

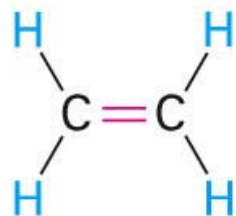
# Alkenes - Structure, Stability, Nomenclature

Also called an olefin but *alkene* is better

General formula  $C_nH_{2n}$  (if one alkene present)

unsaturated - contain fewer than maximum H's possible per C

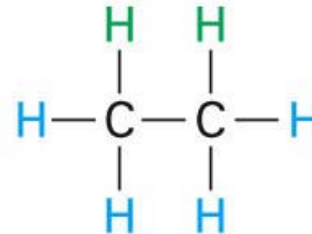
Can act as weak nucleophiles



**Ethylene:  $C_2H_4$**

**(fewer hydrogens—*unsaturated*)**

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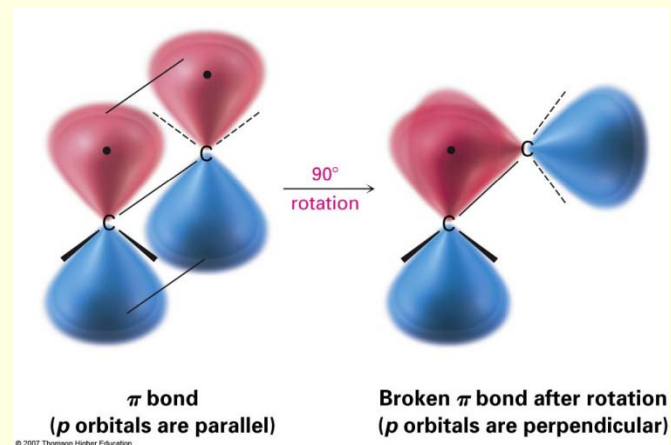
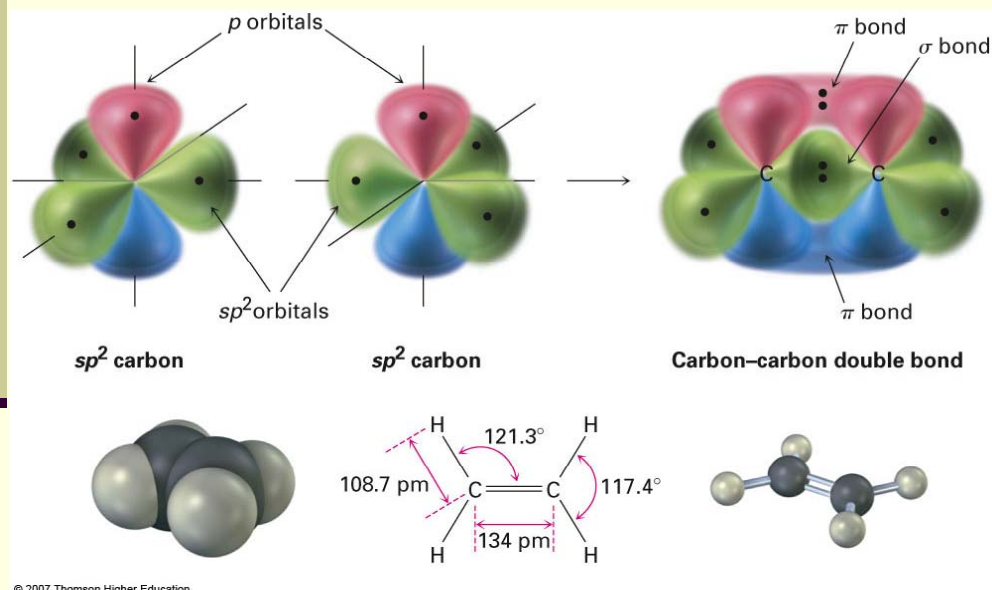
**Ethane:  $C_2H_6$**

**(more hydrogens—*saturated*)**

# Structure of Alkenes

One C-C sigma bond and one C-C pi bond

Presence of C-C pi bond prevents bond rotation!



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# Degree of Unsaturation

Sum of all multiple bonds and/or rings in a molecule  
Compared to saturated alkane ( $C_nH_{2n+2}$ ) where each double bond  
and ring remove two hydrogens.

$$\text{DoU} = (H_{\text{sat}} - H_{\text{actual}})/2$$

where  $H_{\text{sat}}$  is number of hydrogens in saturated compound  
 $H_{\text{actual}}$  is number of hydrogens in compound molecular formula

and 
$$H_{\text{sat}} = 2n + 2 - \#X + \#N$$

X = halogens

N = nitrogens

(ignore other atoms)

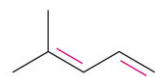
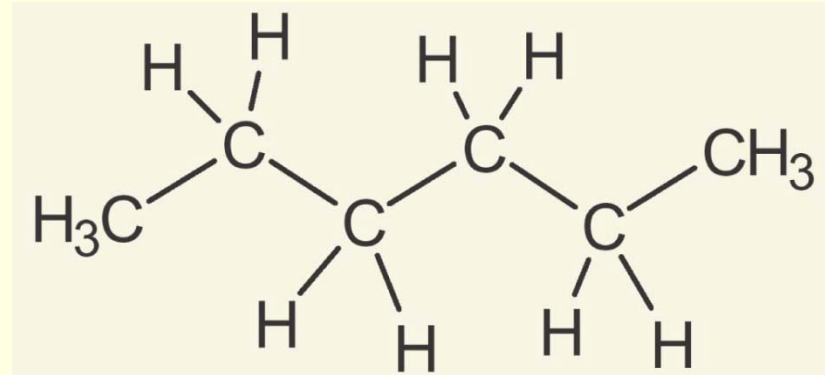
# Example: C<sub>6</sub>H<sub>10</sub>

$$H_{\text{Sat}} = 2(6) + 2 = 14 \text{ (C}_6\text{H}_{14}\text{)}$$

$$H_{\text{actual}} = 10$$

$$\text{DoU} = 2$$

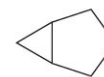
- Two double bonds?
- or triple bond?
- or two rings
- or ring and double bond



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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# Examples



$$\text{H}_{\text{sat}} = 2(7) + 2 + 1 = 17$$

$$\text{H}_{\text{actual}} = 13$$

$$\text{DoU} = 2$$

- Two double bonds?
- or triple bond?
- or two rings
- or ring and double bond



$$\text{H}_{\text{sat}} = 2(8) + 2 + 1 - 3 = 16$$

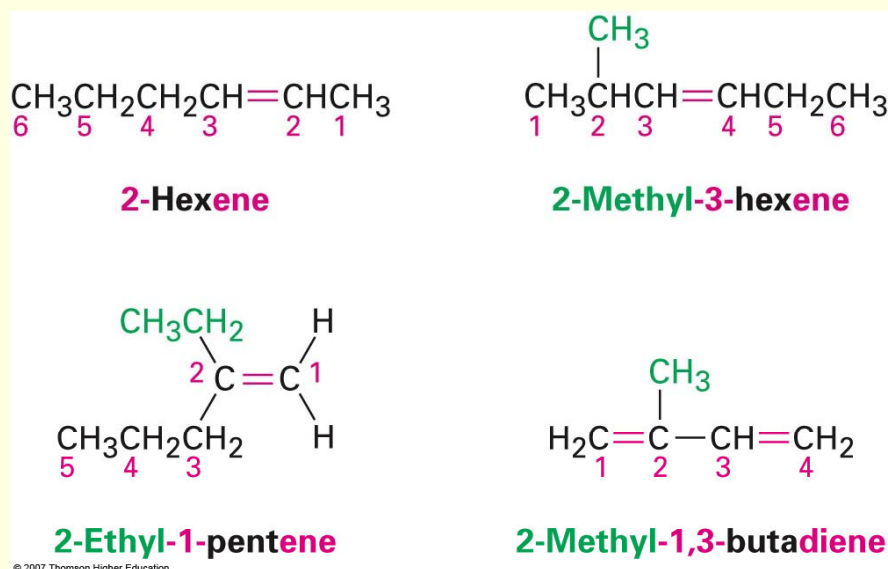
$$\text{H}_{\text{actual}} = 8$$

$$\text{DoU} = 4$$

- Four double bonds?
- two triple bonds?
- two rings/two double bonds?

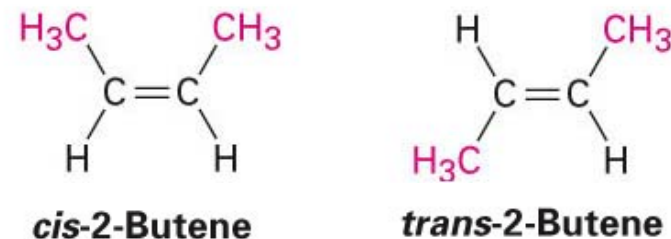
# Alkene Nomenclature

- Identify longest chain containing the alkene (both carbons)
- Number carbons in chain so that double bond carbons have lowest possible numbers (if choice, give sub lowest number)
- Name, number, and list substituents alphabetically as prefix like alkane nomenclature
- Indicate position of alkene with number-followed by name of longest chain with suffix -ane replaced with -ene



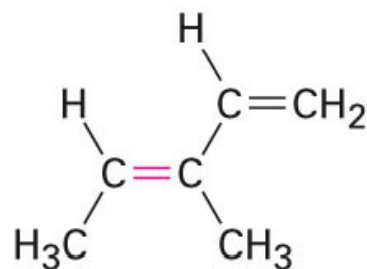
# Alkene Nomenclature: Isomer Prefix

- Disubstituted Alkenes: Cis and Trans

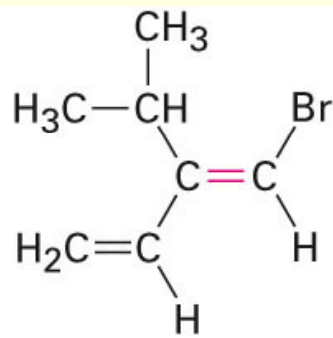


- E and Z System

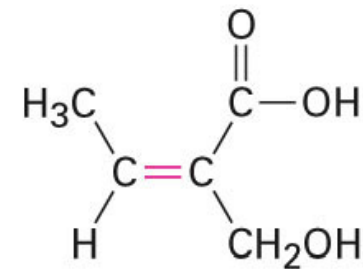
- rank two groups on each individual carbon by atomic number
- if same, find first point of difference
- count multiple bonds multiple times
- Highest Priority Groups same side = Z, opposite = E



**(E)-3-Methyl-1,3-pentadiene**



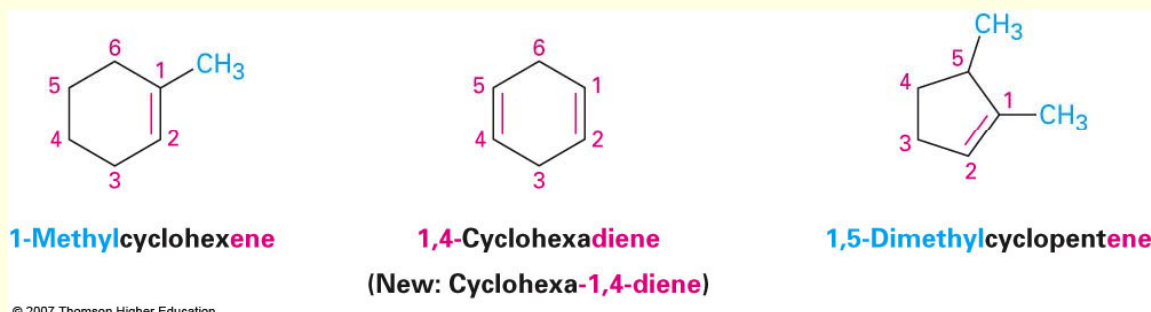
**(E)-1-Bromo-2-isopropyl-1,3-butadiene**



**(Z)-2-Hydroxymethyl-2-butenoic acid**

# Cycloalkene Nomenclature

- Alkene carbons by definition carbons 1 and 2. Give first substituent lowest possible number.
- Name, number, and list substituents alphabetically as prefix like alkane nomenclature
- You do not need to indicate position of alkene with number, simply name ring size with prefix cyclo and followed suffix -ene
- For rings smaller than cyclooctene you do not need to include alkene geometry (only cis is possible)

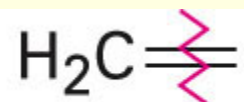




# Alkenes as Substituents

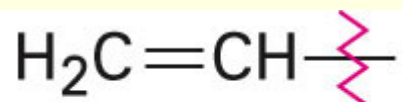
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- Methylene



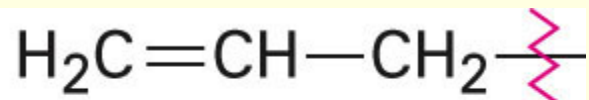
**A methylene group**

- Vinyl



**A vinyl group**

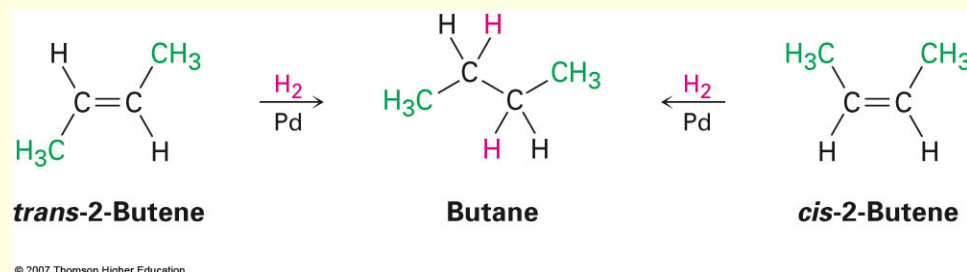
- Allyl



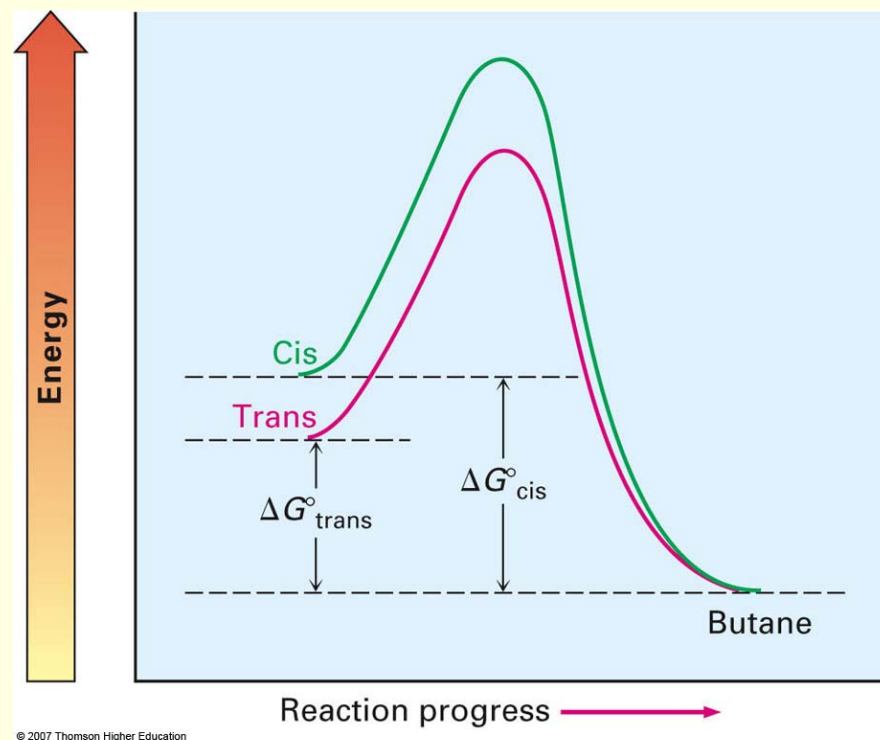
**An allyl group**

# Stability of Alkenes

- Evaluate heat given off when C=C is converted to C-C
- More stable alkene gives off less heat
  - *trans*-Butene generates 4 kJ less heat than *cis*-butene



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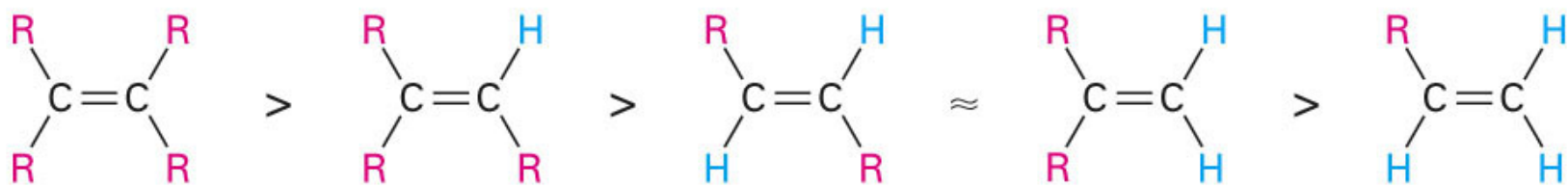


# Stability of Alkenes

**Table 6.2** Heats of Hydrogenation of Some Alkenes

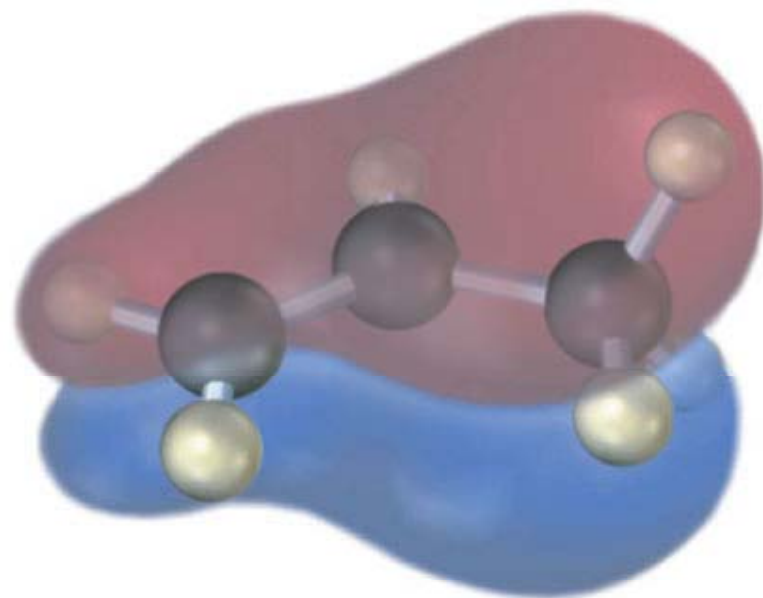
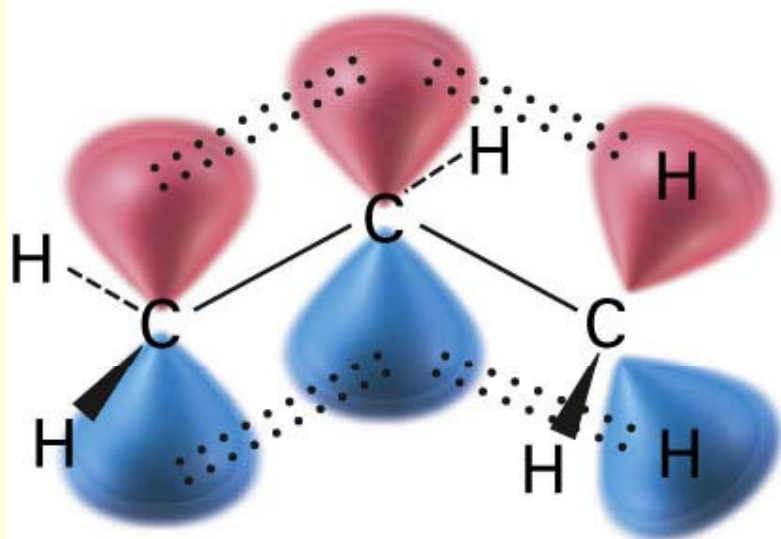
Substitution	Alkene	$\Delta H^\circ_{\text{hydrog}}$	
		(kJ/mol)	(kcal/mol)
Ethylene	$\text{H}_2\text{C}=\text{CH}_2$	-137	-32.8
Monosubstituted	$\text{CH}_3\text{CH}=\text{CH}_2$	-126	-30.1
Disubstituted	$\text{CH}_3\text{CH}=\text{CHCH}_3$ (cis)	-120	-28.6
	$\text{CH}_3\text{CH}=\text{CHCH}_3$ (trans)	-116	-27.6
	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	-119	-28.4
Trisubstituted	$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	-113	-26.9
Tetrasubstituted	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	-111	-26.6

Tetrasubstituted > Trisubstituted > Disubstituted > Monosubstituted



# Stability of Alkenes

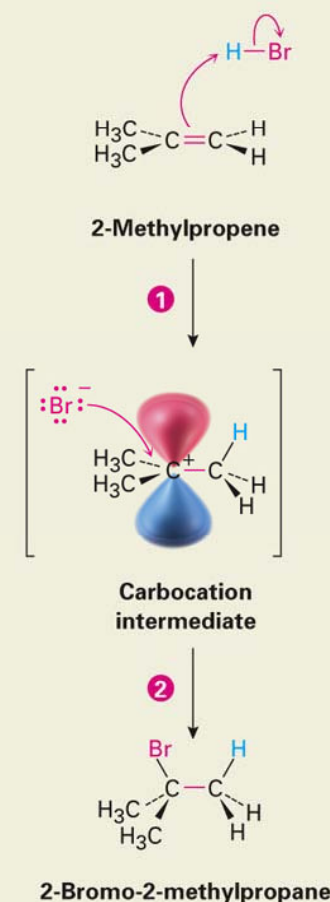
Hyperconjugation - Electrons in neighboring filled  $\sigma$  bond orbital stabilize vacant antibonding  $\pi$  orbital – net positive interaction from delocalization of electrons  
(not possible when only H present)



# Recall: Electrophilic Addition of Alkenes

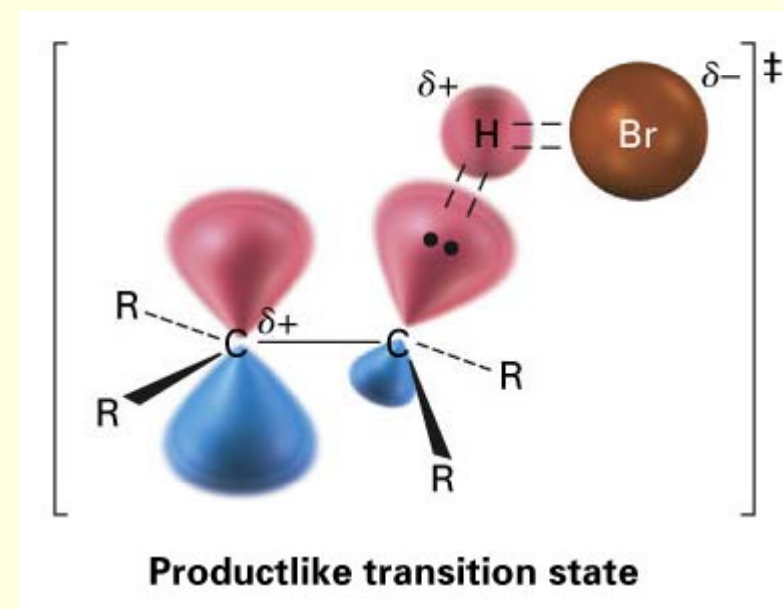
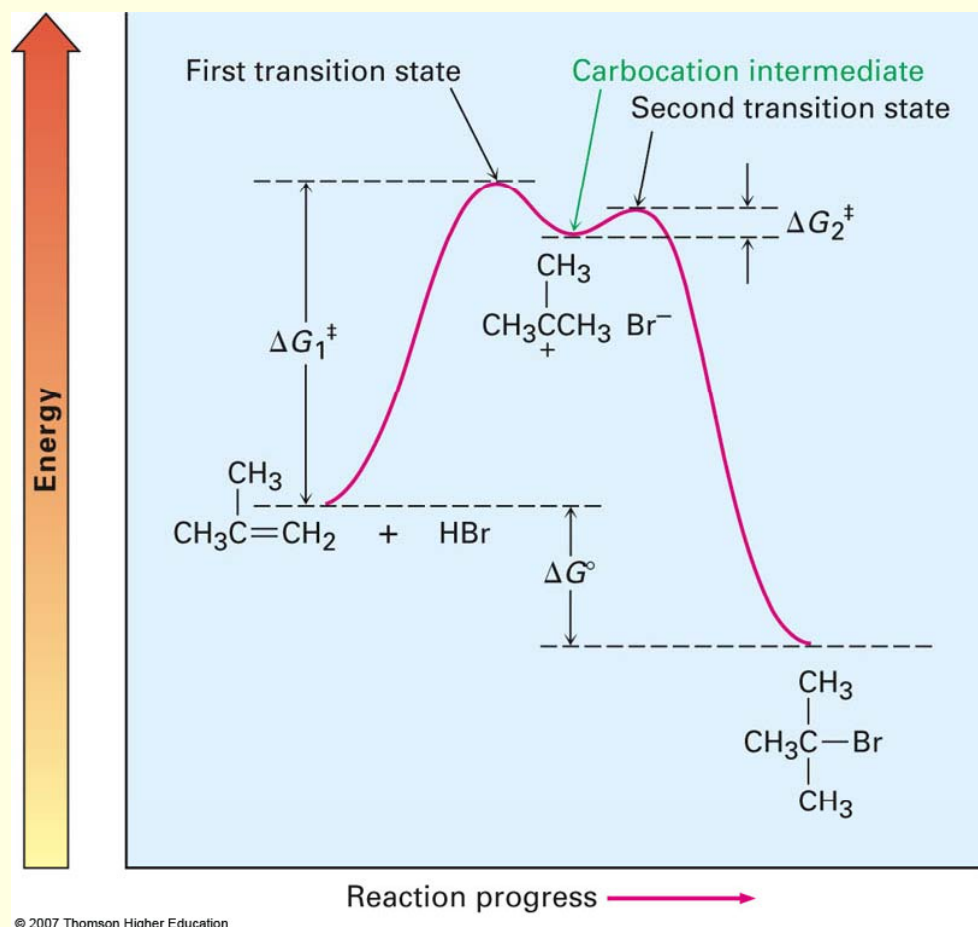
- General reaction mechanism: **electrophilic addition**
- Attack of electrophile (such as HBr) on  $\pi$  bond of alkene
- Produces carbocation and bromide ion
- **Carbocation** is an electrophile, reacting with nucleophilic bromide ion

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.



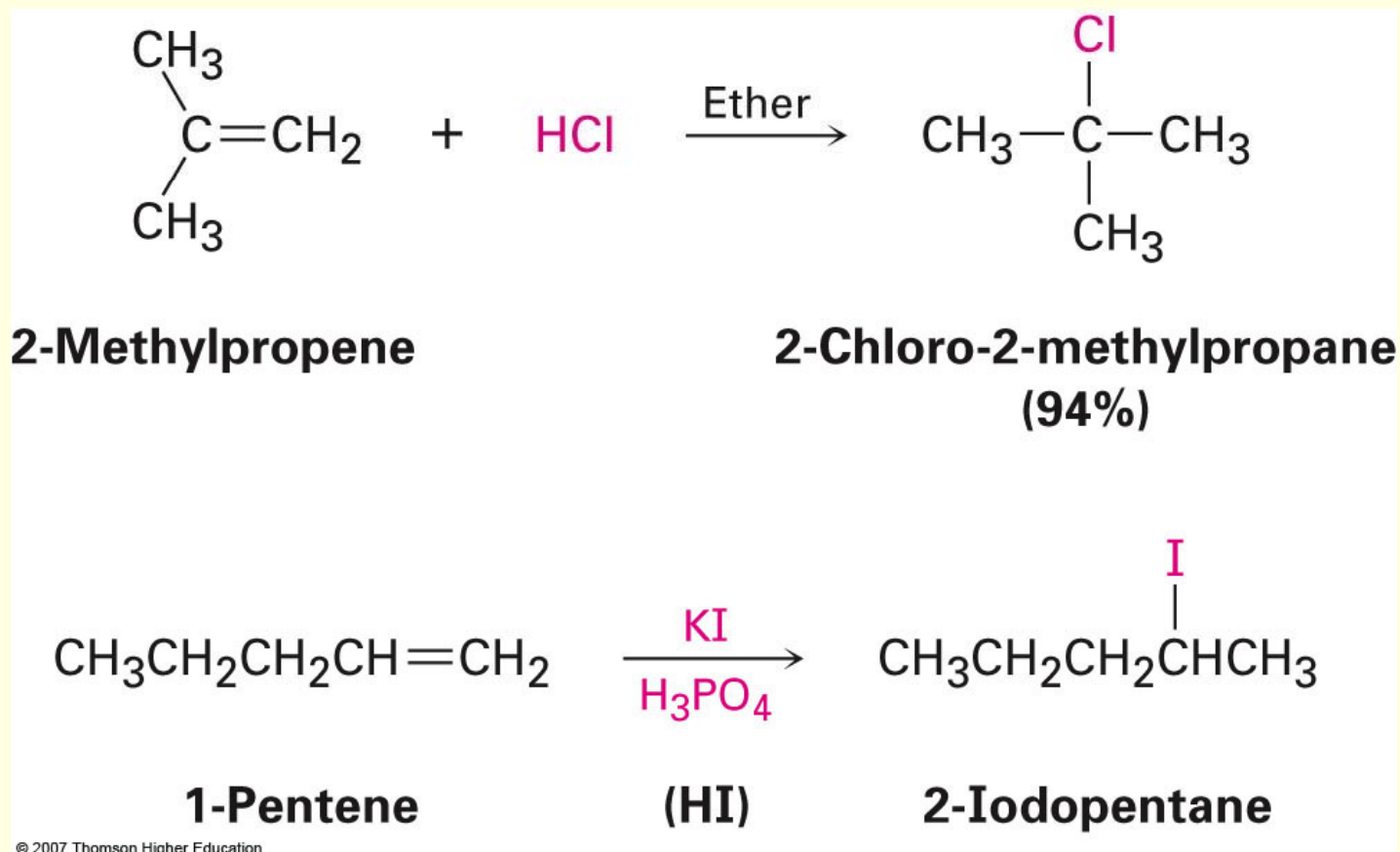
# Recall: Electrophilic Addition Energy Path

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



# Electrophilic Additions

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



# Remaining Notes

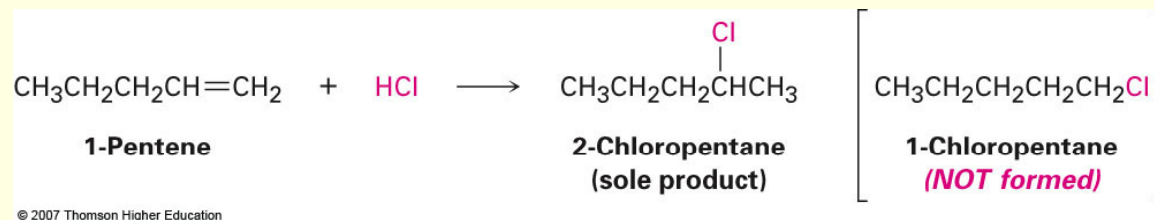
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Rest of the notes are for your benefit and to view pictures.  
Remaining topics will be discussed on the board.



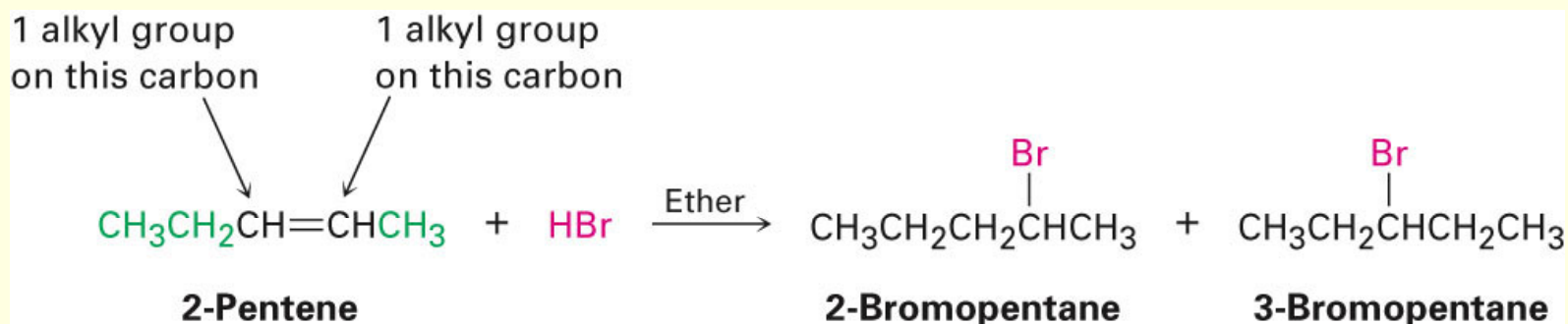
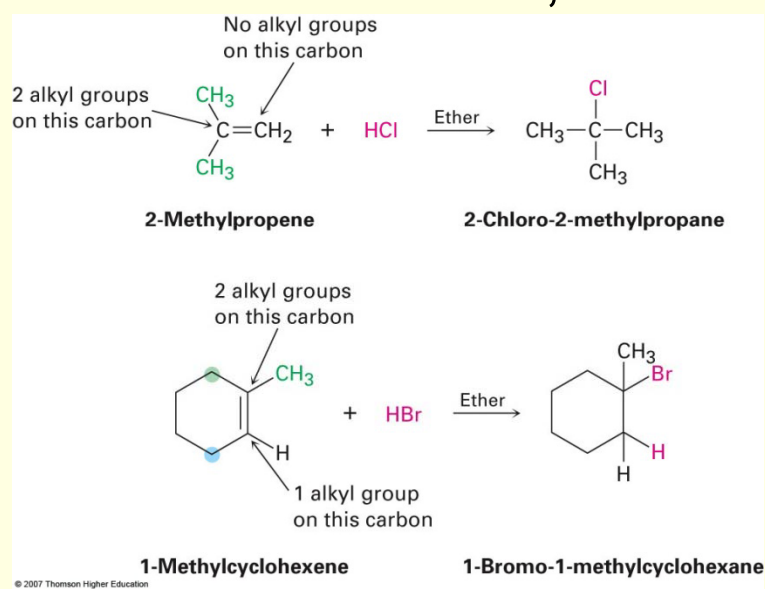
# Orientation of Electrophilic Addition: Markovnikov's Rule

- 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 **regiospecific**
- **Markovnikov** observed in the 19<sup>th</sup> century that in the addition of HX to alkene, the H attaches to the carbon with the most H's and X attaches to the other end (to the one with the most alkyl substituents)
  - This is **Markovnikov's rule**



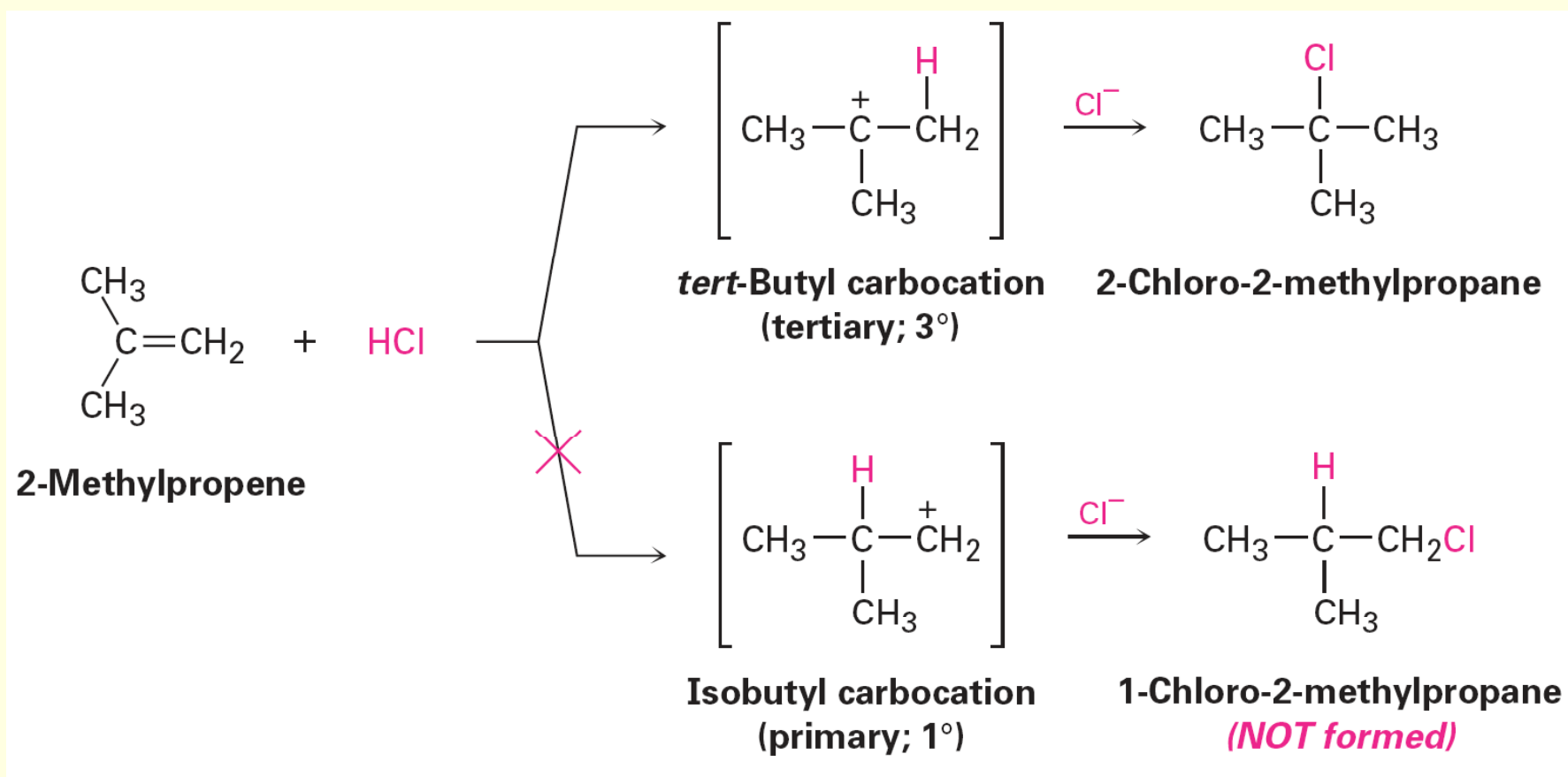
# Example of Markovnikov's Rule

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



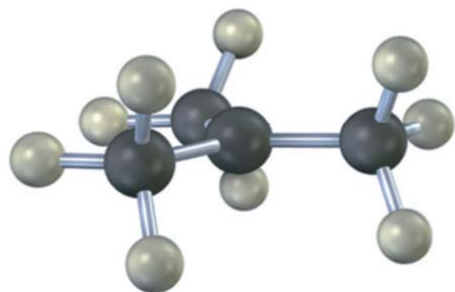
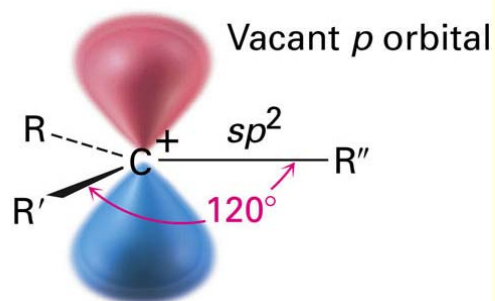
# Markovnikov's Rule (restated)

- 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

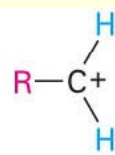


# Carbocation Structure and Stability

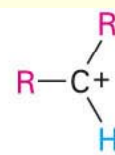
- Carbocations are planar and the tricoordinate carbon is surrounded by only 6 electrons in  $sp^2$  orbitals
- The fourth orbital on carbon is a vacant  $p$ -orbital
- The stability of the carbocation (measured by energy needed to form it from R-X) is increased by the presence of alkyl substituents



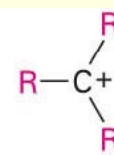
Methyl



Primary ( $1^\circ$ )



Secondary ( $2^\circ$ )



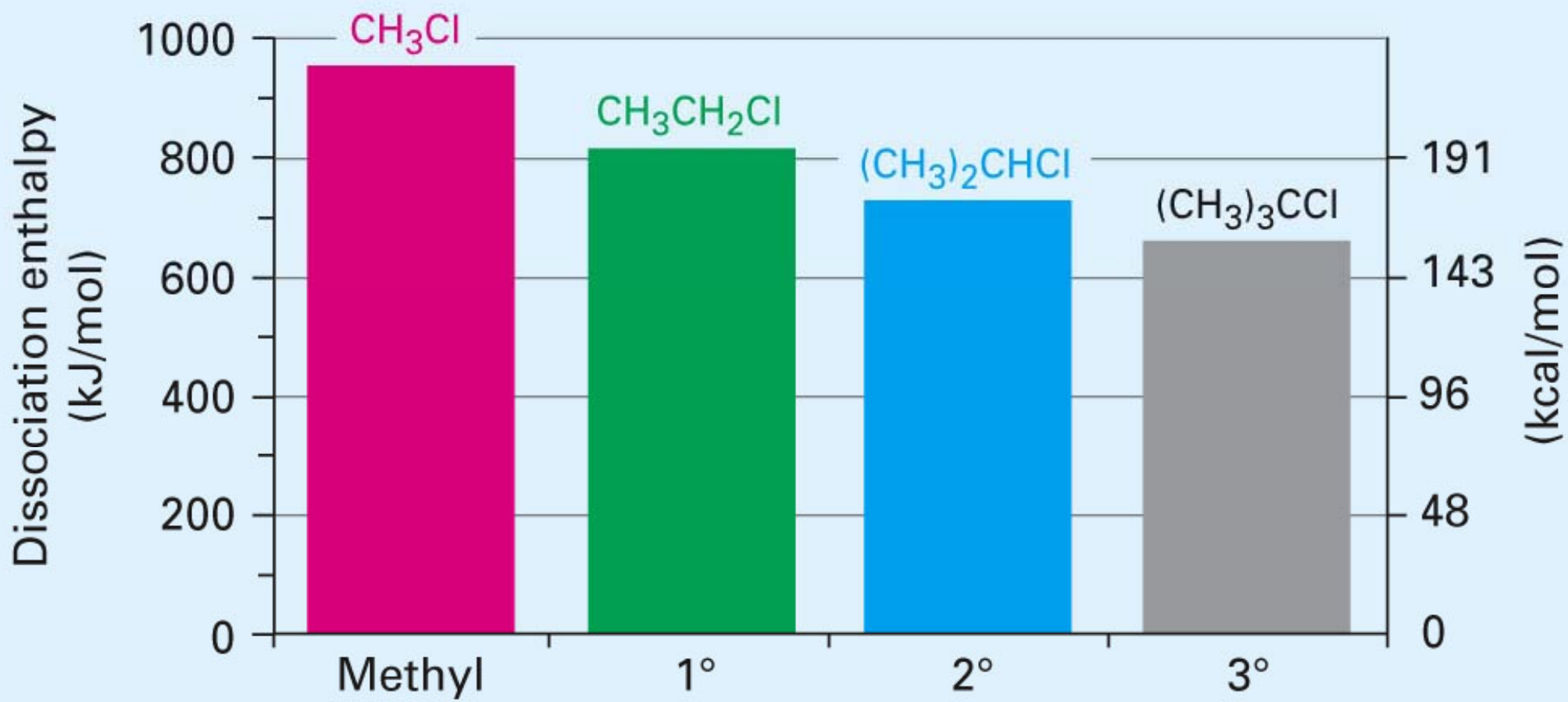
Tertiary ( $3^\circ$ )

Less stable

Stability

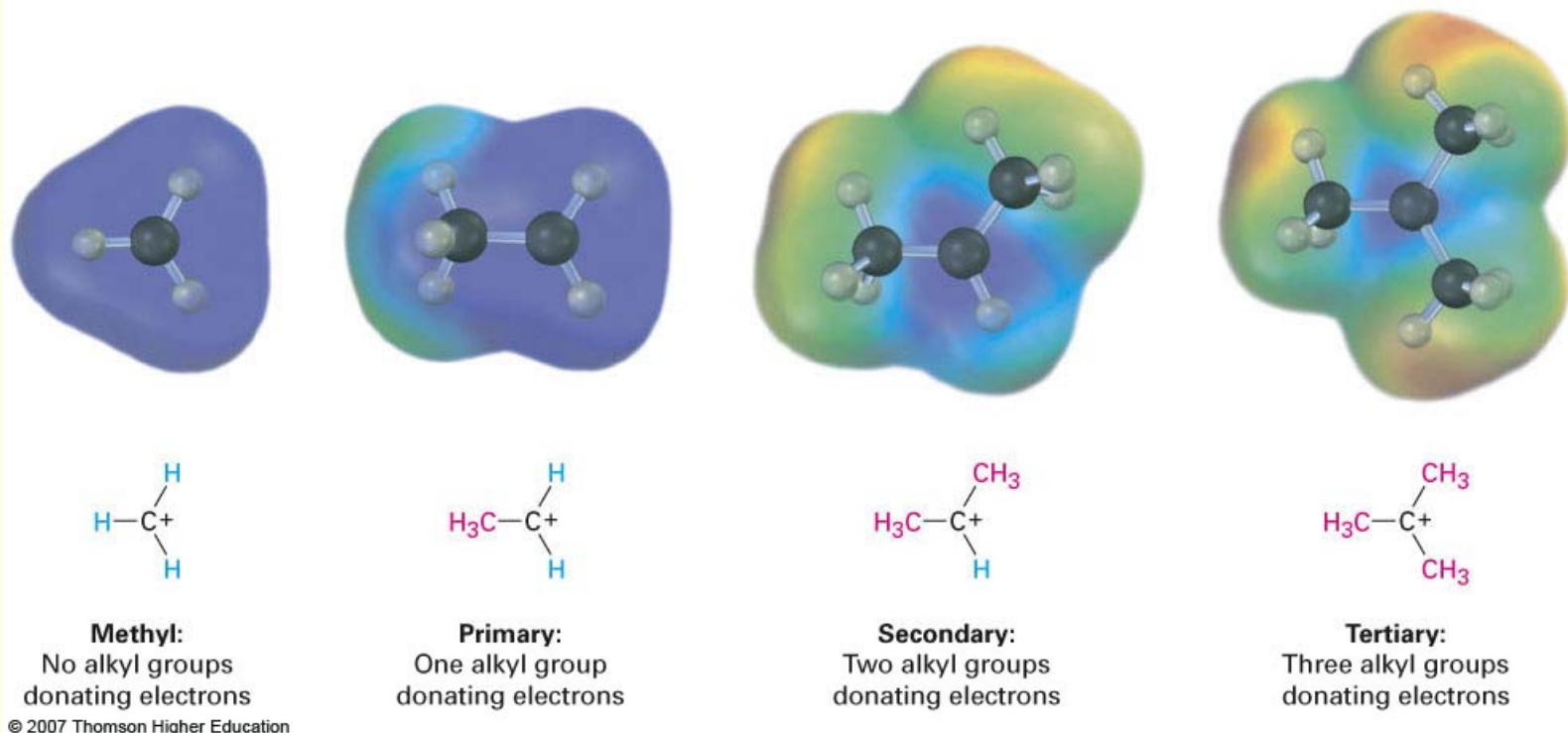
More stable

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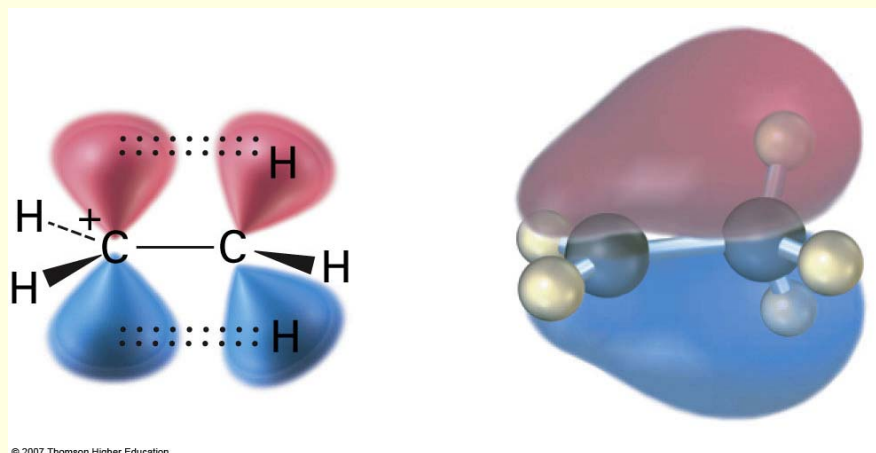


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# Inductive stabilization of cation species



via hyperconjugation!



# The Hammond Postulate

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- 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 ( $\Delta G^0$ )
  - 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

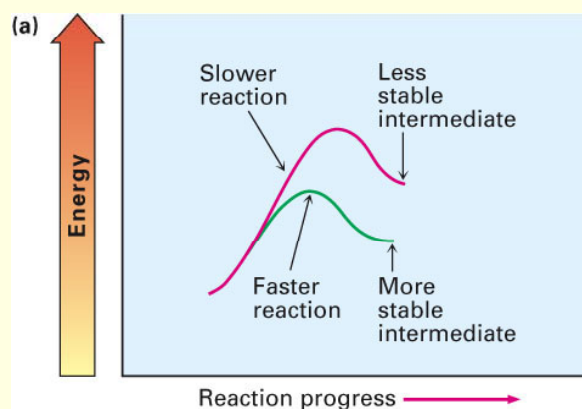
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- A **transition state** is the highest energy species in a reaction step
- By definition, its structure is not stable enough to exist for one vibration
- But the structure controls the rate of reaction
- So we need to be able to guess about its properties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

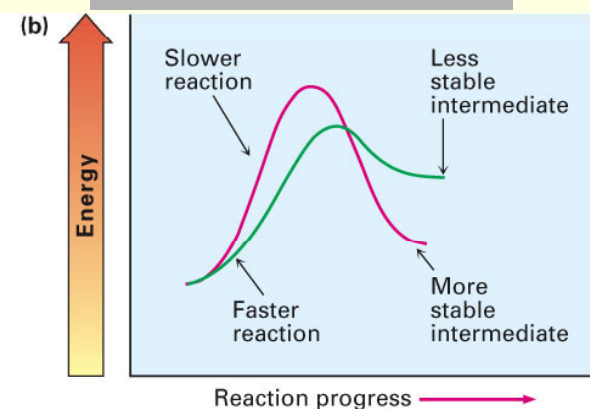


# Examination of the Hammond Postulate

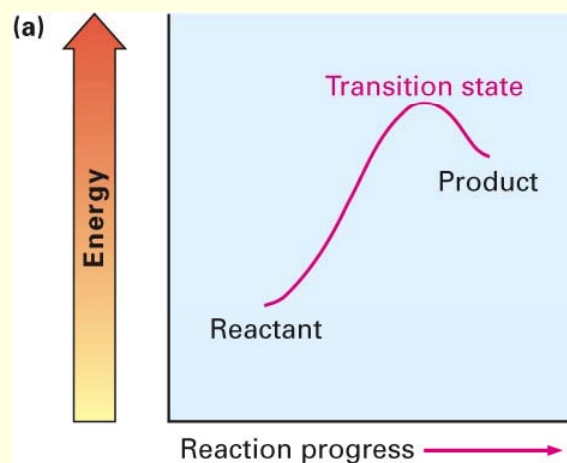
- A transition state should be similar to an intermediate that is close in energy



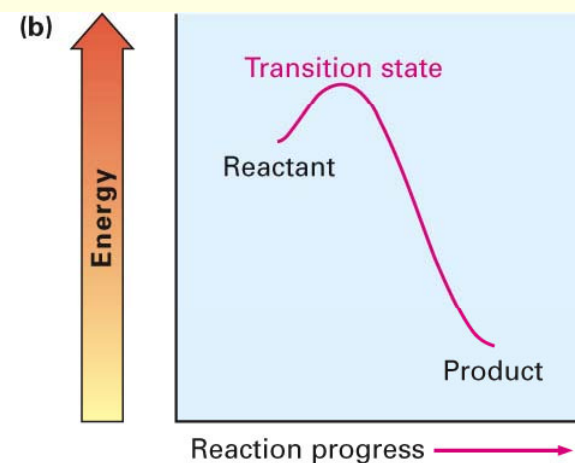
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- Sequential states on a reaction path that are close in energy are likely to be close in structure - G. S. Hammond

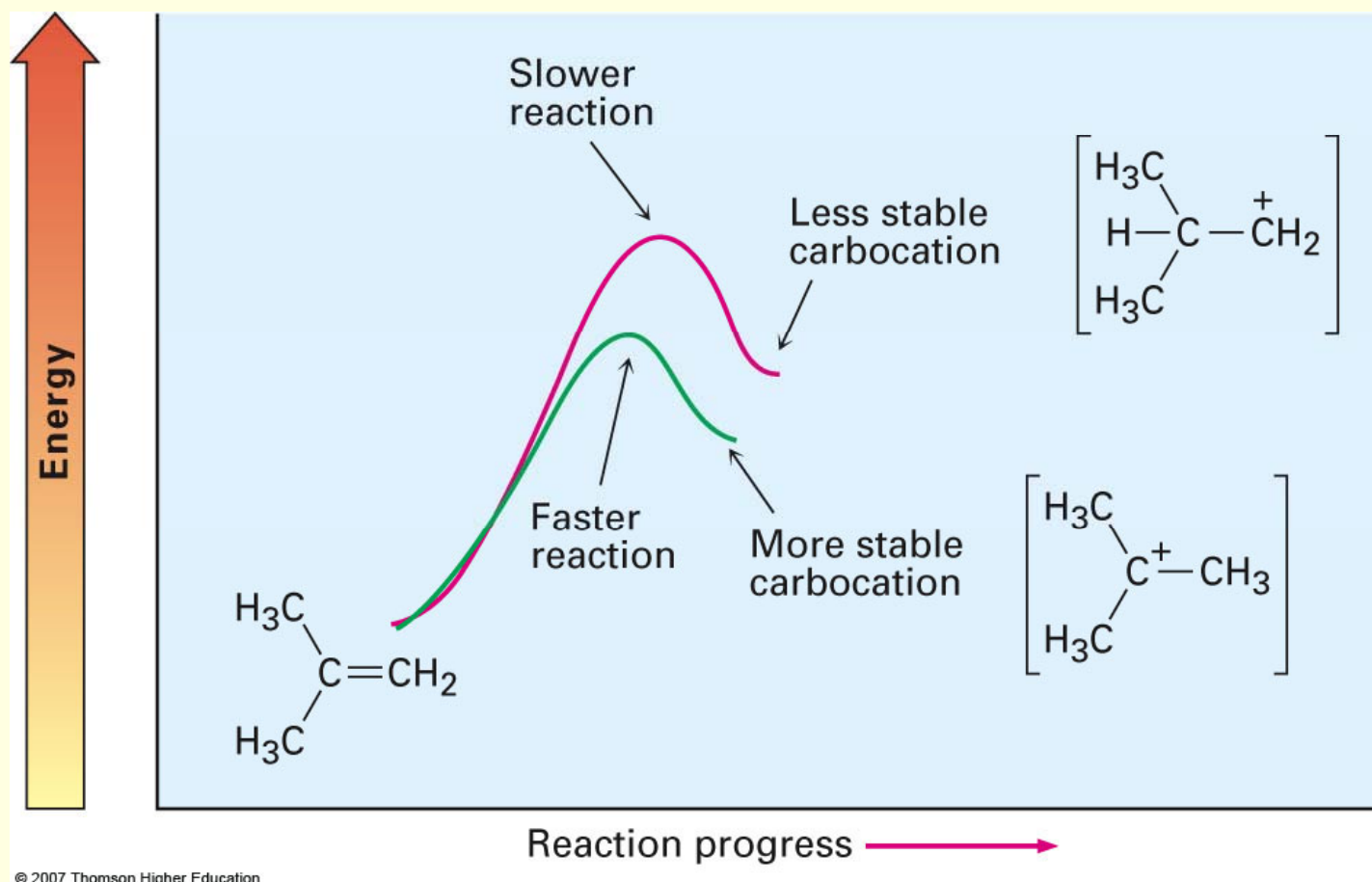


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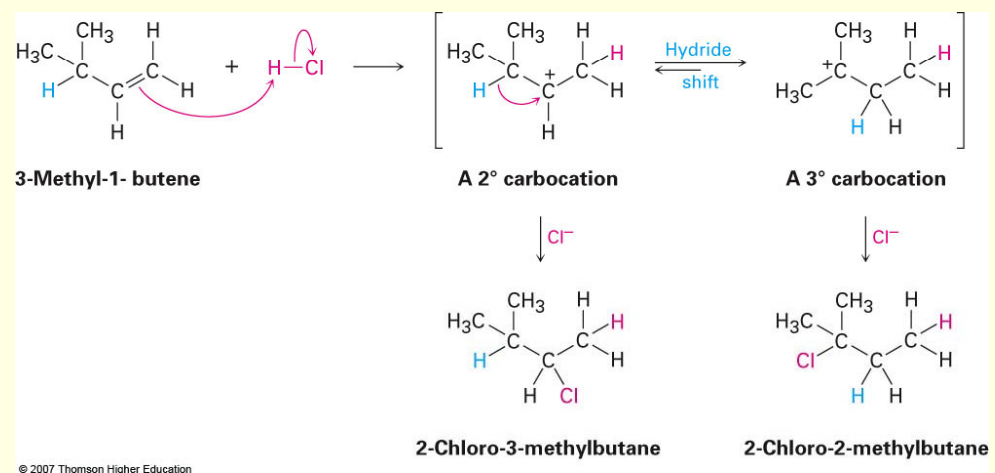
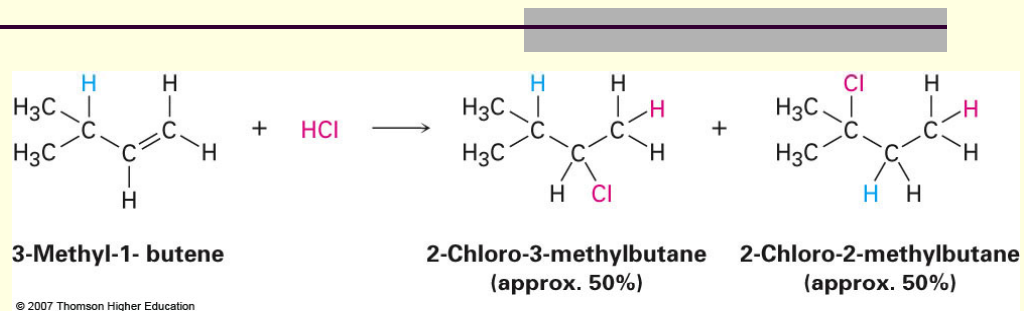
# Competing Reactions and the Hammond Postulate

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

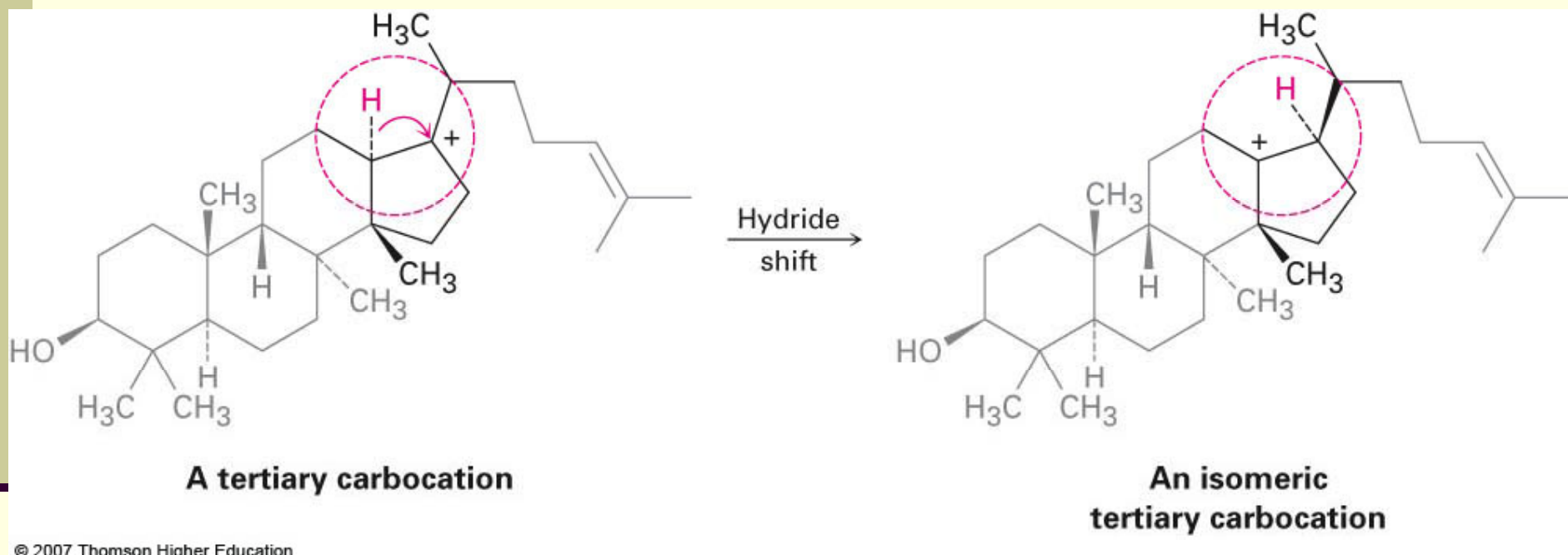


# Mechanism of Electrophilic Addition: Rearrangements of Carbocations

- 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



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