

Chapter 6

Reactions of Alkenes: Addition Reactions

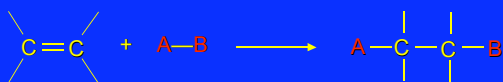
6.1

Hydrogenation of Alkenes

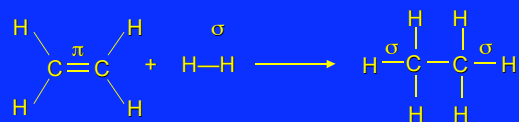
Surface Reaction-
Hydrogenation

Reactions of Alkenes

The characteristic reaction of alkenes is addition to the double bond.



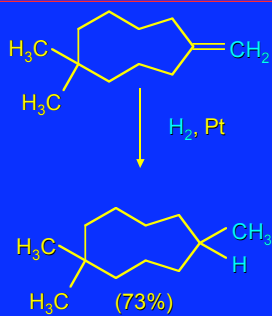
Hydrogenation of Ethylene



exothermic $\Delta H^\circ = -136 \text{ kJ/mol}$

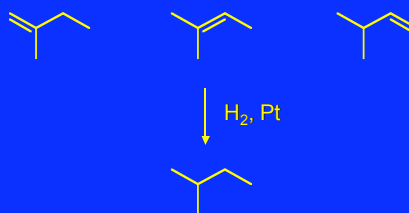
catalyzed by finely divided Pt, Pd, Rh, Ni

Example



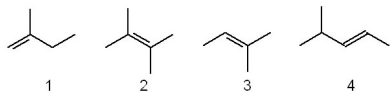
Problem 6.1

What three alkenes yield 2-methylbutane on catalytic hydrogenation?



Question 2

Which of the alkenes below will produce 2-methylbutane on catalytic hydrogenation?



- A) 1 and 3
B) 1, 2 and 3
C) 2 and 4
D) 2, 3 and 4

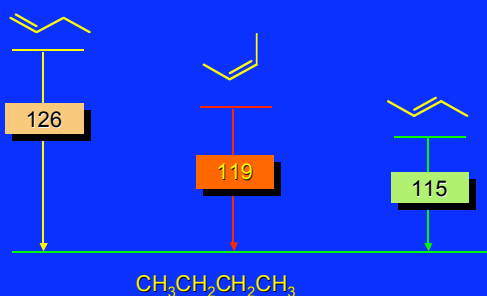
6.2

Heats of Hydrogenation

can be used to measure relative stability of isomeric alkenes

correlation with structure is same as when heats of combustion are measured

Heats of Hydrogenation of Isomers

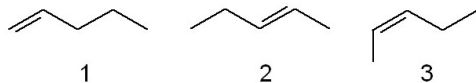


Heats of Hydrogenation (kJ/mol)

Ethylene	136
Monosubstituted	125-126
<i>cis</i> -Disubstituted	117-119
<i>trans</i> -Disubstituted	114-115
Terminally disubstituted	116-117
Trisubstituted	112
Tetrasubstituted	110

Question 1

Rank the following alkenes in order of decreasing heat of hydrogenation.



- A) $1 > 3 > 2$
B) $3 > 2 > 1$
C) $2 > 3 > 1$
D) $1 > 2 > 3$

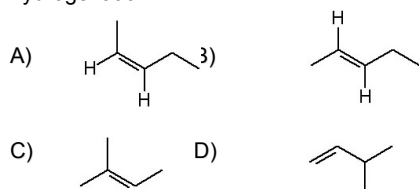
Problem 6.2

Match each alkene of Problem 6.1 with its correct heat of hydrogenation.

126 kJ/mol		highest heat of hydrogenation; least stable isomer
118 kJ/mol		
112 kJ/mol		lowest heat of hydrogenation; most stable isomer

Question 4

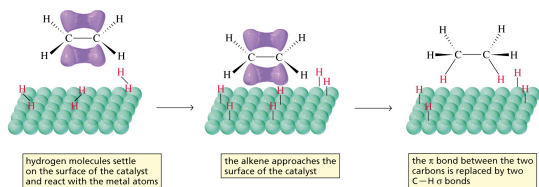
Which alkene has the lowest heat of hydrogenation?



6.3

Stereochemistry of Alkene Hydrogenation

Catalytic Hydrogenation of an Alkene



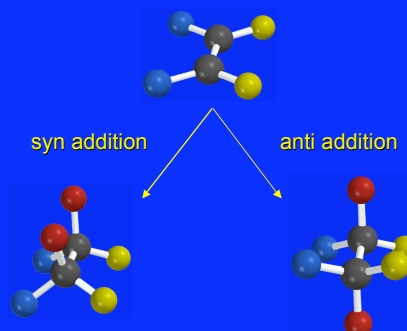
Two Spatial (stereochemical) Aspects of Alkene Hydrogenation

- (1) syn addition of both H atoms to double bond (adds from the same side)
- (2) hydrogenation is stereoselective, corresponding to addition to less crowded face of double bond

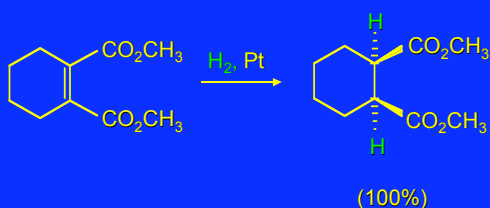
Two Spatial (stereochemical) Aspects of Alkene Hydrogenation

- (1) syn addition of both H atoms to double bond

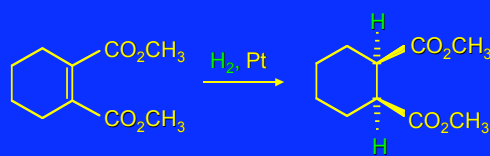
syn Addition versus anti Addition



Example of syn-Addition



Question



True (A) / False (B)

The hydrogenation product is a chiral molecule.

Two Spatial (stereochemical) Aspects of Alkene Hydrogenation

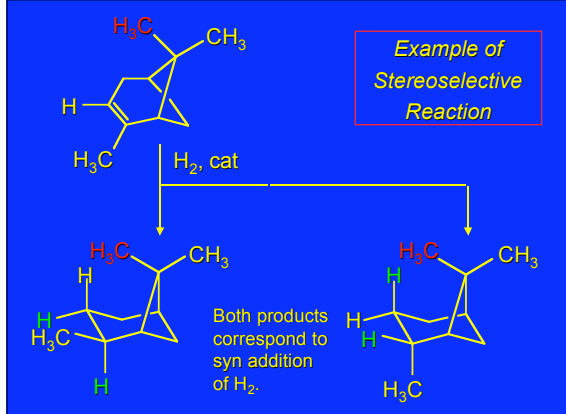
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Two Spatial (stereochemical) Aspects of Alkene Hydrogenation

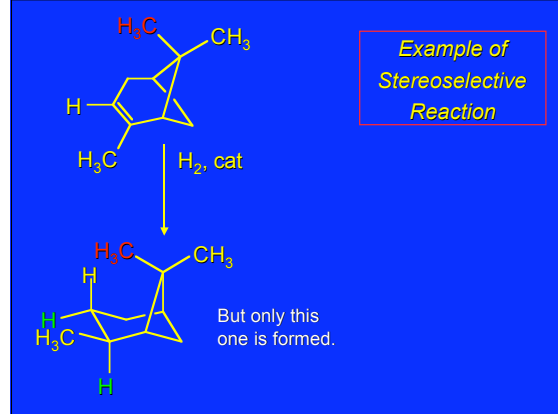
- (2) hydrogenation is stereoselective, corresponding to addition to less crowded face of double bond

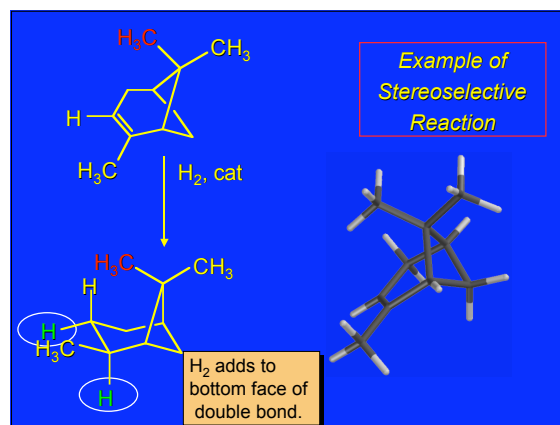
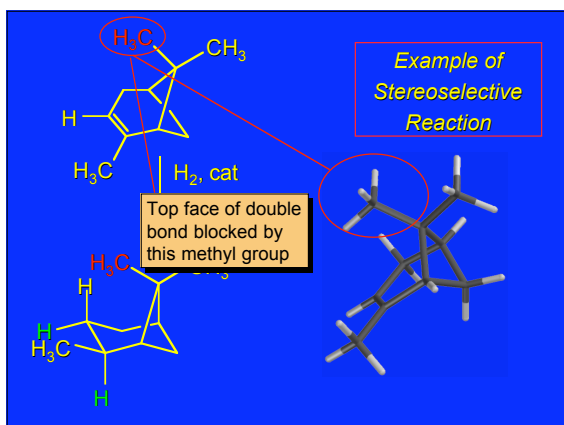
A reaction in which a single starting material can give two or more stereoisomeric products but yields one of them in greater amounts than the other (or even to the exclusion of the other) is said to be stereoselective.

Example of Stereoselective Reaction



Example of Stereoselective Reaction





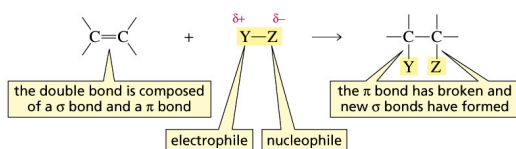
Question 14

Which one of the following terms best applies to the hydrogenation of an alkene in the presence of finely divided platinum? (in ethanol as solvent)

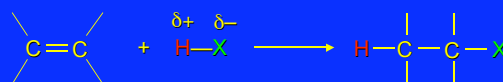
- A) anti addition
- B) concerted reaction
- C) heterogeneous catalysis
- D) endothermic reaction

6.4 Electrophilic Addition of Hydrogen Halides to Alkenes

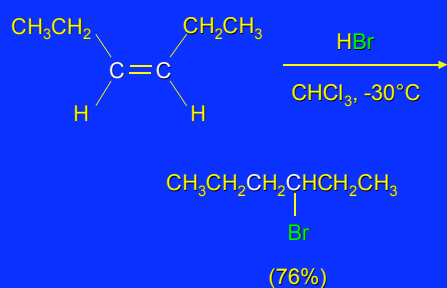
Electrophilic Additions: Alkenes



When the Electrophile is a Hydrogen Halide



Example

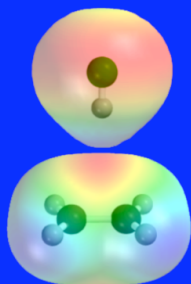


Mechanism

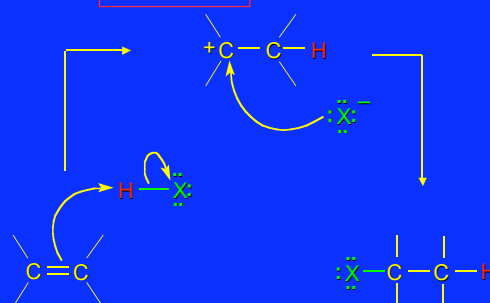
Electrophilic addition of hydrogen halides to alkenes proceeds by rate-determining formation of a carbocation intermediate.

Mechanism

Electrons flow from the π system of the alkene (electron rich) toward the positively polarized proton of the hydrogen halide.



Mechanism



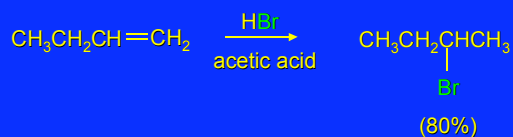
6.5

Regioselectivity of Hydrogen Halide Addition (Markovnikov's Rule)

Markovnikov's Rule

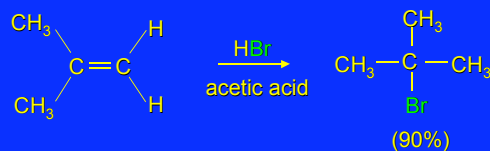
When an unsymmetrically substituted alkene reacts with a hydrogen halide, the hydrogen adds to the carbon that has the greater number of hydrogen substituents, and the halogen adds to the carbon that has the fewer hydrogen substituents.

Markovnikov's Rule



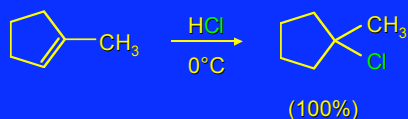
Example 1

Markovnikov's Rule



Example 2

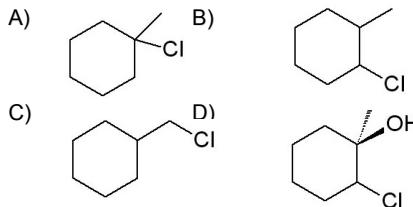
Markovnikov's Rule



Example 3

Question 6

What is the product of the reaction of 1-methylcyclohexene with HCl?



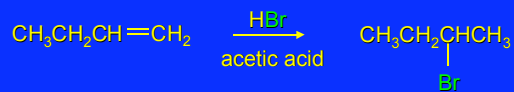
6.6

Mechanistic Basis for Markovnikov's Rule

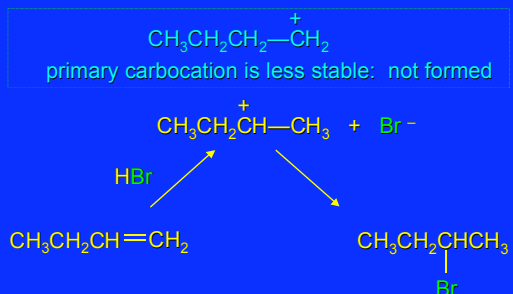
Protonation of double bond occurs in direction that gives more stable of two possible carbocations.

Mechanistic Basis for Markovnikov's Rule:

Example 1

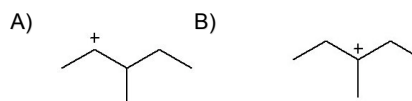


Mechanistic Basis for Markovnikov's Rule:
Example 1

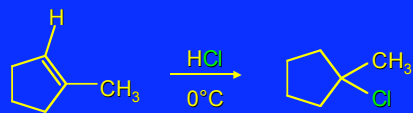


Question 3

Which carbocation forms when 3-methyl-2-pentene is protonated?

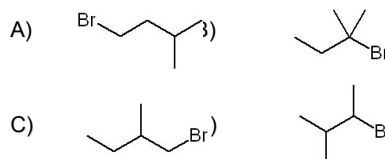


Mechanistic Basis for Markovnikov's Rule:
Example 3

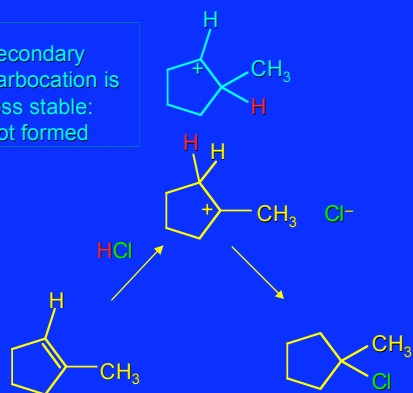


Question 5

The reaction of 3-methyl-1-butene with HBr produces 2-bromo-3-methylbutane and which other alkyl halide?

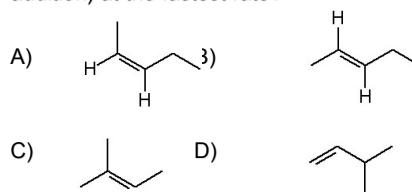


secondary carbocation is less stable: not formed

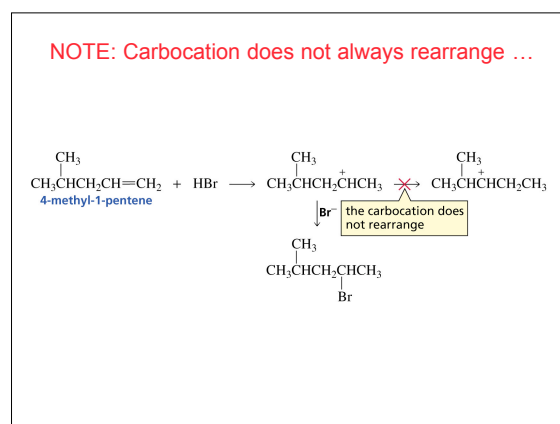
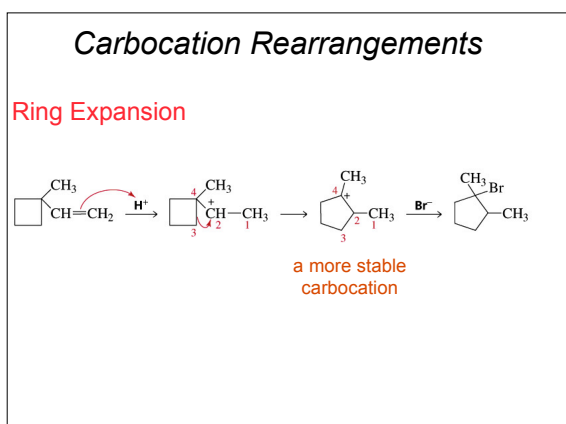
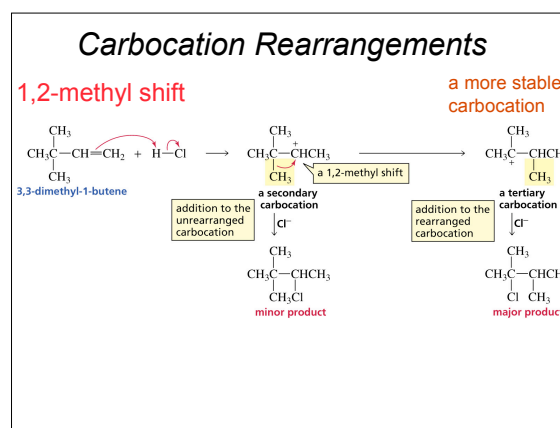
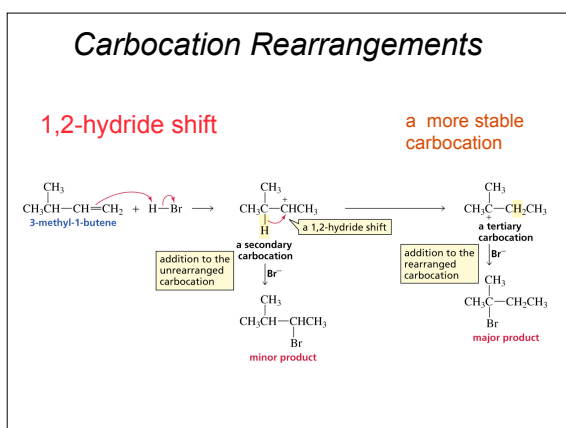
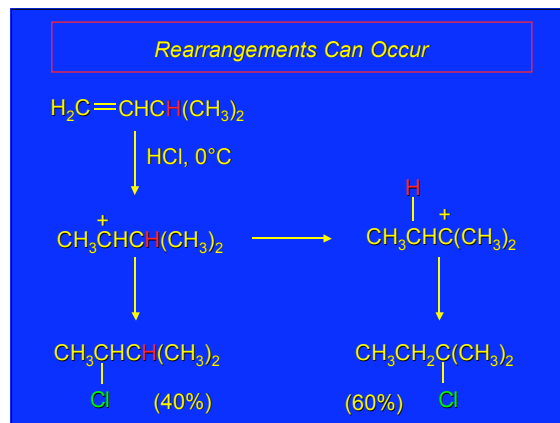


Question 18

Which alkene reacts with HCl (electrophilic addition) at the fastest rate?



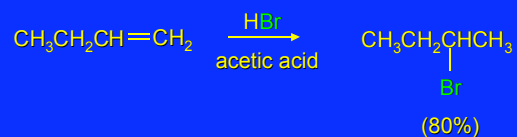
6.7 Carbocation Rearrangements in Hydrogen Halide Addition to Alkenes



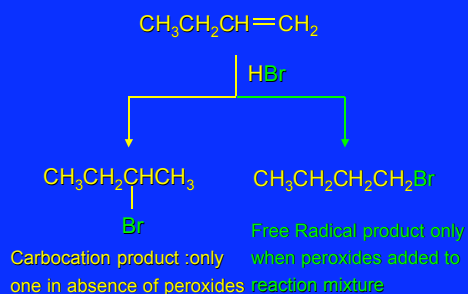
6.8
Free-radical Addition of HBr to
Alkenes

The "peroxide effect"

Markovnikov's Rule

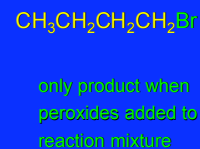


Addition of HBr to 1-Butene

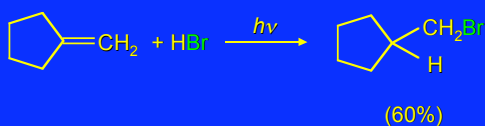


Addition of HBr to 1-Butene

Addition opposite to
Markovnikov's rule



Photochemical Addition of HBr

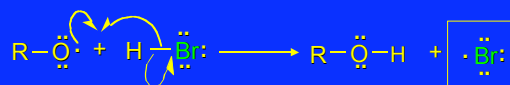
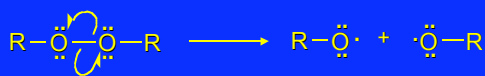


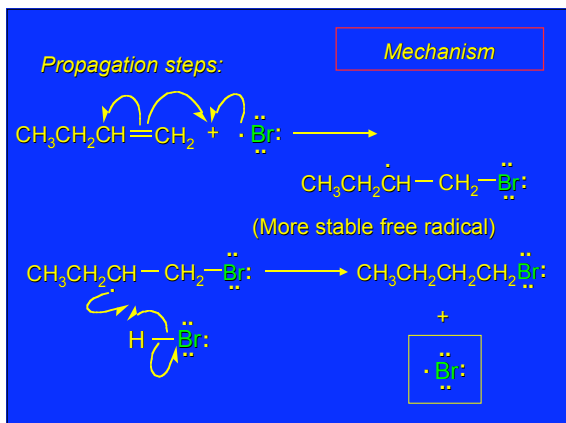
Addition of HBr with a regiochemistry opposite to Markovnikov's rule also occur when initiated with light with or without added peroxides.

Mechanism

Addition of HBr opposite to Markovnikov's rule proceeds by a free-radical chain mechanism.

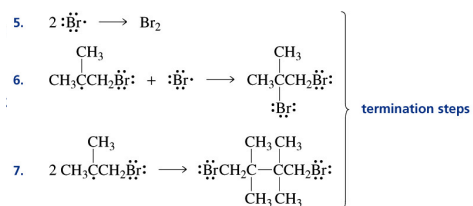
Initiation steps:





Examples of Termination Steps

(Initiation → Propagation → Termination)



Question 7

What is the correct IUPAC name of the compound isolated from the reaction of 2-methyl-2-pentene with HBr in the presence of peroxides?

- A) 3-bromo-4-methylpentane
- B) 3-bromo-2-methylpentane
- C) 2-bromo-2-methylpentane
- D) 2,3-dibromo-2-methylpentane