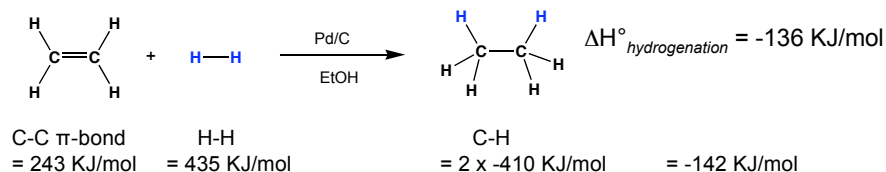


Chapter 6: Reactions of Alkenes: Addition Reactions

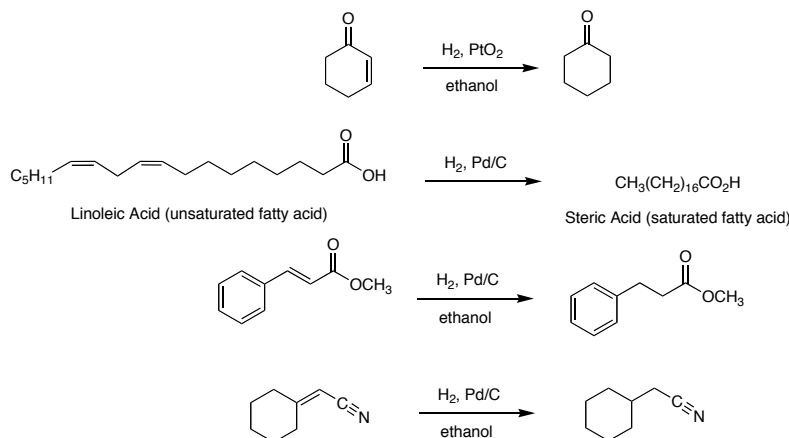
6.1: Hydrogenation of Alkenes – addition of H-H (H_2) to the π -bond of alkenes to afford an alkane. The reaction must be catalyzed by metals such as Pd, Pt, Rh, and Ni.



- The catalyst is not soluble in the reaction media, thus this process is referred to as a *heterogeneous* catalysis.
- The catalyst assists in breaking the π -bond of the alkene and the H-H σ -bond.
- The reaction takes place on the surface of the catalyst. Thus, the rate of the reaction is proportional to the surface area of the catalyst.

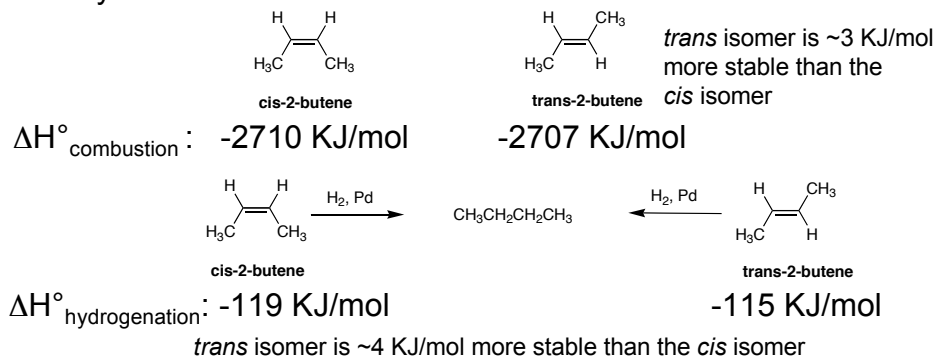
127

- Carbon-carbon π -bond of alkenes and alkynes can be reduced to the corresponding saturated C-C bond. Other π -bond bonds such as C=O (carbonyl) and C \equiv N are not easily reduced by catalytic hydrogenation. The C=C bonds of aryl rings are *not* easily reduced.

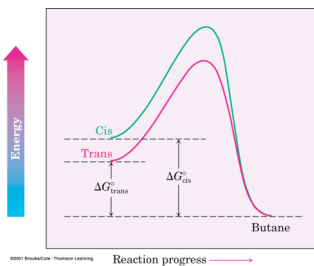


128

6.2: Heats of Hydrogenation - can be used to measure relative stability of isomeric alkenes









The greater release of heat, the less stable the reactant.



129

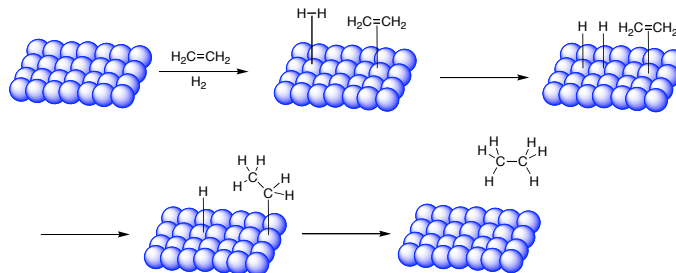
Table 6.1 (pg 228): Heats of Hydrogenation of Some Alkenes

	Alkene	ΔH° (KJ/mol)
	$\text{H}_2\text{C}=\text{CH}_2$	136
monosubstituted		125 - 126
disubstituted		117 - 119
		114 - 115
		116 - 117
trisubstituted		112
tetrasubstituted		110

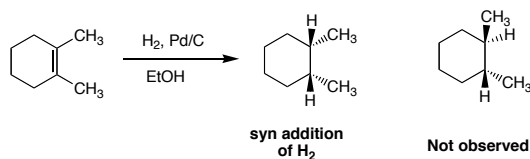
130

6.3: Stereochemistry of Alkene Hydrogenation

Mechanism:

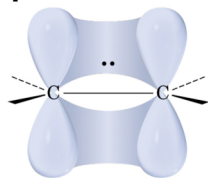


The addition of H₂ across the π-bond is *syn*, i.e., from the same face of the double bond



131

6.4: Electrophilic Addition of Hydrogen Halides to Alkenes

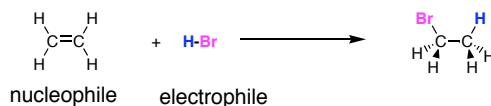


Carbon-carbon π bond:
weaker: more accessible electrons

C-C σ-bond: ΔH° = 368 KJ/mol
C-C π-bond: ΔH° = 243 KJ/mol

π-bond of an alkene can act as a nucleophile!!

Electrophilic addition reaction



Bonds broken

C=C π-bond 243 KJ/mol
H-Br 366 KJ/mol

Bonds formed

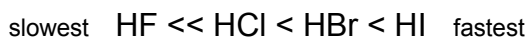
H₃C-H₂C-H -410 KJ/mol
H₃C-H₂C-Br -283 KJ/mol

calc. ΔH° = -84 KJ/mol

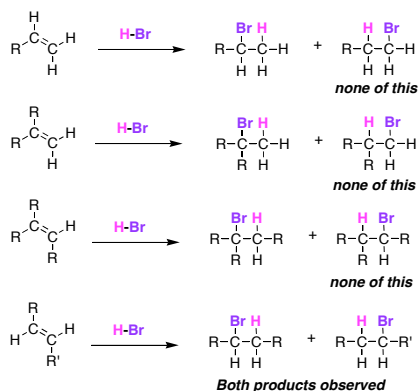
expt. ΔH° = -84 KJ/mol

132

Reactivity of HX correlates with acidity:



6.5: Regioselectivity of Hydrogen Halide Addition: Markovnikov's Rule



For the electrophilic addition of HX across a C=C bond, the H (of HX) will add to the carbon of the double bond with the most H's (the least substituted carbon) and the X will add to the carbon of the double bond that has the most alkyl groups.

133

Mechanism of electrophilic addition of HX to alkenes

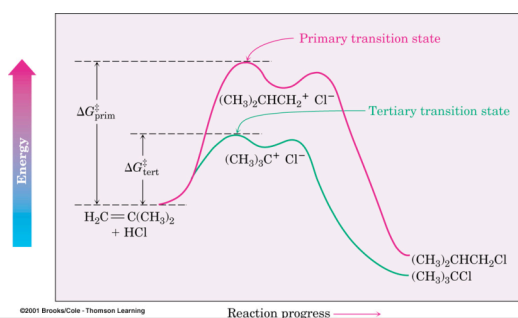
6.6: Mechanistic Basis for Markovnikov's Rule:

Markovnikov's rule can be explained by comparing the stability of the intermediate carbocations

134

For the electrophilic addition of HX to an unsymmetrically substituted alkene:

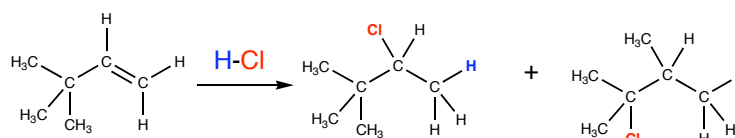
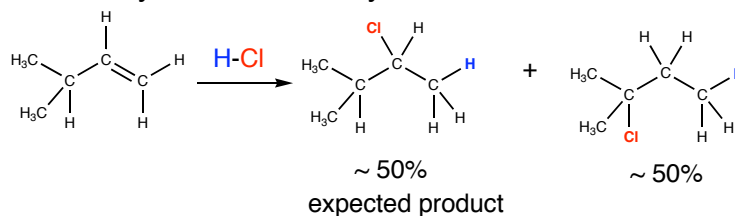
- The more highly substituted carbocation intermediate is formed.
- More highly substituted carbocations are more stable than less substituted carbocations. (hyperconjugation)
- The more highly substituted carbocation is formed faster than the less substituted carbocation. Once formed, the more highly substituted carbocation goes on to the final product more rapidly as well.



135

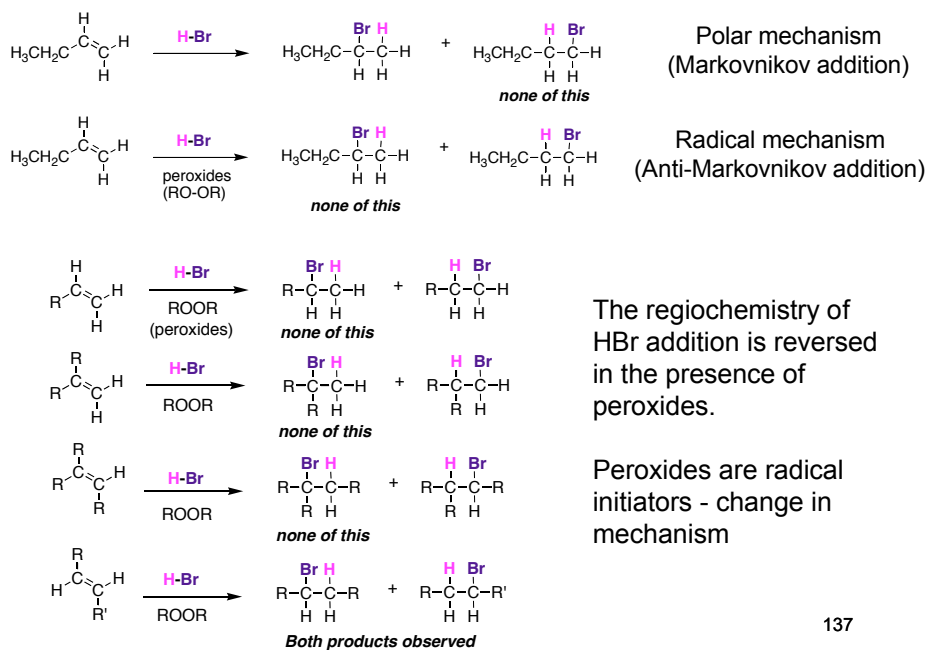
6.7: Carbocation Rearrangements in Hydrogen Halide

Addition to Alkenes - In reactions involving carbocation intermediates, the carbocation may sometimes rearrange if a more stable carbocation can be formed by the rearrangement. These involve hydride and methyl shifts.



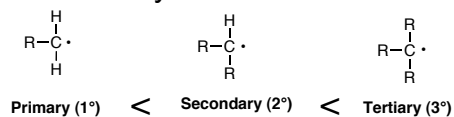
Note that the shifting atom or group moves with its electron pair.
A MORE STABLE CARBOCATION IS FORMED. 136

6.8: Free-radical Addition of HBr to Alkenes



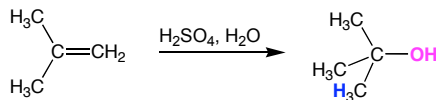
137

The regiochemistry of free radical addition of H-Br to alkenes reflects the stability of the radical intermediate.



138

6.9: Addition of Sulfuric Acid to Alkenes (please read)
6.10: Acid-Catalyzed Hydration of Alkenes - addition of water (H-OH) across the π -bond of an alkene to give an alcohol; opposite of dehydration



This addition reaction follows Markovnikov's rule. The more highly substituted alcohol is the product and is derived from the most stable carbocation intermediate.

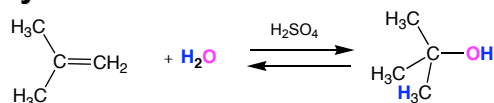
Reaction works best for the preparation of 3° alcohols

139

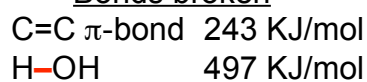
Mechanism is the reverse of the acid-catalyzed dehydration of alcohols: *Principle of Microscopic Reversibility*

140

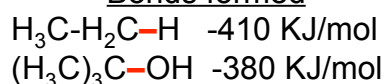
6.11: Thermodynamics of Addition-Elimination Equilibria



Bonds broken



Bonds formed



$$\text{calc. } \Delta H^\circ = -50 \text{ KJ/mol}$$

$$\Delta G^\circ = -5.4 \text{ KJ/mol} \quad \Delta H^\circ = -52.7 \text{ KJ/mol} \quad \Delta S^\circ = -0.16 \text{ KJ/mol}$$

How is the position of the equilibrium controlled?

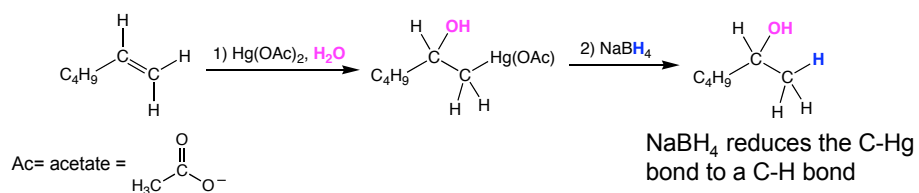
Le Chatelier's Principle - an equilibrium will adjust to any stress

The hydration-dehydration equilibria is pushed toward hydration (alcohol) by adding water and toward alkene (dehydration) by removing water

141

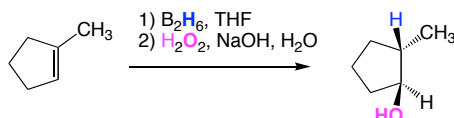
The acid catalyzed hydration is not a good or general method for the hydration of an alkene.

Oxymercuration: a general (2-step) method for the Markovnikov hydration of alkenes



142

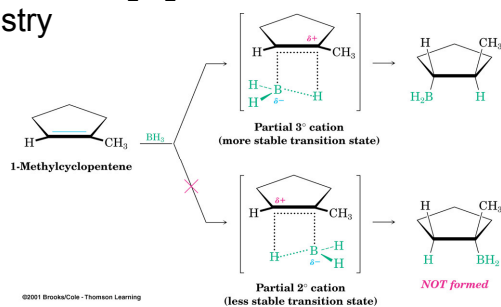
6.12: Hydroboration-Oxidation of Alkenes - *Anti*-Markovnikov addition of H-OH; *syn* addition of H-OH



6.13: Stereochemistry of Hydroboration-Oxidation

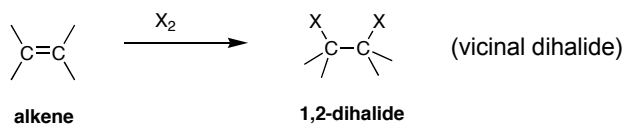
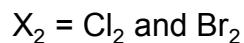
6.14: Mechanism of Hydroboration-Oxidation -

Step 1: *syn* addition of the H₂B-H bond to the same face of the π-bond in an anti-Markovnikov sense; step 2: oxidation of the B-C bond by basic H₂O₂ to a C-OH bond, with retention of stereochemistry

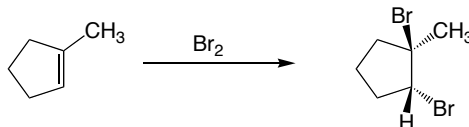
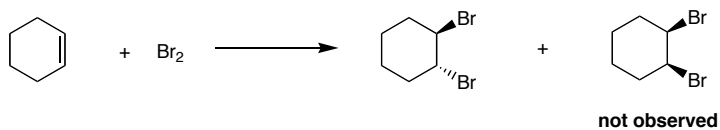


143

6.15: Addition of Halogens to Alkenes



6.16: Stereochemistry of Halogen Addition - 1,2-dibromide has the *anti* stereochemistry

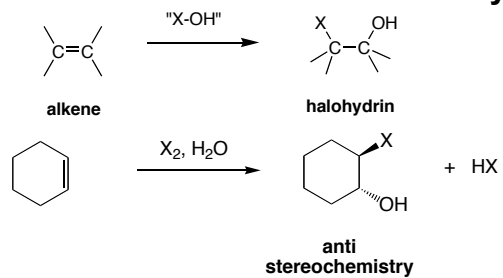


144

6.17: Mechanism of Halogen Addition to Alkenes:
Halonium Ions - Bromonium ion intermediate explains the stereochemistry of Br₂ addition

145

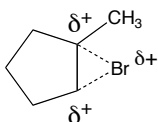
6.18: Conversion of Alkenes to Vicinal Halohydrins



Mechanism involves a halonium ion intermediate

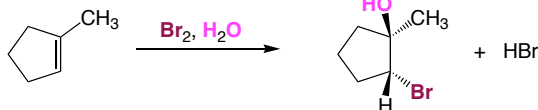
146

For unsymmetrical alkenes, halohydrin formation is Markovnikov-like in that the orientation of the addition of X-OH can be predicted by considering carbocation stability



more δ^+ charge on the more substituted carbon

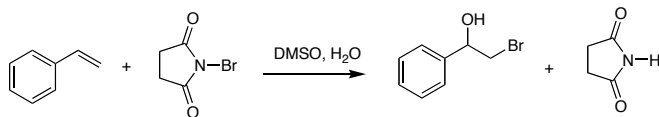
H₂O adds in the second step and adds to the carbon that has the most δ^+ charge and ends up on the more substituted end of the double bond



Br adds to the double bond first (formation of bromonium ion) and is on the least substituted end of the double bond

147

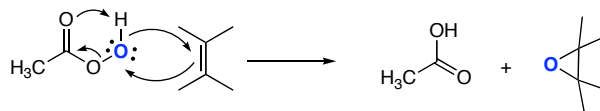
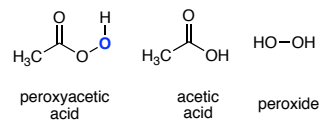
Organic molecules are sparingly soluble in water as solvent. The reaction is often done in a mix of organic solvent and water using N-bromosuccinimide (NBS) as the electrophilic bromine source.



Note that the aryl ring does not react!!!

6.19: Epoxidation of Alkenes - Epoxide (oxirane): three-membered ring, cyclic ethers.

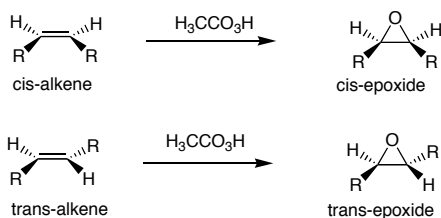
Reaction of an alkene with a peroxyacid:
peroxyacetic acid



148

Stereochemistry of the epoxidation of alkenes: syn addition of oxygen. The geometry of the alkene is preserved in the product

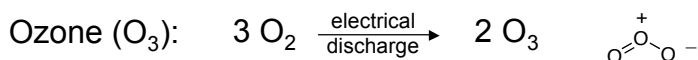
Groups that are trans on the alkene will end up trans on the epoxide product. Groups that are cis on the alkene will end up cis on the epoxide product.



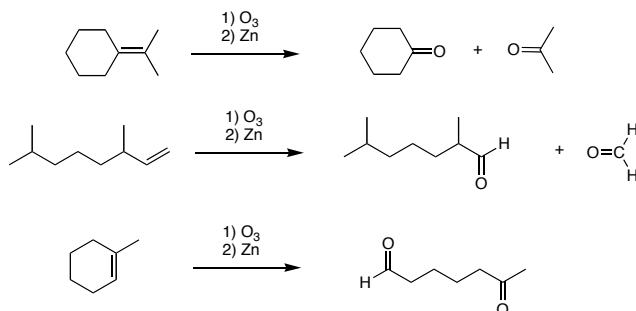
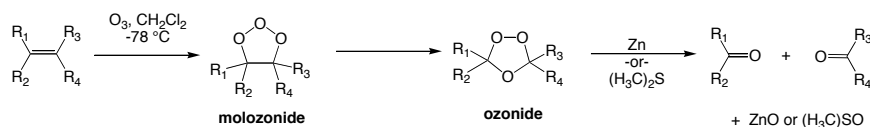
6.20: Ozonolysis of Alkenes - oxidative cleavage of an alkene to carbonyl compounds (aldehydes and ketones). The π - and σ -bonds of the alkene are broken and replaced with C=O double bonds.

C=C of aryl rings, C \equiv N and C=O do not react with ozone, C \equiv C react very slowly with ozone

149



mechanism

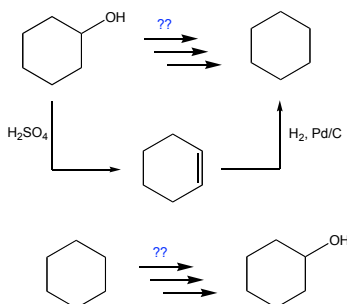


150

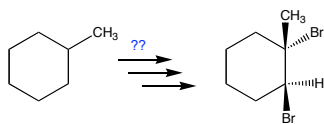
6.21: Introduction to Organic Chemical Synthesis

Synthesis: making larger, more complex molecules out of less complex ones using known and reliable reactions.

devise a synthetic plan by working the problem backward from the target molecule



151



6.22: Reactions of Alkenes with Alkenes: Polymerization (please read)

152