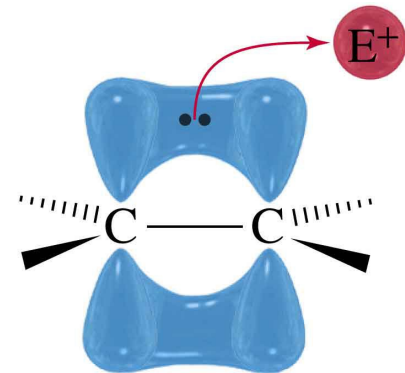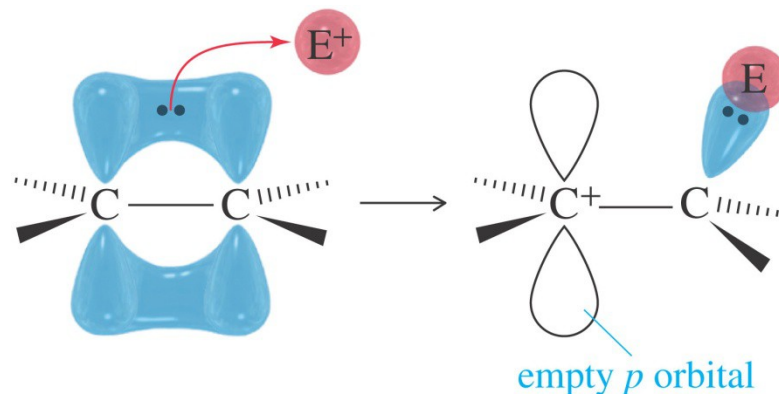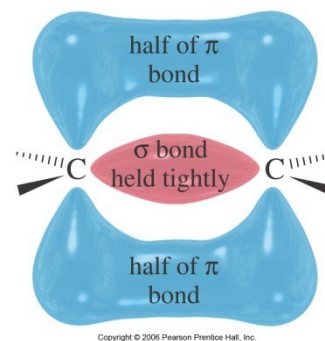*Organic Chemistry*, 7th Edition
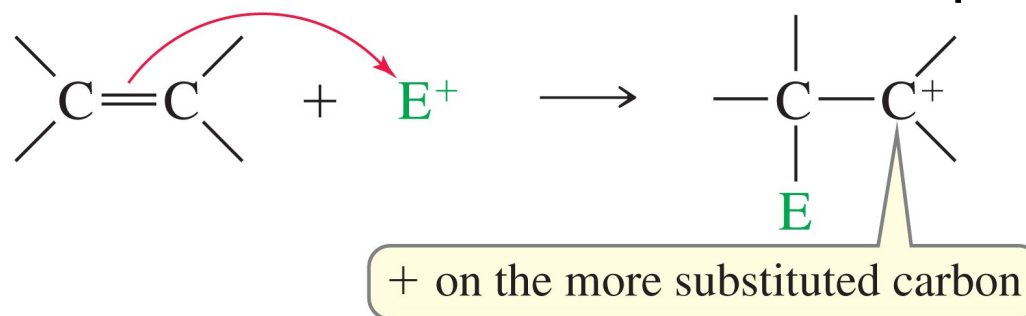L. G. Wade, Jr.

Chapter 8

Reactions of Alkenes

Bonding in Alkenes

- Electrons in pi bond are loosely held.
- The double bond acts as a nucleophile attacking electrophilic species.
- Carbocations are intermediates in the reactions.
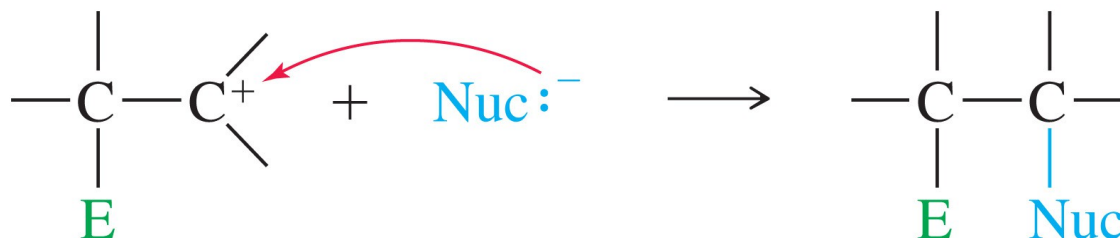- These reactions are called **electrophilic additions**.

Electrophilic Addition

- Step 1: Pi electrons attack the electrophile.

$$\diagdown C = C \diagup \quad + \quad E^+ \quad \longrightarrow \quad -\overset{|}{C}-\overset{+}{C}\diagup$$

+ on the more substituted carbon

- Step 2: Nucleophile attacks the carbocation.

$$-\overset{|}{C}-\overset{+}{C}\diagup \quad + \quad Nuc:^- \quad \longrightarrow \quad -\overset{|}{C}-\overset{|}{C}-$$

Types of Additions

TABLE 8-1

Types of Additions to Alkenes

$C=C$	Type of Addition [Elements Added][a]	Product
hydration [H_2O]		H OH
hydrogenation [H_2], a reduction		H H
hydroxylation [HOOH], an oxidation		OH OH
oxidative cleavage [O_2], an oxidation		$C=O$ $O=C$
epoxidation [O], an oxidation		O
halogenation [X_2], an oxidation		X X
halohydrin formation [HOX], an oxidation		X OH
HX addition [HX] (hydrohalogenation)		H X
cyclopropanation [CH_2]		H H

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

Chapter 8

Addition of HX to Alkenes

- Step 1 is the protonation of the double bond.

- The protonation step forms the most stable carbocation possible.

- In step 2, the nucleophile attacks the carbocation, forming an alkyl halide.

- HBr, HCl, and HI can be added through this reaction.

Mechanism of Addition of HX

Step 1: Protonation of the double bond.
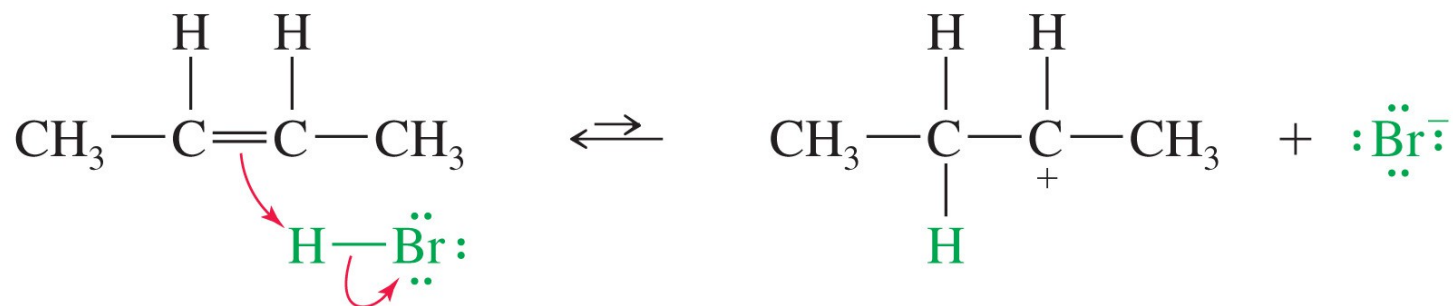
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Step 2: Nucleophilic attack of the halide on the carbocation.
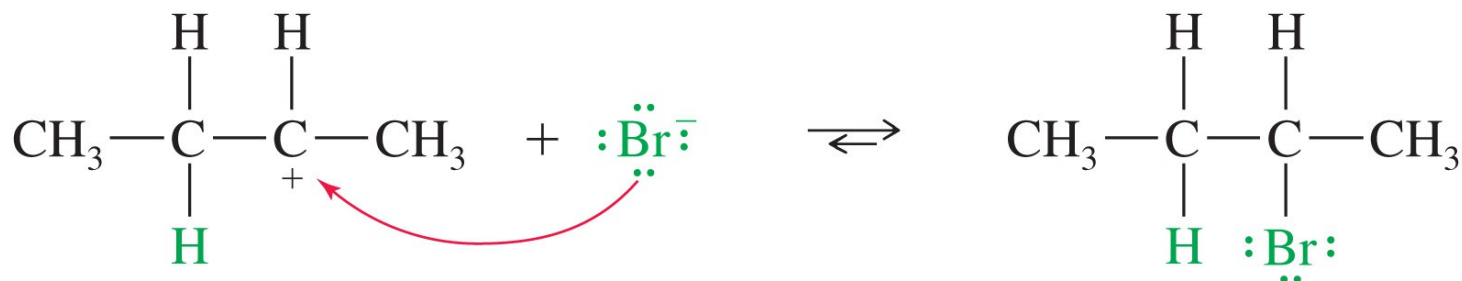
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Regioselectivity

- Markovnikov's Rule: The addition of a proton to the double bond of an alkene results in a product with the acidic proton bonded to the carbon atom that already holds the greater number of hydrogens.

- Markovnikov's Rule (extended): In an electrophilic addition to the alkene, the electrophile adds in such a way that it generates the most stable intermediate.

Markovnikov's Rule
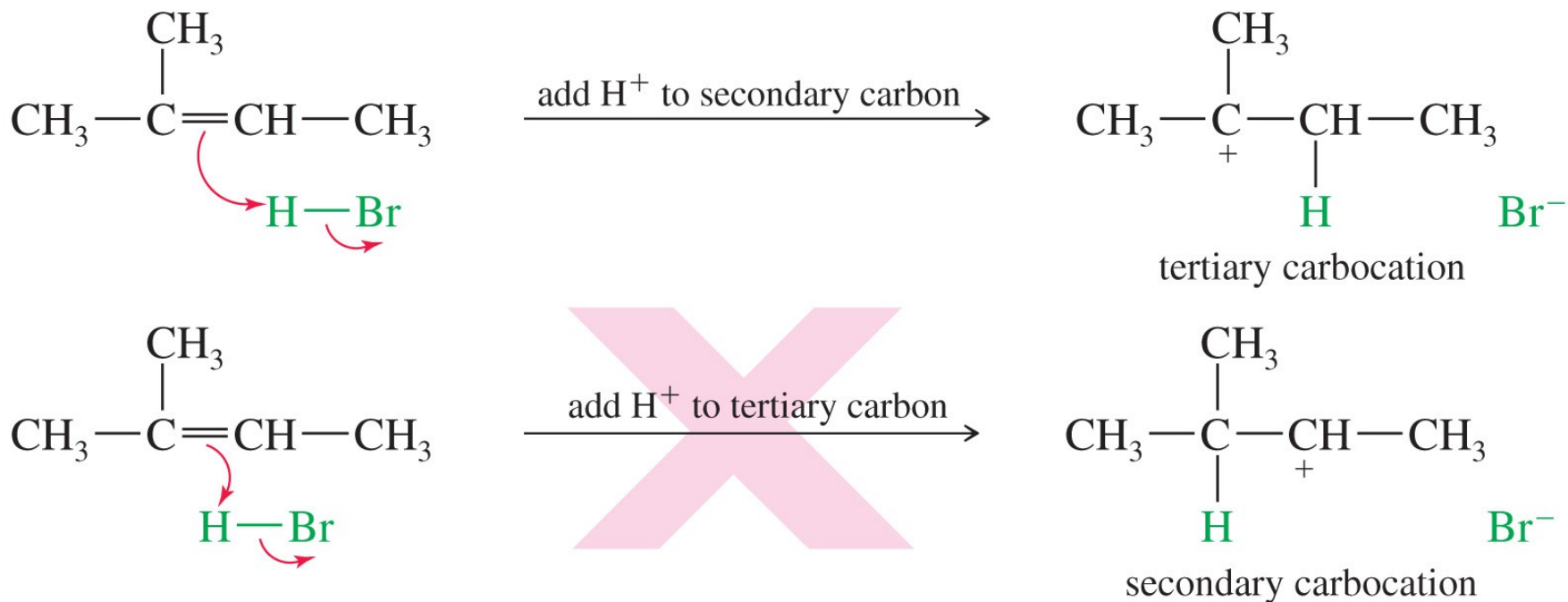
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The acid proton will bond to carbon 3 in order to produce the most stable carbocation possible.

Free-Radical Addition of HBr

- In the presence of peroxides, HBr adds to an alkene to form the "anti-Markovnikov" product.
- Peroxides produce free radicals.
- <u>Only</u> HBr has the right bond energy.
- The HCl bond is too strong, so it will add according to Markovnikov's rule, even in the presence of peroxide.
- The HI bond tends to break heterolytically to form ions, it too will add according to Markovnikov's rule.

Free-Radical Initiation

- The peroxide bond breaks homolytically to form the first radical:

$$R—O—O—R \xrightarrow{heat} R—O\cdot \ + \ \cdot O—R$$

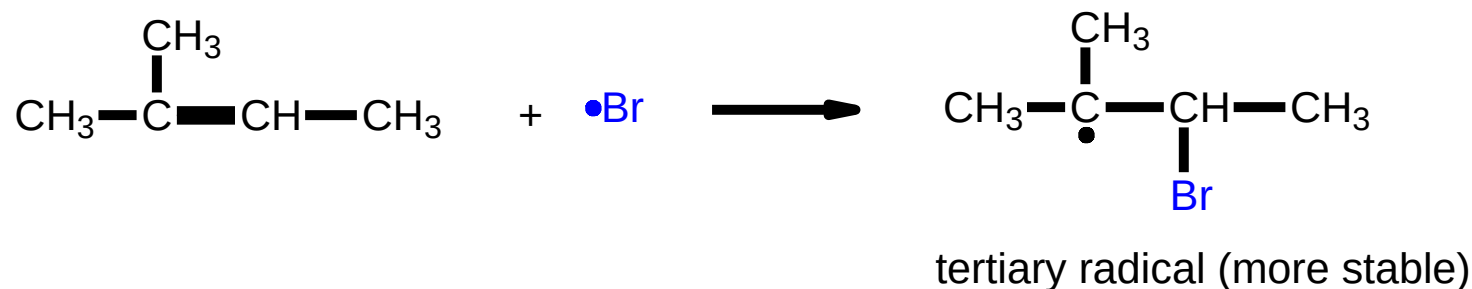$$R—O\cdot \ + \ H—Br \longrightarrow R—O—H \ + \ Br\cdot$$

Copyright © 2010 Pearson Prentice Hall, Inc.
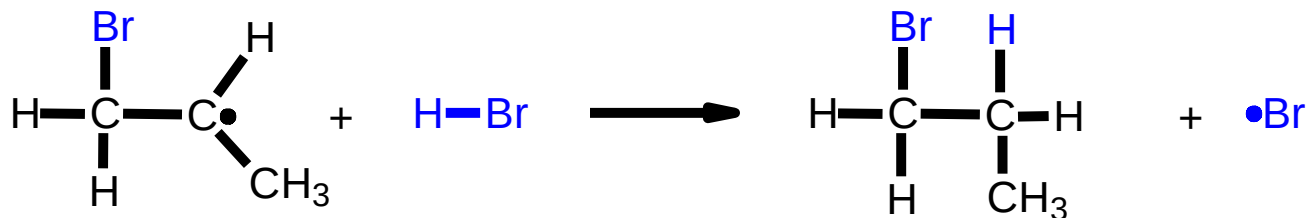
- Hydrogen is abstracted from HBr.

Propagation Steps

- Bromine adds to the double bond forming the most stable radical possible:

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3 \quad + \quad \bullet Br \quad \longrightarrow \quad CH_3-\underset{\underset{\bullet}{\overset{|}{C}}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{Br}{|}}{CH}-CH_3$$

tertiary radical (more stable)

- Hydrogen is abstracted from HBr:

$$H-\underset{\underset{H}{|}}{\overset{\overset{Br}{|}}{C}}-\underset{\underset{CH_3}{}}{\overset{\overset{H}{}}{C}}\bullet \quad + \quad H-Br \quad \longrightarrow \quad H-\underset{\underset{H}{|}}{\overset{\overset{Br}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-H \quad + \quad \bullet Br$$

Anti-Markovnikov Stereochemistry

$$CH_3-C(CH_3)=CH-CH_3 \quad + \quad \bullet Br \quad \longrightarrow$$

tertiary radical (more stable)
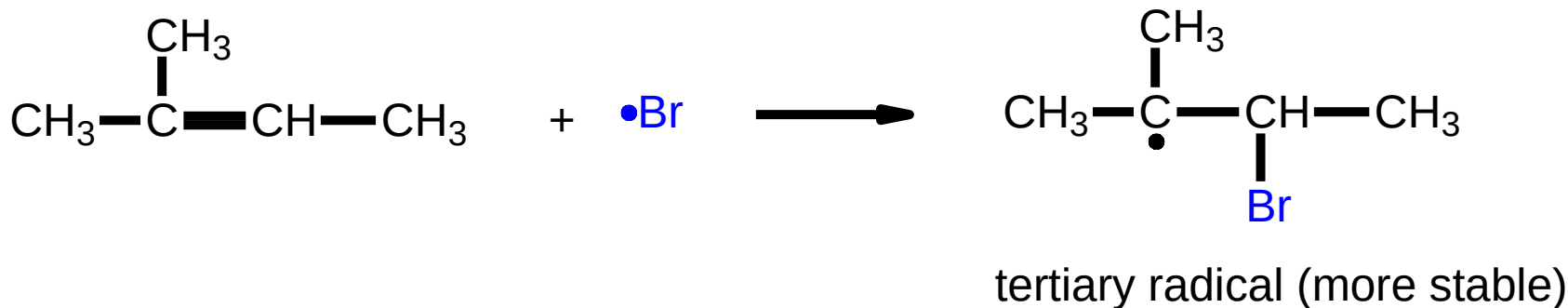
- The intermediate tertiary radical forms faster because it is more stable.

secondary radical (less stable)
not formed
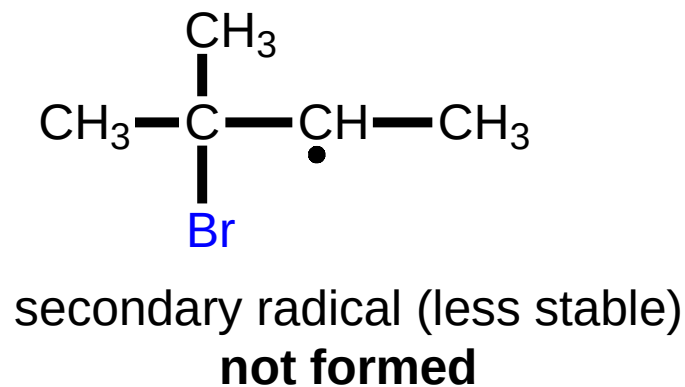
Hydration of Alkenes
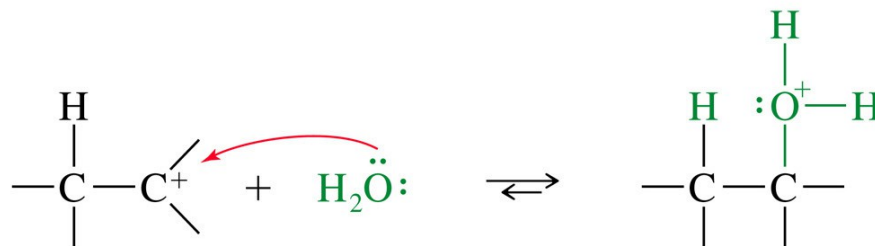
Hydration of an alkene
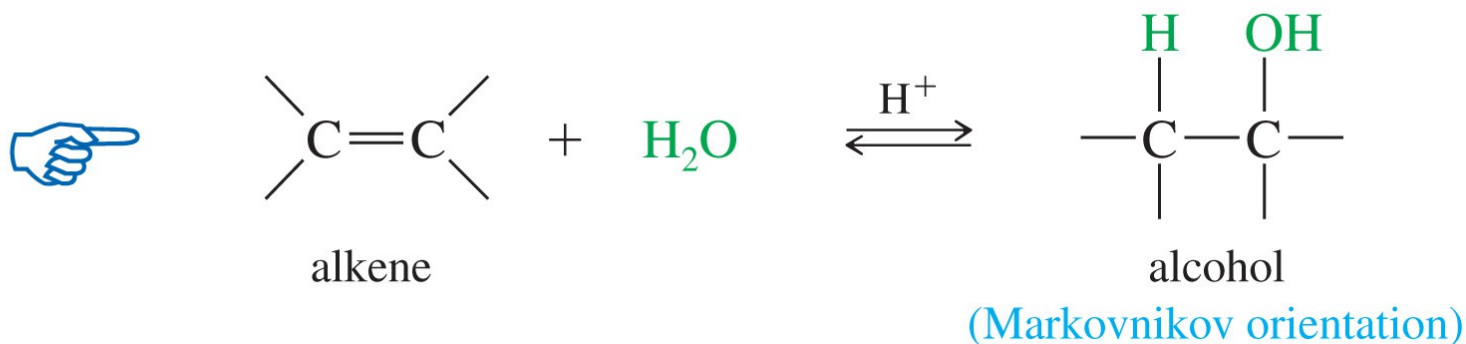
- The Markovnikov addition of water to the double bond forms an alcohol.
- This is the reverse of the dehydration of alcohol.
- Uses dilute solutions of H_2SO_4 or H_3PO_4 to drive equilibrium toward hydration.
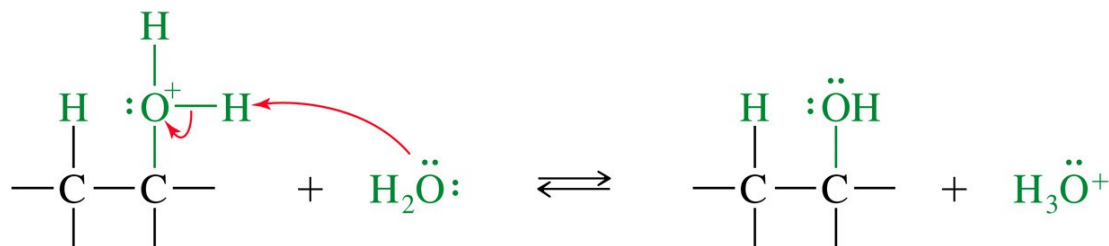
Mechanism for Hydration

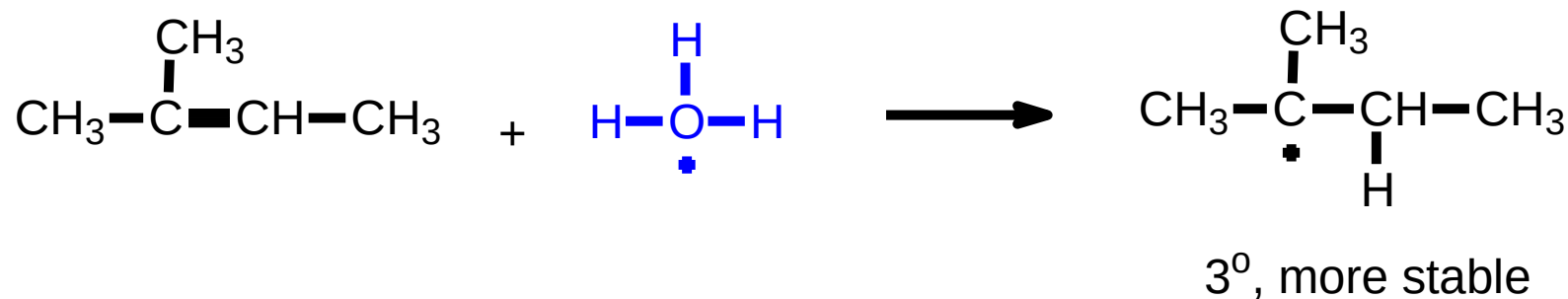*Step 1:* Protonation of the double bond forms a carbocation.
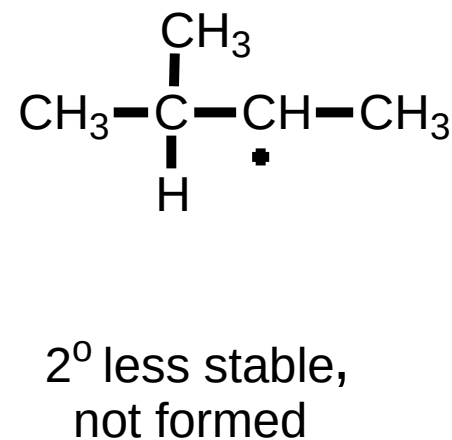

Step 2: Nucleophilic attack by water.
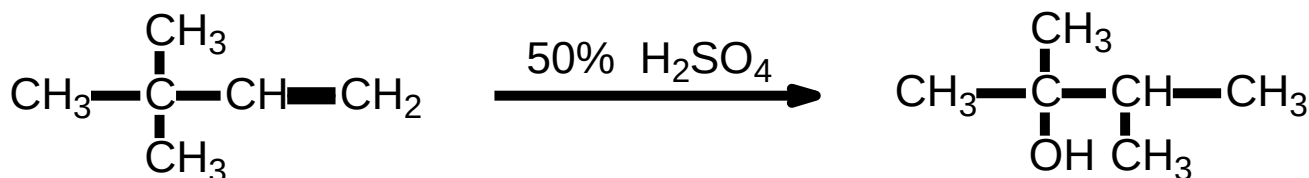

Step 3: Deprotonation to the alcohol.

Orientation of Hydration

$$CH_3-\underset{\underset{}{\overset{\overset{CH_3}{|}}{}}}{C}=CH-CH_3 \quad + \quad H-\underset{\underset{}{\overset{\overset{H}{|}}{}}}{O}-H \quad \longrightarrow$$

$$CH_3-\underset{\underset{}{\overset{\overset{CH_3}{|}}{C^{\bullet}}}}{}-\underset{\underset{H}{|}}{CH}-CH_3$$
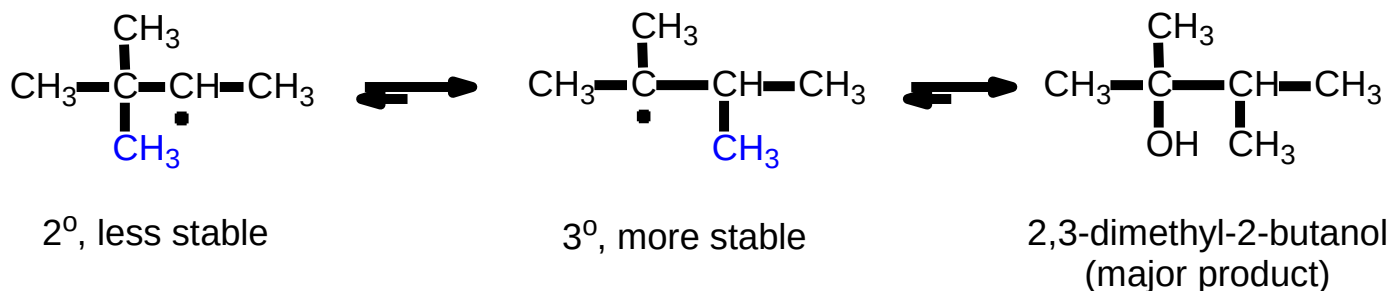
3°, more stable

The protonation follows Markovnikov's rule: The hydrogen is added to the less substituted carbon in order to form the most stable carbocation.

$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH^{\bullet}-CH_3$$

2° less stable,
not formed

Rearrangements

Rearrangement:

2°, less stable   3°, more stable   2,3-dimethyl-2-butanol (major product)

- Rearrangements can occur when there are carbocation intermediates.
- A methyl shift after protonation will produce the more stable tertiary carbocation.
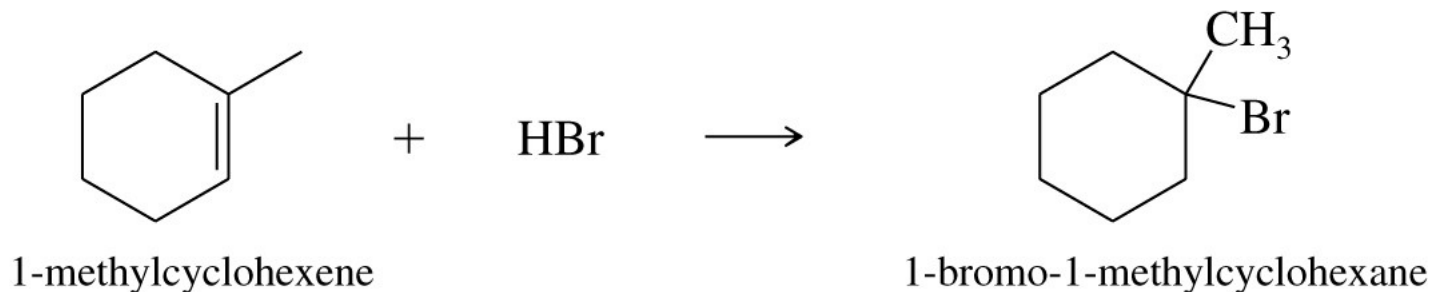
Solved Problem 1

Show how you would accomplish the following synthetic conversions.
(a) Convert 1-methylcyclohexene to 1-bromo-1-methylcyclohexane.

Solution

This synthesis requires the addition of HBr to an alkene with Markovnikov orientation. Ionic addition of HBr gives the correct product.
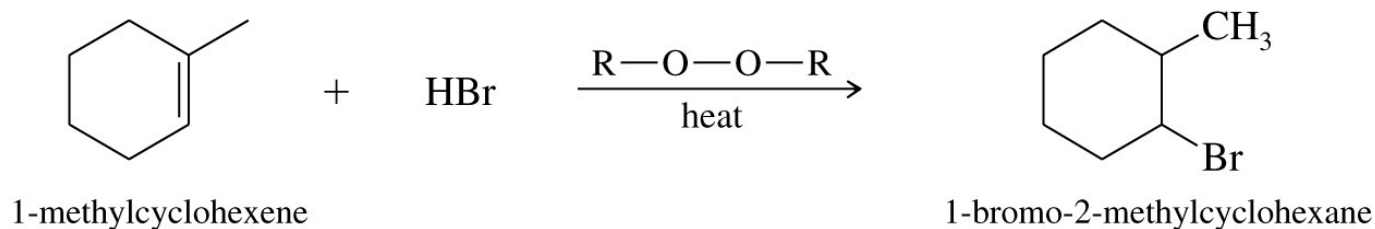

1-methylcyclohexene   +   HBr   ⟶   1-bromo-1-methylcyclohexane
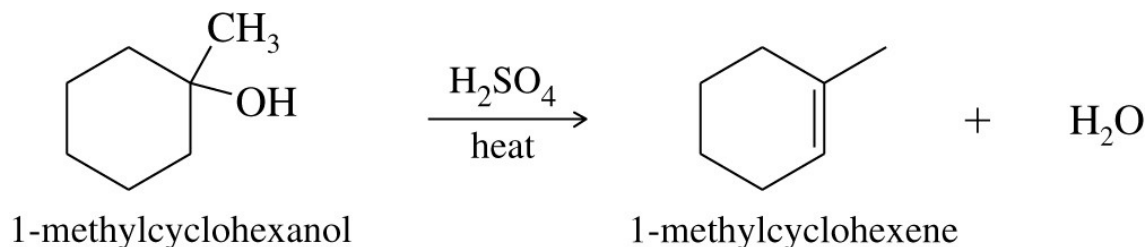
Solved Problem 2

Convert 1-methylcyclohexanol to 1-bromo-2-methylcyclohexane.

Solution

This synthesis requires the conversion of an alcohol to an alkyl bromide with the bromine atom at the neighboring carbon atom. This is the anti-Markovnikov product, which could be formed by the radical-catalyzed addition of HBr to 1-methylcyclohexene.


1-methylcyclohexene   1-bromo-2-methylcyclohexane

1-Methylcyclohexene is easily synthesized by the dehydration of 1-methylcyclohexanol. The most substituted alkene is the desired product.

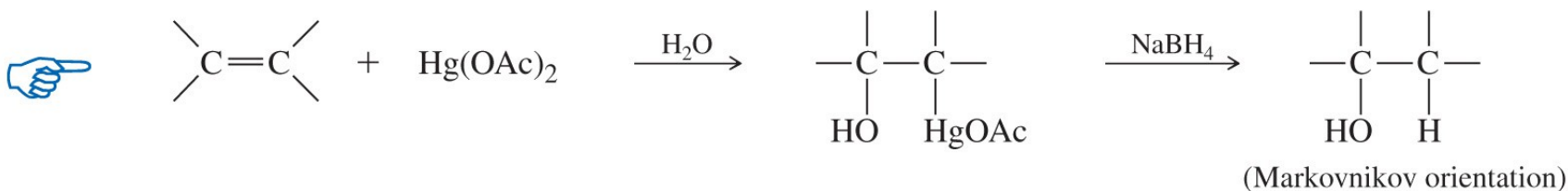1-methylcyclohexanol   1-methylcyclohexene

Solved Problem 2 (Continued)

Solution (Continued)

The two-step synthesis is summarized as follows:

1-methylcyclohexanol → 1-methylcyclohexene → 1-bromo-2-methylcyclohexane
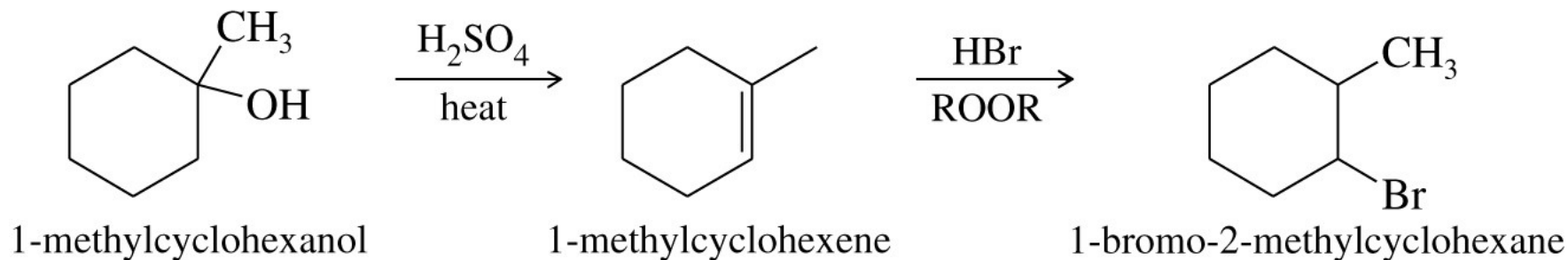
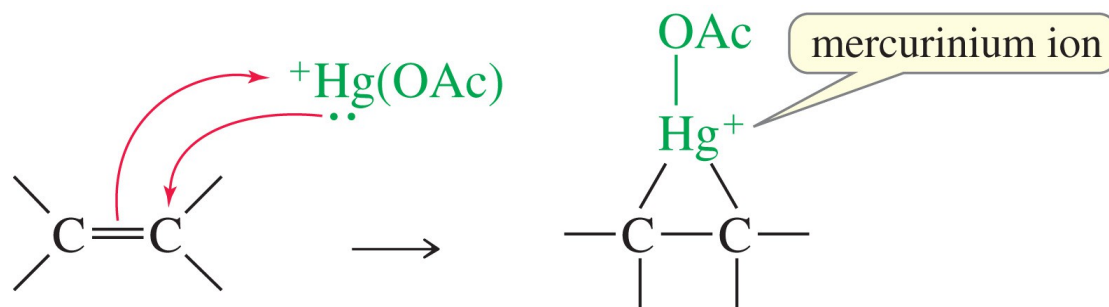# Oxymercuration–Demercuration Reaction

Oxymercuration–Demercuration

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- Markovnikov addition of water to the double bond.

- No rearrangements.

- This is a two-step process.

Oxymercuration Reaction

- Reagent is mercury(II) acetate, which dissociates slightly to form $^{+}$Hg(OAc).

- $^{+}$Hg(OAc) is the electrophile that adds to the pi bond.

- The intermediate is a three-membered ring called the mercurinium ion.

- Overall the addition of water follows Markovnikov's rule.
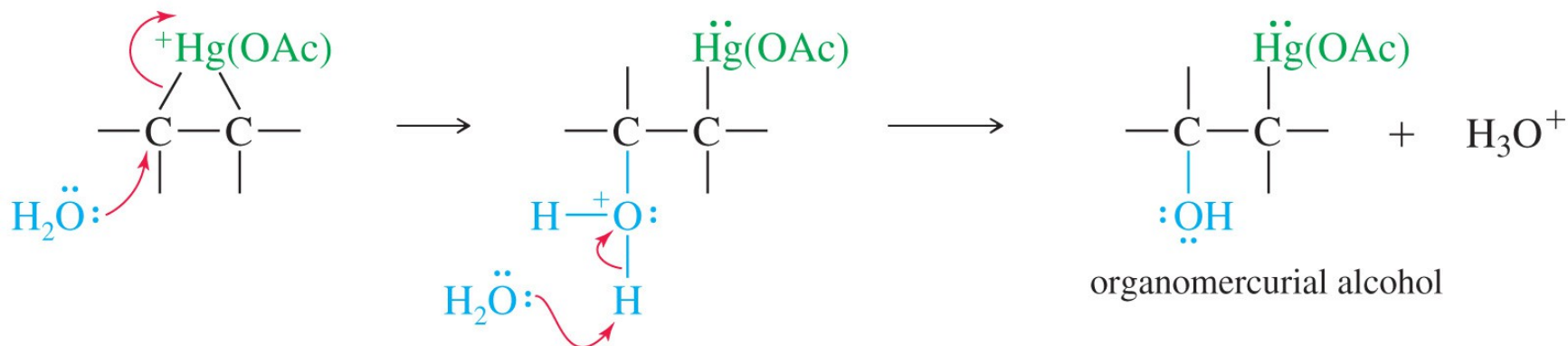
Mechanism of Oxymercuration

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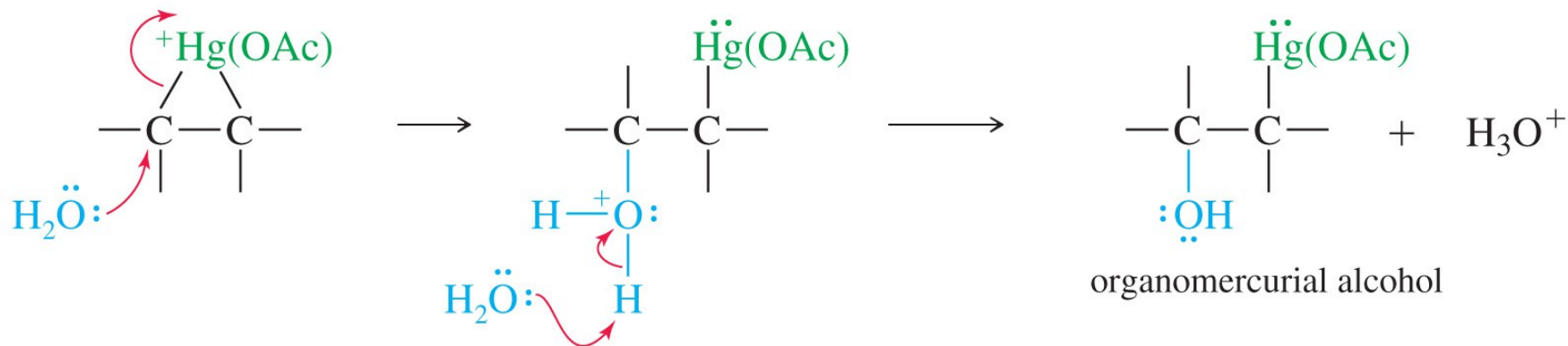
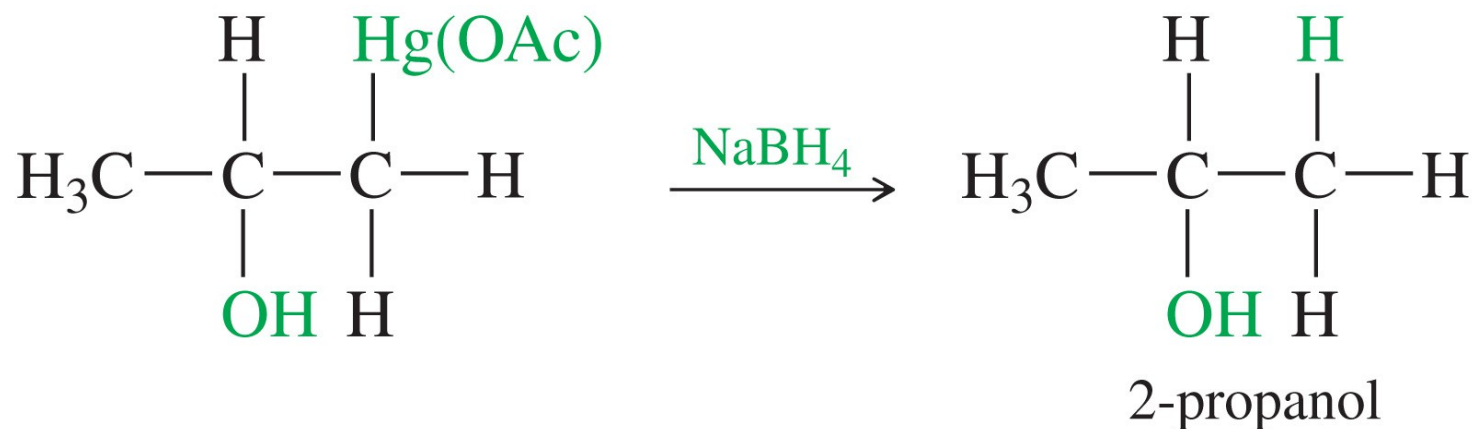Copyright © 2010 Pearson Prentice Hall, Inc.

Mercurinium Ion Opening

- Water adds to the more substituted carbon to form the Markovnikov product.

- Water approaches the mercurinium ion from the side opposite the ring (anti addition).

organomercurial alcohol

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Demercuration Reaction

$$H_3C-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{Hg(OAc)}{|}}{C}}-H \xrightarrow{NaBH_4} H_3C-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H$$

2-propanol

- In the demercuration reaction, a hydride furnished by the sodium borohydride ($NaBH_4$) replaces the mercuric acetate.
- The oxymercuration-demercuration reaction gives the Markovnikov product with the hydroxy group on the most substituted carbon.

Oxymercuration–Demercuration of 3,3,-Dimethyl-1-butene

3,3-dimethyl-1-butene → mercurinium ion → Markovnikov product

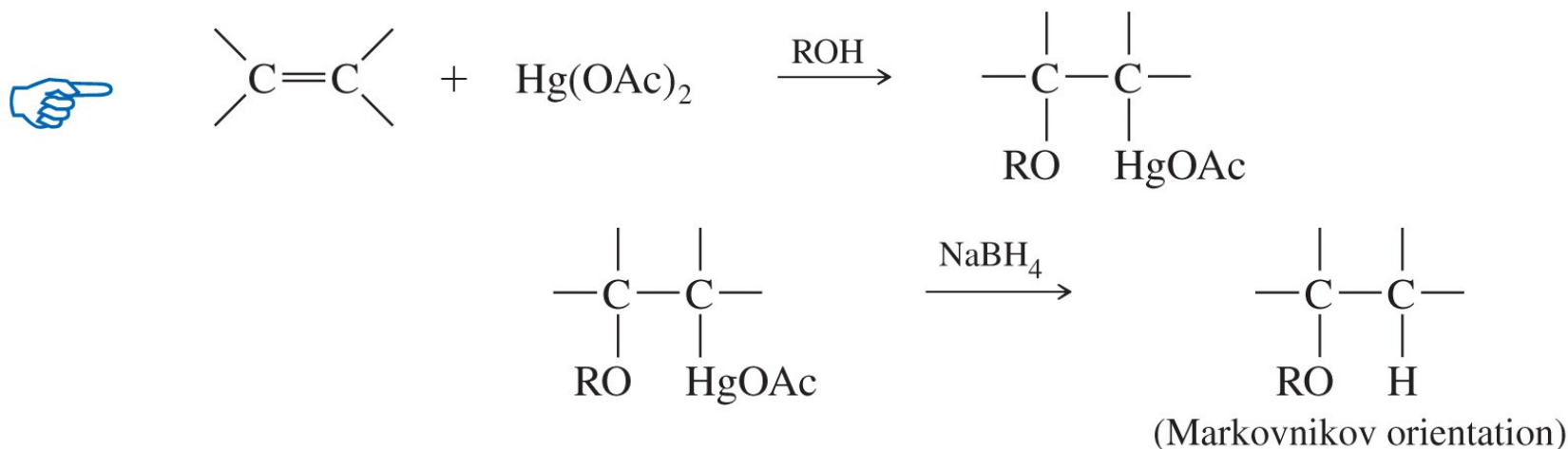Markovnikov product → NaBH$_4$ → 3,3-dimethyl-2-butanol (94% overall)
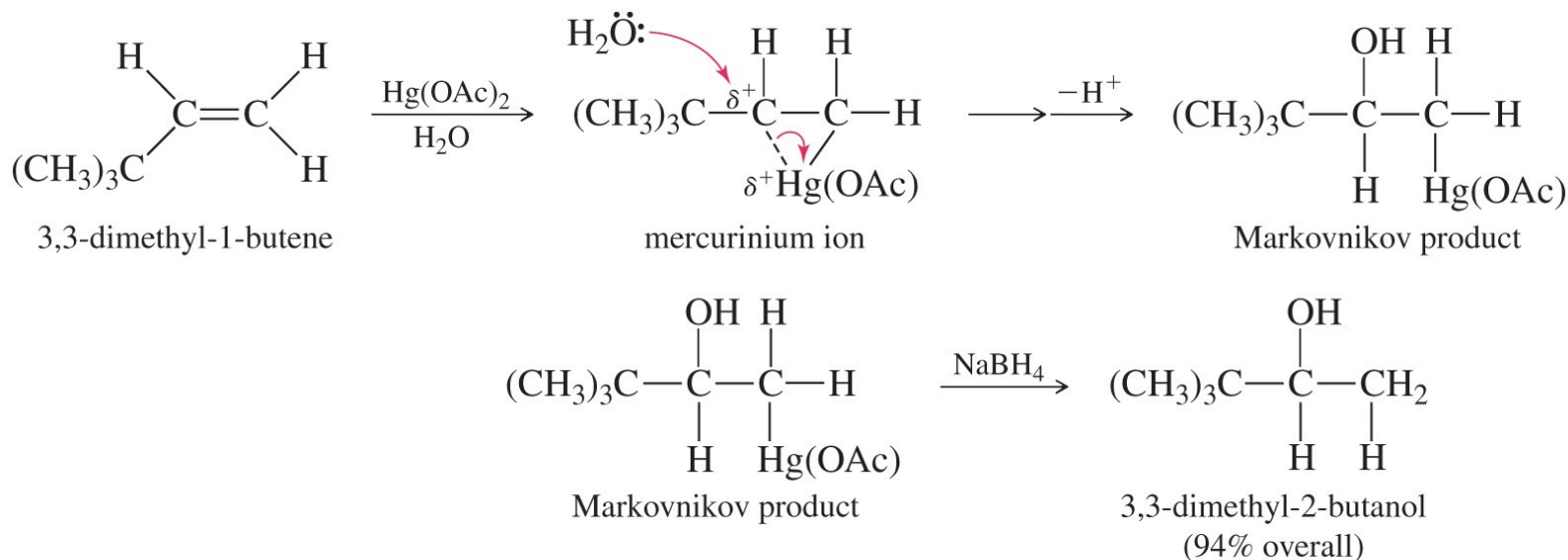
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The reaction does not suffer from rearrangements because there is no carbocation intermediate.

Alkoxymercuration–Demercuration

If the nucleophile is an alcohol, ROH, instead of water, HOH, an ether is produced.
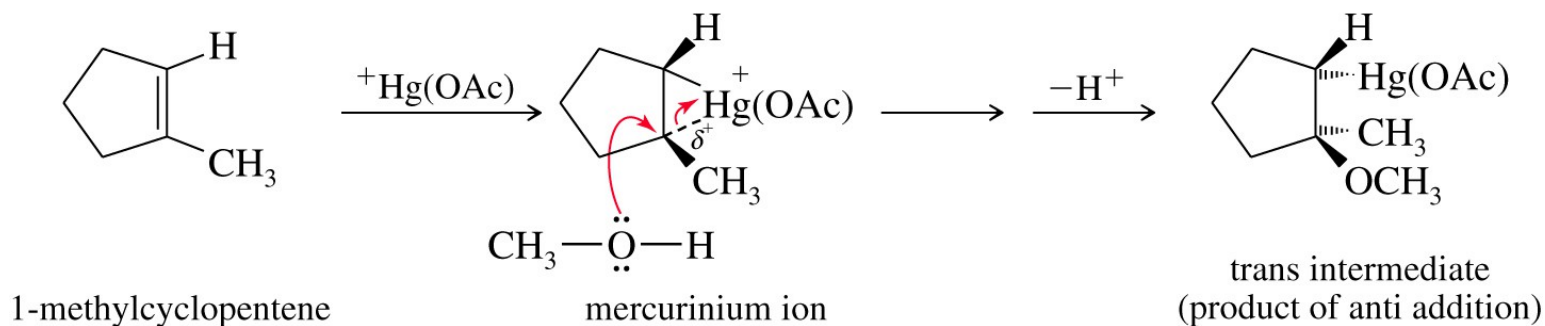

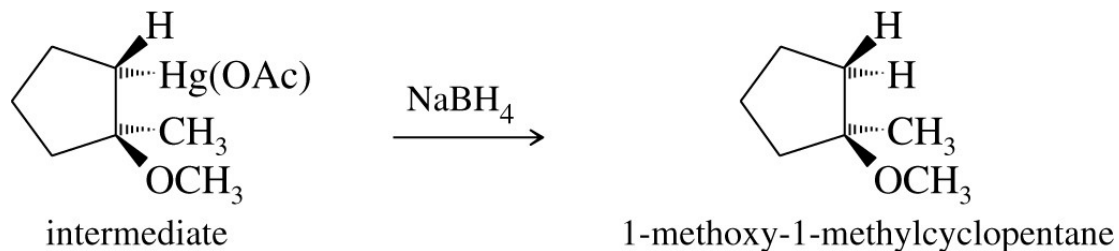Copyright © 2010 Pearson Prentice Hall, Inc.

Solved Problem 3

Show the intermediates and products that result from alkoxymercuration–demercuration of 1-methylcyclopentene, using methanol as the solvent.

Solution

Mercuric acetate adds to 1-methylcyclopentene to give the cyclic mercurinium ion. This ion has a considerable amount of positive charge on the more substituted tertiary carbon atom. Methanol attacks this carbon.
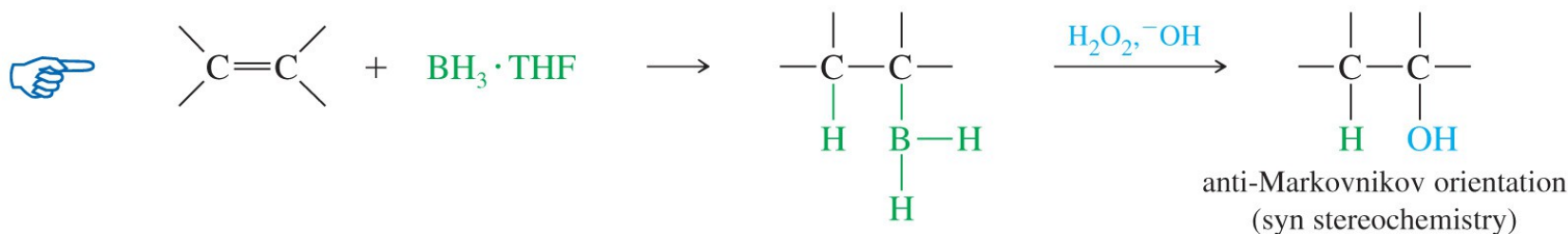

1-methylcyclopentene   mercurinium ion   trans intermediate
                                                        (product of anti addition)

Reduction of the intermediate gives the Markovnikov product, 1-methoxy-1-methylcyclopentane.

intermediate   1-methoxy-1-methylcyclopentane

Hydroboration of Alkenes

Hydroboration–oxidation:

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- The reaction adds water across the double bond with anti-Markovnikov orientation.
- BH_3 (borane) is a strong Lewis acid.
- Diborane (B_2H_6) is a dimer of borane and it is in equilibrium with a small amount of BH_3.
- BH_3•THF is the most commonly used form of borane.

Mechanism of Hydroboration

more stable transition state

less stable transition state
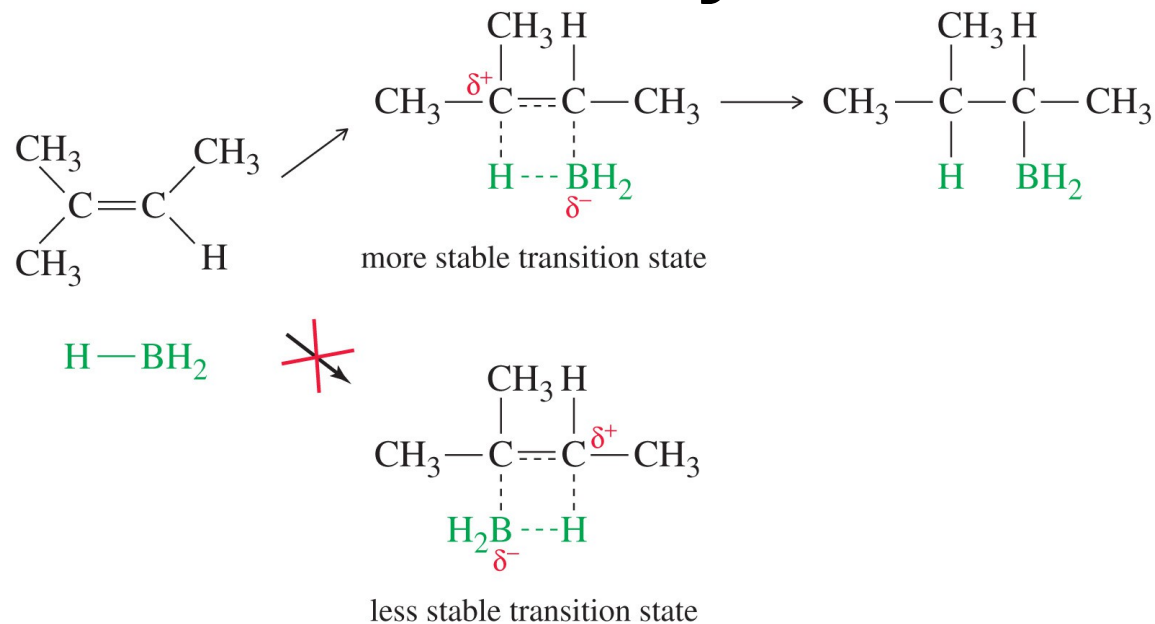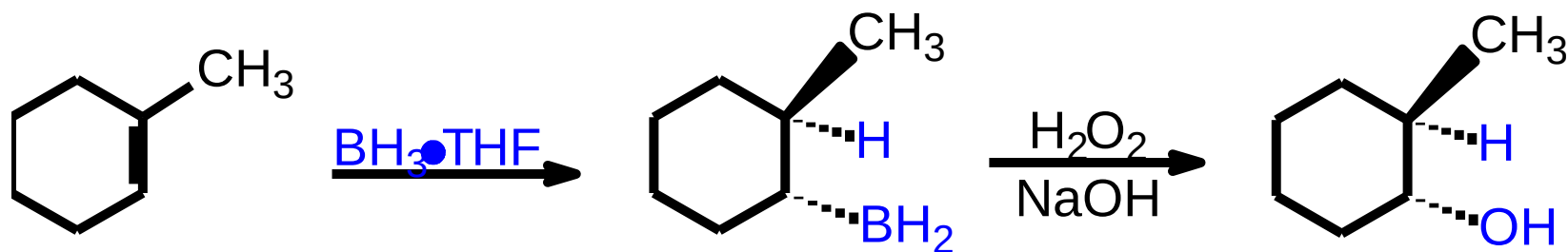
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- Borane adds to the double bond in a single step, with boron adding to the less substituted carbon and hydrogen adding to the more highly substituted carbon.
- This orientation places the partial positive charge in the transition state on the more highly substituted carbon atom.

Stereochemistry of Hydroboration

- The hydroboration steps adds the hydrogen and the boron to the same side of the double bond (**syn addition**).

- When the boron is oxidized, the OH will keep the same stereochemical orientation.
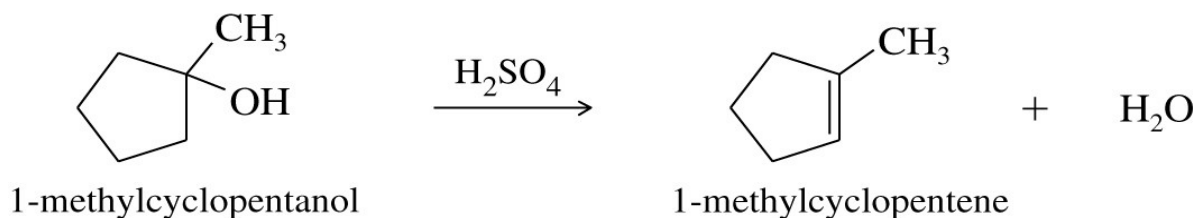
Solved Problem 4

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

Solution

Working backward, use hydroboration–oxidation to form 2-methyl cyclopentanol from 1-methylcyclopentene. The use of (1) and (2) above and below the reaction arrow indicates individual steps in a two-step sequence.
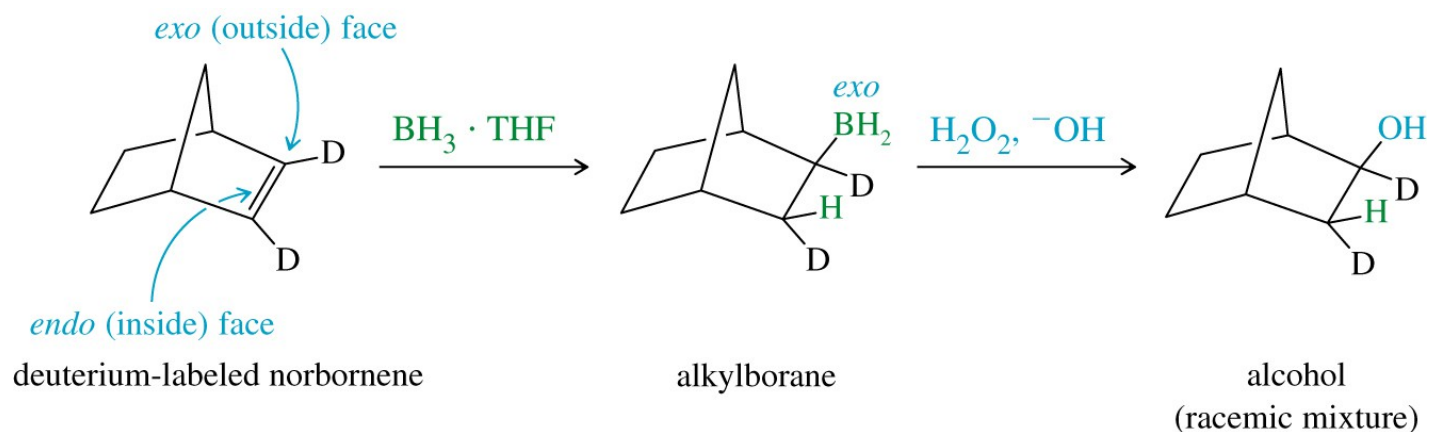

$$\text{1-methylcyclopentene} \quad \xrightarrow[\text{(2) } H_2O_2, \ {}^-OH]{\text{(1) } BH_3 \cdot THF} \quad \textit{trans}\text{-2-methylcyclopentanol}$$
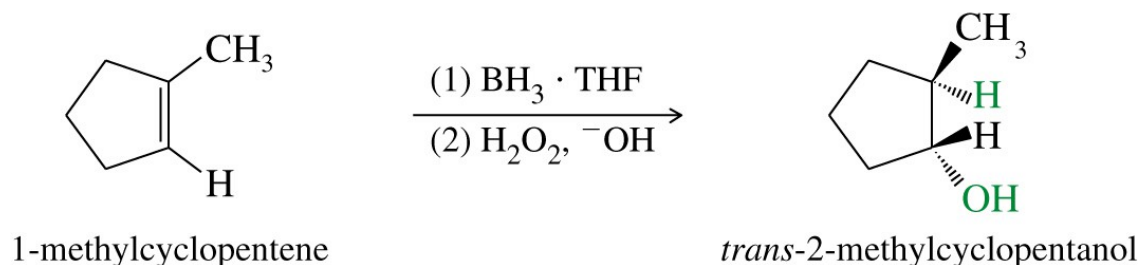
The 2-methylcyclopentanol that results from this synthesis is the pure trans isomer. This stereochemical result is discussed in Section 8-7C. 1-Methylcyclopentene is the most substituted alkene that results from dehydration of 1-methylcyclopentanol. Dehydration of the alcohol would give the correct alkene.

$$\text{1-methylcyclopentanol} \quad \xrightarrow{H_2SO_4} \quad \text{1-methylcyclopentene} \quad + \quad H_2O$$

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Solved Problem 5

A norbornene molecule labeled with deuterium is subjected to hydroboration–oxidation. Give the structures of the intermediates and products.

Solution

exo (outside) face

endo (inside) face

deuterium-labeled norbornene   alkylborane   alcohol (racemic mixture)

The syn addition of BH_3 across the double bond of norbornene takes place mostly from the more accessible outside (exo) face of the double bond. Oxidation gives a product with both the hydrogen atom and the hydroxyl group in exo positions. (The less accessible inner face of the double bond is called the endo face.)

Oxidation to Alcohol
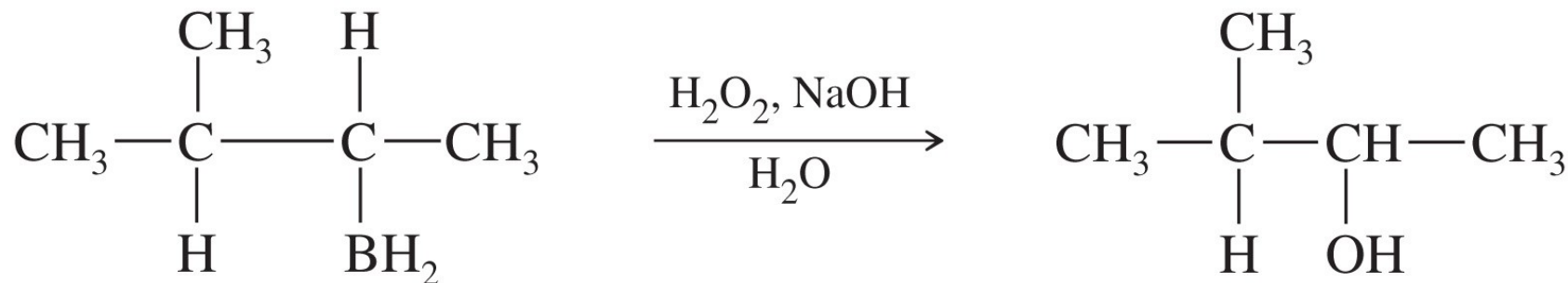
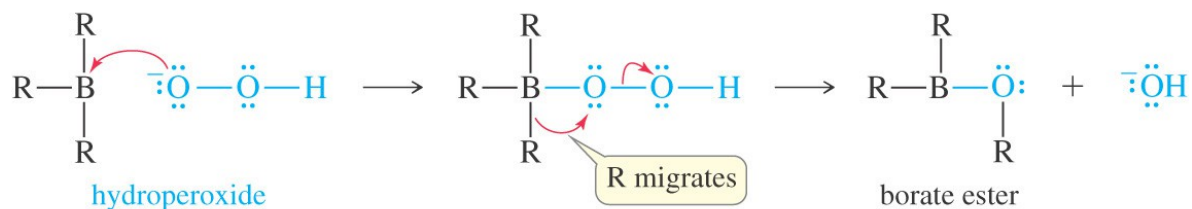Copyright © 2010 Pearson Prentice Hall, Inc.

- Oxidation of the alkyl borane with basic hydrogen peroxide produces the alcohol.
- Orientation is anti-Markovnikov.
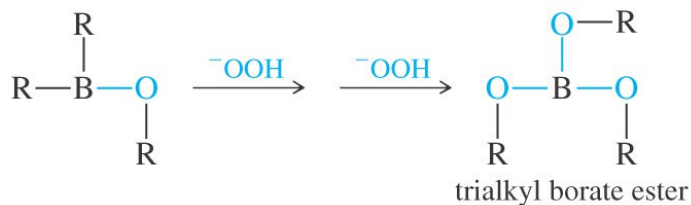
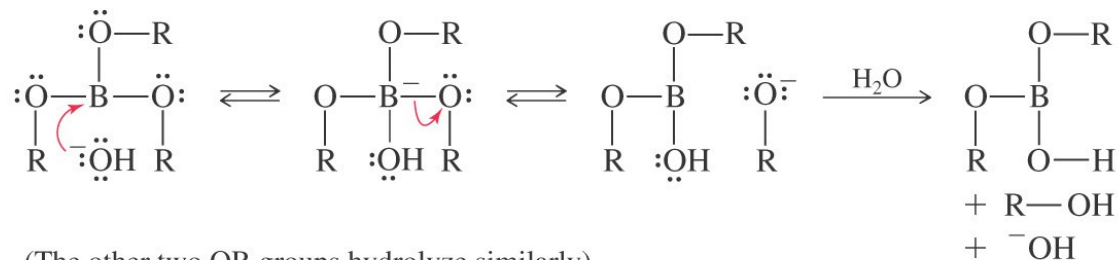# Oxidation of a Trialkylborane

Formation of hydroperoxide ion

$$H—\ddot{O}—\ddot{O}—H \quad + \quad :^-\ddot{O}H \quad \rightleftharpoons \quad H—\ddot{O}—\ddot{O}:^- \quad + \quad H_2\ddot{O}:$$

Addition of hydroperoxide and migration of the alkyl group

hydroperoxide

R migrates

borate ester

Twice more to oxidize the other two alkyl groups

trialkyl borate ester

Hydrolysis of the borate ester

(The other two OR groups hydrolyze similarly)

34

Addition of Halogens

$(X_2 = Cl_2, Br_2, \text{sometimes } I_2)$

usually anti addition
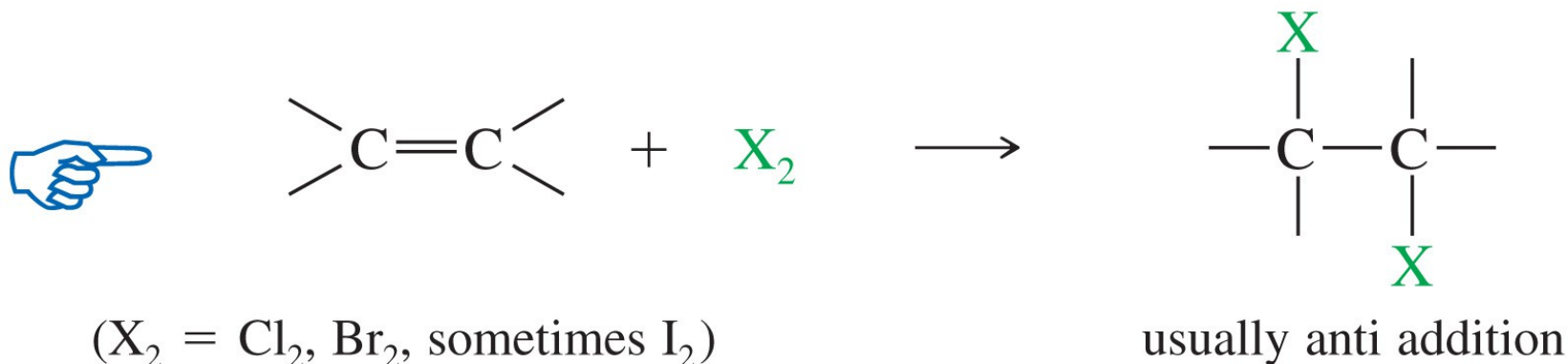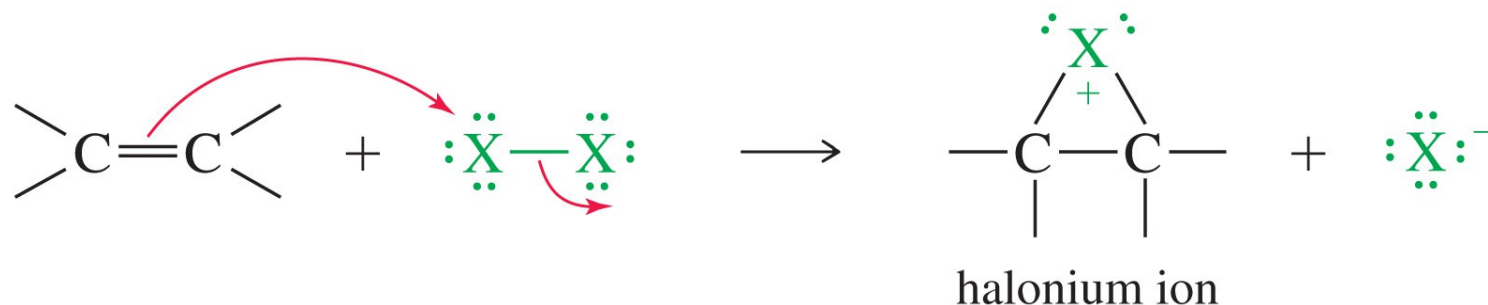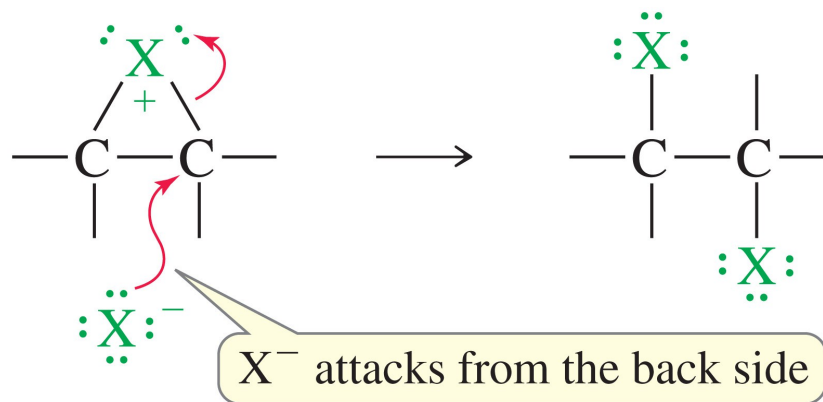
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- Cl_2, Br_2, and sometimes I_2 add to a double bond to form a vicinal dibromide.
- This is an anti addition of halides.
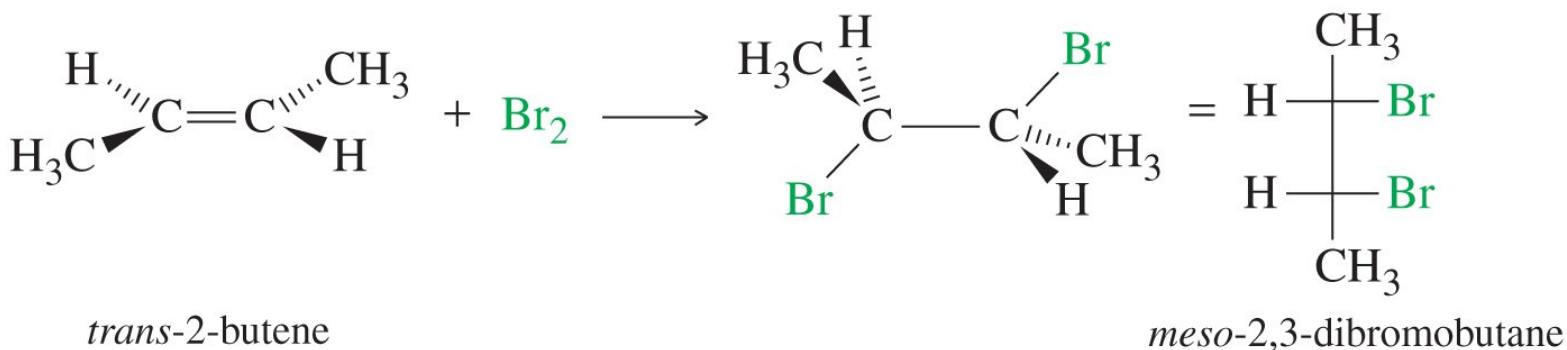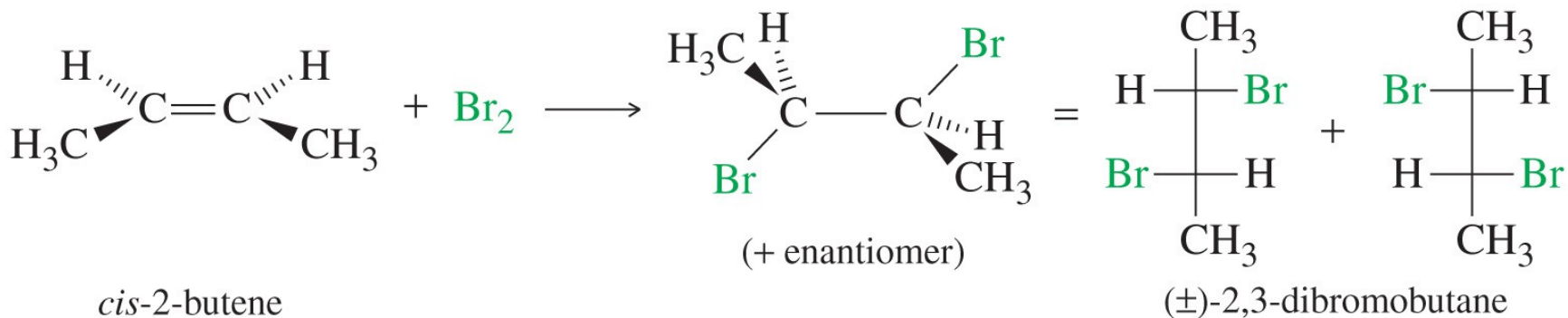
Mechanism of Halogen Addition to Alkenes

halonium ion

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X⁻ attacks from the back side

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- The intermediate is a three-membered ring called the halonium ion.

Examples of Stereospecificity

cis-2-butene + Br₂ ⟶ (+ enantiomer) = (±)-2,3-dibromobutane

trans-2-butene + Br₂ ⟶ = meso-2,3-dibromobutane

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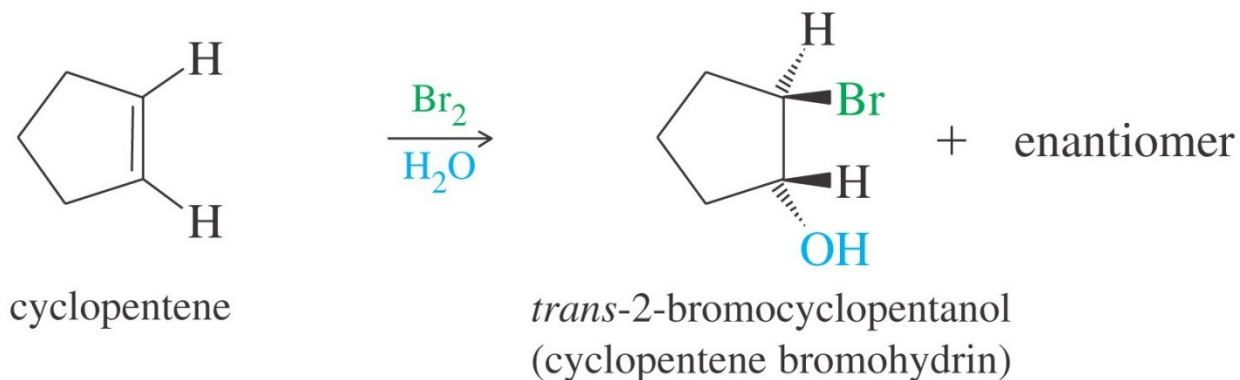
meso

Test for Unsaturation

- Add Br_2 in CCl_4 (dark, red-brown color) to an alkene.

- The color quickly disappears as the bromine adds to the double bond (left-side test tube).

- If there is no double bond present the brown color will remain (right side).

- "Decolorizing bromine" is the chemical test for the presence of a double bond.
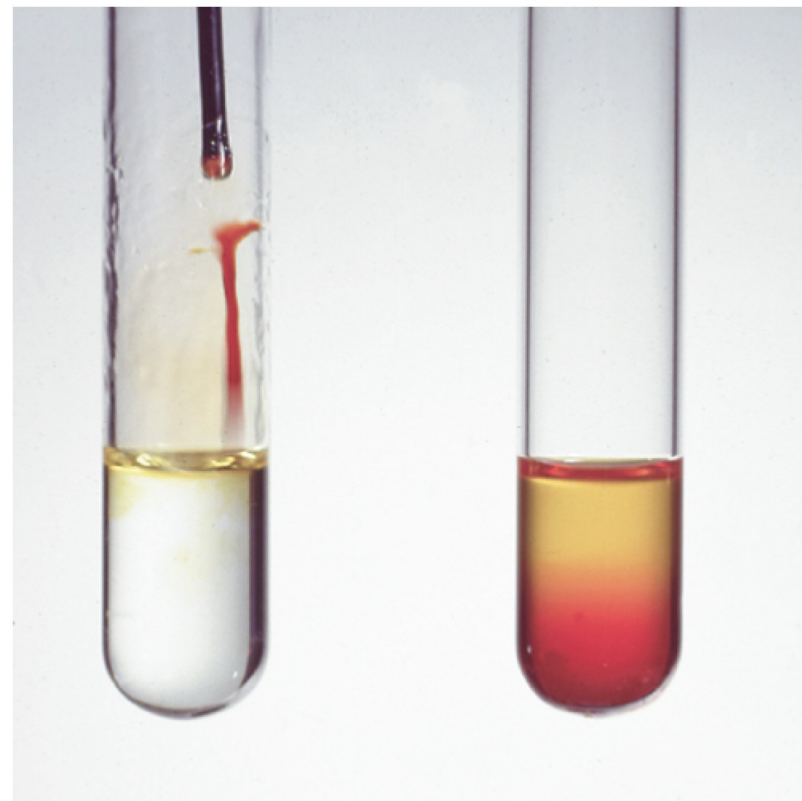
Formation of Halohydrin

cyclopentene

Br₂ / H₂O →

trans-2-bromocyclopentanol
(cyclopentene bromohydrin)

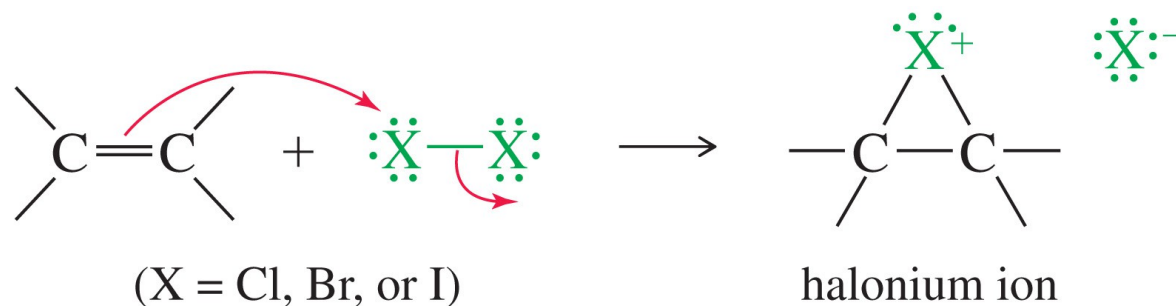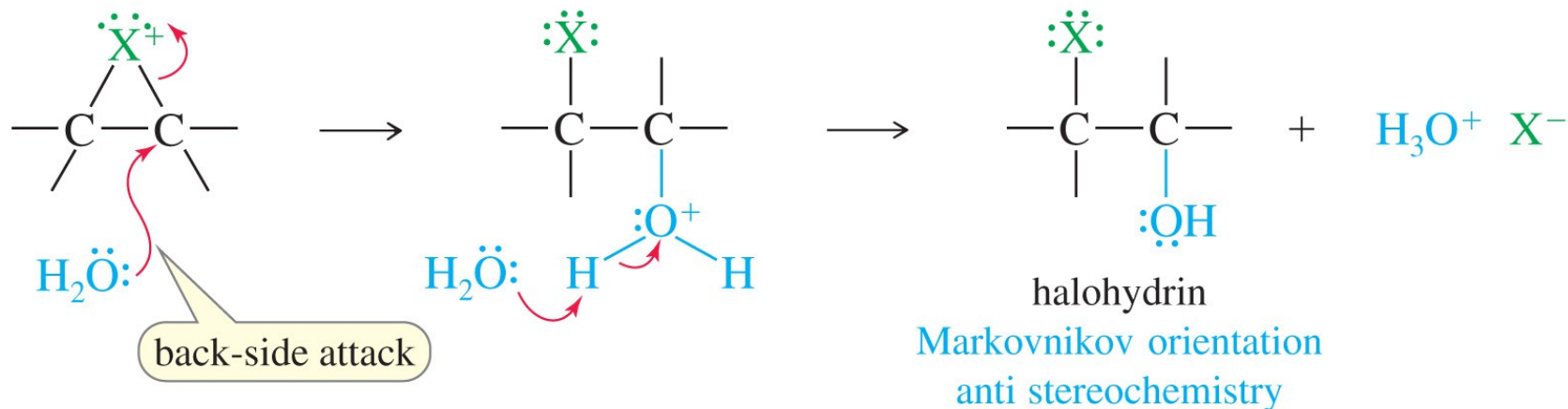+ enantiomer

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- If a halogen is added in the presence of water, a halohydrin is formed.
- Water is the nucleophile.
- This is a Markovnikov addition: The bromide (electrophile) will add to the less substituted carbon.

Mechanism of Halohydrin Formation

$(X = Cl, Br, or I)$ halonium ion

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back-side attack

$H_2O:$ H

halohydrin

Markovnikov orientation
anti stereochemistry

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Solved Problem 6

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.
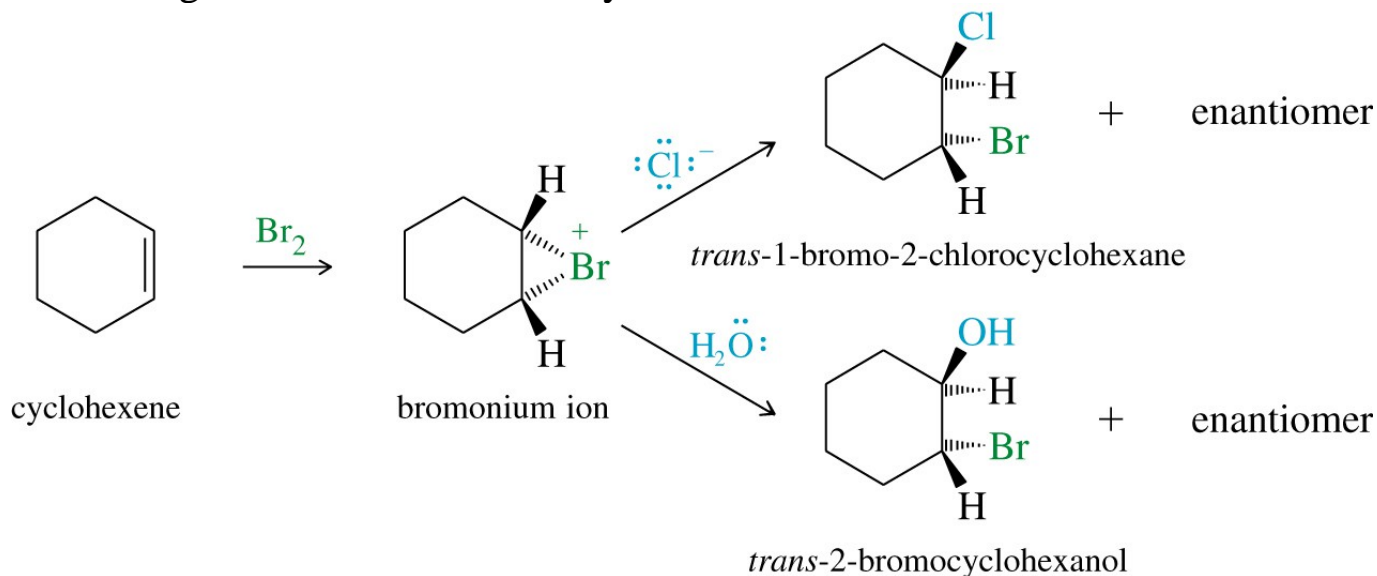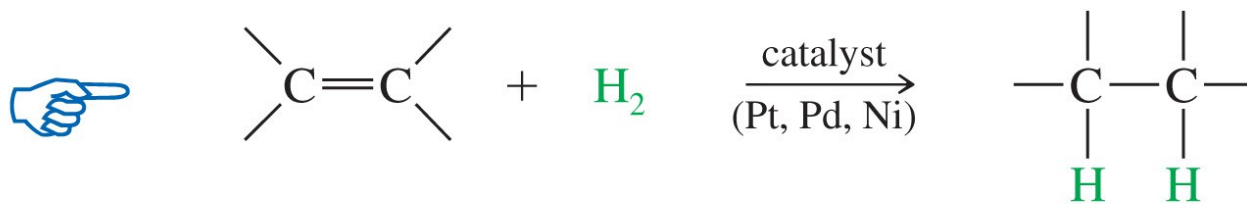

+ enantiomer
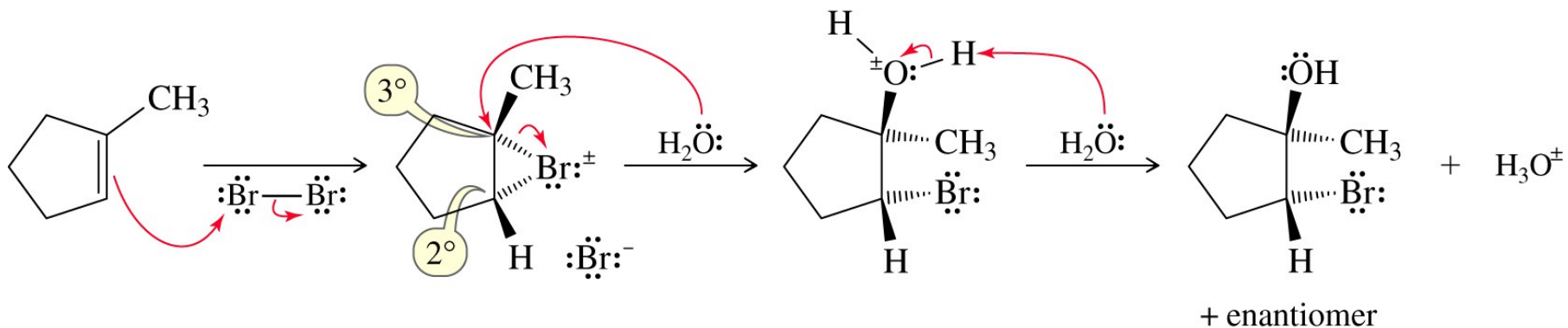
Solved Problem 7

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.
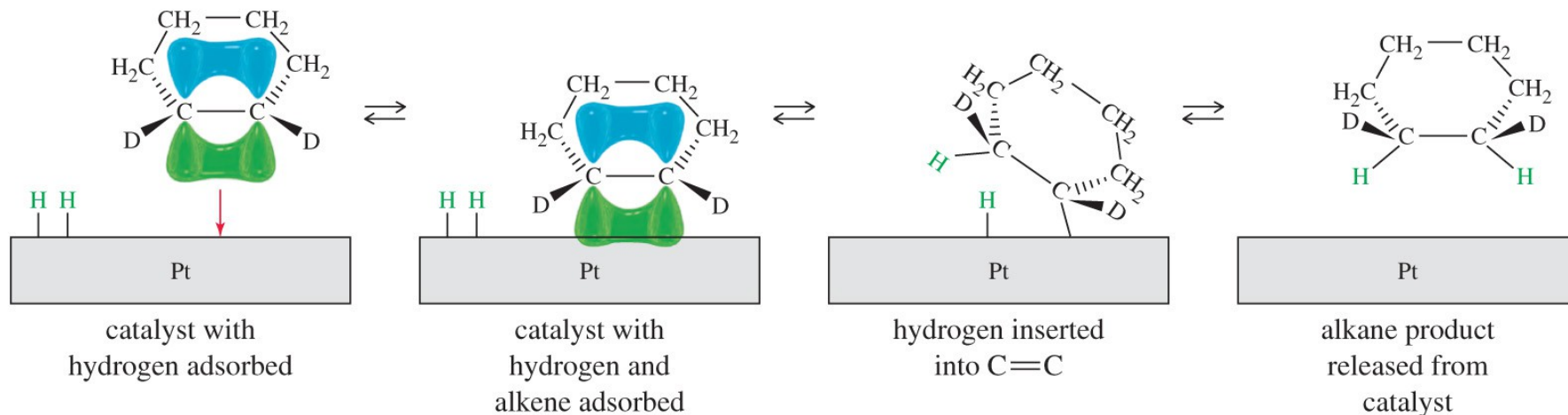
Hydrogenation of Alkenes

$$\text{C}=\text{C} \quad + \quad \text{H}_2 \quad \xrightarrow[\text{(Pt, Pd, Ni)}]{\text{catalyst}} \quad -\text{C}-\text{C}- \atop \text{H} \quad \text{H}$$

Example

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

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- Hydrogen (H_2) can be added across the double bond in a process known as **catalytic hydrogenation**.
- The reaction only takes place if a catalyst is used. The most commonly used catalysts are palladium (Pd), platinum (Pt), and nickel (Ni), but there are other metals that work just as well.
- Syn addition of hydrogen.

Mechanism of Catalytic Hydrogenation

catalyst with hydrogen adsorbed

catalyst with hydrogen and alkene adsorbed

hydrogen inserted into C=C

alkane product released from catalyst

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- The hydrogen and the alkene are adsorbed on the metal surface.
- Once adsorbed, the hydrogens insert across the same face of the double bond and the reduced product is released from the metal.
- The reaction has a syn stereochemistry since both hydrogens will add to the same side of the double bond.
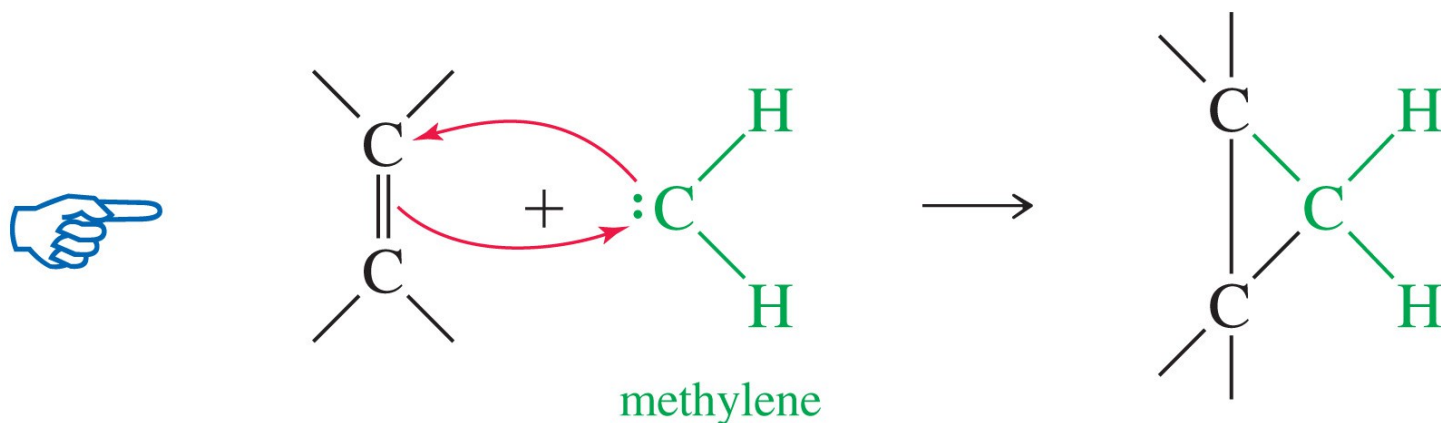
Chiral Hydrogenation Catalysts

$$\text{Ru(BINAP)Cl}_2 =$$
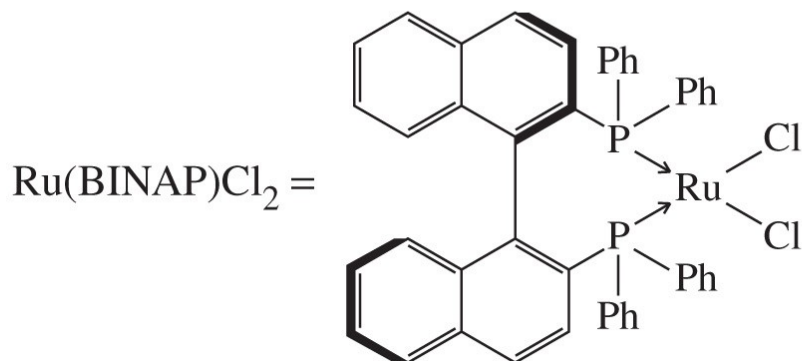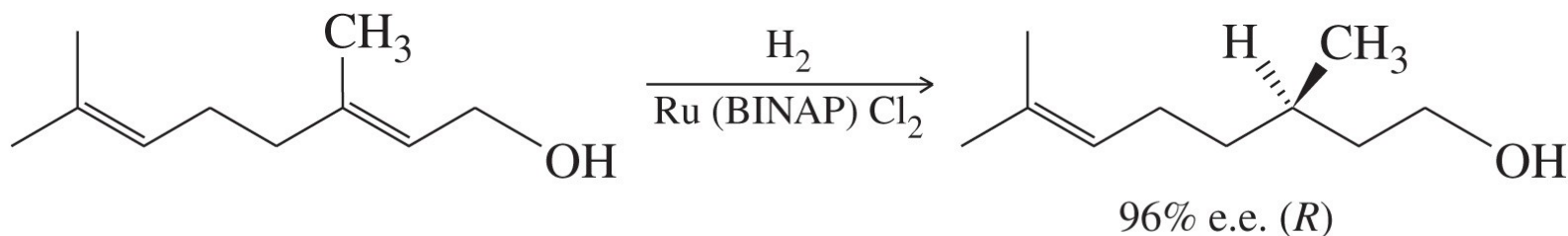
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- Rhodium and ruthenium phosphines are effective homogeneous catalysts for hydrogenation.
- Chiral ligands can be attached to accomplish asymmetric induction, the creation of a new asymmetric carbon as mostly one enantiomer.
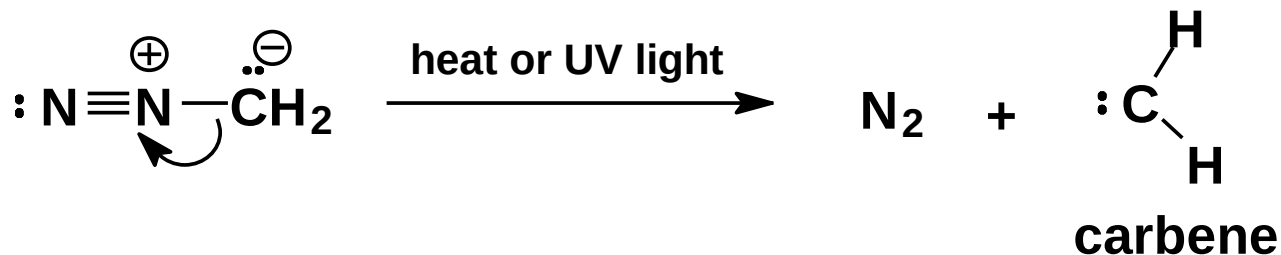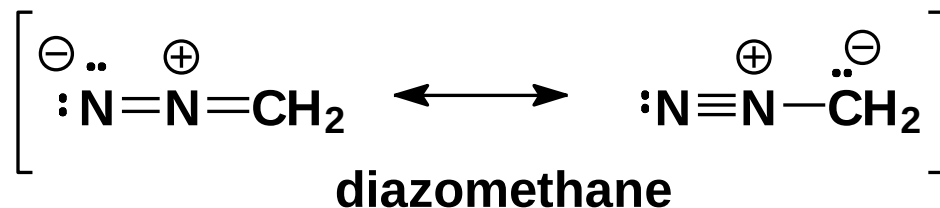
Addition of Carbenes

methylene

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- The nsertion of the —CH_2 group into a double bond produces a cyclopropane ring.
- Three methods:
  - Diazomethane (CH_3N_2, UV light or heat).
  - Simmons–Smith (CH_2I_2 and Zn(Cu)).
  - Alpha elimination of a haloform (CHX_3, NaOH, H_2O).

Carbenes: Diazomethane Method

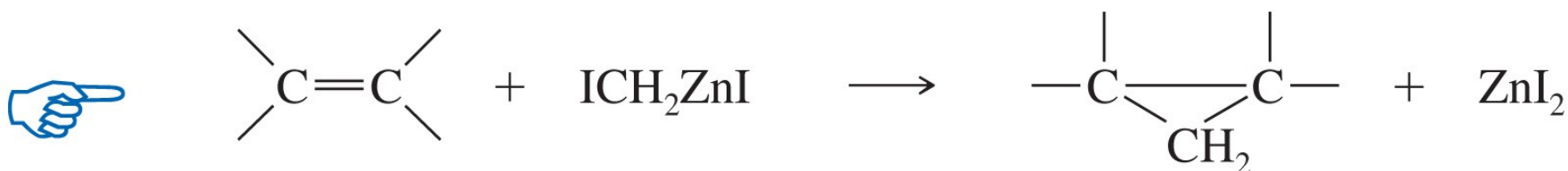$$\left[\overset{\ominus}{:}\overset{..}{N}=\overset{\oplus}{N}=CH_2 \longleftrightarrow \overset{\oplus}{:}N\equiv\overset{\ominus}{N}-\overset{..}{CH_2} \right]$$

diazomethane

$$:N\equiv\overset{\oplus}{N}-\overset{..\ominus}{CH_2} \xrightarrow{\text{heat or UV light}} N_2 \; + \; :C\overset{H}{\underset{H}{<}}$$

carbene

Problems with diazomentane:
    1. Extremely toxic and explosive.
    2. The carbene can insert into C—H bonds too.

Simmons–Smith Reaction
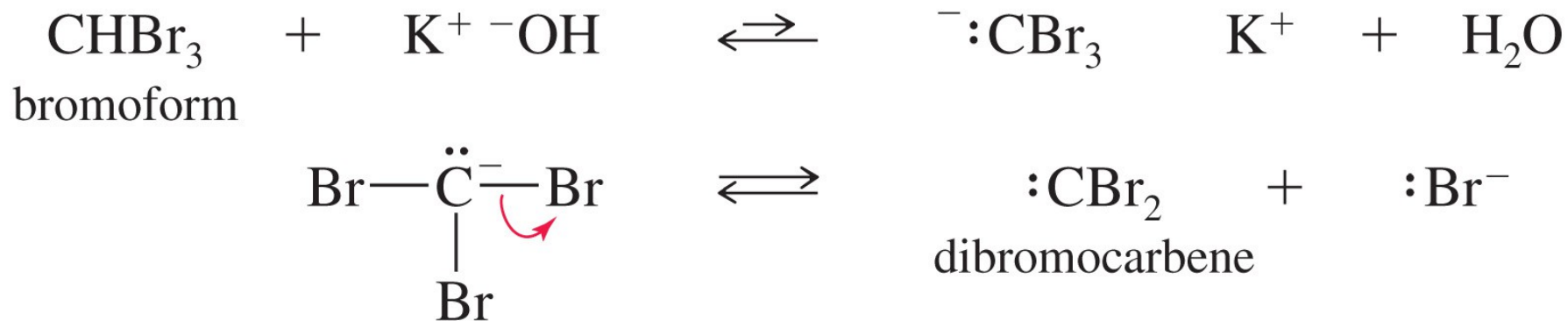
Best method for preparing cyclopropanes.

$$\text{C}=\text{C} \quad + \quad \text{ICH}_2\text{ZnI} \quad \longrightarrow \quad -\text{C}\underset{\text{CH}_2}{\diagdown\diagup}\text{C}- \quad + \quad \text{ZnI}_2$$

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$$\text{CH}_2\text{I}_2 \quad + \quad \text{Zn(Cu)} \rightarrow \quad \text{ICH}_2\text{ZnI}$$

Simmons–Smith
reagent

Alpha Elimination Reaction

$$CHBr_3 \quad + \quad K^+ \, {}^-OH \quad \rightleftharpoons \quad {}^-{:}CBr_3 \quad K^+ \quad + \quad H_2O$$
bromoform

Br—C̈⁻—Br $\rightleftharpoons$ $\quad {:}CBr_2 \quad + \quad {:}Br^-$
|
Br

dibromocarbene

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- In the presence of a base, chloroform or bromoform can be dehydrohalogenated to form a carbene.

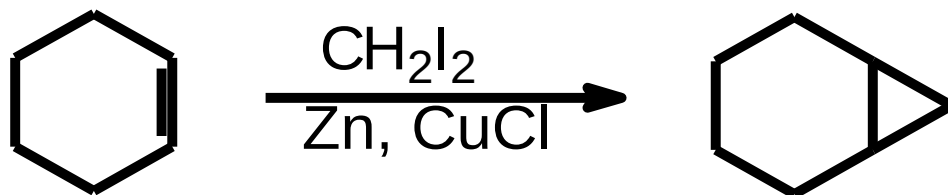# Stereospecificity

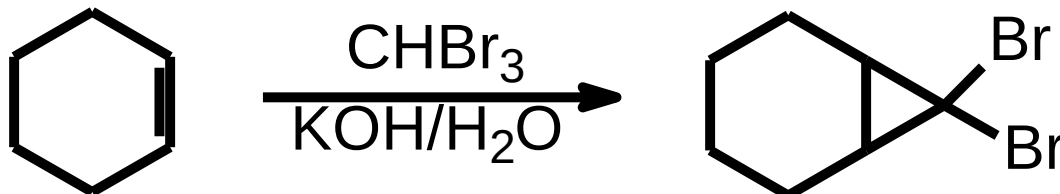- The cylopropanes will retain the cis or trans stereochemistry of the alkene.

$$\underset{CH_3}{\overset{H}{\diagdown}}C = C \underset{H}{\overset{CH_3}{\diagup}} \quad \xrightarrow[\text{KOH/H}_2\text{O}]{\text{CHBr}_2} \quad \underset{CH_3}{\overset{H}{\diagdown}} \underset{Br}{\overset{Br}{\diagup}} \underset{H}{\overset{CH_3}{\diagup}}$$
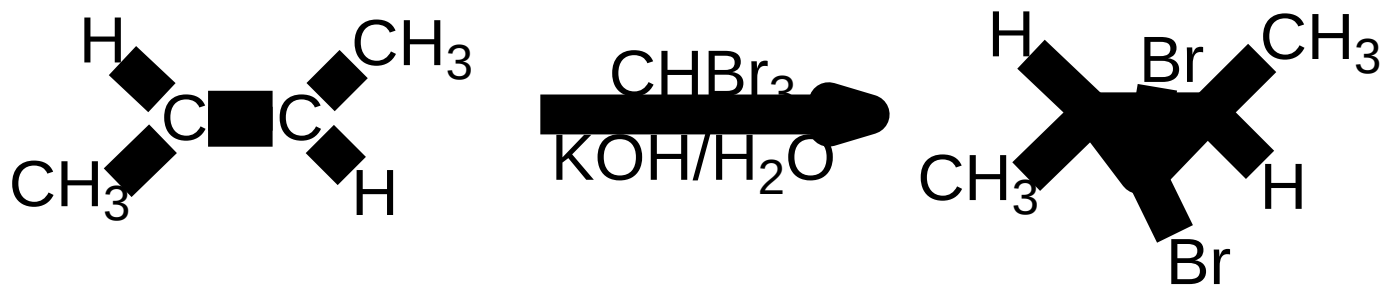
Carbene Examples

Simmons–Smith Reaction

$$\text{CH}_2\text{I}_2 \quad \text{over} \quad \text{Zn, CuCl}$$

Alpha Elimination Reaction

$$\text{CHBr}_3 \quad \text{over} \quad \text{KOH/H}_2\text{O}$$

Br
Br

Epoxidation

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- Alkene reacts with a peroxyacid to form an epoxide (also called oxirane).
- The usual reagent is peroxybenzoic acid.

Mechanism

alkene   peroxyacid

transition state
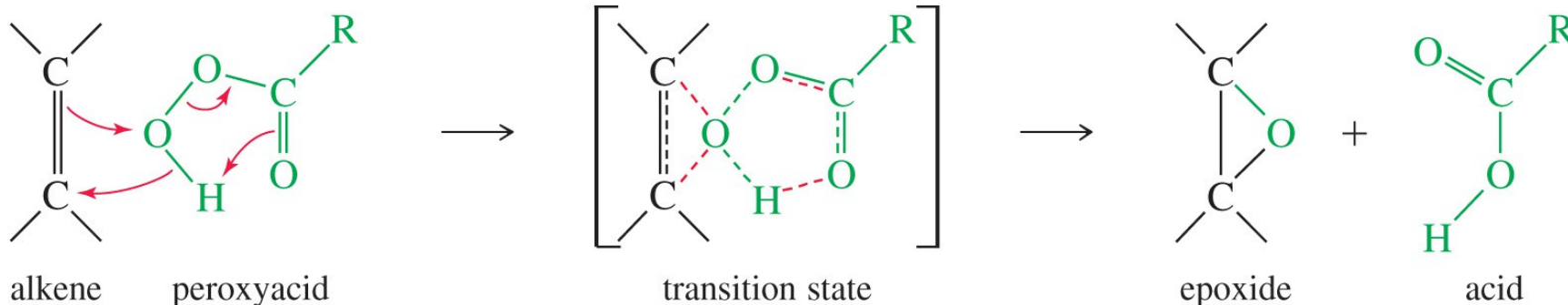
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epoxide   acid

- The peroxyacid and the alkene react with each other in a one-step reaction to produce the epoxide and a molecule of acid.

- The most common peroxyacid used is *meta*-chloroperoxybenzoic acid (MCPBA).

Epoxide Stereochemistry
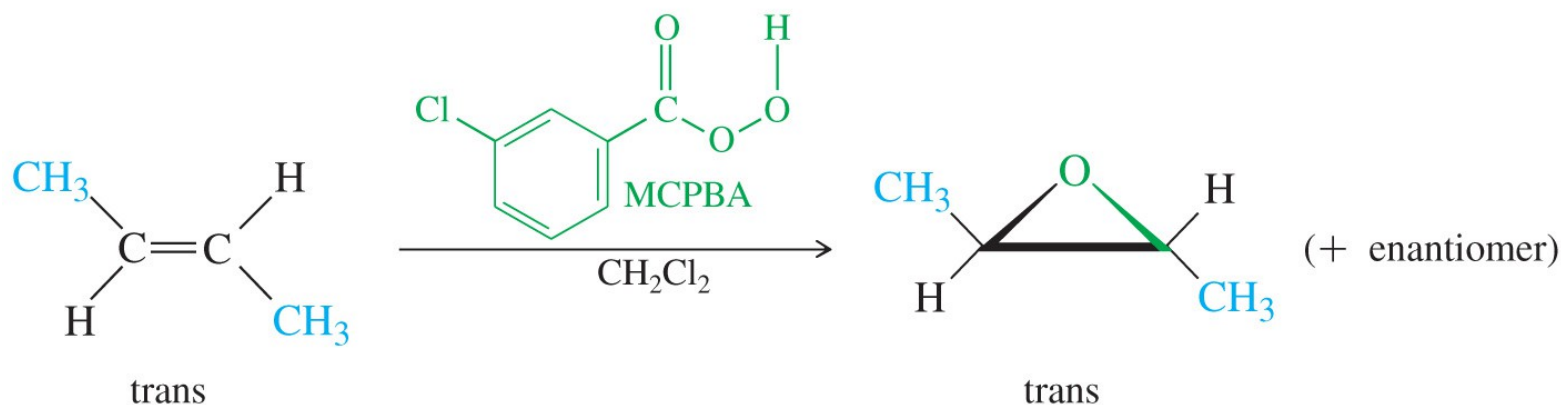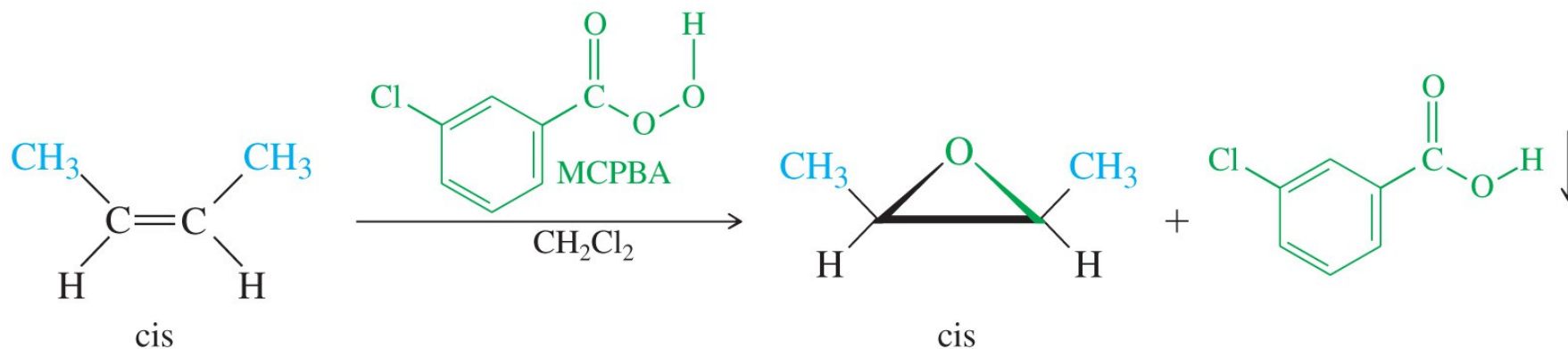
Opening the Epoxide Ring

- This process is acid catalyzed.

- Water attacks the protonated epoxide on the opposite side of the ring (back-side attack).

- Anti–diol is formed.
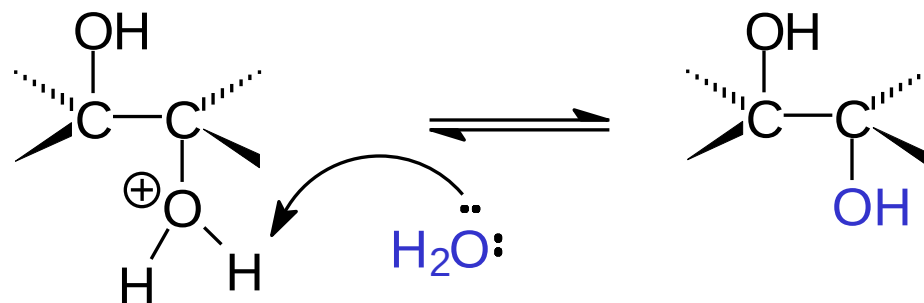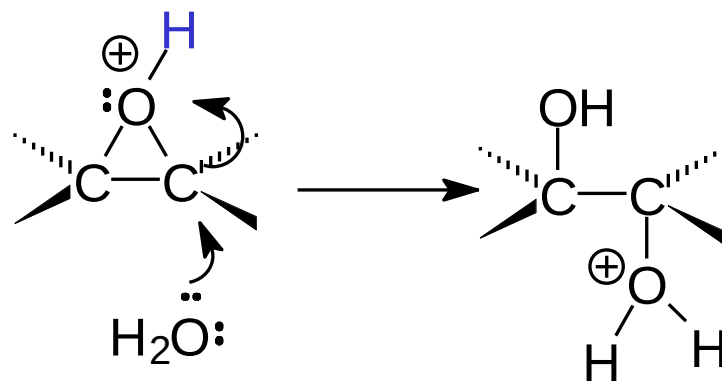
Syn Hydroxylation of Alkenes

- Alkene is converted to a *syn*-1,2-diol

- Two reagents:
  - Osmium tetroxide, OsO_4, followed by hydrogen peroxide *or*
  - Cold, dilute solution of $KMnO_4$ in base.
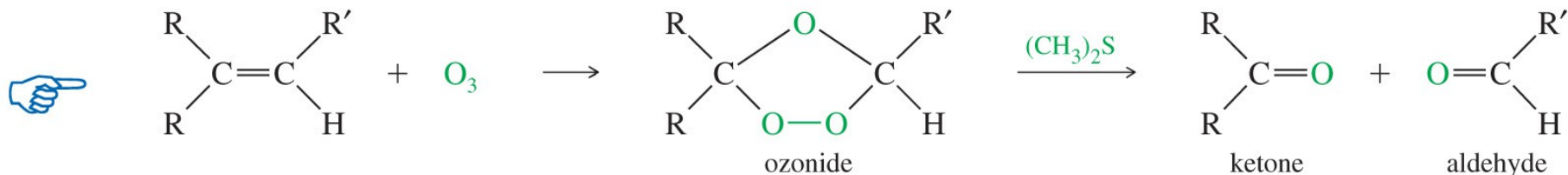
Mechanism with OsO$_4$
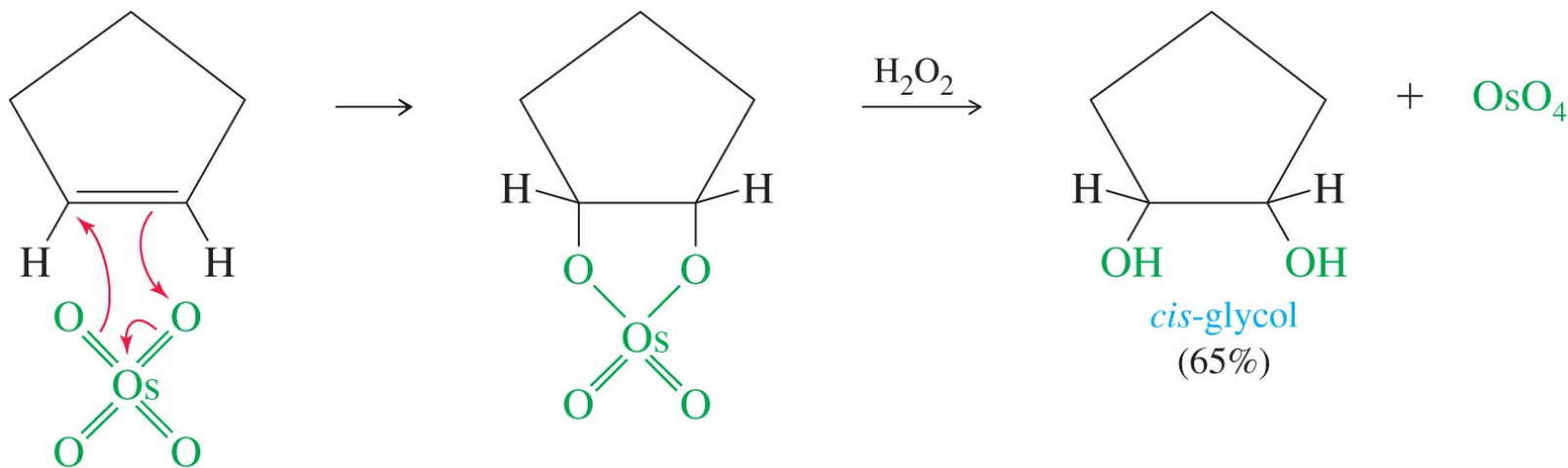
concerted formation of osmate ester

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- The osmium tetroxide adds to the double bond of an alkene in a concerted mechanism forming an osmate ester.

- The osmate ester can be hydrolized to produce a *cis*-glycol and regenerate the osmium tetroxide.

Ozonolysis

ozonide   ketone   aldehyde

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- Ozone will oxidatively cleave (break) the double bond to produce aldehydes and ketones.
- Ozonolysis is milder than $KMnO_4$ and will not oxidize aldehydes further.
- A second step of the ozonolysis is the reduction of the intermediate by zinc or dimethyl sulfide.

Mechanism of Ozonolysis

molozonide
(primary ozonide)
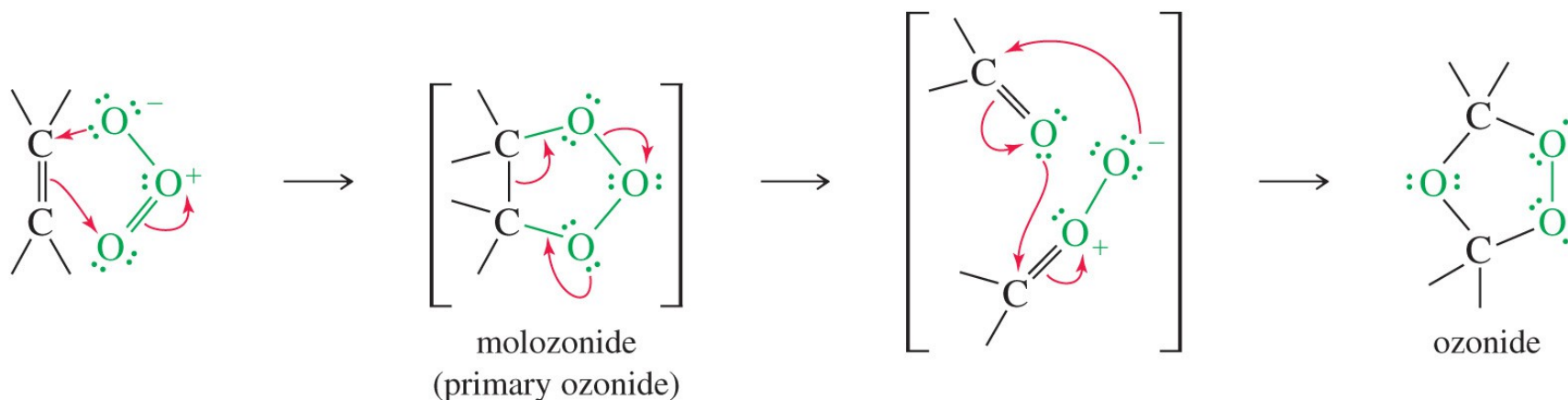
ozonide

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- The ozone adds to the double bond, forming a five-membered ring intermediate called molozonide, which rearranges to form the ozonide.

Reduction of the Ozonide

ozonide

dimethyl sulfide

ketones, aldehydes

dimethyl sulfoxide (DMSO)
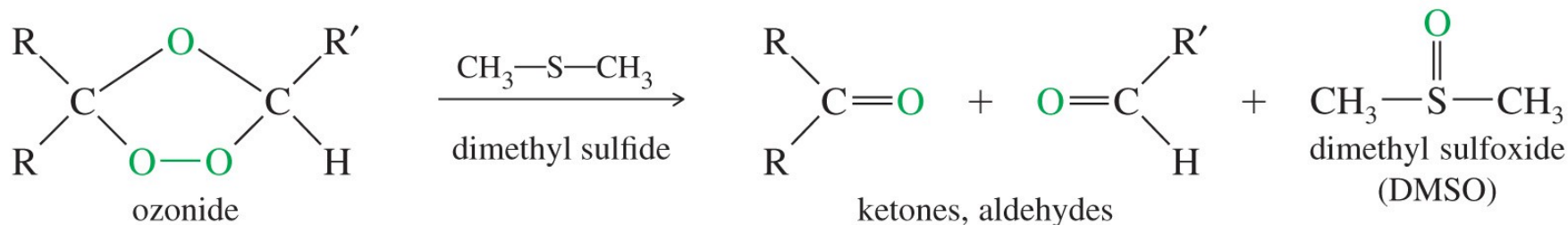
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- The ozonide is not isolated, but is immediately reduced by a mild reducing agent, such as zinc or dimethyl sulfide, to give the aldehydes and ketones as the main products.
- When dimethyl sulfide is used the sulfur atom gets oxidized, forming dimethyl sulfoxide (DMSO).

Solved Problem 8

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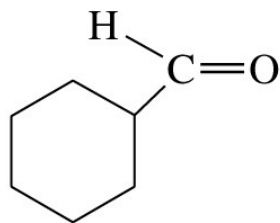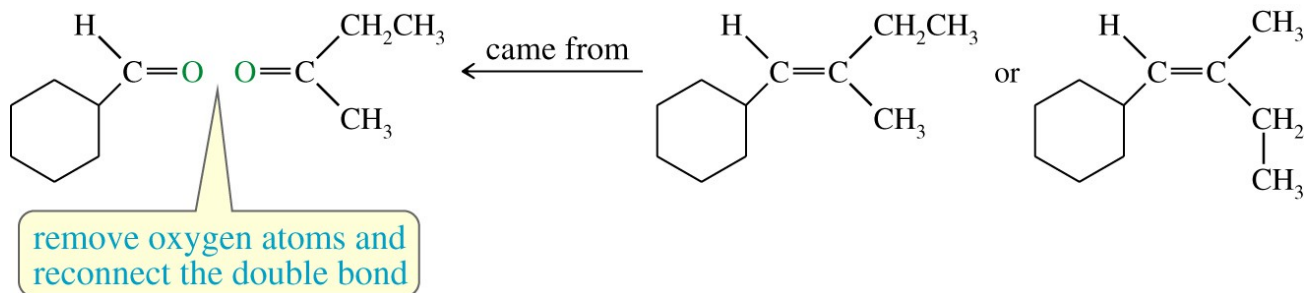

cyclohexanecarbaldehyde
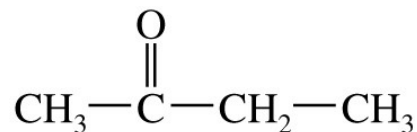
2-butanone

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

Cleavage with $KMnO_4$

- Permanganate is a strong oxidizing agent.
- Glycol initially formed is further oxidized.
- Disubstituted carbons become ketones.
- Monosubstituted carbons become carboxylic acids.
- Terminal $=CH_2$ becomes CO_2.

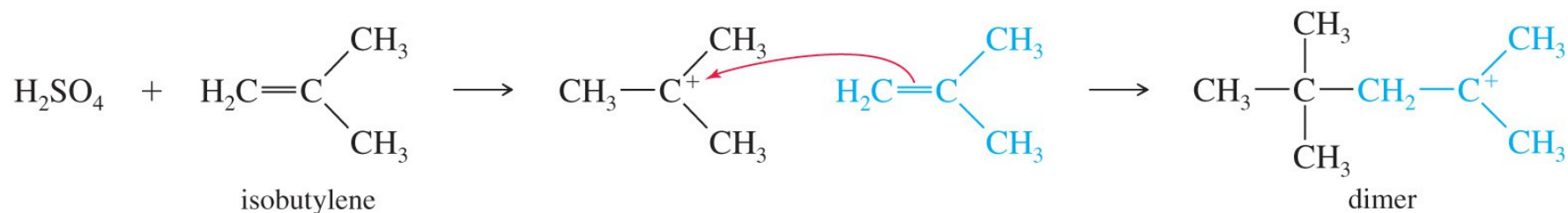# Comparison of Permanganate Cleavage and Ozonolysis

carboxylate

Aldehydes can be isolated.
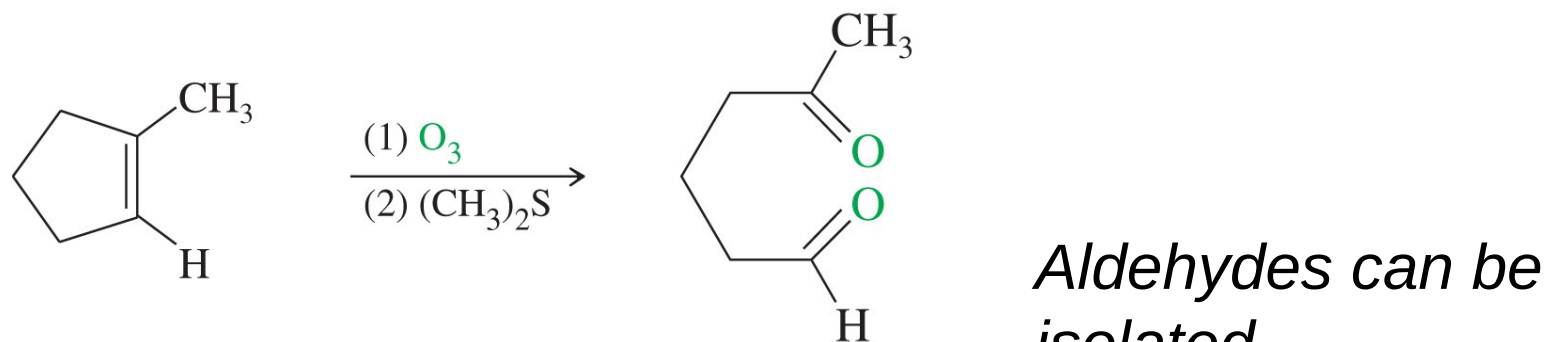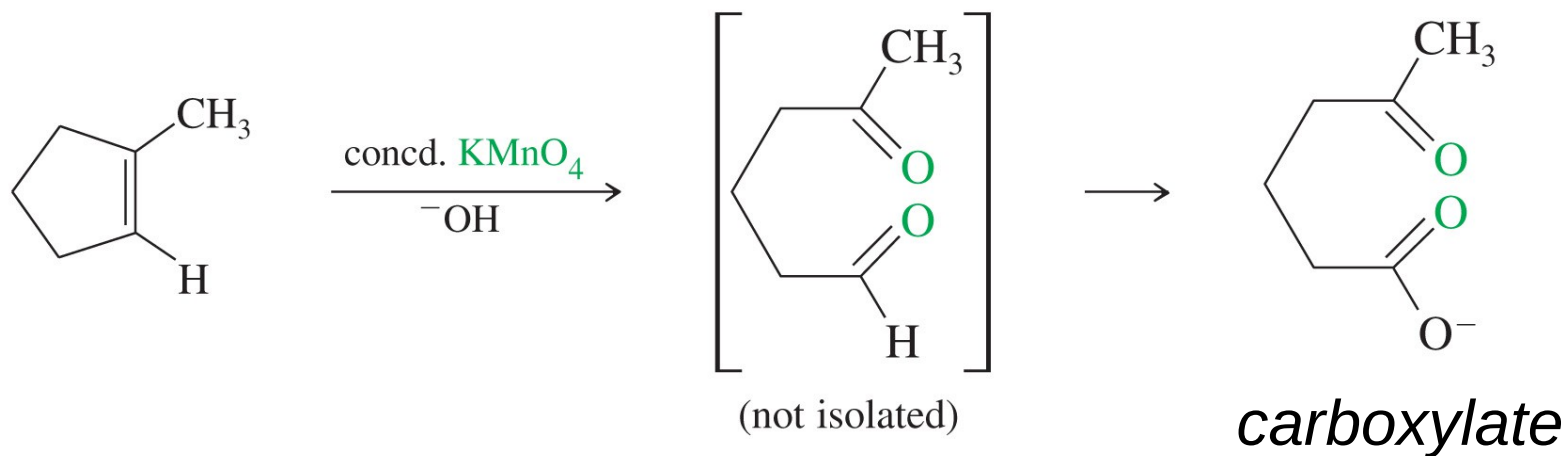
Polymerization

- An alkene (monomer) can add to another molecule like itself to form a chain (polymer).

- Three methods:

  - Cationic, a carbocation intermediate

  - Free radical

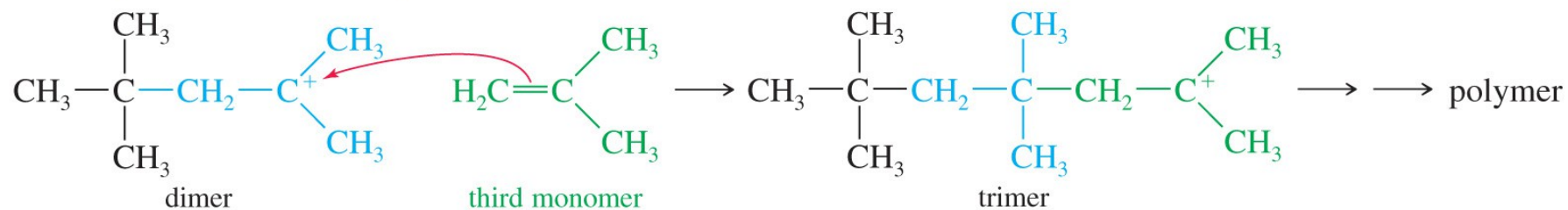 - Anionic, a carbanion intermediate (rare)

Cationic Polymerization

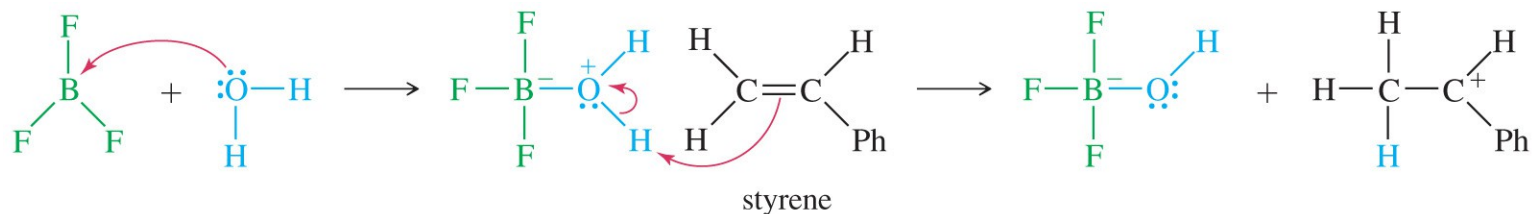Copyright © 2010 Pearson Prentice Hall, Inc.

Termination Step of Cationic Polymerization
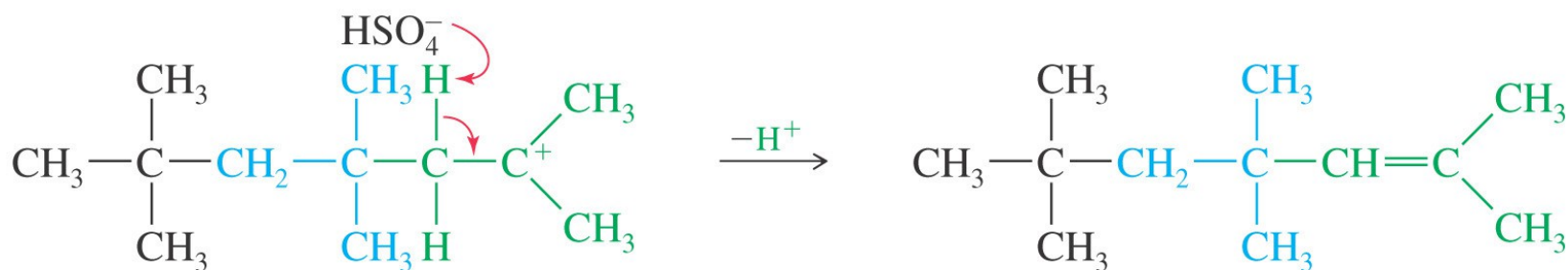
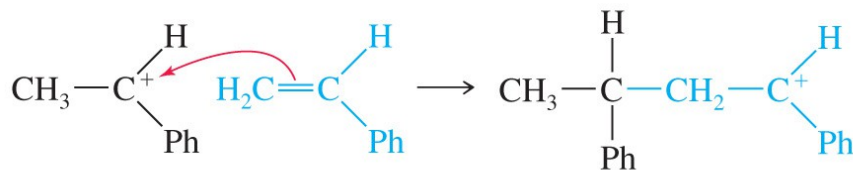Copyright © 2006 Pearson Prentice Hall, Inc.

- The chain growth ends when a proton is abstracted by the weak base of the acid used to initiate the reaction.
- The loss of a hydrogen forms an alkene and ends the chain growth so this is a termination step.
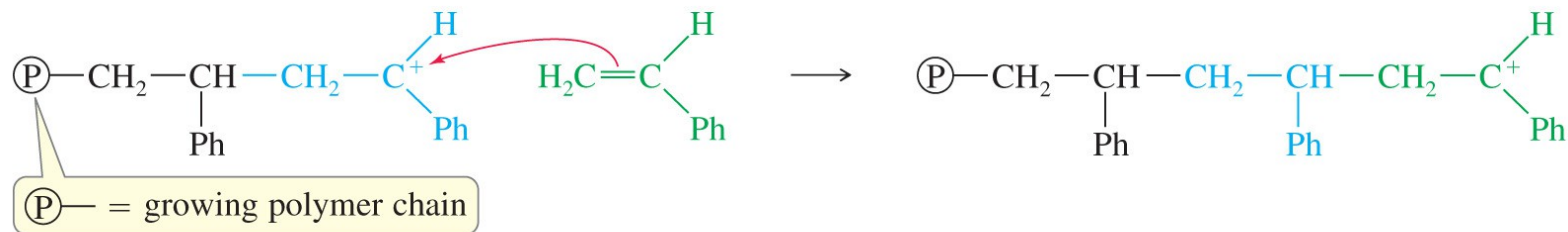
Cationic Polymerization Using BF$_3$ as Catalyst

styrene

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First chain-lengthening step

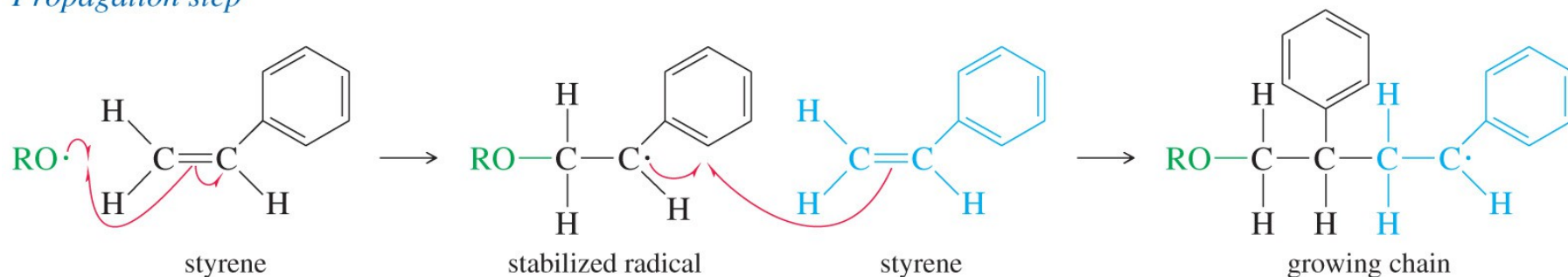

After many steps the polymerization continues

(P)— = growing polymer chain

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Radical Polymerization

Initiation step ROOR $\xrightarrow{\text{heat}}$ 2 RO·

Propagation step

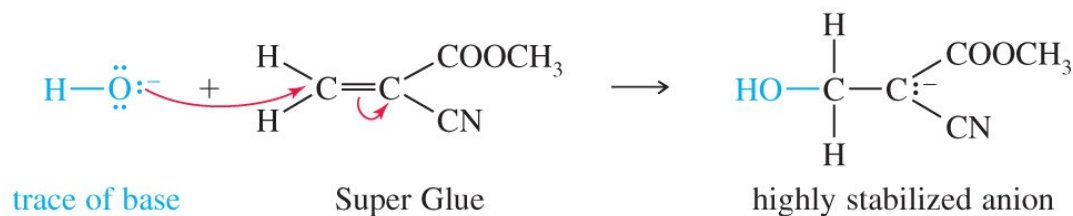styrene → stabilized radical + styrene → growing chain

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- In the presence of an initiator such as peroxide, free-radical polymerization occurs.
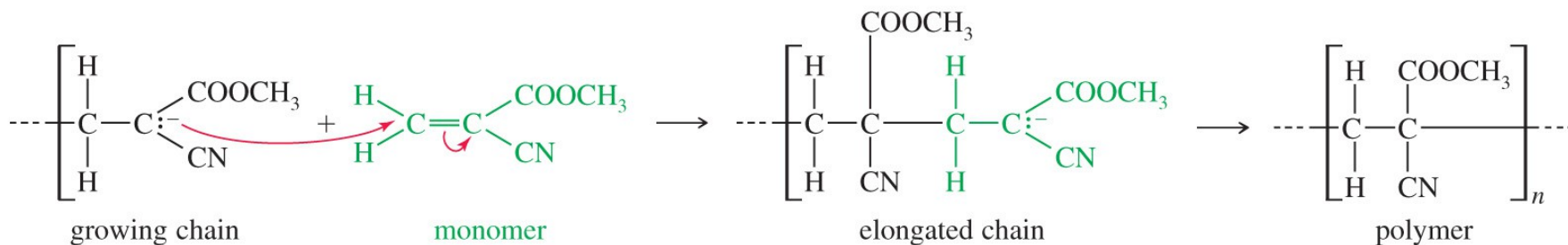
Anionic Polymerization

For an alkene to gain electrons, strong electron-withdrawing groups such as nitro, cyano, or carbonyl must be attached to the carbons in the

Initiation step

trace of base   Super Glue   highly stabilized anion

Chain lengthening step

growing chain   monomer   elongated chain   polymer

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