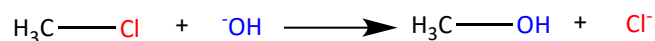


Chapter 8. Organic Reaction Basics

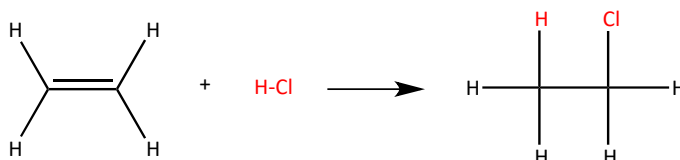
8.1 Types of Reactions

Organic reactions can be placed into several different categories.

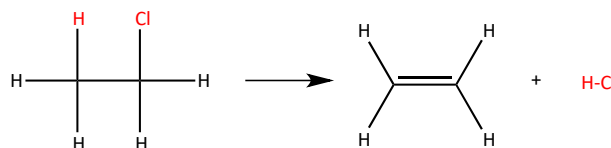
1. **Substitutions.** Much like how a substitute teacher replaces the regular teacher, a substitution reaction is one where one atom or group is replaced, or substituted, with another atom or group. One group replaces another group. In this case, hydroxide (OH^-) replaces chloride (Cl^-).



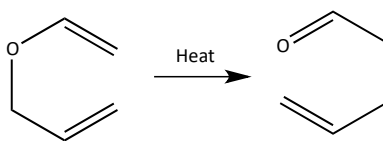
2. **Additions.** In an addition, two atoms or groups are added to a molecule's π bond. In effect, two molecules are added together. Two molecules become one molecule.



3. **Eliminations.** When something is eliminated, it is expelled or removed. In an elimination reaction, two atoms or groups are expelled from a molecule to generate a π bond and make two molecules. Elimination reactions are the opposite of addition reactions. Notice in this example, both H and Cl are removed to form a π bond.

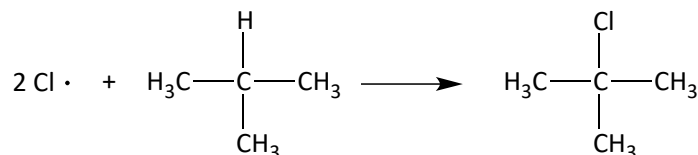
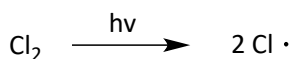


4. **Rearrangements.** In a rearrangement, a molecule reorganizes its bonds and atoms to make an isomer of itself.



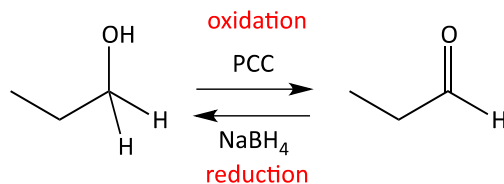
Claisen Rearrangement

5. **Free radical.** In a free radical reaction, the reactive species is one that contains a single, unpaired electron (a free radical). This free radical is often generated by using ultra violet light.

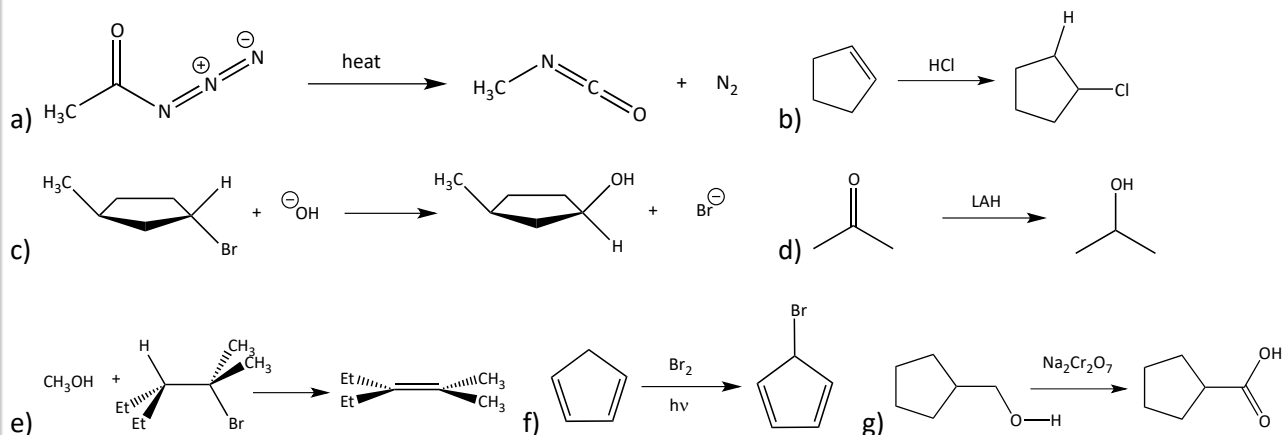


Organic Reaction Basics

6. **Oxidations/Reductions.** In organic oxidations or organic reductions, an organic species either gains oxygen or loses hydrogen. If a molecule makes more carbon-oxygen bonds and/or loses carbon-hydrogen bonds, we say it the organic species is oxidized. If a molecule gains hydrogen bonds, we say it is reduced.



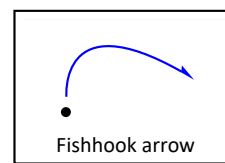
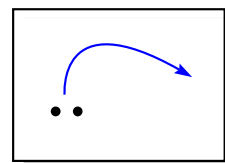
8.1 Identify each of the following reactions as a substitution, addition, elimination, rearrangement, free radical, oxidation, or reduction.



Each organic reaction has a story. Bonds are broken and bonds are formed. Reactants become products. Organic chemists call this story the mechanism of a reaction. It is how a reaction proceeds. The mechanism helps organic chemists understand why and how the reaction happened. Mechanisms are very important in organic chemistry.

A mechanism is a step-by-step story of how a reaction proceeds. Sometimes, you will be given both the reactants and the products of a reaction and be asked to give the mechanism of how the reaction went. At other times, you may be asked to predict what will happen in a reaction given two or more reactants. This is usually the more difficult task.

To be able to tell the mechanism story, you need to know the conventions organic chemists have agreed upon. The agreement is that we will show where electrons move in a reaction. To show this movement of electrons, we use arrows. A regular two-headed arrow shows the movement of two negative electrons. Did you get that? That last sentence may be one of the most important statements I will teach you. *Arrows show the movement of negative electrons.* Arrows DO NOT show the movement of positive charges, atoms, or anything else you can think of. Arrows in organic reaction mechanisms show the movement of negative electrons. Students who fail to learn this are almost never successful in organic chemistry. If you don't learn to focus on the movement of

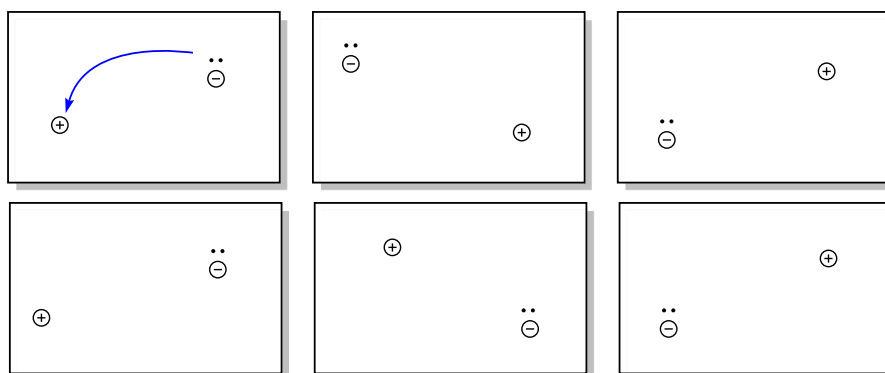


these electrons, organic chemistry will remain a mystery. It is my belief that successful organic chemistry students learn to think in terms of arrows.

There is a small subset of organic reactions called free radical reactions where only one electron is moving at a time. In these cases, we use an arrow with only one barb on its head, sometimes called a fishhook arrow.

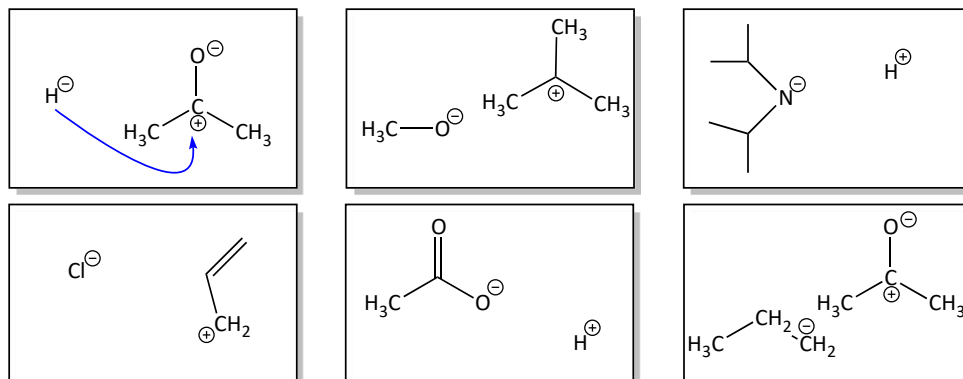
For this chapter, we'll focus on regular, two-headed arrows. Arrows in mechanisms always start at negative electrons and show you where they go. Every time I look at a mechanism, I first ask myself where the electrons are moving. And since electrons have a negative charge, they almost always move towards the most positive atom on another reactant.

8.2 Draw one arrow in each of the following boxes. Your arrow should ALWAYS begin at the negative electrons and travel towards a positive spot. You can curve your arrows a little bit if you want, but it doesn't matter.



Of course, for real molecules, there are several atoms. In the following exercise, I've made several molecules. On each molecule, I've identified one most negative atom and one most positive atom.

8.3 Draw one arrow in each box showing the movement of the electrons from the negative charge on the molecule on the left to the positive charge on the molecule on the right.



8.2 Nucleophiles/Electrophiles

To be a little more technical, the negative molecules are called **nucleophiles** and the negative spots are called **nucleophilic sites**. Nuclei are positively charged and “philic” means “lover of”. Opposites attract, so negative things love positive things; they’re nucleophilic.

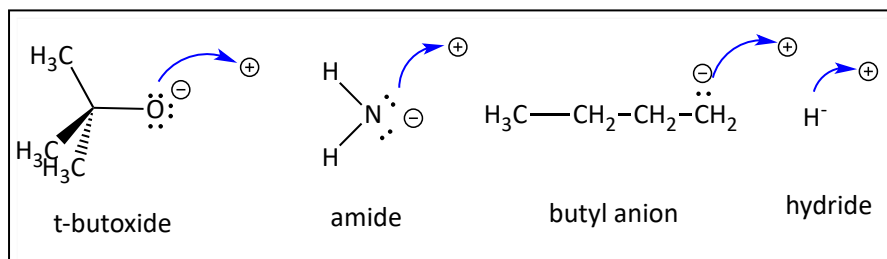
Positive molecules are called **electrophiles**. Positive spots are called **electrophilic sites**. Electrons are negatively charged, so electrophiles are lovers of negative things. Negative things are called nucleophiles, positive things are called electrophiles.

8.4 Circle the appropriate word in each of the following sentences.

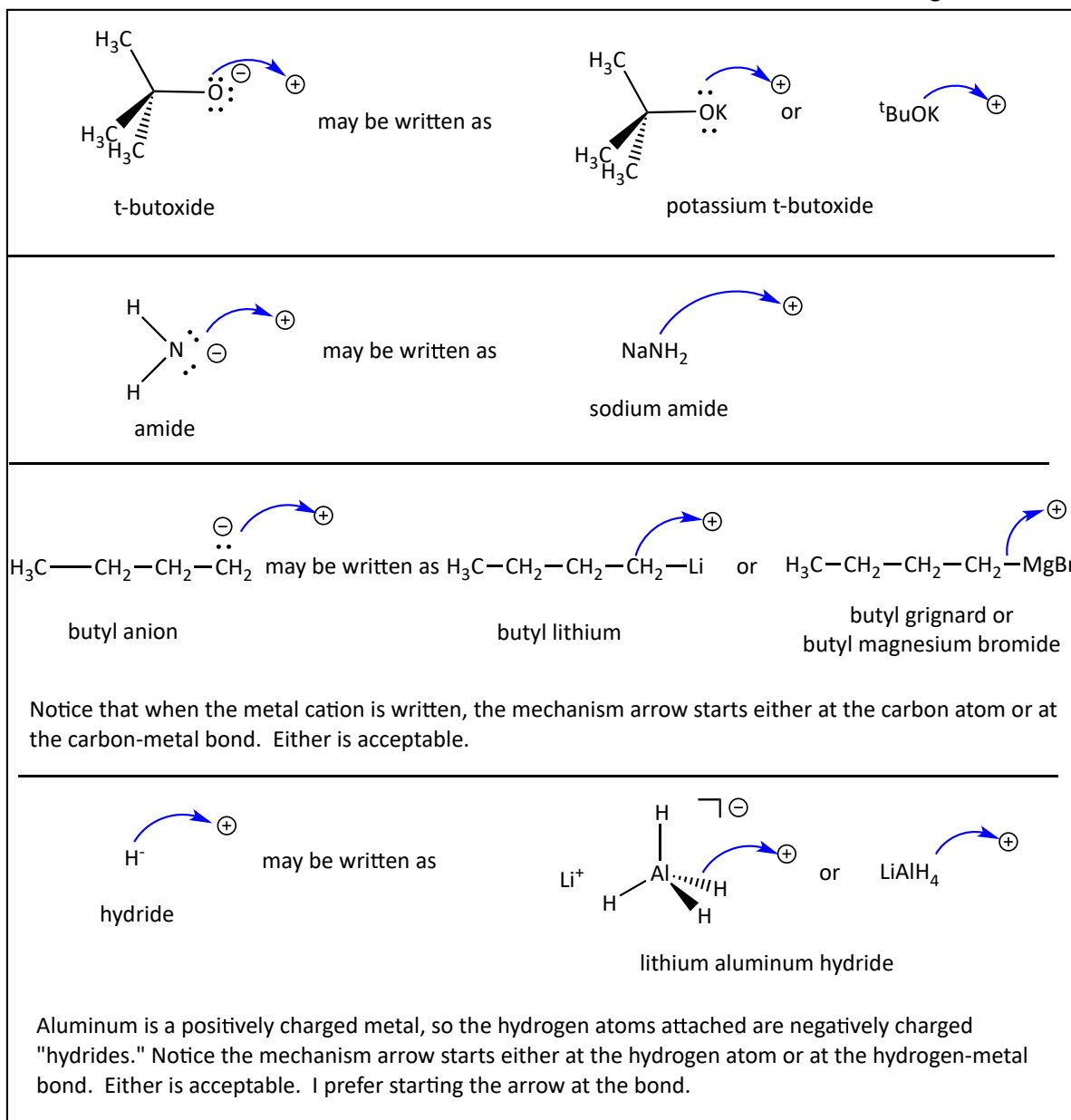
- Negatively charged molecules are called (electrophiles/nucleophiles).
- Positively charged molecules are called (electrophiles/nucleophiles).
- A molecule that is attacked by a negatively charged molecule is called a(n) (electrophile/nucleophile).

8.3 Finding Nucleophilic Sites

Let’s first address how we recognize the most negative spots (nucleophilic sites) in real molecules. Perhaps the most obvious situation is if an atom has a formal negative charge. Examples of this are oxides, amide ions, carbanions, and hydrides. Remember that arrows always show where the negative electrons move. In the following figure, the arrows originate at the negative, nucleophilic sites.

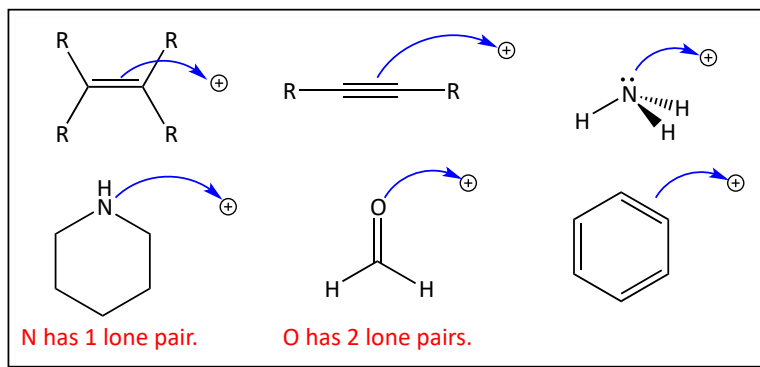


The charges are sometimes drawn on the atoms. When they are, that helps us determine where to start our arrows. But in fact, this negative charge is always balanced out by a counterion. The counterion is a positive cation, usually a metal cation. This metal cation is typically drawn attached to the most negative, nucleophilic site. This can make it a little trickier recognizing the negative atom. Remember that anytime you see a metal in a molecule, the atom attached has a negative charge. A positive metal has a negatively charged atom attached to it! It is this negative atom that will go out and attack in our mechanisms. Our arrow will start there. Here are some examples of how these compounds may be written with the metal. Remember that arrows are pointing away from the most negative, nucleophilic sites.

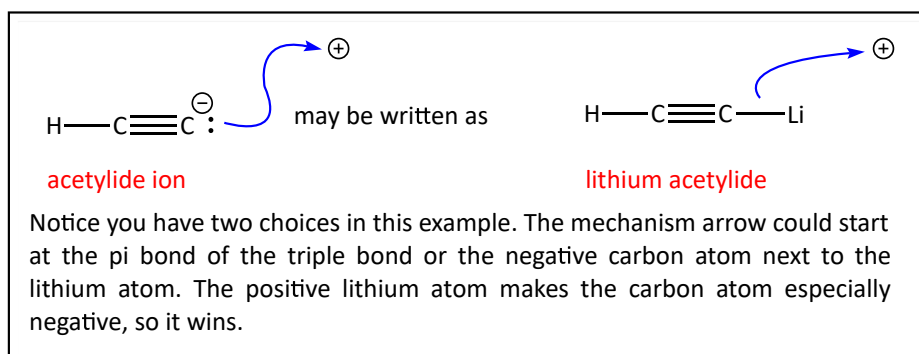


If you don't see a formal negative charge on an atom, or if you don't see a metal to tip you off to the location of a negative atom, look for other locations of nice, juicy negative electrons. The best place to look? Look for double or triple bonds as they contain one or two π bonds respectively. You can also look for lone pairs of electrons. This is a little tricky for beginning students because chemists are lazy when it comes to drawing structures. We quite often do not draw in all of the lone pairs of electrons. It is assumed you will know how many lone pairs there are on each atom. Remember the normal bonding patterns and you will be all right. So, if you have a nitrogen, oxygen, or sulfur atom, be sure to draw in the lone pairs of electrons.

Organic Reaction Basics



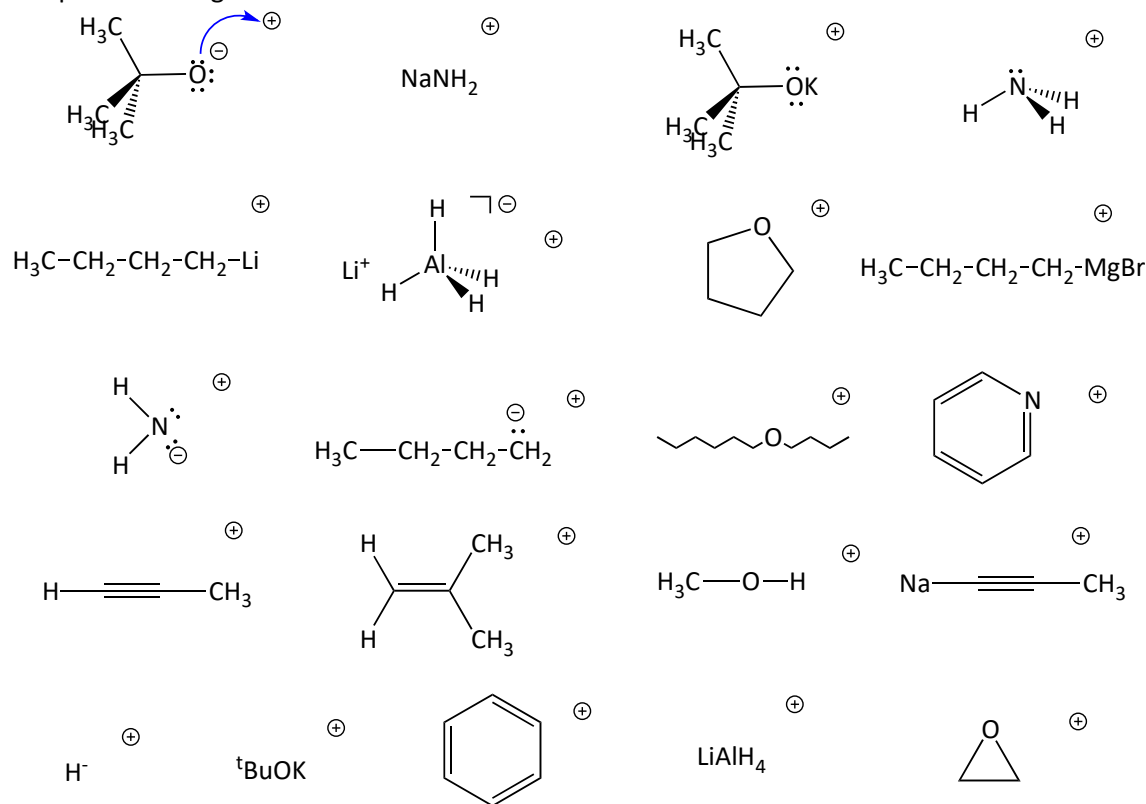
Sometimes, you'll have two sites to choose from. Let's consider lithium acetylide, $\text{H}-\text{C}\equiv\text{C}-\text{Li}$. In this molecule, we see the lithium metal atom which we remember is positively charged. This means that the carbon atom attached to the lithium has a partial negative charge. We can think of it as having a lone pair of electrons on it. But, we also notice that there is a pi bond that is also available for bonding. When you see a molecule with a metal written, our mechanism arrow will almost always start at the atoms attached to it. So, typically, carbon-metal bonds are more negative (more nucleophilic) than pi bonds.



In summary, there are four main locations to look for negatively charged sites on molecules.

- How to find negative sites
1. Formal negative charges
 2. Bonds between nonmetal and metal atoms
 3. Lone pairs of electrons
 4. Pi bonds

8.5 Draw arrows for the following molecule starting at the most negative spots (nucleophilic sites) and pointing towards the positive charges.

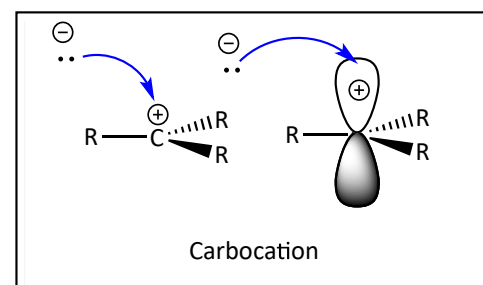


If you struggled at all or missed any of the problems in the previous exercise, go back and reread the beginning of this chapter once again. You should make sure you understand what is going on before proceeding. If you were successful in the previous exercise, great! Let's learn to recognize the positive spots (electrophilic sites) in molecule

8.4 Finding Electrophilic Sites

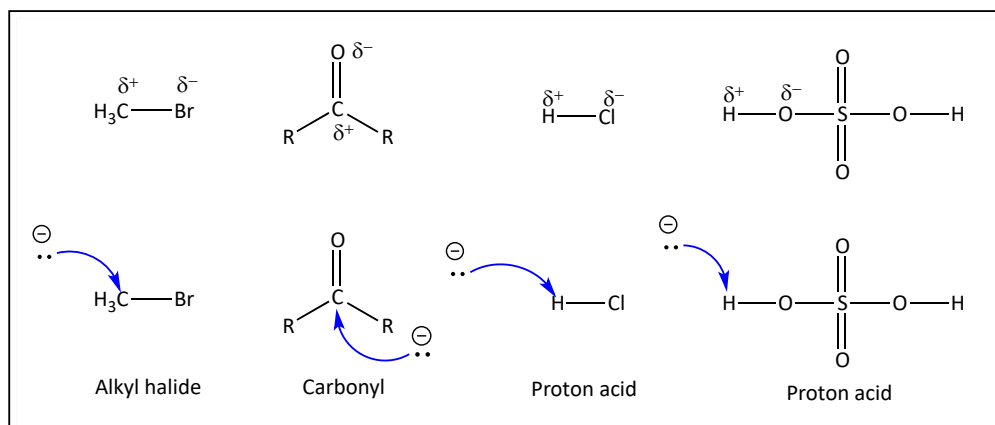
The first and most obvious electrophiles are *atoms with a positive charge explicitly written on them*. A carbocation (positively charged cation on a carbon atom) is a prime example. Carbocations have a carbon atom with three bonds and an empty p orbital.

Other sources of atoms with a positive formal charge, which may seem "hidden", are the acids. Recall that acids are a source of protons, H^+ . So, HCl , H_2SO_4 , H_3PO_4 are all sources of the electronegative H^+ .

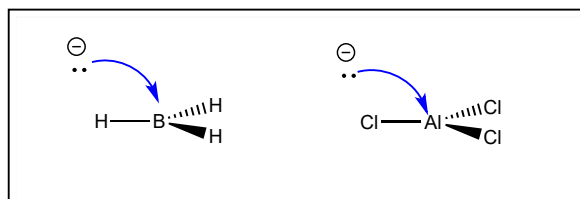


If a carbon or hydrogen is attached to a more electronegative atom, the carbon or hydrogen atom has a partially positive charge. Alkyl halides, carbonyls, and proton acids are also electrophiles.

Organic Reaction Basics



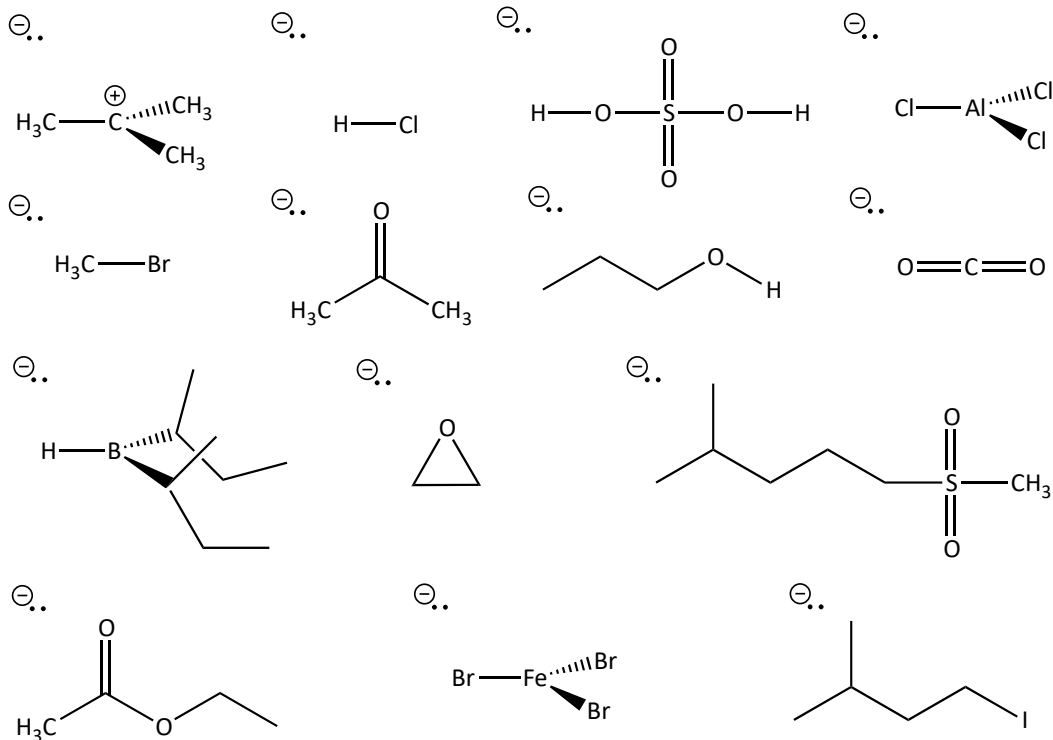
You may remember from general chemistry the strange chemical behavior of *boron (B)* and *aluminum (Al)*. They are atoms that are electron deficient because they normally have six electrons in their Lewis structures. They have an incomplete octet. Since B and Al contain a partial positive charge because they normally lack negative electron density around them.



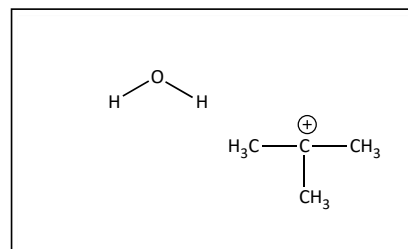
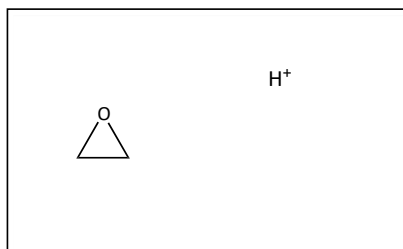
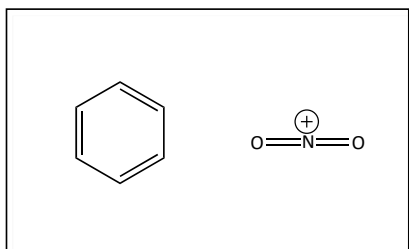
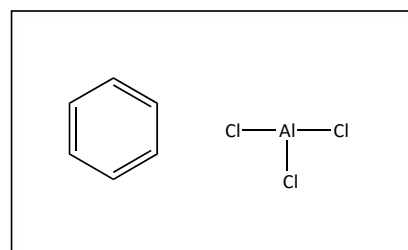
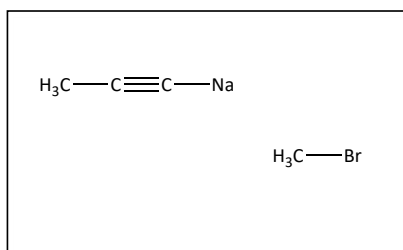
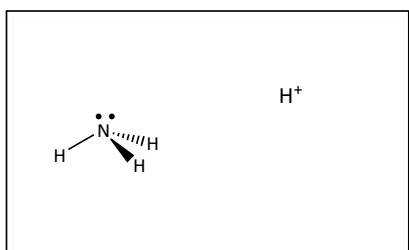
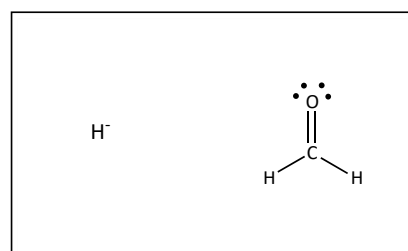
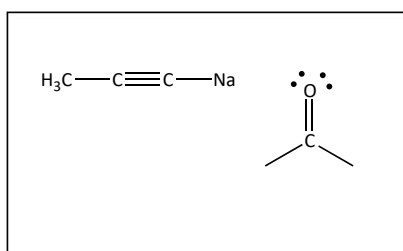
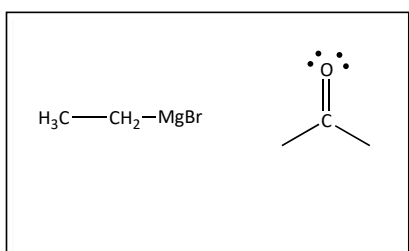
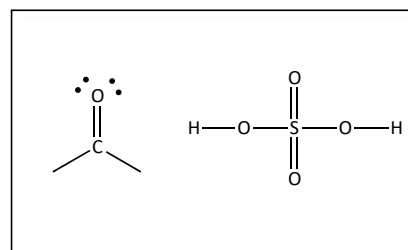
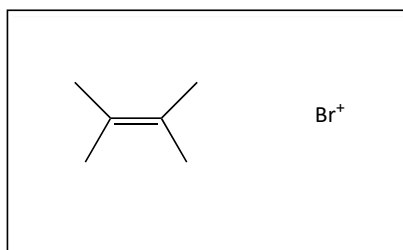
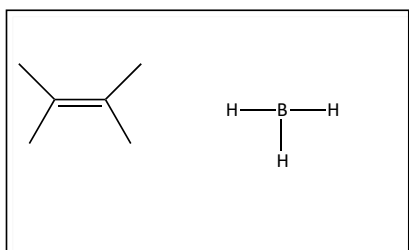
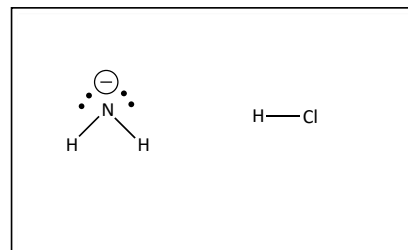
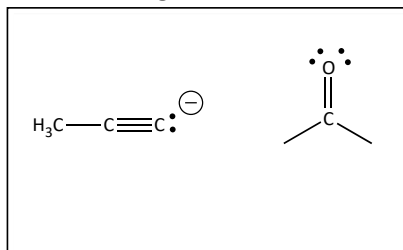
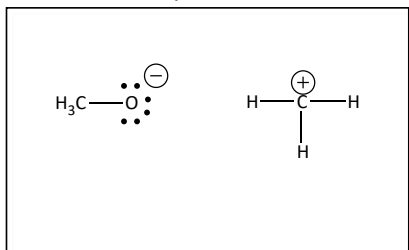
To summarize how to find positively charged electrophilic sites, look for the following.

1. Atoms with a formal positive charge written on them.
 - a. Sometimes the positive formal charge is written right on the atom. Hooray for those times!
 - b. Strong acids are a source of H^+ .
 - c. If you cannot find a positive formal charge, it might help to draw valid resonance forms until you find some good sites.
2. Atoms attached to electronegative elements.
3. Al or B atoms

8.6 Draw an arrow from the negative electrons to the most positive spot (most electrophilic site) in the following molecules.

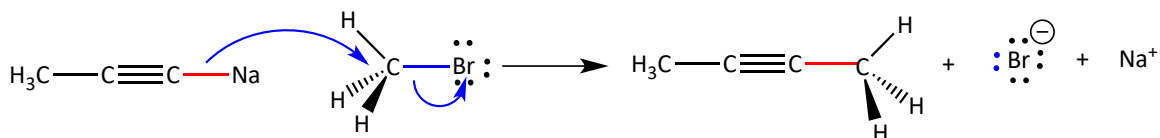


8.7 Draw arrows from the most negative, nucleophilic sites on one molecule on the left towards the most positive, electrophilic sites in the molecule on the right.



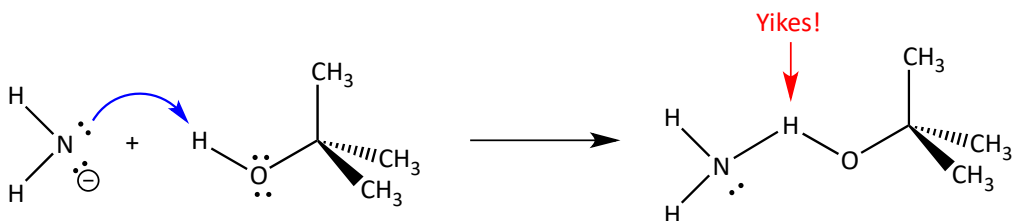
Organic Reaction Basics

Do you see a problem with the product? Of course, there are five bonds around a carbon atom! Ten electrons around the carbon atom break the octet rule. This molecule needs to get rid of two electrons from that carbon. A better mechanism would be the following with two arrows happening at the same time, a concerted mechanism.

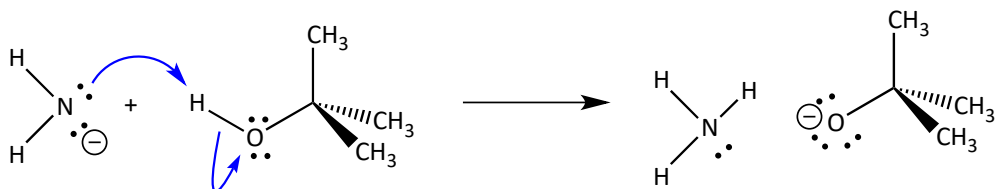


Using this two-arrow, concerted, mechanism we avoid the unsavory 10-electron species from above. Now, the carbon atom in the product only has its octet. So, a rule to follow is that if electrons are coming to an electrophile and it makes more electrons than an octet at an atom, then electrons **MUST** move away from this atom. If this is not the case, *use only one arrow*.

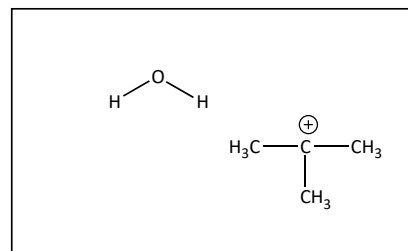
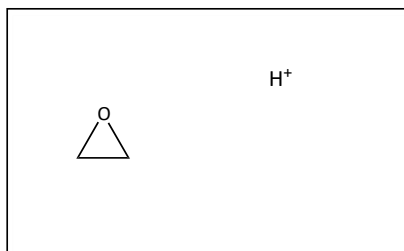
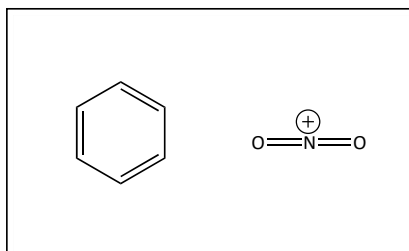
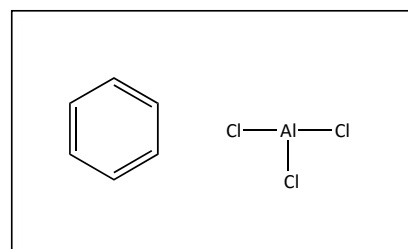
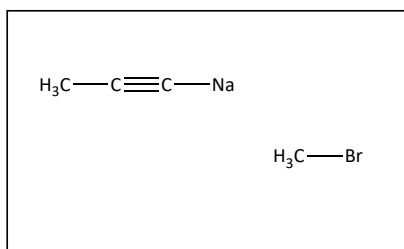
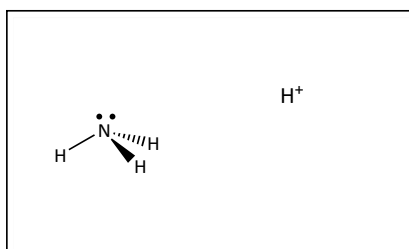
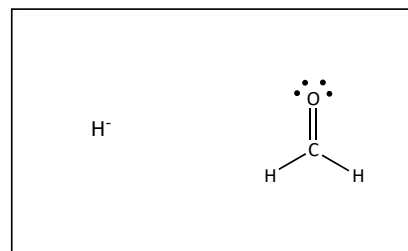
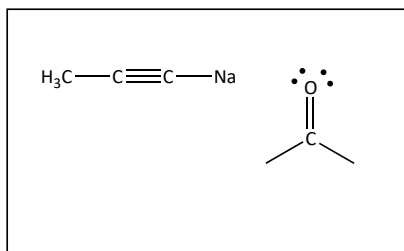
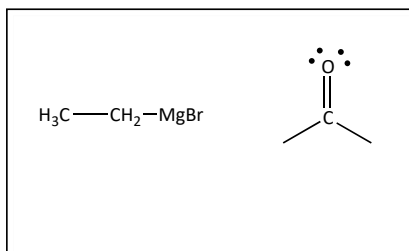
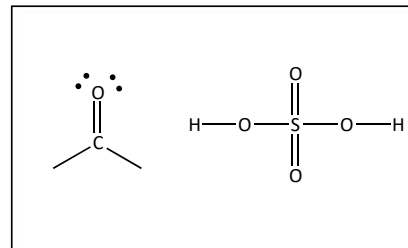
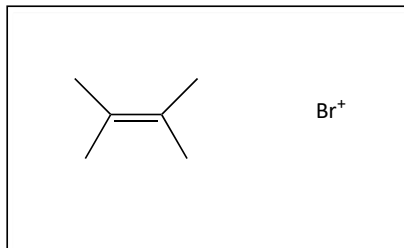
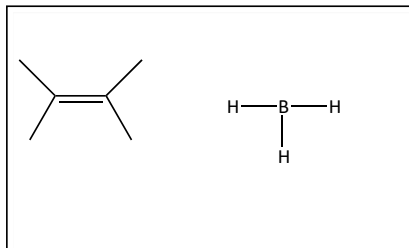
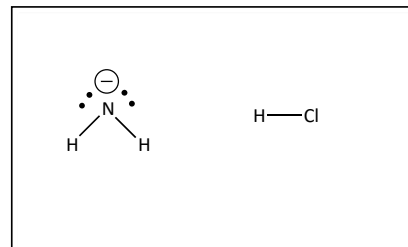
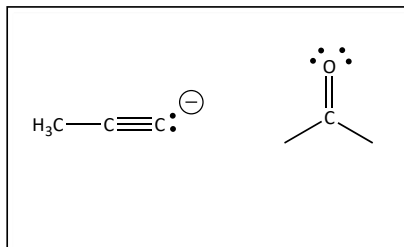
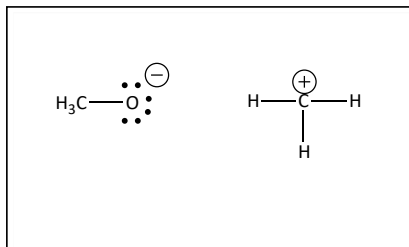
A similar situation occurs with acids. Consider what the following reaction looks like after one arrow has moved two electrons.



Do you see the problem? A hydrogen atom with two bonds in organic chemistry is not going to happen. Let's please have only one bond for every hydrogen atom. In order to avoid a situation like this, we again need two arrows.

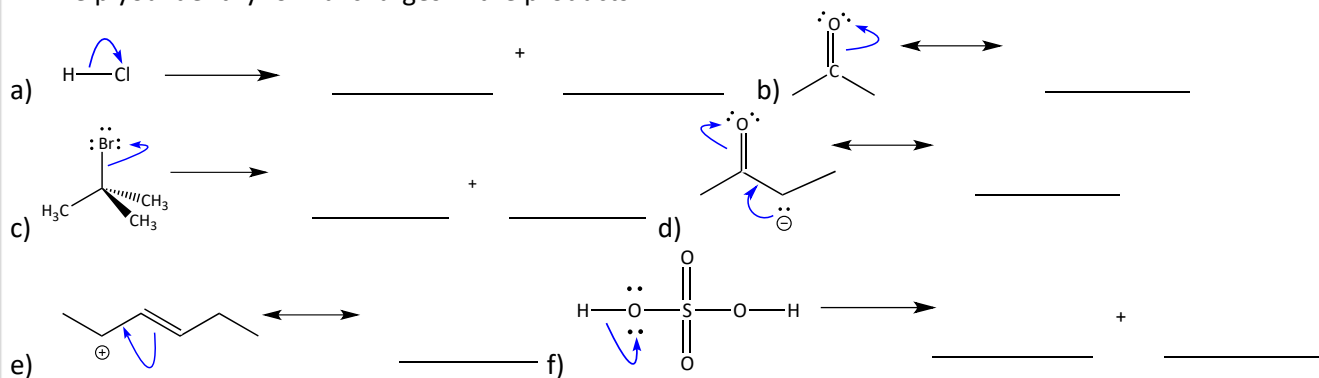


8.8 Draw in either one or two arrows, as appropriate, to complete the mechanism.

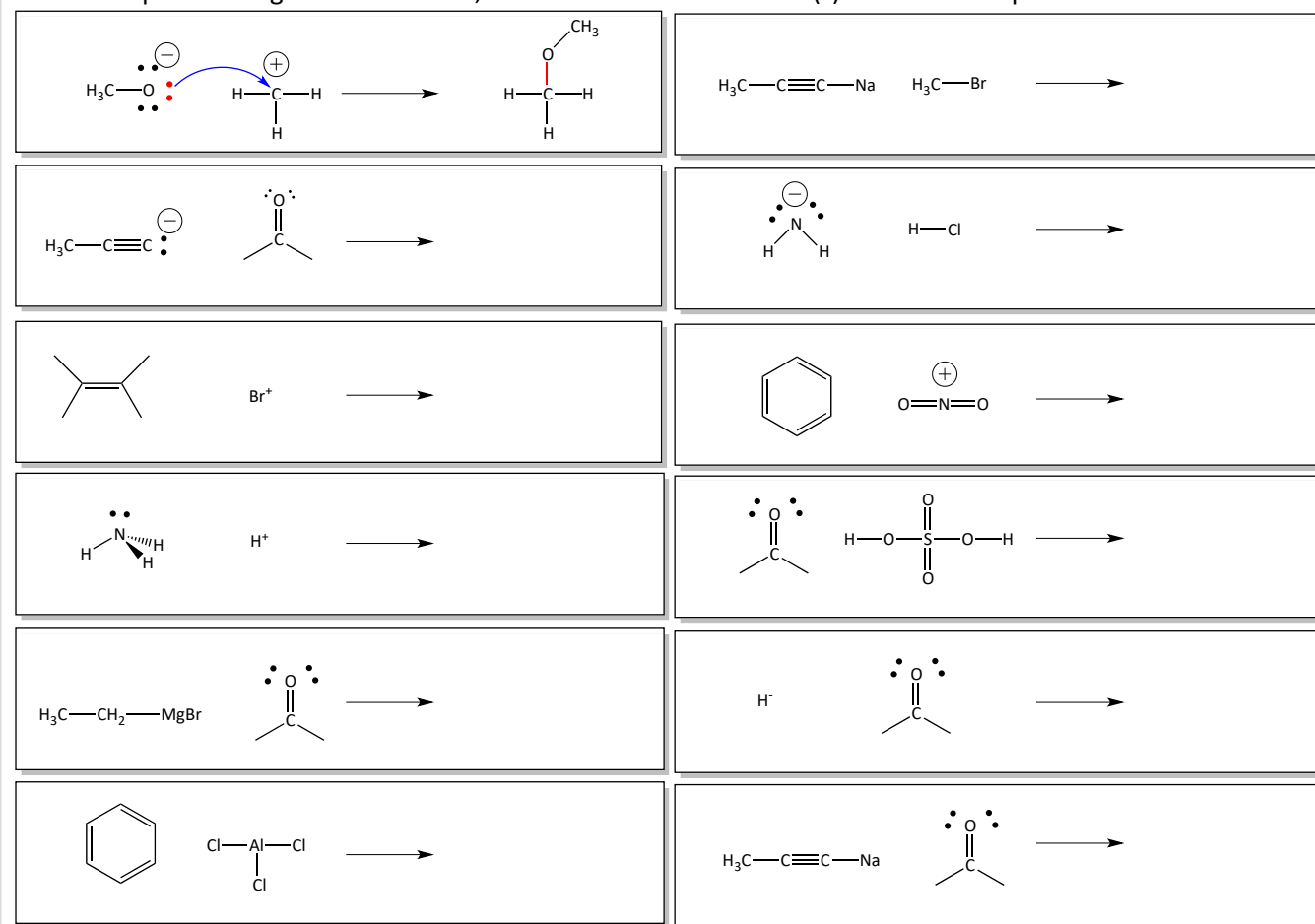


After you have completed this exercise, go and check your answers. If you missed any, make sure you understand why. If you did not miss any, you are ready for the next step.

8.9 Draw in the product or resonance form that is made after pushing the electrons that the arrows show. It is recommended that you draw in all lone pairs of electrons and hydrogen atoms near where the arrows are. This will help you identify formal charges in the products.



8.10 Let's put it all together. This time, draw the mechanism arrow(s) as well as the product that is formed.



8.6 Arrow Review

We have seen several types of arrows so far. Let's review the different types of arrows found in organic chemistry. Most of these are review, but here is one new one. A retrosynthetic arrow is the opposite of a regular reaction arrow. We use it when we are thinking about how we want to synthesize a particular product. When we ask, "What reactants would we mix together to make this product?" we are doing a retrosynthetic analysis. We use a retrosynthetic arrow to show we are thinking how to synthesize something.

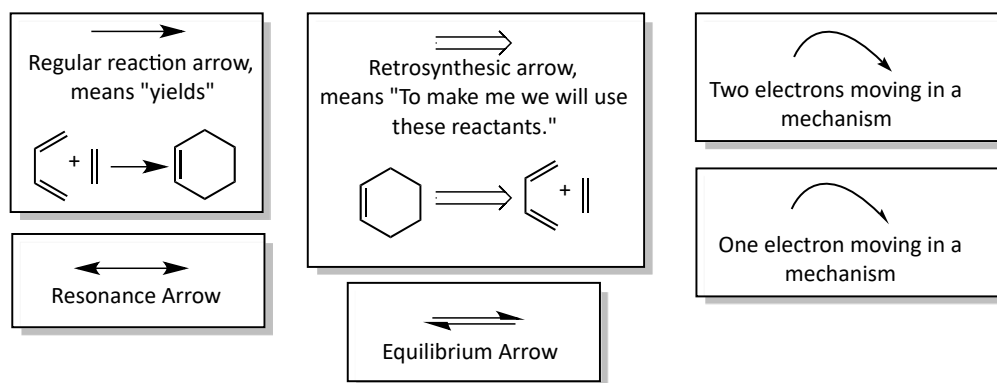


Figure 8.1 Various arrows

8.7 Reaction conditions

Symbols are sometimes written above the reaction arrows to indicate the reaction conditions. A small triangle is written above the arrow if the reaction is heated. It looks like the tip of a flame. One way to heat up an organic reaction to the boiling point of the solvent without losing the solvent is to perform a reflux. The solvent is boiled. The vapors travel up a condenser where they cool down, condense back into a liquid, and fall back into the reaction flask. An arrow pointing up and one pointing down is drawn over the reaction arrow if a reaction is heated to reflux. It represents the path the solvent travels. The symbol $h\nu$ is drawn above the reaction arrow if a reaction is placed under ultraviolet light. This comes from the equation for the energy of light $E=h\nu$.

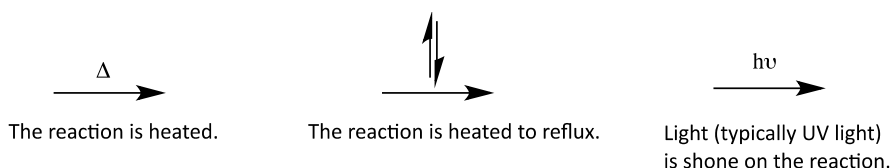


Figure 8.2 Symbols for various reaction conditions

Sometimes, instead of writing all of the reactants in a reaction to the left side of the reaction arrow, they are written above or below the arrow to signify they are added to the reaction. If numbers are placed before the reactants, then they are added in that particular order. If numbers are not written before the reactants, then all reactants are added to the reaction at the same time.

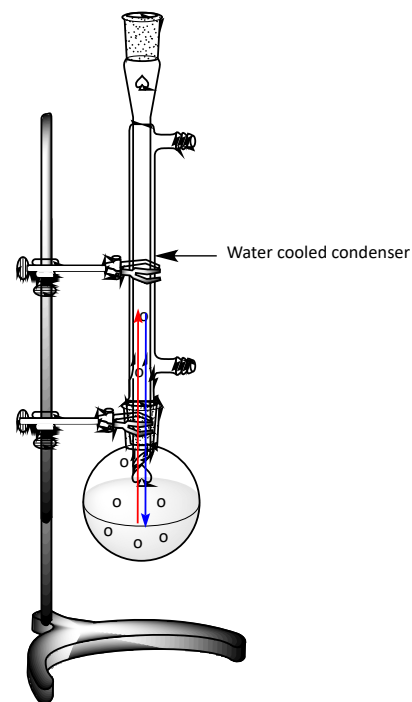


Figure 8.3 Reflux apparatus