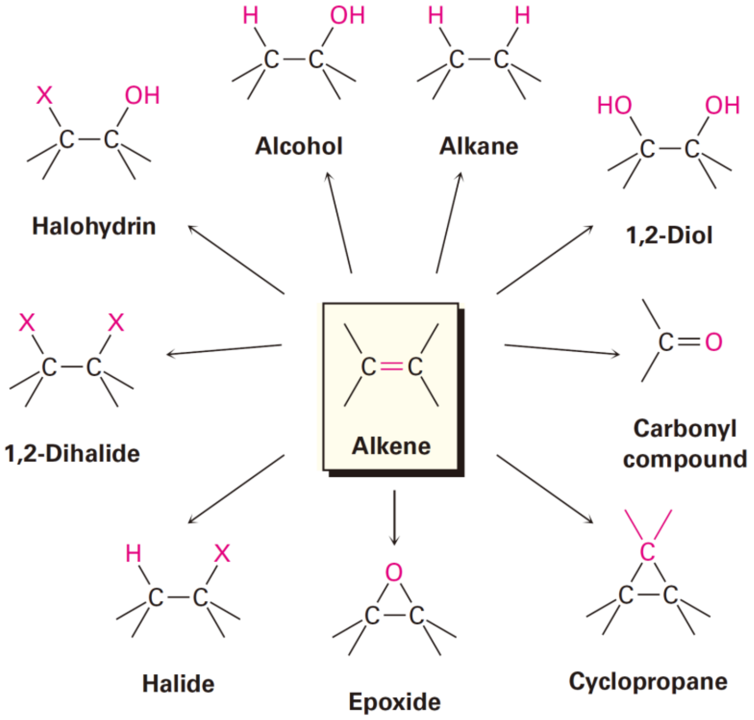
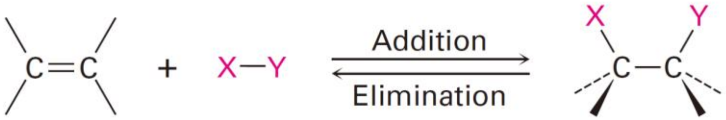

Alcohol
Alkane
Halohydrin
1,2-Diol
1,2-Dihalide
Alkene
Carbonyl compound
Halide
Epoxide
Cyclopropane

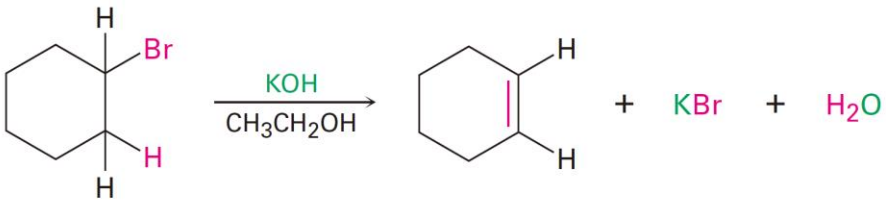
# 8

# 烯烃：反应与合成

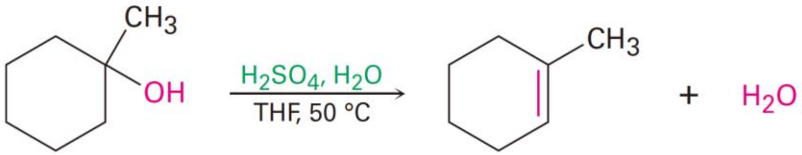
# 8.1 烯烃的制备

- 消除反应





**Bromocyclohexane** **Cyclohexene (81%)**



**1-Methylcyclohexanol** **1-Methylcyclohexene (91%)**

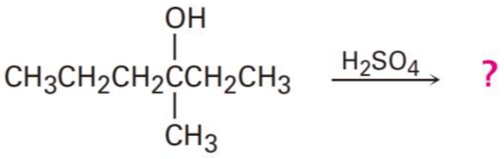
**Tetrahydrofuran (THF)—a common solvent**

***Problem 8.1***

One problem with elimination reactions is that mixtures of products are often formed. For example, treatment of 2-bromo-2-methylbutane with KOH in ethanol yields a mixture of two alkene products. What are their likely structures?

***Problem 8.2***

How many alkene products, including *E,Z* isomers, might be obtained by dehydration of 3-methyl-3-hexanol with aqueous sulfuric acid?

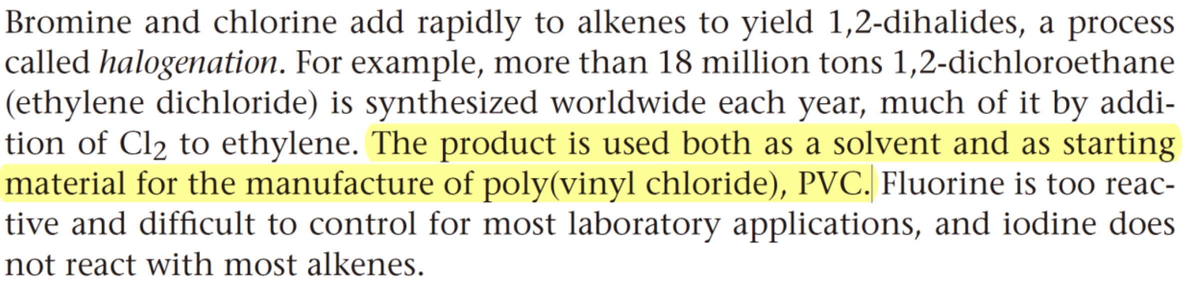


$$CH_3CH_2CH_2\overset{\overset{\large OH}{|}}{\underset{\underset{\large CH_3}{|}}{C}}CH_2CH_3 \xrightarrow{H_2SO_4} ?$$

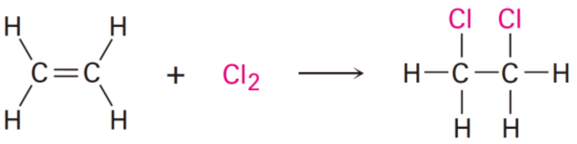
**3-Methyl-3-hexanol**

# 8.2 与卤素加成

- 溴单质和氯气可以与烯烃快速反应得到加成产物。
- 氟气反应太剧烈，通常不用于实验室合成；碘单质一般不与烯烃反应。

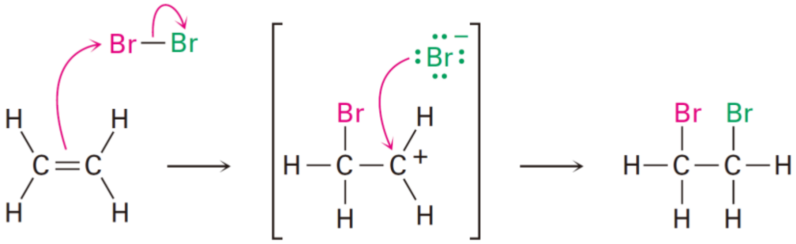


Bromine and chlorine add rapidly to alkenes to yield 1,2-dihalides, a process called *halogenation*. For example, more than 18 million tons 1,2-dichloroethane (ethylene dichloride) is synthesized worldwide each year, much of it by addition of $Cl_2$ to ethylene. The product is used both as a solvent and as starting material for the manufacture of poly(vinyl chloride), PVC. Fluorine is too reactive and difficult to control for most laboratory applications, and iodine does not react with most alkenes.



**Ethylene**

**1,2-Dichloroethane (ethylene dichloride)**

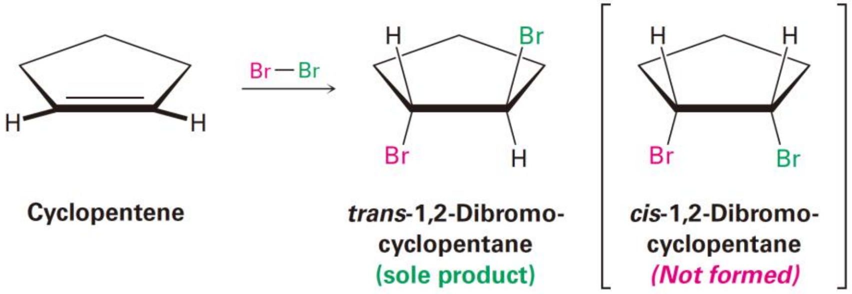


**Possible mechanism?**

**Possible mechanism?**

# 8.2 与卤素加成

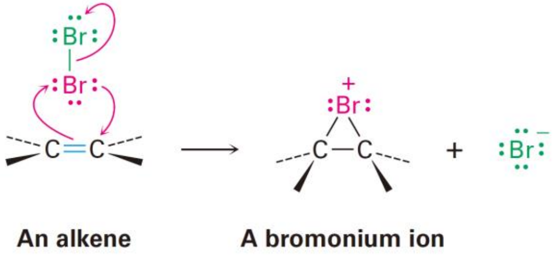
- 加成机理：第一步形成溴鎓离子；第二步从反面进攻。



**Cyclopentene**

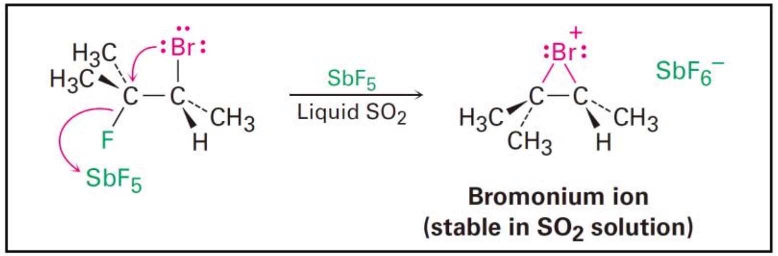
***trans*-1,2-Dibromo-cyclopentane**
**(sole product)**

***cis*-1,2-Dibromo-cyclopentane**
***(Not formed)***

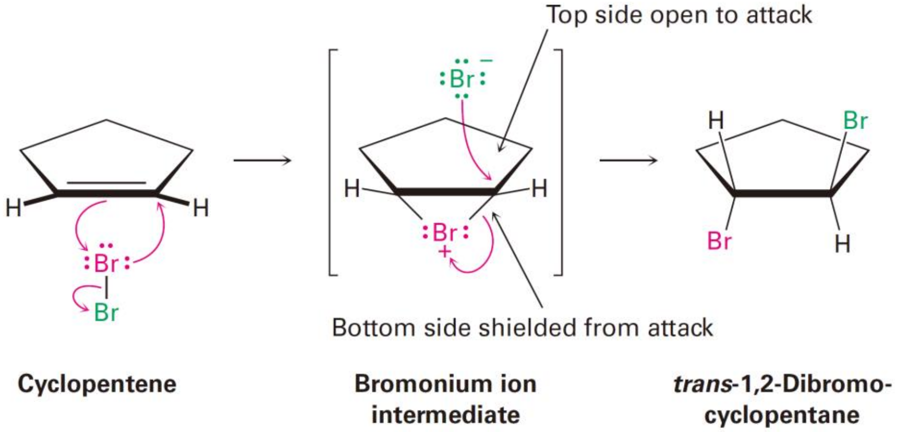


**An alkene**

**A bromonium ion**



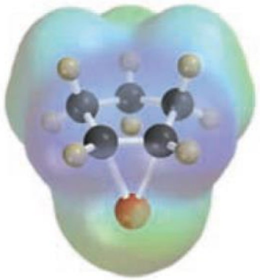
**Bromonium ion**
**(stable in $SO_2$ solution)**



**Cyclopentene**

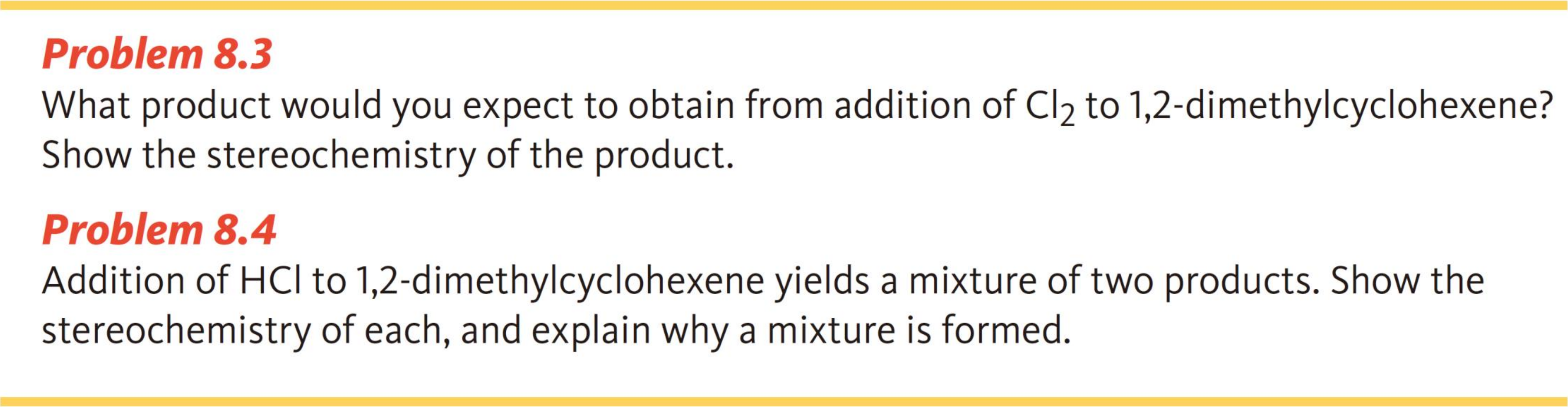
**Bromonium ion intermediate**

***trans*-1,2-Dibromo-cyclopentane**



# 8.2 与卤素加成

- 课堂练习



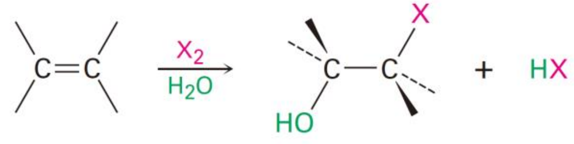
**Problem 8.3**

What product would you expect to obtain from addition of $Cl_2$ to 1,2-dimethylcyclohexene? Show the stereochemistry of the product.

**Problem 8.4**

Addition of HCl to 1,2-dimethylcyclohexene yields a mixture of two products. Show the stereochemistry of each, and explain why a mixture is formed.

# 8.3 与次卤酸加成

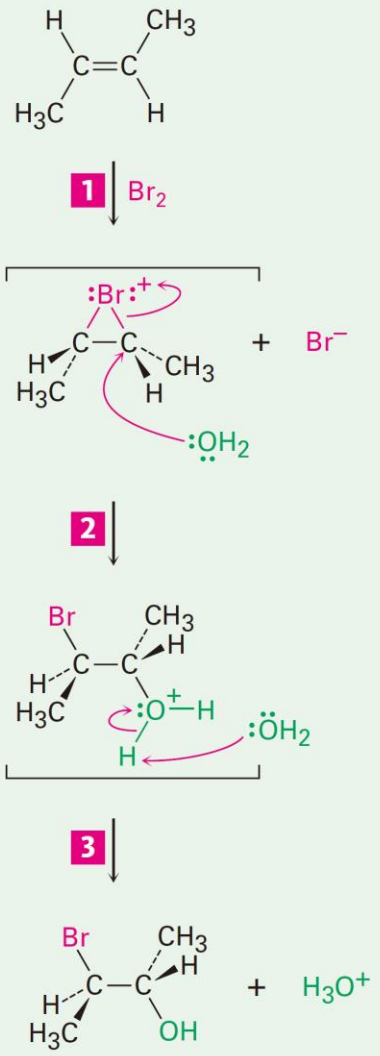


**An alkene** **A halohydrin**

**1** Reaction of the alkene with $Br_2$ yields a bromonium ion intermediate, as previously discussed.

**2** Water acts as a nucleophile, using a lone pair of electrons to open the bromonium ion ring and form a bond to carbon. Since oxygen donates its electrons in this step, it now has the positive charge.

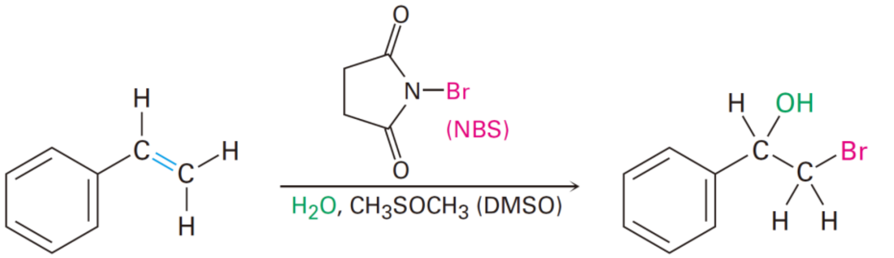
**3** Loss of a proton ($H^+$) from oxygen then gives $H_3O^+$ and the neutral bromohydrin addition product.



**3-Bromo-2-butanol**
**(a bromohydrin)**

# 8.3 与次卤酸加成

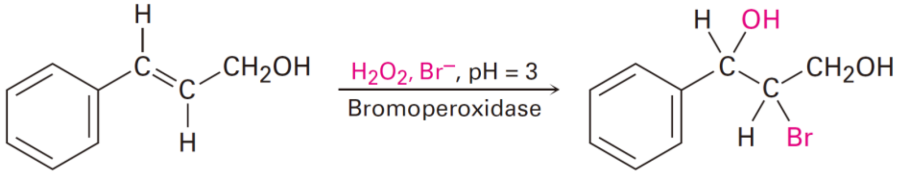
In practice, few alkenes are soluble in water, and bromohydrin formation is often carried out in a solvent such as aqueous dimethyl sulfoxide, $CH_3SOCH_3$ (DMSO), using a reagent called *N*-bromosuccinimide (NBS) as a source of $Br_2$. NBS is a stable, easily handled compound that slowly decomposes in water to yield $Br_2$ at a controlled rate. Bromine itself can also be used in the addition reaction, but it is more dangerous and more difficult to handle than NBS.



**Styrene**

**2-Bromo-1-phenylethanol (70%)**

There are a number of biological examples of halohydrin formation, particularly in marine organisms. As with halogenation **(Section 8.2)**, halohydrin formation is carried out by haloperoxidases, which function by oxidizing $Br^-$ or $Cl^-$ ions to the corresponding HOBr or HOCl bonded to a metal atom in the enzyme. Electrophilic addition to the double bond of a substrate molecule then yields a bromonium or chloronium ion intermediate, and reaction with water gives the halohydrin. For example:



# 8.3 与次卤酸加成

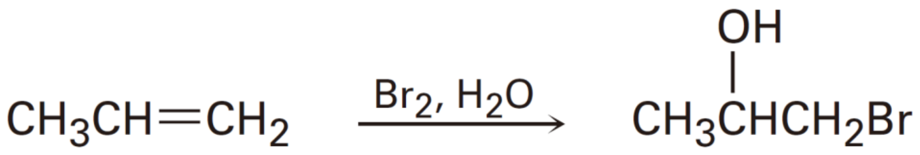
- 课堂练习

**Problem 8.5**

What product would you expect from the reaction of cyclopentene with NBS and water? Show the stereochemistry.

**Problem 8.6**

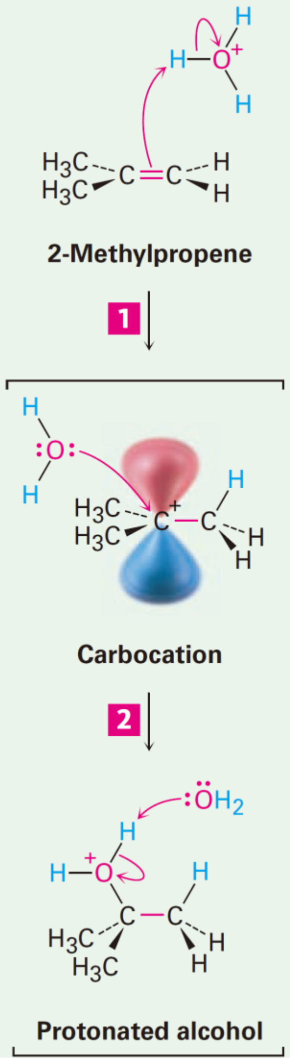
When an unsymmetrical alkene such as propene is treated with *N*-bromosuccinimide in aqueous dimethyl sulfoxide, the major product has the bromine atom bonded to the less highly substituted carbon atom. Is this Markovnikov or non-Markovnikov orientation? Explain.

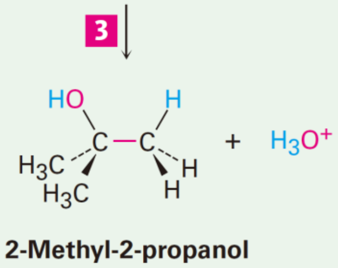


$$CH_3CH{=}CH_2 \xrightarrow{Br_2,\ H_2O} CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_2Br$$

# 8.4 烯烃的水合：乙酸汞法

- 减少碳正离子重排





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

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

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

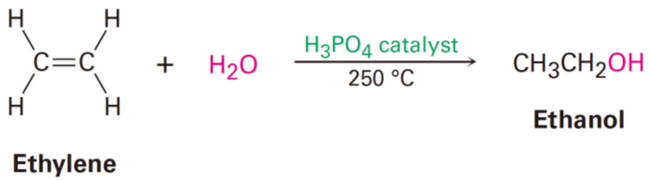
**2-Methylpropene**

**Carbocation**

**Protonated alcohol**

**2-Methyl-2-propanol**

工业制乙醇

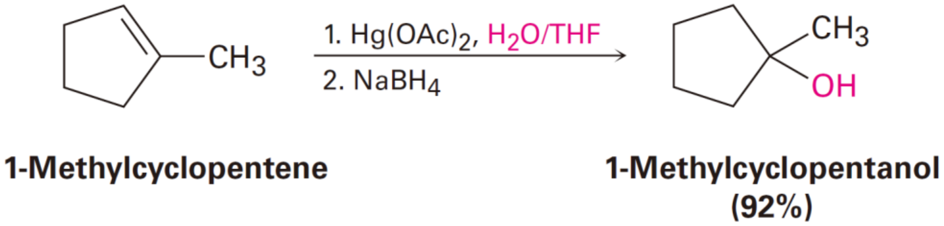


**Ethylene**

**Ethanol**

# 8.4 烯烃的水合：乙酸汞法

- 减少碳正离子重排



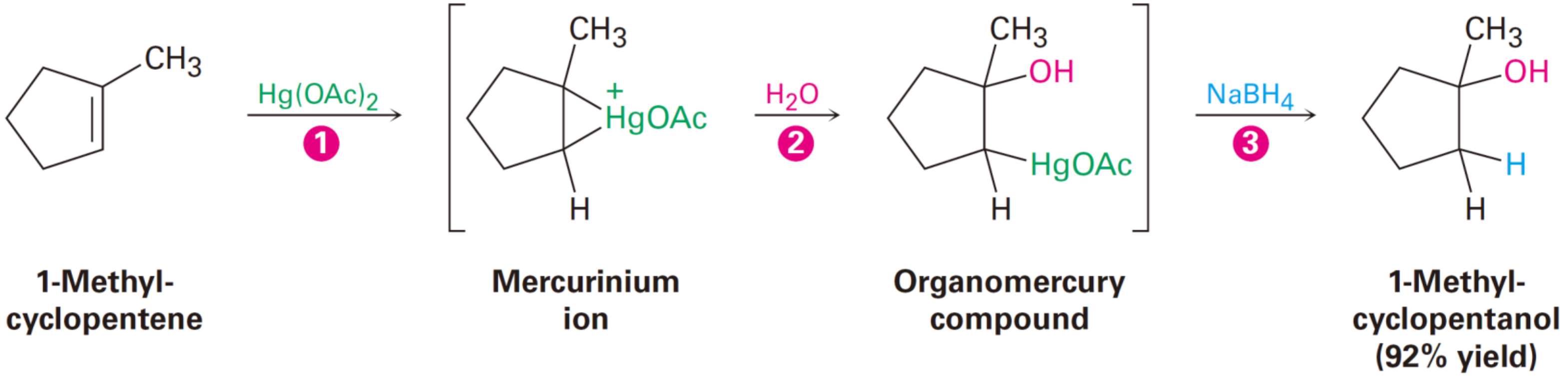
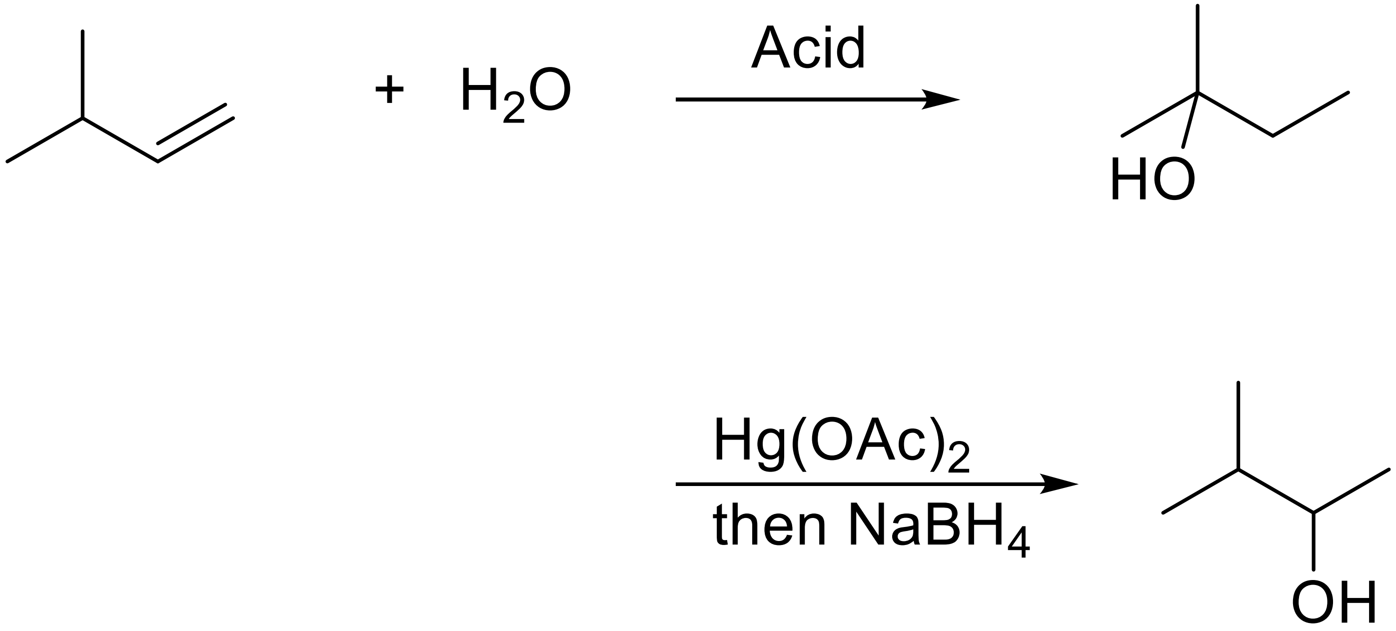


**Figure 8.3** Mechanism of the oxymercuration of an alkene to yield an alcohol. (①) Electrophilic addition of $Hg^{2+}$ gives a mercurinium ion, which (②) reacts with water as in halohydrin formation. Loss of a proton gives an organomercury product, and (③) reaction with $NaBH_4$ removes the mercury. The product of the reaction is the more highly substituted alcohol, corresponding to Markovnikov regiochemistry.

# 8.4 烯烃的水合：乙酸汞法

- 减少碳正离子重排



# 8.4 烯烃的水合：乙酸汞法

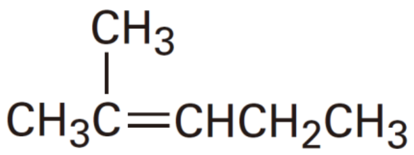
- 课堂练习

### Problem 8.7

What products would you expect from oxymercuration–demercuration of the following alkenes?

**(a)** $CH_3CH_2CH_2CH{=}CH_2$

**(b)**

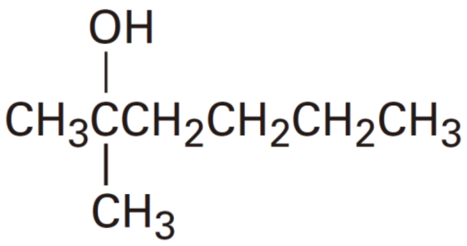


$CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_2CH_3$

### Problem 8.8

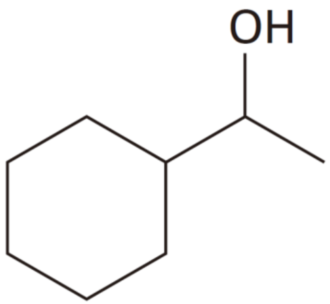
From what alkenes might the following alcohols have been prepared?

**(a)**



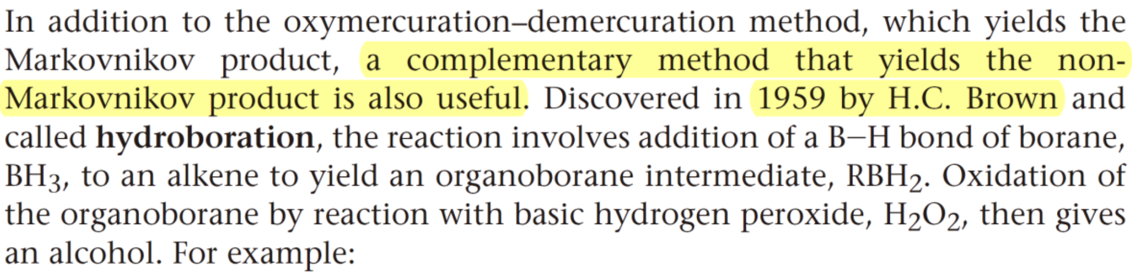
$CH_3\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}CH_2CH_2CH_2CH_3$

**(b)**

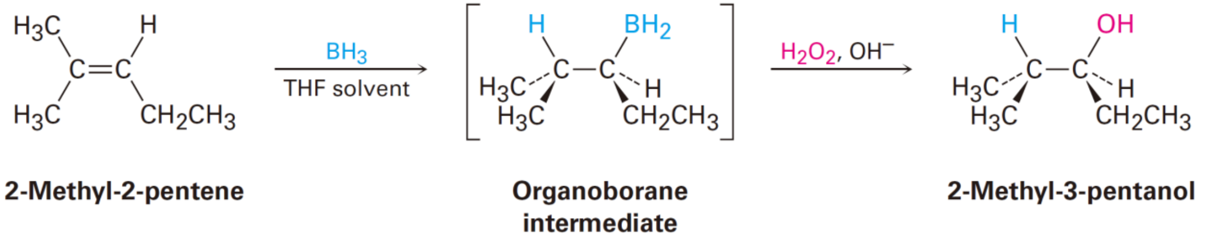


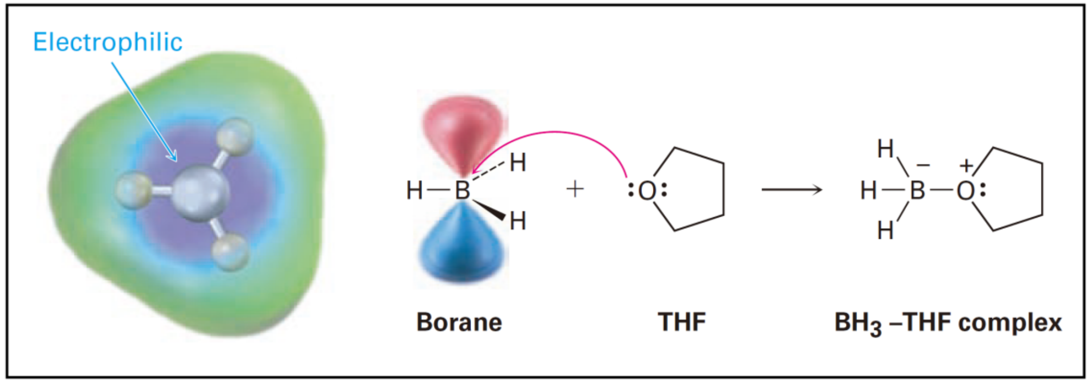
# 8.5 烯烃的硼氢化氧化

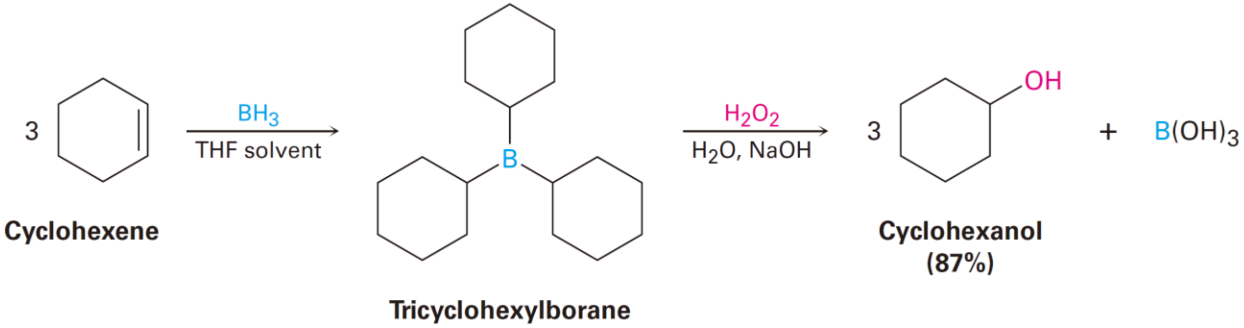
- 区域选择性：反马氏加成



In addition to the oxymercuration–demercuration method, which yields the Markovnikov product, a complementary method that yields the non-Markovnikov product is also useful. Discovered in 1959 by H.C. Brown and called **hydroboration**, the reaction involves addition of a B–H bond of borane, $BH_3$, to an alkene to yield an organoborane intermediate, $RBH_2$. Oxidation of the organoborane by reaction with basic hydrogen peroxide, $H_2O_2$, then gives an alcohol. For example:

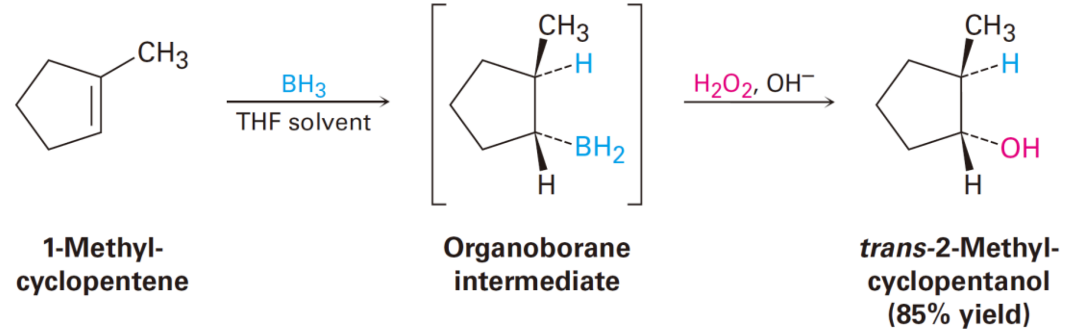


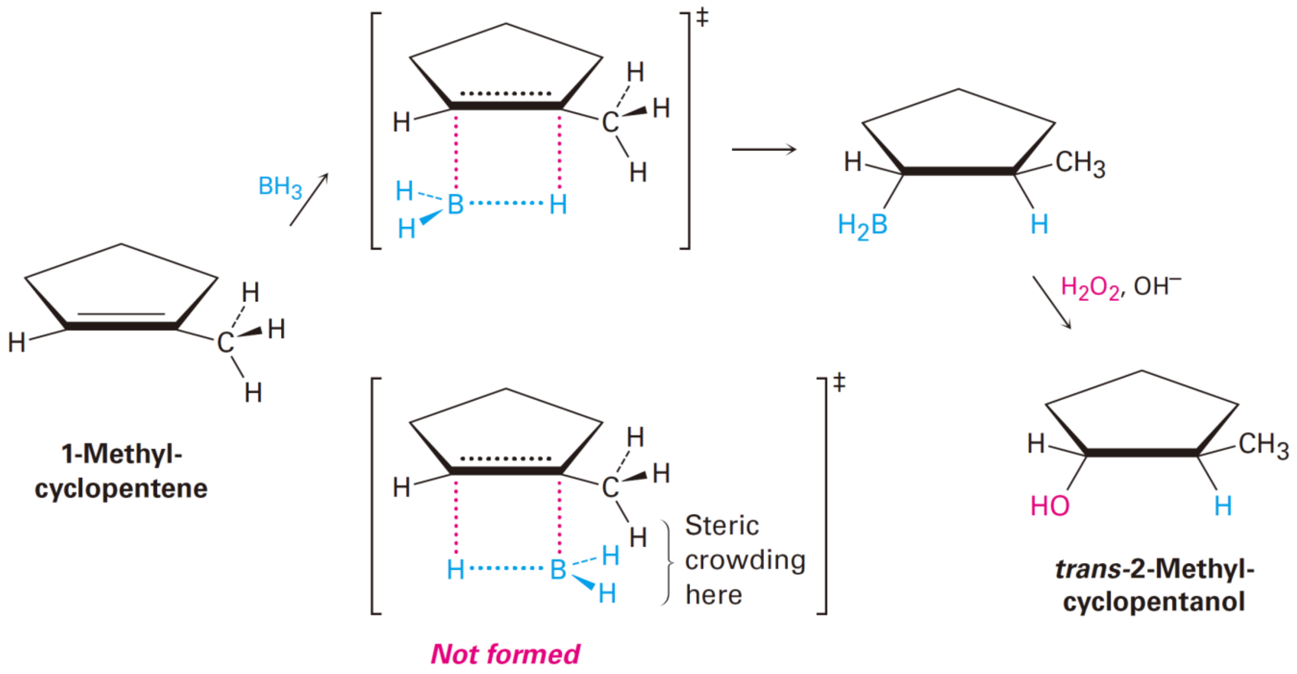




# 8.5 烯烃的硼氢化氧化

- 立体化学：顺式加成

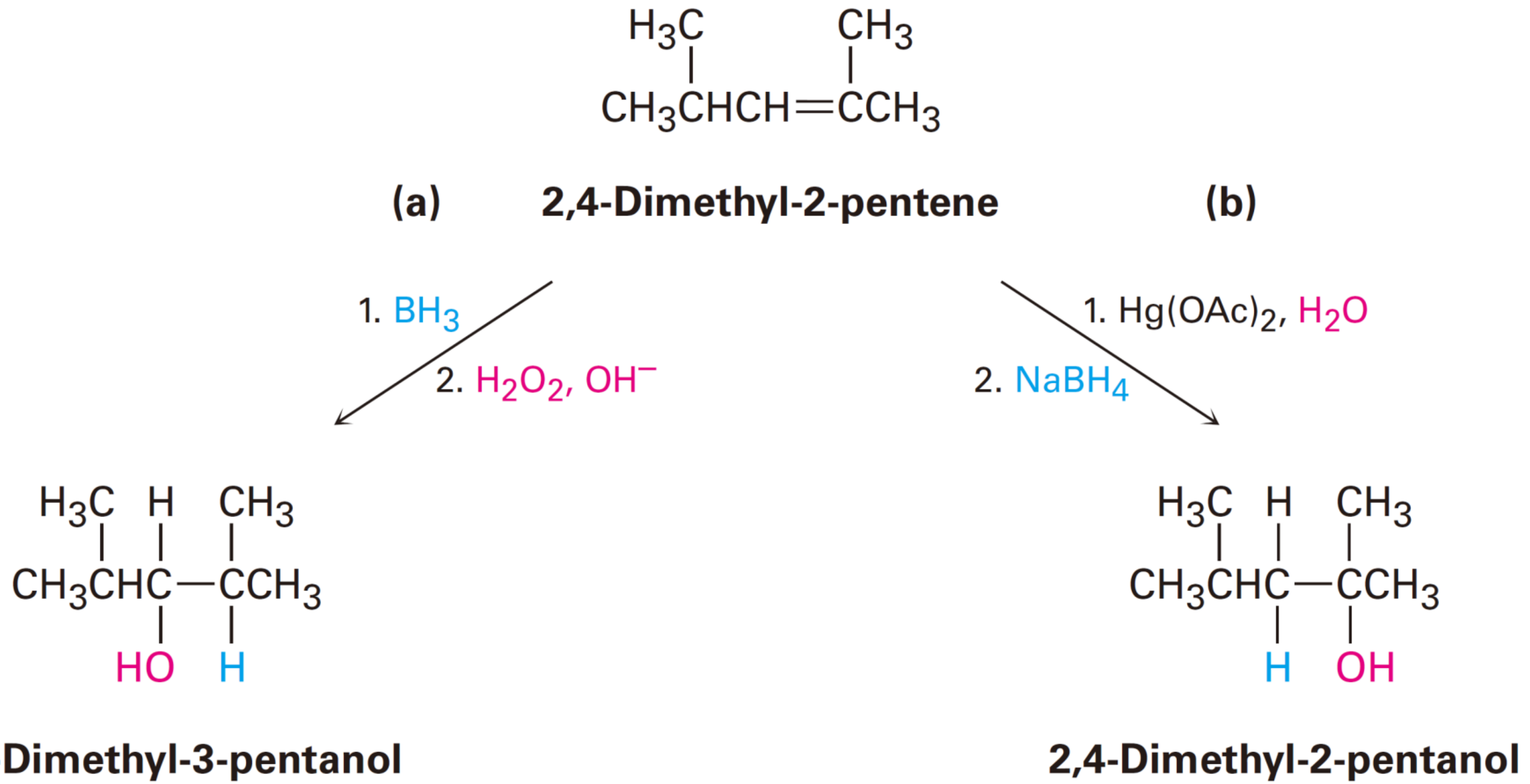




# 8.5 烯烃的硼氢化氧化

- 实例一

***Solution***



$CH_3CH(CH_3)CH{=}C(CH_3)CH_3$

(a) **2,4-Dimethyl-2-pentene** (b)

1. $BH_3$ 2. $H_2O_2$, $OH^-$

1. $Hg(OAc)_2$, $H_2O$ 2. $NaBH_4$

$CH_3CH(CH_3)CH(OH)\text{—}CH(CH_3)CH_3$

**2,4-Dimethyl-3-pentanol**

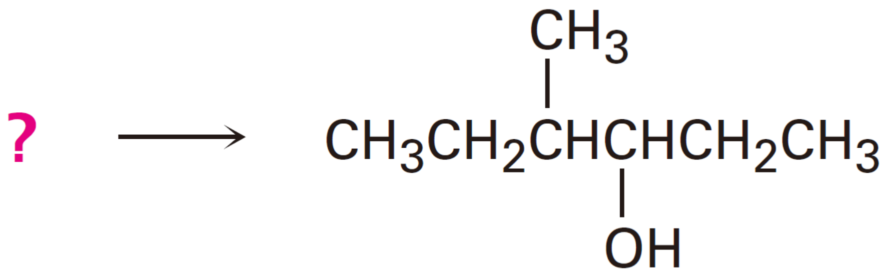
$CH_3CH(CH_3)CH_2\text{—}C(OH)(CH_3)CH_3$

**2,4-Dimethyl-2-pentanol**

# 8.5 烯烃的硼氢化氧化

- 实例二

How might you prepare the following alcohol?



$$? \longrightarrow \mathrm{CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}H\underset{\underset{\displaystyle OH}{|}}{C}HCH_2CH_3}$$

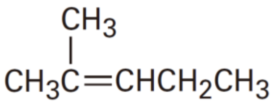
# 8.5 烯烃的硼氢化氧化

- 课堂练习

**Problem 8.9**

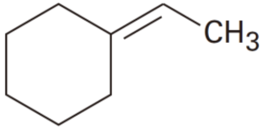
Show the structures of the products you would obtain by hydroboration–oxidation of the following alkenes:

**(a)**



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

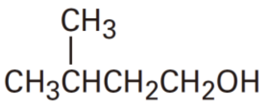
**(b)**



**Problem 8.10**

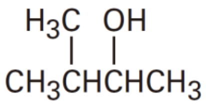
What alkenes might be used to prepare the following alcohols by hydroboration–oxidation?

**(a)**



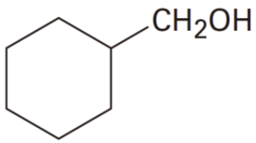
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2OH$

**(b)**



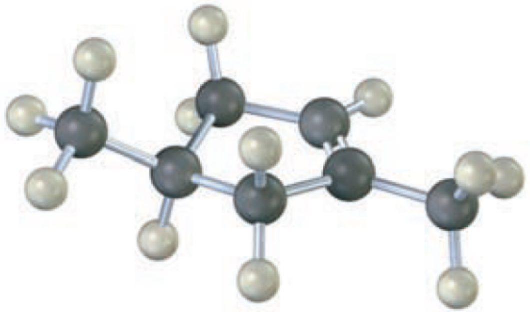
$CH_3\overset{H_3C}{\overset{|}{C}}H\overset{OH}{\overset{|}{C}}HCH_3$

**(c)**



**Problem 8.11**

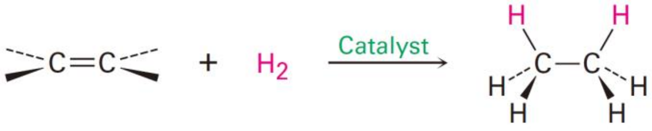
The following cycloalkene gives a mixture of two alcohols on hydroboration followed by oxidation. Draw the structures of both, and explain the result.



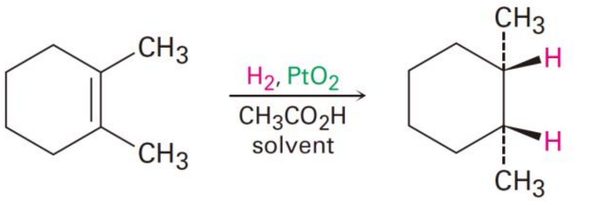
# 8.6 烯烃的催化氢化

**Reduction** Increases electron density on carbon by:
- forming this: C–H
- or breaking one of these: C–O C–N C–X

**A reduction:**

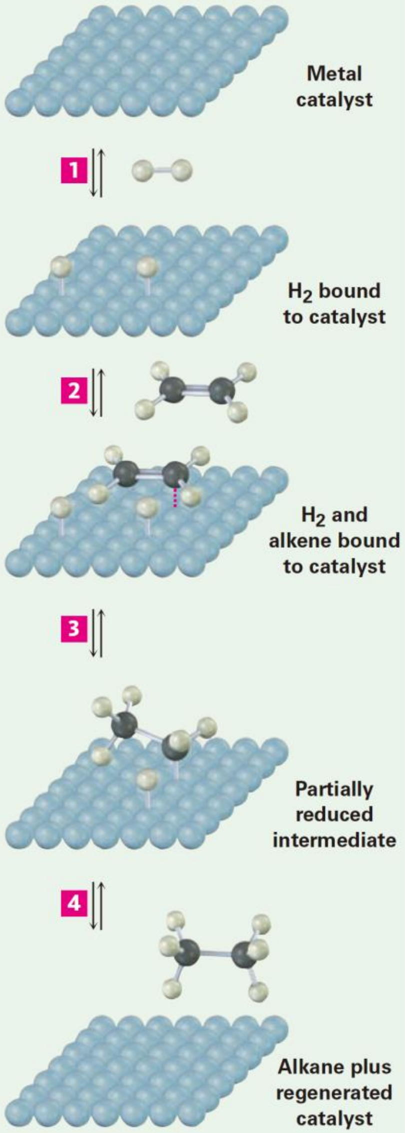


**An alkene** **An alkane**



**1,2-Dimethyl-cyclohexene**

***cis*-1,2-Dimethyl-cyclohexane (82%)**



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

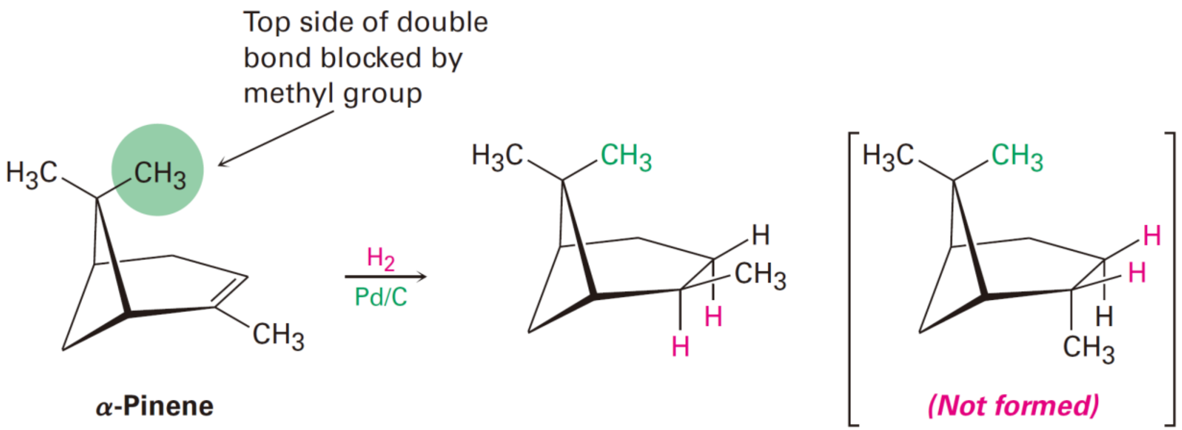
**2** The alkene adsorbs to the catalyst surface, using its $\pi$ bond to complex to the metal atoms.

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

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

# 8.6 烯烃的催化氢化

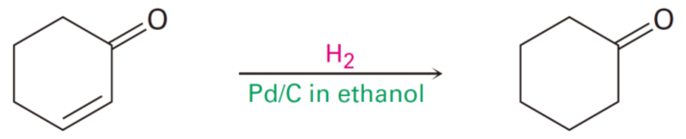
- 区域选择性，立体选择性和化学选择性



Top side of double bond blocked by methyl group

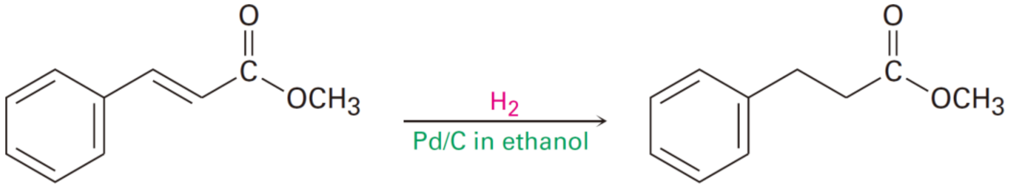
α-Pinene

*(Not formed)*



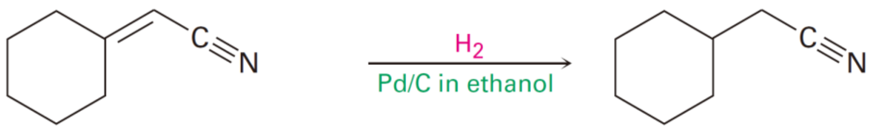
**2-Cyclohexenone**

**Cyclohexanone**
**(ketone not reduced)**



**Methyl 3-phenylpropenoate**

**Methyl 3-phenylpropanoate**
**(aromatic ring not reduced)**



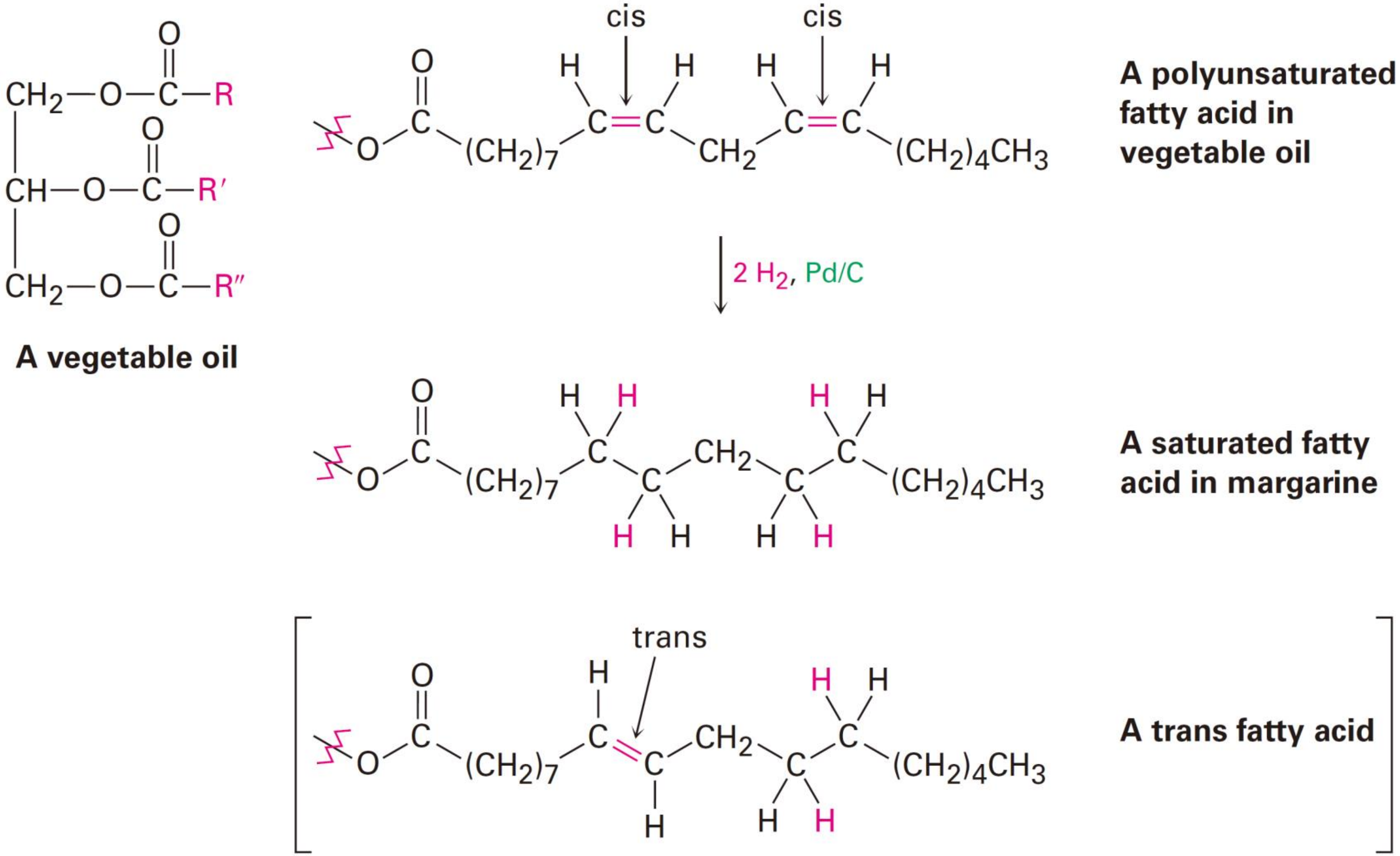
**Cyclohexylideneacetonitrile**

**Cyclohexylacetonitrile**
**(nitrile not reduced)**

# 8.6 烯烃的催化氢化

- 工业应用：氢化植物油

**Figure 8.6** Catalytic hydrogenation of polyunsaturated fats leads to saturated products, along with a small amount of isomerized trans fats.



# 8.6 烯烃的催化氢化

- 生物过程

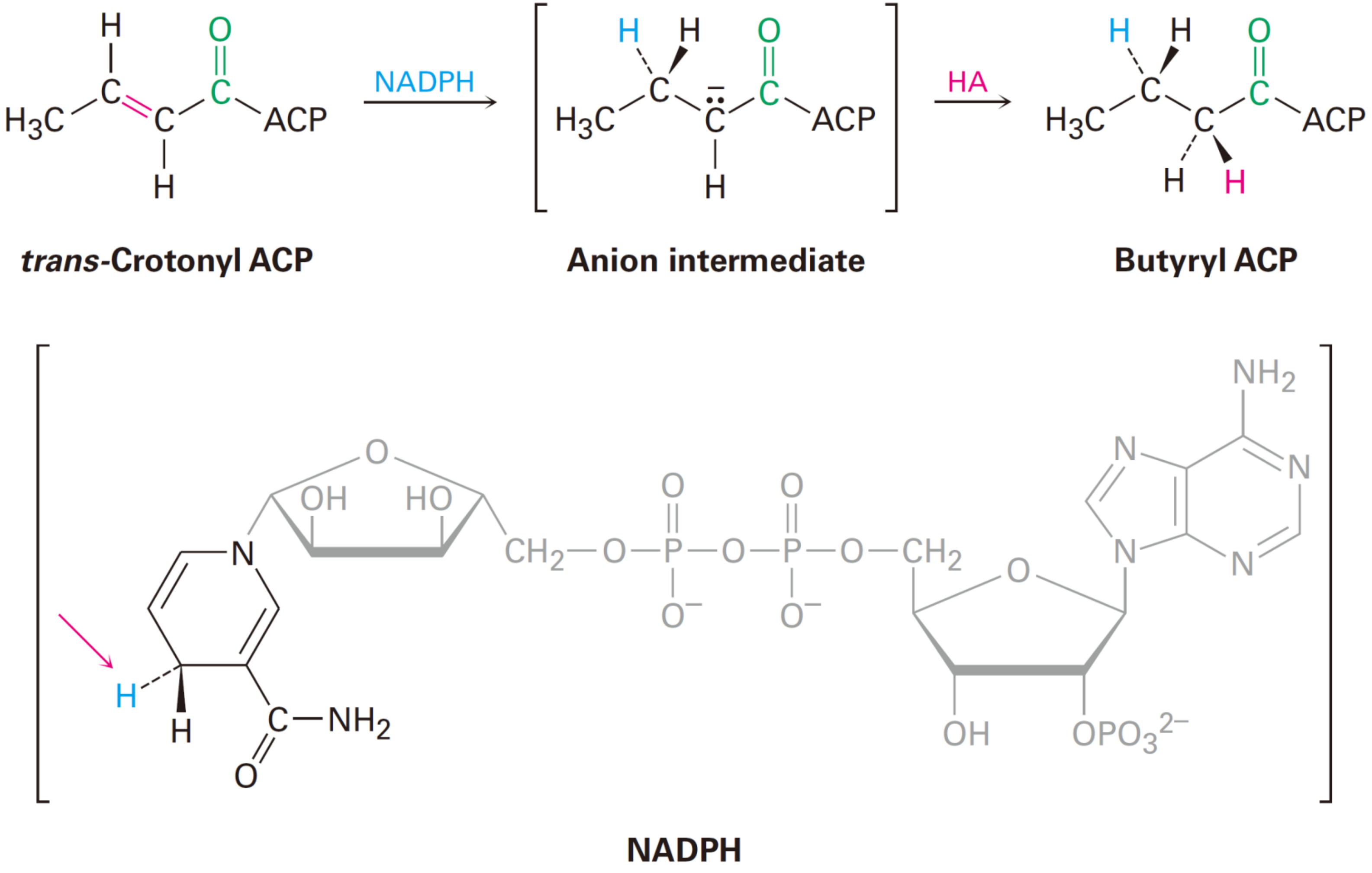


**Figure 8.7** Reduction of the carbon–carbon double bond in *trans*-crotonyl ACP, a step in the biosynthesis of fatty acids. **One hydrogen** is delivered from NADPH as a hydride ion, $H:^-$; the **other hydrogen** is delivered by protonation of the anion intermediate with an acid, HA.

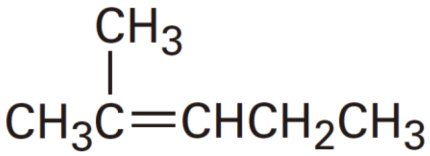
# 8.6 烯烃的催化氢化

- 课堂练习

**Problem 8.12**

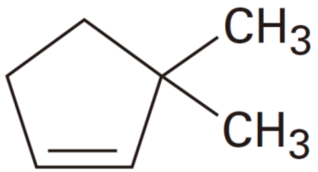
What product would you obtain from catalytic hydrogenation of the following alkenes?

**(a)**

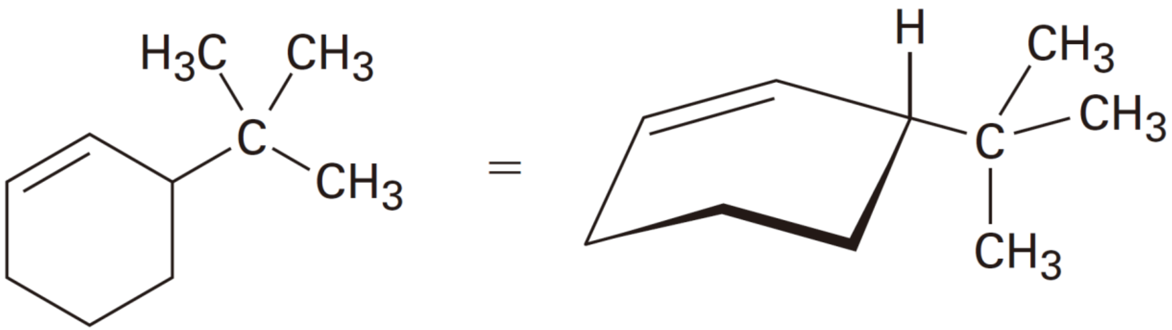


$\mathrm{CH_3\overset{\overset{CH_3}{|}}{C}{=}CHCH_2CH_3}$

**(b)**



**(c)**

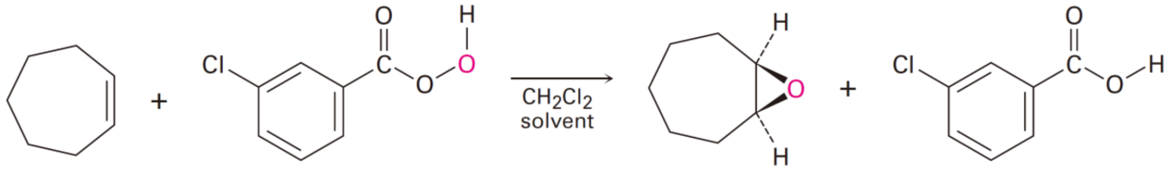


# 8.7 烯烃的氧化

- 烯烃的环氧化

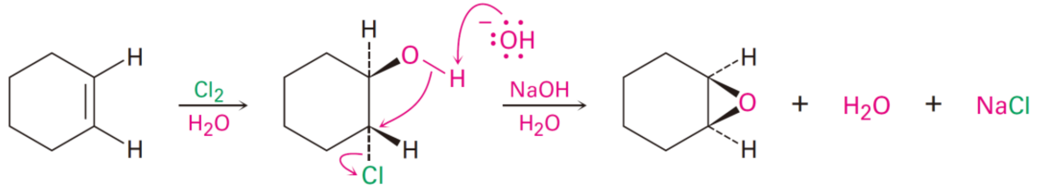
**Oxidation** Decreases electron density on carbon by:
– forming one of these: C–O C–N C–X
– or breaking this: C–H

用过氧羧酸进行环氧化



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

用HOX进行环氧化



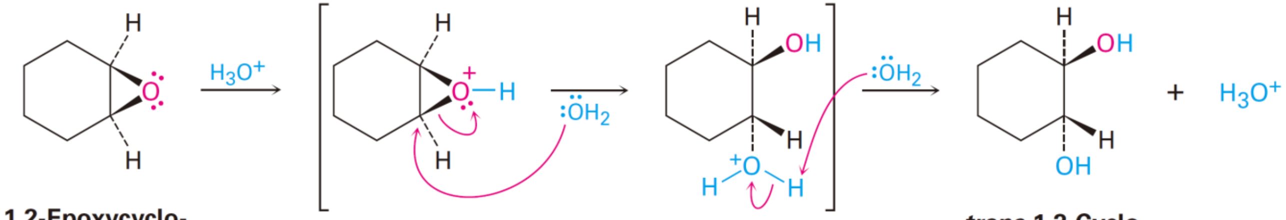
**Cyclohexene** → ***trans*-2-Chlorocyclohexanol** → **1,2-Epoxycyclohexane (73%)**

**Alkene** **Peroxyacid** **Epoxide** **Acid**

# 8.7 烯烃的氧化

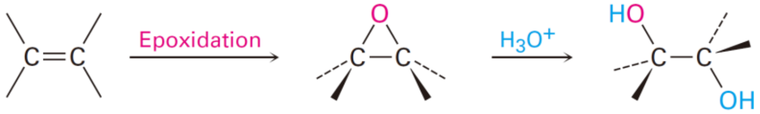
- 烯烃的双羟化：环氧化产物的水合开环
- 反式二醇

Epoxides undergo an acid-catalyzed ring-opening reaction with water (a *hydrolysis*) to give the corresponding 1,2-dialcohol, or *diol*, also called a **glycol**. Thus, the net result of the two-step alkene epoxidation/hydrolysis is **hydroxylation**—the addition of an −OH group to each of the two double-bond carbons. In fact, approximately 18 million metric tons of ethylene glycol, $HOCH_2CH_2OH$, most of it used for automobile antifreeze, is produced worldwide each year by epoxidation of ethylene followed by hydrolysis.



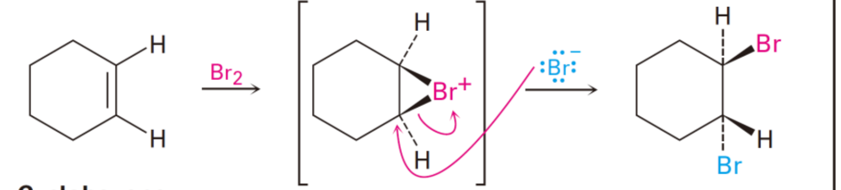
**1,2-Epoxycyclohexane**

***trans*-1,2-Cyclohexanediol (86%)**



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

Recall the following:

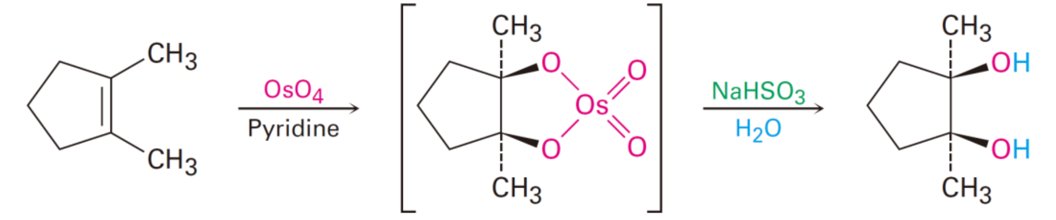


**Cyclohexene**

***trans*-1,2-Dibromocyclohexane**

# 8.7 烯烃的氧化

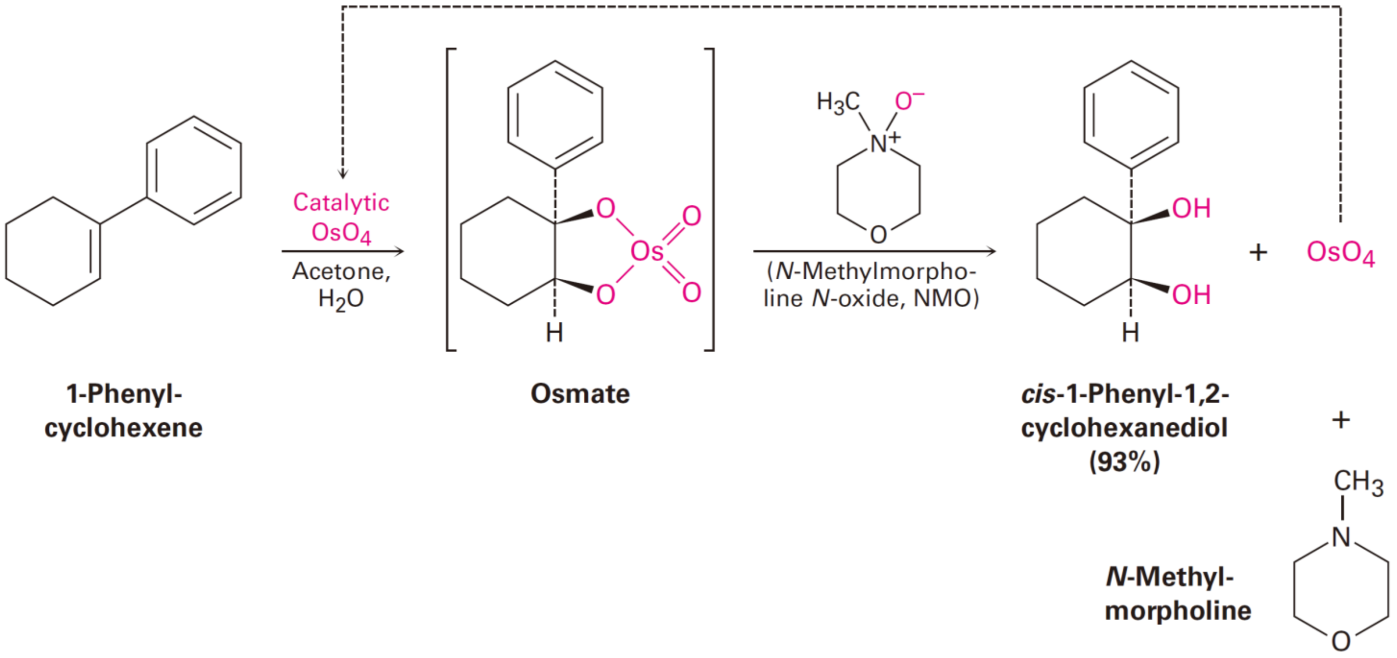
- 烯烃的双羟化：四氧化锇氧化
- 顺式二醇



**1,2-Dimethylcyclopentene**

**A cyclic osmate intermediate**

***cis*-1,2-Dimethyl-1,2-cyclopentanediol (87%)**



**1-Phenyl-cyclohexene**

**Osmate**

***cis*-1-Phenyl-1,2-cyclohexanediol (93%)**

***N*-Methyl-morpholine**

# 8.7 烯烃的氧化

- 课堂练习

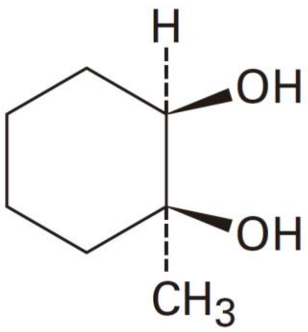
**Problem 8.13**

What product would you expect from reaction of *cis*-2-butene with *meta*-chloroperoxybenzoic acid? Show the stereochemistry.

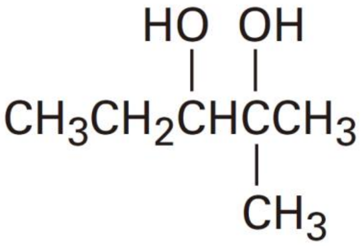
**Problem 8.14**

How would you prepare each of the following compounds starting with an alkene?

**(a)**

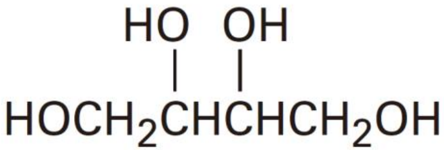


**(b)**



$CH_3CH_2\overset{HO}{C}H\underset{CH_3}{\overset{OH}{C}}CH_3$

**(c)**

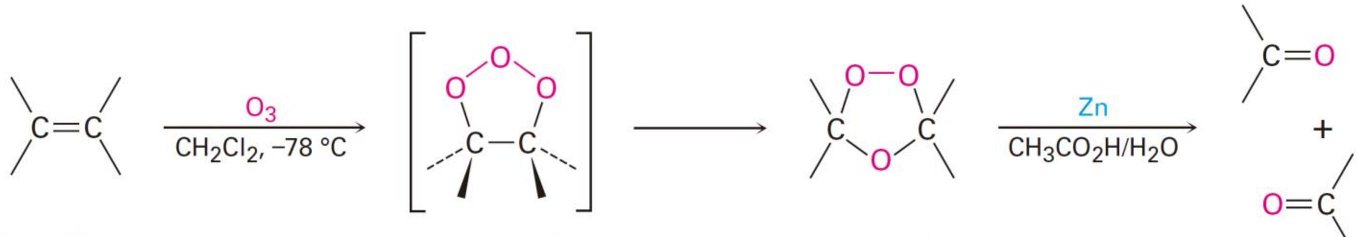


$HOCH_2\overset{HO}{C}H\overset{OH}{C}HCH_2OH$

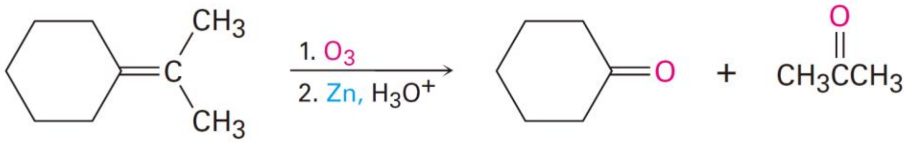
# 8.8 烯烃氧化制备羰基化合物

- 烯烃的臭氧化
- 要点：臭氧和锌试剂的组合

$$3\ O_2 \xrightarrow[\text{discharge}]{\text{Electric}} 2\ O_3$$



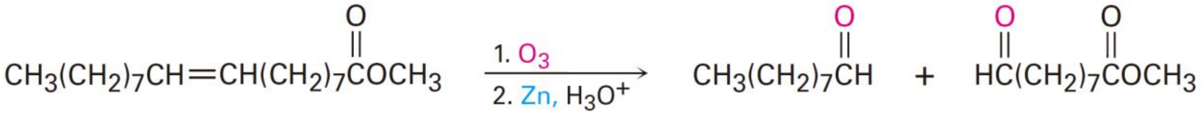
**An alkene** **A molozonide** **An ozonide**



**Isopropylidenecyclohexane (tetrasubstituted)**

**Cyclohexanone** **Acetone**

**84%; two ketones**



$$CH_3(CH_2)_7CH{=}CH(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow[2.\ Zn,\ H_3O^+]{1.\ O_3} CH_3(CH_2)_7\overset{O}{\overset{\|}{C}}H + H\overset{O}{\overset{\|}{C}}(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3$$

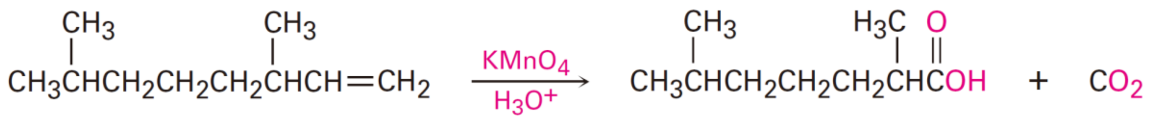
**Methyl 9-octadecenoate (disubstituted)**

**Nonanal** **Methyl 9-oxononanoate**

**78%; two aldehydes**

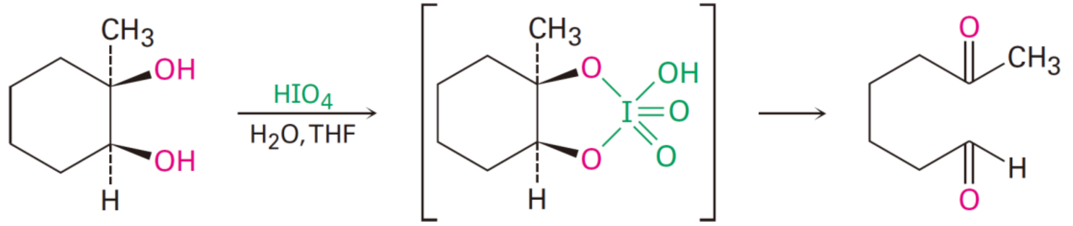
# 8.8 烯烃氧化制备羰基化合物

- 其他氧化剂的氧化：高锰酸钾、高碘酸。

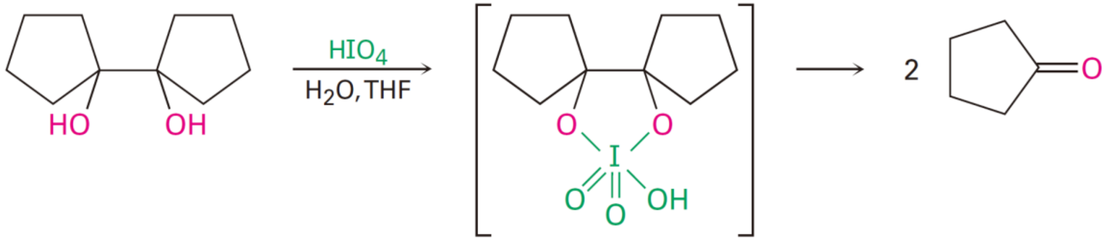


$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH{=}CH_2 \xrightarrow[H_3O^+]{KMnO_4} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_2\overset{H_3C}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}OH + CO_2$$

**3,7-Dimethyl-1-octene** **2,6-Dimethylheptanoic acid (45%)**



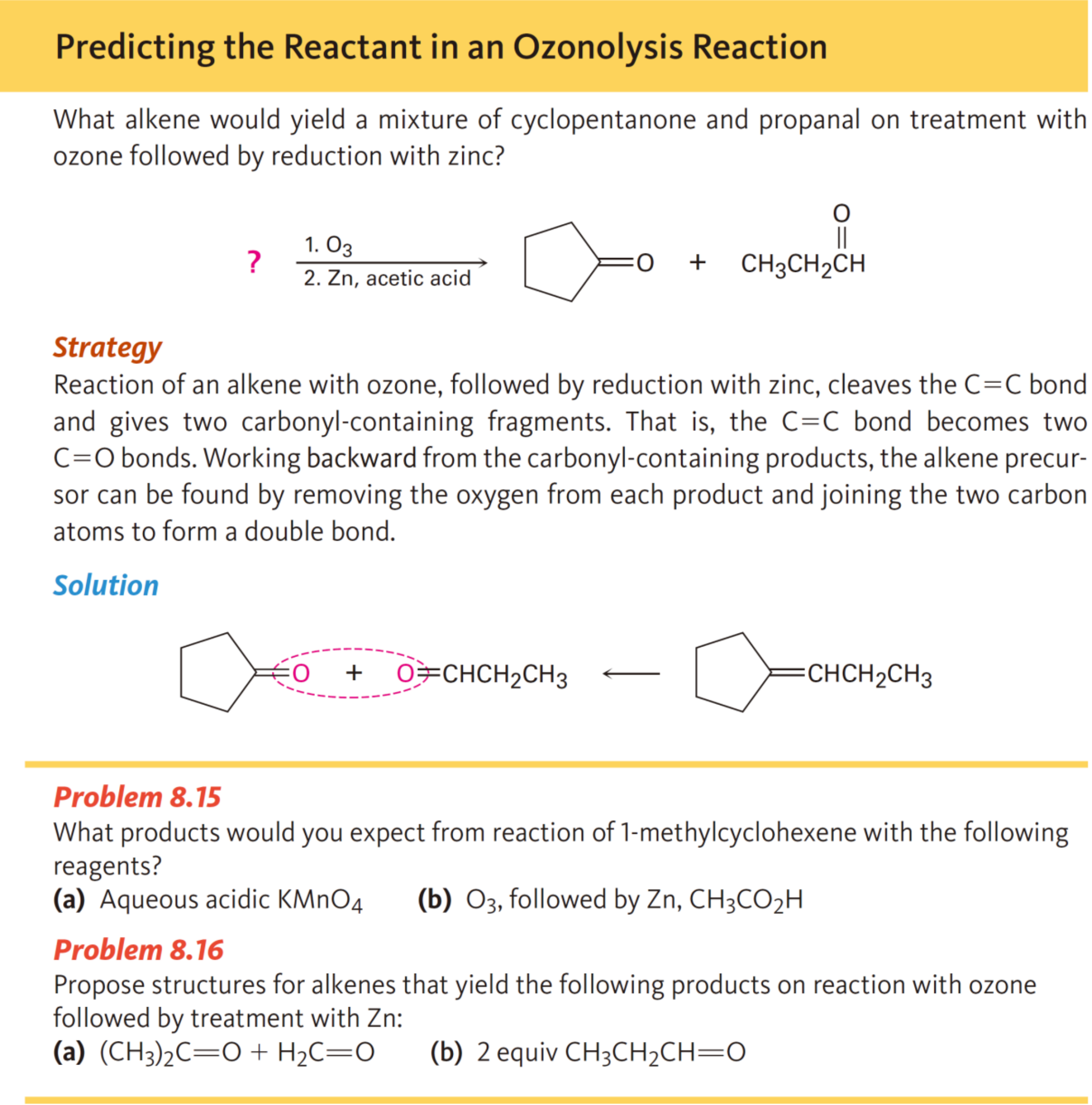
**A 1,2-diol** **Cyclic periodate intermediate** **6-Oxoheptanal (86%)**



**A 1,2-diol** **Cyclic periodate intermediate** **Cyclopentanone (81%)**

# 8.8 烯烃氧化制备羰基化合物

- 课堂练习



## Predicting the Reactant in an Ozonolysis Reaction

What alkene would yield a mixture of cyclopentanone and propanal on treatment with ozone followed by reduction with zinc?

? $\xrightarrow[\text{2. Zn, acetic acid}]{\text{1. } O_3}$ cyclopentanone + $CH_3CH_2\overset{O}{\overset{\|}{C}}H$

***Strategy***

Reaction of an alkene with ozone, followed by reduction with zinc, cleaves the C=C bond and gives two carbonyl-containing fragments. That is, the C=C bond becomes two C=O bonds. Working backward from the carbonyl-containing products, the alkene precursor can be found by removing the oxygen from each product and joining the two carbon atoms to form a double bond.

***Solution***

cyclopentanone =O + O=$CHCH_2CH_3$ ⟵ cyclopentylidene=$CHCH_2CH_3$

***Problem 8.15***

What products would you expect from reaction of 1-methylcyclohexene with the following reagents?

**(a)** Aqueous acidic $KMnO_4$ **(b)** $O_3$, followed by Zn, $CH_3CO_2H$

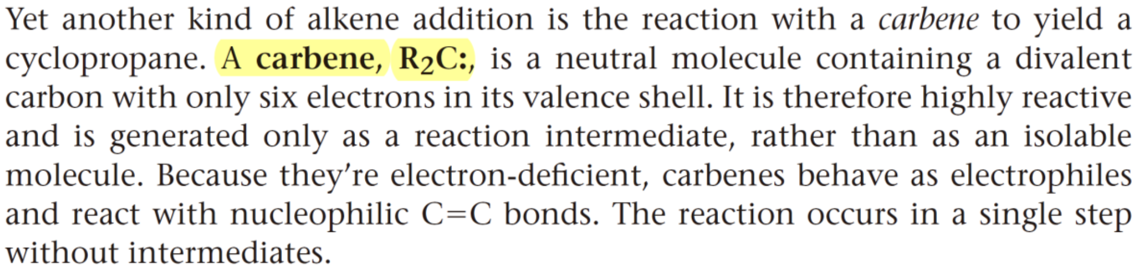
***Problem 8.16***

Propose structures for alkenes that yield the following products on reaction with ozone followed by treatment with Zn:

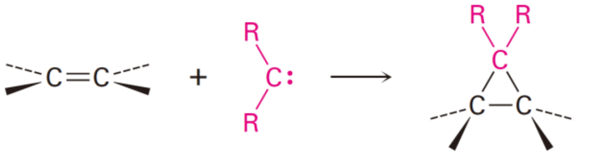
**(a)** $(CH_3)_2C{=}O + H_2C{=}O$ **(b)** 2 equiv $CH_3CH_2CH{=}O$

# 8.9 烯烃的环丙烷化反应

- 卡宾，又称碳烯、碳宾，是含二价碳的电中性化合物。卡宾是由一个碳和其他两个基团以共价键结合形成的，碳上还有两个自由电子。

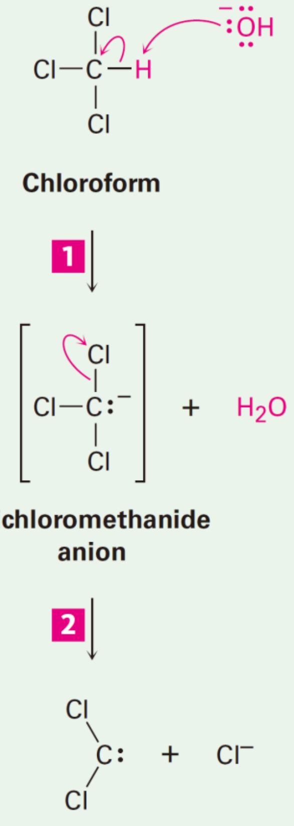


Yet another kind of alkene addition is the reaction with a *carbene* to yield a cyclopropane. A **carbene**, **$R_2C$:**, is a neutral molecule containing a divalent carbon with only six electrons in its valence shell. It is therefore highly reactive and is generated only as a reaction intermediate, rather than as an isolable molecule. Because they're electron-deficient, carbenes behave as electrophiles and react with nucleophilic C=C bonds. The reaction occurs in a single step without intermediates.



**An alkene** **A carbene** **A cyclopropane**

二氯卡宾的制备：



**Chloroform**

**1** Base abstracts the hydrogen from chloroform, leaving behind the electron pair from the C–H bond and forming the trichloromethanide anion.

**Trichloromethanide anion**

**2** Spontaneous loss of chloride ion then yields the neutral dichlorocarbene.

**Dichlorocarbene**

# 8.9 烯烃的环丙烷化反应

二氯卡宾的结构：

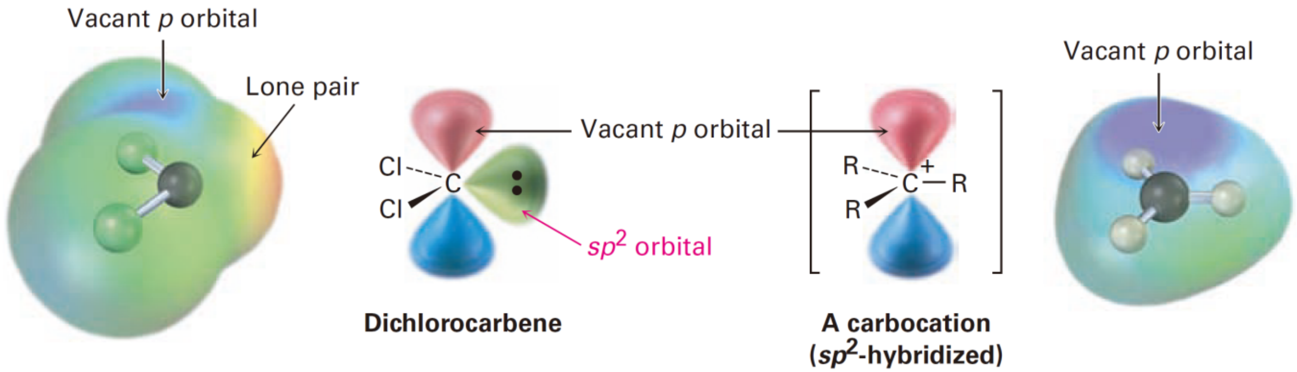
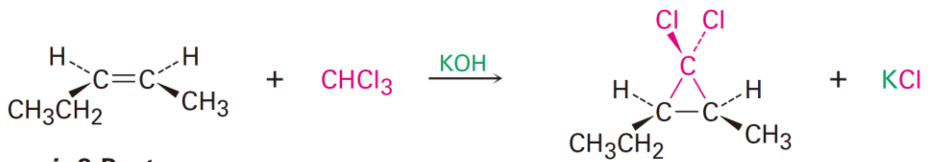
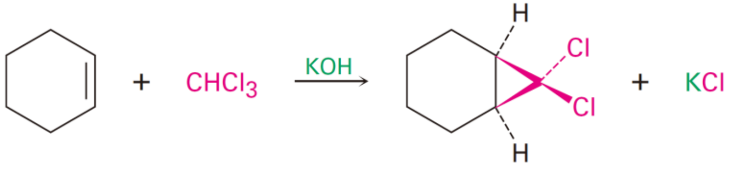


**Figure 8.9** The structure of dichlorocarbene. Electrostatic potential maps show how the **positive region** coincides with the empty *p* orbital in both dichlorocarbene and a carbocation ($CH_3^+$). The **negative region** in the dichlorocarbene map coincides with the lone-pair electrons.



***cis*-2-Pentene**



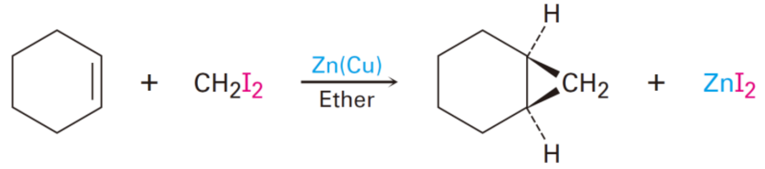
**Cyclohexene**

亚甲基卡宾的形式物：

$CH_2I_2 + Zn(Cu) \longrightarrow ICH_2-ZnI \quad [\text{"}:CH_2\text{"}]$

**Diiodomethane**

**(Iodomethyl)zinc iodide**
**(a carbenoid)**



**Cyclohexene**

**Bicyclo[4.1.0]heptane**
**(92%)**

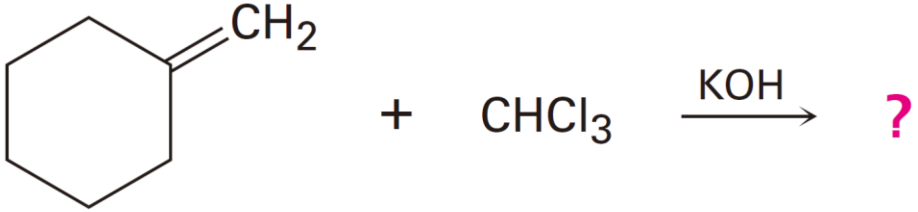
# 8.9 烯烃的环丙烷化反应

- 课堂练习

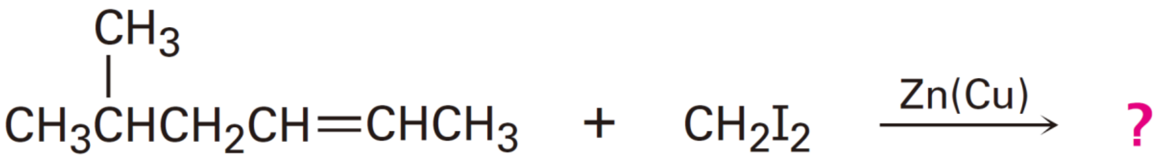
## *Problem 8.17*

What products would you expect from the following reactions?

**(a)**



**(b)**

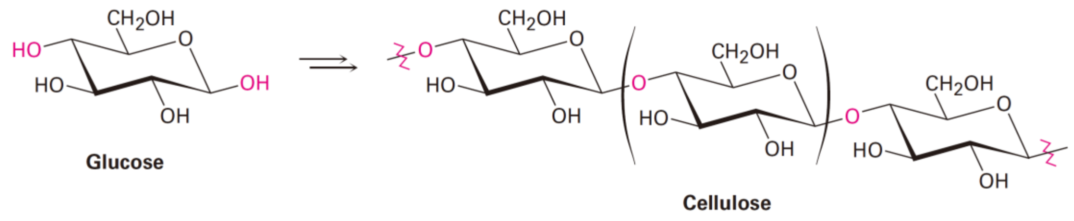


$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH{=}CHCH_3 + CH_2I_2 \xrightarrow{Zn(Cu)} ?$$

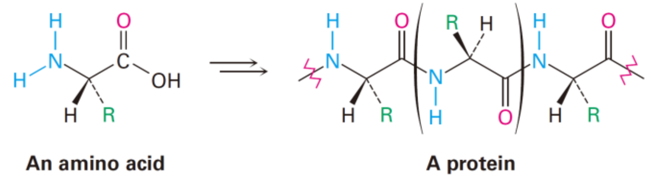
# 8.10 烯烃的自由基聚合

- 高分子是通过一定形式的聚合反应生成具有非常高的分子量的大分子。
- 生命过程的物质基础

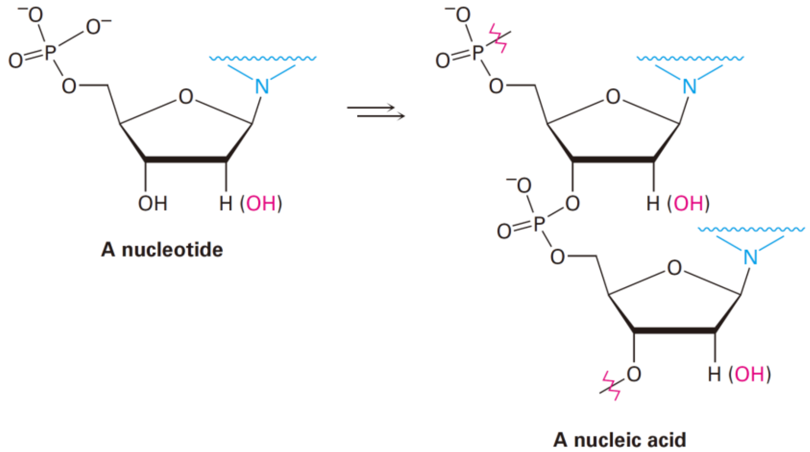
Cellulose—a glucose polymer



Protein—an amino acid polymer



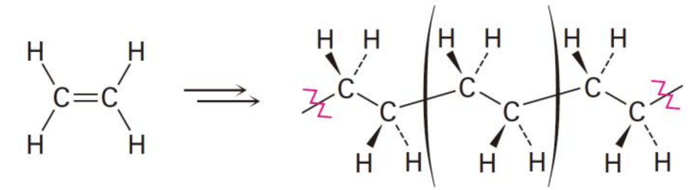
Nucleic acid—a nucleotide polymer



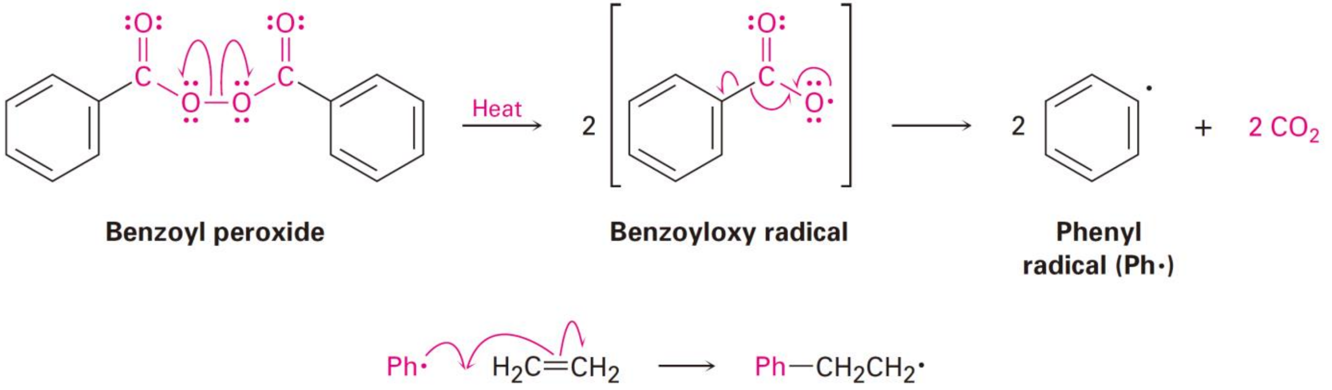
# 8.10 烯烃的自由基聚合

- 乙烯的聚合

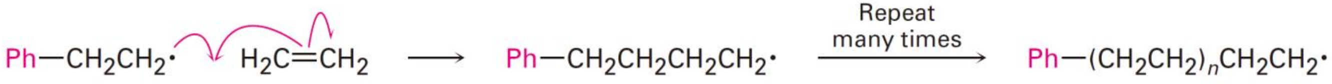
**Polyethylene—a synthetic alkene polymer**



链引发:



链增长:



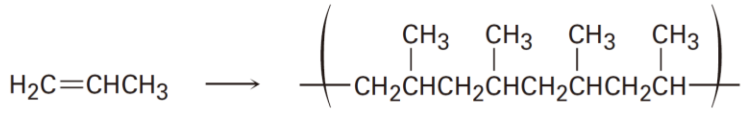
$$\text{Ph—CH}_2\text{CH}_2\cdot\ \ \text{H}_2\text{C=CH}_2 \longrightarrow \text{Ph—CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot \xrightarrow{\text{Repeat many times}} \text{Ph—(CH}_2\text{CH}_2)_n\text{CH}_2\text{CH}_2\cdot$$

链终止:

$$2\ \text{R–CH}_2\text{CH}_2\cdot \longrightarrow \text{R–CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{–R}$$

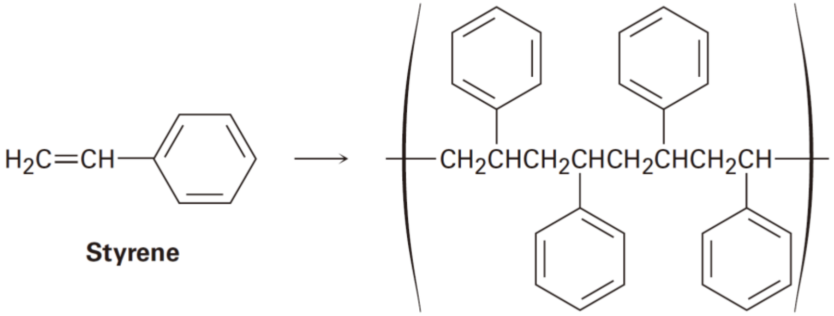
# 8.10 烯烃的自由基聚合

- 其他烯烃的聚合



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

**Propylene** **Polypropylene**



**Styrene**

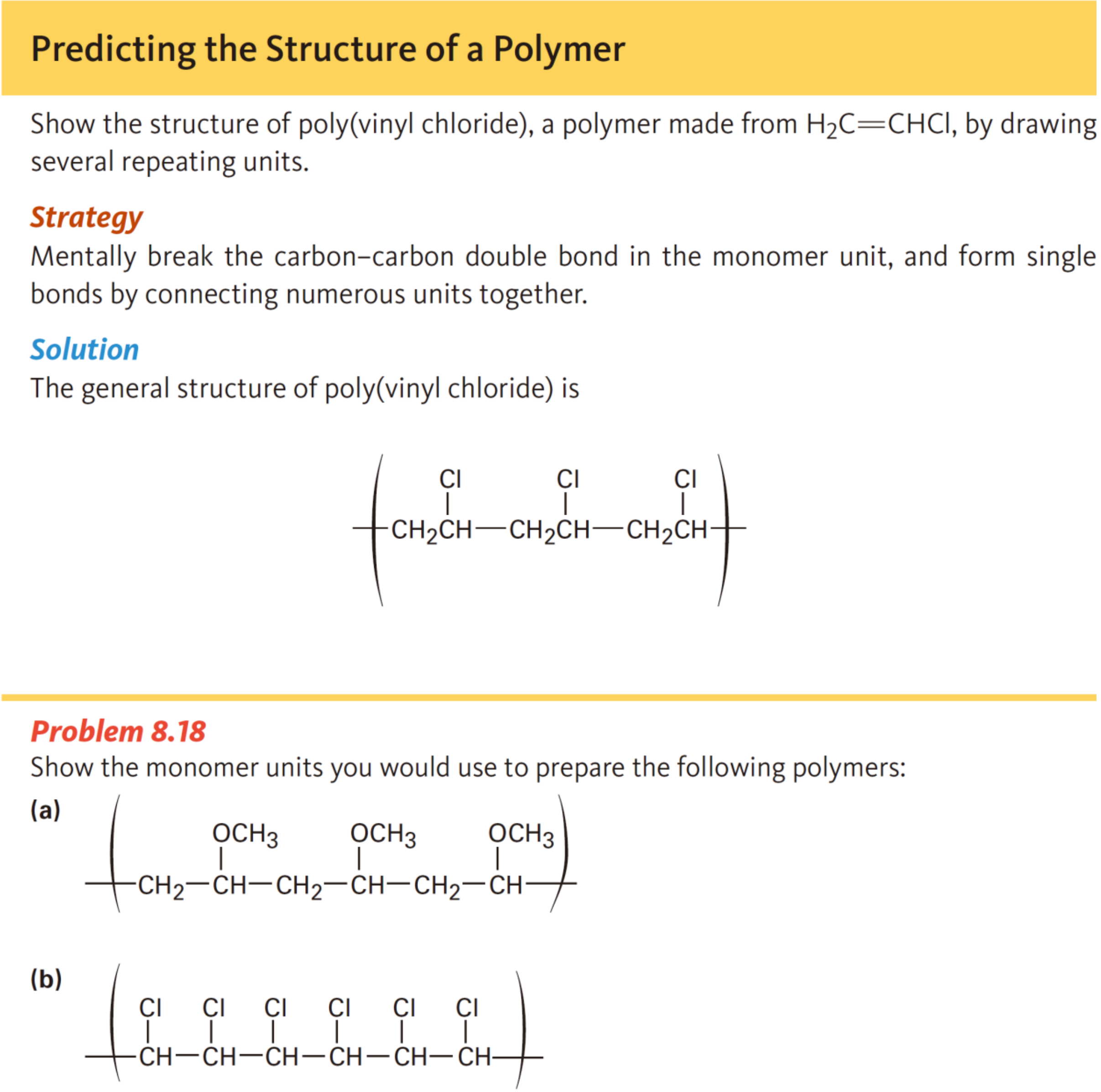
**Polystyrene**

**Table 8.1** Some Alkene Polymers and Their Uses

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

# 8.10 烯烃的自由基聚合

- 课堂练习



## Predicting the Structure of a Polymer

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

***Strategy***

Mentally break the carbon–carbon double bond in the monomer unit, and form single bonds by connecting numerous units together.

***Solution***

The general structure of poly(vinyl chloride) is

$$-\!\!\left(\mathrm{CH_2}\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{CH}}-\mathrm{CH_2}\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{CH}}-\mathrm{CH_2}\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{CH}}\right)\!\!-$$

***Problem 8.18***

Show the monomer units you would use to prepare the following polymers:

**(a)**

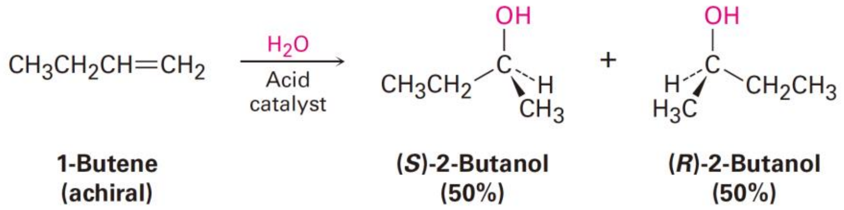
$$-\!\!\left(\mathrm{CH_2}-\overset{\overset{\mathrm{OCH_3}}{|}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\overset{\mathrm{OCH_3}}{|}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\overset{\mathrm{OCH_3}}{|}}{\mathrm{CH}}\right)\!\!-$$

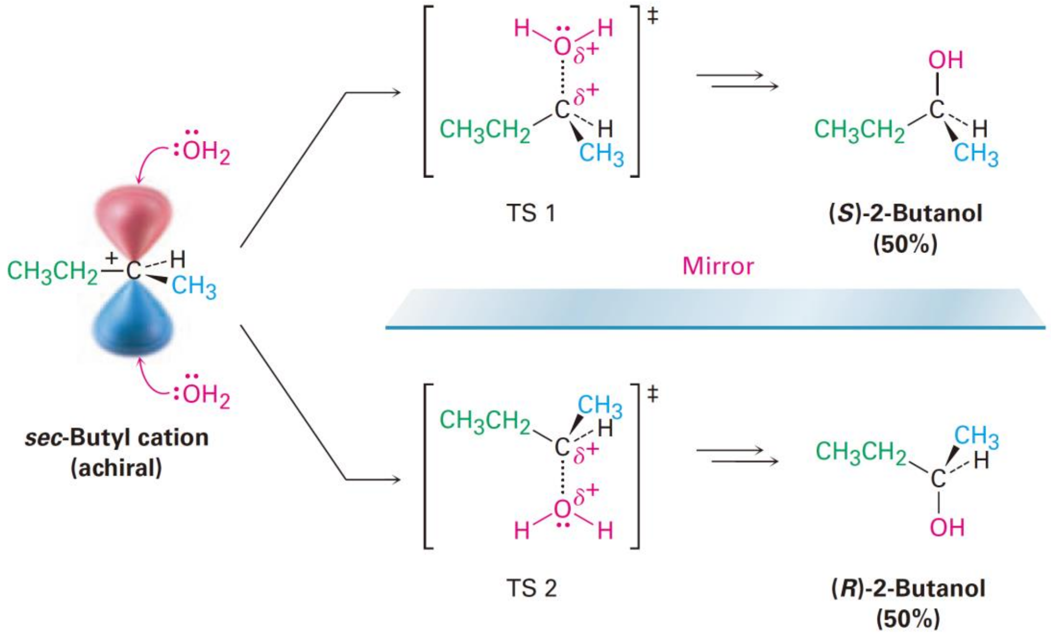
**(b)**

$$-\!\!\left(\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{CH}}-\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{CH}}-\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{CH}}-\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{CH}}-\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{CH}}-\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{CH}}\right)\!\!-$$

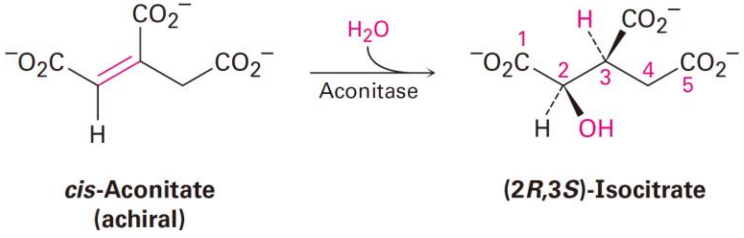
# 8.11 烯烃水合的手性问题

- 非手性底物的反应

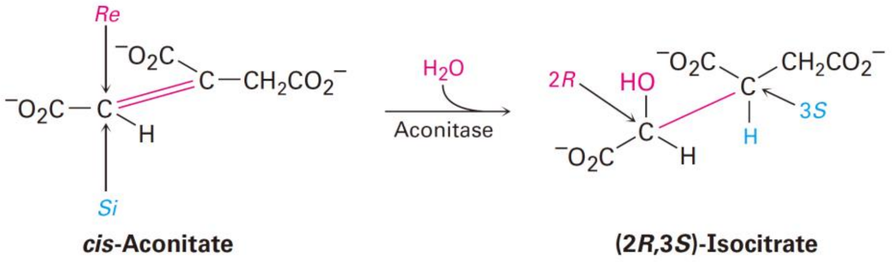




**酶是手性催化剂**



Even though *cis*-aconitate is achiral, only the (2*R*,3*S*) enantiomer of the product is formed. As discussed in **Sections 5.11 and 5.12**, *cis*-aconitate is a prochiral molecule, which is held in a chiral environment by the aconitase enzyme during the reaction. In that chiral environment, the two faces of the double bond are chemically distinct, and addition occurs on only the *Re* face at C2.



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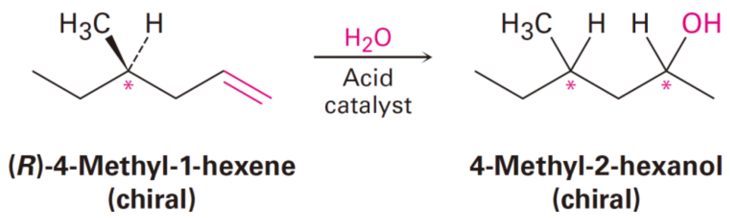

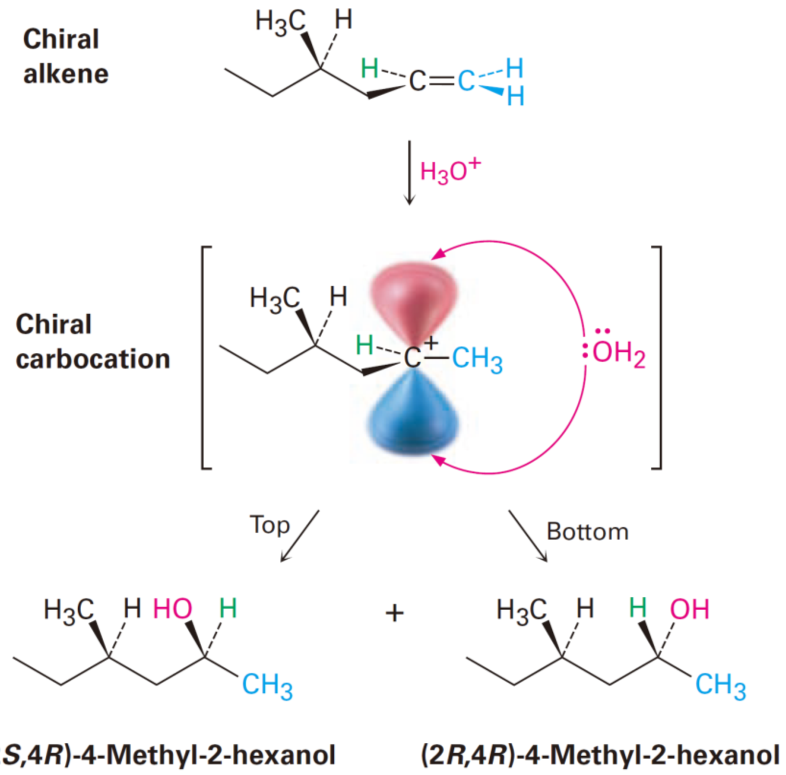

**Figure 8.12** Stereochemistry of the acid-catalyzed addition of $H_2O$ to the chiral alkene, (*R*)-4-methyl-1-hexene. A mixture of diastereomeric 2*R*,4*R* and 2*S*,4*R* products is formed in unequal amounts because reaction of the chiral carbocation intermediate is not equally likely from top and bottom. The product mixture is optically active.

# 作业

- 8.43, 8.44, 8.46, 8.48, 8.52, 8.53, 8.55, 8.56