

## Reactions of Alkenes I

**Reading:** Wade chapter 8, sections 8-1- 8-8

**Study Problems:** 8-47, 8-48, 8-55, 8-66, 8-67, 8-70

### Key Concepts and Skills:

- Predict the products of additions to alkenes, including regiochemistry and stereochemistry.
- Propose logical mechanisms to explain the observed products of alkene addition reactions, including regiochemistry and stereochemistry

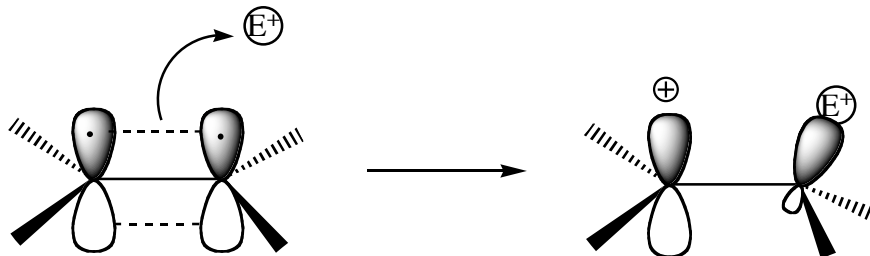
### Lecture Topics:

#### I. Additions to pi bonds

The pi bond of Alkenes requires 63 kcal/mol to break; C-C sigma bond is 83 kcal/mol, thus the reactivity of alkenes is dominated by the addition of reagents that cleave the pi bond to form more stable sigma bonds, such as C-H bonds (100 kcal/mol). Additions to alkenes are thus driven by thermodynamics- the tendency to form stronger bonds.

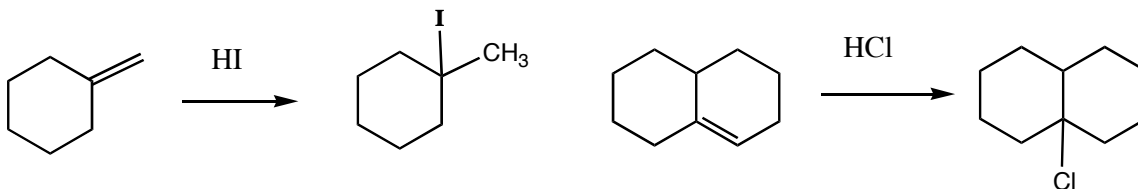
#### A. Electrophilic additions

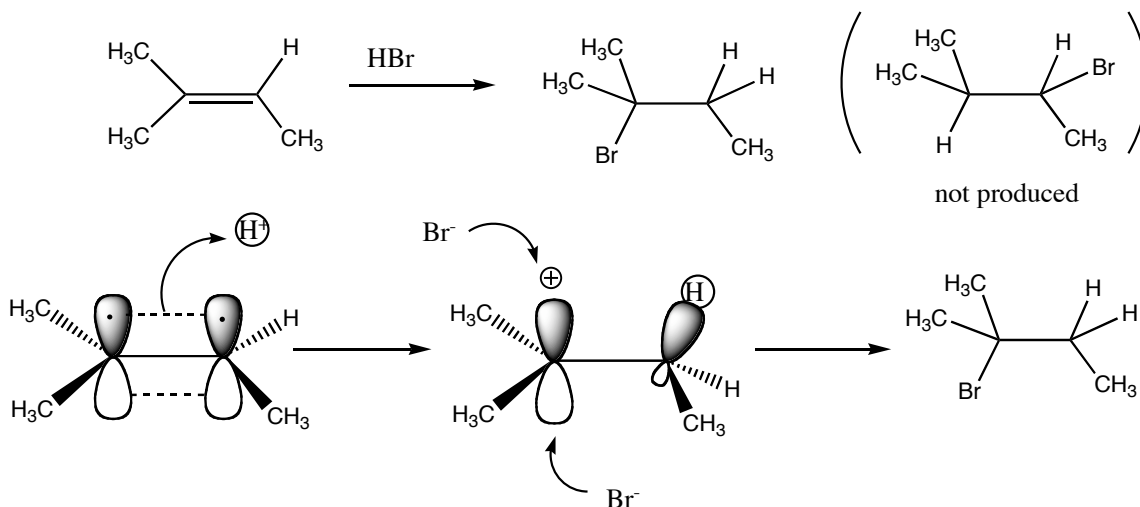
Strong electrophiles shift the electron density of the double bond. Since the electron density of a pi bond is above and below the internuclear axis, the electrons in pi bonds are not as tightly held as those in sigma bonds. Thus the approach of a strong electrophile (or Lewis acid, bearing a partial or formal positive charge, to the pi bond distorts the electron cloud toward the electrophile, leaving one of the carbons of the double bond with a partial or formal positive charge (carbocation):



#### 1. Addition of HBr to alkenes

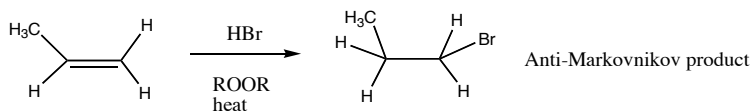
Addition of HBr (HCl, HI) to alkenes is an exothermic process which occurs regioselectively. According to the Markovnikov rule, the proton ends up on the carbon with more hydrogen attached. Alternatively, this may be restated by saying that electrophilic addition of H-X to a double bond occurs in such a way that the more stable carbocation intermediate is produced. Halogen adds to the more highly substituted end of the double bond



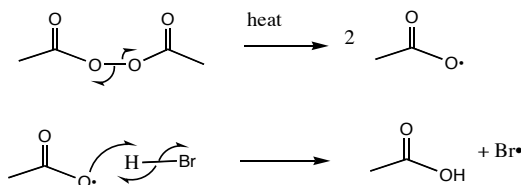


## 2. Free radical additions to double bonds: Anti-Markovnikov regiochemistry

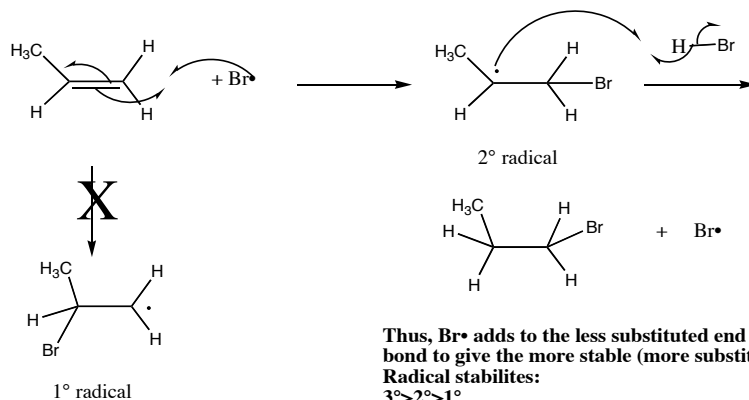
This process was discovered as the “peroxide effect” and only works for HBr addition across alkenes. Peroxides contain a weak O-O bond which homolytically splits upon heating to generate an oxygen radical, initiating a radical chain reaction. Again, reaction of bromine radical ( $\text{Br}\cdot$ , the electrophile) occurs in such a way that the more substituted radical (more stable radical) is produced; reaction of this radical with H-Br generates anti-markovnikov product and  $\text{Br}\cdot$ , which continues the radical chain reaction.



### Initiation:



### Propagation:

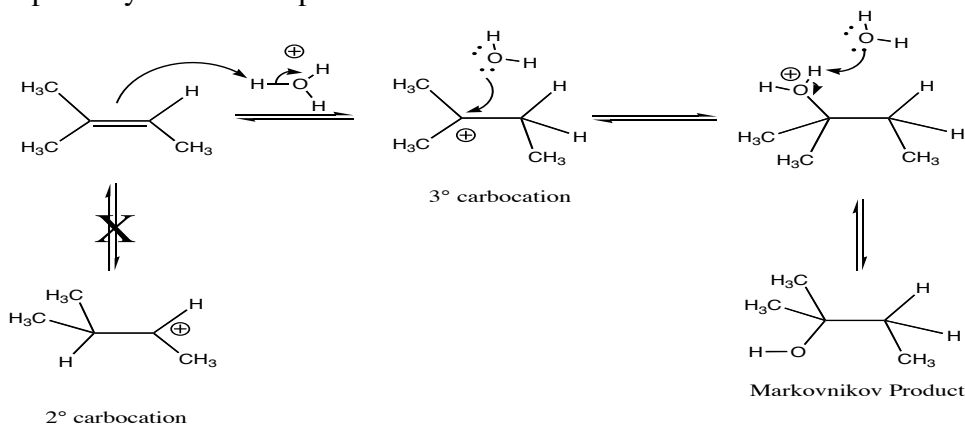


Note again that this peroxide-promoted radical reaction is much faster than ordinary electrophilic addition of H-X only for HBr addition to double bonds.

## II. Hydration of Alkenes

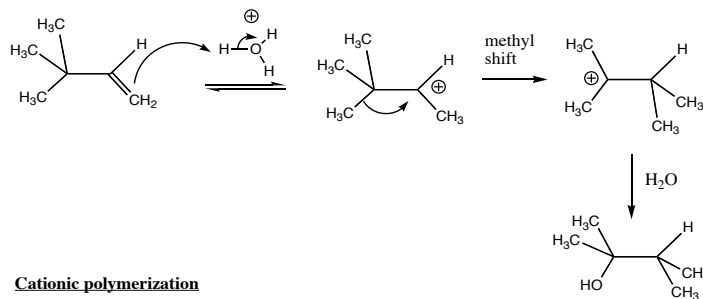
A. Acid-catalyzed hydration of alkenes is the *microscopic reverse* of alcohol dehydration. The equilibrium is driven in the direction of the alcohol product in the presence of excess water. Markovnikov regiochemistry is observed; each step is an equilibrium

*Principle of Microscopic reversibility* → the forward and reverse reaction must follow the same pathway in microscopic detail.

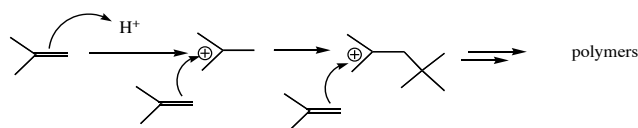


Acid-catalyzed hydration of alkenes is usually not a practical process, since presence of cationic intermediate indicates that rearrangements and polymerization may occur:

### Rearrangement:

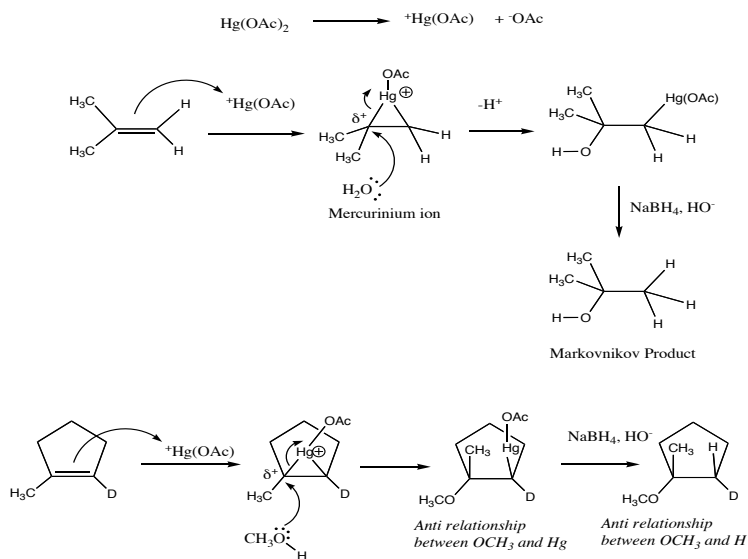


### Cationic polymerization



## B. Oxymercuration/Demercuration of Alkenes: Markovnikov Hydration

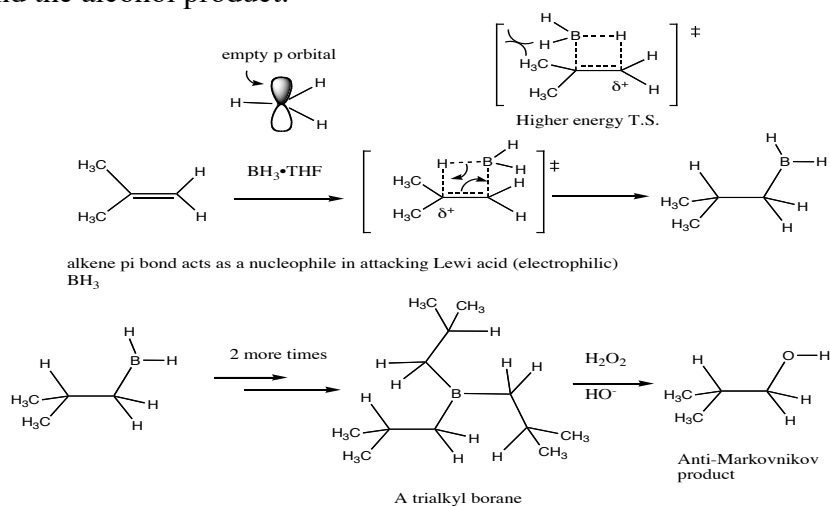
Treating alkenes with mercuric acetate in water or an alcohol solvent is a mild method of obtaining Markovnikov hydration or alkoxylation products. No rearrangements or polymerization is observed in this process, since there is no carbocation intermediate. The reaction occurs through the intermediacy of a mercurinium ion, formed from the reaction of the alkene with  $^+\text{Hg}(\text{OAc})$ . Because of the presence of a partial positive charge on the more substituted carbon of the mercurinium ion intermediate, the nucleophile (water or an alcohol) attacks the more substituted carbon to give the anti-hydroxy-organomercurial intermediate. The C-Hg bond is reduced with  $\text{NaBH}_4$  in  $\text{NaOH}$  to give the alcohol/ether product, in which Markovnikov regiochemistry is observed. Note the anti relationship between the OH (OR) and  $\text{Hg}(\text{OAc})$  in the intermediate.



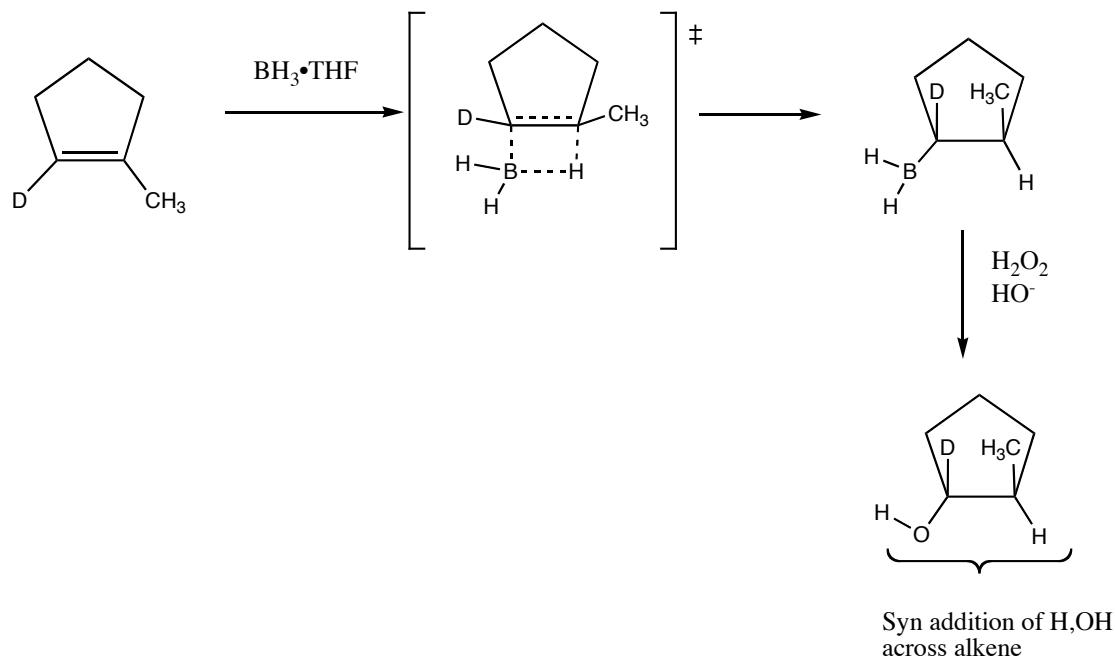
Yields in the oxymercuration/alkoxymercuration/demercuration process are high, the reaction occurs under mild conditions, and no rearrangements or polymerizations are observed

### C. Hydroboration: Anti-Markovnikov hydration of an alkene

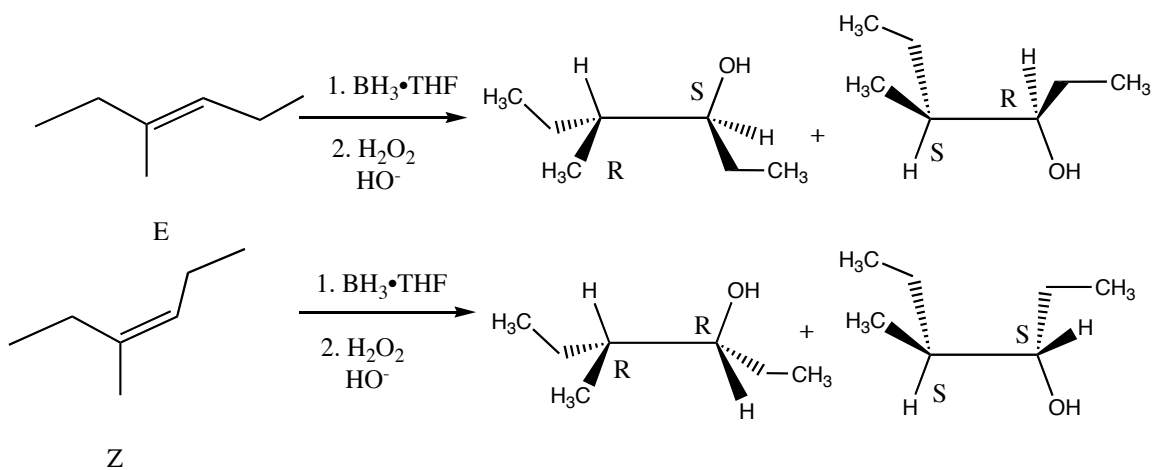
$\text{BH}_3$  is a reagent in which the boron atom is electrophilic (it contains an empty p-orbital on B, since  $\text{BH}_3$  lacks an octet). The reaction occurs in a single step through a four-centered transition state in which the electrophilic boron atom attacks the less hindered carbon atom of the alkene. In so doing, the electron density of the double bond is shifted toward the B atom, leaving the more highly substituted carbon atom with a partial positive charge. This regiochemistry of boron addition to alkenes is also favored by sterics. All three B-H bonds on  $\text{BH}_3$  are reactive, so with 1/3 of an equivalent of  $\text{BH}_3$  to alkene, a trialkyl borane results. The second step of the reaction is treatment of the organoborane with basic peroxide, which oxidizes the C-B bond, producing ultimately boric acid and the alcohol product.



Stereochemically, borane addition to alkenes results in a *syn* addition of H and OH across the double bond:



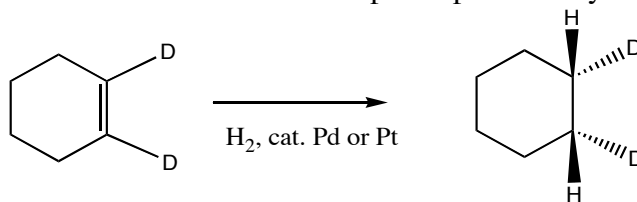
Hydroboration is a Stereospecific Reaction



Hydroboration is also stereospecific: stereoisomeric reactants lead to stereoisomeric products

### III. Catalytic hydrogenation

Addition of H<sub>2</sub> across alkenes requires a transition metal catalyst. The *syn* addition of hydrogen gas occurs at the metal surface in a stepwise process. Hydrogen is added to

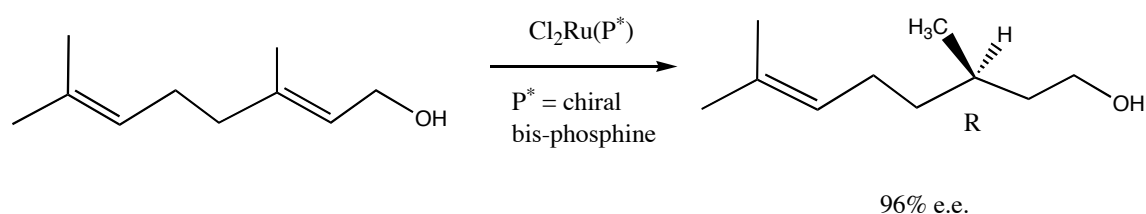
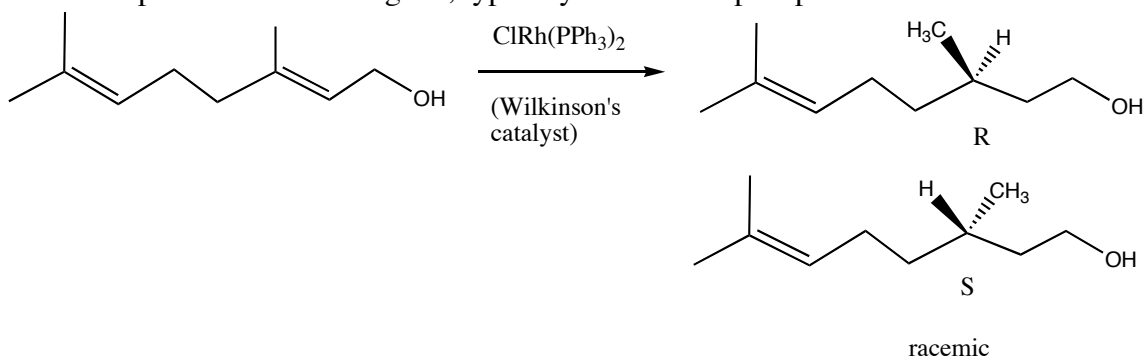


the same side of the alkene that is adsorbed to the metal surface.

**Heterogenous catalysis** takes place when the reactants (alkene, H<sub>2</sub> gas) are in a different phase from the reactants

**Homogenous catalysis** takes place when the reactants and catalyst are in the same phase. Wilkinson's catalyst is an example of a homogenous catalyst.

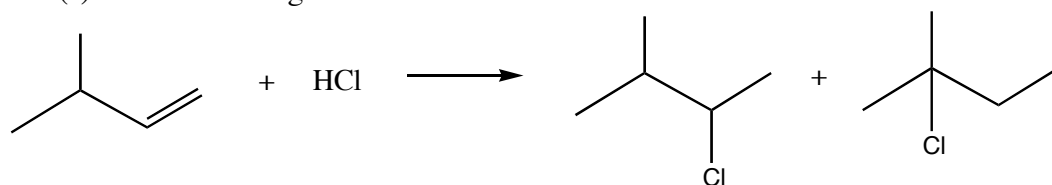
A **chiral catalyst** may be employed to enantioselectively reduce double bonds. This process is very important in chemical industry. A chiral catalyst consists of a transition metal complexed to a chiral ligand, typically a chiral bis-phosphine.



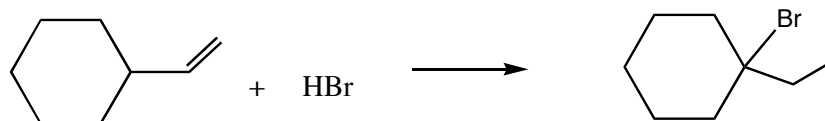
Additional Problems for practice:

1.) Write a mechanism which accounts for the formation of the observed product(s) in the following reactions:

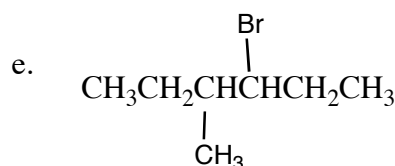
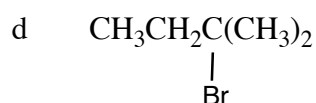
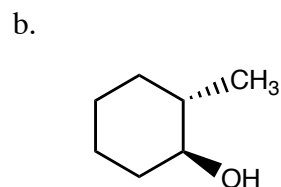
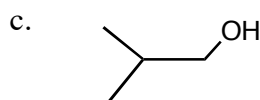
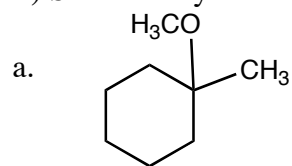
a.



b.



2.) Show how you could prepare the following compounds from an alkene:



3.) Draw mechanisms for and show the products of the following reactions. Remember to indicate the regio- and stereochemistry of the products

