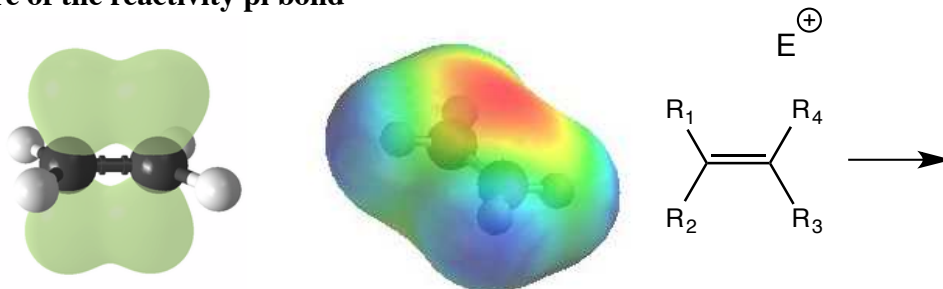


# Chapter 9: Addition Reactions of Alkenes

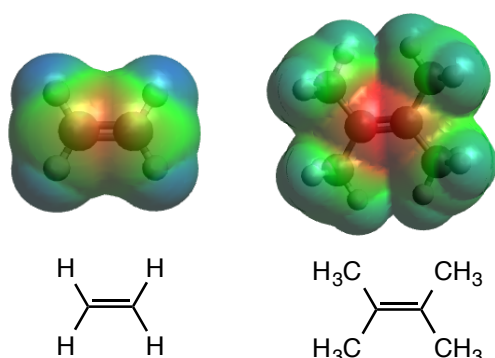
[Sections: 9.1-9.8]

## Nature of the reactivity pi bond

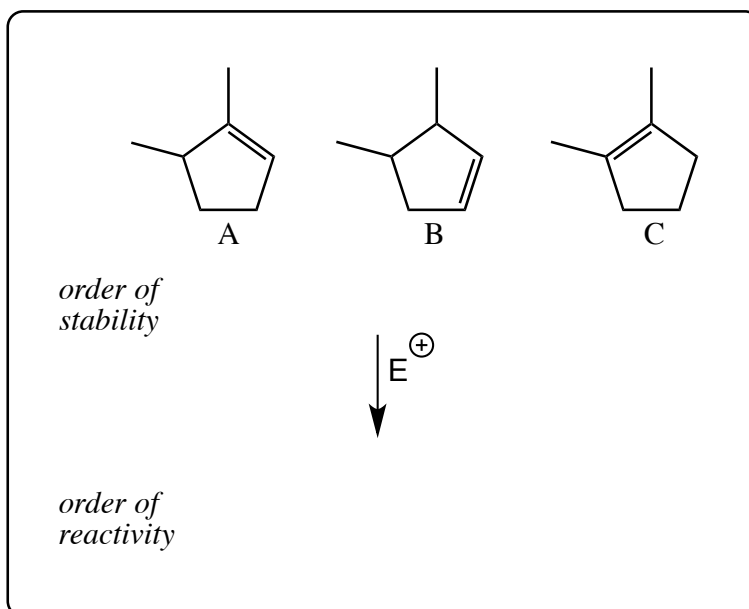
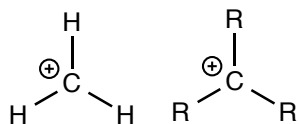


- *pi ( $\pi$ ) bond is weak (compared to sigma ( $\sigma$ ) bond)*
- *clouds of electron density above and below the plane defined by the atoms of the molecule*
- *alkenes are electron-rich, and therefore good electron donors*
- *susceptible to reaction with electrophiles*

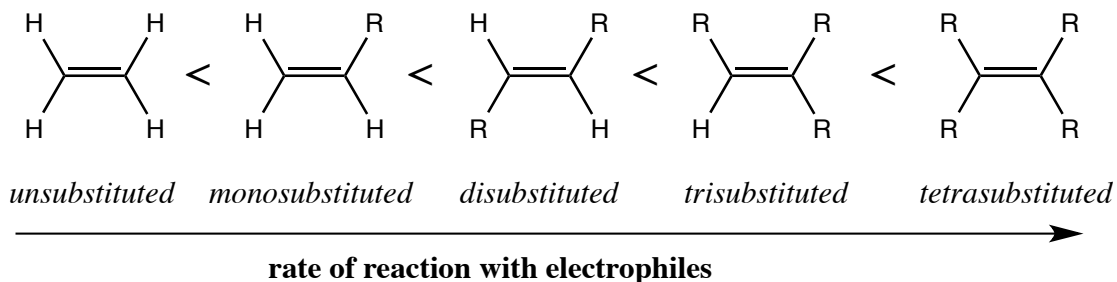
## Relative reactivities of alkenes



*flashback to carbocations:*

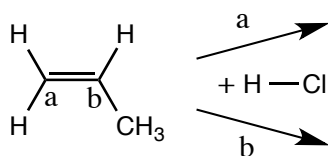
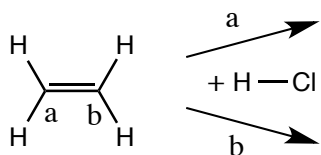


- *electron density of the pi bond increases with increasing substitution about the double bond*

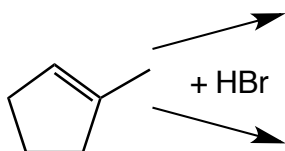


- *remember: earlier we determined that increasing substitution about the double bond increased stability!*
- *thus, if we have a set of isomeric alkenes, the most stable isomer is also be the most reactive towards electrophiles!*

## Hydrohalogenation

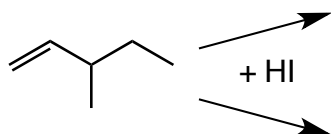


- hydrohalogenations are addition reactions
- generally exothermic since two sigma bonds are formed at the expense of a broken pi bond
- initial protonation favors formation of the more stable carbocation intermediate
- the carbocation intermediate is trapped by the halide nucleophile to form the final product
- since the most stable carbocation intermediate is the more substituted carbocation, the final product corresponds to the nucleophile (the halide) being attached to the more substituted carbon of the C=C bond
- this is called Markovnikov addition



Vladimir Markovnikov  
1838-1904

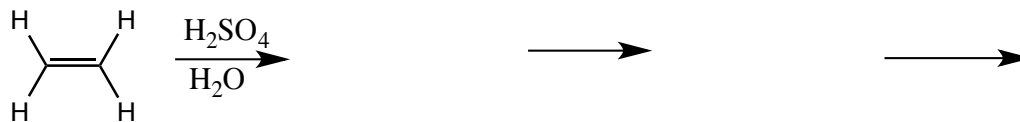
	HF	HCl	HBr	HI
process	hydrofluorination	hydrochlorination	hydrobromination	hydroiodination
$pK_a$	3.2	-8	-9	-10
relative rate in reaction w/ alkenes				



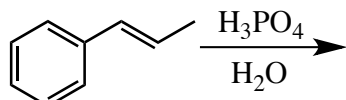
- as with ANY reaction that involves carbocation intermediates, be aware that rearrangements of the intermediate carbocations to more stable carbocations might occur!

Problems: 1 (Alkenes + Reagent A), 2

## Acid-Catalyzed Hydration



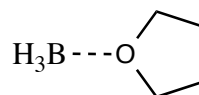
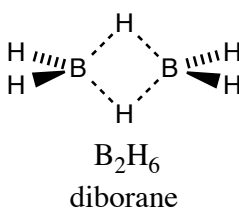
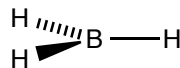
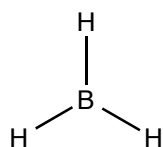
- either  $H_2SO_4$  or  $H_3PO_4$  are utilized for this reaction. Both have non-nucleophilic conjugate bases
- the net result is addition of  $H_2O$  across the double bond
- since a carbocation intermediate is formed, the  $OH$  group ends up at the more substituted carbon
- this is Markovnikov addition



Problems: 1 (Alkenes + Reagent B)

## Hydration via Hydroboration

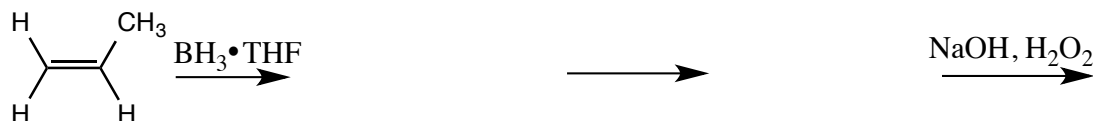
$BH_3$  = borane



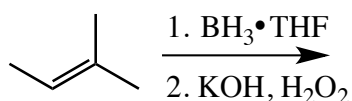
$BH_3 \cdot THF$



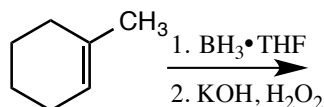
**H.C. Brown**  
1912-2004  
Nobel Prize 1979



Predict the major product(s) of the following reaction:

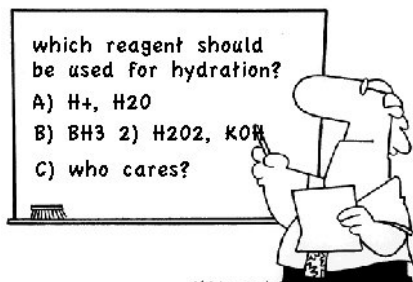


- there is actual never a true carbocation intermediate, so there are no rearrangements possible
- the net result is addition of  $H_2O$  across the double bond
- this is anti-Markovnikov addition

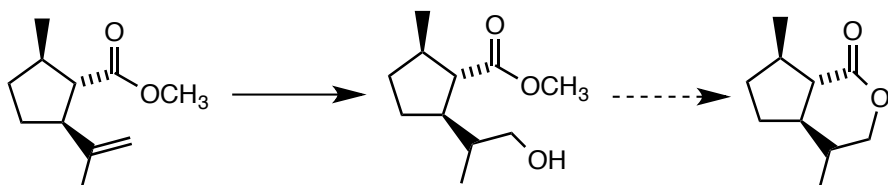


- in hydroboration hydrations, the  $H$  and  $OH$  are delivered to the same face of the  $\pi$  bond
- addition to the same face of a  $\pi$  bond is called "syn" addition
- this is considered to be a "stereospecific" reaction since a single stereoisomer results although two or more might be conceivably formed

Problems: 1 (Alkenes + Reagent C)

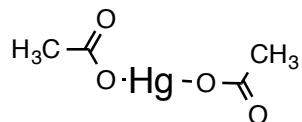
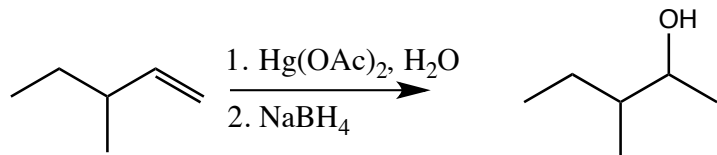
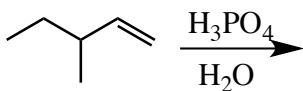
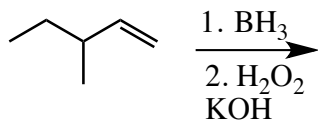
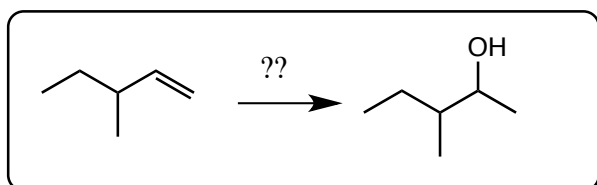


wasp *Alloxysta victrix*



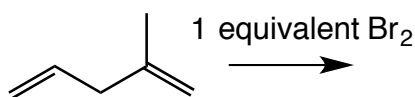
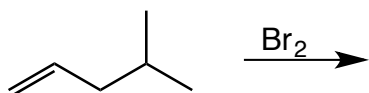
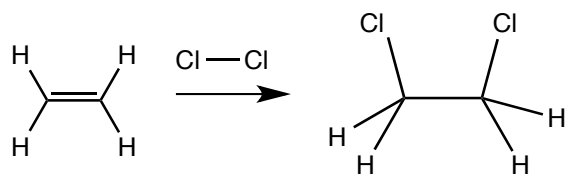
wasp pheromone

### Hydration via Oxymercuration



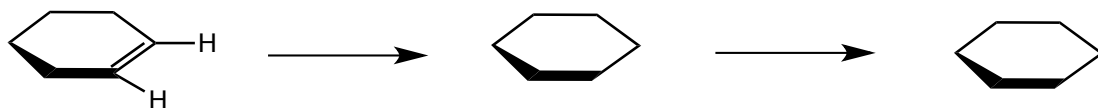
- process of oxymercuration
- two-step process
- result is Markovnikov hydration without possibility of rearrangement!

## Halogenation



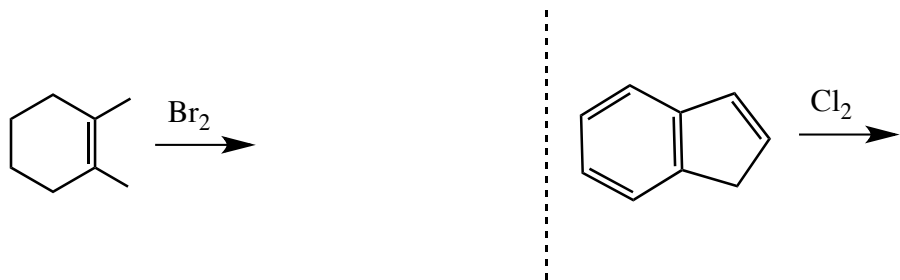
- halogenations are addition reactions
- generally exothermic since two fairly strong C-X bonds are formed at the expense of a broken pi bond and a weak X-X bond
- $\text{Br}_2$  and  $\text{Cl}_2$  engage in reactivity.  $\text{F}_2$  is TOO reactive and  $\text{I}_2$  is too unreactive
- NOTE: HX reactions and  $\text{X}_2$  reactions are completely different!

Observed:



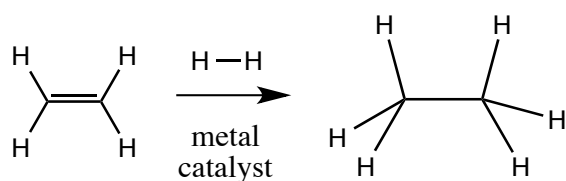
**bromonium ion**

- bromonium ions are very strained intermediates due to angle strain and the fact that a positive charge is forced onto an electronegative atom
- bromonium ions are very reactive and seek to eliminate the characteristics that contribute to the strain
- reaction with  $\text{Br}^-$  to form the 1,2-dibromide relieves these sources of strain
- the net result is addition of the two bromine atoms onto either face of the original pi bond
- such addition is referred to as "anti" addition
- the reaction is therefore stereospecific

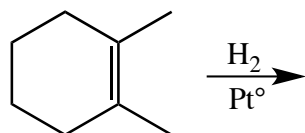
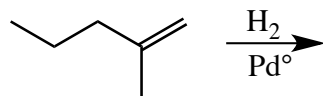
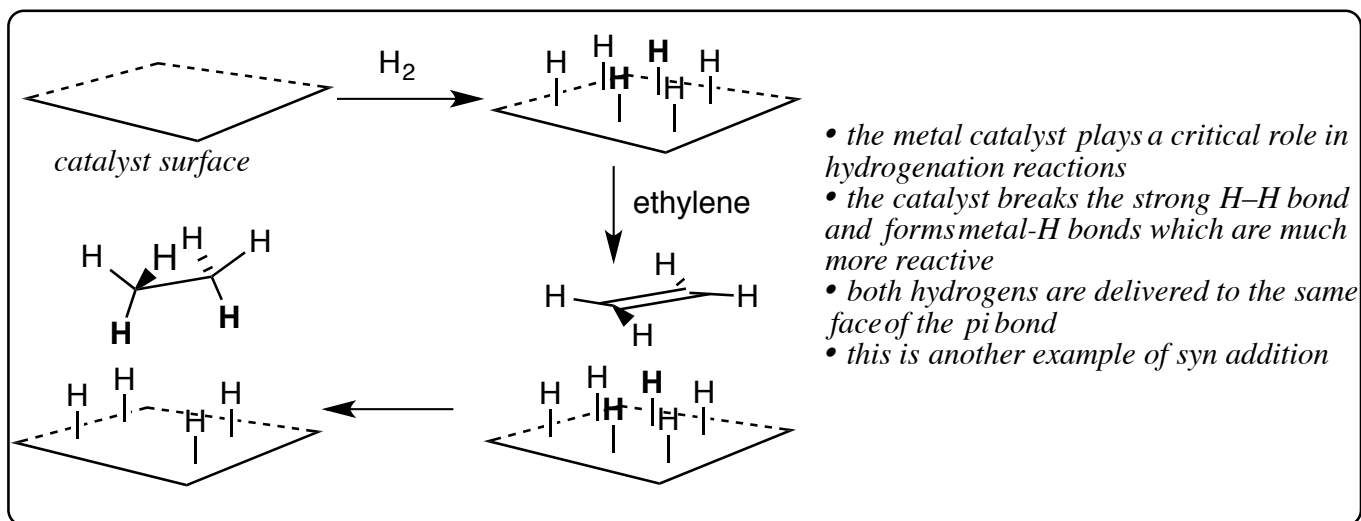


Problems: 1 (Alkenes + Reagent F)

## Hydrogenation



- hydrogenations are addition reactions
- strongly exothermic since two strong CH sigma bonds are formed at the expense of a broken pi bond
- no reaction occurs in the absence of a suitable catalyst!
- the typical catalysts are  $\text{Pd}^\circ$ ,  $\text{Pt}^\circ$ ,  $\text{Rh}^\circ$  or  $\text{Ni}^\circ$

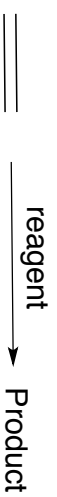


- hydrogenations are stereospecific

## Chapter 9 *Essential Concepts*

1. Understand the differences between  $\pi$  and  $\sigma$  bonds and the ramifications on reactivity
2. Know how and why substitution patterns on C=C bonds affect stability and reactivity
3. Be able to predict reactions of HX with alkenes in the context of Markovnikov addition, the products formed, and the factors that affect rate of reaction including the nature of HX and substitution on the C=C bond. You should be able to draw the mechanism of this reaction.
4. Know the three ways of hydrating C=C bonds (acid catalyzed, hydroboration and oxymercuration) and their impact on products formed (including stereochemistry where relevant for the hydroboration reaction). You should be able to draw the mechanism for the acid catalyzed reaction (you will not need to draw the mechanism for hydroboration or oxymercuration)
5. Know how  $\text{Cl}_2$  and  $\text{Br}_2$  add to C=C bonds (including the mechanism) and be able to predict the products (including stereochemistry where relevant). Know why  $\text{I}_2$  and  $\text{F}_2$  are not used for these reactions.
6. Understand how hydrogenation of C=C bonds takes place, the role of the metal catalyst, and be able to predict products formed, including stereochemistry where relevant.

## Summary of Alkene Reactions



Rearrangements

<u>Reagent</u>	<u>Product Type</u>	<u>Process Name</u>	<u>Product Name</u>	<u>Orientation</u>	<u>Possible?</u>
HX (X = Cl, Br, I)		hydrohalogenation	alkyl halide	Markovnikov	YES
H <sub>2</sub> O, H <sub>2</sub> SO <sub>4</sub> or H <sub>3</sub> PO <sub>4</sub>		hydration	alcohol	Markovnikov	YES
1. BH <sub>3</sub> 2. H <sub>2</sub> O <sub>2</sub> , KOH		hydration	alcohol	syn and anti-Markovnikov	NO
1. H <sub>2</sub> O, Hg(OAc) <sub>2</sub> 2. NaBH <sub>4</sub>		hydration	alcohol	Markovnikov	NO
X <sub>2</sub> (X = Cl, Br)		halogenation	1,2-dihalide	anti	NO
H <sub>2</sub> , Pt (or Pd or Ni)		hydrogenation	alkane	syn	NO