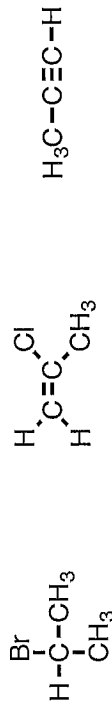


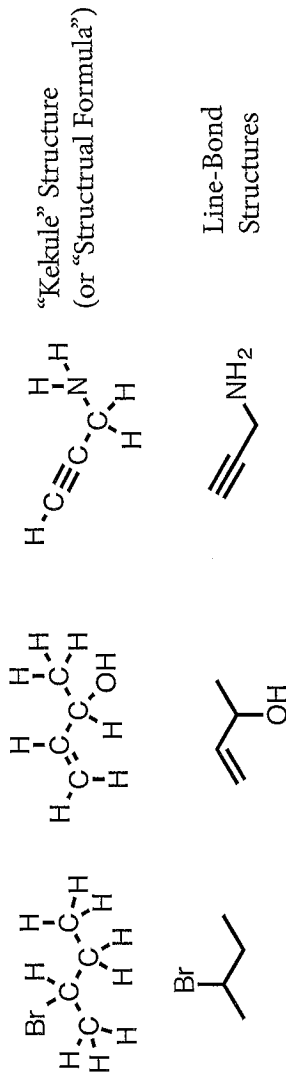
## Chapter 1: The Basics

### Drawing Organic Structures: Kekule and Line-Bond Structures

Let's begin with the basics of an organic structure. The carbon atom always makes four bonds if there is no formal charge on the carbon. Every carbon atom in the molecules below have 4 bonds. A double bond is counted as two bonds to carbon and a triple bond is counted as three bonds to carbon.



There are two common methods for depicting organic structures: the "Kekule" (or structural formula) and the Line-Bond. In the Kekule form all atoms are shown, while in the Line-Bond form of the same molecule, carbons and hydrogens from C—H bonds are implied. The Kekule form gives more information to the beginning student, however the line-bond structure is easier to read and to draw, especially for large molecules. In the figure below, the top line is the Kekule form and the molecule below it is the Line-Bond form for the same molecule.

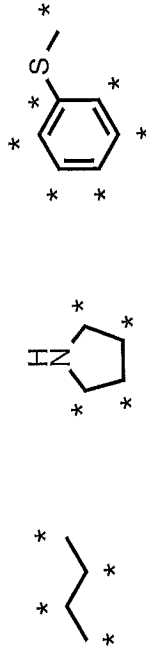


### Rules for Drawing Kekule Structures

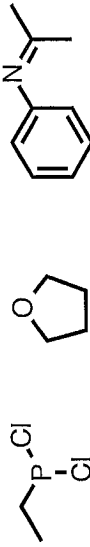
1. Show every atom including carbon and hydrogen.
2. You may wish to show lone pair electrons on heteroatoms. Heteroatoms are classified as atoms other than carbon or hydrogen such as O, N, P, S, Cl, Br, and I.

### Rules for Drawing Line-Bond Structures

1. The beginning and end of every line is a carbon unless otherwise noted. (each carbon is indicated by an \*)



2. The symbol for atoms other than carbon and hydrogen are explicitly shown.



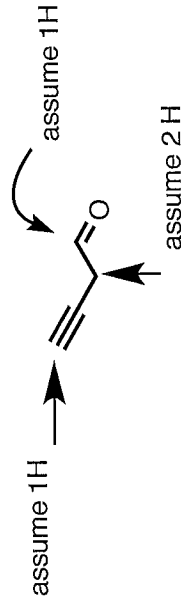
3. Hydrogens attached to non-carbon elements are shown. Hydrogens attached to carbon are implied.



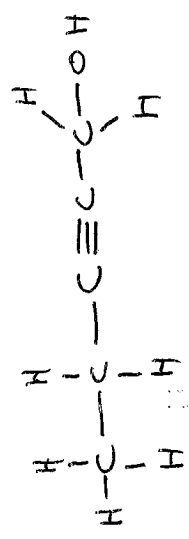
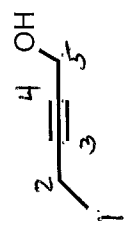
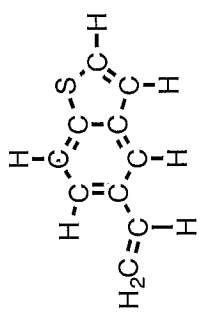
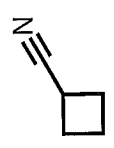
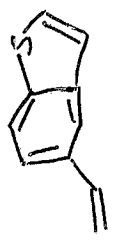
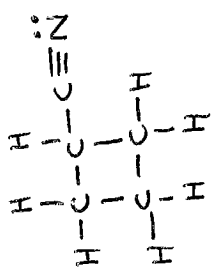
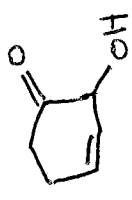
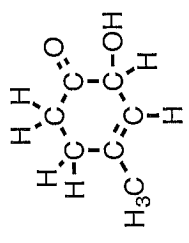
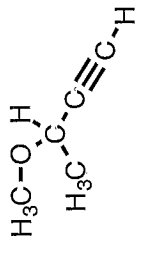
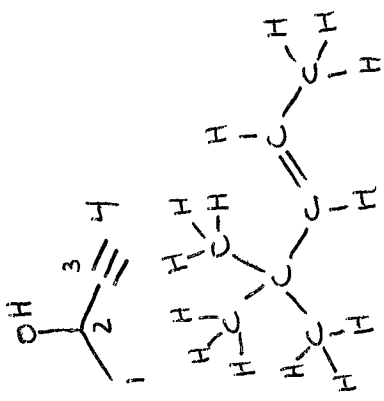
correct

incorrect

4. Always assume each carbon has four total bonds unless a formal charge is shown. This means that you must discern the number of implied hydrogens. (Remember that each carbon takes four bonds in the uncharged state.)

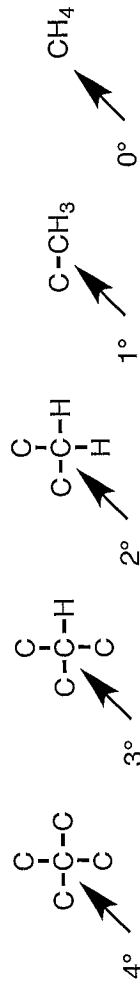


**Exercise:** If the Kekule is shown, draw the corresponding Line-Bond structure and vice versa.



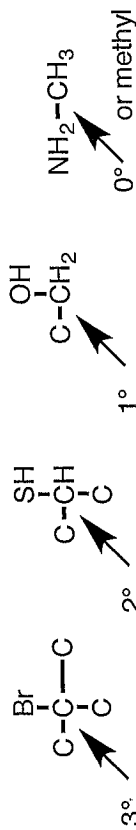
## Degree of Branching or Degree of Substitution

Alkyl groups (carbons) are classified by their attachment to other carbons. We refer to this as the degree of substitution or the degree of branching. This is important because a molecule will follow a specific mechanistic pathway based on the degree of branching of the carbon undergoing reaction. Notice that as the degree of substitution increases from  $1^\circ$  to  $4^\circ$ , the carbon atom becomes more crowded; this has an impact on reactivity which will become apparent in the substitution and elimination chapters.

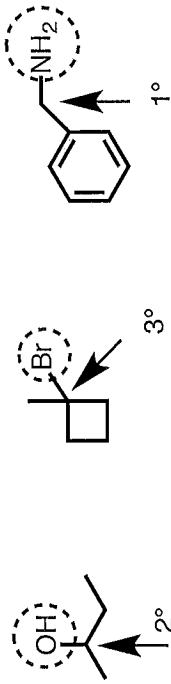


A carbon attached to 4 other carbons is called "quaternary": it has  $4^\circ$  of substitution.  
A carbon attached to 3 other carbons is called "tertiary": it has  $3^\circ$  of substitution.  
A carbon attached to 2 other carbons is called "secondary": it has  $2^\circ$  of substitution.  
A carbon attached to 1 other carbon is called "primary": it has  $1^\circ$  of substitution.

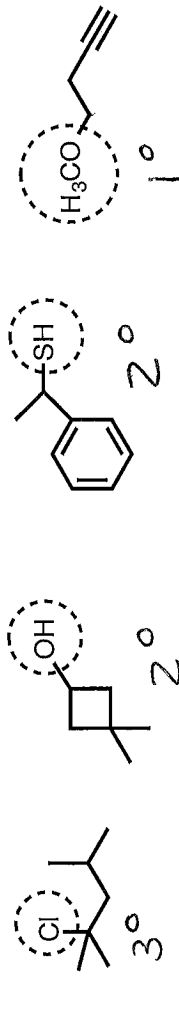
What happens to the degree of branching when a carbon is replaced by a non-carbon atom? Well, the degree of branching is reduced because the degree of branching is calculated on bonds to carbons, not bonds to other atoms.



We often refer to the degree of branching for a functional group or an atom of interest that's not carbon. (A functional group is a group of atoms attached to the carbon framework of a molecule that is primarily responsible for its reactivity). A functional group adopts the degree of branching of the carbon to which it is attached. In the example below, the alcohol is 2° because it is attached to a carbon that is 2°.



**Exercise:** Identify the degree of branching for every carbon and the circled functional groups.



based on degree of branching at the  
"parent" carbon.

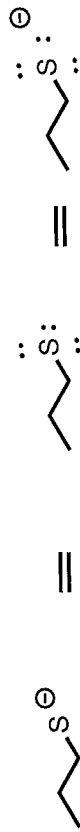
## Implicit or “Hidden” Lone Pair Electrons

Electrons are not always explicitly shown in line-bond structures so we need a way to identify those “hidden” electrons. Look at the following pairs of molecules. Each set is a representation of the exact same molecule. Sometimes we show nonbonding (or lone pair) electrons, sometimes just the formal charge and sometimes both the electrons and the formal charge. It can be confusing at first, but they all mean the same thing.



lone pair electrons  
implied

lone pair electrons  
shown



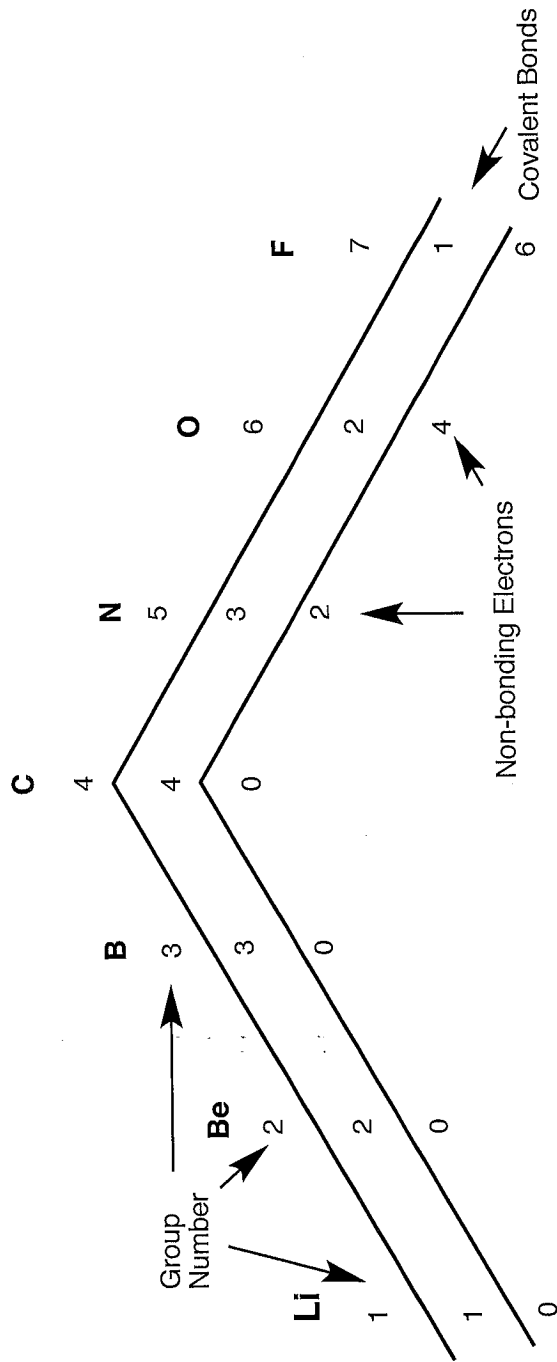
lone pair electrons  
implied

lone pair electrons  
shown

lone pair electrons  
shown and charge indicated

For a neutral molecule, one without a formal charge, we can figure out the number of “hidden” lone pair electrons using a device called the Bonding Triangle. The Bonding Triangle is based on the Group Number which tells us the numbers of valence shell electrons for each element. You can deduce the number of covalent bonds and non-bonding electrons by following the Triangle.

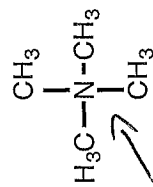
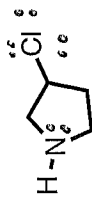
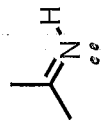
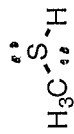
### Example of a bonding triangle



We have a molecule  $\text{CH}_4$ . Find carbon in the Triangle, it is Group IV, so it has 4 valence shell electrons. Carbon takes 4 bonds, which leaves no electrons left over to be used as non-bonding electrons.

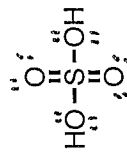
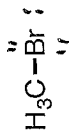
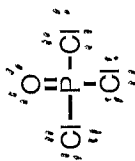
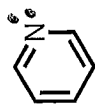
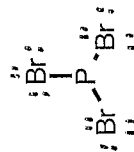
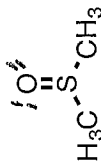
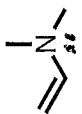
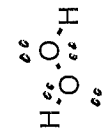
$\text{CH}_4$ (looking at the carbon)	$:\text{NH}_3$ (looking at the nitrogen)	
Group Number	Group Number	
- Covalent bonds from triangle 4	- Covalent bonds from triangle 3	= 2
Non-bonding electrons = 0	Non-bonding electrons	

**Exercise:** Use the Bonding Triangle to determine the number of non-bonding electrons (lone pair) present but not shown. This applies to atoms other than carbon or hydrogen.



+1 charge,

no e-





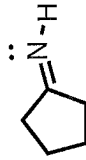
## Determining Formal Charge (FC)

An atom adopts a formal charge (positive or negative) when the number of electrons the atom owns is different than the number of valence electrons (based on the Group Number). The molecules below have no formal charge because the total number of electrons on each atom equals the valence number of electrons for that atom.



Oxygen "owns" 6 electrons

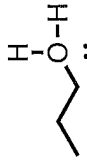
4 non-bonding electrons  
1 electron from each C—O sigma bond



Nitrogen "owns" 5 electrons

2 non-bonding electrons (not shown)  
1 electron from the N—H sigma bond  
2 electrons from the C=N double bond

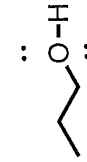
Now, let's look at atoms where the total number of electrons does not equal the valence number for that atom.



Oxygen has 6 valence electrons

2 non-bonding electrons  
1 electron from the C—O bond  
1 electron from each C—H bond

$$FC = 6 - 2 - 3 = +1$$



Oxygen has 6 valence electrons

4 non-bonding electrons  
1 electron from the C—O bond  
1 electron from the C—H bond

$$FC = 6 - 4 - 2 = 0$$



Oxygen has 6 valence electrons

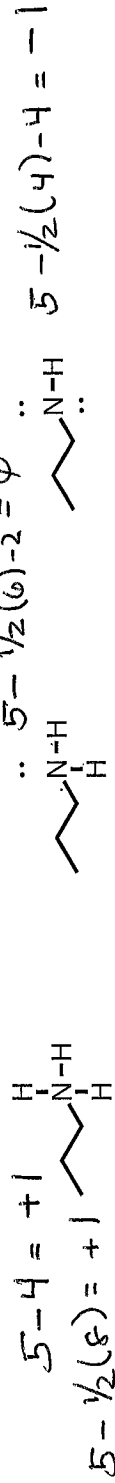
6 non-bonding electrons  
1 electron from the C—O bond

$$FC = 6 - 6 - 1 = -1$$

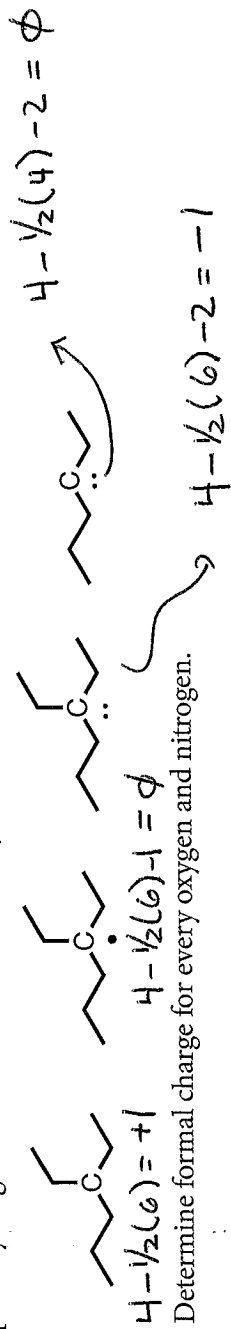
The rule of thumb is that fewer electrons than the valence numbers results in a positive charge and more electrons than the valence number results in a negative charge. A charge results when the atom deviates from its net nuclear charge.

**Exercise:** Determine the formal charge for the indicated atoms.

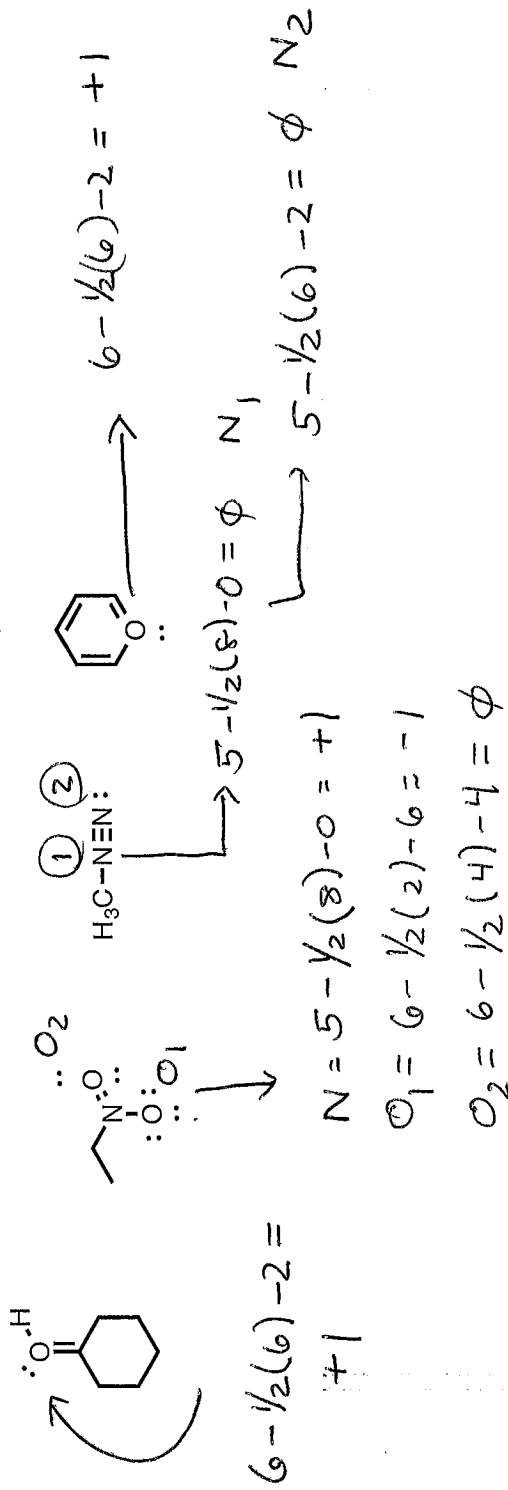
A. Determine the formal charge for nitrogen in each molecule.



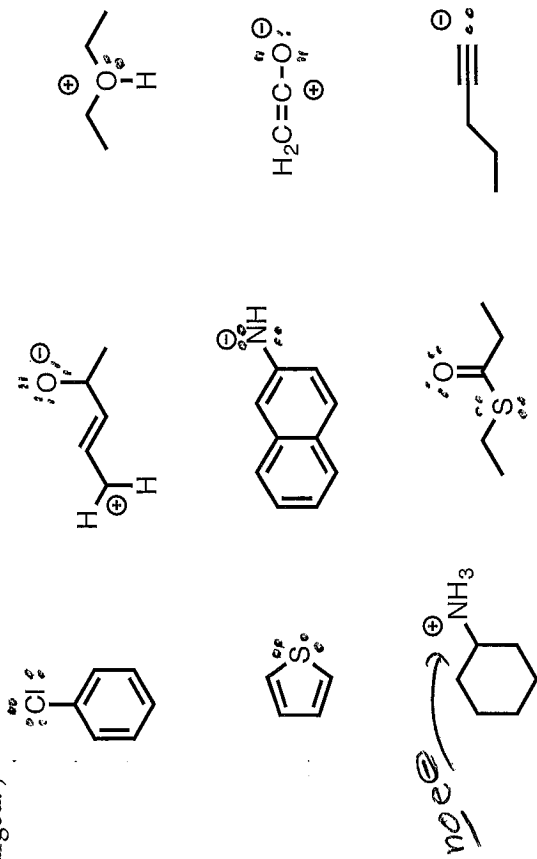
B. Determine the formal charge on the carbon annotated as C. (FYI: There are no implied hydrogen on the annotated carbons).



C. Determine formal charge for every oxygen and nitrogen.



**Exercise:** Draw in the hidden electrons. (This might be a little tricky when the atom is charged.)



Common charges associated with oxygen and nitrogen.

	4 bonds	3 bonds	2 bonds	1 bond
nitrogen	+1 (NH <sub>4</sub> <sup>+</sup> )	0 (NH <sub>3</sub> )	-1 (NH <sub>2</sub> <sup>-</sup> )	n/a
oxygen	n/a	+1 (OH <sub>3</sub> <sup>+</sup> )	0 (OH <sub>2</sub> )	-1 (OH <sup>-</sup> )

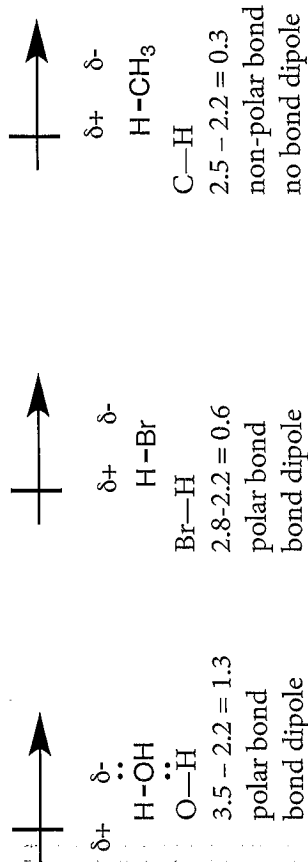
## The "Hidden" Positive Charge, Otherwise Known as a Dipole

The atoms in any given bond may have similar or dissimilar electronegativity values. If the electronegativity of two atoms in a bond is substantially different, then the bond is said to have a dipole. A dipole indicates some degree of charge separation. Most organic molecules have at least a few bonds that have dipoles. It is important to note that the atoms in a dipole adopt a partial positive ( $\delta+$ ) or a partial negative ( $\delta-$ ) charge. Locating dipoles can help us to predict where a chemical reaction will occur and also aids in helping us to discern whether a compound will act as an acid or a base.

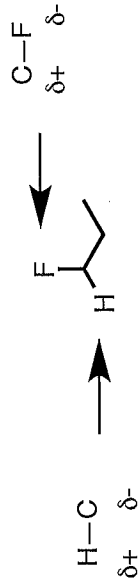
Recall from general chemistry that electronegativity values increase across a row in the Periodic Table and decrease down a column. We usually do not need to know the exact numerical values for electronegativity, just their relative rankings. However, we have shown the important values for organic students.

F	O	Cl	N	Br	C	S	I	P	H	B
4.0	3.5	3.2	3.0	2.8	2.5	2.5	2.5	2.2	2.2	2.0

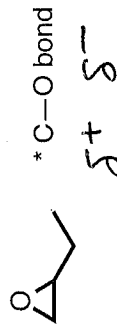
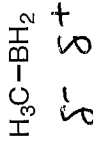
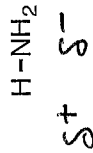
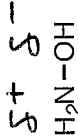
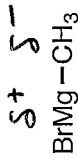
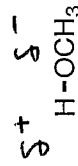
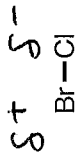
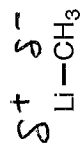
If the difference in electronegativity between two atoms in a bond is  $<0.5$  then it is said to be non-polar, if the difference is greater than 0.5 the bond is considered polar. Polar bonds are said to have a dipole - a difference in electronegative between any two atoms connected by a bond. This dipole can be indicated using a dipole arrow or the  $\delta+$  and  $\delta-$  symbols. The symbol  $\delta+$  means electropositive and  $\delta-$  means electronegative. These symbols can be used to indicate if there is a difference in electronegativity between any two atoms in a bond even if there is no dipole.



Bond polarity has one oddity. An atom may be *partial positive* in reference to one of its bonds but *partial negative* in reference to the other. For the molecule below, the carbon is electronegative in reference to the hydrogen, but electropositive in reference to the fluorine. Typically the bond with the largest dipole difference takes priority in using dipoles to predict reactivity.



**Exercise:** Indicate the difference in electronegativity using  $\delta^+$  and  $\delta^-$  symbols. Then determine if each highlighted bond (X—X) has a dipole.



## How To Quickly Identify Acids And Bases

There are three ways of looking at acids and bases based on how they behave in a reaction: Arrhenius, Bronsted-Lowry and Lewis. Arrhenius is not very useful outside a few specific applications and will not be discussed here. The workhorse of organic chemistry lies in Bronstead and Lewis approaches.

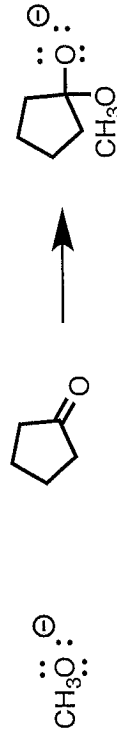
Bronstead-Lowry reactions involve proton transfer. The base accepts a proton donated by the acid. Lewis reactions involve the movement of electrons: bases are electron pair donors (because they are electron rich) and acids are electron pair acceptors (because they are electron poor).

Look at the reactions below, the same structure acts a Bronsted base in the first reaction but as a Lewis base in the second reaction. Same base, different activity. Those bases are tricky buggers.



Proton acceptor  
Bronsted base

Proton donor  
Bronsted acid



Electron donor  
Lewis base

Electron acceptor  
Lewis acid

A word about terminology is warranted. We tend to think of bases as those species which abstract a proton, in other words a Bronsted base. When we think about bases forming sigma bonds to atoms other than hydrogen, we are referring to a Lewis base. To distinguish between the function of Bronsted and Lewis bases we will refer to Lewis bases as nucleophiles. To distinguish between the function of Bronstead and Lewis acids, we will refer to Lewis acids as electrophiles.

Bronsted and Lewis theory don't tell you how to identify a structure as a potential acid or base at all. These theories are descriptions of the process that has already occurred. Luckily there are clues to help us look at a molecule and make an educated guess about whether it will act as a base or acid. Just remember that a base is a base regardless of what theory is used to describe its reactivity.

A list of characteristics that will help us identify a base and an acid in most cases would be a great place to start. The classification below will work most of the time, but not all of the time since some molecules can be amphoteric. (Amphoteric species can act like an acid or base depending upon its chemical environment. Water is the most common example.)

### General Ways to Classify Bases or Nucleophiles

- Hydroxides  
 $\text{NaOH}$ ,  $\text{LiOH}$ ,  $\text{KOH}$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$
- Species with a negative charge (sometimes shown as a salt)  
 $\text{Br}^\ominus$      $\text{N}_3^\ominus$      $\text{CH}_3\text{CH}_2^\ominus$      $\text{CH}_3\text{S}^\ominus$   
 $\text{NaBr}$      $\text{NaN}_3$      $\text{LiCH}_2\text{CH}_3$      $\text{KSCH}_3$
- Species with a pi bond (double or triple)  
 $\text{H}_2\text{C}=\text{CH}_2$      $\text{HC}\equiv\text{CH}$      $\text{H}_2\text{C}=\text{NH}$      $\text{HC}\equiv\text{N}$      $\text{H}_2\text{C}=\text{O}$
- Carbon-metal bonds (the carbon is basic)  
 $\text{H}_3\text{C}-\text{Mg}$      $\text{H}_3\text{C}-\text{Li}$      $(\text{H}_3\text{C})_2\text{CuLi}$
- Hydrogen-metal bonds (the hydrogen is basic)  
 $\text{NaBH}_4$      $\text{LiAlH}_4$     (isobutyl) $_2\text{AlH}$
- Species with lone pair electrons (non-bonded electrons).  
*These are generally weak bases and in many cases these species are also amphoteric, so you need to look at the reaction environment to determine if it will act as an acid or base.*



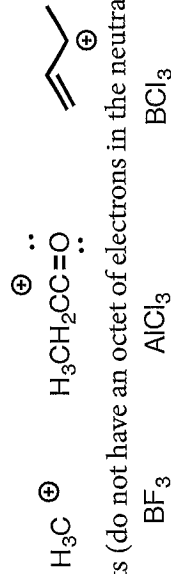
## General Ways to Classify Acids

### 1. Inorganic Proton sources

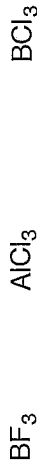


mineral acids  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HCl}$

### 2. All carbon based cations



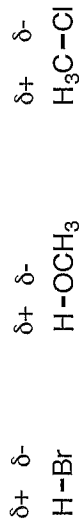
### 3. Group III elements (do not have an octet of electrons in the neutral species)



### 4. Transition metal



### 5. Electropositive site of a bond dipole



### 6. Alcohols of many flavors donate protons.



carboxylic acids      water      alkyl alcohols

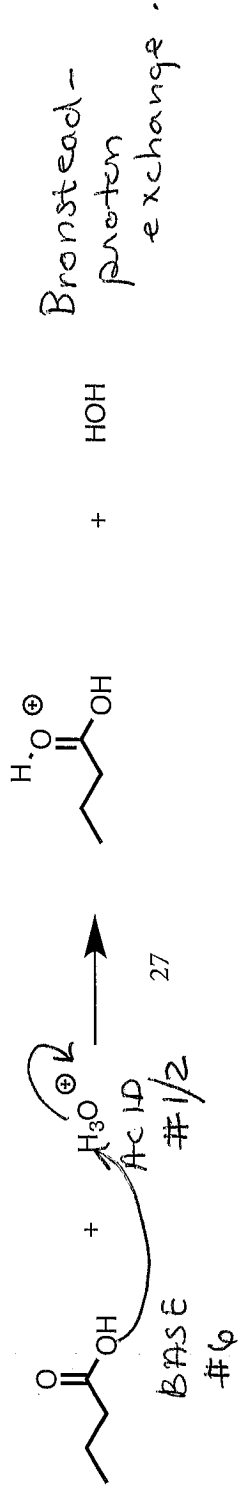
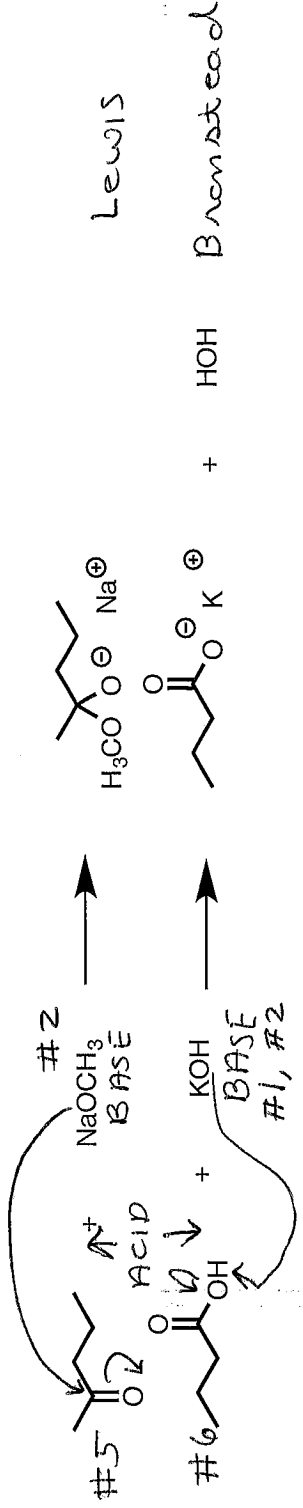
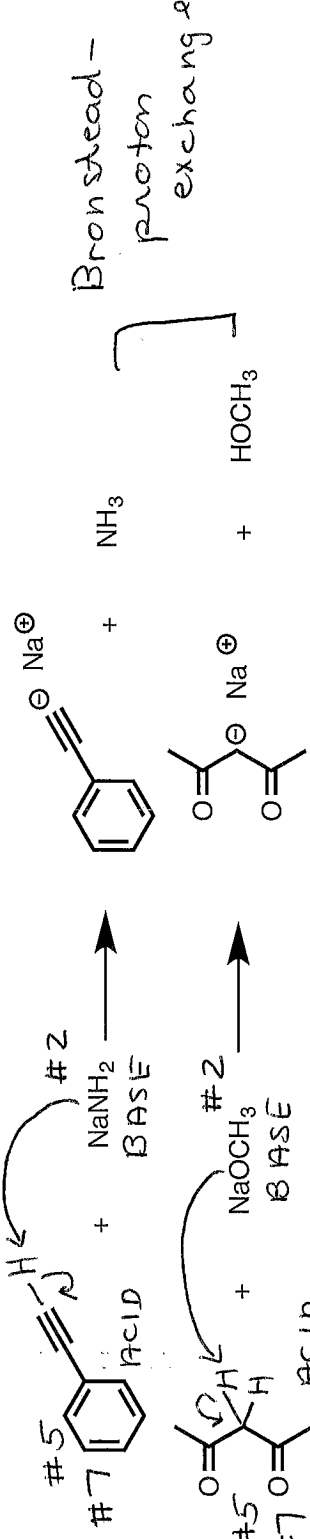
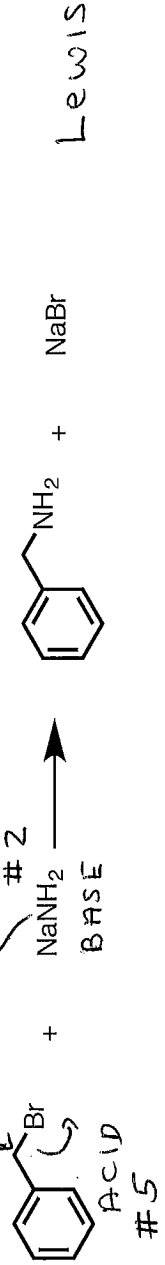
### 7. Acidic C-H bonds, such as terminal alkynes and C-H bonds adjacent to carbonyls

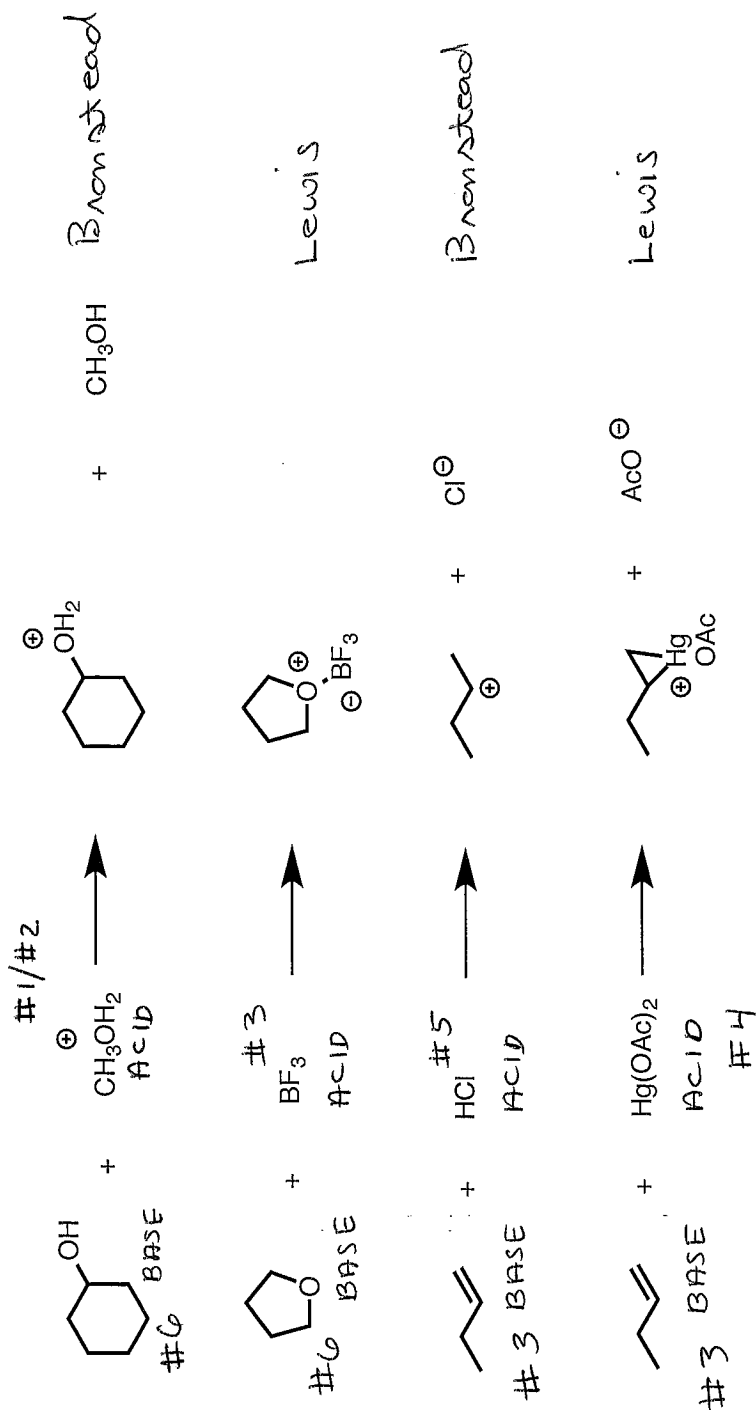




**Exercise:**

**Part I:** Classify each base as Bronsted or Lewis based on how it functions in the reaction. Bronsted bases abstract protons and Lewis bases (aka nucleophiles) form bonds to atoms other than hydrogen. Be sure to look for implied hydrogens!





**Exercise:**

**Part II.** Now go back and look at each acid and base in the above exercise and determine which criteria from the classification list above each species meets. For example  $\text{HO}^-$  is a base using both criteria #1 (hydroxides) and #2 (negative charge) and  $\text{HCl}$  is an acid based on criteria #1 (mineral acid) and #5 (bond dipole)

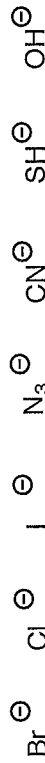
## A Word About Nucleophiles And Leaving Groups

In many organic reactions the goal of a reaction is to make a new compound. This means that we add, replace or remove functional groups to the existing compound. The most common reaction in first semester organic is substitution wherein we replace an existing functional groups with a new functional groups. The incoming functional group is typically a Lewis base or **nucleophile** and the group being displaced must leave, so we call it the **leaving group**.

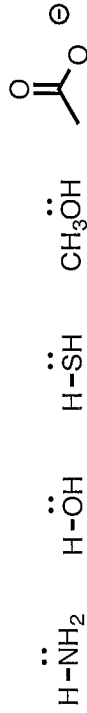


**Nucleophiles** in substitution reactions fall into two categories. **Strong nucleophiles** promote  $S_N2$  substitution reactions and weaker nucleophiles promote  $S_N1$  substitution reactions. This will make sense to you as you proceed through the workbook. For now, just kept this in your far reaches of your mind.

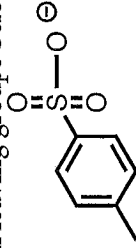
Strong nucleophiles typically have a negative charge and follow base classification criteria #2 (see the acid base section)



Weaker nucleophiles typically have a lone pair of electrons (base classification criteria #6) or a resonance delocalized negative charge.



**Leaving groups** are an essential component of many reactions. You cannot make a new bond without breaking an existing bond. The bond that breaks during a reaction is called the leaving group. You will notice that leaving groups and nucleophiles have a lot in common. Both are bases, both may have negative charges and both will likely contain lone pair electrons. Let's list the most common leaving groups below.



tosylate

There are “good” leaving groups and there are “bad” leaving groups. Reactions are more likely to take place when you can displace a good leaving group. What makes a leaving group “good” or “bad”? Thankfully, there's one simplifying factor to look at when deciding this: its basicity. **Good leaving groups are weak bases.**

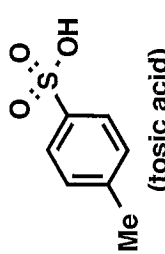
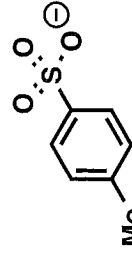
How do we identify a weak base? There's a useful tool for that – it's called a pKa table. Many pKa tables give you the identity of the acid, but if you think about it, it also gives you information about the conjugate base of each acid. The conjugate base is the part left over when you lose H+. The stronger the acid, the weaker the conjugate base. And the weaker the conjugate base, the better the leaving group. So a pKa table is a great guide to leaving group ability. Stabilized electrons make for less reactive species which is typical of good leaving groups. If the electrons are not stabilized, it is more reactive, which is typical of nucleophiles.

## A Ranking Of Leaving Groups

In general: the weaker the base, the better the leaving group.

The conjugate bases of strong acids are very weak bases and excellent leaving groups.

The conjugate bases of very weak acids are very strong bases and very poor leaving groups

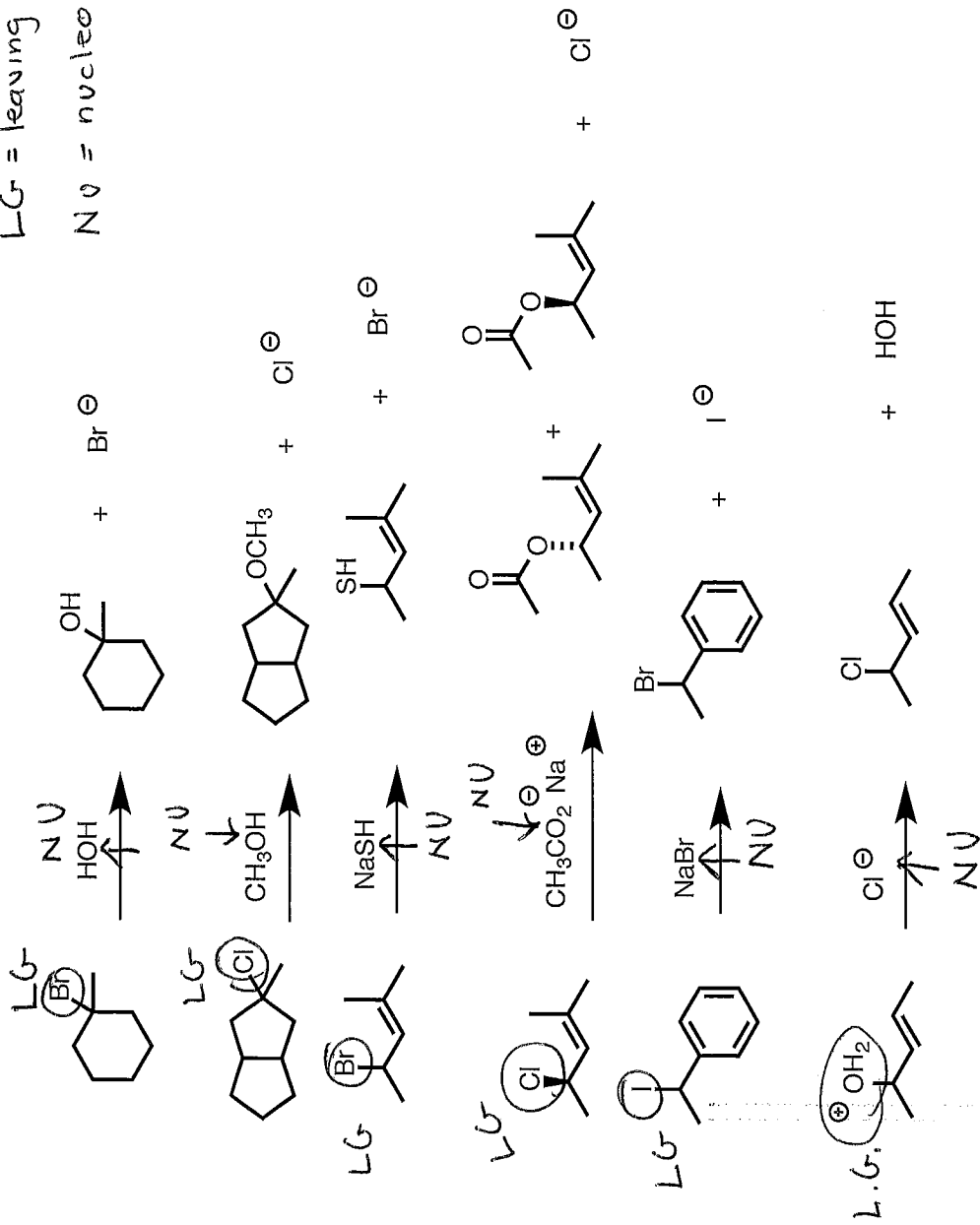
Functional group /Example	pKa	Conjugate base	Functional group /Example	pKa	Conjugate base
<b>STRONG ACIDS</b>		<b>GREAT LEAVING GROUPS</b>	<b>MODERATE ACIDS</b>		<b>GOOD LEAVING GROUPS</b>
Hydroiodic acid HI	-10	I <sup>⊖</sup>	Carboxylic acids H <sub>3</sub> C-C(=O)OH	4	H <sub>3</sub> C-C(=O)O <sup>⊖</sup>
Hydrobromic acid HBr	-9	Br <sup>⊖</sup>	Protonated amines NH <sub>4</sub> <sup>⊕</sup> Cl <sup>⊖</sup>	9-11	NH <sub>3</sub>
Hydrochloric acid HCl	-6	Cl <sup>⊖</sup>	<b>POOR ACIDS</b>		<b>POOR LEAVING GROUPS</b>
Sulfuric acid H <sub>2</sub> SO <sub>4</sub>	-3	HSO <sub>4</sub> <sup>⊖</sup>	Water HO-H	16	HO <sup>⊖</sup>
Sulfonic acids (tosic acid) 	-3		Alcohols CH <sub>3</sub> O-H	16-18	CH <sub>3</sub> O <sup>⊖</sup>
Hydronium ion H <sub>3</sub> O <sup>⊕</sup>	-1.7	H <sub>2</sub> O	<b>VERY POOR ACIDS</b>		<b>VERY POOR LEAVING GROUPS</b>
Hydrofluoric acid H-F	3.2	F <sup>⊖</sup>	Amine NH <sub>3</sub>	~35	NH <sub>2</sub> <sup>⊖</sup>
			Hydrogen H-H	42	H <sup>⊖</sup>
			Alkane H <sub>3</sub> C-CH <sub>2</sub> -CH <sub>3</sub>	~50	H <sub>3</sub> C-CH <sub>2</sub> -CH <sub>2</sub> <sup>⊖</sup>

**Exception:** F<sup>⊖</sup> is typically an extremely poor leaving group (forms strong bonds)

**Exercise:** Label the nucleophile and the leaving group in each reaction. Right now don't worry about what makes a good leaving group or nucleophile, just look at which atoms are moving in this process of substitution.

LG = leaving group

NU = nucleophile



## The Wonderful World Of Arrows

We use a variety of arrows in organic chemistry and they each mean something different. Reaction and equilibrium arrows are used to indicate the progress of a reaction from reactants to products. Resonance arrows are used when we wish to show the different arrangements of electrons in a structure. The dipole arrow is used to illustrate a bond dipole and it travels from the  $\delta+$  site to the  $\delta-$  site of a bond dipole. Curved arrows show electron flow, bond making and bond breaking in a mechanism. The primary focus of this workbook is the use of curved arrows to show how a reaction works, otherwise known as the mechanism.

reaction arrow



equilibrium arrow



resonance arrow



dipole arrow



curved arrow or  
mechanism arrow



shows movement  
of an electron pair

shows movement  
of a single electron

## The Basic Rules For Using Curved Arrows

The curved arrow is a key component of our journey into the organic mechanism. Curved arrows show us where bonds are being made and broken, but more specifically they represent electron flow. In a mechanism, which is just a description of how reactions are working at the electronic level, we used curved arrows to show electron flow not atom movement. Yes atoms are moving, but it is through the action of electrons. Therefore it is key to be able to identify electrons, formal charge and valency of atoms which is why we spent time on that earlier in the chapter. Now we will learn the does and don'ts of moving electrons through the curved arrow convention. If the curved arrow is double-headed it means two electrons are moving, and a single-headed arrow or fishhook indicates the movement of one electron typical of a radical reaction. We will only use double-headed arrows here. Let's begin with some do's and don'ts for using curved arrows.

1. The tail of the arrow originates at the electron rich ( $\delta^-$ ) site (base or nucleophile) and arrow head ends at the electron poor ( $\delta^+$ ) site (acid or electrophile).

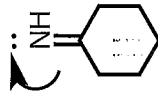


correct

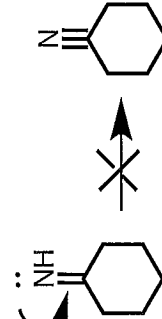
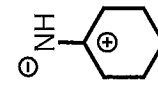


incorrect

2. Maintain an octet for second row elements.



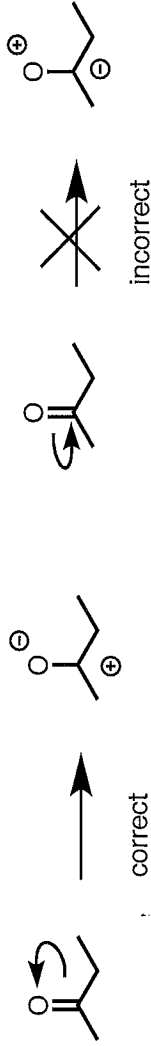
correct



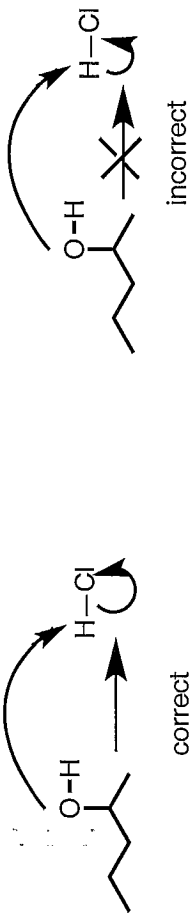
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3. When breaking a pi bond, move the electrons toward the more electronegative atom.

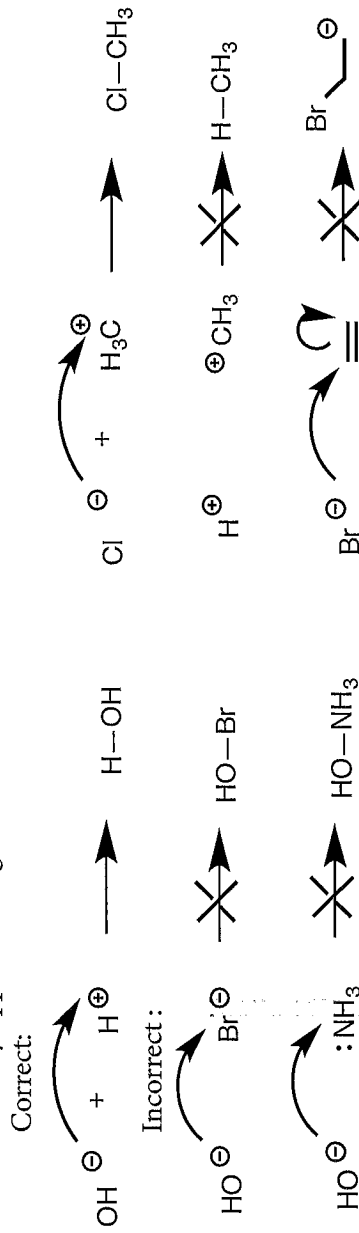


4. In a sequence, each atom or bond has only 1 originating arrow. Two arrows originating from the same atom or bond is typically not allowed.



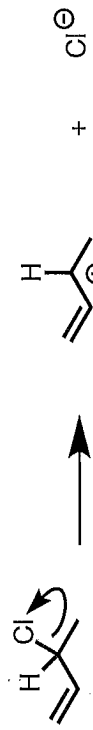
Notice that there are 2 arrows on hydrogen

5. Only opposite charges interact with each other.



### Advanced concepts for mechanisms

6. Sigma Bond Breaking – SINGLE MOVE. In some instances, a sigma bond can break apart without the assistance of an incoming nucleophile. This can only happen with 2°, 3° or allylic leaving groups and is typical of SN1 and E1 mechanism types.



**Exercise:** Identify the leaving group then provide the structure of the carbocation and the leaving group.

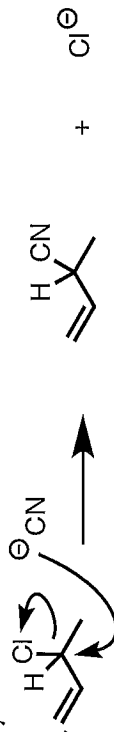
Carbocation      LG



remember implied hydrogens



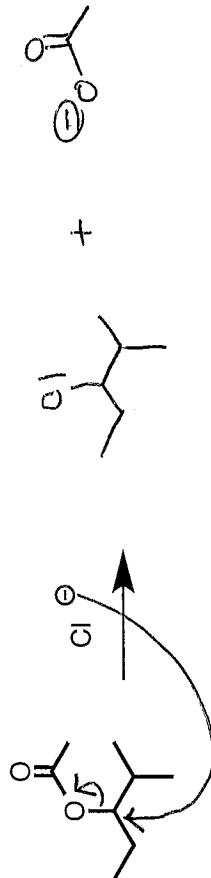
7. Simultaneous Sigma Bond Breaking and Making. In some instances, a sigma bond is broken by the action of an incoming base or nucleophile, i.e. the sigma bond breaking and bond making occur simultaneously. This is typical of reactions that have a strong base and a good leaving group. We will see that SN2 and E2 reactions fall into this category.



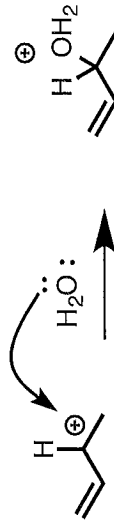
**Exercise:** Show the nucleophile attacking a carbon and displacing the leaving group.



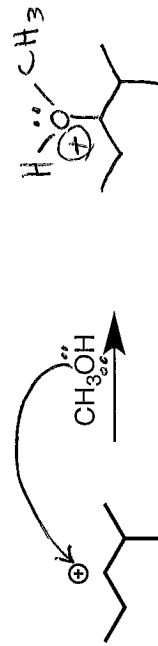
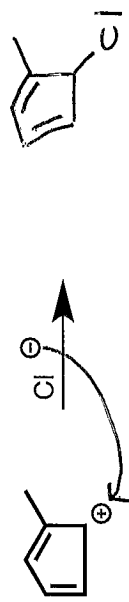
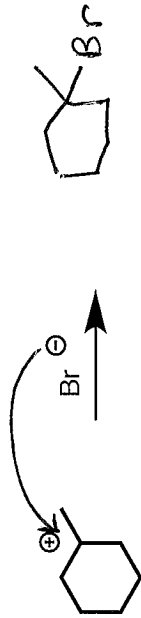
remember implied hydrogens



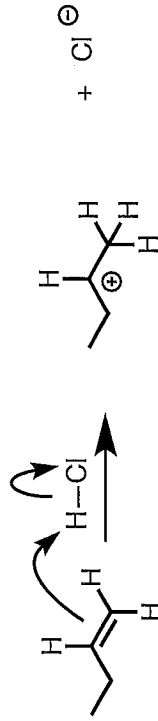
8. Sigma Bond Making . Many reactions proceed through a carbocation or other charged intermediate of carbon. In this case the leaving group has already departed (See item 6) before the nucleophile attacks and creates a new sigma bond. This is typical of SN1 type mechanisms. This move requires only a weak base.



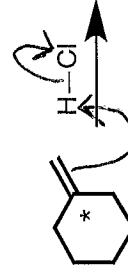
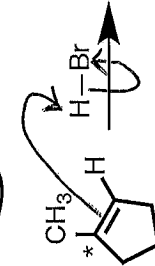
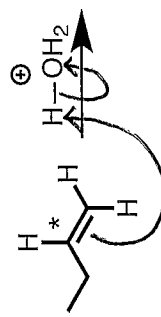
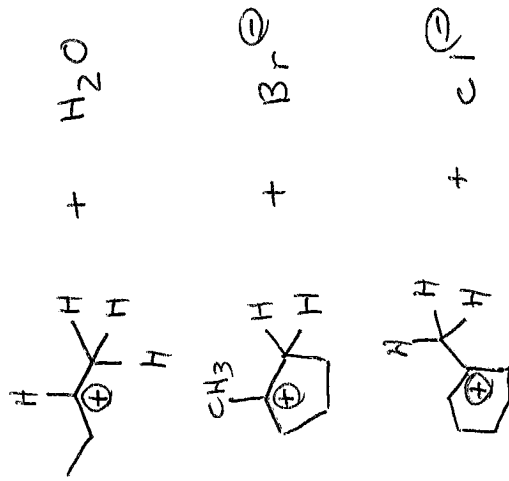
**Exercise:** Show the nucleophile attacking the carbocation and making a new sigma bond. Be sure to keep track of formal charges.



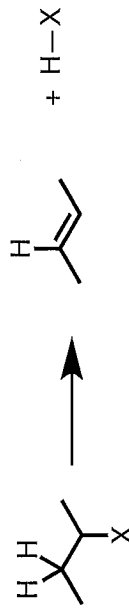
9. Pi-bond Breaking - Pi bonds can break during the course of a reaction. When this happens the pi bond is acting like a nucleophile, recall that pi bonds are electron rich. When the pi bond breaks, you simultaneously form a new sigma bond to one of the pi bond carbons while the other carbon typically becomes a charged carbocation. There is a strong preference to form the most stable carbocation allowed.



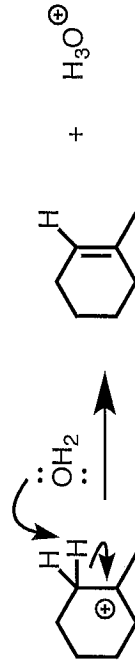
**Exercise:** Show the pi bond attacking a cation or the most electrophilic site of each electrophile (Lewis acid) and making a new sigma bond. Be sure to keep track of formal charges. In the exercise below the placement of the resulting positive charge is indicated by an asterisk.



10. Pi Bond Making – Pi bonds can be created during the course of a reaction. A pi bond is formed when there is a loss of two atoms or groups of atoms on adjacent carbons.



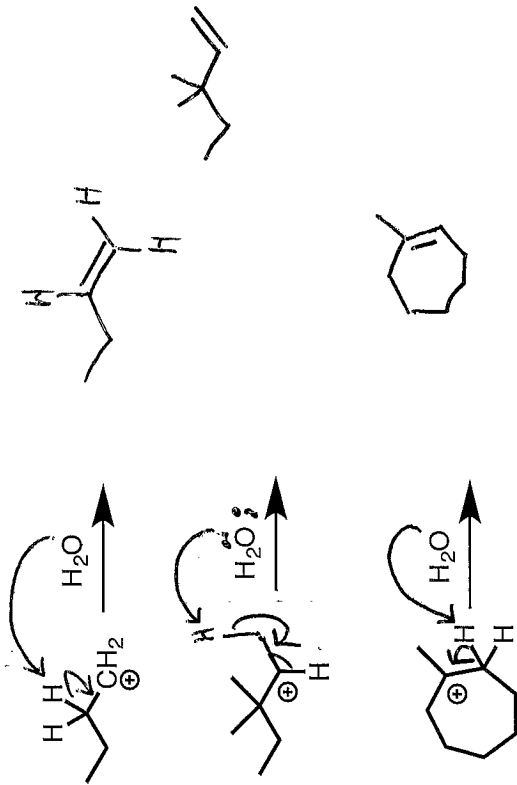
Two Moves: There are two primary pathways to accomplish pi bond making. One pathway is typical of a mechanism we call E1. In this case, we start with a carbocation that collapses into a pi bond. A hydrogen atom adjacent to the carbocation is abstracted by a weak base and the electrons from the C—H sigma bond move in to form the new pi bond.



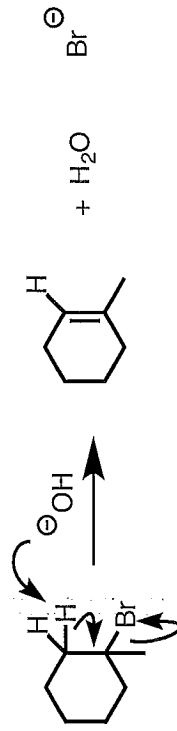
**Exercise:** Show the abstracting a proton adjacent to the carbocation and making a new pi bond. Be sure to keep track of formal charges.

Oops! Missing Exercises  
on the next page.

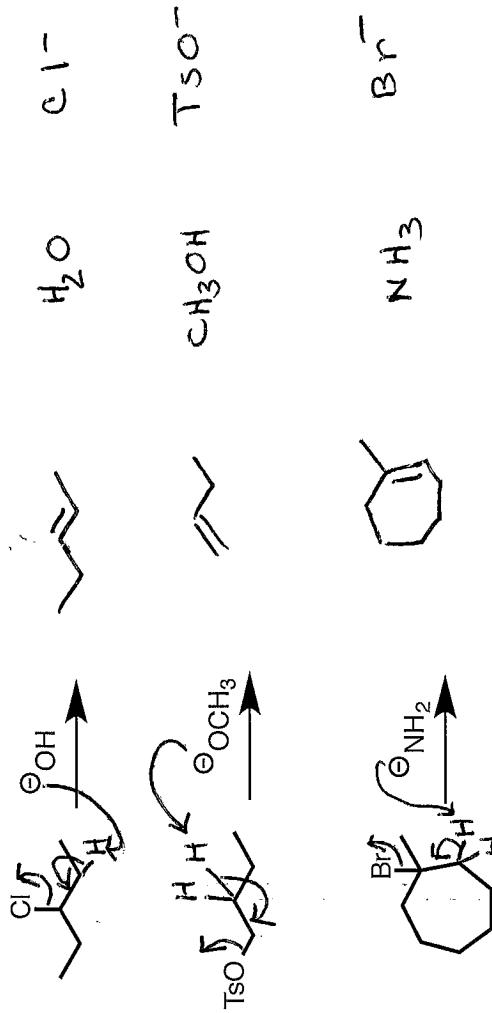
**Exercise:** Show strong base abstracting a hydrogen adjacent to the leaving group. There may be more than one adjacent hydrogen, just choose one for now. Then show the collapse to the pi bond and the leaving group departing. Be sure to keep track of formal charges!



Three Moves: There are two primary pathways to accomplish pi bond making. The second pathway is typical of a mechanism we call E2. In this case, a strong base abstracts a hydrogen atom that is adjacent to a good leaving group. The electrons from the C—O sigma bond being broken collapse to form the pi bond. The leaving group must leave at this time to avoid exceeding an octet of electrons on that carbon.



**Exercise:** Show strong base abstracting a hydrogen on a carbon adjacent to carbon with the leaving group. There may be more than one adjacent hydrogen, just choose one for now. Then show the collapse to the pi bond and the leaving group departing. Be sure to keep track of formal charges!



11. Charge can sometimes be deceiving. In the reaction below, it sure looks like the methoxide ( $\text{CH}_3\text{O}^-$ ) should attack the oxygen of the hydronium ( $\text{H}_3\text{O}^+$ ). After all, negative attacks positive. But let's see what happens when we follow that protocol.



central oxygen exceeds an octet of electrons



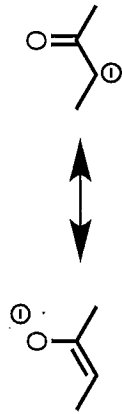
Even though oxygen has the positive charge, it is still more electronegative than the hydrogen (oxygen is 3.5 and hydrogen is 2.2) In some cases dipoles are more predictive of reactivity than formal charge.



## Drawing Reasonable Resonance Structures

A resonance structure is an average of two or more Lewis structures that result from the movement of electrons within the molecule. One structure is often not adequate to describe the properties or the reactivity of a given species. Resonance structures differ only in the arrangement of electrons.

Resonance form



This scheme shows the movement of a negative charge (electrons) from an oxygen to an adjacent carbon.

Not a resonance form

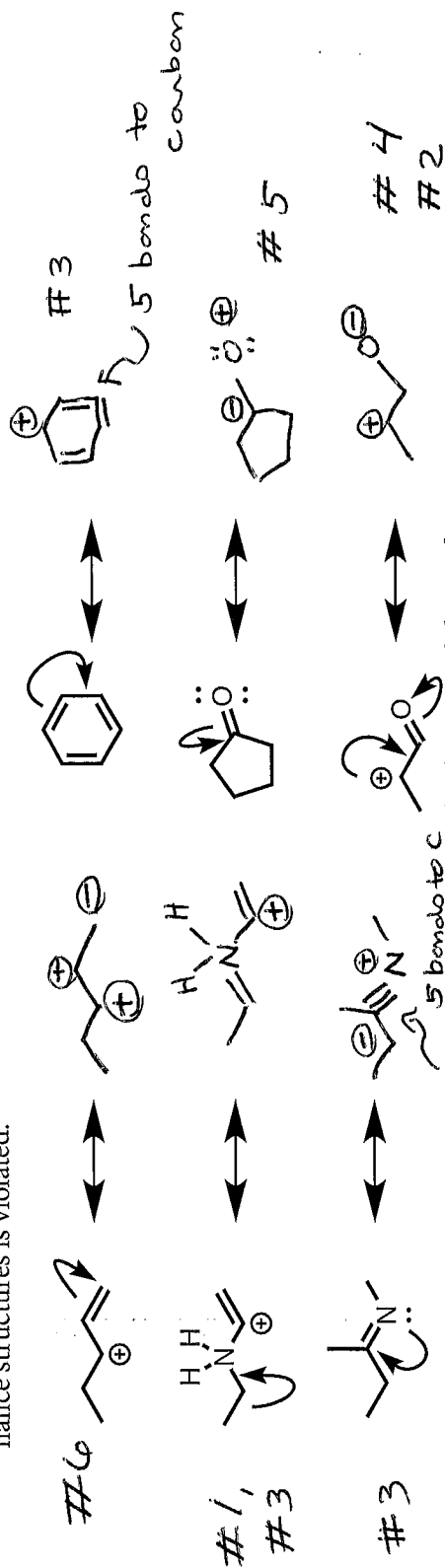


This scheme shows the movement of a hydrogen atom from oxygen to carbon

### Rules for drawing resonance structures:

1. The connectivity of all atoms must be the same. Never break a sigma (single) bond!
2. Each contributing structure must have the same number of electrons and the same net charge.
3. Never exceed the octet-rule for the second row elements (C, N, O, F)
4. Electrons are being moved from non-bonding electron pairs or pi bonds.
5. When breaking a pi bond, electrons typically move to electron rich atoms, place the negative charge or lone pairs on the more electronegative atom in the bond.
6. Do not place like charges on adjacent atoms.

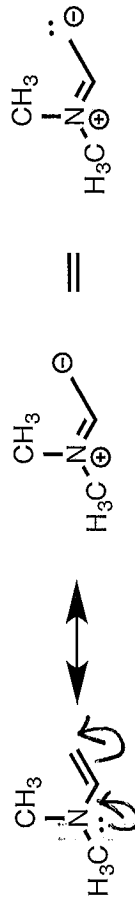
**Exercise:** For each problem below, determine which of the 6 rules for drawing resonance structures is violated.



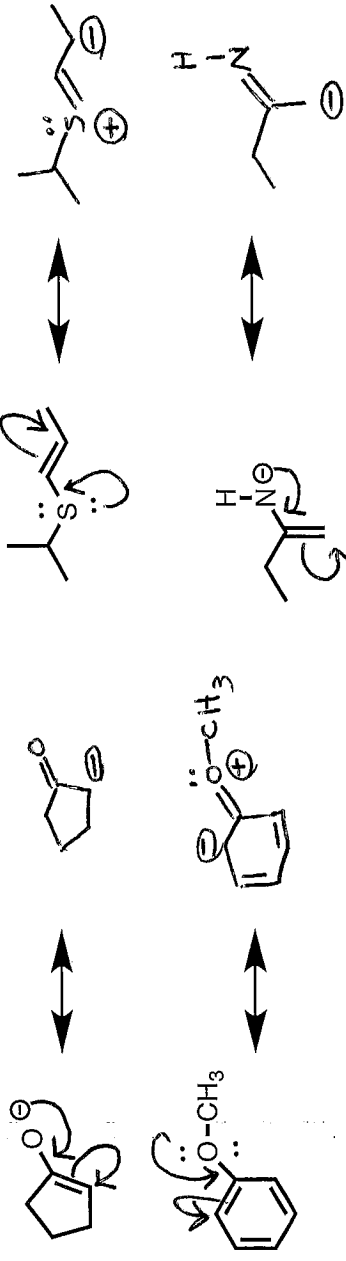
**Pattern Recognition:** Learning to recognize patterns will aid in your ability to draw resonance structures. Look out for the following patterns and draw the curved arrows that get you there.

- Allylic lone pairs - Lone pair electrons or negative charge next to a double bond are pushable electrons. (Allylic refers to any species on the carbon next to a pi bond.)

**Exercise:** Provide the appropriate curved arrows.

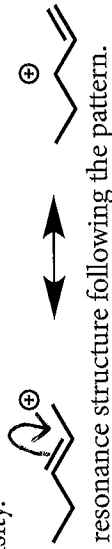


**Exercise:** Provide the resonance structure following the pattern.

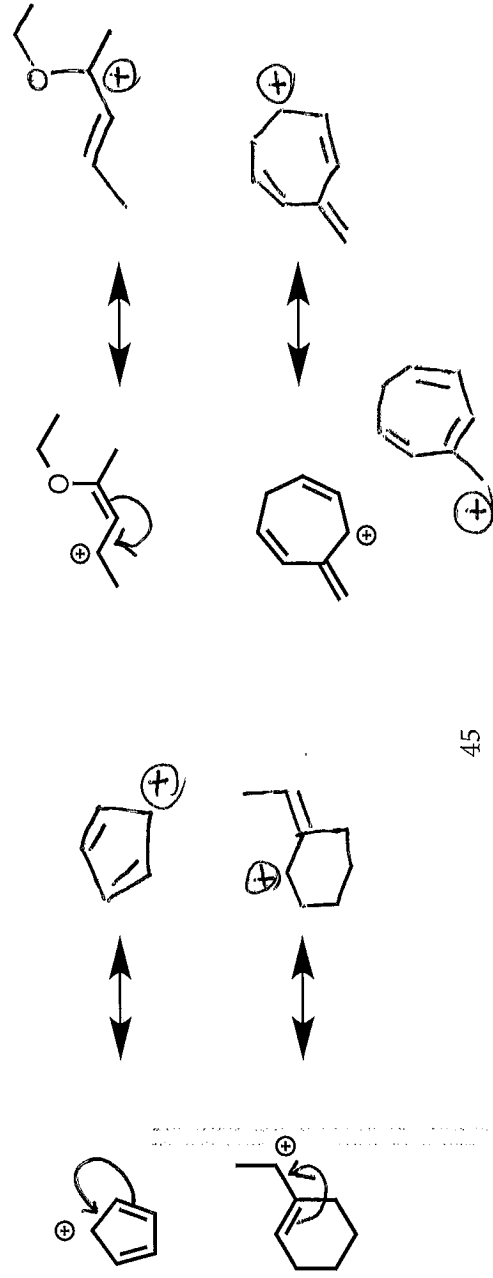


2. Allylic positive charge - Electrons in a  $\pi$  bond adjacent to a positive charge are pushable.

**Exercise:** Provide the appropriate curved arrows. \*Recall that the arrow begins at the source of electron density.

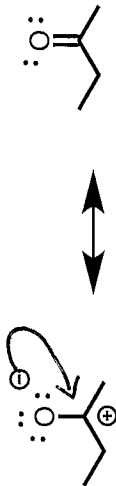


**Exercise:** Provide the resonance structure following the pattern.

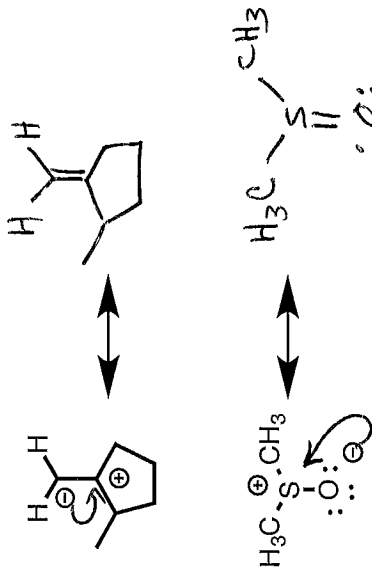
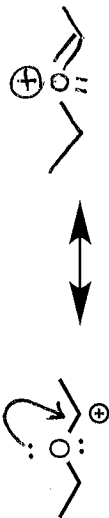


3. Lone pair electrons or a negative charge adjacent to a positive charge

**Exercise:** Provide the appropriate curved arrows.

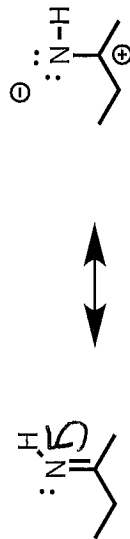


**Exercise:** Provide the resonance structure following the pattern.

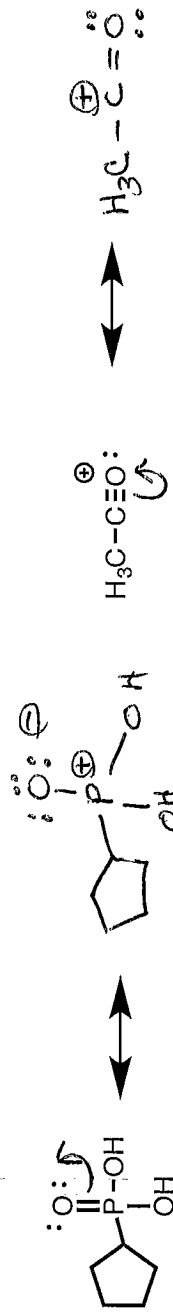
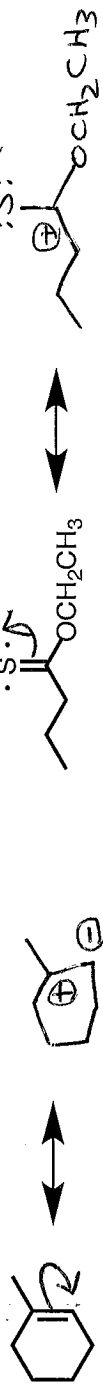


4. A  $\pi$  bond between two atoms of different electronegativity. In this case the electrons flow to the more electronegative atom of the bond. In the case of a  $\pi$  bond between two carbon atoms, the preference for the negative charge is not as clear.

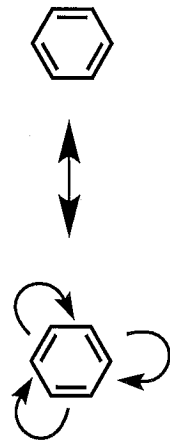
**Exercise:** Provide the appropriate curved arrows.



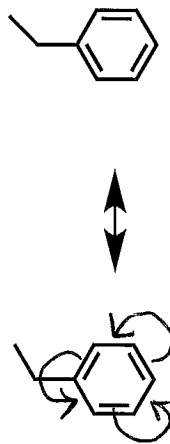
**Exercise:** Provide the resonance structure following the pattern.



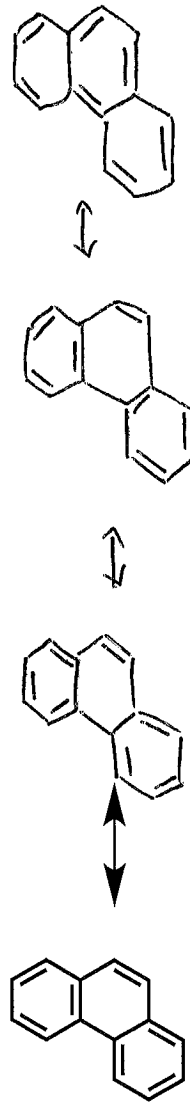
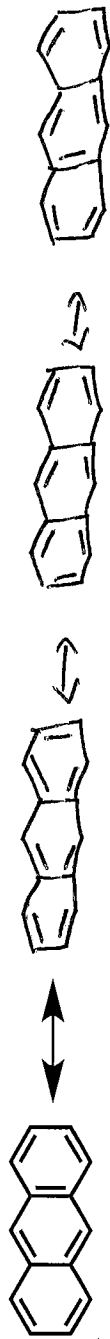
5. Conjugated  $\pi$  bonds enclosed in a ring. The resulting resonance structures typically involve a circulation of pi bonds around the ring. The movement of electrons within a benzene ring typically involve the use of three arrows that move simultaneously.



**Exercise:** Provide the appropriate curved arrows.

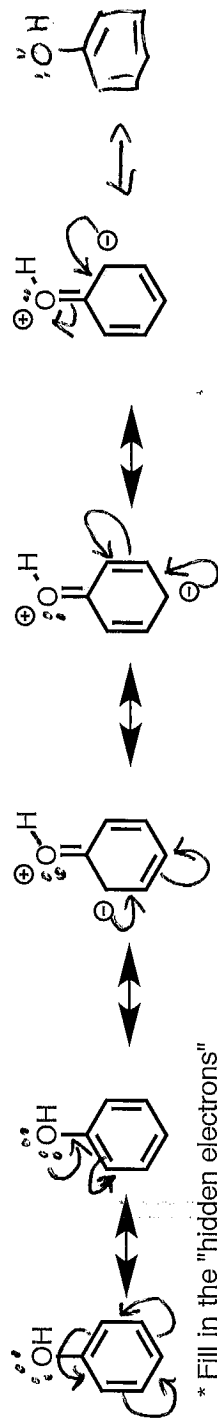


**Exercise:** Provide 3 different resonance structure for each molecule following the pattern.

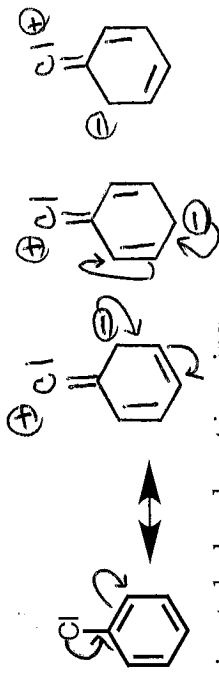
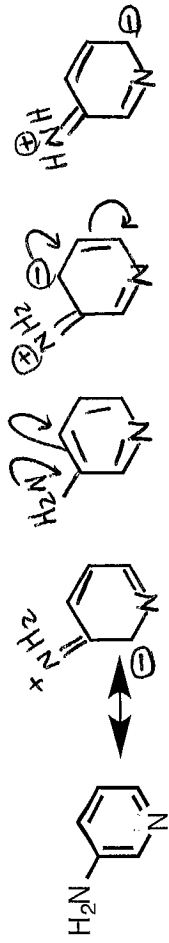
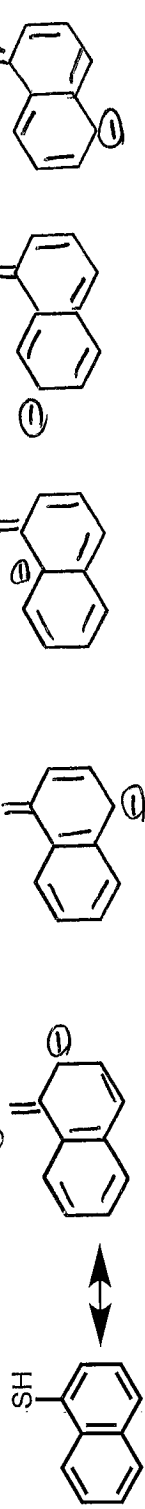


6. Groups outside the ring system can also participate in ring resonance.

**Exercise:** Provide the appropriate curved arrows.



Exercise: Provide 3 different resonance structures for each molecule following the pattern.

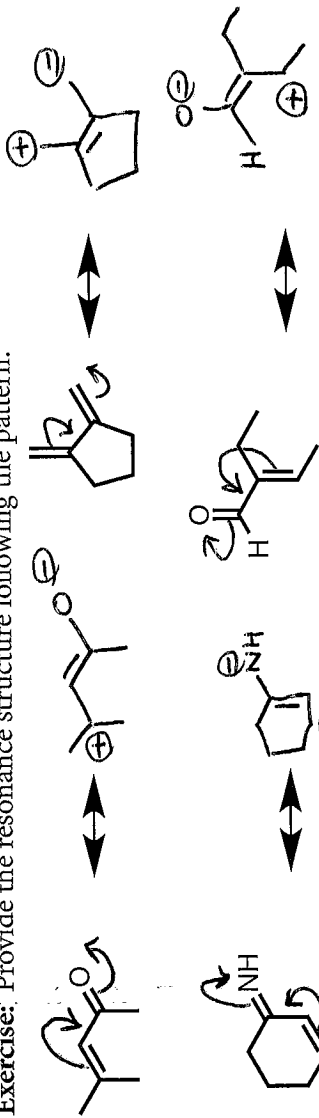


7. Conjugated  $\pi$  bonds not in a ring

Exercise: Provide the appropriate curved arrows.



**Exercise:** Provide the resonance structure following the pattern.



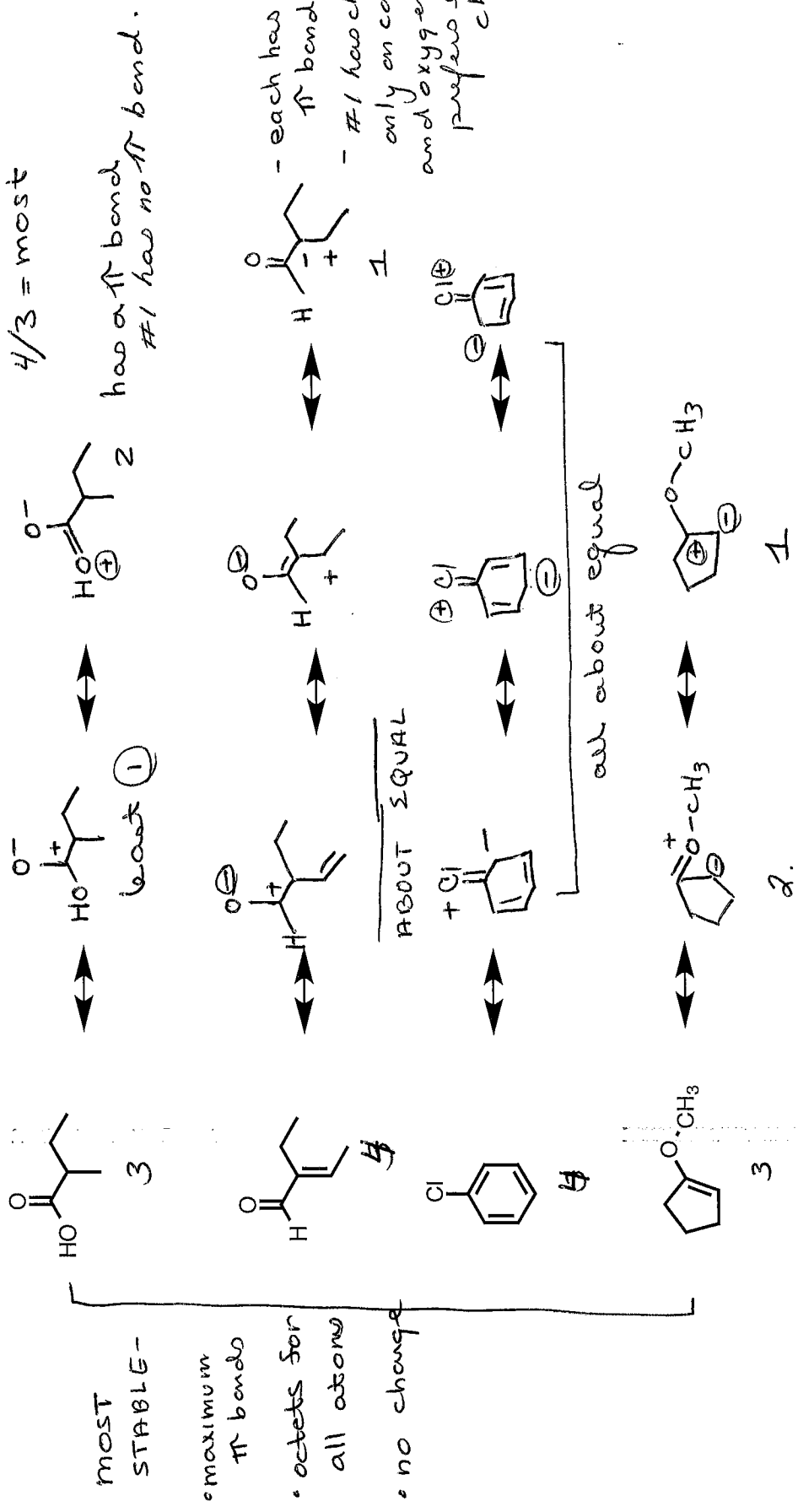
**How do I know which resonance form contributes more?** There are certainly some rules to follow, but in general the more stable resonance forms has (1) less charge separation, (2) more pi bonds rather than less, and (3) places negative charges on electronegative atoms and positive charges on electropositive atoms. These are simple guidelines that will help you to evaluate resonance forms.

- #1: Valence shells prefer to be filled
- #2: Maximize the number of pi bonds when applicable
- #3: Minimize point charges when possible
- #4: Place negative charges on the more electronegative atom and positive charges on the more electropositive atom when breaking a pi bond
- #5 More than two contiguous charges is considered unstable. More than three charges in a molecule is typically not seen (with the notable exception of a nitro group).



Exercise: Provide resonance structures for each molecule and rank their resonance forms from most to least stable using the above criteria.

1 = least  
4/3 = most



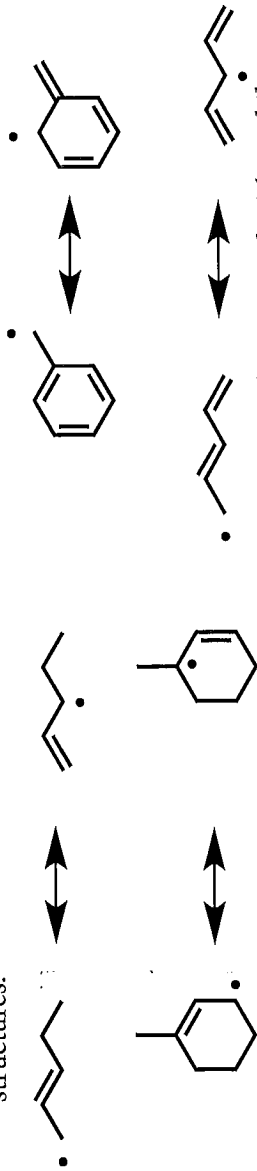
- MOST STABLE -
- maximum  $\uparrow$  bonds
- octets for all atoms
- no charge

## Reactive Intermediates of Carbon: Focus on Carbocations

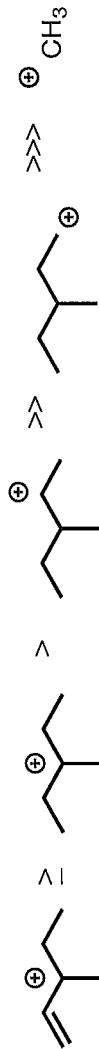
There are four reactive intermediates for carbon: carbanion, carbon radical, carbocation and carbene. The most commonly seen reactive intermediate in first semester is the carbocation. Common characteristics of the reactive intermediates of carbon are outlined in the table below.

	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \cdot\cdot \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \cdot \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{C}^+-\text{CH}_3 \end{array}$	$\begin{array}{c} \text{H}_3\text{C}-\text{C} \\ \cdot\cdot \end{array}$
Name	carbanion	carbon radical	carbocation	carbene
Formal Charge	-1	0	+1	0
Acid / base	base	does not apply to radicals which are all electron deficient	acid	acid
Rearrangement?	no	allylic radicals have resonance forms	yes	no

Carbanions and carbenes do not rearrange. Radicals can undergo resonance delocalization if they are next to a pi bond, in other words, allylic. The radicals below haven't really rearranged because only the electrons are moving. They are really resonance structures.

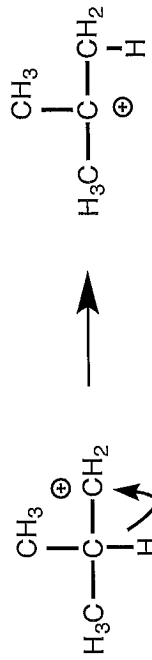


Carbocation rearrangements occur to give a more stable carbocation only. The stability ranking for carbocations allylic =  $3^\circ > 2^\circ > 1^\circ > \text{methyl}$ .

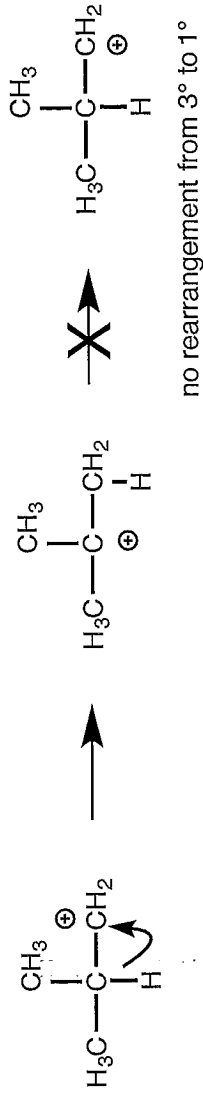


Carbocation stability is based on the inductive effect. The more highly substituted the carbocation is, the more stable it is. Each carbon attached to the carbocation will release some electron density from its C—C sigma bond which helps to alleviate, or lessen, the positive charge on carbon. Carbocations are also stabilized by placement of the charge on a more substituted carbon.

In the case of carbocations, we actually move atoms, and in the process breaking and making sigma bonds. This is a true rearrangement process. Please note that we do not move the + charge. A plus charge really means “missing electrons” and you cannot move what you do not have!

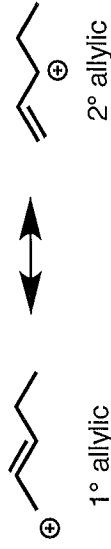


A common mistake is asking the carbocation to rearrange to a less substituted, less stable carbocation.

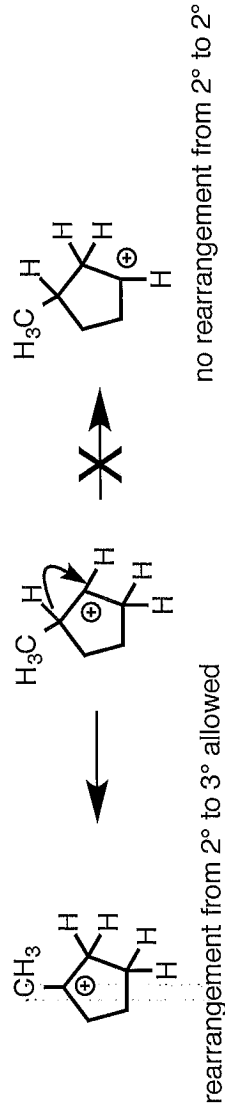


**There are three basic moves for rearrangement.**

A) A simple resonance delocalization via a pi bond is typical for allylic cations. Notice only the pi electrons are moving; no sigma bonds have been broken, so it's technically not a rearrangement but we often place this in the rearrangement category for carbocations.



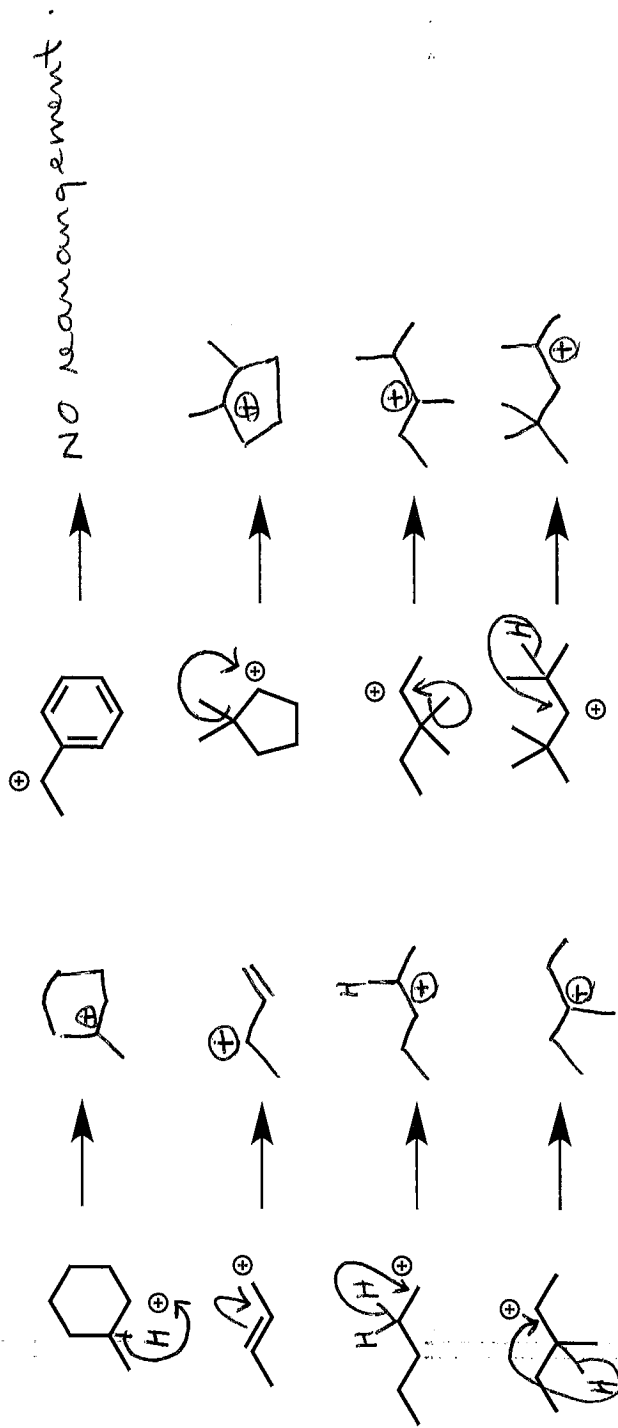
B) The hydride shift is a move that results in a C—H sigma bond breaking and then reforming at the adjacent carbon which originally had the carbocation. Notice that the hydrogen atom and the two electrons from the C—H sigma bond are migrating. A hydride with 2 electrons is a hydride, or H<sup>-</sup>.



C) The methide shift is a move that results in a C-CH<sub>3</sub> sigma bond breaking and then reforming at the adjacent carbon which originally had the carbocation.



**Exercise:** Show the rearrangement product to the more stable carbocation. Don't forget about those implied hydrogens.



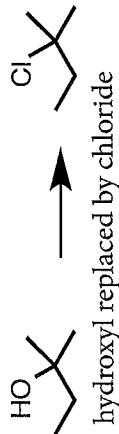
NO rearrangement.

Hydride > methide of both give the same stability for the carbocation

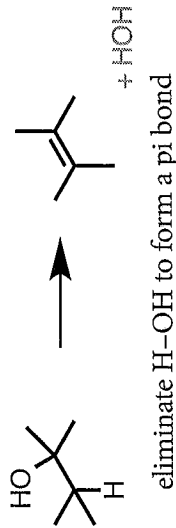
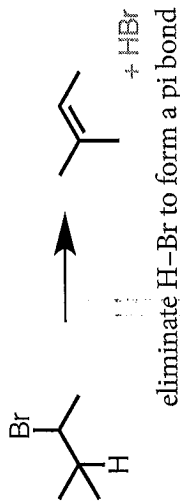
## Classification of Reactions: Substitution, Elimination, and Addition

Most organic reactions can be classified into one of three categories based on the transformation of reactant to product. Knowing how to classify a reaction can give us a clue to the mechanism. For example if we classify a reaction as an elimination, there are only two possible mechanistic pathways - E1 and E2. With just one more piece of information we can choose between E1 and E2 pathways. Classifying the overall reaction helps us to identify the mechanism, or figure out how the reaction actually works at the electronic level.

(1) Substitution Reactions: In a substitution reactions one atom or group of atoms is replaced by another atom or group of atoms. In a very practical sense in first semester organic this normally means replacing one functional group on a carbon atom with a different functional group.



(2) Elimination Reactions: In an elimination reaction two atoms (or groups of atoms) on adjacent carbons are removed to form a pi bond. In first semester organic this normally means the loss of H-X on adjacent carbons.



(3) Addition Reactions: In an addition reaction a pi bond is broken and atoms or groups of atoms are added to the pi bond that was broken. In some cases you can consider addition the reverse form of elimination.



H-Br added across the pi bond

CH<sub>2</sub> is added across the pi bond



**Exercise:** Classify each reaction as substitution, elimination or addition.

