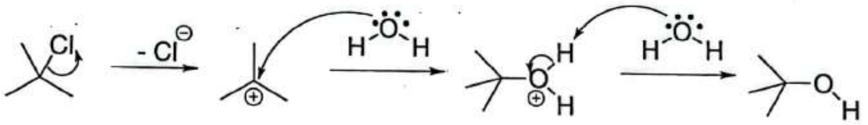
Name: ____________________ Date: __________

CHAPTER **8**

MECHANISMS

Mechanisms are your key to success in this course. If you can master the mechanisms, you will do very well in this class. If you don't master mechanisms, you will do poorly in this class. What are mechanisms and why are they so important?

When two compounds react with each other to form new and different products, we try to understand *how* the reaction occurred. Every reaction involves the flow of electron density—electrons move to break bonds and form new bonds. Mechanisms illustrate how the electrons move during a reaction. The flow of electrons is shown with curved arrows; for example,



These arrows show us how the reaction took place. For most of the reactions that you will see this semester, the mechanisms are well understood (although there are some reactions whose mechanisms are still being debated today). You should think of a mechanism as "bookkeeping of electrons." Just as an accountant will do the bookkeeping of a company's cash flow (money coming in and money going out), the mechanism of a reaction is the bookkeeping of the flow of electrons.

When you understand a mechanism, you will understand why the reaction took place, why the stereocenters turned out the way they did, and so on. If you do not understand the mechanism, then you will find yourself memorizing the exact details of every single reaction. Unless you have a photographie memory, that will be a very difficult challenge. By understanding mechanisms, you will be able to make more sense of the course content, and you will be able to better organize all of the reactions in your mind.

The mechanisms that you will learn in the first half of your course are the most critical ones. This is the time when you will either master arrow pushing and mechanisms or you will not master them. If you don't, you will struggle with all mechanisms in the rest of the course, which will turn your organic chemistry experience into a nightmare. It is absolutely critical that you master the mechanisms for the early reactions that you cover. That way, you will have the tools that you need to understand all of the other mechanisms in your course.

In this chapter, we will *not* learn every mechanism that you need to know. Rather, we will focus on the tools that you need to properly read a mechanism and abstract the important information. You will learn some of the basic ideas behind arrow pushing in mechanisms, and these ideas will help you conquer the early mechanisms that you will learn. The second half of this chapter provides a place for you to keep a list of mechanisms as you progress through the course. This list (which you will fill out as you go along) is arranged so that you will have the key information at your fingertips, and you will be able to use the list as a study guide for your exams.

8.1 CURVED ARROWS

We have already gotten quite a bit of experience with curved arrows in chapter 2 (Resonance). There is one very major difference between curved arrows for drawing resonance structures and curved arrows for drawing mechanisms. With resonance structures, we saw that the electrons were not really moving at all. We were pretending that they were moving so that we could draw all of the resonance structures. By contrast, the curved arrows that we use in mechanisms refer to the actual *movement of electrons.* Electrons are moving to break and form bonds (hence the term *chemical reaction*). Why are we stressing this difference? We first need to understand what arrows represent before we can move on to the rules of pushing arrows.

When we learned how to draw resonance structures, we saw two commandments that we must not violate: (1) never break a single bond, and (2) never violate the octet rule. When drawing mechanisms, we are trying to understand where the electrons actually moved to break and form bonds. Therefore, it is OK to break single bonds. In fact, it happens in almost every reaction. So when drawing mechanisms there is only one commandment to follow: never violate the octet rule.

Now that we have some of the ground rules down, let's just have a quick review of curved arrows, and the different types of arrows that you can draw. Every curved arrow has a *head* and a *tail*. It is essential that the head and tail of every arrow be drawn in precisely the proper place. *The tail shows where the electrons are coming from, and the head shows where the electrons are going:*

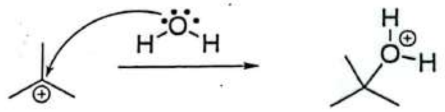
Therefore, there are only two things that you have to get right when drawing each arrow. The tail needs to be in the right place and the head needs to be in the right place. Remember that electrons exist in orbitals, either as lone pairs or as bonds. So the *tail* of an arrow can only come *from a bond* or *from a lone pair:* The *head* of an arrow can only be drawn to *make a bond* or to *make a lone pair:* In total, this gives us four possibilities:

1. Lone pair → bond
2. Bond → lone pair
3. Bond → bond
4. Lone pair → lone pair

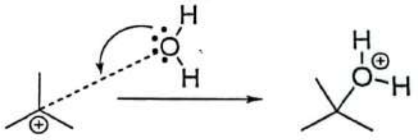
The last possibility does not work, because we cannot push electrons from one lone pair to another (at least not in one step). So we only have to consider the first three possibilities. Every arrow you will see will belong to one of these three categories, so let's see examples of each of the three categories.

From a Lone Pair to a Bond

Consider the second step in the mechanism above, where we are forming a single bond:



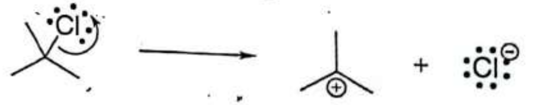
The tail of the arrow is coming from a lone pair on the oxygen atom, and the head of the arrow is going to form a bond between oxygen and carbon. Since the head of the arrow is placed on an atom, it might seem like the electrons are going from a lone pair to a lone pair, but they are not. The electrons are going from the oxygen lone pair to form a bond to the carbon atom. If this makes you unhappy, there is an alternative way of drawing the arrow that shows it more clearly:



The dotted line shows the bond that is about to form, and we draw the arrow to that dotted line. In this drawing it is very clear that the head of the arrow is going to form a bond. When you see an arrow drawn the first way (where it looks like it is going to an atom rather than to form a bond), don't be confused by this—it really is just going to form a bond.

From a Bond to a Lone Pair

Consider the first step of the mechanism above, where we are breaking a single bond:

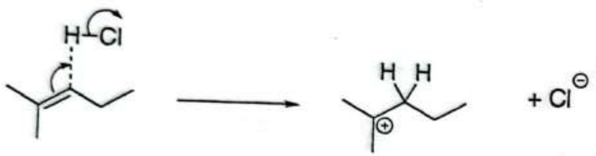


The tail of the arrow is on a bond, and the head of an arrow is forming a lone pair on the chlorine atom. The two electrons of the bond used to be shared between the carbon and the chlorine atoms. But now, both electrons are going on the chlorine. So the carbon has lost an electron, and the chlorine has gained one. This is why the carbon ends up with a positive charge, and the chlorine gets a negative charge.

By the way, a chlorine atom with a negative charge is called a chlor*ide ion* (-ide- implies the negative charge). So in this reaction chloride is *popping off of the* molecule to form a carbocation (a carbon with a positive charge).

From a Bond to a Bond

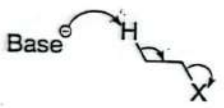
Consider the first arrow in the example below, where we are using the electrons of the pi bond to attack a proton (H^+), and kicking off Cl^- in the process:



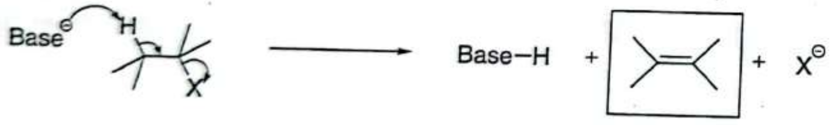
The first arrow has its tail on the pi bond, and the head is being used to form a bond between a carbon atom and the proton.

You will notice in the example above that there are two arrows. The first arrow is going from a bond to a bond. But the second arrow is going from a bond to form a lone pair. So we see that you can have more than one type of arrow together in one step of a mechanism.

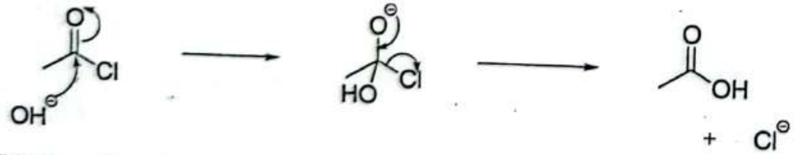
In fact, it is possible to have all three types of arrows in one step of a mechanism. Consider the example below:



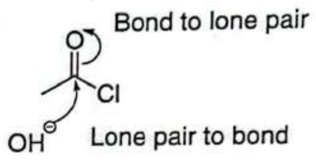
Notice that there is one long flow of electron density, illustrated with three arrows. We begin at the tail of the arrow on the base, because that is where the flow starts. This arrow is going from a lone pair to form a bond. The second arrow goes from a bond to form a bond, and the third arrow goes from a bond to form a lone pair on X. This type of reaction is called an elimination reaction, because we are *eliminating* H^+ and X^- to form a double bond:



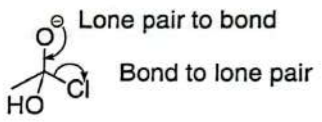
Notice that the arrows are all going from one end of the molecule to the other. *Never* draw arrows going in opposite directions. That would not make any sense! To see what we mean by this, consider the example below:



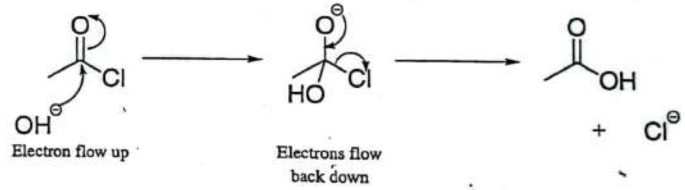
This type of reaction will be covered much later on in your course, but let's use it now as an example. Notice that there are two steps to this mechanism. In the first step, we have two arrows: from a lone pair to form a bond, and then from a bond to form a lone pair:



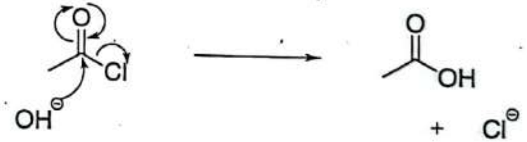
In the second step of the mechanism, we also have two arrows: from a lone pair to form a bond, and then from a bond to form a lone pair:



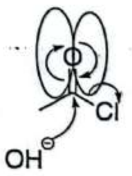
If we consider the overall reaction, we notice that the OH^- is replacing the Cl. If we look at how the electrons flowed, we see that it all started at the negative charge of the attacking OH^-. This charge flowed up temporarily on to the oxygen atom of the C=O in step 1 of the mechanism, and then the charge flowed back down to kick off Cl^-:



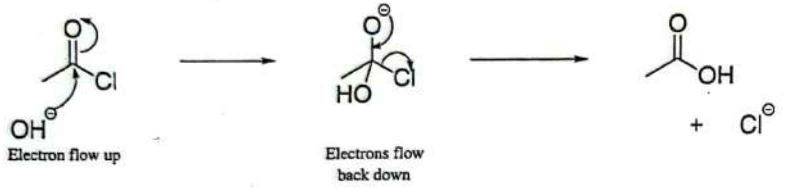
When we consider how the charge flowed throughout the whole reaction, it might be tempting to draw it all in one step, like this:



However, this is no good, because we have two arrows going in opposite directions:



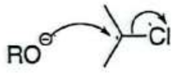
Never draw arrows in opposite directions. That would imply that the electrons were flowing in opposite directions *at the same time*. That is not possible. In this reaction, the electrons first flowed up, and then they flowed back down. So we have to draw it as two steps:



Before we can practice drawing arrows, we first need to make sure that we can identify the three different arrow types. This is important, because it will get you accustomed to the types of arrows that are acceptable to draw.

EXERCISE 8.1 In the example below, classify each arrow that you see into one of the following three types:

1. Bond → bond
2. Bond → lone pair
3. Or lone pair → bond

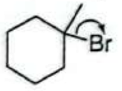


Answer The first arrow is going from a lone pair on the oxygen to form a bond between the oxygen and carbon. So, this arrow is of the type lone pair → bond.

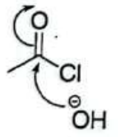
The second arrow is going from a bond to form a lone pair, so the second arrow is of the type bond → lone pair.

PROBLEMS For each of the following examples, classify each arrow that you see into one of the three types that we discussed.

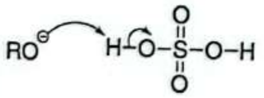
8.2



8.3



8.4



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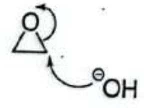
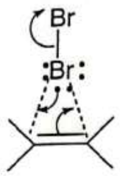
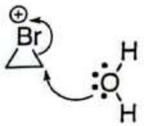


8.6



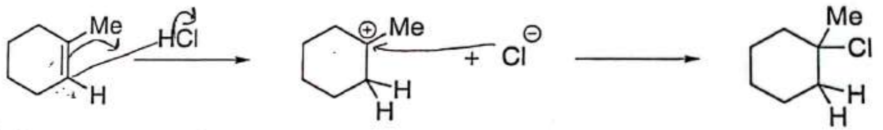
8.7



8.2 ARROW PUSHING

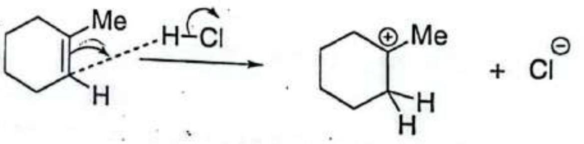
Now that we know what kinds of arrows are acceptable, we can begin to practice drawing them (or "pushing" them, as its called). To do this, we need to learn how to analyze a step in a mechanism, and train our eyes to look for all of the lone pairs and all of the bonds. We have said that all arrows are coming from or going to either lone pairs or bonds. So it makes sense that we need to be able to look at a step in a mechanism and determine which bonds have changed and which lone pairs have changed. Let's see this in an example.

EXERCISE 8.8 Complete the mechanism of the following reaction by drawing the proper arrows in each step:

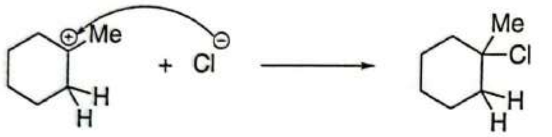


Answer We need to look for all changes for bonds or lone pairs. In the first step, the double bond is disappearing, one of the carbon atoms of the double bond is forming a new bond to a proton (H^+), and we are breaking the H—Cl bond to kick off Cl^-. So we have broken two bonds (C=C, and H—Cl) and we have formed one bond (C—H) and one extra lone pair (on Cl). Therefore, we will need two arrows to make this happen. Where do we start?

Keep in mind that electron density always flows in one direction. In this example we can see which direction the flow went, because in the end we had a positive charge on one side and a negative charge developed on the chlorine. We can use that information to figure out the direction of the flow. The first arrow needs to show the double bond going to form a bond to the proton (from a bond to a bond) and then we need a second arrow to show the bond from the H—Cl going to form a negative charge on the chlorine atom (from a bond to a lone pair):

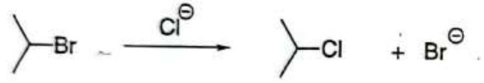


In the next step, again we look for all changes to lone pairs or bonds. We see that the Cl is giving up one of its lone pairs to form a bond with a carbon (C$^+$). So, we need only one arrow, from a lone pair to form a bond:

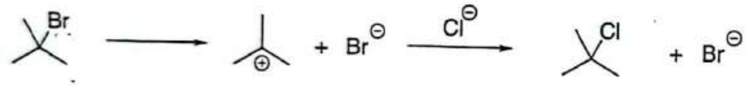


PROBLEMS For each transformation below, complete the mechanism by drawing the proper arrows.

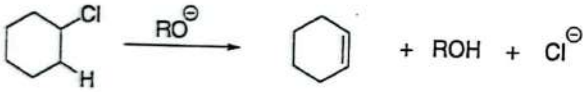
8.9



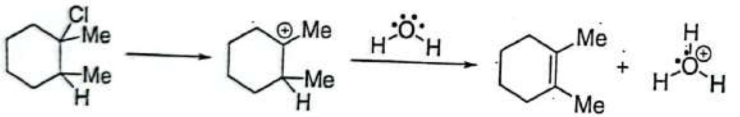
8.10



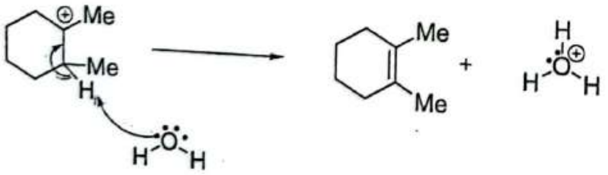
8.11



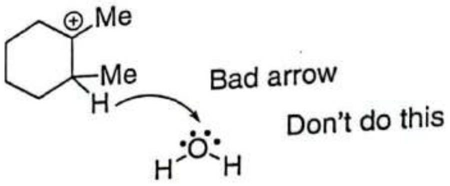
8.12



Consider the second step of problem 8.12. A lone pair from the oxygen is pulling off a proton to form a double bond:



Remember that arrows indicate the flow of electrons. Arrows do not show where atoms went. Many students will accidentally draw it like this:



Students often make this mistake because they want to show where the H is going. But this is wrong. Remember that arrows show the *movement of electrons, not atoms*. The H was able to move only because the electrons came from the oxygen and grabbed the H.

8.3 DRAWING INTERMEDIATES

We have seen the different types of arrows and how to draw them. Now we need to get practice drawing intermediates when we are given the arrows. Intermediates are compounds that exist for a very short time before reacting further. Let's consider an analogy. Imagine that you are trying to climb a mountain and it is very cold (below freezing). You are wearing a hat that keeps your ears warm, but it is loose and keeps slipping off. Your friend offers you a spare hat that he brought, and you borrow it. Now you need to take your old hat off to replace it with the new hat. If someone were to take a picture of you while you have nothing on your head, the picture would look very strange. There you are, in the freezing cold, with no hat on. You were only like that for 3 seconds, but it was long enough for someone to take a picture. Intermediates of reactions are similar.

Intermediates are intermediate structures in going from the starting material to the product. They do not live for very long, and it is rare that you can isolate one and store it in a bottle, but they do exist for very short periods of time. Their structures are often critical in understanding the next step of the reaction. Going back to the analogy, if I saw the picture of you without your hat on, and I knew how cold it was on that mountain, then I would have been able to predict that you put on a hat right after the picture was taken. I would have known this because I would have been able to immediately identify an uncomfortable situation, and I could have predicted what resolution must have taken place to alleviate the problem. The same is true of intermediates. If we can look at an intermediate and determine which part of the intermediate is unstable, and we also know what options are available to alleviate the instability, then we can predict the products of the reaction based on an analysis of the intermediate. That's why they are so important.

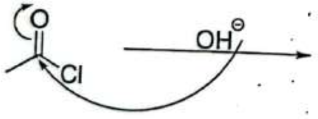
So let's get practice drawing intermediates. If you look closely at any step of a mechanism, you will see that the arrows tell you exactly how to draw the intermediate. Since you know how to classify every arrow into one of three categories (previous section of this chapter), now you will be able to read each arrow as a road map of how to draw the intermediate. Here's an example:

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

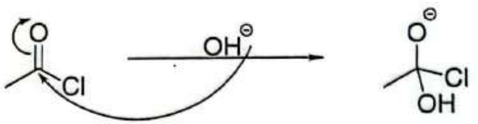
The trickiest part is getting the formal charges correct. If you have trouble assigning formal charges, then you will need to go back and review the sections on formal charges in Chapter 1 and Chapter 2 of this book. Assigning formal charges is a very important part of drawing the intermediates. Drawing the structure without the charges would be like taking the photograph in the analogy above, but digitally removing all of the snow. Without the snow, I wouldn't know that it was cold, so I would not be able to predict that you put a hat on shortly after the picture was taken. If you don't draw the source of instability on the intermediate, then what good is it?

One trick will help you in some situations when you have a flow of electrons represented by a few arrows (as in the example above). Notice that the only change in formal charges comes on the first and last atom of the system where the electrons are flowing. In our example above, the nucleophile loses its negative charge by using its lone pair to form a bond with a carbon atom. At the other end of the system, the oxygen is gaining a negative charge as a bond is converted into a lone pair on oxygen. Notice the conservation of charge. If the overall charge is negative at the beginning of the reaction, then it must also be negative at the end of the reaction. If something starts off with no charge, then it can split up into a positive charge and a negative charge, because the *total* charge is still conserved.

EXERCISE 8.13 Look at the arrows below, and draw the intermediate that you get after pushing the arrows:



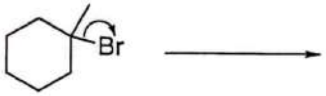
Answer We need to read the arrows like a road map: the first arrow is going from a lone pair on HO^- to form a bond with the carbon of the C═O. The second arrow goes from the C═O bond to form a lone pair on oxygen. We use this info to draw the products:



The hard part was assigning formal charges. Notice that we had two arrows moving in a flow. We had a negative charge in the beginning, so we must have a negative charge in the end. It started off on the first atom in the flow of arrows, and it ended on the last atom of the flow (the oxygen).

PROBLEMS For each problem below, draw the intermediate that you get after pushing the arrows.

8.14



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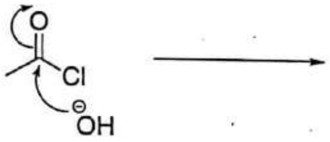

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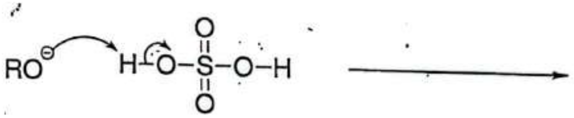

8.17

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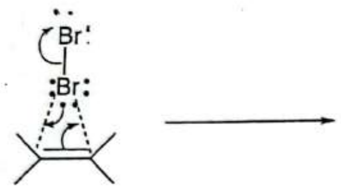

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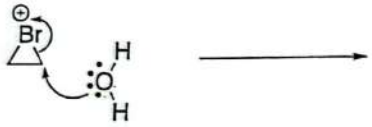
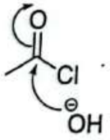


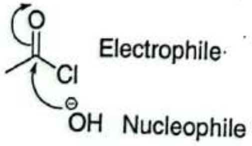
8.4 NUCLEOPHILES AND ELECTROPHILES

Whenever one compound uses its electrons to attack another compound, we call the attacker a *nucleophile,* and we call the compound being attacked an *electrophile.* It is very simple to tell the difference between an electrophile and a nucleophile. You just look at the arrows and see which compound is attacking the other. A nucleophile will always use a region of high electron density (either a lone pair or a bond) to attack the electrophile (which, by definition, has a region of low electron density that can be attacked). These are important terms, so let's make sure we know how to identify nucleophiles and electrophiles.

EXERCISE 8.20 In the reaction below, determine which compound is the nucleophile and which compound is the electrophile:

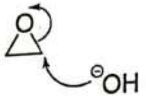


Answer The OH is attacking the C=O bond, so the OH is the nucleophile and the other compound is the electrophile:

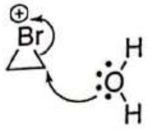


PROBLEMS In each of the reactions below, determine which compound is the nucleophile and which compound is the electrophile.

8.21

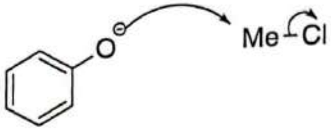


8.22



8.23

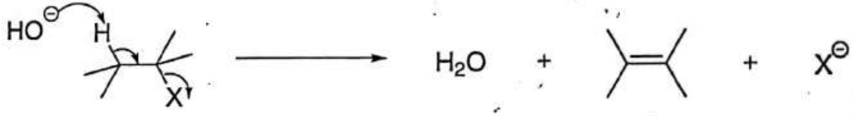
8.24



8.5 BASES VERSUS NUCLEOPHILES

Students are often unclear about the difference between nucleophiles and bases. Since most mechanisms involve the use of nucleophiles and bases, it will be worth our time to clear up the difference.

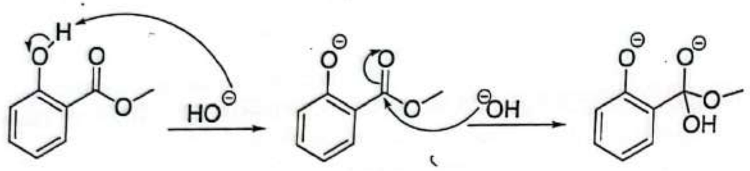
Consider the hydroxide ion (OH^-). Sometimes it acts like a base and pulls off a proton from another compound:



At other times it acts like a nucleophile and attacks another compound (forming a new bond to an atom in that compound):

The difference between basicity and nucleophilicity is a difference of *function.* In other words, the hydroxide ion can function in two ways: as a base (which means it is pulling off a proton and then running away with that proton) or as a nucleophile (latching onto a compound). In some cases, the hydroxide ion might function mostly as a base; while in other situations, the hydroxide ion might function mostly as a nucleophile. To understand mechanisms well, it is important to be able to distinguish between the two roles. Let's see an example.

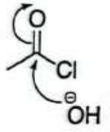
EXERCISE 8.25 Below you will find the first two steps of a mechanism. In each step, determine whether the hydroxide ion is functioning as a nucleophile or as a base:



Answer In the first step, the hydroxide ion is pulling off a proton, so it is functioning as a base. In the second step, it is attacking the C=O and latching on to the compound, so it is functioning as a nucleophile.

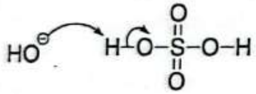
PROBLEMS In each step below, determine whether the hydroxide ion is functioning as a nucleophile or as a base.

8.26



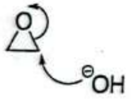
Answer: ____________

8.27



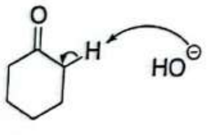
Answer: ____________

8.28



Answer: ____________

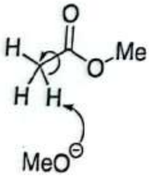
8.29



Answer: ____________

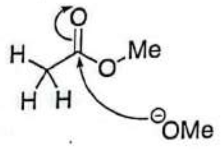
PROBLEMS In each step below, determine whether the methoxide ion (MeO⁻) is functioning as a nucleophile or as a base.

8.30



Answer: ____________

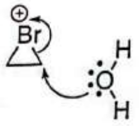
8.31



Answer: ____________

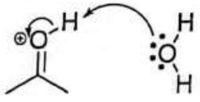
PROBLEMS In each step below, determine whether water is functioning as a nucleophile or as a base.

8.32



Answer: ____________

8.33



Answer: ____________

There is another subtle difference between nucleophiles and bases that is worth mentioning, because it illustrates a common theme in organic chemistry. We can see the difference by defining the terms nucleophilicity and basicity.

Once we determine that a reagent is acting as a nucleophile, we measure how fast it functions that way with the term *nucleophilicity*. Nucleophilicity measures *how quickly* a reagent will attack another compound. For example, we saw above that water can function as a nucleophile because it has lone pairs that can attack a compound. But the hydroxide ion will clearly be more nucleophilic—the hydroxide ion has a negative charge, so it will attack compounds *faster.*

Basicity measures base strength (or how unstable the base is) by *the position of equilibrium.* The term *basicity* does not reflect how quickly the equilibrium was reached. The equilibrium might have been established in a fraction of a second or it could have taken several hours. It doesn't matter, because we are not measuring speed of reaction. We are measuring stability and the position of the equilibrium.

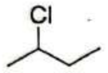
Now we can understand this difference between nucleophilicity and basicity. Nucleophilicity measures how fast things happen, which is called *kinetics*. Basicity measures stability and the position of equilibrium, which is called *thermodynamics.* Throughout your course, you will see many reactions where the product is determined by kinetic concepts, and you will also see many reactions where the product is determined by thermodynamic concepts. In fact, there will even be times, where these two factors are competing with each other and you will need to make a choice of which factor wins: kinetics or thermodynamics.

So the difference between nucleophiles and bases is a difference of function. And now we can also appreciate that nucleophilicity is a measure of a kinetic phenomenon (rate of reaction), while basicity is a measure of stability (thermodynamic phenomenon).

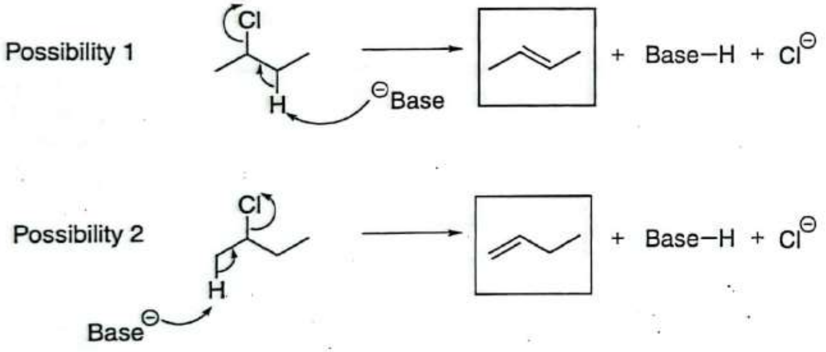
8.6 THE REGIOCHEMISTRY IS CONTAINED WITHIN THE MECHANISM

Regiochemistry refers to *where* the reaction takes place. In other words, in what region of the molecule is the reaction taking place? Let's see examples of this for different types of reactions. In the process, we will uncover some new terminology as we learn about different reactions.

Let's consider elimination reactions. When we eliminate H and X (where X is some leaving group that can leave with a negative charge, like Cl or Br), it is possible to form the double bond in different locations. Consider the following compound:



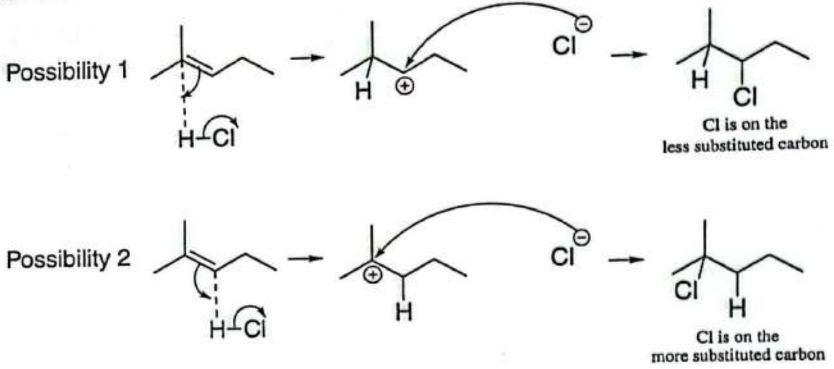
This compound can undergo two possible elimination reactions (to make it easier to see, we are drawing the H that gets eliminated in each case, even though we usually do not draw hydrogen atoms on bond-line drawings):



Where does the double bond form? This is a question of regiochemistry. We distinguish between these two possibilities by considering how many groups are attached to each double bond. Double bonds can have anywhere from 1 to 4 groups attached to them:

So if we look back at the reaction above, we find that the two possible products are monosubstituted and disubstituted double bonds. Whenever we have an elimination reaction where more than one possible double bond can be formed, we have names for the different products based on which one is more substituted and which one is less substituted. The more substituted product is called the Zaitsev product, and the less substituted product is called the Hoffmann product. Usually, we get the Zaitsev product, but under special circumstances we get the Hoffman product. You will learn about this in detail in your textbook when you cover elimination reactions. For now, you just need to realize that this is an issue of regiochemistry. The difference between the Zaitsev product and the Hoffman has to do with where the double bond formed. This is regiochemistry.

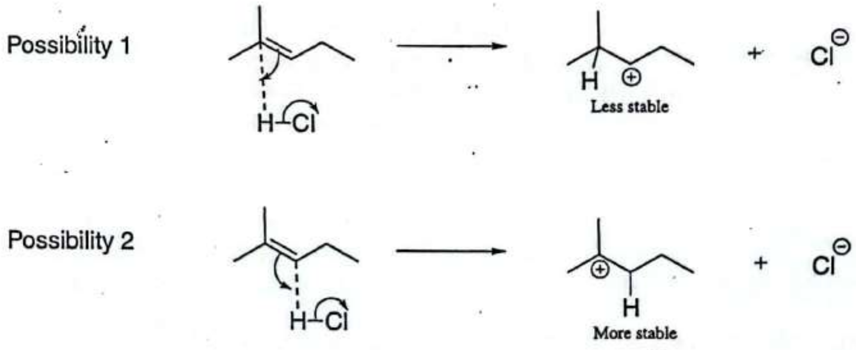
Let's consider another example of regiochemistry, in a completely different type of reaction. Consider the addition reaction of HCl across a double bond:



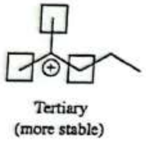
There are two possible ways to add the H and the Cl. Which product do we get?

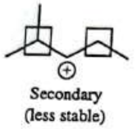
One possibility would be to put the Cl on the less substituted carbon (carbon connected to two other carbon atoms), and the other possibility would be to put the Cl on the more substituted carbon (carbon connected to three other carbon atoms). If we put the Cl on the more substituted carbon, we call this a Markovnikov addition. If we put the Cl on the less substituted carbon, we call it an anti-Markovnikov addition. How do we know whether we get Markovnikov addition or anti-Markovnikov addition? This is an issue of regiochemistry.

For the reaction above, let's analyze the two possible outcomes. In each case, the first step involves the electrons of the double bond attacking the proton of HCl to form a carbocation (a carbon with a positive charge). The difference between the two possibilities is where the carbocation is formed:

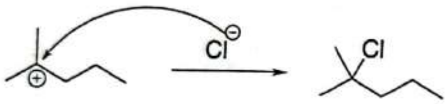


Recall that alkyl groups are electron donating, so the carbocation on the bottom (called a tertiary carbocation because it has three alkyl groups) will be more stable than the carbocation on the top (called a secondary carbocation because it has only two alkyl groups).


Tertiary
(more stable)


Secondary
(less stable)

Therefore, possibility 2 is a better mechanism (because it involves a more stable intermediate. If we follow the last step of the mechanism for possibility 2, we see that the Cl will attach where the carbocation is, which will be at the more substituted carbon:



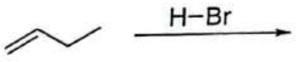
We see that the final position of the chlorine is determined by the stability of the intermediate carbocation, which becomes evident as we work through the mechanism. Since the chlorine ends up at the more substituted carbon, we call this a Markovnikov addition. The mechanism for this reaction helped explain the regiochemistry of the reaction.

Sometimes regiochemistry is not an issue. For example, if we are adding H and H across a double bond, then it does not matter which carbon gets the first H and which carbon gets the second H. Either way, they both end up with an H. Similarly, if we add two OH groups across a double bond, regiochemistry also does not matter. Any time we add two of the same group across a double bond, we do not have to worry about the regiochemistry.

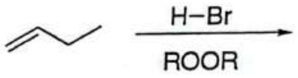
Here is where we get back to mechanisms. Whether we are talking about Zaitsev vs. Hoffman elimination reactions or about Markovnikov vs. anti-Markovnikov addition reactions, the explanation of the regiochemistry for every reaction is contained within the mechanism. If we completely understand the mechanism, then we will understand why the regiochemistry had to be the way it turned out. By understanding the mechanism, we eliminate the need to memorize the regiochemistry for every reaction. With every reaction you encounter, you should consider the regiochemistry of the reaction and look at the mechanism for an explanation of the regiochemistry.

PROBLEMS You will, over the course of your studies, learn the mechanisms for the following reactions. In the meantime, you will be given the regiochemical information that you need to answer each of the problems below. These problems are intended to ensure that you understand what regiochemistry means.

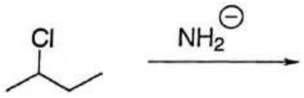
8.34 Consider the reaction shown. If you were to add HBr across the double bond, what would the product be? Assume a Markovnikov addition.



8.35 When you do the same reaction (as above) in the presence of peroxides (R-O-O-R), you get an anti-Markovnikov addition of HBr across the double bond. Draw the product of an anti-Markovnikov addition.



8.36 Consider the elimination reaction below, which uses a strong base. The product will be a double bond. This reaction will produce two Zaitsev products. One will be cis and one will be trans. Draw these products, and identify which is cis and which is trans.

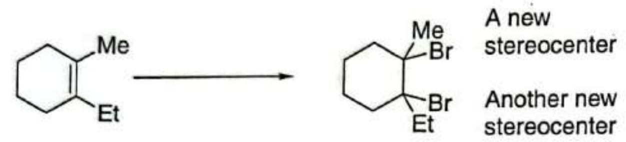


8.37 Consider the elimination reaction below, which uses a strong, sterically hindered base (LDA). The product will be a double bond. This reaction will produce the Hoffmann product. Draw this product.

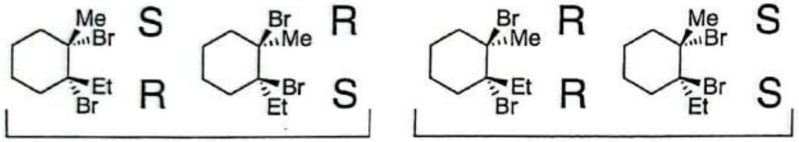
8.7 THE STEREOCHEMISTRY IS CONTAINED WITHIN THE MECHANISM

Stereochemistry is all about configurations of stereocenters (R vs. S) and double bonds (E vs. Z). Whenever we have a reaction where we are forming a stereocenter, we need to ask whether we get a racemic mixture (equal amounts of R and S) or only one configuration. And, if so, why? Also, whenever we form a double bond, we need to ask whether we get both E and Z isomers or only one of them? And, if so, why?

This information is also contained within the mechanism. Let's see an example. Consider the addition of Br and Br across a double bond. We already saw that we don't need to worry about the regiochemistry of this reaction, because we are adding two of the same group. But what about the stereochemistry? We are creating two new stereocenters:



Each stereocenter has two possibilities (R or S). Since there are two stereocenters, we will have four total possibilitites: SR, RS, RR, and SS. These four compounds represent two sets of enantiomers:

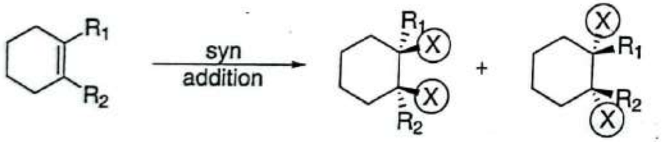


One set of enantiomers, Br and Br are on the same side of the ring

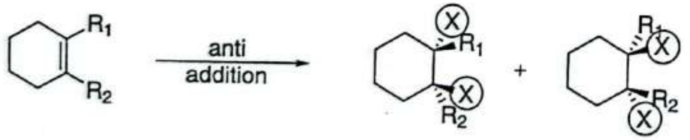
Another set of enantiomers, Br and Br are on opposite sides of the ring

How many of them do we get? Do we get both sets of enantiomers as our products (meaning all four products), or do we only get one set (meaning two out of the four possible products)? This depends on how the reaction took place.

If an addition reaction can take place only through a mechanism that allows a syn addition, then the two groups that we added must be on the same side of the double bond in the product. So we will get only that one set of enantiomers:



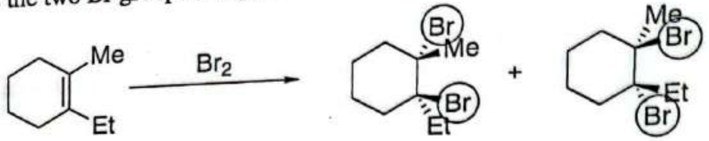
If a reaction can go through only an anti addition, then the two groups we added must be on opposite sides of the double bond. So we will get only the set of enantiomers where the groups are on opposite sides:



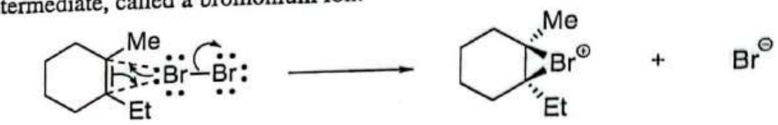
Sometimes, the reaction is not stereoselective. In other words, we get both syn and anti addition. So we get all four products (both sets of enantiomers).

Each reaction will be different. Some will give only syn addition, some will give only anti addition, and others will not be stereoselective. For every addition reaction, we need to know the stereochemistry of the addition, and that information is contained within the mechanism.

So let's go back to our example above with the addition of Br and Br across a double bond. This reaction is an anti addition, so we get only the set of enantiomers that has the two Br groups on opposite sides of the ring:

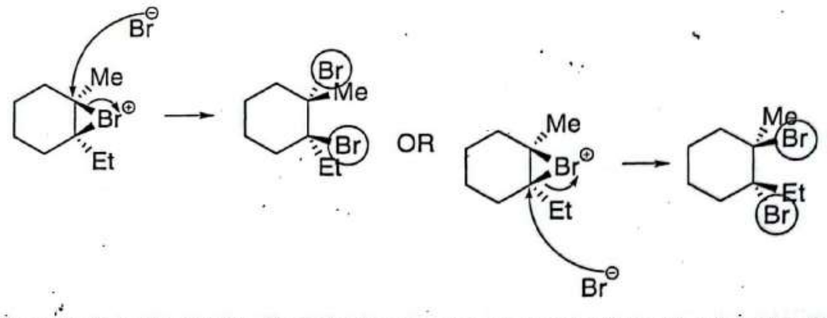


Let's look at the mechanism to understand why. In the first step, we form a bridged intermediate, called a bromonium ion:



In this step, the double bond is acting as a nucleophile that attacks Br_2 (the electrophile in this reaction). The arrows are not going in opposite directions—they are actually moving in a small circle to form a ring.

Then, in the next step, the bromide (formed in the first step) comes back and attacks the bromonium ion, opening up the bridge. The bromide can attack either carbon (both possibilities shown below):

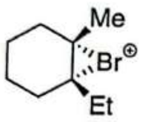


When the bromide attacks, it must attack on the other side of the ring (not the side of the bromonium bridge, but rather on the opposite side of the ring) to break open the bridge. So the addition must be an *anti addition*.

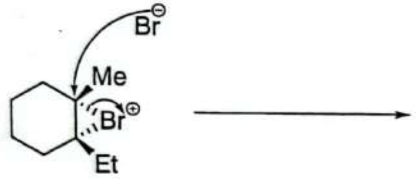
We see that the mechanism explains why the addition must be anti. For every reaction, the stereochemistry will always be explained by the mechanism.

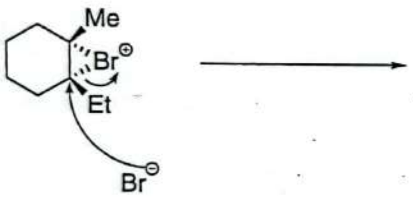
PROBLEM 8.38 In the reaction above, we saw that the first step involved formation of a bromonium ion.

You will notice that the bromonium ion drawn above has the bridge coming out towards you (on wedges), but we did not say at the time that it could also have formed with the bridge going away from you (on dashes):



We did not talk about this at the time, because the end products would still have been the same as the way we did it before. Draw what happens if the bromide (Br^-) attacks this other bromonium ion. Remember that there are two carbon atoms that the bromide could attack, so draw both possibilities:



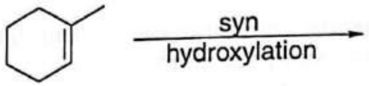


When you finish drawing the two products, compare them to the two products that we got before. You should find that the two products you get here are the same as the two products we got before. Think about why. Remember that the reaction can happen only as an anti addition.

Every new class of reactions (additions, eliminations, substitutions, etc.) has its own terminology for stereochemistry. As you learn each of these classes of reactions, keep a watchful eye on what terminology is used to describe the stereochemistry. Then, look at the mechanism of each reaction within each class, and try to understand why the mechanism dictates the stereochemistry.

PROBLEMS For the following reactions, you will (over the course of your studies) learn the mechanisms for these reactions. In the meantime, you will be given the stereochemical information that you need to answer each of the problems below. These problems are intended to ensure that you understand what stereochemistry means.

8.39 If you add OH and OH across the following double bond in a syn addition, what will the products be?

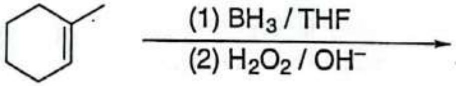


8.40 If you add Br and Br across the following double bond in an anti addition, what will the products be?

8.41 If you add Br and Br across the following double bond in an anti addition, you get only one product. If you draw the two products that you would expect, you will find that they are the same compound (a meso compound). Draw this product.

Do not confuse the concepts of regiochemistry and stereochemistry. For instance, in addition reactions, the term "anti-Markovnikov addition" refers to the *regiochemistry* of the addition, but the term "anti" refers to the *stereochemistry* of the addition. Students often confuse these concepts (probably because both terms have the word "anti"). It is possible for an addition reaction to be anti-Markovnikov and a syn addition (hydroboration is an example that you will learn about at some point in time). You must realize that regiochemistry and stereochemistry are two totally different concepts.

8.42 In the following reaction, we will add H and OH across a double bond. The regiochemistry is anti-Markovnikov, and the stereochemistry is a syn addition. Draw the products you would expect now that you know all of the information.



You must know the stereochemistry and regiochemistry for every reaction, and each of them is contained within the mechanism. In the problems above, you were told what to expect for the stereochemistry and the regiochemistry. When you are doing problems in your textbook and on your exams, you will be expected to know what these pieces of information are simply from looking at the reagents. A solid understanding of every mechanism will be an invaluable asset to you in this course.

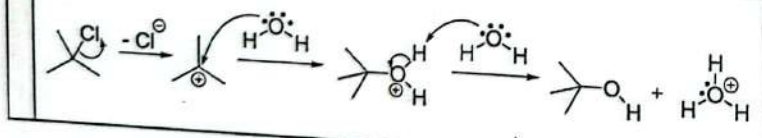
8.8 A LIST OF MECHANISMS

Now you need to begin to keep a list of all reaction mechanisms that you cover. The rest of the pages in this chapter are set up specifically for you to generate this list in such a way that you will record the critical information: the regiochemistry and the stereochemistry. You should fill in these pages as you proceed through the course and you learn more mechanisms. As your list gets larger, you will have one central place where you can go to review all of the mechanisms.

A few example mechanisms have been filled in for you, so that you can see how to fill in the each mechanism from now on. Depending on the order that your course follows, these reactions may or may not be the first ones you cover. Whatever the case might be, you will definitely see these reactions early on in the course:

Reaction type	**Stereochemistry**	**Regiochemistry**
Substitution (S_N2)	Inversion	Not applicable (nucleophile attacks carbon next to LG)

Reaction type	**Stereochemistry**	**Regiochemistry**
Substitution (S_N1)	Racemization	Not applicable (nucleophile attacks carbon next to LG)



Now, for every reaction that you cover, fill in the templates below, and then use this list as a study guide for all of your mechanisms:

Reaction type	**Stereochemistry**	**Regiochemistry**

Reaction type	**Stereochemistry**	**Regiochemistry**

Reaction type	Stereochemistry	Regiochemistry

Reaction type	Stereochemistry	Regiochemistry

Reaction type	Stereochemistry	Regiochemistry

Reaction type	Stereochemistry	Regiochemistry