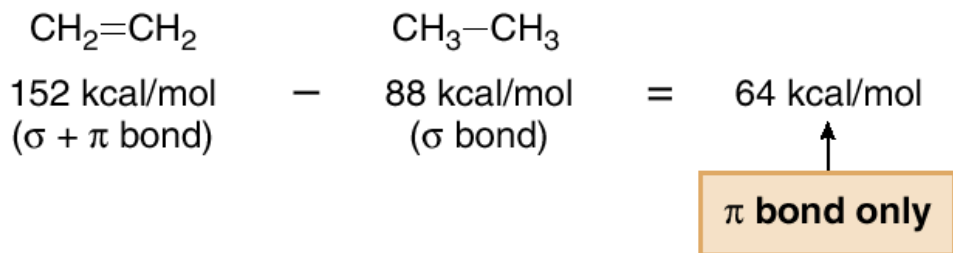# Alkenes (Olefins)

Chapters 7 & 8
Organic Chemistry, *8th Edition*
John McMurry
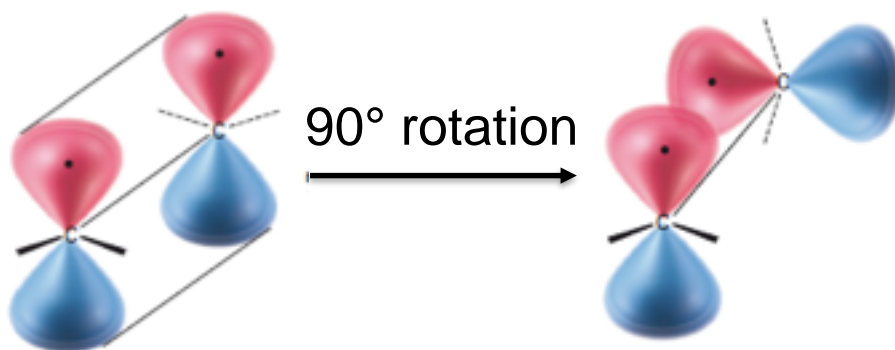
Structure and Bonding

$$CH_2=CH_2 \qquad CH_3-CH_3$$

|		
152 kcal/mol	−	88 kcal/mol	=	64 kcal/mol
($\sigma + \pi$ bond)		(σ bond)		

π **bond only**
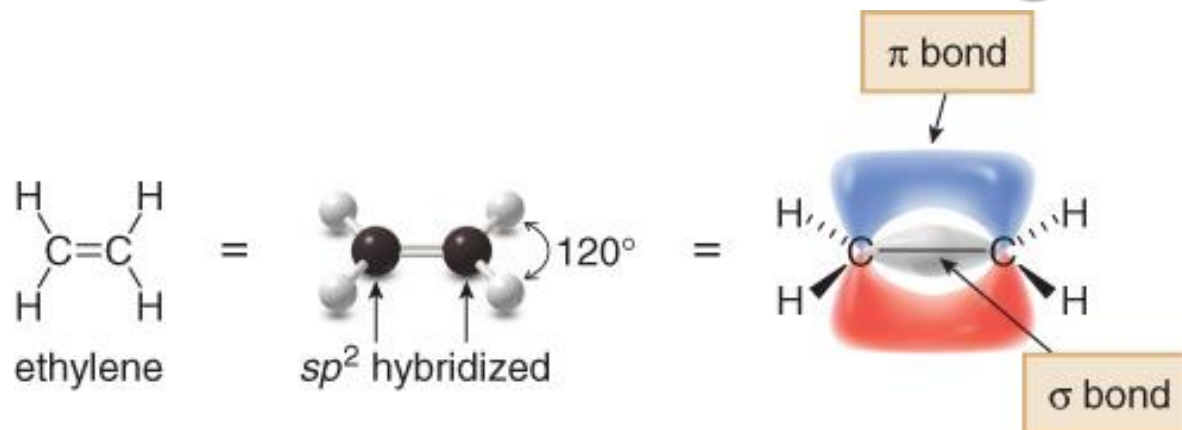
- The π bond is much weaker than the σ bond of a C−C double bond, making it much more easily broken. As a result, alkenes undergo many reactions that alkanes do not.

Structure and Bonding

Rotation around the C=C bond is restricted

90° rotation

The p orbitals are orthogonal
the π bond is broken

cis-2-Butene
p.f. −139°C, p.e. 4°C

trans-2-Butene
p.f. −106°C, p.e. 1°C
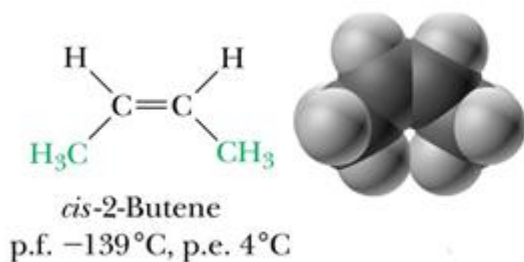
Cis and *trans* are diastereomers.
The *trans* is more stable than *cis* because of the steric interaction between the substitutes which is larger in *cis*.

Simple Alkenes

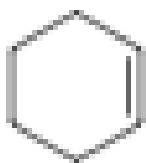$H_3C=CH_2$ ethene   (ethylene)

$H_2C=CH-CH_3$ propene   (propylene)

$\begin{array}{c} CH_3 \\ | \\ H_3C=CH-CH_3 \end{array}$ 2-methylpropene   (isobutene)

cyclohexene

Positional isomers

1-hexene   2-hexene   3-hexene

4

Unsaturation Degree

- In hydrocarbons the **degree of unsaturation** is half the difference between the number of hydrogens present compared to the maximum possible number.
- Alkenes are unsaturated hydrocarbons.
- An acyclic alkene has the general structural formula C_nH_{2n}.
- Cycloalkanes also have the general formula C_nH_{2n}.
- Each π bond or ring removes two hydrogen atoms from a molecule, and this introduces one degree of unsaturation.

- es. C_4H_6

Maximun number of hydrogens is 10 (2n+2)

Number of hydrogen present is 6; degree of unsaturation (10-6)/2 = 2
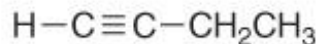
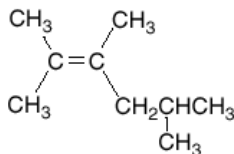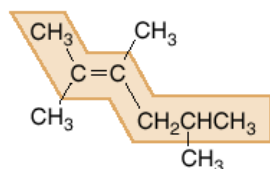| two rings | or | two π bonds | or | one ring and one π bond |

Possible structures
for C_4H_6:

$H-C\equiv C-CH_2CH_3$

Nomenclature

How To — Name an Alkene

Example   Give the IUPAC name of the following alkene:

$$CH_3 \quad CH_3$$
$$C=C$$
$$CH_3 \quad CH_2CHCH_3$$
$$CH_3$$

Step [1]   Find the longest chain that contains *both* carbon atoms of the double bond.

$$CH_3 \quad CH_3$$
$$C=C$$
$$CH_3 \quad CH_2CHCH_3$$
$$CH_3$$

6 C's in the longest chain

hex*ane* ---→ hex*ene*

• Change the *-ane* ending of the parent alkane to *-ene*.

Step [2]   Number the carbon chain to give the double bond the lower number, and apply all other rules of nomenclature.

a. **Number** the chain, and name using the *first* number assigned to the C=C.

$$1 \to CH_3 \quad CH_3 \quad 5 \quad 6$$
$$2 \to C=C$$
$$CH_3 \quad 3 \quad CH_2CHCH_3$$
$$4 \quad CH_3$$
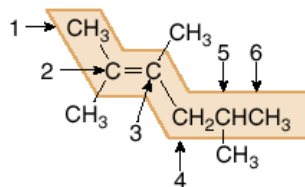
• Number the chain to put the C=C at C2, not C4.

2-hexene

b. **Name** and **number** the substituents.

$$CH_3 \quad CH_3 \quad 5$$
$$2 \to C=C$$
$$CH_3 \quad 3 \quad CH_2CHCH_3$$
$$CH_3$$
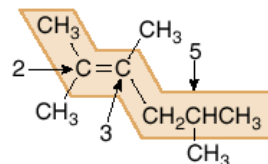
three methyl groups at C2, C3, and C5

Answer: 2,3,5-trimethyl-2-hexene

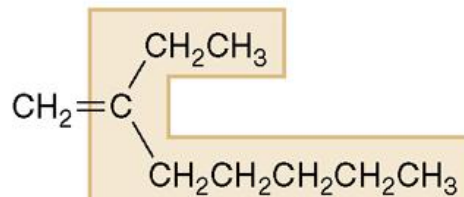# Nomenclature

CH₂=C with CH₂CH₃ branch and CH₂CH₂CH₂CH₂CH₃ chain
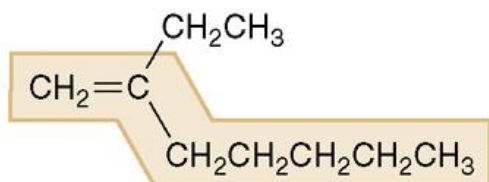
7 C's ---→ heptene

Both C's of the C=C are contained in this long chain.

Correct: **2-ethyl-1-heptene**

CH₂=C with CH₂CH₃ branch and CH₂CH₂CH₂CH₂CH₃ chain

8 C's

Both C's of the C=C are NOT contained in this long chain.
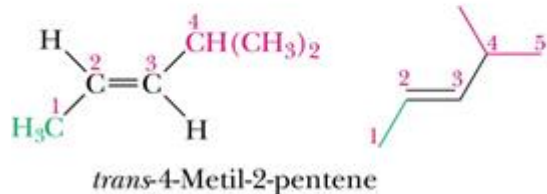
Incorrect

cis-4-Metil-2-pentene

trans-4-Metil-2-pentene
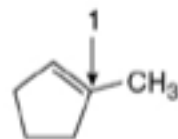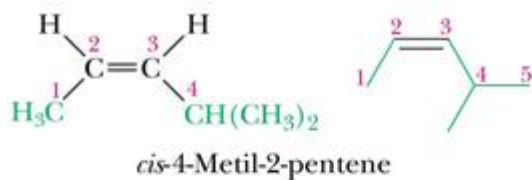
1-methylcyclopentene
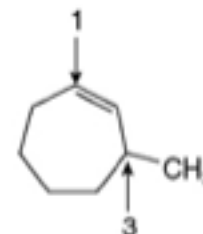
3-methylcycloheptene
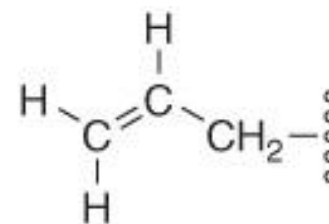
Number clockwise beginning at the C=C and place the CH₃ at C3.

7

Nomenclature
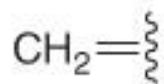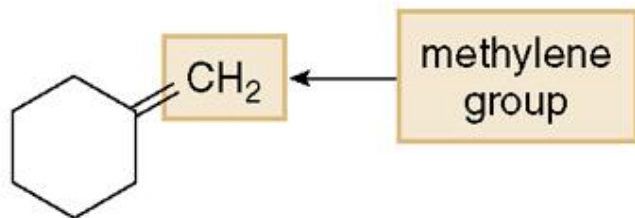

methylene group

vinyl group

allyl group

methylenecyclohexane

1-vinylcyclohexene
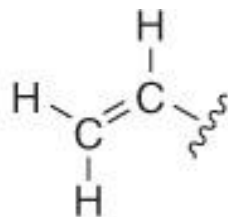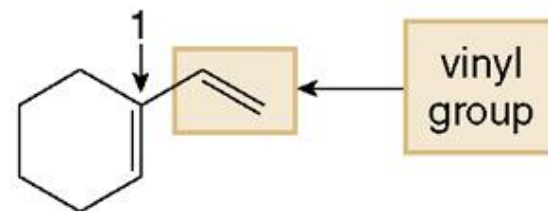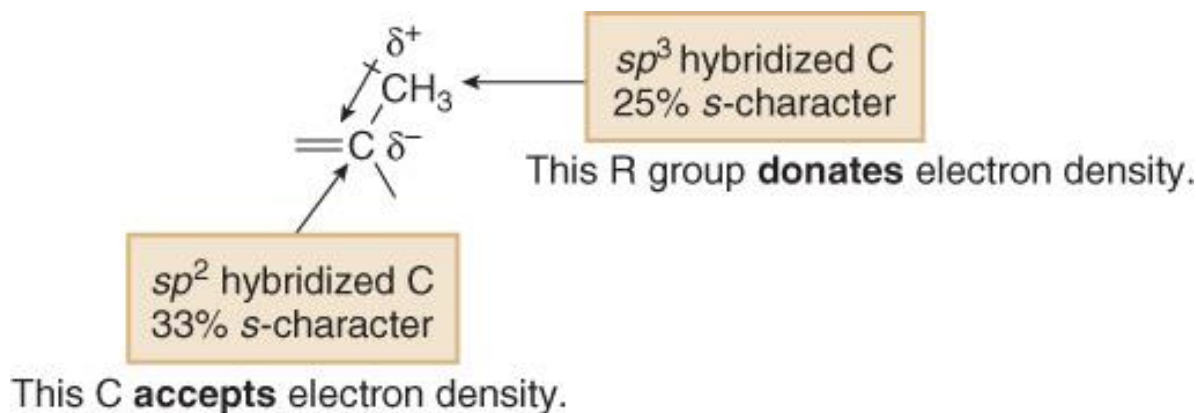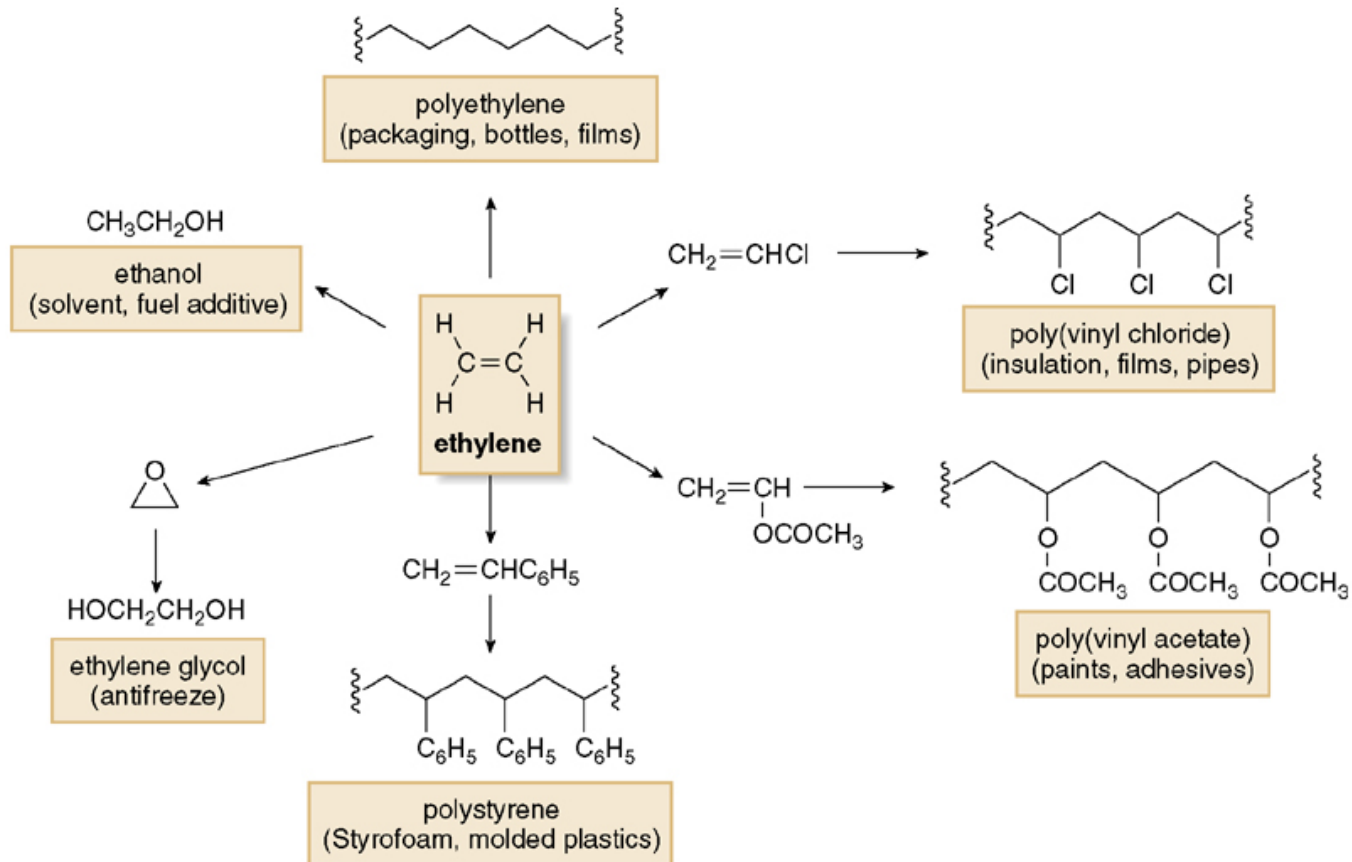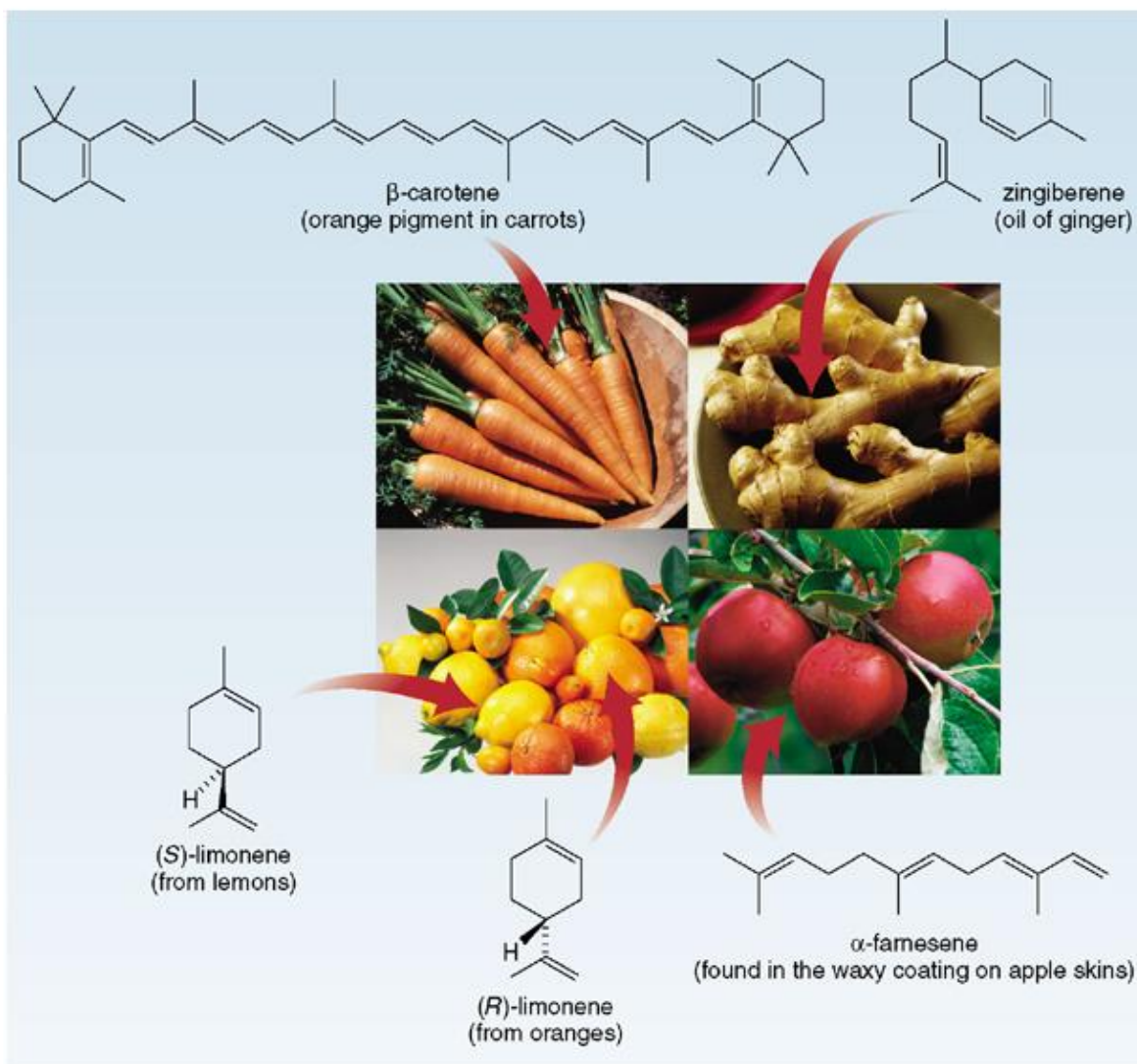
Physical Properties

- Their physical properties are similar to alkanes of comparable molecular weight.
- Alkenes have low melting points and boiling points.
- M.p. and b.p. increase as the number of carbons increases because of increased surface area.
- Alkenes are soluble in organic solvents and insoluble in water.
- The C—C single bond between an alkyl group and one of the double bond carbons of an alkene is slightly polar.
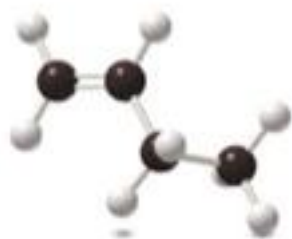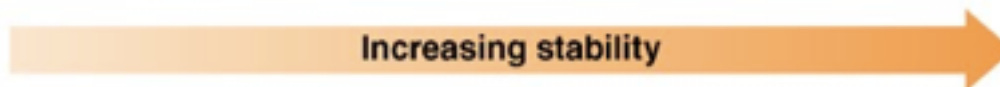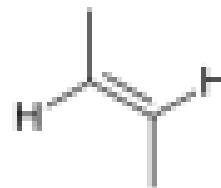

sp^3 hybridized C
25% s-character

This R group **donates** electron density.

sp^2 hybridized C
33% s-character

This C **accepts** electron density.

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Interesting Alkenes

Interesting Alkenes

β-carotene
(orange pigment in carrots)

zingiberene
(oil of ginger)

(S)-limonene
(from lemons)

(R)-limonene
(from oranges)

α-farnesene
(found in the waxy coating on apple skins)

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Geometrical Isomerism

Increasing stability
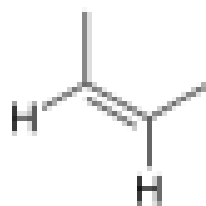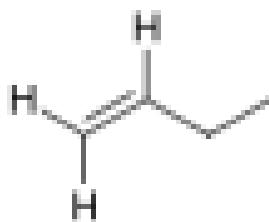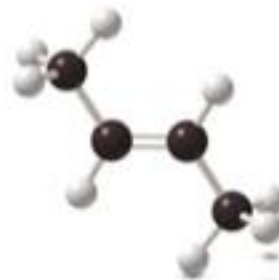
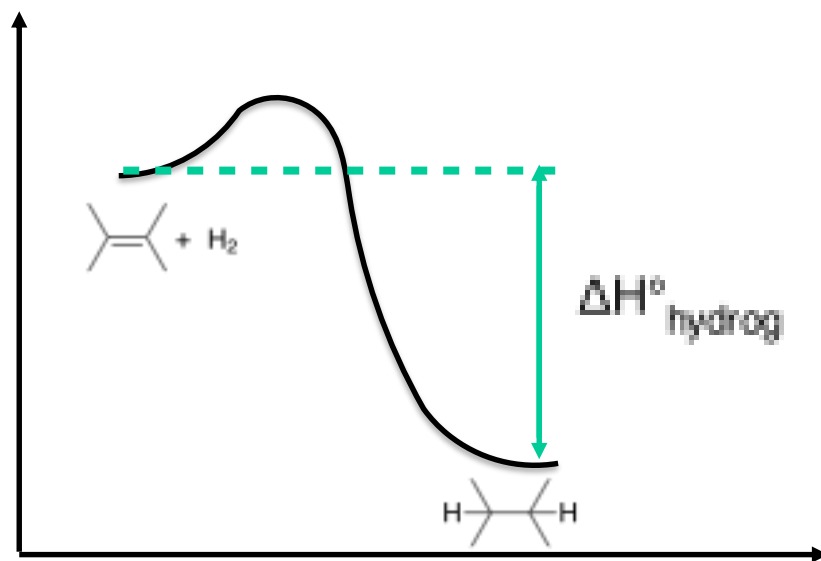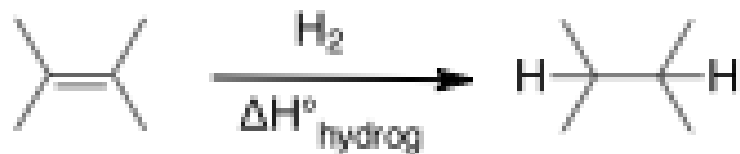1-butene   *cis*-2-butene   *trans*-2-butene

Stability of Alkenes

- Hydrogenation of alkenes is exothermic
- The heat of hydrogenation can be used as a measure of the relative stability of different alkenes.

Stability of Alkenes

Substitution	Alkene	ΔH°hydrog (Kcal/mol)
Unsubstituted	$H_2C=CH_2$	-32.8
Monosubstituted	$CH_3CH=CH_2$	-30.1
Disubstituted	$(CH_3)_2C=CH_2$	-28.4
	$CH_3CH=CHCH_3$ (cis)	-28.6
	$CH_3CH=CHCH_3$ (trans)	-27.6
Trisubstituted	$(CH_3)_2C=CHCH_3$	-26.9
Tetrasubstituted	$(CH_3)_2C=C(CH_3)_2$	-26.6

Geometrical Isomerism

- *trans*-Cyclooctene is the smallest isolable trans cycloalkene, but it is considerably less stable than *cis*-cyclooctene, making it one of the few alkenes having a higher energy trans isomer.
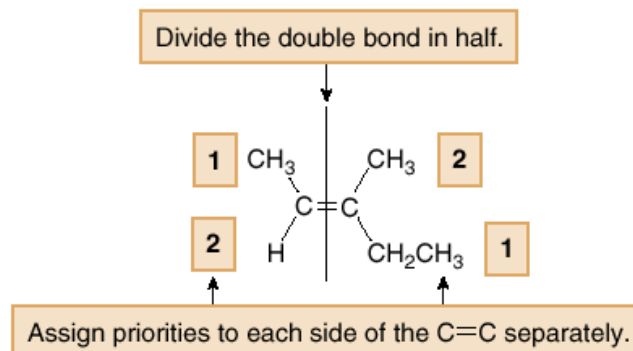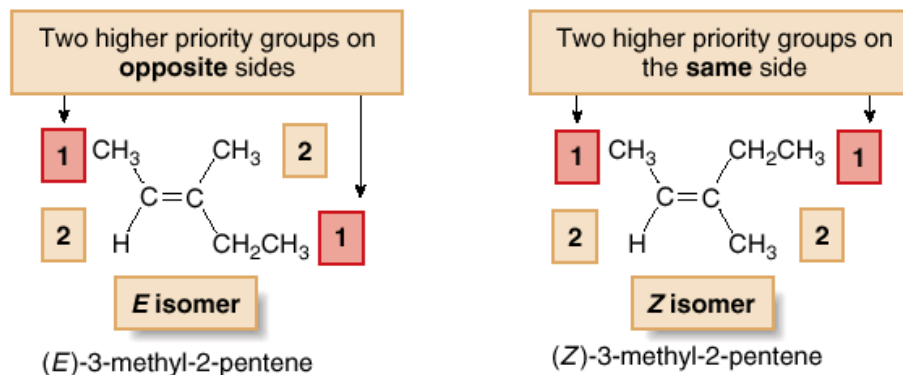
trans

cis

trans-cyclooctene

cis-cyclooctene
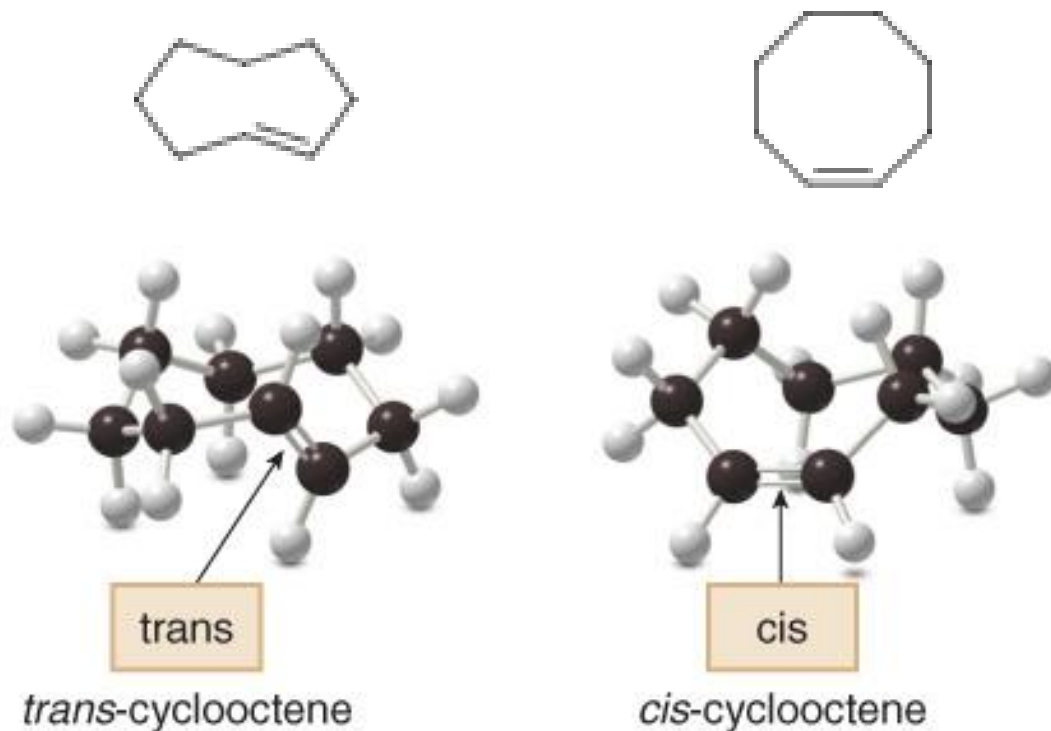
E/Z Nomenclature

Step [1]   Assign priorities to the two substituents on each end of the C=C by using the priority rules for *R,S* nomenclature (Section 5.6).

- Divide the double bond in half, and assign the numbers **1** and **2** to indicate the relative priority of the two groups on each end—the higher priority group is labeled **1,** and the lower priority group is labeled **2**.

Divide the double bond in half.

| 1 | CH₃ | CH₃ | 2 |

$$1 \quad CH_3 \qquad CH_3 \quad 2$$
$$C=C$$
$$2 \quad H \qquad CH_2CH_3 \quad 1$$

Assign priorities to each side of the C=C separately.

Step [2]   Assign *E* or *Z* based on the location of the two higher priority groups (1).

Two higher priority groups on **opposite** sides

$$1 \quad CH_3 \qquad CH_3 \quad 2$$
$$C=C$$
$$2 \quad H \qquad CH_2CH_3 \quad 1$$

E isomer

(*E*)-3-methyl-2-pentene

Two higher priority groups on the **same** side

$$1 \quad CH_3 \qquad CH_2CH_3 \quad 1$$
$$C=C$$
$$2 \quad H \qquad CH_3 \quad 2$$

Z isomer

(*Z*)-3-methyl-2-pentene

- The **E** isomer has the two higher priority groups on the **opposite sides.**
- The **Z** isomer has the two higher priority groups on the **same side.**

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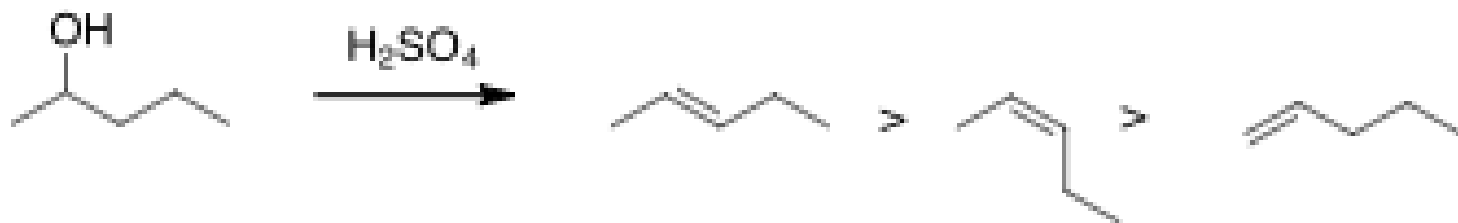# Preparation of Alkenes.
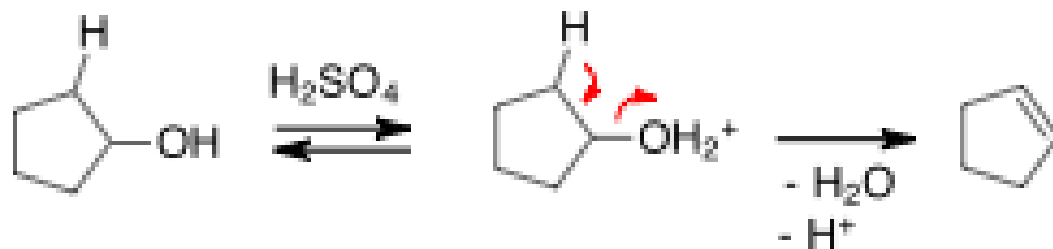# 1 Dehydroalogenation

major
product
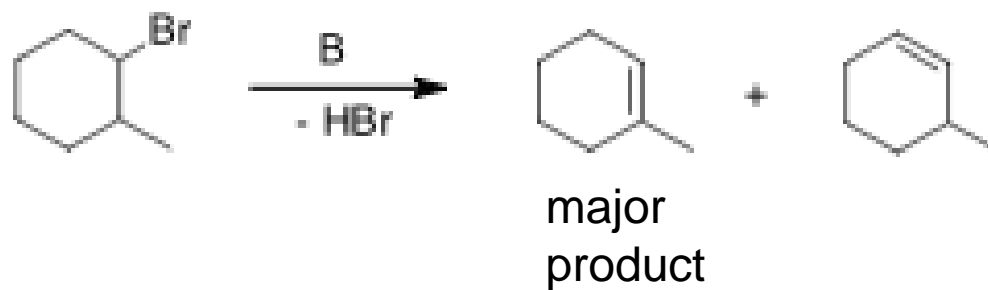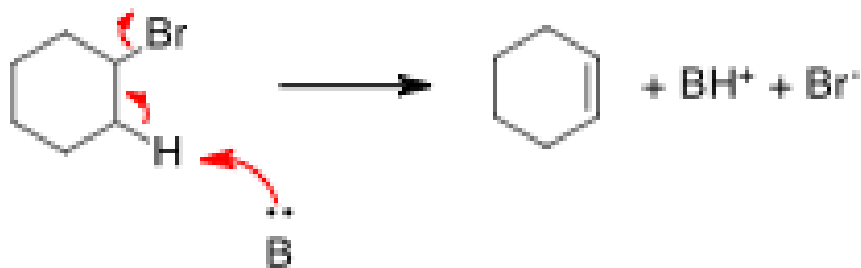
Saytzev's rule.
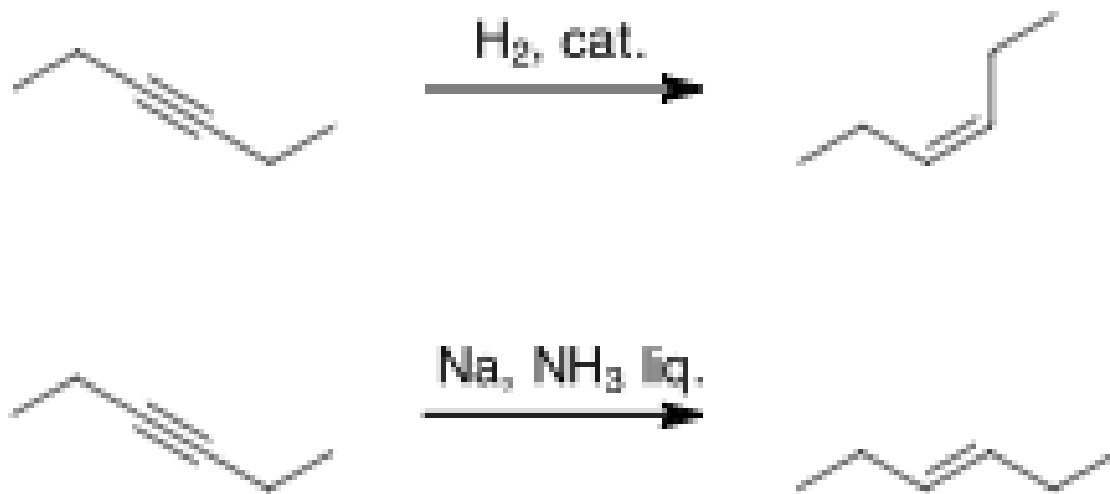The more substituted alkene (more stable) is favoured

18

Preparation of Alkenes.
2 Dehydration

Preparation of Alkenes. 3 Hydrogenation/Reduction of Alkynes
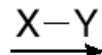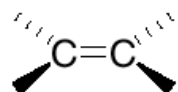
Introduction to Addition Reactions

Addition reaction

$$\text{C=C} \quad + \quad \text{X-Y} \quad \longrightarrow \quad -\text{C-C}-$$
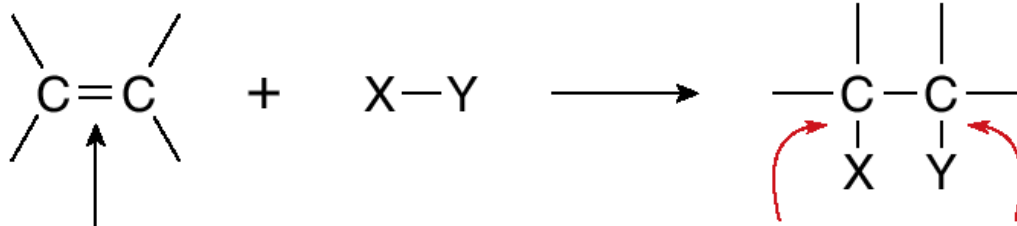
This π bond is broken.

Two σ bonds are formed.

- Alkenes are electron rich, with the electron density of the π bond concentrated above and below the plane of the molecule.
- **Alkenes react with electrophiles.** Simple alkenes do not react with nucleophiles or bases.
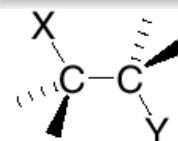
Introduction to Addition Reactions

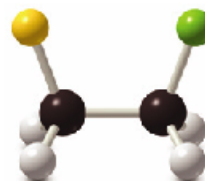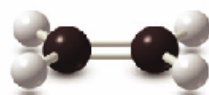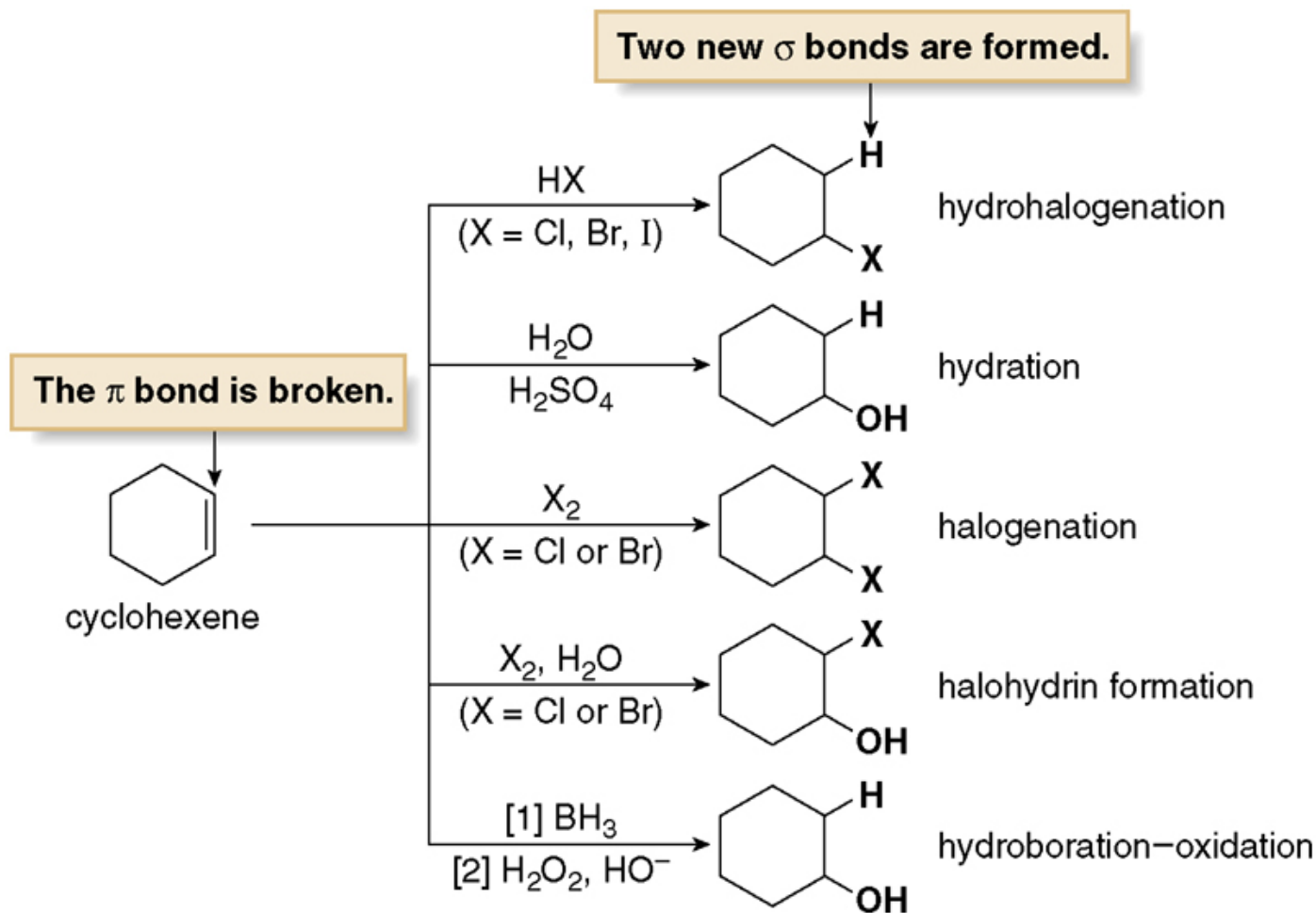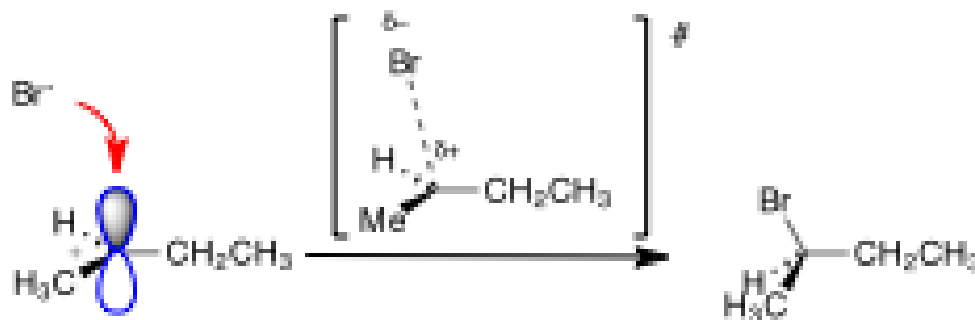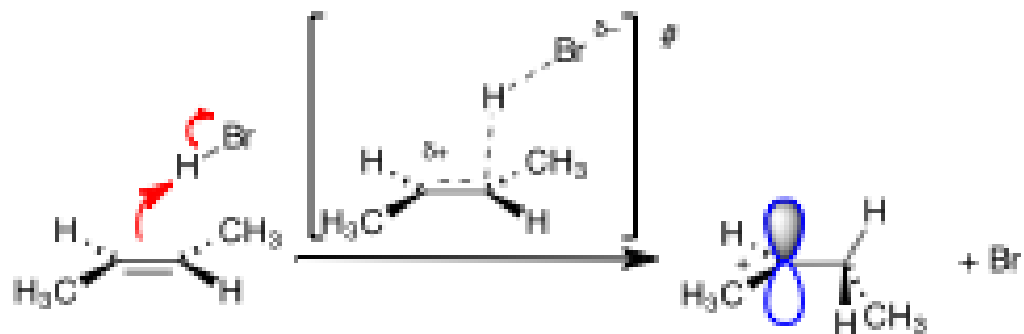- *Syn addition* takes place when both X and Y are added from the *same* side.
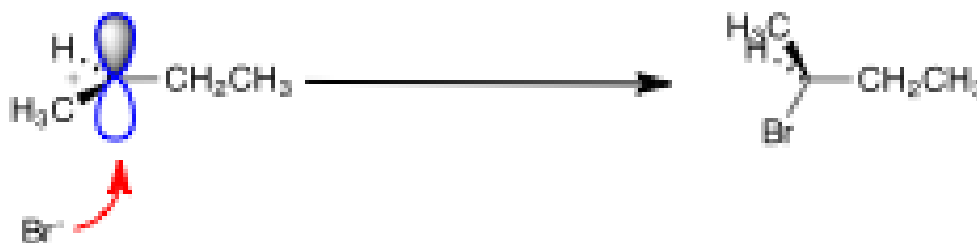- *Anti addition* takes place when X and Y are added from *opposite* sides.
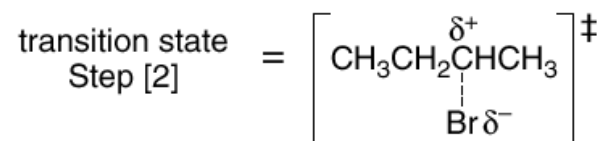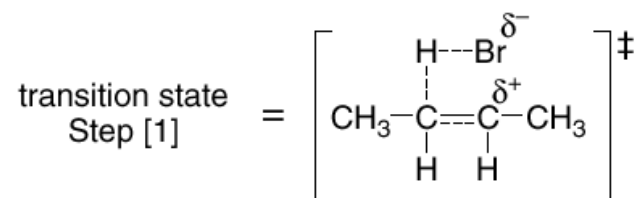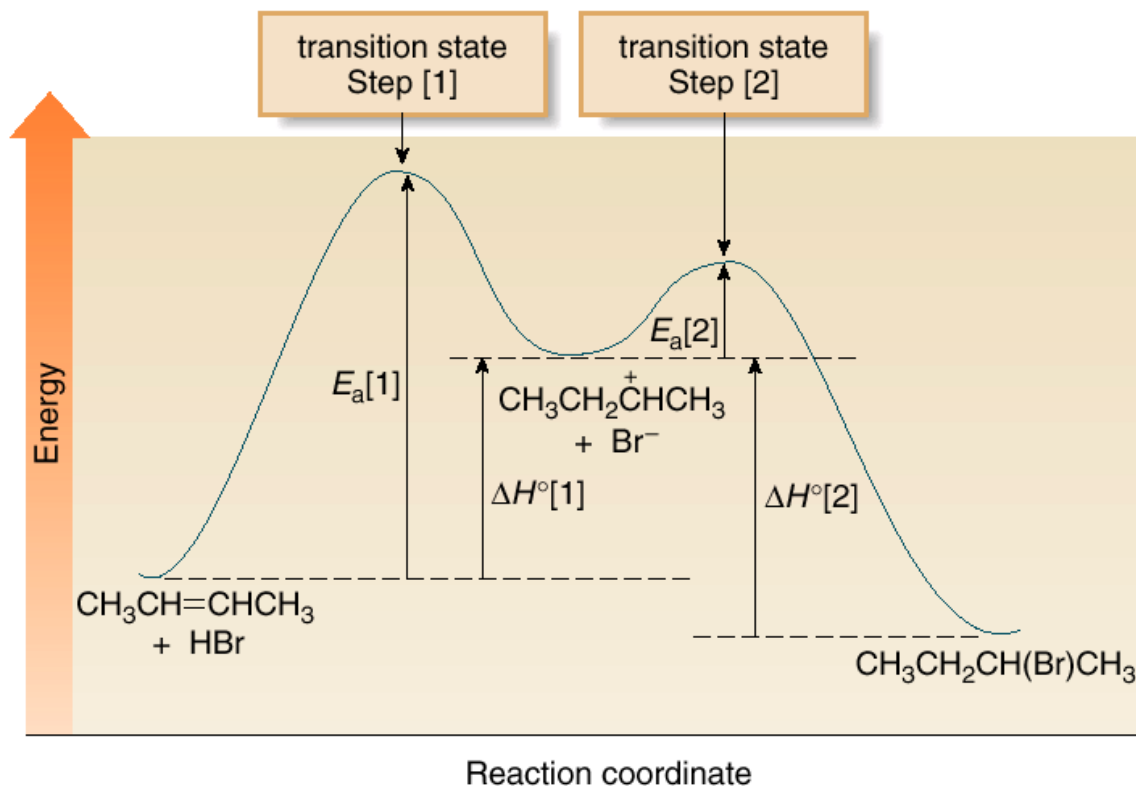
Introduction to Addition Reactions

Hydrohalogenation. Mechanism
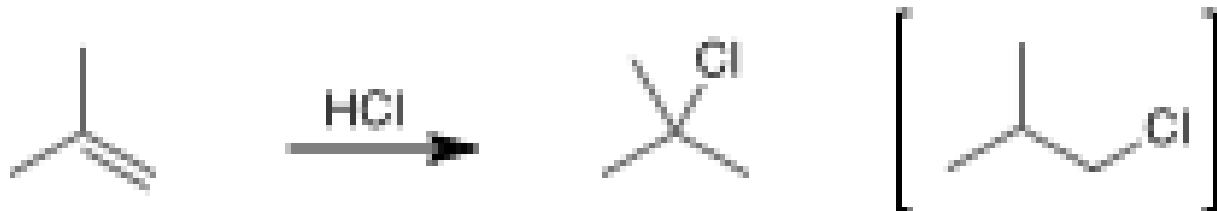

enantiomers
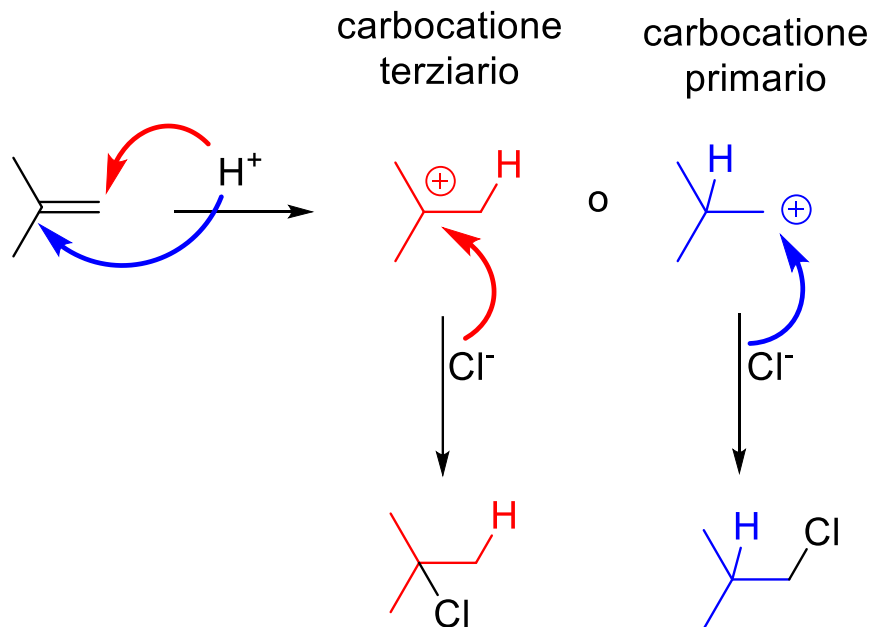
25

Hydrohalogenation

- The mechanism has two steps, so there are two energy barriers.
- Step [1] is rate-determining.
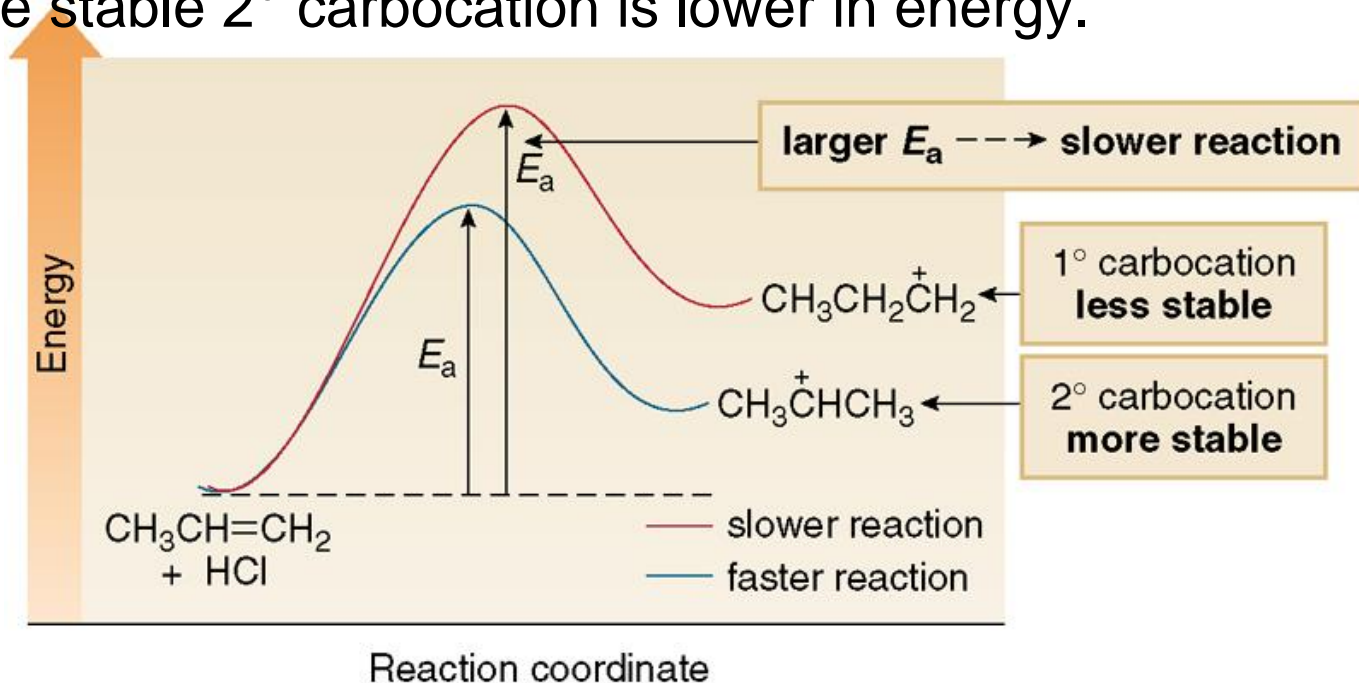
Hydrohalogenation — Markovnikov's Rule

not formed

- The electrophile (H$^+$) adds to the less substituted carbon; the nucleophile (Cl$^-$) to the more substituted one.

carbocatione terziario

carbocatione primario
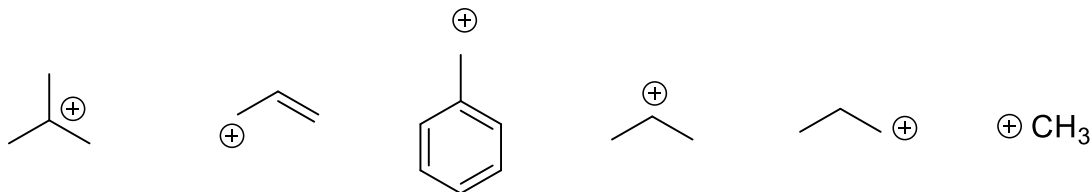
o

Cl$^-$

Cl$^-$

Hydrohalogenation—Markovnikov's Rule

According to the Hammond postulate, the transition state to form the more stable 2° carbocation is lower in energy.

The stability of carbocationi follows a trend similar to that of radicals for the same effects (induction, hyperconjugation, resonance).

Terziario > allilico ~ benzilico ~ secondario > primario > metilico

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Hydrohalogenation—Stereochemistry

- Addition of HX to 1,2-dimethylcyclohexene forms two new stereogenic centers.

1,2-dimethyl-
cyclohexene

HCl →
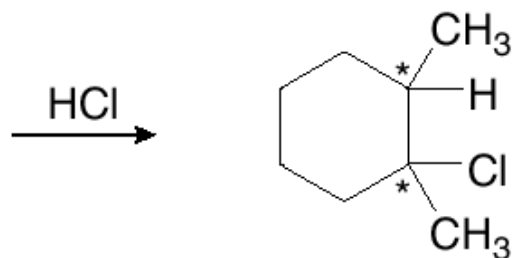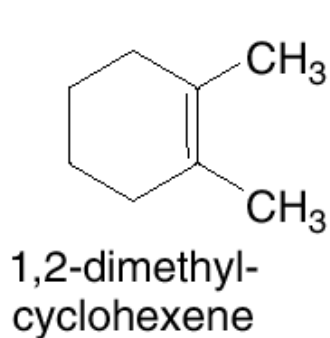
Two new stereogenic centers
are formed.

[* denotes a stereogenic center]

Hydrohalogenation—Stereochemistry

Hydrohalogenation—Summary

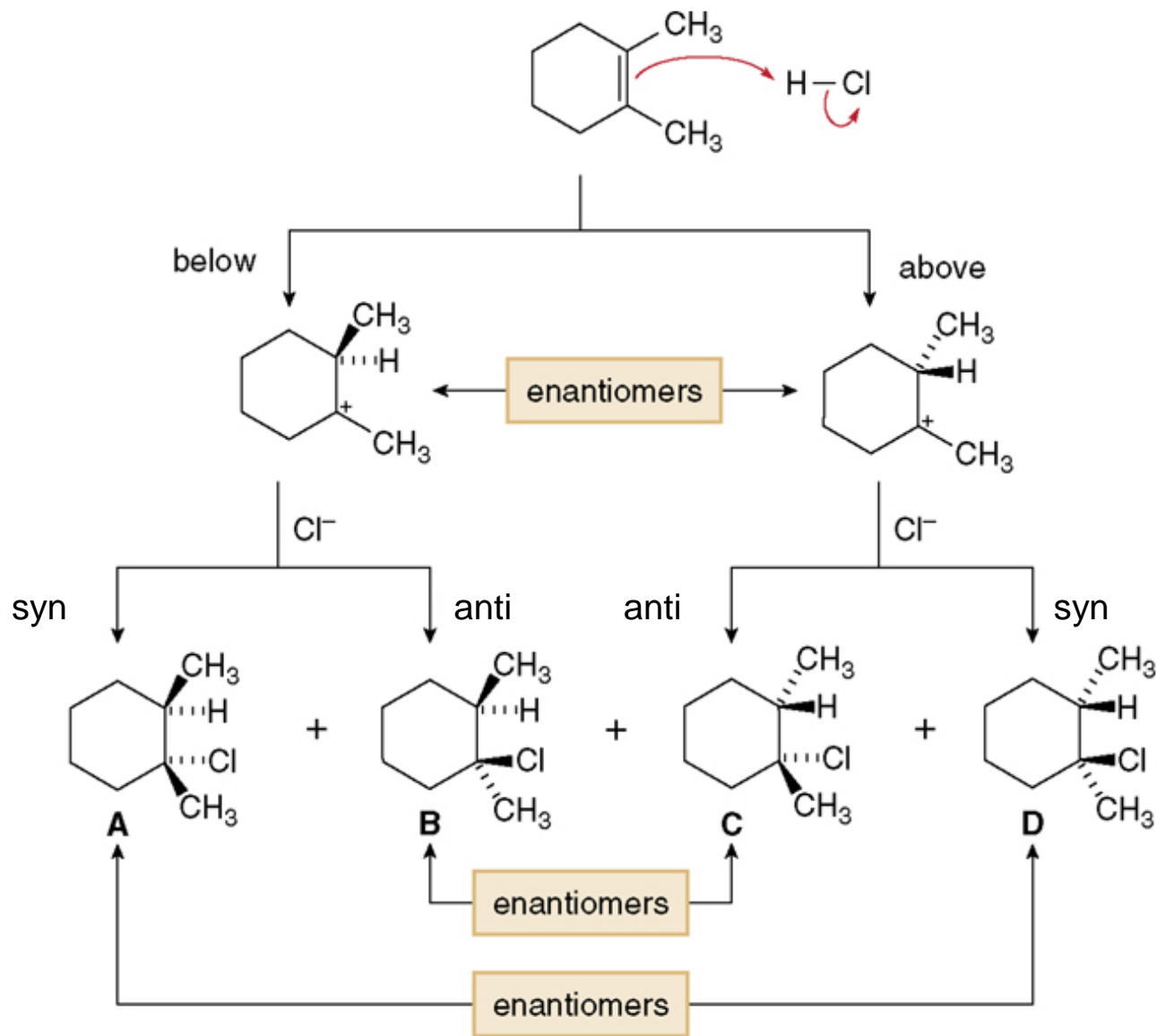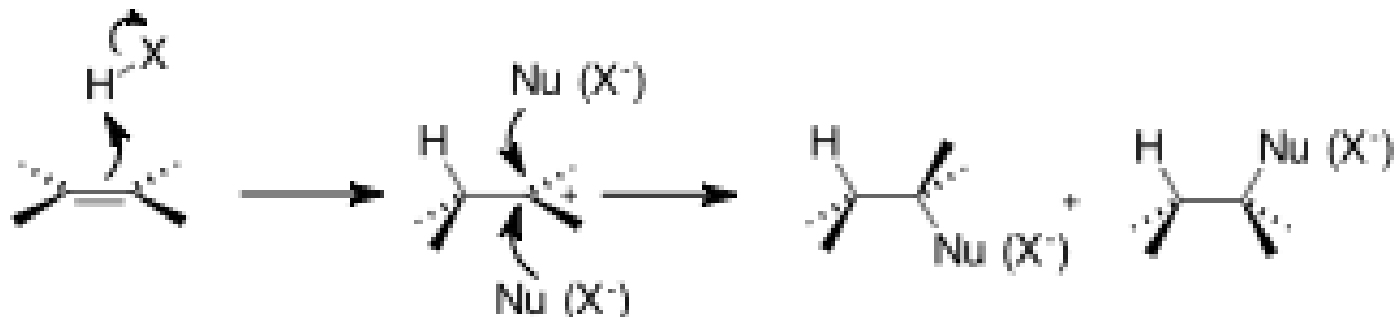| Mechanism	• The mechanism involves two steps. • The rate-determining step forms a carbocation. • Rearrangements can occur.
Regioselectivity	• Markovnikov's rule is followed. In unsymmetrical alkenes, H bonds to the less substituted C to form the more stable carbocation.
Stereochemistry	• Syn and anti addition occur.

Hydration—Electrophilic Addition of Water

This π bond is broken.

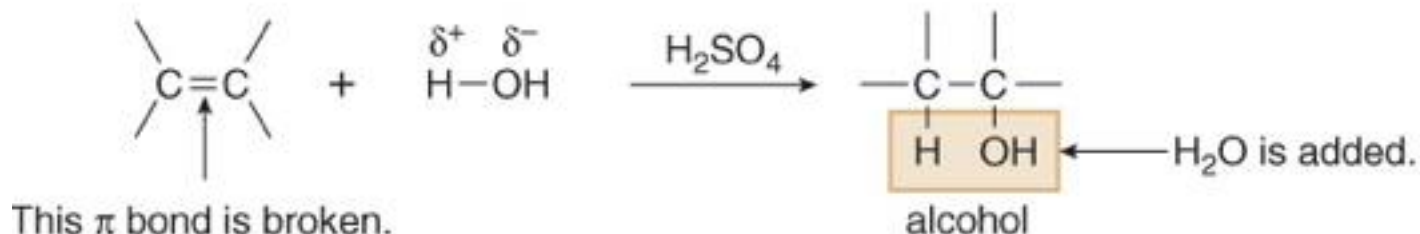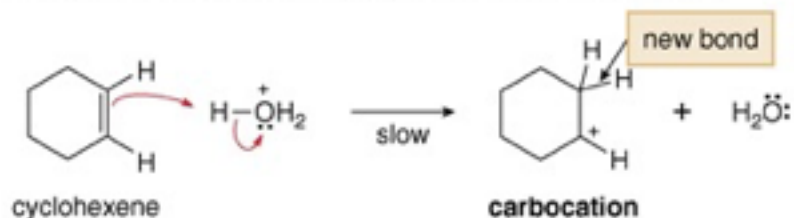$C=C$ + $\overset{\delta^+ \quad \delta^-}{H-OH}$ $\xrightarrow{H_2SO_4}$ $-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OH}{C}}-$ ← H_2O is added.

alcohol

Step [1] Addition of the electrophile (H^+) to the π bond

cyclohexene $H-\overset{+}{\underset{\cdot\cdot}{O}}H_2$ $\xrightarrow{slow}$ new bond   + $H_2\ddot{O}:$ **carbocation**

- The π bond attacks H_3O^+, thus forming a new C−H bond while breaking the H−O bond. Because the remaining carbon atom of the original double bond is left with only six electrons, a **carbocation** intermediate is formed. This step is **rate-determining** because two bonds are broken but only one bond is formed.

Step [2] Nucleophilic attack of H_2O

+ $H_2\ddot{O}:$ ⟶
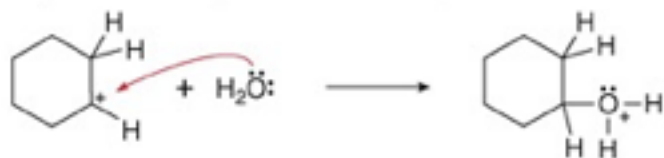
- **Nucleophilic attack of H_2O** on the carbocation forms the new C−O bond.

Step [3] Loss of a proton

+ $H_2\ddot{O}:$ ⟶ cyclohexanol + $H_3\ddot{O}^+$
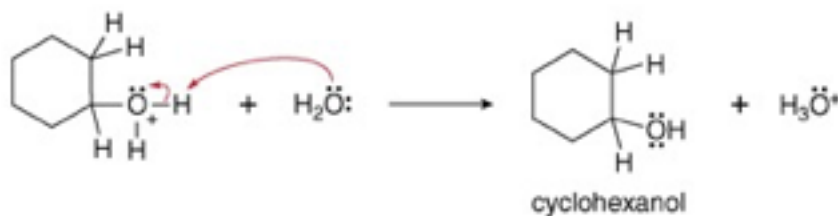
- Removal of a proton with a base (H_2O) forms a neutral alcohol. Because the acid used in Step [1] is regenerated in Step [3], hydration is **acid-catalyzed**.
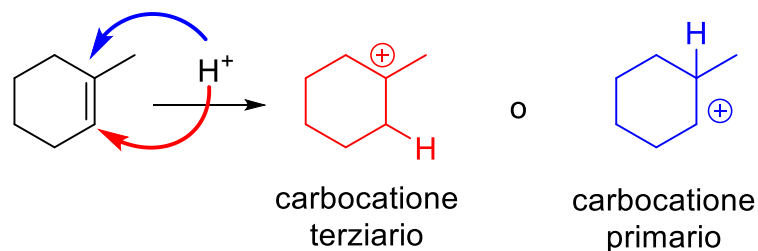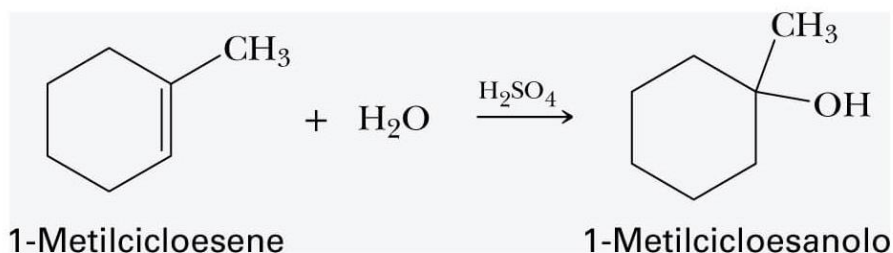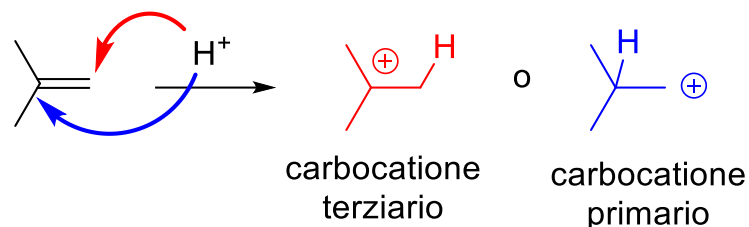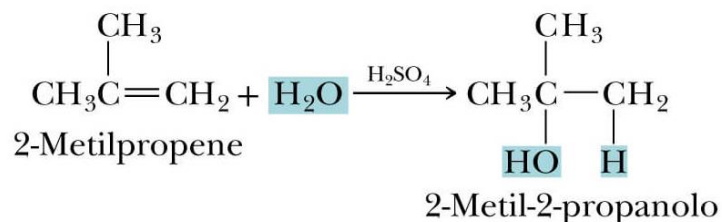
33

Electrophilic Addition of Alcohols

- Alcohols add to alkenes, forming ethers by the same mechanism. For example, addition of CH_3OH to 2-methylpropene, forms *tert*-butyl methyl ether (MTBE), a high octane fuel additive.

tert-butyl methyl ether
MTBE
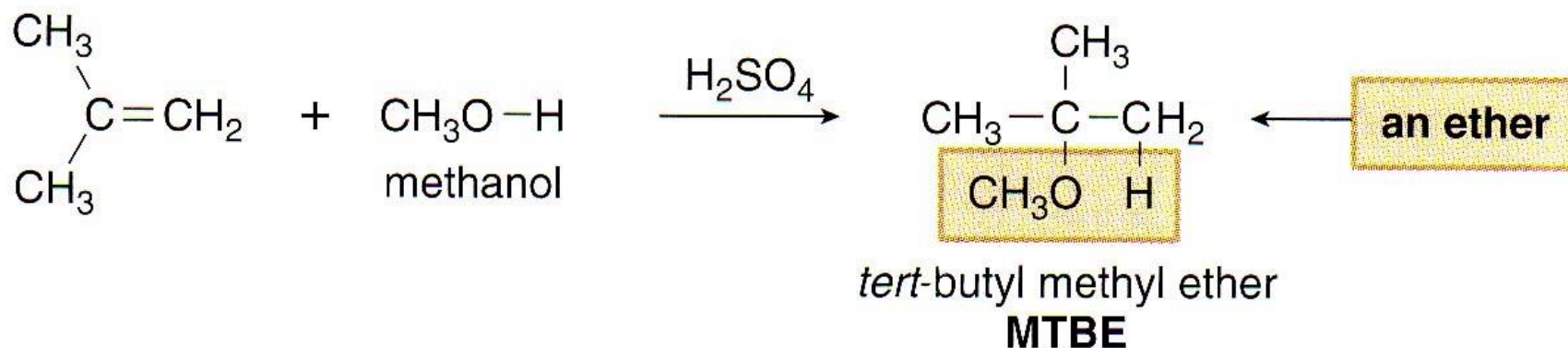
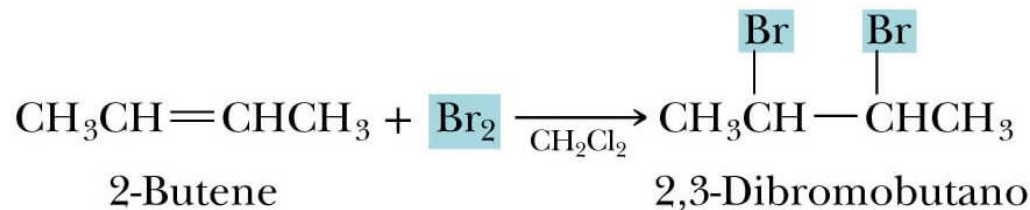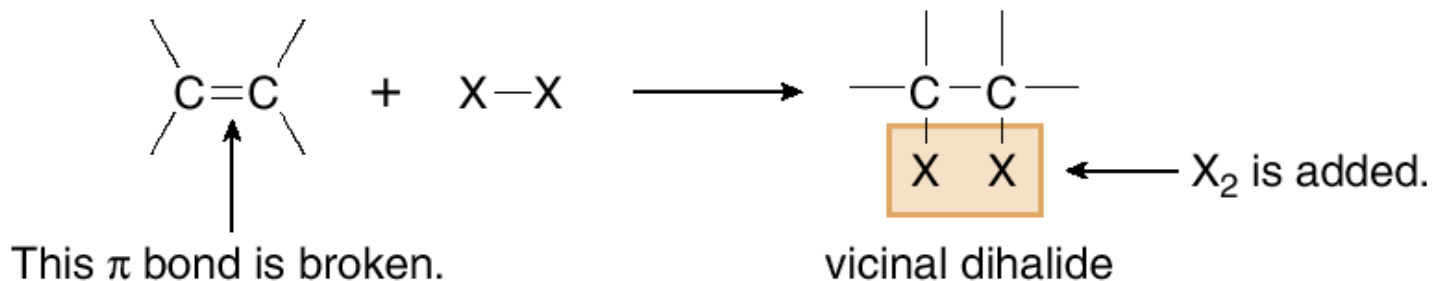# Hydration—Electrophilic Addition of Water

Hydration is a **Markovnikov type addition** (follows the Markovnikov rule)

2-Metilpropene + H_2O $\xrightarrow{H_2SO_4}$ 2-Metil-2-propanolo

carbocatione terziario

carbocatione primario

1-Metilcicloesene + H_2O $\xrightarrow{H_2SO_4}$ 1-Metilcicloesanolo

carbocatione terziario

carbocatione primario

Halogenation—Addition of Halogen

Halogenation

This π bond is broken.

X_2 is added.

vicinal dihalide

$$CH_3CH = CHCH_3 + Br_2 \xrightarrow{CH_2Cl_2} CH_3CH - CHCH_3$$

2-Butene

2,3-Dibromobutano

Anti addition

Br_2

trans

cis
not formed
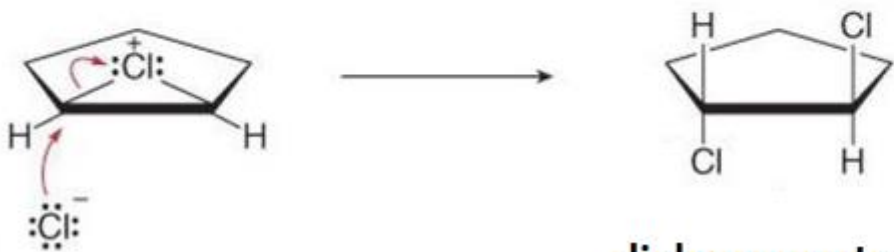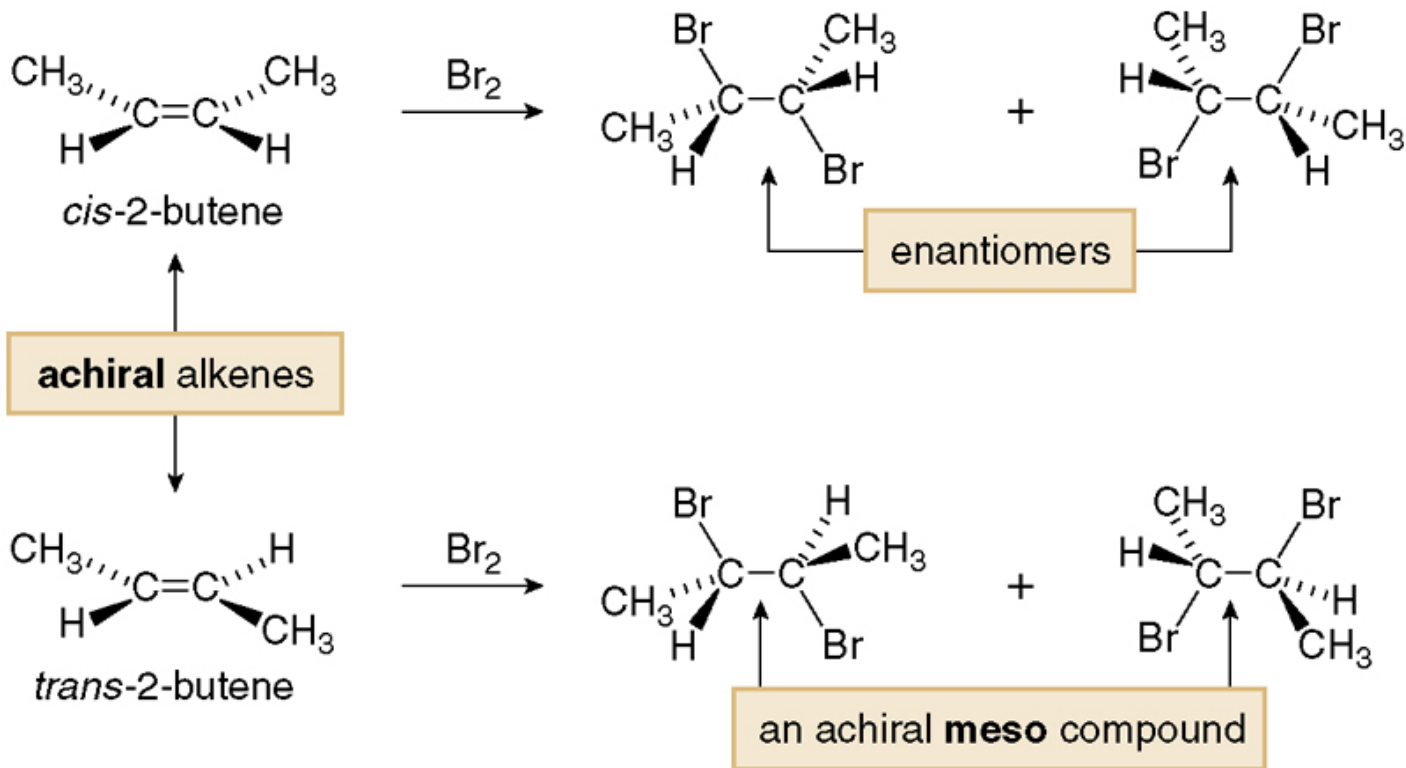
36
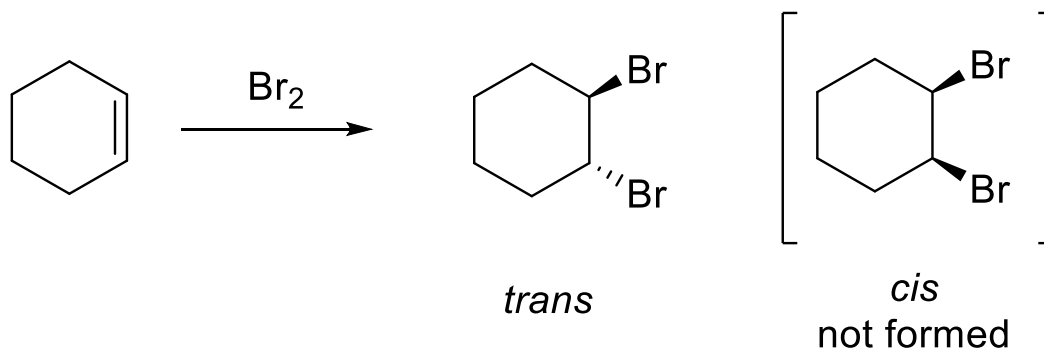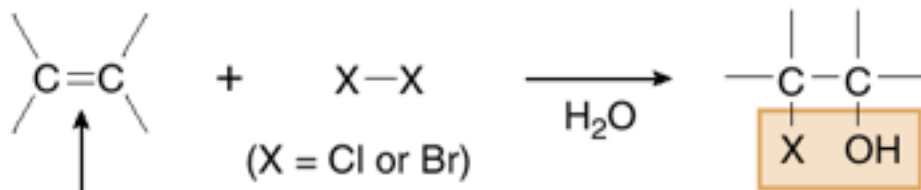
Halogenation—Mechanism
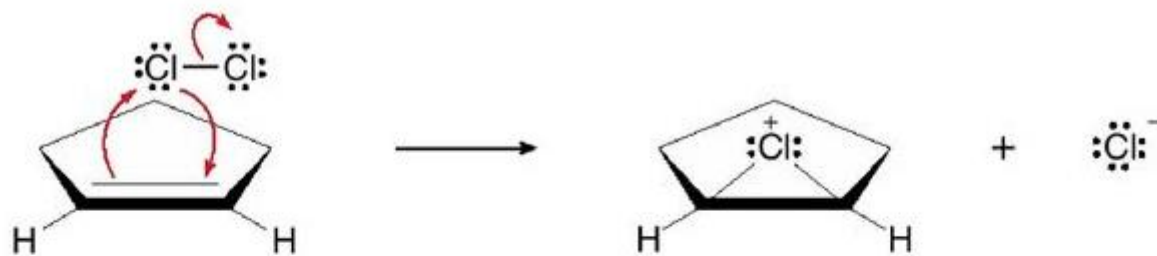
ione epicloronio

dialogenuro trans

Halogenation—Stereochemistry

Halohydrin Formation

General reaction

$$\begin{array}{c} \diagdown \\ \diagup \end{array}C = C\begin{array}{c} \diagup \\ \diagdown \end{array} \quad + \quad X-X \quad \xrightarrow{\;H_2O\;} \quad -\overset{|}{\underset{X}{C}}-\overset{|}{\underset{OH}{C}}-$$

(X = Cl or Br)

This π bond is broken.

halohydrin

X and OH added

$$\xrightarrow[H_2O]{Br_2}$$

\+

anti addition of Br and OH

Br   OH   Br   OH
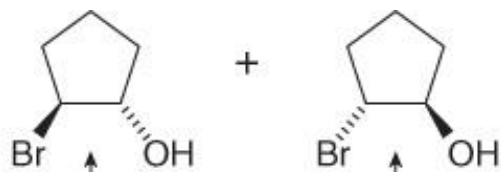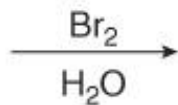
trans enantiomers

39

Halohydrin Formation

nucleophilic attack at the
more substituted C
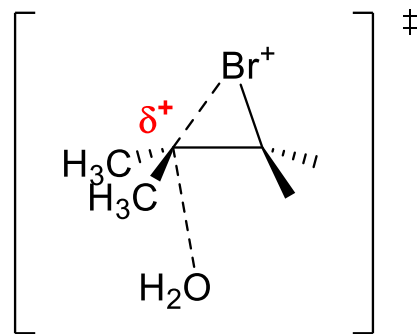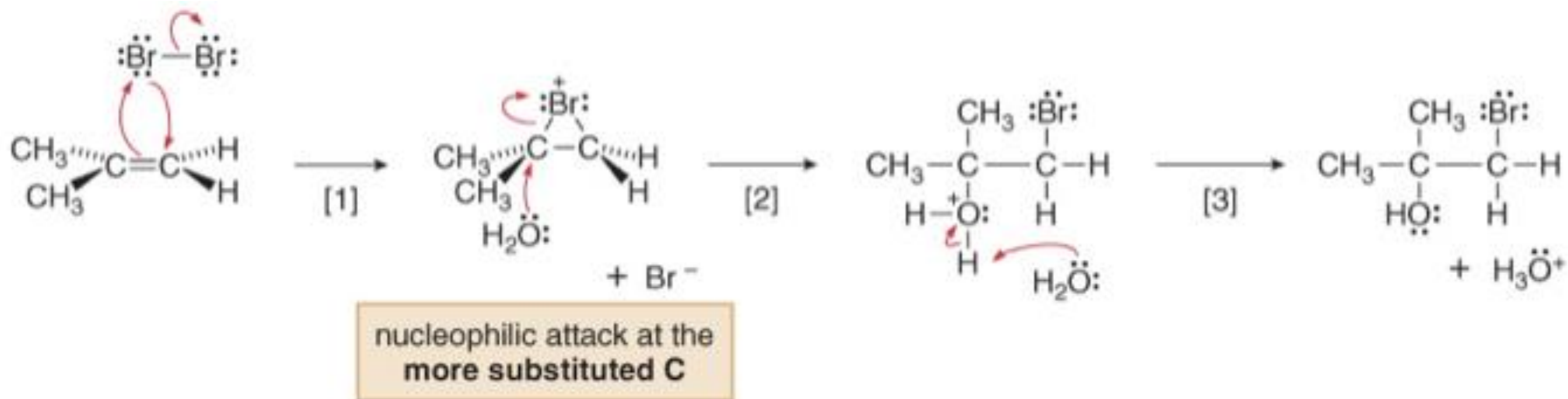
Halohydrin Formation is a **Markovnikov type addition** with X$^+$ as electrophile

Halohydrin Formation

- Bromohydrins are also formed with *N*-bromosuccinimide (NBS) in aqueous DMSO [$(CH_3)_2S=O$].
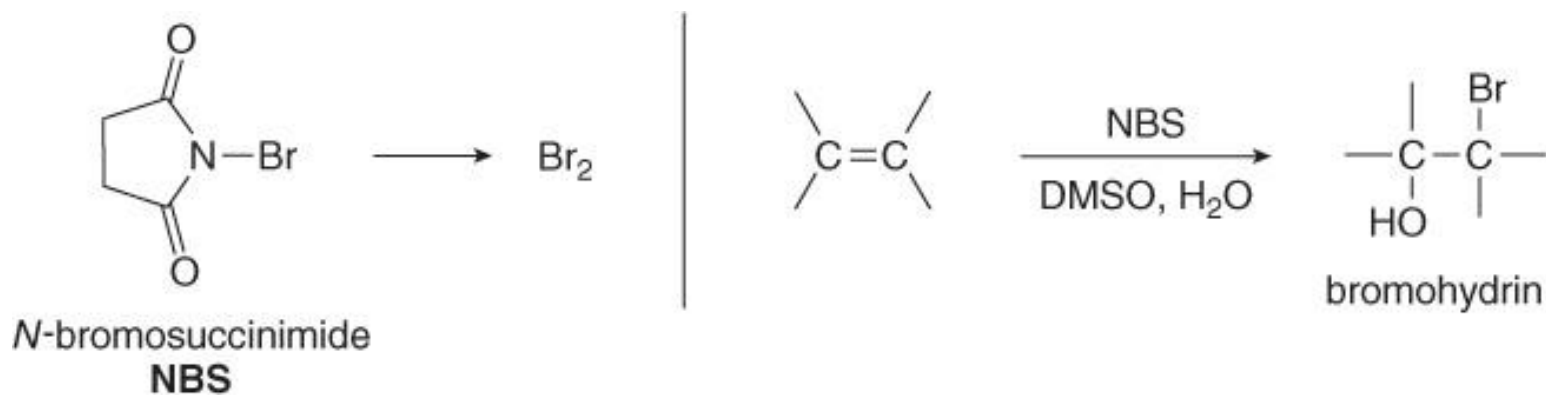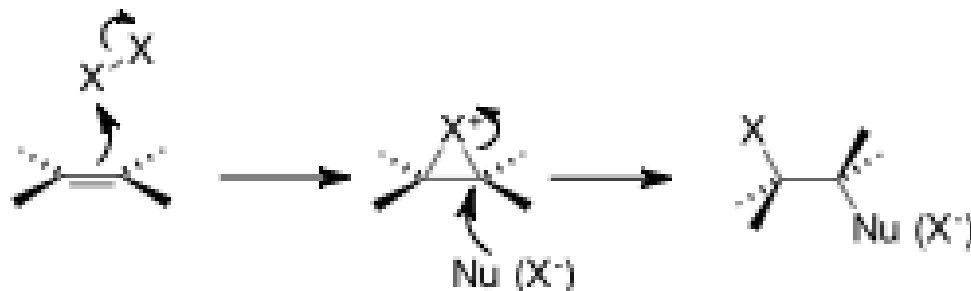- In H_2O, NBS decomposes to form Br_2, which then goes on to form a bromohydrin by the same reaction mechanism.

N-bromosuccinimide
NBS

bromohydrin

Halogenation and Halohydrin Formation

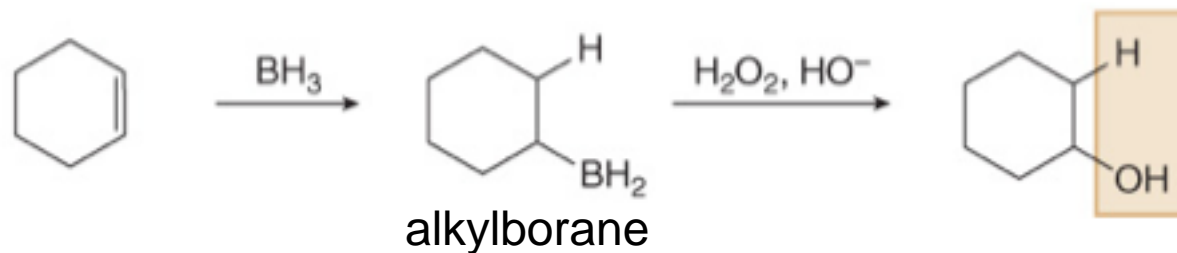| Mechanism	• The mechanism involves two steps.
	• The rate-determining step forms a bridged halonium ion.
	• No rearrangements can occur.
Regioselectivity	• Markovnikov's rule is followed. X^+ bonds to the less substituted carbon.
Stereochemistry	• Anti addition occurs.

Hydroboration—Oxidation

alkylborane

- *Hydroboration* is the addition of borane (BH_3) to an alkene, forming an alkylborane.
- *Oxidation* converts the C−B bond of the alkylborane to a C−O bond.
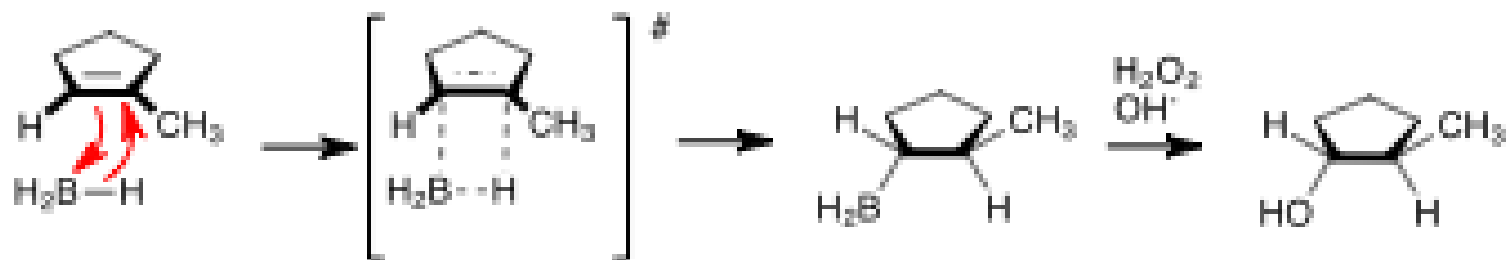

43
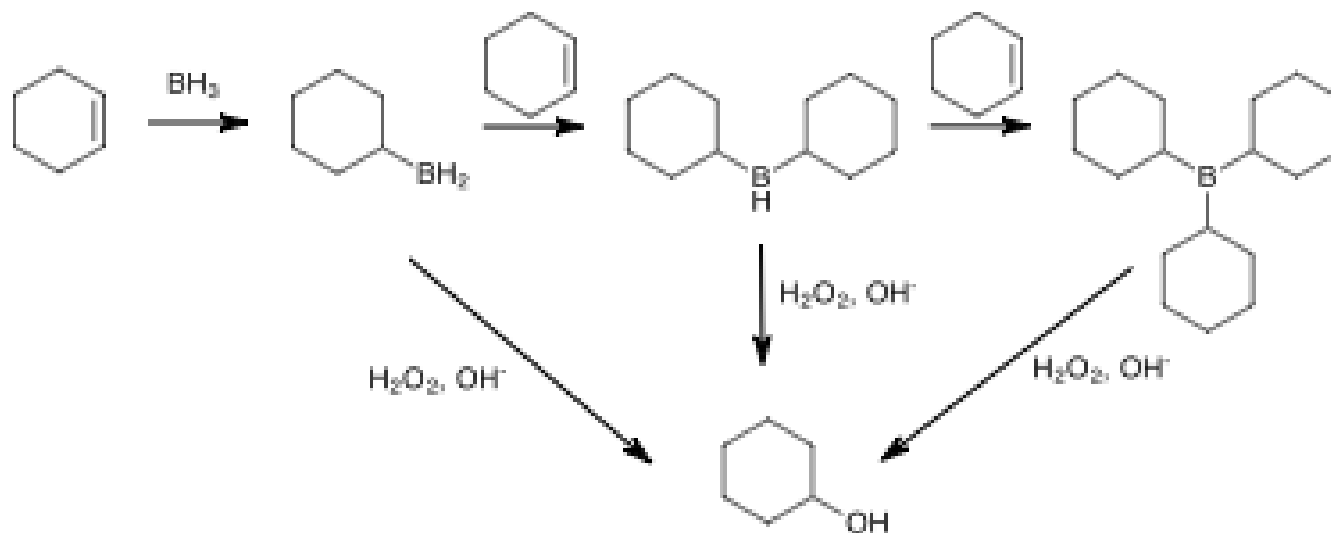
Hydroboration—Oxidation

- Alkylboranes react rapidly with water and spontaneously burn when exposed to air; they are oxidized, without isolation, with basic hydrogen peroxide (H_2O_2, ^-OH).

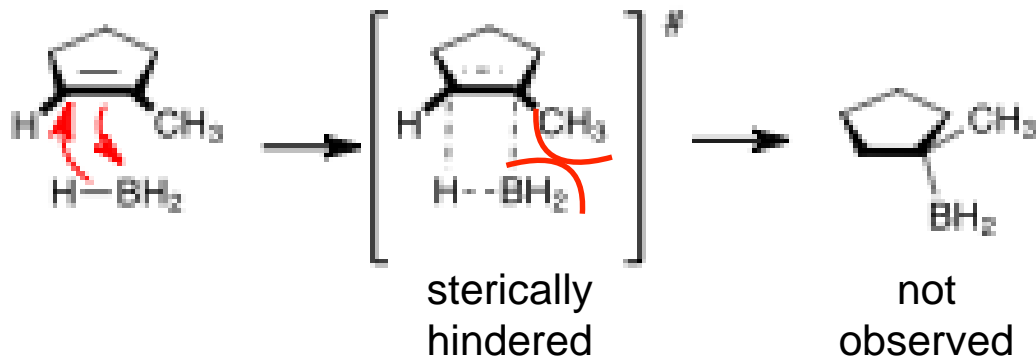$$CH_3-CH_2-CH_2-BH_2 \xrightarrow{\quad H_2O_2,\ OH^- \quad} CH_3-CH_2-CH_2-OH$$
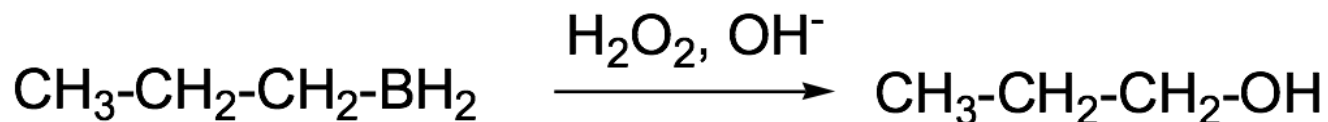
- Oxidation replaces the C—B bond with a C—O bond, forming a new OH group with retention of configuration.

Hydroboration—Oxidation

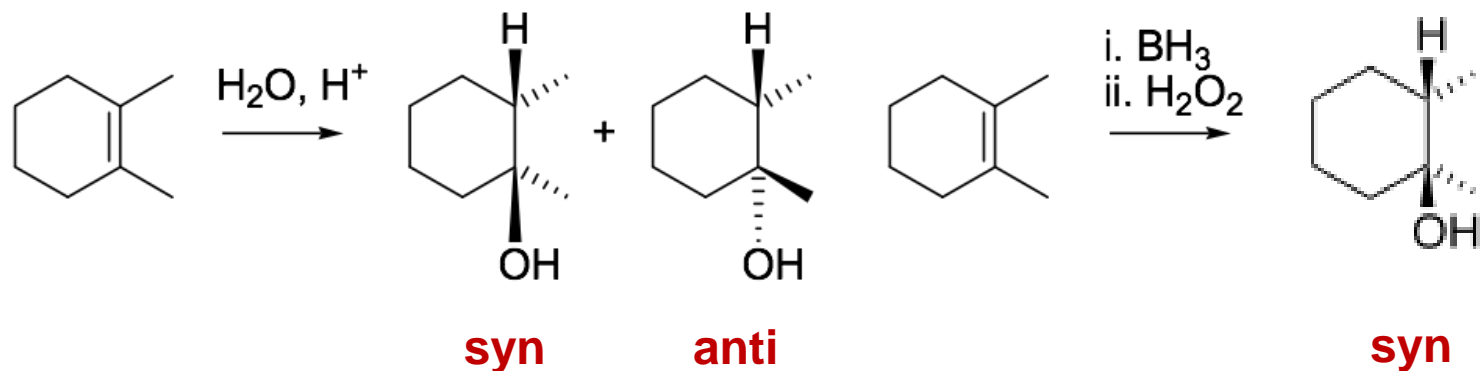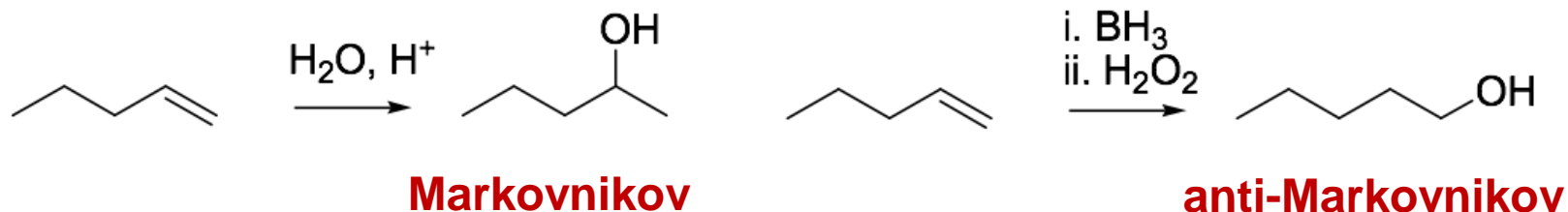1-methyl
cyclopentane

trans, secondary
alcohol

sterically
hindered

not
observed

45

Hydroboration—Oxidation

- The overall result is syn addition of H and OH to a double bond in an "anti-Markovnikov" fashion.

Hydroboration—Oxidation

Observation

Mechanism	• The addition of H and BH_2 occurs in one step.
	• No rearrangements can occur.
Regioselectivity	• The BH_2 group bonds to the less substituted carbon atom.
Stereochemistry	• Syn addition occurs.
	• OH replaces BH_2 with retention of configuration.

Alkenes in Organic Synthesis
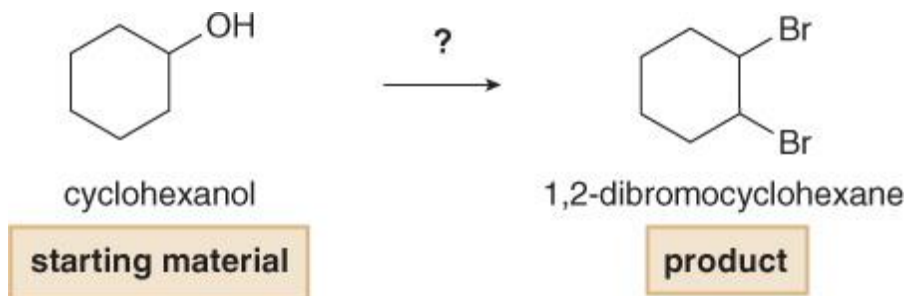

To solve this problem we must:

- Work backwards from the product by asking: What type of reactions introduce the functional groups in the product?
- Work forwards from the starting material by asking: What type of reactions does the starting material undergo?
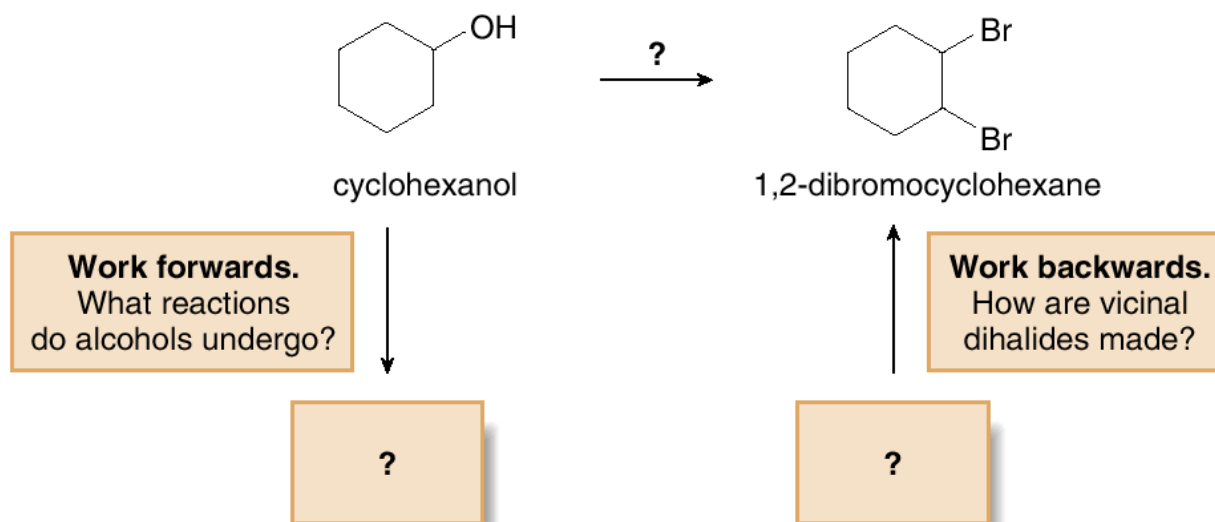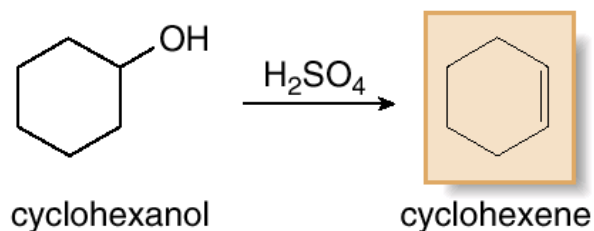
Alkenes in Organic Synthesis

Working backwards:

[1] 1,2-Dibromocyclohexane, a vicinal dibromide, can be prepared by the addition of Br_2 to **cyclohexene.**

cyclohexene   1,2-dibromocyclohexane
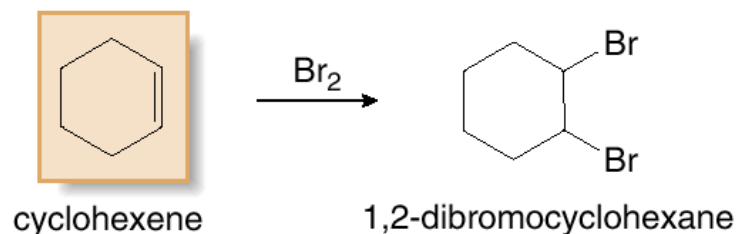
Working forwards:

[2] Cyclohexanol can undergo acid-catalyzed dehydration to form **cyclohexene.**


cyclohexanol   cyclohexene

Cyclohexene is called a **synthetic intermediate,** or simply an **intermediate,** because it is the **product of one step and the starting material of another.** We now have a two-step sequence to convert cyclohexanol to 1,2-dibromocyclohexane, and the synthesis is complete. Take note of the central role of the alkene in this synthesis.
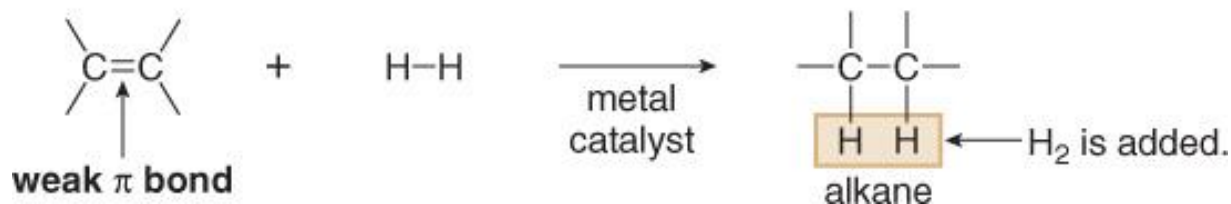
A two-step synthesis

a synthetic intermediate
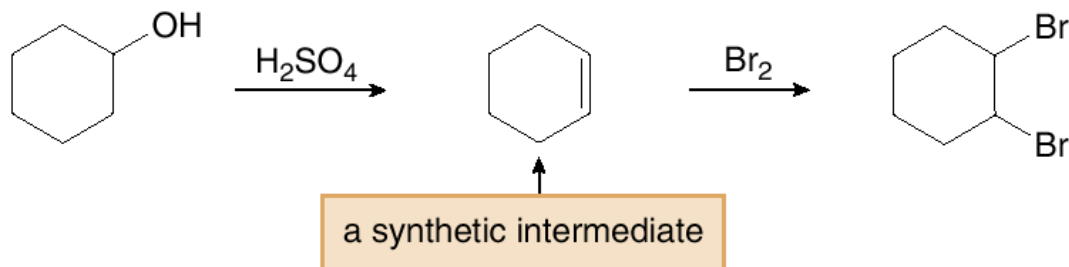
Oxidation and Reduction

- Oxidation: increase of C—O bonds or decrease of C—H bonds.
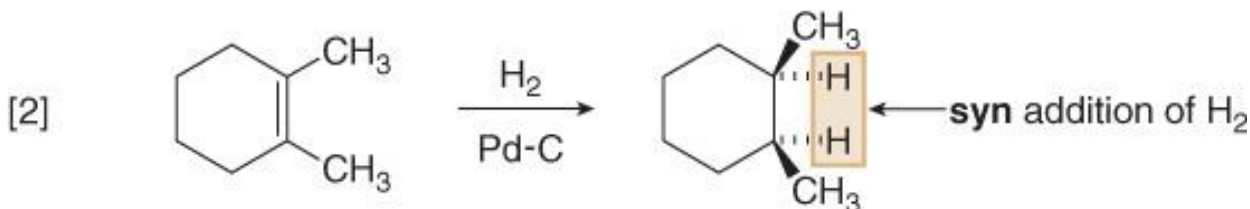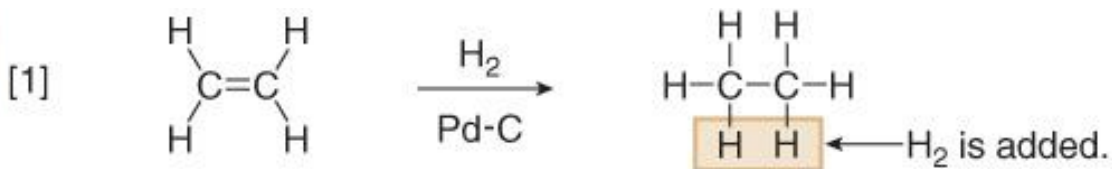- Reduction: decrease of C—O bonds or increase of C—H bonds.

50
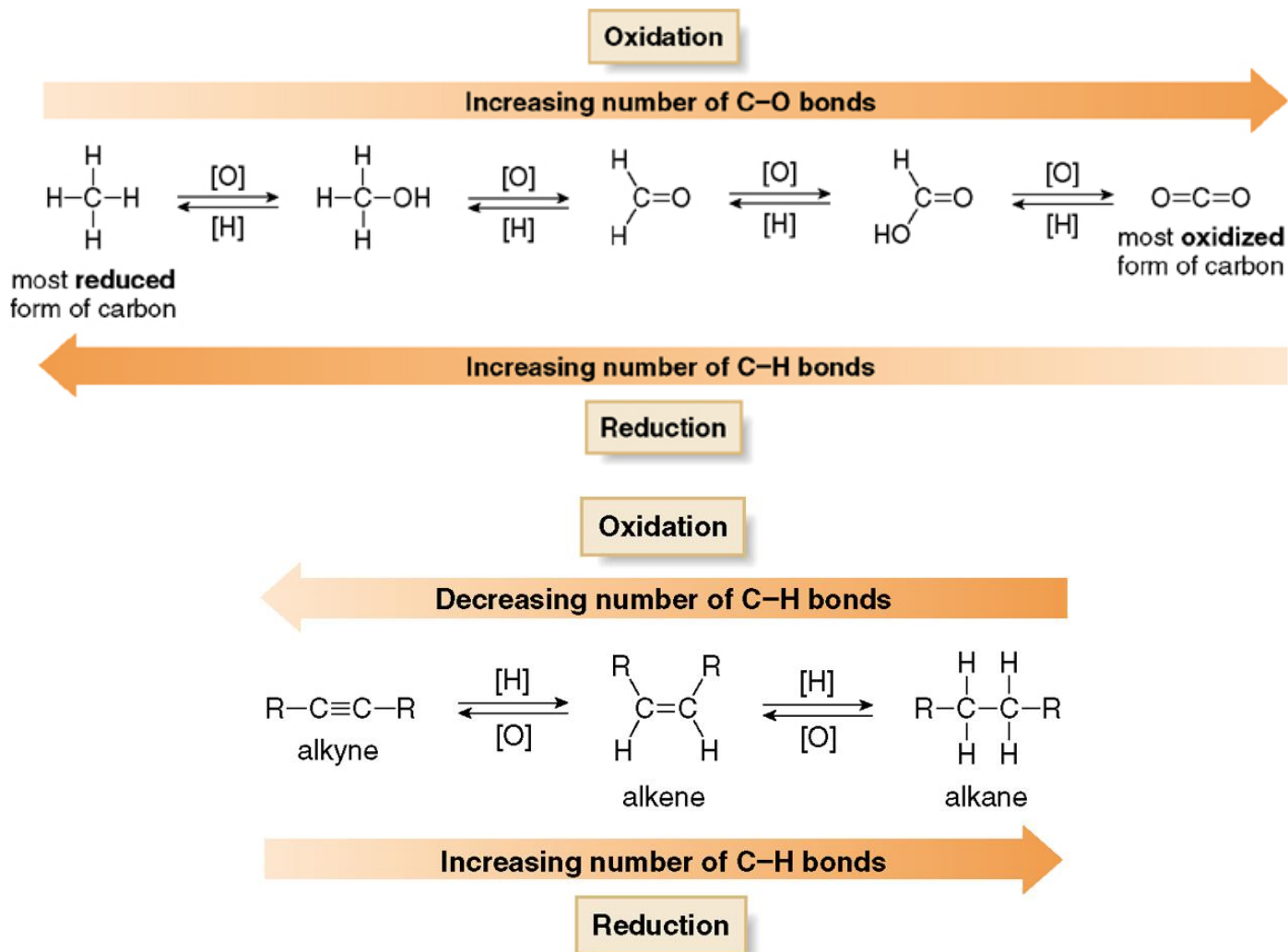
Catalytic Hydrogenation

Hydrogenation—General reaction

- The addition of H_2 occurs only in the presence of a metal catalyst—usually Pd, Pt, or Ni, adsorbed onto a finely divided inert solid, such as charcoal.
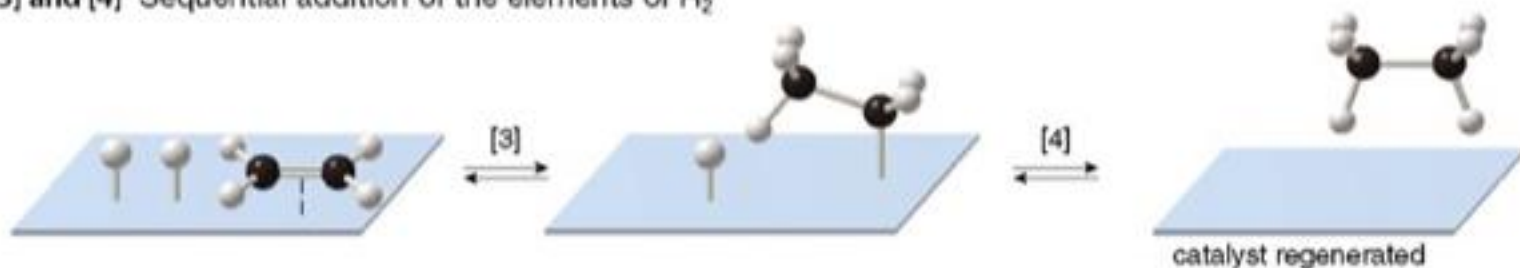- H_2 adds in a syn fashion.

Examples

Catalytic Hydrogenation

Steps [1] and [2] Complexation of H_2 and the alkene to the catalyst

- **H_2 adsorbs to the catalyst surface** with partial or complete cleavage of the H–H bond.
- The π bond of the alkene complexes with the metal.

Steps [3] and [4] Sequential addition of the elements of H_2

- **Two H atoms are transferred sequentially** to the π bond in Steps [3] and [4], forming the alkane.
- Because the product alkane no longer has a π bond with which to complex to the metal, it is released from the catalyst surface.
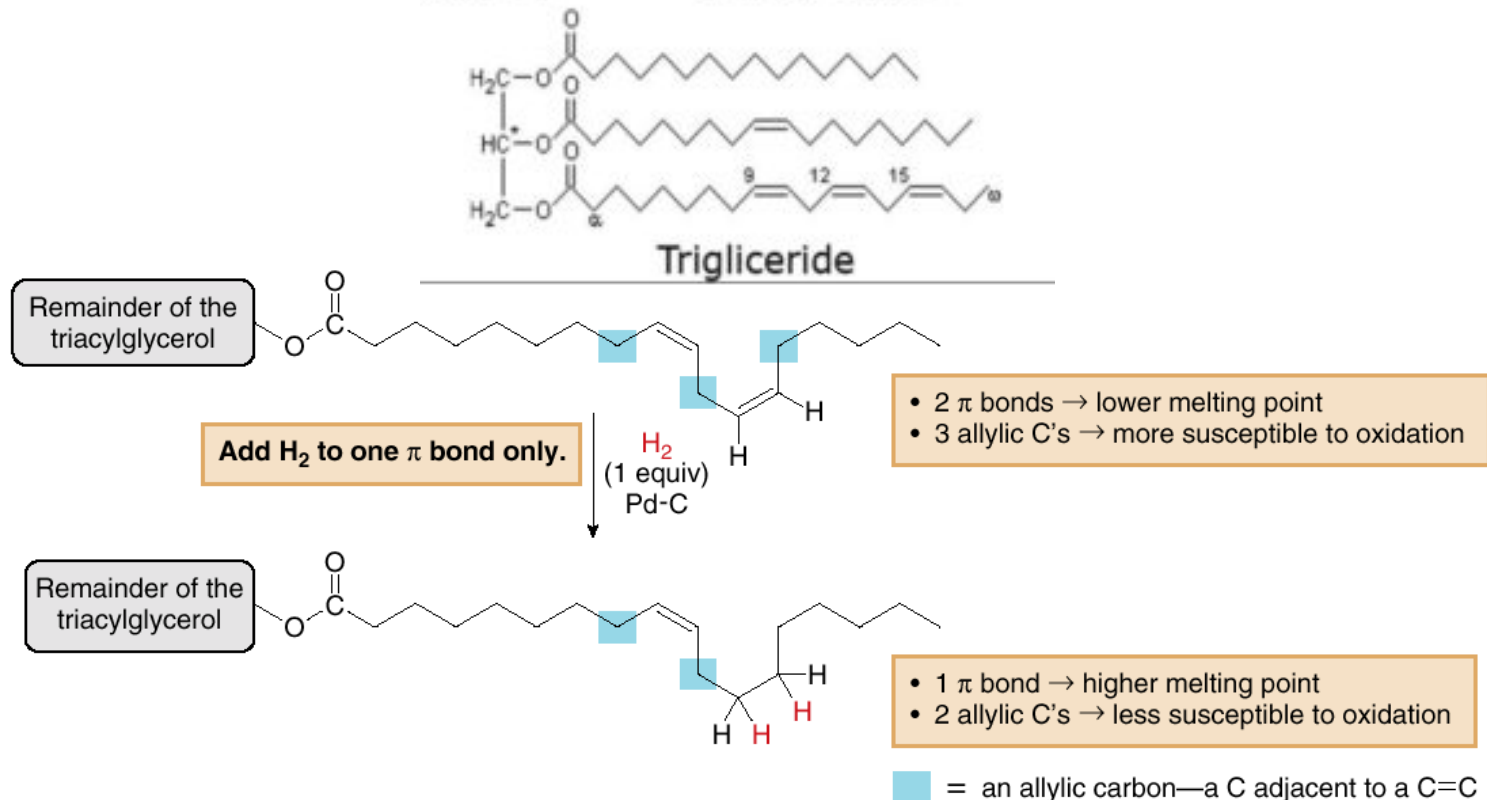
Catalytic Hydrogenation

- Rapid, sequential addition of H_2 occurs from the side of the alkene complexed to the metal surface, resulting in syn addition.
- Less crowded double bonds complex more readily to the catalyst surface, resulting in faster reaction.

Increasing rate of hydrogenation

most reactive   least reactive

Increasing alkyl substitution
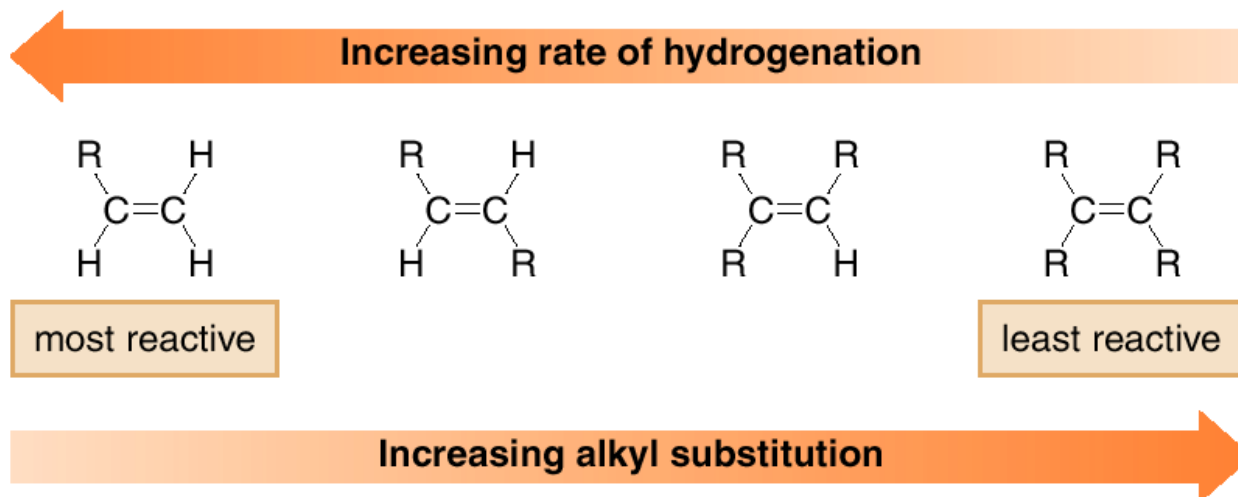
Catalytic Hydrogenation

- When unsaturated vegetable oil is treated with hydrogen, some or all of the π bonds add H_2. This increases the melting point of the oil.
- Margarine is prepared by partially hydrogenating vegetable oils to give a product with a consistency that more closely resembles butter.

Trigliceride

Remainder of the triacylglycerol

Add H₂ to one π bond only.

H_2
(1 equiv)
Pd-C

- 2 π bonds → lower melting point
- 3 allylic C's → more susceptible to oxidation

Remainder of the triacylglycerol

- 1 π bond → higher melting point
- 2 allylic C's → less susceptible to oxidation

▢ = an allylic carbon—a C adjacent to a C=C

- **Decreasing** the number of degrees of unsaturation **increases** the melting point.
- When an oil is *partially* hydrogenated, some double bonds react with H_2, whereas some double bonds remain in the product.
- Partial hydrogenation **decreases** the number of allylic sites, making a triacylglycerol **less** susceptible to oxidation, thereby increasing its shelf life.
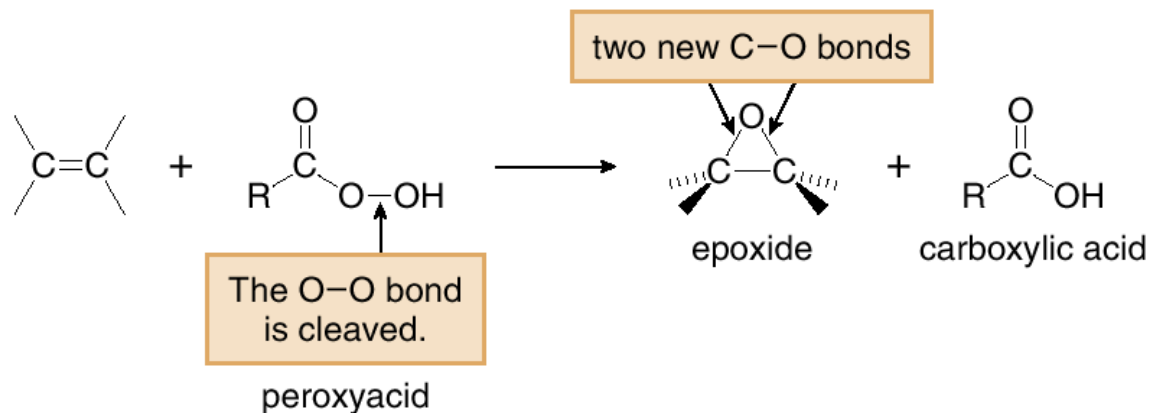
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Oxidations

Oxidizing agents:

- Reagents containing an O—O bond: O_2, O_3, H_2O_2, ROOH, RCOOOH.

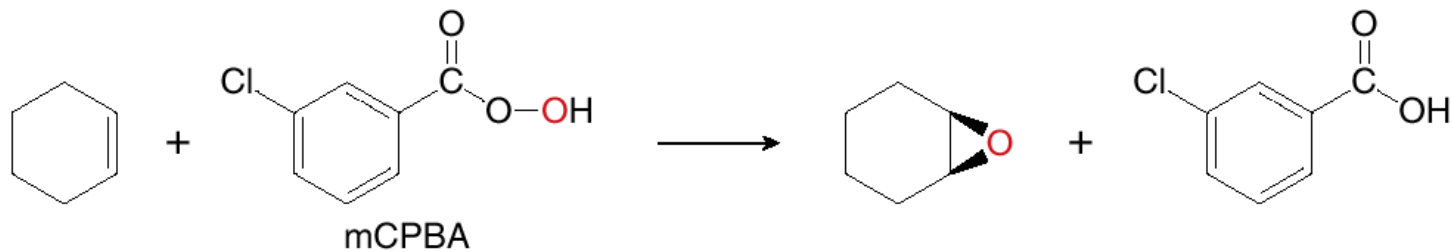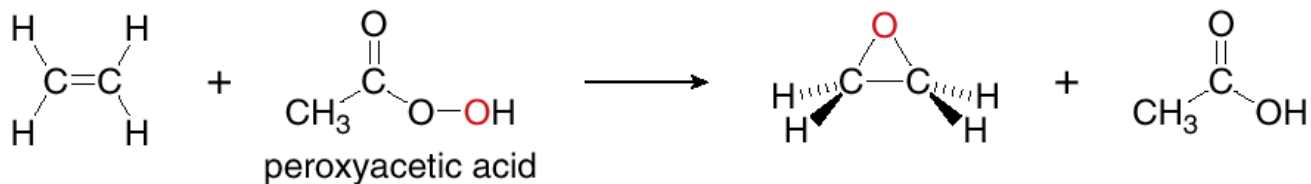- Reagents containing metal-oxygen bonds: Cr(VI), Mn(VII), Os(VIII), Ag(I).
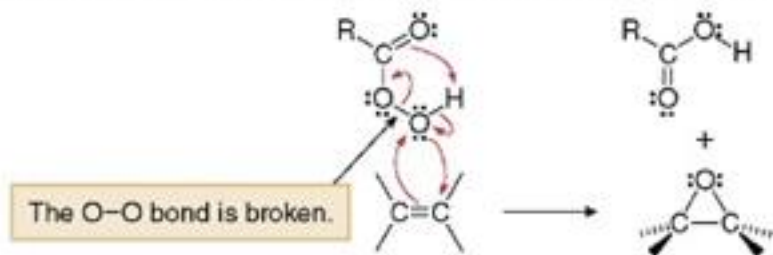
Reactions:
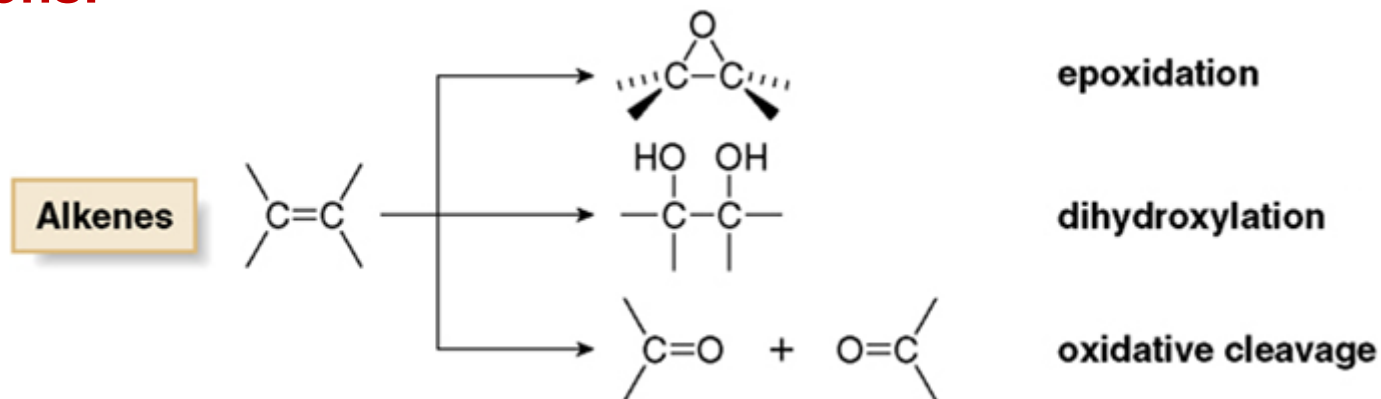
Epoxidation

Epoxidation

One step All bonds are broken or formed in a single step.
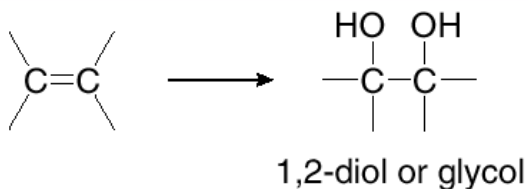

The O—O bond is broken.

- Two C—O bonds are formed to one O atom with one electron pair from the peroxyacid and one from the π bond.
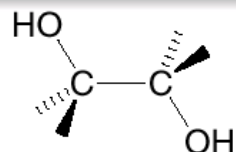- The weak O—O bond is broken.

• Epoxidation is stereospecific.

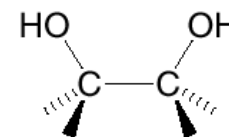# Dihydroxylation

Dihydroxylation—General reaction

HO OH

C=C → —C—C—

1,2-diol or glycol

Stereochemistry

anti addition product

2 OH's added on **opposite** sides of the C=C

or

syn addition product

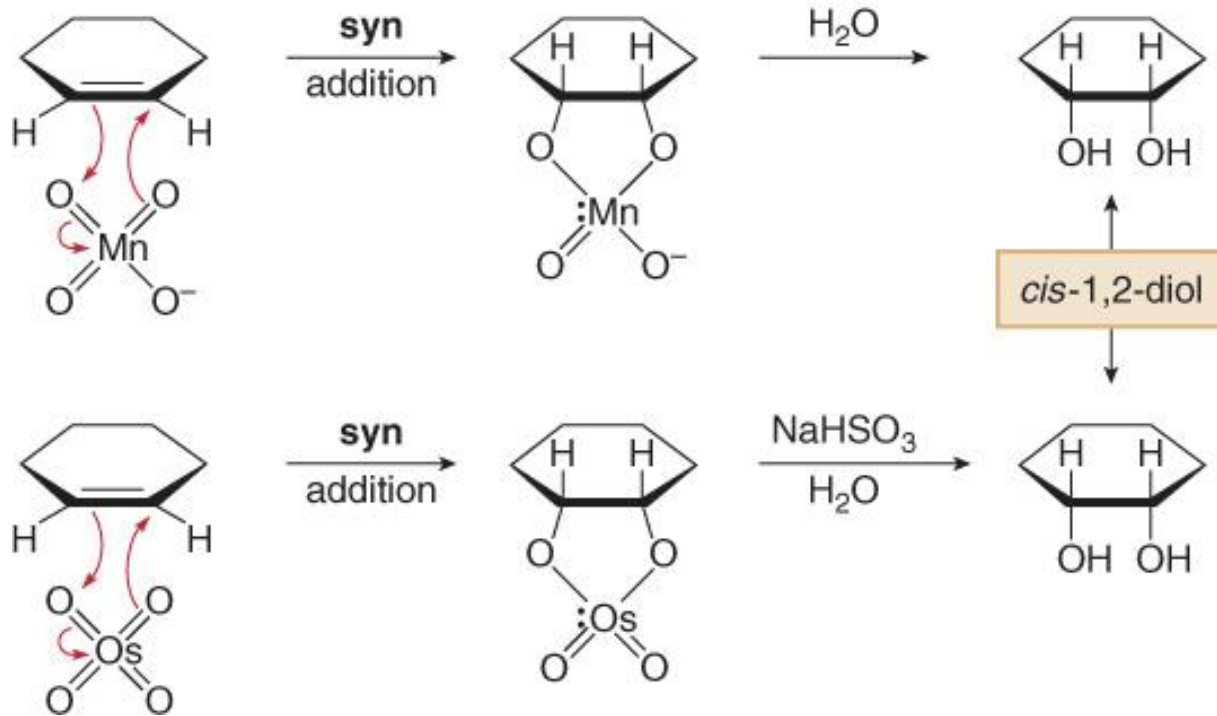2 OH's added on the **same** side of the C=C

cis-1,2-diols

Syn dihydroxylation

KMnO₄ / H₂O, HO⁻

cis-1,2-cyclohexanediol

[1] OsO₄ / [2] NaHSO₃, H₂O

cis-1,2-cyclopentanediol

trans-1,2-diols

Anti dihydroxylation

[1] RCO₃H / [2] H₂O (H⁺ or ⁻OH)

+

enantiomers

58
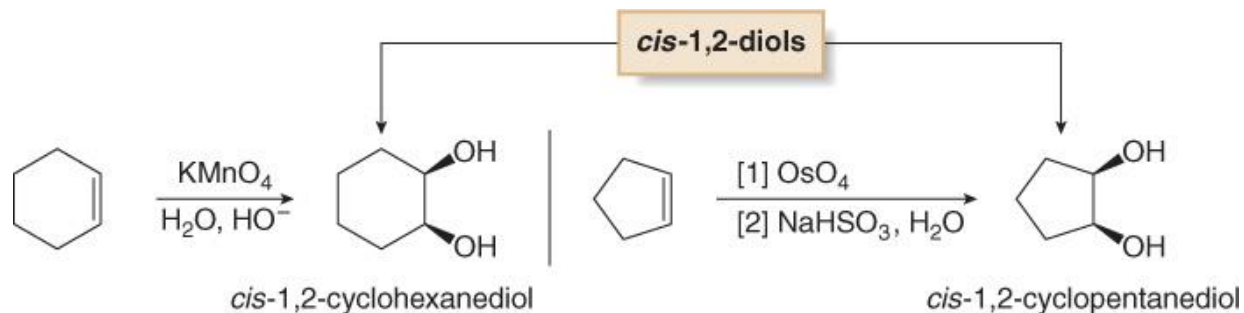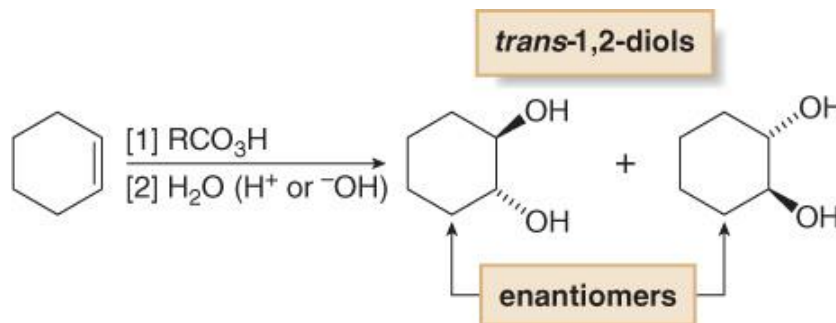
Syn Dihydroxylation

Two O atoms are added to the **same** side of the C=C.
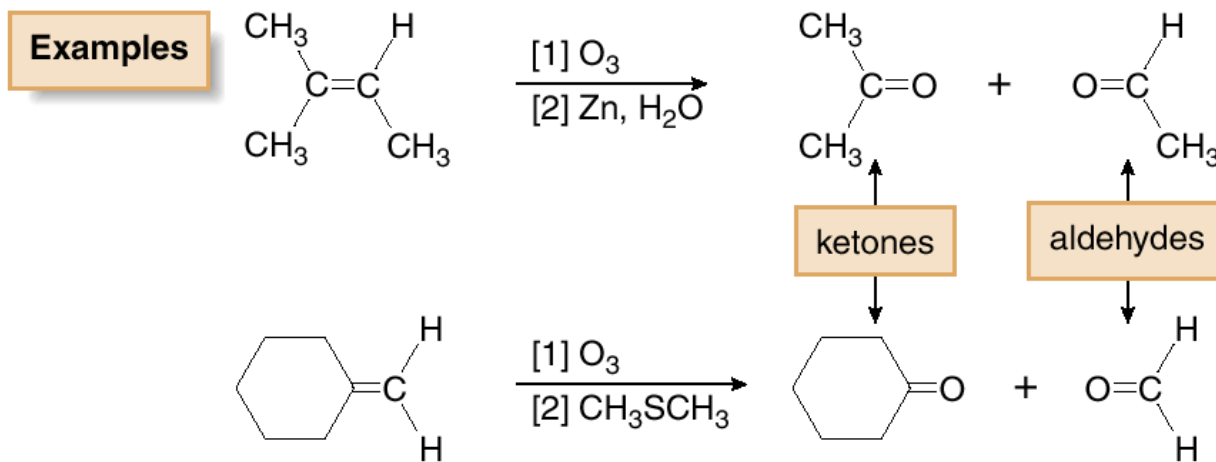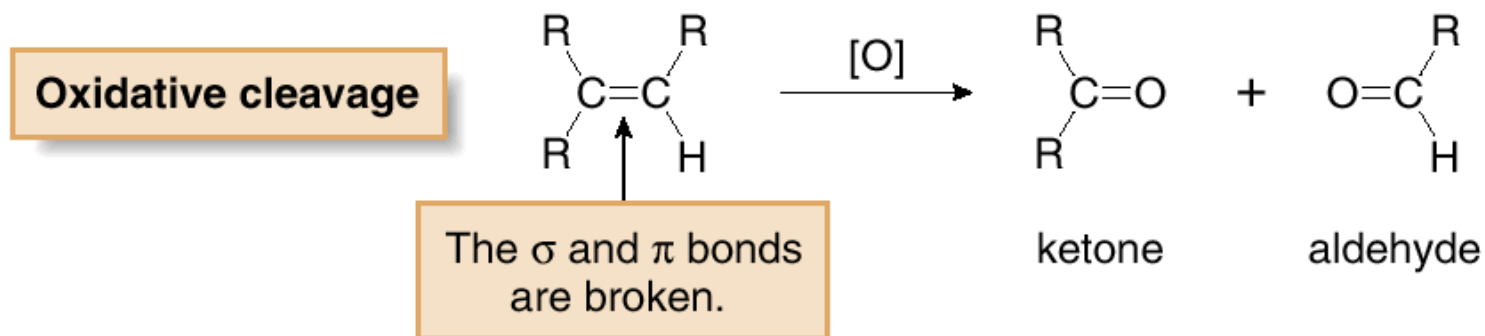
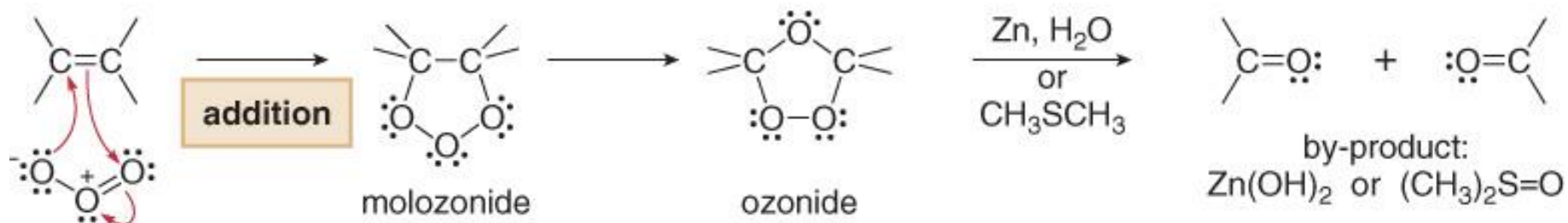*cis*-1,2-diol

Anti Dihydroxylation
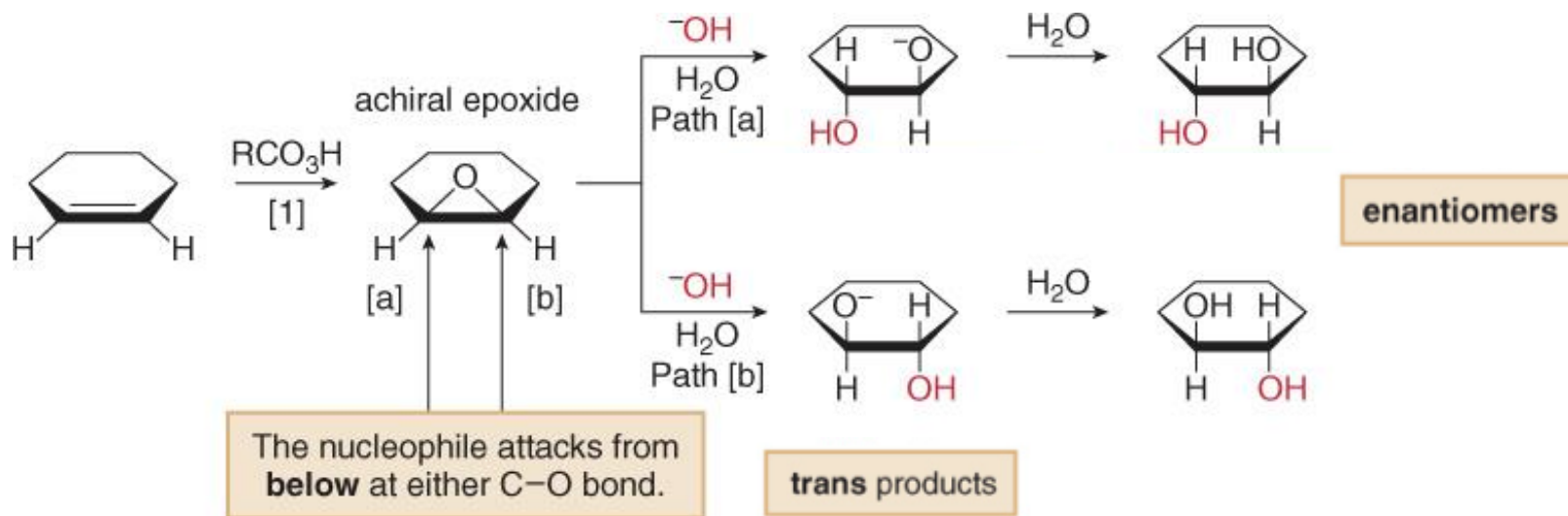
Oxidative Cleavage

- Oxidative cleavage of an alkene breaks both the σ and π bonds of the double bond to form two carbonyl compounds. Cleavage with ozone (O_3) is called ozonolysis.
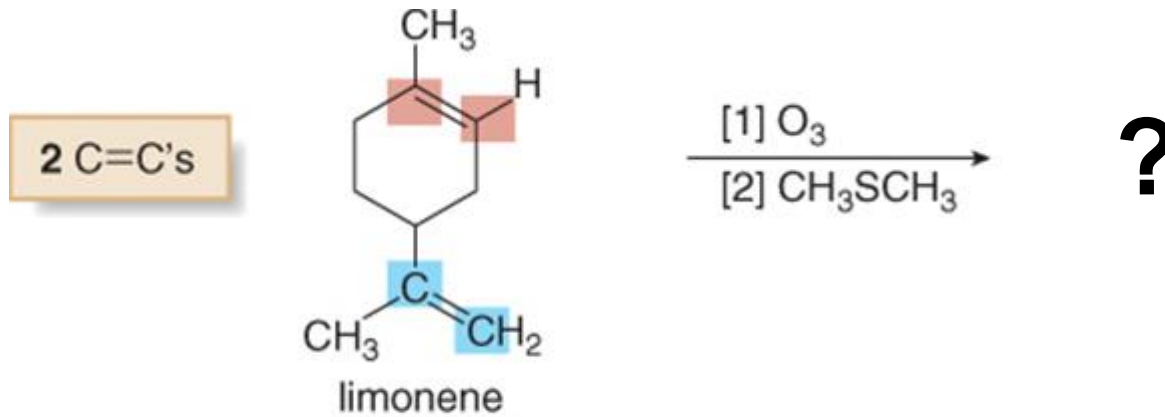

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Oxidative Cleavage

- Addition of O_3 to the π bond of an alkene forms a molozonide, which rearranges to an ozonide in a stepwise process.
- The unstable ozonide is reduced to afford carbonyl compounds.
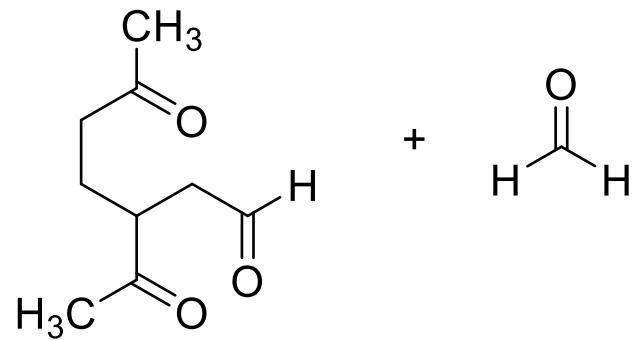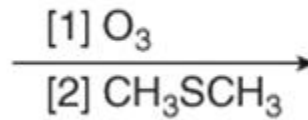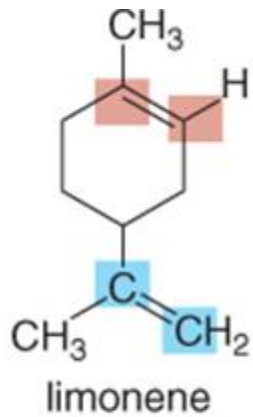

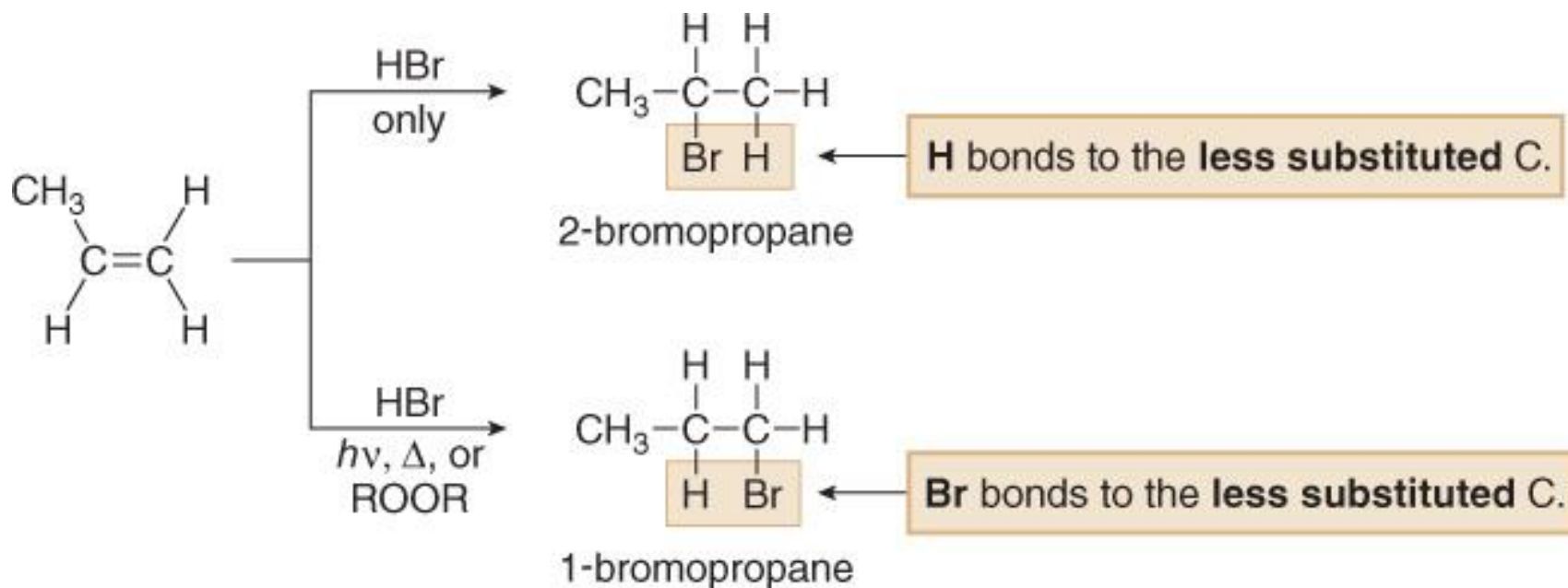The key intermediates in ozonolysis

Oxidative Cleavage

2 C=C's

limonene

$$\xrightarrow[\text{[2] } CH_3SCH_3]{\text{[1] } O_3}$$

?

Oxidative Cleavage

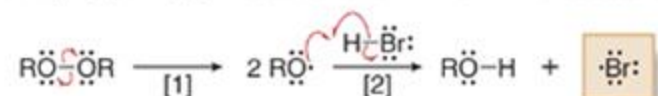# Radical Additions to Double Bonds

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Radical Additions to Double Bonds

Limited utility: HBr only

Initiation
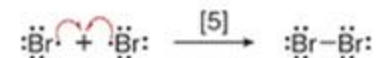**Steps [1] and [2]** Abstraction of H from HBr occurs by a two-step process.

RÖ—ÖR $\xrightarrow{[1]}$ 2 RÖ· $\xrightarrow[\text{[2]}]{\text{H—Br:}}$ RÖ—H + ·Br:

Propagation
Steps [3] and [4] The π bond is broken and the C−H and C−Br σ bonds are formed.

CH₃, H
　C=C $\xrightarrow{[3]}$ CH₃−C−C−H ← new bond
H   H ·Br: 　　　:Br:
·Br: 　　　　　2° radical

CH₃−C−C−H $\xrightarrow{[4]}$ CH₃−C−C−H + ·Br:
　　:Br: 　　　　　H :Br:
H—Br: 　　new bond
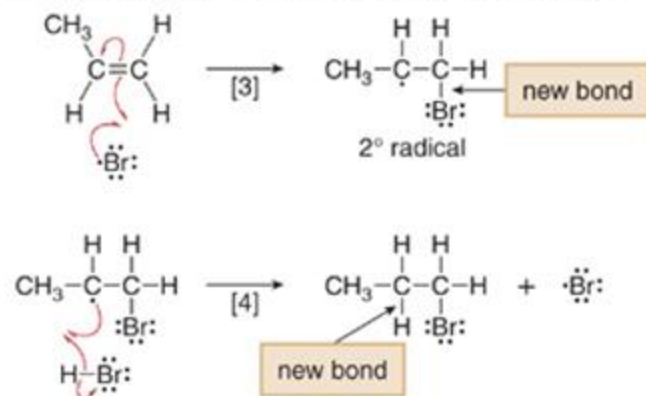
Repeat Steps [3], [4], [3], [4], and so forth.

Termination
Step [5] Two radicals react to form a bond.

:Br· + ·Br: $\xrightarrow{[5]}$:Br—Br:

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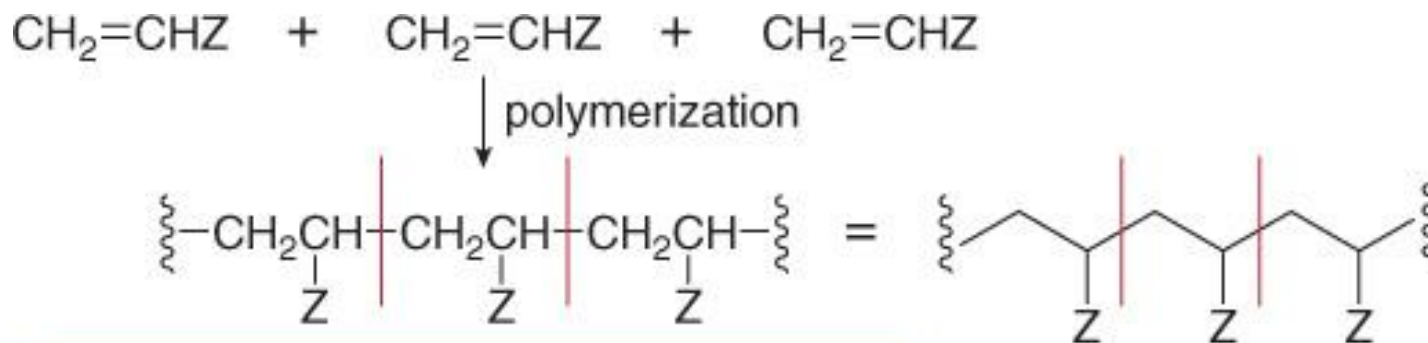# Polymers and Polymerization

- Polymers are large molecules made up of repeating units of smaller molecules called monomers. They include biologically important compounds such as proteins and carbohydrates, as well as synthetic plastics such as polyethylene, polyvinyl chloride (PVC) and polystyrene.

- Polymerization is the joining together of monomers to make polymers. For example, joining ethylene monomers together forms the polymer polyethylene, a plastic used in milk containers and plastic bags.
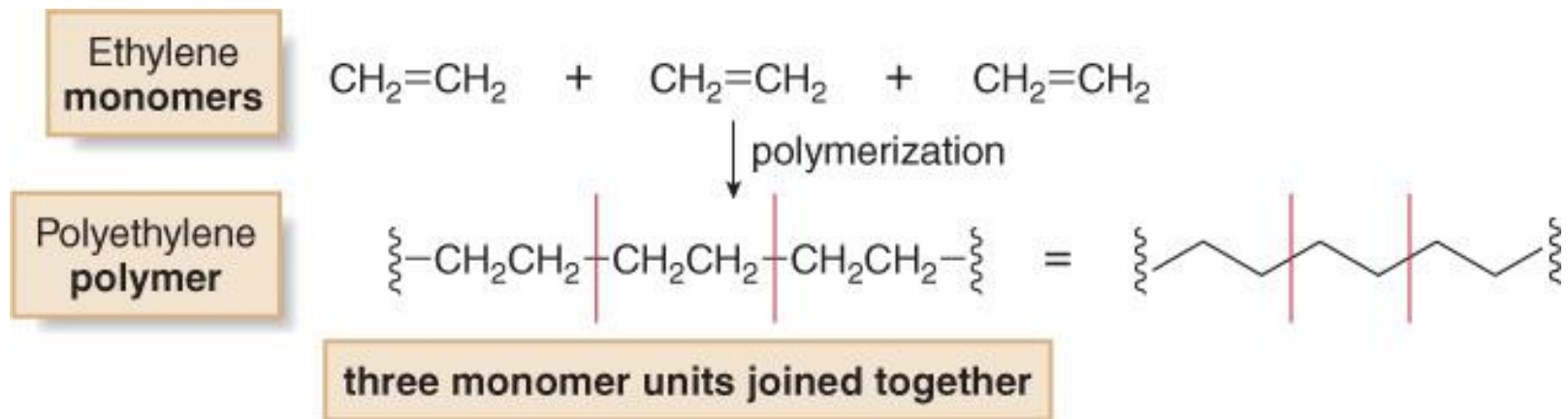
Polymers and Polymerization

- Many ethylene derivatives having the general structure $CH_2=CHZ$ are also used as monomers for polymerization.

- The identity of Z affects the physical properties of the resulting polymer.

- Polymerization of $CH_2=CHZ$ usually affords polymers with Z groups on every other carbon atom in the chain.

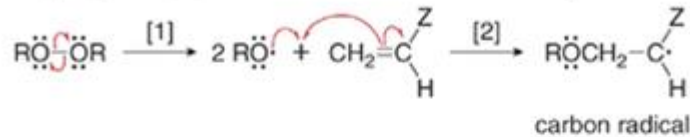$$CH_2=CHZ \quad + \quad CH_2=CHZ \quad + \quad CH_2=CHZ$$

polymerization

$$-CH_2CH-CH_2CH-CH_2CH- \quad = \quad$$
$$\quad\quad | \quad\quad\quad | \quad\quad\quad |$$
$$\quad\quad Z \quad\quad\quad Z \quad\quad\quad Z$$

three monomer units joined together

Polymers and Polymerization

Initiation
Steps [1] and [2] A carbon radical is formed by a two-step process.
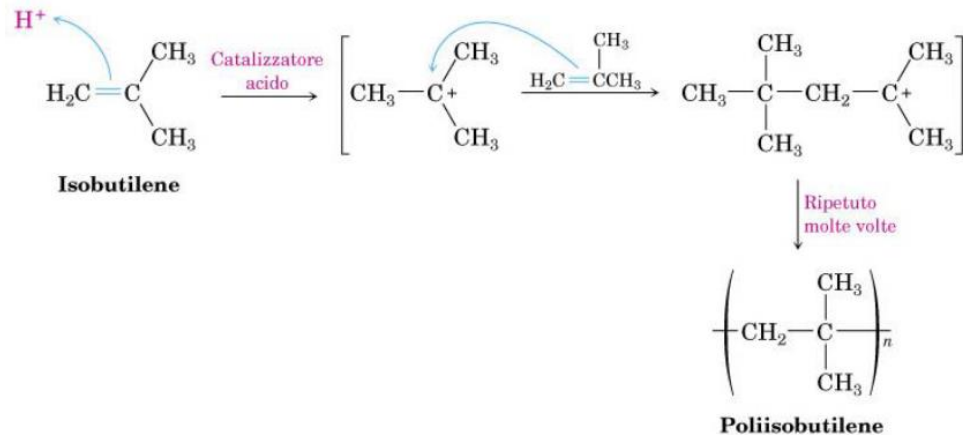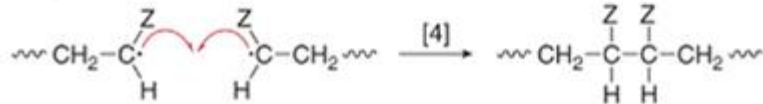

carbon radical

Propagation
Step [3] The polymer chain grows.
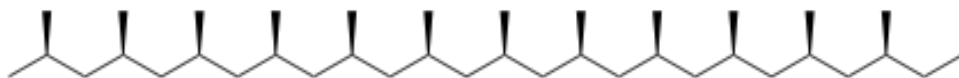

Repeat Step [3] over and over.

new C−C bond
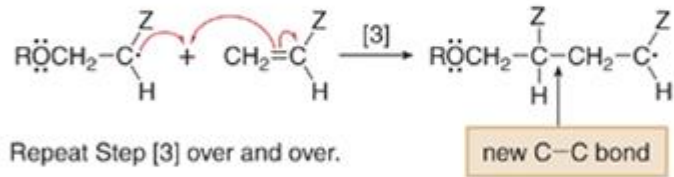
The more substituted radical always adds to the less substituted end of the monomer, a process called head-to-tail polymerization.
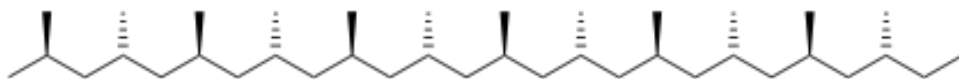
Termination
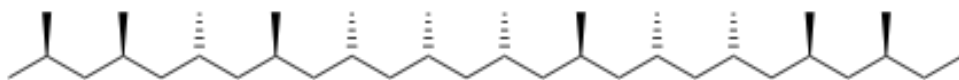**Step [4]** Two radicals combine to form a bond.

Isobutilene

Ripetuto molte volte

Poliisobutilene

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Polymers and Polymerization

Isotactic (TiCl$_3$, AlEt$_2$Cl)

sindiotactic (TiCl$_4$, AlR$_3$)
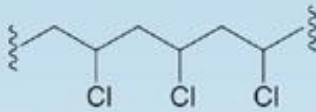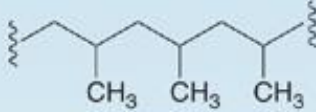
atactic (TiCl$_3$, AlCl$_3$)

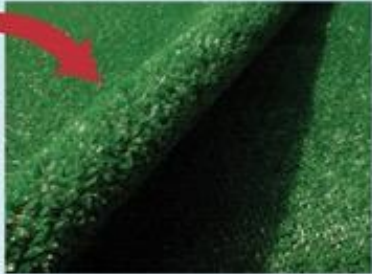# Polymers and Polymerization

Table 15.2 Common Industrial Monomers and Polymers

Monomer →	Polymer	Consumer product

$CH_2=CHCl$
vinyl chloride → poly(vinyl chloride) PVC → PVC pipes

$CH_2=CHCH_3$
propene → polypropylene → polypropylene carpeting

$CH_2=CH$—(benzene ring)
styrene → polystyrene → Styrofoam products

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