

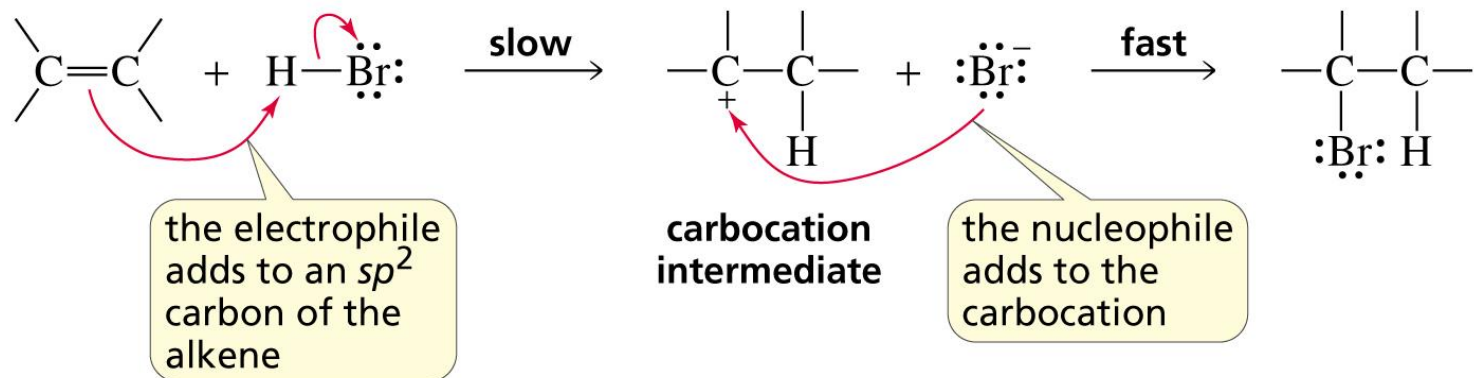
# Chapter 6



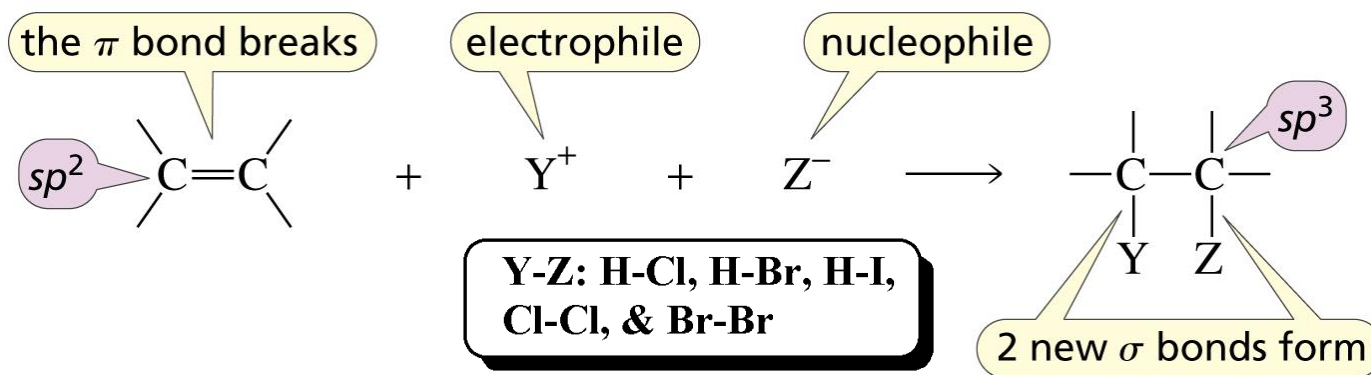
## The Reactions of Alkenes

### The Stereochemistry of Addition Reactions

# Electrophilic Addition of Alkenes

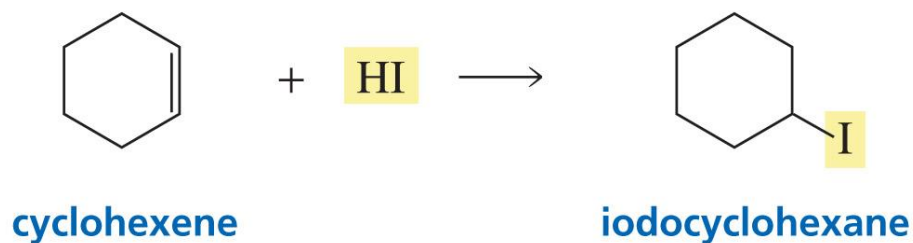
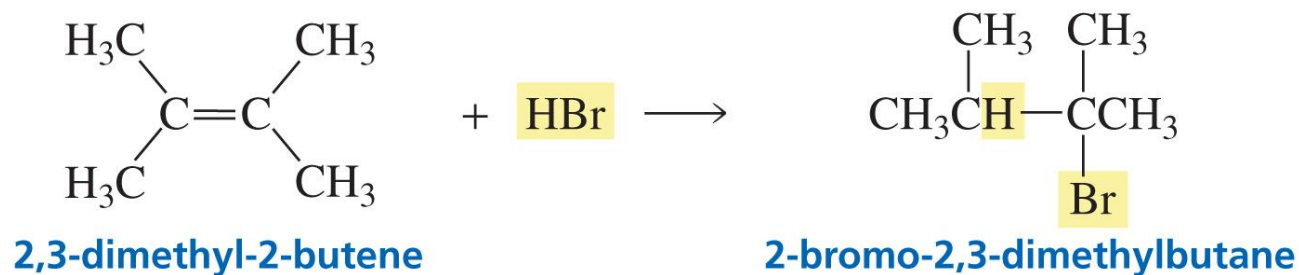


**Reaction of alkene:  
addition reaction.**

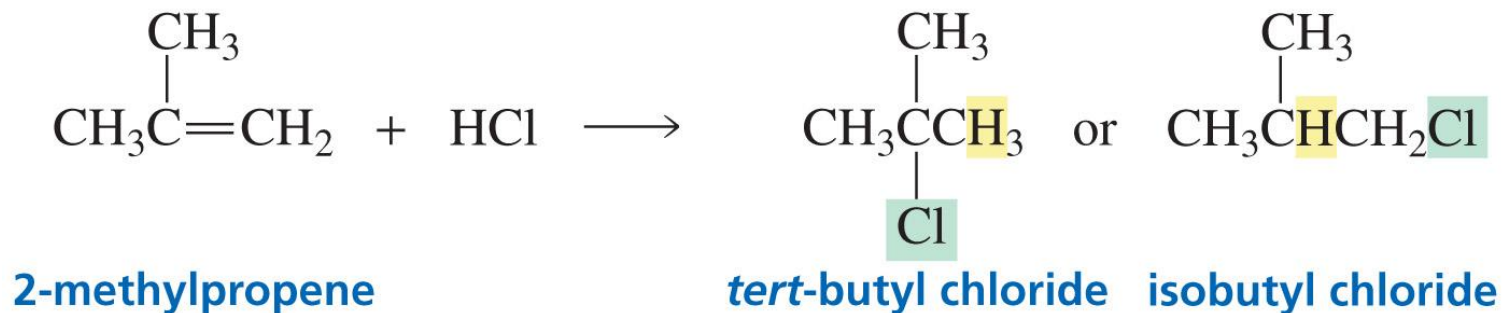


**Synthesis of alkene:  
elimination reaction**

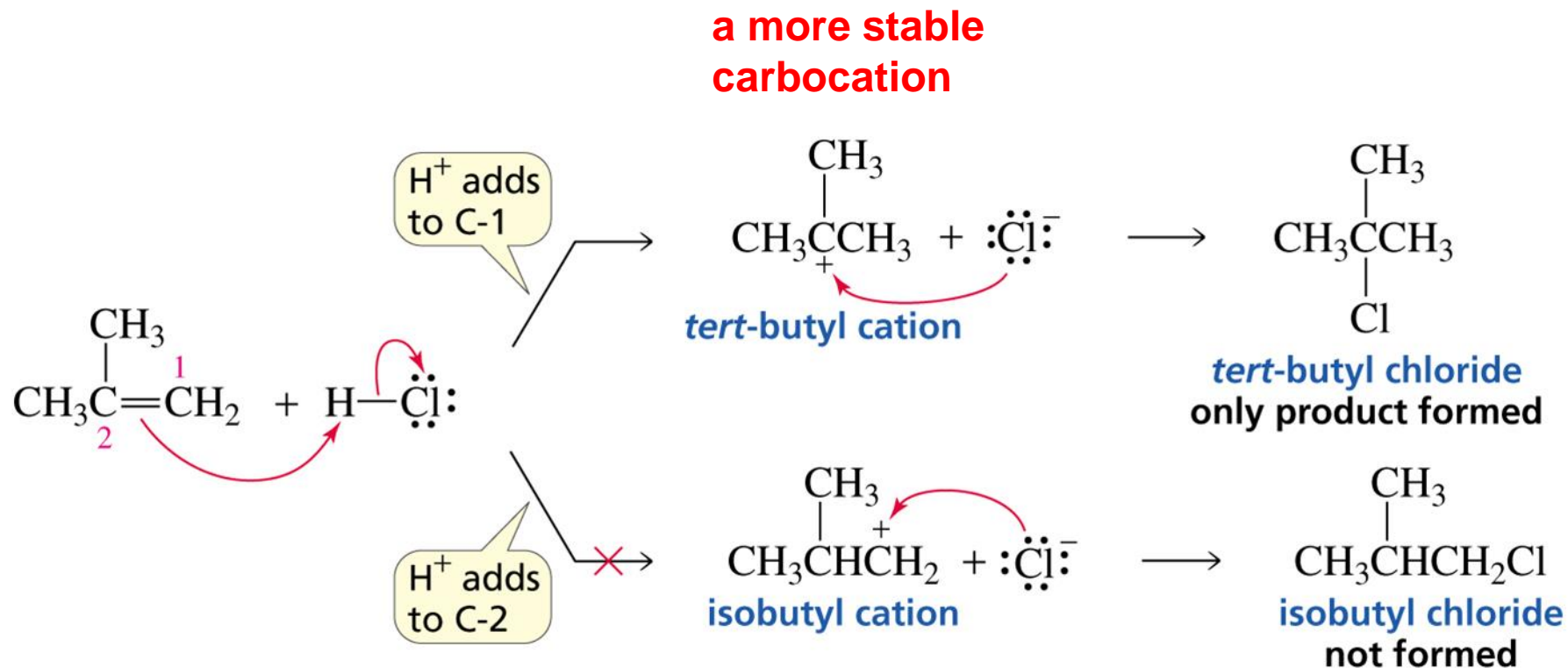
# 6.1 THE ADDITION OF A HYDROGEN HALIDE TO AN ALKENE



*What is the product?*

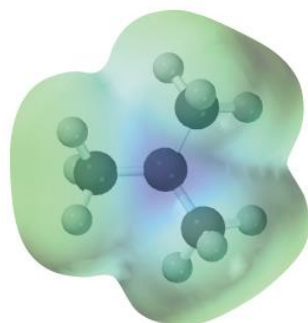
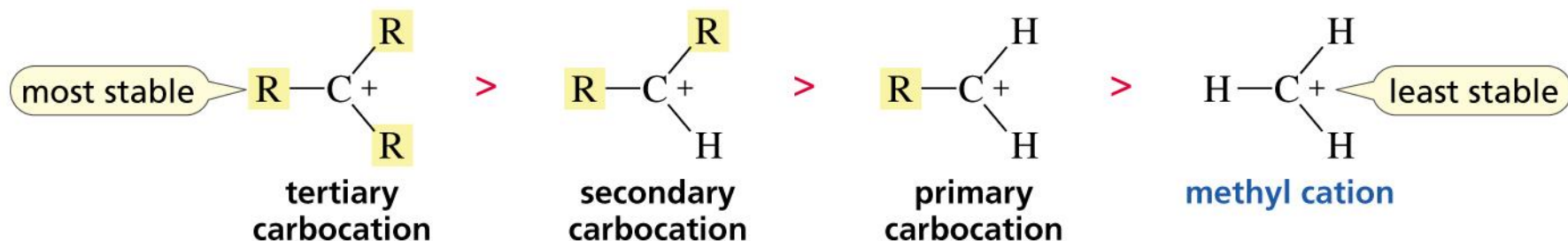


Formation of the carbocation is the rate-limiting step.

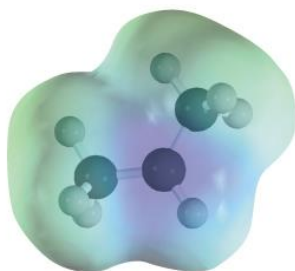


## 6.2 CARBOCATION STABILITY DEPENDS ON THE NUMBER OF ALKYL GROUPS ATTACHED TO THE POSITIVELY CHARGED CARBON

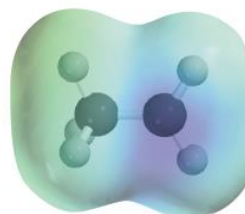
relative stabilities of carbocations



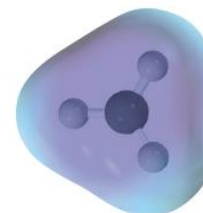
*tert*-butyl cation



isopropyl cation



ethyl cation



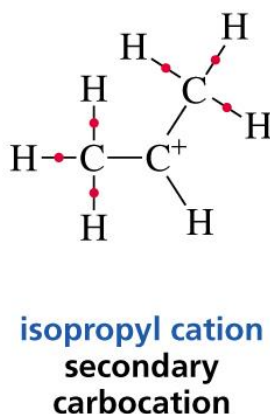
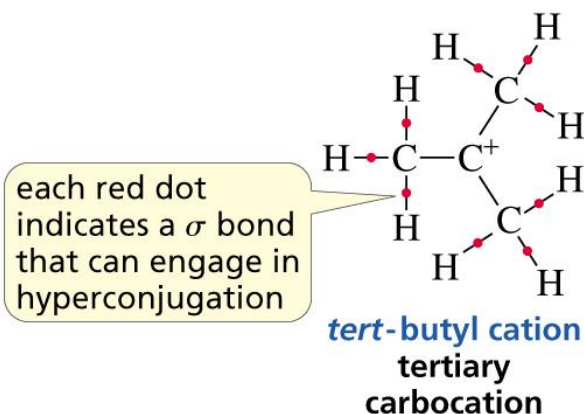
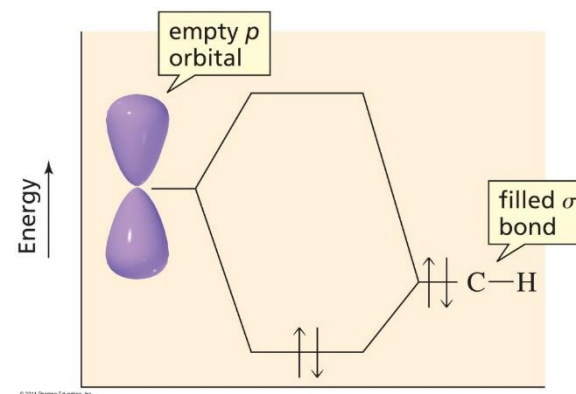
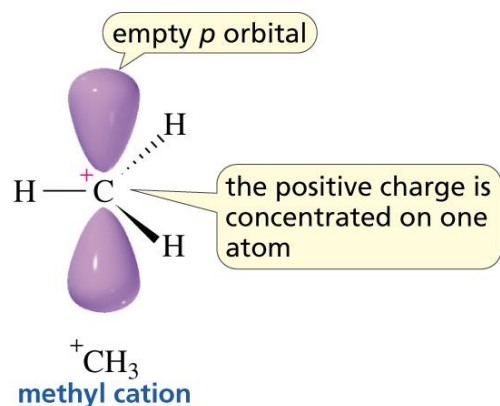
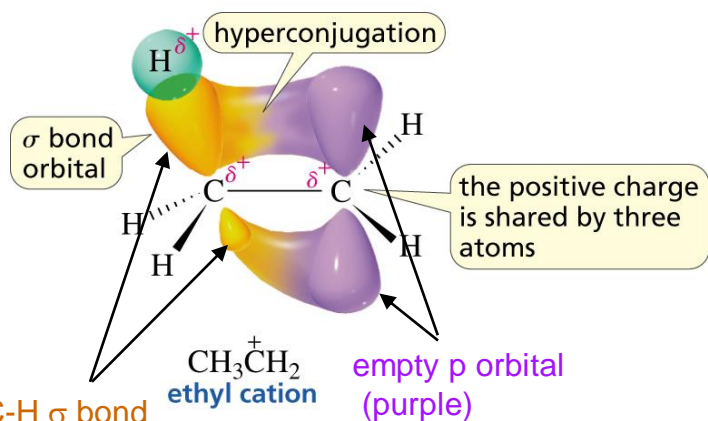
methyl cation

the most intense blue indicates the carbon with the highest concentration of positive charge

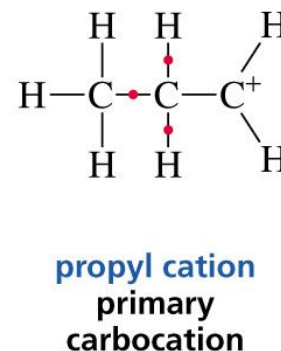
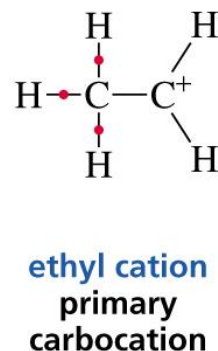
Alkyl groups decrease the concentration of positive charge in the carbocation



# Stabilization of a Carbocation by Hyperconjugation



*electron-donating alkyl groups*

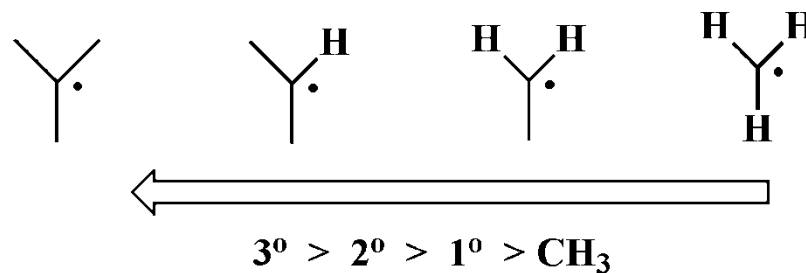


*Remember other hyperconjugations?  
in staggered conformation. in alkene stability.*

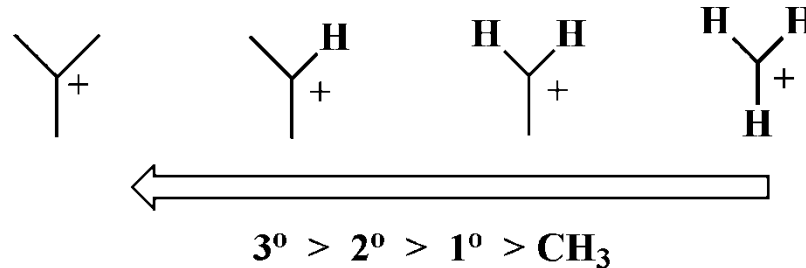
**Note that both C-H and C-C  $\sigma$  bond orbitals can overlap the empty p orbital**

# Species Stability Predicted by Hyperconjugation

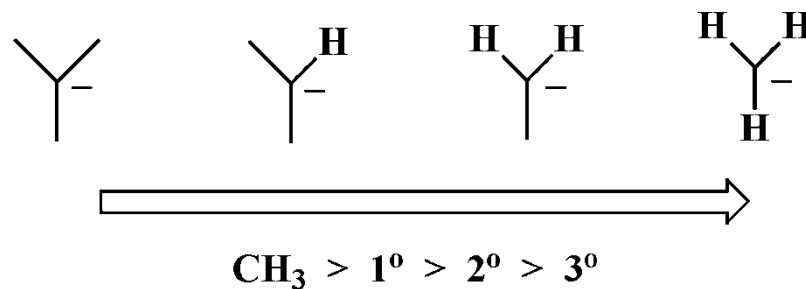
## Radical Stability



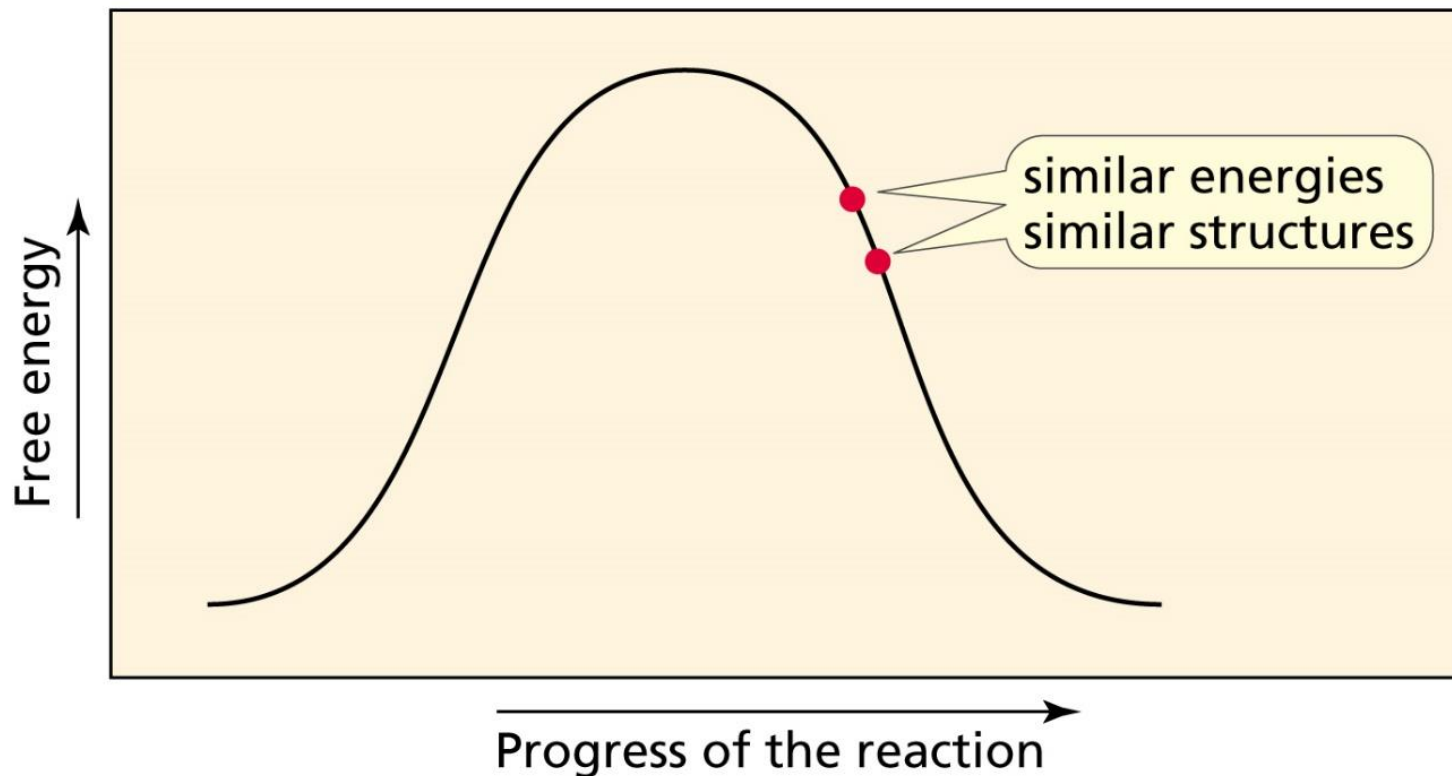
## Carbocation Stability



## Carbanion Stability



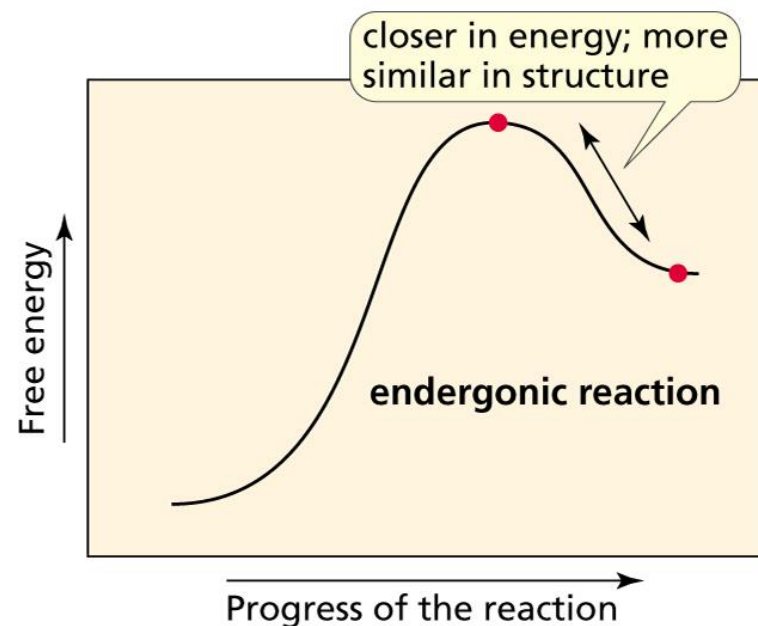
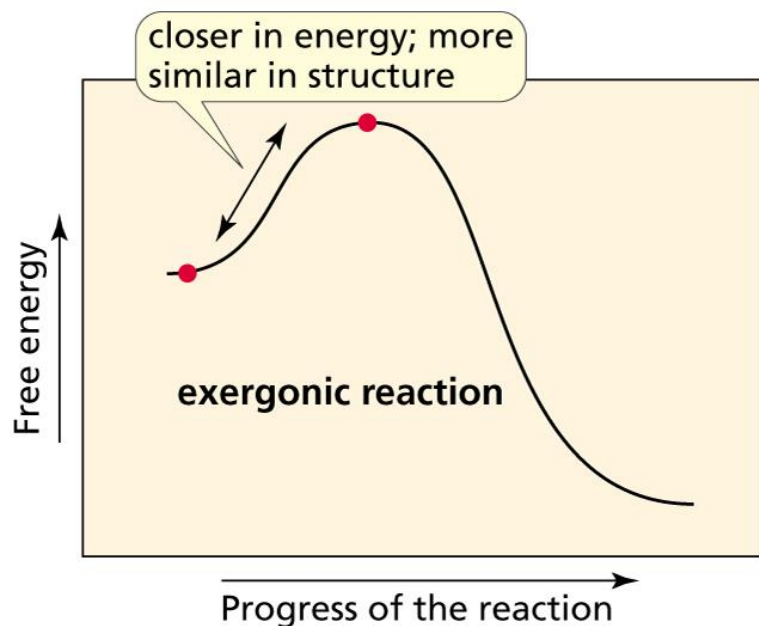
## 6.3 WHAT DOES THE STRUCTURE OF THE TRANSITION STATE LOOK LIKE?





# Hammond Postulate

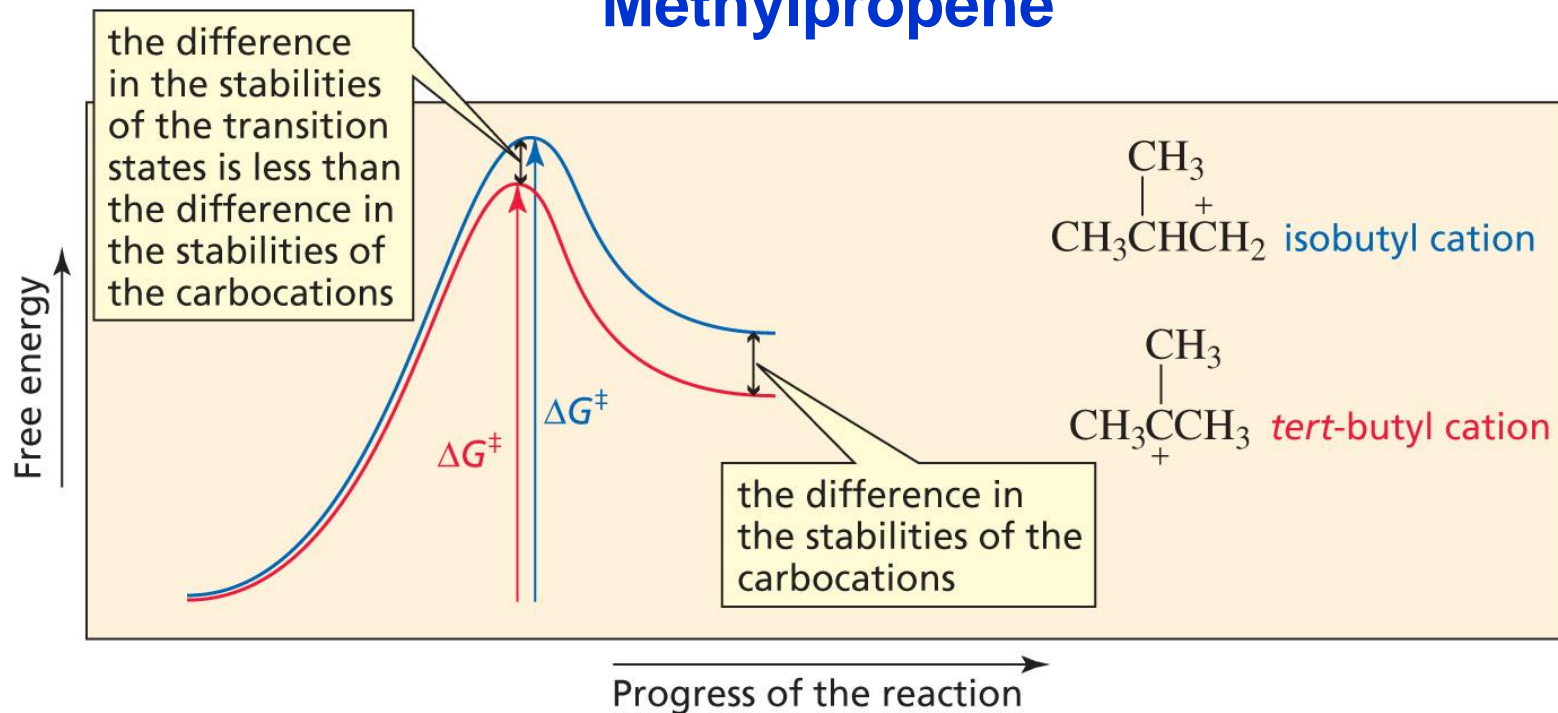
The transition state will be more similar in structure to the species to which it is more similar in energy.



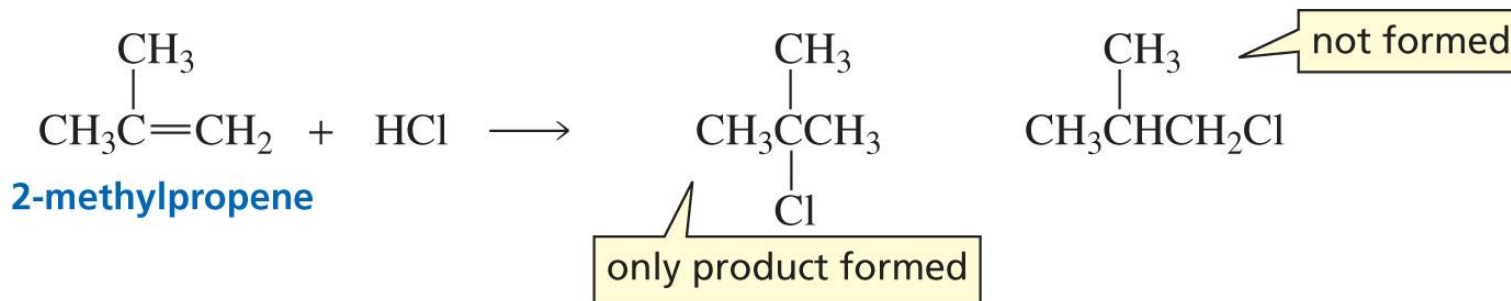
exergonic reaction: The transition state resembles the reactants.

endergonic reaction: The transition state resembles the products.

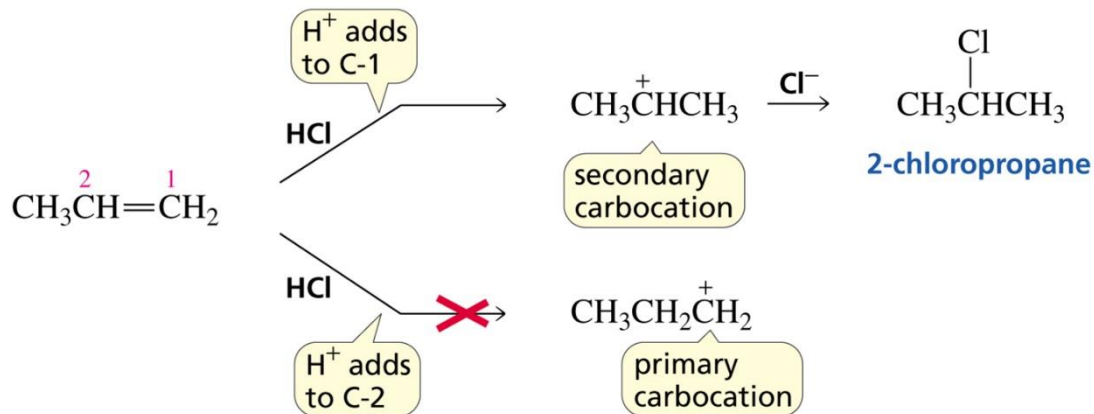
# Reaction Coordinate Diagram for the Addition of H<sup>+</sup> to 2-Methylpropene



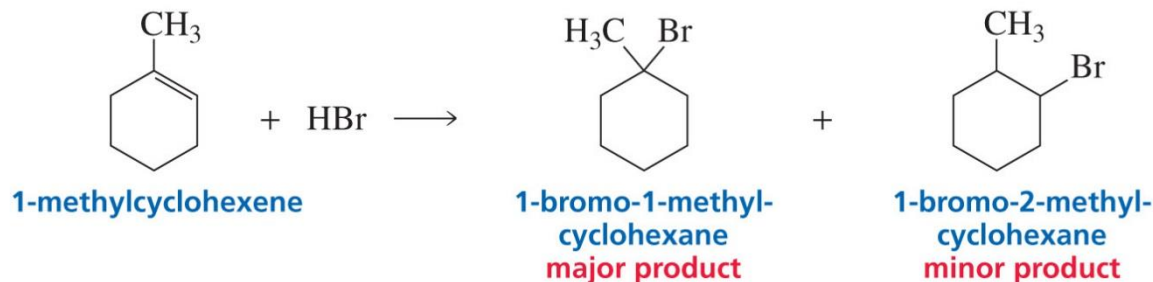
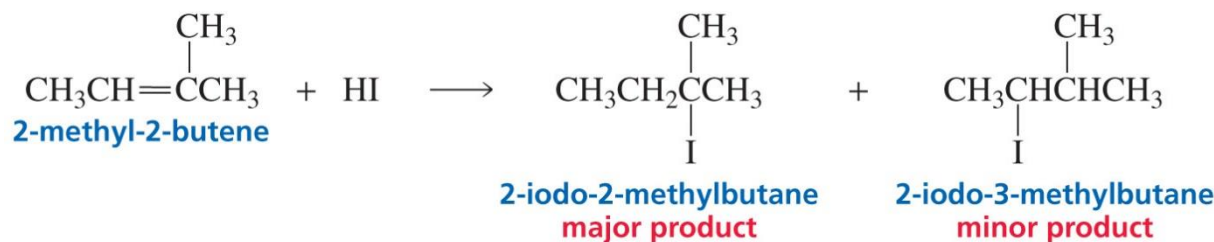
- ✓ In an electrophilic addition reaction, **the more stable carbocation forms faster.**
- ✓ The **relative rates of formation of two carbocations** determine the **relative amounts of products** formed. If difference is large, only product is formed.



# 6.4 ELECTROPHILIC ADDITION REACTIONS ARE REGIOSELECTIVE



## Regioselective Reactions:

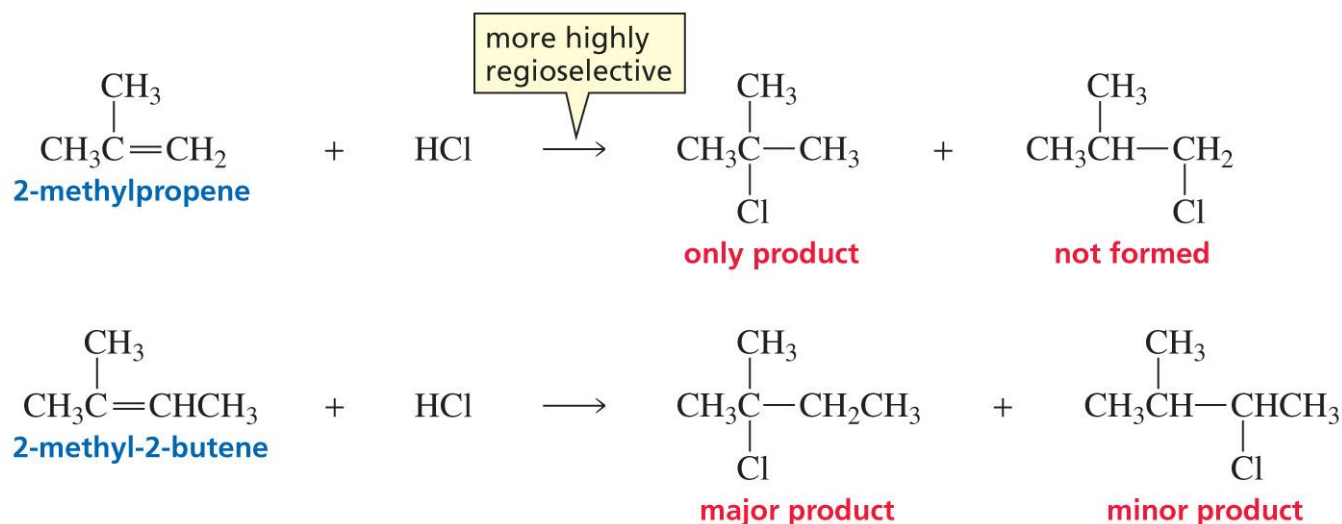


Electrophile adds to the  $sp^2$  carbon bonded to the most hydrogens

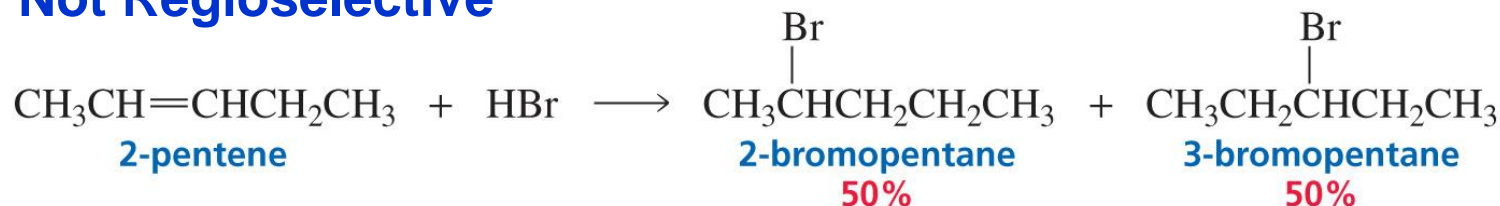
## Degrees of Regioselectivity:

A regioselective reaction is a reaction that forms more of one **constitutional isomer** than of another.

The reaction can be: **moderately regioselective**  
**highly regioselective**  
**completely regioselective**



## Not Regioselective

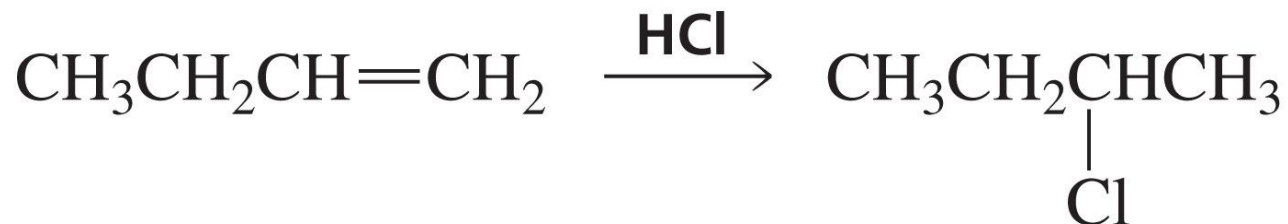


# Markovnikov's Rule

- The  $\text{H}^+$  of  $\text{HX}$  adds to the  $\text{sp}^2$  carbon that is bonded to the greater number of hydrogens
- valid only for addition rxn of  $\text{HX}$
- A better rule is to use “electrophile ( $\text{E}^+$ )” instead of  $\text{H}^+$



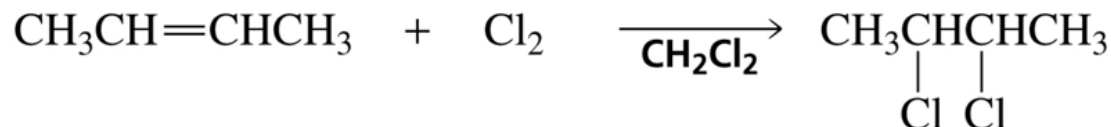
**Same**



**In a regioselective reaction, one constitutional isomer is the major or the only product.**

# Writing organic reactions

- reactants left, products right

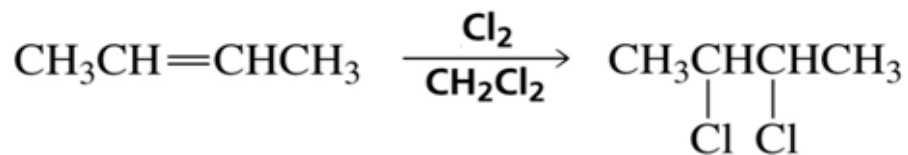


- conditions above or below arrow

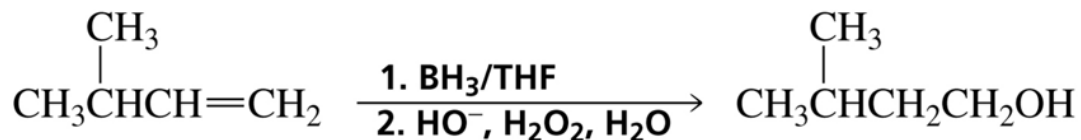
- catalyst, solvent, temperature, heat [ $\Delta$ ]

- sometimes substrate only on the left

- substrate = (C-containing) organic comp'd



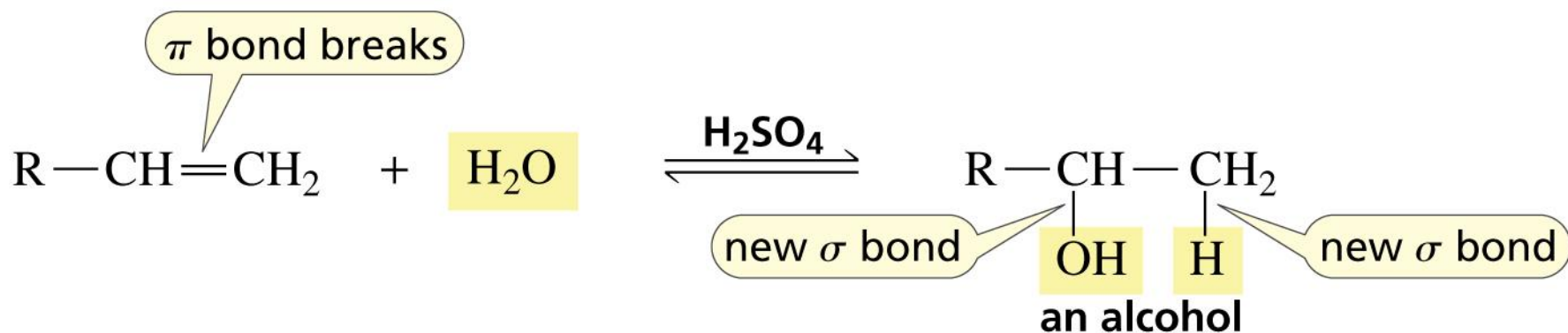
- in multi-step rxn



## 6.5 THE ADDITION OF WATER TO AN ALKENE

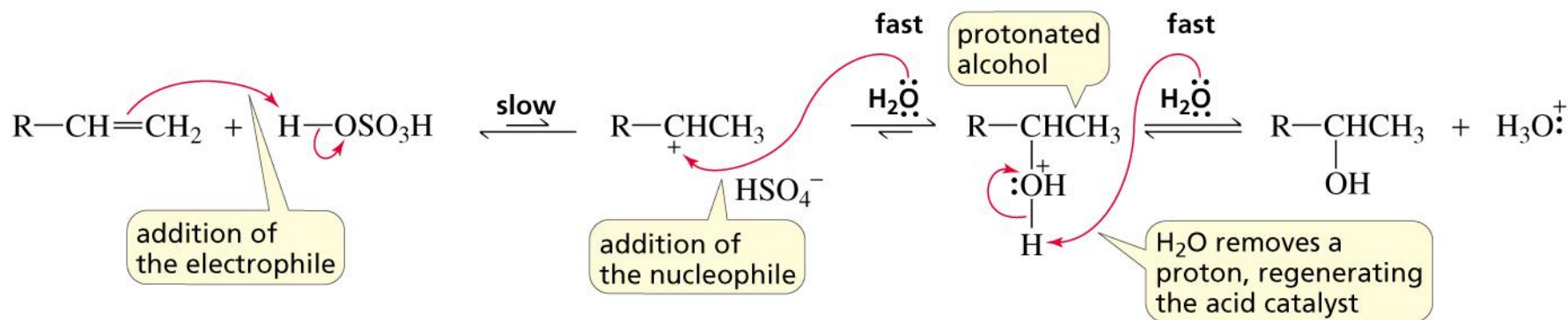


A reaction takes place if an acid is added.



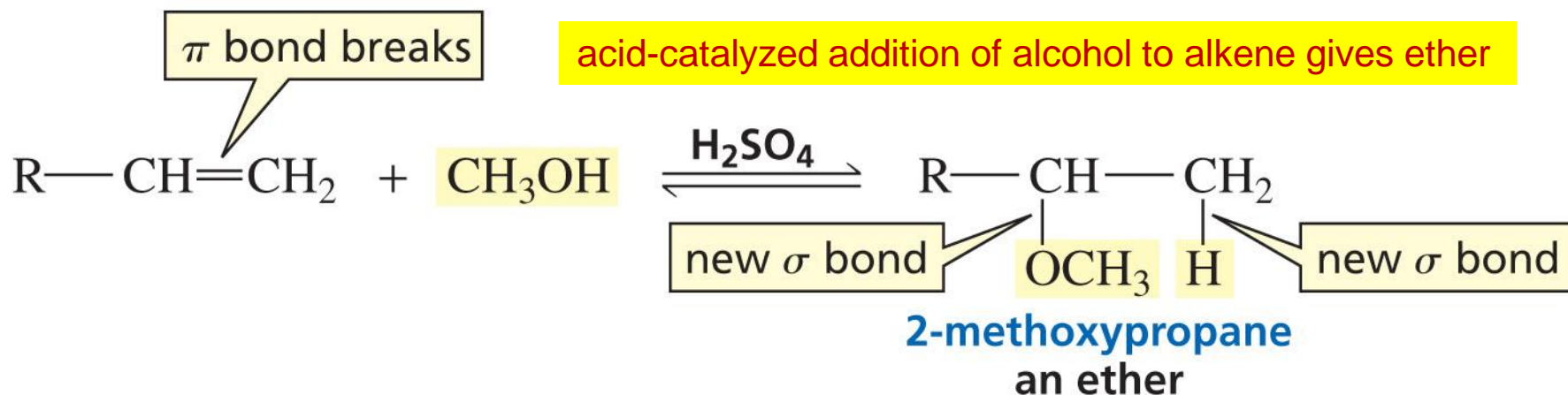


# Mechanism for the Acid-Catalyzed Addition of Water to an Alkene

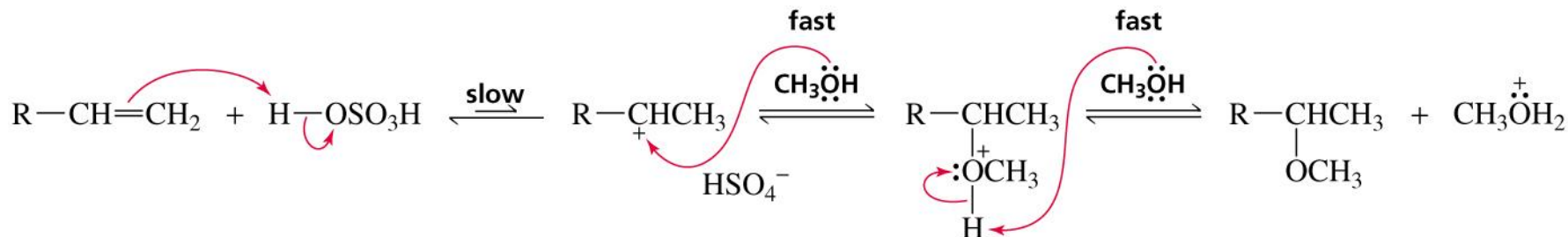


- $\text{H}^+$  (an electrophile) adds to the  $sp^2$  carbon of the alkene (a nucleophile) that is bonded to the most hydrogens.
- $\text{H}_2\text{O}$  (a nucleophile) adds to the carbocation (an electrophile), forming a protonated alcohol.
- The protonated alcohol loses a proton because the pH of the solution is greater than the  $\text{p}K_a$  of the protonated alcohol (Section 2.10). (We have seen that protonated alcohols are very strong acids; Section 2.6.)

# 6.6 THE ADDITION OF AN ALCOHOL TO AN ALKENE



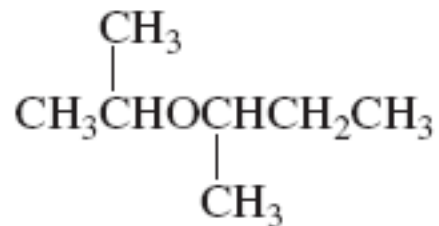
## Mechanism:



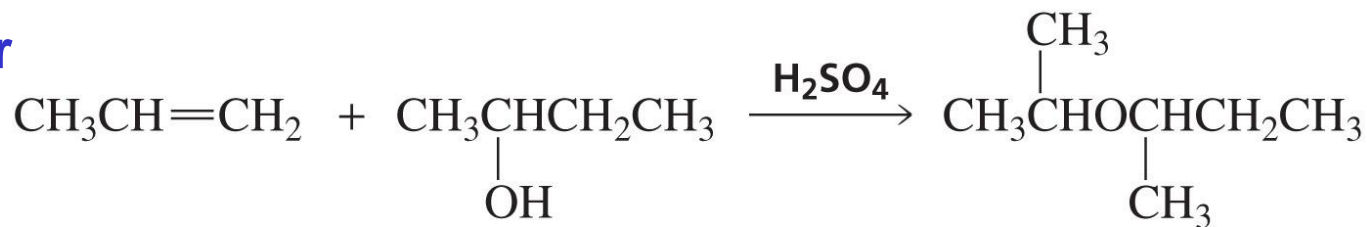
- The electrophile ( $\text{H}^+$ ) adds to the  $\text{sp}^2$  carbon that is bonded to the greater number of hydrogens.
- The nucleophile ( $\text{CH}_3\text{OH}$ ) adds to the carbocation, forming a protonated ether.
- The protonated ether loses a proton, because the pH of the solution is greater than the  $\text{pK}_a$  of the protonated ether ( $\text{pK}_a \sim -3.6$ ).

## Problem 13

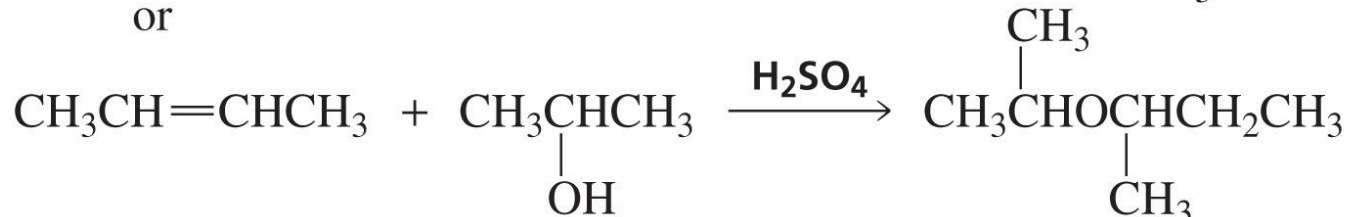
How could the following compound be prepared, using an alkene as one of the starting materials?



### Answer



or



or

