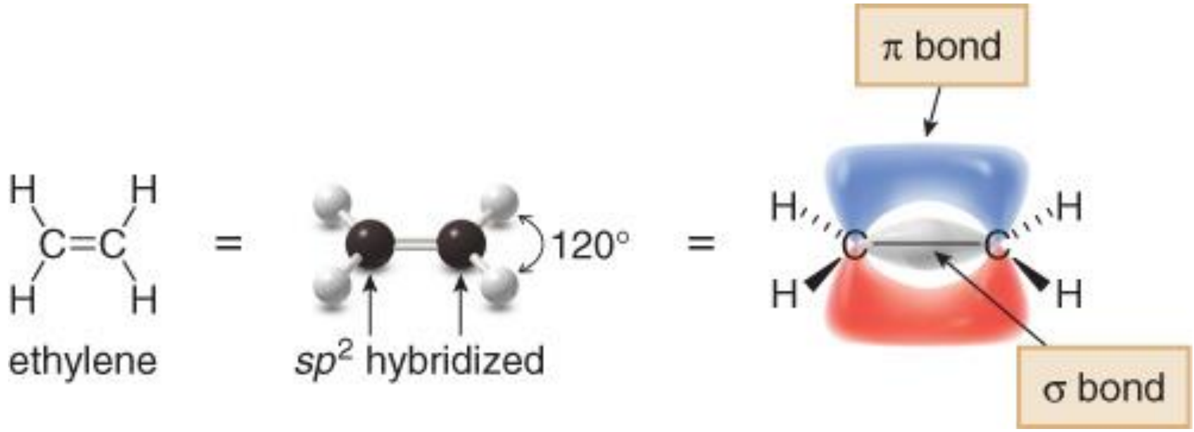
Alkenes (Olefins)

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

Structure and Bonding



$CH_2{=}CH_2$ $\qquad$ $CH_3{-}CH_3$

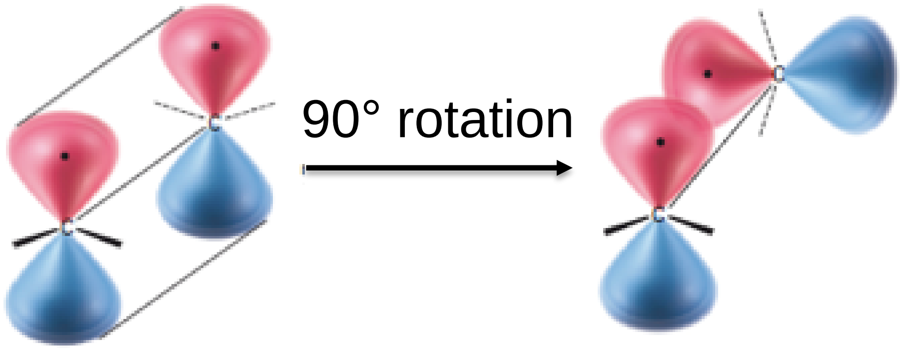
152 kcal/mol (σ + π bond) − 88 kcal/mol (σ bond) = 64 kcal/mol

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

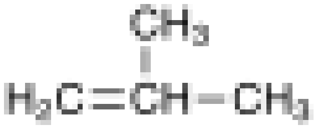
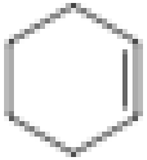
Rotation around the C=C bond is restricted



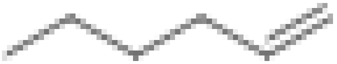
90° rotation

The p orbitals are orthogonal
the π bond is broken

Simple Alkenes

$H_2C{=}CH_2$	ethene	(ethylene)
$H_2C{=}CH{-}CH_3$	propene	(propylene)
 $\overset{CH_3}{\overset{\vert}{H_2C{=}CH{-}CH_3}}$	2-methylpropene	(isobutene)
	cyclohexene	

Positional isomers



1-hexene

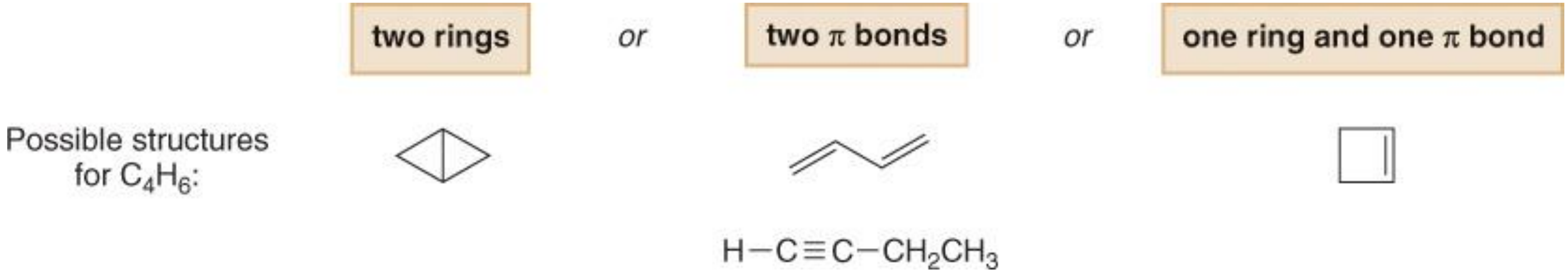
2-hexene

3-hexene

Unsaturation Degree

- 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.

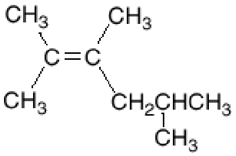
- es. C_4H_6



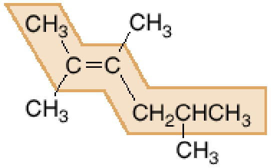
Nomenclature

How To Name an Alkene

Example Give the IUPAC name of the following alkene:



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



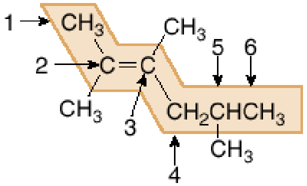
6 C's in the longest chain

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.

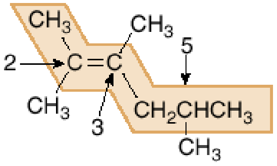
a. **Number** the chain, and name using the ***first* number** assigned to the C=C.



- Number the chain to put the C=C at C2, not C4.

2-hexene

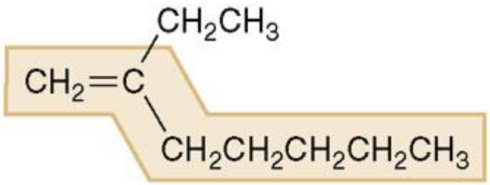
b. **Name** and **number** the substituents.



three methyl groups at C2, C3, and C5

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

Nomenclature

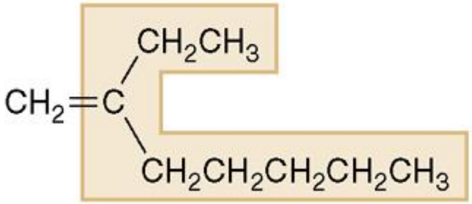


$CH_2{=}C(CH_2CH_3)CH_2CH_2CH_2CH_2CH_3$

7 C's ---→ heptene

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

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

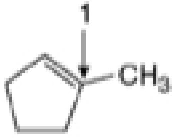


$CH_2{=}C(CH_2CH_3)CH_2CH_2CH_2CH_2CH_3$

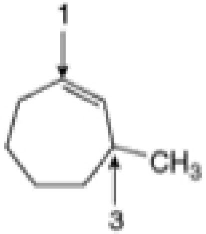
8 C's

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

Incorrect



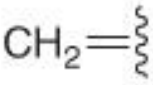
1-methylcyclopentene



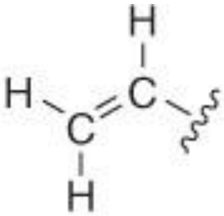
3-methylcycloheptene

[Number clockwise beginning at the C=C and place the CH_3 at C3.]

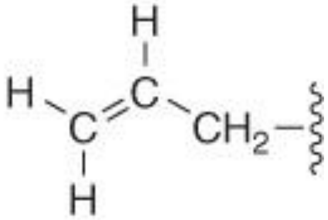
Nomenclature



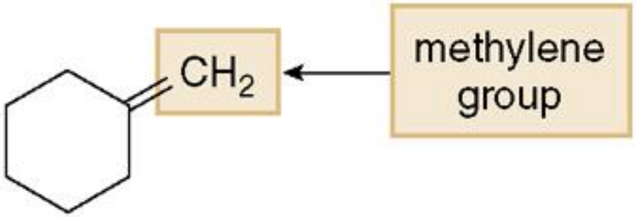
methylene group



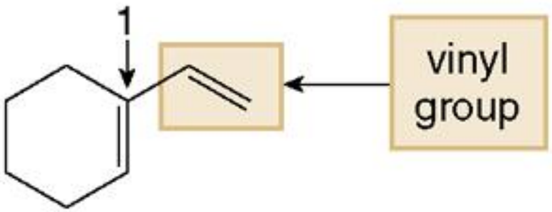
vinyl group



allyl group



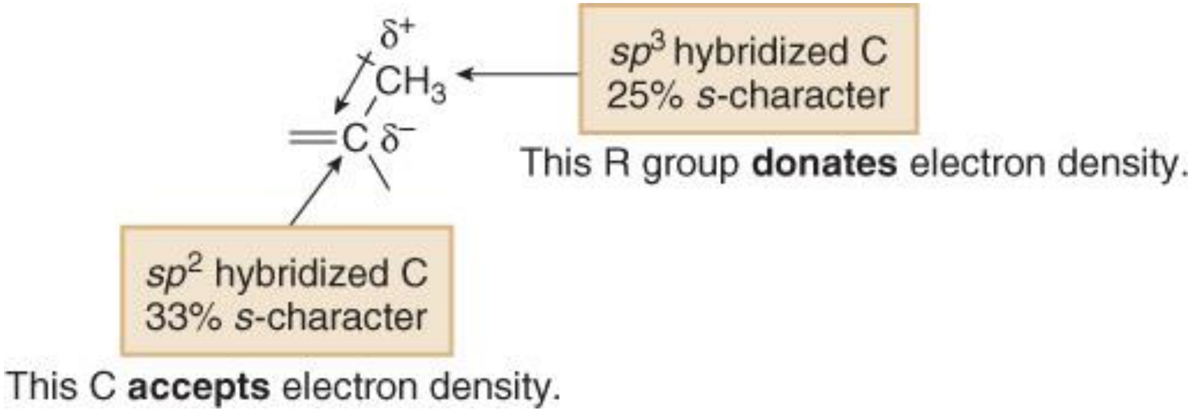
methylenecyclohexane



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.



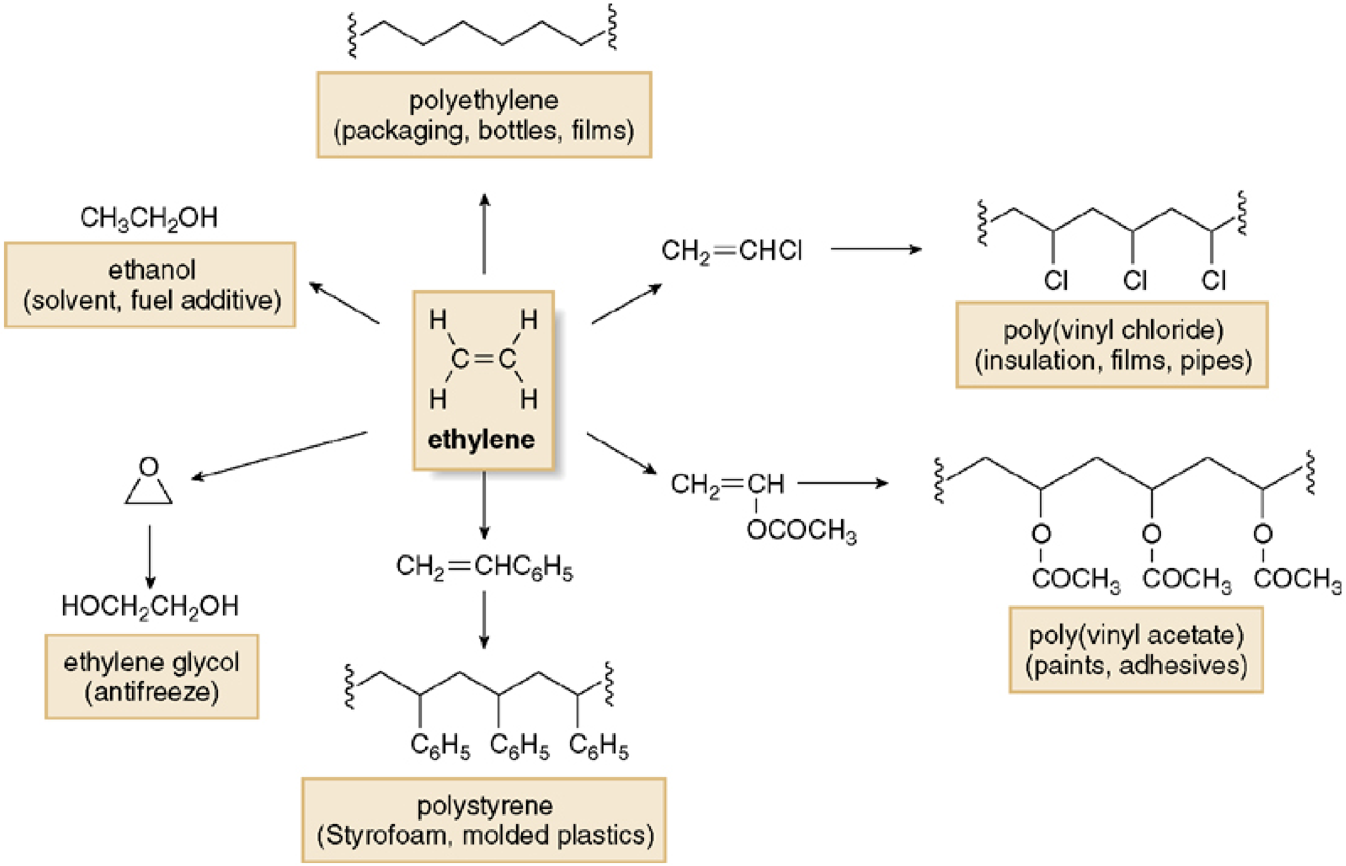
sp^3 hybridized C
25% *s*-character

This R group **donates** electron density.

sp^2 hybridized C
33% *s*-character

This C **accepts** electron density.

Interesting Alkenes



polyethylene
(packaging, bottles, films)

CH_3CH_2OH

ethanol
(solvent, fuel additive)

ethylene

$CH_2{=}CHCl$

Cl Cl Cl

poly(vinyl chloride)
(insulation, films, pipes)

$CH_2{=}CH$–$OCOCH_3$

O O O

$COCH_3$ $COCH_3$ $COCH_3$

poly(vinyl acetate)
(paints, adhesives)

O

$HOCH_2CH_2OH$

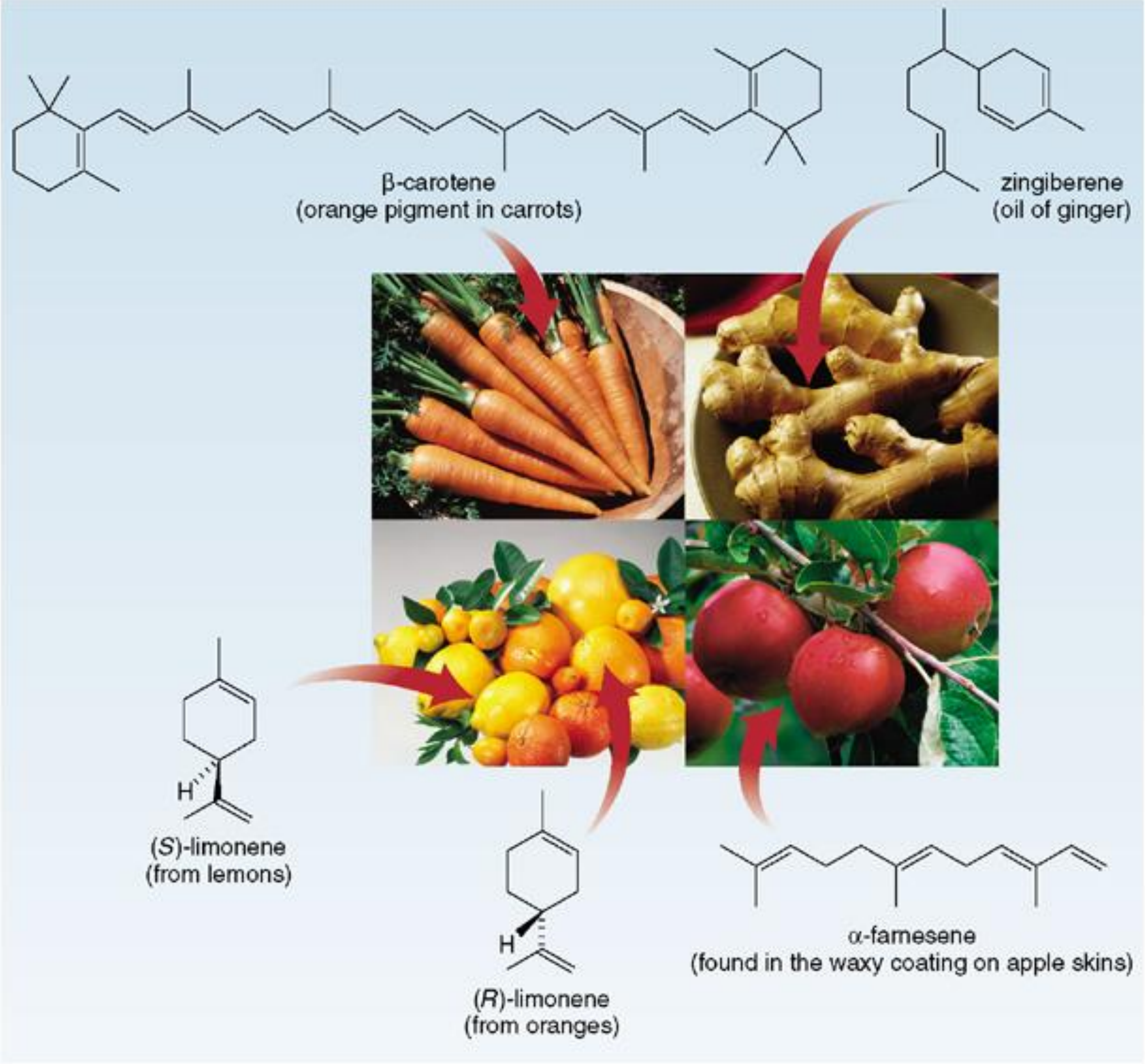
ethylene glycol
(antifreeze)

$CH_2{=}CHC_6H_5$

C_6H_5 C_6H_5 C_6H_5

polystyrene
(Styrofoam, molded plastics)

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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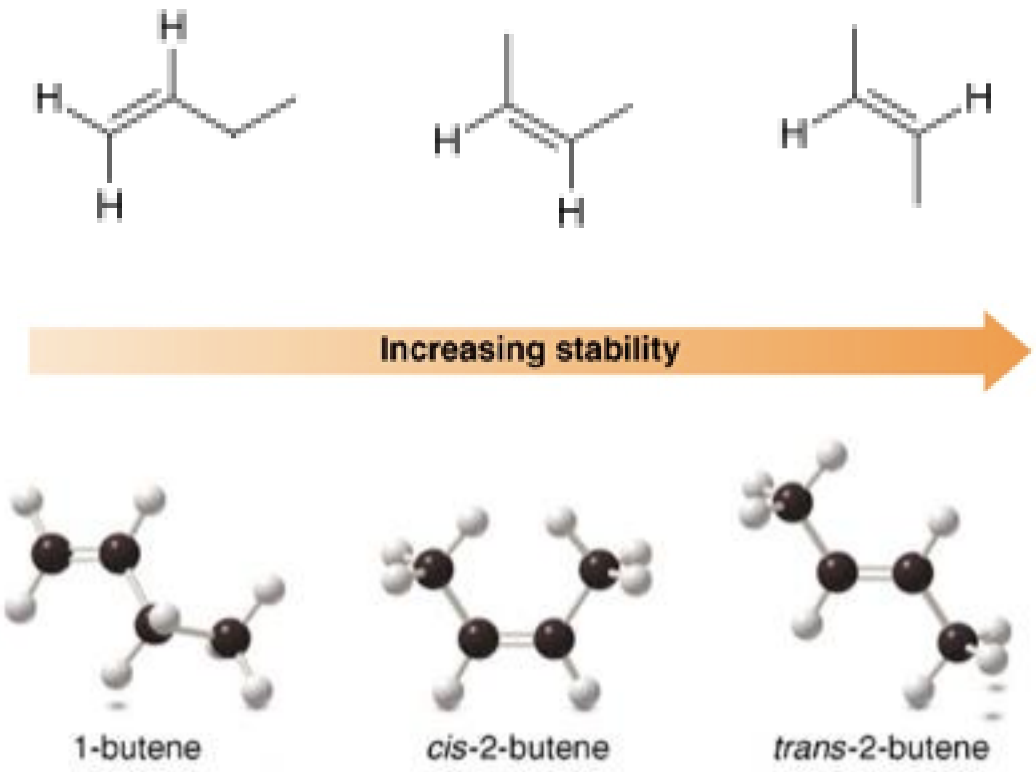
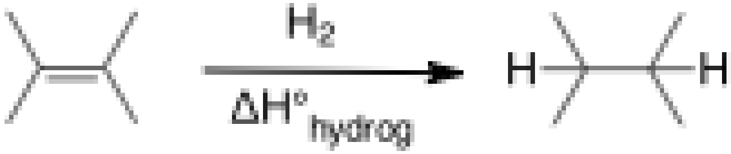
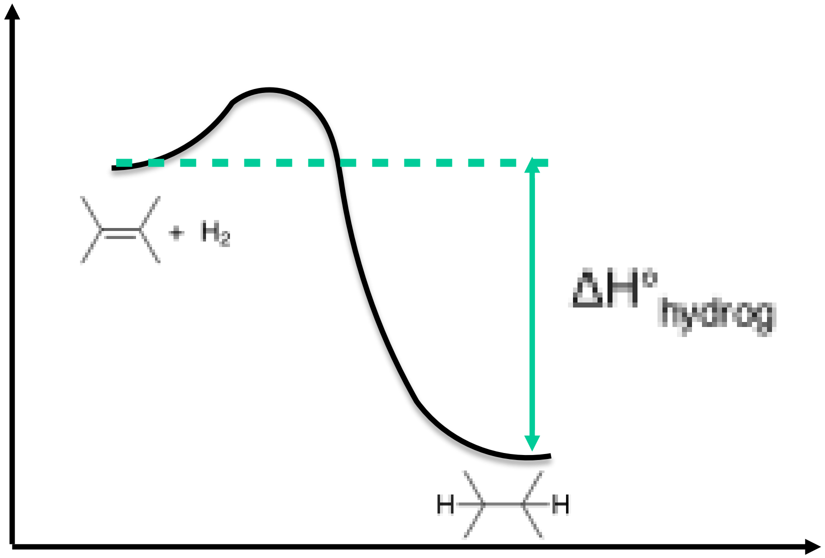
Geometrical Isomerism



Stability of Alkenes





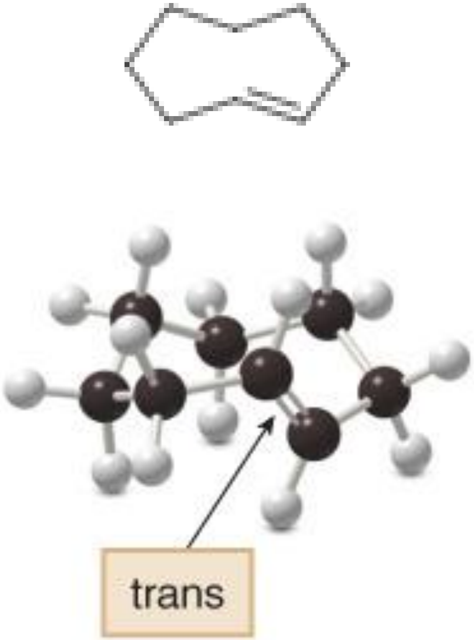
- Hydrogenation of alkenes is exothermic
- The heat of hydrogenation can be used as a measure of the relative stability of different alkenes.

Stability of Alkenes

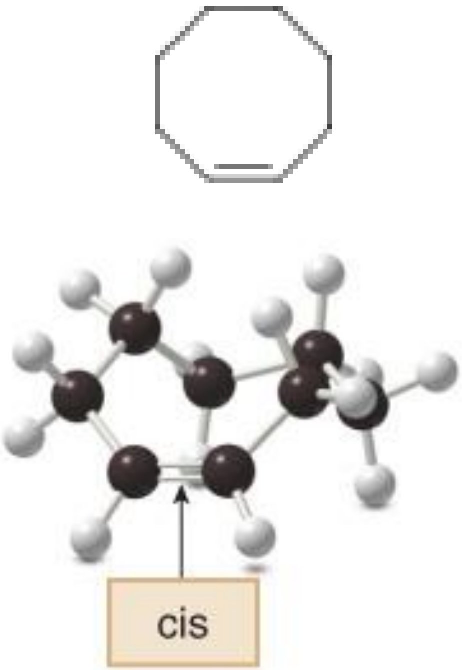
Substitution	Alkene	ΔH°hydrog (Kcal/mol)
Unsubstituted	$H_2C=CH_2$	-32.8
Monosubstituted	$CH_3CH=CH_2$	-30.1
Disubstituted	$(CH_3)_2C=CH_2$	-28.4
	$CH_3CH=CHCH_3$ (cis)	-28.6
	$CH_3CH=CHCH_3$ (trans)	-27.6
Trisubstituted	$(CH_3)_2C=CHCH_3$	-26.9
Tetrasubstituted	$(CH_3)_2C=C(CH_3)_2$	-26.6

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-cyclooctene



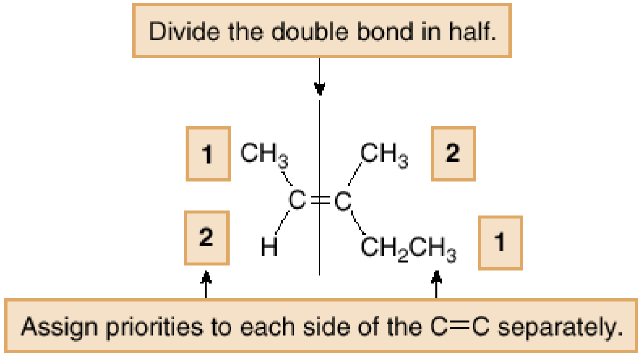
cis-cyclooctene

E/*Z* Nomenclature

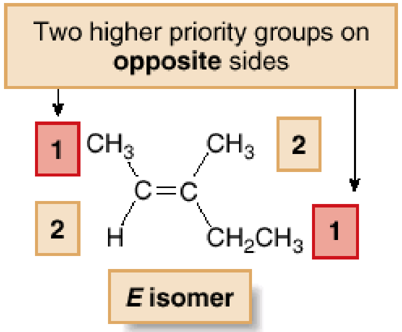
How To Assign the Prefixes *E* and *Z* to an Alkene

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).

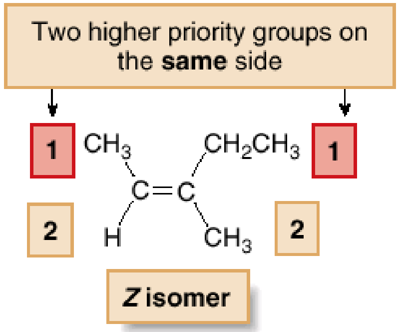
- Divide the double bond in half, and assign the numbers **1** and **2** to indicate the relative priority of the two groups on each end—the higher priority group is labeled **1,** and the lower priority group is labeled **2.**



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



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



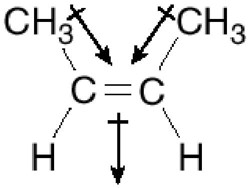
(*Z*)-3-methyl-2-pentene

- 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.**

Physical Properties

- A small dipole is associated with the C(sp2)-C(sp3) bond.
- A consequence of this dipole is that cis and trans alkenes often have different physical properties.
- *cis*-2-Butene has a higher b. p.(4°C) than *trans*-2-butene (1°C).

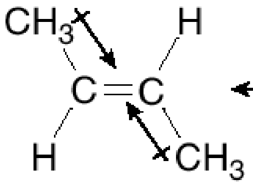
more polar isomer



a small net dipole

cis-2-butene

higher bp



no net dipole

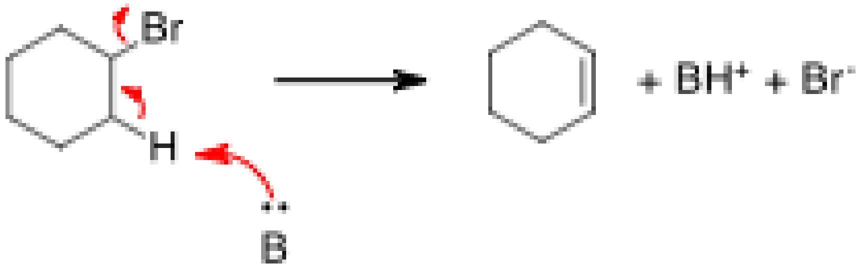
trans-2-butene

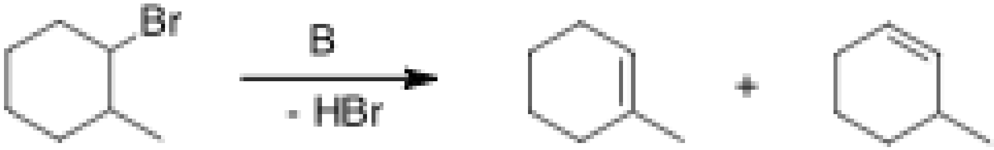
lower bp

less polar isomer

- A cis alkene is more polar than a trans alkene, giving it a slightly higher boiling point and making it more soluble in polar solvents.

Preparation of Alkenes.
1 Dehydroalogenation



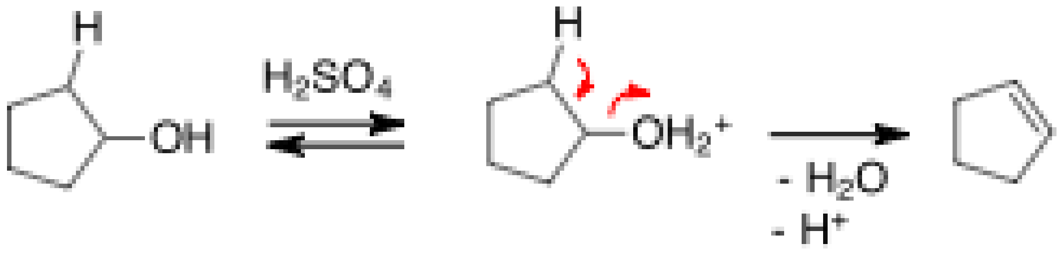


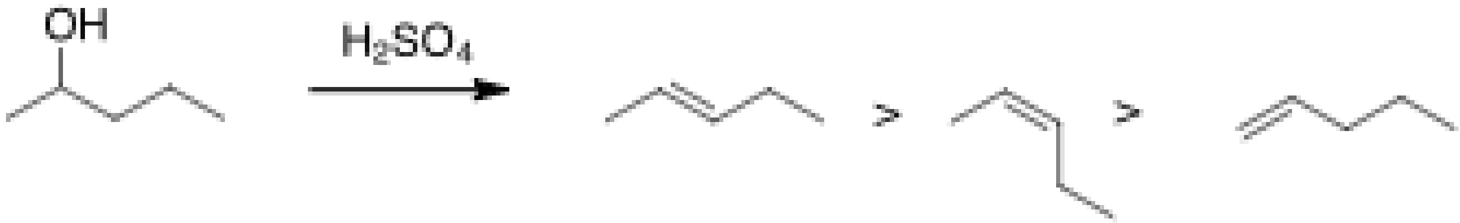
major
product

Saytzev's rule.

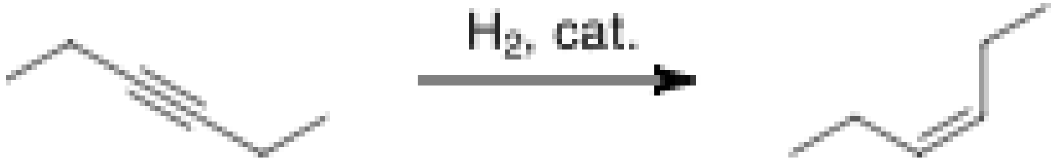
The more substituted alkene (more stable) is favoured

Preparation of Alkenes.
2 Dehydration



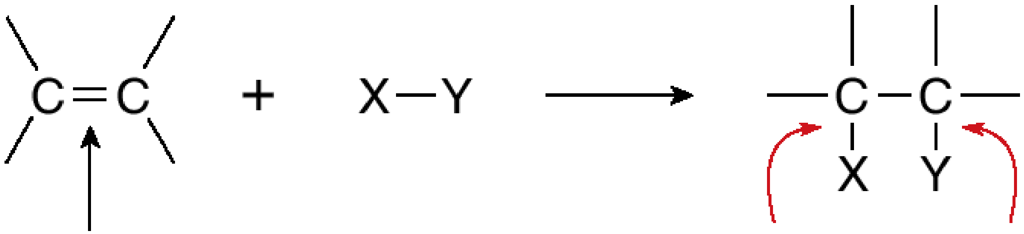


Preparation of Alkenes. 3
Hydrogenation/Reduction of Alkynes



Introduction to Addition Reactions

Addition reaction



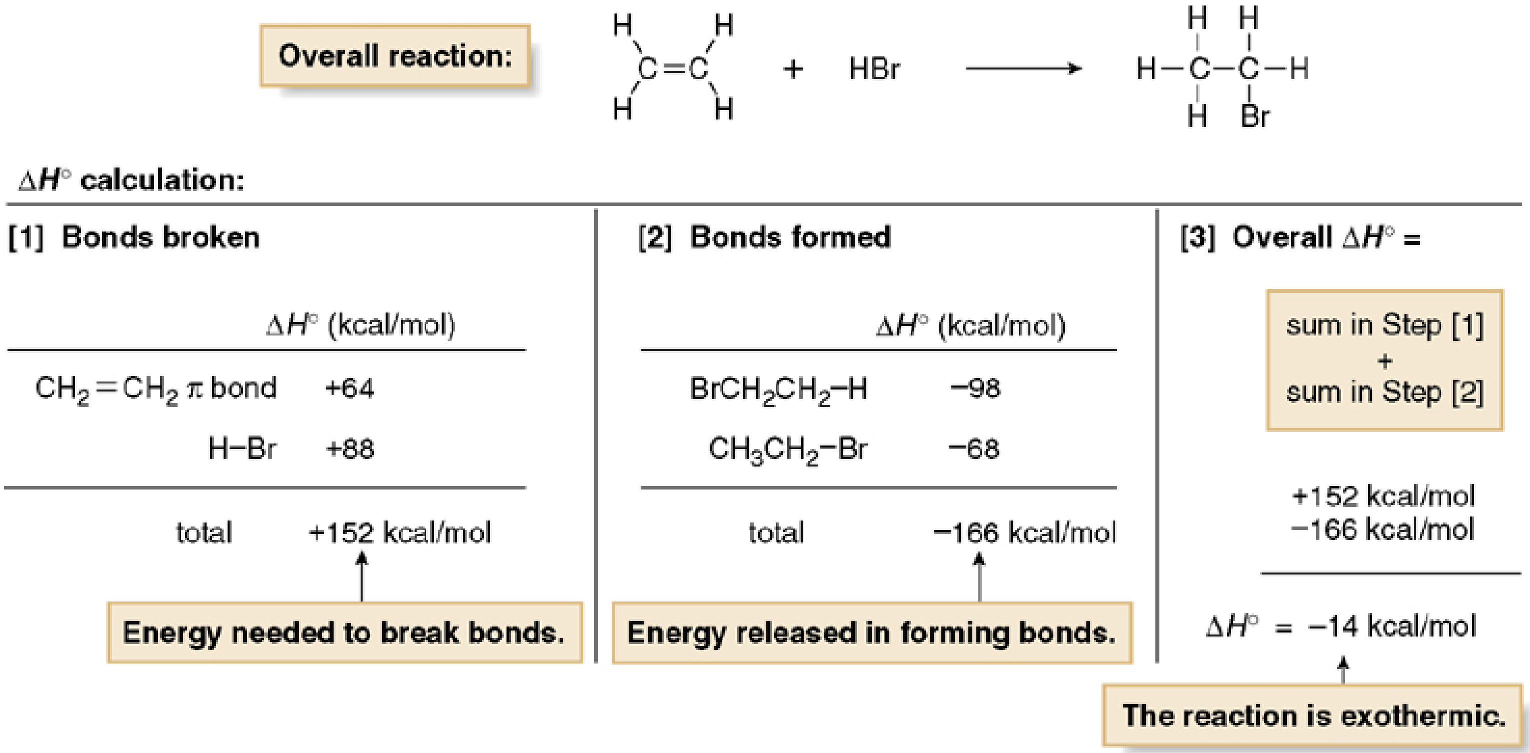
This π bond is broken.

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.

Thermodynamics of Addition Reactions

- Addition reactions are exothermic because the two σ bonds formed in the product are stronger than the σ and π bonds broken in the reactants.



Overall reaction:

$\Delta H°$ calculation:

[1] Bonds broken

	$\Delta H°$ (kcal/mol)
$CH_2=CH_2$ π bond	+64
H–Br	+88
total	+152 kcal/mol

Energy needed to break bonds.

[2] Bonds formed

	$\Delta H°$ (kcal/mol)
$BrCH_2CH_2–H$	−98
$CH_3CH_2–Br$	−68
total	−166 kcal/mol

Energy released in forming bonds.

[3] Overall $\Delta H°$ =

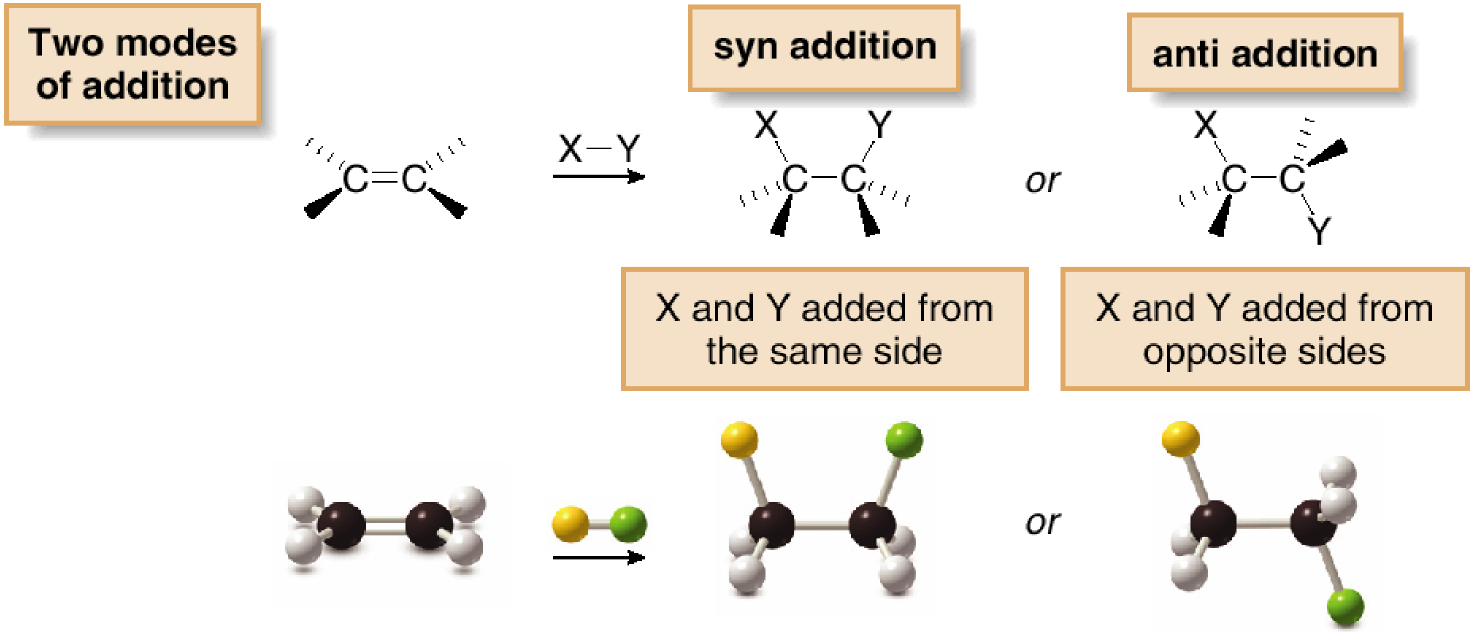
sum in Step [1]
+
sum in Step [2]

+152 kcal/mol
−166 kcal/mol

$\Delta H° = −14$ kcal/mol

The reaction is exothermic.

Introduction to Addition Reactions



Two modes of addition

syn addition

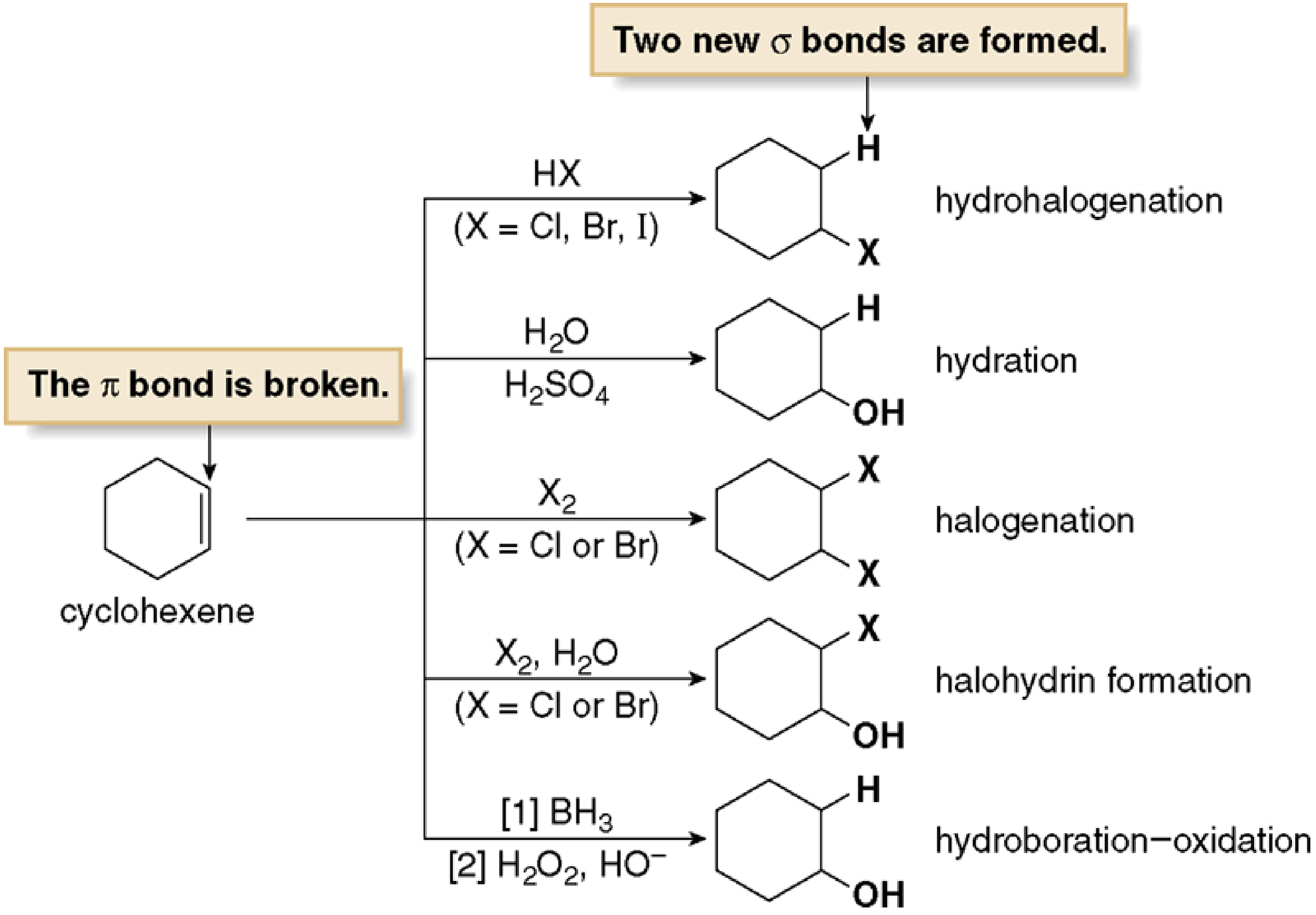
X and Y added from the same side

anti addition

X and Y added from opposite sides

- *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



Two new σ bonds are formed.

The π bond is broken.

cyclohexene

HX (X = Cl, Br, I) — hydrohalogenation

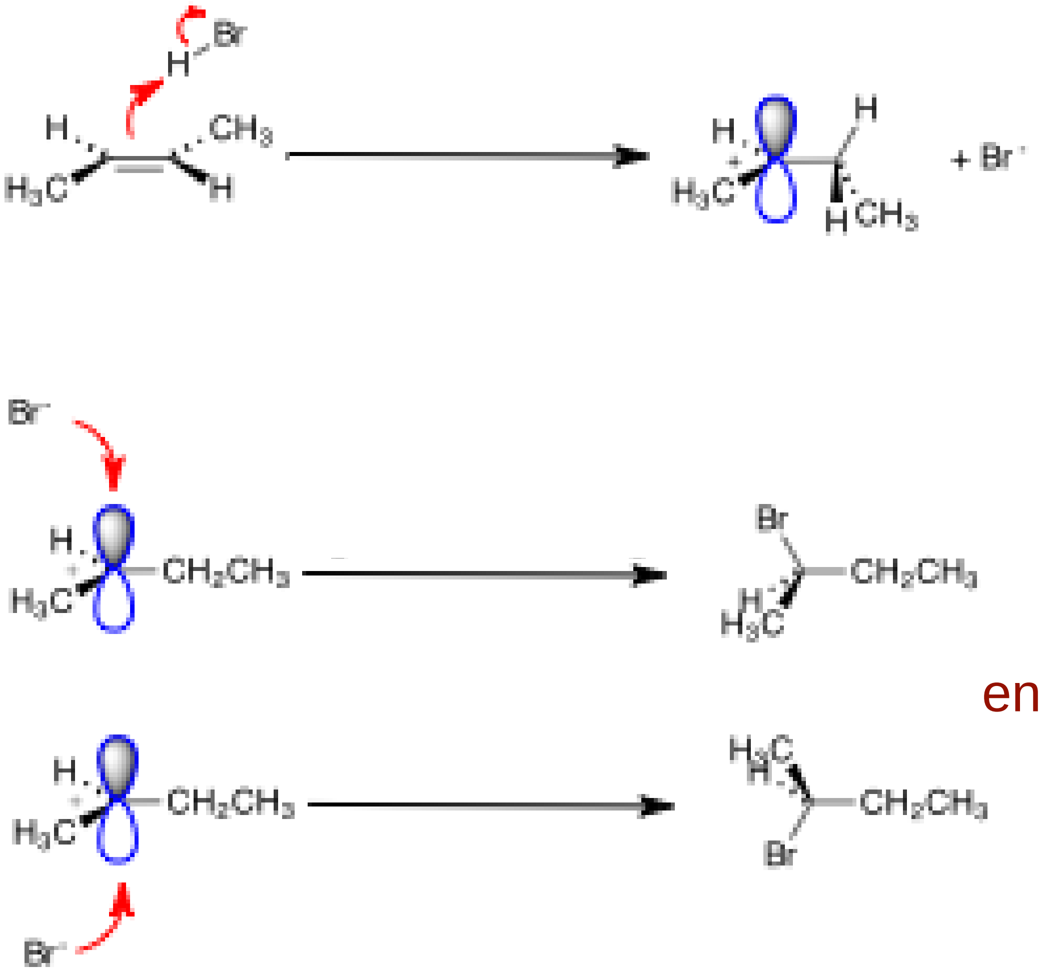
H_2O, H_2SO_4 — hydration

X_2 (X = Cl or Br) — halogenation

X_2, H_2O (X = Cl or Br) — halohydrin formation

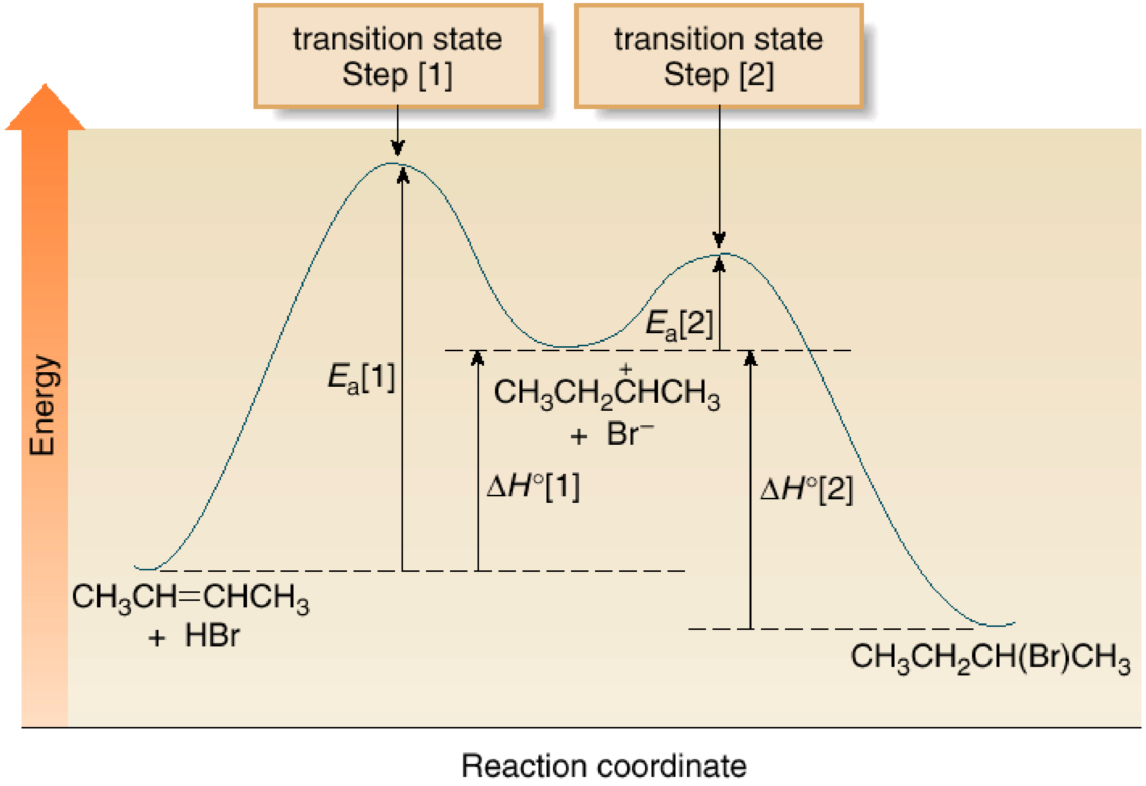
[1] BH_3 [2] H_2O_2, HO^- — hydroboration–oxidation

Hydrohalogenation. Mechanism

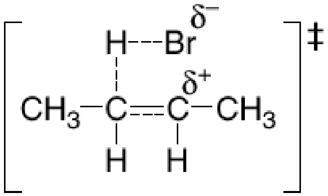


enantiomers

Hydrohalogenation

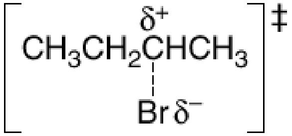


transition state Step [1] =



$$\left[CH_3-\underset{H}{\overset{H---Br^{\delta-}}{C}}{=}{=}\underset{H}{\overset{\delta+}{C}}-CH_3 \right]^{\ddagger}$$

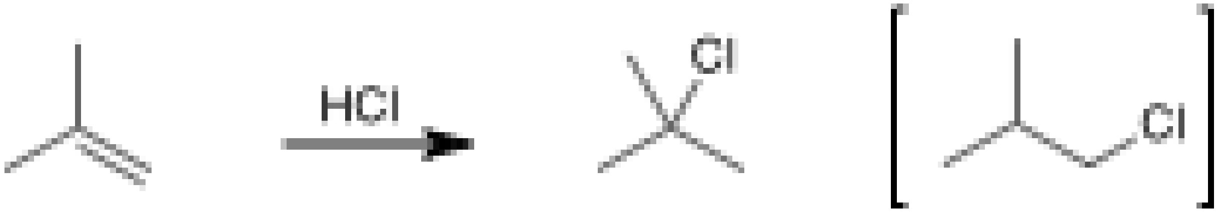
transition state Step [2] =



$$\left[CH_3CH_2\underset{Br\,\delta^-}{\overset{\delta+}{C}}HCH_3 \right]^{\ddagger}$$

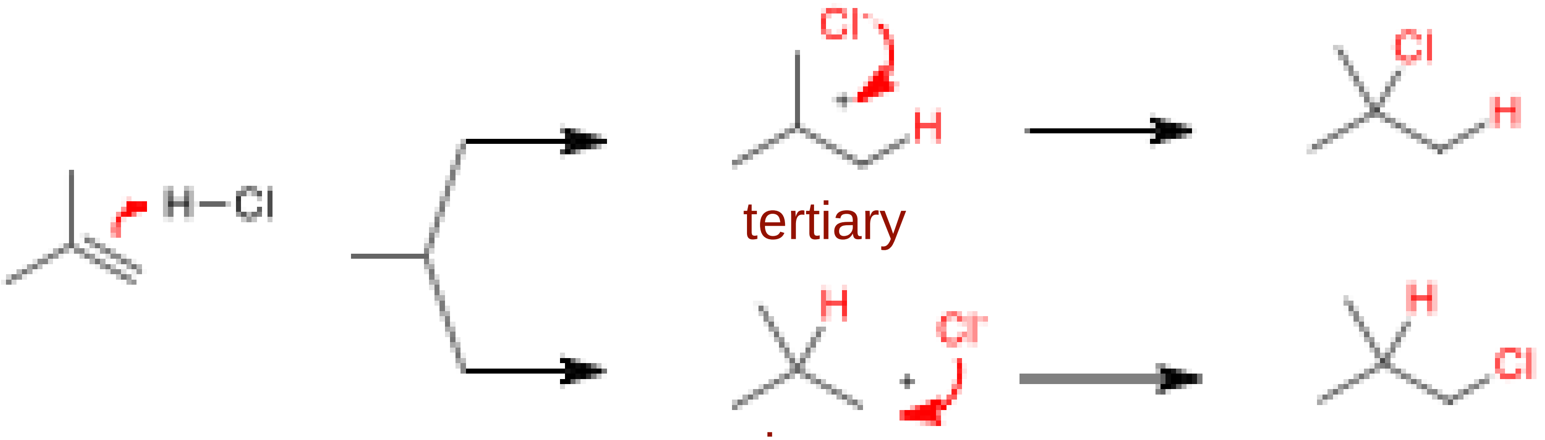
- The mechanism has two steps, so there are two energy barriers.
- Step [1] is rate-determining.

Hydrohalogenation — Markovnikov's Rule



not formed

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



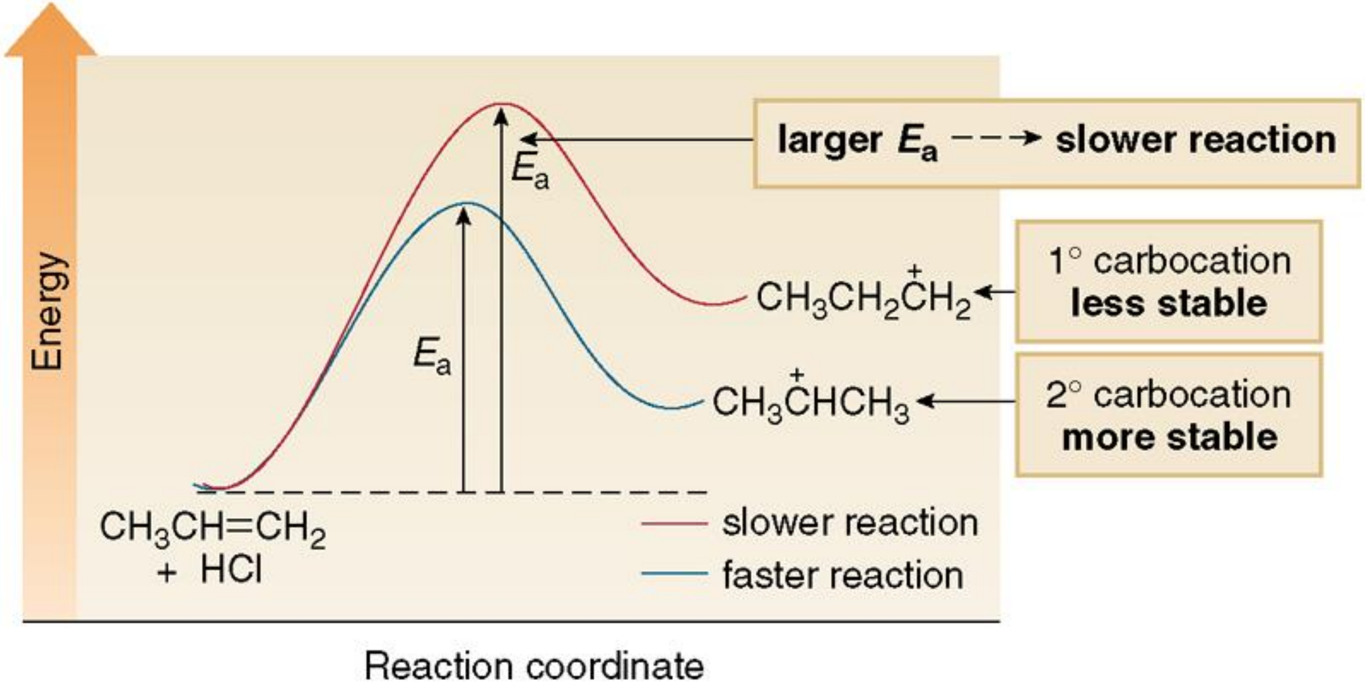
tertiary

primary

not observed

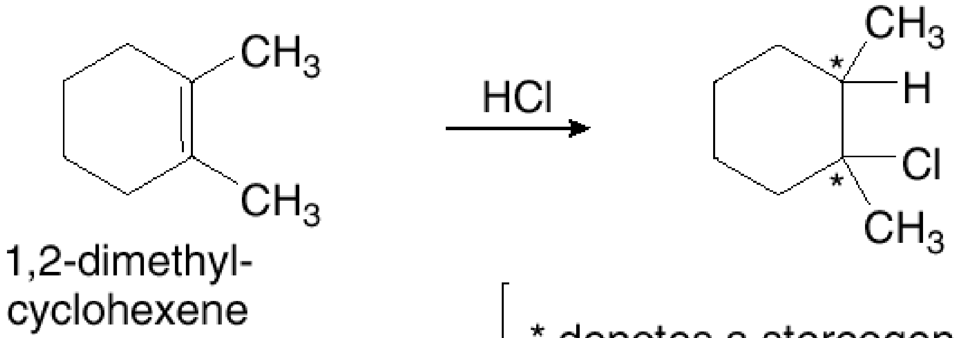
Hydrohalogenation—Markovnikov's Rule

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



Hydrohalogenation—Stereochemistry

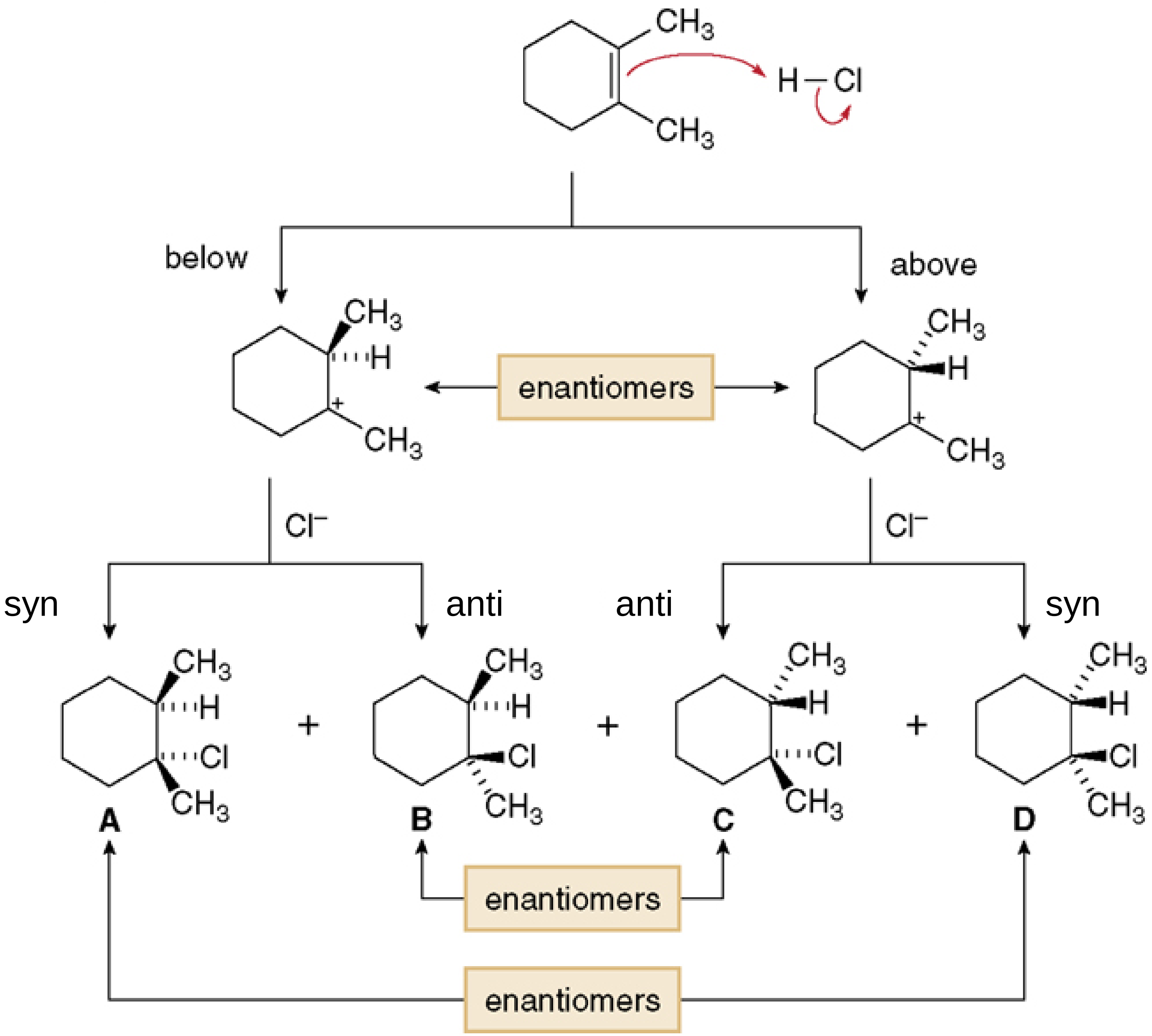
- Addition of HX to 1,2-dimethylcyclohexene forms two new stereogenic centers.



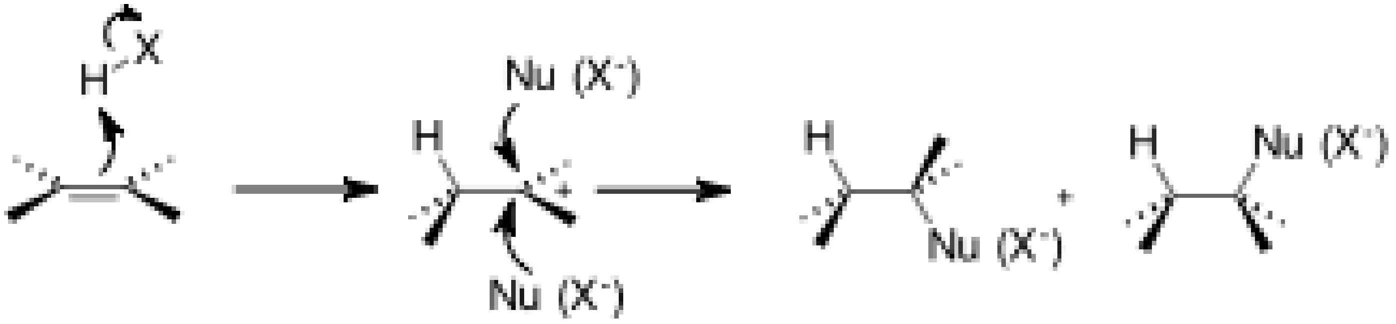
Two new stereogenic centers are formed.

[* denotes a stereogenic center]

Hydrohalogenation—Stereochemistry

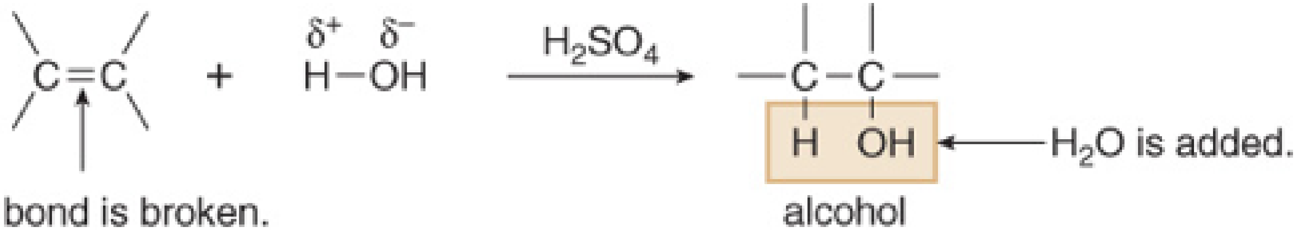


Hydrohalogenation—Summary



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

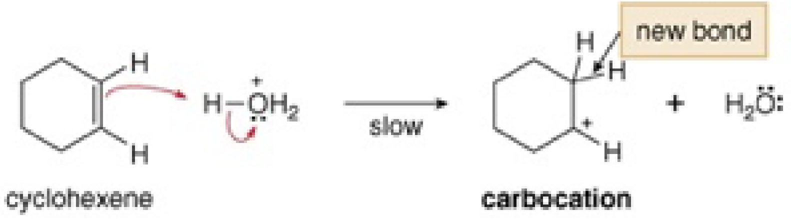


This π bond is broken.

alcohol

H_2O is added.

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

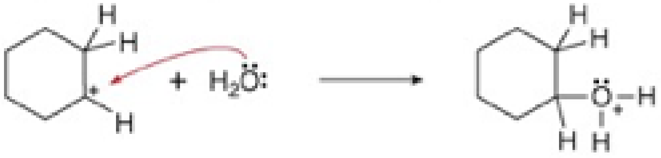


cyclohexene

carbocation

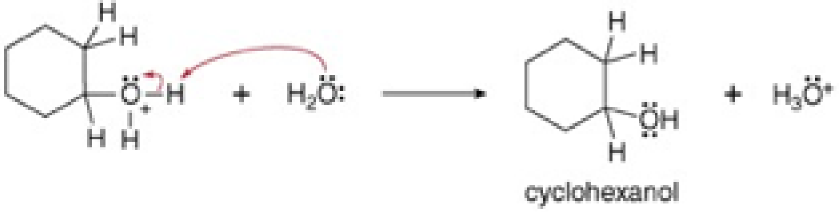
- The π bond attacks H_3O^+, thus forming a new C−H bond while breaking the H−O bond. Because the remaining carbon atom of the original double bond is left with only six electrons, a **carbocation** intermediate is formed. This step is **rate-determining** because two bonds are broken but only one bond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

Step [2] Nucleophilic attack of H_2O



- **Nucleophilic attack of H_2O** on the carbocation forms the new C−O bond.

Step [3] Loss of a proton

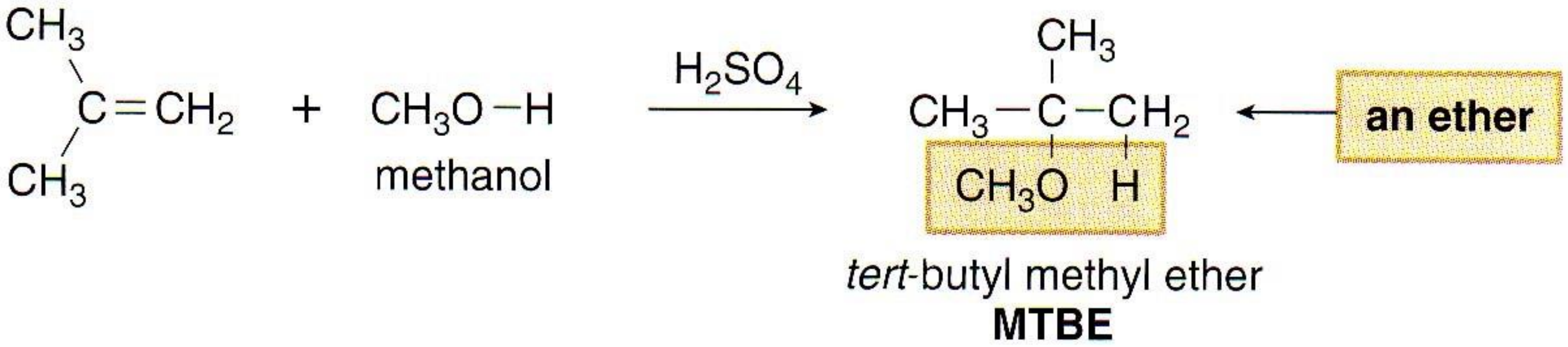


cyclohexanol

- 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.**

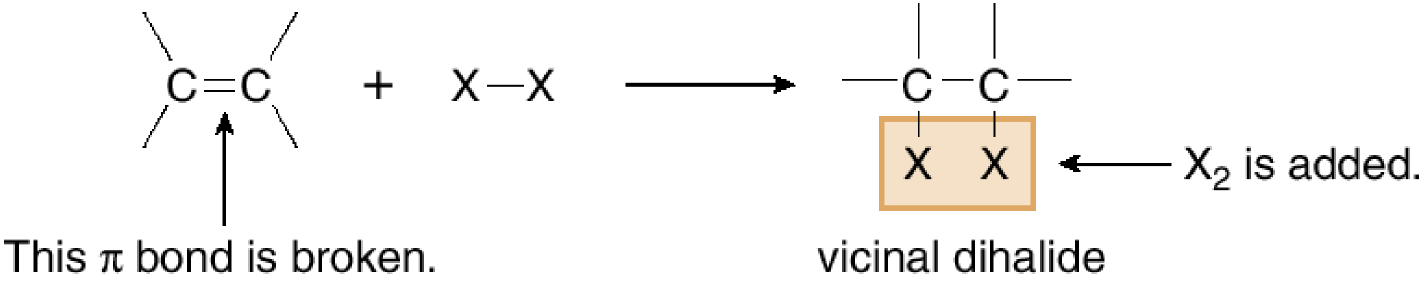
Electrophilic Addition of Alcohols

- 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.



Halogenation—Addition of Halogen

Halogenation

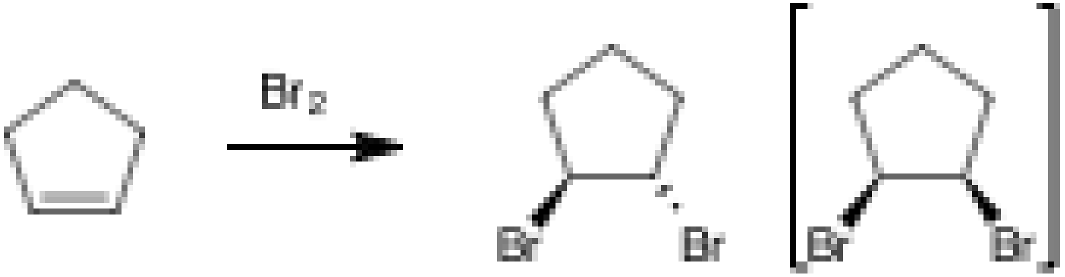


This π bond is broken.

vicinal dihalide

X_2 is added.

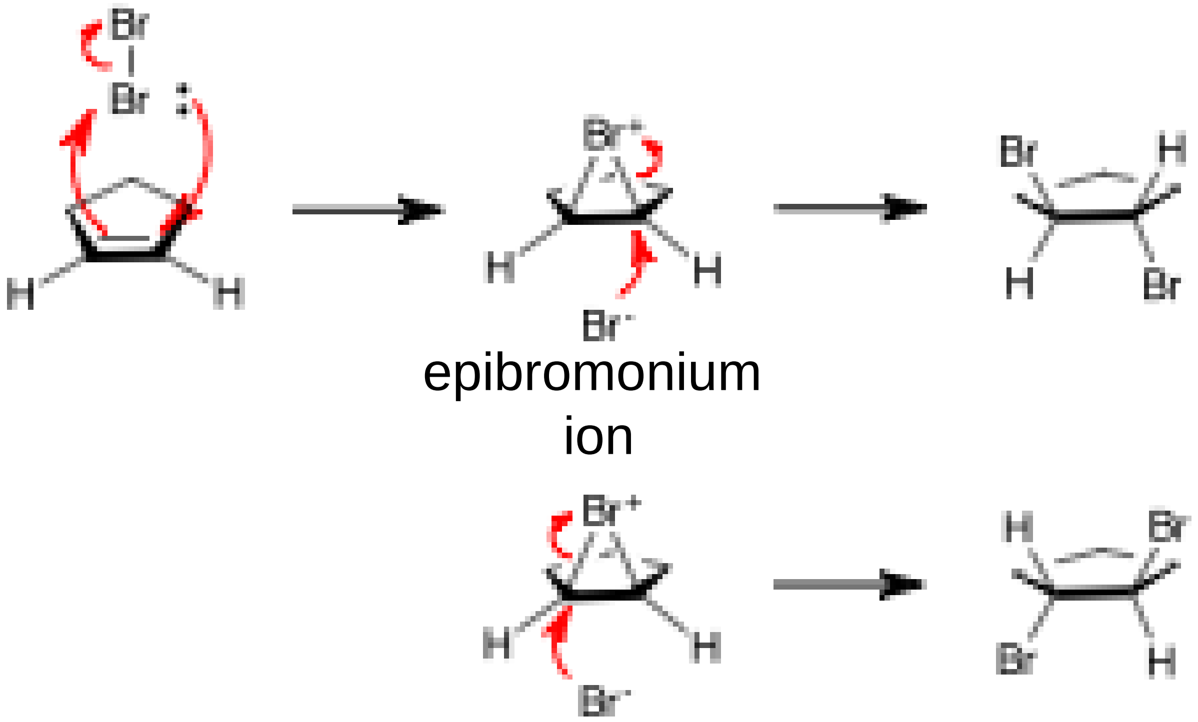
Anti addition



trans

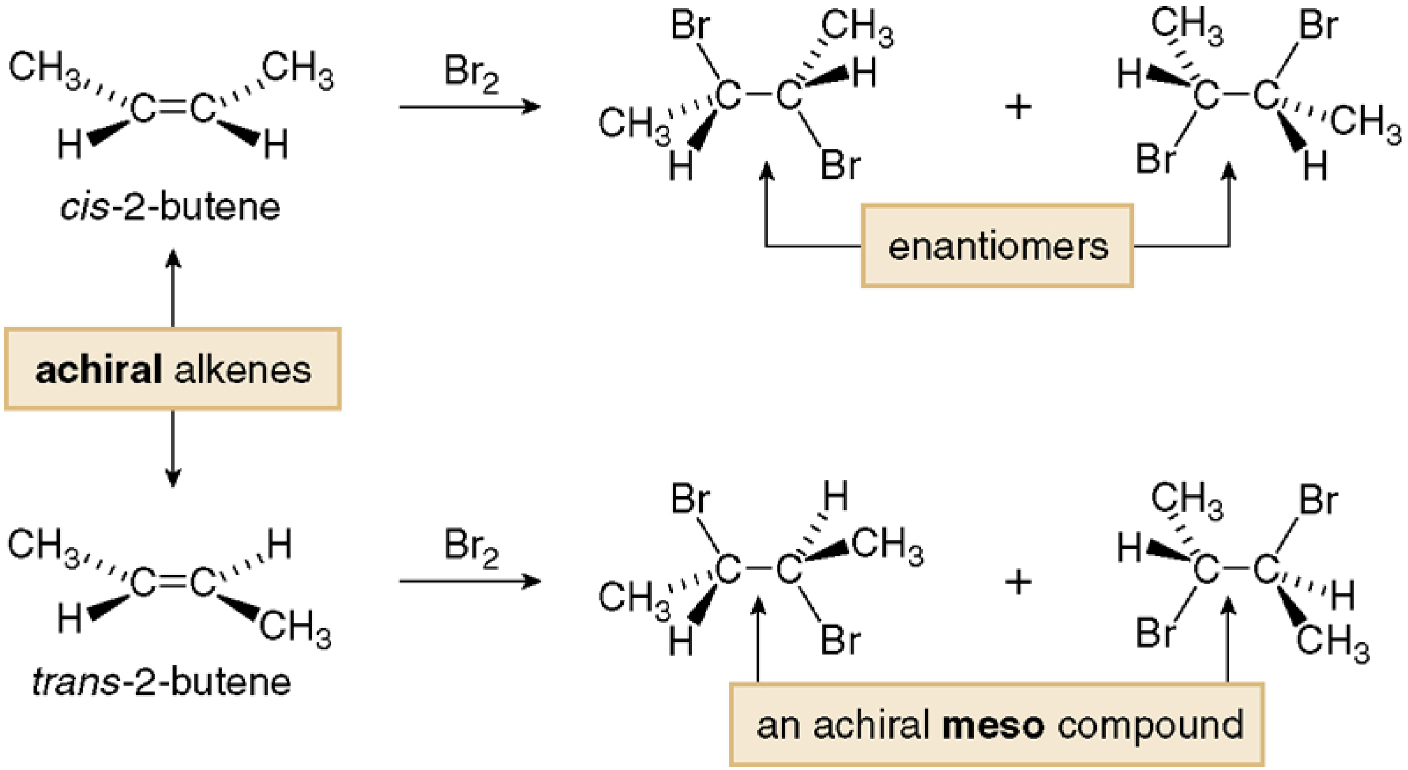
cis
(not observed)

Halogenation—Mechanism



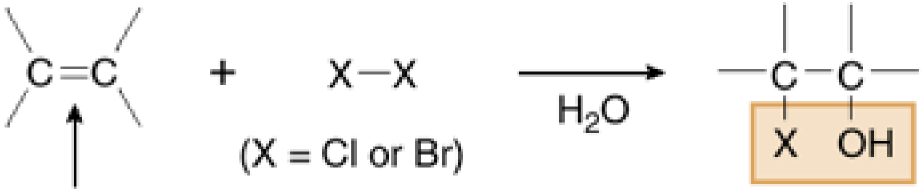
epibromonium ion

Halogenation—Stereochemistry



Halohydrin Formation

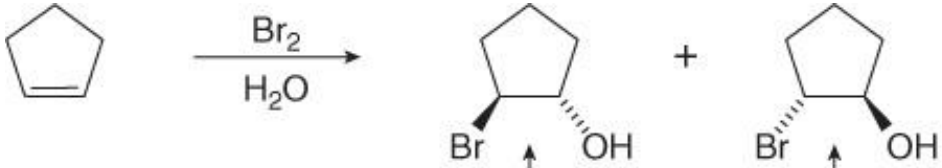
General reaction



This π bond is broken.

halohydrin

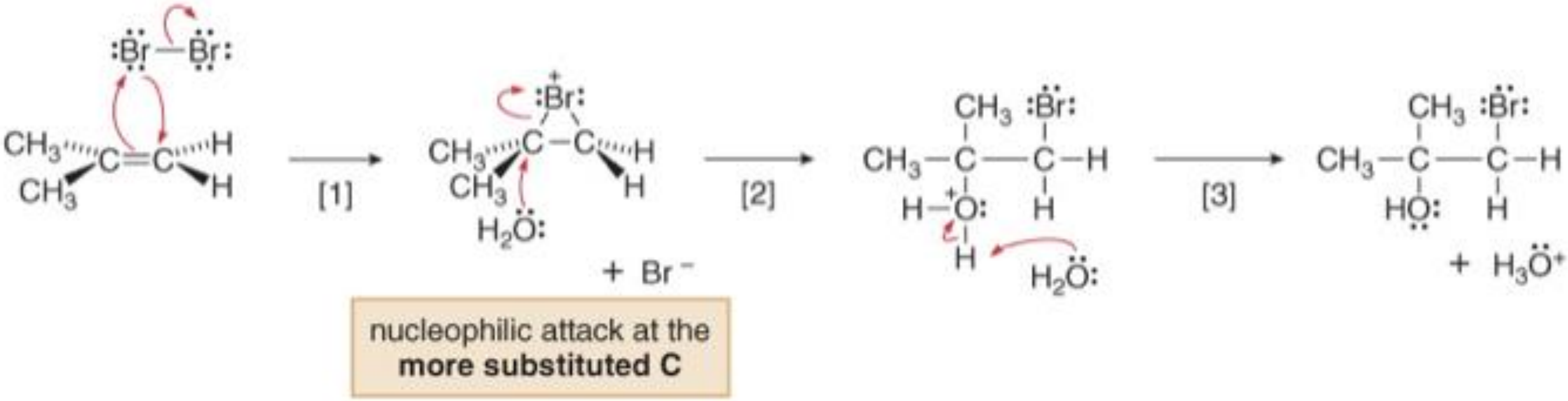
X and OH added



anti addition of Br and OH

trans enantiomers

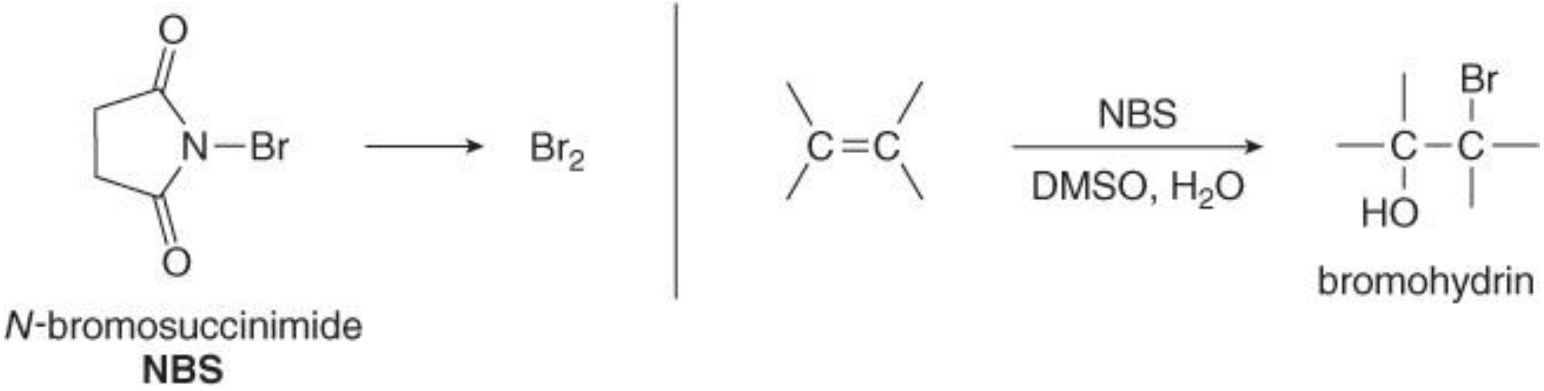
Halohydrin Formation



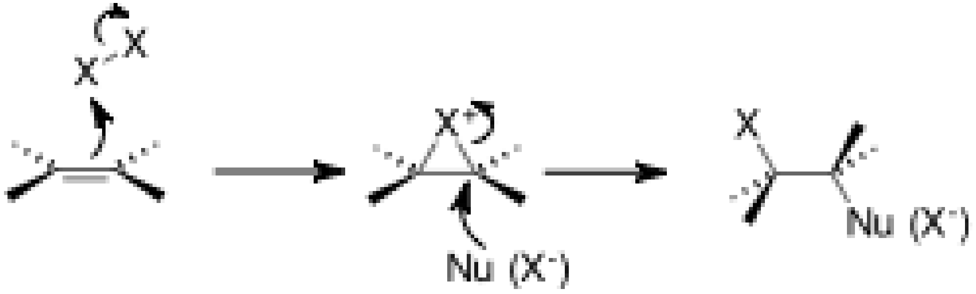
nucleophilic attack at the **more substituted C**

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.

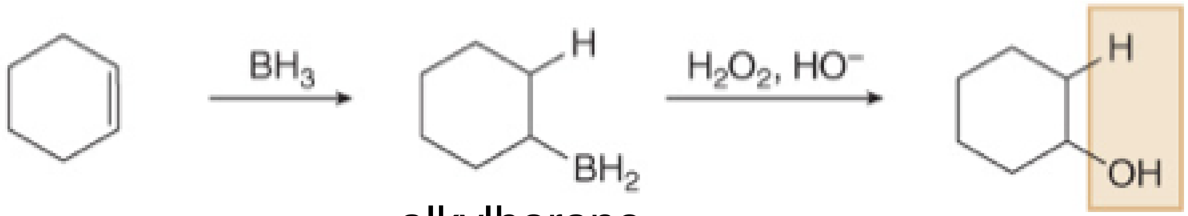


Halogenation and Halohydrin Formation



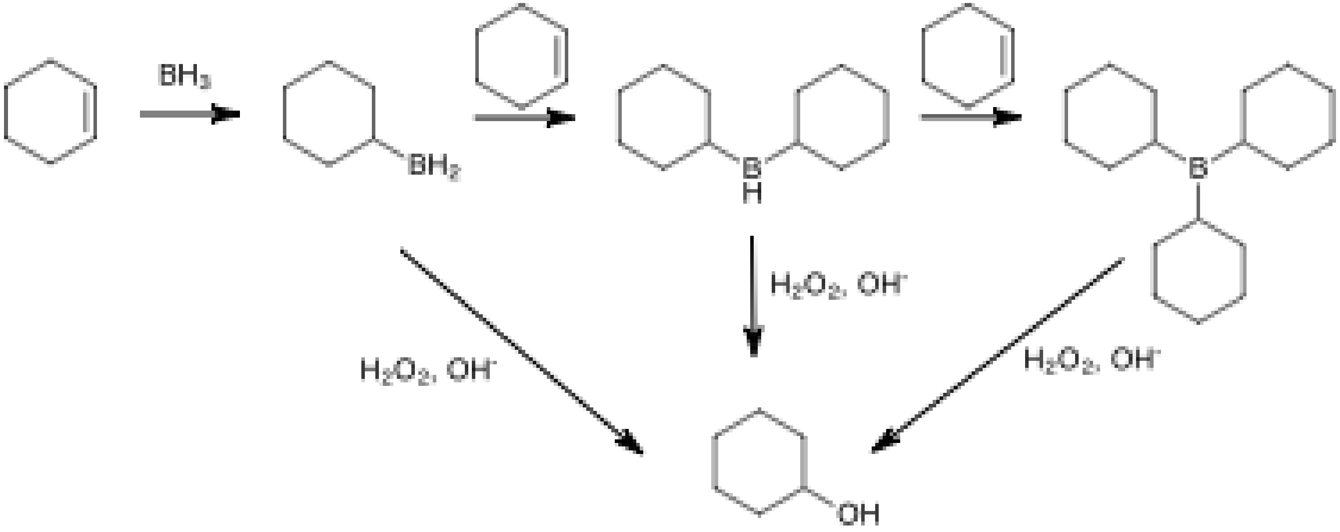
Mechanism	• The mechanism involves two steps. • The rate-determining step forms a bridged halonium ion. • No rearrangements can occur.
Regioselectivity	• Markovnikov's rule is followed. X^{+} bonds to the less substituted carbon.
Stereochemistry	• Anti addition occurs.

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.



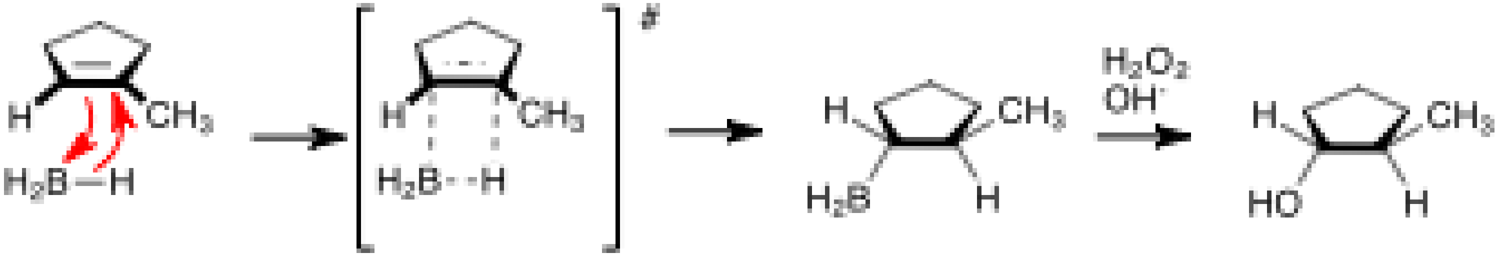
Hydroboration—Oxidation

- 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).

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}BH_2 \xrightarrow{H_2O_2,\ OH^-} CH_3\text{-}CH_2\text{-}CH_2\text{-}OH$$

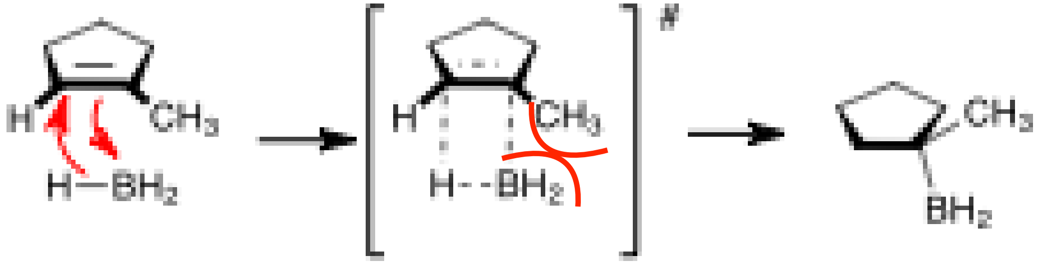
- Oxidation replaces the C—B bond with a C—O bond, forming a new OH group with retention of configuration.

Hydroboration—Oxidation



1-methyl
cyclopentane

trans, secondary
alcohol

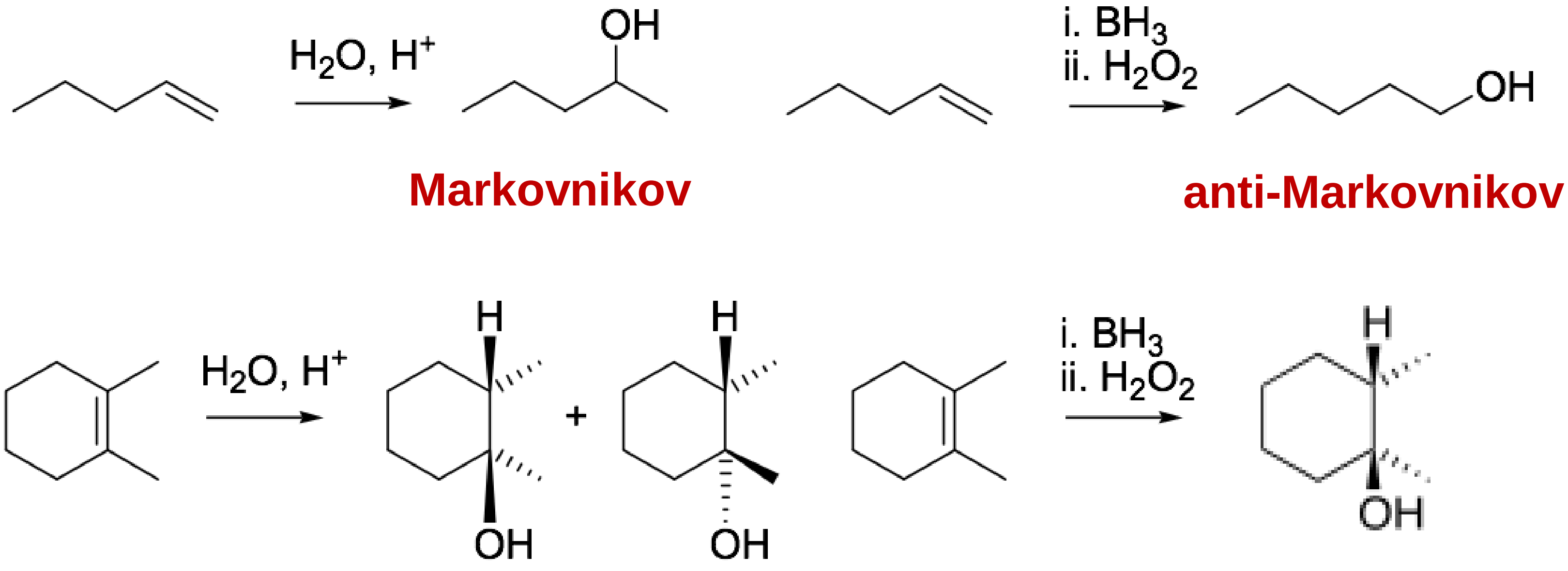


sterically
hindered

not
observed

Hydroboration—Oxidation

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



Markovnikov

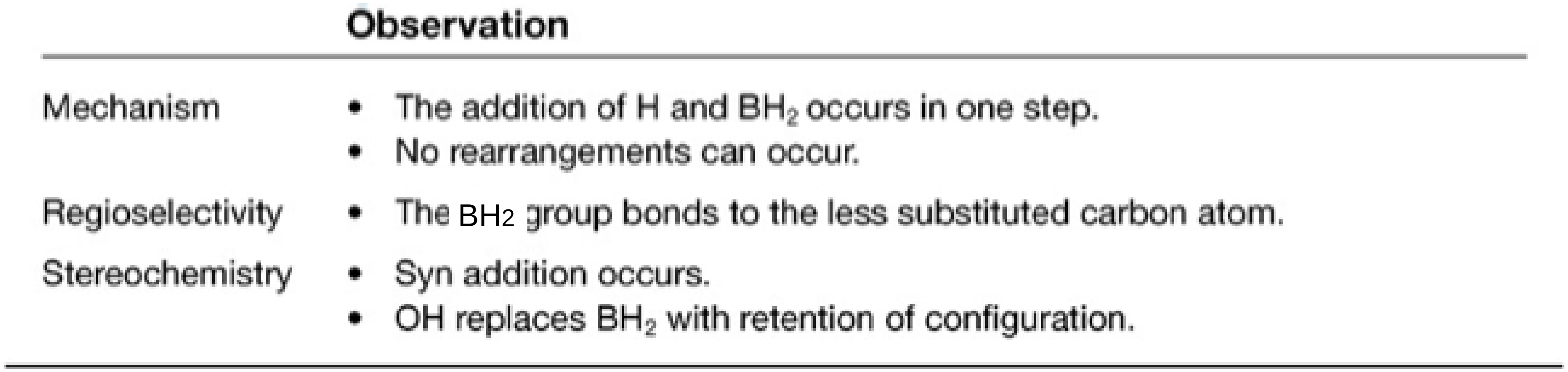
anti-Markovnikov

syn

anti

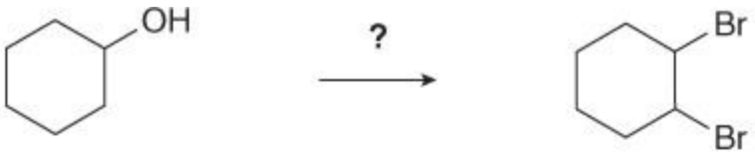
syn

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



cyclohexanol

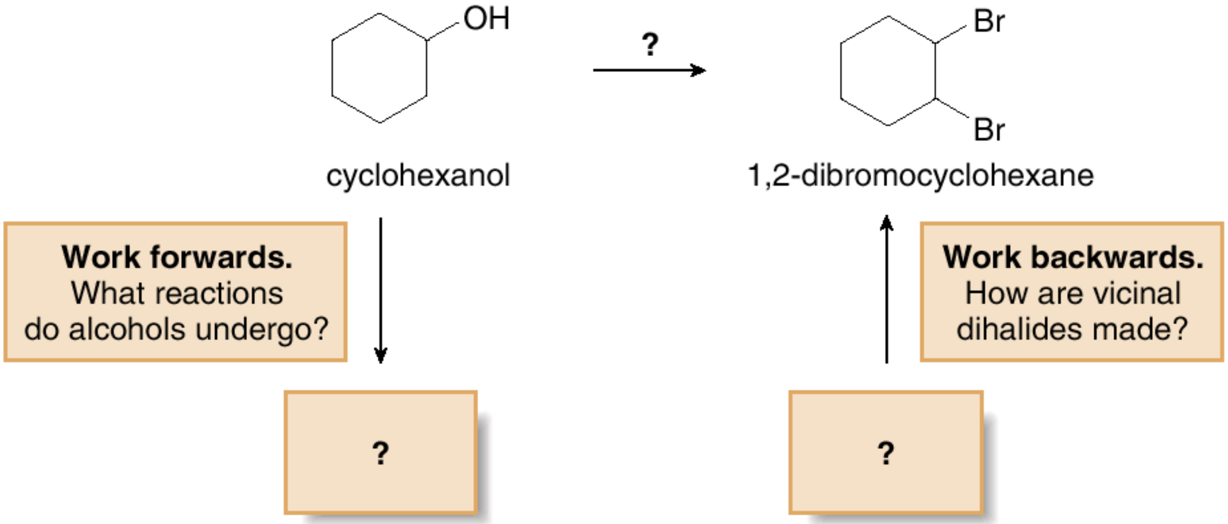
starting material

1,2-dibromocyclohexane

product

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?



cyclohexanol

1,2-dibromocyclohexane

Work forwards.
What reactions
do alcohols undergo?

Work backwards.
How are vicinal
dihalides made?

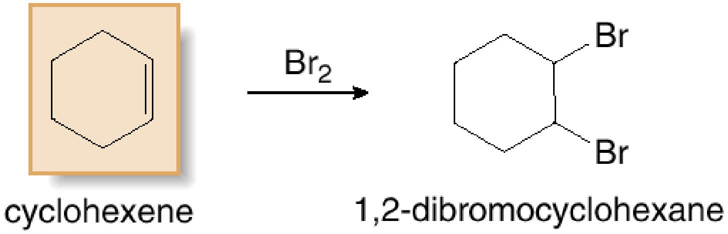
?

?

Alkenes in Organic Synthesis

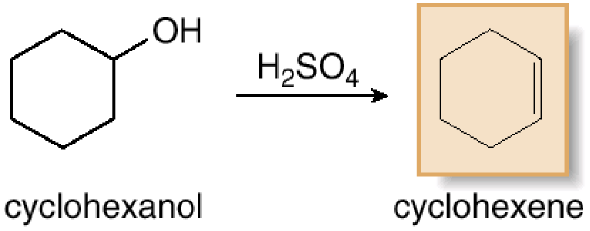
Working backwards:

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



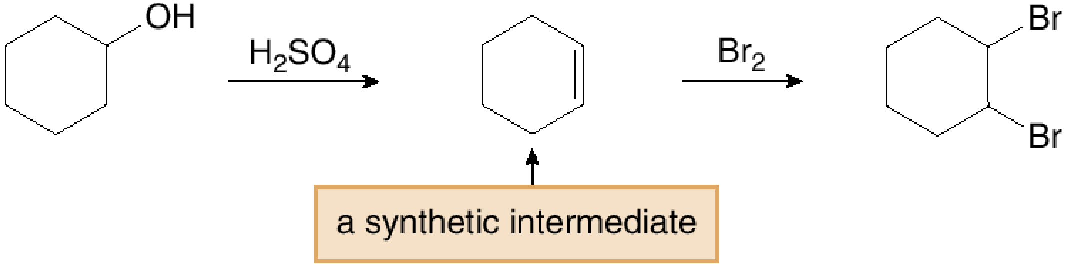
Working forwards:

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



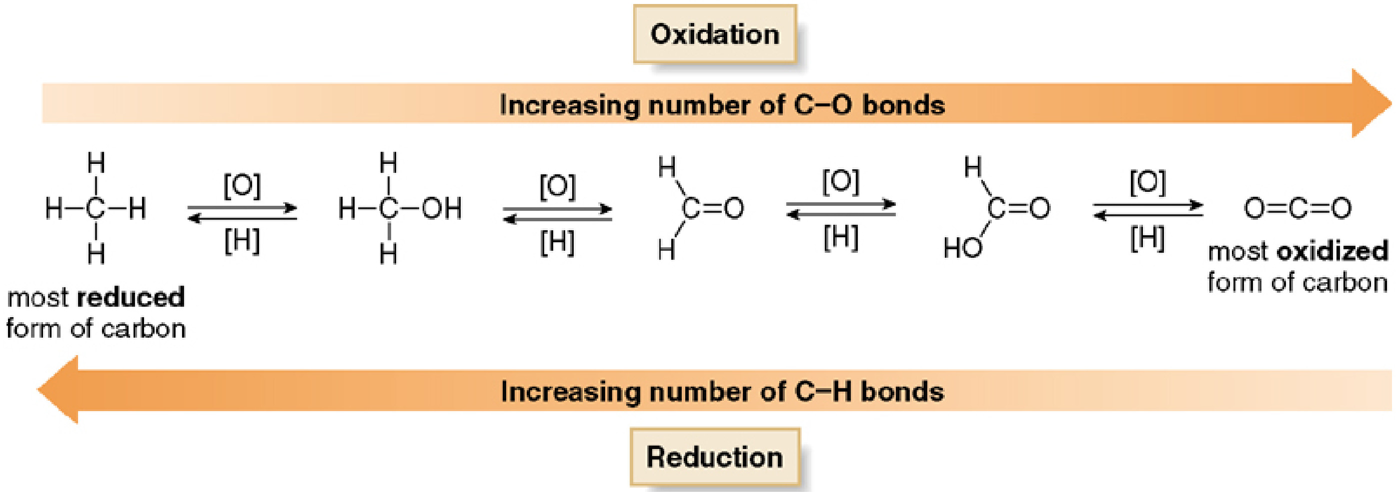
Cyclohexene is called a **synthetic intermediate,** or simply an **intermediate,** because it is the **product of one step and the starting material of another.** We now have a two-step sequence to convert cyclohexanol to 1,2-dibromocyclohexane, and the synthesis is complete. Take note of the central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

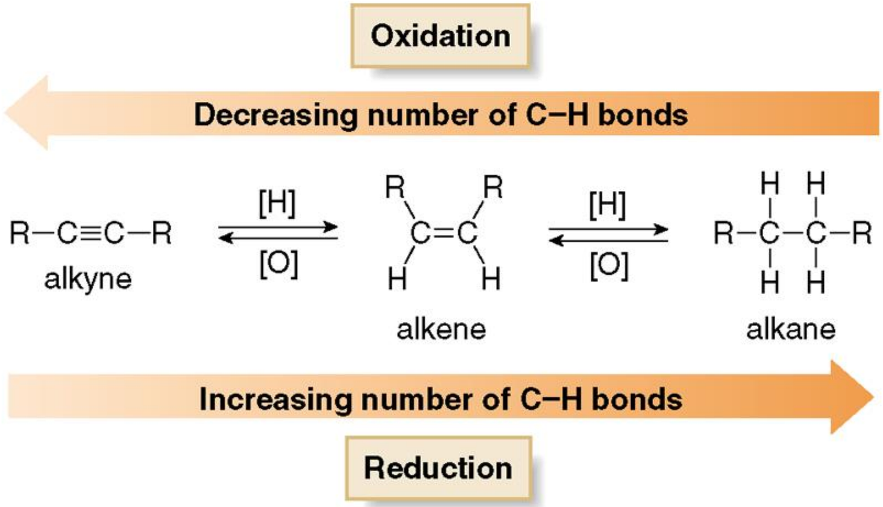
A two-step synthesis



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.



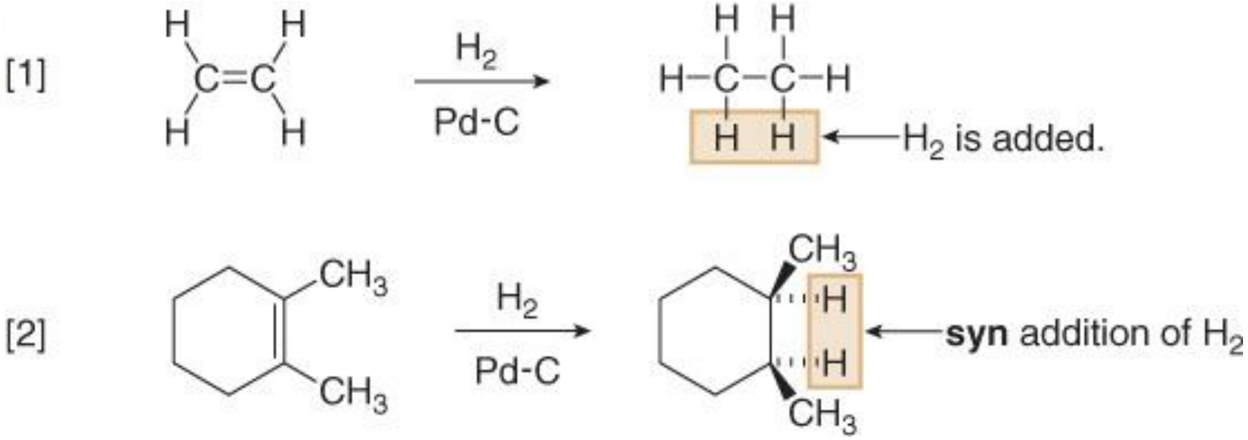


Catalytic Hydrogenation

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

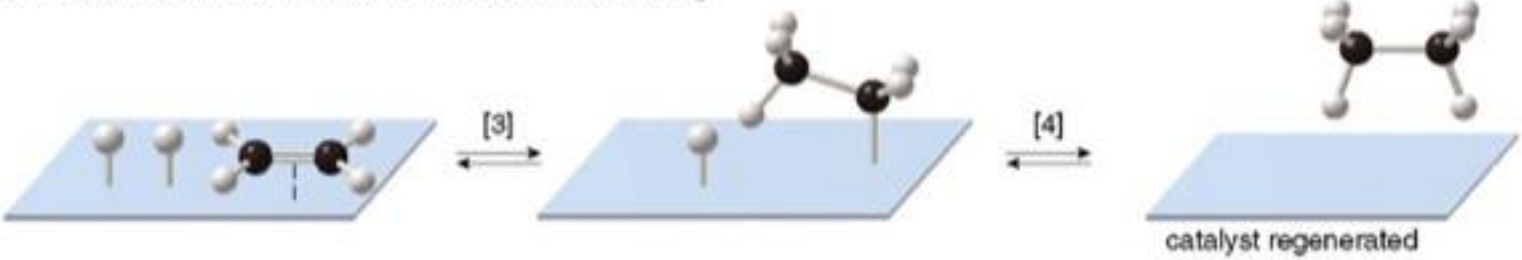


Catalytic Hydrogenation

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.

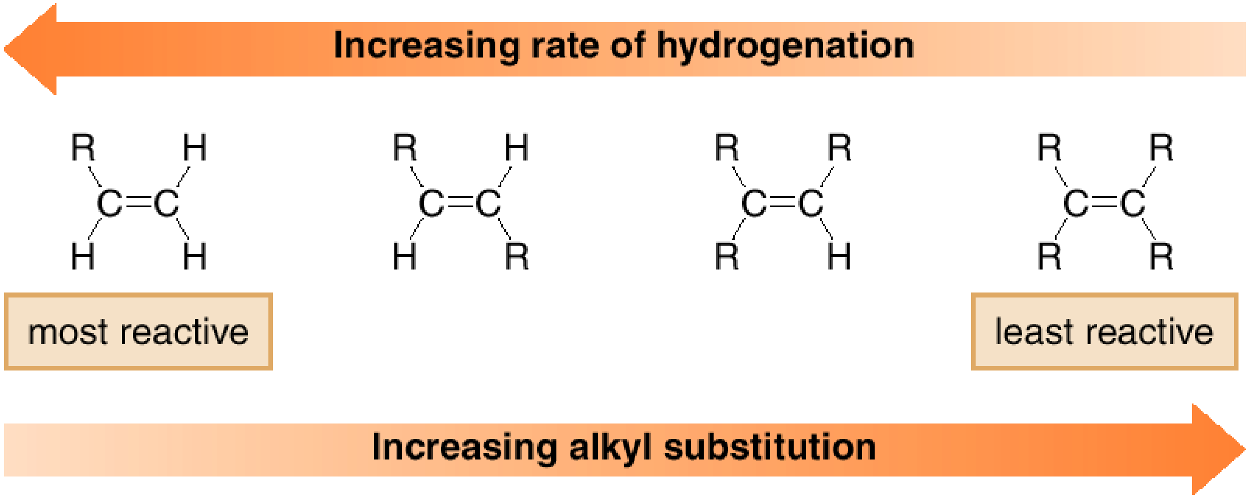
Steps [3] and [4] Sequential addition of the elements of H_2



- **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

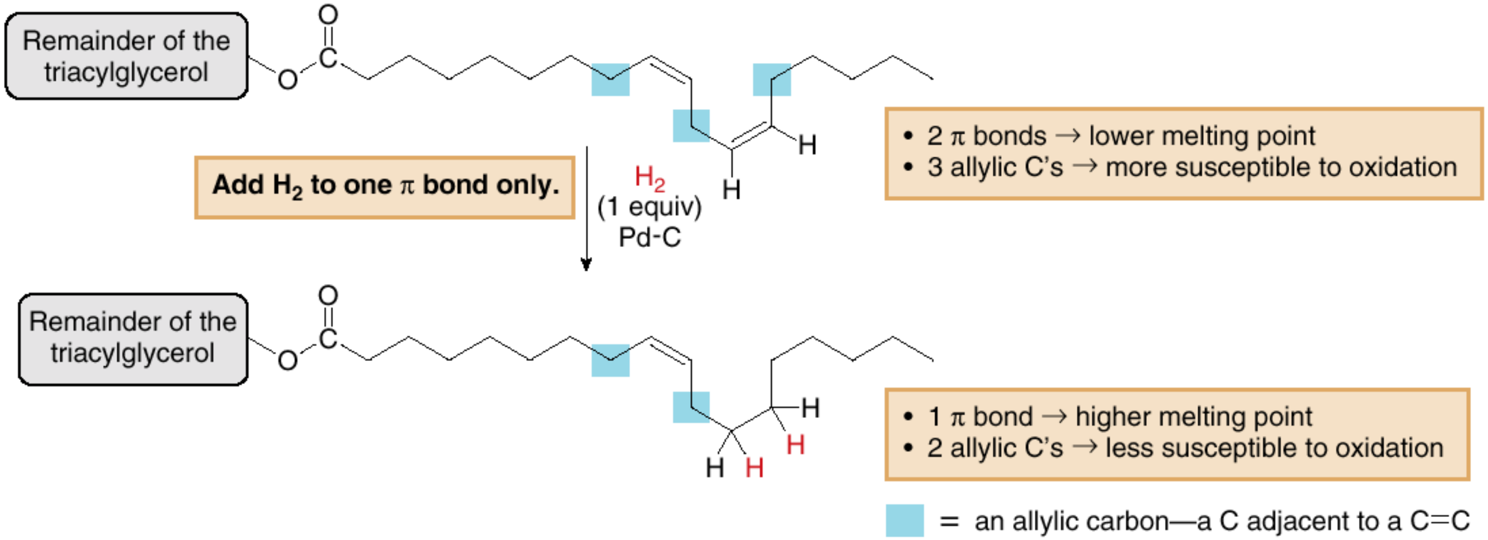
most reactive

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.



Add H_2 to one π bond only.

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

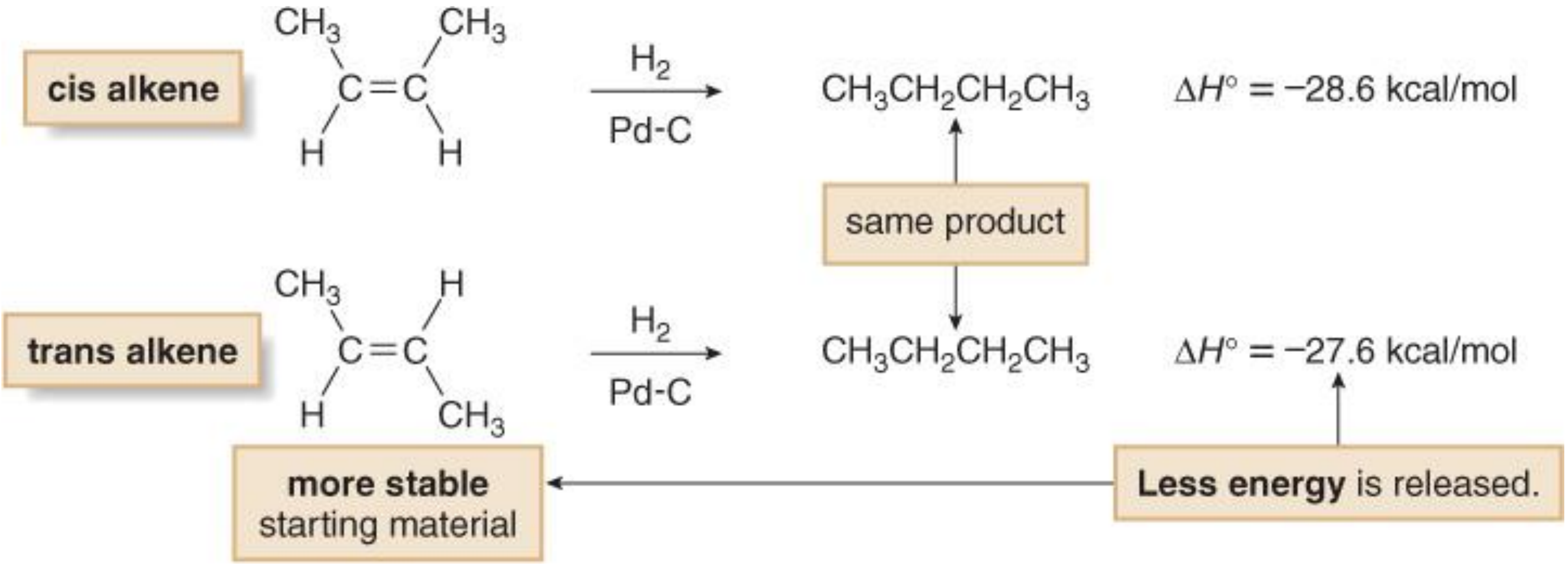
- 1 π bond → higher melting point
- 2 allylic C's → less susceptible to oxidation

🟦 = 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.

Catalytic Hydrogenation

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

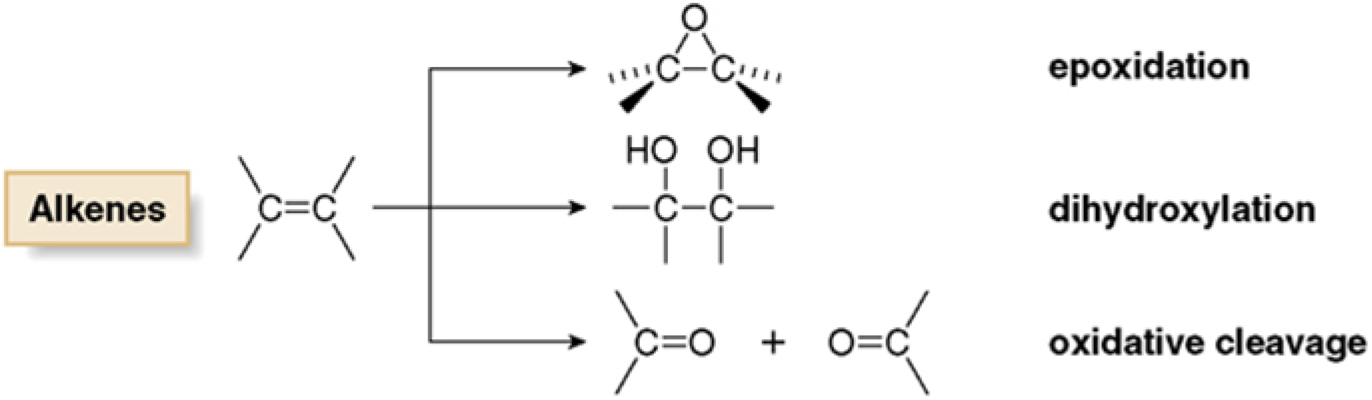


Oxidations

Oxidizing agents:

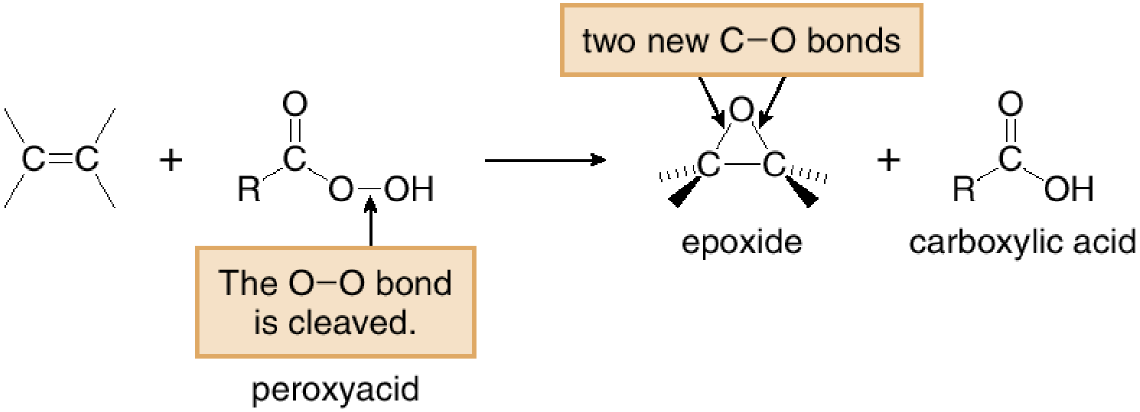
- Reagents containing an O—O bond: O_2, O_3, H_2O_2, ROOH, RCOOOH.
- Reagents containing metal-oxygen bonds: Cr(VI), Mn(VII), Os(VIII), Ag(I).

Reactions:



Epoxidation

Epoxidation



two new C–O bonds

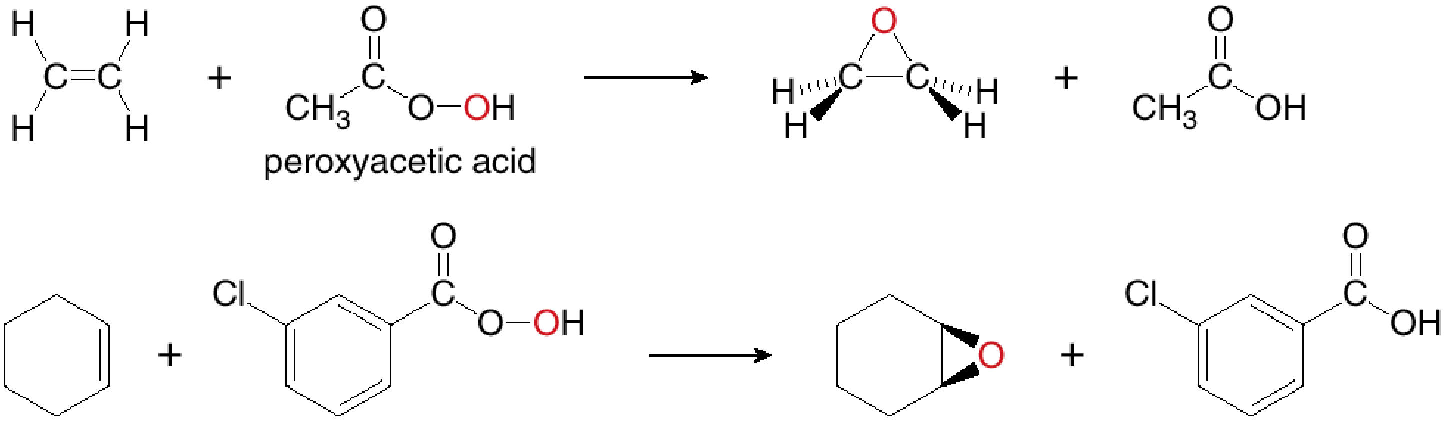
The O–O bond is cleaved.

peroxyacid

epoxide

carboxylic acid

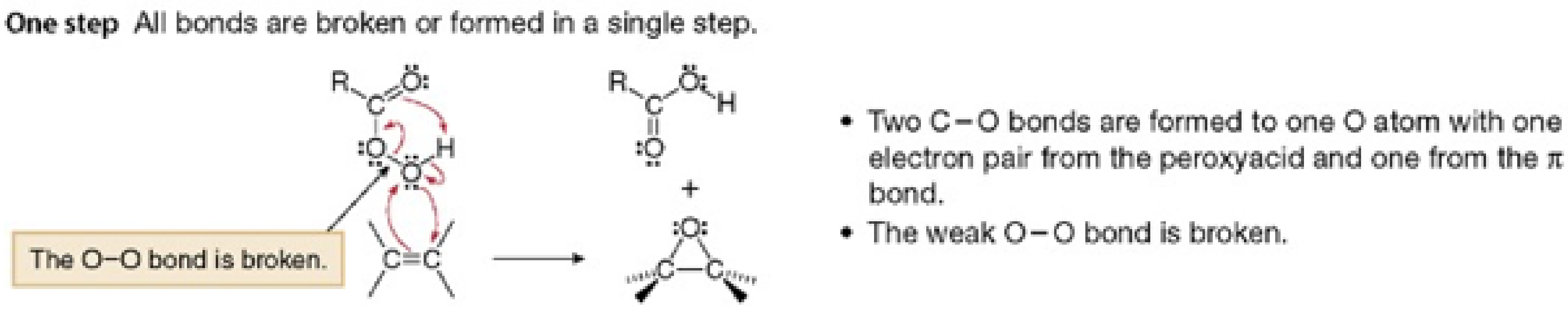
Examples



peroxyacetic acid

mCPBA

Epoxidation

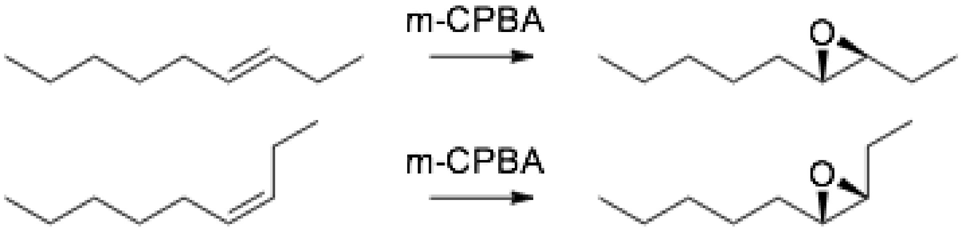


One step All bonds are broken or formed in a single step.

The O–O bond is broken.

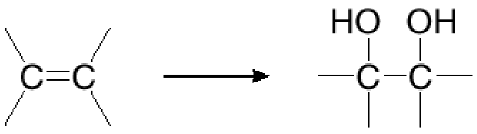
- Two C–O bonds are formed to one O atom with one electron pair from the peroxyacid and one from the π bond.
- The weak O–O bond is broken.

- Epoxidation is stereospecific.



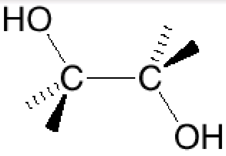
Dihydroxylation

Dihydroxylation—General reaction

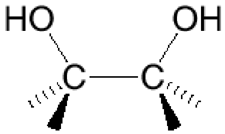


1,2-diol or glycol

Stereochemistry



or



anti addition product

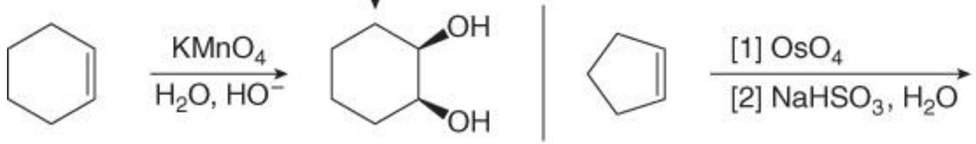
2 OH's added on **opposite** sides of the C=C

syn addition product

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

Syn dihydroxylation

***cis*-1,2-diols**

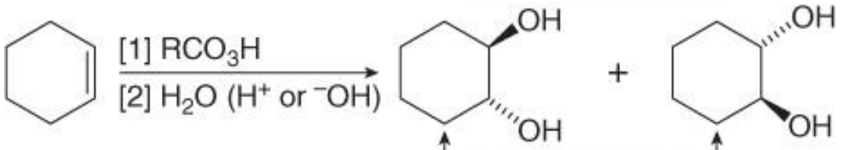


cis-1,2-cyclohexanediol

cis-1,2-cyclopentanediol

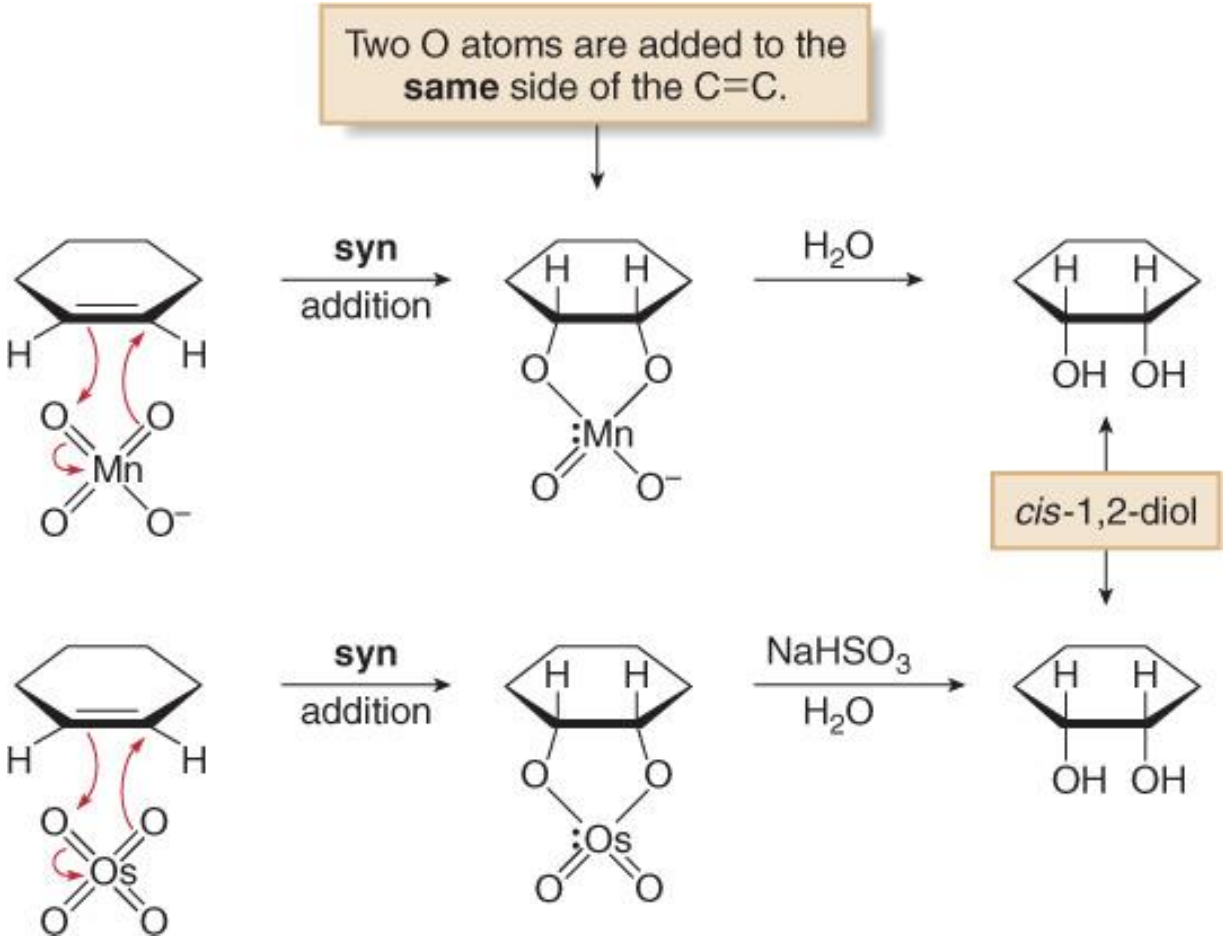
Anti dihydroxylation

***trans*-1,2-diols**



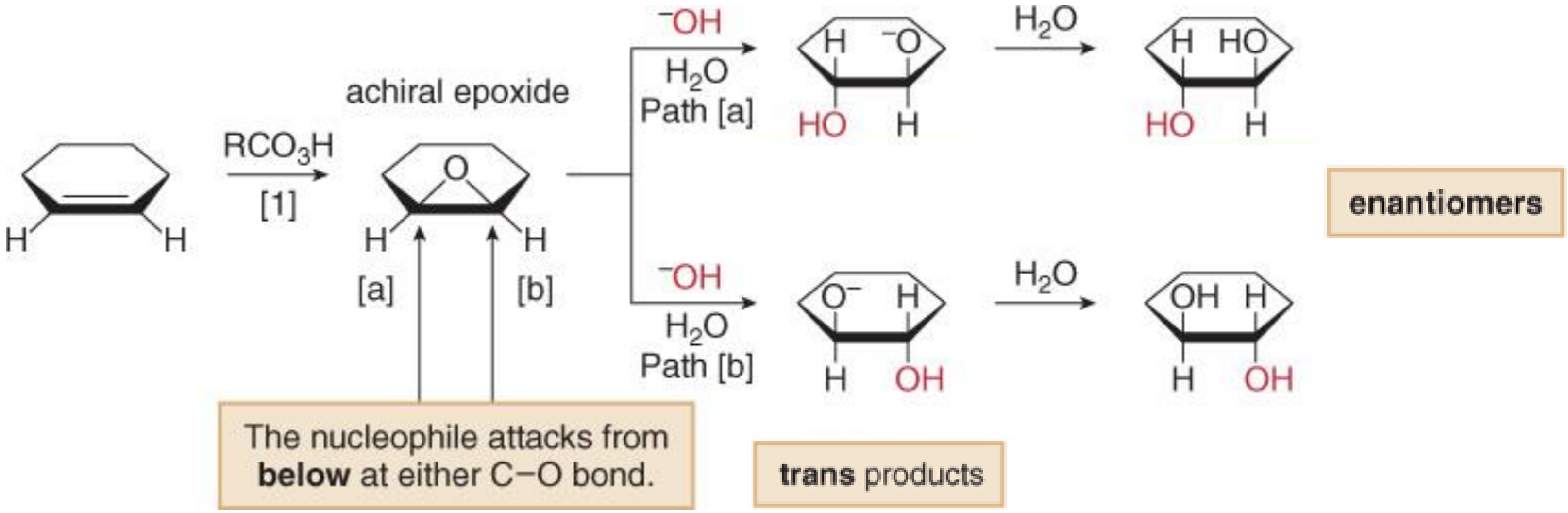
enantiomers

Syn Dihydroxylation


Two O atoms are added to the **same** side of the C=C.

cis-1,2-diol

Anti Dihydroxylation



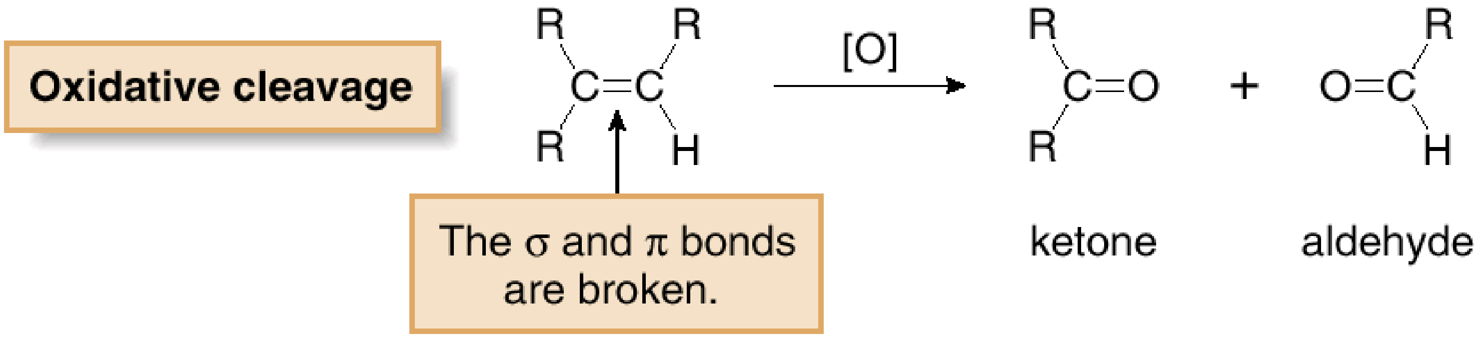
The nucleophile attacks from **below** at either C–O bond.

trans products

enantiomers

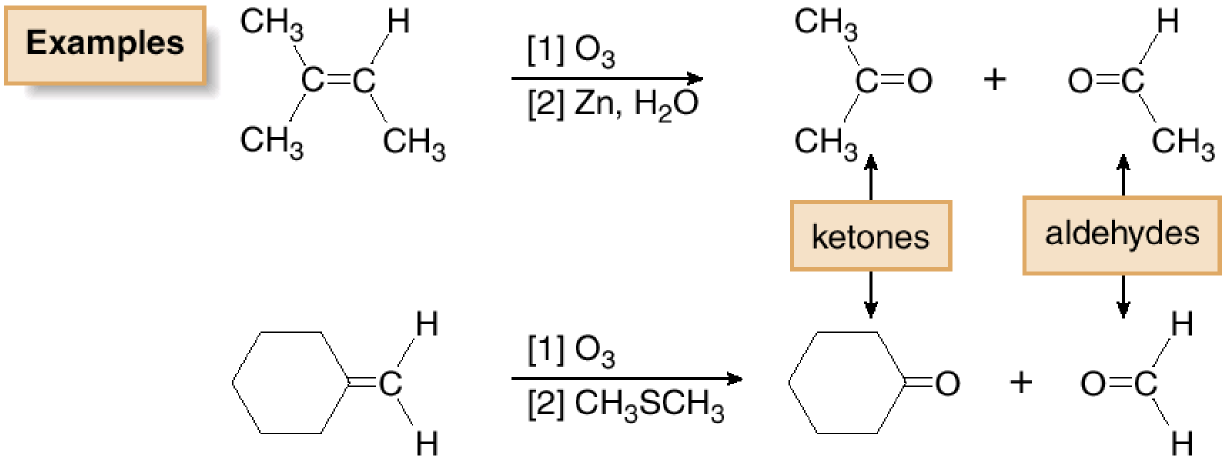
Oxidative Cleavage

- 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.



Oxidative cleavage

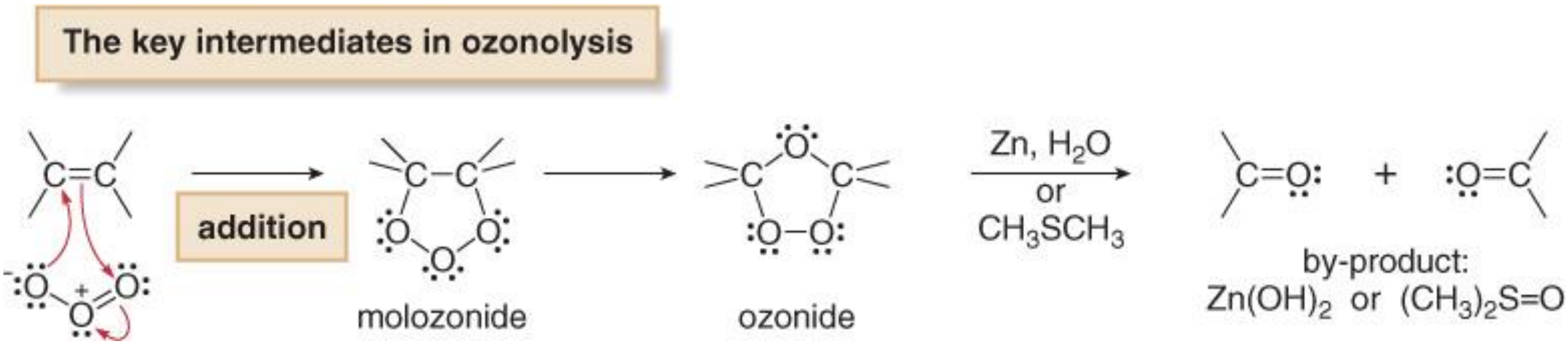
The σ and π bonds are broken.



Examples

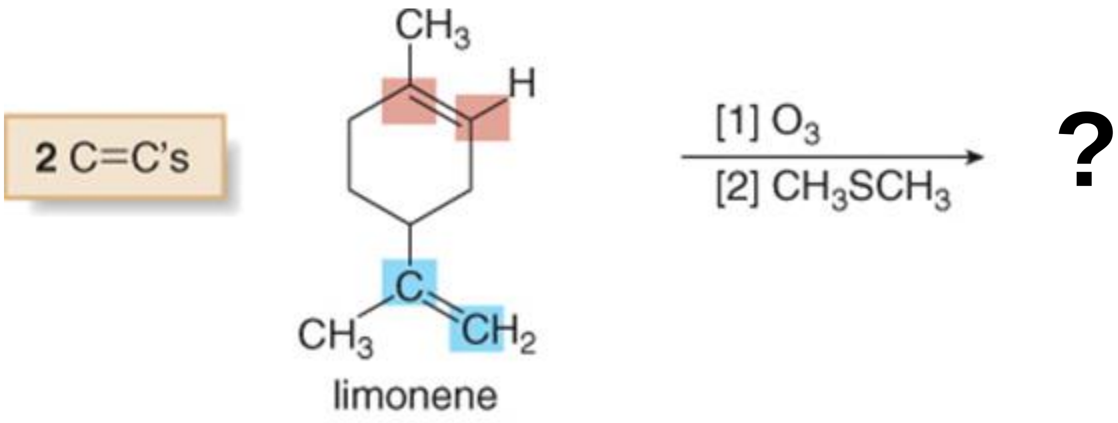
Oxidative Cleavage

- 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.



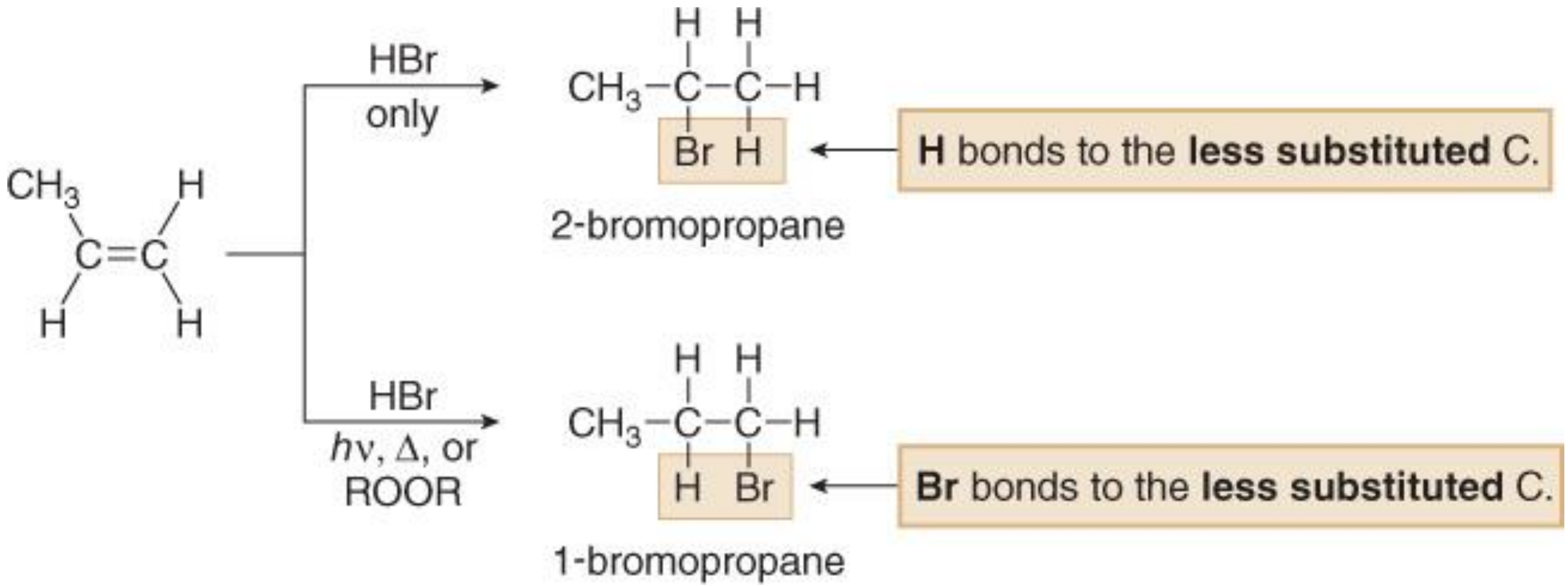
The key intermediates in ozonolysis

Oxidative Cleavage



limonene

Radical Additions to Double Bonds



2-bromopropane

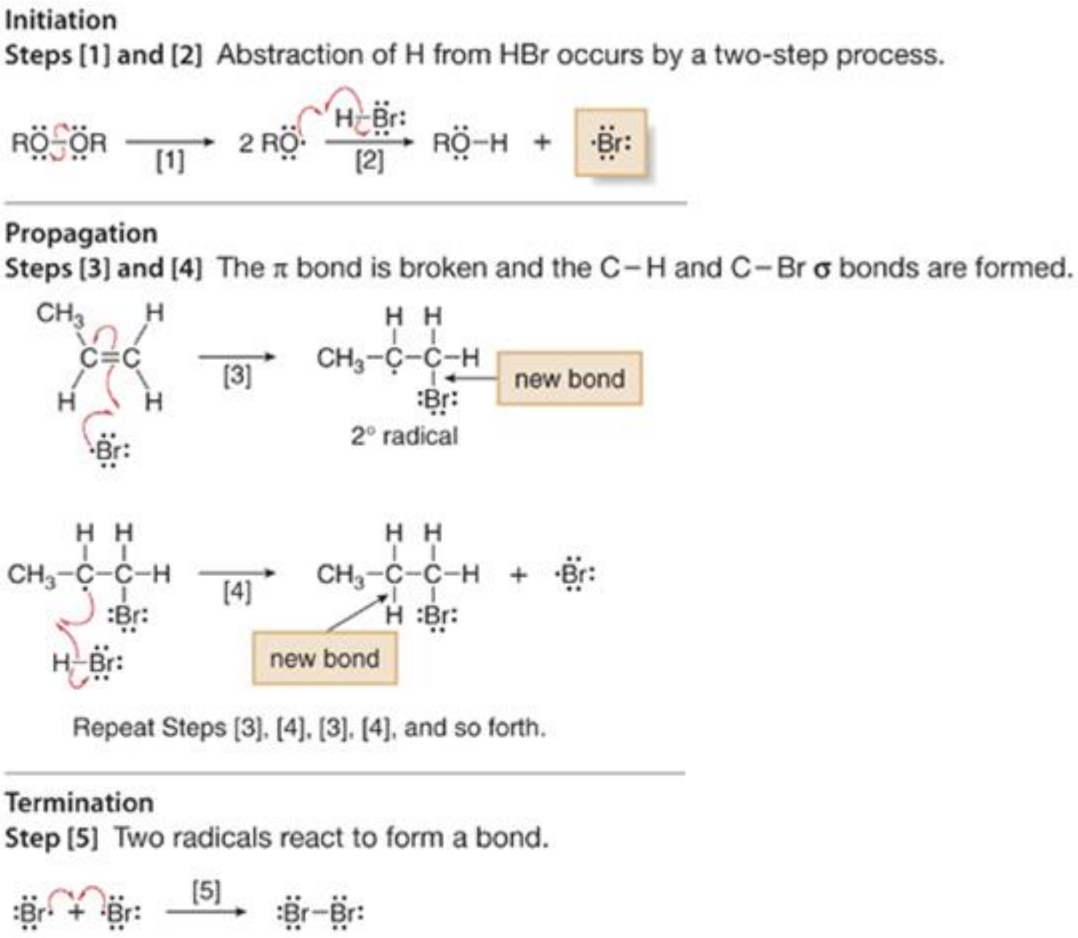
H bonds to the **less substituted** C.

1-bromopropane

Br bonds to the **less substituted** C.

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.

Propagation

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

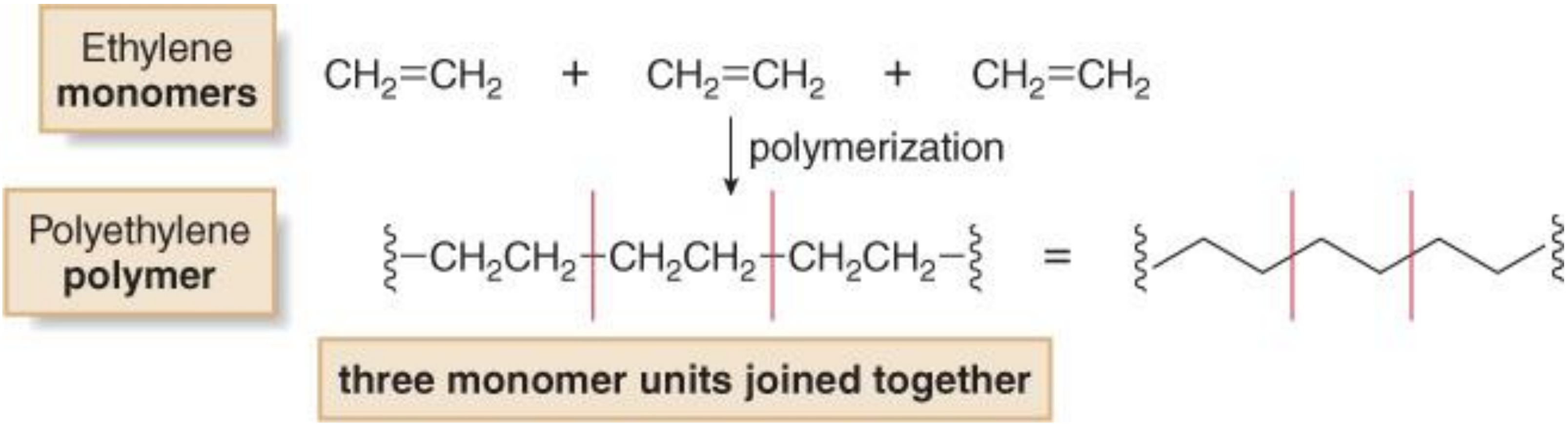
Repeat Steps [3], [4], [3], [4], and so forth.

Termination

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

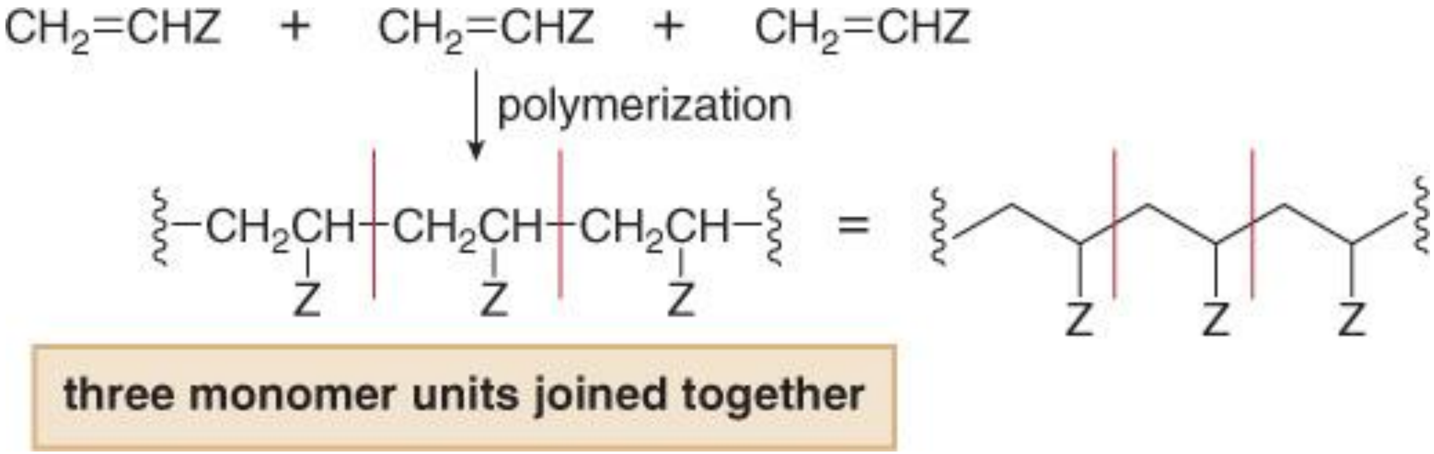
Polymers and Polymerization

- 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.

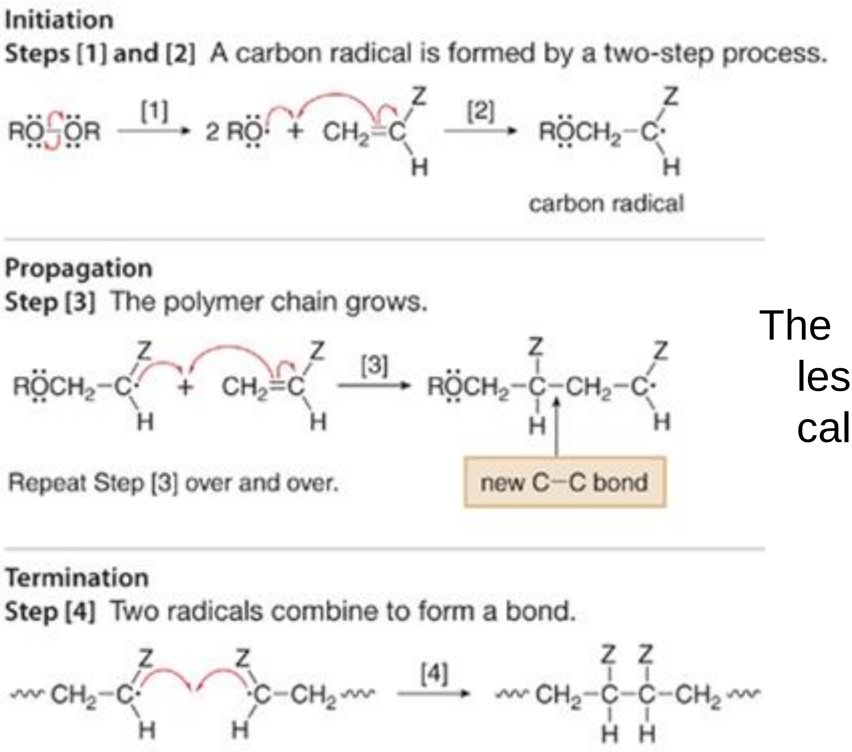


Polymers and Polymerization

- 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.



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.

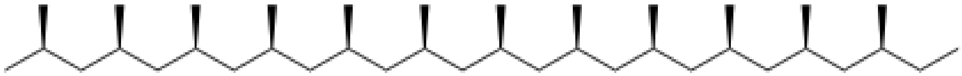
new C–C bond

Termination

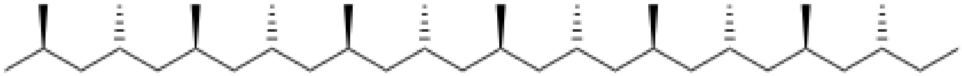
Step [4] Two radicals combine to form a bond.

The more substituted radical always adds to the less substituted end of the monomer, a process called head-to-tail polymerization.

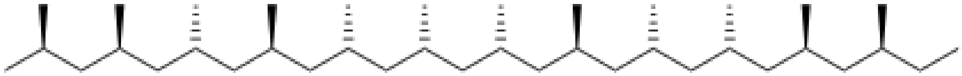
Polymers and Polymerization



Isotactic ($TiCl_3$, $AlEt_2Cl$)



sindiotactic ($TiCl_4$, AlR_3)



atactic ($TiCl_3$, $AlCl_3$)

Cationic polymerization

Polymers and Polymerization

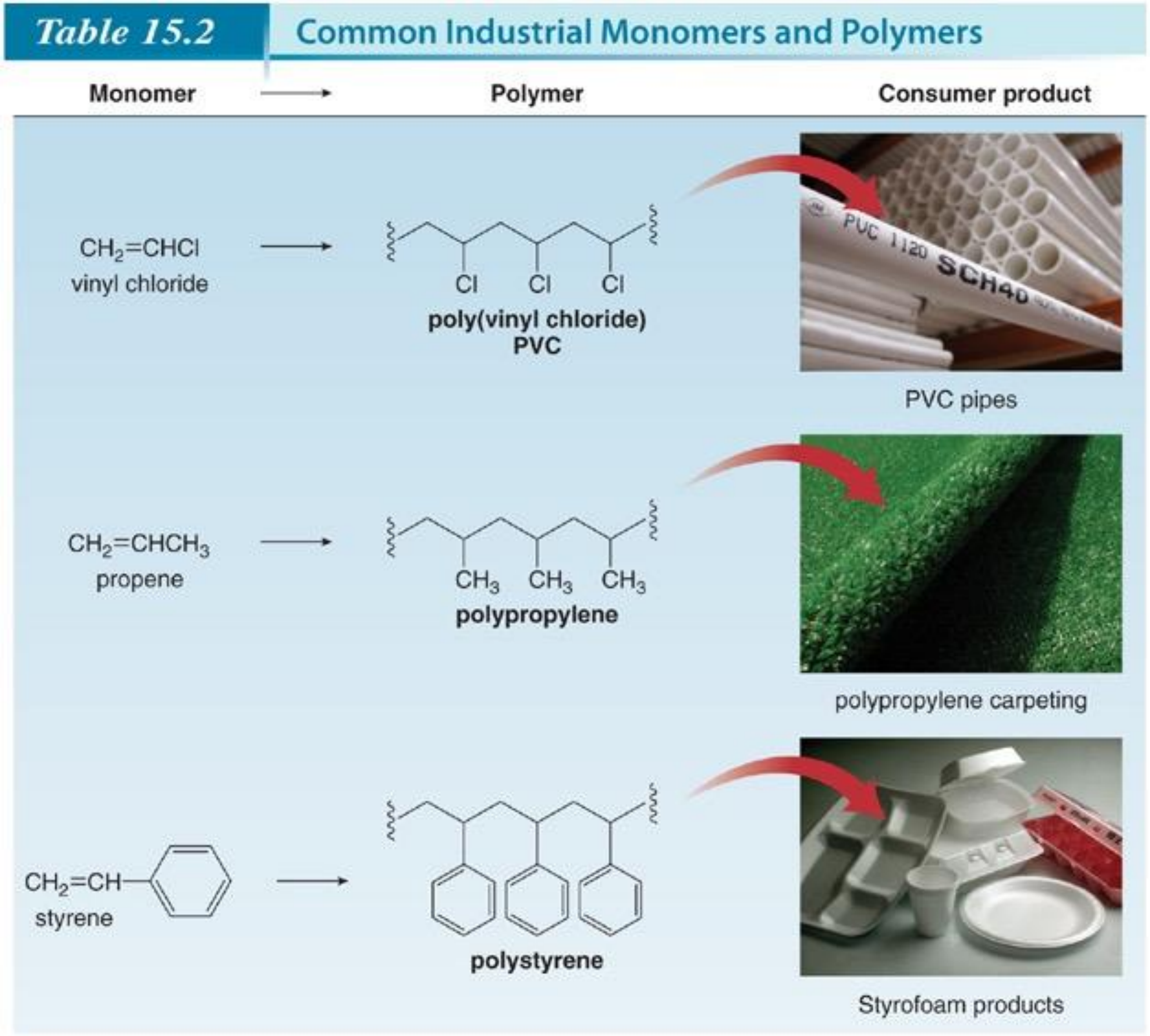


Table 15.2 Common Industrial Monomers and Polymers

Monomer	→	Polymer	Consumer product
$CH_2{=}CHCl$ vinyl chloride	→	**poly(vinyl chloride)** **PVC**	PVC pipes
$CH_2{=}CHCH_3$ propene	→	**polypropylene**	polypropylene carpeting
$CH_2{=}CH-$ styrene	→	**polystyrene**	Styrofoam products

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