

Chapter 11. Alkene & Alkyne Reactions

11.1 Electrophilic attack

Electrophiles are species that love negative electrons. They are normally electron deficient or have a slight positive charge. The pi-bond of an alkene can be thought of as a large, juicy, pair of electrons that can go out and attack these electrophiles. When the pi-bond grabs hold of an electrophile, it leaves a positive charge behind on the other carbon atom.

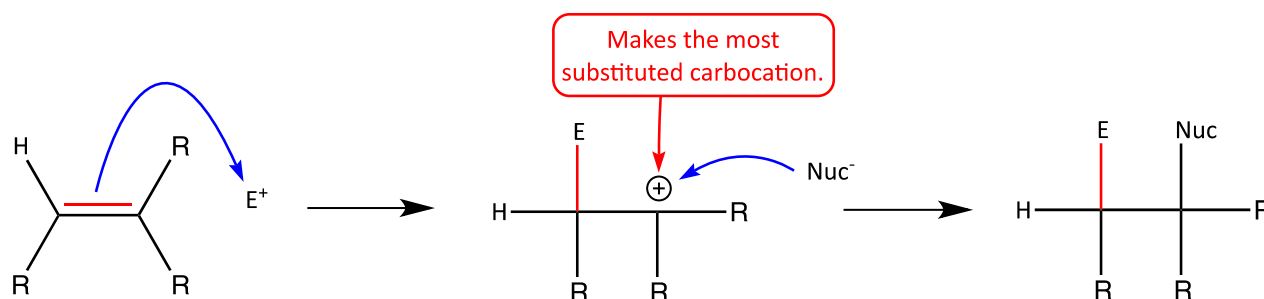


Figure 11.1 A Generic Electrophilic Attack

11.2 Markovnikov hydrohalogenation

11.2.1 Of an alkene

The addition of hydrogen halide, HBr, HCl, HI, is a regioselective reaction. One of the two possible orientations is favored. Vladimir Markovnikov, a Russian chemist, noticed this preference for one regioisomer over the other. In 1869, Markovnikov wrote how to predict which regioisomer is favored. He wrote, when H-X is added to an alkene, the hydrogen atom adds to the carbon atom of the double bond that starts with more hydrogen atoms on it. Another way to think about it is the "special group", the non-hydrogen group, is added to the more substituted carbon atom of the double bond (the carbon atom with the most R groups). Reactions that follow this rule are called Markovnikov reactions. The products of these reactions are Markovnikov products.

Although Markovnikov wrote his rule for hydrogen halide reactions of alkenes, chemists today use this rule for any reactions that add a hydrogen atom to one side of an alkene and a different group to the other carbon atom of the alkene.

Why does Markovnikov's rule work? For the reaction of H-X, the more substituted carbocation is lower in energy. Its pathway is easier to follow, resulting in more of the Markovnikov product, where the special group is on the more substituted carbon atom (where the carbocation was).

Markovnikov's rule is not always followed. Sometimes what appears to be the wrong product, the anti-Markovnikov product, is formed. But, in these instances, the more stable intermediate is still the one whose path is followed. This idea, where the more stable intermediate is the path that is followed more, is ALWAYS obeyed.

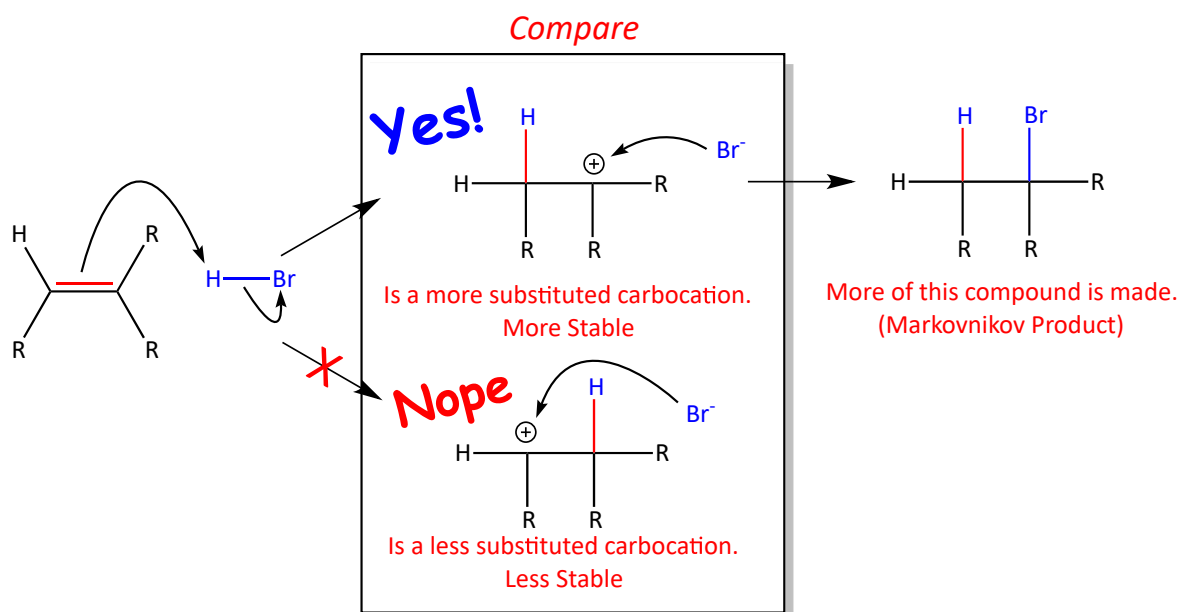


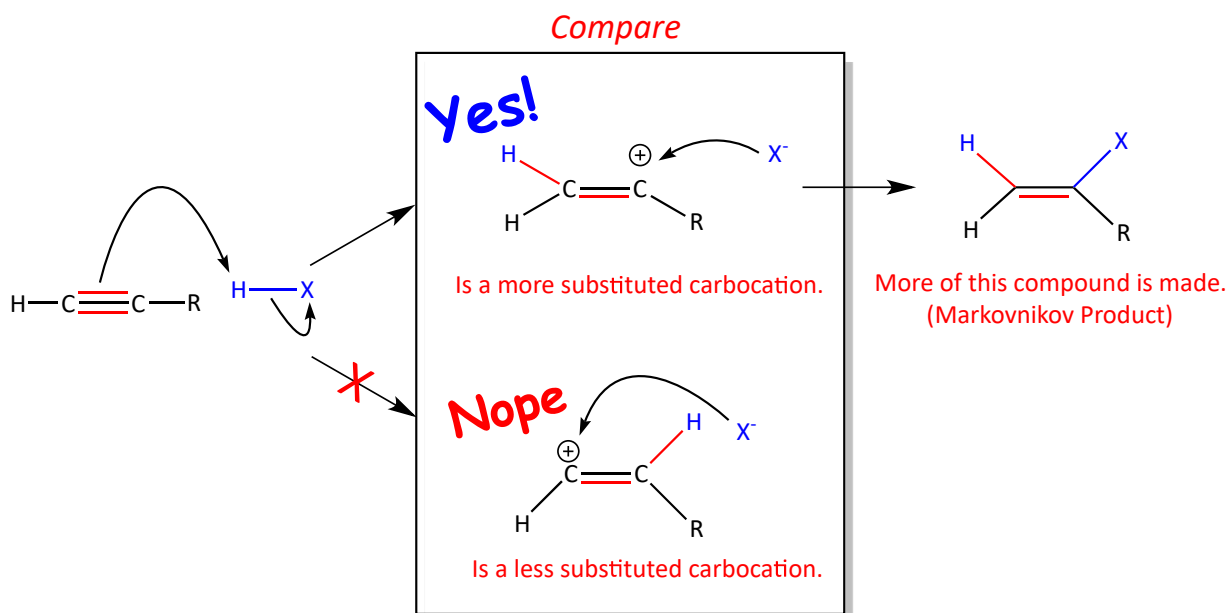
Figure 11.2 Markovnikov hydrohalogenation of an alkene

11.2.2 Of an alkyne

The same reaction can be performed on an alkyne. But, since an alkyne contains two pi-bonds, the reaction with H-X (HCl, HBr, or HI) can occur twice. If a terminal alkyne is a reactant, a Markovnikov product is made.

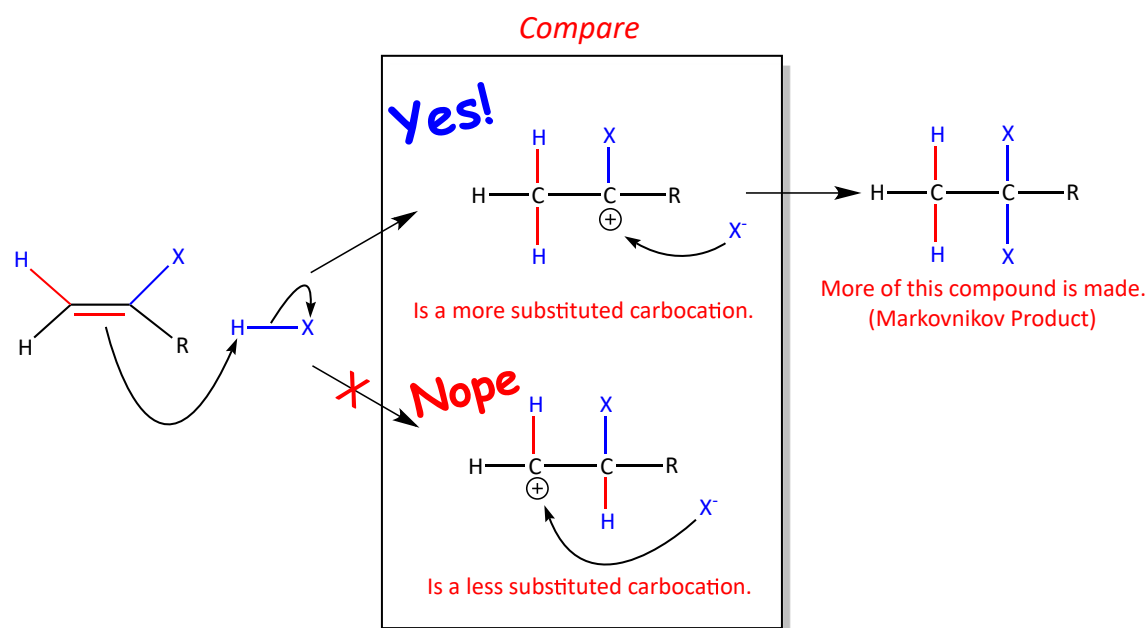
Mechanism

1. Addition to first pi-bond.

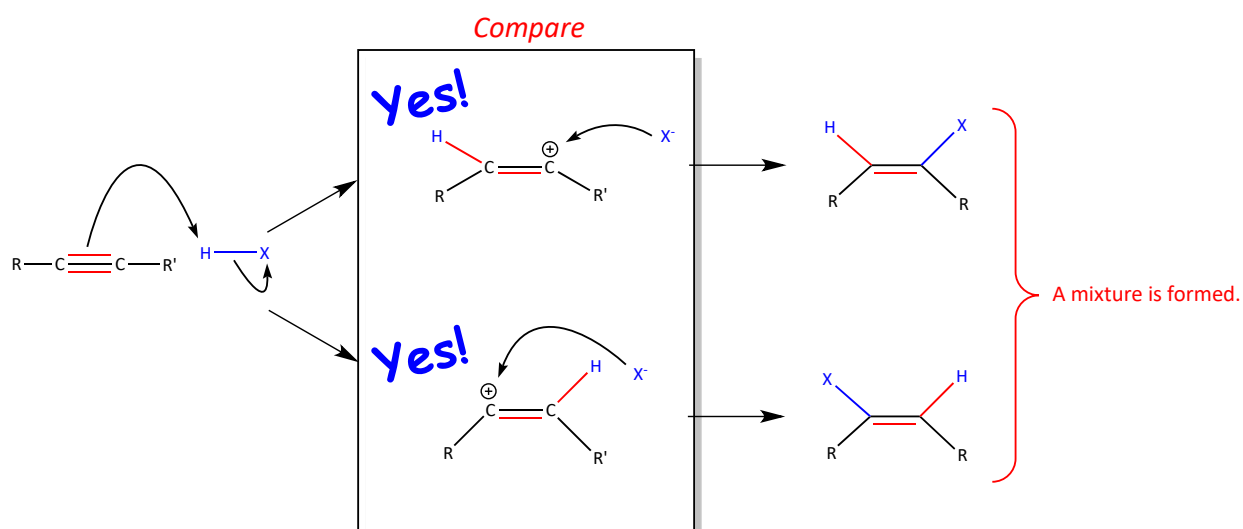


Alkene & Alkyne Reactions

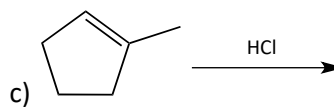
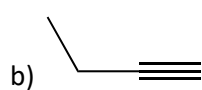
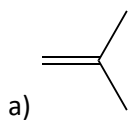
2. Addition to second pi-bond.



If an internal alkyne is a reactant, it doesn't matter which side the hydrogen adds. Both are equally stable. Therefore, a mixture of products is formed.



11.1 Draw the product of the following reactions.

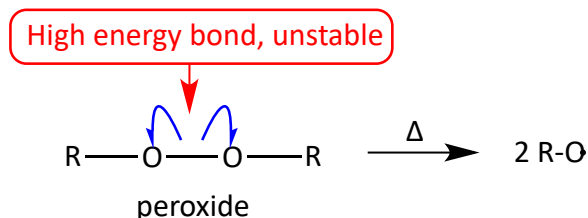


11.3 Anti-Markovnikov hydrobromination

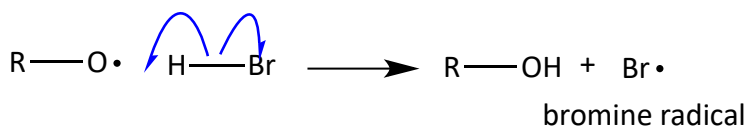
11.3.1 Of an alkene

Anti-Markovnikov halides can also be synthesized. When peroxide is added to the reaction of HBr and an alkene, a different mechanism occurs than the one we saw previously. When peroxide is added, a free radical mechanism occurs.

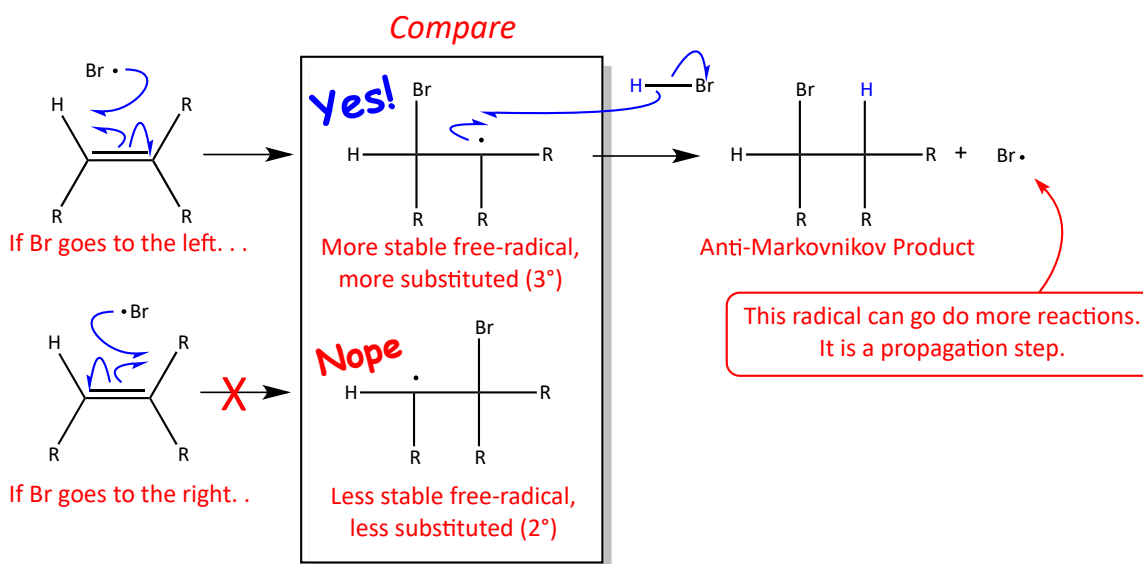
The first step of this mechanism is that the peroxide breaks apart to form free radicals.



The oxygen free radicals react with H-Br to make bromine radicals.



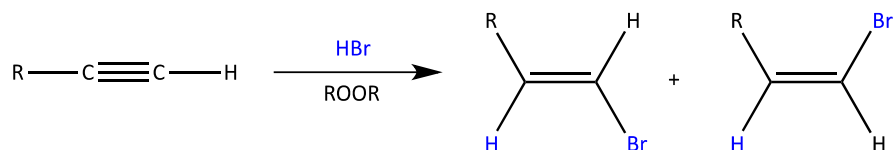
The bromine radical can attack one of two ways. We'll look at both possibilities and choose the one with the more stable intermediate. Remember, we ALWAYS do this. But, in the end, we will make more of the anti-Markovnikov product.



11.3.2 Of an alkyne

If HBr and peroxide are reacted with an alkyne, a free radical reaction occurs giving anti-Markovnikov addition of HBr.

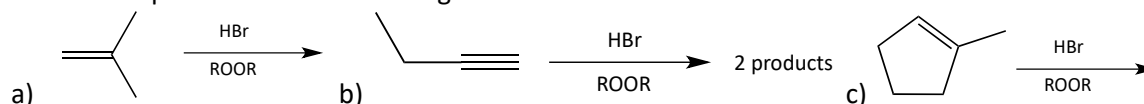
Alkene & Alkyne Reactions



Both are anti-markovnikov
Mixture of *cis* and *trans*

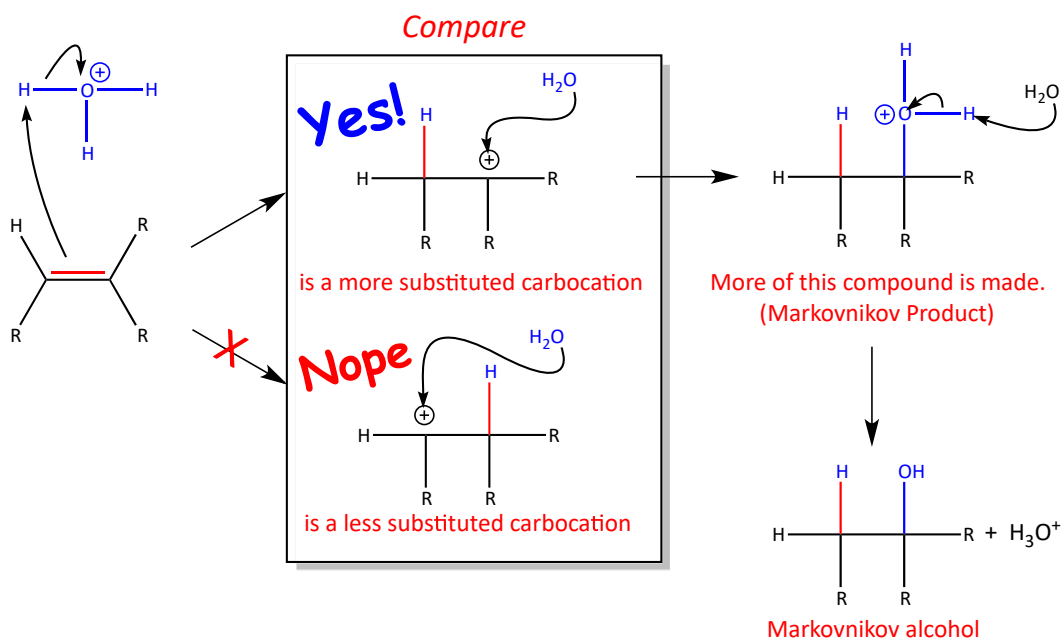
The reaction usually does not occur again. It tends to stop at the double bond.

11.2 Draw the products of the following reactions.



11.4 Hydration of alkene

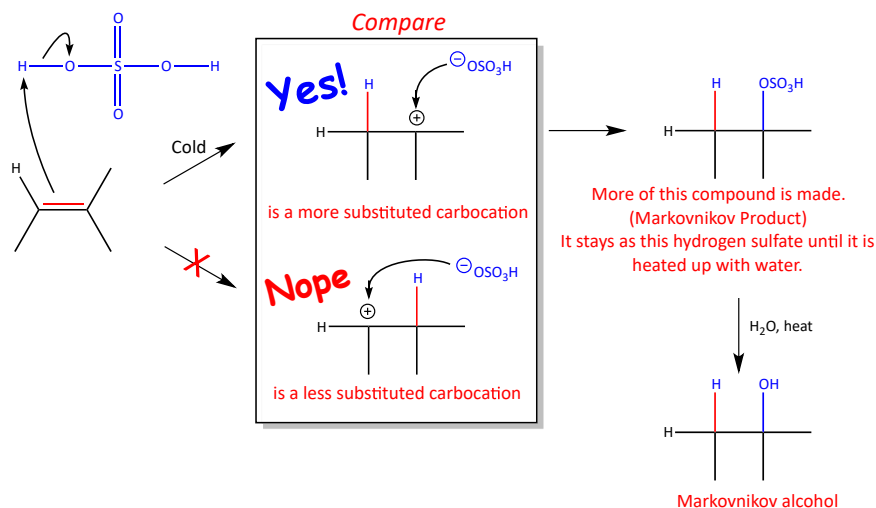
In the hydration of an alkene, acid and water are added to an alkene. In the mechanism, the pi bond of the alkene attacks H^+ of the hydronium (H_3O^+). The two possible carbocations that can be formed are compared. The more stable one, which is usually the more substituted one, is lower energy and its path followed. This leads to more of the Markovnikov alcohol.



If the reaction is performed with concentrated H_2SO_4 or H_3PO_4 , the reaction equilibrium is driven to the alkene starting material because H_2SO_4 or H_3PO_4 are dehydrating acids and absorb the water. If the acid is diluted with plenty of water, the reaction equilibrium is driven to the alcohol. One difficulty with this reaction is that alkenes are not usually very water soluble, so it is difficult to run this reaction. Also, rearrangements are possible since a carbocation is formed. For these reasons, there are better ways to make Markovnikov alcohols.

11.5 Hydrosulfonation

Hydrosulfonation could be a better way to make Markovnikov alcohols. Since alkenes do not dissolve very well in water, concentrated sulfuric acid (H_2SO_4) can be used. Normally, sulfuric acid drives the equilibrium to the alkene, but sulfuric acid does dissolve the alkene. If the reaction is run cold, it leads to the Markovnikov hydrogen sulfonate. At this point in the reaction mechanism, if plenty of water is added and the reaction is heated, the hydrogen sulfonate becomes a Markovnikov alcohol.



The problem with this reaction is concentrated sulfuric acid is used for the first part of the reaction. Sulfuric acid reacts with many functional groups. If there are any sensitive functional groups on the alkene, the sulfuric acid will chew them up. If a chemistry student spent six months of research making a large, beautiful, complicated molecule that contains an alkene and they want to make a Markovnikov alcohol out of it, they would not want to add concentrated sulfuric acid to it! Also, since a carbocation is formed, rearrangements are possible.

11.6 Triangle reactions

There are two types of reactions that I call “triangle reactions”. It is important to have a general understanding of them before we encounter them in the remainder of this chapter. An analogy helps explain how triangle reactions work. This analogy is the story of a victim and two criminals. This analogy is a little bizarre, but I think it helps us remember how these reactions happen, so bear with me. The victim of the crime is somebody who is totally honest. He is so honest, he cannot help but announce to the world the amount of money he has by carrying a sign above his head. The victim has two options available to him. One is to hold a sign that reads “0” indicating that he has zero money on him. The other option is a sign that reads “+” indicating that he is carrying a positive amount of money on him. The victim sometimes has bags slung over his shoulders. In order to protect any money he holds, the victim puts his money in the pocket that is hidden under the most bags.

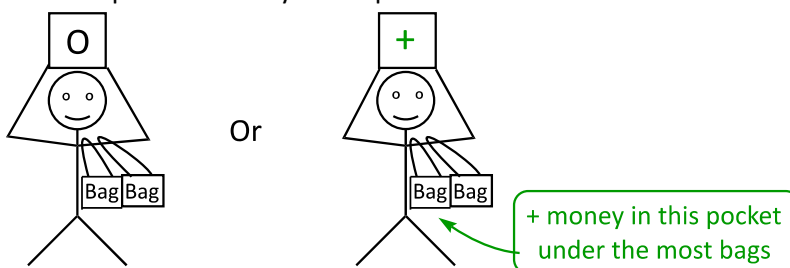


Figure 11.3 The victim of a Triangle Reaction

One of the two criminals is a weak, scared, but greedy pickpocket. This weak pickpocket will not attack a victim unless he knows the victim is *definitely* carrying money. If he doesn't know this, he will leave the victim alone. So, if the victim is carrying the "O" sign, the weak criminal leaves him alone. If the victim is carrying a "+" sign, the pickpocket will reach into his pocket under the bags, where the money is kept.

The second criminal is a strong, aggressive, violent criminal. The strong criminal doesn't really care about money. He is so violent, he wants to punch the victim in the gut immediately. This aggressive criminal will attack any type of victim. If the strong criminal encounters the victim carrying the "O" sign, he punches the victim immediately in the gut. The strong criminal wants to do as much damage as *quickly* as he can to the victim, so he punches him in the side that has the fewest bags on it.

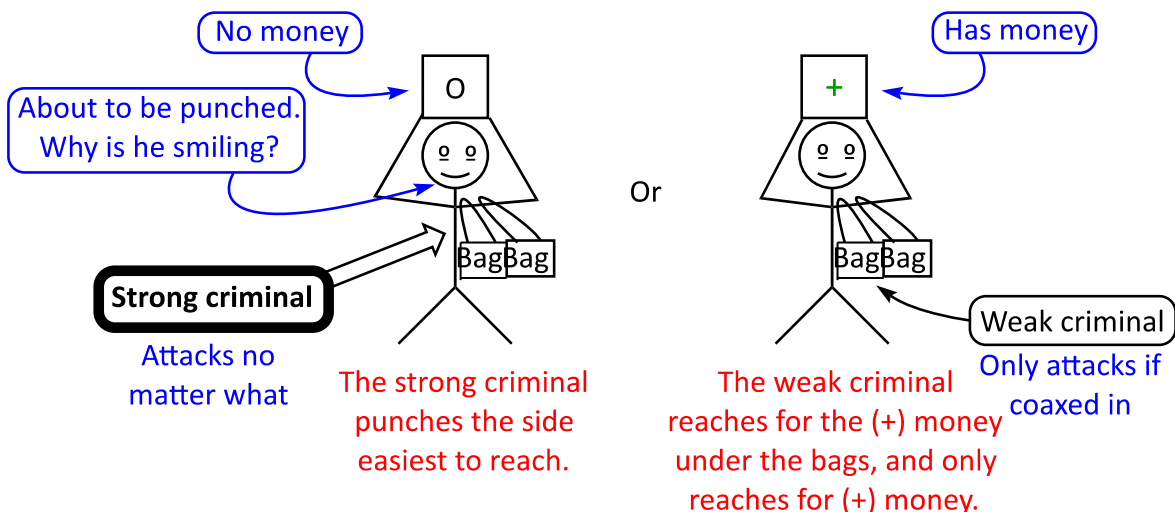


Figure 11.4 How criminals attack in a triangle reaction

If we have a "triangle reaction" the top atom is usually either neutral or it has a positive charge. If the top atom is neutral, it is like a victim that is holding an "O" sign. If the top atom has a positive charge, it is like a victim that is holding a "+" sign. The criminals in the analogy are either strong nucleophiles (the strong criminal) or weak nucleophiles (the weak criminal). Strong nucleophiles tend to attack the least crowded side of the triangle because it is easiest to get to. Weak nucleophiles tend to attack the side of the triangle with the most alkyl groups on it. The bags the victim is carrying are "R" groups or alkyl groups. If the top atom has a positive charge, the positive charge is shared somewhat on the other two atoms of the triangle. The atom of the triangle with the most R groups attached holds more of the partially positive charge. This is because more substituted carbon atoms are more stable carbocations. That more substituted carbon atom of the triangle has enough positive charge (+ money) that even a weak nucleophile (weak criminal) cannot resist and will attack it. Below is an example of a neutral epoxide on the left and a positive, protonated epoxide on the right.

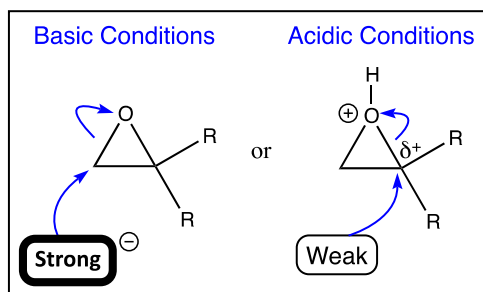


Figure 11.5 How strong or weak nucleophiles attack epoxides

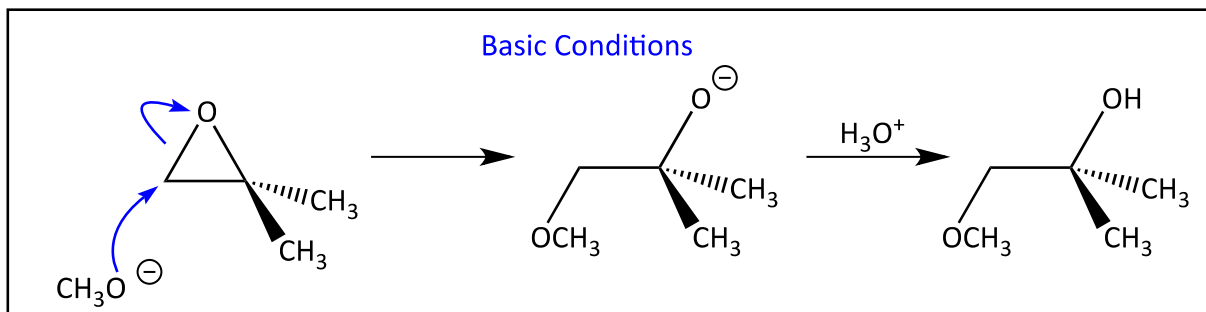


Figure 11.6 Example of a strong nucleophile attacking a neutral epoxide

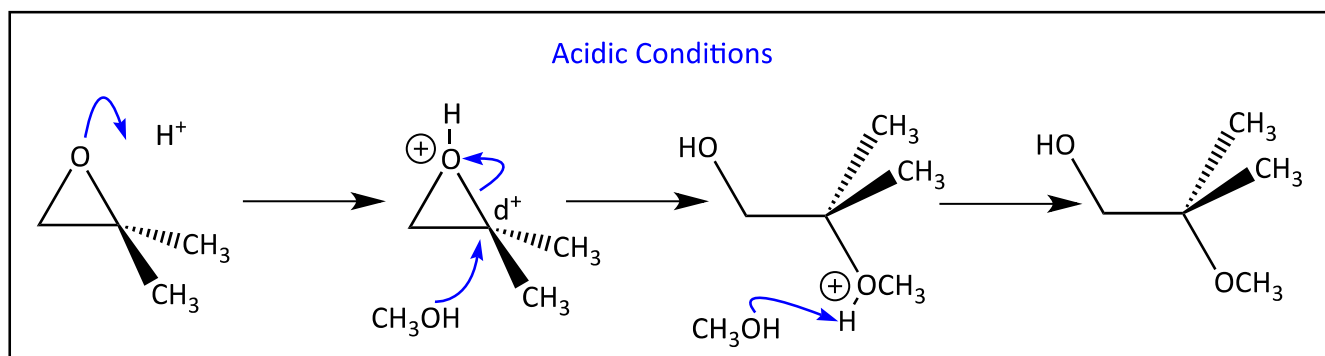


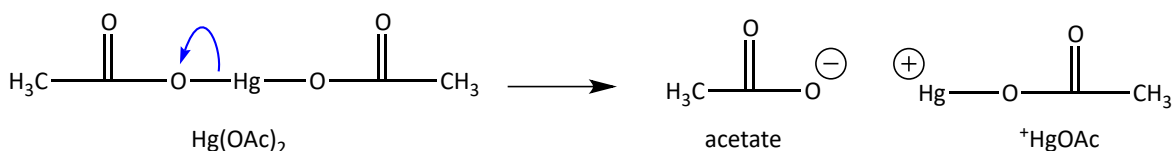
Figure 11.7 Example of a weak nucleophile attacking a protonated epoxide

11.7 Oxymercuration/Demercuration-with water- A triangle reaction

A good, gentle way to make Markovnikov alcohols is oxymercuration in water followed by demercuration.

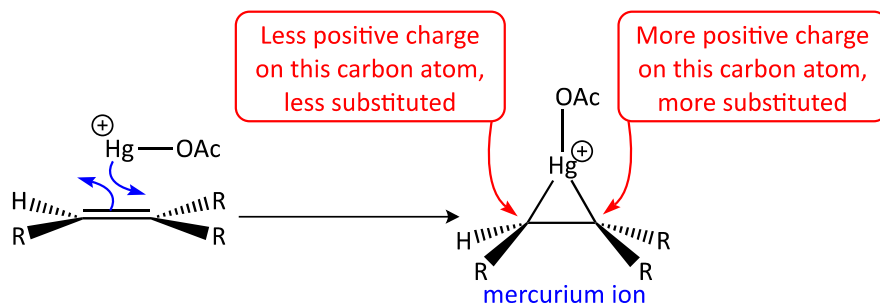
11.7.1 Oxymercuration in water

To perform the oxymercuration, mercuric acetate, $\text{Hg}(\text{OAc})_2$, is used. There are two common oxidation states of mercury, 1^+ and 2^+ . Mercuric refers to the higher oxidation state, Hg^{2+} . Acetate (OAc) is CH_3CO_2^- . There needs to be two of these 1^- acetates to balance the 2^+ charge of the mercury. The key first step in the oxymercuration of an alkene is the breaking apart of the mercuric acetate to form the electrophilic $^+\text{HgOAc}$.

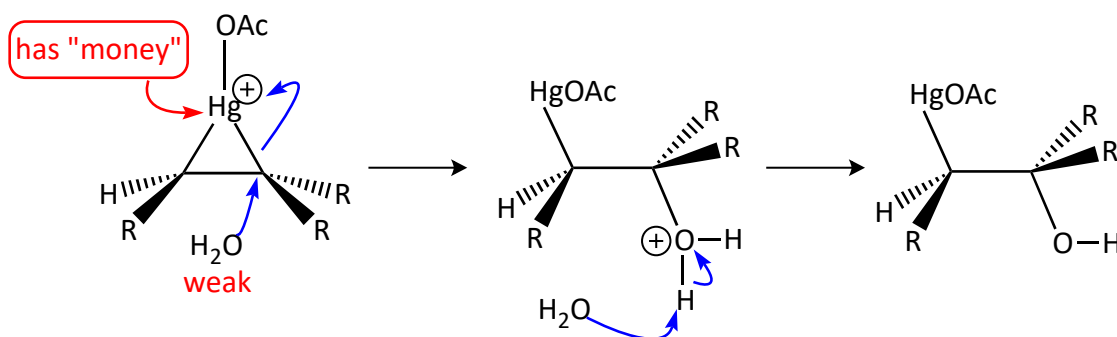


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The negative pi-electrons of the alkene eagerly attack the positively charged, electrophilic $^+\text{HgOAc}$. The pi-electrons attack to form the triangular mercurium ion. The two electrons from the pi bond go towards the Hg^+ , and two electrons return towards the pi bond. This causes the oxidation state of the mercury not to change so it remains Hg^+ . These triangles are formed when very large, soft atoms like mercury are used in the electrophile. The mercury atom is so large, it takes both carbon atoms to hold up. The victim in our triangle analogy is now holding a "+" over his head indicating he has money.

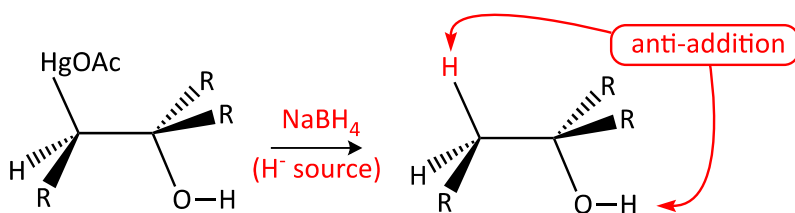


When the reaction is run in water, a weak nucleophile is present. Water is a stable, happy molecule. It will not attack a triangle compound unless it is coaxed in by money in some bags. In this case, the positive charge is shared over the two carbon atoms of the triangle. The more substituted carbon atom (on the right) carries a greater partial positive charge. Water then attacks the carbon atom with the greatest partial positive charge. In our criminal/victim analogy, the right carbon atom of the triangle is holding more bags and the + money is kept on the right carbon atom of the triangle under the bags. From what direction will the water attack the triangle? The large HgOAc blocks the topside of the mercurium ion triangle from attack, so the water must attack from the backside. It attacks, and the electrons go up onto the positive mercury. The neutral mercury acetate that is formed is a good leaving group—even though it is still attached to the left triangle carbon of our molecule. Finally, another water molecule cleans up the protonated alcohol to give us a mercury-alcohol compound.



11.7.2 Demercuration

The final step is demercuration, where HgOAc is replaced with H . Sodium borohydride (NaBH_4) is a source of hydride (H^-). This H^- directly replaces the HgOAc . Don't worry about the mechanism of this step. The mechanism will only confuse you at this state, so this is one of those instances where you should simply memorize this.



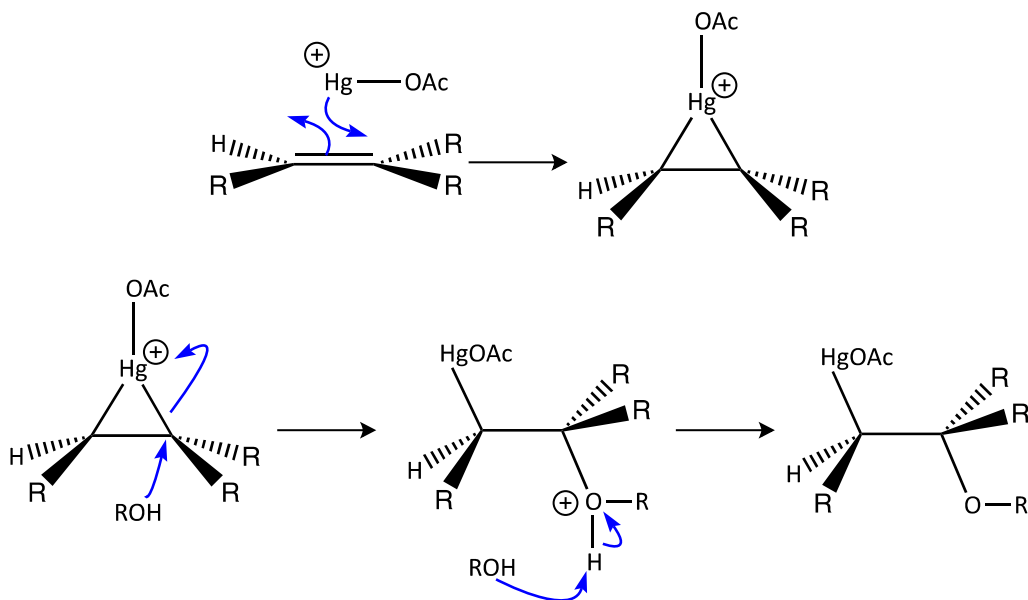
The benefits of oxymercuration/demercuration are: 1) a regular carbocation is not formed, so there is no chance for rearrangements. 2) the reaction is gentler than using sulfuric acid. 3) the reaction tends to go in high yield.

Are there any drawbacks to the oxymercuration/demercuration reaction? You may have already guessed it. Any time a reaction uses mercury, we need to be careful. Mercuric acetate and our mercury-containing products are toxic. We need to be very careful using them and be careful that we properly dispose of our waste.

11.8 Oxymercuration/Demercuration-with alcohol- A triangle reaction

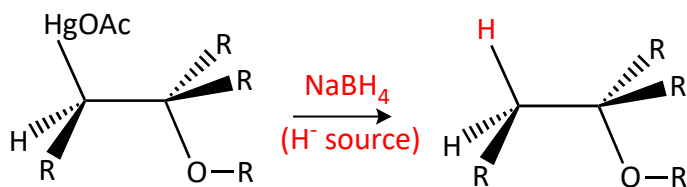
11.8.1 Oxymercuration in alcohol

Once again, mercuric acetate is used to make the triangular mercurium ion. If water is not used as our solvent, it cannot react as the nucleophile. If alcohol is used as the solvent, the lone pair of electrons on the alcohol can act as a weak nucleophile and attack the mercurium. Again, it attacks the carbon atom of the mercurium triangle with the greatest partially positive charge. The electron bond goes up onto the mercury cation to make a good, neutral mercury leaving group. The protonated $-OR$ group is deprotonated with another molecule of solvent to make a mercury-ether containing compound. Many different Markovnikov ethers can be made depending on the alcohol used as the solvent. $R = CH_3$ for methanol, $R = CH_2CH_3$ for ethanol, etc.



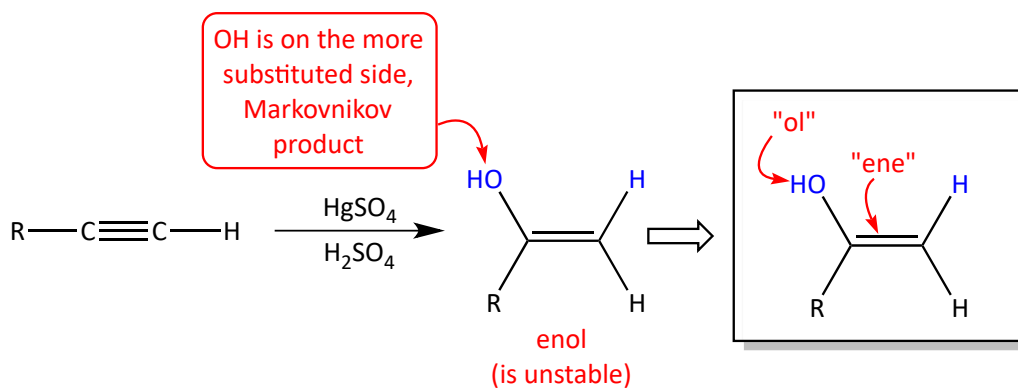
11.8.2 Demercuration

Sodium borohydride ($NaBH_4$) is once again used to replace $HgOAc$ with H^- making a Markovnikov ether.



11.9 Markovnikov hydration of alkyne

Alkynes, with their two pi-bonds, can also react in an oxymercuration-demercuration reaction. The reaction is very similar to that for an alkene with a twist at the end. Instead of mercuric acetate, the oxymercuration of alkynes usually involves mercuric sulfate and aqueous sulfuric acid. Like with alkenes, this results in the addition of water across a pi-bond resulting in a Markovnikov alcohol. Only one pi-bond of the triple bond reacted, so alkene remains. This vinyl alcohol is called an enol (pronounced "een-awl"). The "enol" name comes from this compound being an alkene (*ene*) and an alcohol (*ol*).



Enols tend to be unstable. Enols are in equilibrium with their isomer, the ketone. These isomers differ only in the location of one proton and a double bond. Such isomers are called tautomers (pronounced "taw-toe-mers"). The ketone and enol are called keto-enol tautomers. The transformation of one into another is called a keto-enol tautomerization. The process itself is called keto-enol tautomerism. In the equilibrium of the two, the keto form predominates. Take careful notice of the transformation. The hydrogen atom moves from the alcohol of the enol to the alpha carbon. The pi-bond of the alkene of the enol moves to make a carbonyl (a ketone).

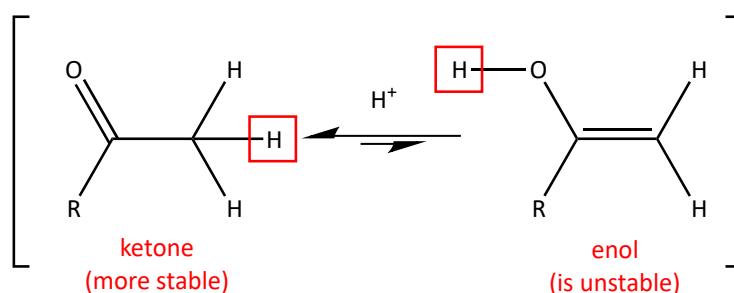
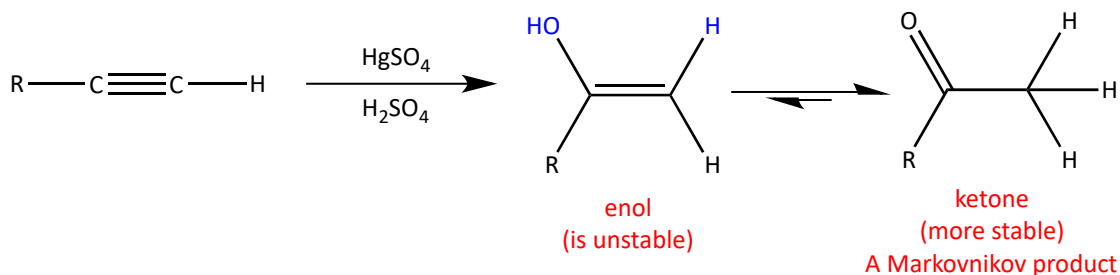


Figure 11.8 Keto-enol tautomerization

Overall Reaction



The tautomerization is acid-catalyzed since sulfuric acid is used in the reaction. H^+ is available because of the acid. To write the mechanism of the acid-catalyzed keto-enol tautomerization, protonate the enol at the alpha-carbon, draw resonance forms, and clean it up to make a ketone.

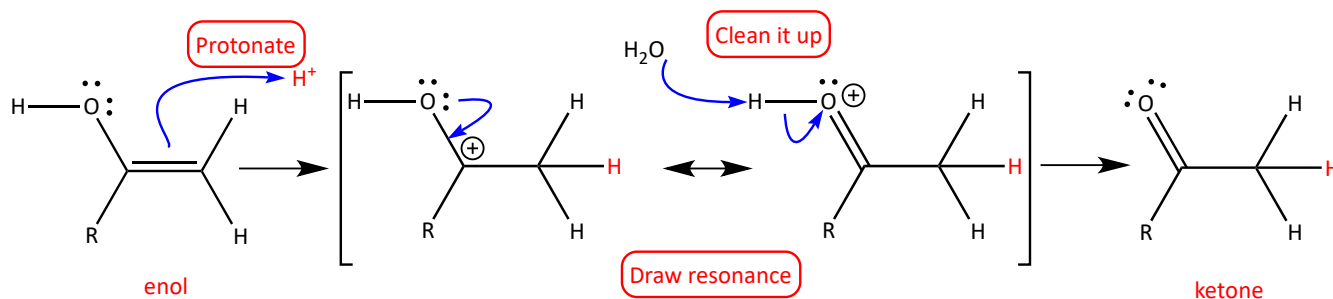
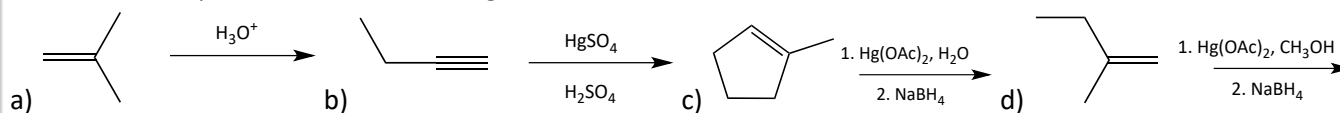


Figure 11.9 Acid-catalyzed keto-enol tautomerization

11.3 Draw the products of the following reactions.



11.10 Hydroboration – Anti-Markovnikov hydration

11.10.1 Hydroboration of alkene

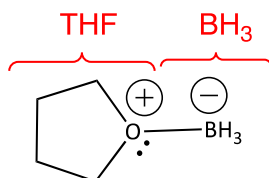
In 1979, Purdue University professor Herbert C. (H.C.) Brown won the Nobel Prize in chemistry for his work on the hydroboration of alkenes. Brown discovered that hydroboration is a way to make anti-Markovnikov alcohols. The simplest hydroborane, BH_3 , has six valence electrons on the boron atom. Remembering the octet rule, we should realize this is electron deficient and therefore an electrophile. It just so happens that there is a nice, juicy pair of negative electrons in an alkene which is more than happy to attack the BH_3 !

BH_3 is available in a couple of forms. One possibility is to buy diborane, B_2H_6 . Diborane breaks apart to make BH_3 .

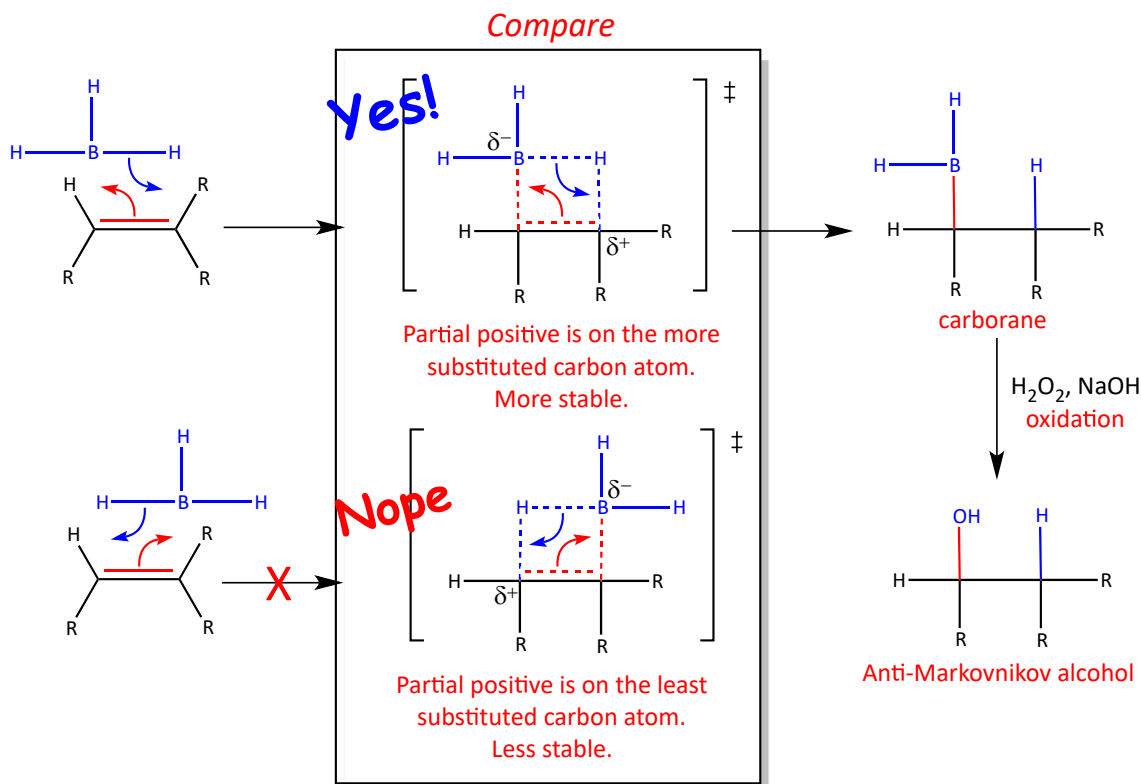


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But, diborane is a toxic, flammable, explosive gas. So, this is not the preferred method. More commonly, BH_3 is purchased dissolved in a solvent like THF. This is a much safer way to use BH_3 . Since it is an adduct with the solvent, it is a liquid that can be measured out.



The mechanism for the hydroboration reaction begins when a B-H bond of BH_3 adds across the C=C in one step to make a square transition state. The boron atom gains a little negative electron density and therefore becomes partially negative. The carbon atom opposite the boron in the square loses some negative electron density and becomes partially positive. When the two transition states are compared, the partially positive carbon atom that is more substituted is more stable. It is the pathway that is followed more. When this carborane is oxidized with H_2O_2 and NaOH , the BH_2 is replaced with OH making an anti-Markovnikov alcohol. This is an extremely important reaction. Now we can make either Markovnikov or anti-Markovnikov alcohols. And, we'll learn later in organic chemistry, that we can turn alcohols into many different types of functional groups.



11.10.2 Hydroboration of alkyne

The hydroboration of an alkyne can lead to an anti-Markovnikov enol. Since alkynes contain two pi-bonds, two molecules of borane could add to it. A big, bulky, sterically hindered borane must be used in order to prevent this addition of two boranes. Usually, the borane used is di(*sec*-isoamyl)borane, commonly called disiamylborane. Instead of the small BH_3 molecule, disiamylborane has two big, large, deer antler-like alkyl

groups attached to it. There are five carbon atoms in each alkyl branch. Amyl is an old, common name for pentyl.

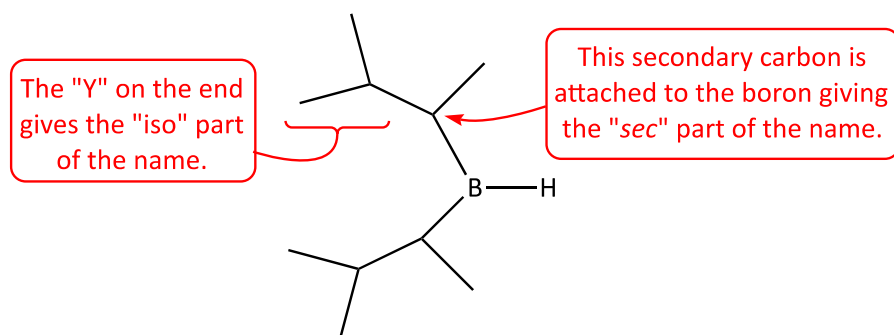
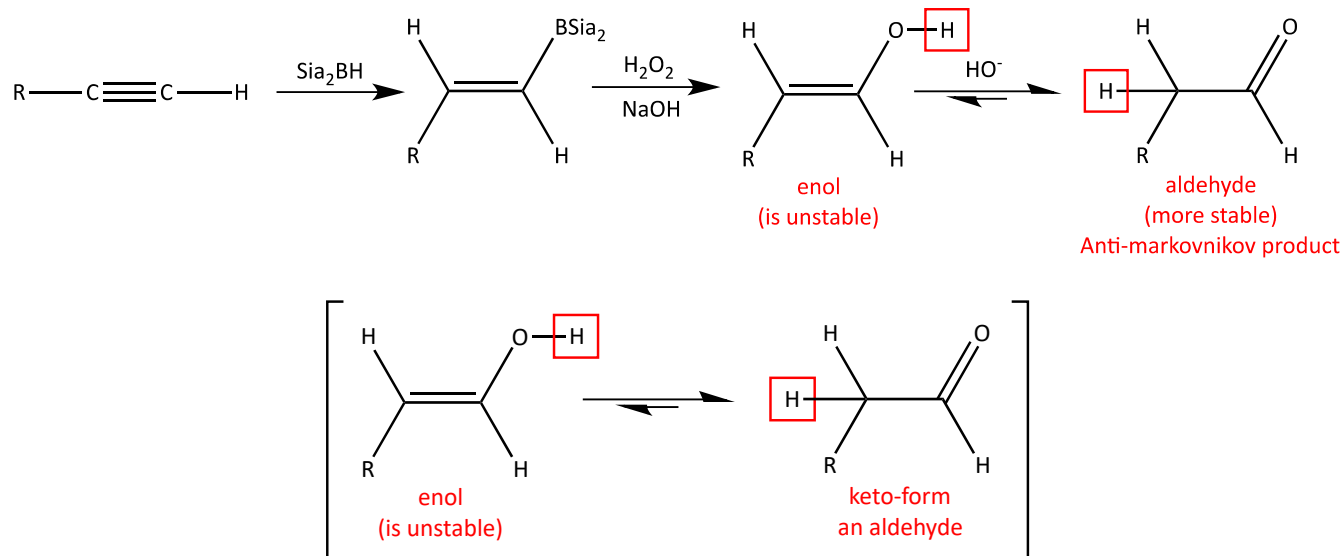


Figure 11.10 Di(sec-isoamyl)borane or disiamylborane

Disiamylborane reacts with an alkyne to make an anti-Markovnikov borane. This borane can be oxidized with peroxide and sodium hydroxide to make an anti-Markovnikov enol. This enol can tautomerize to the keto-form. In the case of a terminal alkyne, this keto-form is an aldehyde with a hydrogen attached to the carbonyl group.



The mechanism of the base catalyzed keto-enol tautomerization is different than the mechanism was in acid. Bases deprotonate. So, the first step of this mechanism is the deprotonation of the enol at the alcohol position. This is pretty easy to remember because we are turning the alcohol portion of the enol into a carbonyl group. Once deprotonated, we draw resonance forms to get us closer to the keto product, then clean it up with some water to make the final aldehyde.

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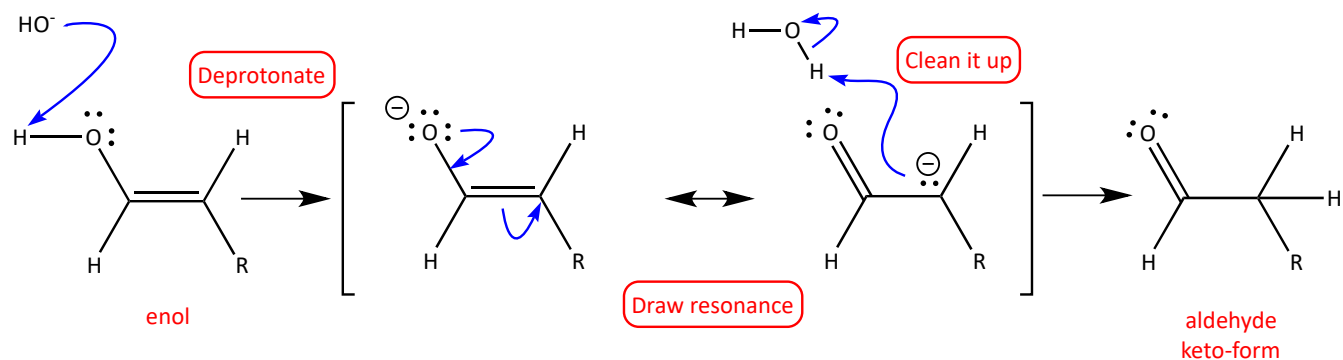
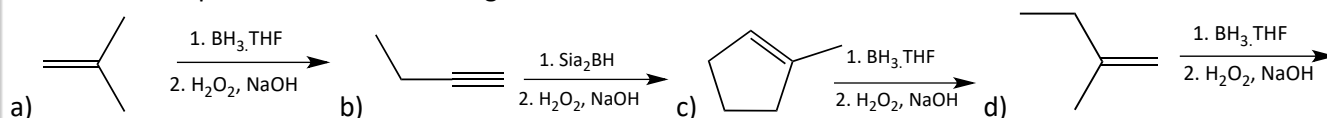


Figure 11.11 Base-catalyzed keto-enol tautomerization

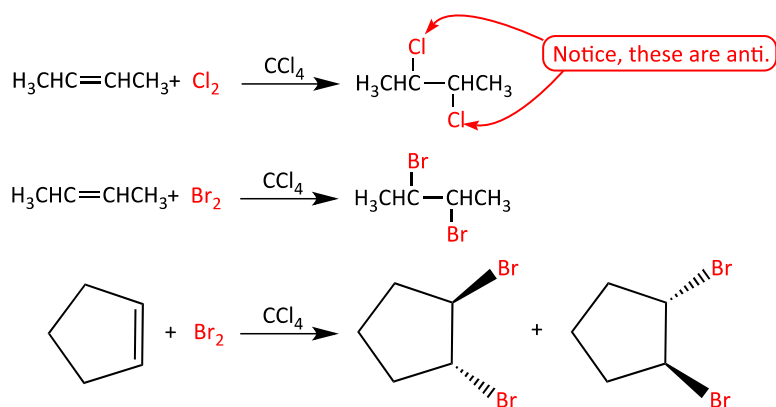
11.4 Draw the products of the following reactions.



11.11 Halogenation-A triangle reaction

11.11.1 Halogenation of alkenes

Alkenes can undergo a halogenation reaction. This is a reaction with Cl_2 or Br_2 to make vicinal dichlorides or dibromides. This reaction must be run in an inert, non-reactive solvent like CCl_4 .



If one looks closely, the two halogens end up on neighboring carbon atoms which makes the product a vicinal dihalide. The third reaction, the bromination of cyclopentene, clearly shows the two bromides of the product are on opposite sides of the ring to each other in a *trans* configuration. This addition where the two groups end up on opposite sides is called *anti-addition*. This anti-addition occurs because a halonium intermediate is formed in the course of the reaction.

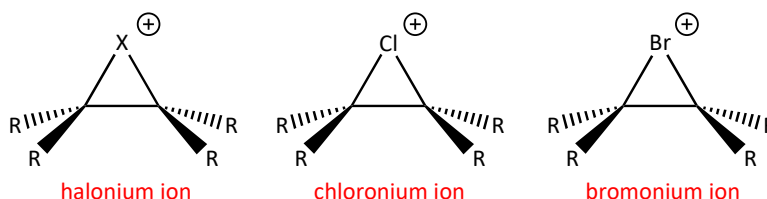
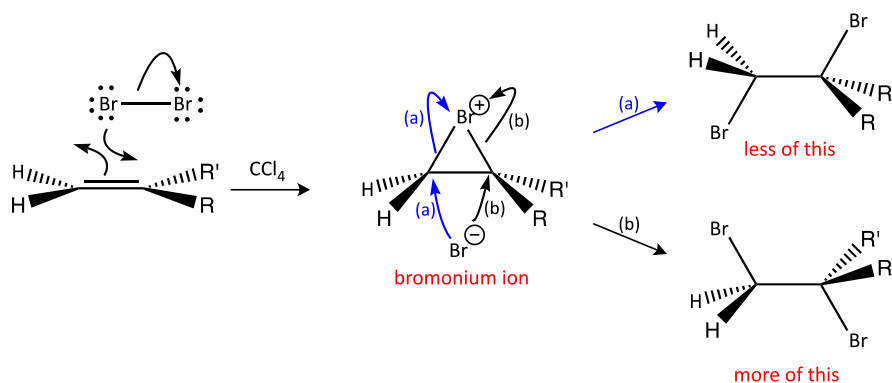


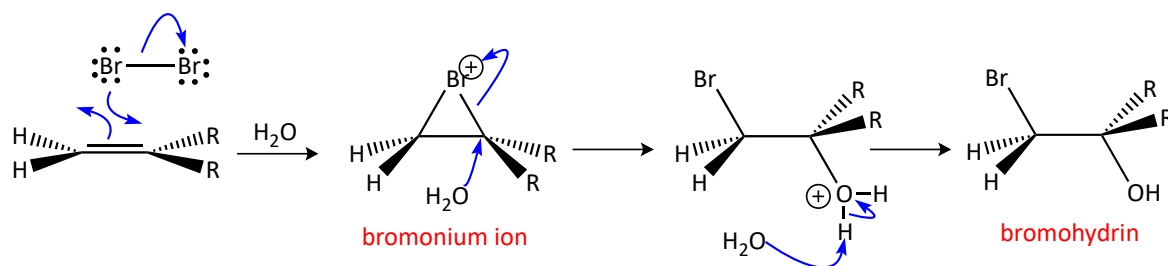
Figure 11.12 Halonium ions

The mechanisms for the chlorination or bromination of alkenes are identical. Bromination is shown here. When the alkene reacts with Br_2 , a triangular bromonium ion is produced with Br^- as the leaving group. This Br^- does a backside attack at either carbon atom of the bromonium ion. In this triangle reaction, the Br^- would attack using pathway (b) more often than (a) since this carbon is more substituted and would have a greater partial positive charge.



11.11.2 Halohydrin formation - A triangle reaction

If the solvent used in a bromination or chlorination reaction is not inert but instead is slightly nucleophilic, different products are formed. As an example, a bromohydrin is formed if water is present in the bromination reaction. In this mechanism, a bromonium ion is formed as before. But, if water is the solvent, there are numerous water molecules for every one Br^- nucleophile. Water ends up being the nucleophile that attacks. In this triangle reaction, a "+" sign is being held up. So, the weak H_2O nucleophile attacks the more substituted carbon atom where more of the + money is held in the pocket under the bags. Once another water molecule cleans it up by deprotonation, it leads to the bromohydrin.



If Cl_2 and water are used, a chlorohydrin is formed. These *halohydrins* are molecules with neighboring halogens and hydroxyl groups.