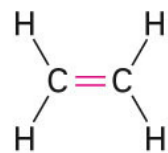


# 6. Alkenes: Structure and Reactivity

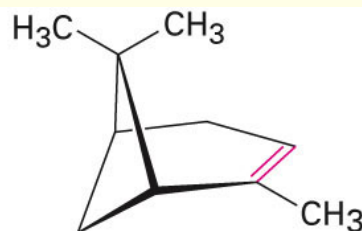
Based on McMurry's *Organic Chemistry*, 7<sup>th</sup> edition

# Alkene - Hydrocarbon With Carbon-Carbon Double Bond

- Also called an olefin but *alkene* is better
- Includes many naturally occurring materials
  - Flavors, fragrances, vitamins



**Ethylene**



**$\alpha$ -Pinene**



**$\beta$ -Carotene**  
(orange pigment and vitamin A precursor)

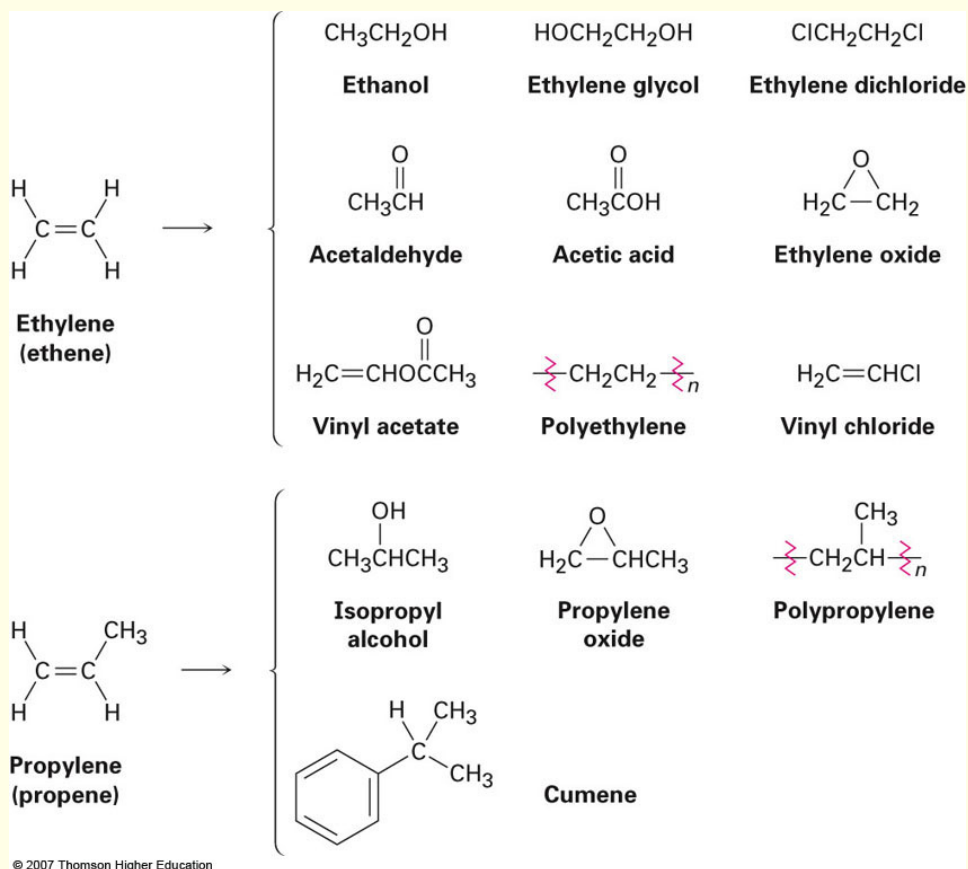
# Why this Chapter?

---

- **C-C double bonds** are present in most organic and biological molecules
- To examine consequences of alkene stereoisomerism
- To focus on general alkene reaction: electrophilic addition

# 6.1 Industrial Preparation and Use of Alkenes

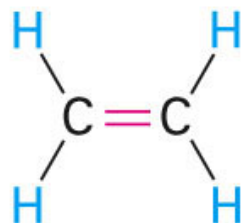
- Ethylene and propylene are the most important organic chemicals produced



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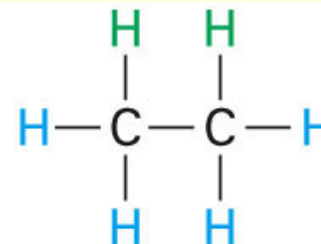
# 6.2 Calculating Degree of Unsaturation

- Relates molecular formula to possible structures
- **Degree of unsaturation:** number of multiple bonds or rings
- Formula for a saturated acyclic compound is  $C_nH_{2n+2}$
- Each ring or multiple bond replaces 2 H's



**Ethylene:  $C_2H_4$**

**(fewer hydrogens—*unsaturated*)**

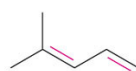
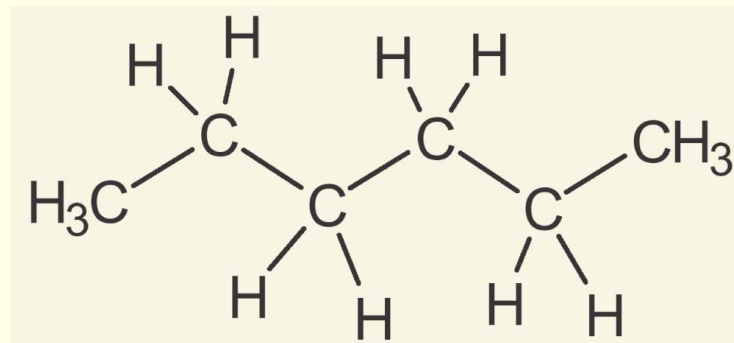


**Ethane:  $C_2H_6$**

**(more hydrogens—*saturated*)**

# Example: C<sub>6</sub>H<sub>10</sub>

- Saturated is C<sub>6</sub>H<sub>14</sub>
  - Therefore 4 H's are not present
- This has two degrees of unsaturation
  - Two double bonds?
  - or triple bond?
  - or two rings
  - or ring and double bond



4-Methyl-1,3-pentadiene  
(two double bonds)



Cyclohexene  
(one ring, one double bond)



Bicyclo[3.1.0]hexane  
(two rings)



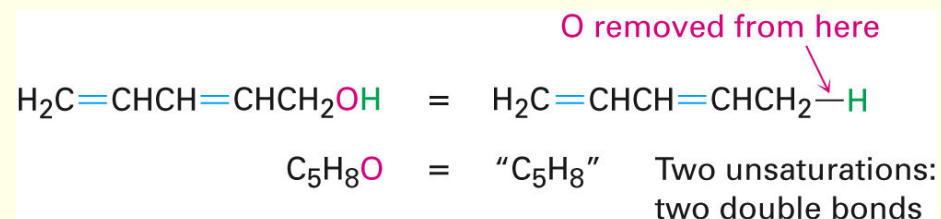
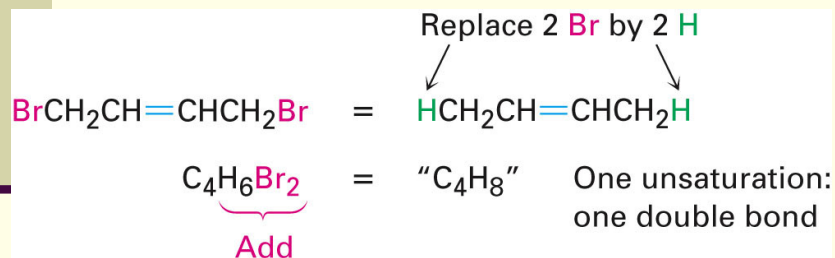
4-Methyl-2-pentyne  
(one triple bond)

C<sub>6</sub>H<sub>10</sub>

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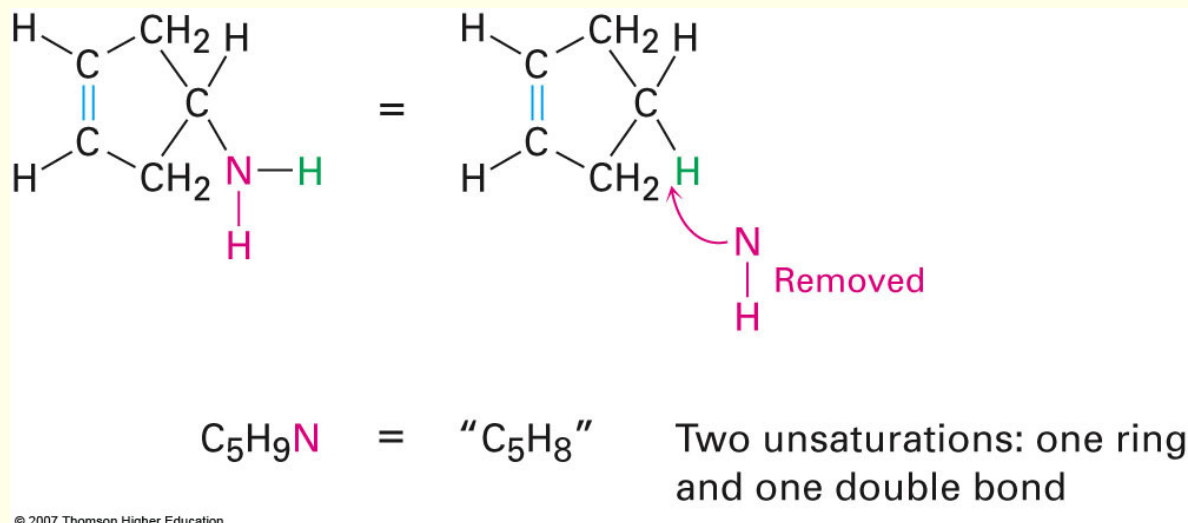
# Degree of Unsaturation With Other Elements

- Organohalogens (X: F, Cl, Br, I)
  - Halogen replaces hydrogen
- $C_4H_6Br_2$  and  $C_4H_8$  have one degree of unsaturation
- Organooxygen compounds (C,H,O) - if connected by single bonds
  - These don't affect the total count of H's



# Organonitrogen compounds

- Nitrogen has three bonds
  - So if it connects where H was, it adds a connection point
  - Subtract one H for equivalent degree of unsaturation in hydrocarbon





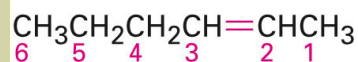
# Summary - Degree of Unsaturation

---

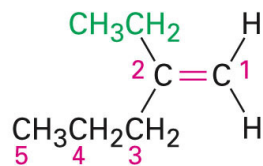
- Count pairs of H's below  $C_nH_{2n+2}$
- Add number of halogens to number of H's (X equivalent to H)
- Ignore oxygens (oxygen links H)
- Subtract N's - they have two connections

# 6.3 Naming of Alkenes

- Name the parent hydrocarbon
- Number carbons in chain so that double bond carbons have lowest possible numbers
- Rings have “**cyclo**” prefix

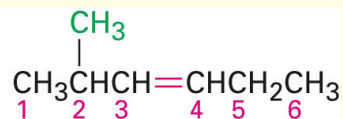


**2-Hexene**

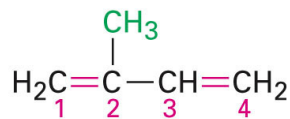


**2-Ethyl-1-pentene**

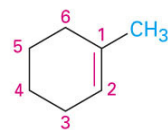
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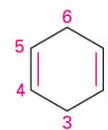
**2-Methyl-3-hexene**



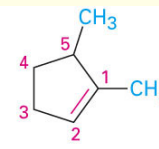
**2-Methyl-1,3-butadiene**



**1-Methylcyclohexene**



**1,4-Cyclohexadiene**  
(New: Cyclohexa-1,4-diene)



**1,5-Dimethylcyclopentene**

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# Many Alkenes Are Known by Common Names

**Table 6.1** | Common Names of Some Alkenes

Compound	Systematic name	Common name
$\text{H}_2\text{C}=\text{CH}_2$	Ethene	Ethylene
$\text{CH}_3\text{CH}=\text{CH}_2$	Propene	Propylene
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{C}=\text{CH}_2 \end{array}$	2-Methylpropene	Isobutylene
$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_2\text{C}=\text{C}-\text{CH}=\text{CH}_2 \end{array}$	2-Methyl-1,3-butadiene	Isoprene

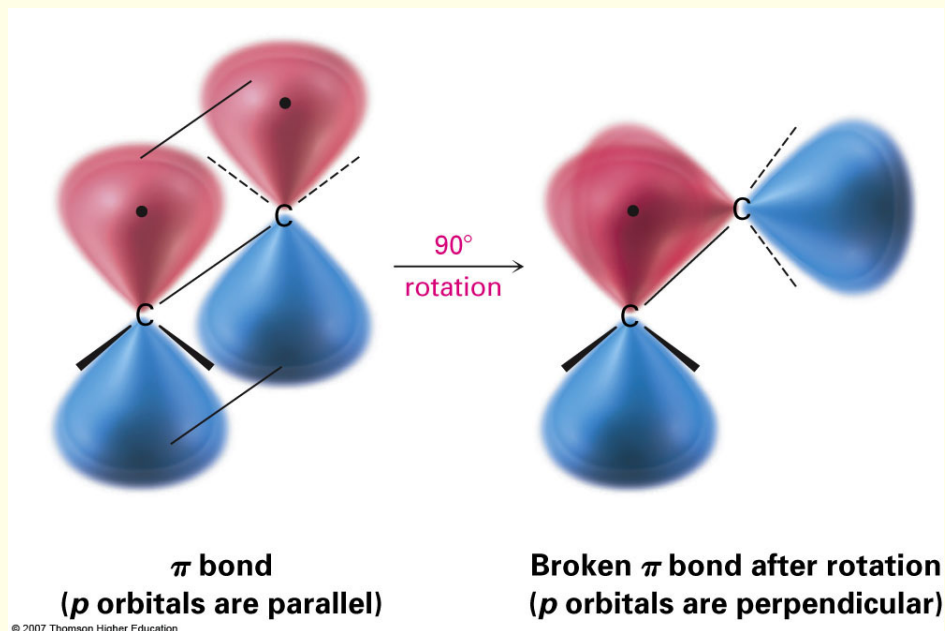
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## 6.4 Cis-Trans Isomerism in Alkenes

---

- Carbon atoms in a double bond are  $sp^2$ -hybridized
  - Three equivalent orbitals at  $120^\circ$  separation in plane
  - Fourth orbital is atomic  $p$  orbital
- Combination of electrons in two  $sp^2$  orbitals of two atoms forms  $\sigma$  bond between them
- Additive interaction of  $p$  orbitals creates a  $\pi$  bonding orbital
  - Subtractive interaction creates a  $\pi$  anti-bonding orbital
- Occupied  $\pi$  orbital prevents rotation about  $\sigma$ -bond
- Rotation prevented by  $\pi$  bond - high barrier, about 268 kJ/mole in ethylene

# Rotation of $\pi$ Bond Is Prohibitive

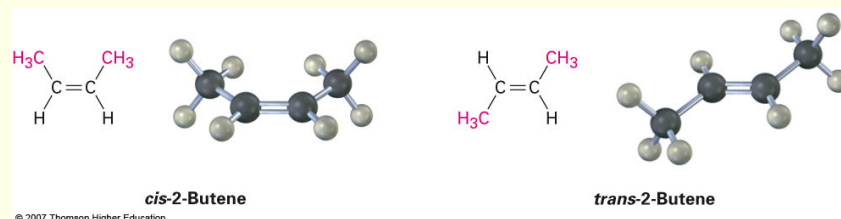


- This prevents rotation about a carbon-carbon double bond (unlike a carbon-carbon single bond).
- Creates possible alternative structures

- The presence of a carbon-carbon double bond can create two possible structures

- ***cis* isomer** - two similar groups on same side of the double bond
- ***trans* isomer** - similar groups on opposite sides

- Each carbon must have two different groups for these isomers to occur

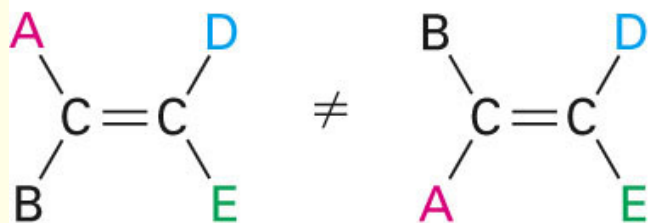


# Cis, Trans Isomers Require That End Groups Must Differ in Pairs

- 180° rotation superposes
- Bottom pair cannot be superposed without breaking C=C



These two compounds are identical; they are not cis-trans isomers.



These two compounds are not identical; they are cis-trans isomers.

# 6.5 Sequence Rules: The *E,Z* Designation

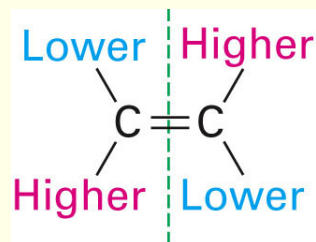
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- Neither compound is clearly “*cis*” or “*trans*”
  - Substituents on C1 are different than those on C2
  - We need to define “similarity” in a precise way to distinguish the two stereoisomers
- *Cis, trans* nomenclature only works for disubstituted double bonds

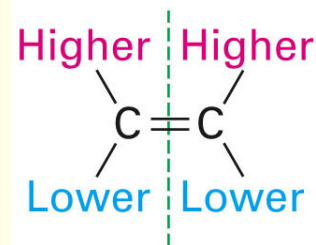


# E,Z Stereochemical Nomenclature

- Priority rules of **Cahn, Ingold, and Prelog**
- Compare where higher priority groups are with respect to bond and designate as prefix
- **E -*entgegen***, opposite sides
- **Z -*zusammen***, together on the same side



*E* double bond  
(Higher-priority groups are on **opposite** sides.)



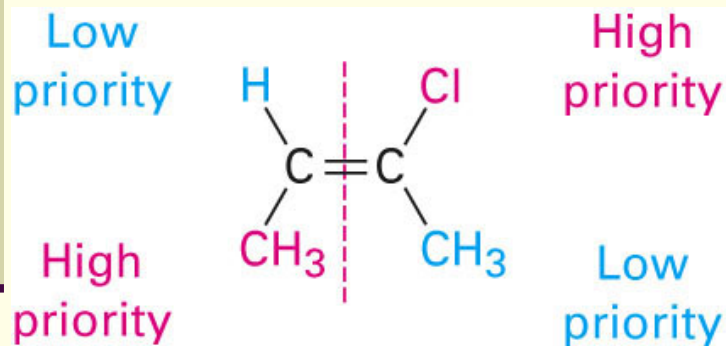
*Z* double bond  
(Higher-priority groups are on the **same** side.)

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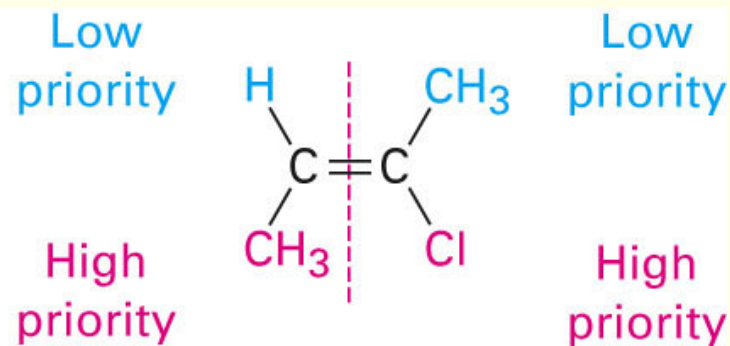
# Ranking Priorities: Cahn-Ingold-Prelog Rules

## RULE 1

- Must rank atoms that are connected at comparison point
- Higher atomic number gets higher priority
  - $\text{Br} > \text{Cl} > \text{S} > \text{P} > \text{O} > \text{N} > \text{C} > \text{H}$



(a) (*E*)-2-Chloro-2-butene



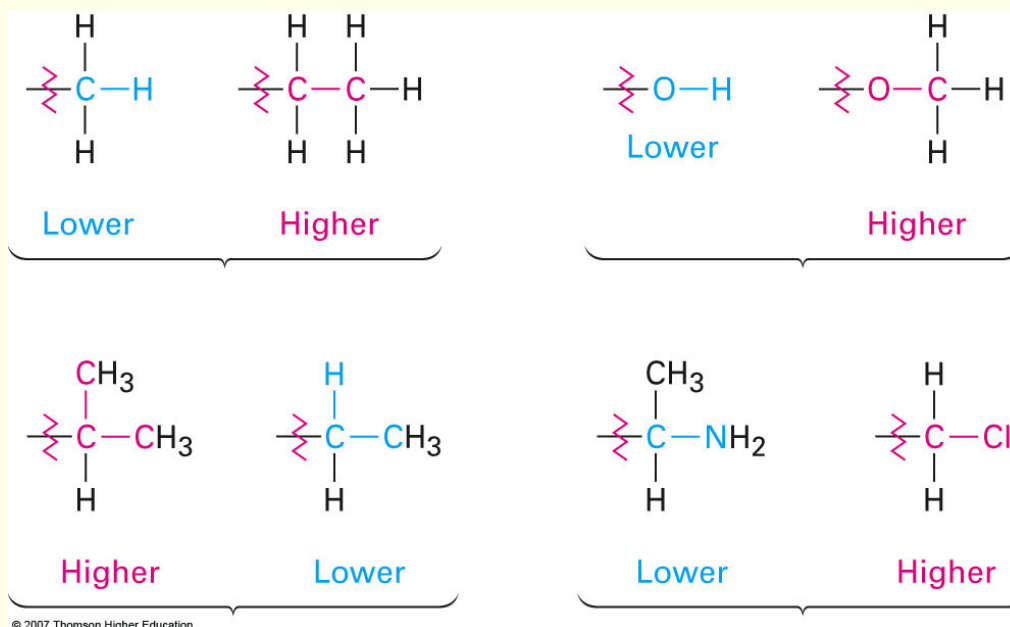
(b) (*Z*)-2-Chloro-2-butene

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# Extended Comparison

## RULE 2

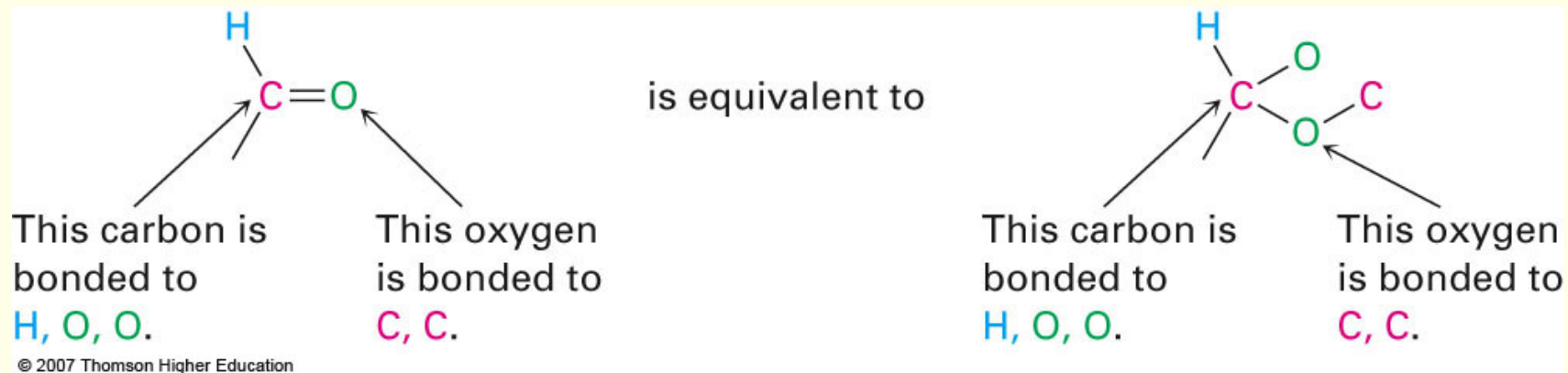
- If atomic numbers are the same, compare at next connection point at same distance
- Compare until something has higher atomic number
- Do not combine – always compare



# Dealing With Multiple Bonds:

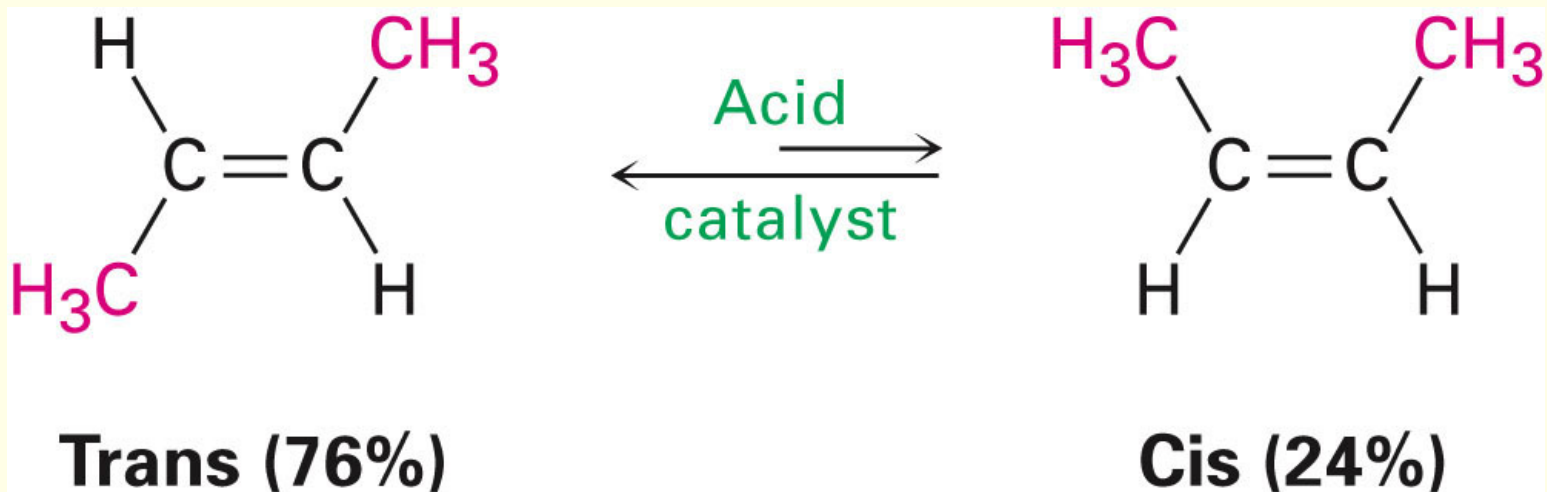
## RULE 3

- Substituent is drawn with connections shown and no double or triple bonds
- Added atoms are valued with 0 ligands themselves



## 6.6 Stability of Alkenes

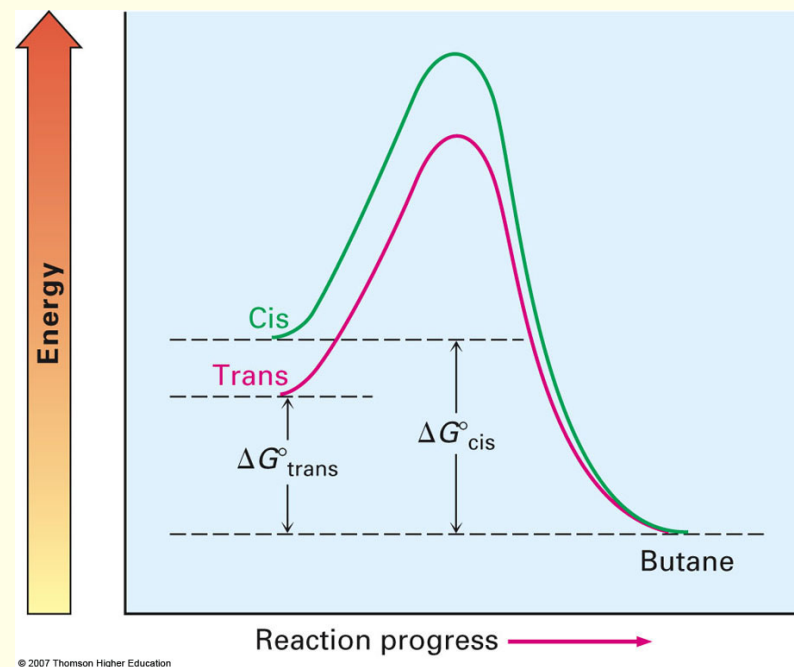
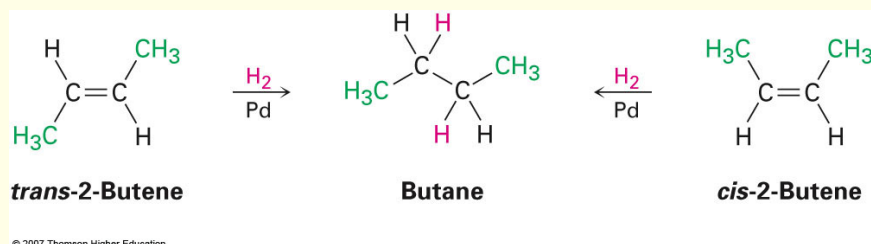
- Cis alkenes are less stable than trans alkenes
- Compare heat given off on hydrogenation:  $\Delta H^\circ$
- Less stable isomer is higher in energy
  - And gives off more heat
  - tetrasubstituted > trisubstituted > disubstituted > monosubstituted
  - *hyperconjugation* stabilizes



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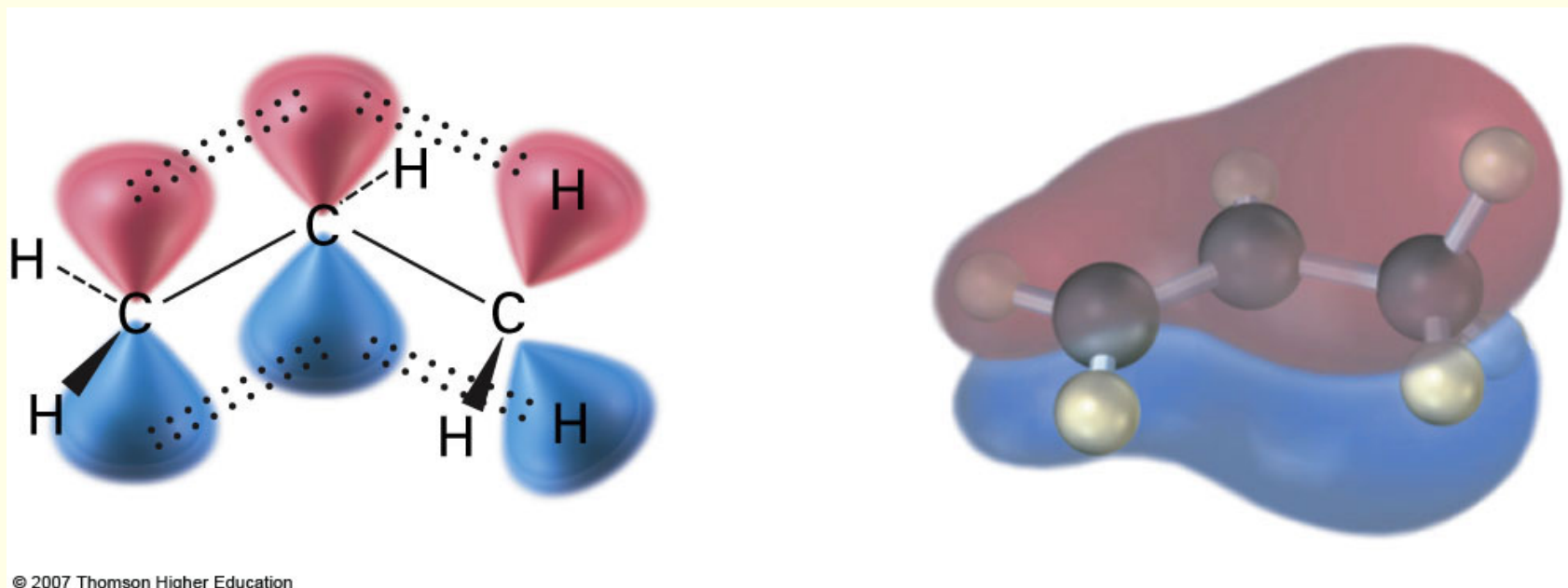
# Comparing Stabilities of Alkenes

- Evaluate heat given off when C=C is converted to C-C
- More stable alkene gives off less heat
  - trans-Butene generates 5 kJ less heat than cis-butene



# Hyperconjugation

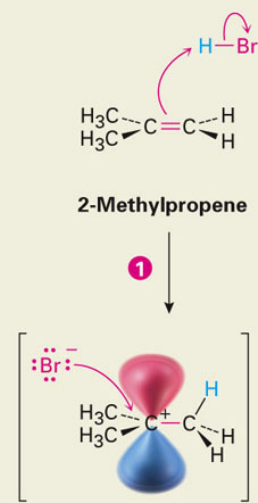
- Electrons in neighboring filled  $\sigma$  orbital stabilize vacant antibonding  $\pi$  orbital – net positive interaction
- Alkyl groups are better than H



# 6.7 Electrophilic Addition of Alkenes

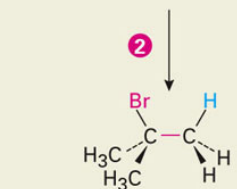
- General reaction mechanism:  
**electrophilic addition**
- Attack of electrophile (such as HBr) on  $\pi$  bond of alkene
- Produces carbocation and bromide ion
- **Carbocation** is an electrophile, reacting with nucleophilic bromide ion

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.



Carbocation intermediate

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

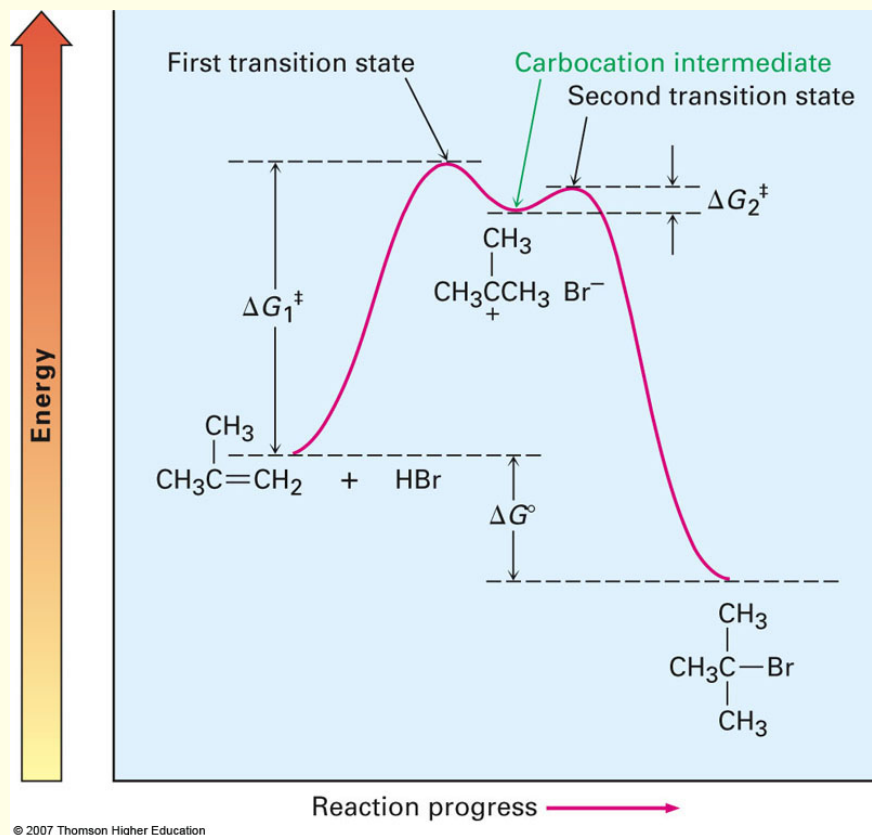


2-Bromo-2-methylpropane



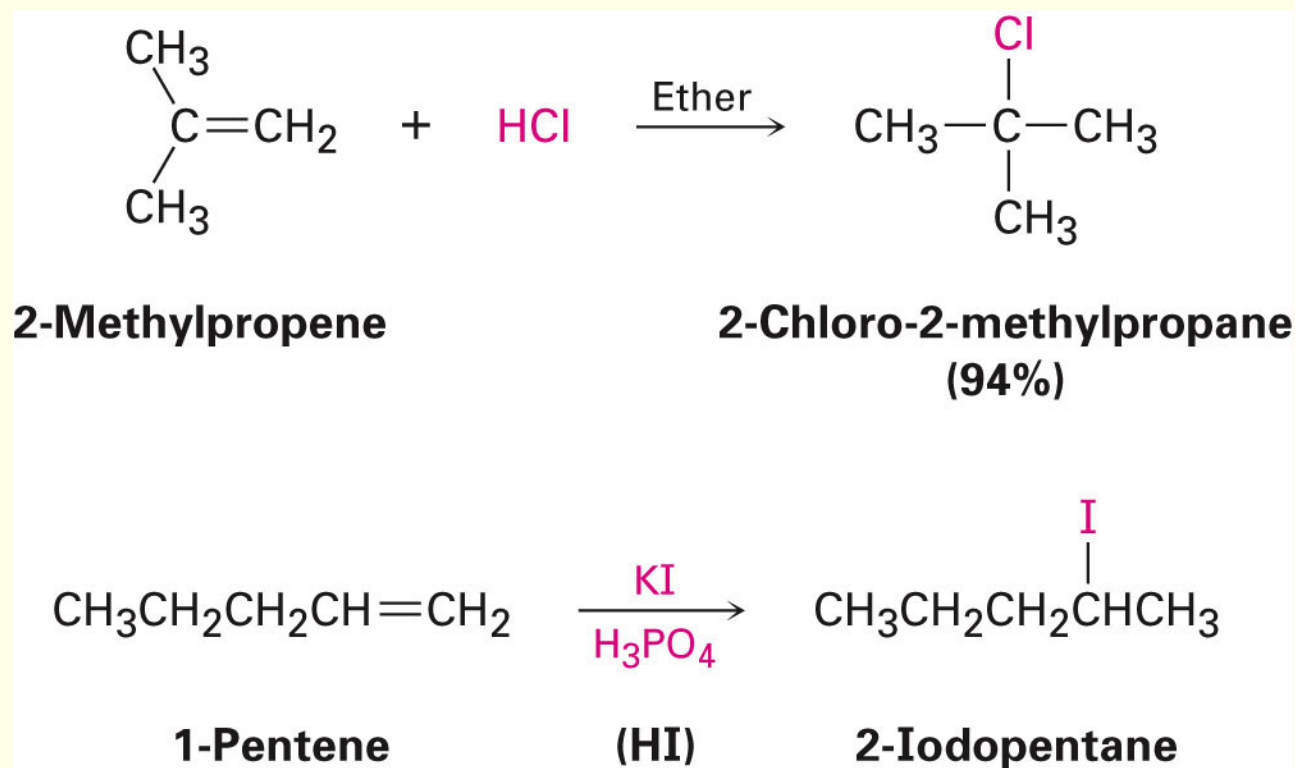
# Electrophilic Addition Energy Path

- Two step process
- First transition state is high energy point



# Electrophilic Addition for preparations

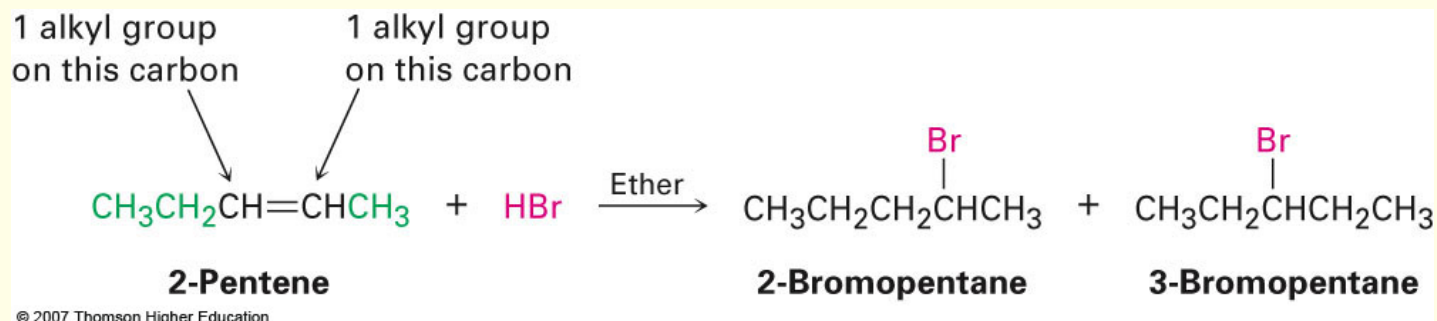
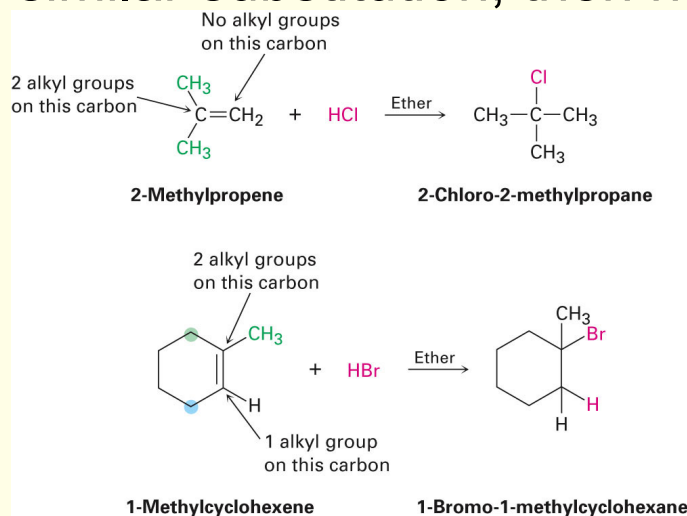
- The reaction is successful with HCl and with HI as well as HBr
- HI is generated from KI and phosphoric acid





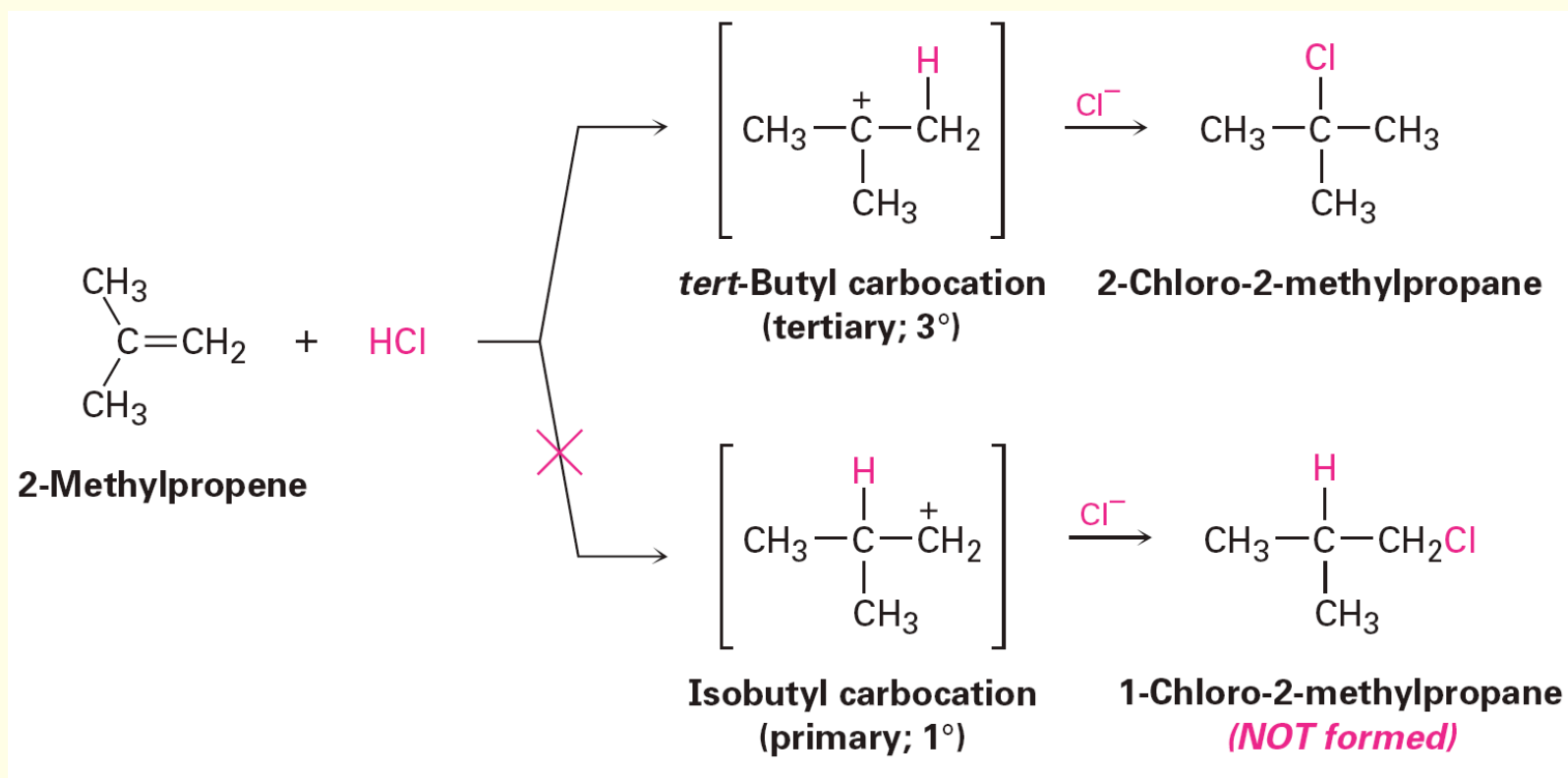
# Example of Markovnikov's Rule

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



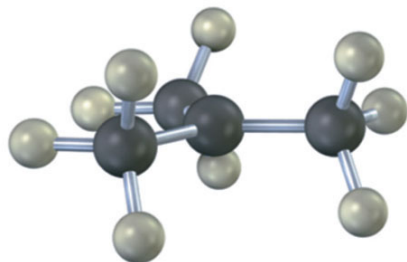
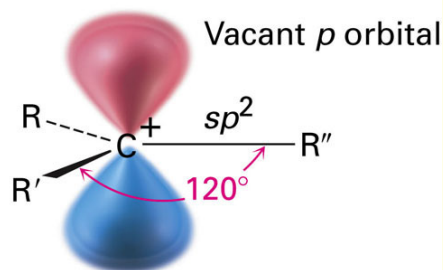
# Markovnikov's Rule (restated)

- 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

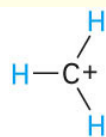


# 6.9 Carbocation Structure and Stability

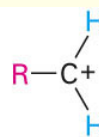
- Carbocations are planar and the tricoordinate carbon is surrounded by only 6 electrons in  $sp^2$  orbitals
- The fourth orbital on carbon is a vacant  $p$ -orbital
- The stability of the carbocation (measured by energy needed to form it from R-X) is increased by the presence of alkyl substituents



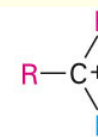
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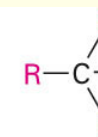
Methyl



Primary ( $1^\circ$ )



Secondary ( $2^\circ$ )



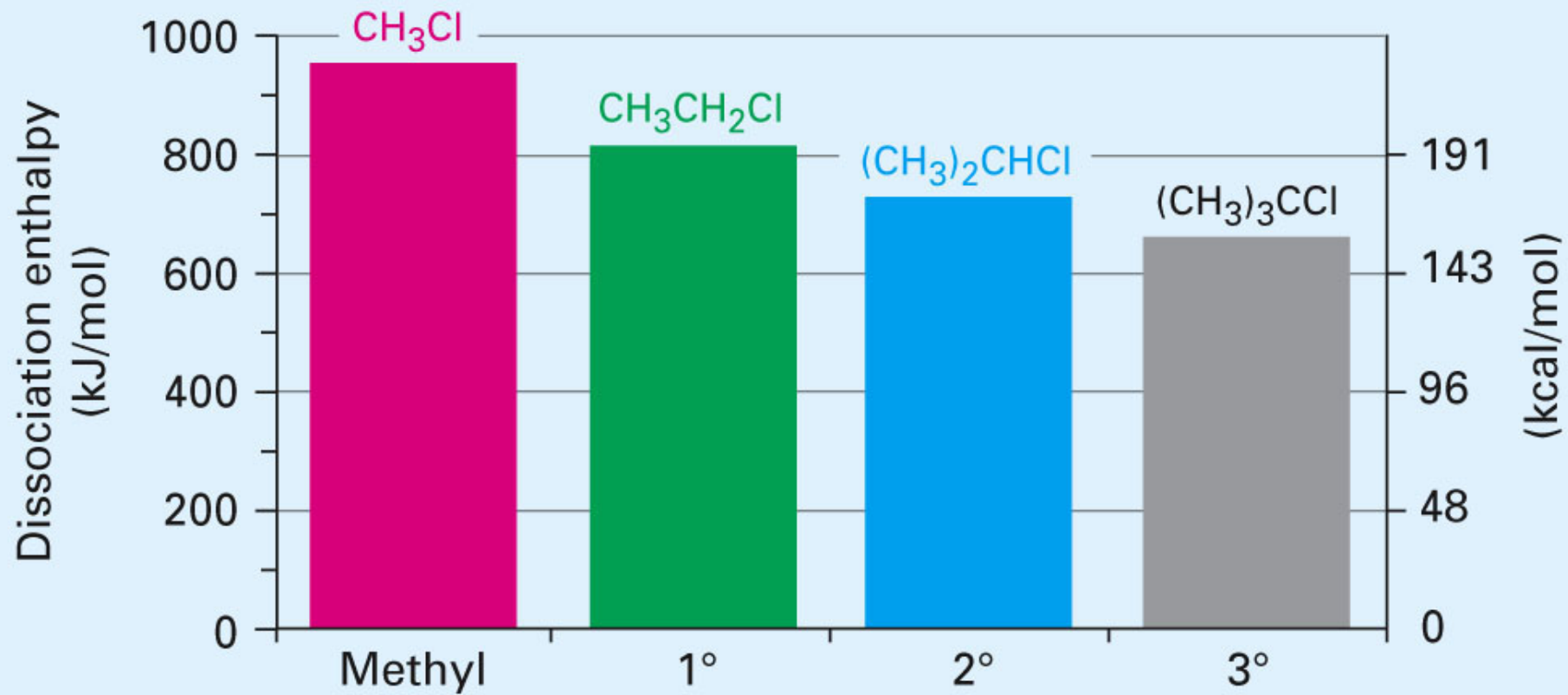
Tertiary ( $3^\circ$ )

Less stable

Stability

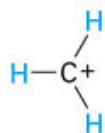
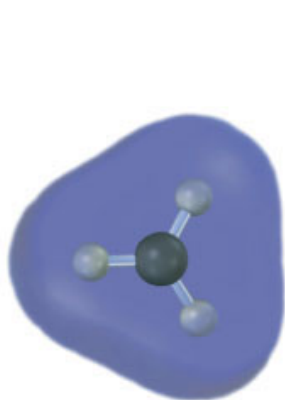
More stable

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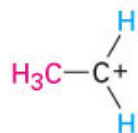
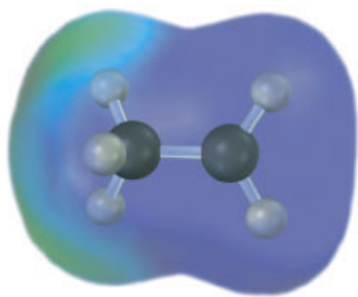
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# Inductive stabilization of cation species

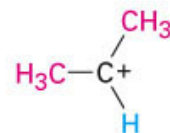
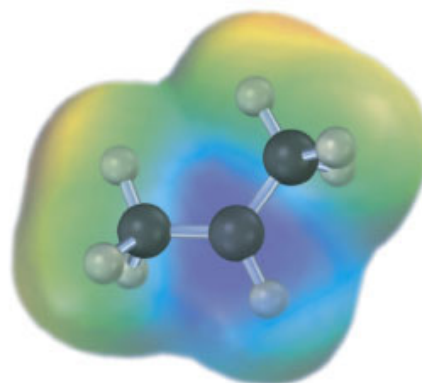


**Methyl:**  
No alkyl groups  
donating electrons

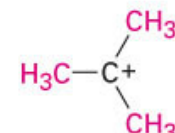
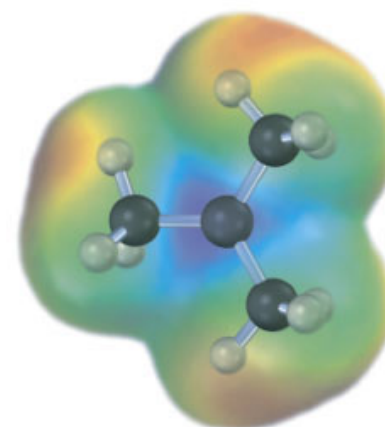
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**Primary:**  
One alkyl group  
donating electrons



**Secondary:**  
Two alkyl groups  
donating electrons



**Tertiary:**  
Three alkyl groups  
donating electrons



# 6.10 The Hammond Postulate

---

- If 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

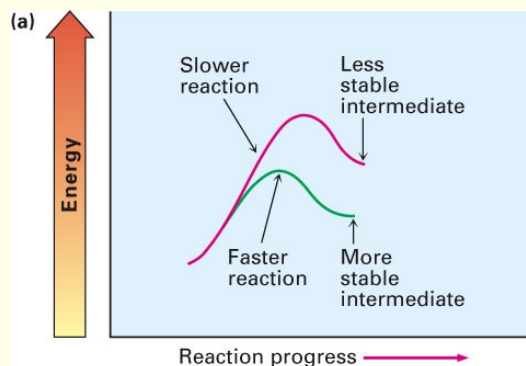
# Transition State Structures

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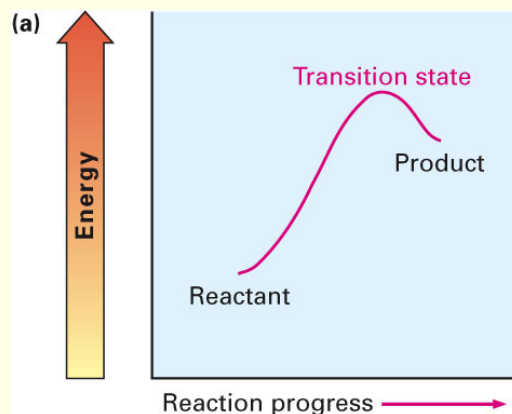
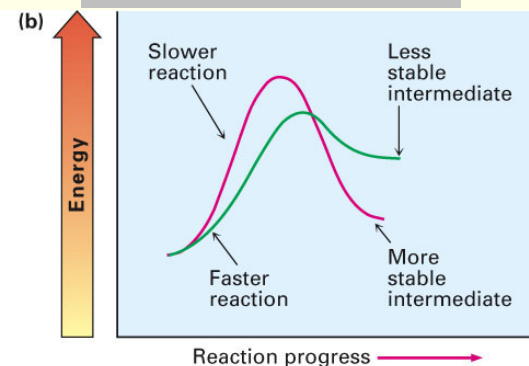
- A **transition state** is the highest energy species in a reaction step
- By definition, its structure is not stable enough to exist for one vibration
- But the structure controls the rate of reaction
- So we need to be able to guess about its properties in an informed way
- We classify them in general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

# Examination of the Hammond Postulate

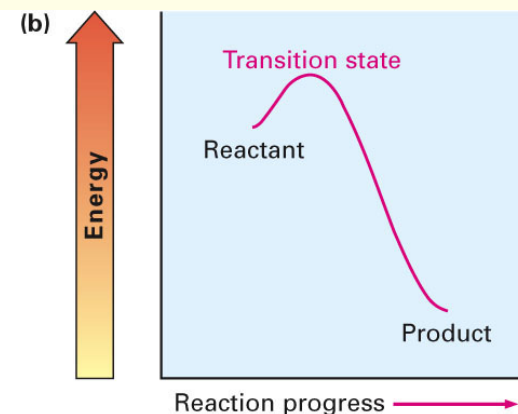
- A transition state should be similar to an intermediate that is close in energy
- Sequential states on a reaction path that are close in energy are likely to be close in structure - G. S. Hammond



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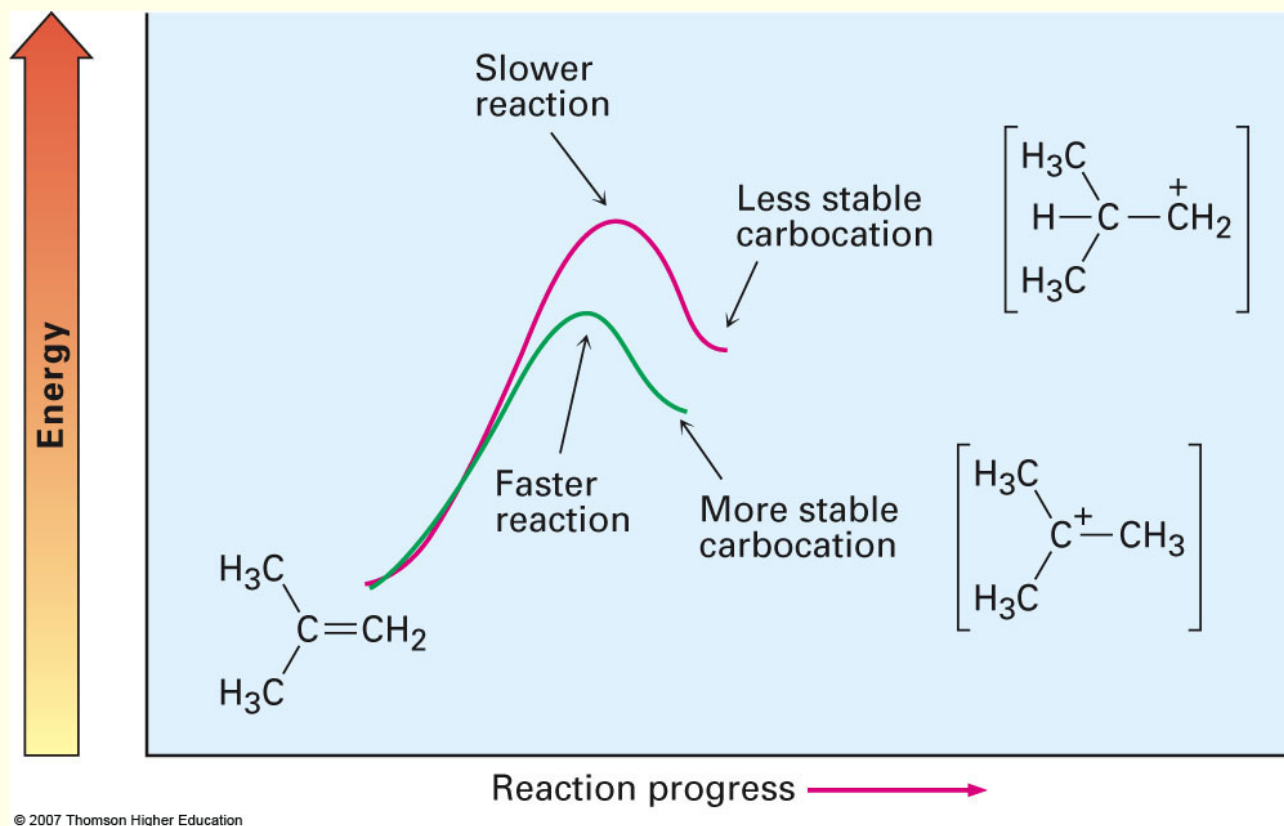


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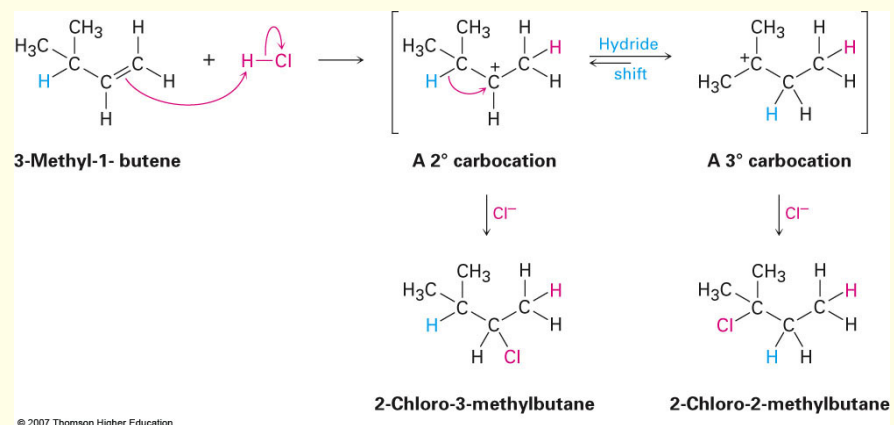
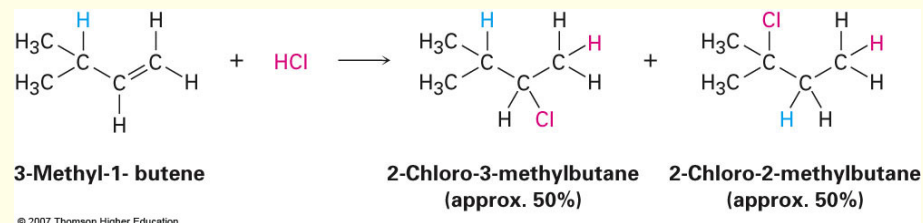
# Competing Reactions and the Hammond Postulate

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



# 6.11 Mechanism of Electrophilic Addition: Rearrangements of Carbocations

- Carbocations undergo structural rearrangements following set patterns
- 1,2-H and 1,2-alkyl shifts occur
- Goes to give more stable carbocation
- Can go through less stable ions as intermediates



# Hydride shifts in biological molecules

