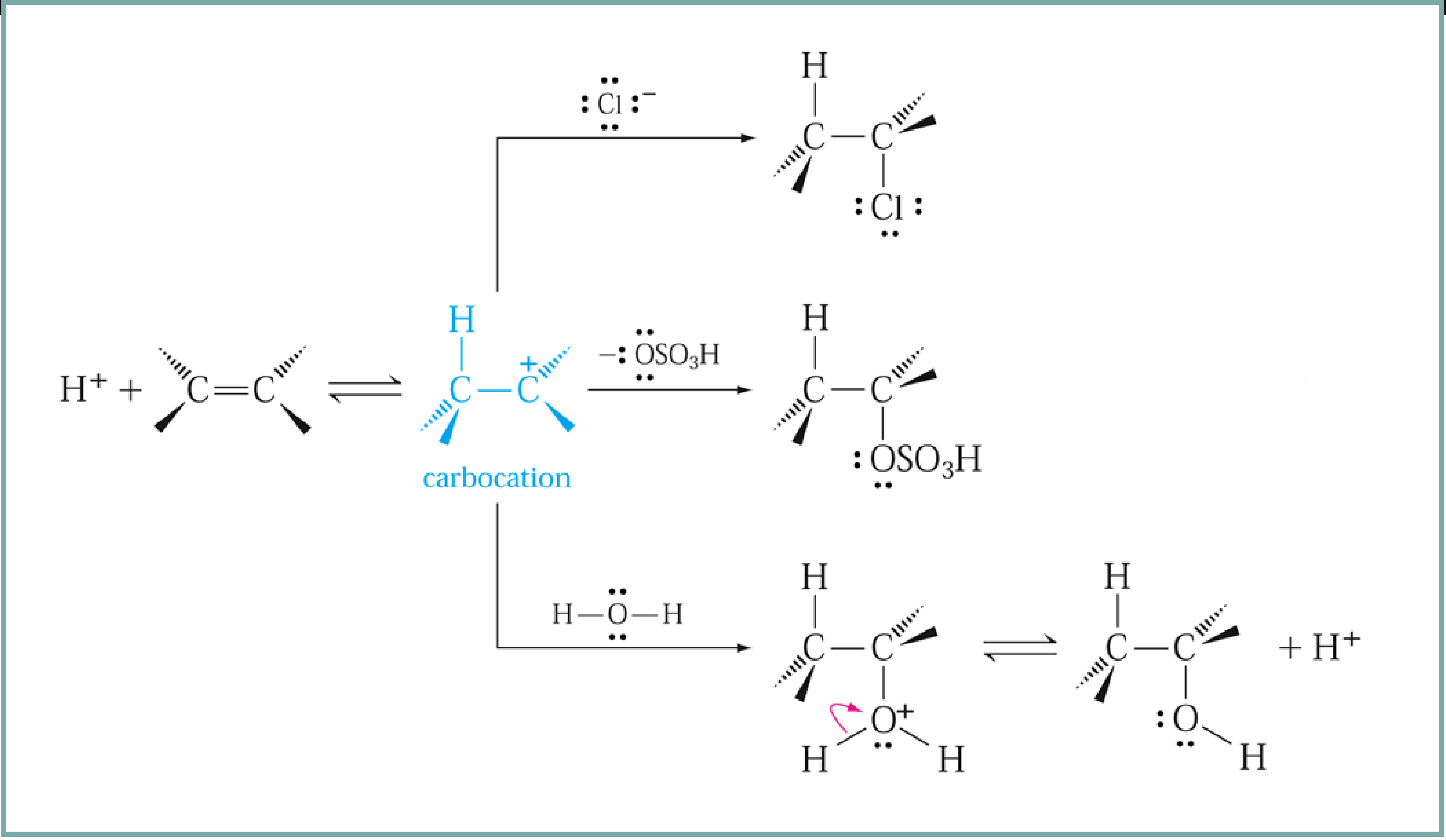


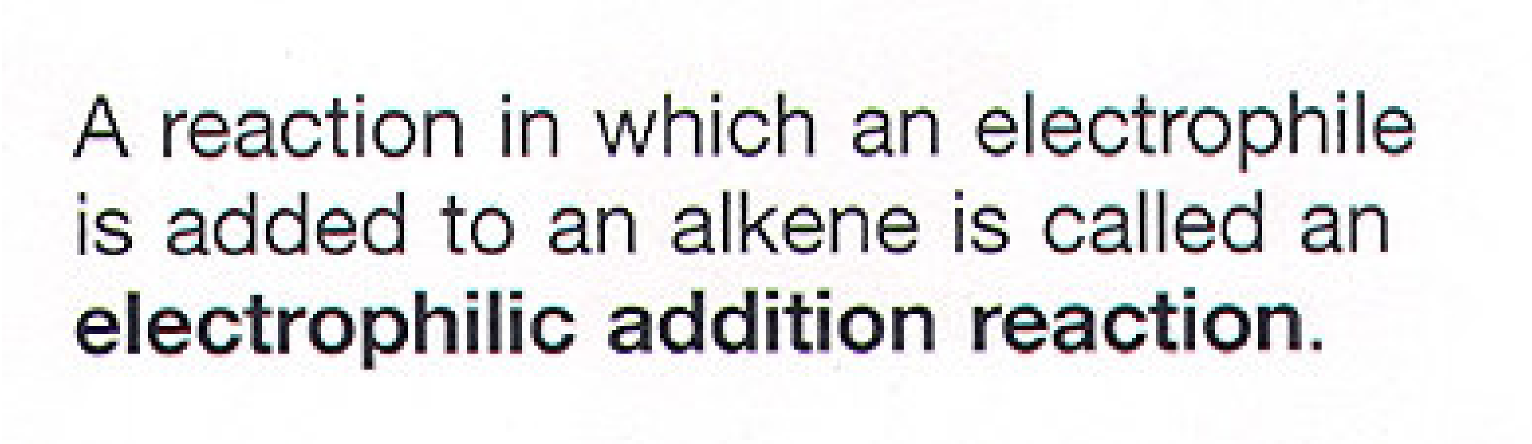
A **carbocation** is a positively charged carbon atom bonded to three other atoms.



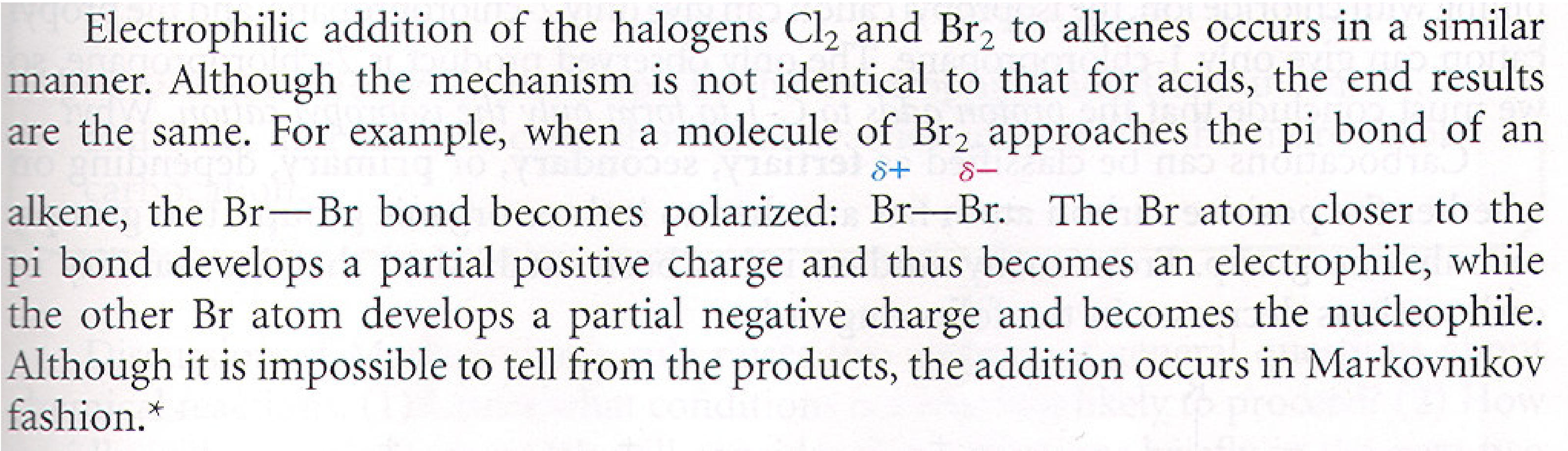
(3.19)

Equation 3.20 Addition reactions of alkenes



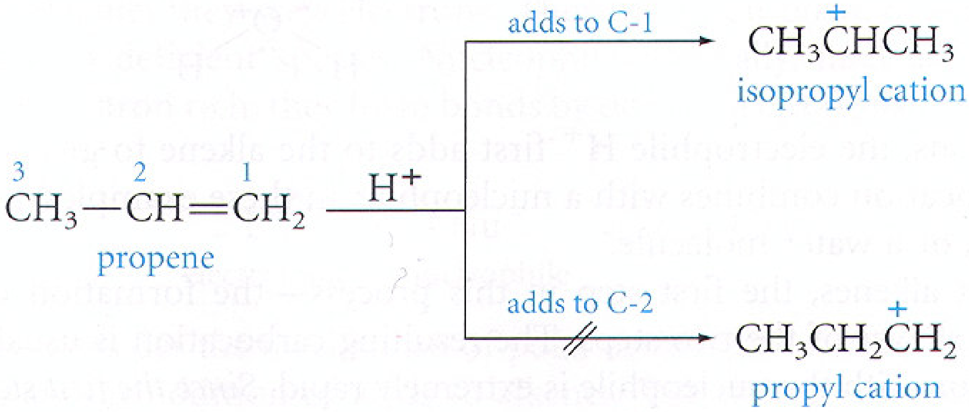


A reaction in which an electrophile is added to an alkene is called an **electrophilic addition reaction**.



Electrophilic addition of the halogens Cl_2 and Br_2 to alkenes occurs in a similar manner. Although the mechanism is not identical to that for acids, the end results are the same. For example, when a molecule of Br_2 approaches the pi bond of an alkene, the Br—Br bond becomes polarized: $\overset{\delta+}{\text{Br}}\text{—}\overset{\delta-}{\text{Br}}$. The Br atom closer to the pi bond develops a partial positive charge and thus becomes an electrophile, while the other Br atom develops a partial negative charge and becomes the nucleophile. Although it is impossible to tell from the products, the addition occurs in Markovnikov fashion.*

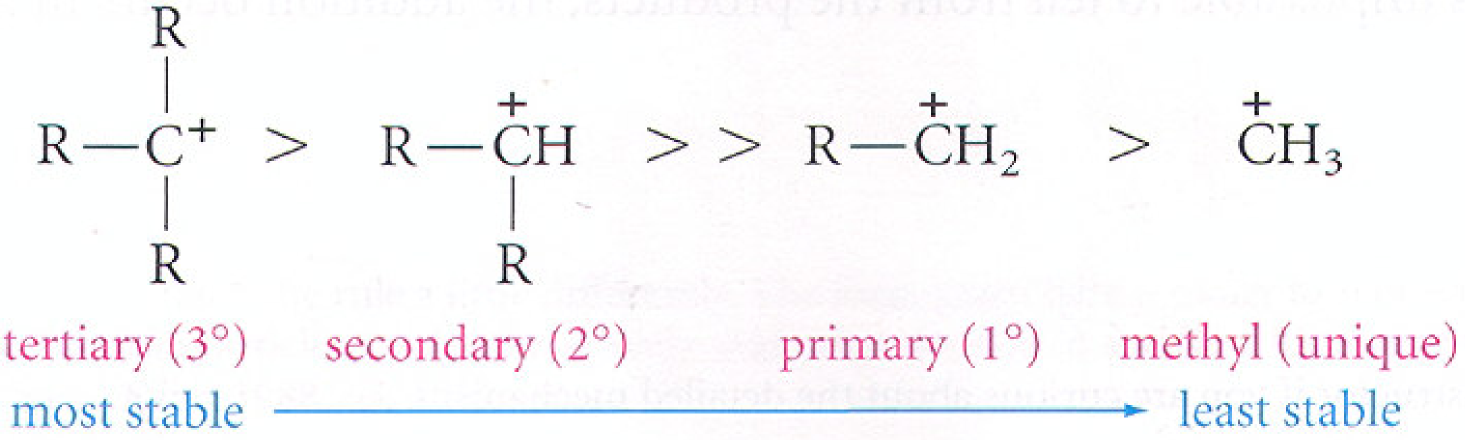
3.10 Markovnikov's Rule Explained



(3.21)

Carbocations are classified as **primary**, **secondary**, and **tertiary** when one, two, and three R groups, respectively, are attached to the positively charged carbon atom.

Relative Stability of Carbocations



$$R-\underset{R}{\overset{R}{\underset{|}{\overset{|}{C^{+}}}}} \;>\; R-\underset{R}{\underset{|}{\overset{+}{C}H}} \;>>\; R-\overset{+}{C}H_2 \;>\; \overset{+}{C}H_3$$

tertiary (3°) secondary (2°) primary (1°) methyl (unique)

most stable → least stable

One reason for the observed order

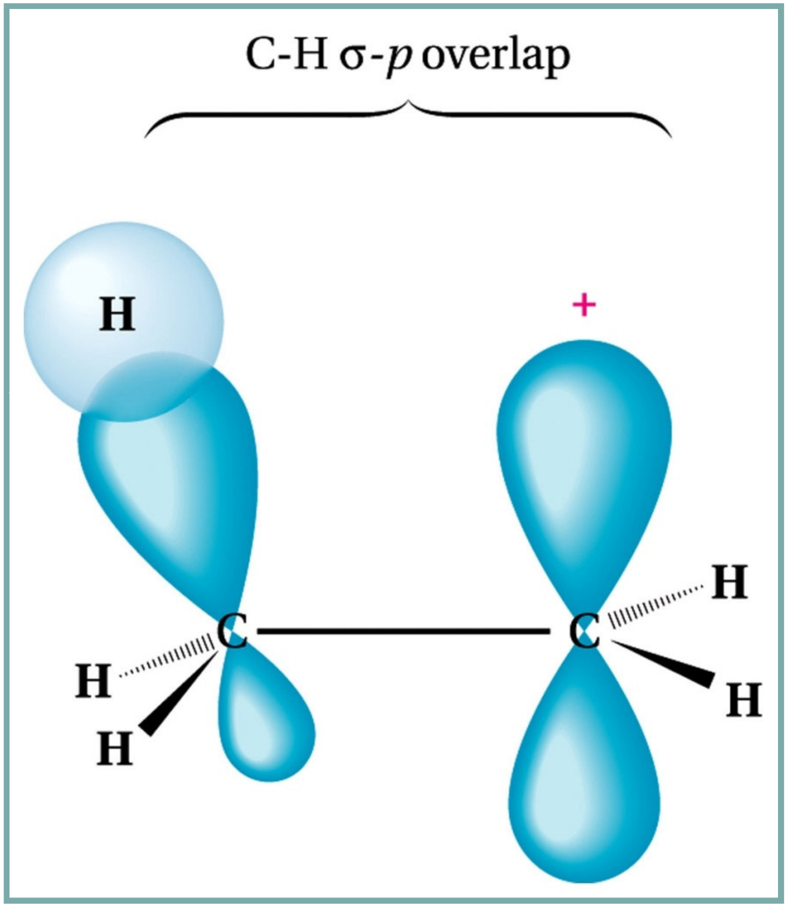
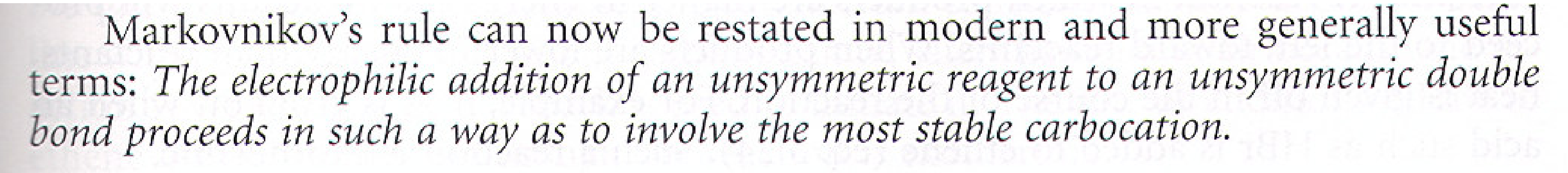


FIGURE 3.9

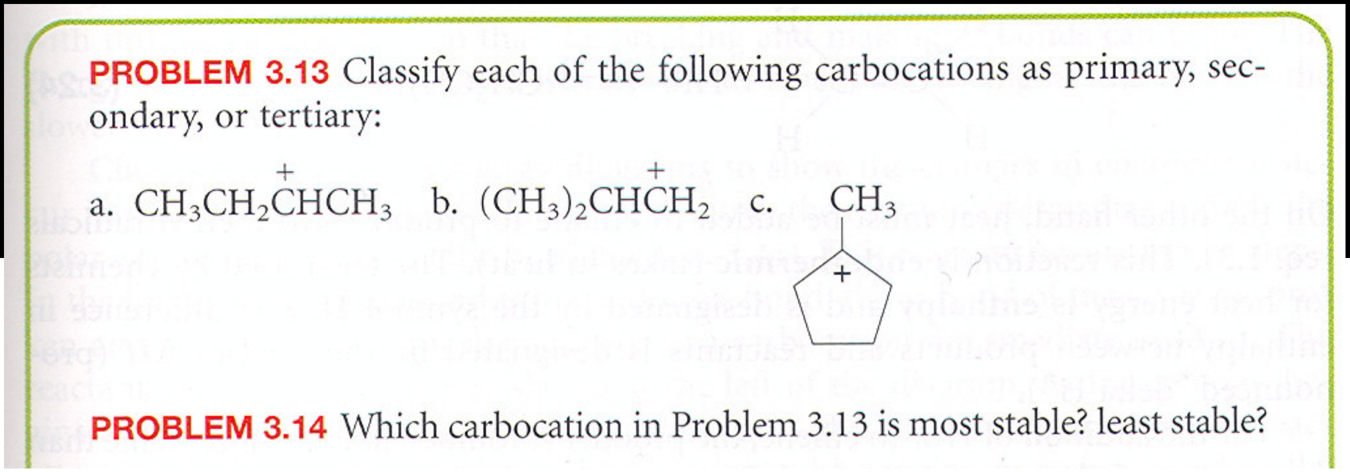
Alkyl groups stabilize carbocations by donating electron density from C—H and C—C sigma bonds that can line up with the empty *p* orbital on the positively charged carbon atom.

Markovnikov's Rule Restated



Markovnikov's rule can now be restated in modern and more generally useful terms: *The electrophilic addition of an unsymmetric reagent to an unsymmetric double bond proceeds in such a way as to involve the most stable carbocation.*

Q&A



PROBLEM 3.13 Classify each of the following carbocations as primary, secondary, or tertiary:

a. $CH_3CH_2\overset{+}{C}HCH_3$ b. $(CH_3)_2CH\overset{+}{C}H_2$ c.

PROBLEM 3.14 Which carbocation in Problem 3.13 is most stable? least stable?

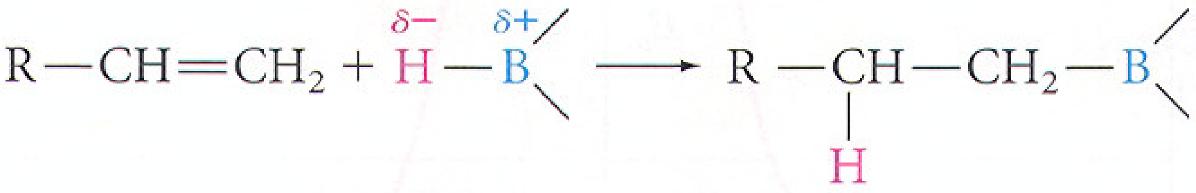
3.13

a. Secondary; there are two carbons bonded to the positively charged carbon.
b. Primary; one carbon is bonded to the positively charged carbon.
c. Tertiary; three carbons are bonded to the positively charged carbon.

3.14 The order of stability is c > a > b.

3.13 Hydroboration of Alkenes

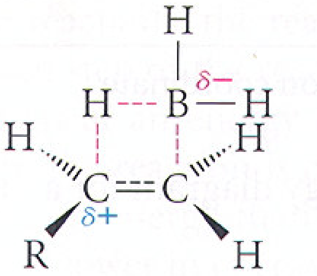
Hydroboration is the addition of $\mathrm{H-B}\langle$ to an alkene.



$$\mathrm{R-CH{=}CH_2} + \overset{\delta-}{\mathrm{H}}-\overset{\delta+}{\mathrm{B}}\langle \longrightarrow \mathrm{R-\underset{\displaystyle H}{\underset{|}{CH}}-CH_2-B}\langle \qquad \textbf{(3.25)}$$

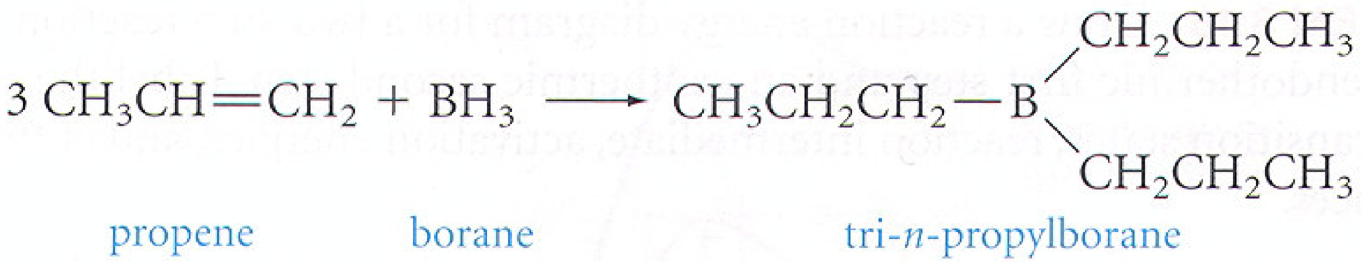
$\mathrm{H-B}\langle$ bond is polarized with the hydrogen $\delta-$ and the boron $\delta+$. Addition occurs so that the boron (the electrophile) adds to the less substituted carbon.

Thus, it resembles a normal electrophilic addition to an alkene, following Markovnikov's rule, even though the addition is concerted (that is, all bond-breaking and bond-making occurs in one step).



transition state
for hydroboration

Because it has three B—H bonds, one molecule of borane, BH_3, can react with three molecules of an alkene. For example, propene gives tri-*n*-propylborane.



$$3\ CH_3CH{=}CH_2 + BH_3 \longrightarrow CH_3CH_2CH_2{-}B(CH_2CH_2CH_3)_2$$

(3.26)

The trialkylboranes made in this way are usually not isolated but are treated with some other reagent to obtain the desired final product. For example, trialkylboranes can be oxidized by hydrogen peroxide and base to give alcohols.

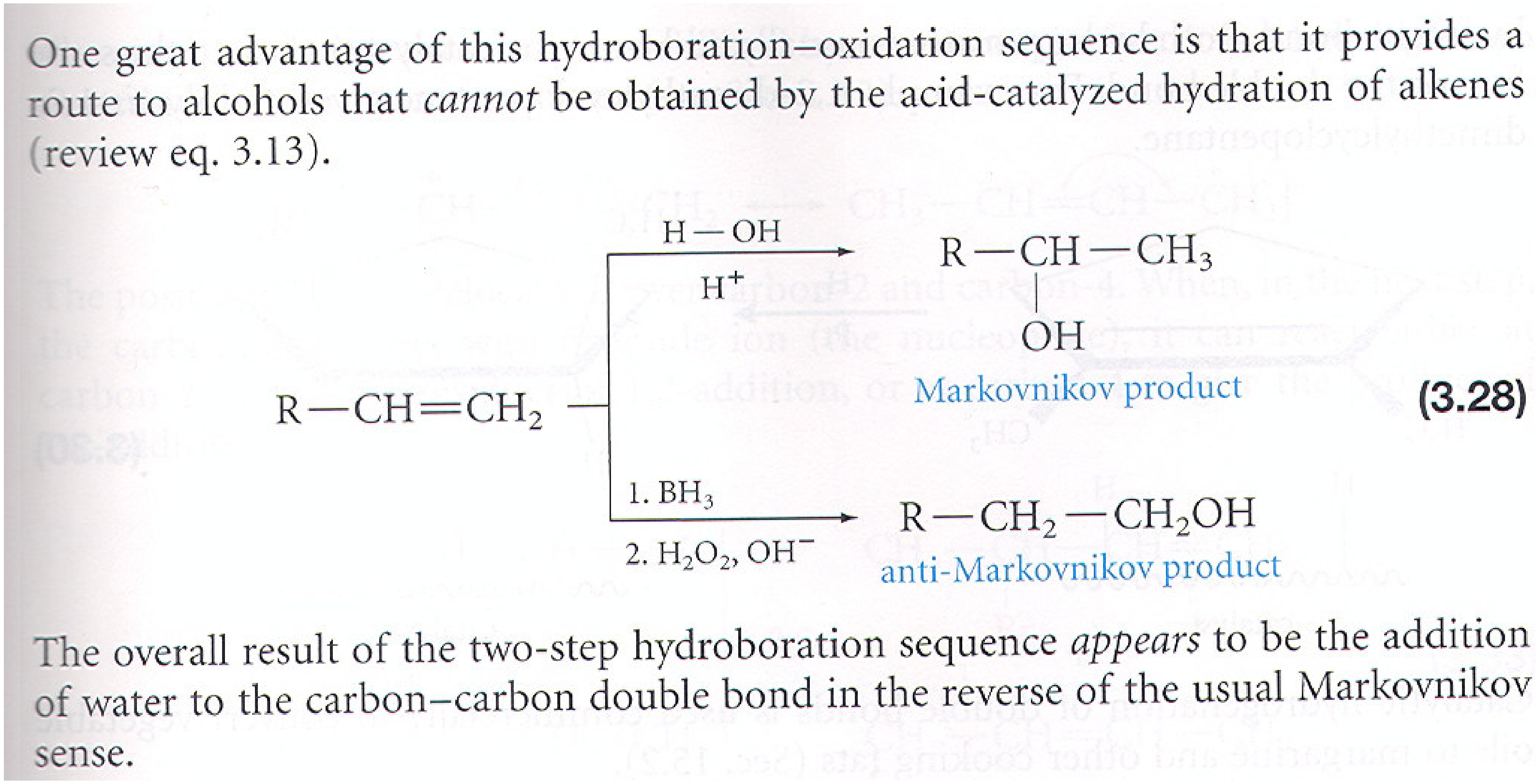
$$(CH_3CH_2CH_2)_3B + 3\,H_2O_2 + 3\,NaOH \longrightarrow$$

tri-*n*-propylborane

$$3\,CH_3CH_2CH_2OH + Na_3BO_3 + 3\,H_2O \qquad \textbf{(3.27)}$$

n-propyl alcohol

sodium borate



One great advantage of this hydroboration–oxidation sequence is that it provides a route to alcohols that *cannot* be obtained by the acid-catalyzed hydration of alkenes (review eq. 3.13).

$$R-CH=CH_2 \xrightarrow[H^+]{H-OH} R-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

Markovnikov product

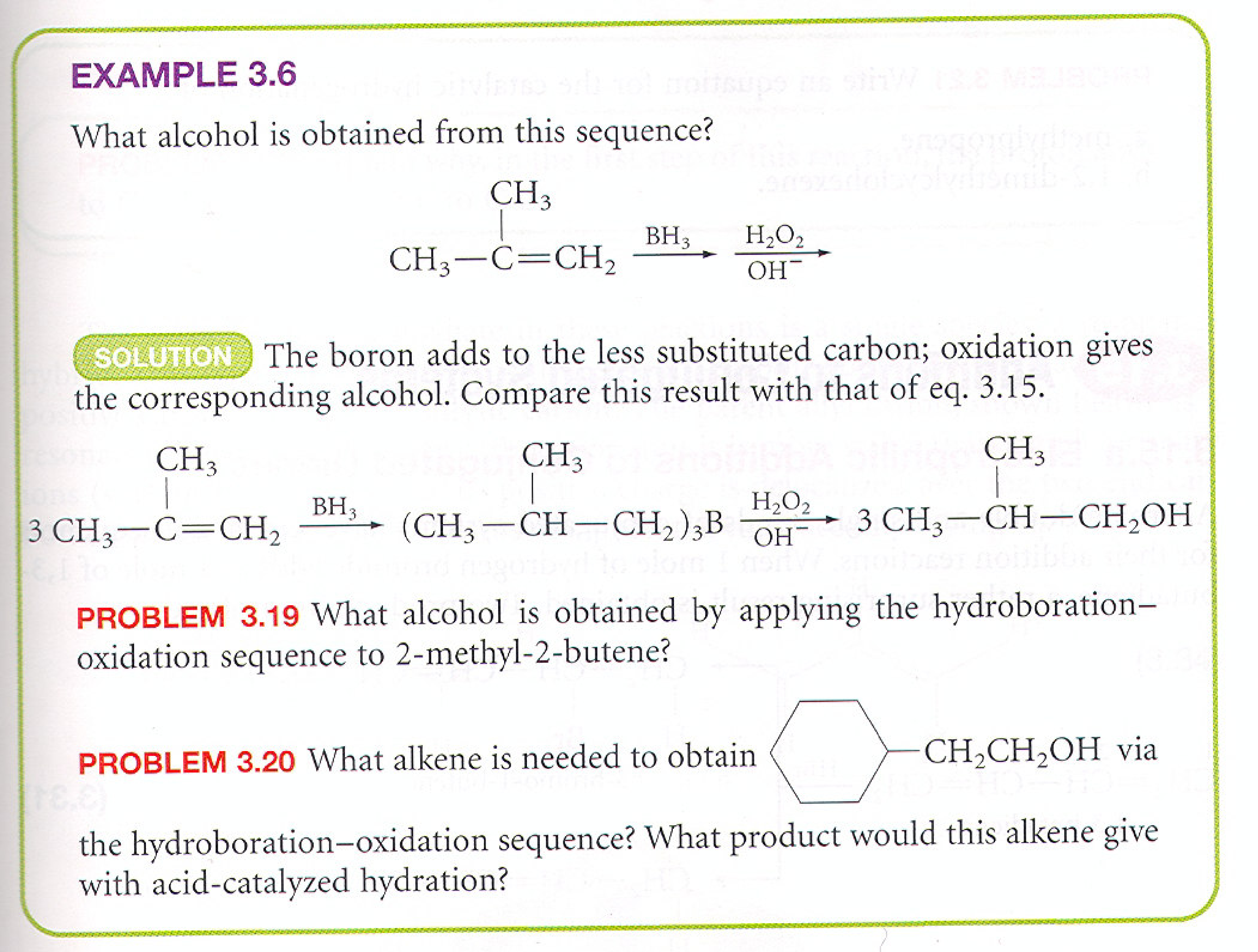
(3.28)

$$R-CH=CH_2 \xrightarrow[2.\ H_2O_2,\ OH^-]{1.\ BH_3} R-CH_2-CH_2OH$$

anti-Markovnikov product

The overall result of the two-step hydroboration sequence *appears* to be the addition of water to the carbon–carbon double bond in the reverse of the usual Markovnikov sense.

Q&A



EXAMPLE 3.6

What alcohol is obtained from this sequence?

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{BH_3} \xrightarrow[OH^-]{H_2O_2}$$

SOLUTION The boron adds to the less substituted carbon; oxidation gives the corresponding alcohol. Compare this result with that of eq. 3.15.

$$3\ CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{BH_3} (CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2)_3B \xrightarrow[OH^-]{H_2O_2} 3\ CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2OH$$

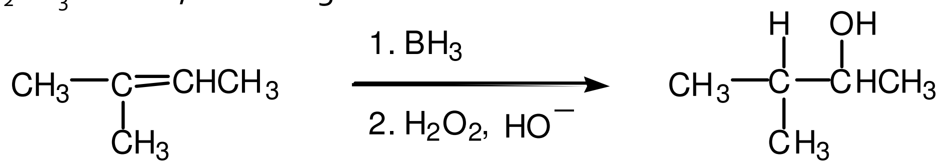
PROBLEM 3.19 What alcohol is obtained by applying the hydroboration–oxidation sequence to 2-methyl-2-butene?

PROBLEM 3.20 What alkene is needed to obtain $-CH_2CH_2OH$ via the hydroboration–oxidation sequence? What product would this alkene give with acid-catalyzed hydration?

Answers

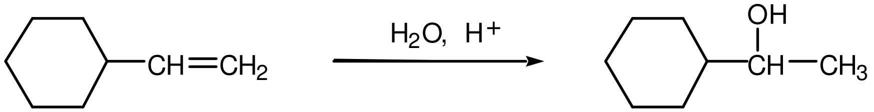
3.19

The boron adds to the *less* substituted carbon of the double bond, and, in the oxidation, the boron is replaced by an OH group. Note that the acid-catalyzed hydration of the same alkene would give the alcohol (CH$_3$)$_2$C(OH)CH$_2$CH$_3$ instead, according to Markovnikov's rule.

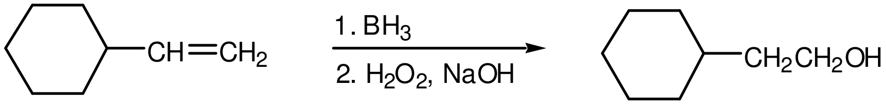


3.20

Acid-catalyzed hydration of vinylcyclohexane occurs in the Markovnikov sense:

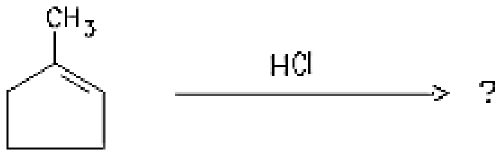


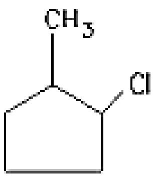
vinylcyclohexane



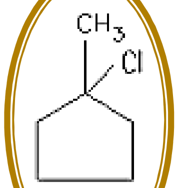
More Questions

What would be the major product of the following reaction?

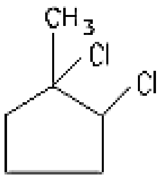




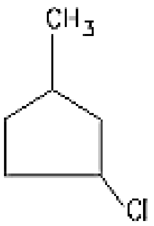
I



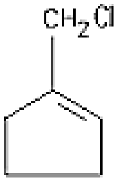
II



III



IV



V

A) I

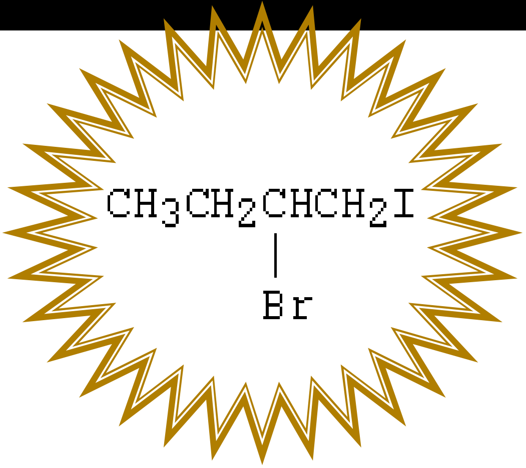
[✓ B) II]

C) III

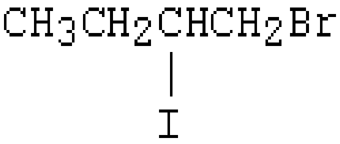
D) IV

E) V

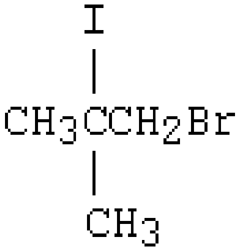
What is the chief product of the reaction of IBr with 1-butene?



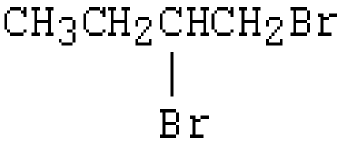
$CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_2I$



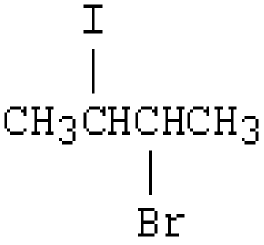
$CH_3CH_2\underset{\underset{I}{|}}{C}HCH_2Br$



$CH_3\overset{\overset{I}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2Br$

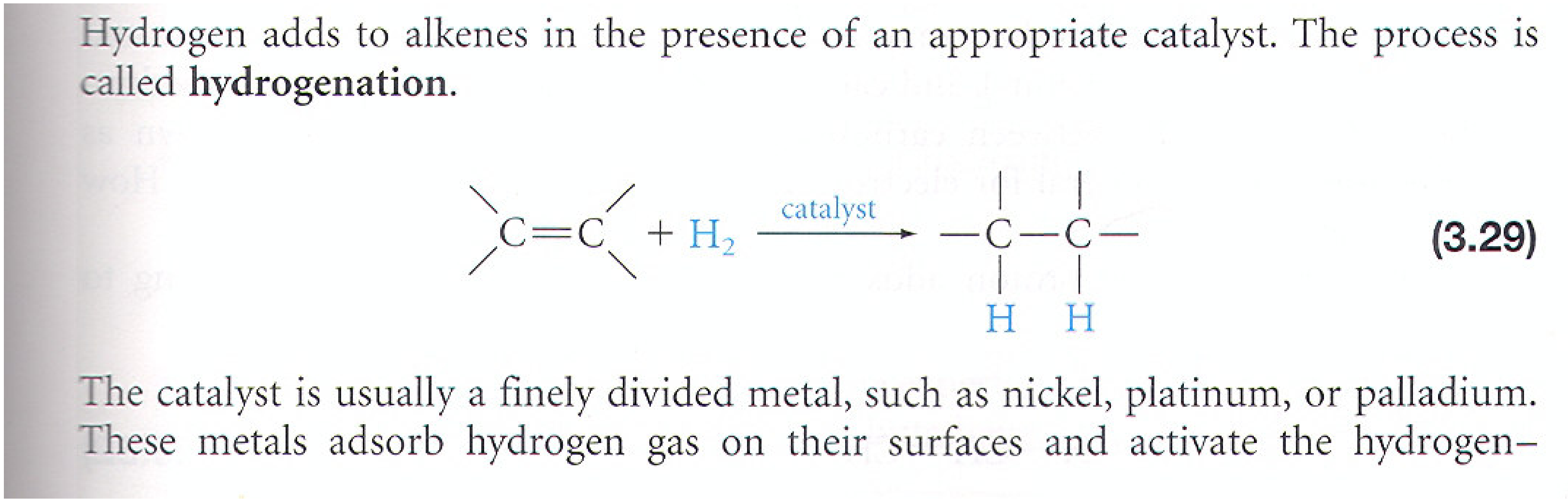


$CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_2Br$



$CH_3\overset{\overset{I}{|}}{C}H\underset{\underset{Br}{|}}{C}HCH_3$

3.14 Addition of Hydrogen



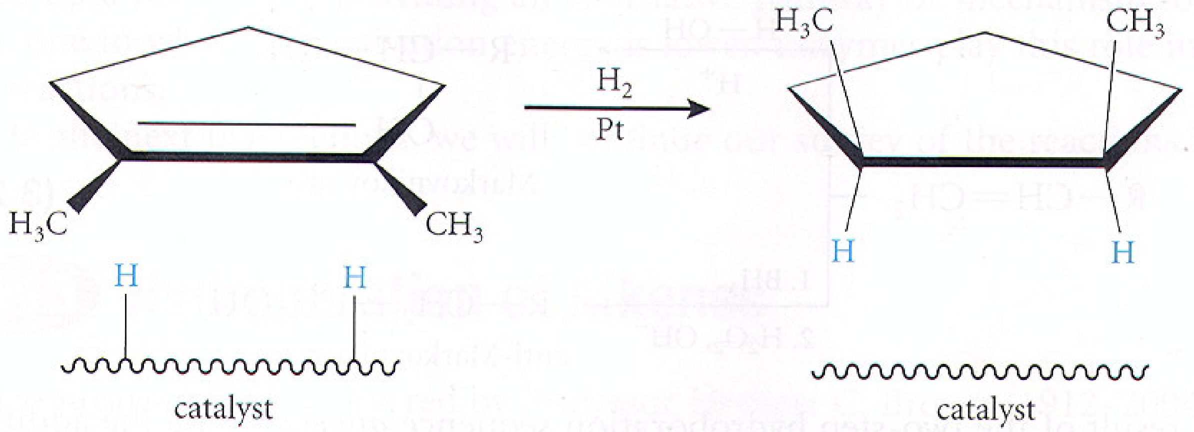
Hydrogen adds to alkenes in the presence of an appropriate catalyst. The process is called **hydrogenation.**

$$\rangle C{=}C\langle + H_2 \xrightarrow{\text{catalyst}} -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}- \qquad \textbf{(3.29)}$$

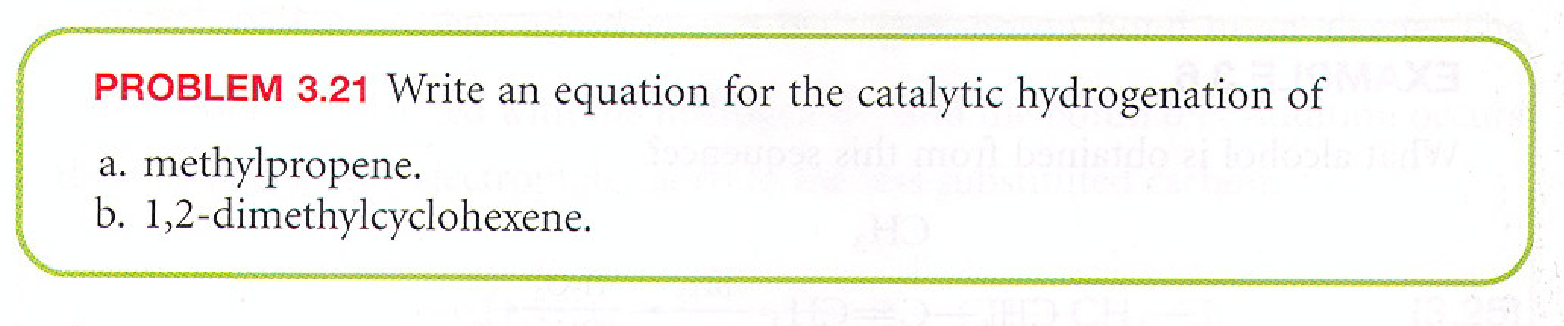
The catalyst is usually a finely divided metal, such as nickel, platinum, or palladium. These metals adsorb hydrogen gas on their surfaces and activate the hydrogen–

3.14 Addition of Hydrogen

. Both hydrogen atoms usually add from the catalyst surface to the same face of the double bond. For example, 1,2-dimethylcyclopentene gives mainly *cis*-1,2-dimethylcyclopentane.



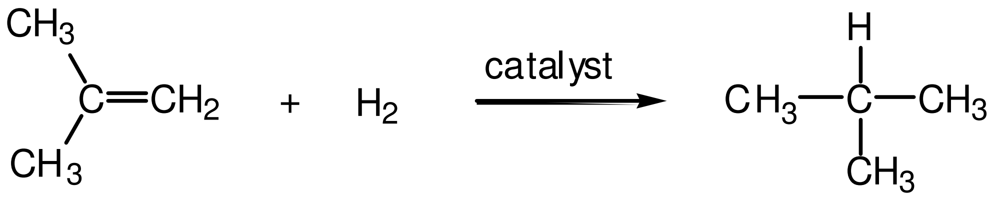
(3.30)



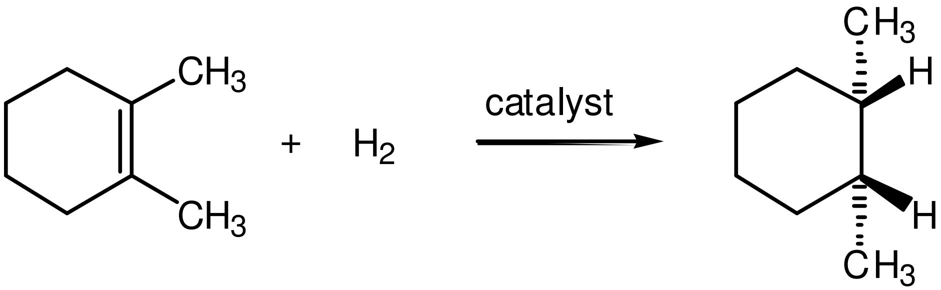
PROBLEM 3.21 Write an equation for the catalytic hydrogenation of

a. methylpropene.
b. 1,2-dimethylcyclohexene.

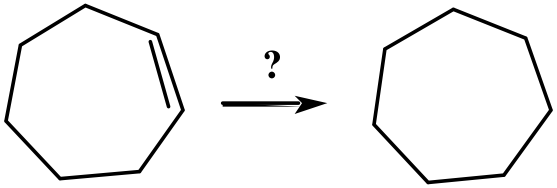
a.



b.

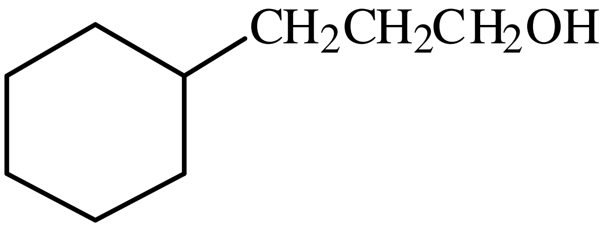


Select the necessary reagent(s) to convert cycloheptene to cycloheptane.



[✓ **a.**] H_2 and Ni   **b.** H_2O **c.** H_2SO_4 and heat
d. Zn and H^+ **e.** KOH in alcohol and heat

Which of the following alkenes is needed to prepare 3-cyclohexyl-1-propanol via a hydroboration-oxidation reaction?



3-cyclohexyl-1-propanol

a. cyclohexene   **b.** vinyl cyclohexane
[✓ **c.**] allyl cyclohexane   **d.** propyl cyclohexene
e. 1- octene