CHEM 261 Nov. 1, 2018

## Recall:

## **Addition Reactions**

- Occurs on double bonds and triple bonds

$$C = C$$

$$A - B$$

$$\delta + \delta -$$

$$C = C$$

$$A - B$$

$$\delta + \delta -$$

## Example: Hydrogenation

$$H_2$$
, Pd

## Halogenation: Addition of halogens across a double bond

$$X = C$$
 $X = C$ 
 $X =$ 

## Ex #1) Cyclopentene

**Achiral** 

trans-1,2-Dibromocyclopentane

Both enantiomers formed (1:1 racemate)

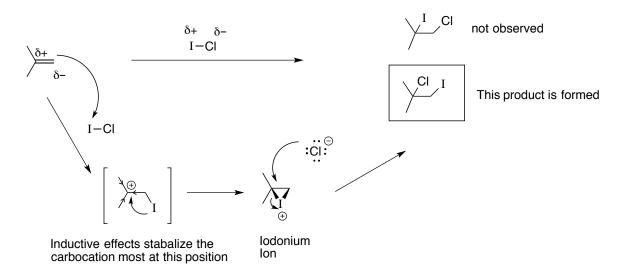
# Ex #2) 1,2-dimethylcyclopentene

$$Br_2$$
 $Br_2$ 
 $Br_2$ 
 $Br_3$ 
 $Br_4$ 
 $Br_5$ 
 $Br_5$ 
 $Br_5$ 

trans-1,2-Dibromo-1,2-dimethylcyclopentane

## Mechanism:

## Ex #3) 2-Methylpropene



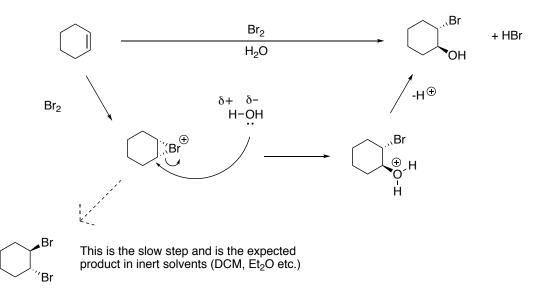
**Markovnikov's Rule:** In an addition reaction, the positive end of an A–B system (e.g. I–Cl) adds to the least substituted end of the double bond to make the more stable carbocation.

# Ex #4) Cyclohexene

$$\begin{array}{c} Cl_2 \\ \hline \\ Cl_2 \\ \hline \\ H_2O \end{array} \begin{array}{c} Cl \\ \hline \\ OH \end{array} \begin{array}{c} Chlorohydrin \\ \hline \\ OMe \end{array}$$

## **Mechanisms:**

#1) Addition of an alcohol functional group (in H<sub>2</sub>O)



#2) Addition of an ether functional group (in CH<sub>3</sub>OH)

$$\begin{array}{c|c} & & & & \\ & & & \\ \hline & & & \\ \hline & & \\ \hline$$

## **Summary:**

$$c=c$$
  $x_2$   $x_2$ 

$$C=C$$
 $X_2$ 
 $R=H \text{ or Alkyl}$ 
 $X_2$ 
 $X_3$ 
 $X_4$ 
 $X_5$ 
 $X_6$ 
 $X_7$ 
 $X_8$ 
 $X_8$ 
 $X_9$ 
 $X_9$ 

#### Ex #5)

$$\begin{array}{c|c} & & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$

#### Ex #6)

In the above example, the intramolecular reaction (meaning within the same molecule) occurs much much  $\underline{FASTER}$  than the intermolecular reaction (between two or more molecules). This means that the -OH group will attack the iodonium ion much faster than the  $\Gamma$  group because it is an intramolecular reaction.

Intramolecular reaction almost always beats intermolecular reactions.

# Ex #7)

