

Week 15
CHE 3332 - Organic Chemistry 2

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

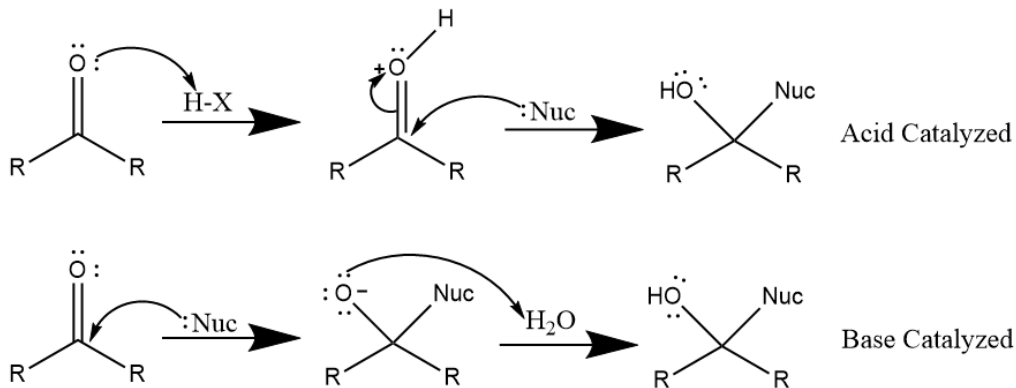
This week is Week 15 of class, so this will be a review oriented resource, covering important topics from previous weeks.

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: Final Review


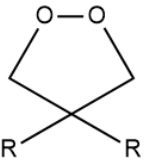
TOPIC #1: Nucleophilic Attack on Ketones

Another good idea for tackling the final is to go over topics which have a variety of possible products. Thus ketones, and all the different forms that we can create from them are a good way to cover a lot of ground. As a reminder, the general mechanism is:



And here is a table including some of the various products we can get from ketones:

Reagent	Product
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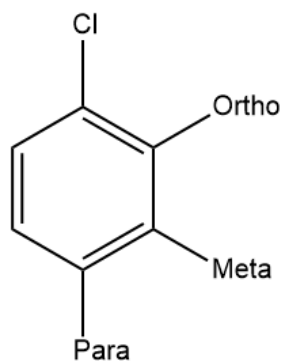
	 <p>Ketal</p>
Ethylene Glycol	 <p>Cyclic Acetal</p>

HIGHLIGHT #1: Aromatic Substitution Reactions

Aromatic Substitution is another good topic with a bunch of different reactions to make use of. Considering that benzyne can be used in so many different reactions (these, as well as reactions involving the benzylic carbon), aromatic molecules in general would be a good topic to go over.

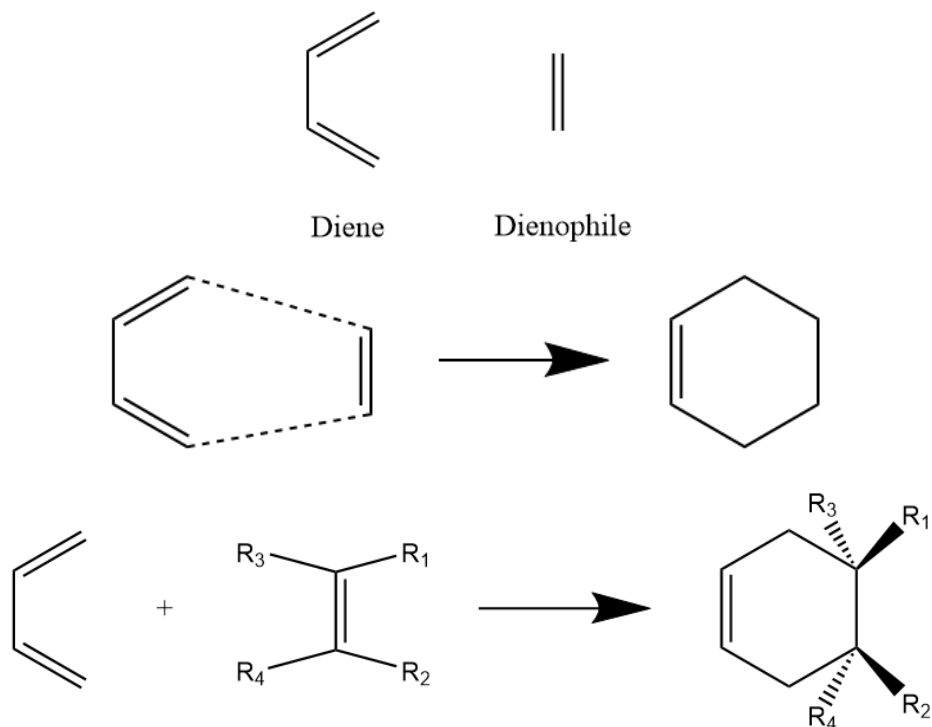
Reaction	Reagent	Product
Halogenation	FeBr ₃ or AlBr ₃ (for bromine) AlCl ₃ (for chlorine)	Addition of a halogen on the benzene ring
Sulfonation	“Fuming” H ₂ SO ₄ (concentrated)	Addition of a HSO ₃ group on the benzene, can be reversed using dilute H ₂ SO ₄
Nitration	1. HNO ₃ 2. H ₂ SO ₄	Addition of a NO ₂ (nitro) group on the benzene
Reduction of Nitro Groups	1. Fe or Zn, HCl 2. NaOH	The nitro group gets reduced to an amine
Friedel-Crafts Alkylation	1. Halocarbon (w/ chlorine) 2. AlCl ₃	The carbon chain is added to the benzene ring
Friedel-Crafts Acylation	1. Acid Chloride 2. AlCl ₃	The acyl group (from the acid chloride) is added to the benzene ring
Clemmensen Reduction	1. ZnHg 2. HCl, Heat	Reduces the ketone group of a previously performed Friedel-Crafts Acylation

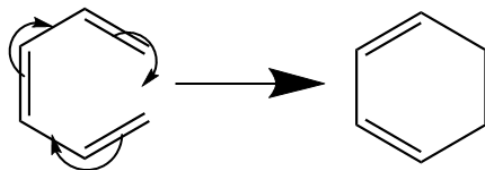
Additionally, here are the names of the different positions on a benzene ring:



HIGHLIGHT #2: Pericyclic Reactions

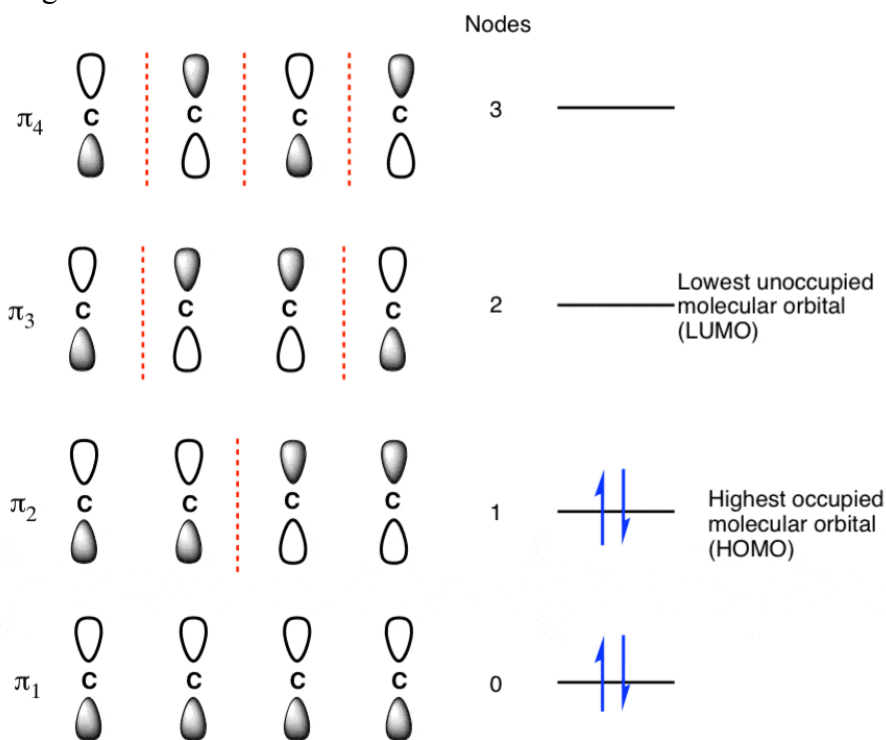
Pericyclic reactions also provide a myriad of different possibilities for questions that could show up on the final. Perhaps the most prominent of all these are the Diels-Alder reactions that can be produced. As you might remember, these will involve a diene (a compound with two separated double bonds), and a dienophile (a compound containing a singular double bond). In the process of these two coming together, we will be creating **two σ** bonds and breaking **two π** bonds.



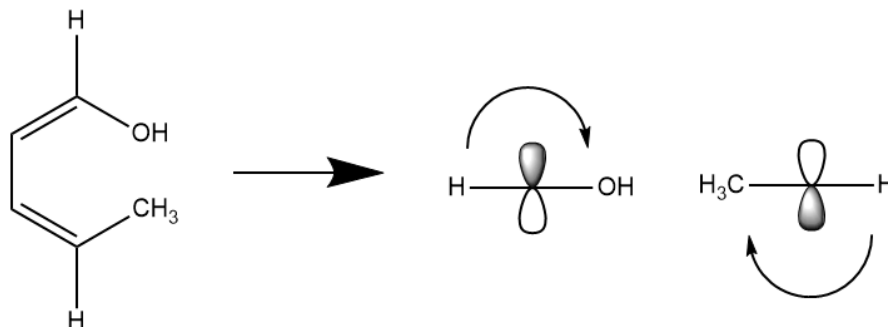


General electrocyclic reaction

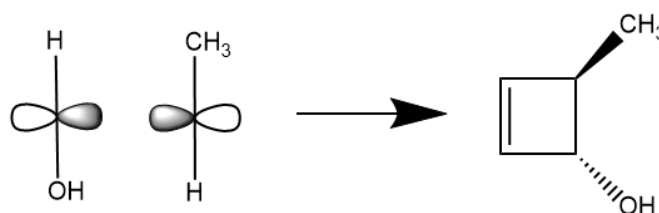
Another important pericyclic reaction is the electrocyclic reaction. This reaction involves knowledge about the molecule's M.O. diagram, which will influence the outcome of a reaction. For example, let's take a molecule with two conjugated double bonds, which would have an M.O. diagram like this:



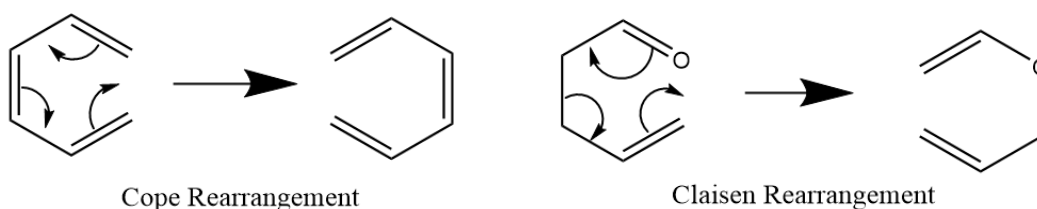
We specifically want to focus on π_2 and π_3 or our HOMO and LUMO, as these will tell us about which configuration the molecule's p-orbitals are in. For example, if we were to react a molecule with two double bonds, using heat, we would know that presently, the two end p-orbitals would be out of phase with each other (judging from the figure above for π_2). Because of this reality, our first p-orbital (with the white phase on top) would rotate clockwise, and our last p-orbital (with the black phase on top) would rotate clockwise to both be in-phase with each other (they are conrotatory). Here's an example:



Once this is figured out, we will move around our double bonds, using one of them to create a sigma bond between the two terminal carbons. Due to the rotation of our p-orbitals, the -OH is facing downwards, whereas the methyl group is facing upwards.

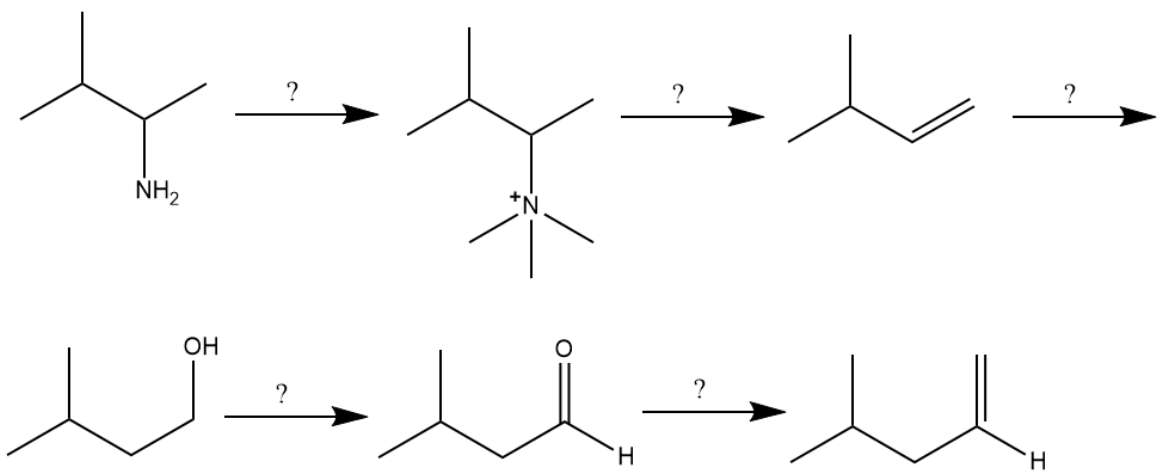


Finally, there are sigmatropic rearrangements, which as the name suggests, this type of reaction involves the movement of one σ bond within a molecule. No other bonds (σ or π) are created, but are instead moved around the molecule. There are two types of sigmatropic rearrangement, the Cope and the Claisen rearrangement. The first reaction involves a molecule whose atoms are all carbon atoms, whereas in a Claisen rearrangement, one atom is an oxygen, usually in the form of an ether or ketone.

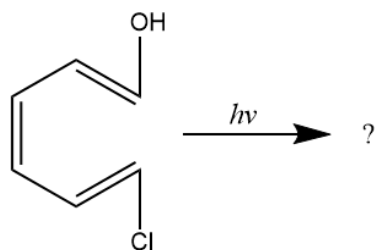


CHECK YOUR LEARNING:

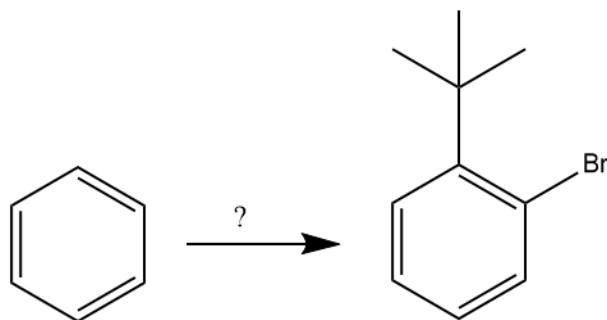
1. Provide the proper reagents for each of the following reactions:



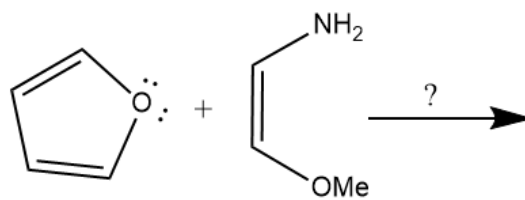
2. Give the product for this reaction:



3. Provide a synthesis for the following transformation:



4. Give the product for this reaction:



THINGS YOU MAY STRUGGLE WITH:

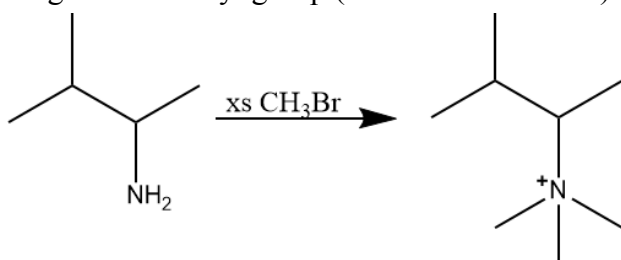
- At this point in OChem 2, you have learned so many reactions, and so many of them share similar topics, so for a single problem, you may be tasked with remembering topics from many different chapters.
 - Additionally, it can sometimes be easy to forget about some of the more niche reactions. It is a good idea to really scour through your book for some of the less common reactions, and to compile them as you go.
 - Of course this week is finals week, so you may get a bit flustered with the amount of OChem knowledge you have to retain. Don't worry about it though, study hard & you all will do well.
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Thanks for checking out these weekly resources!

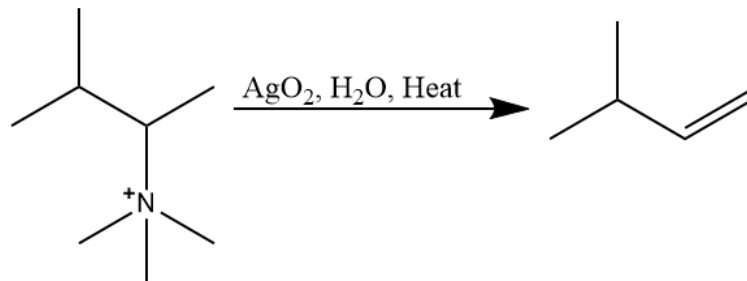
Don't forget to check out our website for group tutoring times, video tutorials and lots of other resources: www.baylor.edu/tutoring! Answers to check your learning questions are below!

ANSWERS FOR THE PRACTICE PROBLEMS:

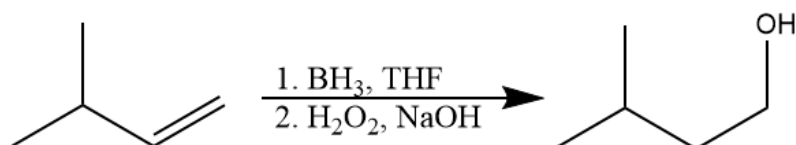
1. In this problem, we only need to provide the reagents, although these reactions span many chapters, so you may have forgotten some of the more obscure ones. Starting with the first reaction, we go from a primary to a quaternary amine. This reaction is from Chapter 22, and involves an excess of a halogenated methyl group (we can use bromine).



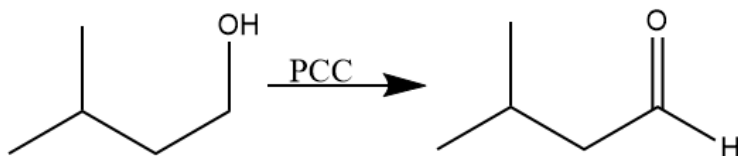
The next step involves the elimination of this quaternary amine. This will be the second step of the Hoffman elimination, which we had started in the last step. This will involve a silver oxide, water, and heat.



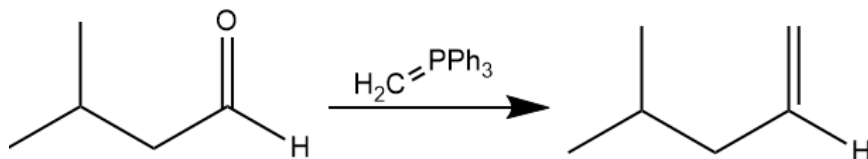
Next up, we are adding a hydroxyl, in the less substituted spot, to the double bond. From Ochem 1, you should remember this as hydroboration oxidation.



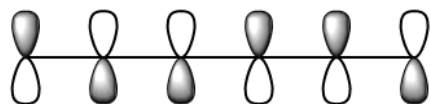
After this, we are oxidizing the hydroxyl into an aldehyde. While it may be tempting to use $\text{Na}_2\text{Cr}_2\text{O}_7$, remember that that will yield a carboxylic acid with a primary alcohol. Thus PCC, which is less commonly used, will be the reagent of choice.



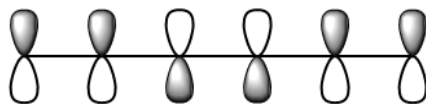
Finally, we are transforming an aldehyde to a carbon carbon double bond. This one should immediately stand out to you all since it's not commonly performed, unless we are using a Wittig reaction, which is the only way to perform such a reaction.



2. For this problem, we are dealing with an electrocyclic reaction. So, the best plan of action is to start by finding the M.O. diagram, and the HOMO and LUMO. Because we are dealing with $h\nu$ (U.V. light), the orbital we want to focus on will be the LUMO. For brevity's sake, I'll show both the HOMO and LUMO only:

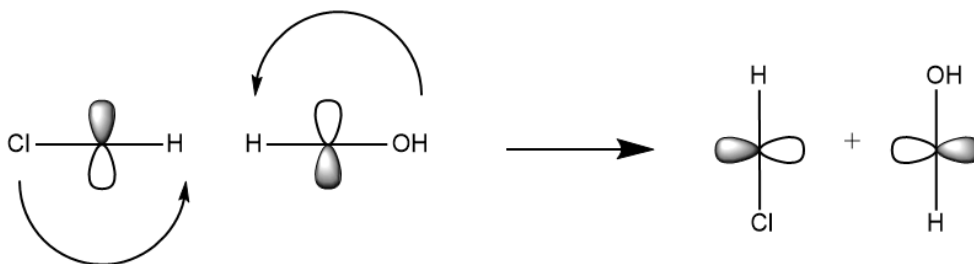


This was originally the LUMO, but using $h\nu$ an electron will be excited up to this level

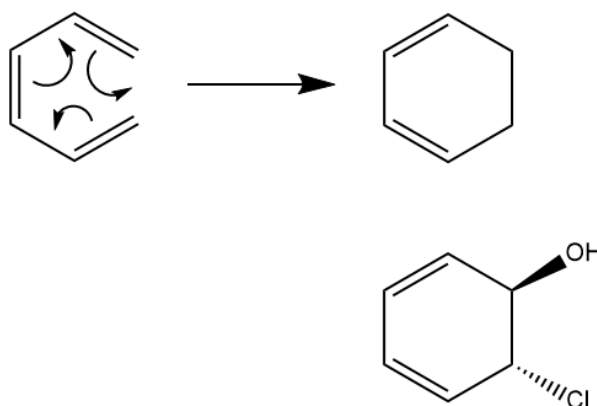


The molecule's original HOMO

Now that we have figured that out, we can draw what our terminal orbitals look like. Judging from the LUMO, the two p-orbitals should be out of phase with each other. Because of this, they will be conrotatory (in this case, both are rotating counter-clockwise).



Because of this, we know our chlorine will be facing down, and our hydroxyl will be facing up. Finally, it is helpful to diagram what our ring will be doing in this case. Since electrocyclic create ring structures, by turning a pi bond into a sigma bond, the reaction should look a little something like this:

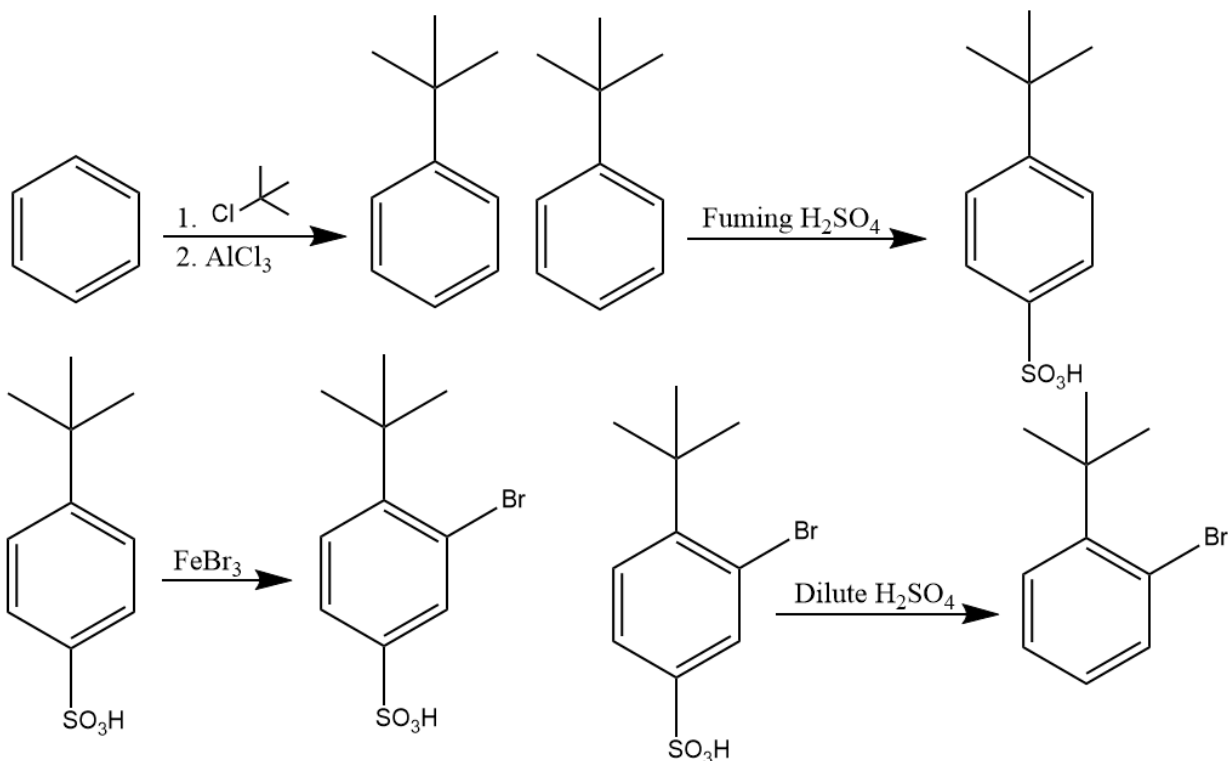


So, by putting all this together our final product will be:

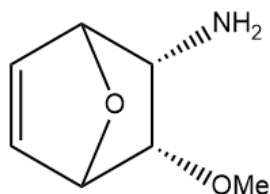
3.

So, for this reaction, we are dealing with a bulky alkyl group, and a bromine placed on the ortho position. Usually we cannot add halogens right next a tert-butyl group, as they would rather add

to the less sterically hindered para position. So, we need a blocking group to keep the bromine from adding at the para position, such as making use of fuming sulfuric acid. This action will place HSO_3 at the para position, thus directing bromine towards the ortho position. We can then take the HSO_3 off using dilute H_2SO_4 .



4. This last problem is simply a Diels-Alder reaction, which will involve the creation of bridgehead carbons within the ring. Because we are using a ring as the diene, the two substituents on the dienophile will prefer to add in the endo position. The final molecule will end up like this diagram:



Thanks for using these weekly resources this semester! Good luck on your final exam!

All tables are courtesy of Organic Chemistry by David Klein.
All drawings of molecules and mechanisms are made by staff of the Tutoring Center.