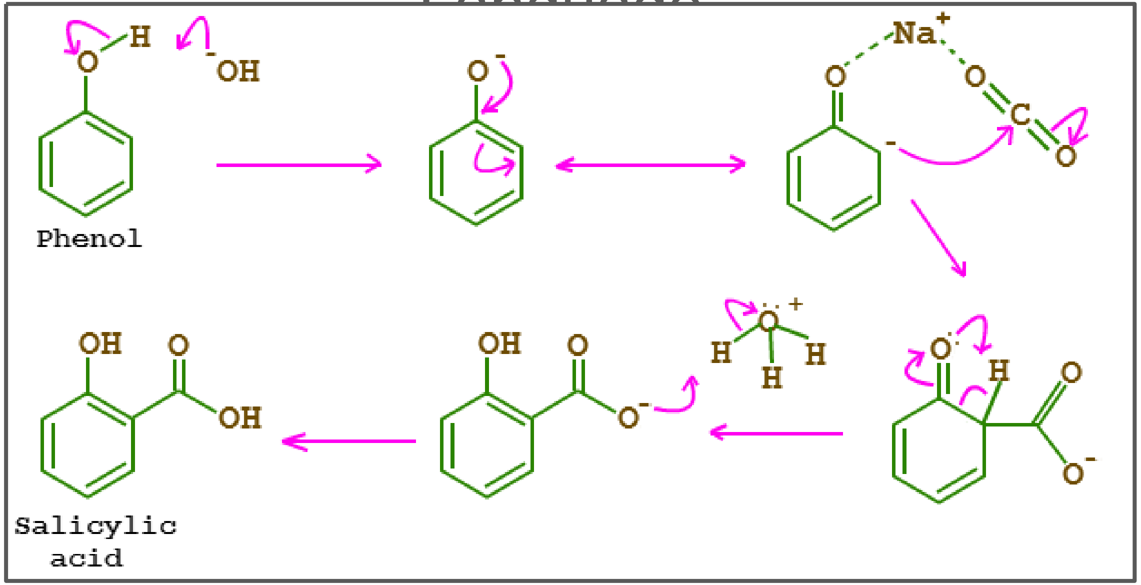
Chapter 8 - Organic Chemistry

Mechanisms

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

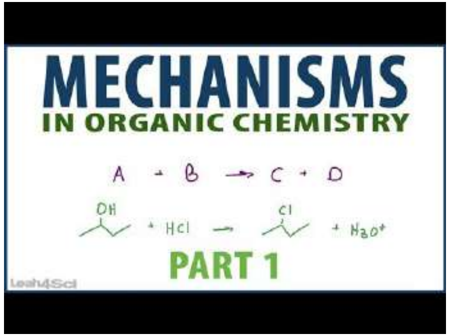


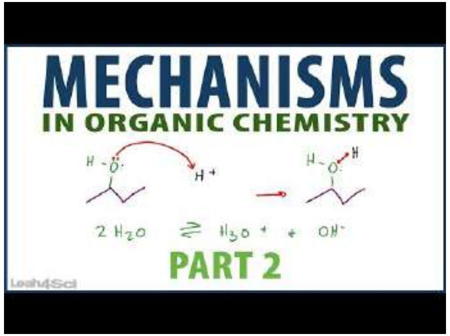
8.0 Introduction to Mechanisms

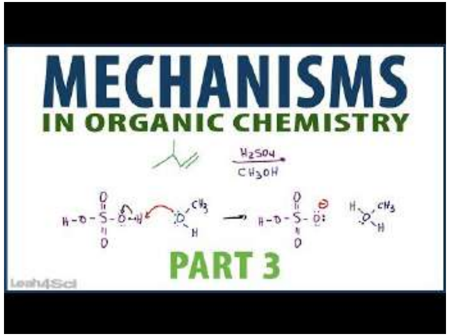
Mechanisms illustrate how the electrons move during a chemical reaction

- 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:





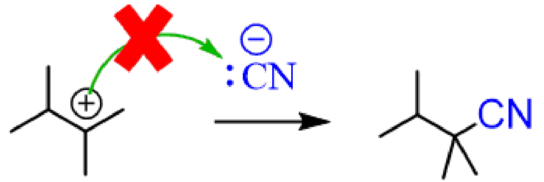


8.1 Curved Arrows

- 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

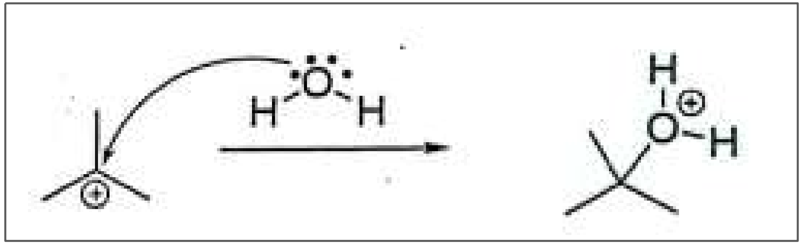
- **Tails of arrows** show where electrons are coming from (donor)
  - So they have to come from an electron source



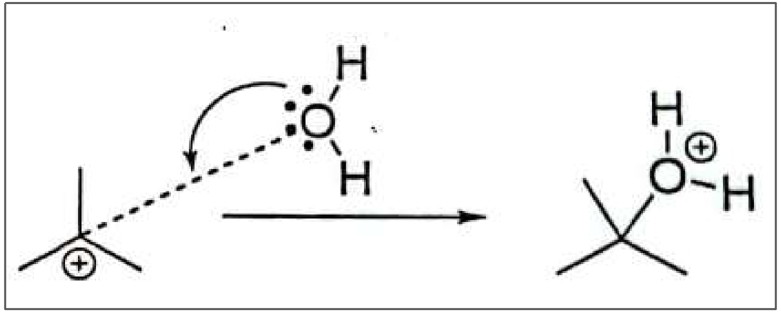
Wrong - arrow cannot start from a (+) charge

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)*

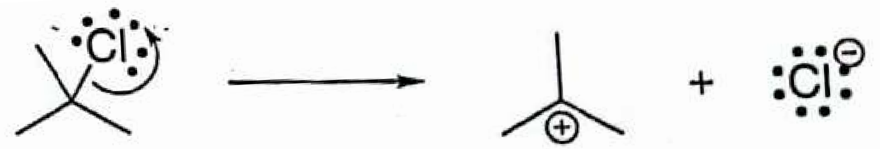


- You may also see it depicted like this *(less common)*

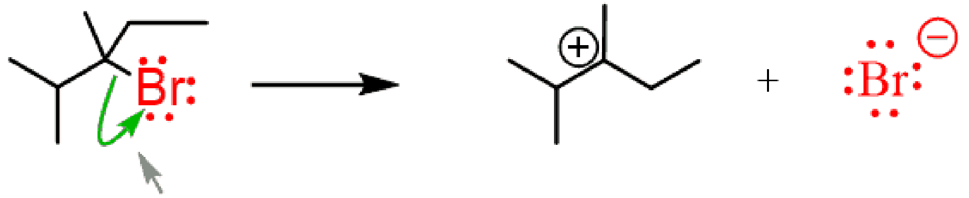


8.1 #2 Curved Arrows from a Bond to a LP

- 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)*



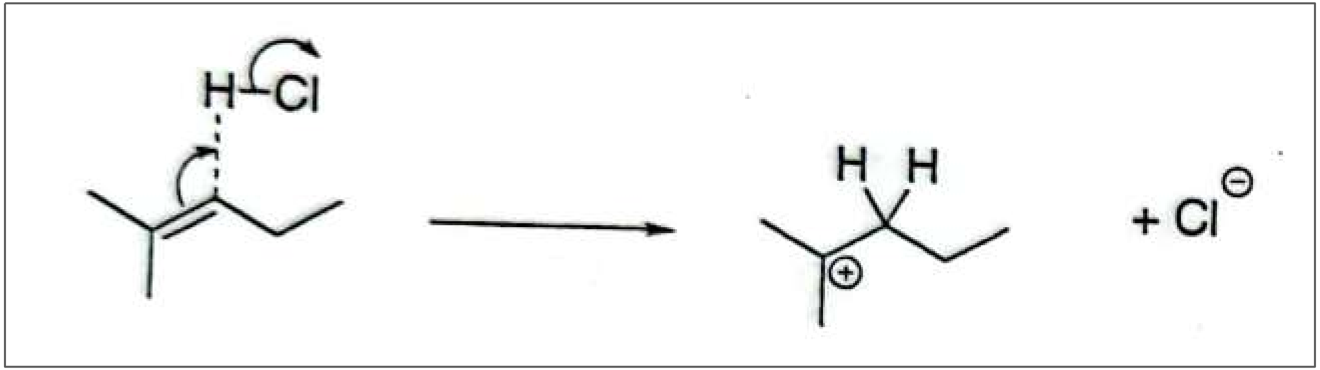
- *Make sure the head of the arrow points at the atom the electrons are attaching to….*



Breaking the bond, giving the e⁻ pair to Br

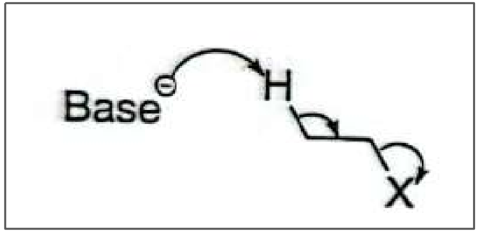
8.1 #3 Curved Arrows from a Bond to a Bond

- 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)*

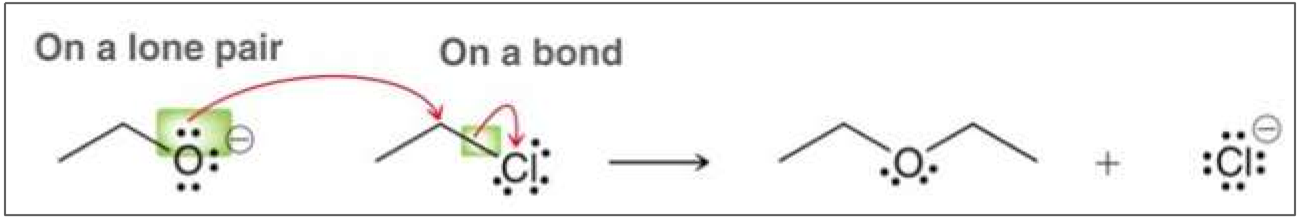


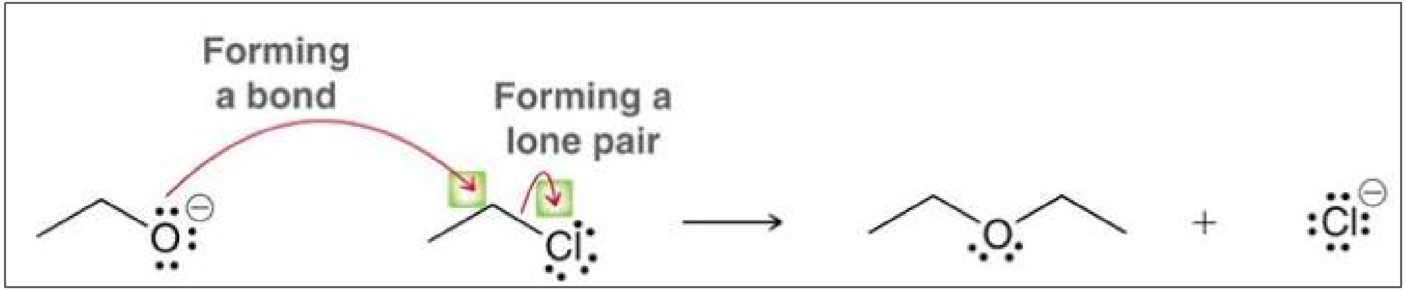
8.1 ALL 3 TYPES of Curved Arrows

- 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!

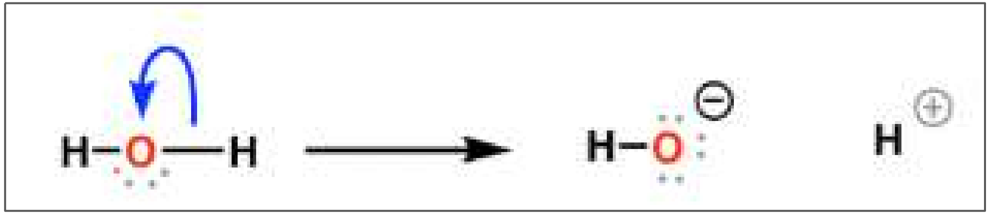


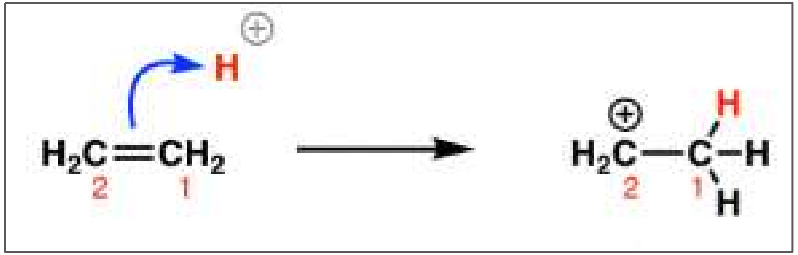


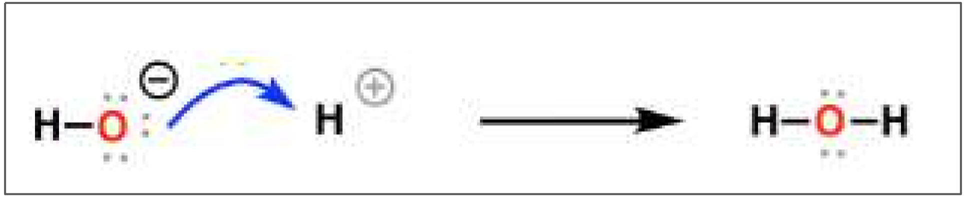
8.1 Practice for Curved Arrows

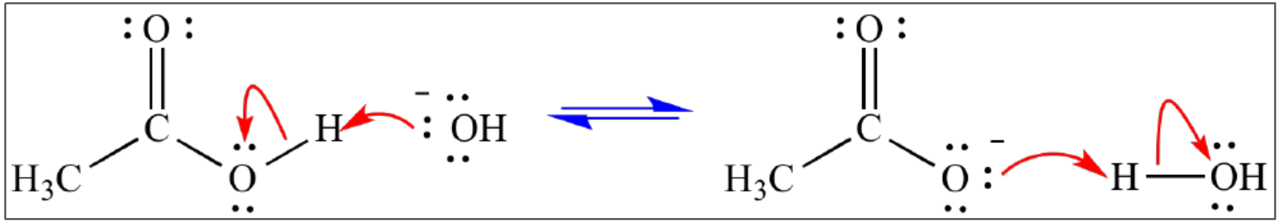
- Classify each of the arrows shown as one of the 3 types:

  1 = LP → B　　**2** = B → LP　　**3** = B → B







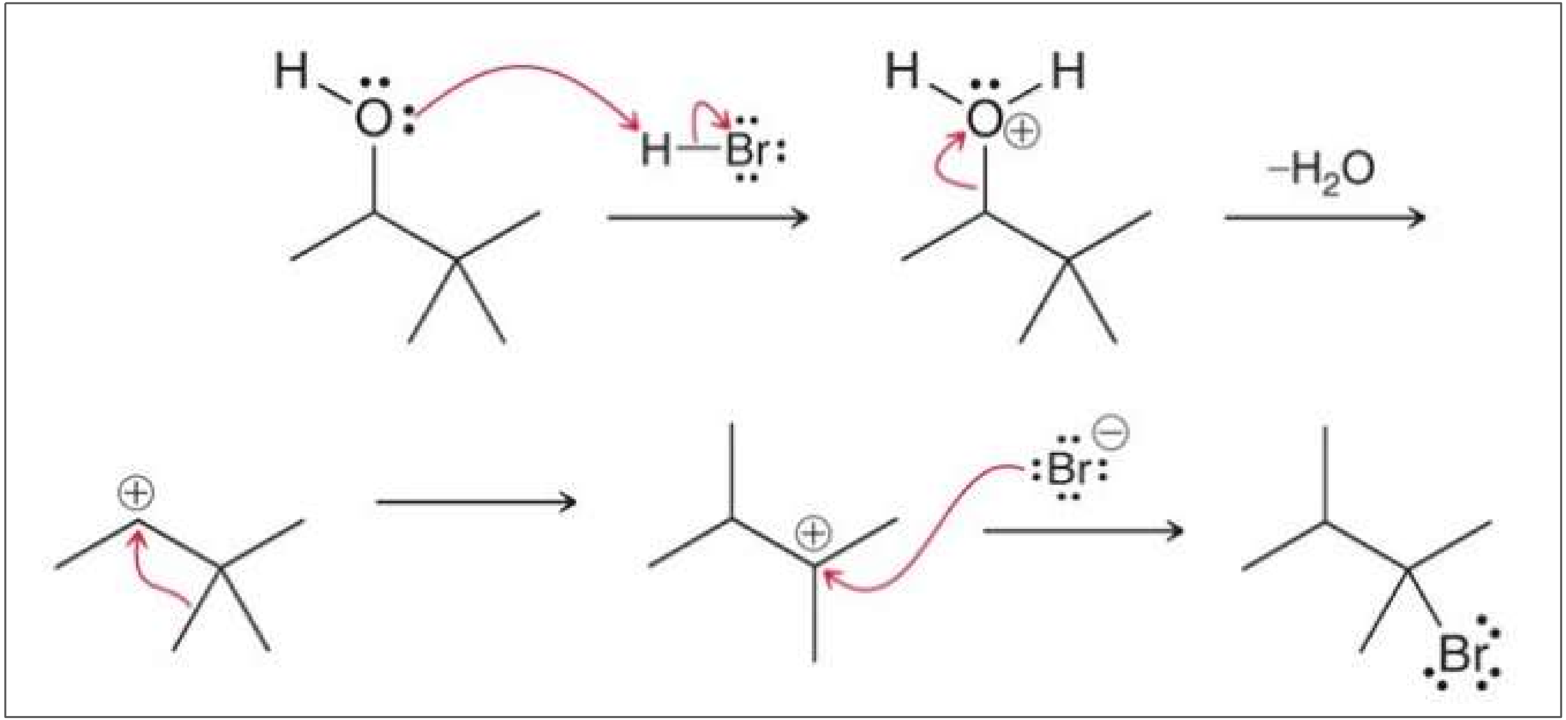


Read 8.1 then complete the practice problems 8.2 - 8.7 on pages 172 - 173.

8.1 Practice for Curved Arrows

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

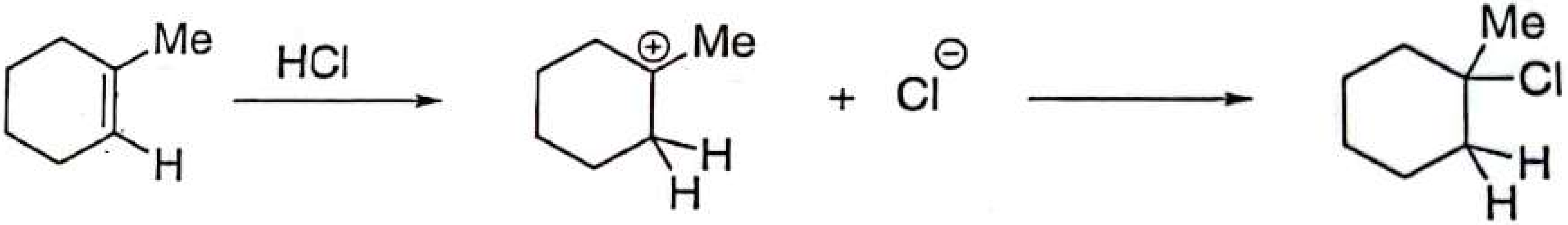
  1 = LP → B **2** = B → LP **3** = B → B



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



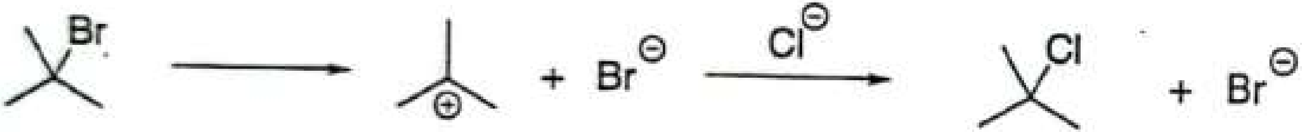
8.2 Arrow Pushing Practice

These are the 8.2 Klein Practice problems from page 174!

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

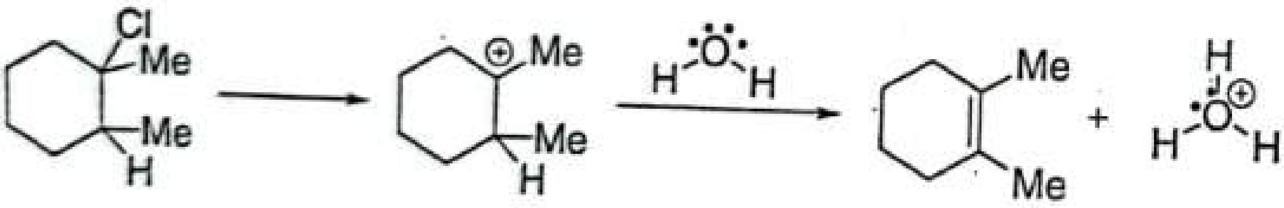
8.9

8.10



8.11

8.12



8.3 Drawing Intermediates & Predicting Products

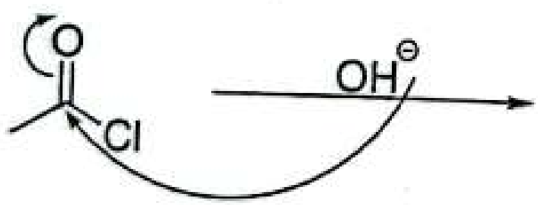
- Intermediates are short-lived structures that exist for a very small amount of time before reacting further.
  - Often critical in understanding the the next step of the reaction
  - Often have “unstable” regions that will help to predict what will happen next

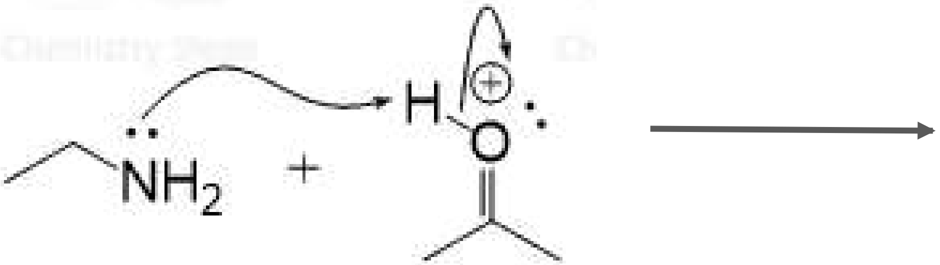
Let’s read the arrows. The first arrow is from a lone pair to form a bond. The arrow shows electrons in a lone pair on a nucleophile (anything that is electron rich) forming a bond with a carbon atom. The second arrow is from a bond to a bond. The third arrow goes from a bond to form a lone pair. All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

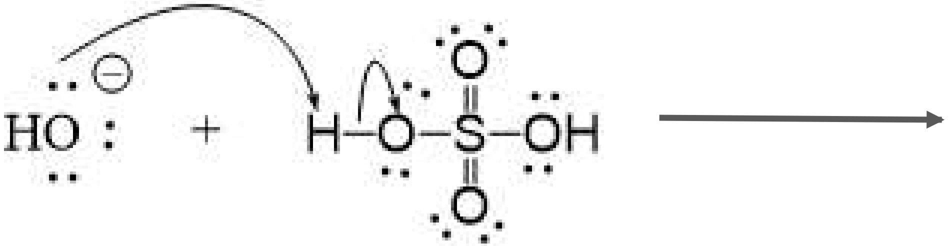
8.3 Practice Drawing Intermediates & Predicting Products

- “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

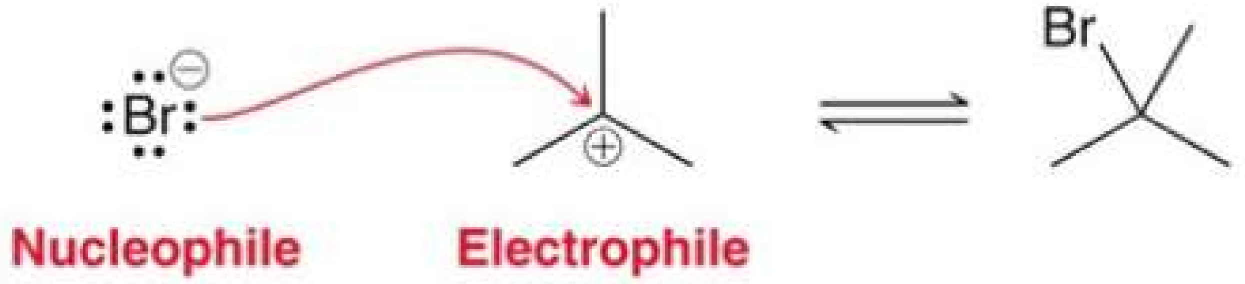
<u>Nucleophiles</u> are the "attacker" compounds.

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

<u>Electrophiles</u> are the compounds that are "being attacked".

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

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



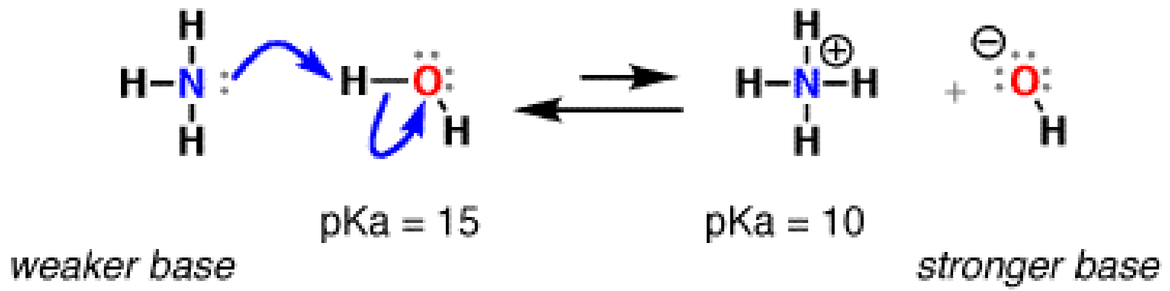
8.5 Bases Versus Nucleophiles

Base - removes an H+ then “runs away with it”

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

- A base donates a pair of electrons to a proton

Example



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.

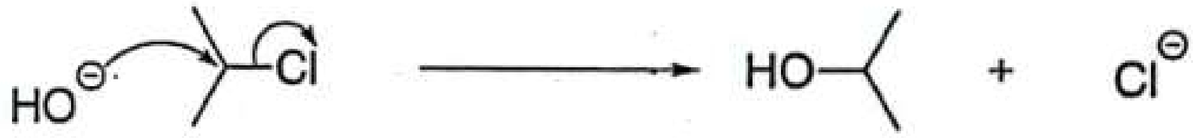
Acid-base reactions reflect relative stabilities

8.5 Bases Versus Nucleophiles

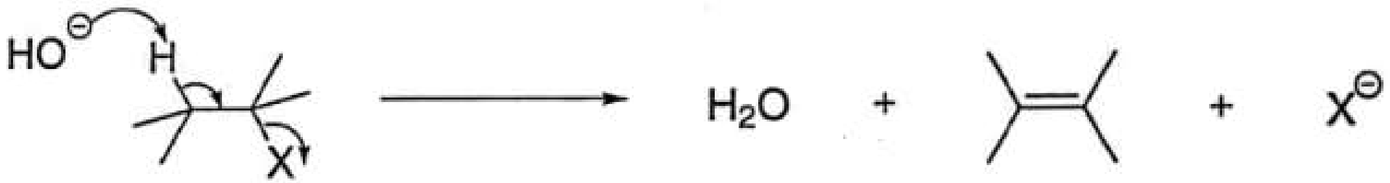
The difference between bases and nucleophiles is a difference of ***function.***

For example, -OH can act as either a Nuc. or a base!

Nucleophile - latches onto a compound (the attacker)



Base - removes an H+ then “runs away with it”



8.5 Bases Versus Nucleophiles

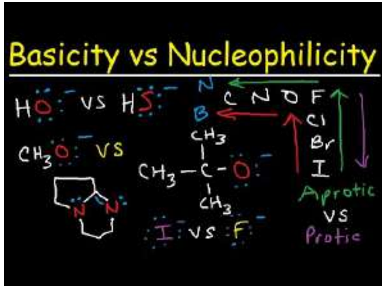
Nucleophile - latches onto a compound

- 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.

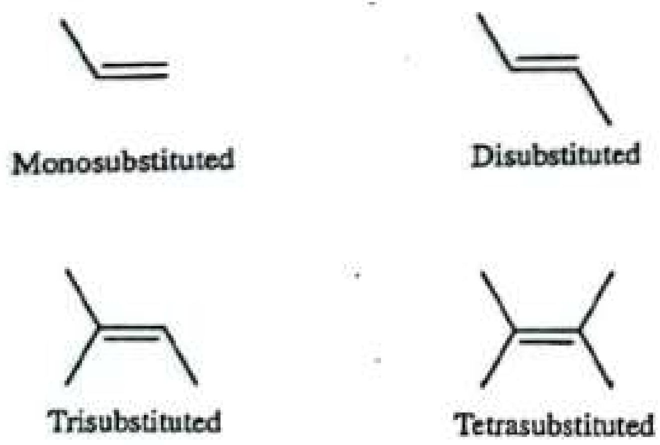
8.6 The Regiochemistry is contained within the Mechanism

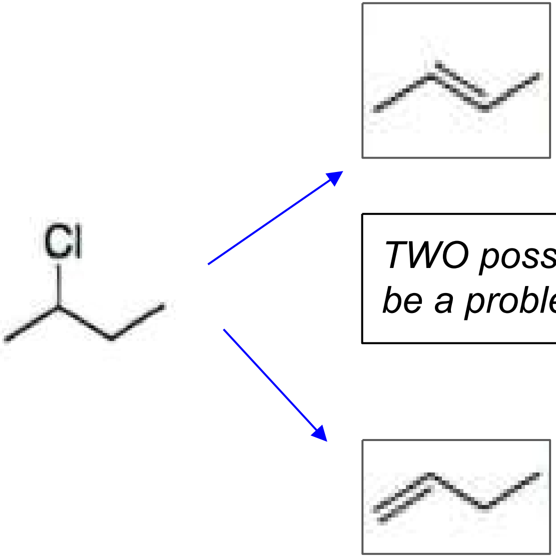
Regiochemistry: refers to where the reaction takes place within the molecule

*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!

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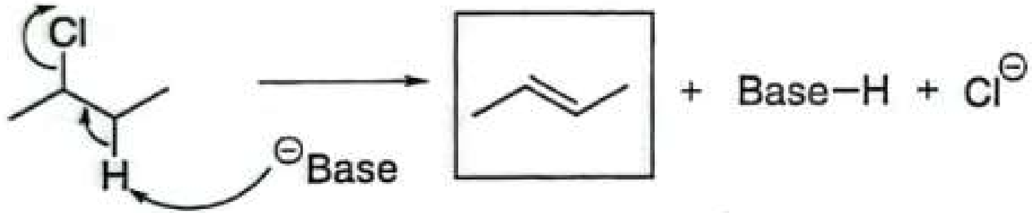
8.6 The Regiochemistry is contained within the Mechanism

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)*

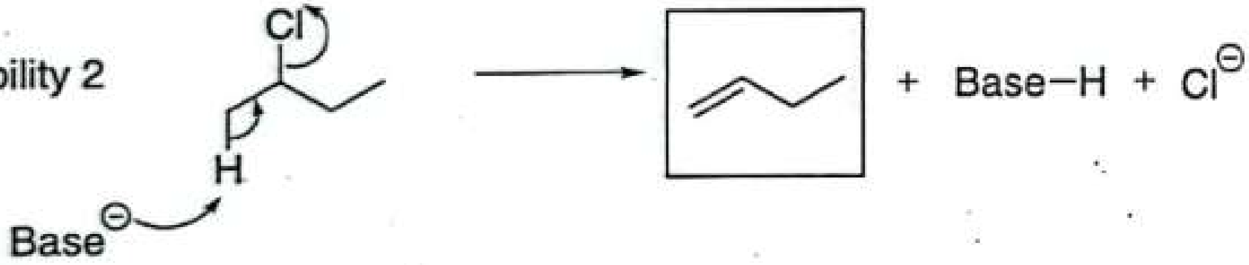
Check out the reaction below, it could form two different products! *The mechanism behind the reactions are what will tell us which one is more likely to occur.*

Possibility 1



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

Possibility 2



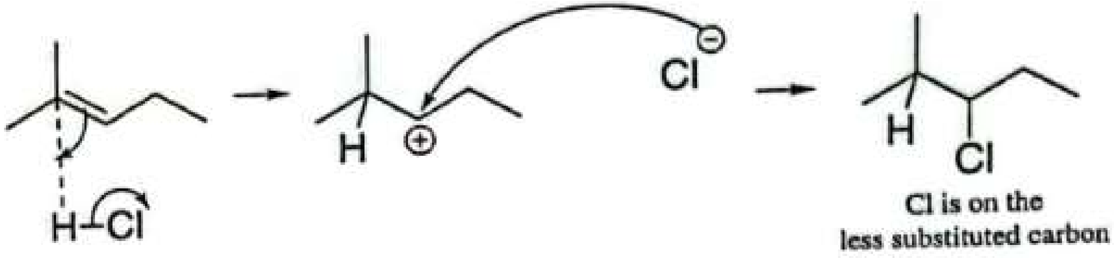
The “lower substituted” product is called the **Hoffman Product** *(typically less common)*

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)*

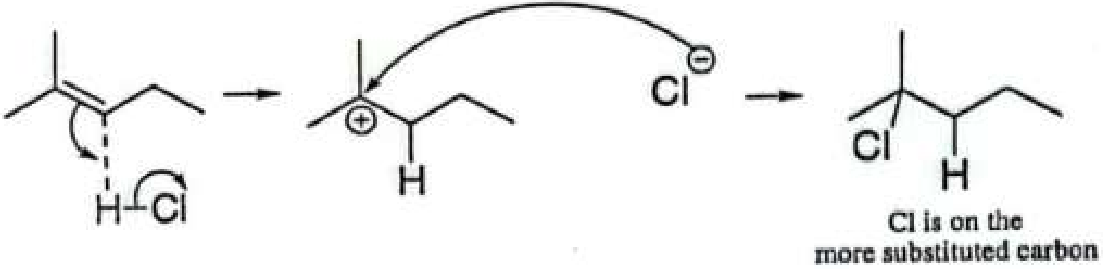
Check out the reaction below, it could form two different products! *The mechanism behind the reactions are what will tell us which one is more likely to occur.*

Possibility 1



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

Possibility 2



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