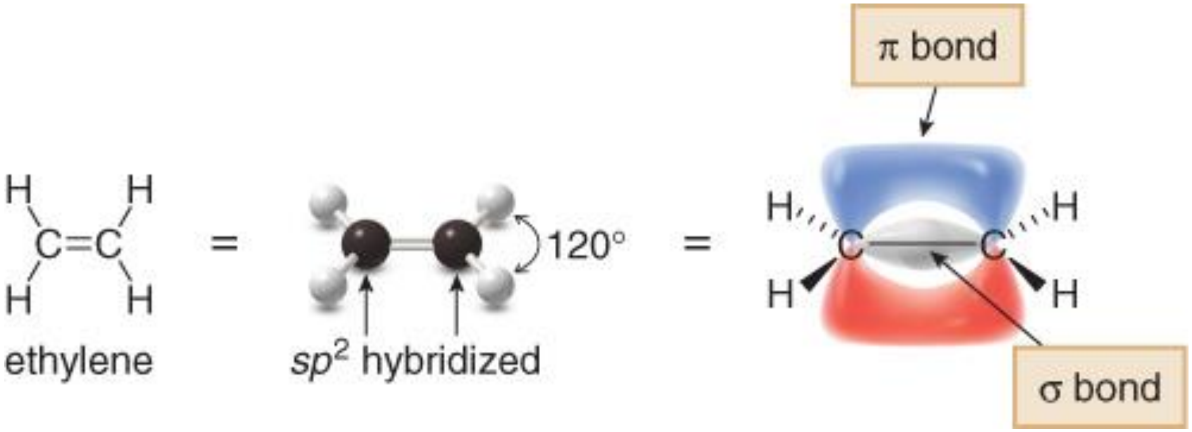
Alkenes (Olefins)

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

Structure and Bonding

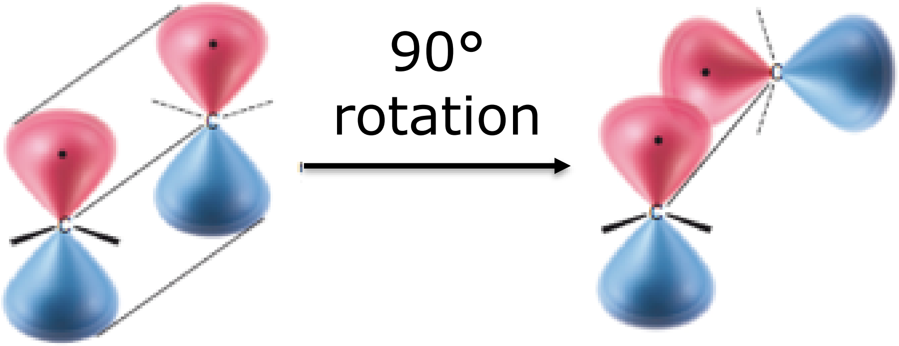


$CH_2{=}CH_2$		$CH_3{-}CH_3$		
152 kcal/mol	−	88 kcal/mol	=	64 kcal/mol
(σ + π bond)		(σ bond)		↑
				π bond only

- 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

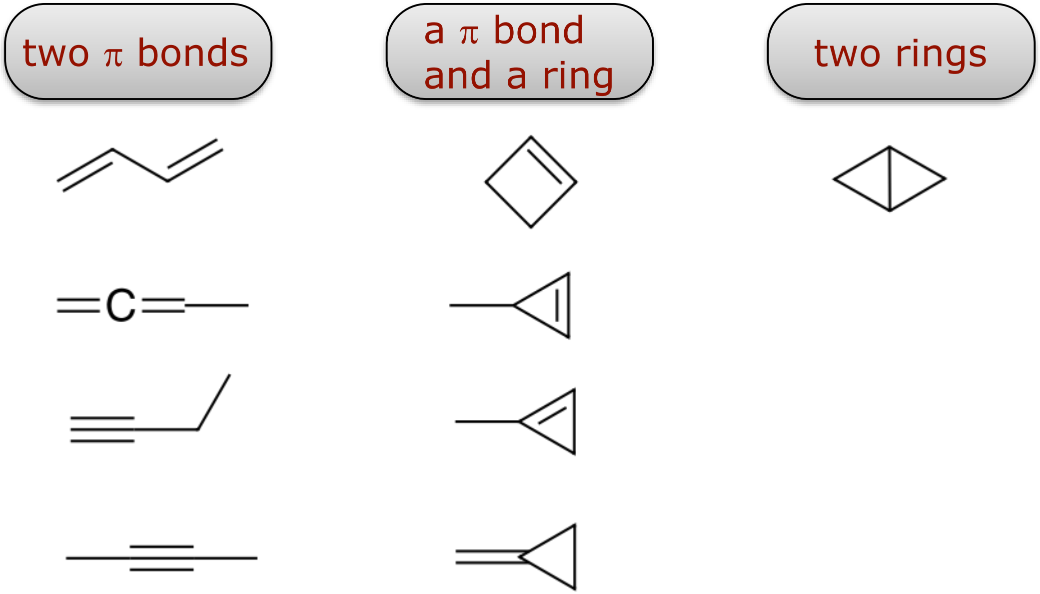
The p orbitals are orthogonal

the π bond is broken

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

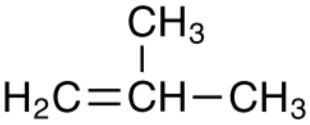


two π bonds

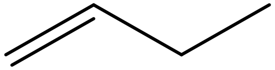
a π bond and a ring

two rings

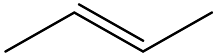
Simple Alkenes

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

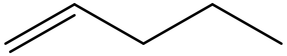
Positional isomers



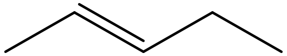
1-butene



2-butene



1-pentene

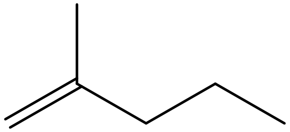


2-pentene

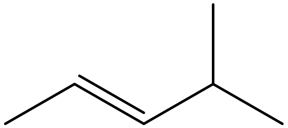
1-hexene

2-hexene

3-hexene

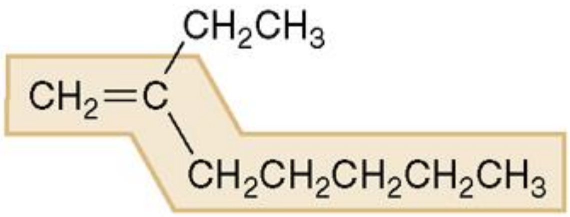


2-methyl-1-pentene



4-methyl-2-pentene

Nomenclature

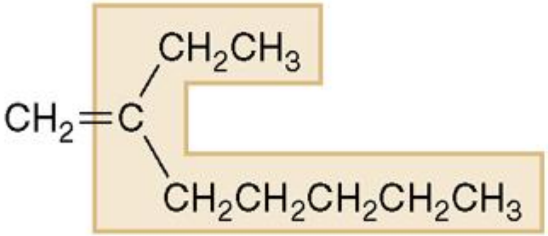


$CH_2{=}C(CH_2CH_3)CH_2CH_2CH_2CH_2CH_3$

7 C's ---→ heptene

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

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

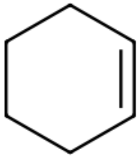


$CH_2{=}C(CH_2CH_3)CH_2CH_2CH_2CH_2CH_3$

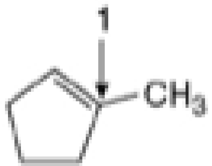
8 C's

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

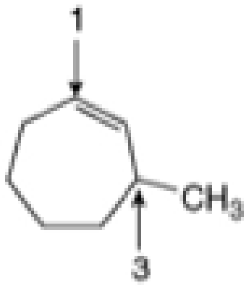
Incorrect



cyclohexene



1-methylcyclopentene



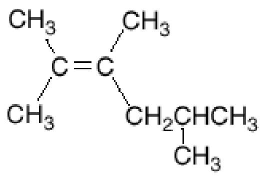
3-methylcycloheptene

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

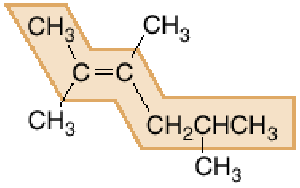
Nomenclature

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.



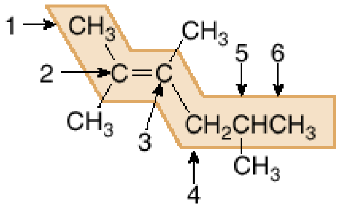
6 C's in the longest chain

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.

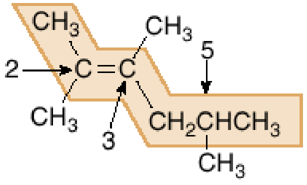
a. **Number** the chain, and name using the ***first* number** assigned to the C=C.



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

2-hexene

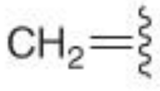
b. **Name** and **number** the substituents.



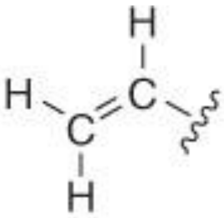
three methyl groups at C2, C3, and C5

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

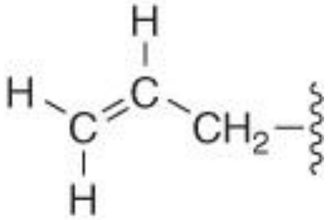
Nomenclature



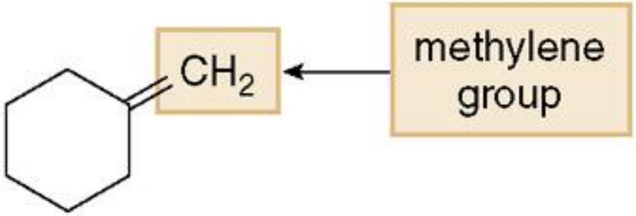
methylene group



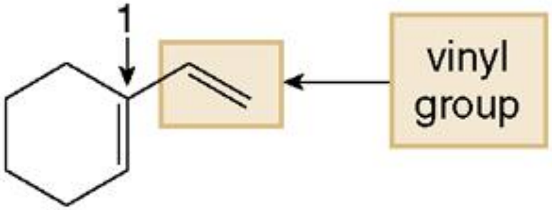
vinyl group



allyl group

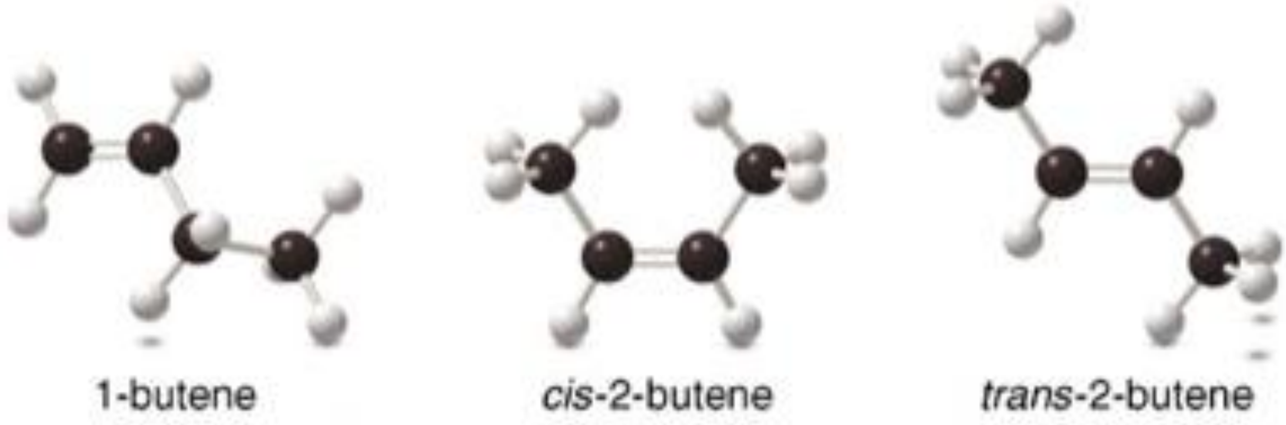


methylenecyclohexane



1-vinylcyclohexene

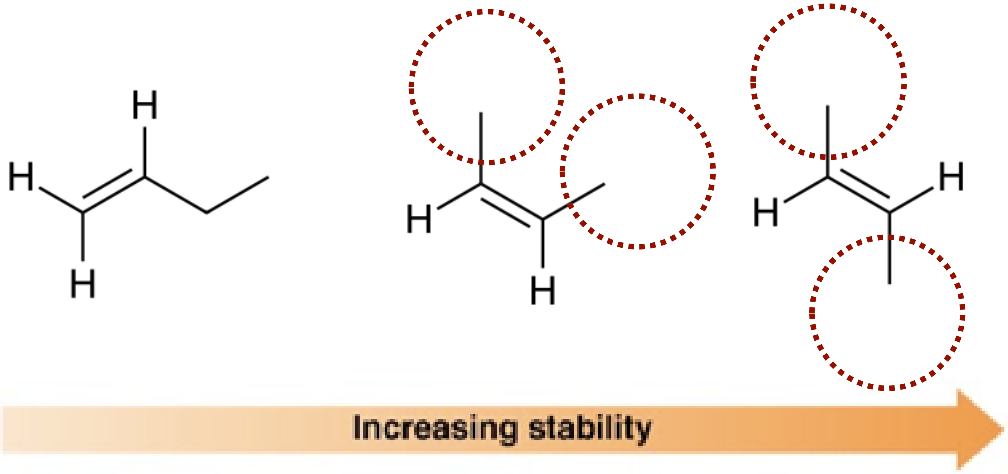
Geometrical Isomerism



1-butene

cis-2-butene

trans-2-butene

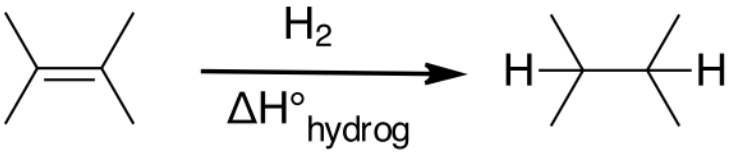


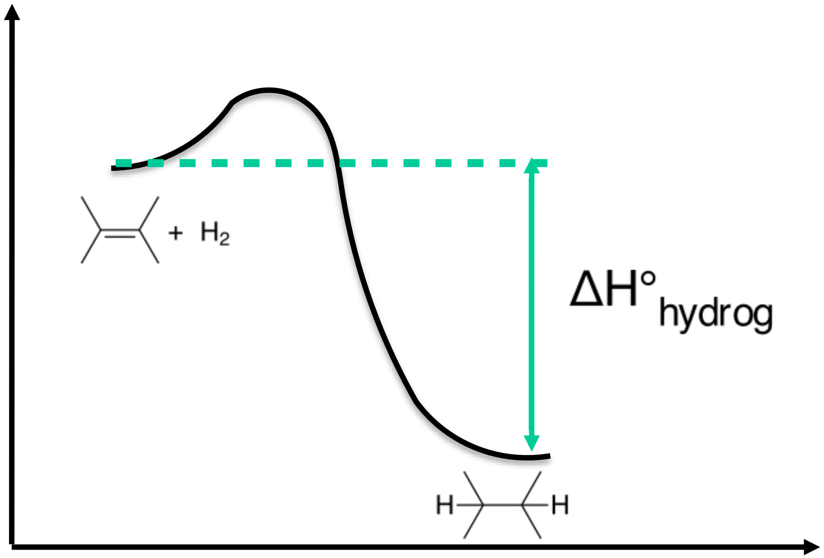
steric strain

no interaction

modelli 3D

Stability of Alkenes





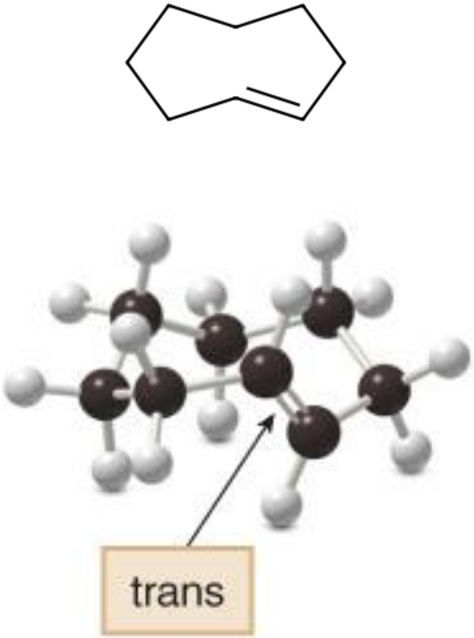
- Hydrogenation of alkenes is exothermic
- The heat of hydrogenation can be used as a measure of the relative stability of different alkenes.

Stability of Alkenes

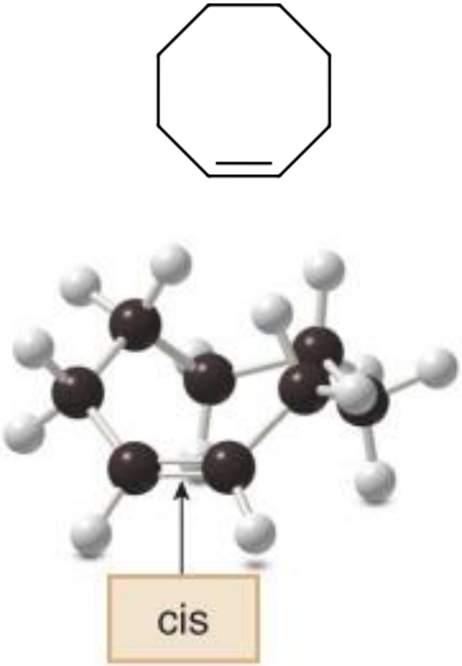
Substitution	Alkene	$\Delta H°_{hydr}$ (Kcal/mol)	stability
Unsubstituted	$H_2C{=}CH_2$	-32.8	less stable
Monosubstituted	$CH_3CH{=}CH_2$	-30.1	
Disubstituted	$(CH_3)_2C{=}CH_2$	-28.4	
	$CH_3CH{=}CHCH_3$ (cis)	-28.6	
	$CH_3CH{=}CHCH_3$ (trans)	-27.6	
Trisubstituted	$(CH_3)_2C{=}CHCH_3$	-26.9	
Tetrasubstituted	$(CH_3)_2C{=}C(CH_3)_2$	-26.6	more stable

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

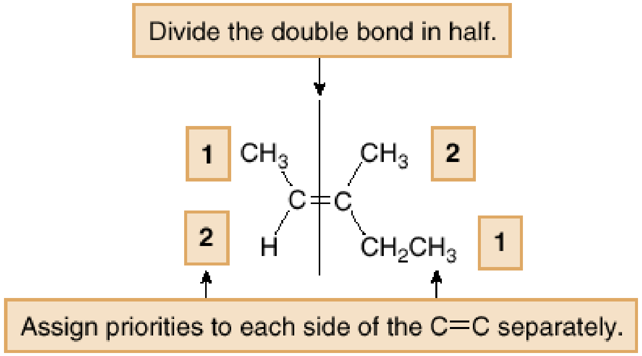
modelli 3D

E/*Z* Nomenclature

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

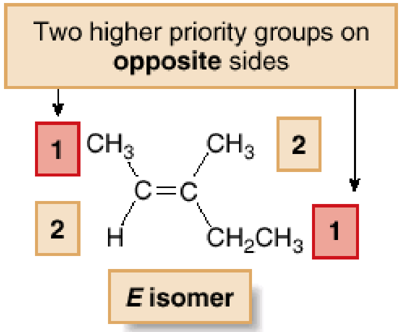
Step [1] Assign priorities to the two substituents on each end of the C=C by using the priority rules for *R,S* nomenclature (Section 5.6).

- 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.**

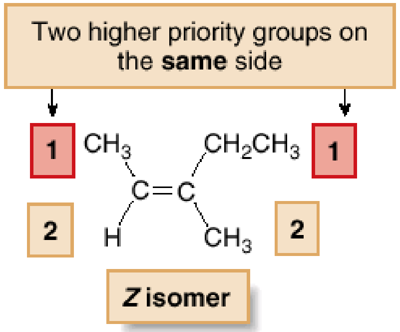

Divide the double bond in half.

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

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

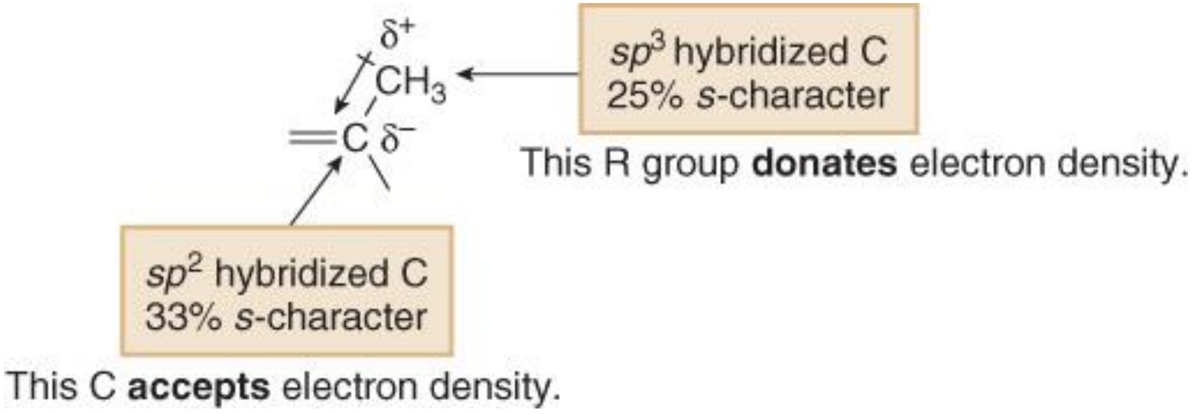

Two higher priority groups on the **same** side

(*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

- 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.

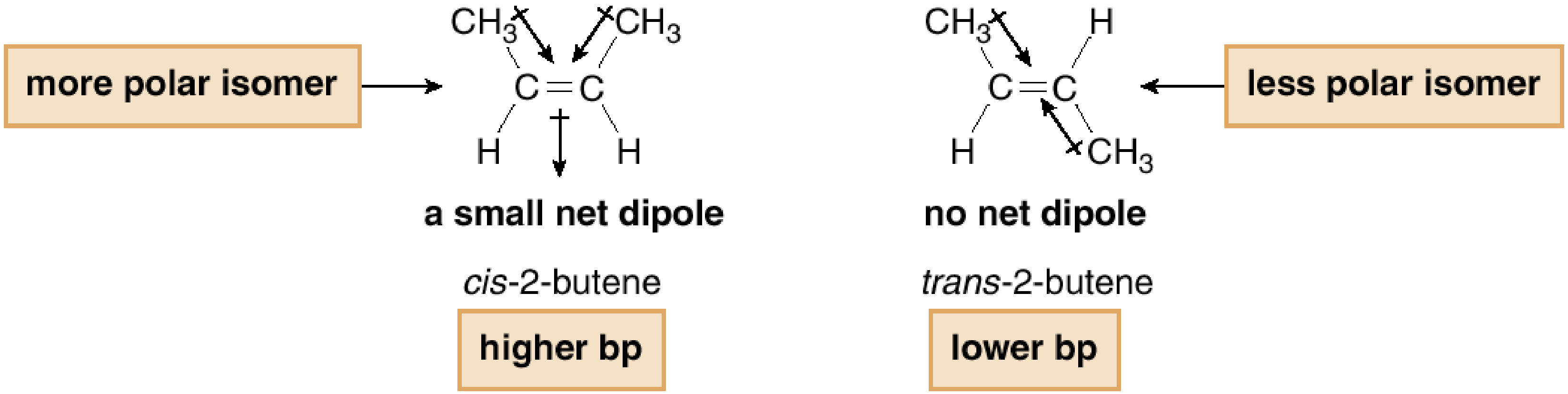


This R group **donates** electron density.

This C **accepts** electron density.

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

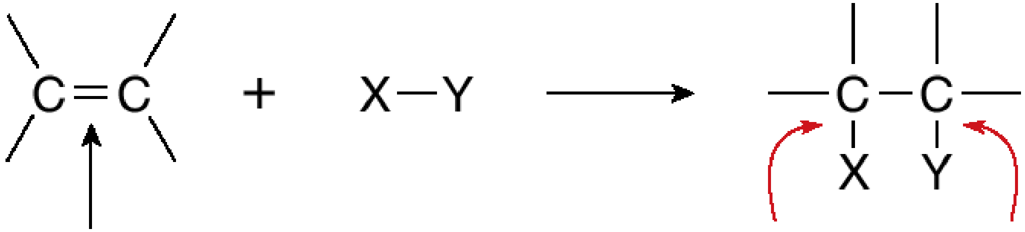
lower bp

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.

Introduction to Addition Reactions

Addition reaction



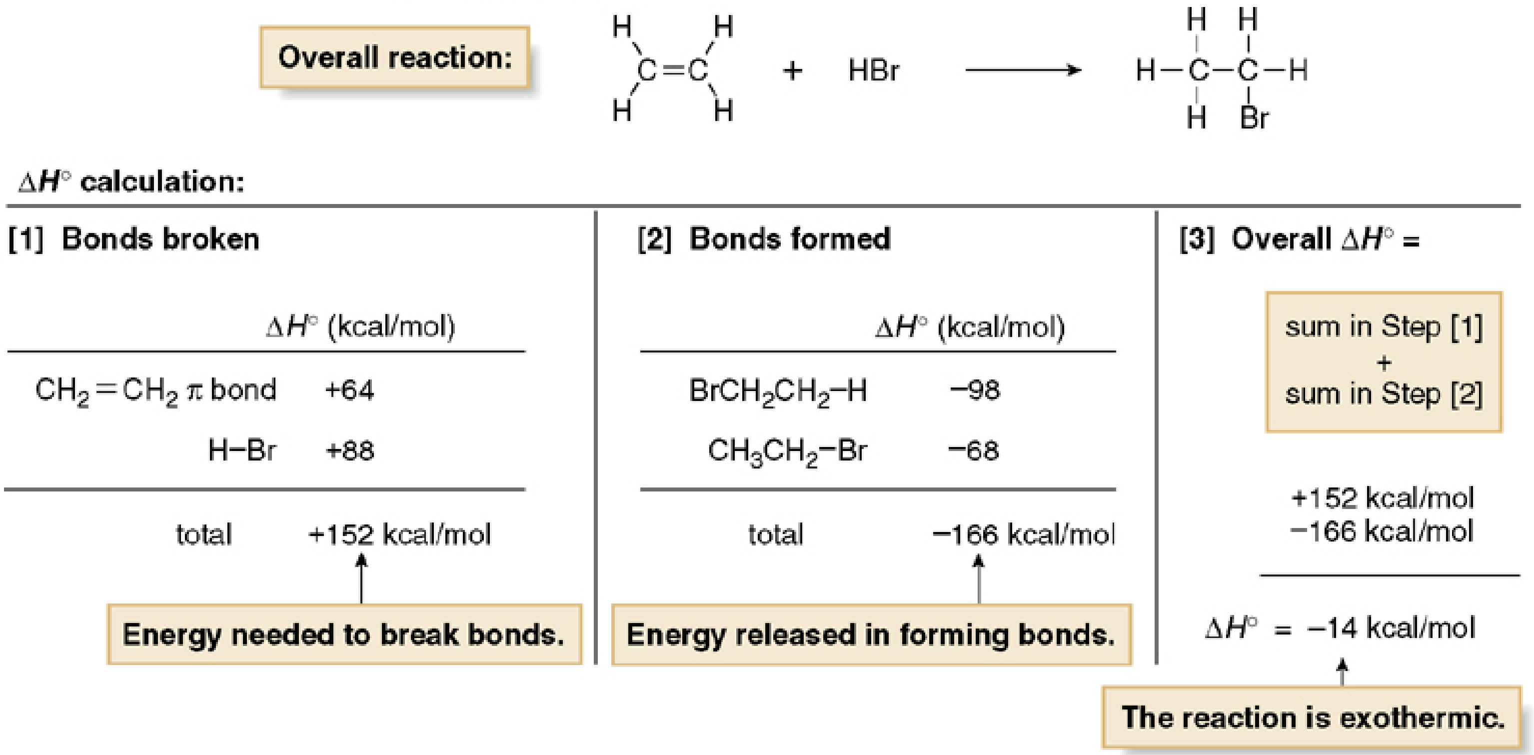
This π bond is broken.

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: Electrophilic addition
- 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 $\Delta H°$ =

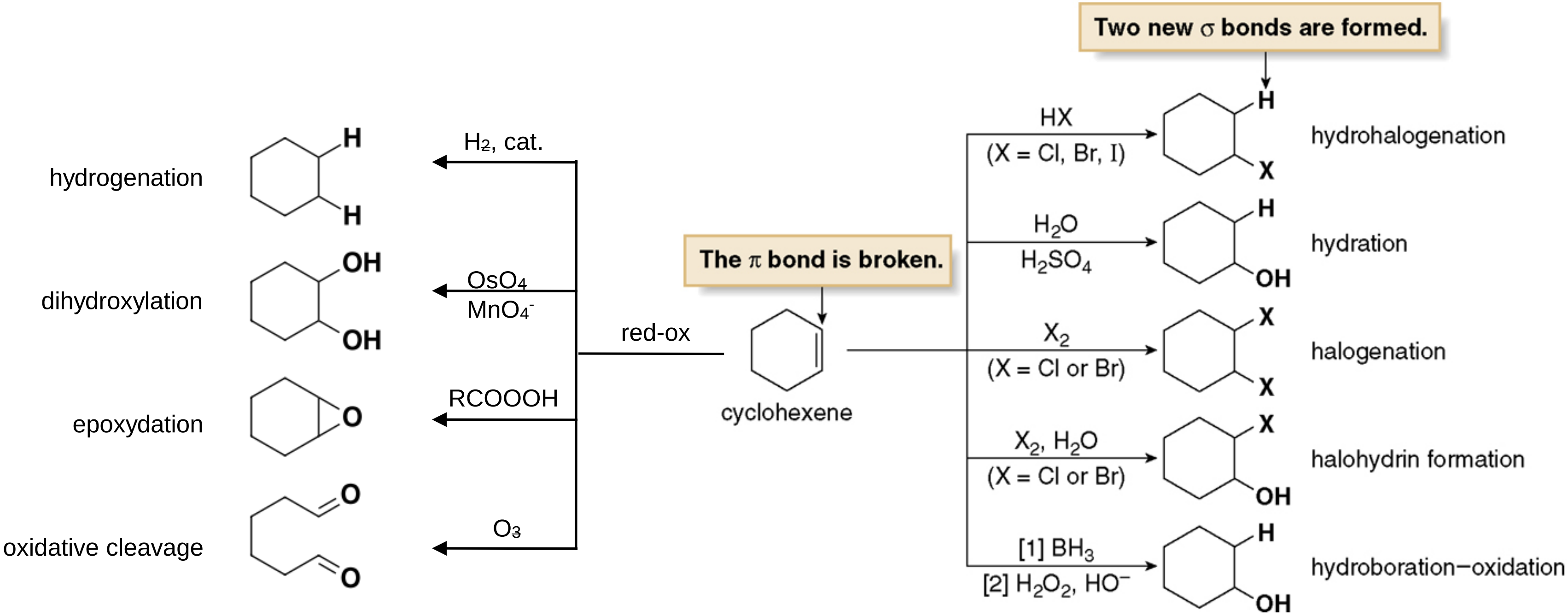
sum in Step [1]
+
sum in Step [2]

$$\begin{array}{r} +152 \text{ kcal/mol} \\ -166 \text{ kcal/mol} \\ \hline \end{array}$$

$\Delta H° = -14$ kcal/mol

The reaction is exothermic.

Introduction to Addition Reactions



Two new σ bonds are formed.

The π bond is broken.

cyclohexene

red-ox

hydrogenation — H_2, cat.

dihydroxylation — OsO_4 / MnO_4^-

epoxydation — RCOOOH

oxidative cleavage — O_3

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

hydration — H_2O / H_2SO_4

halogenation — X_2 (X = Cl or Br)

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

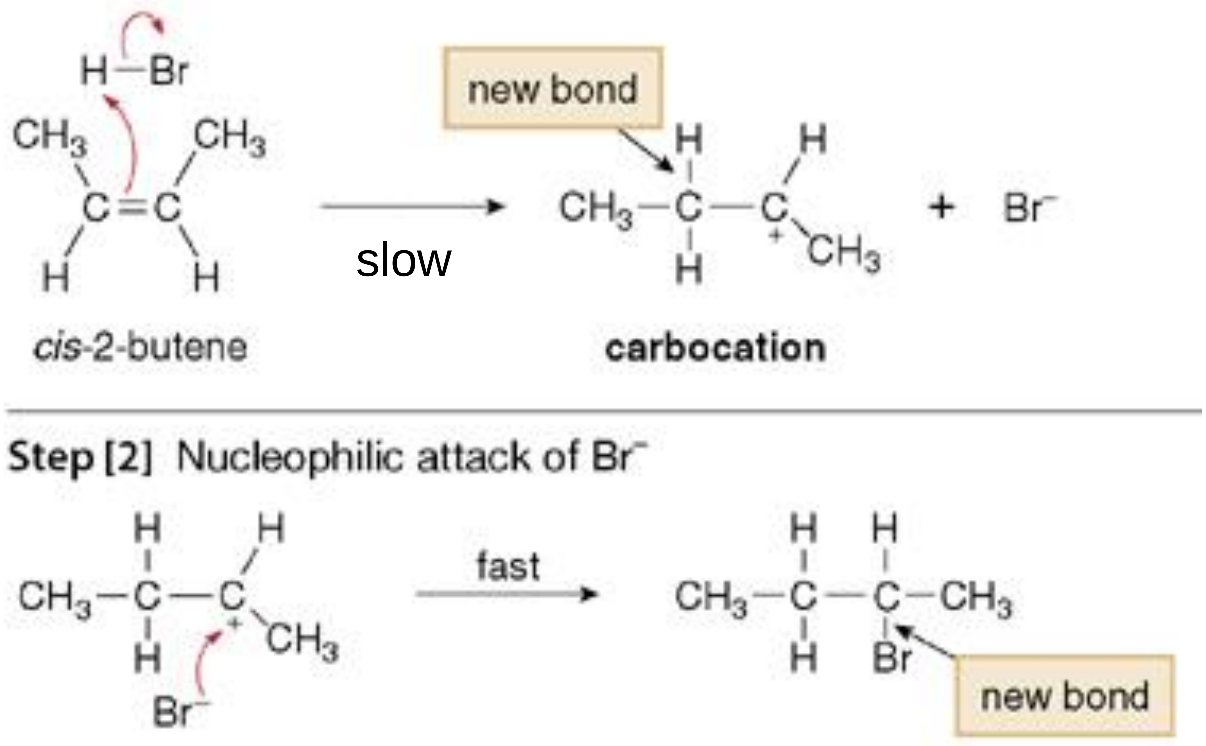
hydroboration−oxidation — [1] BH_3 [2] H_2O_2, HO^-

Hydrohalogenation. Mechanism

- Two-step mechanism. Electrophilic addition
- Step [1] Alkene donates a π electron pair to H-Br, with formation of a C-H bond and a carbocation
- Step [2], Br^- donates the electron pair to the C+, forming the C-Br bond

[1]

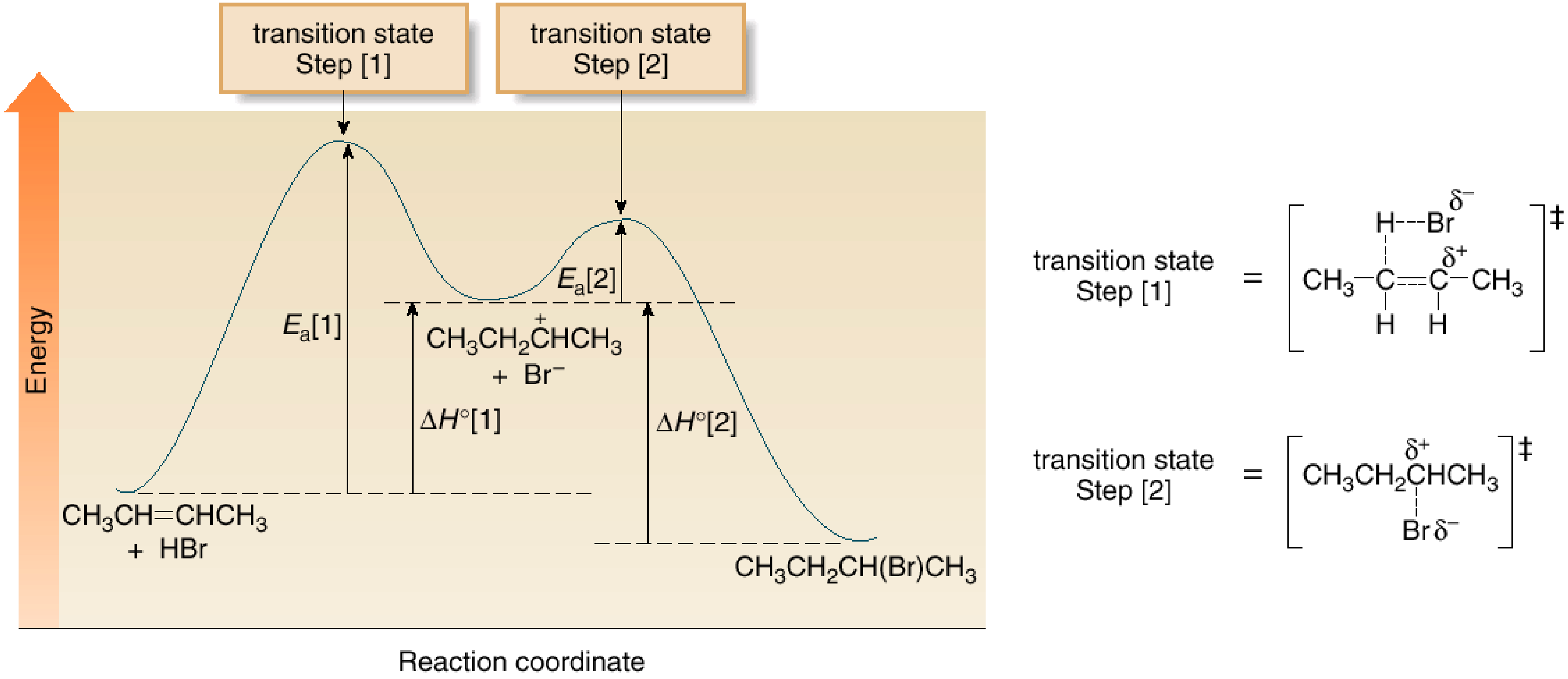
[2]



slow

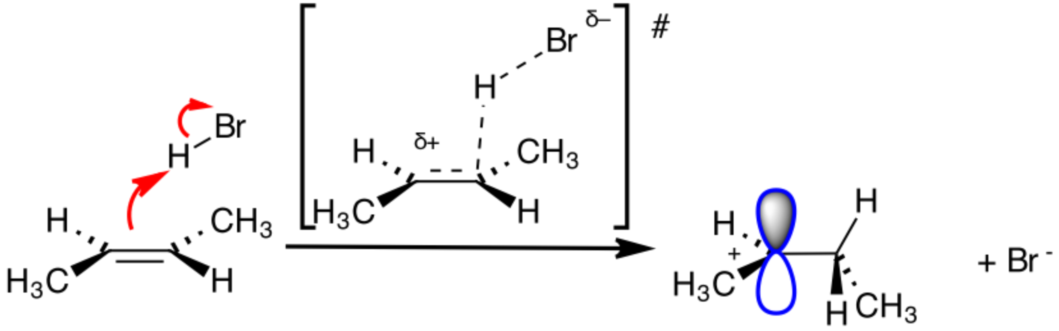
2-bromobutane

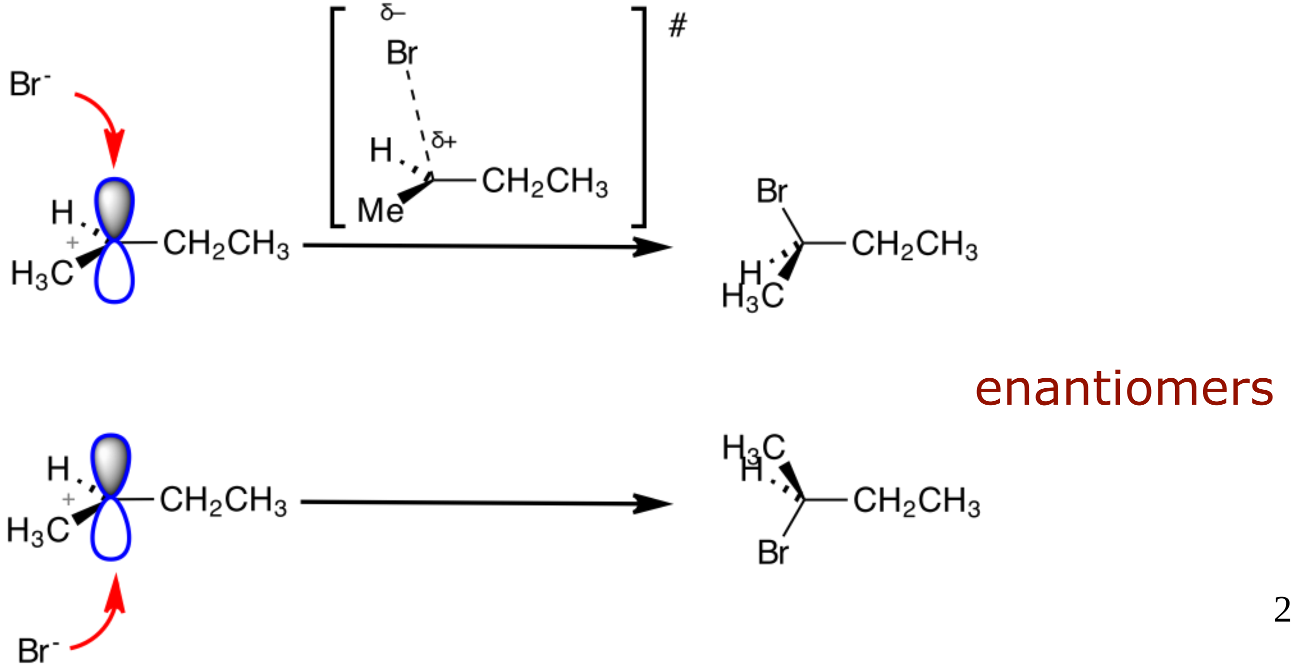
Hydrohalogenation



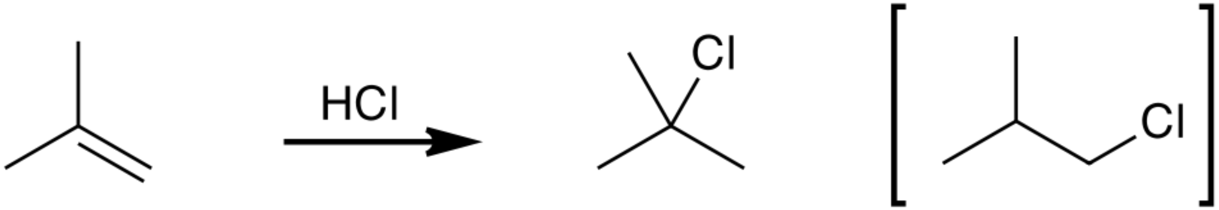
- The mechanism has two steps, so there are two energy barriers.
- Step [1] is rate-determining.

Hydrohalogenation. Mechanism and stereochemistry



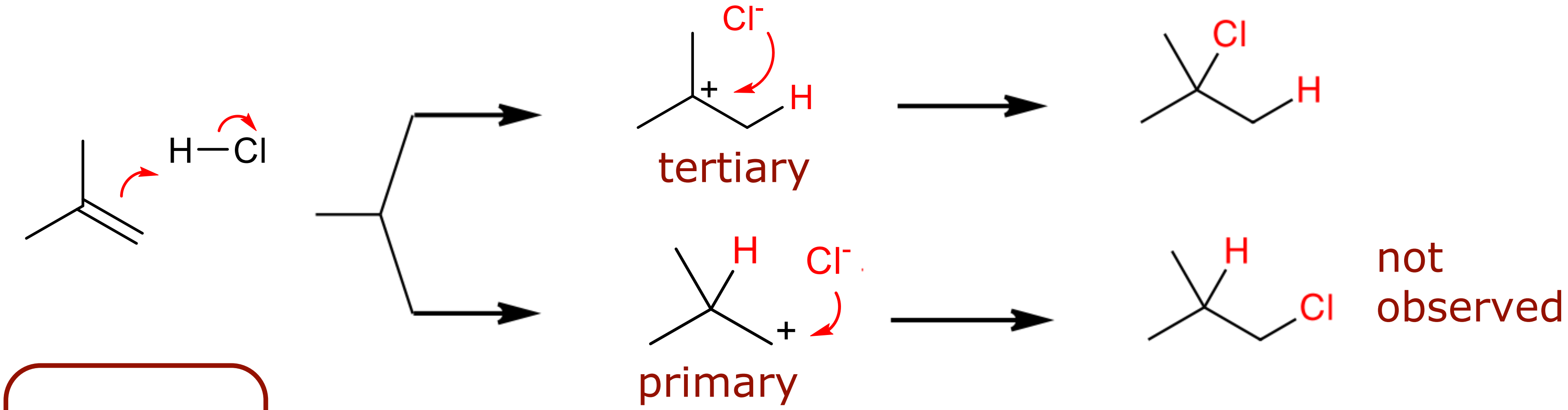


Hydrohalogenation — Regioselectivity



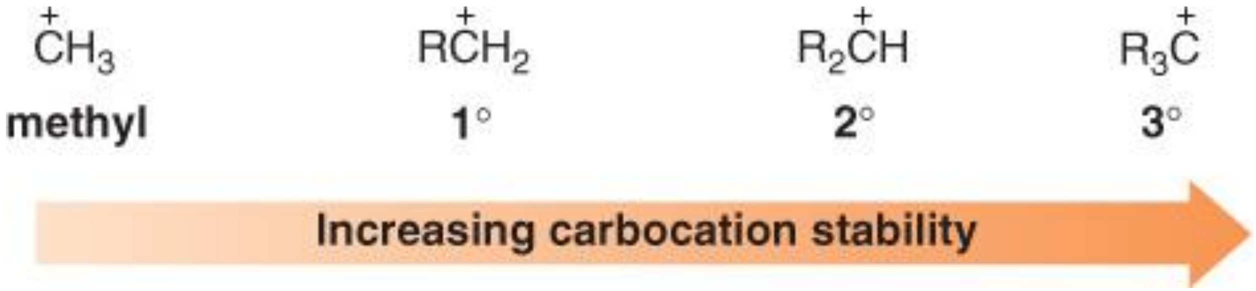
not formed

- Markovnikov's Rule: The electrophile (H^+) adds to the less substituted carbon; the nucleophile (Cl^-) to the more substituted one.

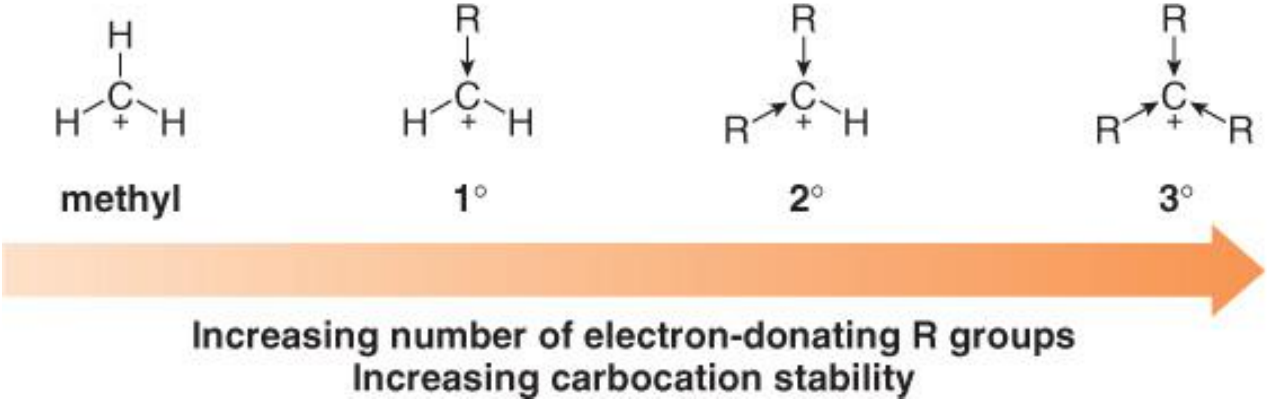


video

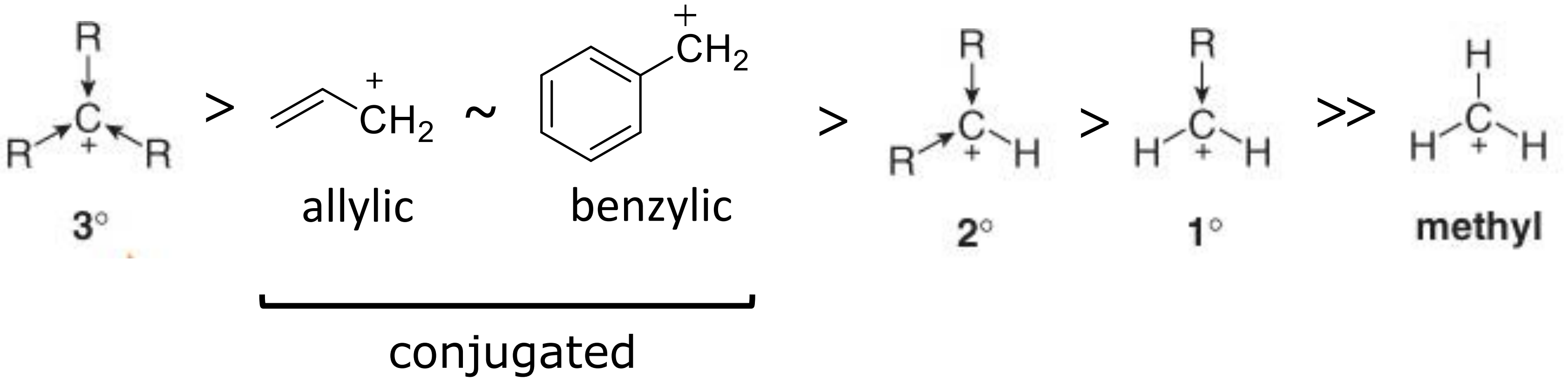
Alkyl Carbocation Stability



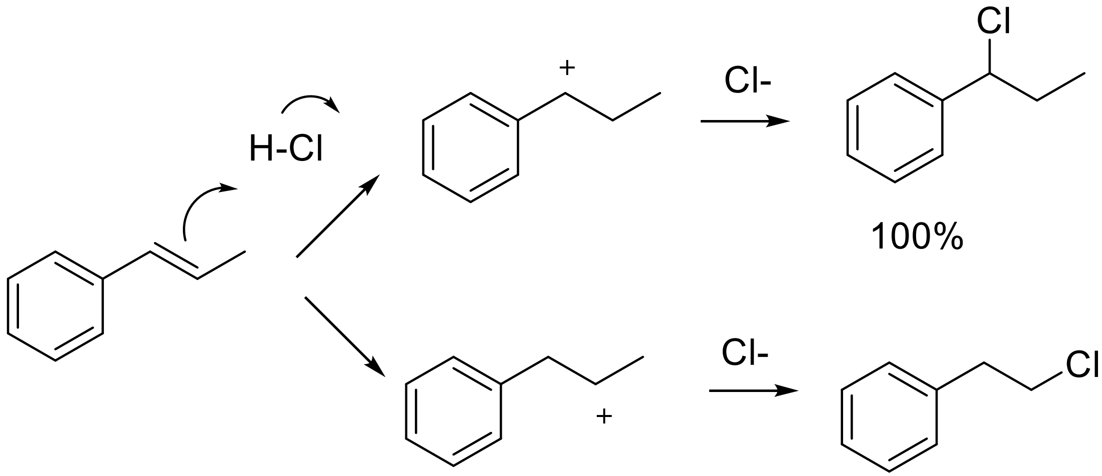
Alkyl groups are electron donating. Since an alkyl group has several σ bonds, each containing electron density, it is more polarizable than a hydrogen atom, and better able to donate electron density.



Carbocation stability



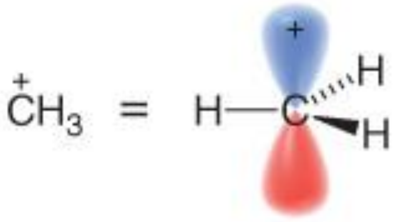
Allylic and benzylic carbocations are conjugated
They are stabilized by resonance



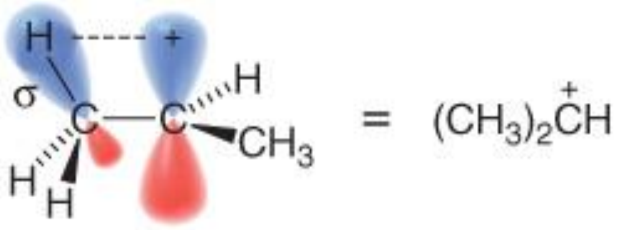
Alkyl Carbocation Stability

- **Hyperconjugation** is the spreading out of charge by the overlap of an empty *p* orbital with an adjacent σ bond. This overlap (hyperconjugation) delocalizes the positive charge on the carbocation, spreading it over a larger volume, and this stabilizes the carbocation.

- Example: CH_3^+ cannot be stabilized by hyperconjugation, but $(CH_3)_2CH^+$ can.



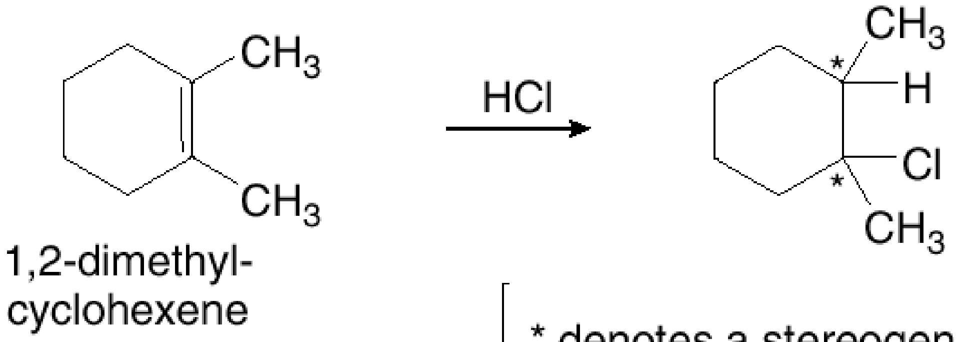
This carbocation has no opportunity for orbital overlap with the vacant *p* orbital.



Overlap of the C−H σ bond with the adjacent vacant *p* orbital stabilizes the carbocation.

Hydrohalogenation - Stereochemistry

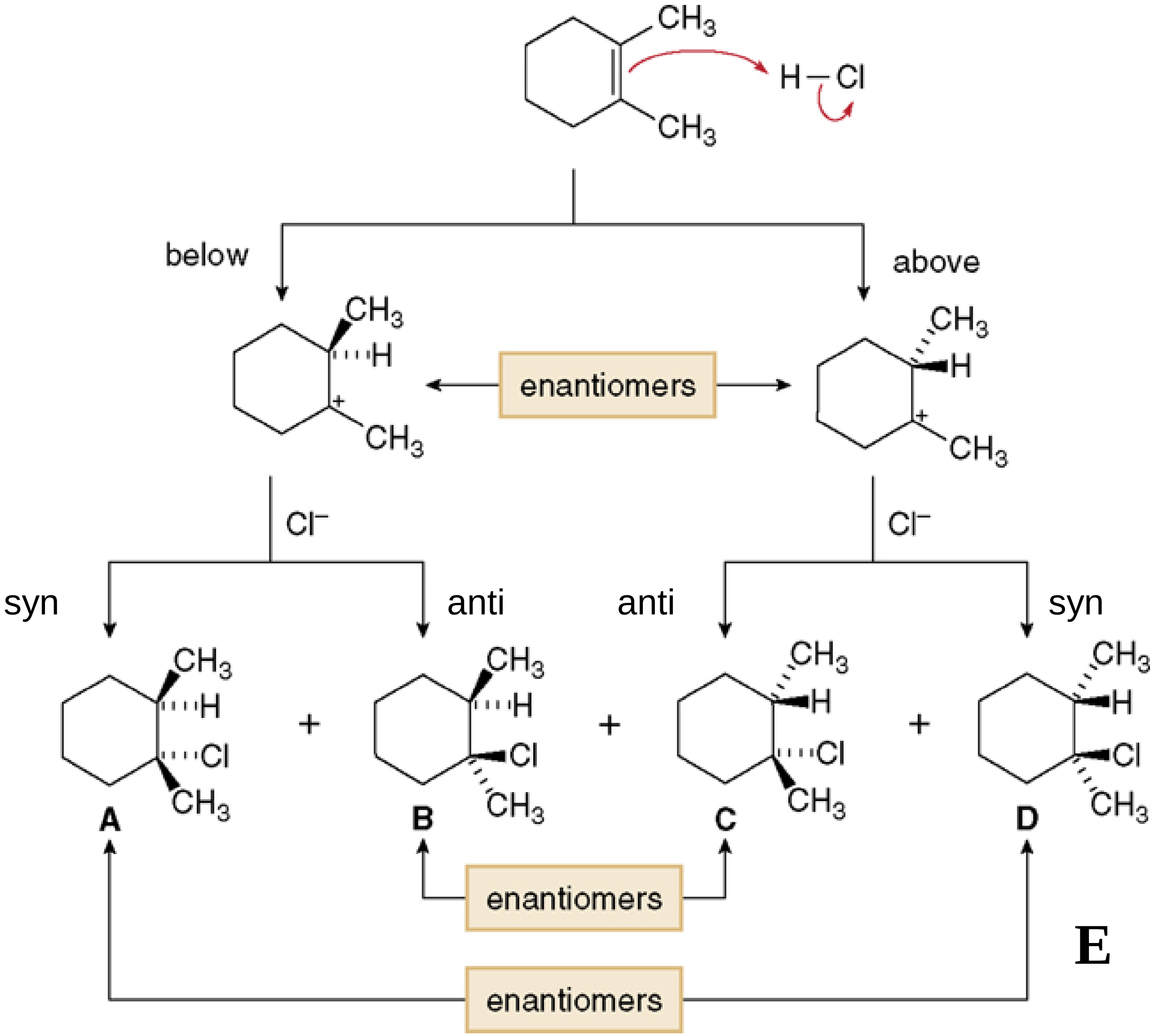
- Addition of HX to 1,2-dimethylcyclohexene forms two new stereogenic centers.



Two new stereogenic centers are formed.

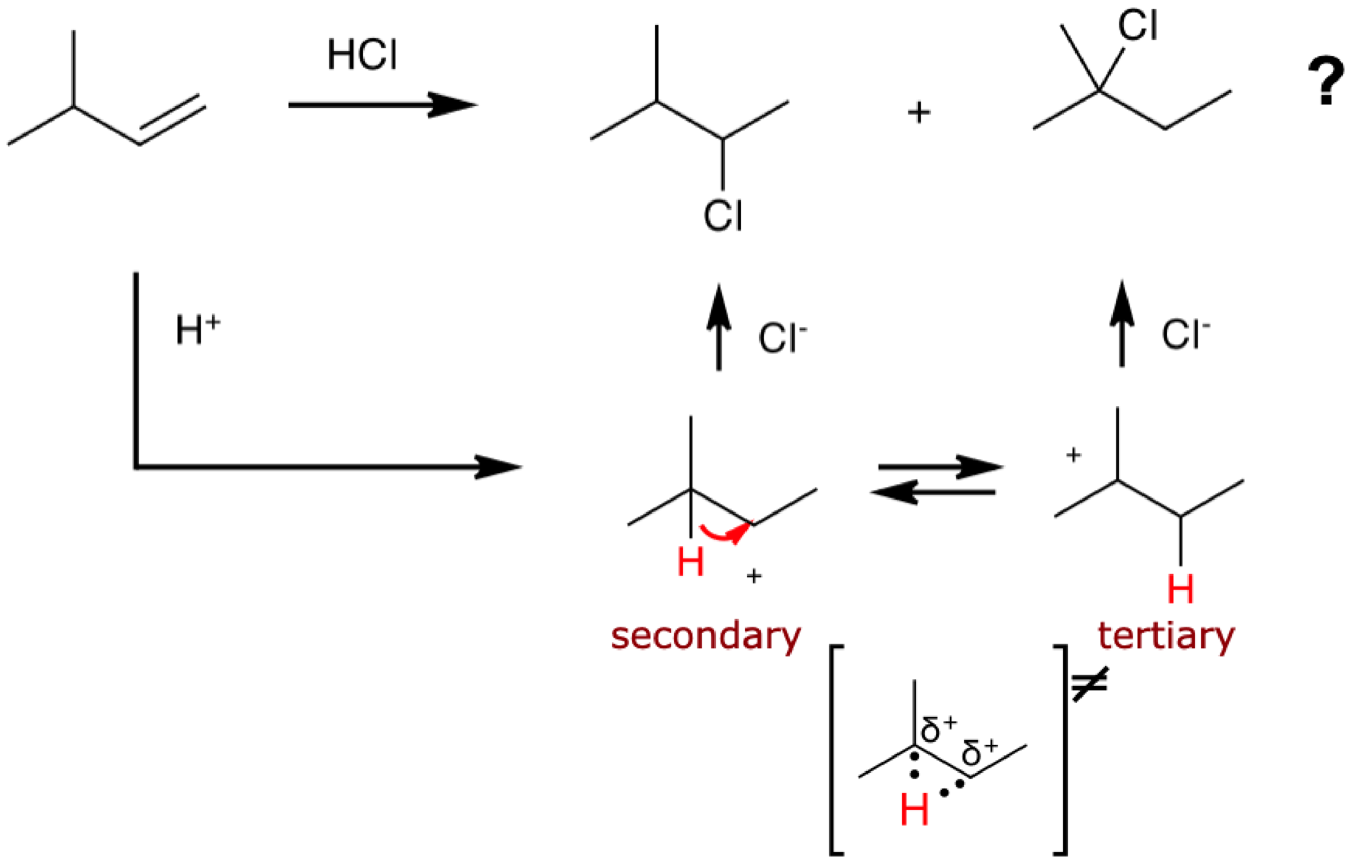
[* denotes a stereogenic center]

Hydrohalogenation—Stereochemistry



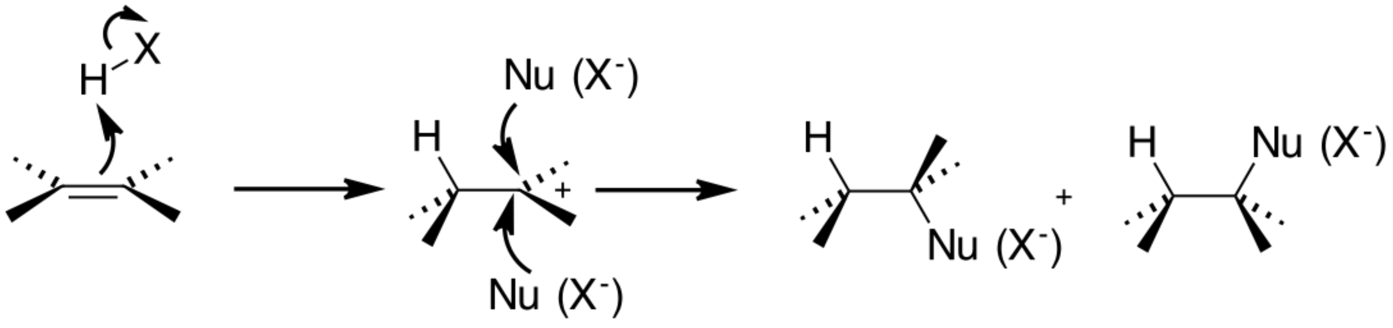
E

Carbocation Rearrangements



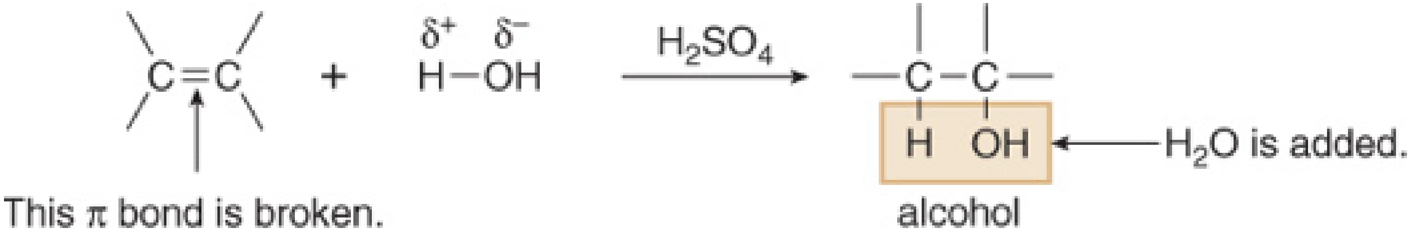
Groups prone to migration: H, Me, Ph

Hydrohalogenation—Summary

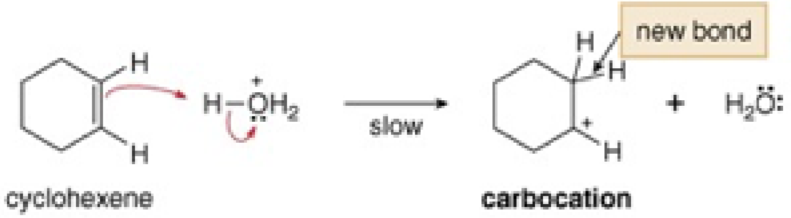


Mechanism	• The mechanism involves two steps. • The rate-determining step forms a carbocation. • Rearrangements can occur.
Regioselectivity	• Markovnikov's rule is followed. In unsymmetrical alkenes, H bonds to the less substituted C to form the more stable carbocation.
Stereochemistry	• Syn and anti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

Hydration—Electrophilic Addition of Water

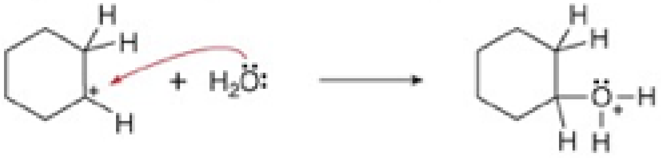


Step [1] Addition of the electrophile (H^+) to the π bond



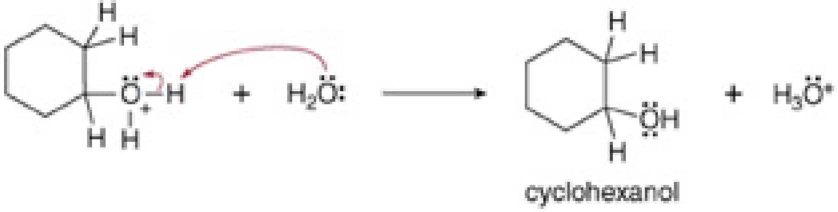
- The π bond attacks H_3O^+, thus forming a new C−H bond while breaking the H−O bond. Because the remaining carbon atom of the original double bond is left with only six electrons, a **carbocation** intermediate is formed. This step is **rate-determining** because two bonds are broken but only one bond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

Step [2] Nucleophilic attack of H_2O



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

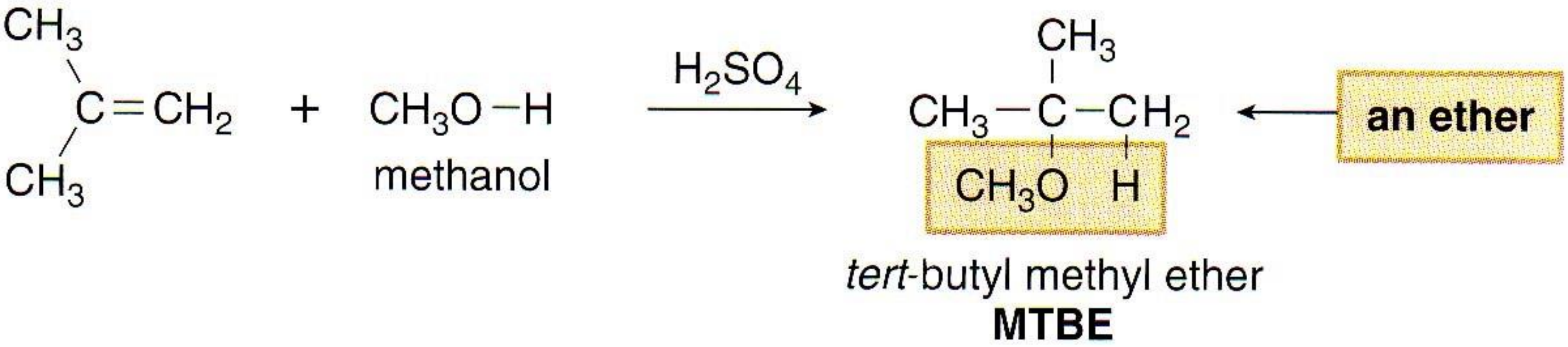
Step [3] Loss of a proton



- 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.**

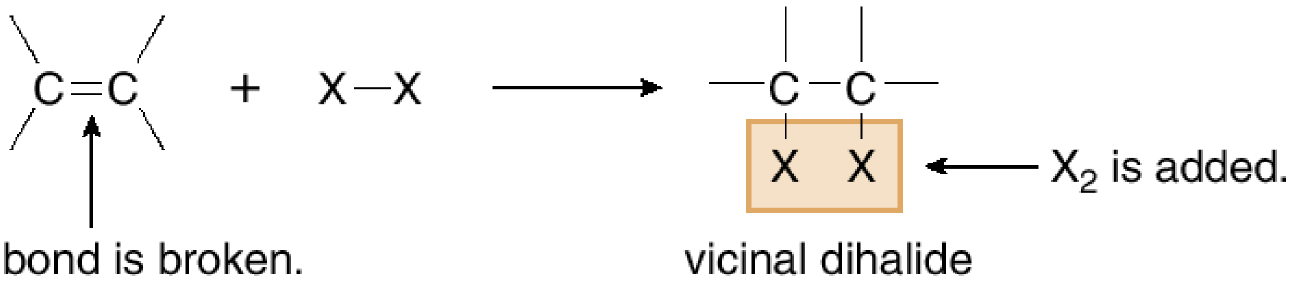
Electrophilic Addition of Alcohols

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.

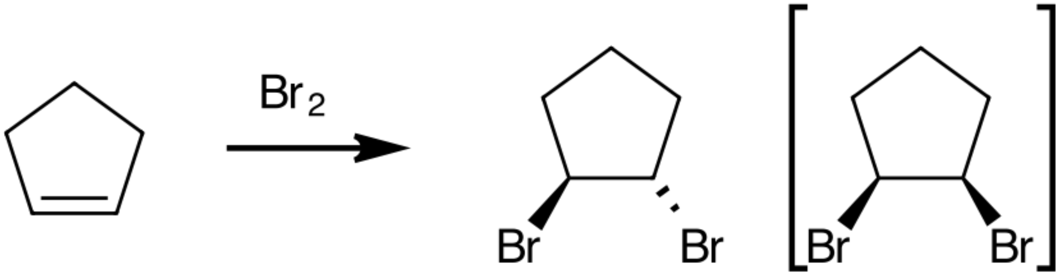


Halogenation - Addition of Halogens

Halogenation



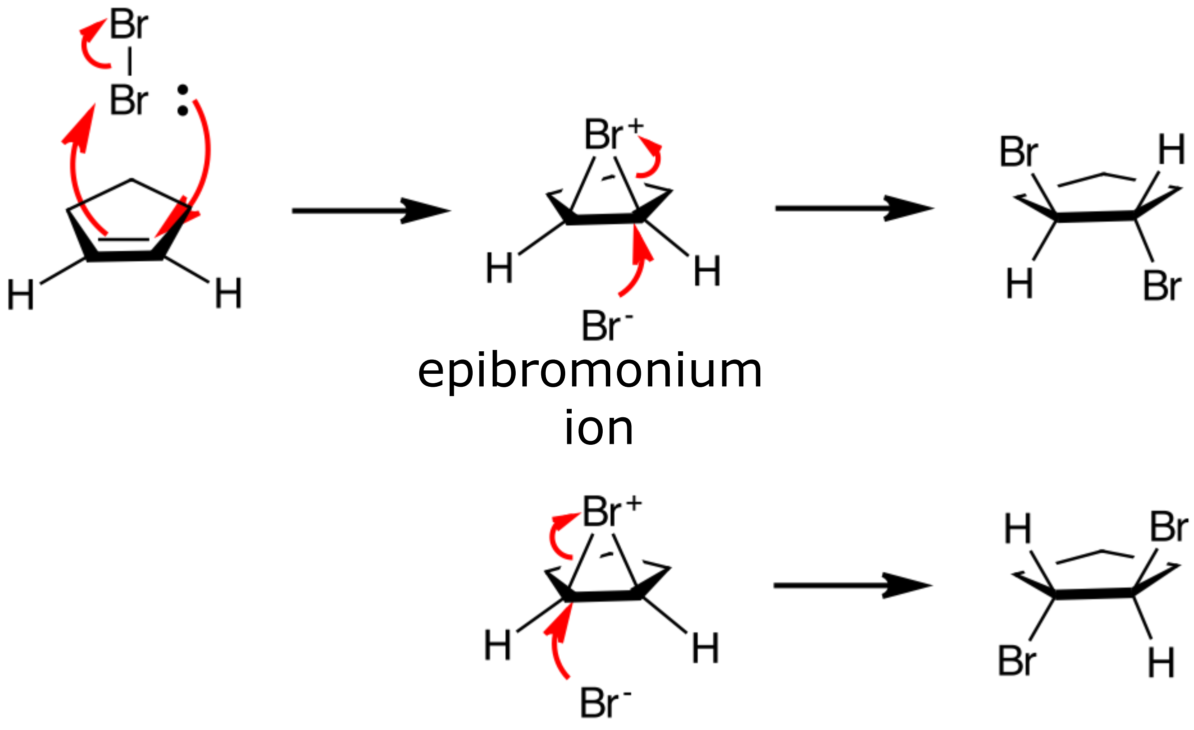
Anti addition



trans

cis
(not observed)

Halogenation - Mechanism

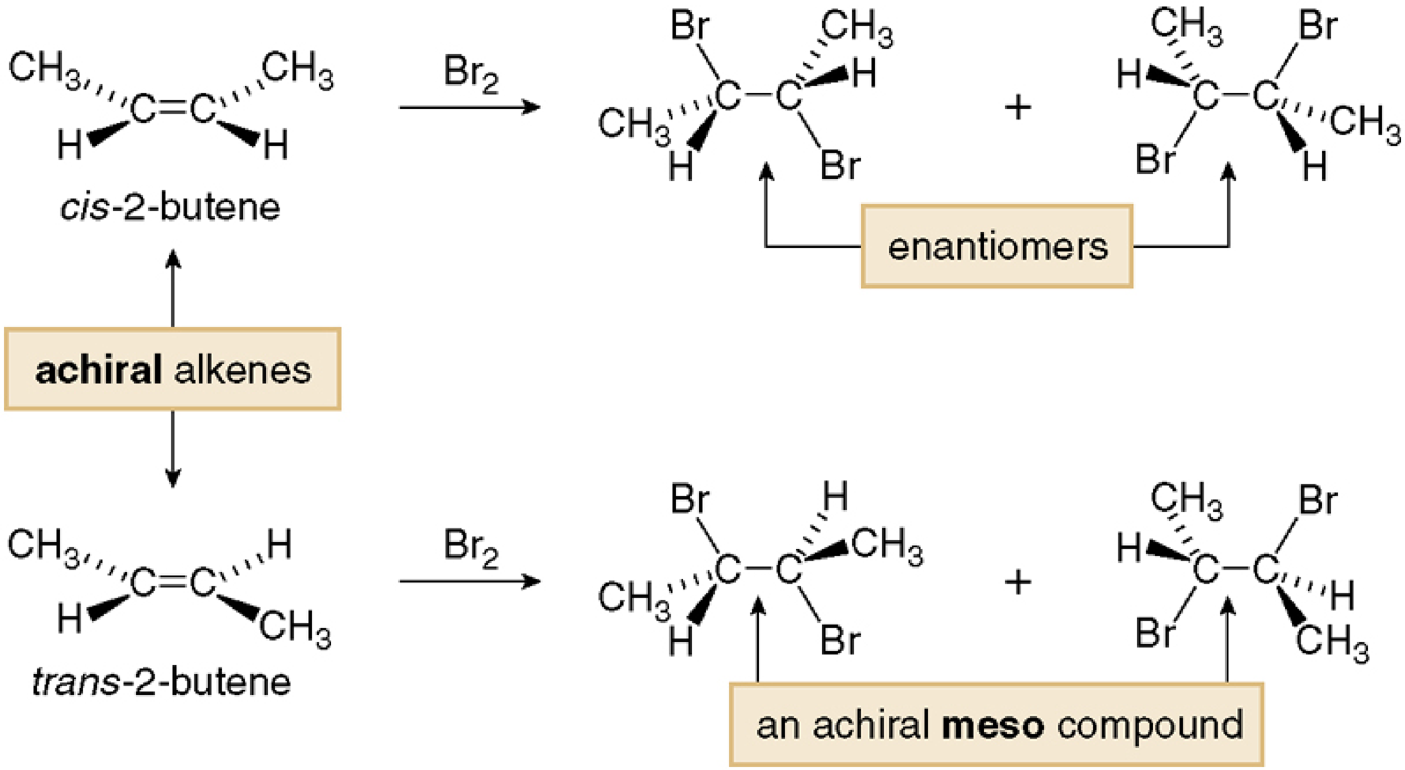


epibromonium
ion

enantiomers

video

Halogenation - Stereochemistry



cis-2-butene

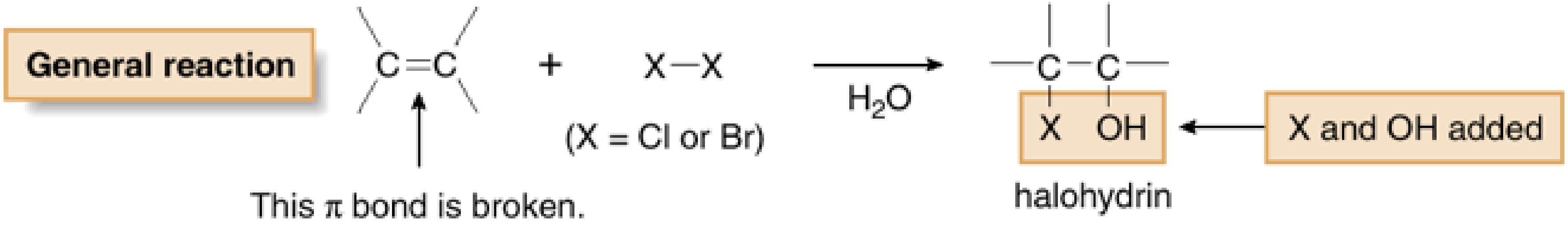
enantiomers

achiral alkenes

trans-2-butene

an achiral **meso** compound

Halohydrin Formation



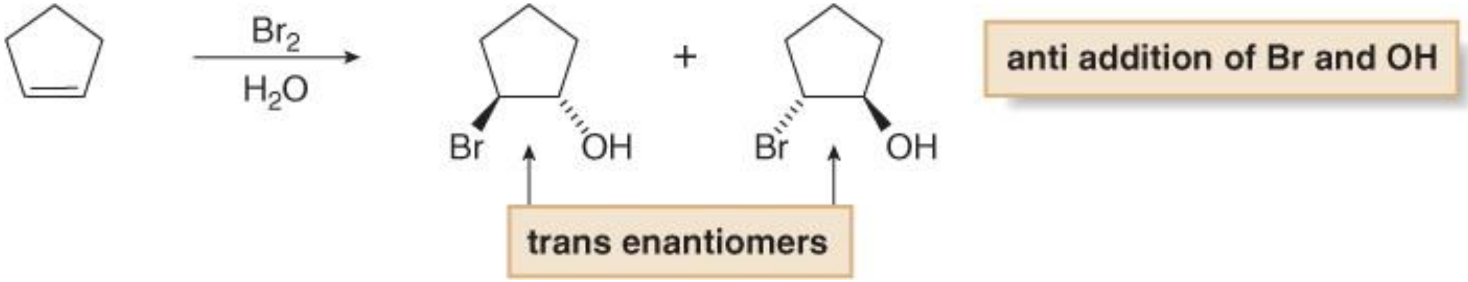
General reaction

$C{=}C + X{-}X \xrightarrow{H_2O}$ halohydrin

(X = Cl or Br)

This π bond is broken.

X and OH added

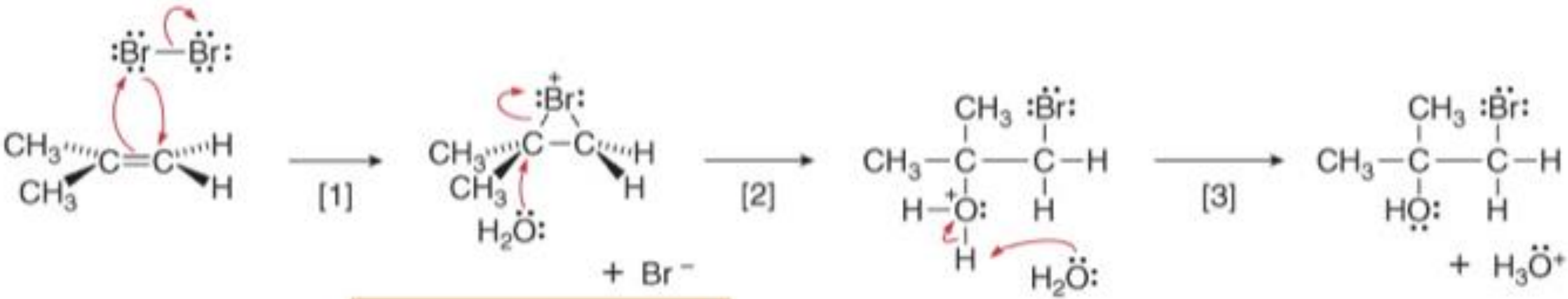


$\xrightarrow[H_2O]{Br_2}$

anti addition of Br and OH

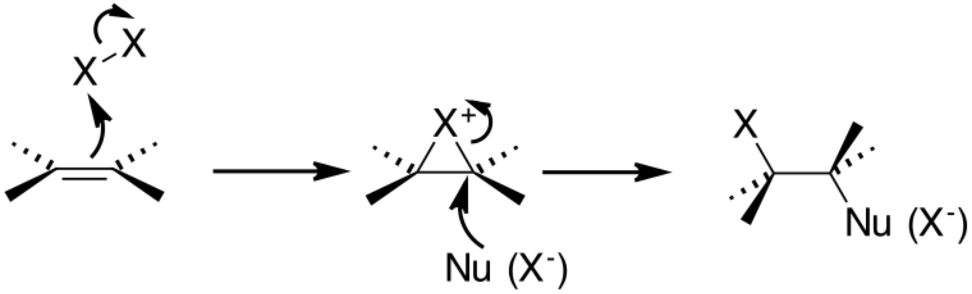
trans enantiomers

Halohydrin Formation



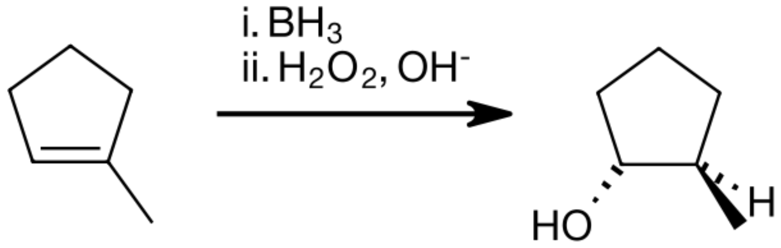
nucleophilic attack at the **more substituted C**

Halogenation and Halohydrin Formation



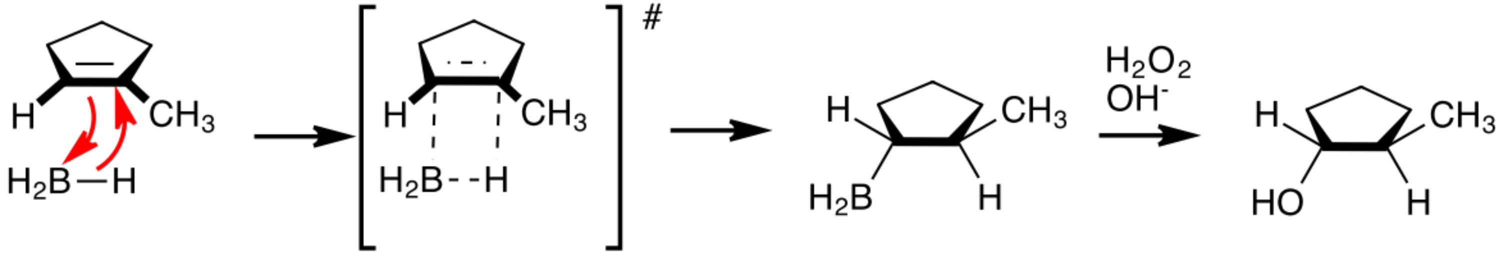
Mechanism	• The mechanism involves two steps. • The rate-determining step forms a bridged halonium ion. • No rearrangements can occur.
Regioselectivity	• Markovnikov's rule is followed. X^+ bonds to the less substituted carbon.
Stereochemistry	• Anti addition occurs.

Hydroboration - Oxidation



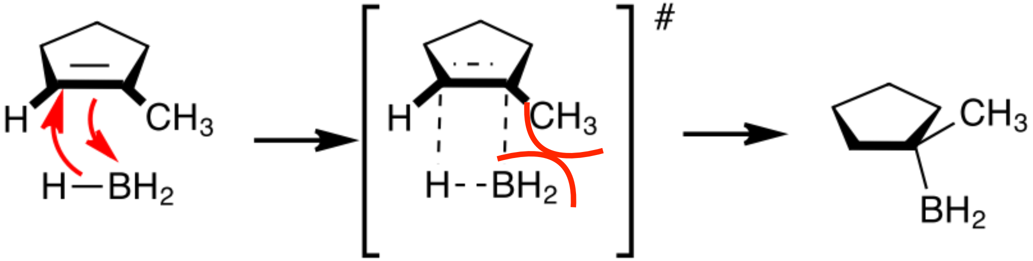
anti-Markovnikow
stereoselective (syn addition)

Hydroboration - Oxidation



1-methylcyclopentene

trans, secondary alcohol



sterically hindered

not observed

video

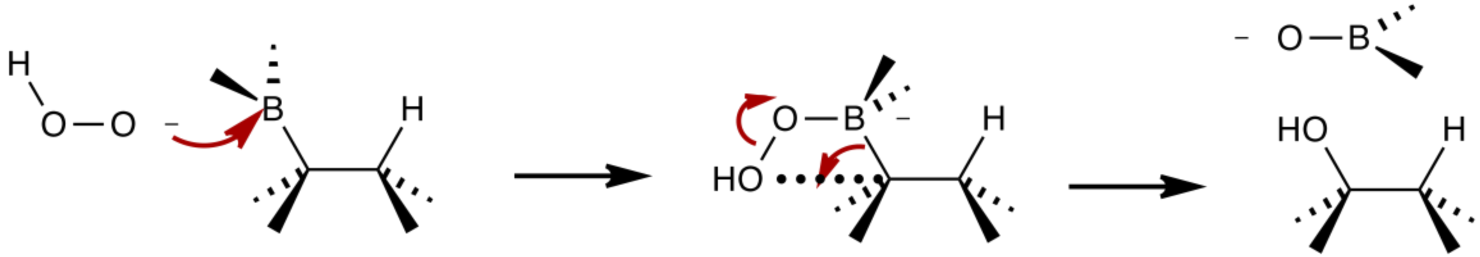
Regioselective addition of BH_3

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).

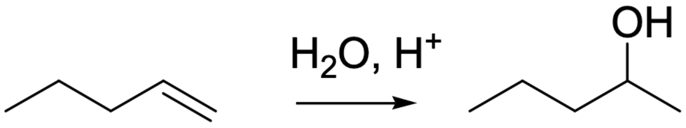
$$CH_3\text{-}CH_2\text{-}CH_2\text{-}BH_2 \xrightarrow{H_2O_2,\ OH^-} CH_3\text{-}CH_2\text{-}CH_2\text{-}OH$$

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

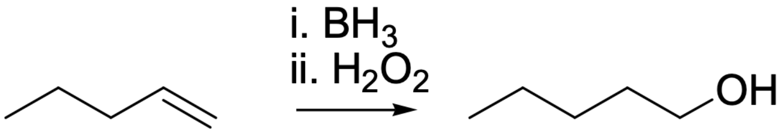


Hydroboration - Oxidation

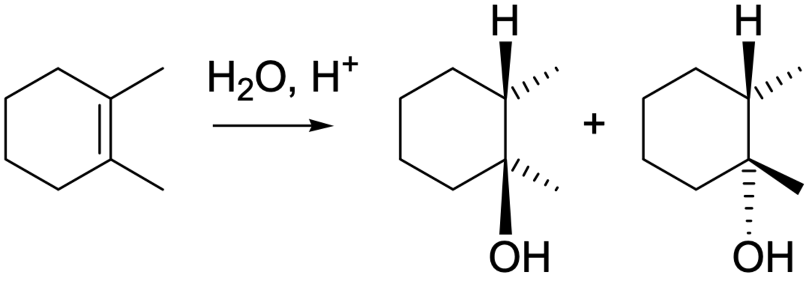
- The overall result is syn addition of the elements of H and OH to a double bond in an "anti-Markovnikov" fashion.



Markovnikov



anti-Markovnikov

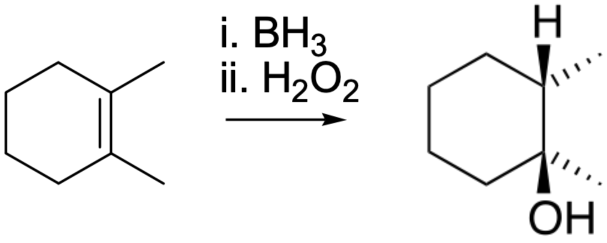


syn

(±)

anti

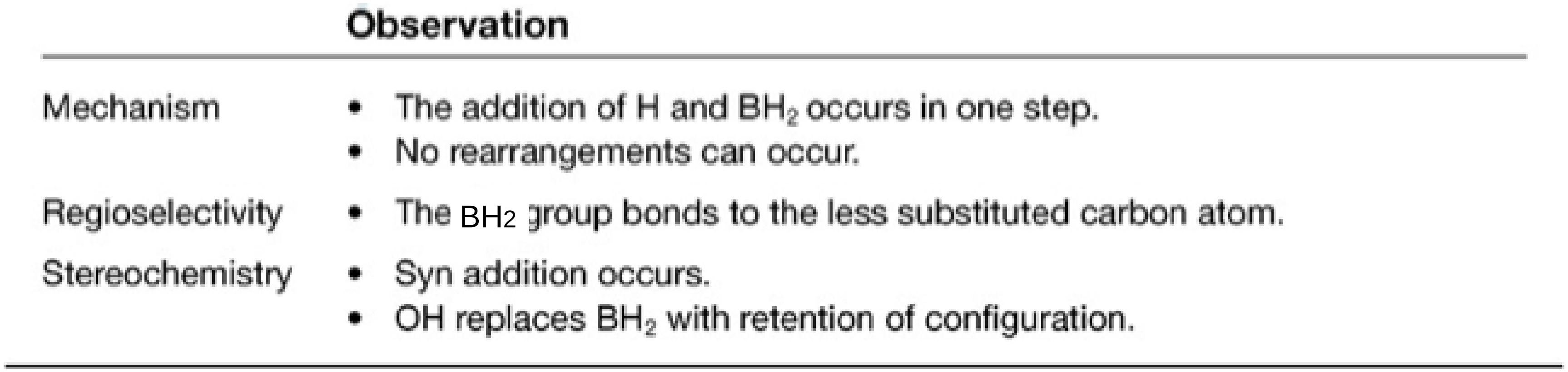
(±)



syn

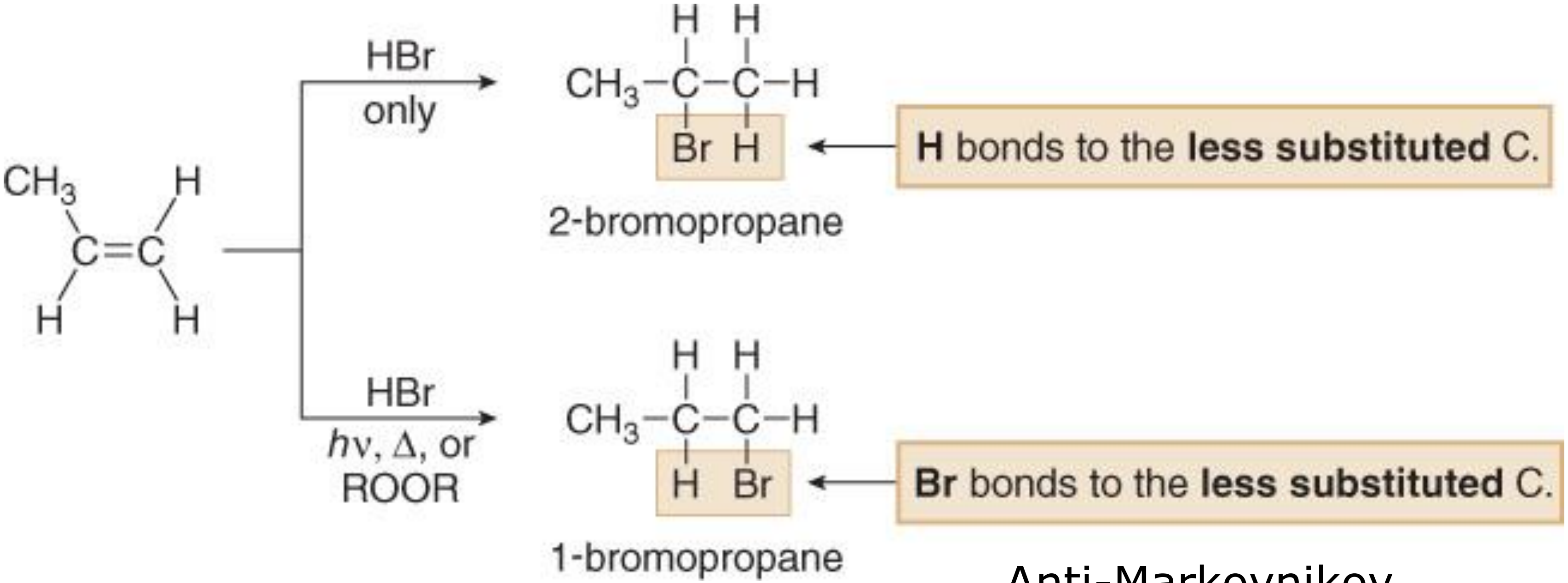
(±)

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.

Radical Additions to Double Bonds



2-bromopropane

1-bromopropane

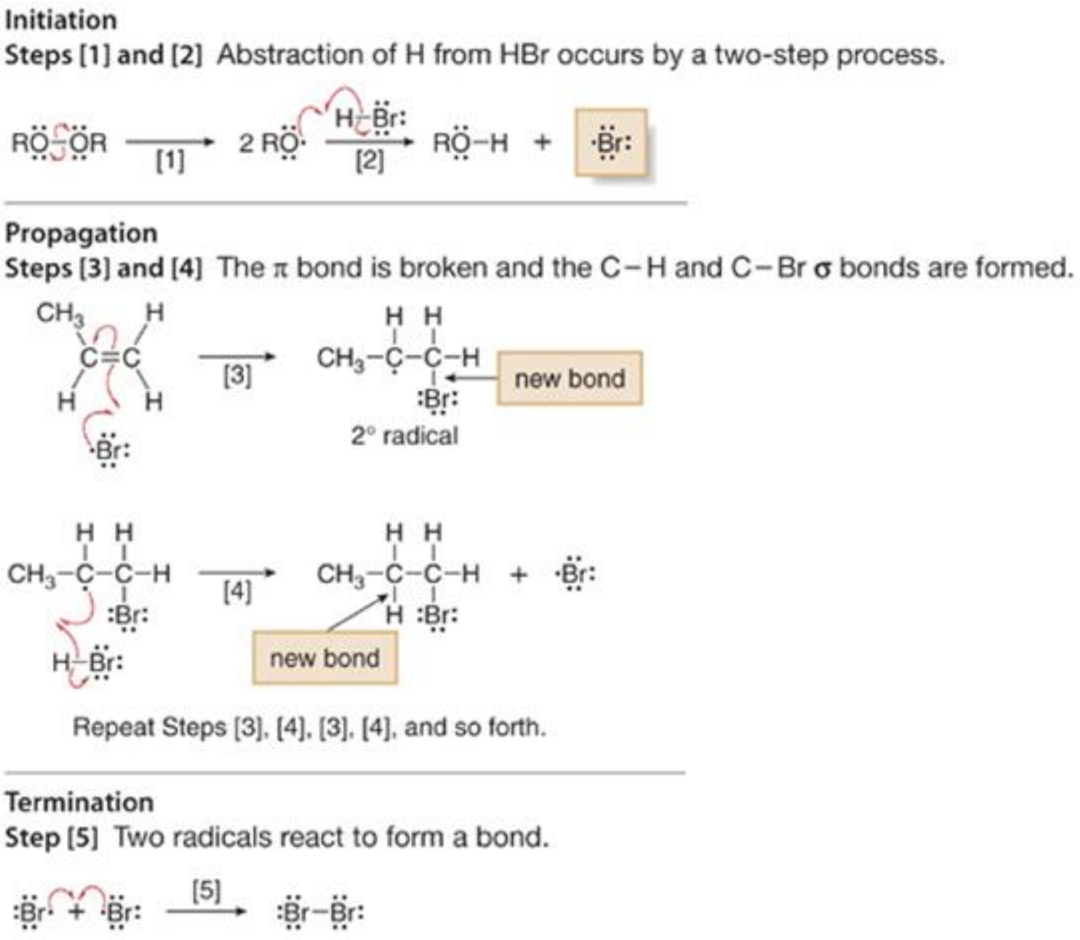
H bonds to the **less substituted** C.

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

Anti-Markovnikov

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.

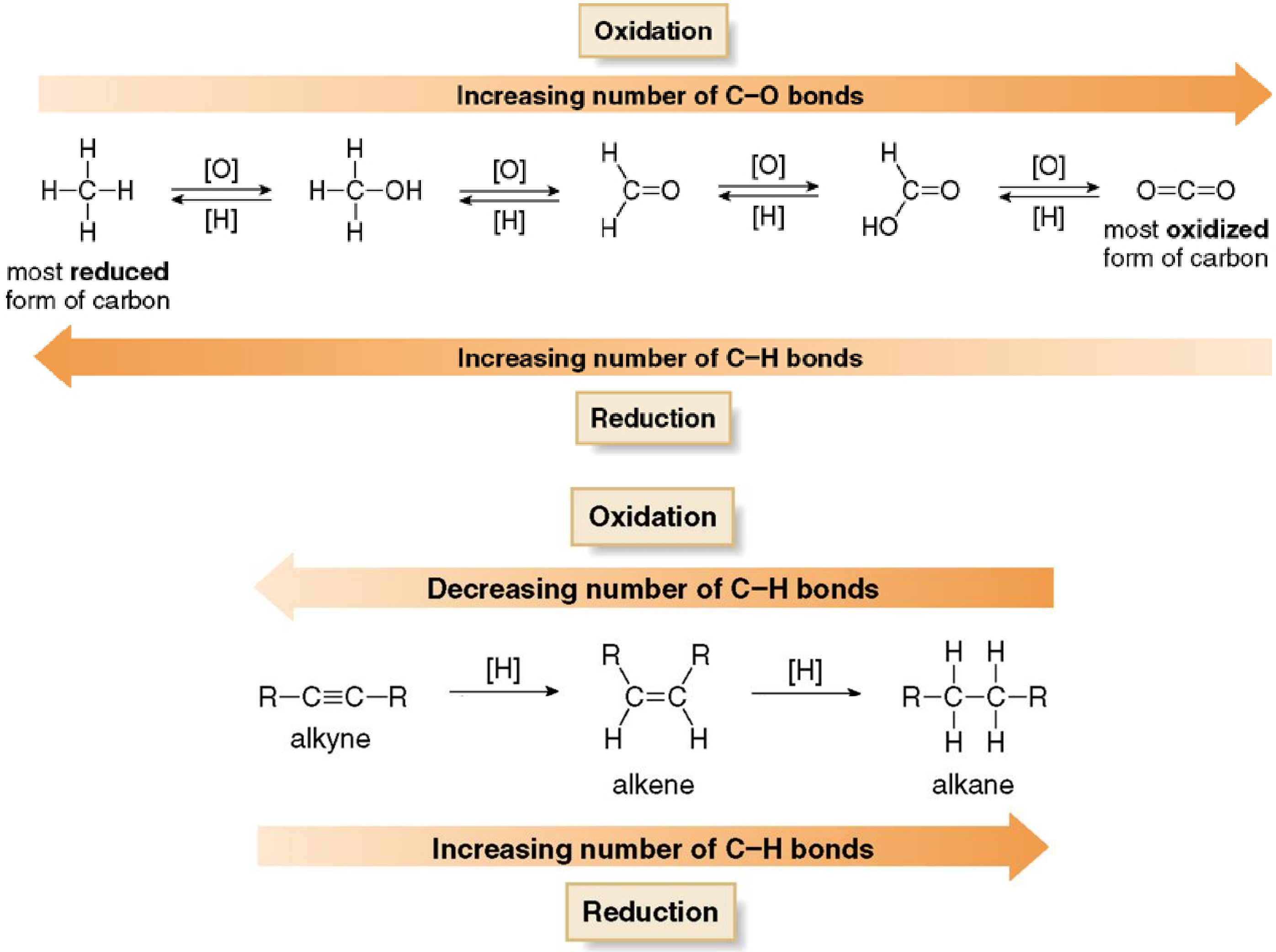
Termination

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

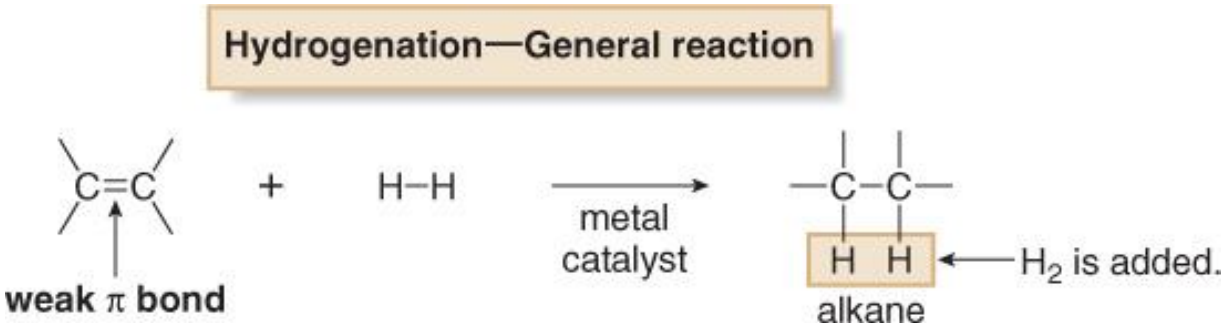
Oxidation and Reduction

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

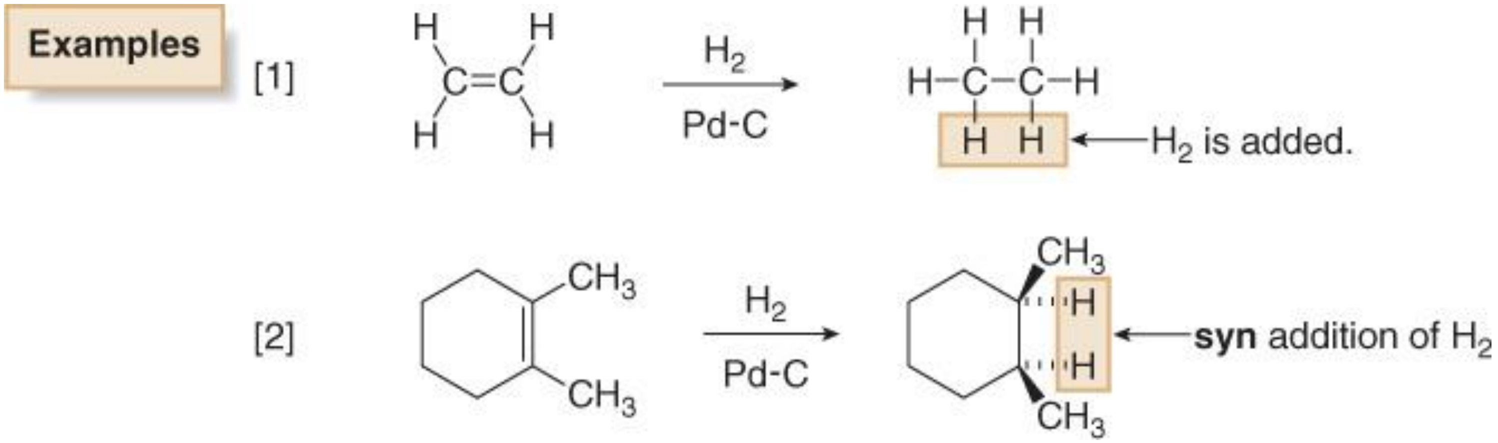
Reduction: decrease of C—O bonds or increase of C—H bonds.



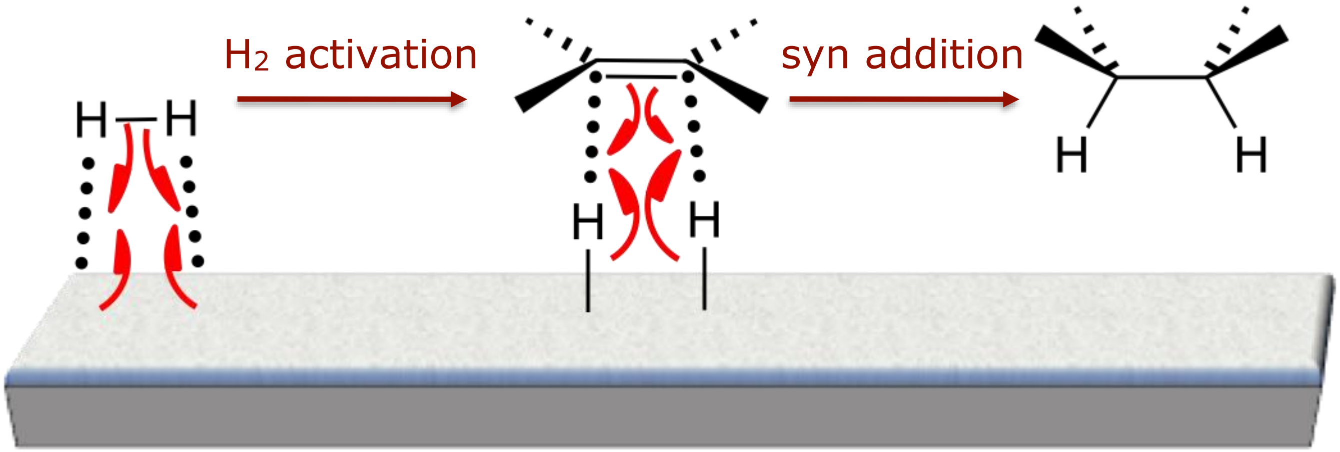
Catalytic Hydrogenation



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

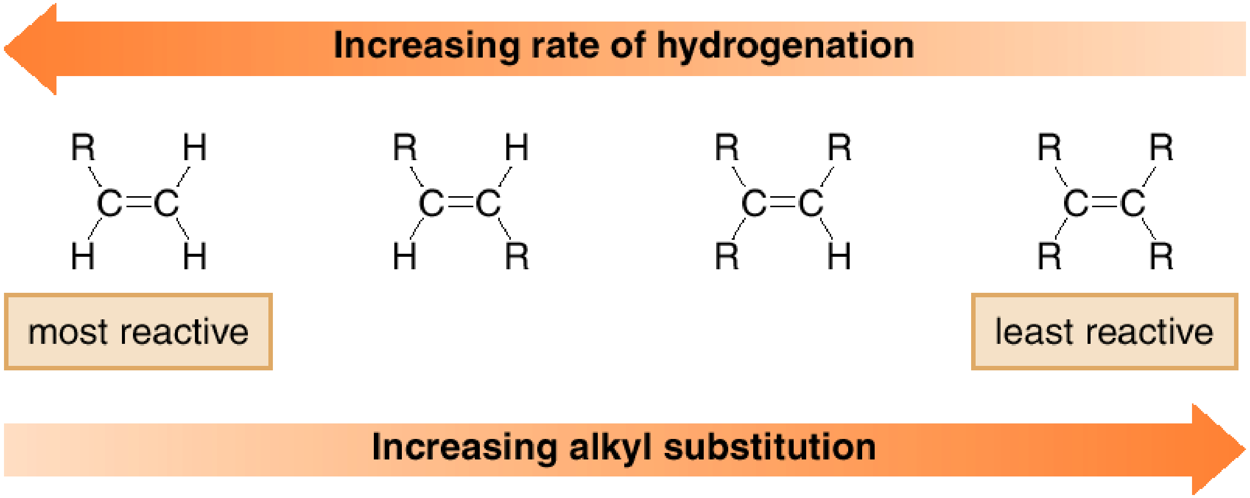


Catalytic Hydrogenation



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

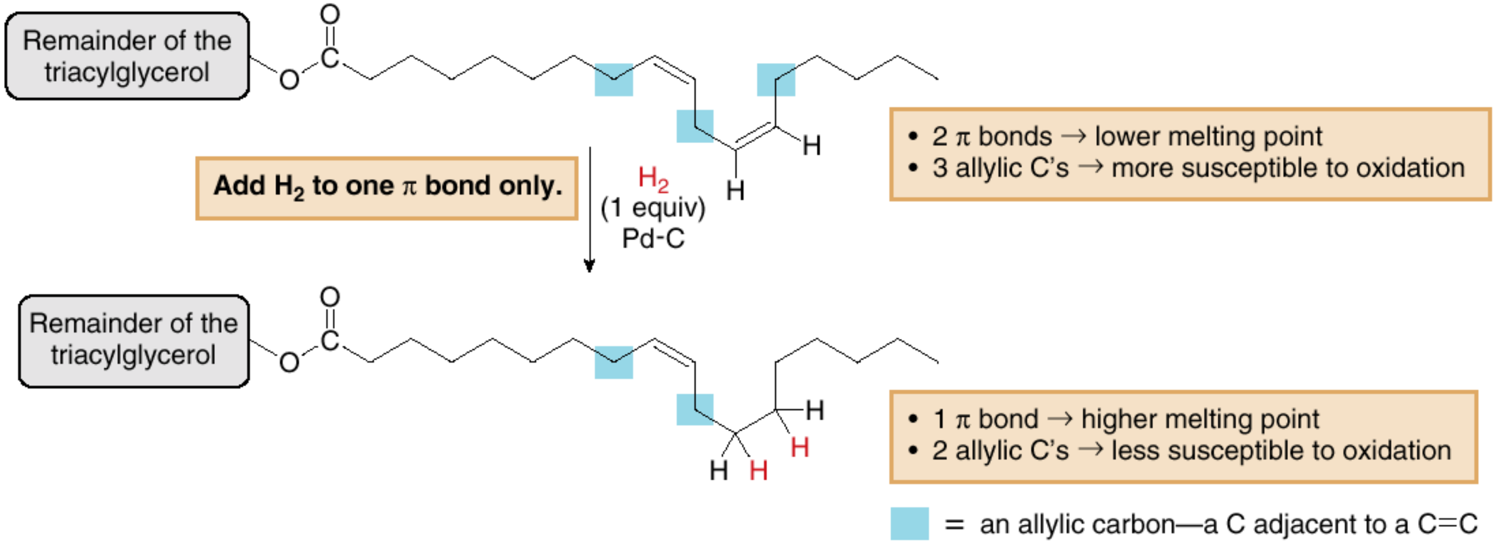
most reactive

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

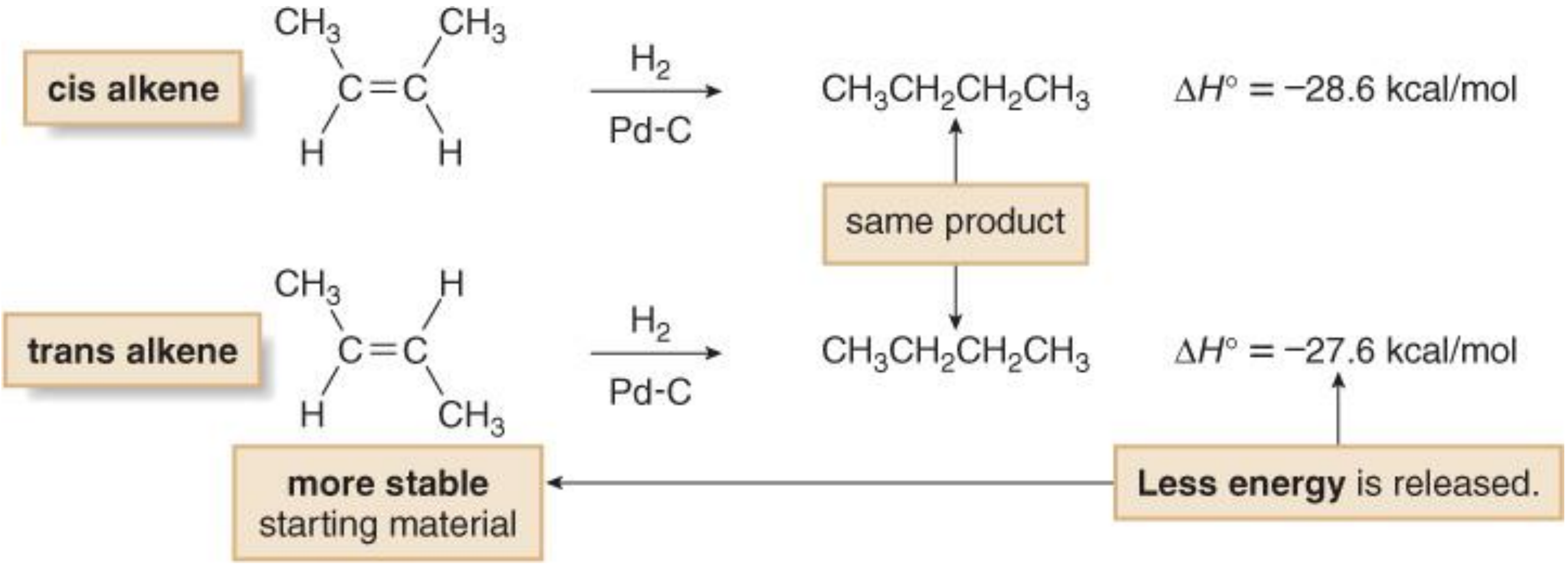
- 1 π bond → higher melting point
- 2 allylic C's → less susceptible to oxidation

🟦 = 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.

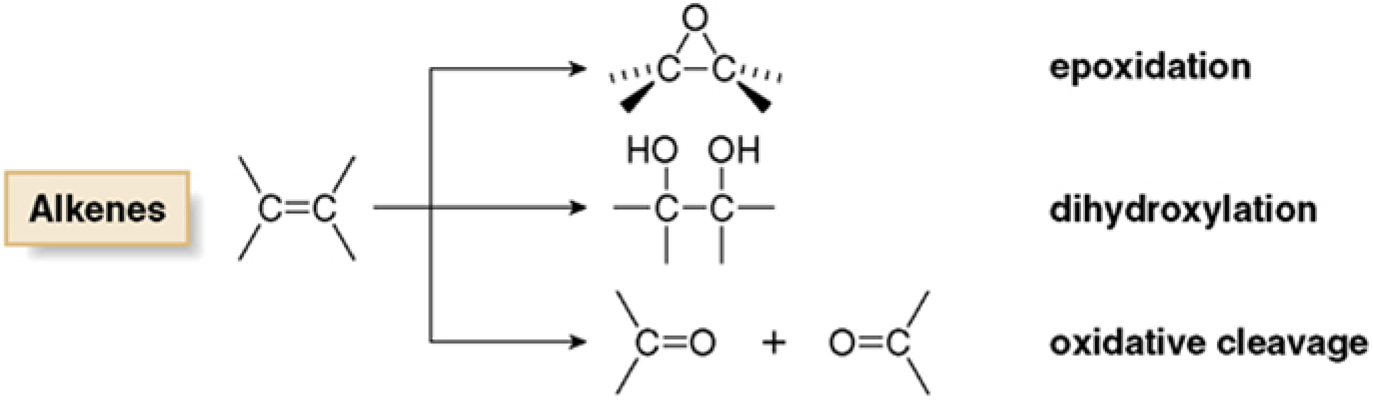


Oxidations

Oxidizing agents:

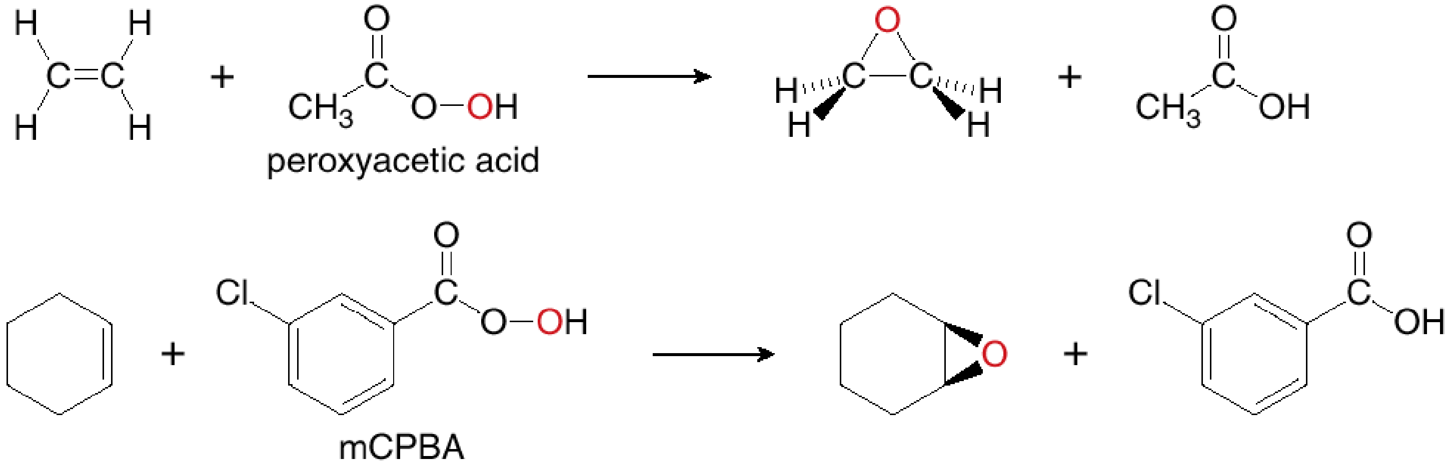
- Reagents containing an O—O bond: O_2, O_3, H_2O_2, ROOH, RCOOOH.
- Reagents containing metal-oxygen bonds: Cr(VI), Mn(VII), Os(VIII).

Reactions:



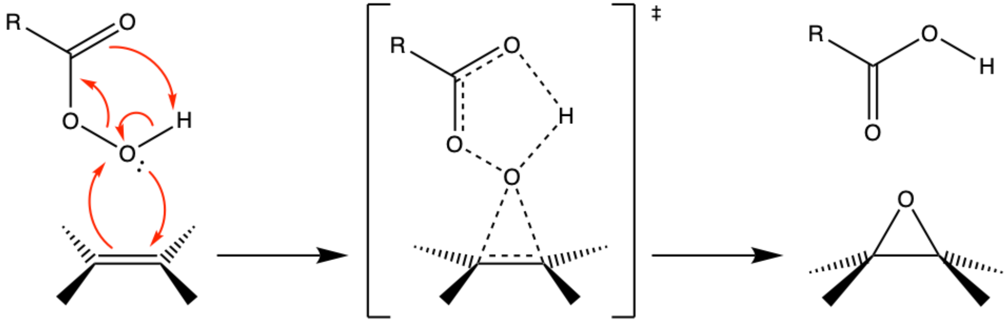
Epoxidation

Examples

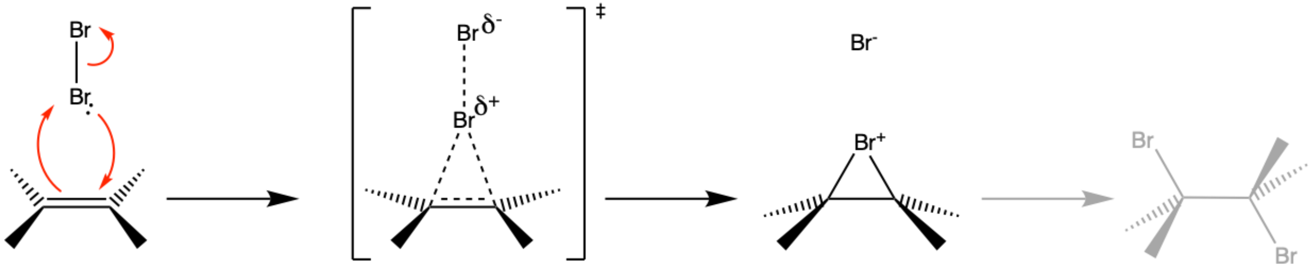


Epoxidation

One step: all bonds are broken/formed in a single step



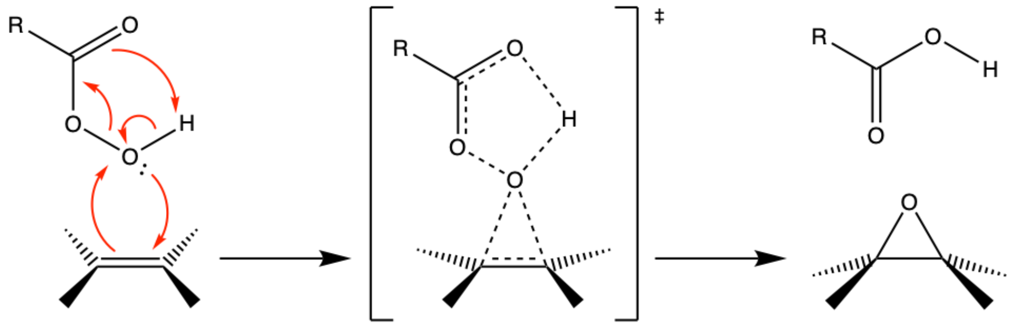
epoxidation and halogenation have similar mechanisms



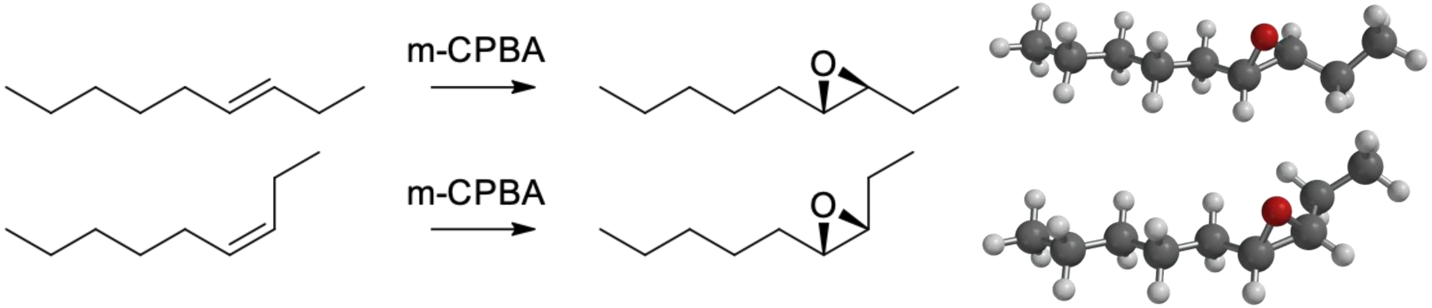
video

Epoxidation

One step: all bonds are broken/formed in a single step

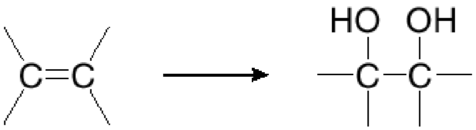


Epoxidation is stereospecific.



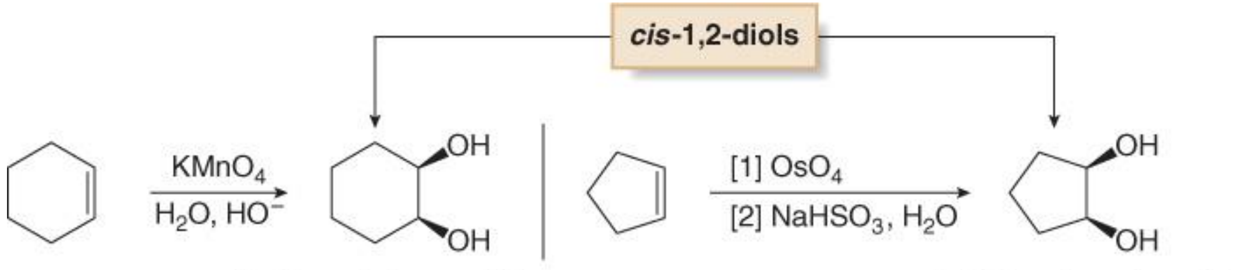
Dihydroxylation

Dihydroxylation—General reaction



1,2-diol or glycol

Syn dihydroxylation



$KMnO_4$

H_2O, HO^-

[1] OsO_4

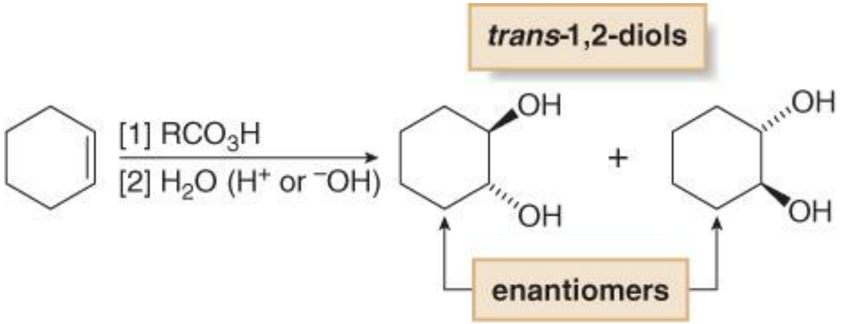
[2] $NaHSO_3$, H_2O

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

cis-1,2-cyclohexanediol

cis-1,2-cyclopentanediol

Anti dihydroxylation



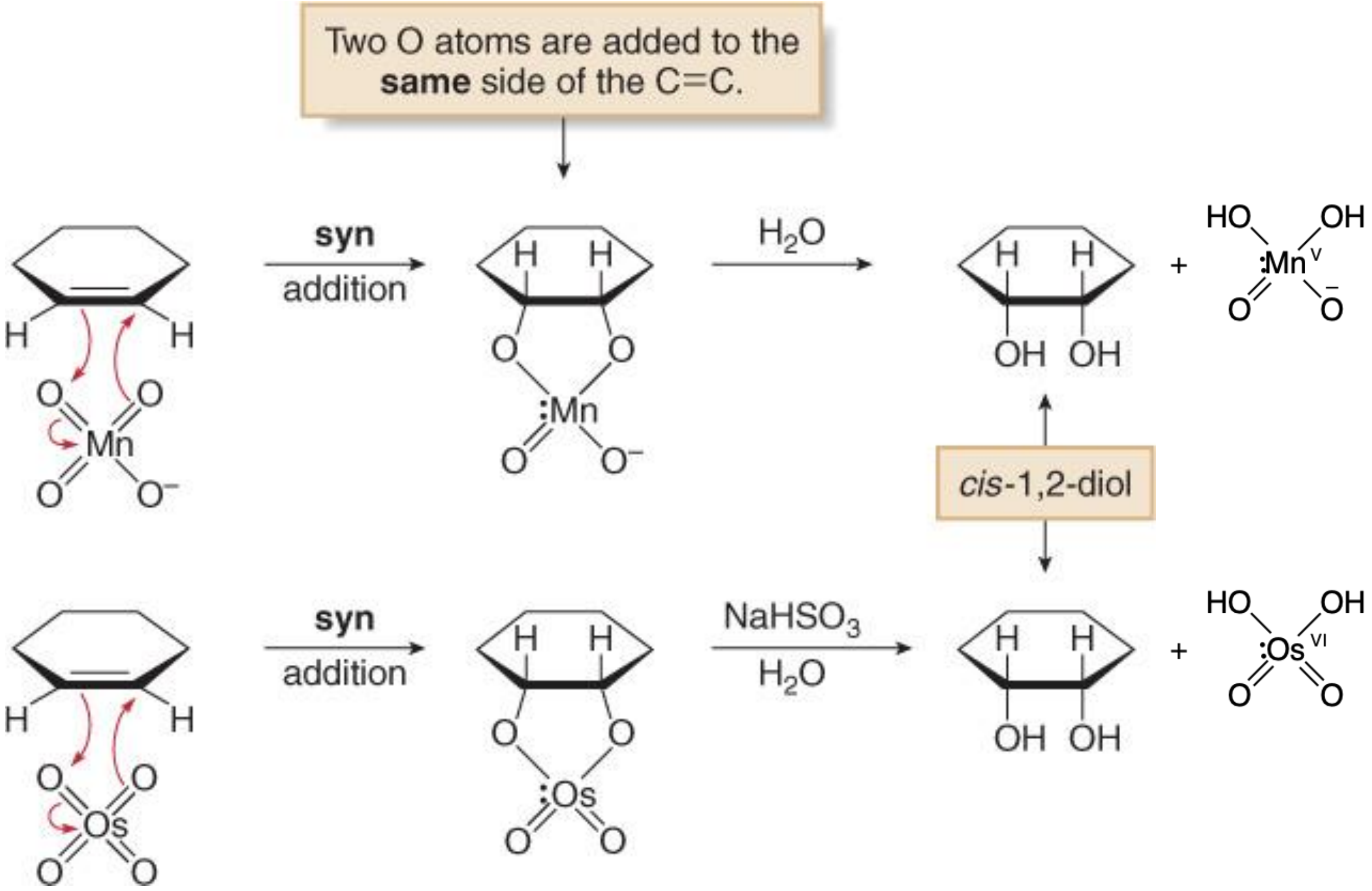
[1] RCO_3H

[2] H_2O (H^+ or ^-OH)

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

enantiomers

Syn Dihydroxylation

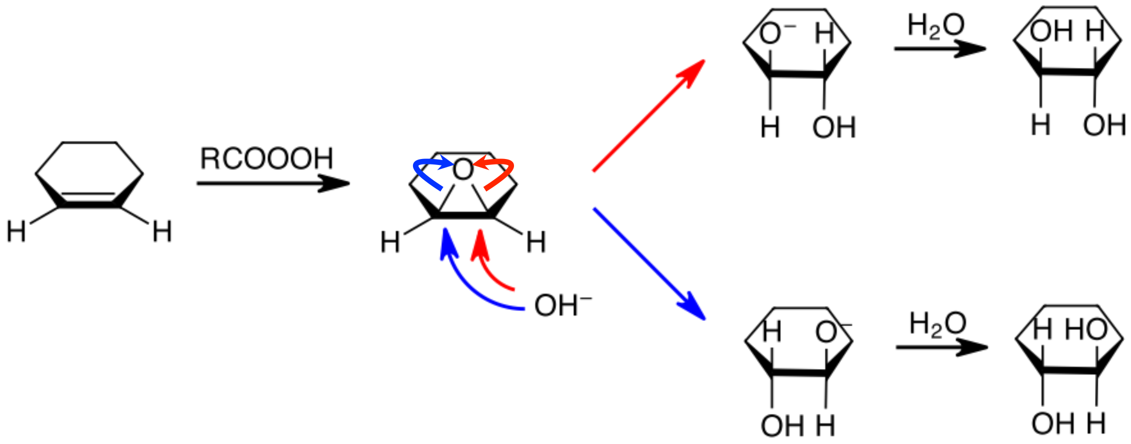


Two O atoms are added to the **same** side of the C=C.

cis-1,2-diol

video

Anti Dihydroxylation

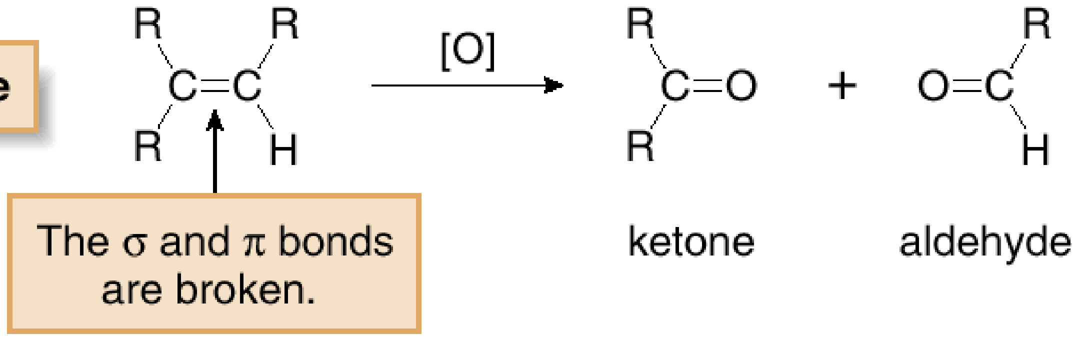


enantiomers

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

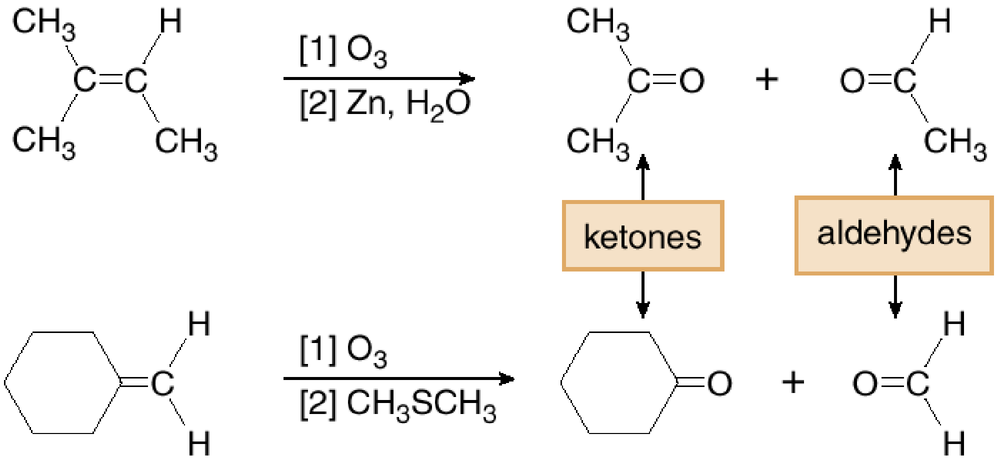


The σ and π bonds are broken.

ketone

aldehyde

Examples

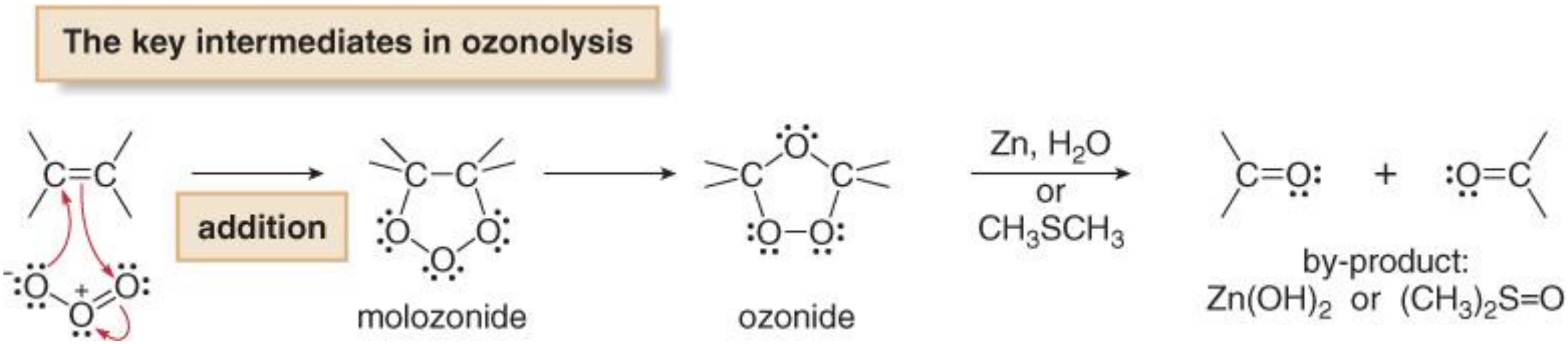


ketones

aldehydes

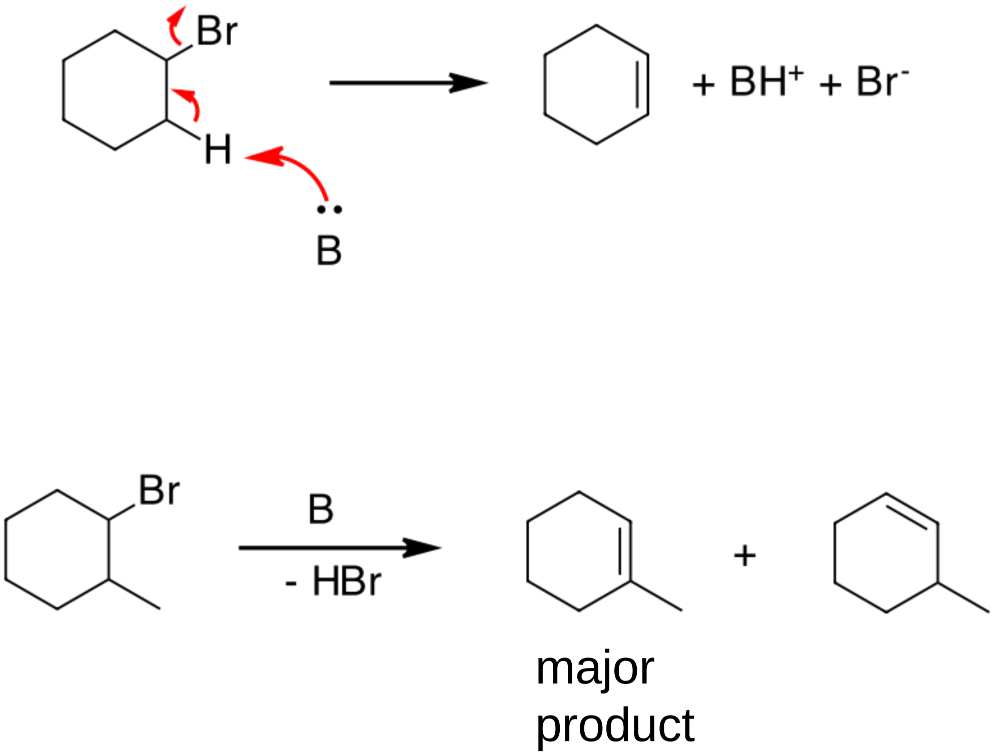
Oxidative Cleavage

- 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

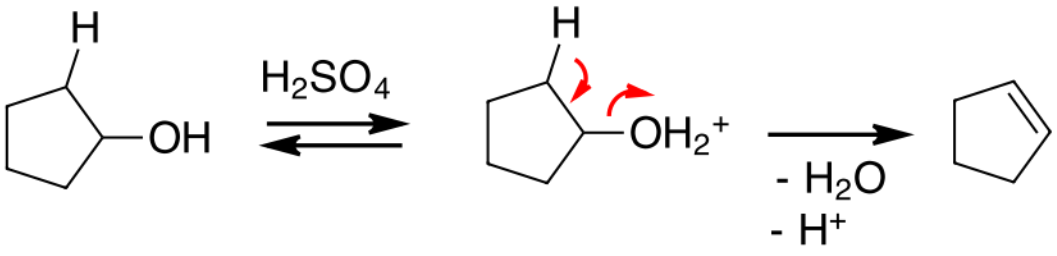
Preparation of Alkenes.
1 Dehydroalogenation

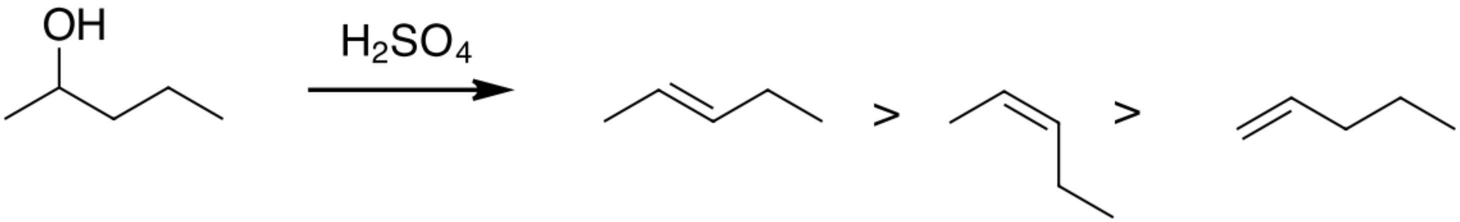


Saytzev's rule.

The more substituted alkene (more stable) is favoured

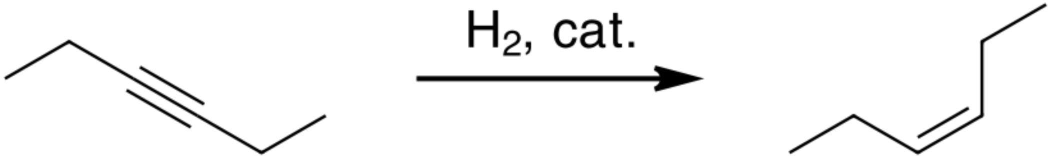
Preparation of Alkenes.
2 Dehydration

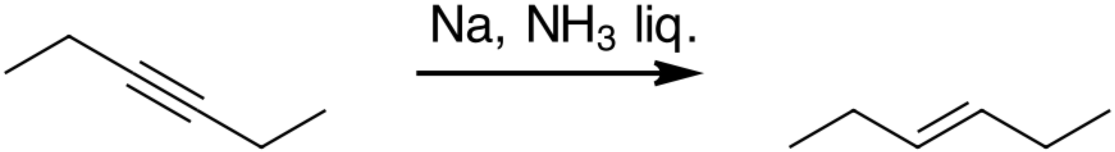




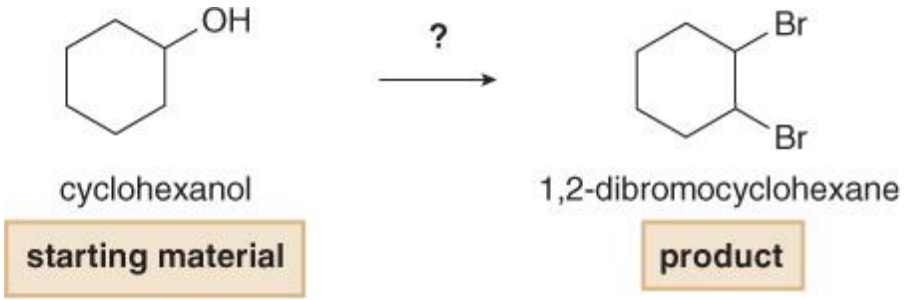
Saytzev's rule.
The more substituted alkene (more stable) is favoured.
Trans alkene formation is favoured over cis

Preparation of Alkenes.
3 Hydrogenation/Reduction of Alkynes



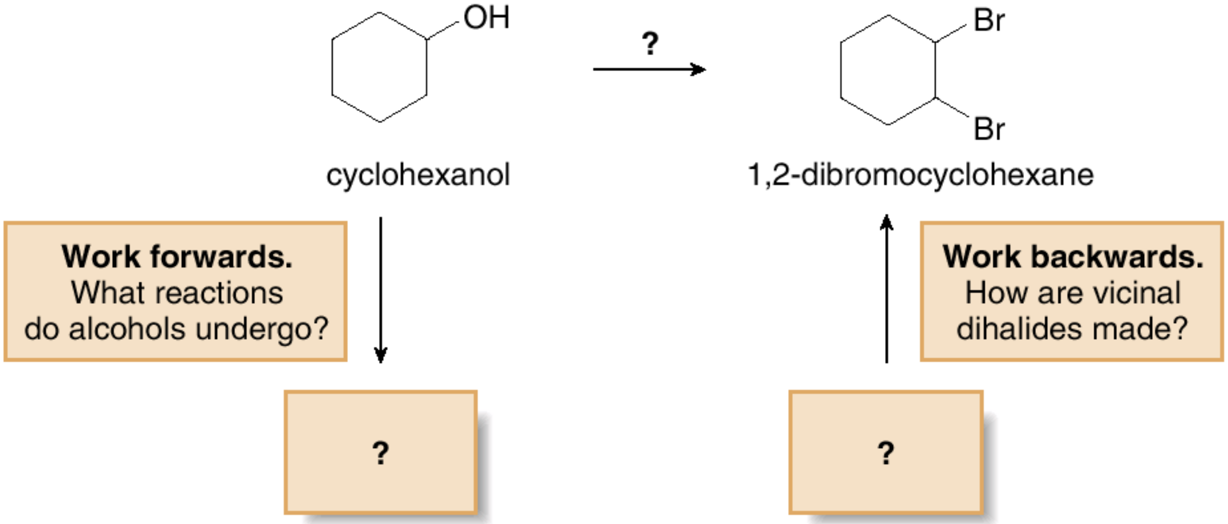


Alkenes in Organic Synthesis



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?



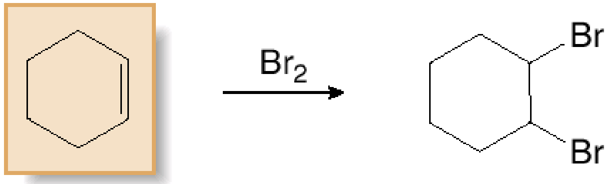
Work forwards. What reactions do alcohols undergo?

Work backwards. How are vicinal dihalides made?

Alkenes in Organic Synthesis

Working backwards:

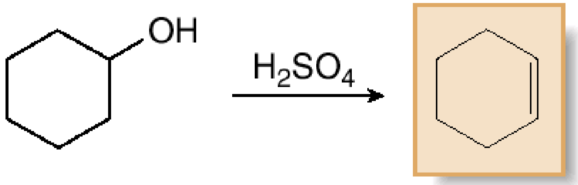
[1] 1,2-Dibromocyclohexane, a vicinal dibromide, can be prepared by the addition of Br_2 to **cyclohexene.**



cyclohexene 1,2-dibromocyclohexane

Working forwards:

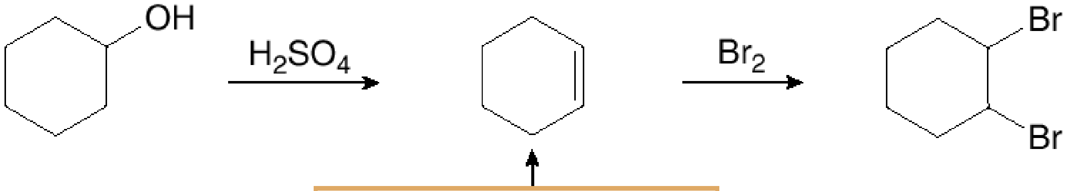
[2] Cyclohexanol can undergo acid-catalyzed dehydration to form **cyclohexene.**



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.

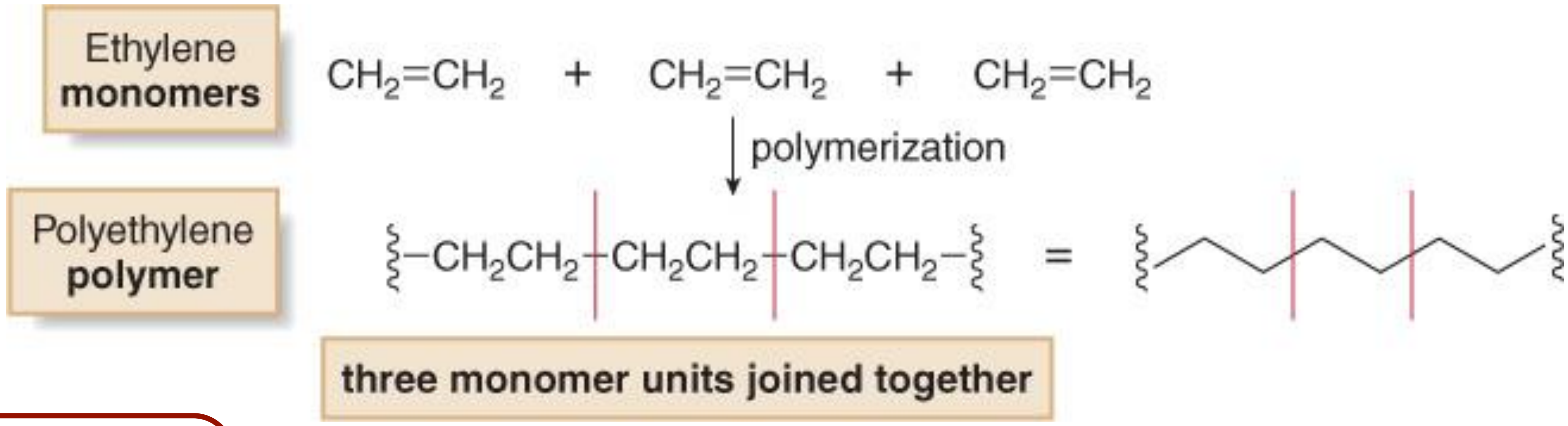
A two-step synthesis



a synthetic intermediate

Polymers and Polymerization

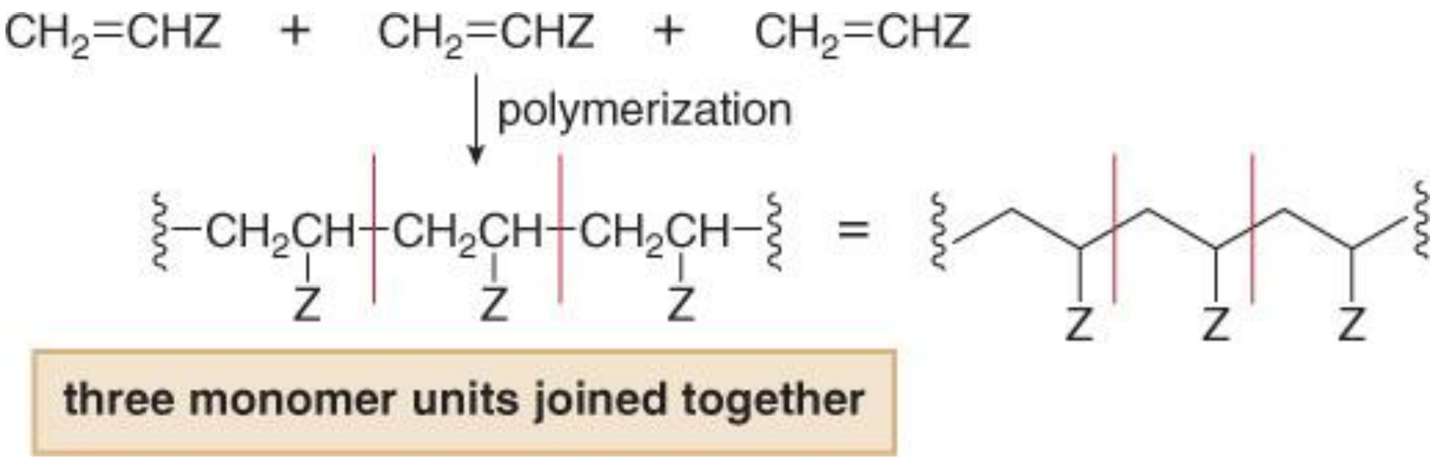
- Polymers are large molecules made up of repeating units of smaller molecules called monomers. They include biologically important compounds such as proteins and carbohydrates, as well as synthetic plastics such as polyethylene, polyvinyl chloride (PVC) and polystyrene.
- Polymerization is the joining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



Polyethylene (PE)

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.



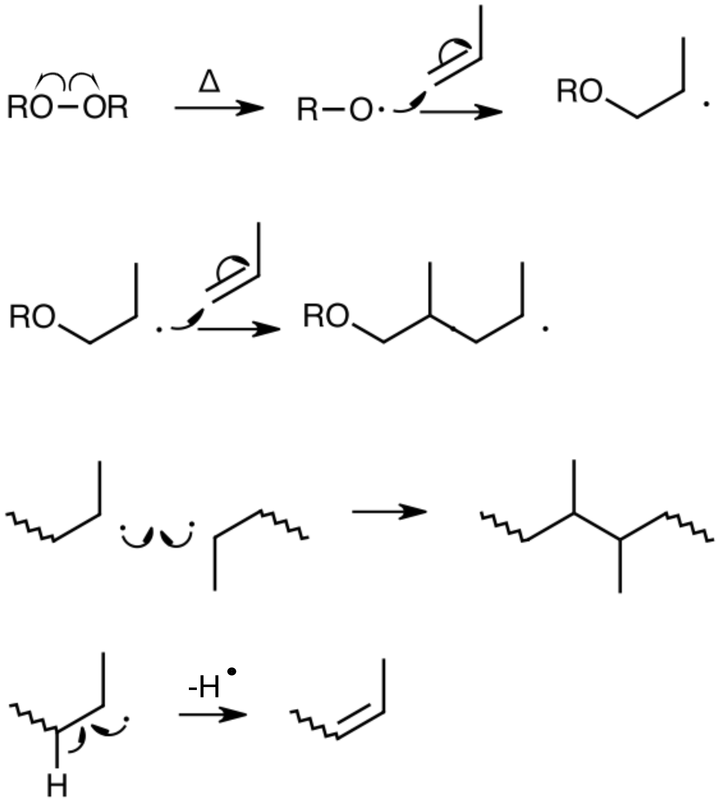
Polymers and Polymerization

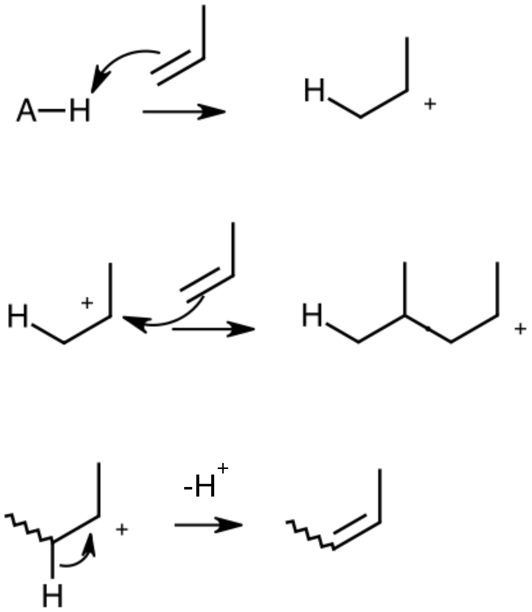
Radical Polymerization

(with a radical initiator, e.g. RO-OR)

Cationic Polymerization

(with a Broensted or a Lewis acid
e.g. $AlCl_3$, $TiCl_3$)





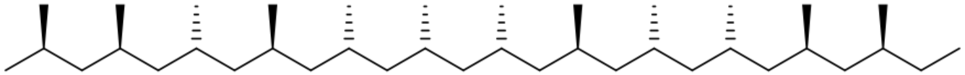
Initiation

Propagation

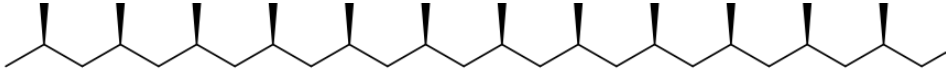
Termination

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

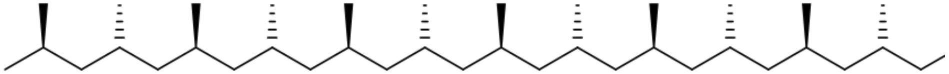
Polymers and Polymerization



atactic ($TiCl_3$, $AlCl_3$)



isotactic ($TiCl_3$, $AlEt_2Cl$)



sindiotactic ($TiCl_4$, AlR_3)

Cationic polymerization - Ziegler-Natta catalysts

Polymers and Polymerization

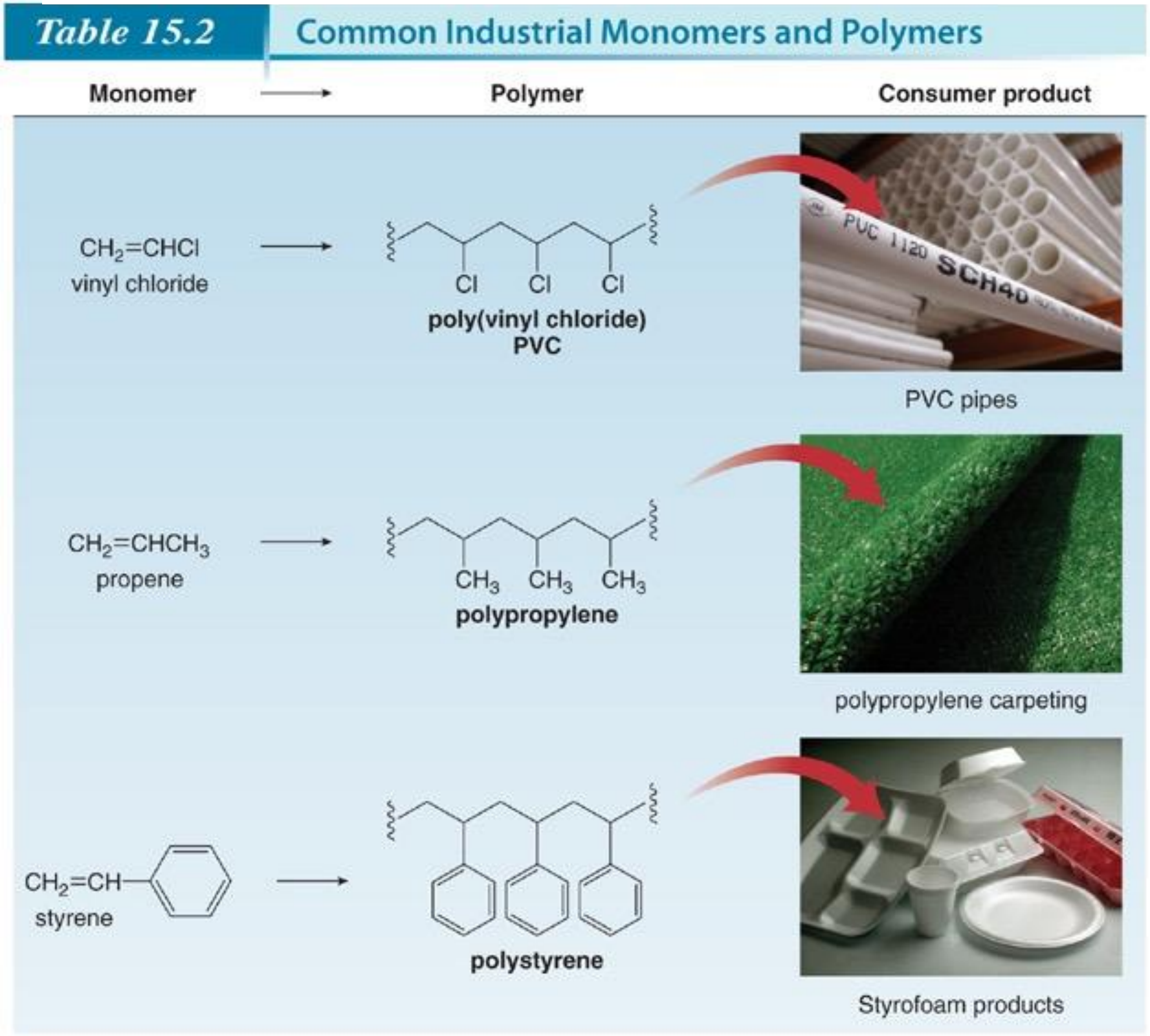


Table 15.2 Common Industrial Monomers and Polymers

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

© The McGraw-Hill Companies, Inc./John Thoeming, photographer