Week 12
CHE 3331- Organic Chemistry

This week is Week 12 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.

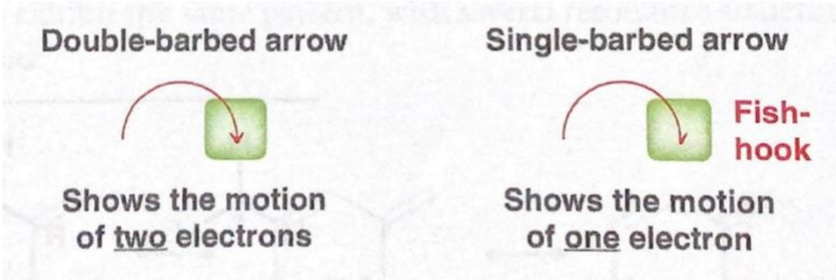
Keywords: Radical Mechanisms, Homolytic Cleavage, Resonance, Initiation, Propagation, Termination, Fishhook Arrows

TOPIC OF THE WEEK: RADICAL MECHANISMS

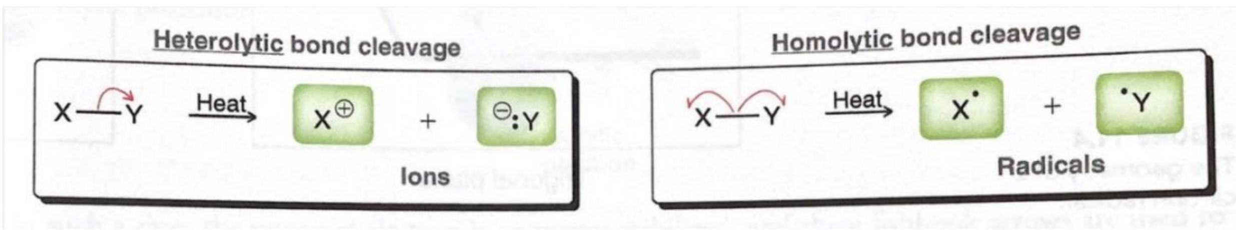
Hello everyone! This week we will be talking about radicals and how to draw mechanisms with radicals! If you are still struggling with alkenes or alkynes, be sure to check out last week's resource and make sure that you understand those completely before moving on to radicals!

Radicals are a little bit different than any other mechanism we have done, so before we jump into mechanisms, let's start off by understanding their differences. One of the first differences between radical mechanisms and normal mechanisms are **the arrows**! For normal mechanisms, we used the typical **double-barbed arrow** to symbolize the movement of **two** electrons! This typical double-barbed arrow represents heterolytic cleavage which cleaves compounds to form two separate ions in which one ion gets both electrons and the other gets none.

However, a radical is an atom or molecule with **one unpaired valence electron**. This is strange because we typically see electrons traveling in pairs, but radicals are created through homolytic cleavage, which cleaves a bond in which both electrons to go to different species, one electron to each! For this reason, we will not be using double-barbed arrows. Radicals use **single-barbed arrows** because we are only moving **one** electron.



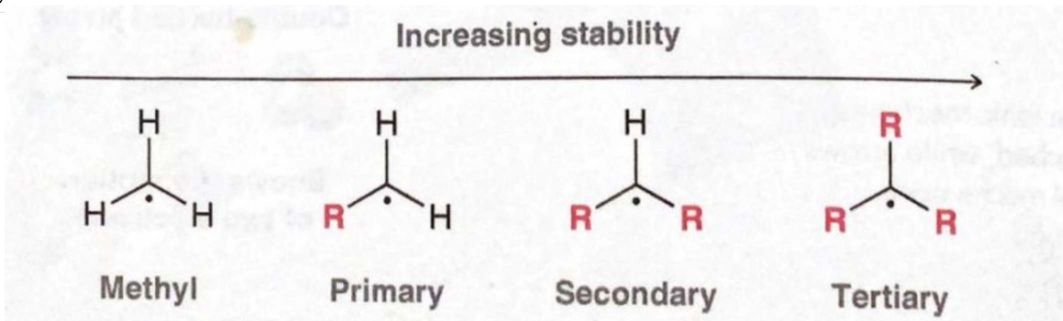
This type of arrow is called a **fish-hook arrow**. Since we are moving only one electron, we will create a radical, which is a molecule with only one unpaired electron. Remember that there are 2 electrons in a bond, so if we are breaking a bond, there must be 2 electrons that are accounted for. Since a radical only has one unpaired electron, the other electron must be drawn alone with a fishhook arrow. Look below for an example of homolytic cleavage, which involves the formation of two different radicals.



It is important to remember that homolytic cleavage will create two new radicals because you move two individual electrons to two separate species. **Following electrons will be the most important thing to do this entire chapter!**

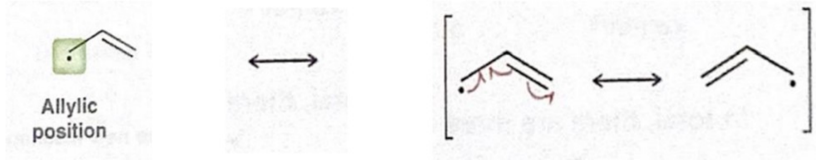
HIGHLIGHT #1: Radical Stability

The order of stability follows a similar idea that we have seen for the past couple of weeks with O-Chem. A radical will always be most stable on a tertiary carbon and least stable on a primary carbon.



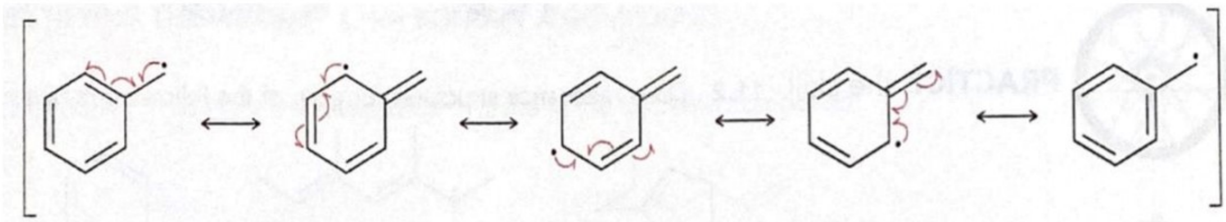
HIGHLIGHT #2: Resonance Structures of Radicals

Just like many of your other structures, radical mechanisms typically have several resonance patterns (around 5-6). The only time you will have only one other resonance structure is when the unpaired electron is next to a pi bond in an allylic position. In that case, then you should only have one other resonance structure, as shown below.



When drawing resonance structures, it will usually involve breaking an already present double bond and combining it with the radical and then leaving the other electron from the double bond to create the radical.

However, if you have a radical at the benzylic position, a radical next to a ring, you will have multiple resonance structures. Try looking at these resonance structures and understanding the patterns.



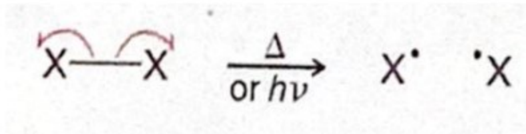
Notice that every resonance structure involves using the double bond as a source to "quench" the radical, creating a new bond. The other electron from the double bond will then go on to make a new radical!
One thing to memorize for this chapter is that radicals that are allylic and benzylic will be stabilized by resonance, but vinylic radicals will not be.

HIGHLIGHT #3: Drawing a Radical Mechanism

There are 3 important steps when learning how to draw a radical mechanism and understanding them will be very helpful in approaching new radical problems.

The first step in drawing a radical mechanism is **INITIATION.**

Many times, in any given solution, we do not typically have radicals. Radicals are very harmful in your body so we will not naturally have radicals "hanging around" in solution. The first step in drawing a radical mechanism, is **homolytically breaking** a bond to **create a radical.**

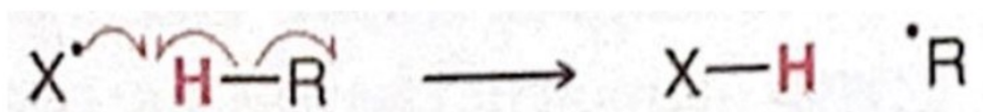


This may seem counterintuitive, but the first step in a radical mechanism will be to break a bond to create **two radical species**. You have probably learned in General Chemistry that breaking bonds requires a large input of energy, so this energy can be supplied in the form of heat (D) or light (hv).

The next step in drawing a radical mechanism is **PROPAGATION**.

This step is where you can add the radical to an already existing pi bond and generate a new radical. This step is where you will have your resonance structures!

Throughout this resource, we have seen how a radical adds to a pi bond. However, what if you do not have a double bond in your molecule? There are many other ways in which you can quench your radical and create new ones. Oftentimes, a radical can steal a hydrogen or halogen from a compound and generate a new radical.



OR

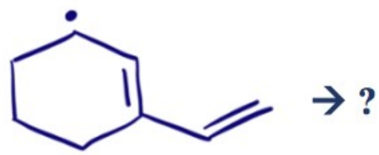
On the top example, we quenched our radical with a hydrogen and created an R radical. On the bottom example, we quenched our radical with a halogen, making a new species, and created a new radical! There are many ways to quench a radical even if you don't have a double bond!

The last step in a radical mechanism is **TERMINATION**.

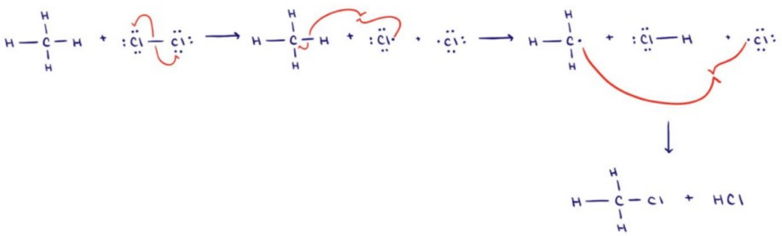
During this step, we quench our last radical which will eliminate all the radicals remaining in solution.

CHECK YOUR LEARNING:

1. Try drawing all resonance structures of this molecule



2. Analyze this mechanism. Try to understand how to use the three steps of radical mechanisms to ensure you understand how to write it out. Then, write out where INITIATION, ELONGATION, AND TERMINATION occur.



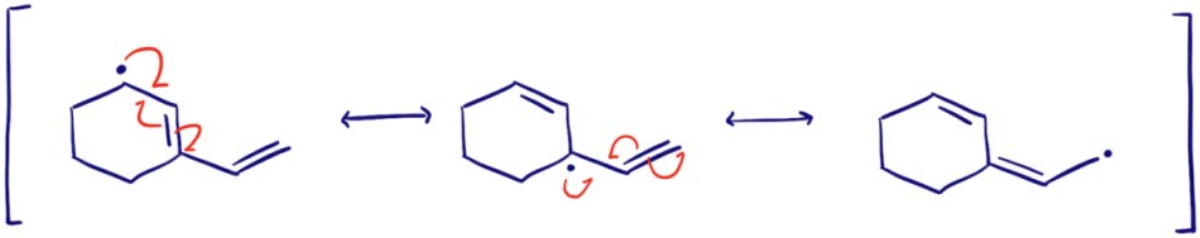
THINGS YOU MAY STRUGGLE WITH:

- Radical mechanisms are difficult to understand. They are tricky and very easy to get confused on. Makes sure you are following electrons!! Try to visualize where the electrons are going and make sure to keep track of where your electrons are! It is easy to forget that a bond has two electrons and forget to draw the last electron!
- If your mechanisms steps do not somewhat resemble the 3 steps: initiation, propagation, and termination, then you are most likely doing something wrong. Use that to your advantage! Check your work with those steps and make sure they align with the general idea of how to draw a radical mechanism.
- Be sure to remember the fishhook arrows when you are using radical mechanisms! Professors will take off points if you use the wrong arrows!

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.



2.