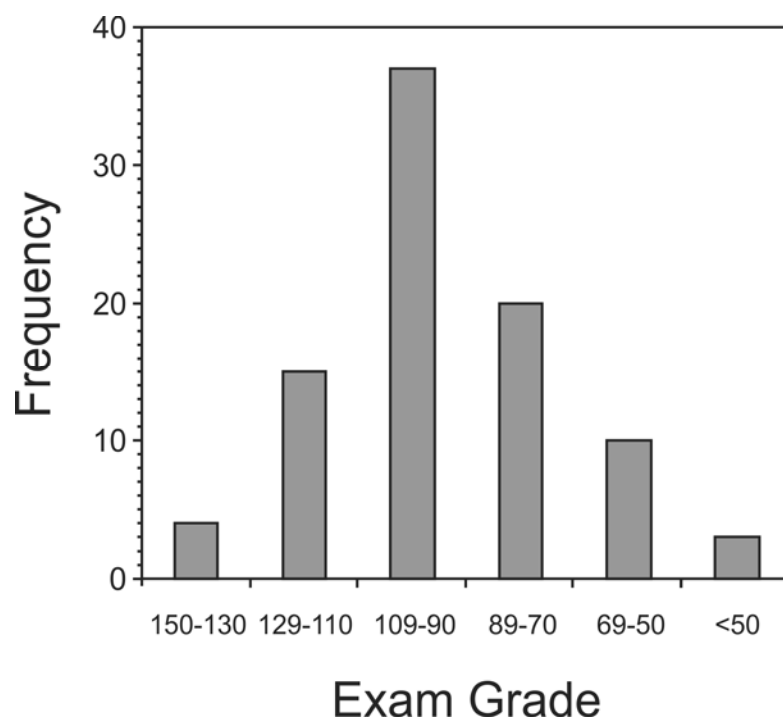
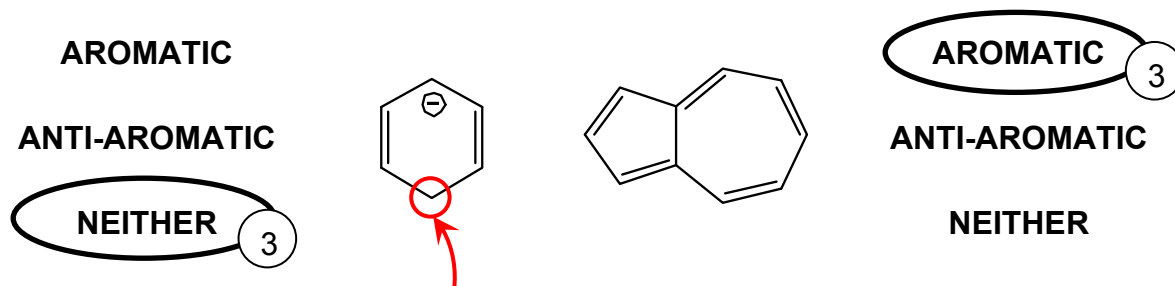


**Final Exam  
Answer Key**

Final Exam Mean: 93  
Final Exam Median: 95  
Final Exam St. Dev.: 22



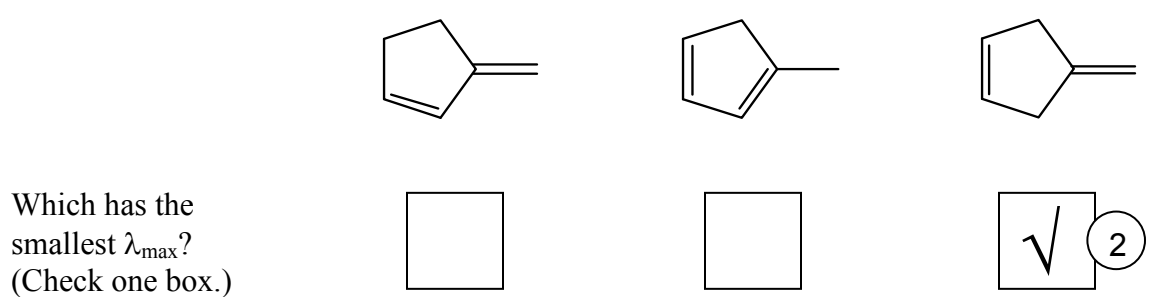
1. (6 pts) For each of the following molecules, circle whether the molecule is aromatic, anti-aromatic, or neither.



This ring has one saturated  $-\text{CH}_2-$  carbon, so the ring of  $p$  orbitals is not continuous. Therefore, it's not aromatic or anti-aromatic.

The cyclic  $\pi$  system in this molecule has 10  $\pi$  electrons, from the five double bonds. That's an odd number of pairs of electrons (or, as Hückel's rule puts it,  $4n+2$ ), and that means aromatic.

2. (10 pts)  
 a. Of the three  $\text{C}_6\text{H}_8$  isomers shown below,

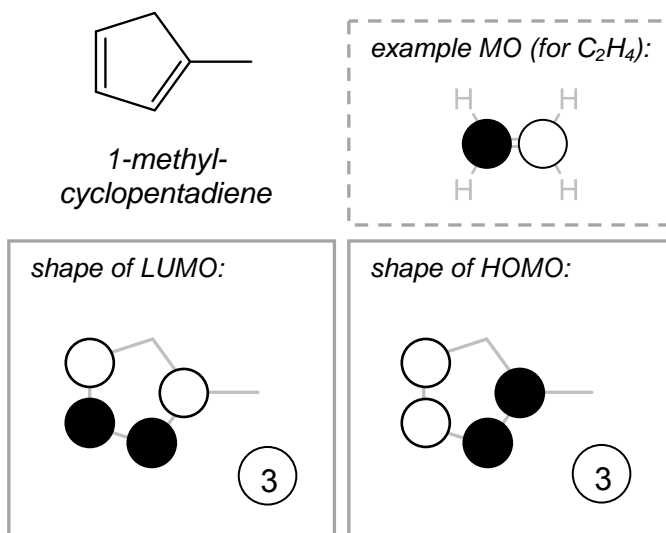


Conjugation increases  $\lambda_{\text{max}}$ , because it decreases the energy difference between HOMO and LUMO. So the molecule with the smallest  $\lambda_{\text{max}}$  will be the one that isn't conjugated.



All of these molecules are dienes that will hydrogenate twice, exothermically, to the same molecule. They will give off energy based on how stable they are—the least stable starting material will give off the most amount of energy. The least stable molecule is the one that isn't conjugated.

- b. In the boxes on the right, draw the shapes of the HOMO and LUMO of 1-methylcyclopentadiene (the middle molecule on the previous page, reproduced at right). Draw each orbital as a combination of atomic orbital lobes, viewed from the top of the molecule. If there is more than one HOMO or LUMO, just draw one. I have drawn the carbon backbone in each box; draw your orbitals right on top of that scaffold.



Even though these orbitals are in a ring, the set of *p* orbitals doesn't make it all the way around the ring, so the diene here is represented by a set of molecular orbitals for a *linear* arrangement of *p* orbitals.

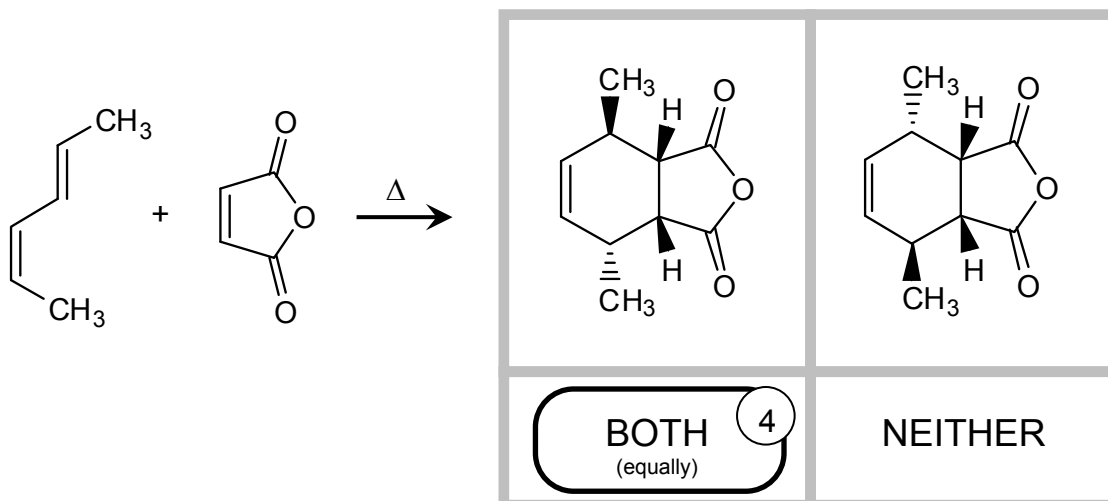
HOMO has one node,

Rubric:

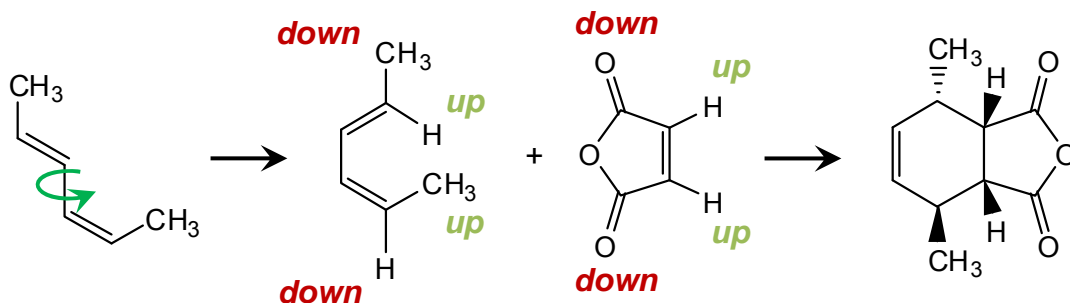
3 points for each MO. (6 points total.)

1 point partial (on each) for switching HOMO and LUMO.

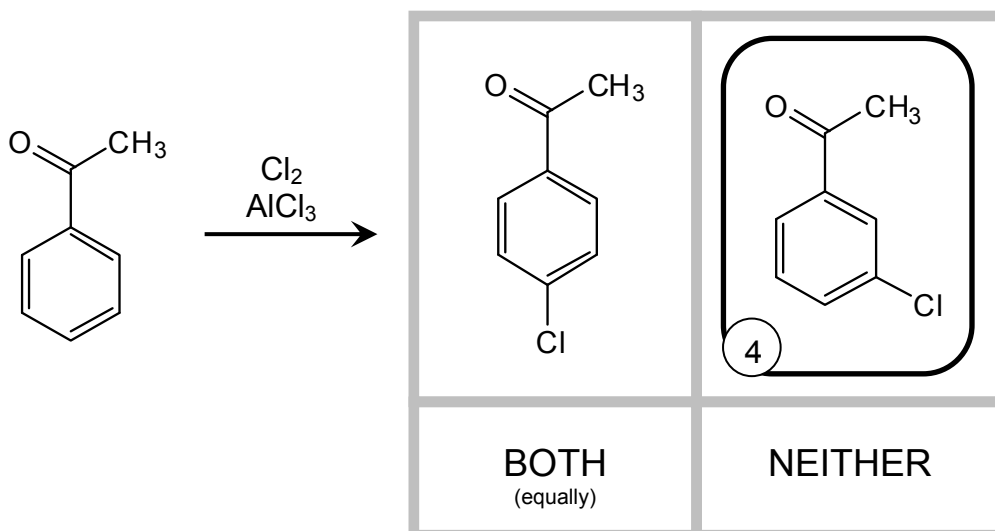
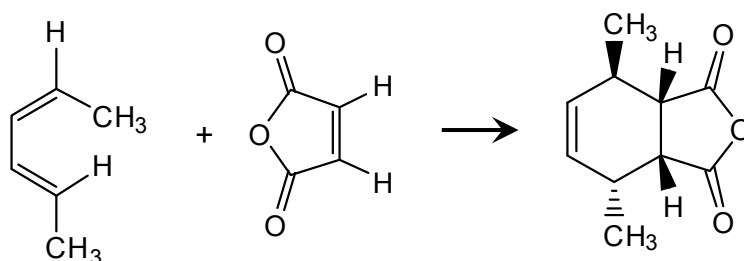
3. (32 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**



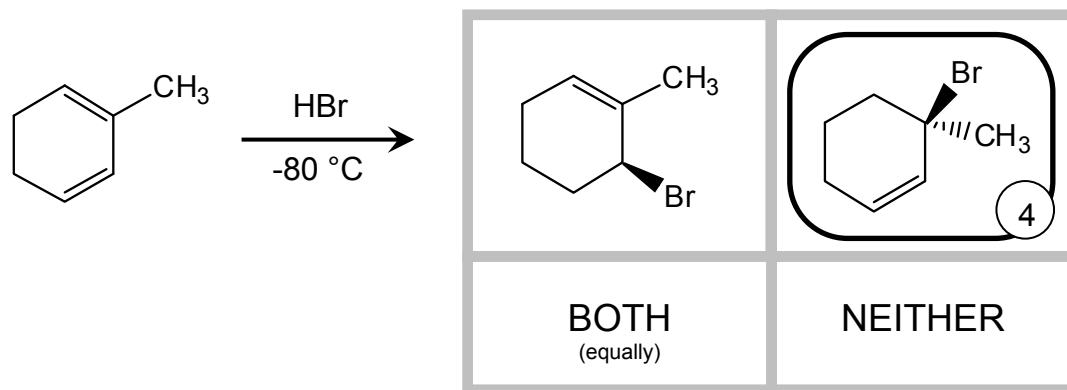
In order to determine what product is formed, we need to redraw the diene so that it is in its reactive, *s-cis* conformation, and redraw the dienophile so that the  $\pi$ -substituents are pointed towards the diene:



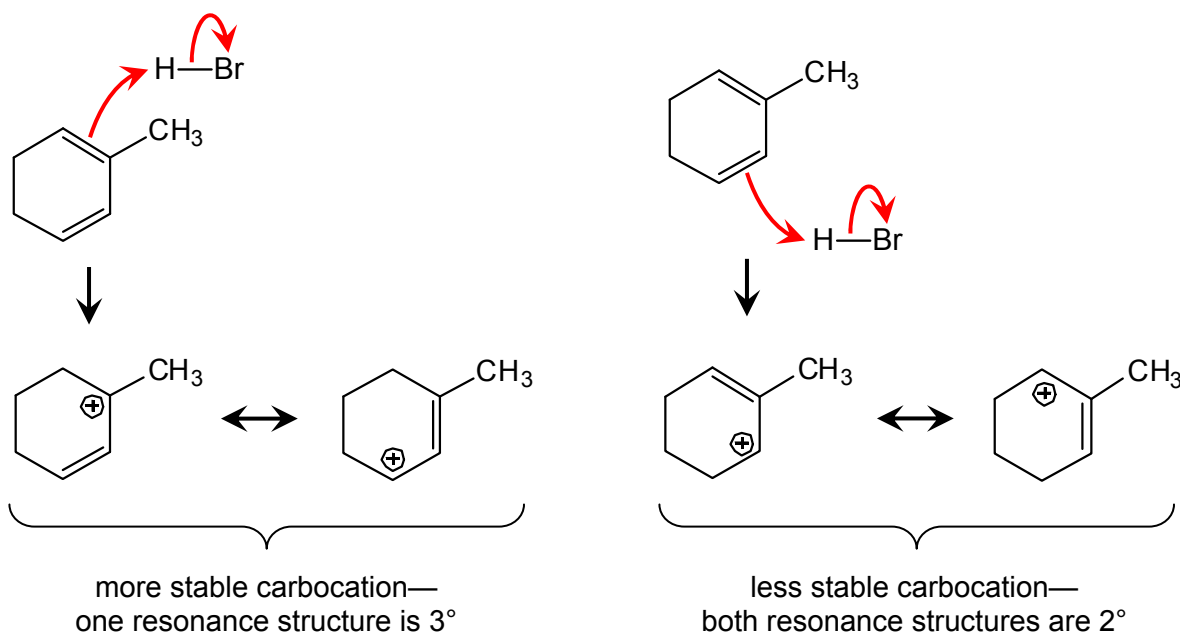
I drew the diene with its (*E*)-alkene up and its (*Z*)-alkene down. But these reactants don't have any partial negative or positive charges that direct regiochemistry, so I could also have drawn the diene (*Z*)-up and (*E*)-down. This gives the other product.



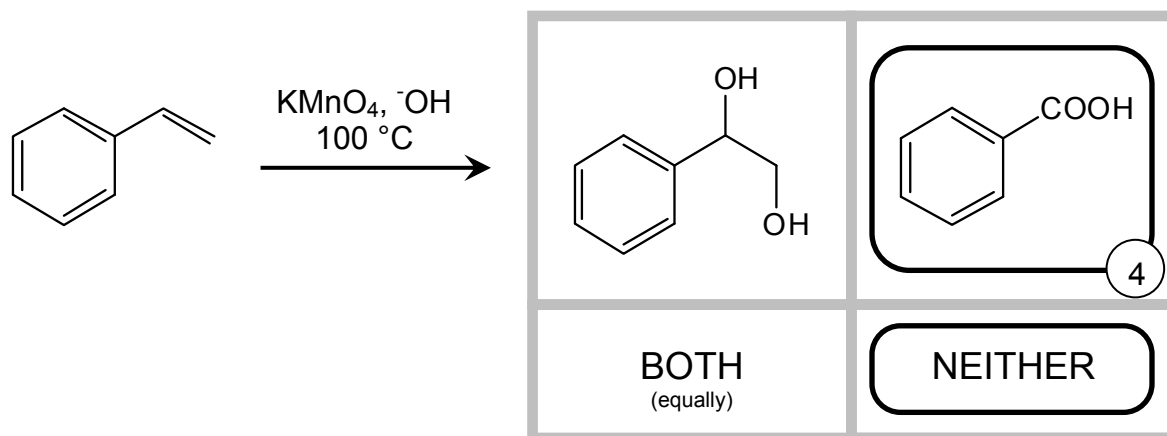
The electron-withdrawing ketone group is meta-directing. Chlorination occurs at the meta position, selectively.



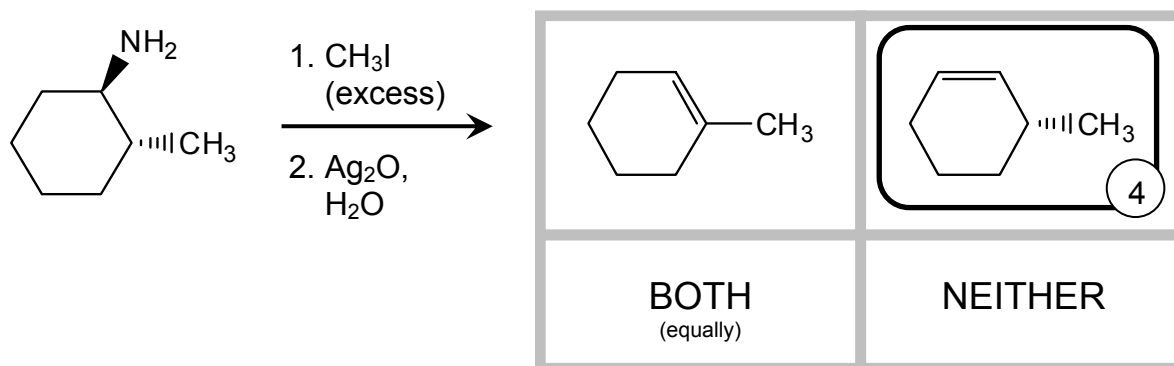
HBr initially reacts with a conjugated diene by protonating it on the end, to yield an allyl cation intermediate. Here, our diene has two ends, and protonating on either end yields two different cations (next page):



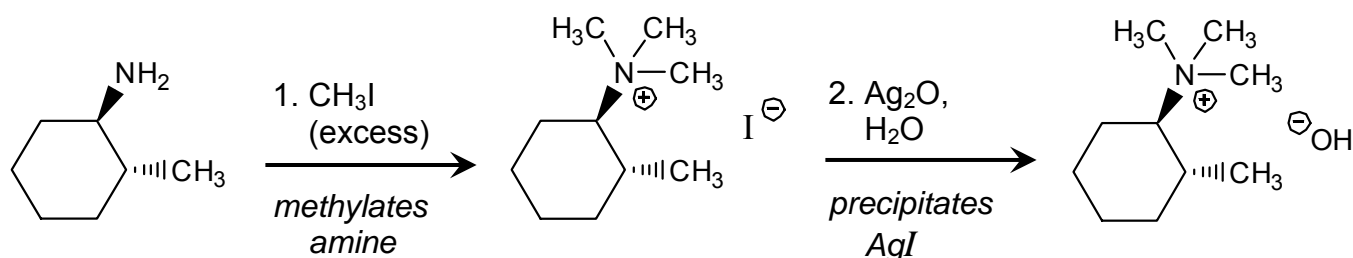
The preferred carbocation will be the one on the left. This can then react with  $\text{Br}^-$  at either of the positively charged carbons in the resonance structures. Because the reaction is conducted at low temperature, the kinetic (1,2) product will be favored.

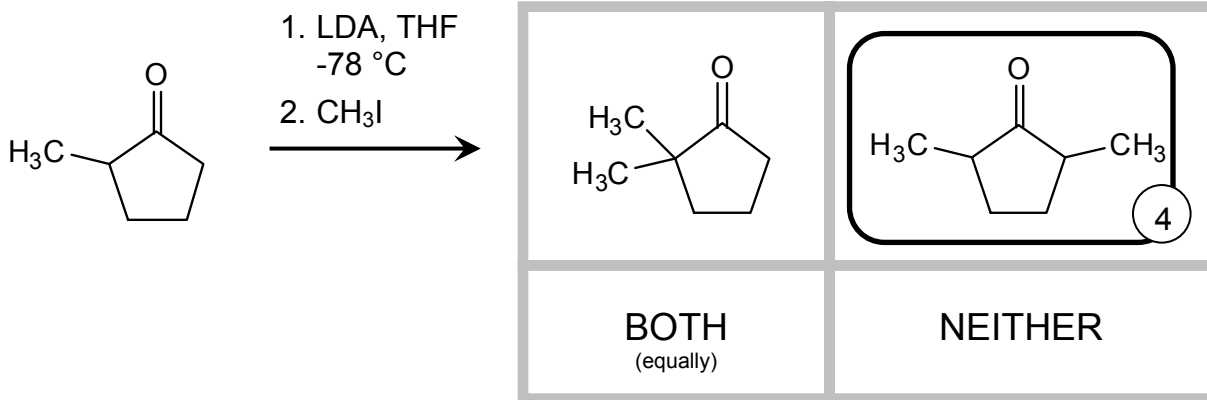
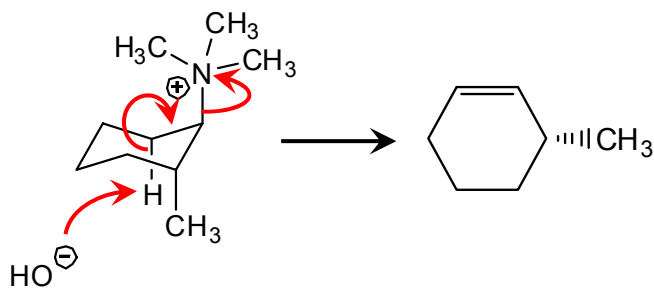


It is true that  $\text{KMnO}_4$  is a dihydroxylating reagent, and in cold dilute solution, it would convert the alkene to a diol. In this case, however, under hot basic conditions,  $\text{KMnO}_4$  converts any benzylic carbon to a carboxylic acid group. Technically, the  $\text{OH}^-$  part of the reagent set would deprotonate the carboxylic acid to the carboxylate, so we also accepted “NEITHER” here.

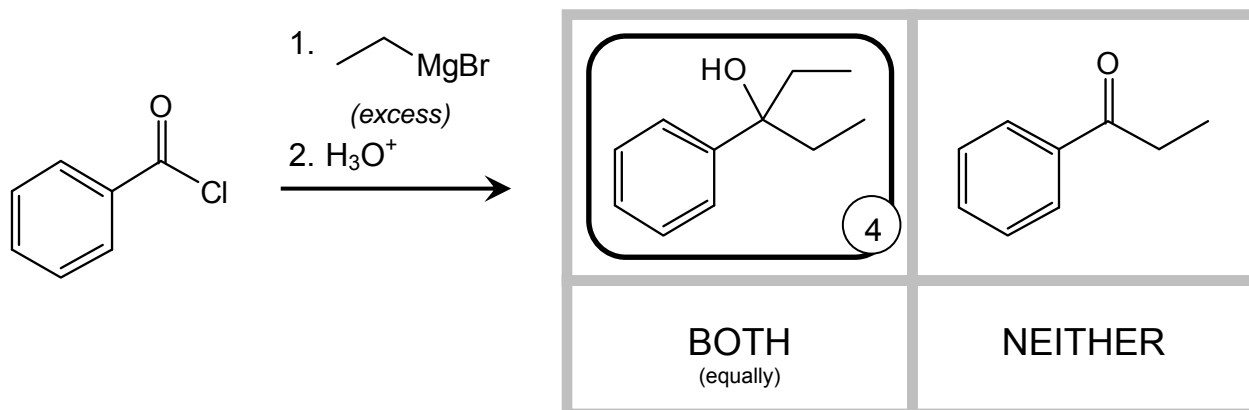


The reaction conditions are for a Hofmann elimination, which prefers the less substituted alkene product (due to the steric hindrance provided by both the trimethylammonium and the substituents). In fact, in this case, the more substituted alkene can't be formed by E2 because the tertiary proton can't be anti-periplanar to the trimethylammonium leaving group.

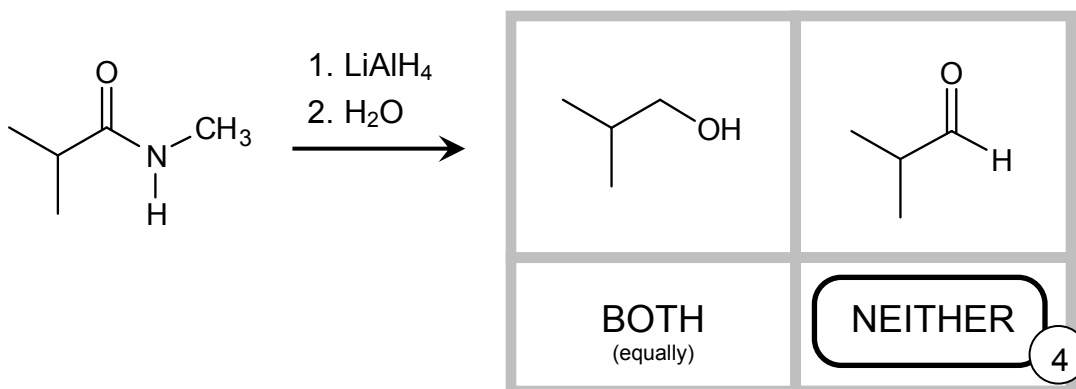




LDA is a big bulky base, and when it is used at low temperature, it will selectively form the kinetic, less-substituted enolate. Methylation will therefore take place at the less-substituted carbon.

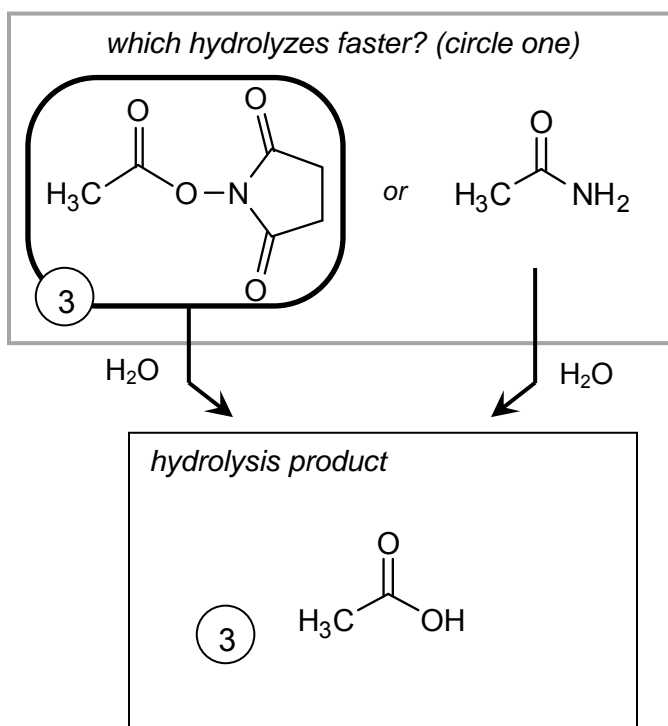


The Grignard adds twice to the ester.



Amides are reduced to amines by  $\text{LiAlH}_4$ .

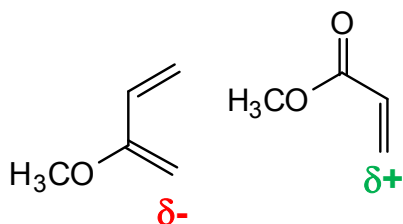
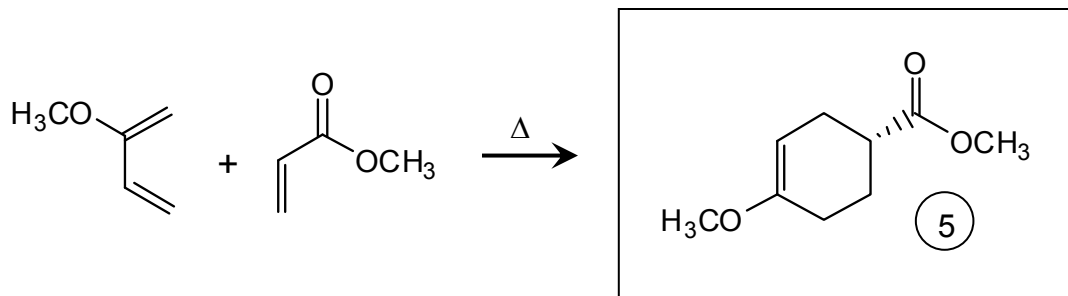
4. (6 pts) Each of the carboxylic acid derivatives on the right reacts with water, at very different rates. **Circle the molecule that hydrolyzes faster.**



What do both of these molecules hydrolyze to?



5. (35 pts) For each of the reactions below, fill in the empty box corresponding to reactants or products. Give only one answer in each box. For reactions that you expect to yield multiple products, give the major product. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note “+ enantiomer”.



To line up partial charges, we need to flip diene vertically. (And to point dienophile  $\pi$ -substituent towards diene, we need to flip dienophile horizontally, though here you would actually also get the right answer if you didn't).

Rubric:

5 points for correct structure.

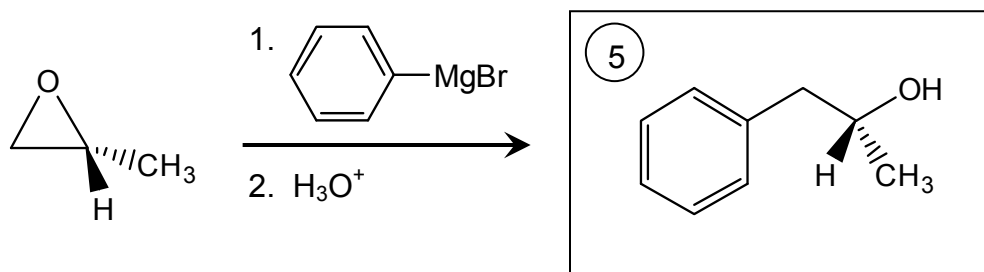
*Full credit for not illustrating stereochemistry (because it doesn't matter here).*

*-1 point for showing stereochemistry, and then not writing “+ enantiomer”.*

*-2 points for incorrect regiochemistry (1,3-substituted instead of 1,4).*

*-3 points for other incorrect substitution/alkene patterns (as long as all substituents are present).*

*-2 points for each trivial structure mistake. (I.e., where it is clear that correct answer was intended, but simple omission or error made the answer incorrect. Intent must be clear.) This includes omitting the double bond.*



The Grignard adds to the less-substituted carbon of the epoxide to give an alkoxide; this then protonates to give the alcohol.

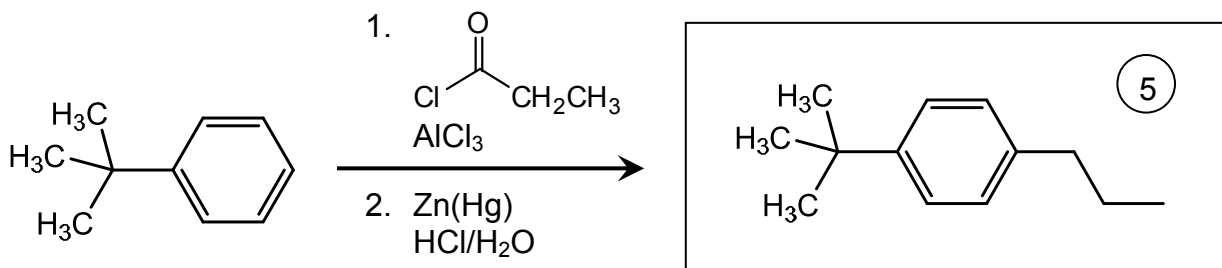
Rubric:

5 points for correct structure.

3 points for incorrect stereochemistry, or for not indicating stereochemistry.

3 points partial for incorrect regiochemistry (attack at more substituted carbon).

-2 points for each trivial structure mistake.

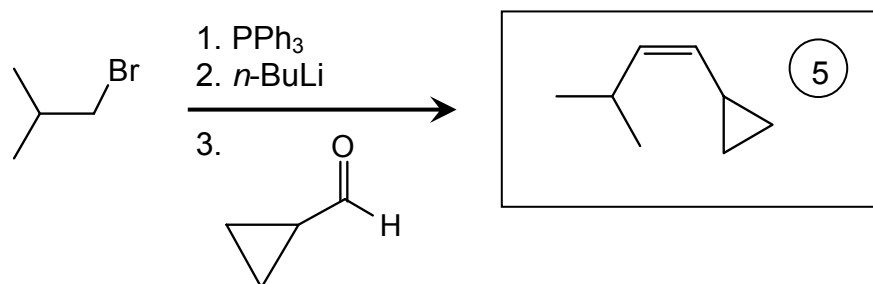


Rubric:

5 points for correct structure.

3 points partial for acylation product instead of alkylation (i.e., for not doing step 2).

-2 points for each trivial structure mistake.



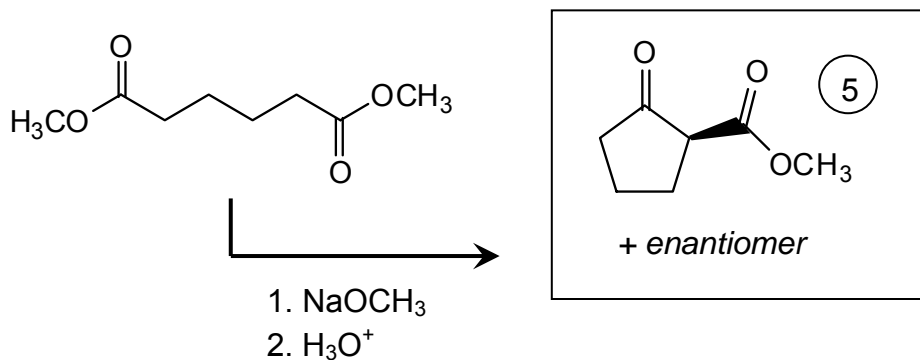
This is a Wittig reaction, which creates a double bond between carbons on two different molecules: an alkyl halide on one side, and an aldehyde or ketone on the other. The Wittig reaction has a preference for *cis*-alkene products.

Rubric for this part:

5 points for correct structure.

4 points partial for *trans*-olefin.

-2 points for each clearly trivial structure mistake. This includes losing/gaining a carbon.

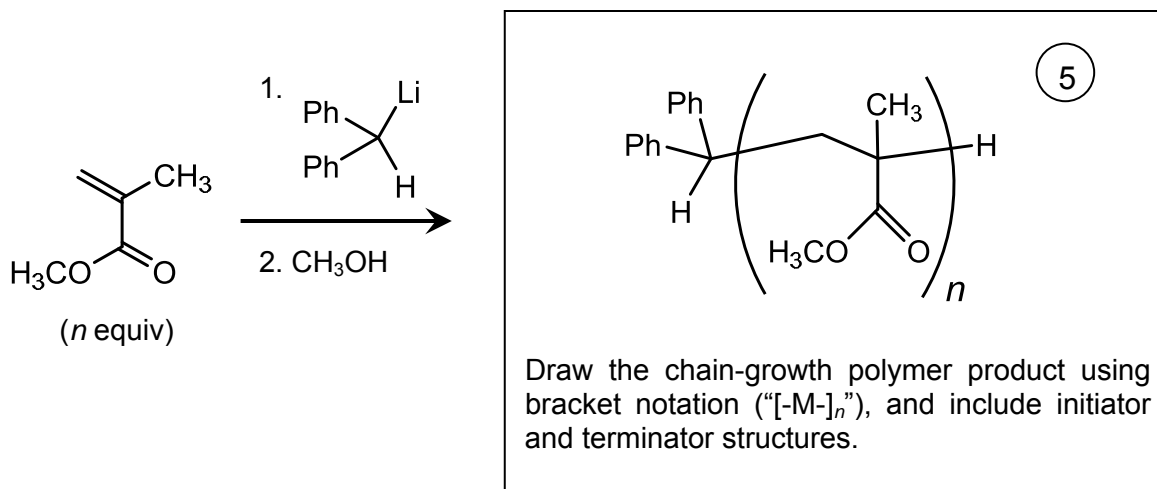


Rubric:

5 points for correct structure.

-1 for omitting "+enantiomer" or not illustrating stereochemistry.

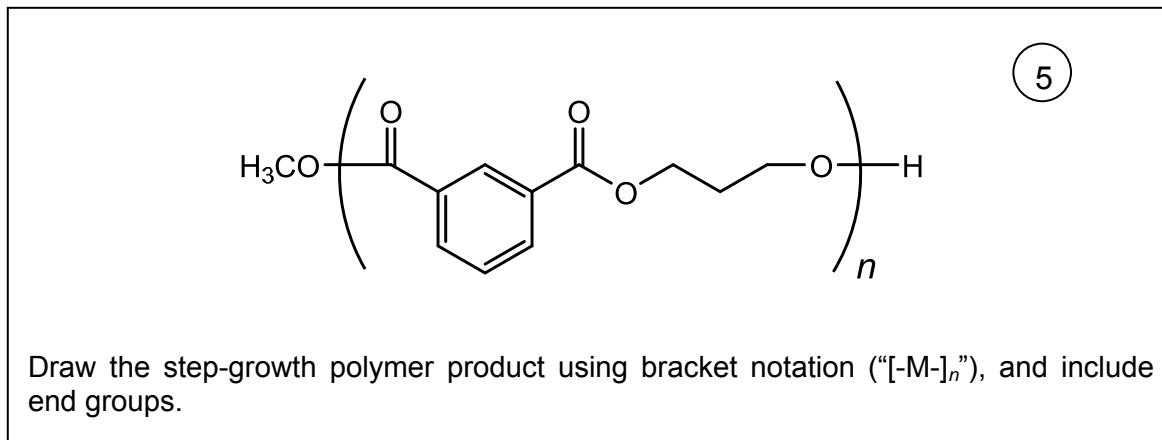
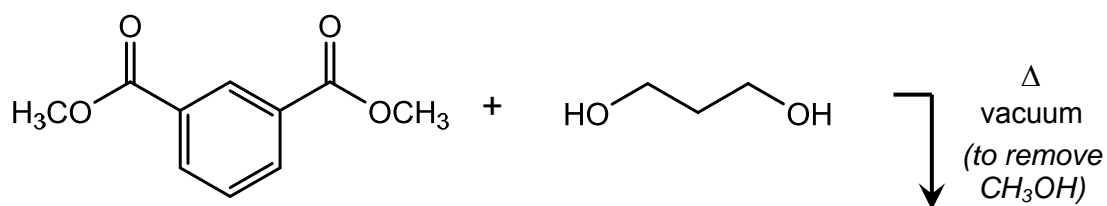
-2 points for each trivial structure mistake.



Rubric:

5 points for correct structure.

-2 points for each error in the initiator part, the terminator part, the attachment points, the bracket position, or other trivial error.



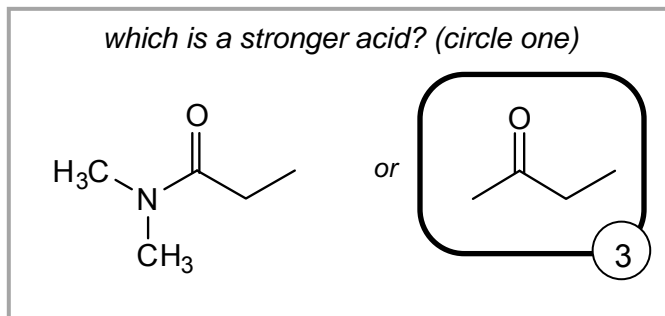
**Rubric:**

5 points for correct structure.

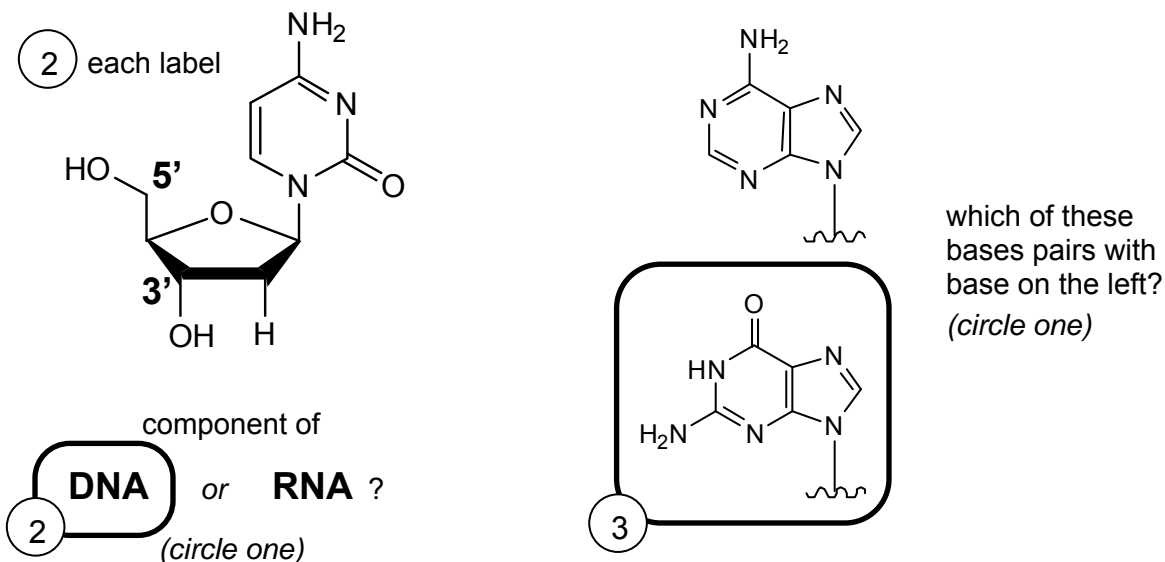
*The brackets can be drawn in a number of different spots; all they need to do is reflect the repeating alternation of di-ester and di-ol units.*

*-2 points for each error in the initiator part, the terminator part, the attachment points, the bracket position, or other trivial error.*

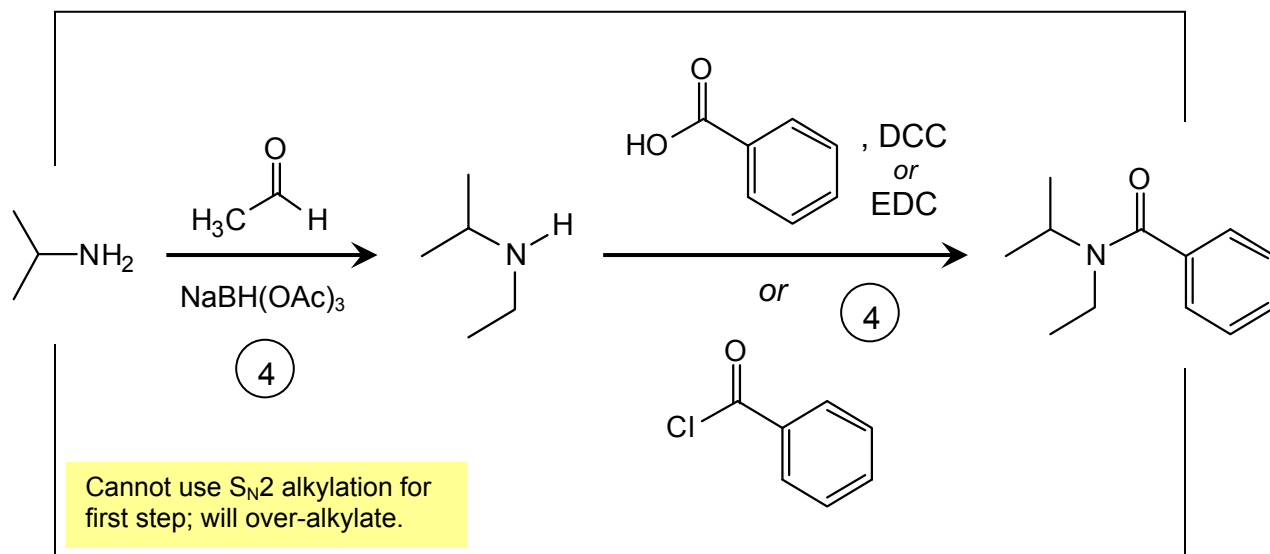
6. (3 pts) Each of the carbonyl-containing compounds on the right is acidic, and can be deprotonated to form an enolate anion. **Circle the stronger acid.**



7. (9 pts) For the nucleoside below on the left:
- Label the 3'- and 5'-carbons with their numbers;
  - Circle whether the nucleoside is a component of DNA or RNA;
  - Circle the base on the right that the base is normally paired with in a double helix.



9. (25 pts) Each of the syntheses shown below can be accomplished in a few steps. For each synthesis, fill in the empty boxes with any appropriate reagents (or sets of reagents) and synthetic intermediates. You must use the starting materials I have shown, but you may also use any other reagents you like.



Rubric:

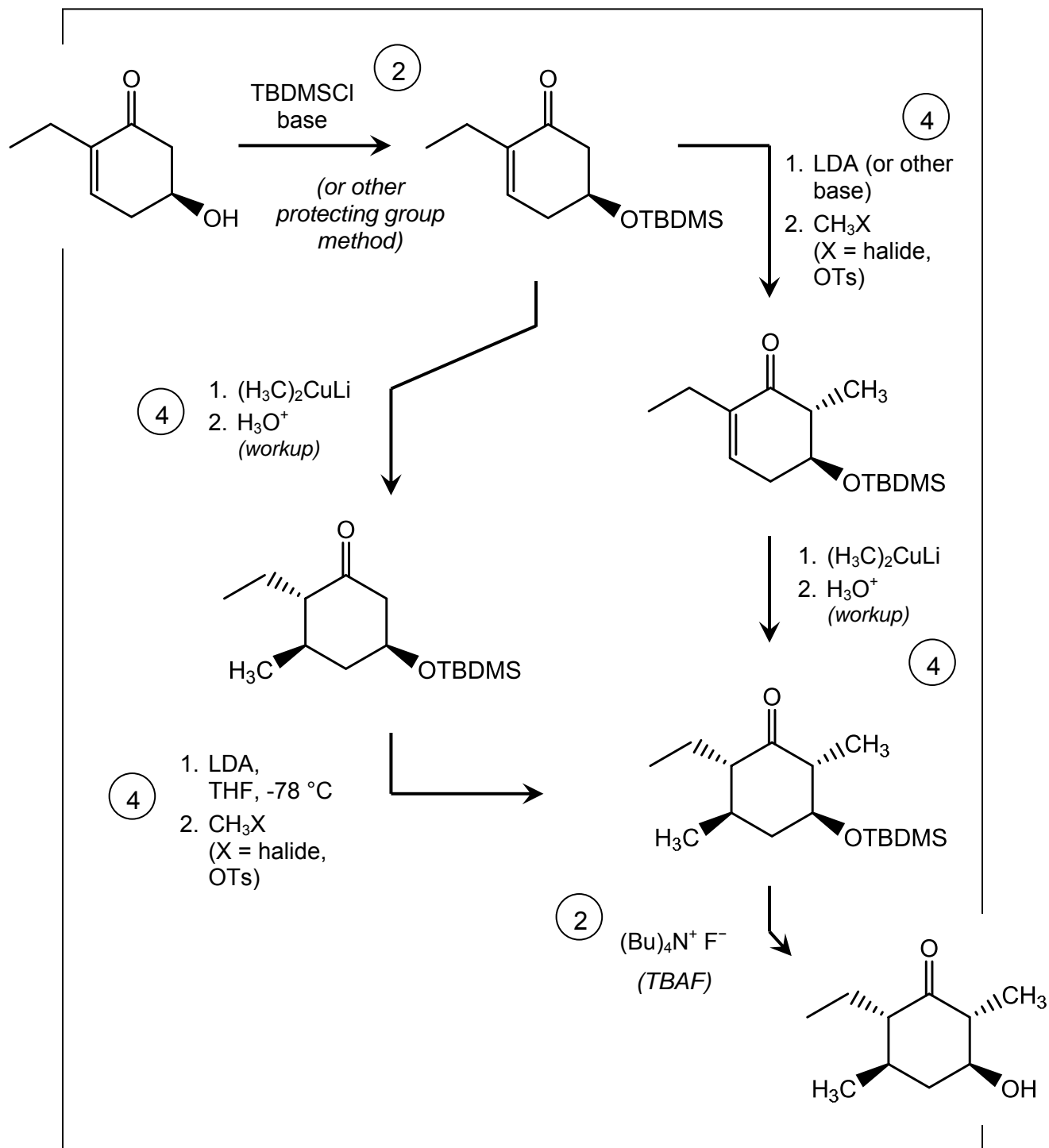
This synthesis requires two tasks: (1) alkylation of amine nitrogen, and (2) acylation of the amine. Each task is judged separately, and does not require that the synthesis makes sense, or that other task was correct. You could also do the tasks in either order, although alkylation of a primary amide works poorly.

4 points each task.

Full credit for making amide first, but -2 for alkylating the amide; is a poor nucleophile, and E2 will compete.

-1 point for each minor error in structures or reagents; if error propagates, points are taken off only for initial error.

-2 points if step reagents are incorrect, but reaction could otherwise be accomplished with correct reagents.



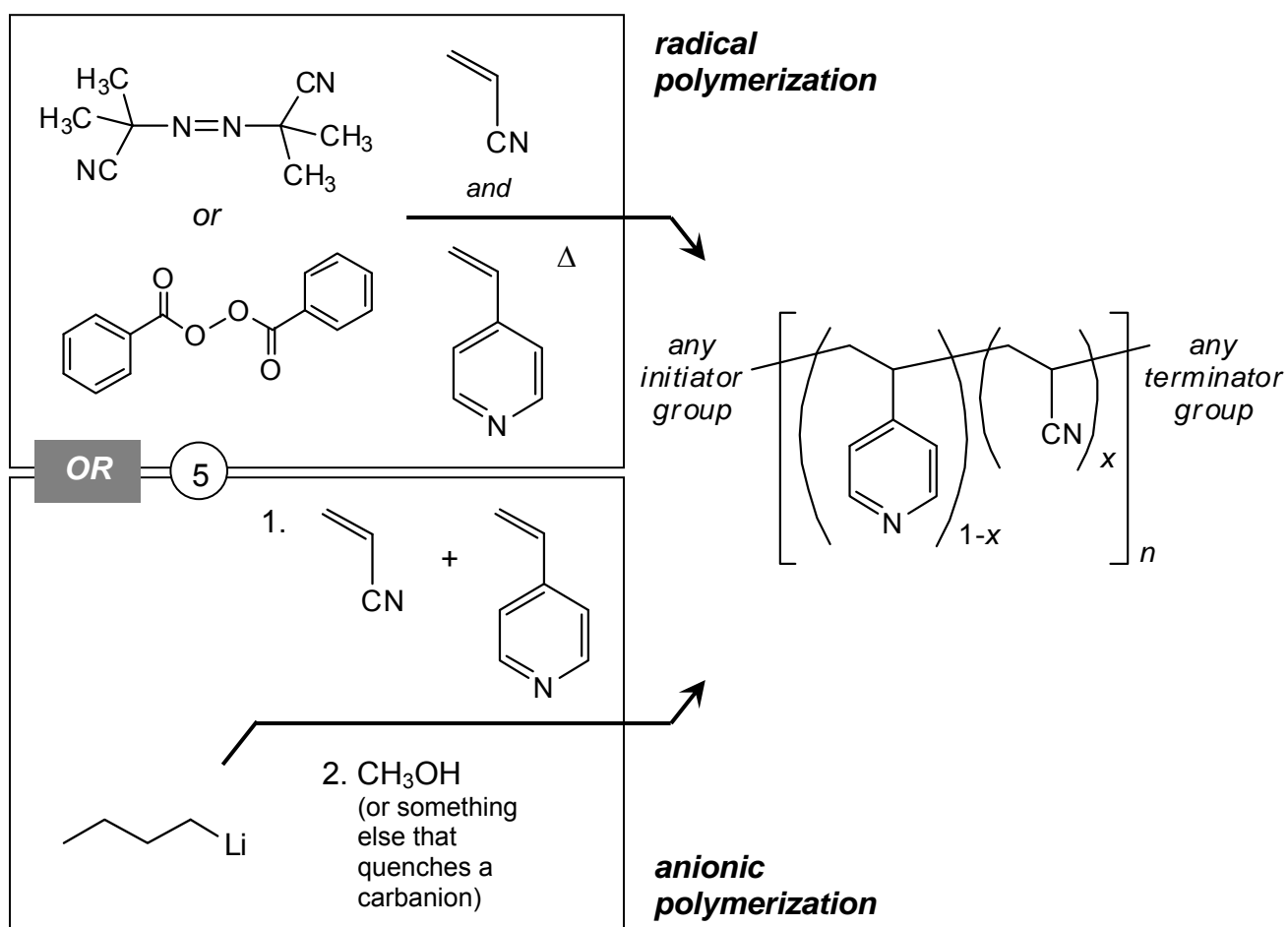
Rubric:

This synthesis requires three tasks: (1) protection and deprotection of the alcohol; (2) Michael addition of a cuprate to the conjugated enone; and (3)  $\alpha$ -alkylation via an enolate. Each task is judged separately, and does not require that the synthesis makes sense, or that other task was correct. You could do some of the tasks in a different order (as shown in my synthesis), although protection had to precede alkylation, and I think deprotection had to happen last.

4 points each task.

-1 point for each minor error in structures or reagents; if error propagates, points are taken off only for initial error.

-2 points if step reagents are incorrect, but reaction could otherwise be accomplished with correct reagents.

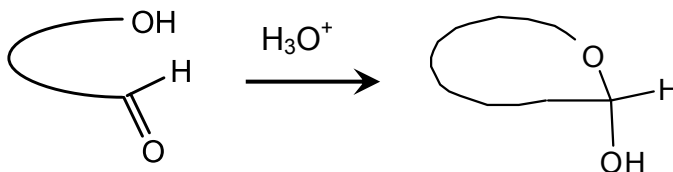


Rubric:

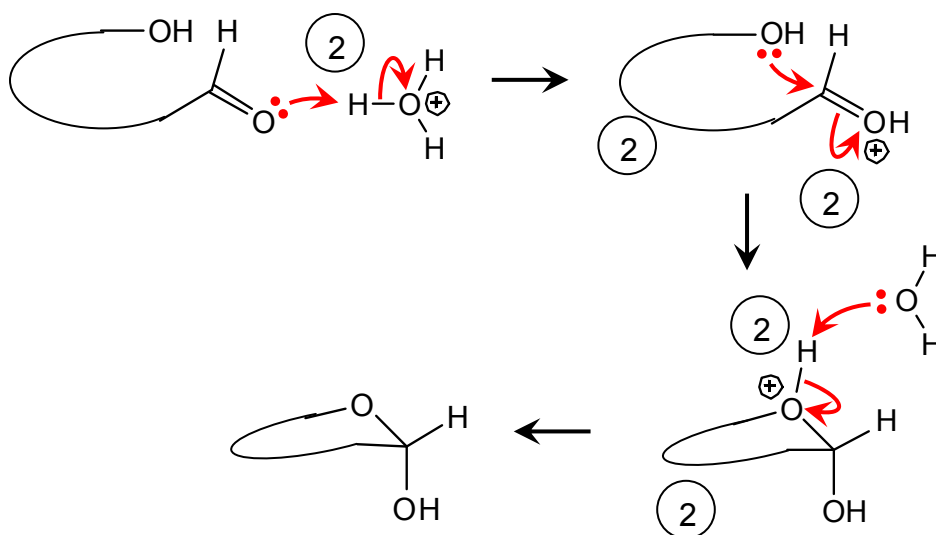
5 points for either correct recipe.

-2 points for depicting monomer addition as sequential rather than together, or for each other minor error.

8. (24 pts) **Draw a mechanism** (using “electron pushing”) for the reaction shown below. Draw each mechanistic step explicitly; don’t cheat by combining multiple processes in a single step, or by taking shortcuts. Use only the molecules shown in the problem.



Mechanism:



Rubric: (10 points total this part).

2 points for each correct intermediate structure in your mechanism.

-1 point for each minor error in charge, valency, structure, etc.; if error propagates, points are taken off only for initial error.

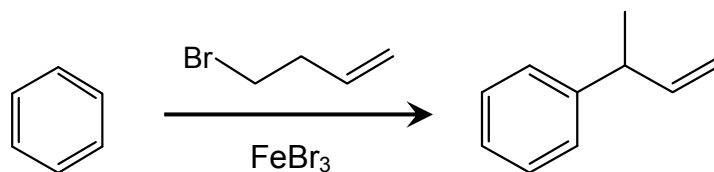
Any molecule can be depicted in any resonance state; no points are lost for drawing a molecule as a minor resonance contributor.

2 points for each electron-pushing step in your mechanism.

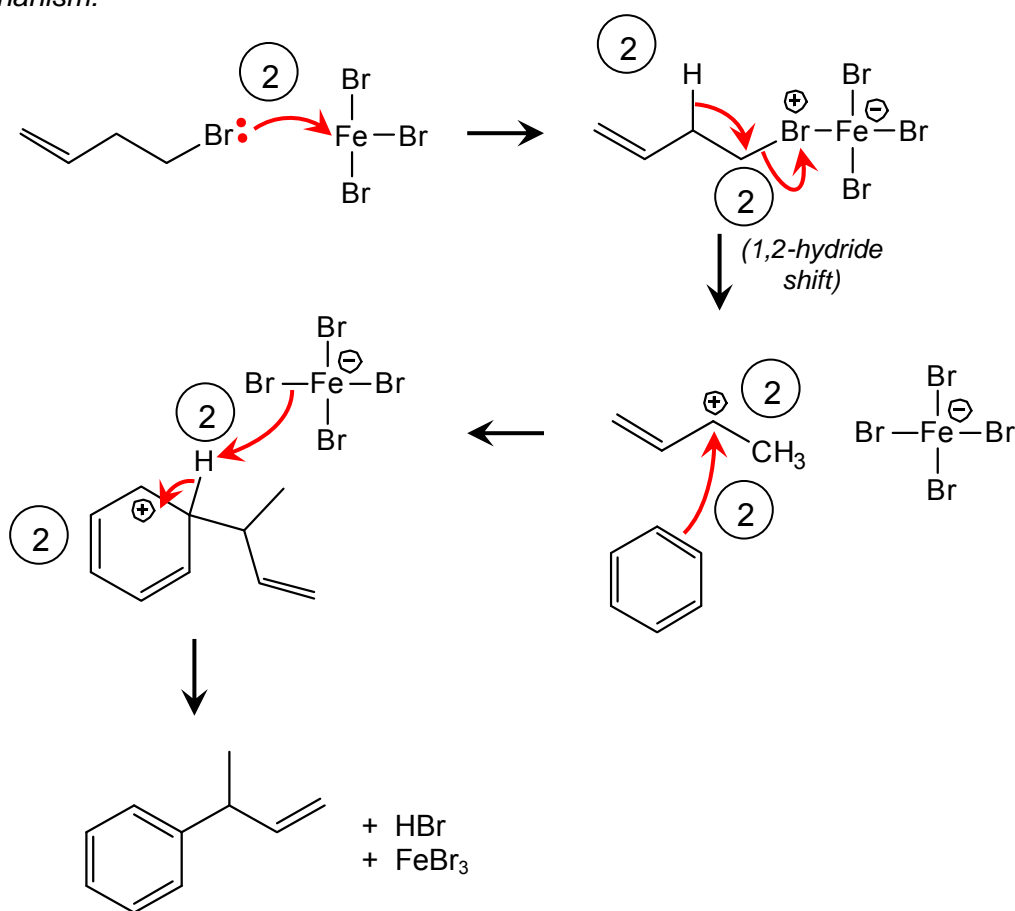
Arrow must start at an electron pair, and end at nucleus or bond where electrons will newly interact. If error is minor, grader may assign partial credit (1 point).

No credit for arrows that involve a generic or incorrect base/acid. For example, “H-A” couldn’t be used to protonate anything here.





Mechanism:



Rubric for part (a): 16 points total.

Overall notes:

Overall, the minimum score for each step is zero; errors in a step cannot earn you negative points that count against another, correct step.

Things that have left for good (e.g.,  $\text{HBr}$ ) and spectators (e.g.,  $\text{FeBr}_4^-$  in the step it isn't used) may be omitted.

-1 point for each minor error in charge, valency, structure, etc.; if error propagates, points are taken off only for initial error.

2 points for each correct intermediate structure in your mechanism.

-1 point for each minor error in charge, valency, structure, etc.; if error propagates, points are taken off only for initial error.

*Any molecule can be depicted in any resonance state; no points are lost for drawing a molecule as a minor resonance contributor.*

2 points for each electron-pushing step in your mechanism.

*Arrow must start at an electron pair, and end at nucleus or bond where electrons will newly interact. If error is minor, grader may assign partial credit (1 point).*

*-2 points for each step combined with another. (Say, steps 2 and 3.) You lose the points on each step you combine; so two 4-point steps (including the arrow-pushing points) could be combined into a step that would be worth a maximum of 4 points total (out of 8).*

*-2 points for each use of a generic or incorrect nucleophile/base. For example, in the last step you needed to use  $\text{FeBr}_4^-$  as the base; other bases like  $\text{OH}^-$ , or a generic base  $X$ , couldn't be used to deprotonate the intermediate.*