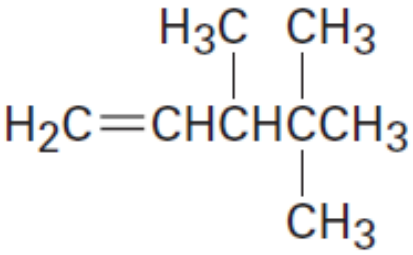
1. Problem

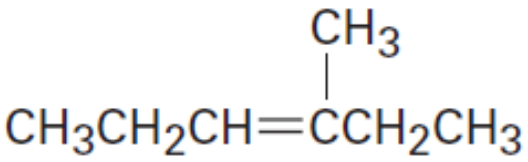
PROBLEM 7-4 (đọc tên IUPAC các chất sau)

Give IUPAC names for the following compounds:

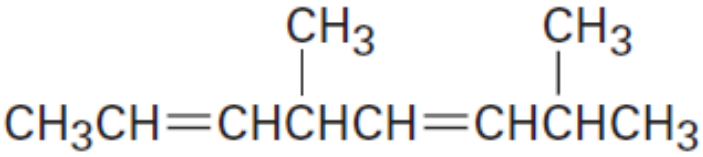
(a)



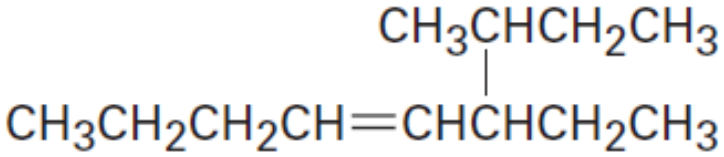
(b)



(c)



(d)



2. Problem

(vẽ công thức cấu tạo các chất sau với tên IUPAC cho dưới đây)

PROBLEM 7-5

Draw structures corresponding to the following IUPAC names:

(a) 2-Methyl-1,5-hexadiene

(b) 3-Ethyl-2,2-dimethyl-3-heptene

(c) 2,3,3-Trimethyl-1,4,6-octatriene

(d) 3,4-Diisopropyl-2,5-dimethyl-3-hexene

3. Problem 7.8

Which of the following compounds can exist as pairs of cis-trans isomers? Draw each cis-trans pair

(chất nào sau đây có đồng phân cis-trans, hãy vẽ chúng).

(a) $CH_3CH{=}CH_2$ **(b)** $(CH_3)_2C{=}CHCH_3$

(c) $CH_3CH_2CH{=}CHCH_3$ **(d)** $(CH_3)_2C{=}C(CH_3)CH_2CH_3$

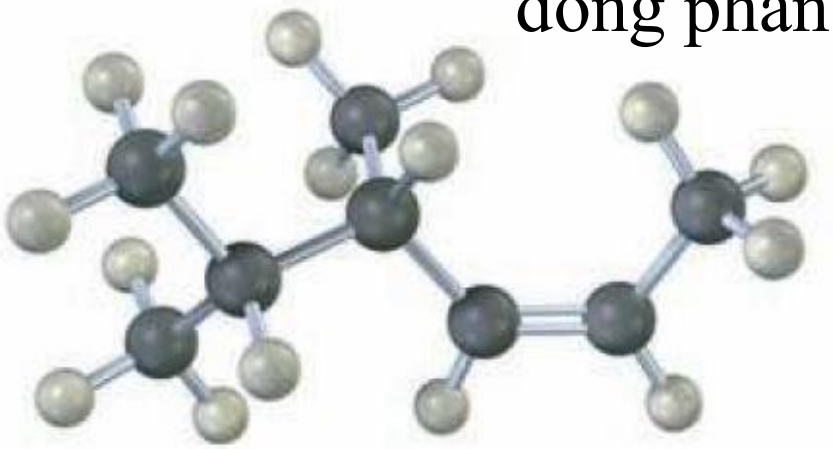
(e) $ClCH{=}CHCl$ **(f)** $BrCH{=}CHCl$

4. Problem 7.8

Name the following alkenes, including a cis/trans designation.

(đọc tên các alkene sau và sử dụng đồng phân cis/trans

(a)



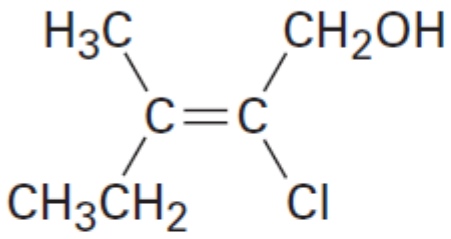
(b)

5. Problem

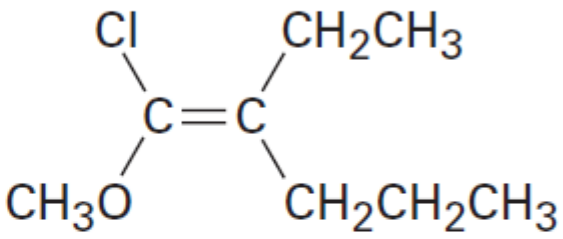
PROBLEM 7-13 (các chất sau có cấu hình E hay Z?)

Assign *E* or *Z* configuration to the following alkenes:

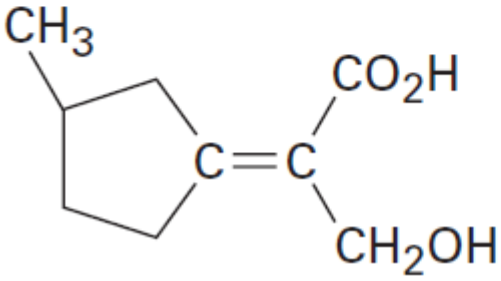
(a)



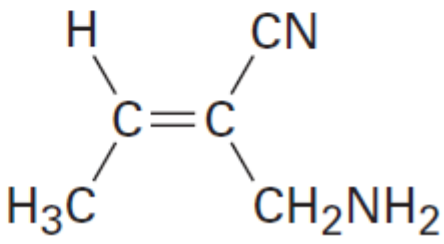
(b)



(c)



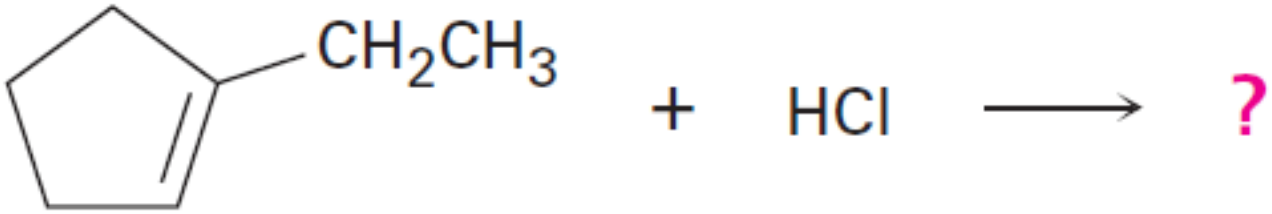
(d)



6. Problem

What product would you expect from the reaction of HCl with 1-ethylcyclopentene?

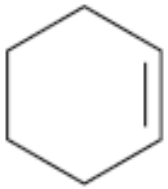
(phản ứng này tạo ra sản phẩm nào)



7. Problem 7.16

PROBLEM 7-16 (dự đoán sản phẩm của những phản ứng sau)

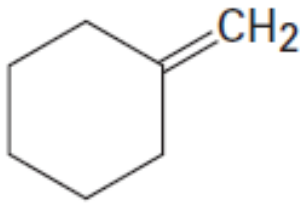
Predict the products of the following reactions:

(a)  $\xrightarrow{HCl}$?

(b) $CH_3CH_3C{=}CHCH_2CH_3$ $\xrightarrow{HBr}$?

(c) $CH_3CHCH_2CH{=}CH_2$ $\xrightarrow[H_2SO_4]{H_2O}$?

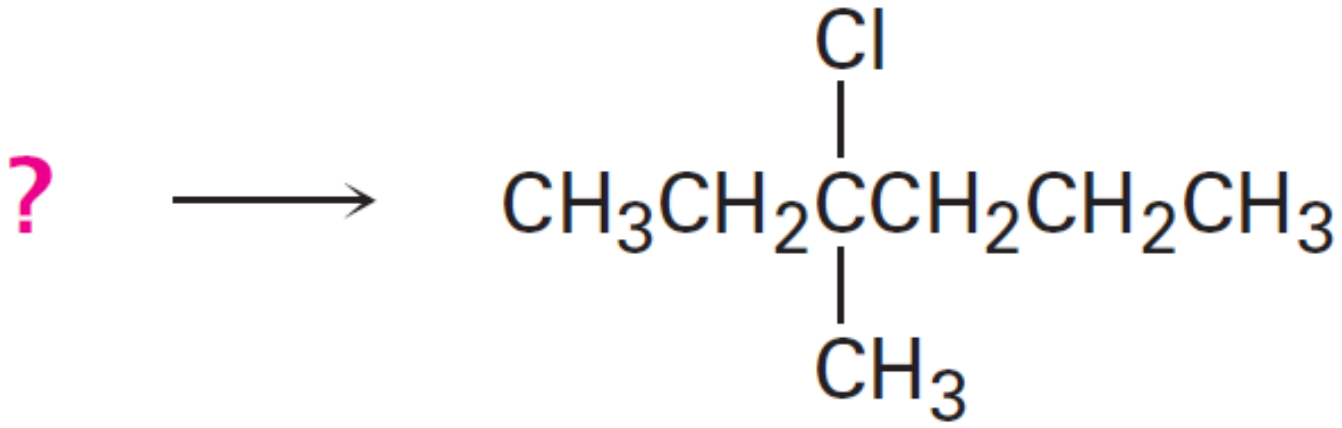
(Addition of H_2O occurs.)

(d)  $\xrightarrow{HBr}$?

8. Problem

8. What alkene would you start with to prepare the following alkyl halide?

(có thể tổng hợp chất này từ alkene nào)



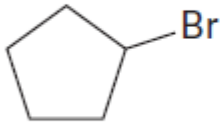
Work backward!

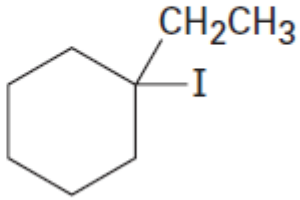
9. Problem 7.16

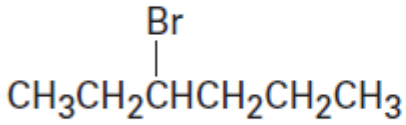
(có thể tổng hợp những chất sau từ các alkene nào)

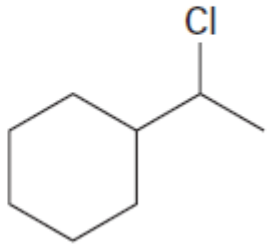
PROBLEM 7-17

What alkenes would you start with to prepare the following products?

(a) 

(b) 

(c) 

(d) 

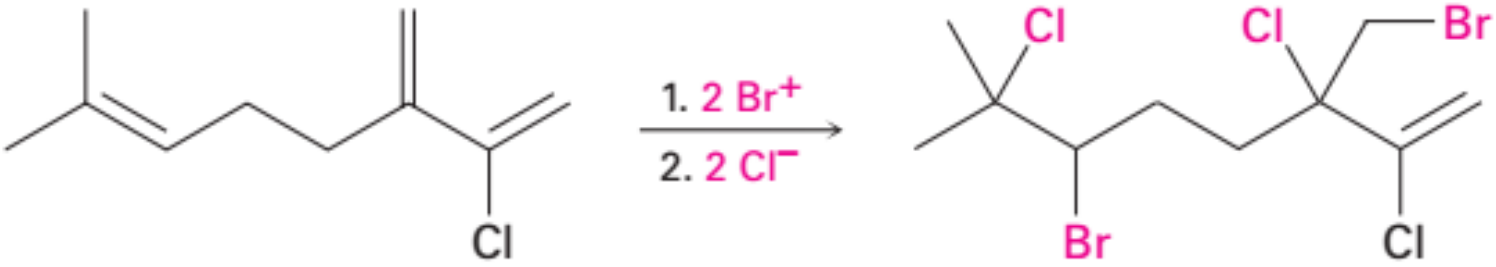
Cancer

Cancer is a group of diseases involving abnormal cell growth with the potential to invade or spread to other parts of the body. Over 100 types of cancers affect humans. In 2015, about 90.5 million people had cancer. About 14.1 million new cases occur a year. It caused about 8.8 million deaths (15.7% of deaths)

Treatment: Radiation therapy, surgery, chemotherapy, and targeted therapy

Tumor
(Colectomy specimen)

Halogenation of alkenes



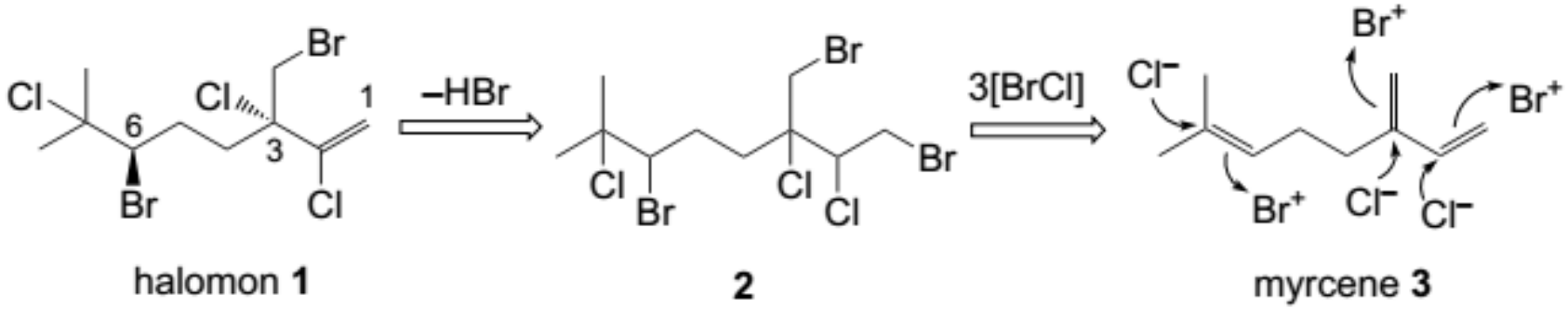
Halomon

Anticancer pentahalide
Extract from **red alga**

A Three-Step Synthesis of Halomon

Takayuki Sotokawa, Takeshi Noda, Sun Pi, and
Masahiro Hirama*

Halomon (**1**), which was isolated from the red algae *Portieria hornemannii*,[1] is a member of a novel class of antitumor agents with selective cytotoxicity against various tumor cell lines (see Scheme 1).[2] Detailed studies on the biological activity of **1** have been hampered due to its limited accessibility. Halomon (**1**) is a small molecule that can be easily synthesized; however, the presence of five halogen atoms on the acyclic carbon chain has created a number of difficulties for regio- and stereocontrolled synthesis.[3, 4] We report herein a very short and straightforward synthesis of **1**.



Scheme 1. Retrosynthetic scheme for the synthesis of halomon (**1**) from myrcene (**3**).

Organic Chemistry

CHE 203

Lecture 8: Reactions of alkenes

Le Quoc Chon – Duy Tan University

Key concepts
(những khái niệm quan trọng)

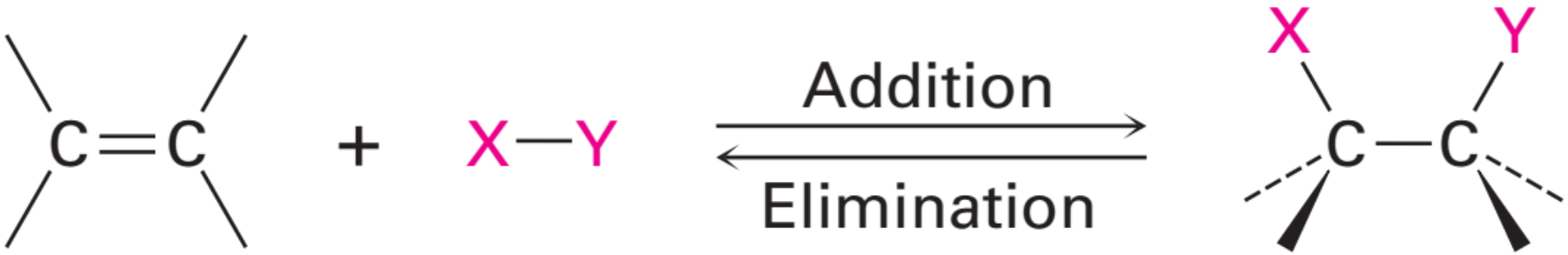
Electrophilic addition reactions

Markovnikov's rules

(Phản ứng cộng ái điện tử,
Quy tắc Markovnikov)

Preparing alkenes

(tạo alkenes, điều chế alkenes)

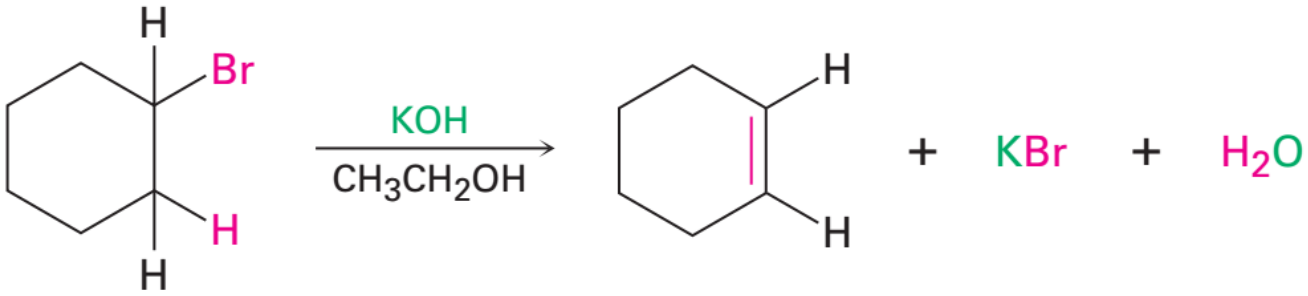


elimination to generate alkenes
(tách loại tạo alkenes)

Preparing alkenes: elimination

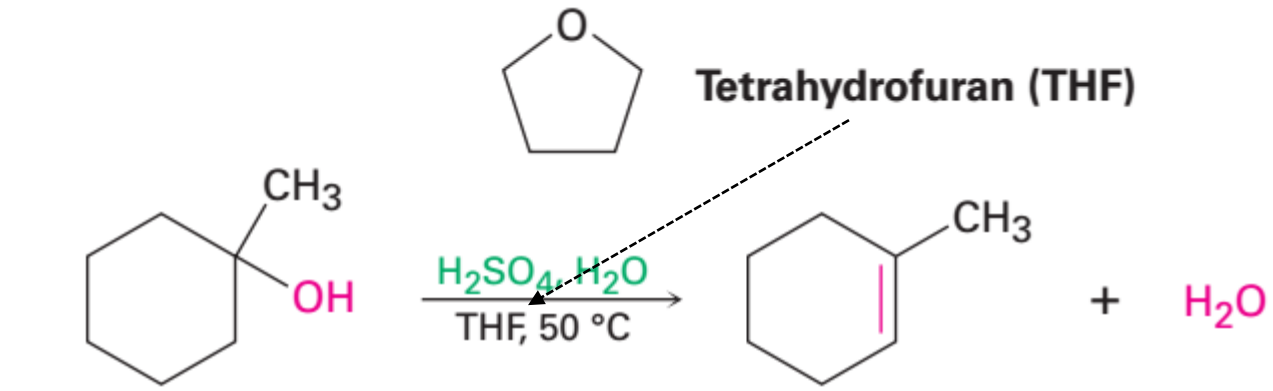
(điều chế alkenes với phản ứng tách loại)

Dehalogenation



Bromocyclohexane **Cyclohexene (81%)**

Dehydration



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

Problem

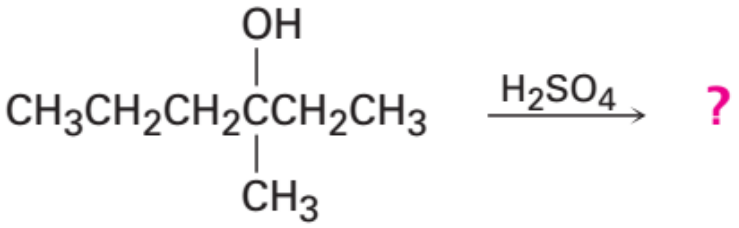
PROBLEM 8-1 (phản ứng tách loại thường tạo hỗn hợp)

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

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?



3-Methyl-3-hexanol

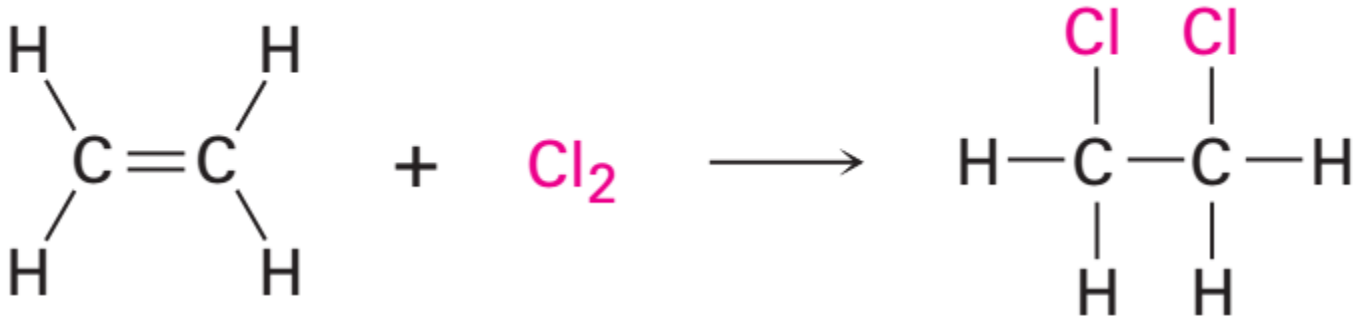
Reactions of alkenes

- Halogenation (halogen hóa)
- Hydration (hydrate hóa)
- Reduction (khử)
- Oxidation (oxy hóa)
- Addition to alkene (cộng vào alkenes)

Halogenation of alkenes

(halogen hóa alkenes)

Addition of X_2



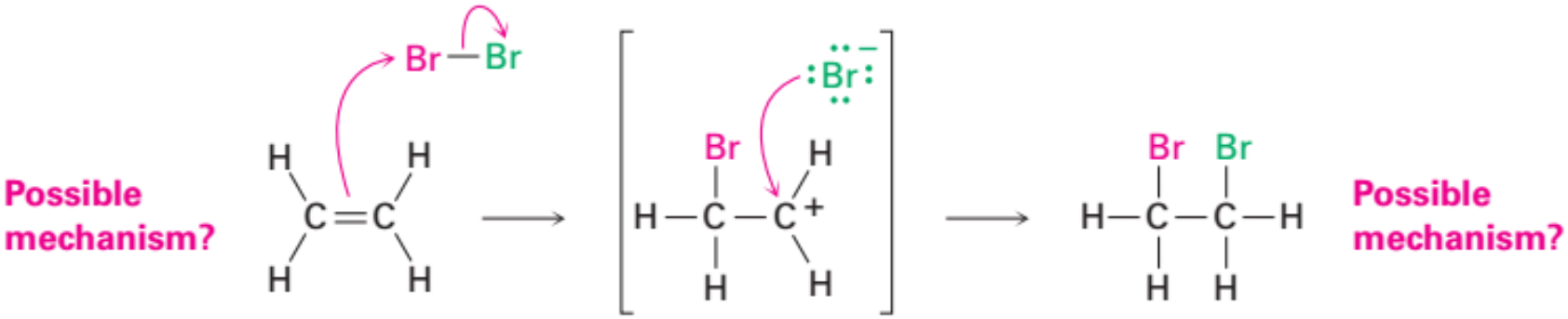
Ethylene

1,2-Dichloroethane (ethylene dichloride)

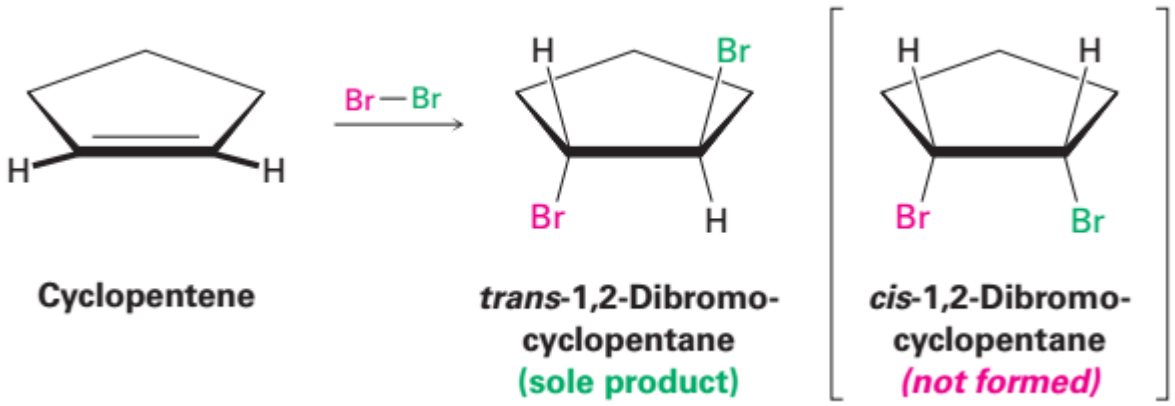
- Only chlorine and bromine react
- Fluorine is too reactive
- Iodine does not react with most alkene

Halogenation of alkenes

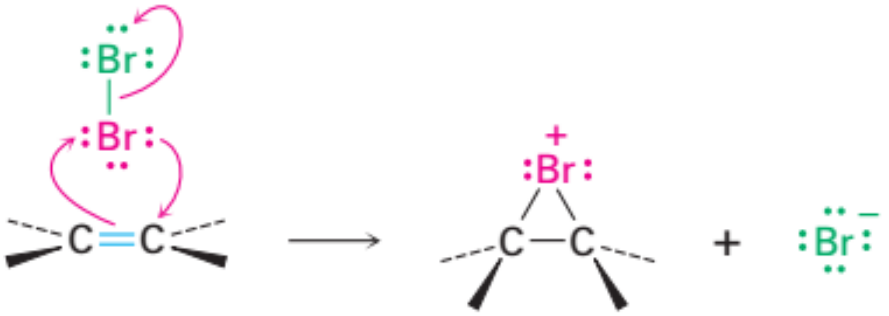
(halogen hóa alkenes)

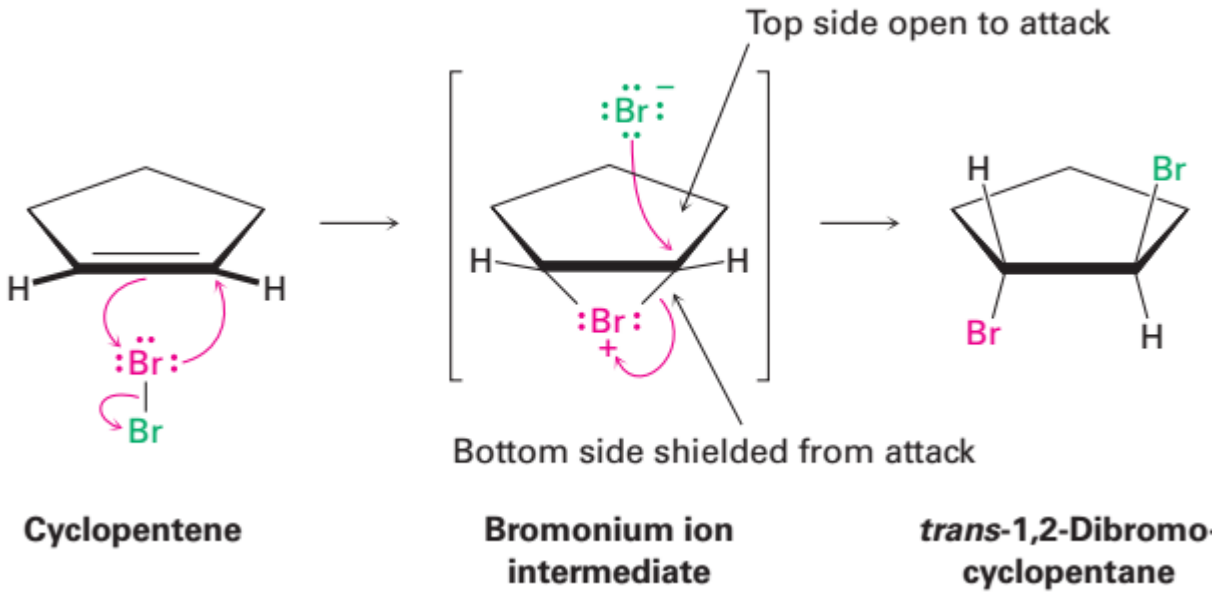


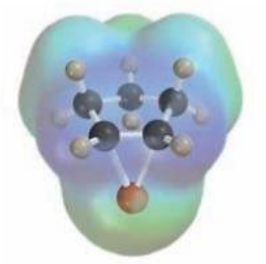
Anti-stereochemistry



Halogenation of alkenes

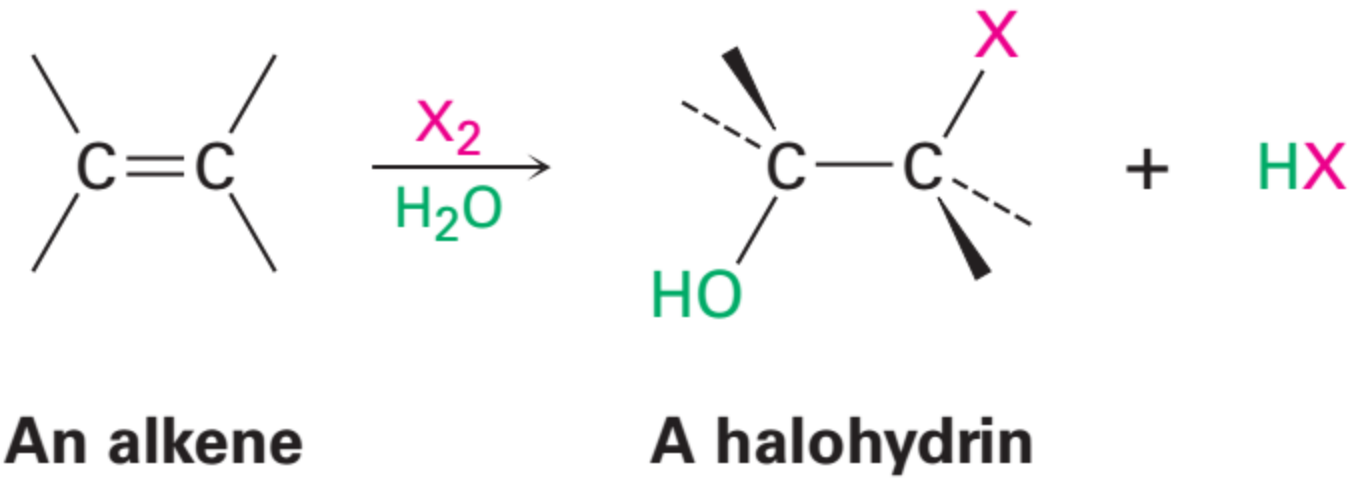






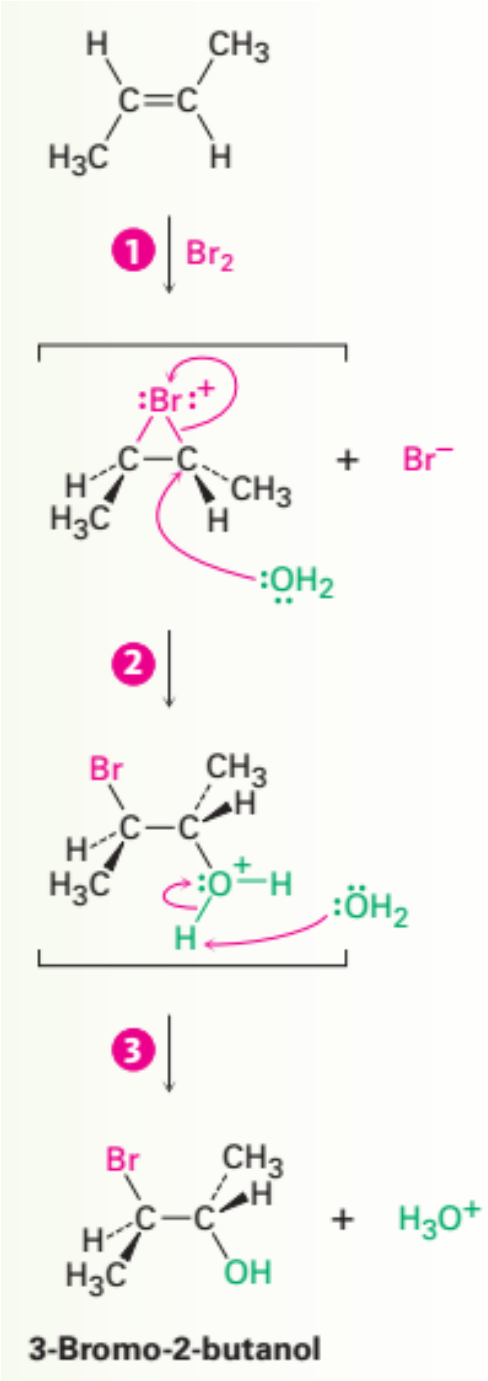
Halohydrin of alkenes

Addition HOX

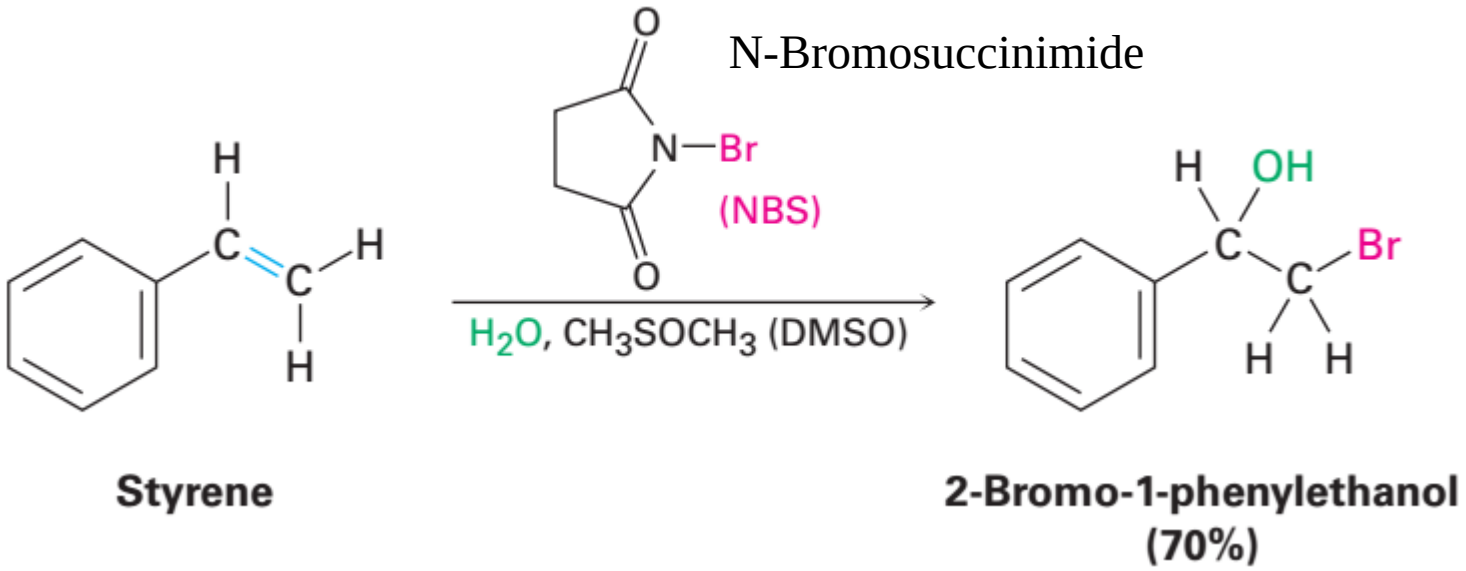


Halohydrin of alkenes

Mechanism

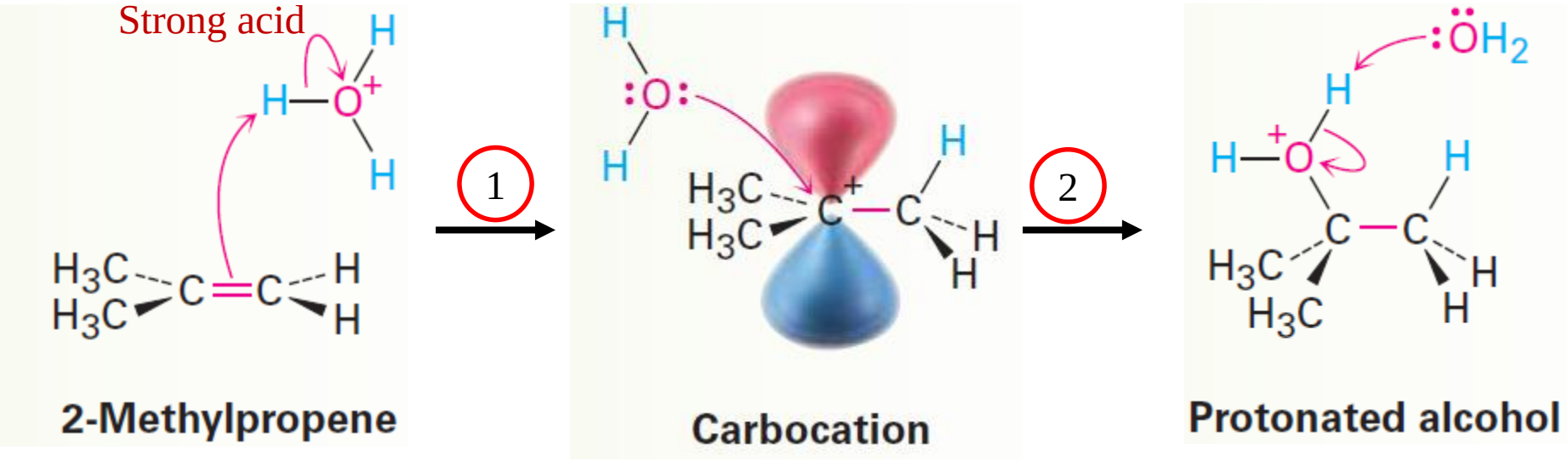


Halohydrin of alkenes

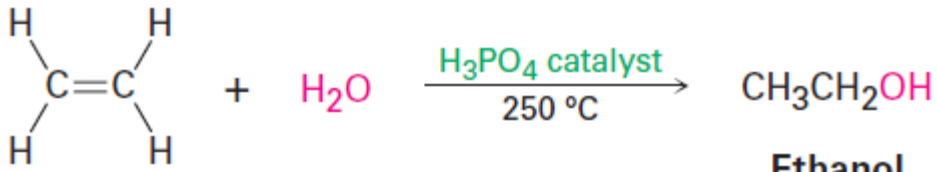


- Few alkene solubilize in water
- NBS is easier to handle than Br_2

Acid-catalyzed hydration to form alcohol

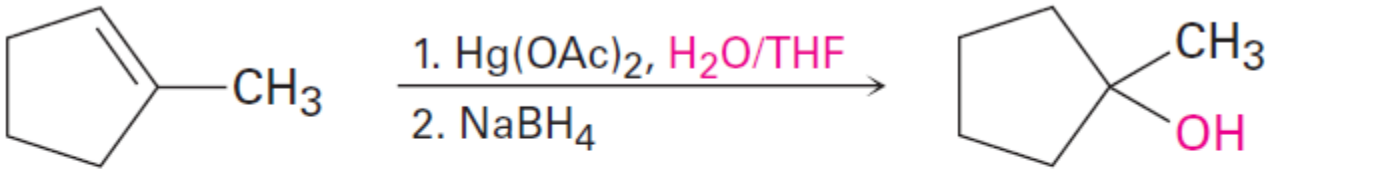


Acid-catalyzed hydration of alkene



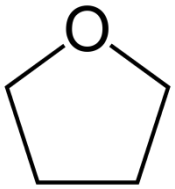
Industrial scale!

Hydration of alkenes by Oxymercuration



1-Methylcyclopentene

1-Methylcyclopentanol (92%)

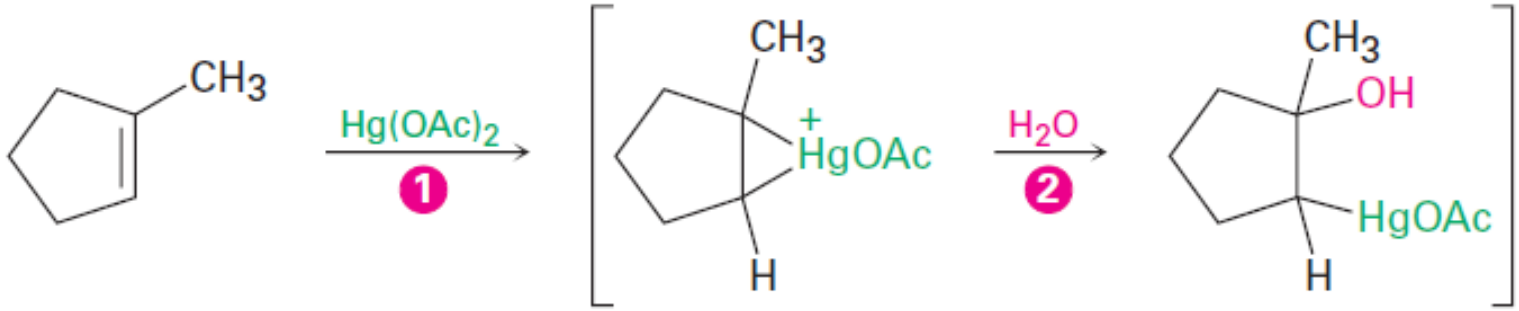


THF: tetrahydrofuran

$NaBH_4$: sodium borohydride

$Hg(OAc)_2$ = mercury (II) acetate $Hg(CH_3CO_2)_2$

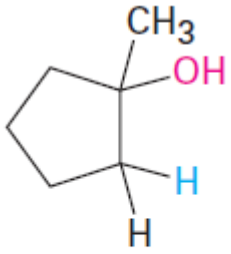
Oxymercuration mechanism



1-Methyl-cyclopentene

Mercurinium ion

Organomercury compound



1-Methyl-cyclopentanol (92% yield)

Gegiochemistry: Markovnikov

-OH attaches to the more highly substituted C

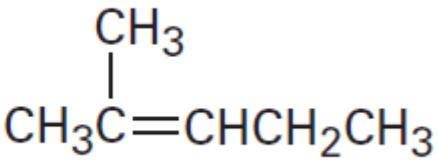
-H attaches to the less highly substituted C

Problem 8.7

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

(a) $CH_3CH_2CH_2CH{=}CH_2$

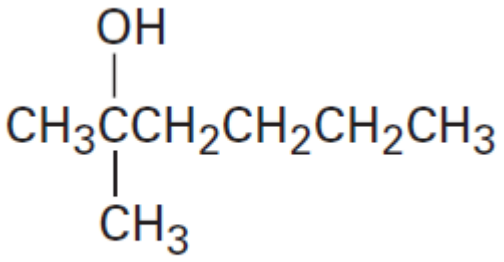
(b)



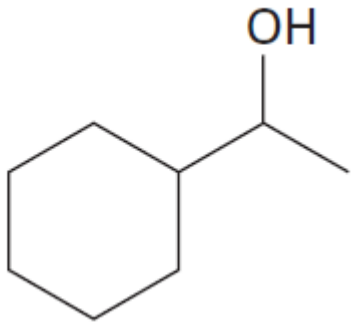
Problem 8.8

From what alkenes might the following alcohols have been prepared?

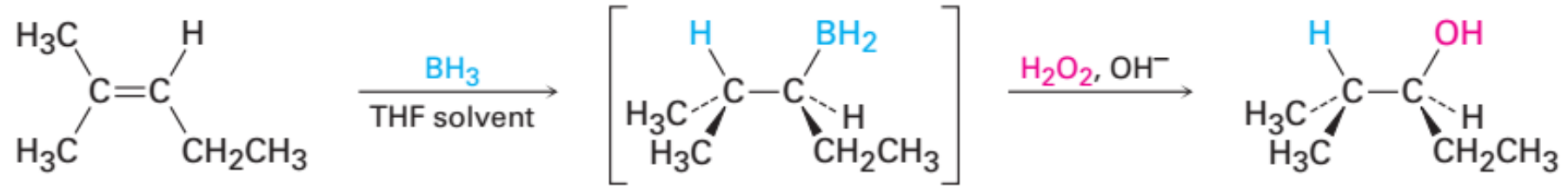
(a)



(b)



Hydration: addition H_2O by hydroboration



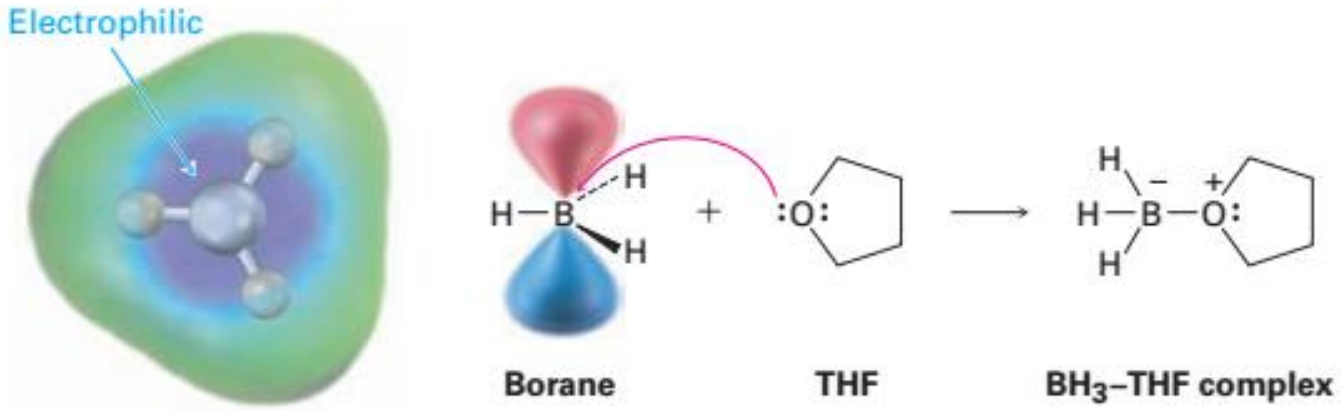
2-Methyl-2-pentene | **Organoborane intermediate** | **2-Methyl-3-pentanol**

Non-Markonikov product

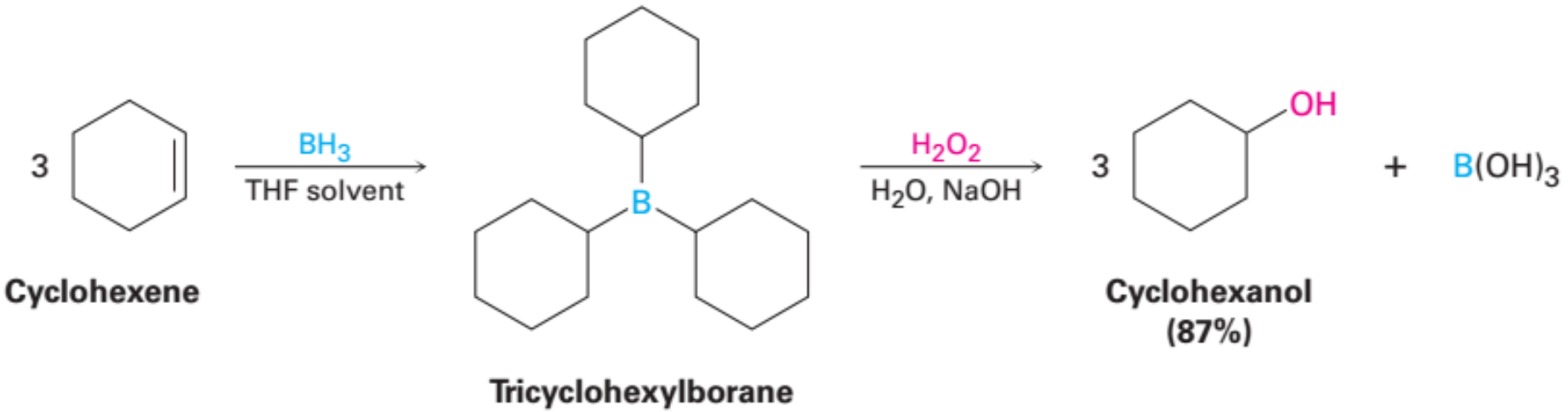
Different with oxymercuration

Hydration: addition H_2O by hydroboration

Borane is very reactive as Lewis acid, the Boron atom has only six electron in its valence shell,

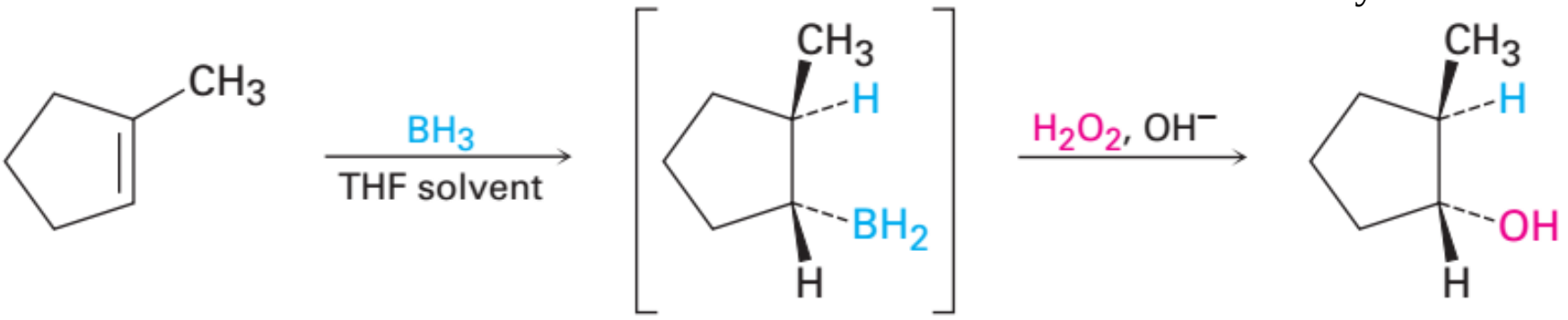


Hydration: addition H_2O by hydroboration



Hydration: addition H_2O by hydroboration

Boron is replaced by –OH with the same stereochemistry



1-Methyl-cyclopentene

Organoborane intermediate

***trans*-2-Methyl-cyclopentanol (85% yield)**

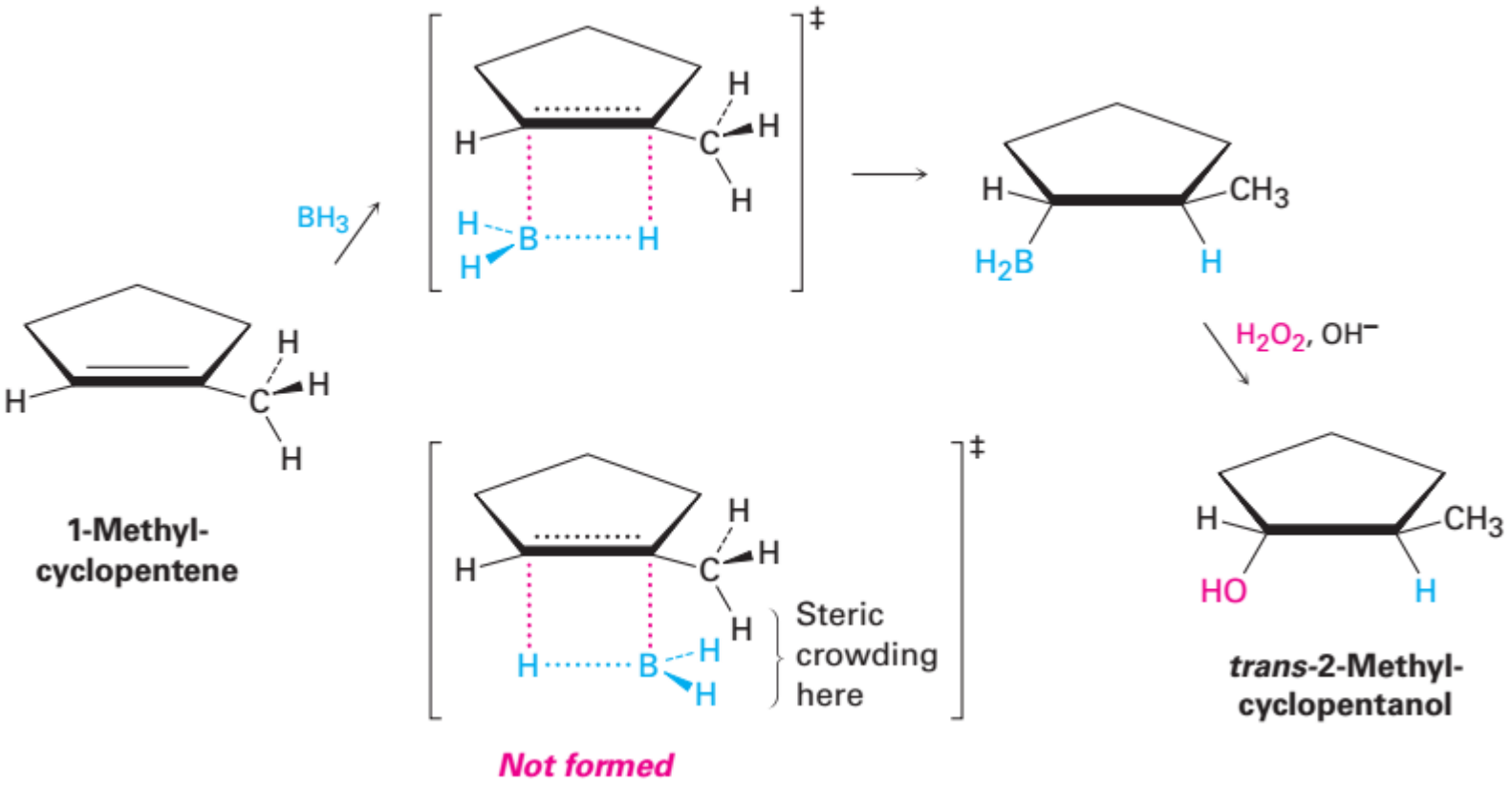
Syn-stereochemistry: Boron and H added to alkene from the same face of the double bond.

Syn non-Markovnikov addition: hydroboration - oxidation

≠ Markovnikov stereochemistry: oxymercuration – demercuration

Hydration: addition H_2O by hydroboration

Syn stereochemistry and non-Markovnikov addition

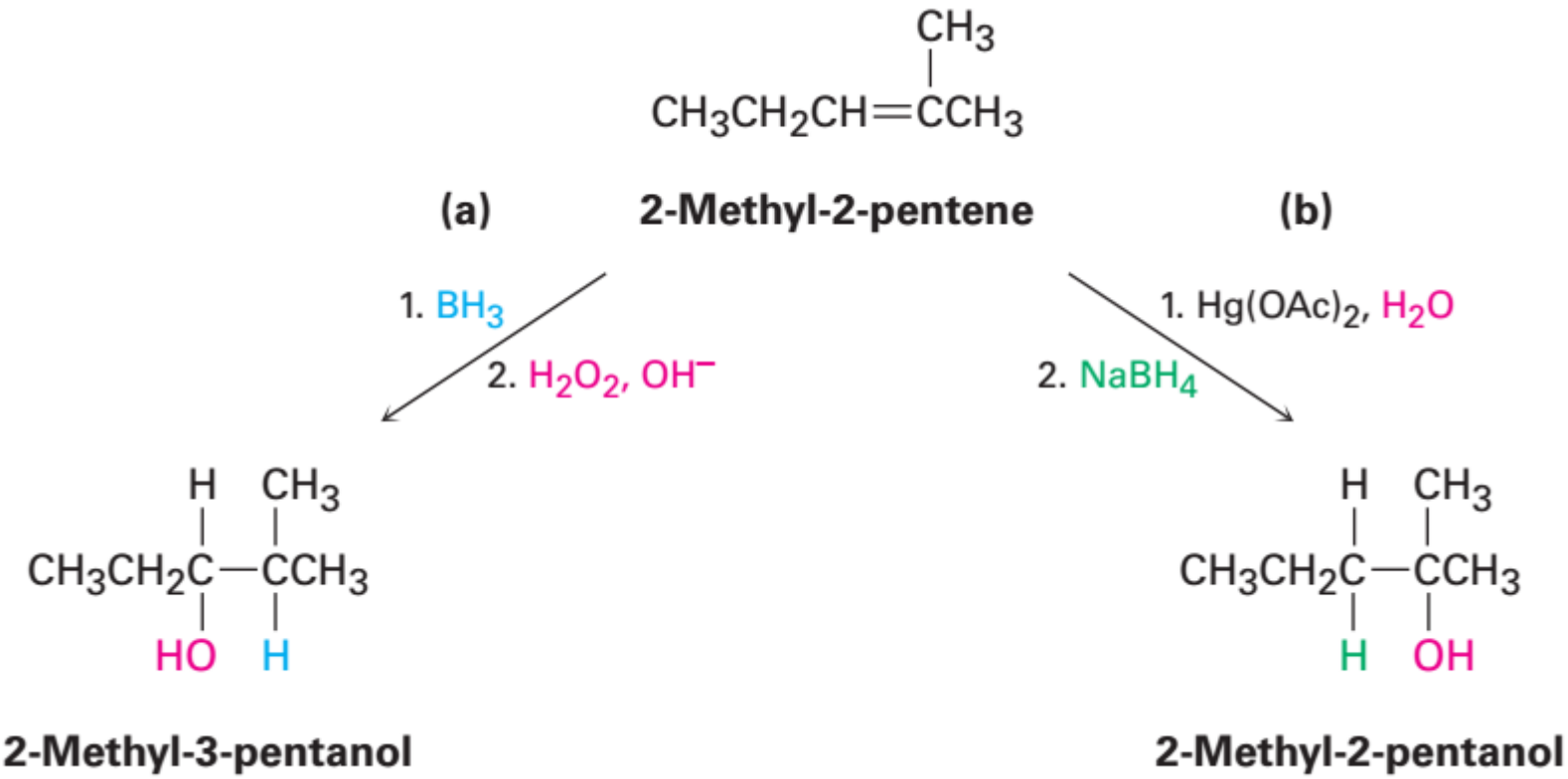


(dự đoán sản phẩm của các phản ứng sau)

Predicting the Products of a Hydration Reaction

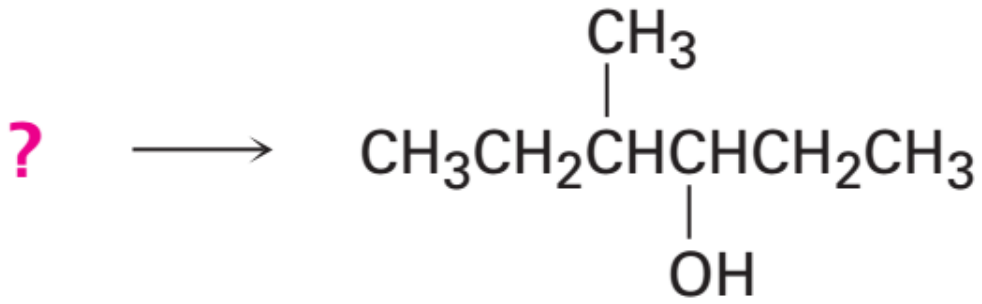
What products would you obtain from reaction of 2-methyl-2-pentene with:
(a) BH_3, followed by H_2O_2, OH^- **(b)** $Hg(OAc)_2$, followed by $NaBH_4$

Answer

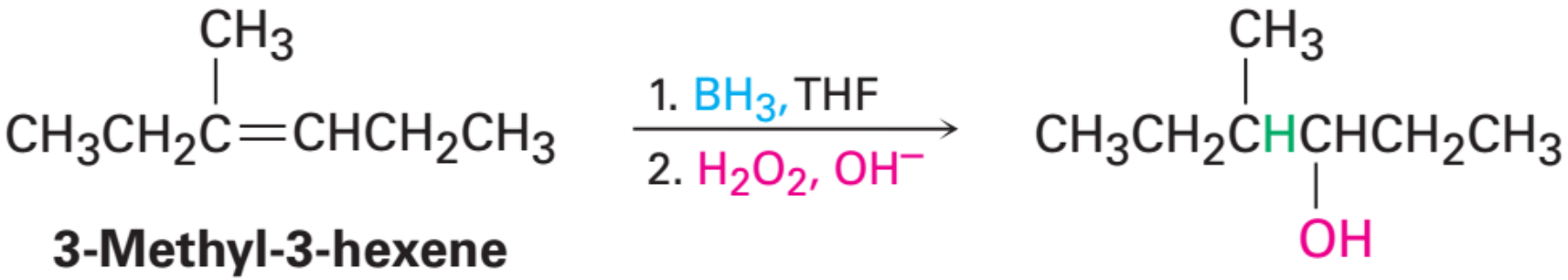

CH3
CH3CH2CH=CCH3
(a)
2-Methyl-2-pentene
(b)
1. BH3
2. H2O2, OH−
1. Hg(OAc)2, H2O
2. NaBH4
H CH3
CH3CH2C—CCH3
HO H
H CH3
CH3CH2C—CCH3
H OH
2-Methyl-3-pentanol
2-Methyl-2-pentanol

(điều chế rượu sau như thế nào)

How might you prepare the following alcohol?



Answer



3-Methyl-3-hexene

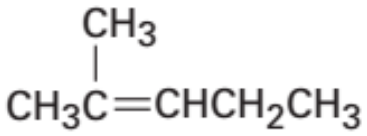
Problem

(vẽ cấu trúc phân tử sản phẩm tạo ra khi thực hiện hydroboration-oxidation các alkene sau)

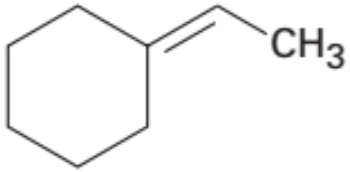
PROBLEM 8-9

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

(a)



(b)



Problem

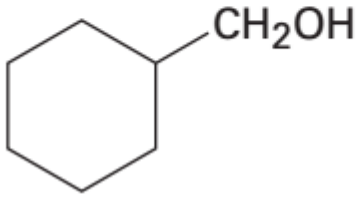
(sử dụng alkene nào để điều chế các rượu sau)

PROBLEM 8-10

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

(a) $CH_3CHCH_2CH_2OH$ (with CH_3 branch)

(b) $CH_3CHCHCH_3$ (H_3C and OH branches)

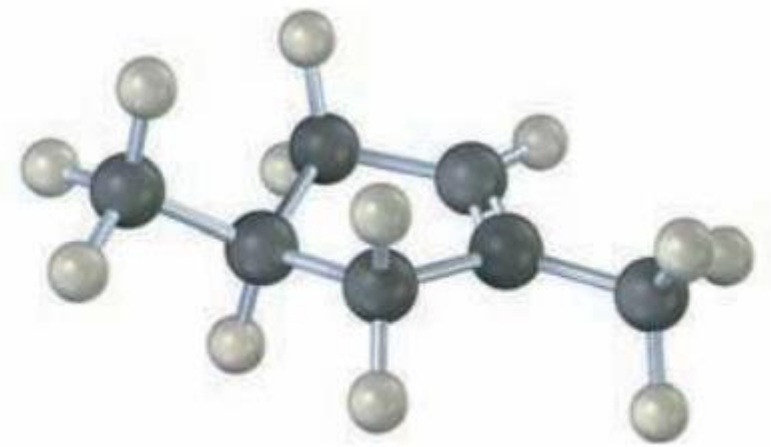
(c) 

Problem

(hydroboration-oxidation alkene sau tạo ra hỗn hợp hai rượu. Hãy vẽ cấu trúc hai rượu đó)

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.



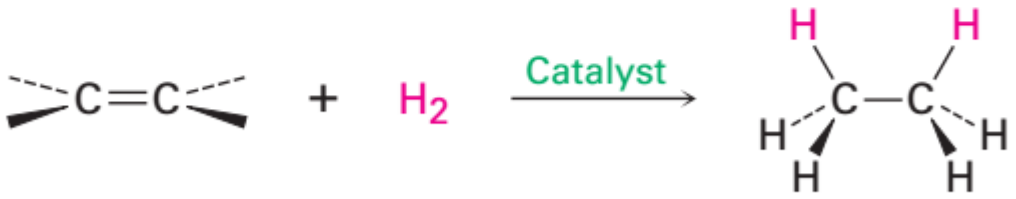
Reduction of alkene: halogenation

Reduction Increases electron density on carbon by:

– forming this: C–H

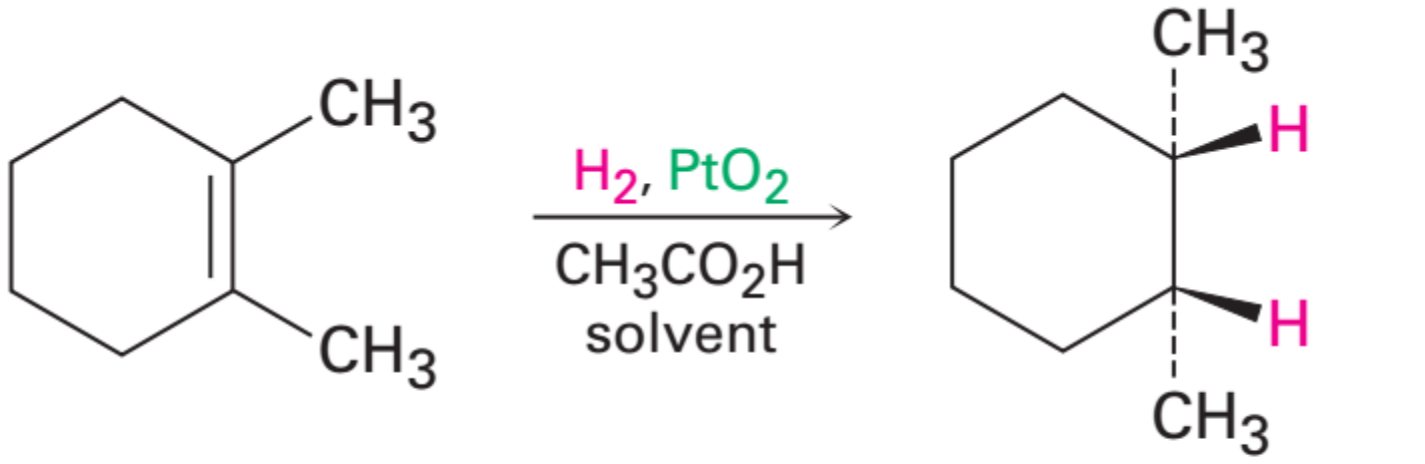
– or breaking one of these: C–O C–N C–X

A reduction:



An alkene **An alkane**

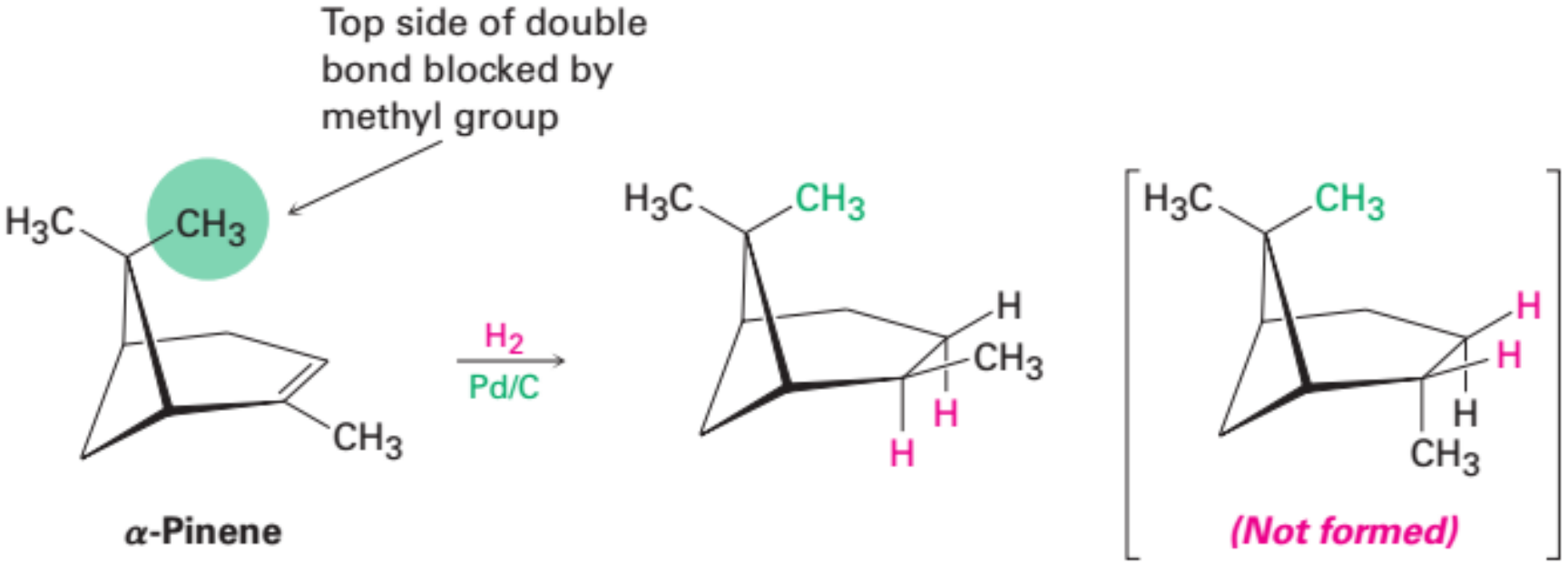
Reduction of alkene: hydrogenation



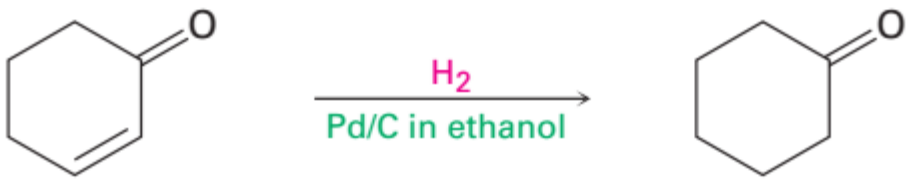
1,2-Dimethyl-cyclohexene

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

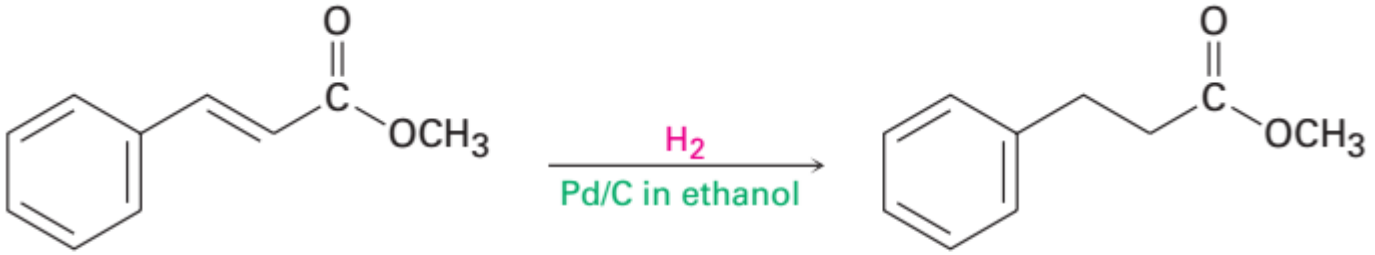
Reduction of alkene: hydrogenation



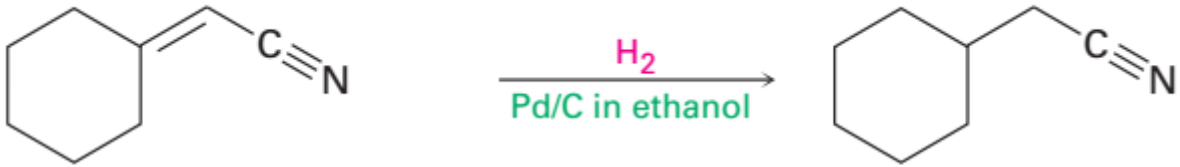
Stability?



Cyclohex-2-enone → **Cyclohexanone**
(ketone not reduced)



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



Cyclohexylideneacetonitrile → **Cyclohexylacetonitrile**
(nitrile not reduced)

Oxidation of alkenes: Epoxidation & hydroxylation

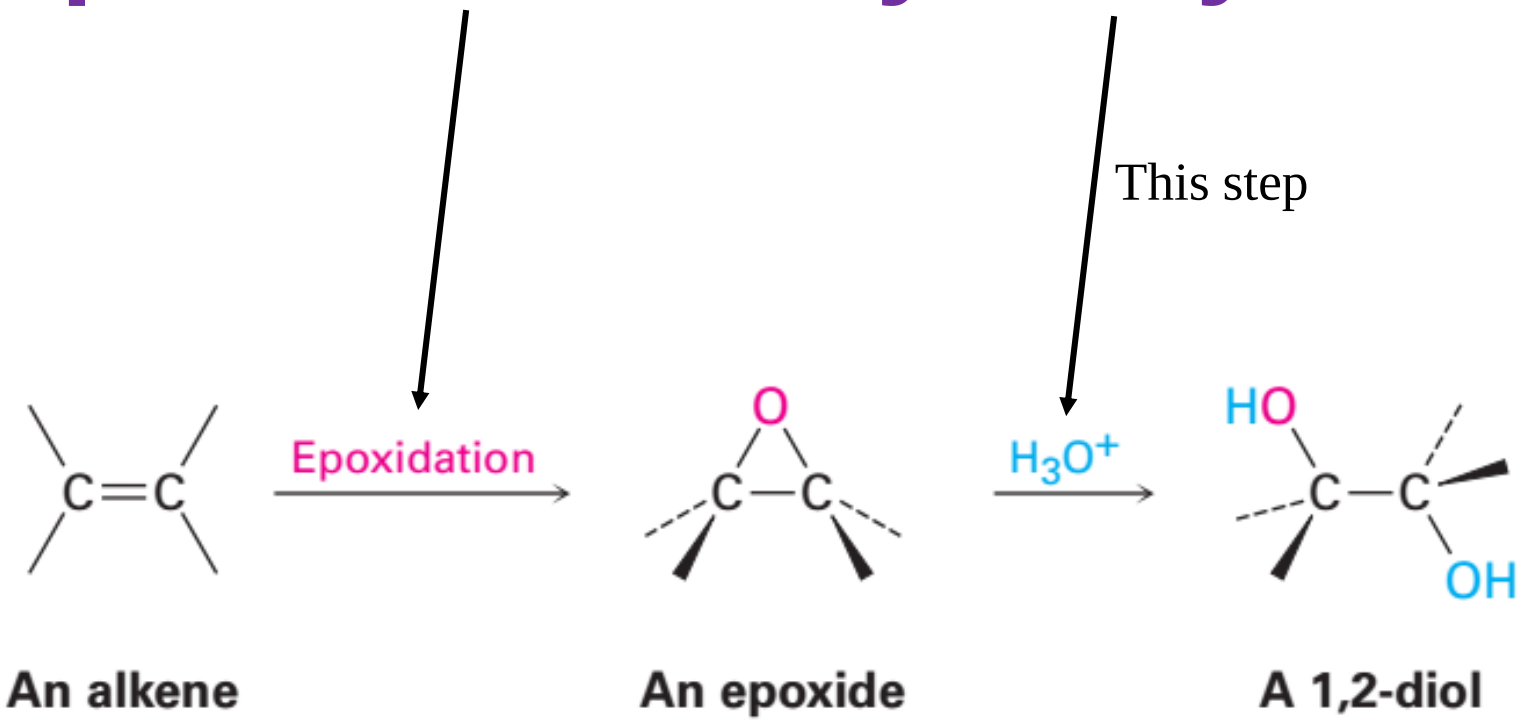
Oxidation Decreases electron density on carbon by:

– forming one of these: C–O C–N C–X

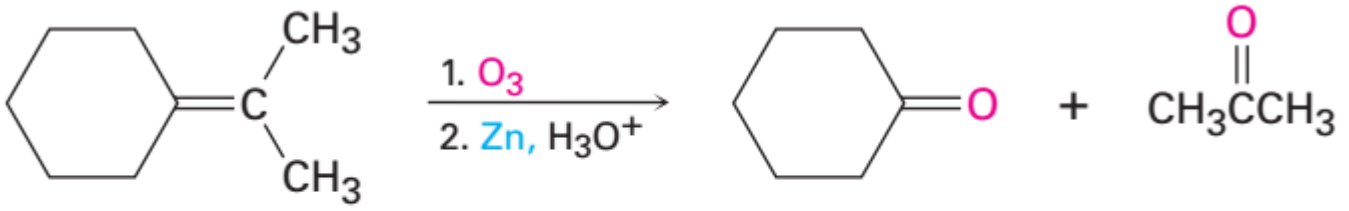
– or breaking this: C–H

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

Epoxidation & hydroxylation



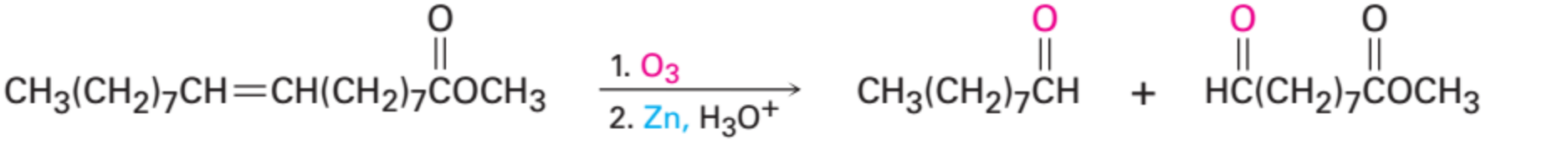
Oxidation of alkenes to carbonyl carbon



Isopropylidenecyclohexane (tetrasubstituted)

Cyclohexanone + **Acetone**

84%; two ketones

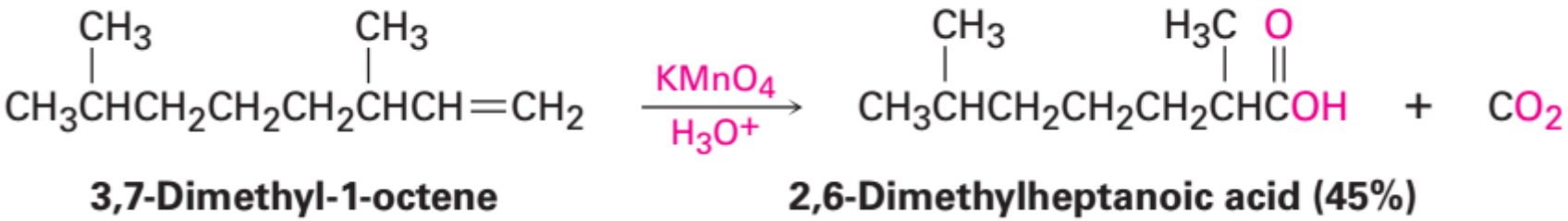


Methyl 9-octadecenoate (disubstituted)

Nonanal + **Methyl 9-oxononanoate**

78%; two aldehydes

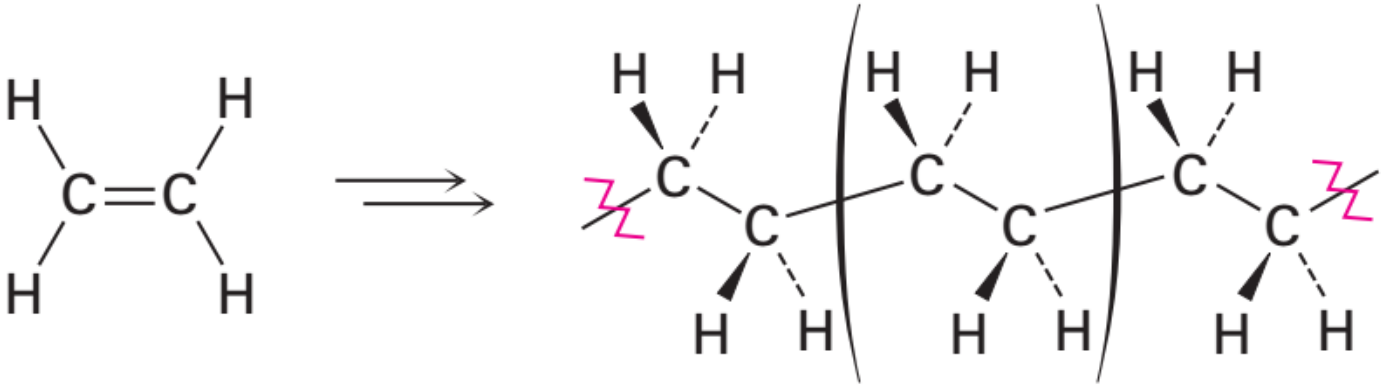
Oxidation of alkenes



3,7-Dimethyl-1-octene

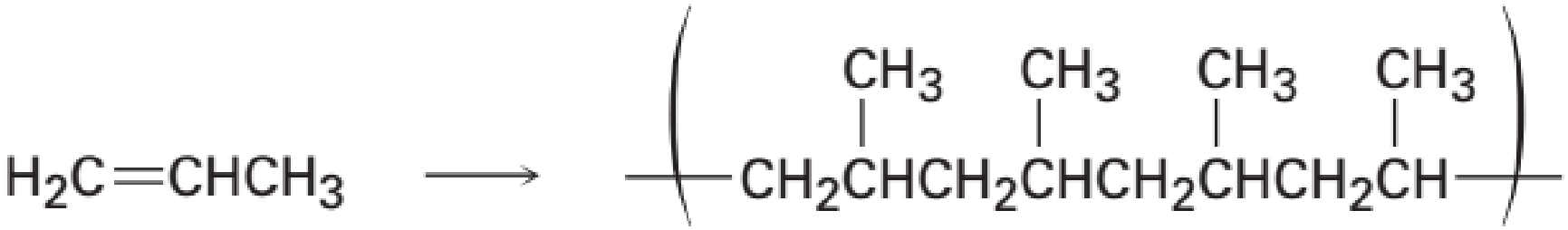
2,6-Dimethylheptanoic acid (45%)

Polymerization



Ethylene

Polyethylene



Propylene

Polypropylene

Some polymers

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)	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	$H_2C{=}C(CH_3)CO_2CH_3$	Plexiglas, Lucite	Paint, sheets, moldings
Vinyl acetate	$H_2C{=}CHOCOCH_3$	Poly(vinyl acetate)	Paint, adhesives, foams