

Week 14
CHE 3332 - Organic Chemistry 2

Hello and Welcome to the weekly resources for CHE 3332 – Organic Chemistry 2!

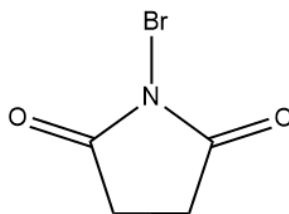
This week is Week 14 of class, and typically in this week of the semester your professors are covering these topics below. If you do not see the topics your particular section of class is learning this week, please take a look at other weekly resources listed on our website for additional topics throughout 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: NBS, Peroxide, Anti-Mark, Polymers

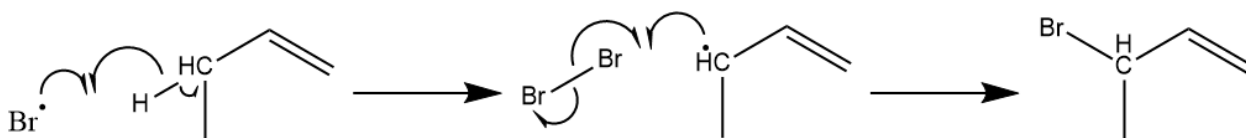
TOPIC OF THE WEEK: Continuing Radicals

Last week we tackled radical reactions, but we did not cover the whole chapter, so we will clean up some loose ends here. There are two other ways in which we can add a bromine radical to an alkene, either by adding it adjacent to the double bond, or directly onto the double bond. The former method is done through NBS bromination. NBS itself is a special bromine bearing molecule which has a nitrogen bonded to a bromine. This bromine can easily break off, and become a radical.

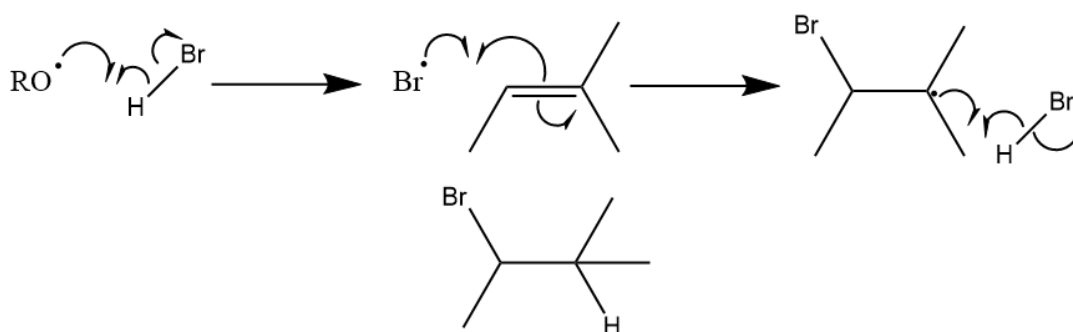


NBS molecule

Because of this bromine radical forming mechanism, which takes place rather slowly, the bromine will **add adjacent to a double bond, instead adding to the double bond itself.** This is unlike what we have seen earlier, where Br_2 added to an alkene **will add directly** to a double bond, because of how common Br_2 is in solution.

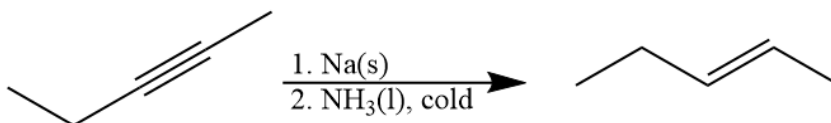


Another reaction that can add bromine is a radical reaction, using peroxides. Because peroxides add Anti-Mark, the bromine will be added first, to the **least substituted side** (as with other peroxide reactions), which is preferred in this case as our radical will be added to the more substituted carbon. Peroxides are great at becoming radicals and initiating reactions (RO indicates a peroxide radical).

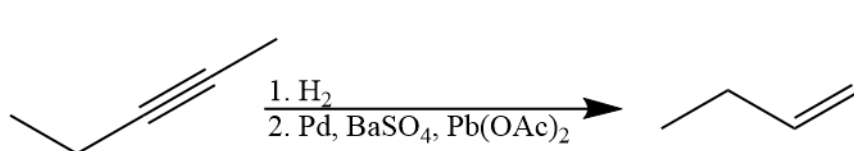


Final product with Anti-Mark positioning

Another series of reactions that this chapter covers, which is tacked onto the end, are reactions which involve the reduction of an **alkyne** to an **alkene**. This doesn't connect much to resonance, but it is still important to cover. While you all have likely talked about catalytic hydrogen (which can take an alkyne to an **alkane**), these will stop at a double bond, and will also have an effect on the cis/ trans stereochemistry. The first reaction is a “metal dissolving” reaction.

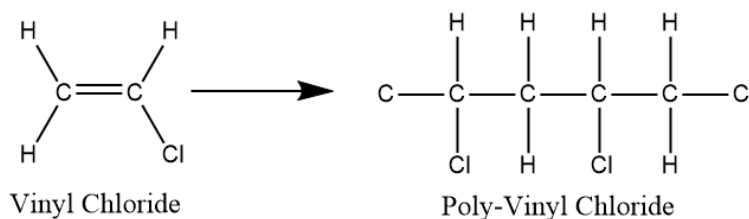


This entails the use of sodium, with liquid ammonia, to perform an electron transfer between the two. Through this, we can reduce alkynes to alkenes, **but notice that the stereochemistry produces a trans alkene**. This will **happen every time**. On the other hand, we can use catalytic hydrogenation with a poisoned metal catalyst. This will also reduce a triple bond to a double bond, **but will always produce a cis alkene**.



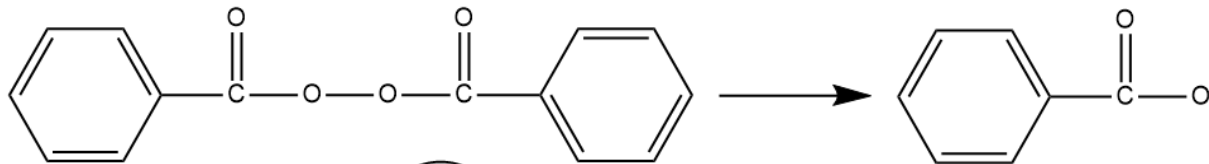
HIGHLIGHT #1: Polymers

Polymers are molecules, which are comprised of a chain of repeating units. These units are known as monomer units. When multiple monomers come together, they form a polymer.

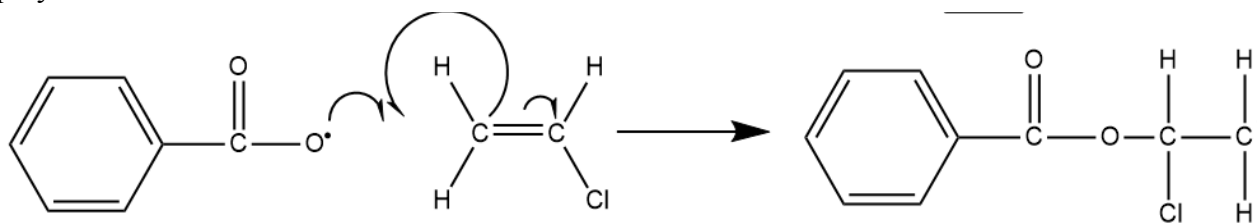


Example of a monomer unit and its respective polymer form

In this chapter, the main topic is polymers, and how to create them. Since the previous chapter was based on radicals, to start this chapter, we will talk about radical polymerization. This can be done with a special peroxide molecule, benzoyl peroxide. As we know, peroxides are great at becoming radicals, so this molecule will split in two, and yield a radical.



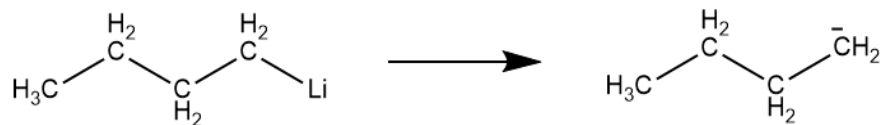
When this happens, the radical peroxide can attack a monomer unit. This in turns creates a **monomer radical which will then easily attack other monomer units** to continue to build the polymer chain.



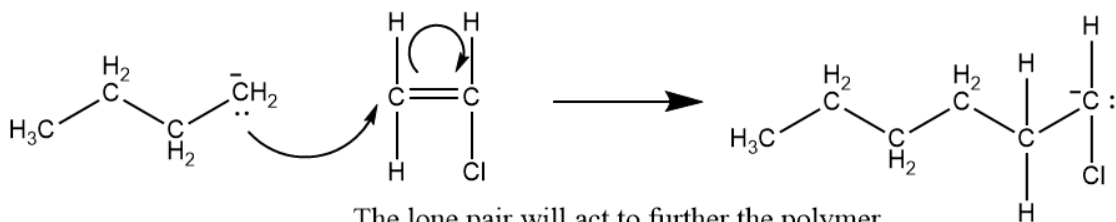
The newly created polymer radical will go to attack other monomers

Another way in which we can create polymers is through cation/ anion initiation. These behave in the same way as radical initiation, and all use their own unique starting material to create the polymer chain. For example, to create polymers using an anion, a lithiated carbon group will be used, which yields a carbanion. This is done **through the umpolung mechanism**

you all have likely talked about earlier in the semester. The lone pair on the terminal carbon will then go to attack a monomer unit, which adds to the chain, and creates another carbanion, which will seek out more monomers.

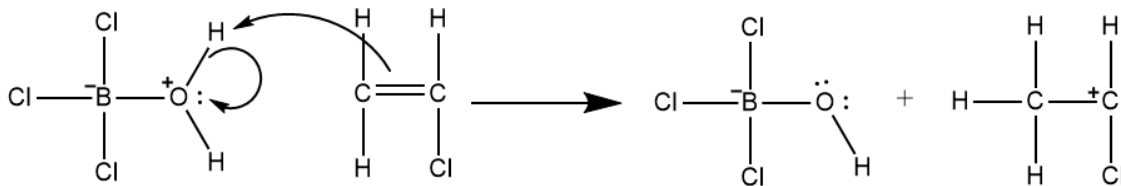


Umpolung reaction yielding a carbanion



The lone pair will act to further the polymer

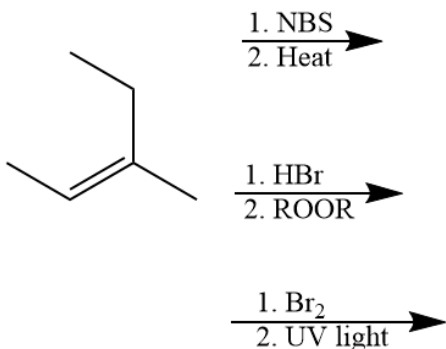
Alternatively, a cation can be used for similar results. This is started using a $\text{BCl}_3 \cdot \text{H}_2\text{O}$ group, which contains a positively charged oxygen. The oxygen will then donate this positive charge to a monomer, through proton transfer, with the monomer going on to create a new polymer.



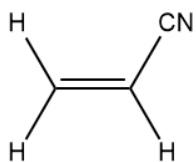
The carbocation will act to initiate polymerization

CHECK YOUR LEARNING:

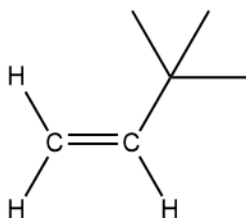
1. Provide the resulting product for each different reagent:



2. Give a mechanism for the radical polymerization of this monomer unit:



3. Give the propagating radical product that would result from reacting this monomer using cation polymerization:



THINGS YOU MAY STRUGGLE WITH:

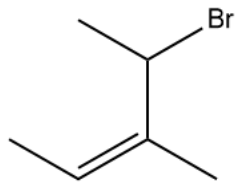
- For radical reactions, there are many different reactions which all do something very similar, but have different regiochemistry. It is best to memorize them well, as well as recognizing when reagents will impact regiochemistry.
- Honestly, this last portion in general is not too hard, and I have faith in you all that it won't be much of a challenge. That being said though, we are approaching finals season, so don't let reviewing fall behind. In fact it may just be a good idea to start now.

Thanks for checking out these weekly resources!

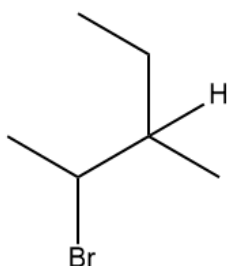
Don't forget to check out our website for group tutoring times, video tutorials and lots of other resources: www.baylor.edu/tutoring! Answers to check your learning questions are below!

ANSWERS FOR THE PRACTICE PROBLEMS:

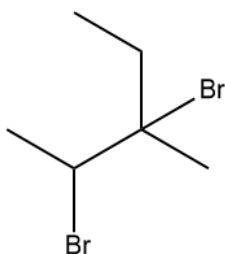
1. This problem is simply testing the different ways we can add a bromine to an alkene. Our first portion is simply just using NBS. Because NBS generates bromine radicals slowly, we will only add one bromine adjacent to the double bond.



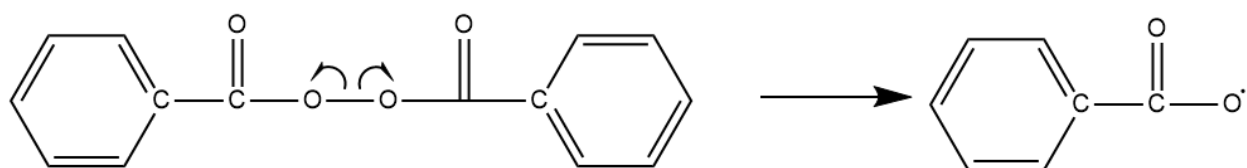
Using the second reagent, we can identify the presence of peroxides. This indicates Anti-Mark addition to the double bond.



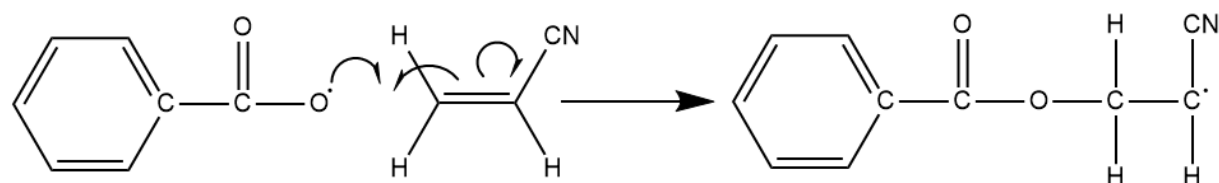
Finally, the third set of reagents indicates a simple addition of bromine to a double bond using U.V. light. This will add two bromines.



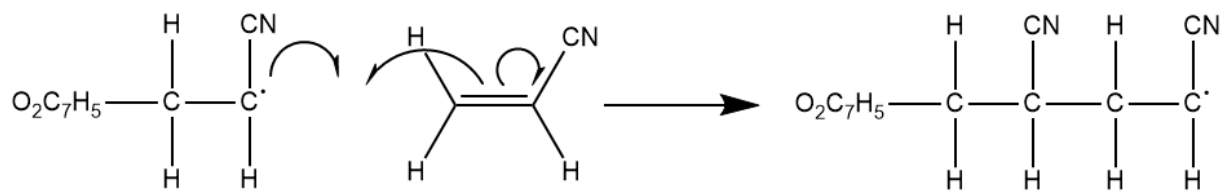
2. For this problem, we need to use a benzoyl radical to initiate the reaction:



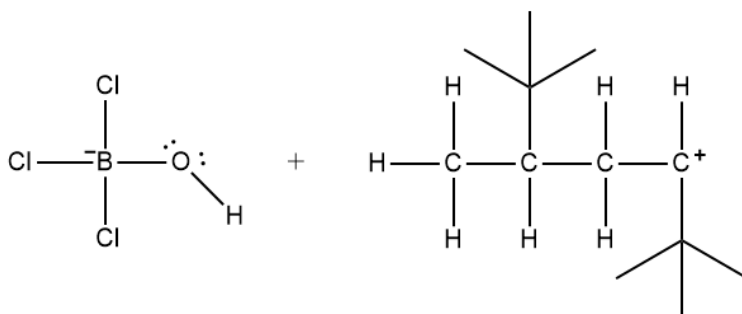
Next, we can use this radical to attack a monomer unit, starting our polymer chain:



Finally, this monomer will go on to build up the polymer chain (I condensed the benzoyl portion towards the end):



3. For this problem, since the tert-butyl group is really big and bulky, we want to keep it as far away from itself in the polymer chain, with it either facing up or down throughout the polymer. Since this is through cationization, the terminal carbon will only have two attached substituents, and then a positive charge, with our starting $\text{BCl}_3 \cdot \text{H}_2\text{O}$ molecule bearing a negative charge.



All tables are courtesy of Organic Chemistry by David Klein. All drawings of molecules and mechanisms are made by me.