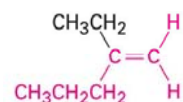


Alkenes: Structure and Reactivity

Alkenes, also called **olefins**, are hydrocarbons containing one or more **double bonds**.

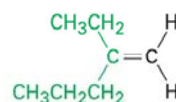
Naming the alkenes:

- Rule 1:** Find the longest chain containing the double bond and name the compound by replacing the alkane suffix -ane with -ene.
- Rule 2:** Number carbons in the chain so that double bond carbons have the lowest possible numbers; if the double bond is equidistant from two ends, begin at the end nearer the first substituent.



Named as a **pentene**

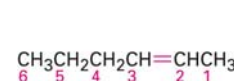
NOT



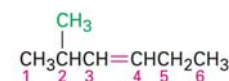
as a hexene, since the double bond is not contained in the six-carbon chain

8-1

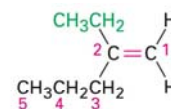
Nomenclature of Alkenes



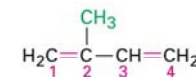
2-Hexene
Hex-2-ene



2-Methyl-3-hexene
2-Methylhex-3-ene

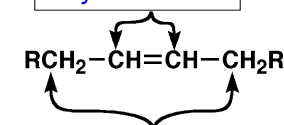


2-Ethyl-1-pentene
2-Ethylpent-1-ene

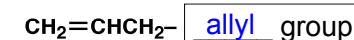


2-Methyl-1,3-butadiene
2-Methylbuta-1,3-diene
-diene and -triene

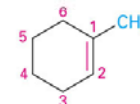
vinyl carbons



allylic carbons



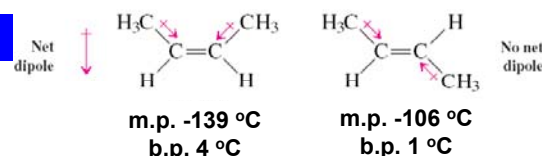
Cycloalkenes:



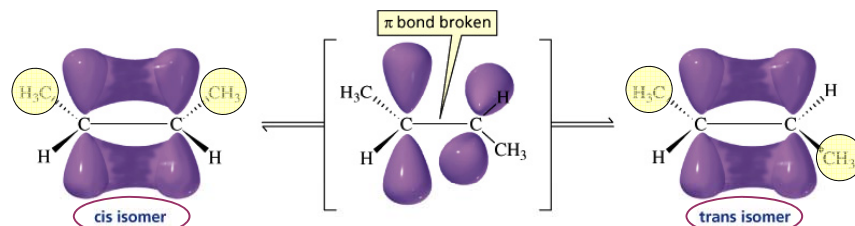
8-2

Factoids of Alkenes

Polarization of Alkenes



Rotation about the π -Bond

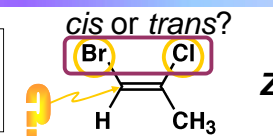


The barrier to rotation is very **large**. This leads to the possibility of *cis* and *trans* **isomers**, stable, separable compounds with **different properties**.

8-3

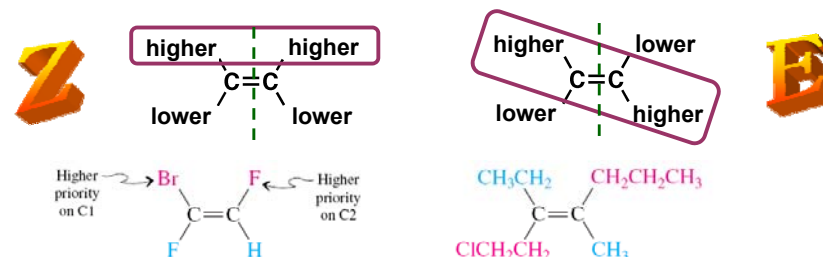
E,Z Nomenclature

Sometimes "*cis*" and "*trans*" are ambiguous; in such cases we resort to the more formal *E,Z* nomenclature.



Steps to assign *E* and *Z* descriptors

- For each C atom, assign substituent priority
- Z* if highest priority substituents on **same** side of double bond
- E* if highest priority substituents on **opposite** side of double bond

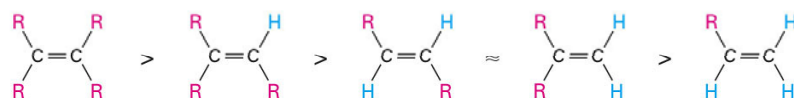


8-4

Stability of Alkenes



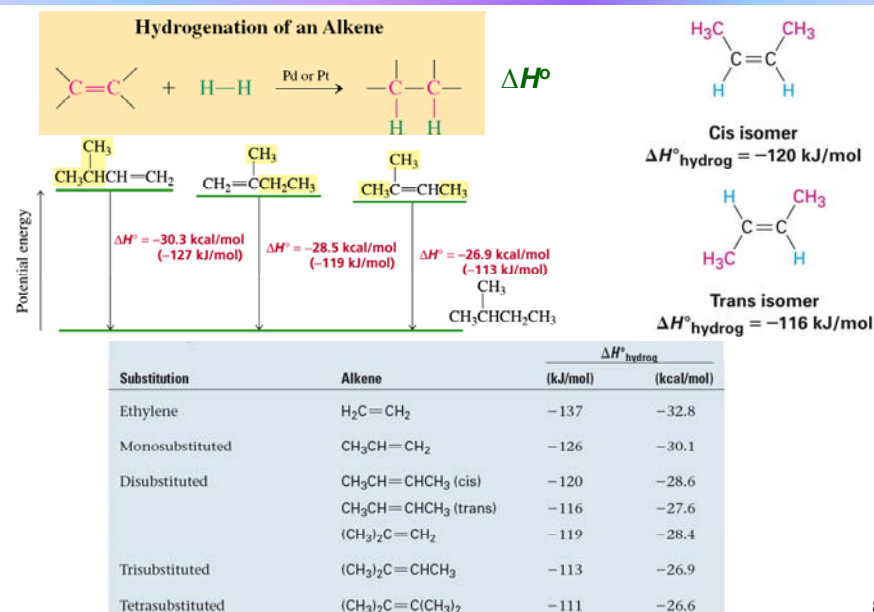
Tetrasubstituted > Trisubstituted > Disubstituted > Monosubstituted



more hyperconjugation

8-5

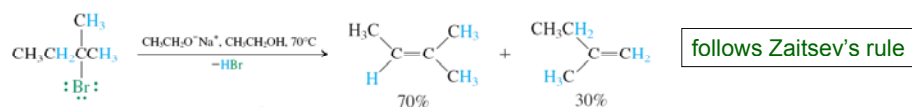
Heat of Hydrogenation: a Measure of Stability



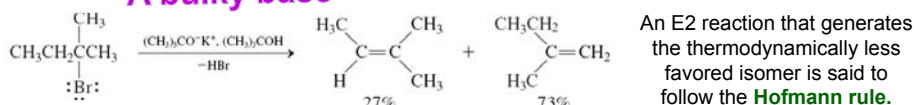
8-6

Preparation of Alkenes

Elimination Reactions:

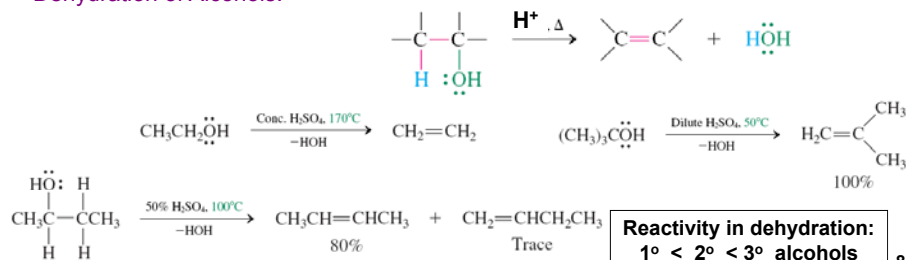


A bulky base



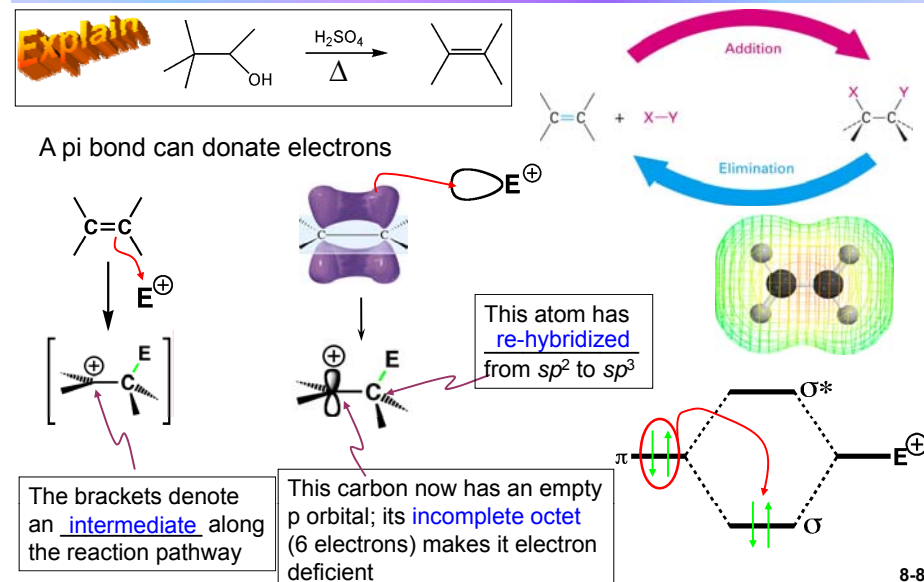
Dehydration of Alcohols:

Acid-Mediated Dehydration of Alcohols



8-7

Reactions of Alkenes: The C=C Double Bond as a Nucleophile

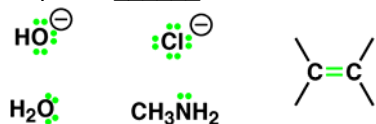


8-8

Classifying Reactants

Many steps in the mechanisms that we will encounter involve bond formation between nucleophiles and electrophiles.

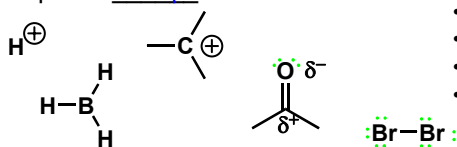
Nucleophiles donate electrons.



Identifying nucleophiles

- Lone pairs
- (-) charges
- π bonds

Electrophiles accept electrons.

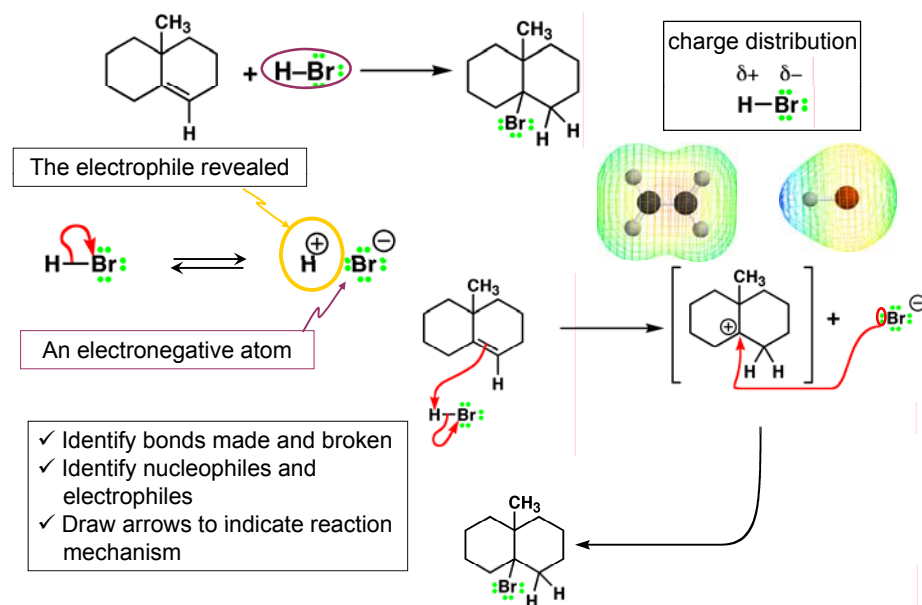


Identifying electrophiles

- Empty orbitals (incomplete octet)
- (+) charges
- Polarized bonds
- Weak σ bonds

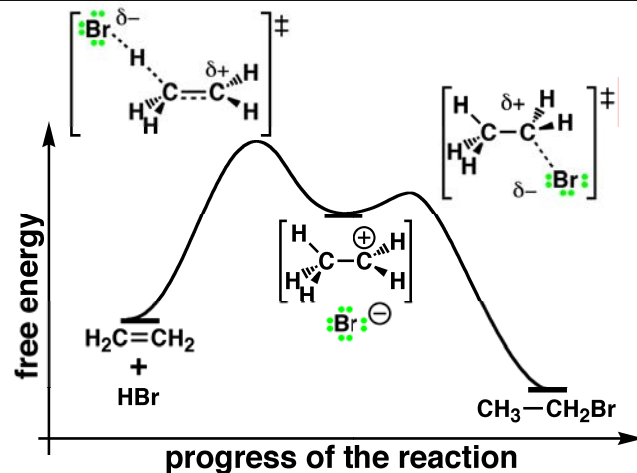
8-9

HBr as an Electrophile



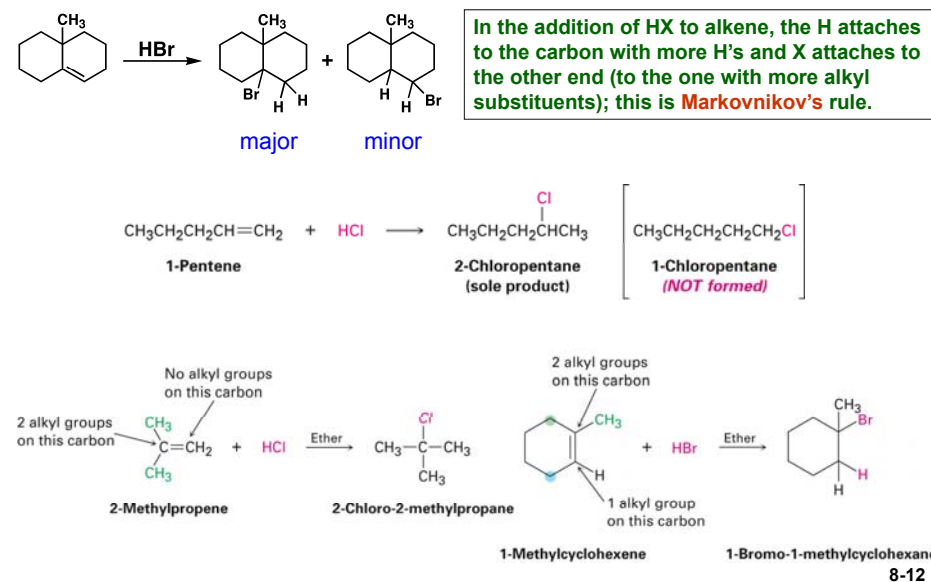
The Reaction Coordinate Diagram for HBr Addition to Alkenes

Transition states along the reaction paths are typically high-energy, unstable species. Unlike TS^\ddagger however, they have fully formed bonds and lie in minima on reaction coordinate diagrams.



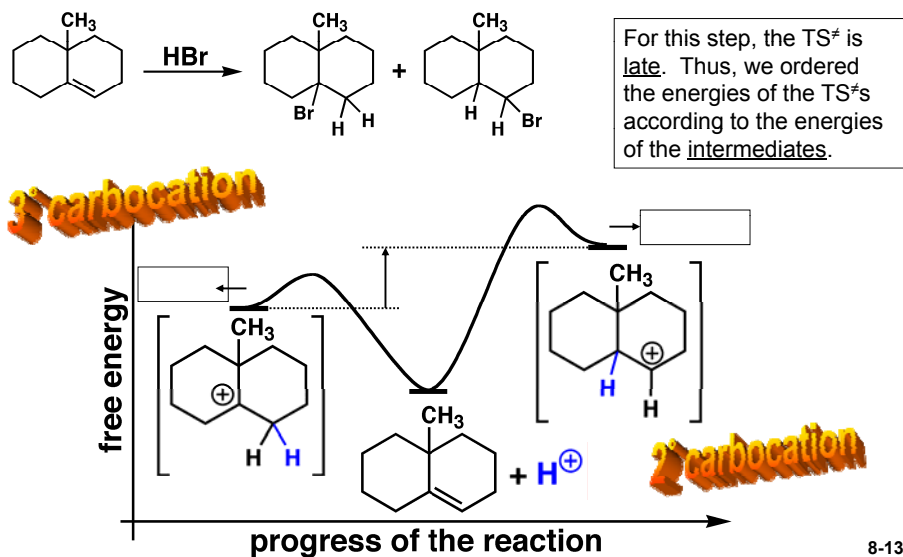
8-11

Product Distribution in HX Addition to Alkenes



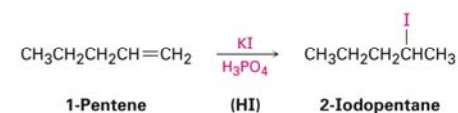
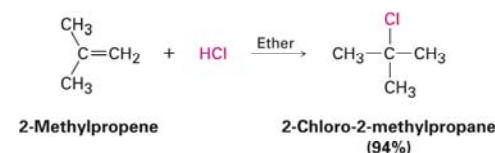
8-12

Product Distribution and the Reaction Coordinate Diagram



Electrophilic Addition: Alkyl Halide Preparation

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

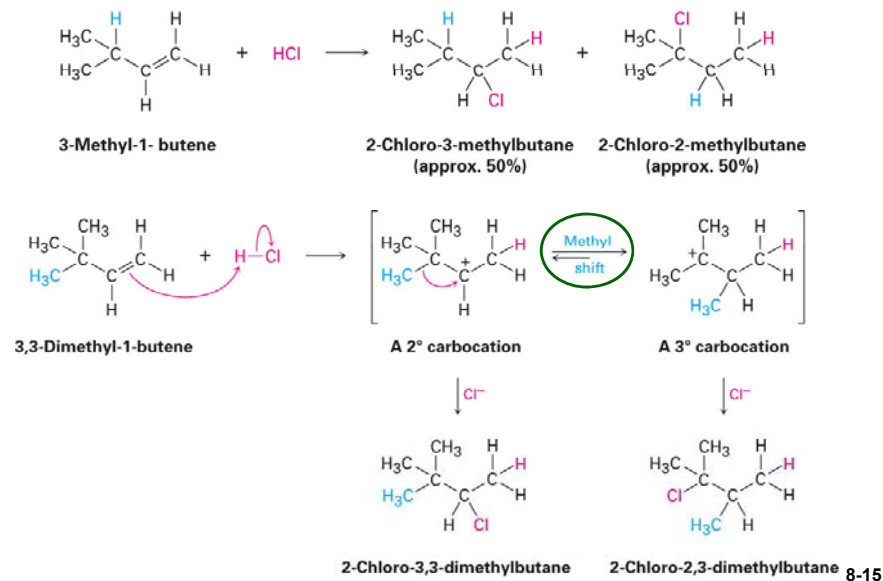


Predict the relative reactivity of the following alkenes toward electrophilic addition of HX and give your explanations.

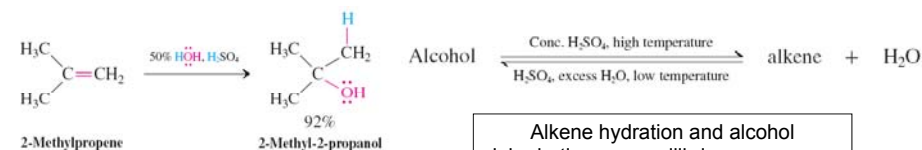


8-14

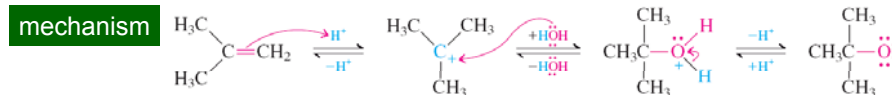
Rearrangement of Carbocations



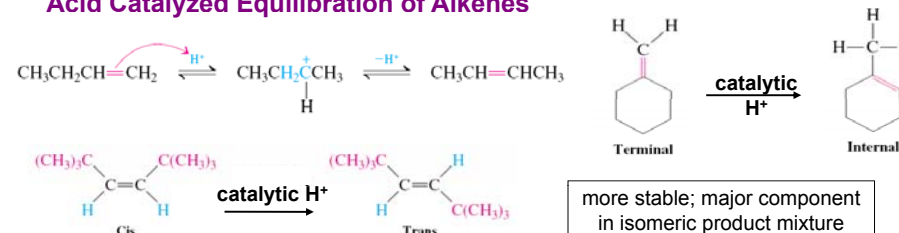
Electrophilic Hydration of Alkenes



Alkene hydration and alcohol dehydration are equilibrium processes.

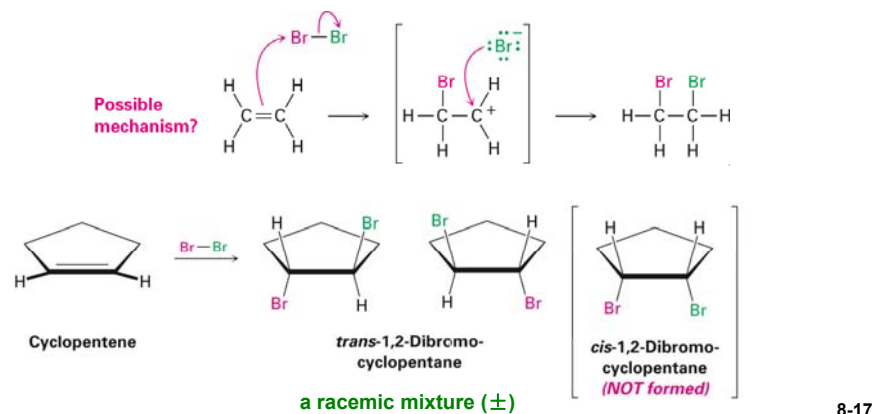
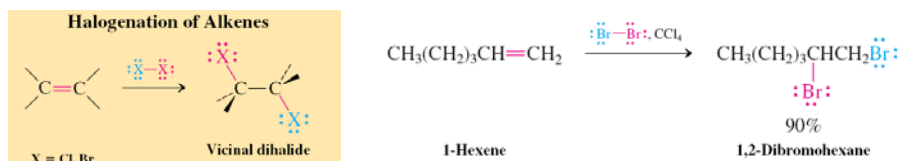


Acid Catalyzed Equilibration of Alkenes

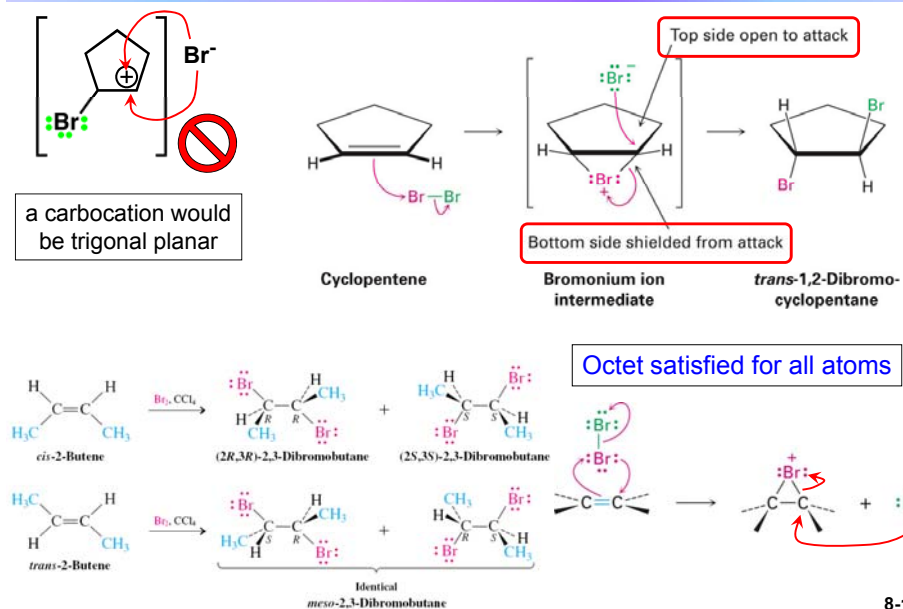


8-16

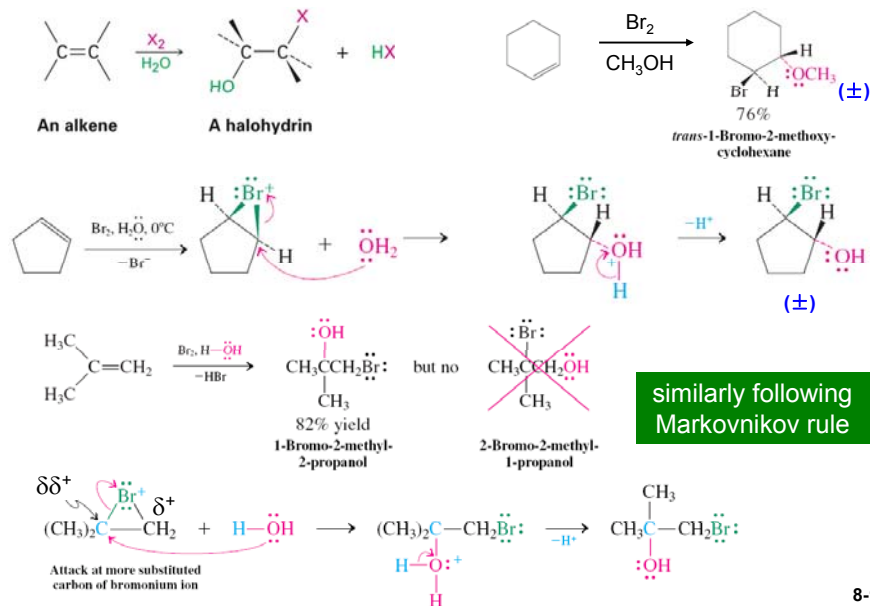
Electrophilic Addition of Halogen to Alkenes



Stereochemistry Elucidates the Mechanism



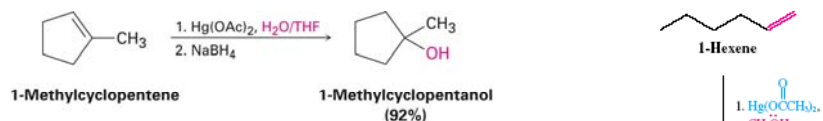
Bromonium Trapped by Other Nucleophiles



Regioselectivity in Halonium Ion Opening

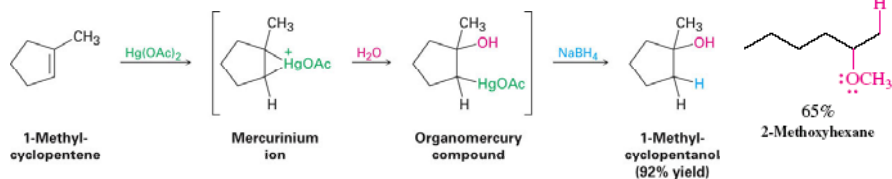
Name	Structure	Addition Product to 2-methylpropene
Bromine chloride	$\text{Br}-\text{Cl}$	$\text{BrCH}_2\text{C}(\text{CH}_3)_2$
Cyanogen bromide	$\text{Br}-\text{CN}$	$\text{BrCH}_2\text{C}(\text{CH}_3)_2$
Iodine chloride	$\text{I}-\text{Cl}$	$\text{ICH}_2\text{C}(\text{CH}_3)_2$
Sulfonyl chlorides	$\text{RS}-\text{Cl}$	$\text{RSCH}_2\text{C}(\text{CH}_3)_2$
Mercuric salts	$\text{XHg}-\text{X}^+$	$\text{XHgCH}_2\text{C}(\text{CH}_3)_2$

Oxymercuration and Demercuration

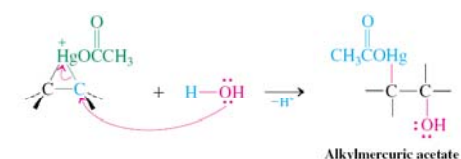


Step 1: oxymercuration

Step 2: demercuration



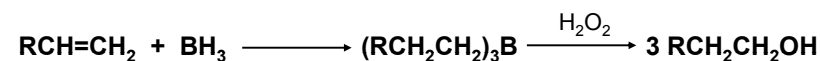
Nucleophilic opening (Markovnikov regioselectivity)



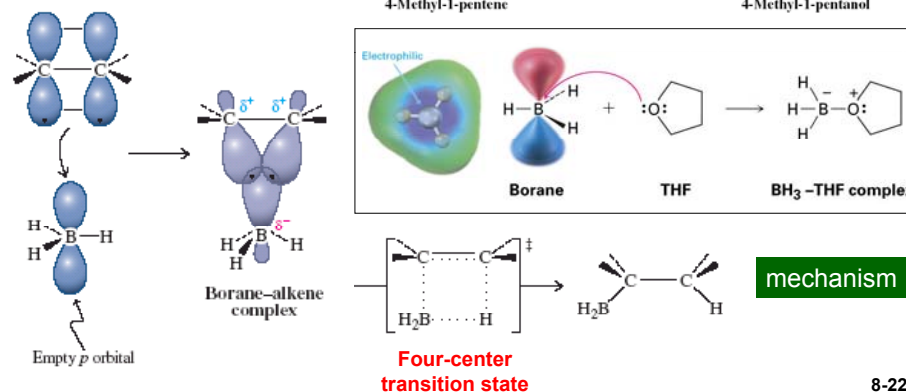
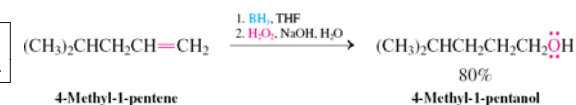
In many cases, the alcohol from demercuration is the same as acid-catalyzed hydration of alkenes; however, because no carbocation intermediate is involved, oxymercuration-demercuration is **not susceptible to rearrangement** of carbocation intermediate.

8-21

Hydroboration-Oxidation: an Anti-Markovnikov Hydration

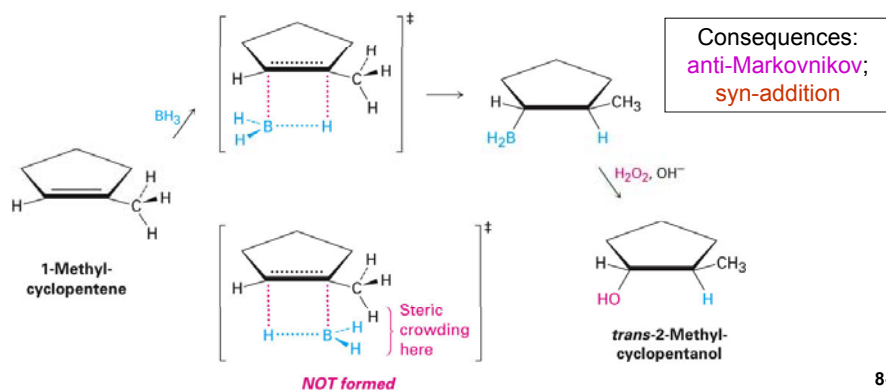
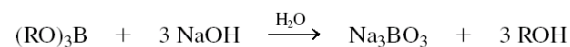


Borane is commercially available in an ether-tetrahydrofuran solvent.



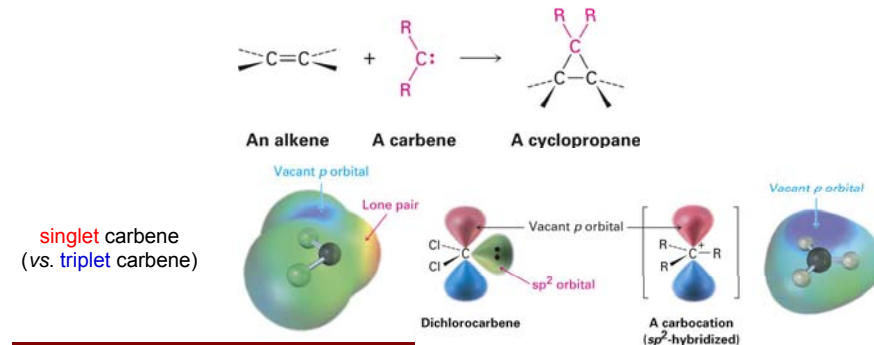
8-22

Mechanism of Hydroboration-Oxidation

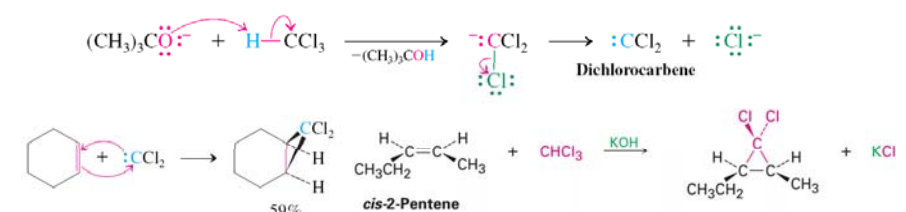


8-23

Carbene Formation and Cyclopropane Synthesis

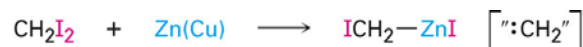
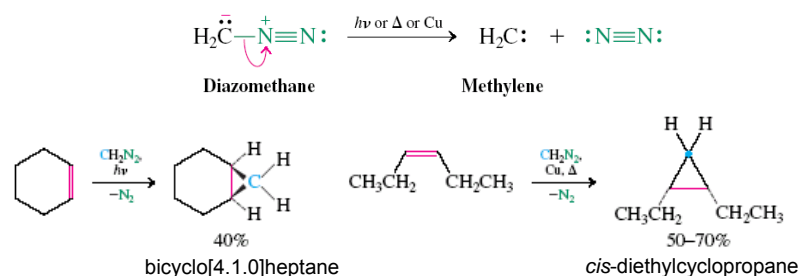


Carbene formations and reactions:

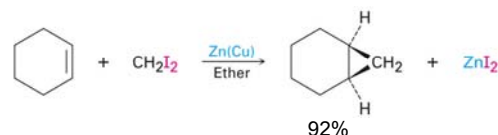


8-24

Carbene and Carbenoid Reactions

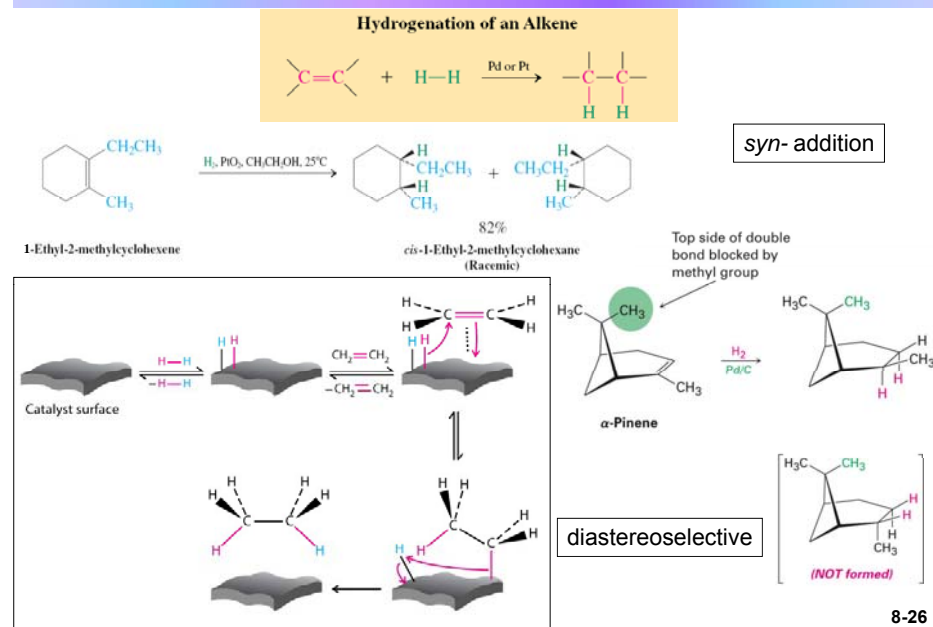


Simmons-Smith reagent: (iodomethyl)zinc iodide
"carbenoid" (a carbene-like substance)



8-25

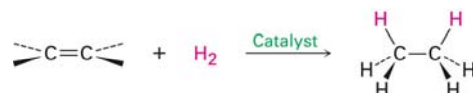
Reduction of Alkenes: Catalytic Hydrogenation



Oxidation and Reduction in Organic Chemistry

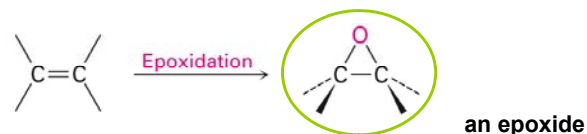
Reduction increase electron density on carbon by:

- forming: C-H
- or breaking: C-O C-N C-X



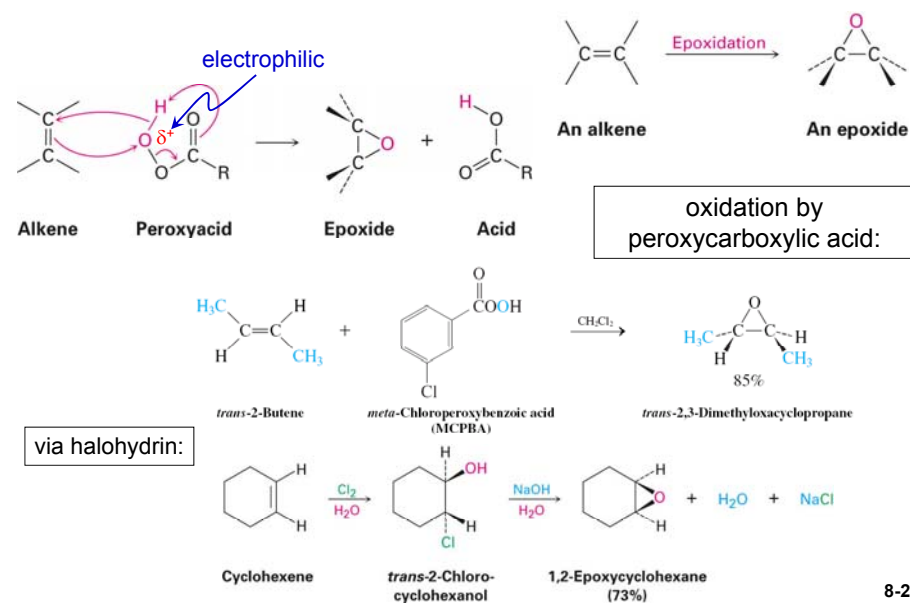
Oxidation decrease electron density on carbon by:

- forming: C-O C-N C-X
- or breaking: C-H



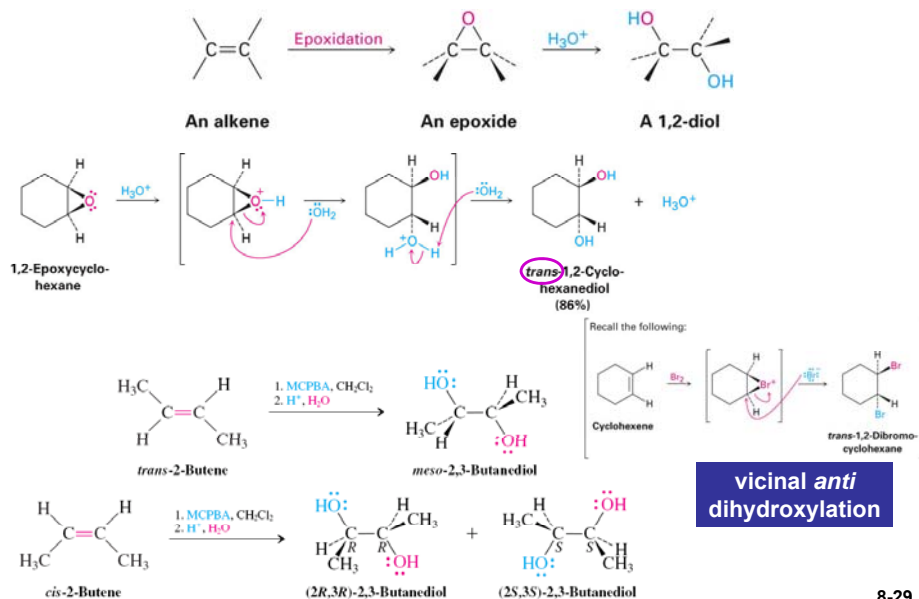
8-27

Epoxide Synthesis



8-28

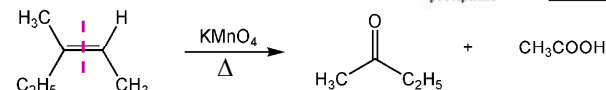
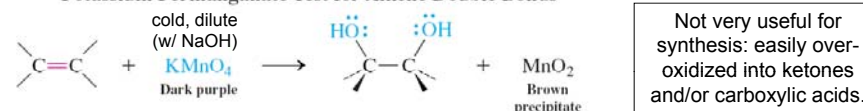
Diol Formation: Epoxide Ring-Opening



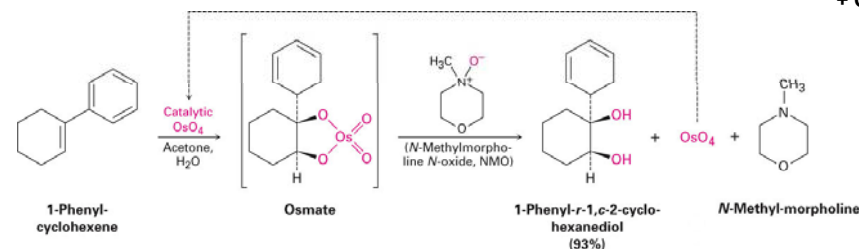
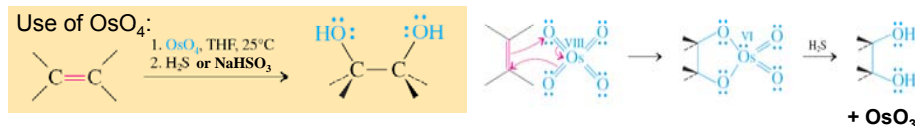
8-29

Vicinal Syn Dihydroxylation of Alkenes

Potassium Permanganate Test for Alkene Double Bonds

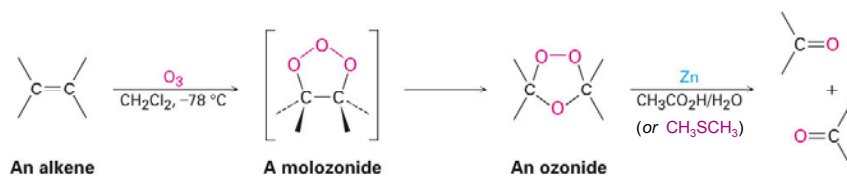


Use of OsO_4 :



8-30

Oxidative Cleavage: Ozonolysis

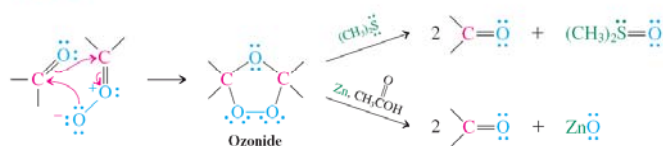


mechanism:

STEP 1. Molozonide formation and cleavage



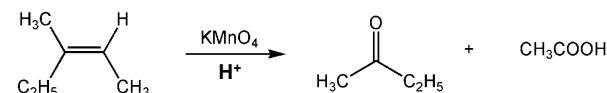
STEP 2. Ozonide formation and reduction



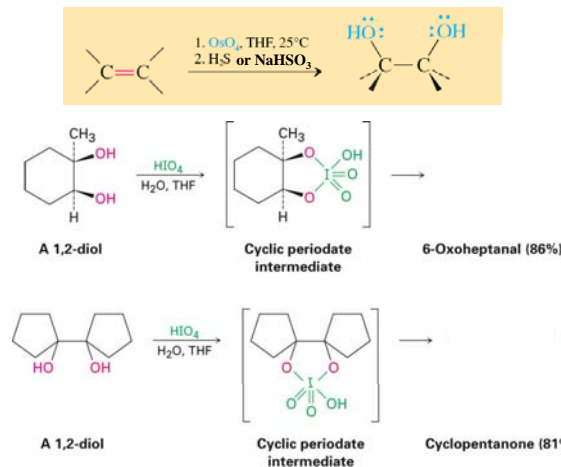
8-31

More Oxidative Cleavages to Carbonyl Compounds

KMnO_4



HIO_4

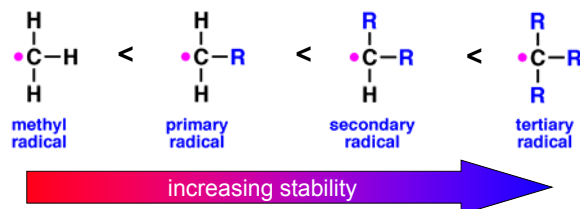
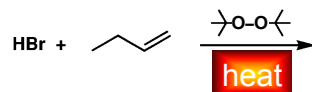
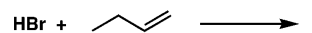


8-32

Anti-Markovnikov Product Formation from Radical Addition of Alkenes

Some weak bonds have a tendency to fragment homolytically e.g., peroxides $\text{RO}-\text{OR}$

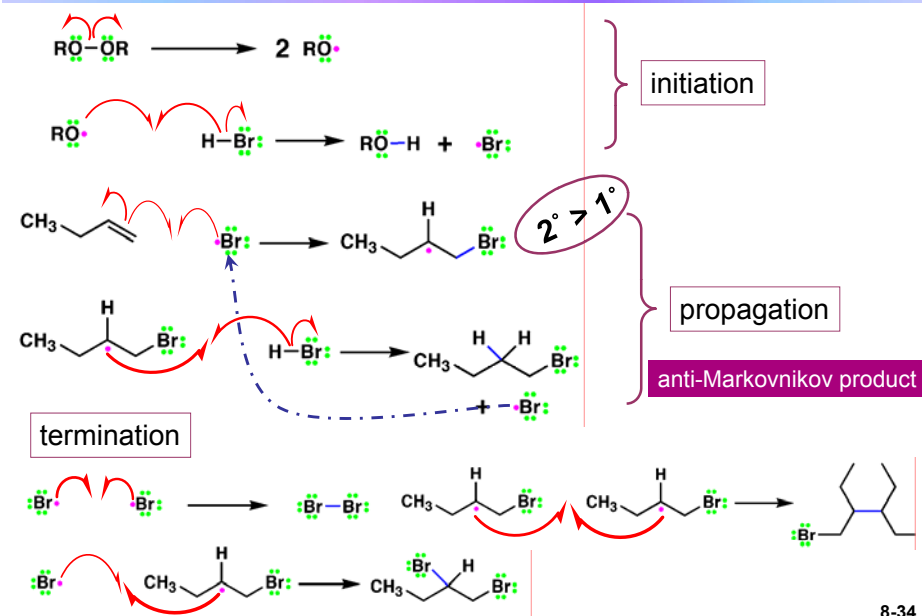
This provides a pathway to initiate radical reactions. Compare:



Review stability of carbon-centered radicals

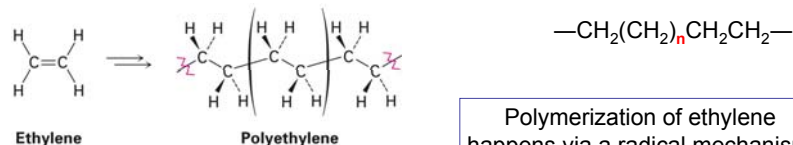
8-33

Mechanism of Radical Chain Addition

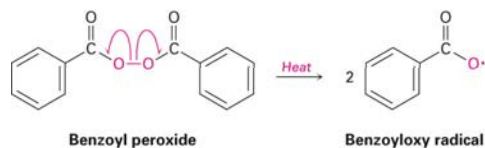


8-34

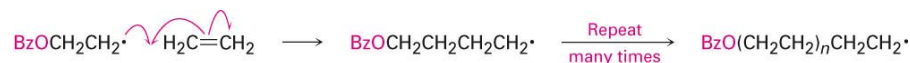
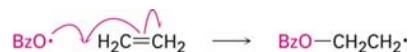
Radical Polymerization of Ethylene



Initiation:



Propagation:

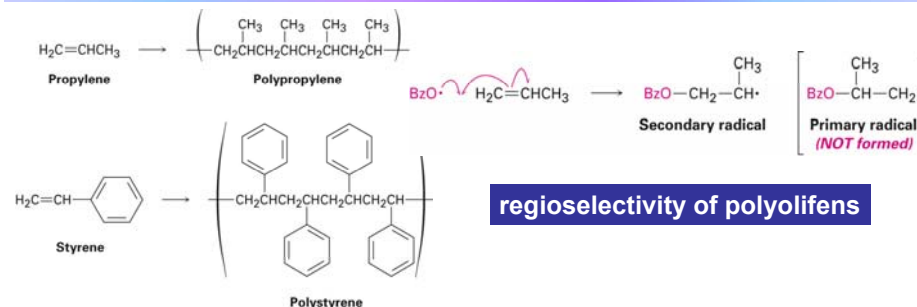


Termination:



8-35

Polymerization of Other Alkenes



Monomer	Formula	Trade or common name of polymer	Uses
Ethylene	$\text{H}_2\text{C}=\text{CH}_2$	Polyethylene	Packaging, bottles
Propene (propylene)	$\text{H}_2\text{C}=\text{CHCH}_3$	Polypropylene	Moldings, rope, carpets
Chloroethylene (vinyl chloride)	$\text{H}_2\text{C}=\text{CHCl}$	Poly(vinyl chloride) Teflon	Insulation, films, pipes
Styrene	$\text{H}_2\text{C}=\text{CHC}_6\text{H}_5$	Polystyrene	Foam, moldings
Tetrafluoroethylene	$\text{F}_2\text{C}=\text{CF}_2$	Teflon	Gaskets, nonstick coatings
Acrylonitrile	$\text{H}_2\text{C}=\text{CHCN}$	Orlon, Acrilan	Fibers
Methyl methacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$	Plexiglas, Lucite	Paint, sheets, moldings
Vinyl acetate	$\text{H}_2\text{C}=\text{CHOCOCH}_3$	Poly(vinyl acetate)	Paint, adhesives, foams

8-36