

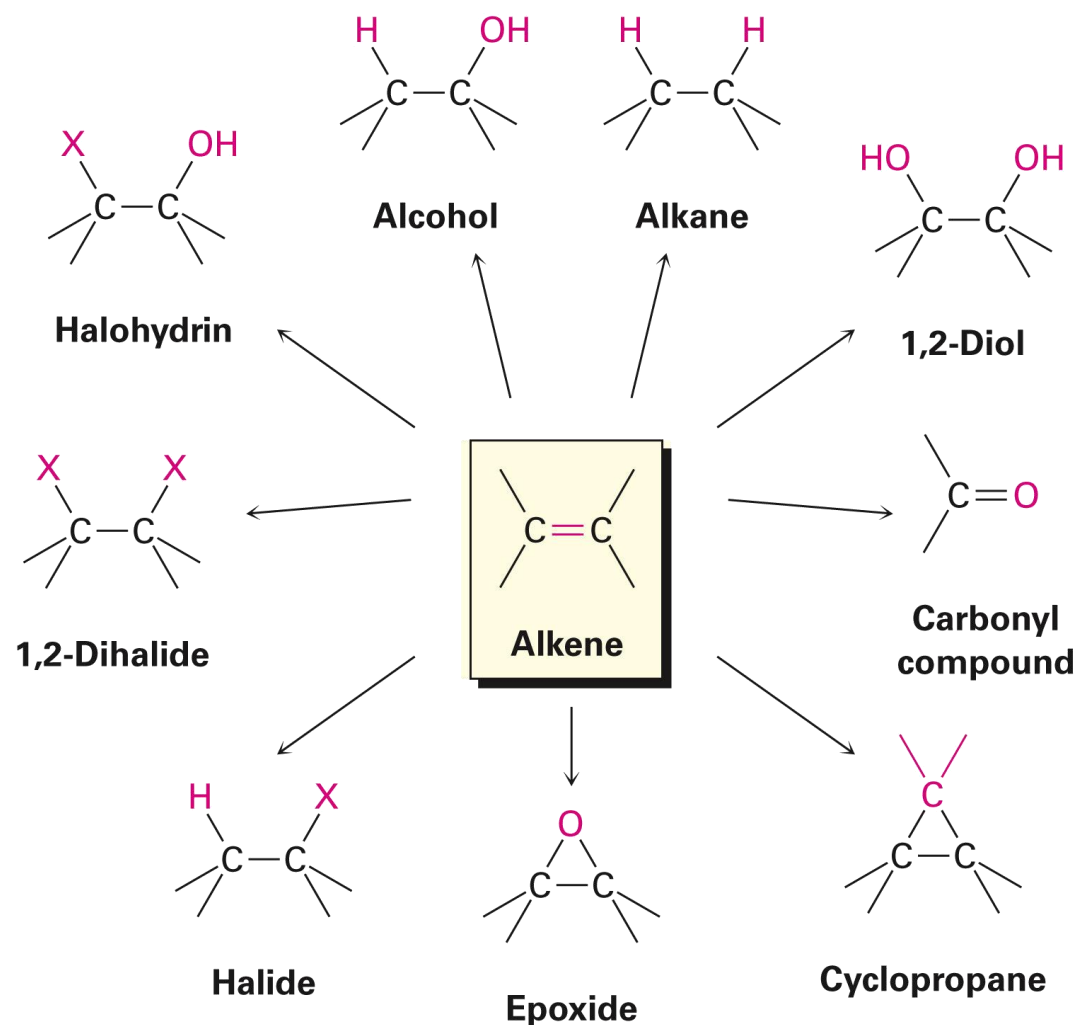
# Lecture 5

## Alkene Reactions

Organic Chemistry, Chapter 8, McMurry, Alkenes-II

# Diverse Reactions of Alkenes

- ▶ Alkenes react with many electrophiles to give useful products by addition (often through special reagents)

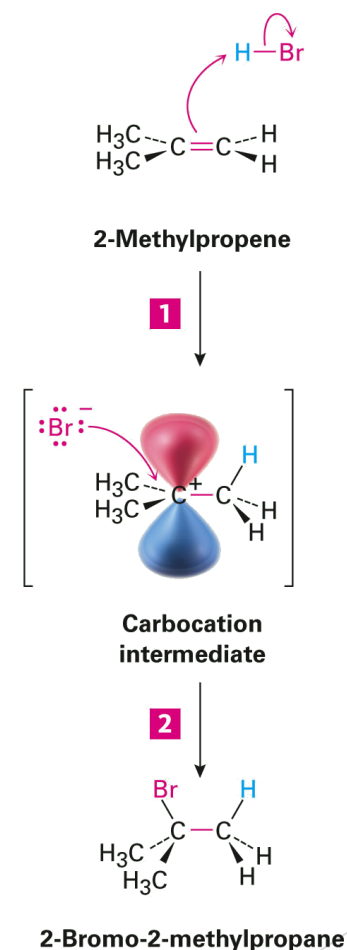


# Electrophilic Addition of Alkenes

- ▶ General reaction mechanism of electrophilic addition
- ▶ Attack on electrophile (such as HBr) by  $\pi$  bond of alkene
- ▶ Produces carbocation and bromide ion
- ▶ Carbocation is an electrophile, reacting with nucleophilic bromide ion

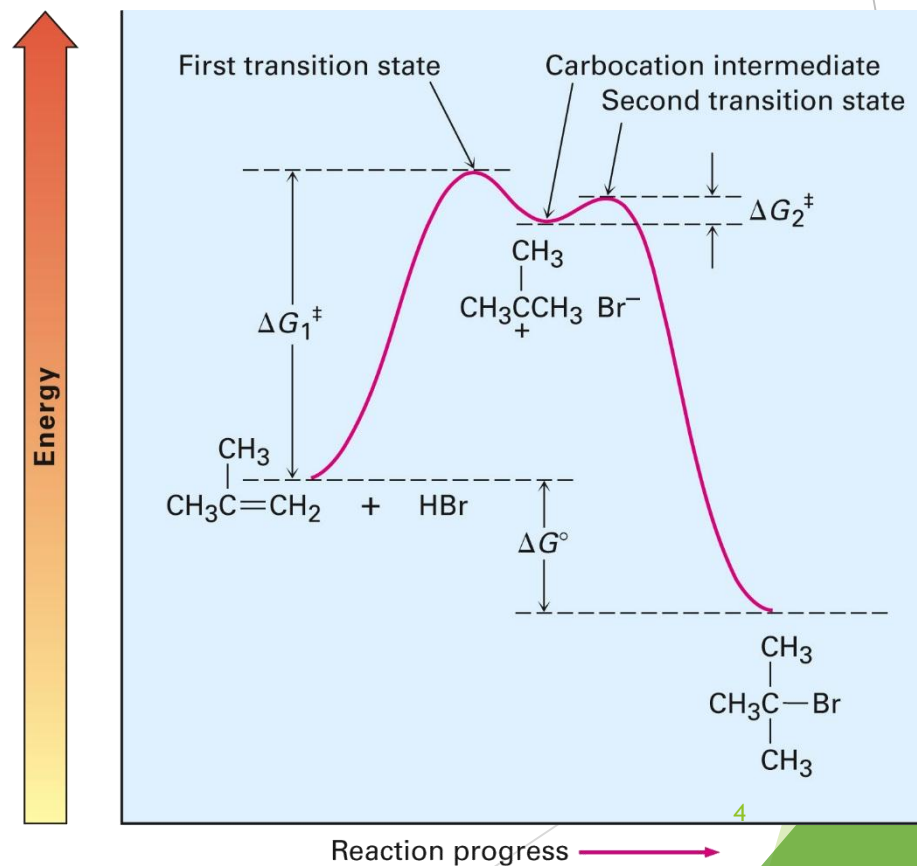
**1** A hydrogen atom on the electrophile HBr is attacked by  $\pi$  electrons from the nucleophilic double bond, forming a new C-H bond. This leaves the other carbon atom with a + charge and a vacant  $p$  orbital. Simultaneously, two electrons from the H-Br bond move onto bromine, giving bromide anion.

**2** Bromide ion donates an electron pair to the positively charged carbon atom, forming a C-Br bond and yielding the neutral addition product.



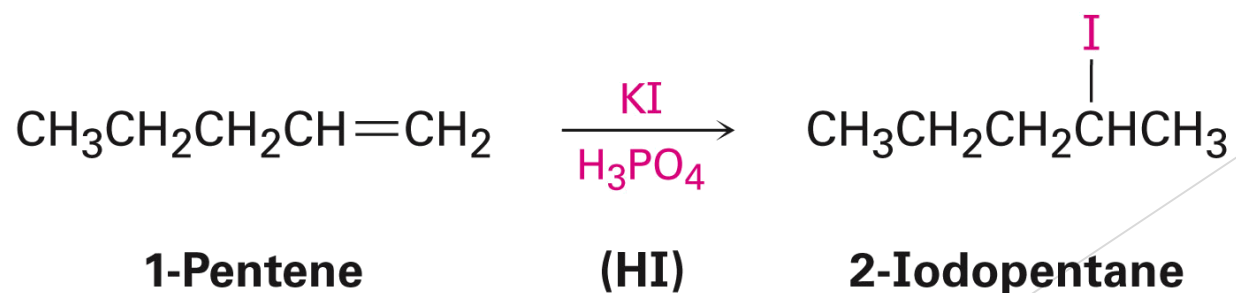
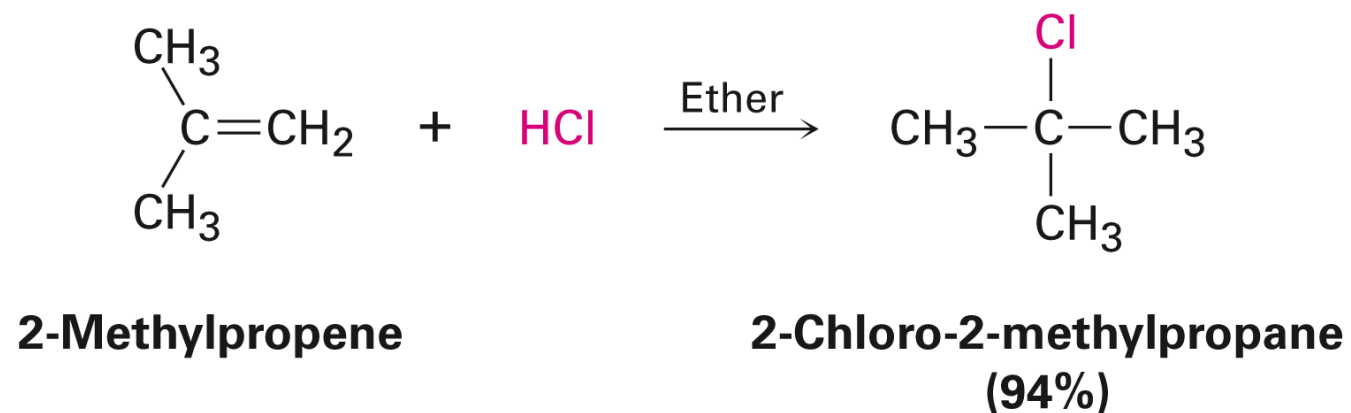
# Electrophilic Addition of Alkenes (Continued): Electrophilic Addition Energy Path

- ▶ Two step process
- ▶ First transition state is high energy point
- ▶ First step is slower than second



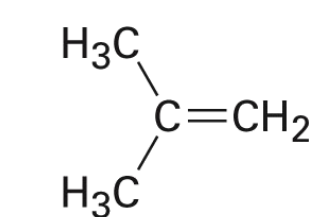
# Electrophilic Addition of Alkenes (Continued)

- ▶ The reaction is successful with HCl and with HI as well as HBr
- ▶ HI is generated from KI and phosphoric acid

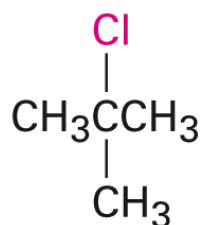


# Orientation of Electrophilic Additions: Markovnikov's Rule

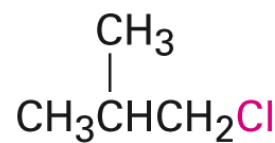
- ▶ In an unsymmetrical alkene, HX reagents can add in two different ways, but one way may be preferred over the other
- ▶ If one orientation predominates, the reaction is **regioselective**
- ▶ **Markovnikov** observed in the 19<sup>th</sup> century that in the addition of HX to alkene, the H attaches to the carbon with more H's and X attaches to the other end (to the one with more alkyl substituents)
  - ▶ This is **Markovnikov's rule**



**2-Methylpropene**



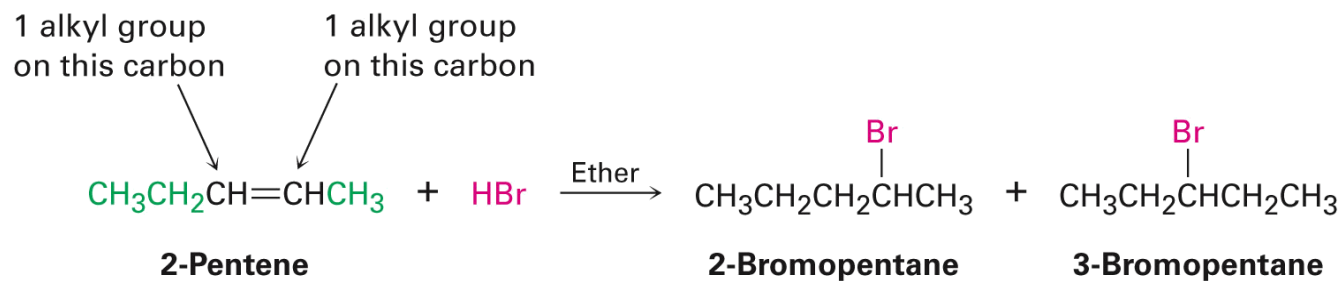
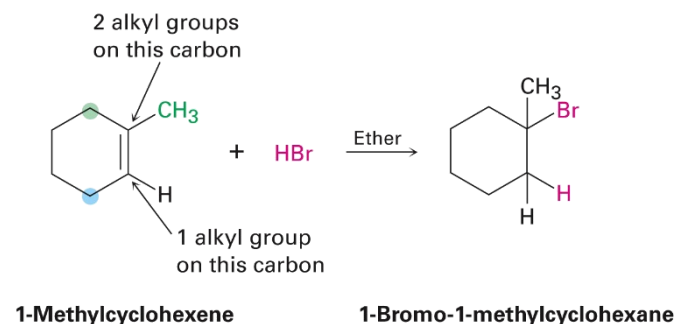
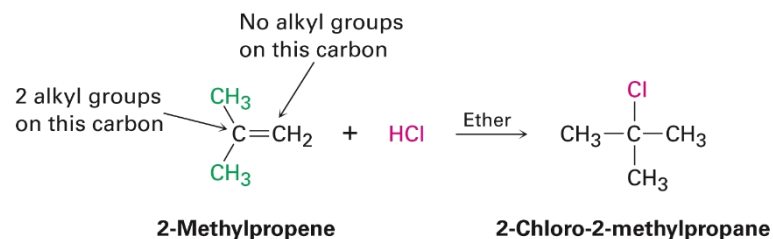
**2-Chloro-2-methyl-  
propane  
(Sole product)**



**1-Chloro-2-methyl-  
propane  
(Not formed)**

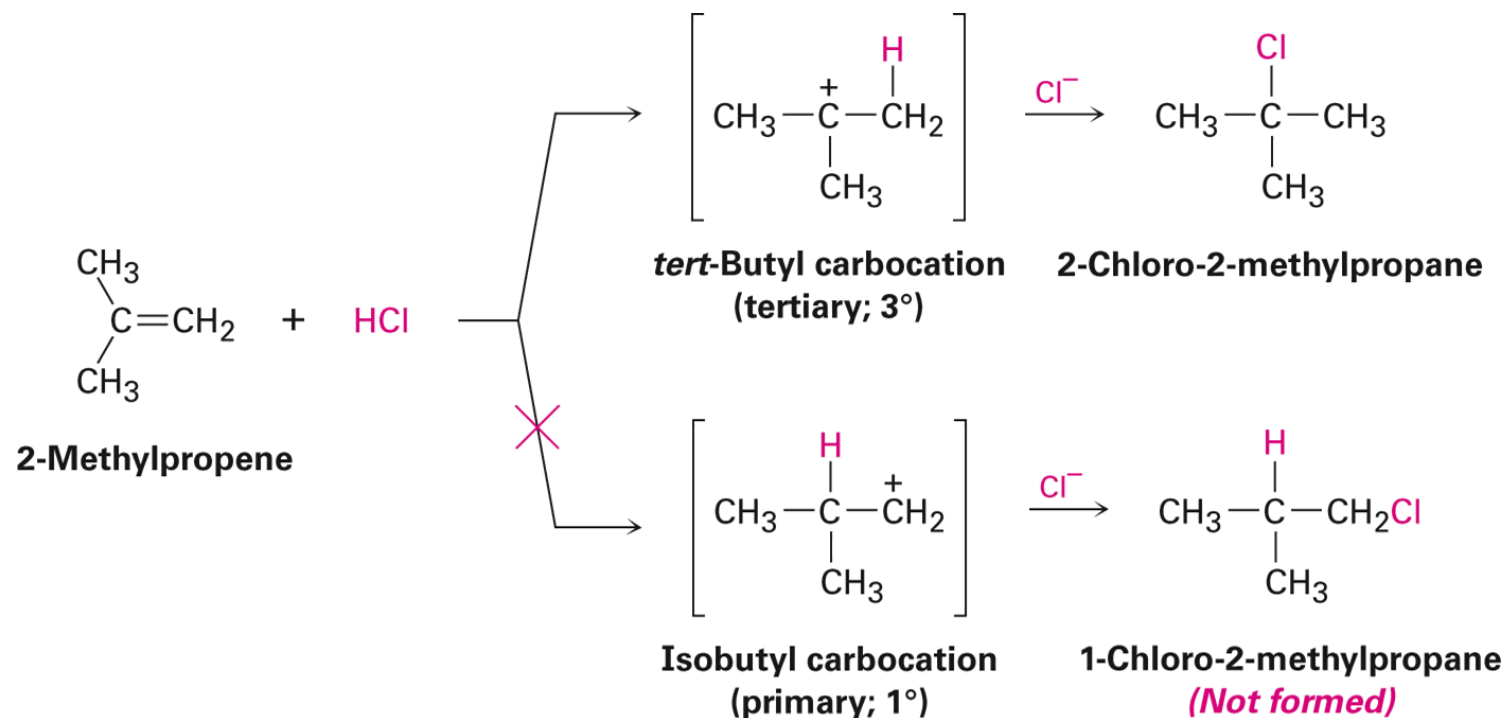
# Example of Markovnikov's Rule

- ▶ Addition of HCl to 2-methylpropene
- ▶ Regiospecific - one product forms where two are possible
- ▶ If both ends have similar substitution, then not regiospecific



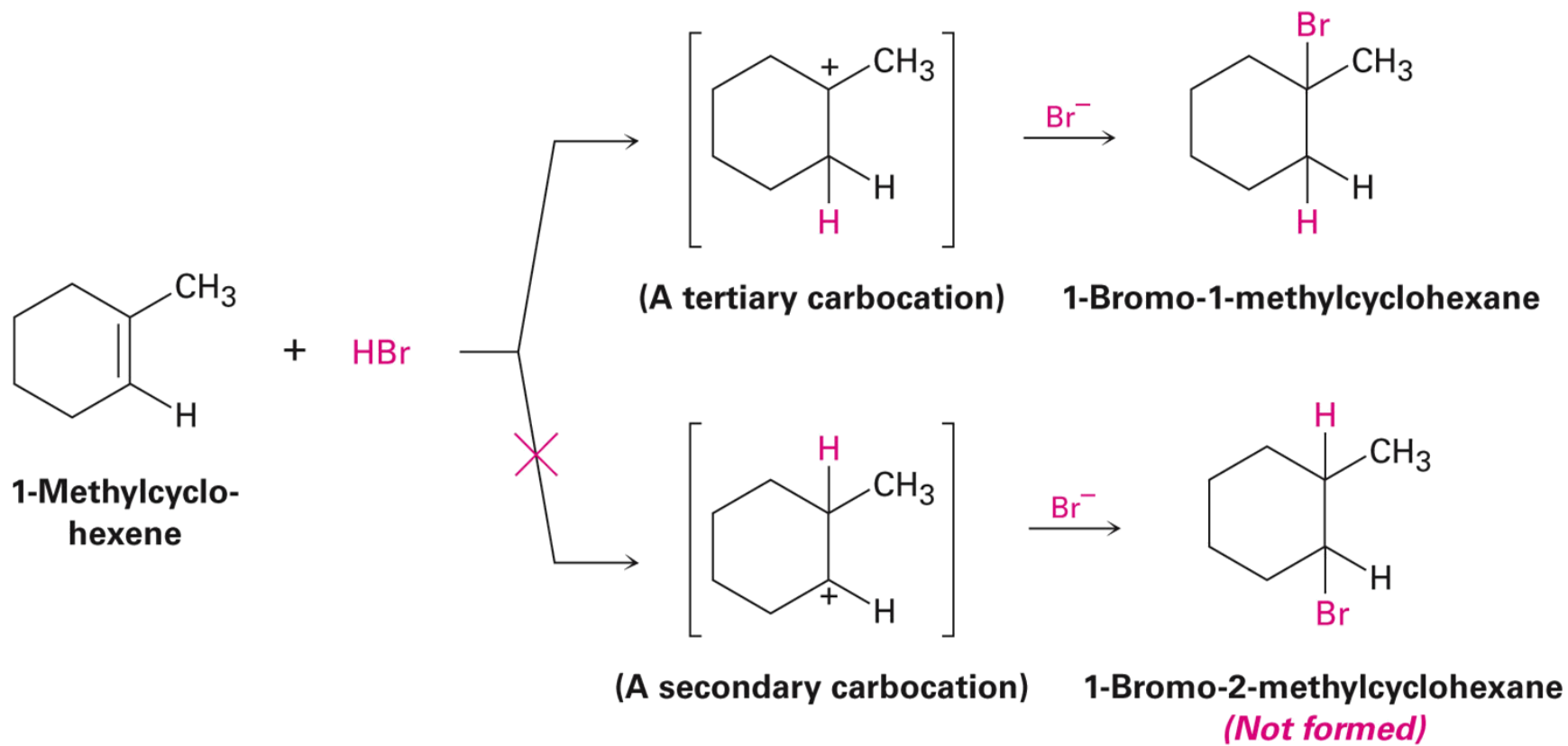
# Markovnikov's Rule (restated)

- ▶ More highly substituted carbocation forms as intermediate rather than less highly substituted one
- ▶ Tertiary cations and associated transition states are more stable than primary cations



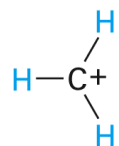
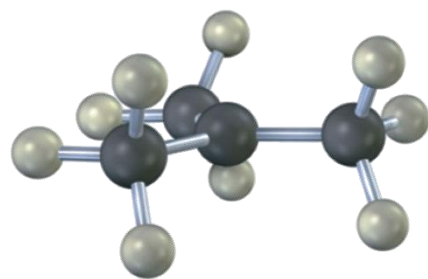
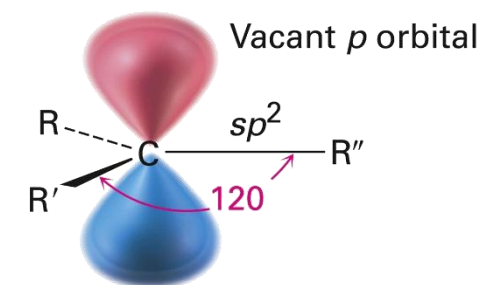


# Markovnikov's Rule (restated)

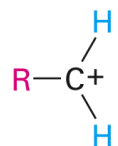


# Carbocation Structure and Stability

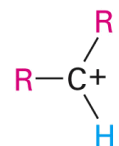
- ▶ Carbocations are planar and the tricoordinate carbon is surrounded by only 6 electrons in  $sp^2$  orbitals
- ▶ the fourth orbital on carbon is a vacant  $p$ -orbital
- ▶ the stability of the carbocation (measured by energy needed to form it from R-X) is increased by the presence of alkyl substituents



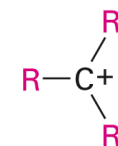
Methyl



Primary ( $1^\circ$ )



Secondary ( $2^\circ$ )



Tertiary ( $3^\circ$ )



# The Hammond Postulate

- ▶ If a carbocation intermediate is more stable than another, why is the reaction through the more stable one faster?
  - ▶ the relative stability of the intermediate is related to an equilibrium constant ( $\Delta G^\circ$ )
  - ▶ the relative stability of the transition state (which describes the size of the rate constant) is the activation energy ( $\Delta G^\ddagger$ )
  - ▶ the transition state is transient and cannot be examined
  - ▶ What does the Hammond Postulate state?

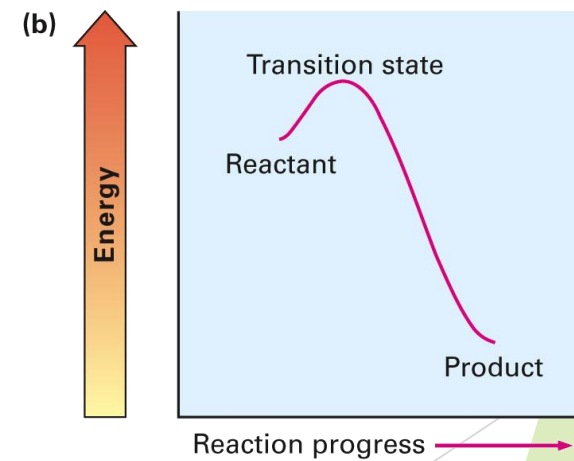
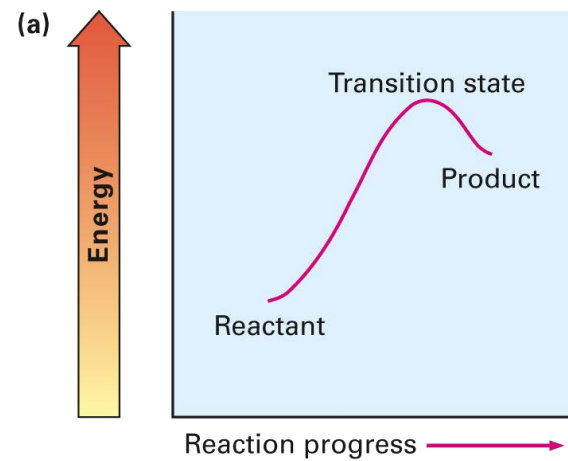
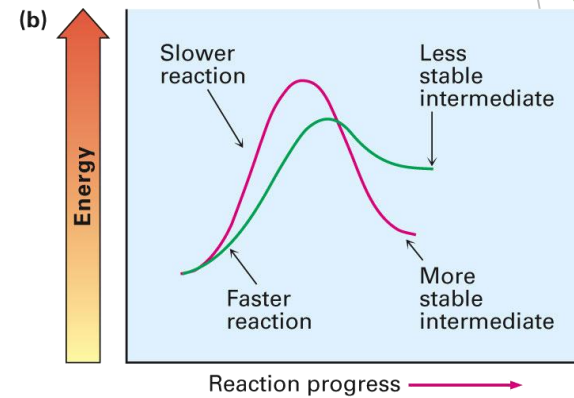
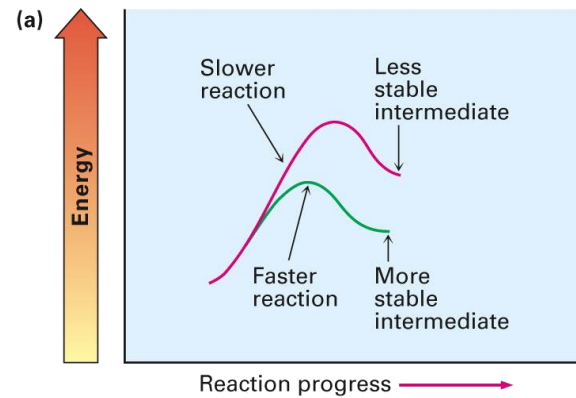
“the structure of a transition state resembles the structure of the nearest stable species. Transition states for endergonic steps structurally resemble products, and transition states for exergonic steps structurally resemble reactants”

# The Hammond Postulate (Continued): Transition State Structures

- ▶ A **transition state** is the highest energy species in a reaction step
- ▶ By definition, its structure is not stable enough to exist for one vibration
- ▶ But the structure controls the rate of reaction
- ▶ So we need to be able to guess about its properties in an informed way
- ▶ We classify them in general ways and look for trends in reactivity - the conclusions are in the Hammond Postulate

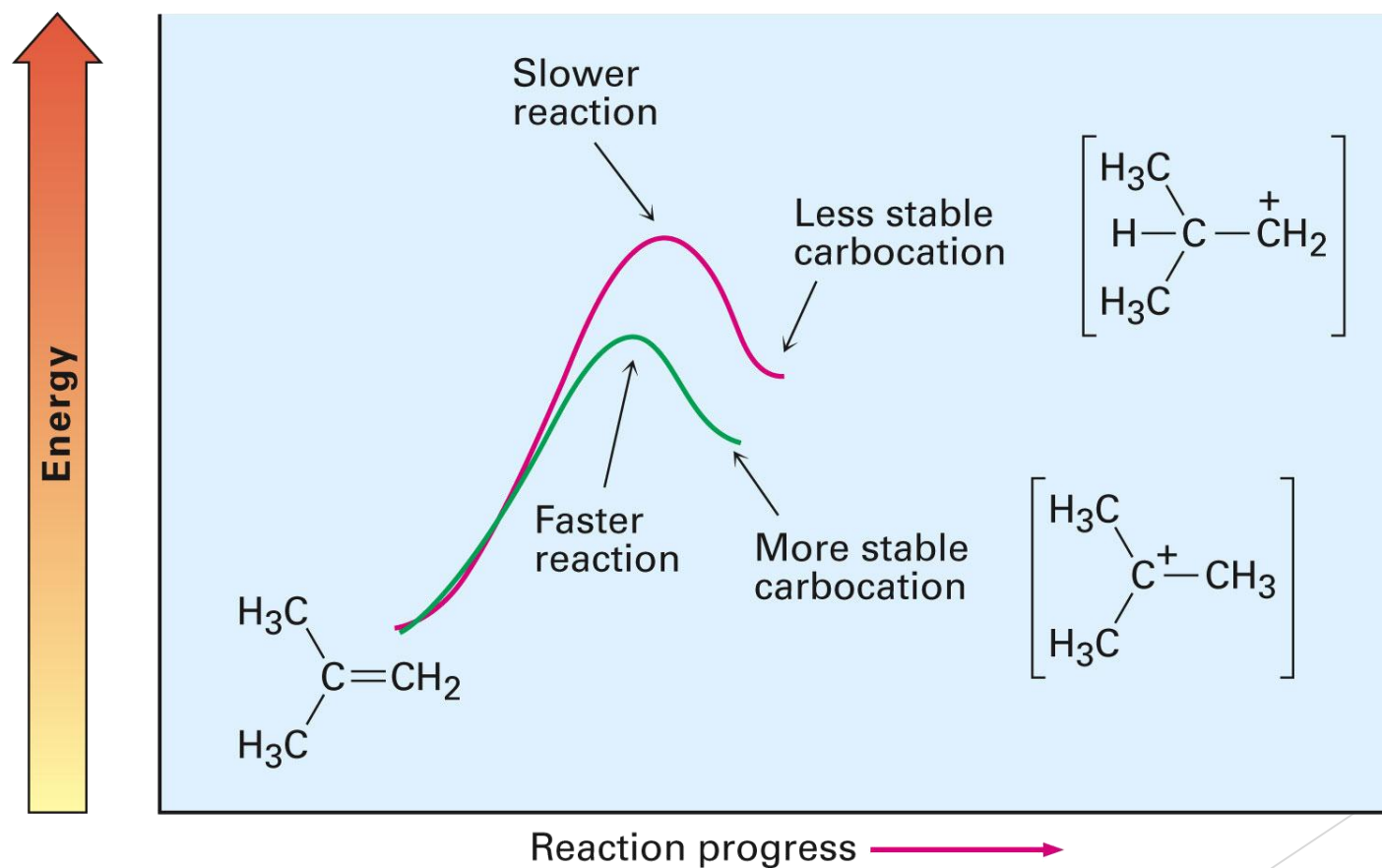
# Examination of the Hammond Postulate

- ▶ A transition state should be similar to an intermediate that is close in energy
- ▶ Sequential states on a reaction path that are close in energy are likely to be close in structure - G. S. Hammond



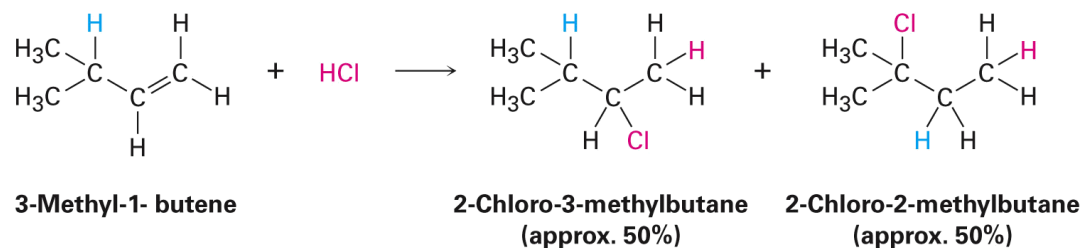
# Competing Reactions and the Hammond Postulate

- ▶ Normal Expectation: Faster reaction gives more stable intermediate
- ▶ Intermediate resembles transition state



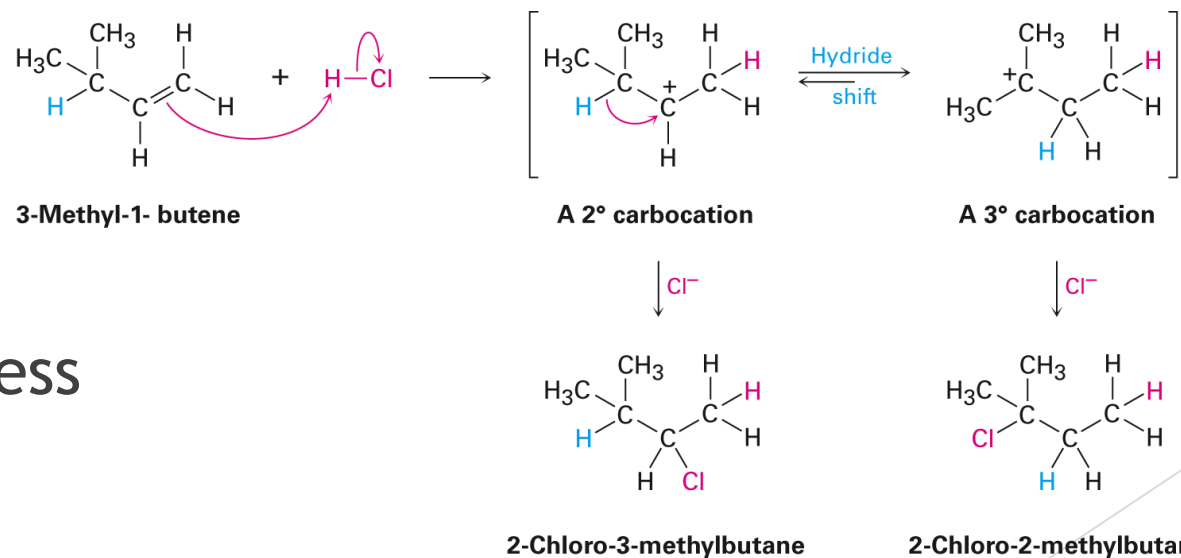
# Evidence for the Mechanism of Electrophilic Addition: Carbocation Rearrangements

- ▶ Carbocations undergo structural rearrangements following set patterns



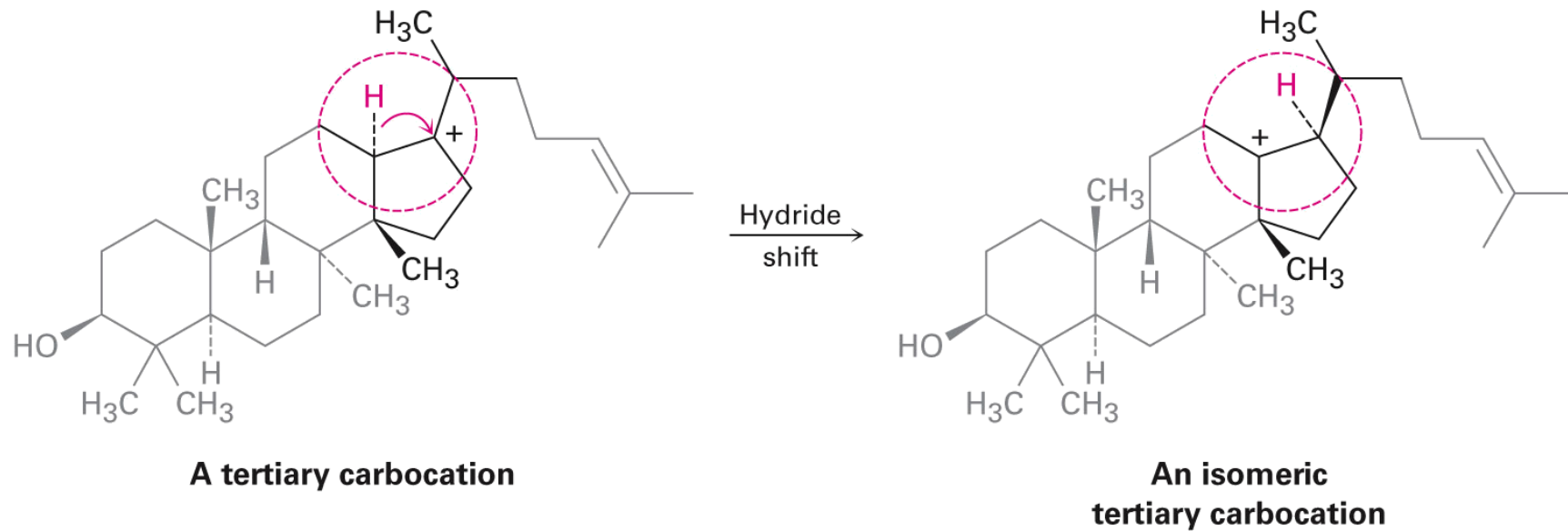
- ▶ 1,2-H and 1,2-alkyl shifts occur

- ▶ Goes to give most stable carbocation



- ▶ Can go through less stable ions as intermediates

# Hydride shifts in biological molecules





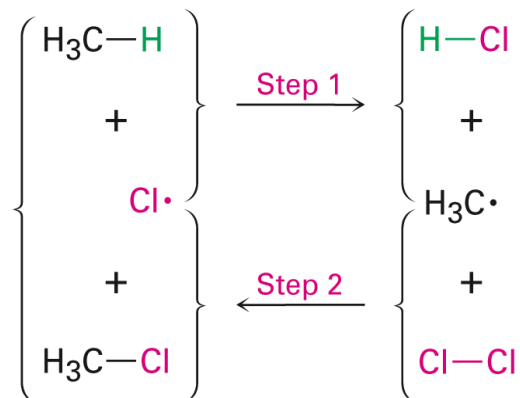
# Preparing Alkyl Halides from Alkenes: Radical Halogenation

- ▶ Alkyl halide from addition of HCl, HBr, HI to alkenes to give Markovnikov product (see Alkenes chapter)
- ▶ Alkyl dihalide from *anti* addition of bromine or chlorine

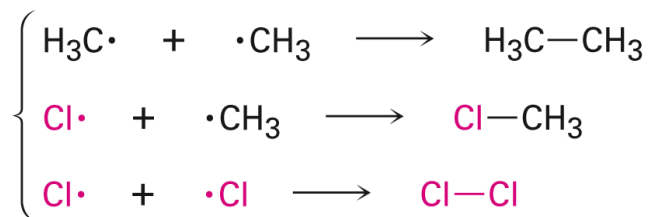
Initiation step



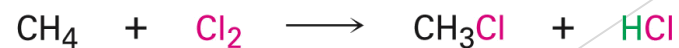
Propagation steps  
(a repeating cycle)



Termination steps

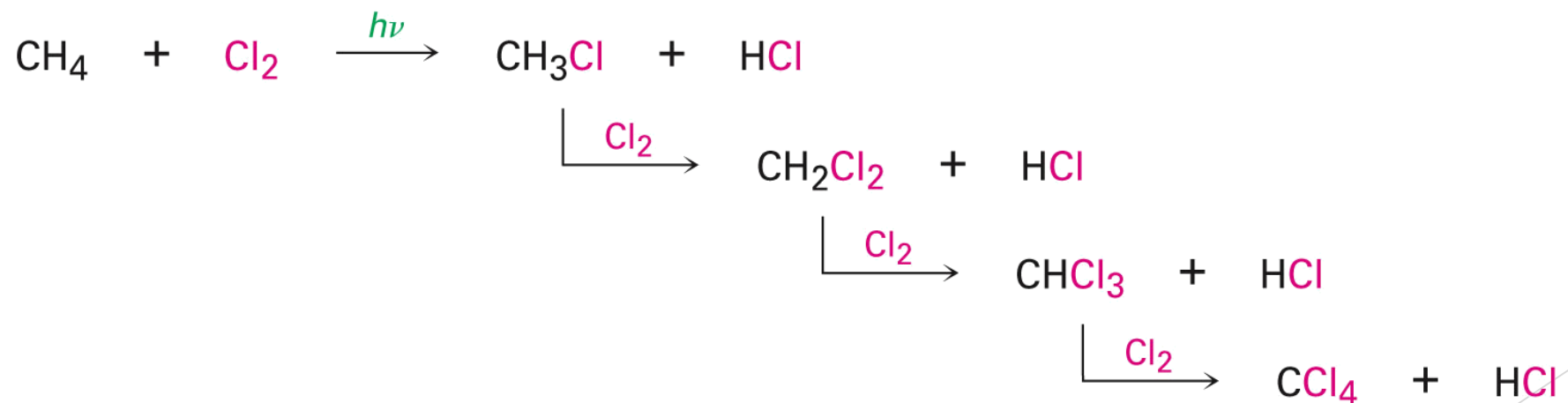


Overall reaction



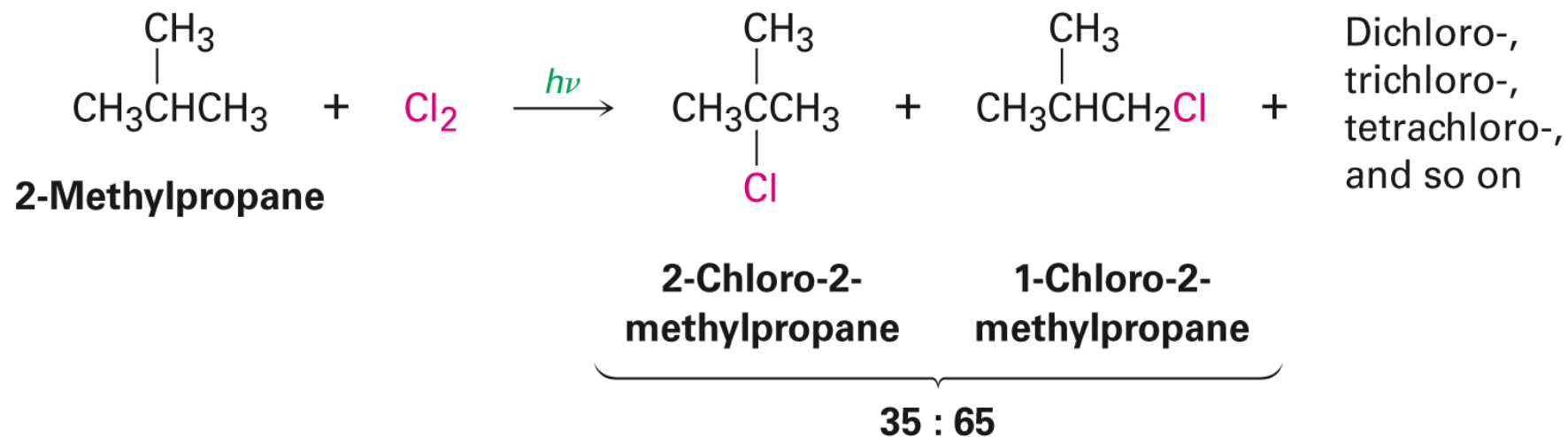
# Preparing Alkyl Halides from Alkenes: Radical Halogenation

- ▶ Alkane + Cl<sub>2</sub> or Br<sub>2</sub>, heat or light replaces C-H with C-X but gives mixtures
  - ▶ Hard to control
  - ▶ Via free radical mechanism
- ▶ It is usually not a good idea to plan a synthesis that uses this method



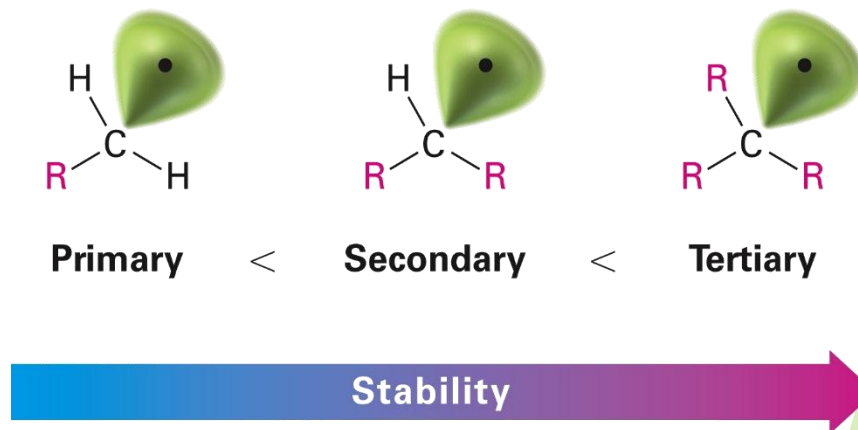
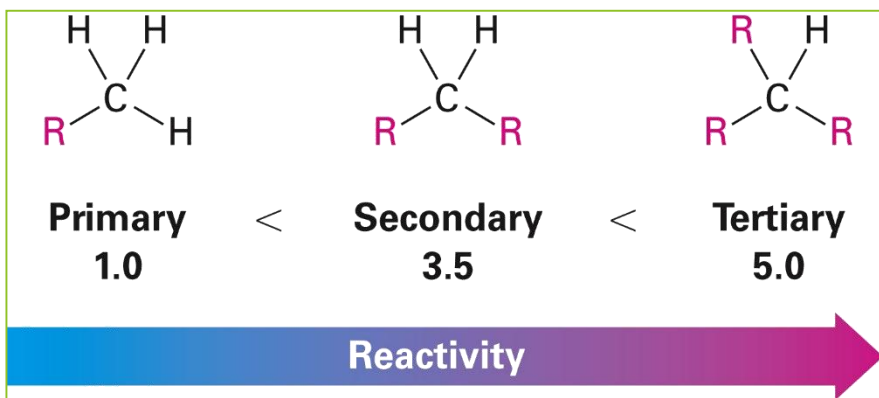
# Radical Halogenation of Alkanes

- ▶ If there is more than one type of hydrogen in an alkane, reactions favor replacing the hydrogen at the most highly substituted carbons (not absolute)



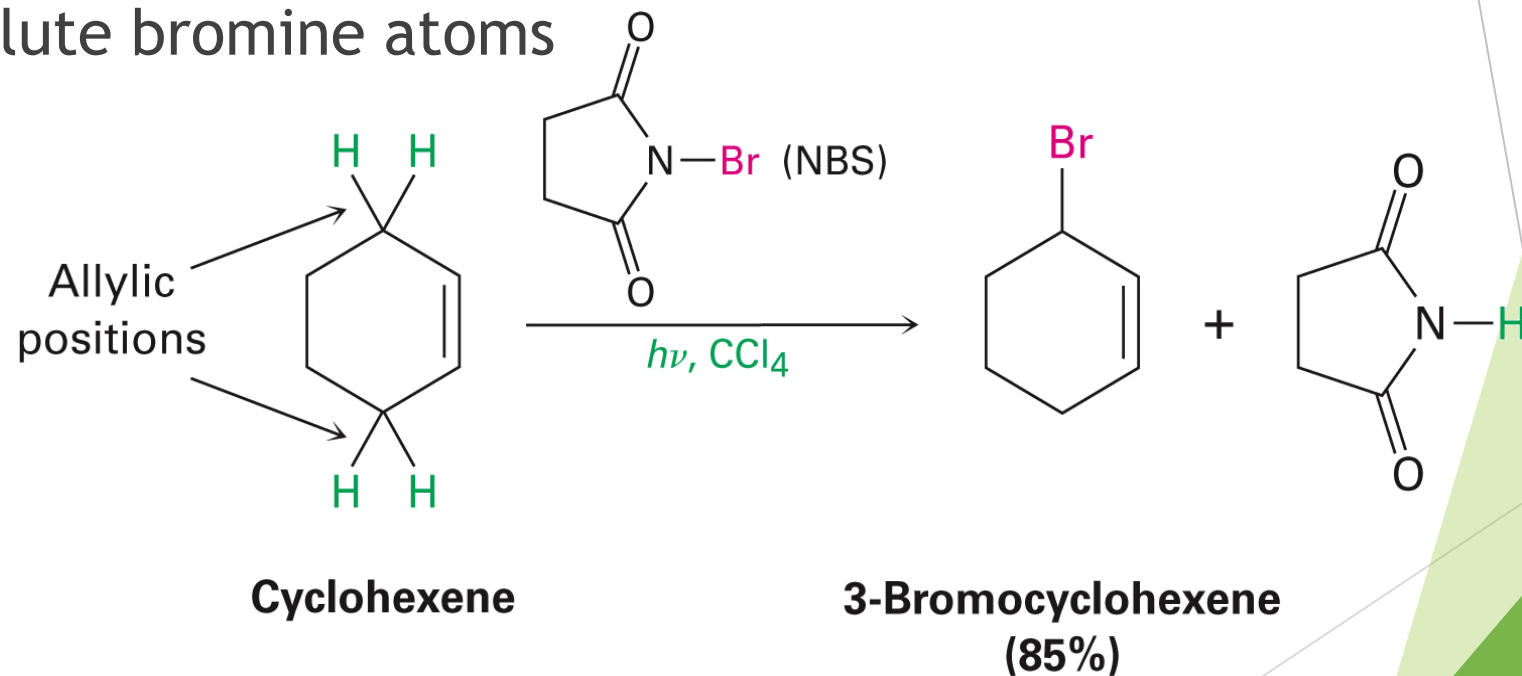
# Relative Reactivity

- ▶ Based on quantitative analysis of reaction products, relative reactivity is estimated
- ▶ Order parallels stability of radicals
- ▶ Reaction distinction is more selective with bromine than chlorine



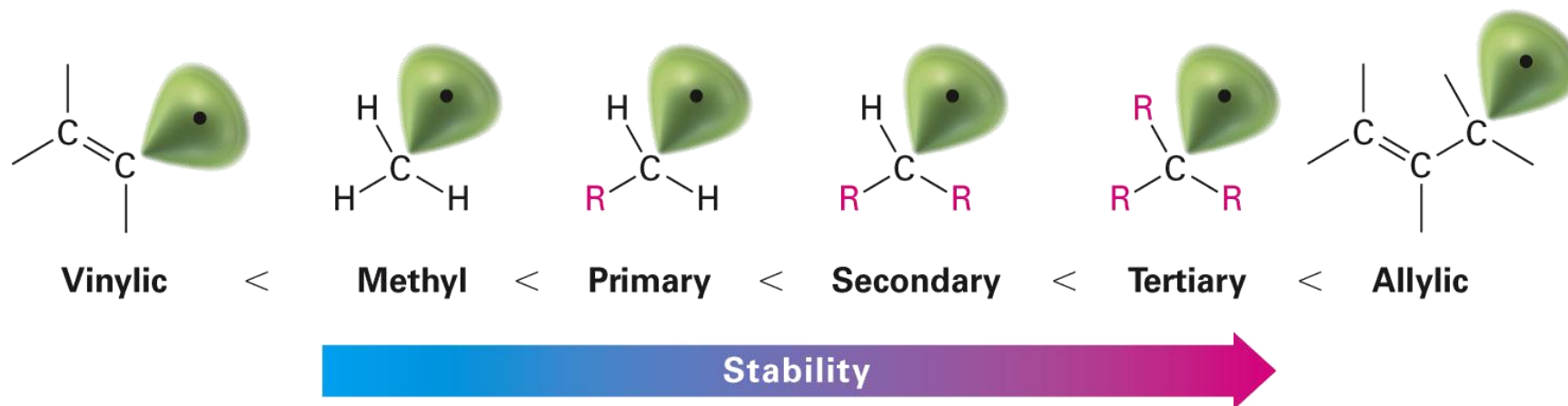
# Preparing Alkyl Halides from Alkenes: Allylic Bromination

- ▶ N-bromosuccinimide (NBS) selectively brominates allylic positions
- ▶ Requires light for activation
- ▶ A source of dilute bromine atoms



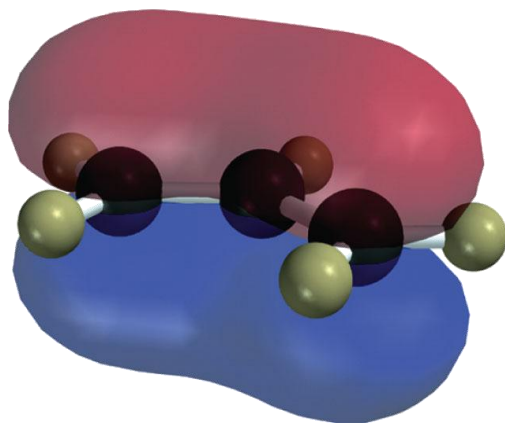
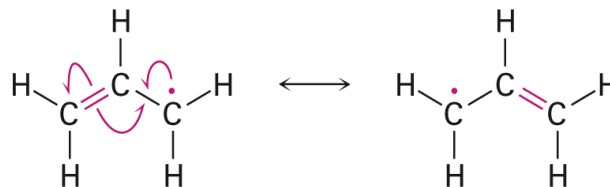
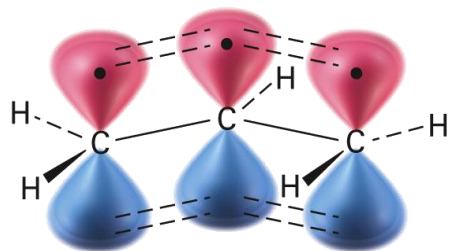
# Allylic Stabilization

- ▶ Allyl radical is delocalized
- ▶ More stable than typical alkyl radical by 40 kJ/mol (9 kcal/mol)
- ▶ Allylic radical is more stable than tertiary alkyl radical



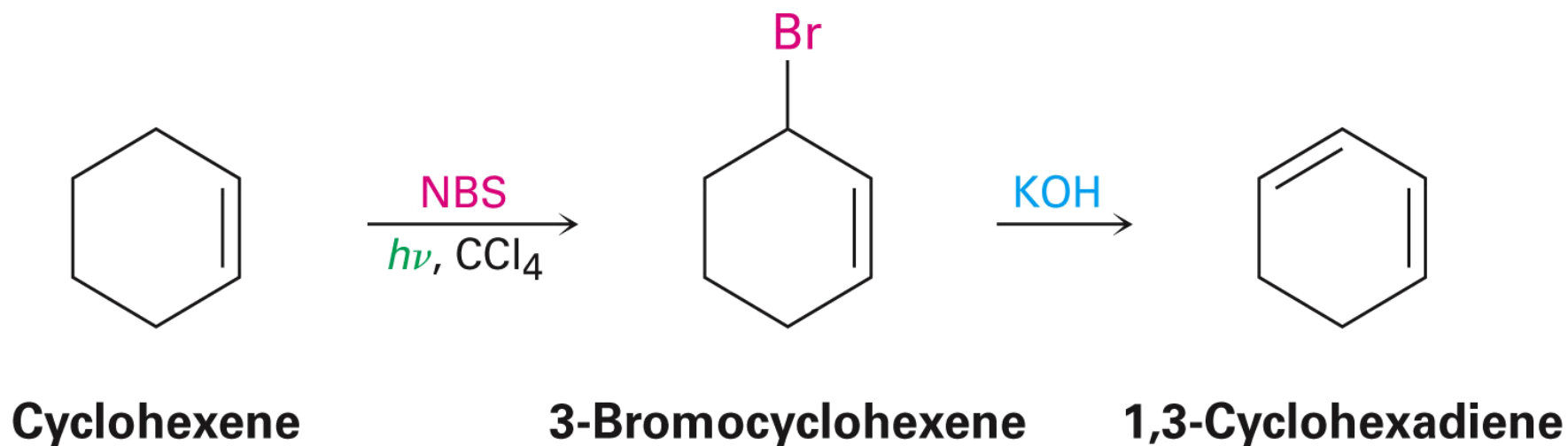
# Stability of the Allyl Radical: Resonance Revisited

- ▶ Three electrons are delocalized over three carbons
- ▶ Spin density surface shows single electron is dispersed



# Use of Allylic Bromination

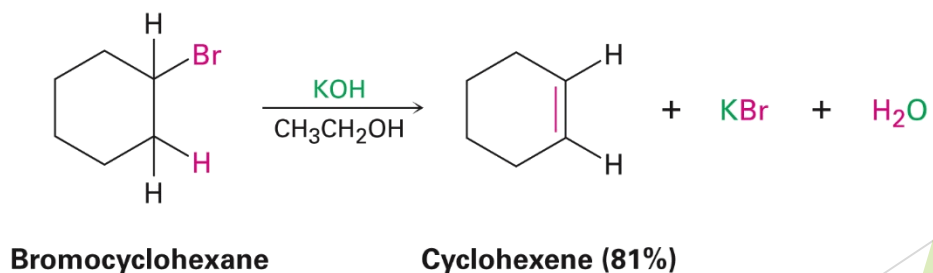
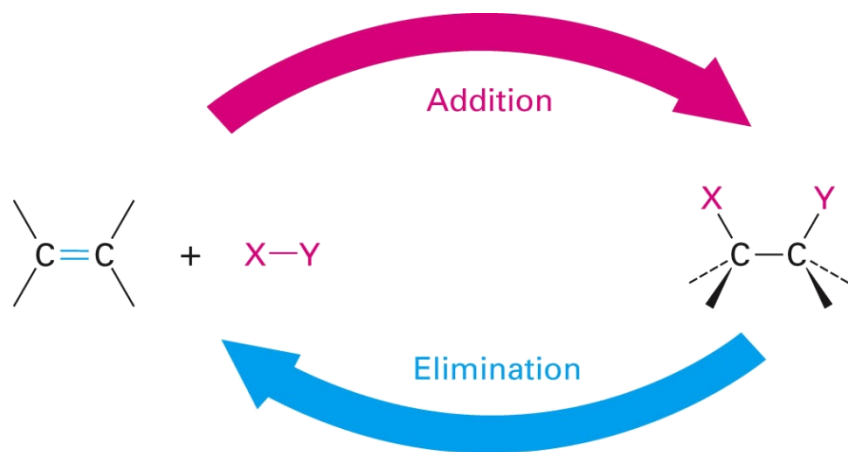
- ▶ Allylic bromination with NBS creates an allylic bromide
- ▶ Reaction of an allylic bromide with base produces a conjugated diene, useful in the synthesis of complex molecules





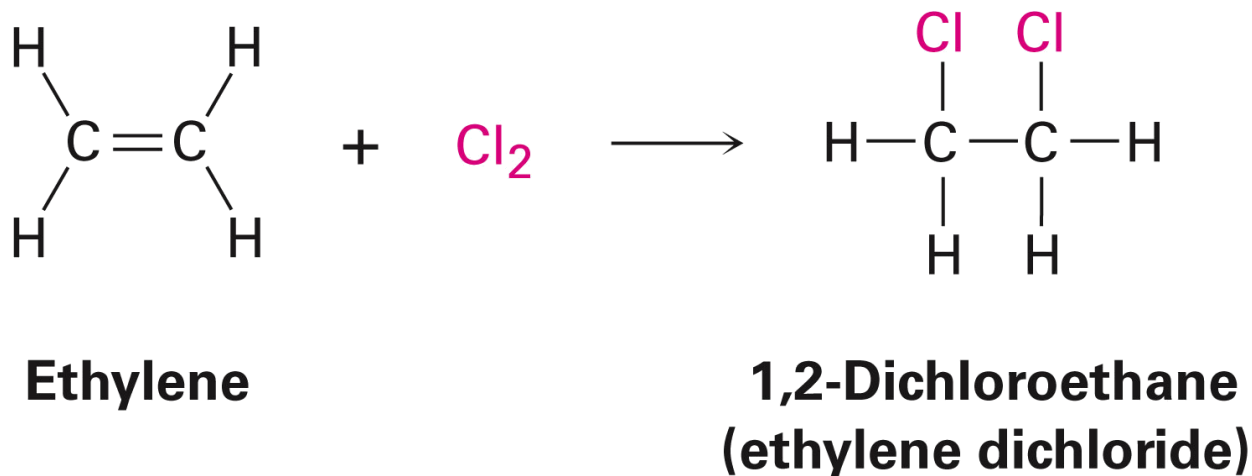
# Preparation of Alkenes: A Preview of Elimination Reactions

- ▶ Alkenes are commonly made by
  - ▶ elimination of HX from alkyl halide (**dehydrohalogenation**)
    - ▶ Uses heat and KOH
  - ▶ elimination of H-OH from an alcohol (**dehydration**)
    - ▶ requires strong acids (sulfuric acid, 50 °C)



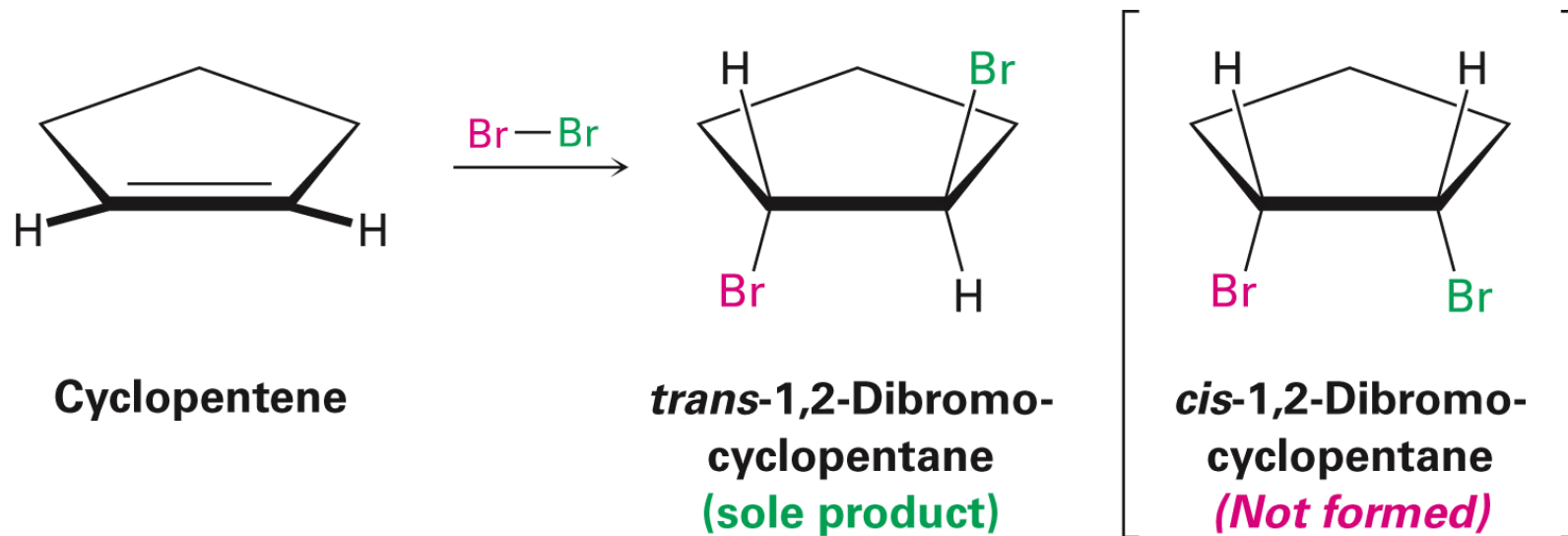
# Addition of Halogens to Alkenes

- ▶ Bromine and chlorine add to alkenes to give 1,2-dihalides, an industrially important process
- ▶  $F_2$  is too reactive and  $I_2$  does not add
- ▶  $Cl_2$  reacts as  $Cl^+ Cl^-$
- ▶  $Br_2$  is similar



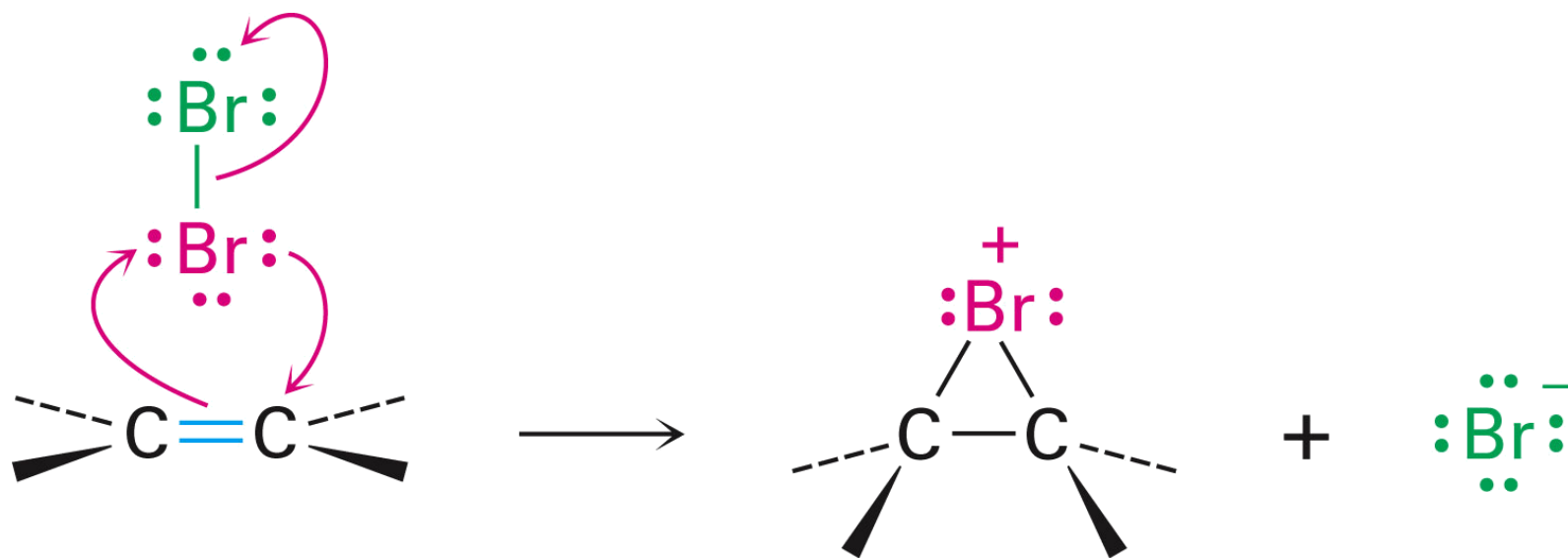
# Addition of Br<sub>2</sub> to Cyclopentene

- Addition is exclusively *trans*



# Mechanism of Bromine Addition

- ▶  $\text{Br}^+$  adds to an alkene producing a cyclic ion
- ▶ Bromonium ion, bromine shares charge with carbon
  - ▶ Gives *trans* addition

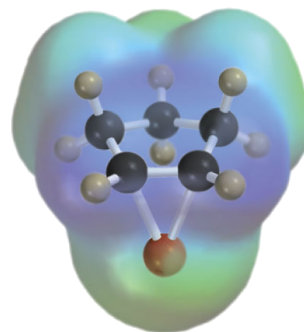
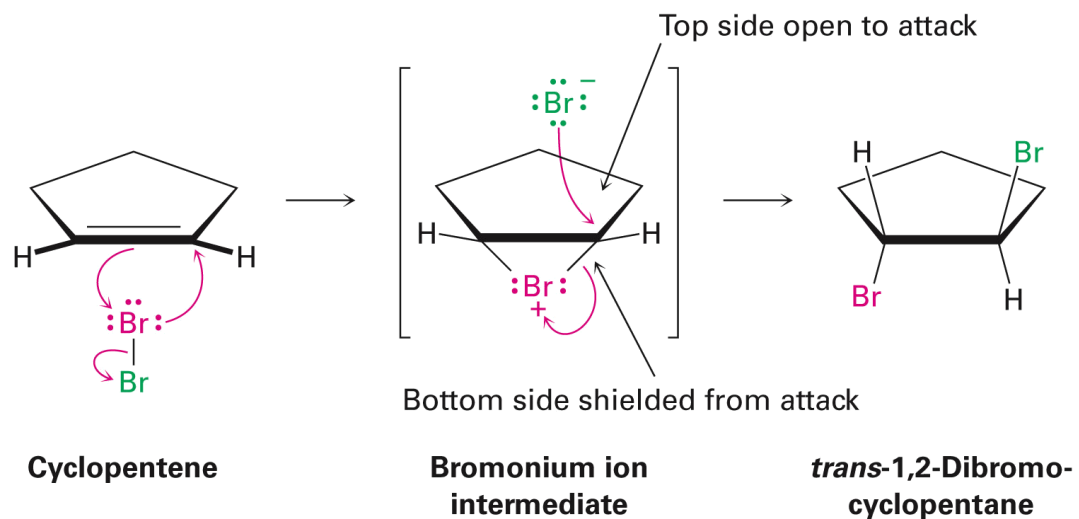


**An alkene**

**A bromonium ion**

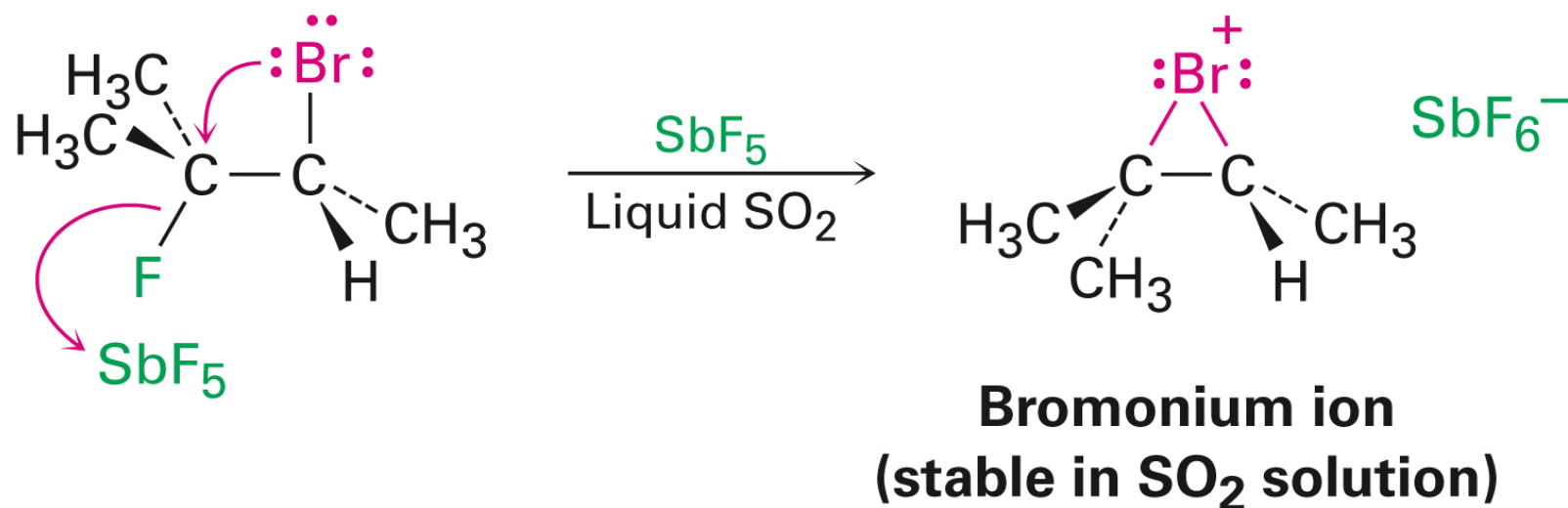
# Bromonium Ion Mechanism

- ▶ Electrophilic addition of bromine to give a cation is followed by cyclization to give a *bromonium ion*
- ▶ This bromonium ion is a reactive electrophile and bromide ion is a good nucleophile



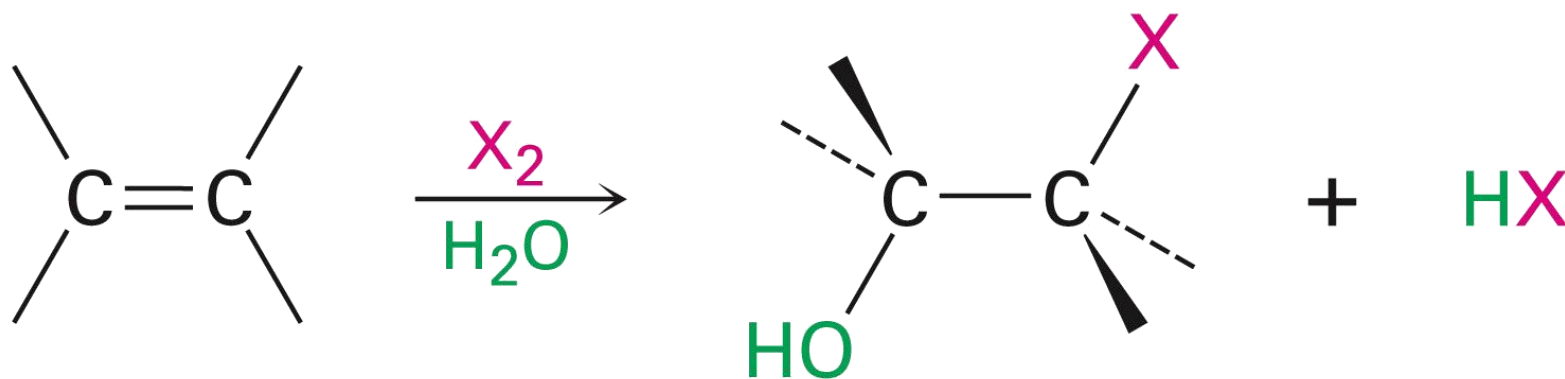
# The Reality of Bromonium Ions

- ▶ Bromonium ions were postulated more than 60 years ago to explain the stereochemical course of the addition (to give the *trans*-dibromide from a cyclic alkene)
- ▶ Olah showed that bromonium ions are stable in liquid  $\text{SO}_2$  with  $\text{SbF}_5$  and can be studied directly



# Halohydrins from Alkenes: Addition of HOX

- ▶ This is formally the addition of HO-X to an alkene to give a 1,2-halo alcohol, called a halohydrin
- ▶ The actual reagent is the dihalogen ( $\text{Br}_2$  or  $\text{Cl}_2$ ) in water in an organic solvent)



**An alkene**

**A halohydrin**

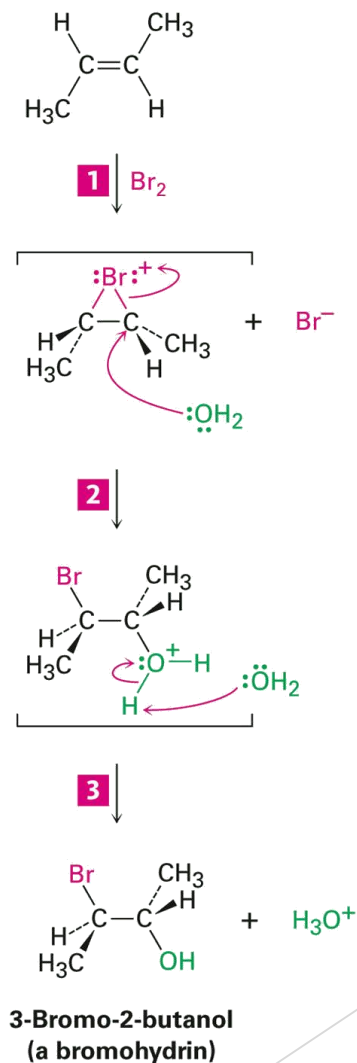
# Mechanism of Formation of a Bromohydrin

- ▶  $\text{Br}_2$  forms bromonium ion, then water adds
- ▶ Orientation toward stable  $\text{C}^+$  species
- ▶ Aromatic rings do not react

**1** Reaction of the alkene with  $\text{Br}_2$  yields a bromonium ion intermediate, as previously discussed.

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

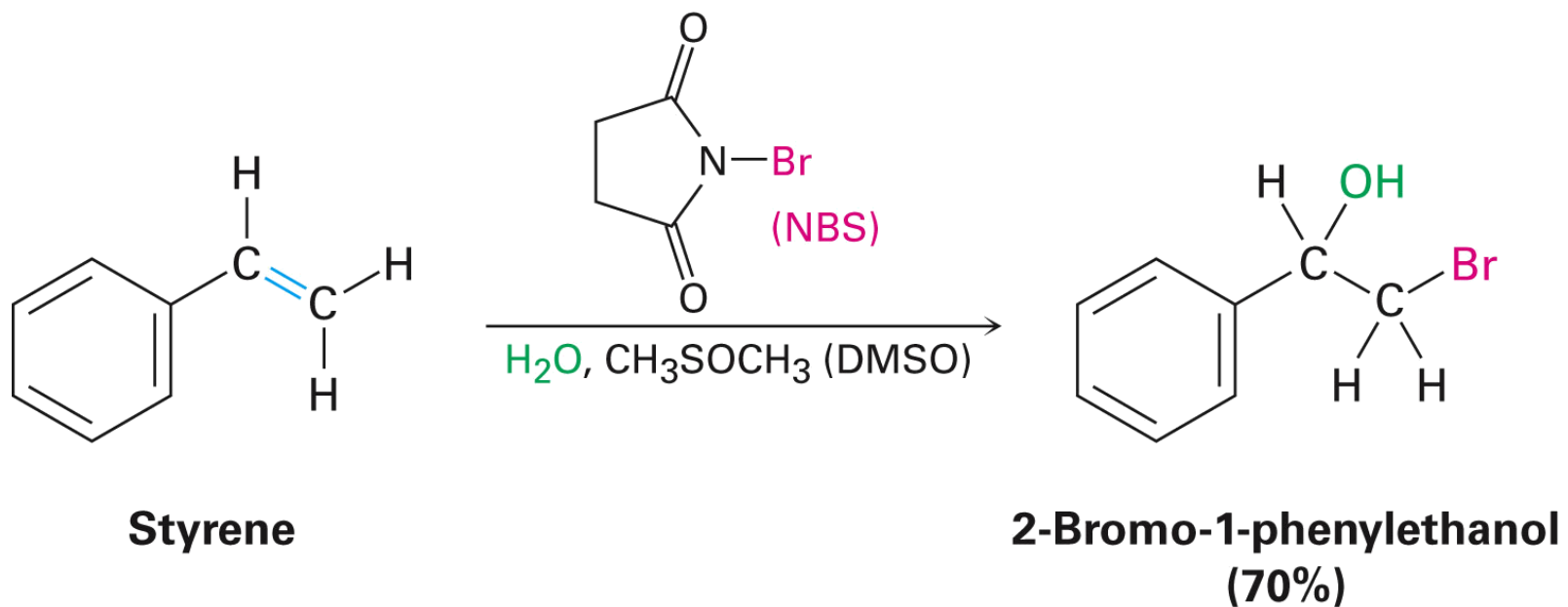
**3** Loss of a proton ( $\text{H}^+$ ) from oxygen then gives  $\text{H}_3\text{O}^+$  and the neutral bromohydrin addition product.





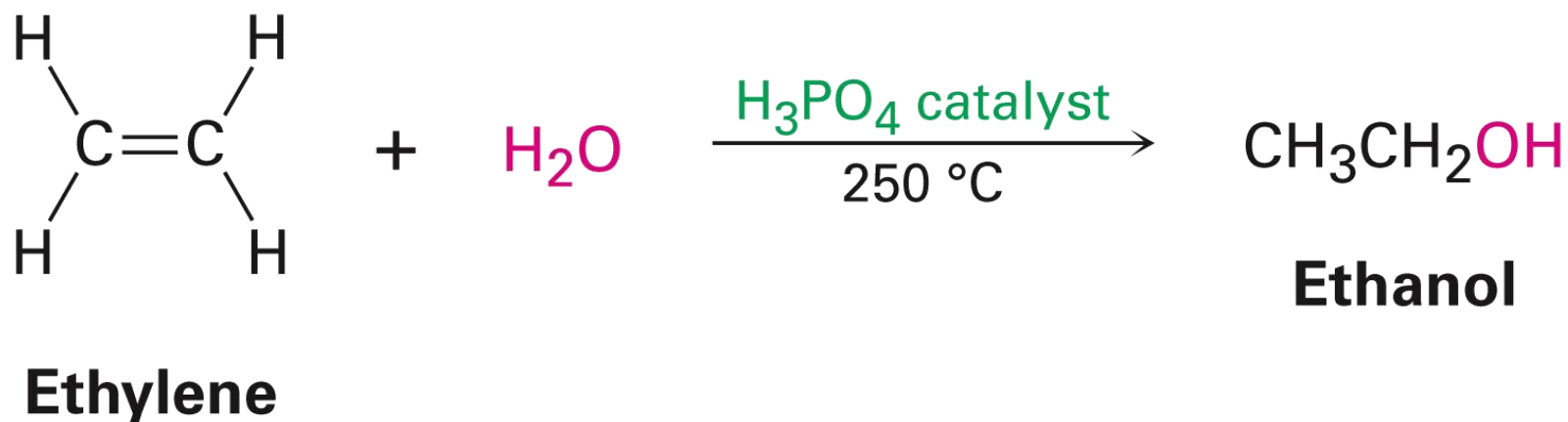
# An Alternative to Bromine

- ▶ Bromine is a difficult reagent to use for this reaction
- ▶ **N-Bromosuccinimide (NBS)** produces bromine in organic solvents and is a safer source



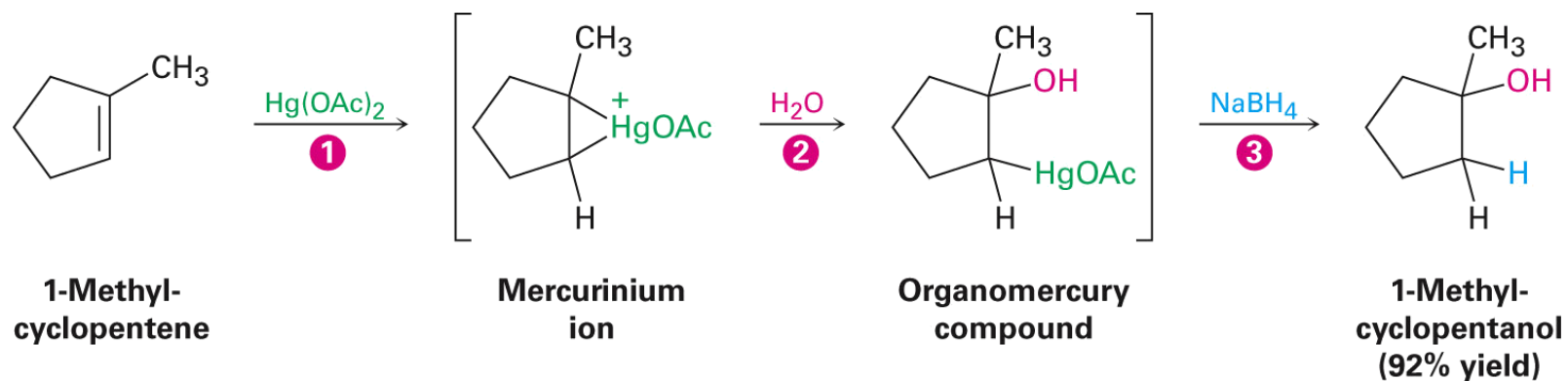
# Hydration of Alkenes: Addition of H<sub>2</sub>O by Oxymercuration

- ▶ Hydration of an alkene is the addition of H-OH to give an alcohol
- ▶ Acid catalysts are used in high temperature industrial processes: ethylene is converted to ethanol



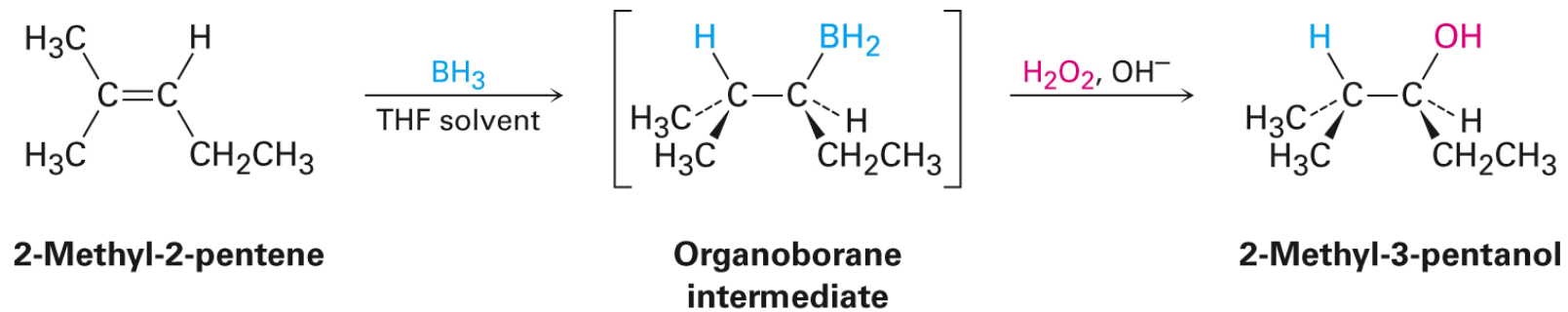
# Oxymercuration Intermediates

- ▶ For laboratory-scale hydration of an alkene
- ▶ Use mercuric acetate in THF followed by sodium borohydride
- ▶ Markovnikov orientation
  - ▶ via mercurinium ion



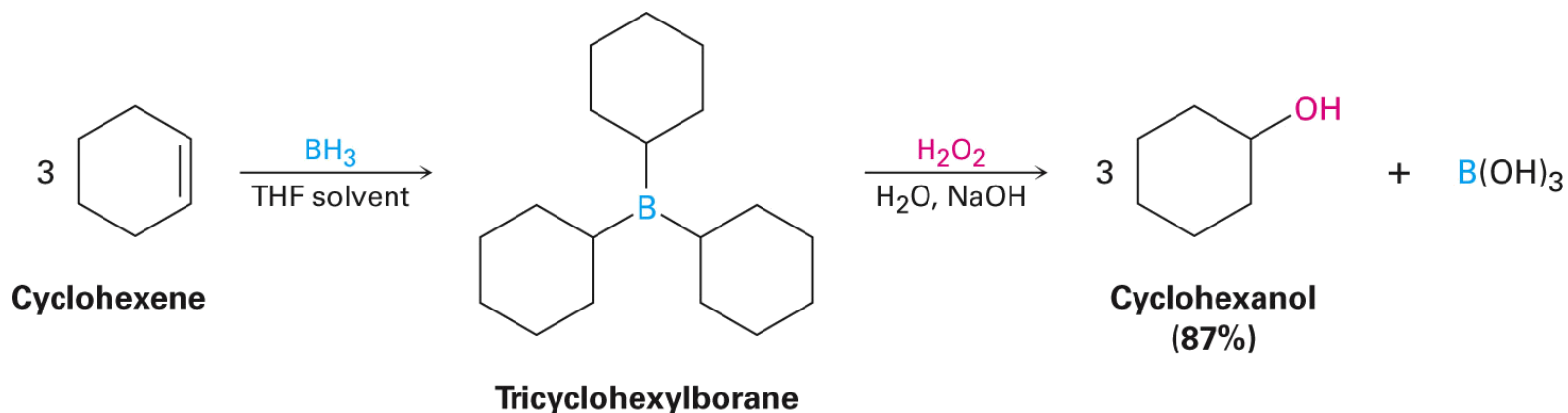
# Hydration of Alkenes: Addition of H<sub>2</sub>O by Hydroboration

- Borane (BH<sub>3</sub>) is electron deficient
- Borane adds to an alkene to give an organoborane



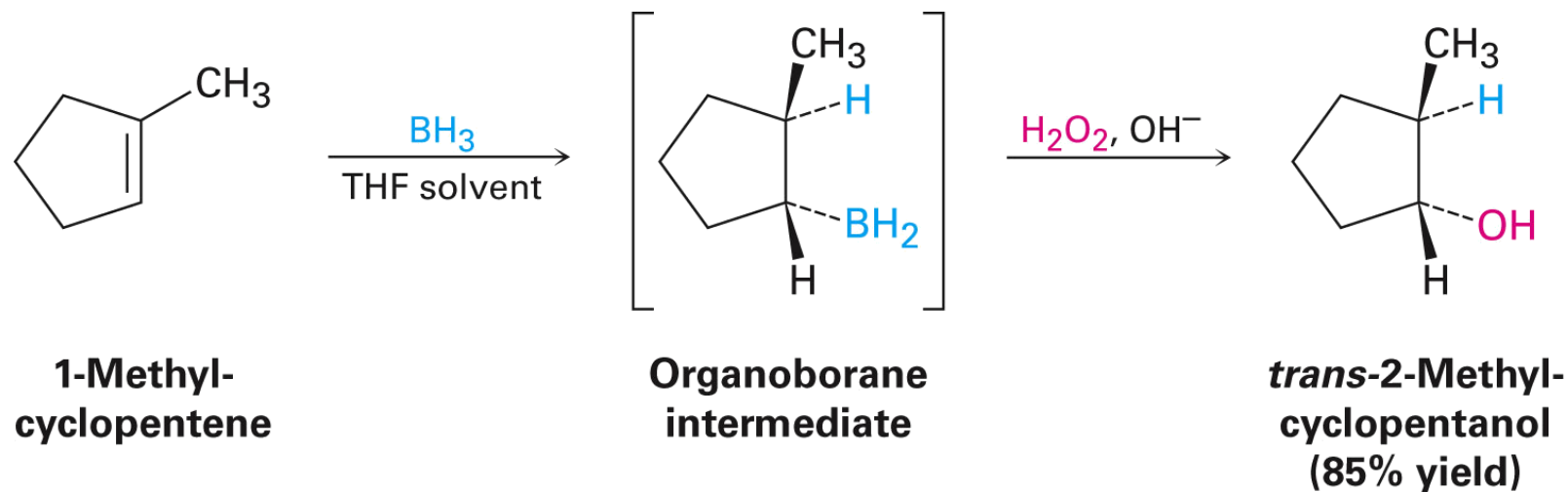
# Hydroboration-Oxidation Forms an Alcohol from an Alkene

- ▶ Addition of H-BH<sub>2</sub> (from BH<sub>3</sub>-THF complex) to three alkenes gives a trialkylborane
- ▶ Oxidation with alkaline hydrogen peroxide in water produces the alcohol derived from the alkene



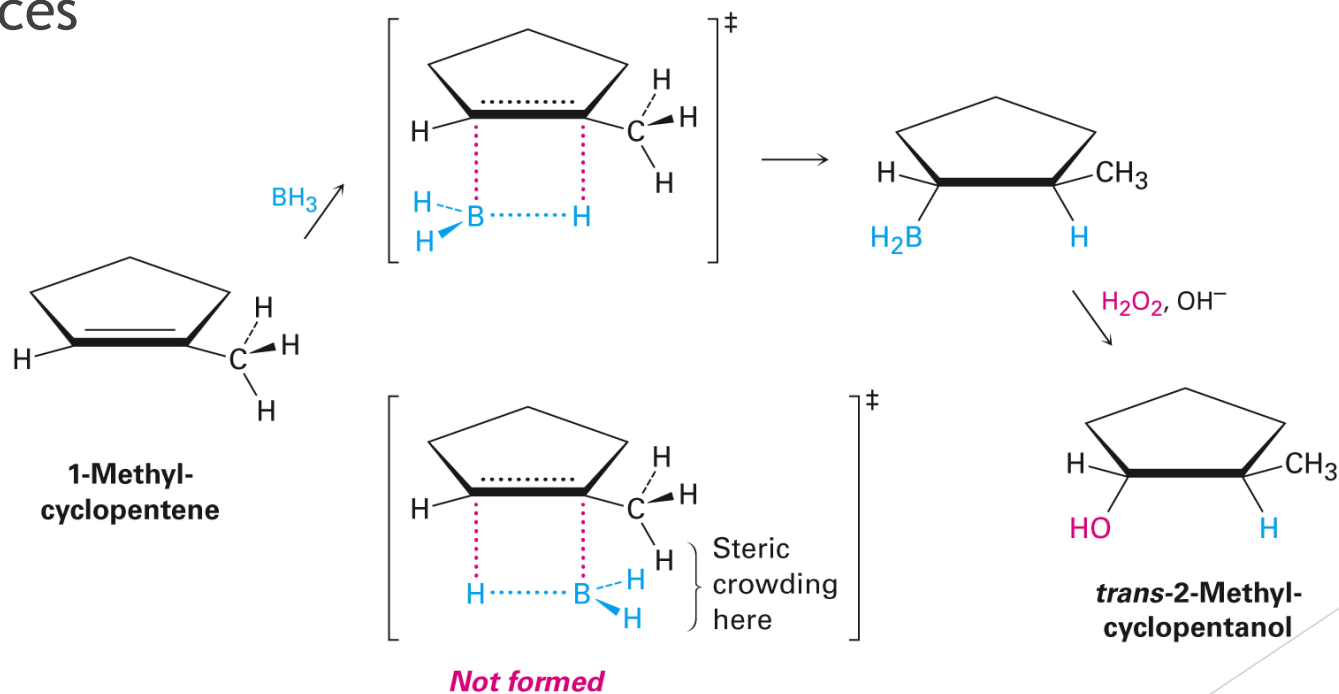
# Orientation in Hydration via Hydroboration

- ▶ Regiochemistry is opposite to Markovnikov orientation
  - ▶ OH is added to carbon with most H's
- ▶ H and OH add with **syn stereochemistry**, to the same face of the alkene (opposite of anti addition)



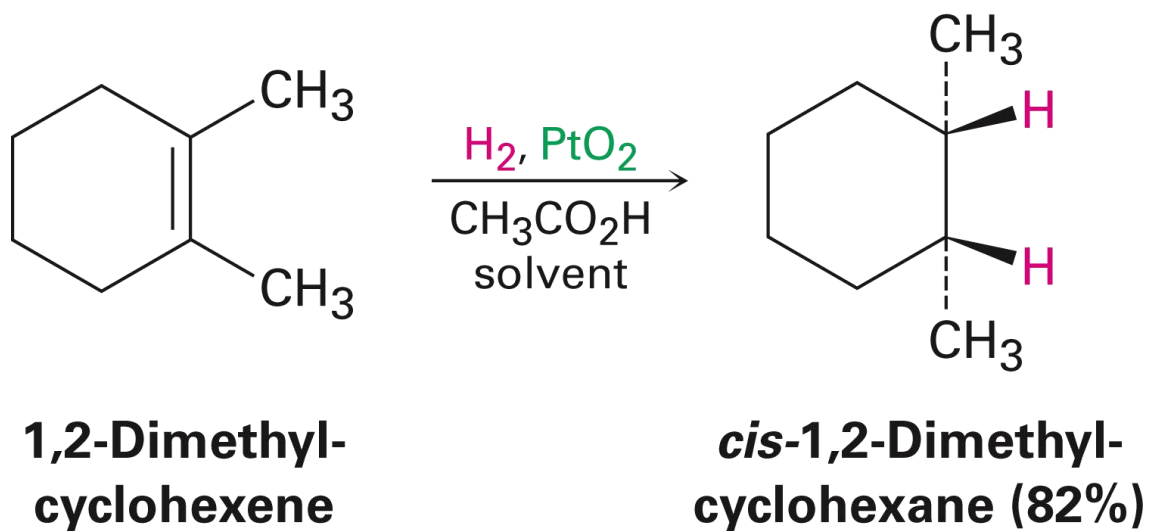
# Mechanism of Hydroboration

- ▶ Borane is a Lewis acid
- ▶ Alkene is Lewis base
- ▶ Transition state involves anionic development on B
- ▶ The components of  $\text{BH}_3$  are added across  $\text{C}=\text{C}$
- ▶ More stable carbocation is also consistent with steric preferences



# Reduction of Alkenes: Hydrogenation

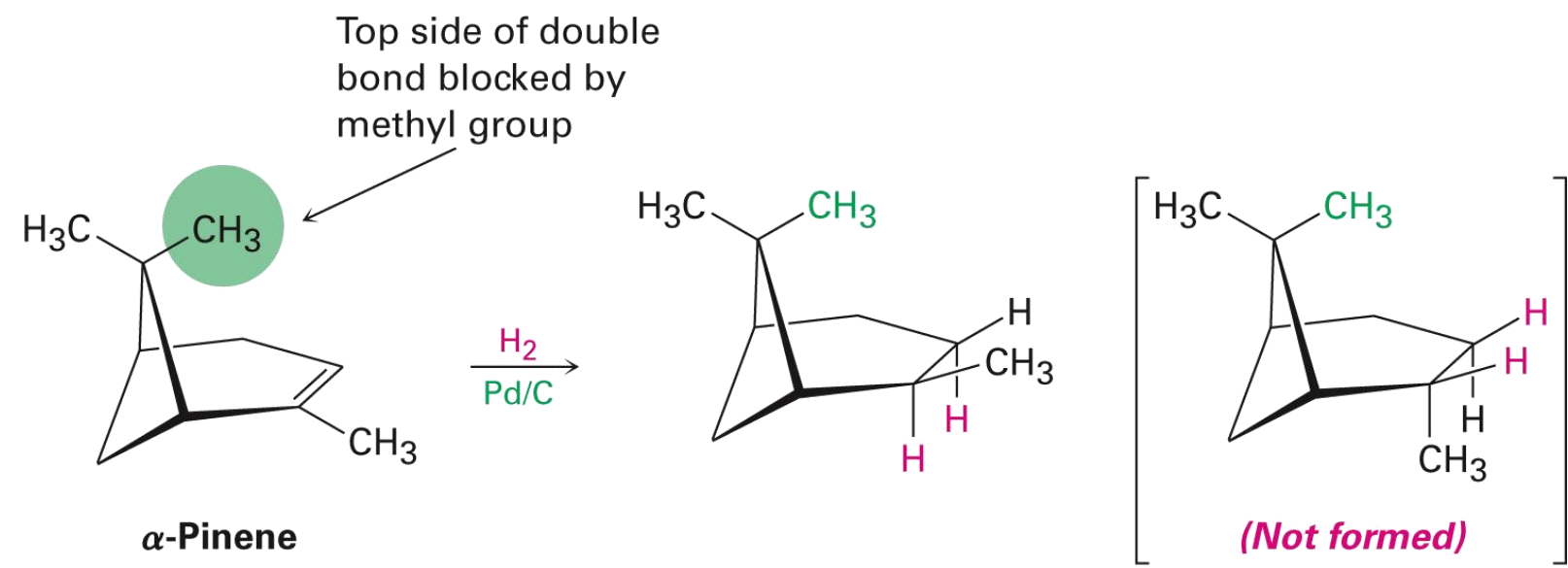
- ▶ Addition of H-H across C=C
- ▶ Reduction in general is addition of H<sub>2</sub> or its equivalent
- ▶ Requires Pt or Pd as powders on carbon and H<sub>2</sub>
- ▶ Hydrogen is first adsorbed on catalyst
- ▶ Reaction is heterogeneous (process is not in solution)





# Hydrogen Addition - Selectivity

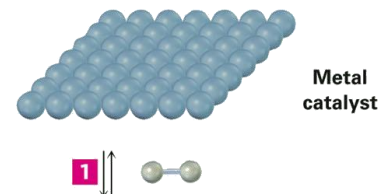
- ▶ Selective for C=C. No reaction with C=O, C=N
- ▶ Polyunsaturated liquid oils become solids
- ▶ If one side is blocked, hydrogen adds to other



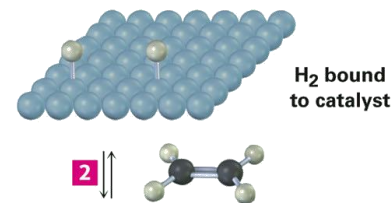
# Mechanism of Catalytic Hydrogenation

- ▶ Heterogeneous - reaction between phases
- ▶ Addition of H-H is *syn*

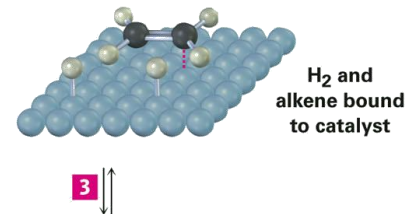
**1** Molecular hydrogen adsorbs to the catalyst surface and dissociates into hydrogen atoms.



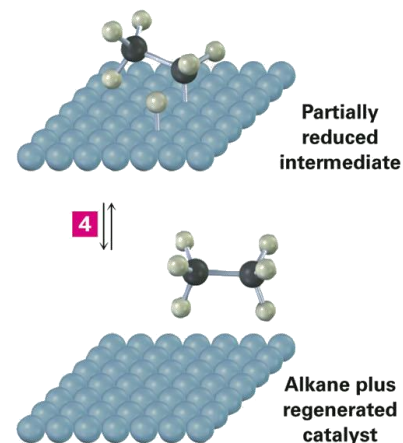
**2** The alkene adsorbs to the catalyst surface, using its  $\pi$  bond to complex to the metal atoms.



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

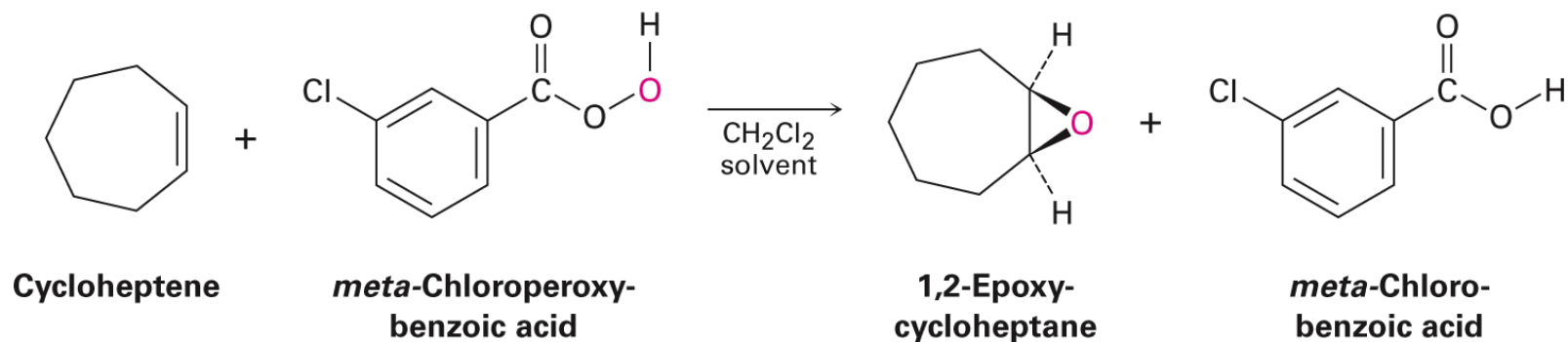


**4** A second hydrogen is transferred from the metal to the second carbon, giving the alkane product and regenerating the catalyst. Because both hydrogens are transferred to the same face of the alkene, the reduction has *syn* stereochemistry.



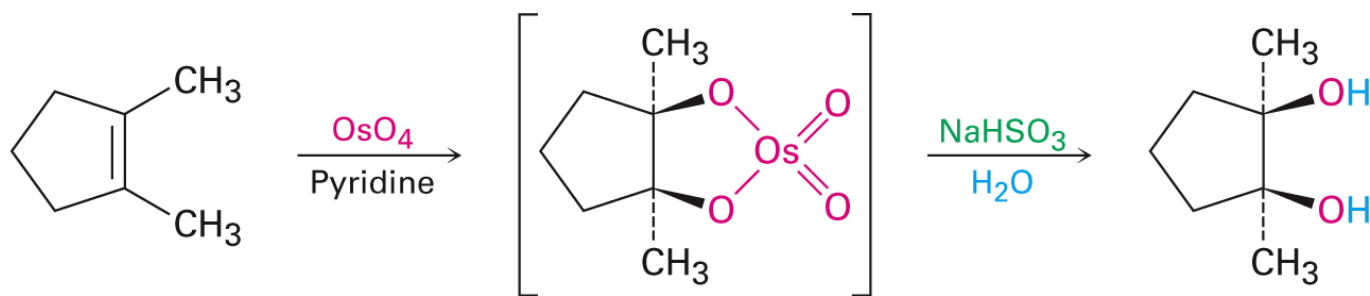
# Oxidation of Alkenes: Epoxidation and Hydroxylation

- ▶ Epoxidation results in a cyclic ether with an oxygen atom
- ▶ Stereochemistry of addition is syn



# Osmium Tetroxide Catalyzed Formation of Diols

- ▶ Hydroxylation - converts to syn-diol
- ▶ Osmium tetroxide, then sodium bisulfite
- ▶ Via cyclic osmate di-ester



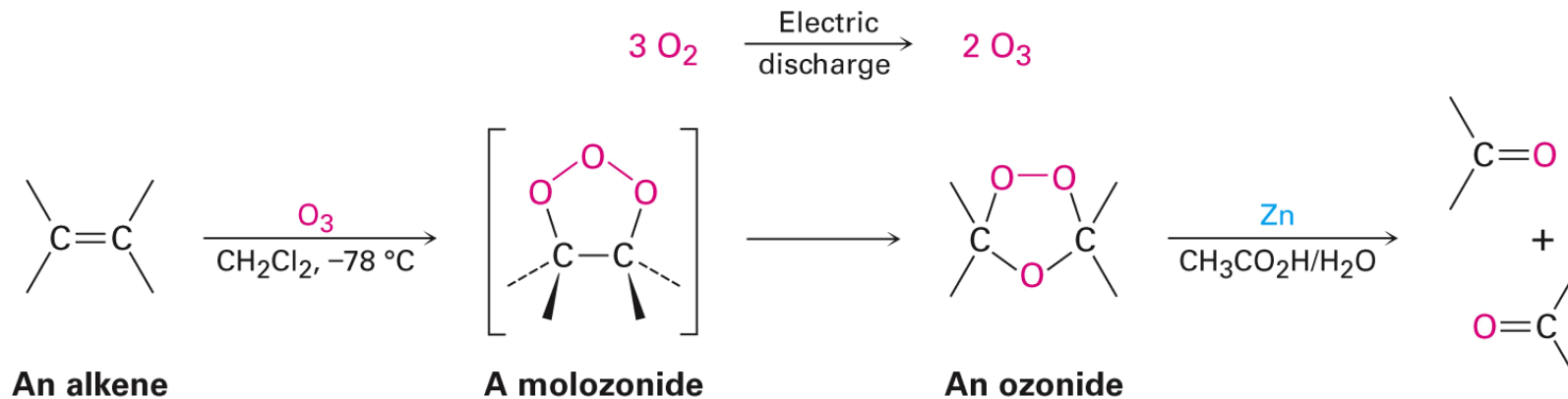
1,2-Dimethylcyclopentene

A cyclic osmate intermediate

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

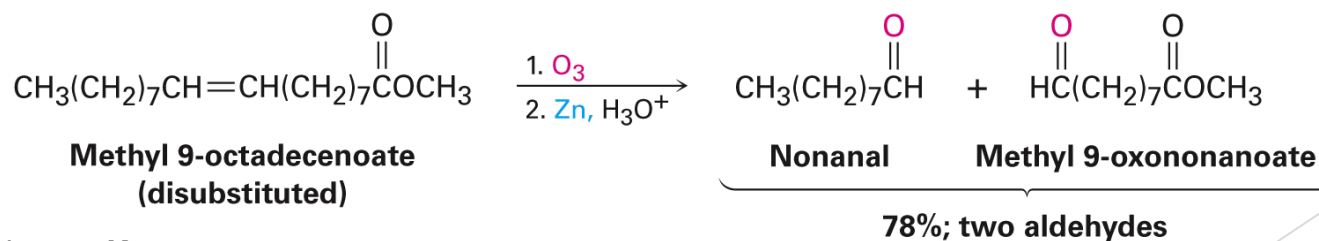
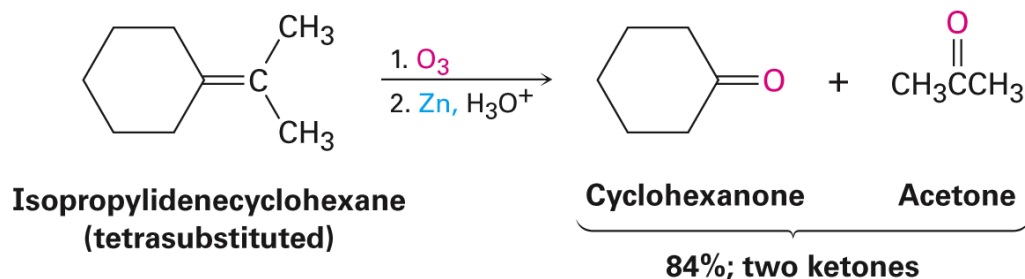
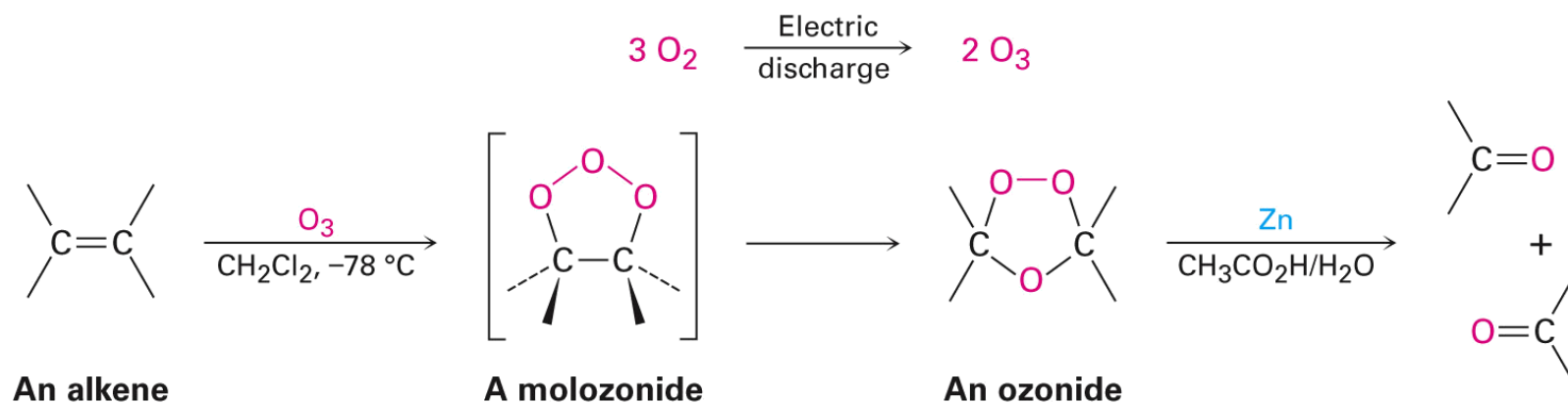
# Oxidation of Alkenes: Cleavage to Carbonyl Compounds

- ▶ **Ozone**,  $O_3$ , adds to alkenes to form molozonide
- ▶ Molozonide is converted to ozonide that may be reduced to obtain ketones and/or aldehydes



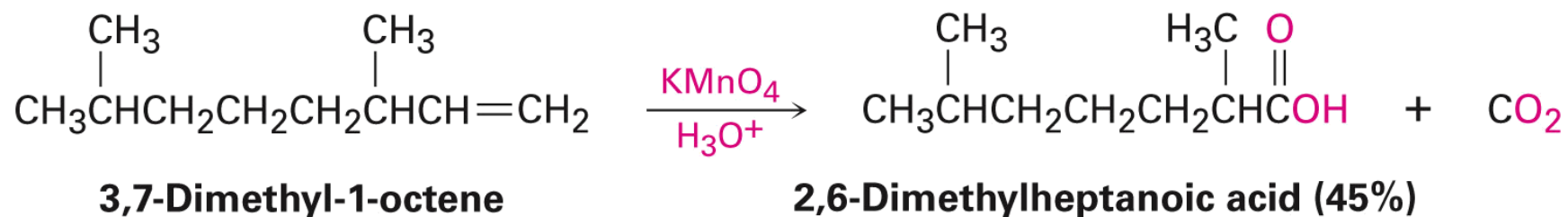
# Examples of Ozonolysis of Alkenes

- Used in determination of structure of an unknown alkene



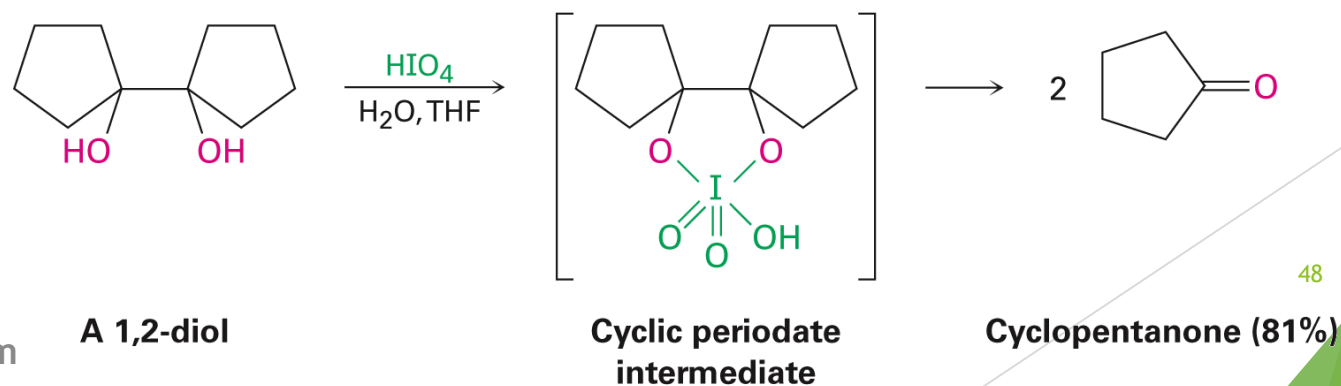
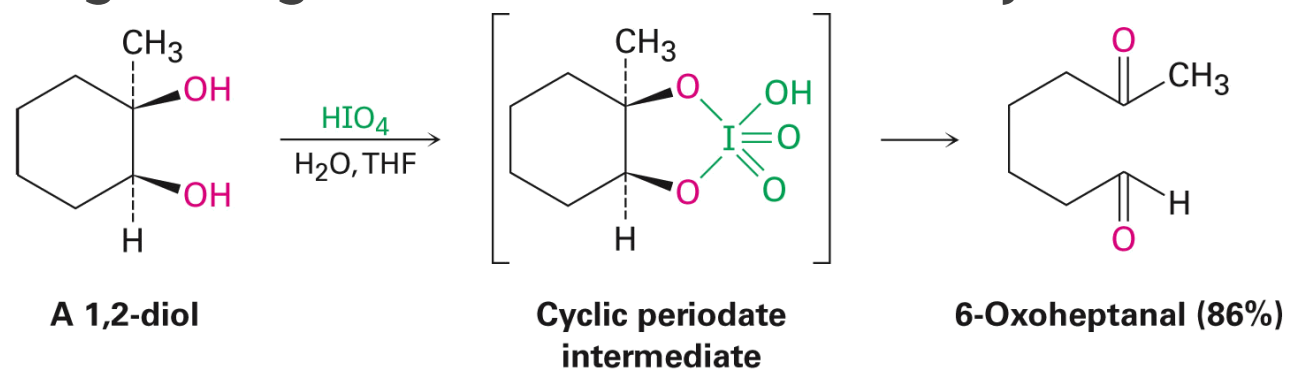
# Permanganate Oxidation of Alkenes

- ▶ Oxidizing reagents other than ozone also cleave alkenes
- ▶ Potassium permanganate ( $\text{KMnO}_4$ ) can produce carboxylic acids and carbon dioxide if H's are present on  $\text{C}=\text{C}$



# Cleavage of 1,2-diols

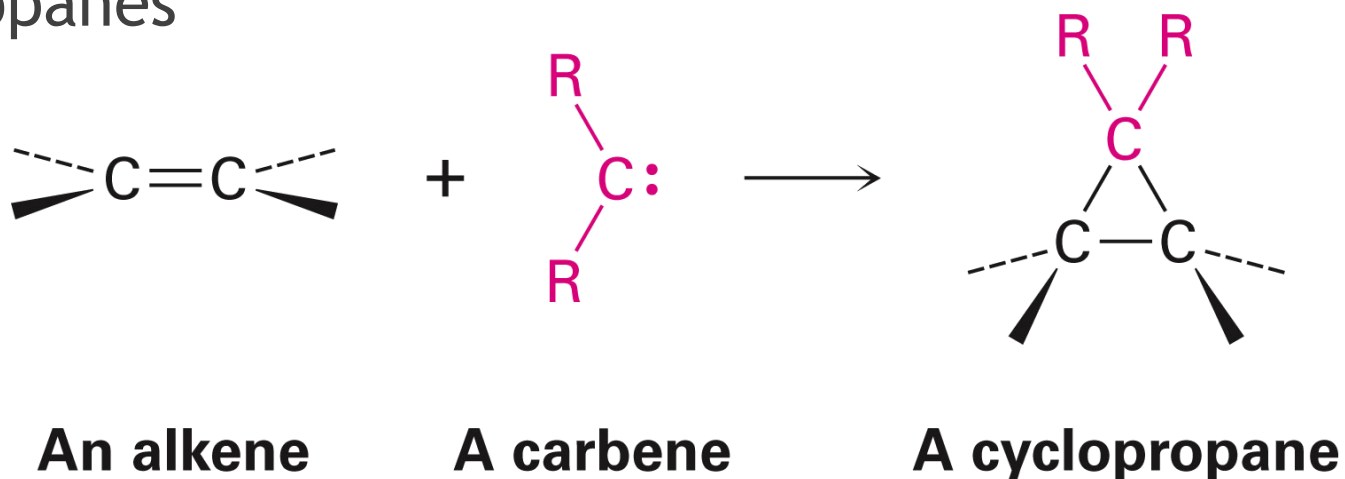
- ▶ Reaction of a 1,2-diol with **periodic** (*per-iodic*) acid,  $\text{HIO}_4$ , cleaves the diol into two carbonyl compounds
- ▶ Sequence of diol formation with  $\text{OsO}_4$  followed by diol cleavage is a good alternative to ozonolysis





# Addition of Carbenes to Alkenes: Cyclopropane Synthesis

- ▶ The **carbene** functional group is “half of an alkene”
- ▶ Carbenes are electronically neutral with six electrons in the outer shell
- ▶ They add symmetrically across double bonds to form cyclopropanes

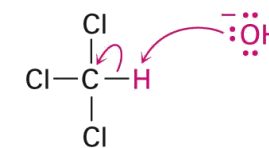


# Formation of Dichlorocarbene

- ▶ Base removes proton from chloroform
- ▶ Stabilized carbanion remains
- ▶ Unimolecular elimination of  $\text{Cl}^-$  gives electron deficient species, dichlorocarbene

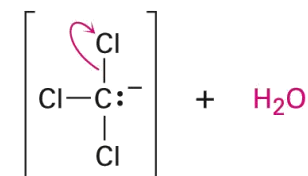
**1** Base abstracts the hydrogen from chloroform, leaving behind the electron pair from the C-H bond and forming the trichloromethanide anion.

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



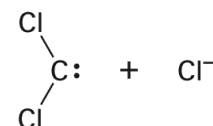
Chloroform

**1** ↓



Trichloromethanide anion

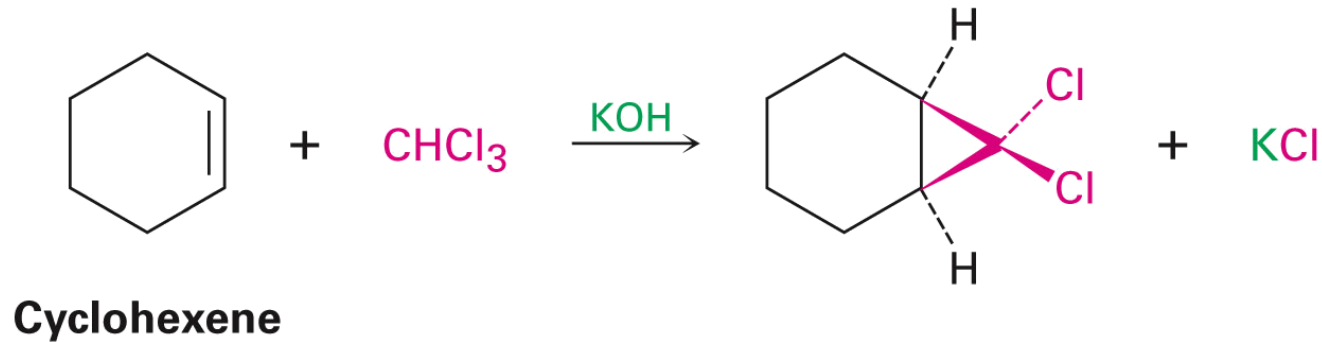
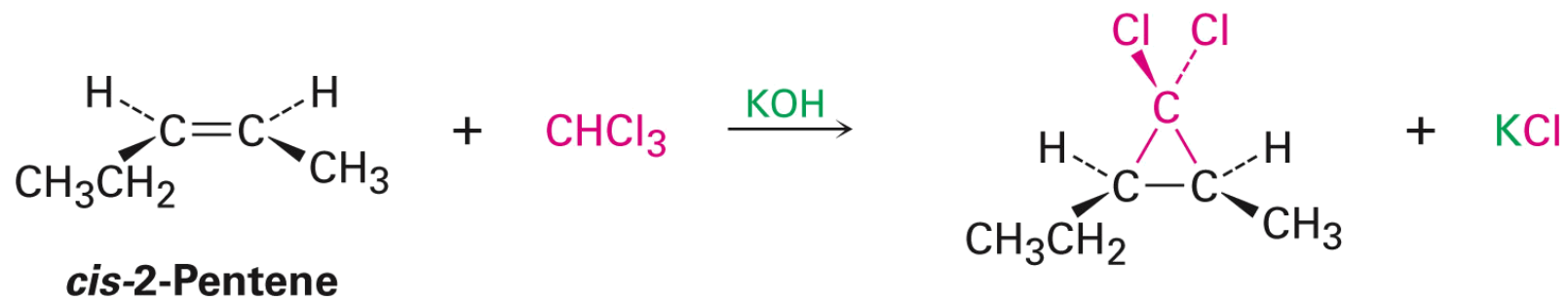
**2** ↓



Dichlorocarbene

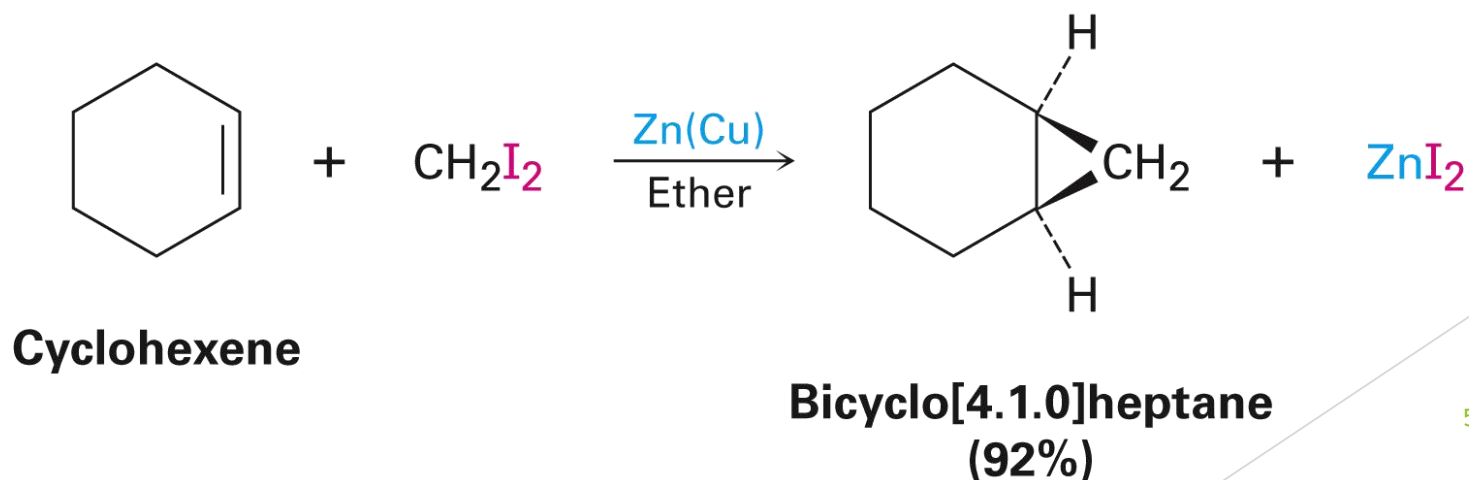
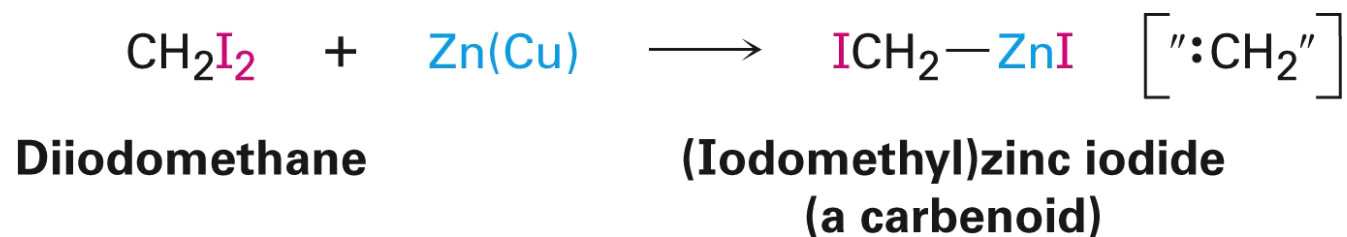
# Reaction of Dichlorocarbene

- Addition of dichlorocarbene is stereospecific *cis*



# Simmons-Smith Reaction

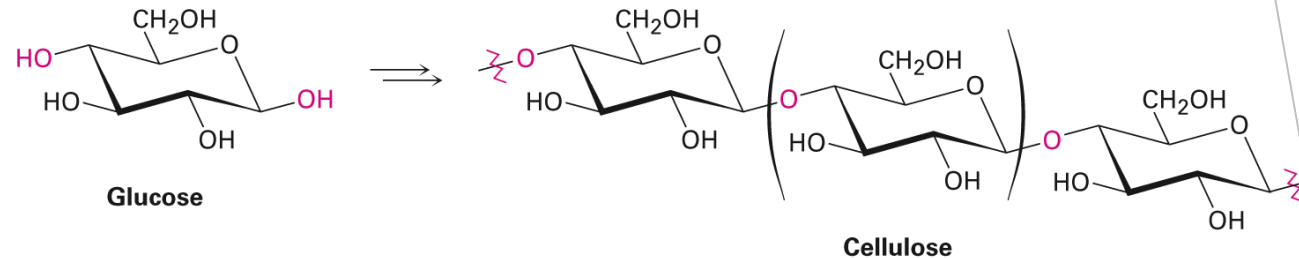
- ▶ Equivalent of addition of  $\text{CH}_2$ :
- ▶ Reaction of diiodomethane with zinc-copper alloy produces a carbenoid species
- ▶ Forms cyclopropanes by **cycloaddition**



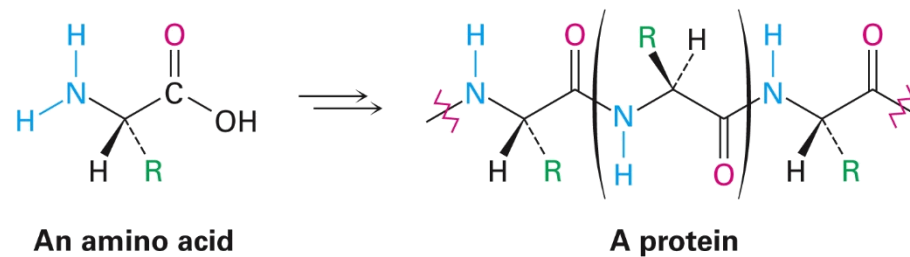
# Radical Additions to Alkenes: Chain-Growth Polymers

- ▶ A **polymer** is a very large molecule consisting of repeating units of simpler molecules, formed by *polymerization*
- ▶ Alkenes react with radical catalysts to undergo radical polymerization
- ▶ Ethylene is polymerized to polyethylene, for example

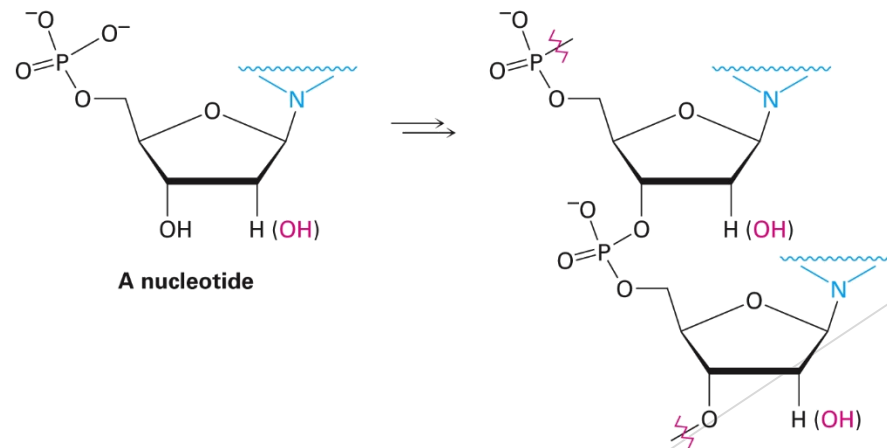
Cellulose—a glucose polymer



Protein—an amino acid polymer



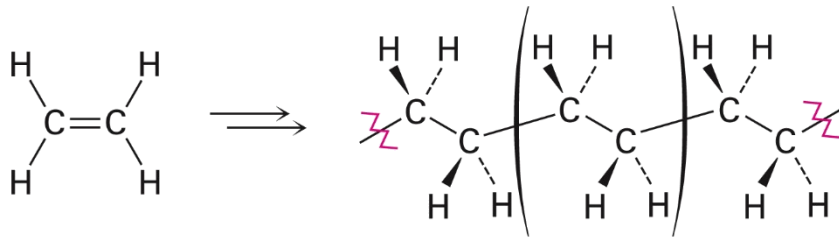
Nucleic acid—a nucleotide polymer



# Free Radical Polymerization: Initiation

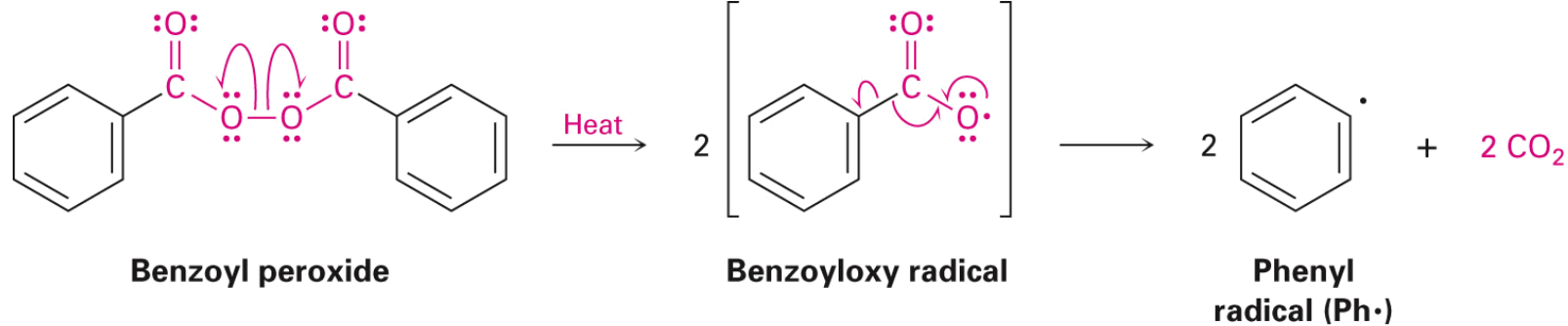
- ▶ **Initiation** - a few radicals are generated by the reaction of a molecule that readily forms radicals from a nonradical molecule
- ▶ A bond is broken homolytically

Polyethylene—a synthetic alkene polymer



Ethylene

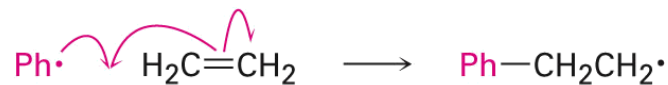
Polyethylene



Benzoyl peroxide

Benzoyloxy radical

Phenyl radical (Ph·)



# Polymerization: Propagation

- ▶ Radical from initiation adds to alkene to generate alkene derived radical
- ▶ This radical adds to another alkene, and so on many times



# Polymerization: Termination

- ▶ Chain propagation ends when two radical chains combine
- ▶ Not controlled specifically but affected by reactivity and concentration





# Other Polymers

- ▶ Other alkenes give other common polymers

