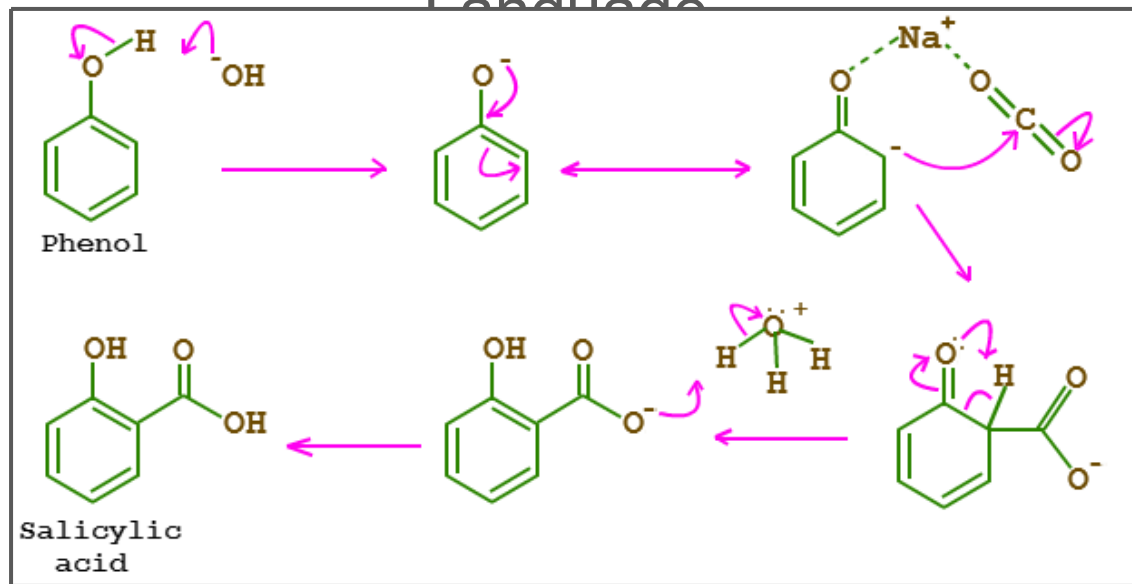


# Chapter 8 - Organic Chemistry

## Mechanisms

Based on David Klein's Organic Chemistry as a Second Language

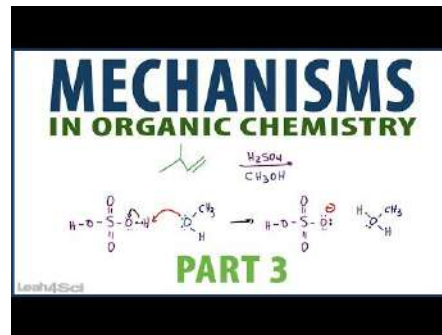
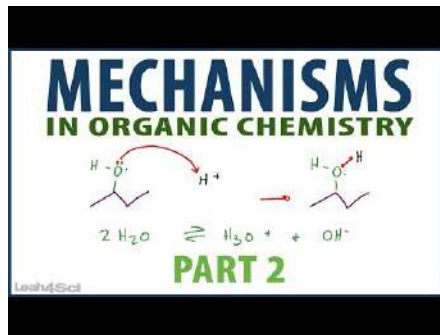
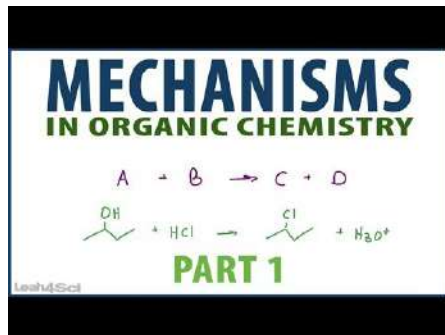


# 8.0 Introduction to Mechanisms

**Mechanisms** illustrate how the electrons move during a chemical reaction

- All reactions involve the flow of electron density
- Mechanisms use curved arrows to show this flow of electrons
  - They use curved arrows like we saw in resonance

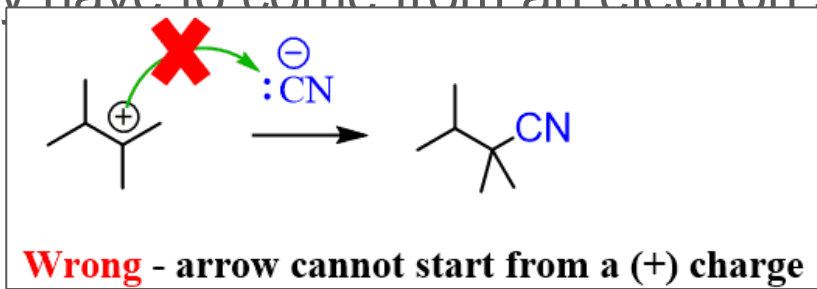
Below are a series of videos that are helpful when learning about mechanisms:



# 8.1 Curved Arrows

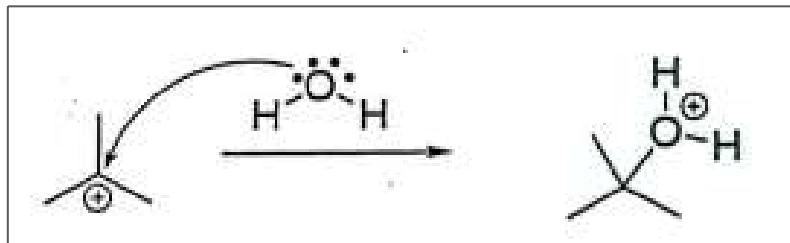
**Tail**  **Head**

- Similar to arrows from resonance
  - BUT we are actually moving atoms/electrons now to break and form bonds
  - We still cannot violate an octet for second row elements
  - 3 basic types or categories of what arrows show
- **Heads of arrows** show where the electrons are going (acceptor)
  - Kind of like little sticky slap hands that “grab” onto atoms
- **Tails of arrows** show where electrons are coming from (donor)
  - So they have to come from an electron source

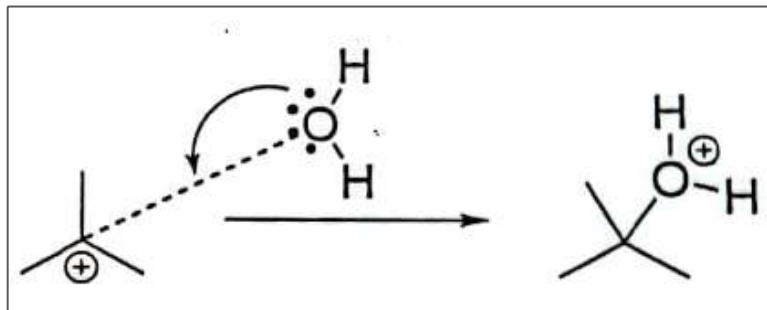


## 8.1 #1 Curved Arrows from a LP to a Bond

- The electrons from a lone pair reach out and “grab” onto an atom to form a single bond, joining them together.
- Notice the overall charge is conserved (*like in resonance*)

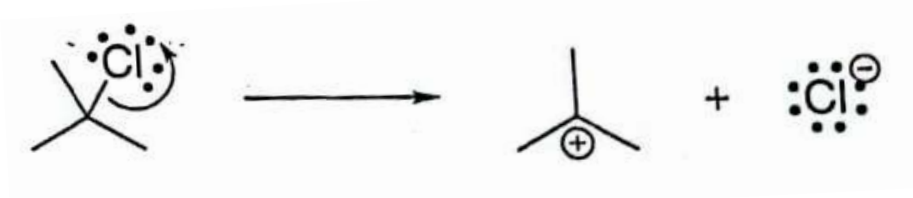


- You may also see it depicted like this (*less common*)

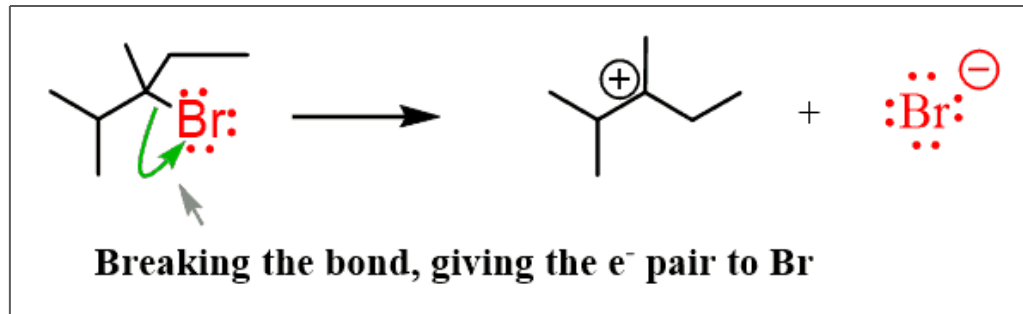


## 8.1 #2 Curved Arrows from a Bond to a LP

- The electrons that were involved in a bond will form a lone pair on one of the attached atoms, severing it from the original molecule.
- Notice the overall charge is conserved (*like in resonance*)

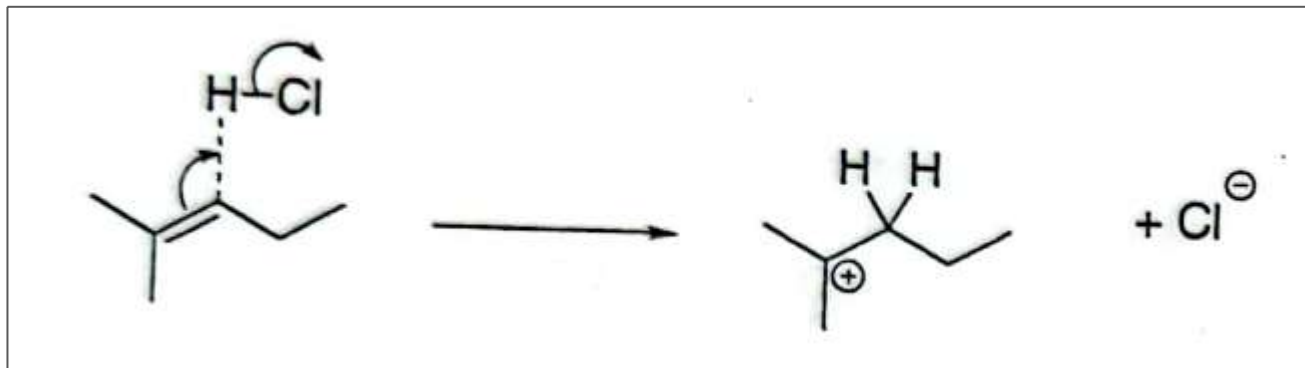


- *Make sure the head of the arrow points at the atom the electrons are attaching to....*



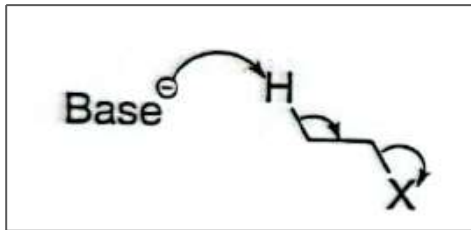
## 8.1 #3 Curved Arrows from a Bond to a Bond

- The electrons that were involved in a pi bond will “reach out” and “grab” onto an atom to form a single bond to.
  - The pi bond goes away, but a new single bond is formed
  - Sometimes the atom that was attached will need to be released from another atom (*see example below*)
- Notice the overall charge is conserved (*like in resonance*)

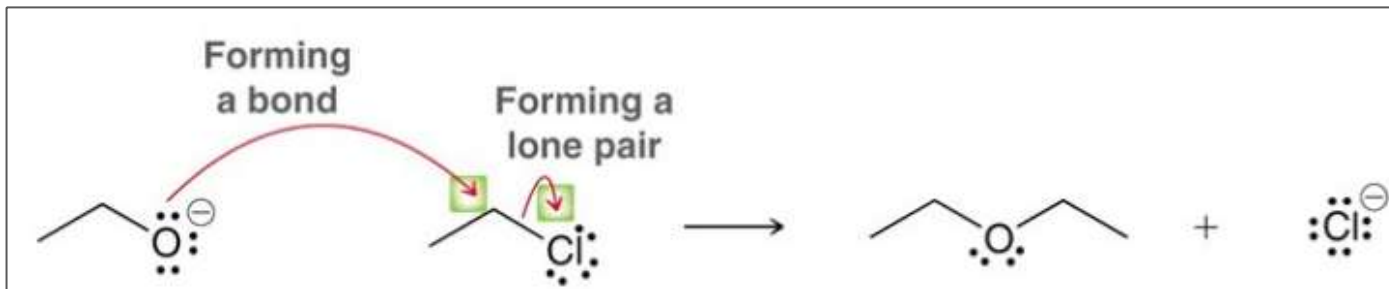
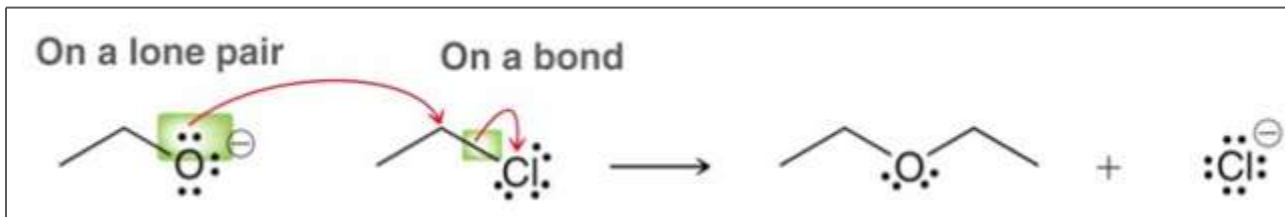


## 8.1 ALL 3 TYPES of Curved Arrows

- As we saw in the last example, sometimes you will need multiple curved arrows throughout a mechanism.



You could even see all three types of arrows used in one problem!



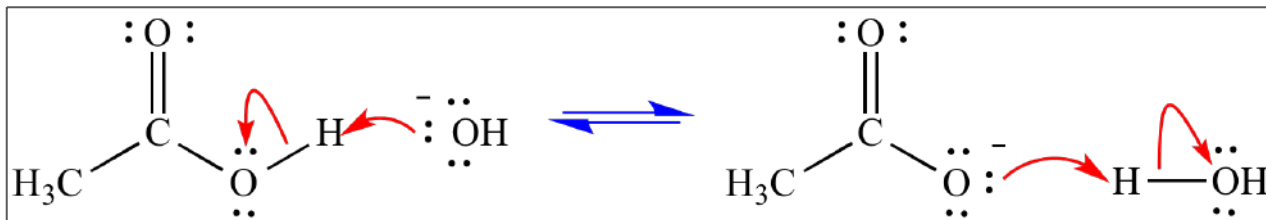
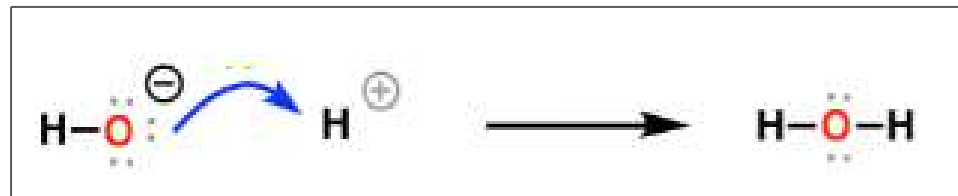
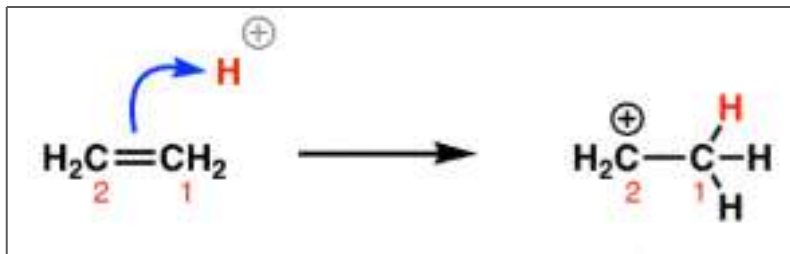
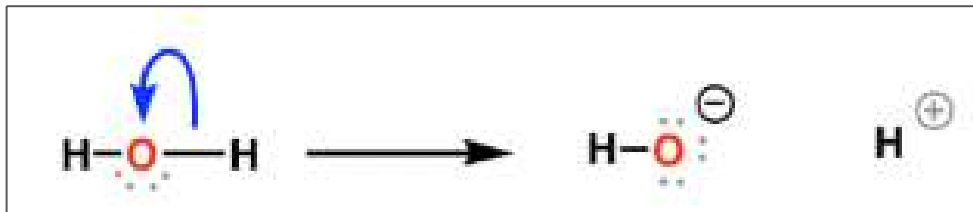
# 8.1 Practice for Curved Arrows

- Classify each of the arrows shown as one of the 3 types:

**1** = LP  $\rightarrow$  B

**2** = B  $\rightarrow$  LP

**3** = B  $\rightarrow$  B



Read 8.1 then complete the practice problems 8.2 - 8.7 on pages 172 - 173.

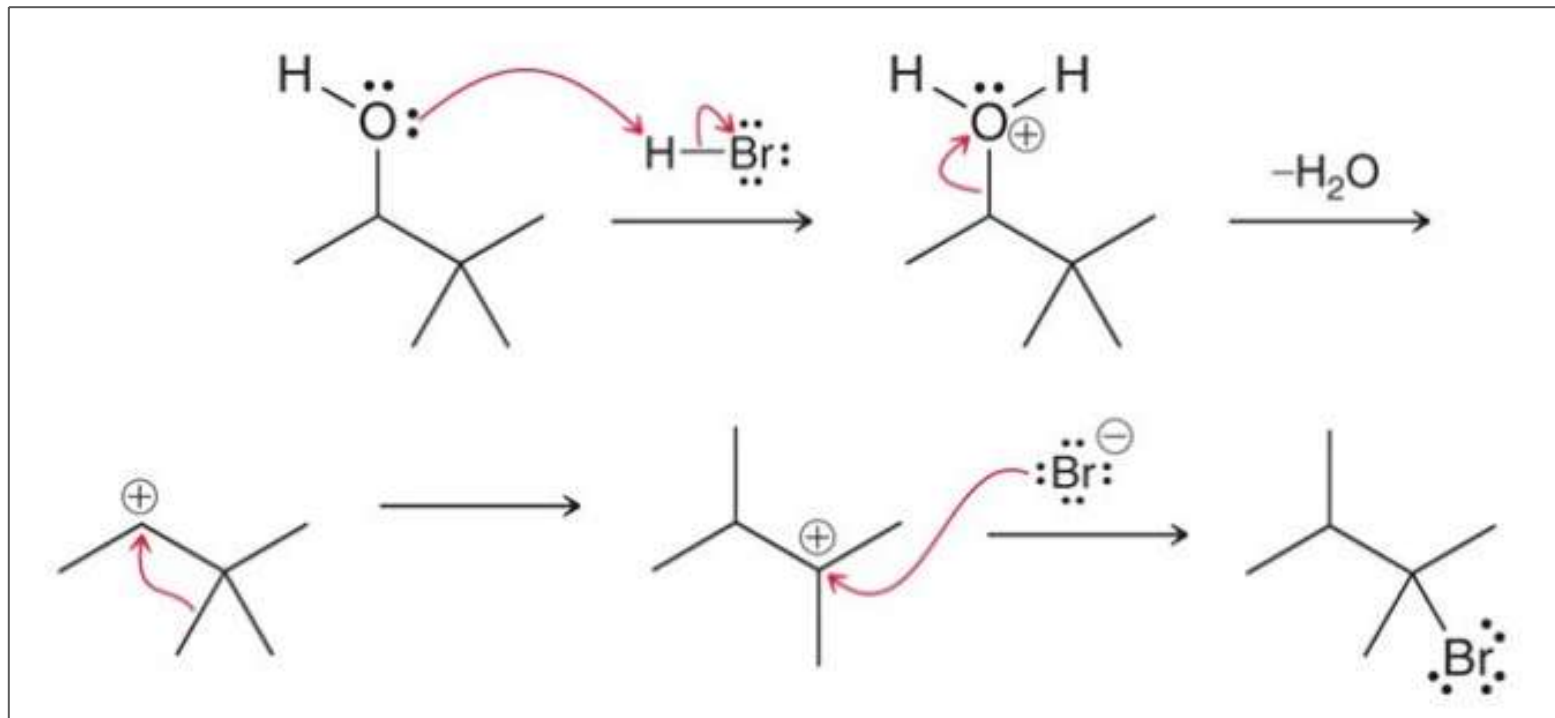
## 8.1 Practice for Curved Arrows

- Classify each of the arrows shown as one of the 3 types:

**1** = LP  $\rightarrow$  B

**2** = B  $\rightarrow$  LP

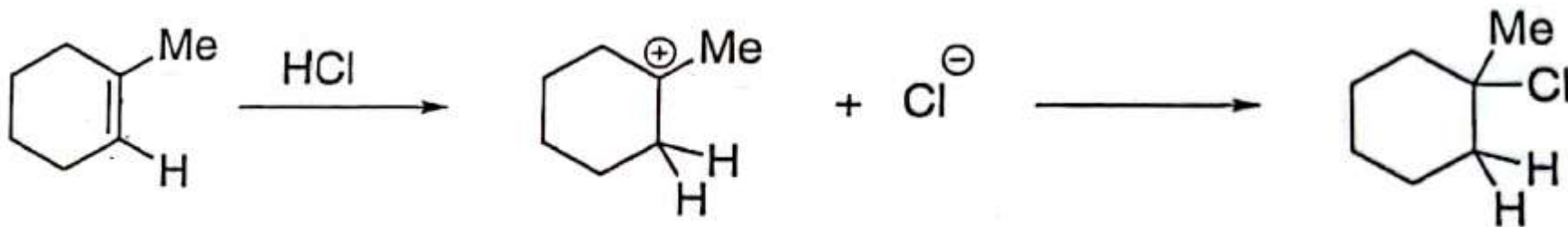
**3** = B  $\rightarrow$  B



## 8.2 Arrow Pushing

- Now that we know the 3 types of arrows, we can apply them to looking at the beginning and ending products of a chemical reaction.
  - Electron density always flows in one direction
  - Use the charges to help you determine where the “push” went to

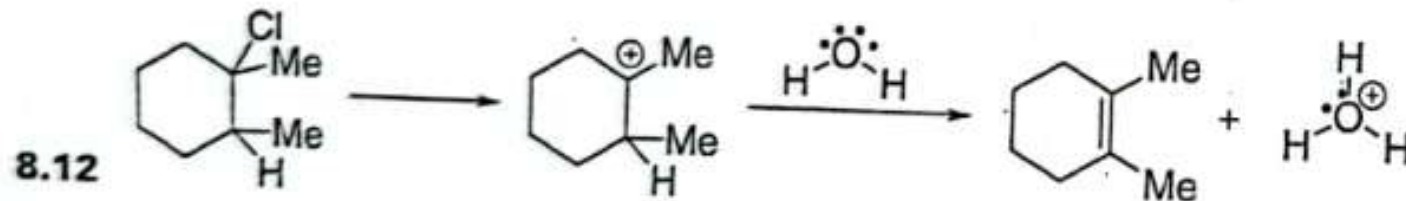
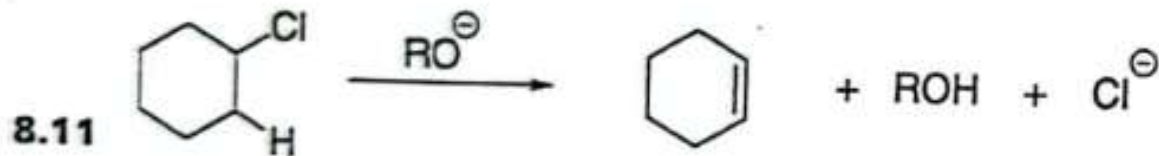
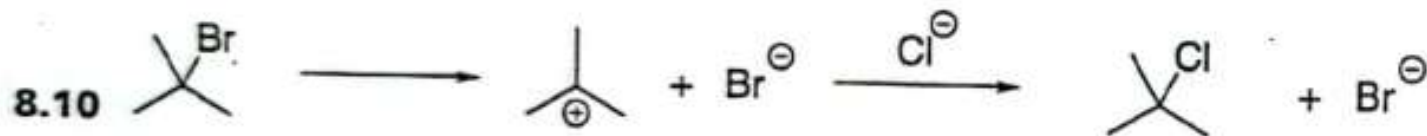
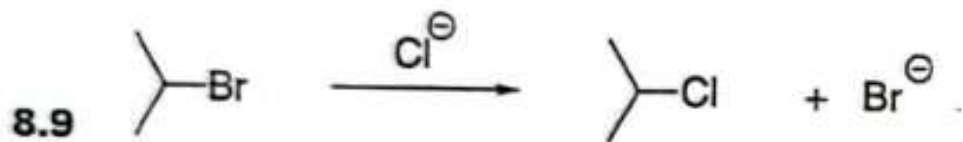
*Draw in the curved arrows for each step of the reaction*



## 8.2 Arrow Pushing Practice

These are the 8.2 Klein Practice problems from page 174!

*Remember, arrows show the movement of electrons, NOT atoms!*



## 8.3 Drawing Intermediates & Predicting Products

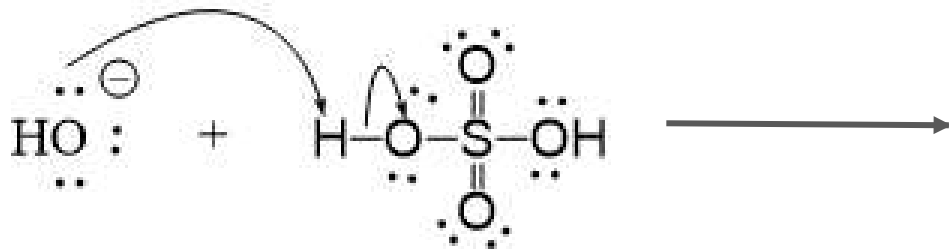
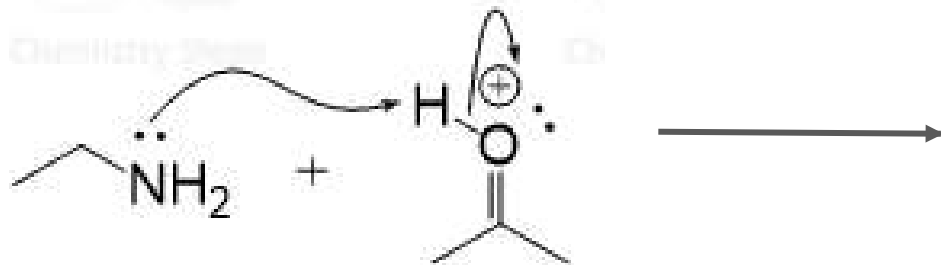
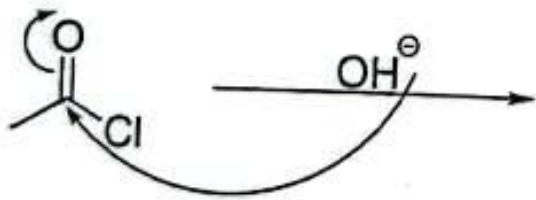
- Intermediates are short-lived structures that exist for a very small amount of time before reacting further.
  - Often critical in understanding the the next step of the reaction
  - Often have “unstable” regions that will help to predict what will happen next

Let's read the arrows. The first arrow is from a lone pair to form a bond. The arrow shows electrons in a lone pair on a nucleophile (anything that is electron rich) forming a bond with a carbon atom. The second arrow is from a bond to a bond. The third arrow goes from a bond to form a lone pair. All in all, these arrows serve as a road map for drawing the intermediate:



## 8.3 Practice Drawing Intermediates & Predicting Products

- “Follow” the arrows and draw the intermediate(s) created.



Read 8.3 then  
complete the  
practice  
problems 8.14 -  
8.19 on pages  
177 - 178.

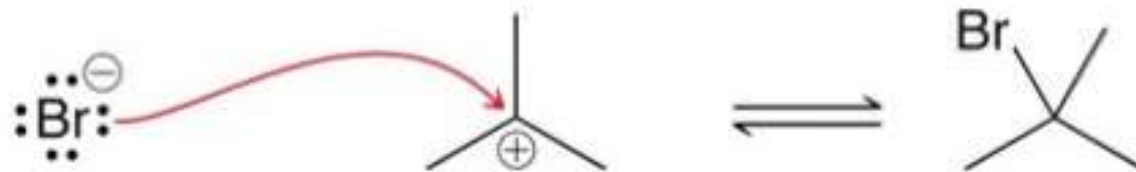
## 8.4 Nucleophiles and Electrophiles

**Nucleophiles** are the “attacker” compounds.

- They have a region that is electron-rich where the arrow will originate. (LP or bond)

**Electrophiles** are the compounds that are “being attacked”.

- They have a region that is electron-poor where the arrow will attach to/bond.



**Nucleophile**

**Electrophile**

Read 8.4 then complete the practice problems 8.21 - 8.24 on pages 178 - 179.

**Nucleophiles  
and  
Electrophiles  
MADE EASY!**

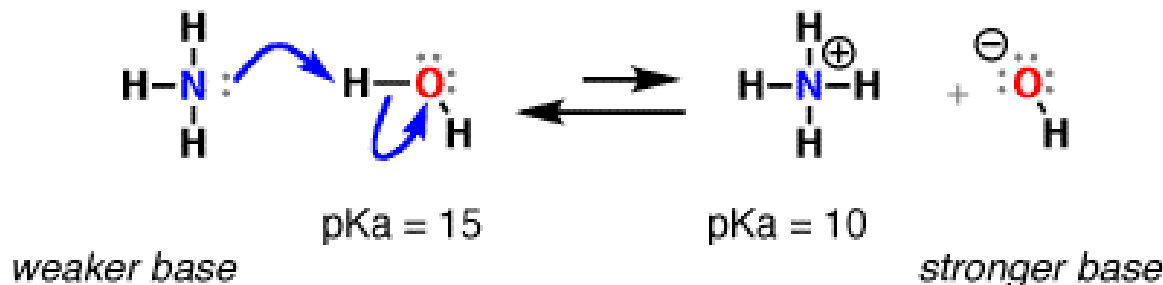


## 8.5 Bases Versus Nucleophiles

**Base** - removes an  $\text{H}^+$  then “runs away with it”

- A base donates a pair of electrons to a proton

*Example*



**These can be confused with Nuc. because they appear to be attacking the electrophile!**

### How do we measure basicity?

- Because most species can participate in reversible acid-base reactions, we can measure basicity by the position of an *equilibrium*.
- In other words, we're measuring *relative stability* of the species involved. "Stability" is a *thermodynamic* property.

**Acid-base reactions reflect relative stabilities**

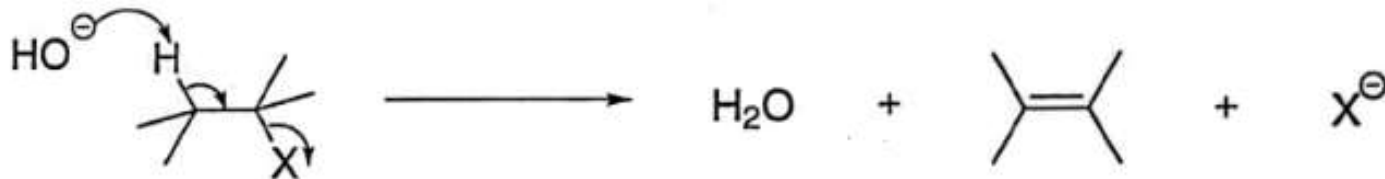
## 8.5 Bases Versus Nucleophiles

The difference between bases and nucleophiles is a difference of **function**.  
*For example, -OH can act as either a Nuc. or a base!*

**Nucleophile** - latches onto a compound (the attacker)



**Base** - removes an  $\text{H}^+$  then “runs away with it”



# 8.5 Bases Versus Nucleophiles

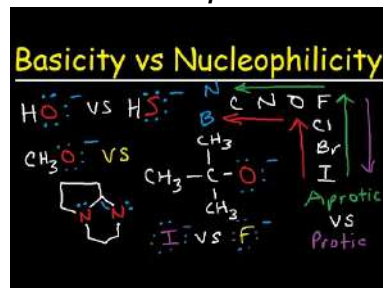
**Nucleophile** - latches onto a compound

- Analyzed by nucleophilicity: measures how quickly a reagent will attack another compound
- Argument of **kinetics** (speed/rate of reaction)
- **Factor #1: Steric hindrance.** Reactions where nucleophiles attack carbon-based electrophiles are significantly more sensitive to steric effects, because empty orbitals on carbon are not as accessible. Steric hindrance is like a fat goalie.
- **Factor #2: Solvents.** The medium (solvent) in which a reaction takes place can greatly affect the rate of a reaction. Specifically, the solvent can greatly attenuate (reduce) the nucleophilicity of some Lewis bases through hydrogen bonding.

**Base** - removes an  $H^+$

- Basicity measure base strength
- Determined from stability of the base and the position of equilibrium
- Does not reflect how quickly the equilibrium is reached
- Argument of **thermodynamics**

Helpful video - but gets more into chapters 9/10



Read 8.5 then complete the practice problems 8.26 - 8.33 on pages 180 - 181.

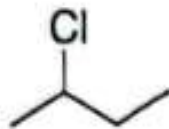
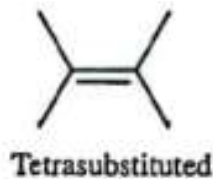
## 8.6 The Regiochemistry is contained within the Mechanism

**Regiochemistry:** refers to where the reaction takes place within the molecule

\*Very important in elimination and addition reactions!

Take a look at this reaction. There are two possible products - *determine how the double bond is substituted for each option.*

### Double Bond Substitutions:



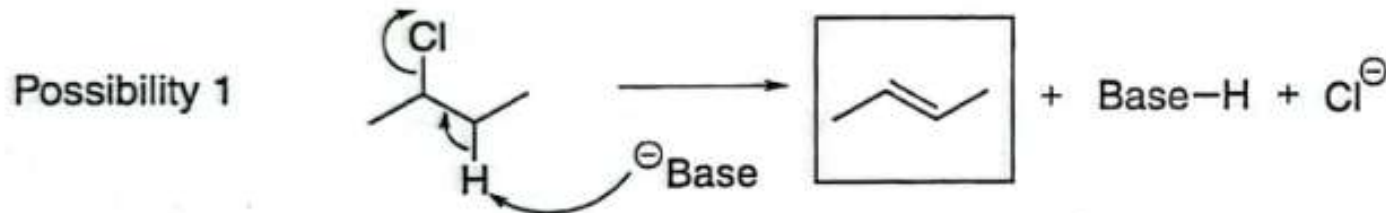
*TWO possible products! This will be a problem of regiochemistry!*



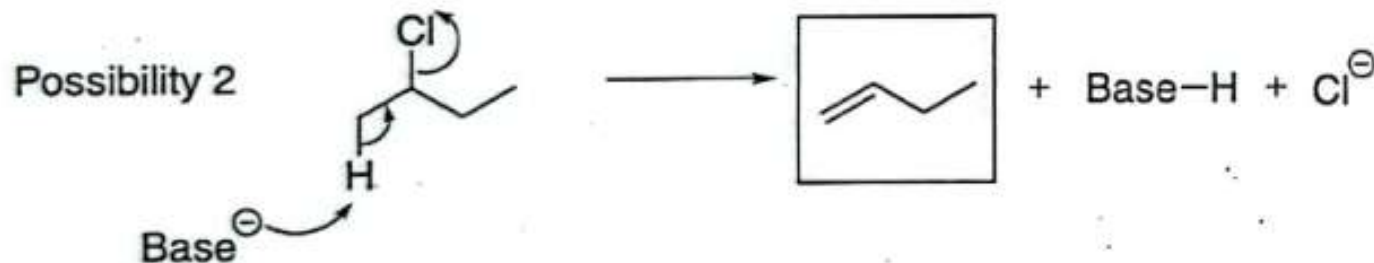
## 8.6 The Regiochemistry is contained within the Mechanism

**Elimination Reactions:** a “leaving group” leaves and a double bond forms. (*There is also a H that usually gets ripped off somewhere too, but it isn't as obvious*)

Check out the reaction below, it could form two different products! *The mechanism behind the reactions are what will tell us which one is more likely to occur.*



The “higher substituted” product is called the **Zaitsev Product** (*typically more common*)

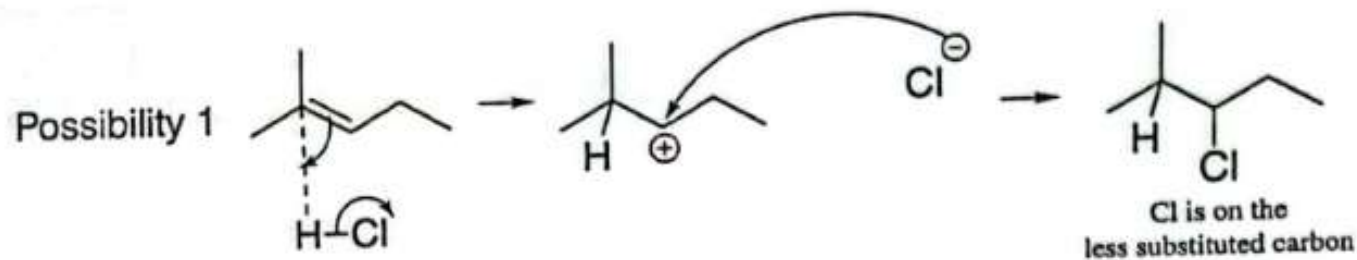


The “lower substituted” product is called the **Hoffman Product** (*typically less common*)

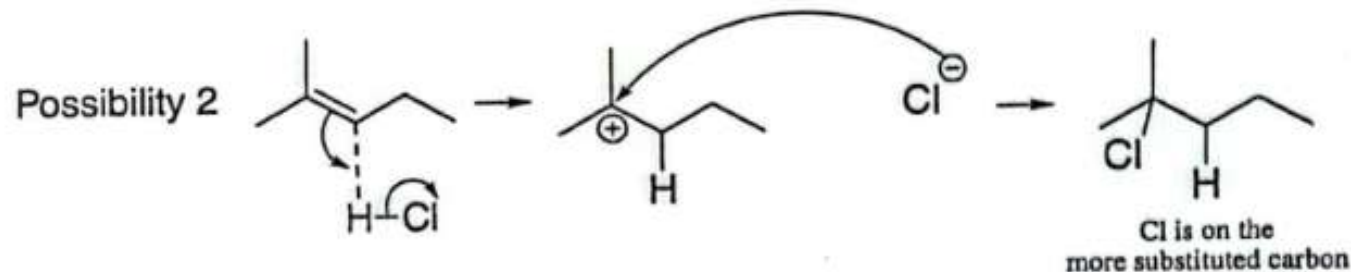
## 8.6 The Regiochemistry is contained within the Mechanism

**Addition Reactions:** The electrons from a double bond “reach out” and grab onto an atom. (*There is also a H that gets added on. Looks like the opposite of elimination*)

Check out the reaction below, it could form two different products! *The mechanism behind the reactions are what will tell us which one is more likely to occur.*



The “higher substituted” product is called the **Markovnikov Product** (“markov = more sub!”)



The “lower substituted” product is called the **Anti-Markovnikov Product** (typically less common)