

Week 10

CHE 3331- Organic Chemistry

This week is Week 10 of class, and typically in this week of the semester, your professors are covering these topics below. If you do not see the topics your particular section of class is learning this week, please take a look at other weekly resources listed on our website for additional topics throughout of the semester.

We also invite you to **look at the group tutoring chart on our website to see if this course has a group tutoring session offered this semester.**

If you have any questions about these study guides, group tutoring sessions, private 30 minute tutoring appointments, the Baylor Tutoring YouTube channel or any tutoring services we offer, please visit our website www.baylor.edu/tutoring or call our drop in center during open business hours. M-Th 9am-8pm on class days 254-710-4135.

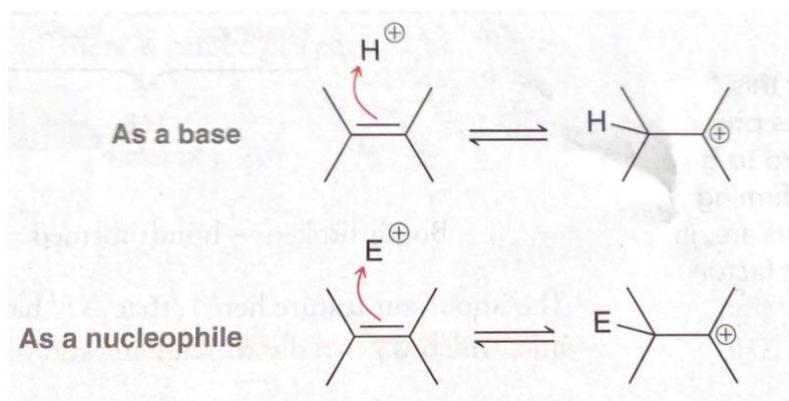
Keywords: Addition Reactions Across Alkenes, Hydrohalogenation, Markovnikov Addition, Anti-Markovnikov Addition, Oxymercuration-Demercuration

TOPIC OF THE WEEK: ADDITION REACTIONS OF ALKENES

Last week, we taught you guys how to create alkenes through elimination reactions! This week, we will be teaching you different kinds of reactions with alkenes and how we can add different groups across the double bond to break it and add new groups!

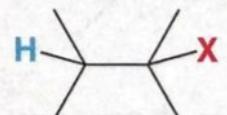
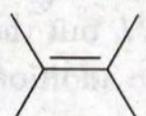
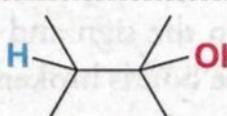
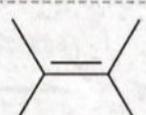
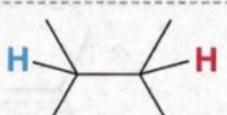
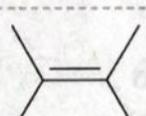
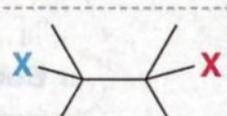
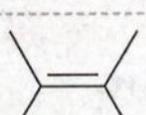
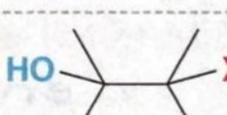
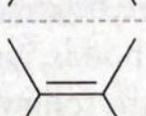
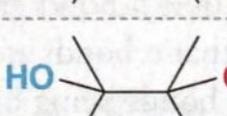
First, it is important to get a brief overview on how alkenes can become reactive. The pi bond of a molecule can function either as a **weak base** or a **weak nucleophile**!

- **If it functions as a weak base**, it will add one hydrogen molecule to one carbon of the double bond and leave a + charge on the other carbon of the double bond
- **If it functions as a weak nucleophile**, it will attach other electrophilic centers and will cause one carbon of the double bond to become attached to the electrophile and leave a + charge on the other carbon of the double bond



- **Remember: Sigma bonds are more stable than pi bonds, so the most common reactions of pi bonds will be to transform it into 2 sigma bonds!** *in a double bond, there is one sigma and one pi bond*

These are some of the most common addition reactions. You will want to memorize each reaction and reagent! I would recommend putting them in a Quizlet and committing them to memory because they will be very helpful!

TYPE OF ADDITION REACTION	NAME	SECTION
 Addition of H and X 	Hydrohalogenation (X=Cl, Br, or I)	9.3
 Addition of H and OH 	Hydration	9.6
 Addition of H and H 	Hydrogenation	9.7
 Addition of X and X 	Halogenation (X=Cl or Br)	9.8
 Addition of OH and X 	Halohydrin formation (X=Cl, Br, or I)	9.8
 Addition of OH and OH 	Dihydroxylation	9.9, 9.10

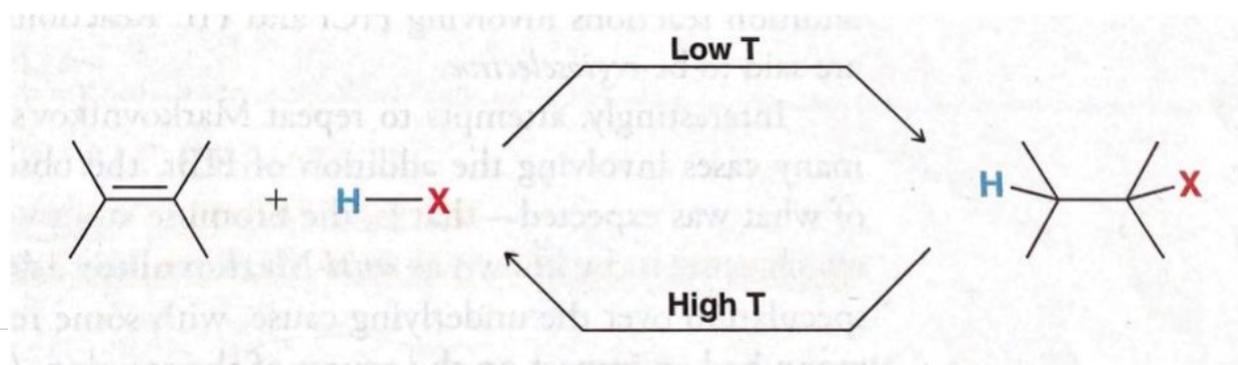
HIGHLIGHT #1: Addition vs. Elimination from a Thermodynamic Perspective

Remember the things we talked about in the thermodynamics' chapter! We discussed that the sign of the ΔG will determine whether the equilibrium favors the reactants or the products.

- If ΔG is *negative*, the reaction will *favor the products!*
- If ΔG is *positive*, the reaction will *favor the reactants!*

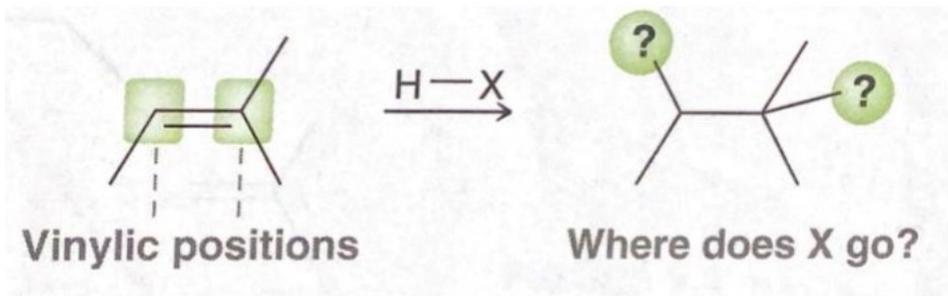
Addition and Elimination reactions are very temperature dependent, and both are favored under different conditions.

Addition reactions are favored at a low temperature, while elimination reactions are favored at a high temperature!



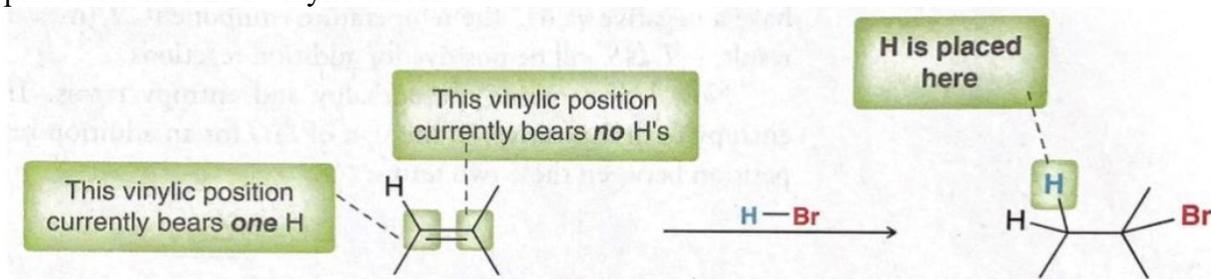
HIGHLIGHT #2: Hydrohalogenation and Regioselectivity

When an alkene reacts with HX, (where X = any halogen, such as Bromine, Chlorine, Iodine, etc.) the addition reaction is called a *hydrohalogenation*. Consider the case below.

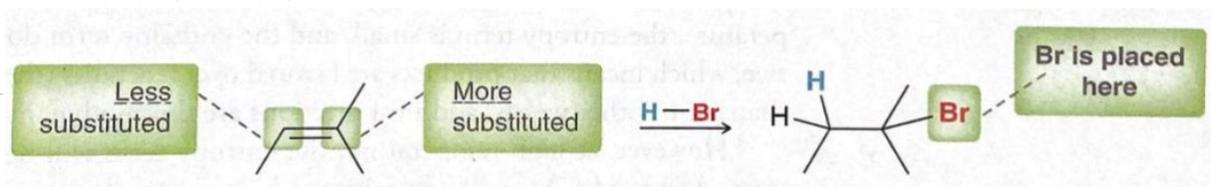


There are instances where we can add an H and X (a halogen) across a double bond that is asymmetrical, so in this case, does it matter where we add the H and the X? The answer is YES!

Typically, we will place the hydrogen on the vinylic position that has the larger number of hydrogen atoms already! So, in the case of the example above, the H would be placed on the LEFT vinylic carbon!



Therefore, we leave the halogen to be placed at the more substituted position. This regiochemical preference for the halogen to be in the more substituted position is called a **Markovnikov addition!**



If we were to place the Halogen on the **LESS** substituted carbon, this regiochemical preference would be called **anti-Markovnikov addition**

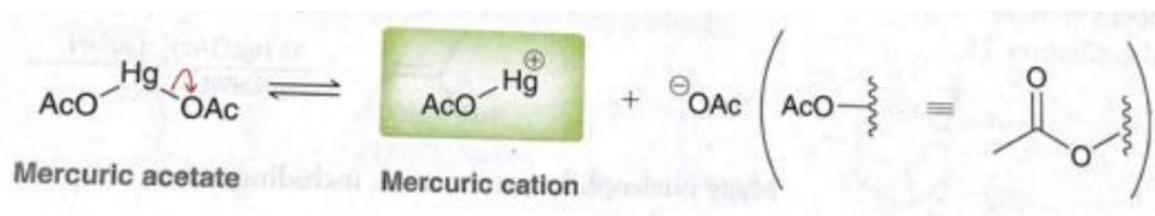
Note: Because we create a carbocation when the double bond attacks, do not forget about the possibility for a methyl shift or a hydride shift! Everything in Organic Chemistry builds upon itself, so we can use our notes and logic from S_N1 reactions and apply them to our addition reactions!

HIGHLIGHT #3: Oxymercuration-Demercuration

For the past couple of pages, we have dived into the different ways in which we can achieve a

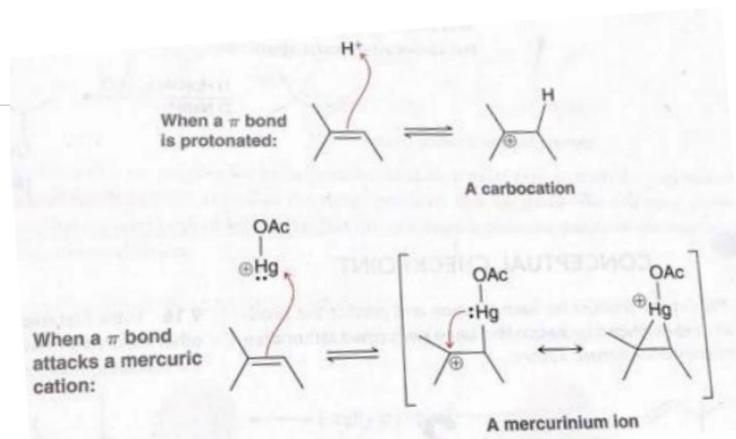
Markovnikov addition of water across an alkene, which adds an OH group to one carbon and an H to the other carbon. However, there are many other ways which are *more* efficient in catalyzing the addition of a water across an alkene **without the carbocation rearrangement!** This is where **Oxymercuration-Demercuration** occurs!

This addition reaction occurs through a couple of steps, and will begin with mercuric acetate $\text{Hg}(\text{OAc})_2$, which will dissociate and form a **mercuric cation** seen below.



The mercuric cation is a very powerful electrophile and is a great place for a nucleophile to attack, like the pi bond of a double bond!

1. **FIRST**, the pi bond is going to attack the mercuric cation and will result in a positive charge on a carbon! Do not confuse this with a carbocation, because the extra lone pairs on the mercury atom will interact with the positive charge to form a bridge, which is an intermediate called a mercurinium ion!



When you see the positive charge on the carbon, do not worry about carbocation rearrangements! This structure will not undergo rearrangement! Instead, it will be attacked by a nucleophile!

Note: The attack will take place at the more substituted carbon, leading to a Markovnikov addition. Then, we can remove the mercury through a demercuration!

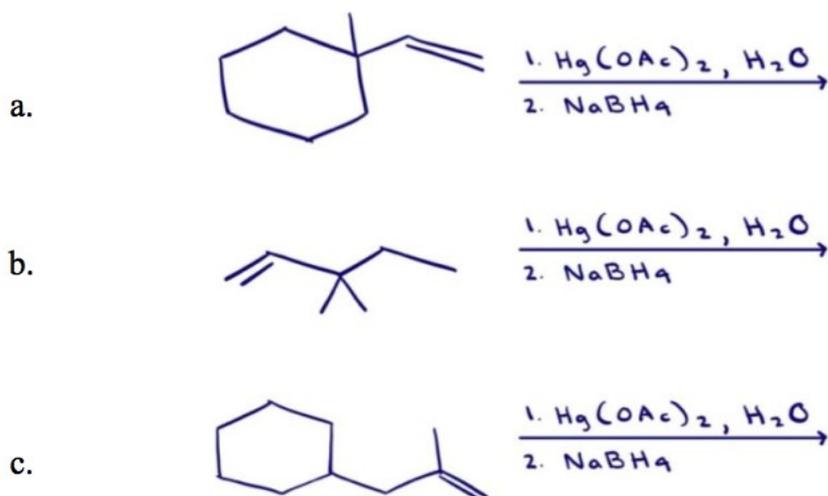
2. After the mercurium ion has been formed, it will create two different resonance structures. The resonance structure that has a positive charge on a carbon will be your primary resonance structure!
3. This intermediate will NOT undergo carbocation rearrangement! Instead of rearranging, it will simply be attacked by a nucleophile!
4. Many nucleophiles can be used! It can be water, or any other nucleophile can be added across the alkene!
5. The attack will always occur on the more substituted position, which will always yield a Markovnikov addition!
6. After the attack, demercuration will remove the mercury atom! The reagent used to accomplish this will be sodium borohydride!

CHECK YOUR LEARNING:

1. Draw a mechanism for the following reaction and state if they are added Markovnikov or anti-Markovnikov addition.



2. Try out drawing the mechanisms for extra practice! If you do not understand how to yet, we will go over it in more detail in Group Tutoring! To answer each question, simply predict the product for each of the following examples.



THINGS YOU MAY STRUGGLE WITH:

- The mechanisms for Oxymercuration-Demercuration are a bit more difficult to understand because it involves a resonance stabilized state and no carbocation rearrangement! This will just take practice to understand, and to get used to writing the mechanism in this distinct way. Watch a bunch of videos and do a lot of practice problems on this material so you understand the mechanism well!
- There are also other reactions that are important for additions across alkenes, such as hydroboration-oxidation! This resource is not exhaustive, so please be sure to learn those reactions well also! I added summary videos that also cover the hydroboration-oxidation reaction, so please watch those!

Thanks for checking out these weekly resources!
Don't forget to check out our website for group tutoring times, video tutorials and lots of other resources: www.baylor.edu/tutoring ! Answers to check your learning questions are below!

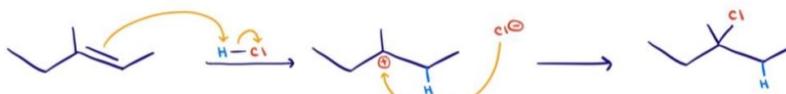
ANSWERS TO CHECK YOUR LEARNING:

1.

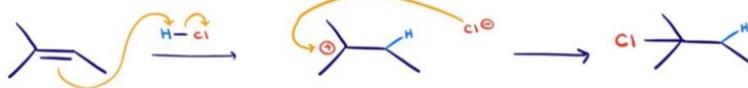
a. Mark addition



b. Mark addition

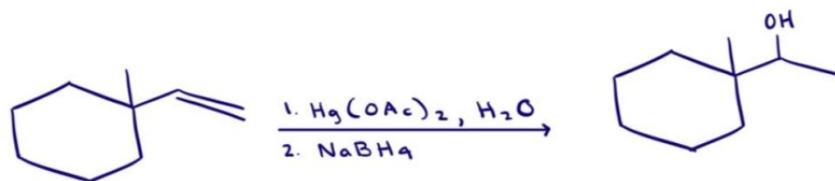


c. Mark addition

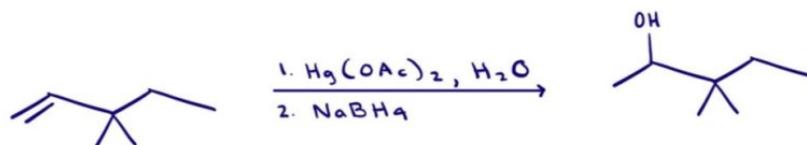


2.

a.



b.



c.

