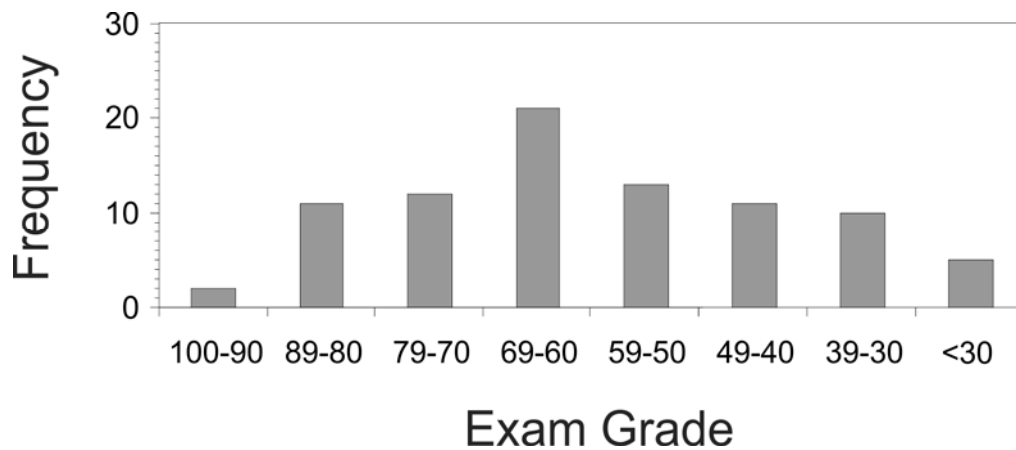


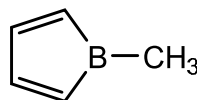
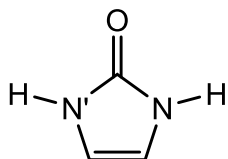
**Exam 1
Answer Key**

Exam 1 Mean: 60
Exam 1 Median: 62
Exam 1 St. Dev.: 18



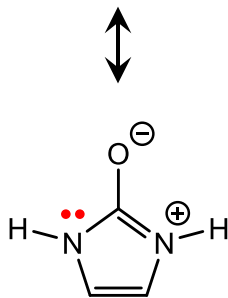
1. (12 pts) For each of the molecules below, circle whether the molecule is aromatic, anti-aromatic, or neither.

AROMATIC (3)
 ANTI-AROMATIC
 NEITHER



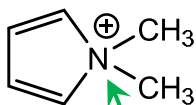
AROMATIC
 ANTI-AROMATIC (3)
 NEITHER

This molecule has a resonance structure that has 6 π electrons in the ring—4 from the two double bonds, and 2 from the lone pair on N. If a molecule has an aromatic resonance structure, it's aromatic.

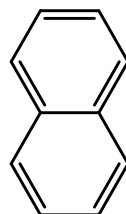


The boron atom is sp^2 -hybridized, because it has 3 σ bonds and no lone pairs. So this molecule has a complete ring of p orbitals. It has 4 π electrons total in the ring from the two double bonds, which is an even number of pairs (or $4n$, where $n = 1$). Hückel's rule says that's anti-aromatic.

AROMATIC
 ANTI-AROMATIC
 NEITHER (3)



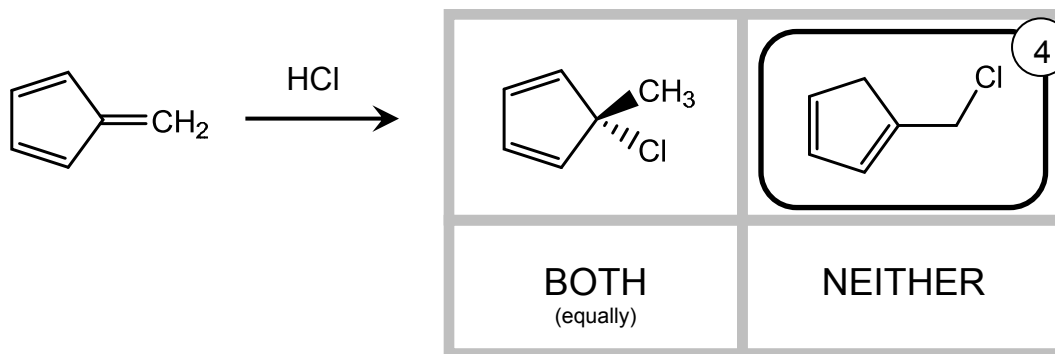
This nitrogen is sp^3 -hybridized, so this molecule doesn't have a complete cycle of p orbitals. It can't be aromatic or anti-aromatic.



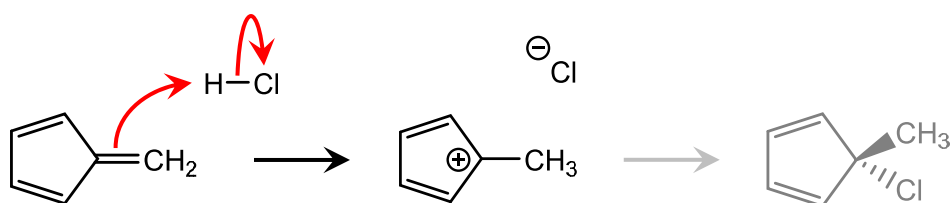
AROMATIC (3)
 ANTI-AROMATIC
 NEITHER

10 π electrons total = an odd number of e^- pairs. (Or, put in Hückel's terms, $4n + 2$, where $n = 2$, from the 5 double bonds). Hückel's rule says that's aromatic.

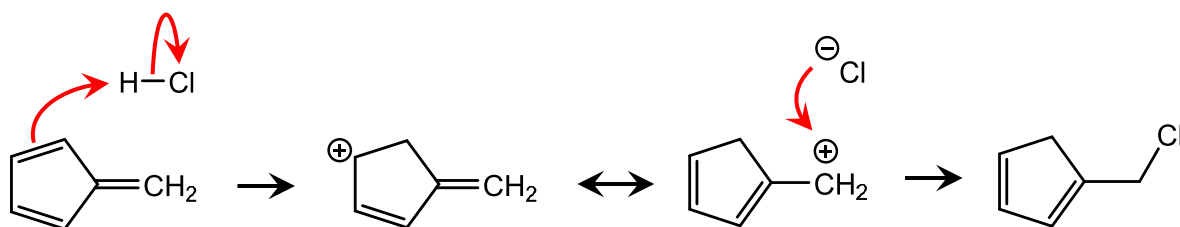
2. (20 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**



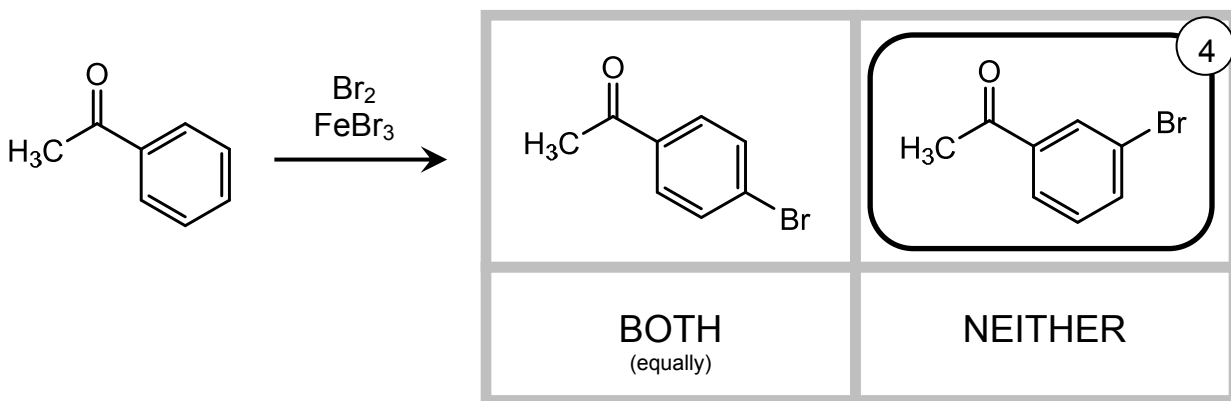
Both of the products come from electrophilic addition to one of the double bonds. Let's examine the mechanisms of those electrophilic additions to see whether they would happen or not:



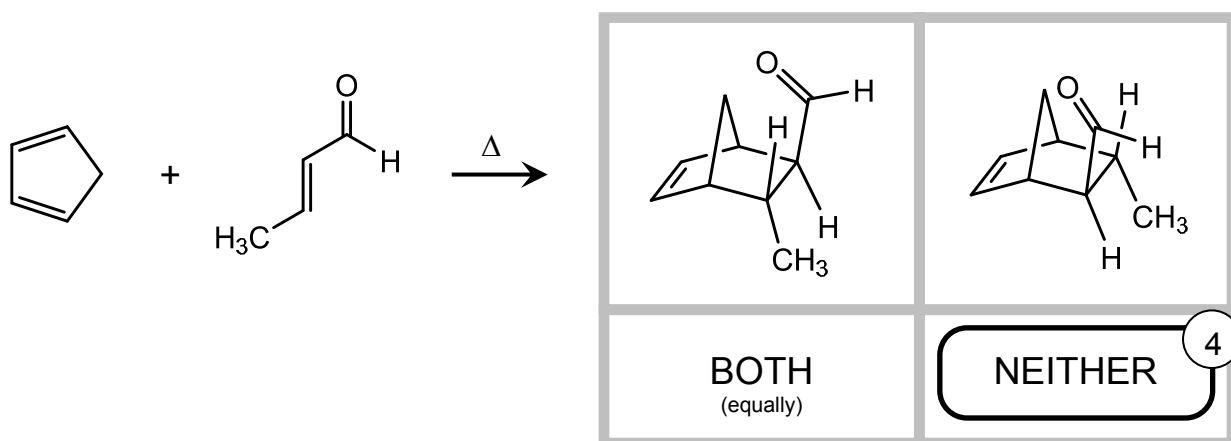
This intermediate is anti-aromatic; it has 4 π electrons in its cycle of p orbitals. The molecule really really doesn't want to be anti-aromatic, so it will do everything it can to avoid that situation. This first product will never be made.



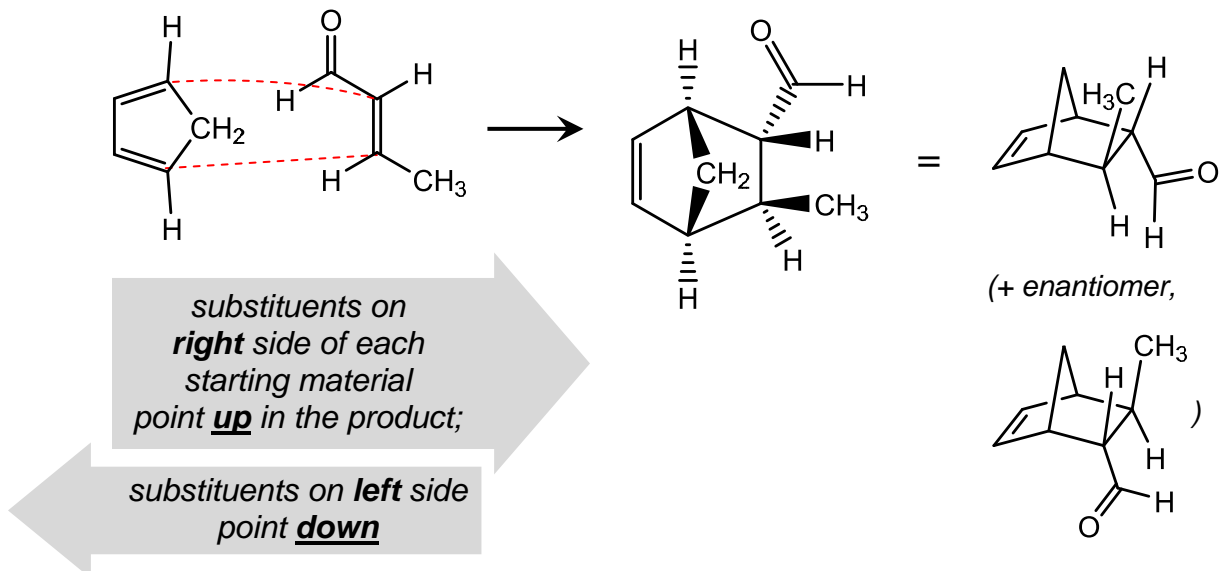
This intermediate isn't anti-aromatic but it isn't aromatic either; it doesn't have a complete cycle of p orbitals. But it is conjugated, and that's pretty good. This should be preferred over the cation above.

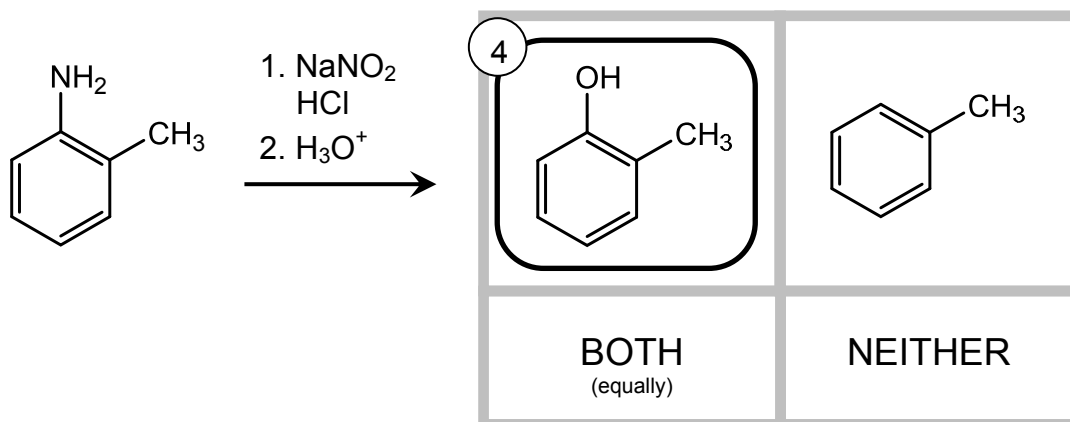


The $-(C=O)R$ group in the starting material is a *meta*-director. The *meta*-product would be preferred.

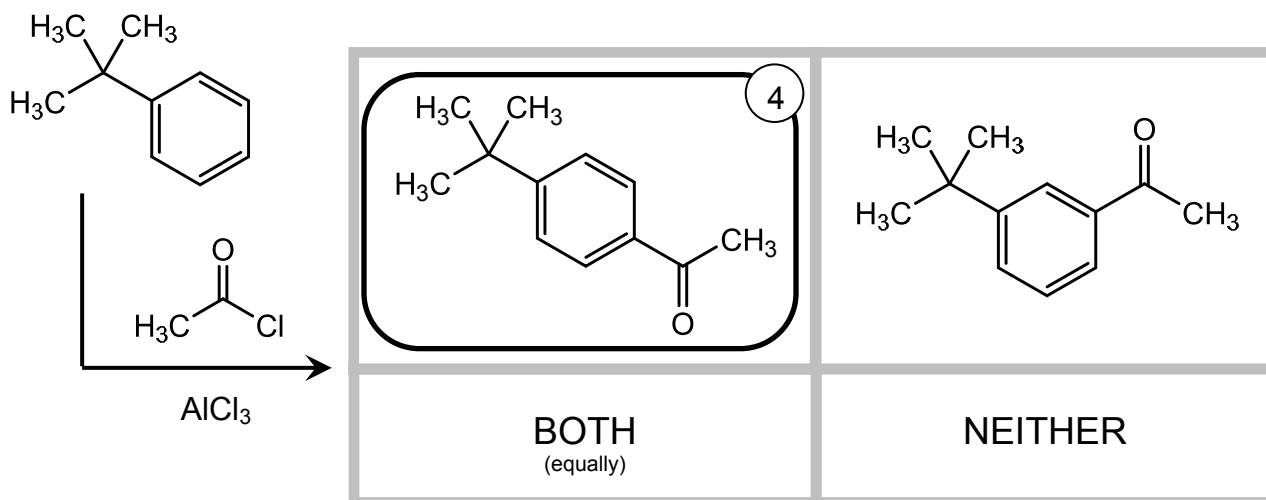
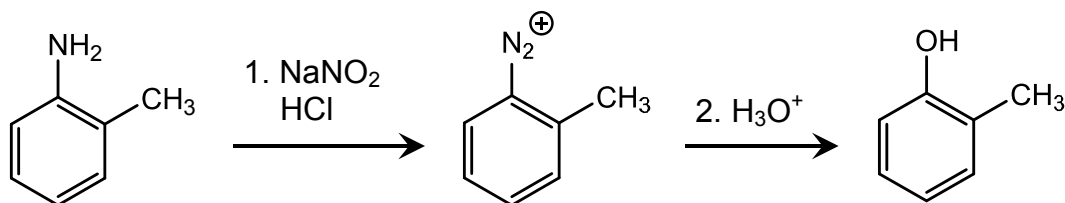


Whenever we solve a Diels-Alder problem like this one, we generally have to think about both regiochemistry and stereochemistry in the product. Here, our cyclopentadiene starting material is symmetric, so it doesn't have partial positive or negative charges, and we don't have to worry about regiochemistry. (Yay!) But we do have to think about stereochemistry. The dienophile always points its π -substituent—here, the aldehyde group—towards the diene:



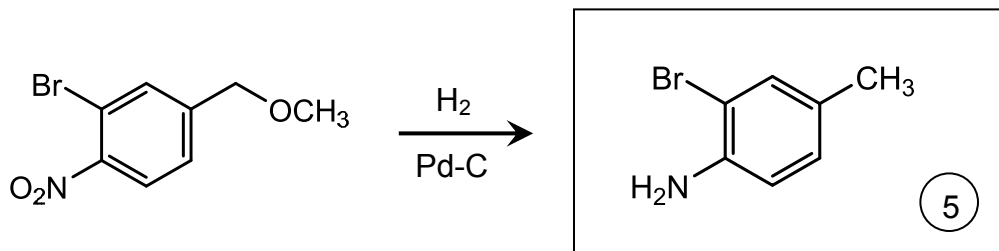


This is a Sandmeyer reaction sequence. The first step of the recipe generates a diazonium salt, and the second step substitutes the diazo group with an OH:



Alkyl groups, like the *tert*-butyl group in the starting material, are *ortho*-/*para*-directors. (They are also activating, which means the group won't prevent the Friedel-Crafts acylation from happening.) The *para*-product should be preferred. (*ortho*-Substitution might also occur, but it will be limited by the steric bulk of the *tert*-butyl group.)

3. (10 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”.



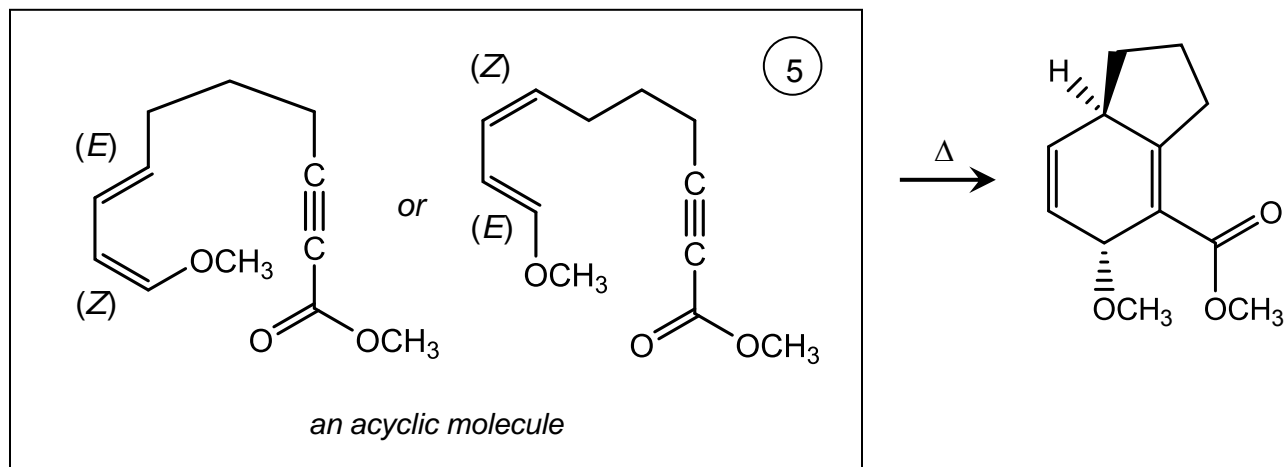
This problem is like three problems in one: it asks, how would hydrogenation conditions affect the three functional groups in this molecule?

1. The benzylic ether would get reduced to a methyl group. Reductions of single bonds like this only occur at benzylic carbons—carbon atoms that are one step away from a benzene ring—and they only happen for benzylic C-O, C-N and C-X bonds.
2. The nitro (-NO₂) group would get reduced to an amine. Smith and I described that both hydrogenation and acidic metal treatment (e.g., Fe/HCl) would do this reaction.
3. The bromine would change. It isn't benzylic, so it wouldn't get reduced.

Rubric for this part:

5 points for correct structure.

-2 points for each error in the three tasks above. So, if your answer did (1) and (3) but not (2), you would get 3 points partial credit.



The diene side of the molecule has to have its two substituents—the OCH₃ group and the connecting alkyl chain—with opposite stereochemistries, because the two

end up trans to each other in the product. But either an (*E,Z*) or a (*Z,E*) alkene combination will lead to the expected product.

Rubric for this part:

5 points for correct structure.

-2 points for incorrect stereochemistry on the diene side.

-2 points for double bond instead of triple bond in the dienophile.

-2 points for each clearly trivial structure mistake. (By “trivial”, I mean your intent must be clear—it must be obvious that you meant to write the correct answer, but you accidentally made a minor change that keeps your intent clear.) This includes drawing the incorrect number of carbon atoms in the connecting chain.

4. (5 pts) How would you use acid-base extraction to separate a carboxylic acid from an alcohol? Below are listed five possible steps you might take to selectively remove an alcohol from a chloroform (CHCl_3) solution of an acid. **Write the letters of these steps in the empty boxes, in the correct order.** Keep in mind that you may not need to use all the letters, or all the boxes. (I may have given you extra boxes.)

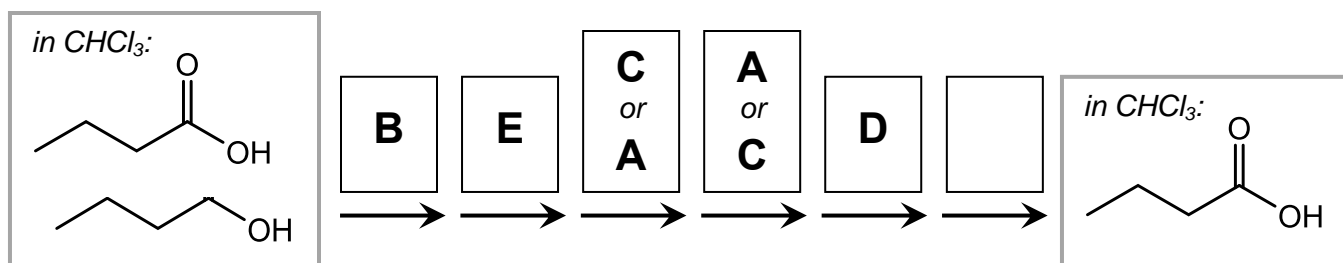
A	Add H_2O and HCl (such that the water layer is acidic). Shake.
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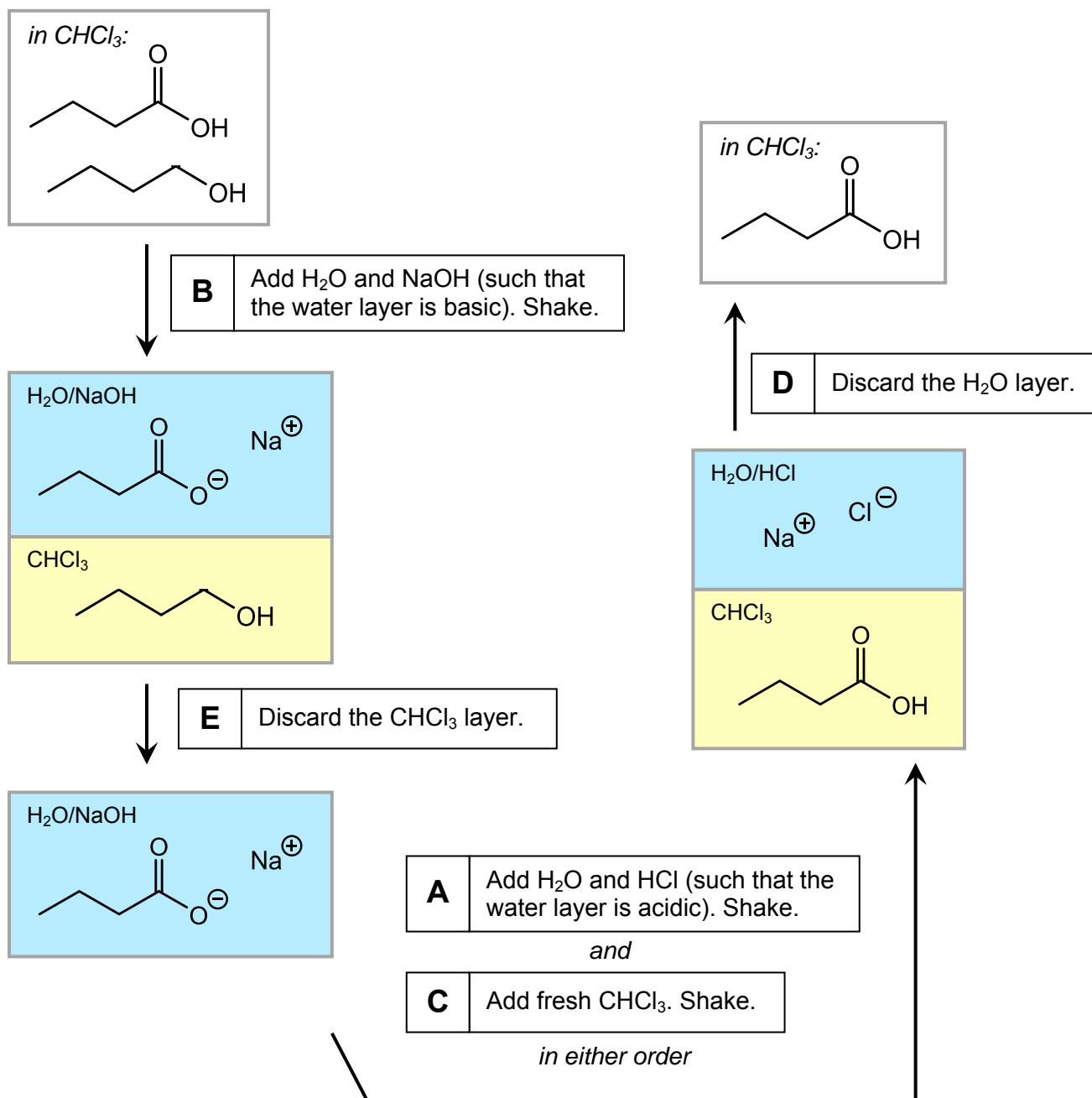
C	Add fresh CHCl_3 . Shake.
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B	Add H_2O and NaOH (such that the water layer is basic). Shake.
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D	Discard the H_2O layer.
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E	Discard the CHCl_3 layer.
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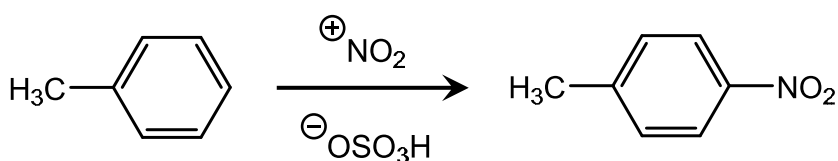
Rubric:

5 points for correct answer.

1 point partial for each letter correct starting from the beginning.

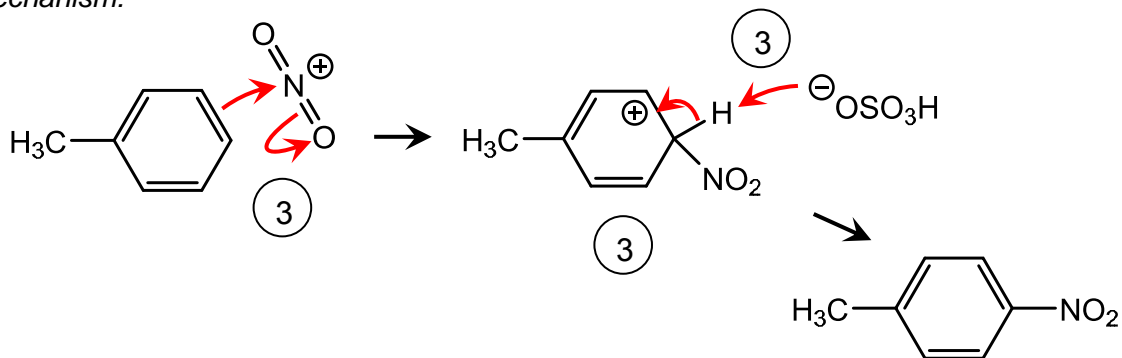
1 point partial for each letter correct starting from the end.

5. (9 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. Use only the molecules shown in the problem; don’t invoke generic species. (E.g., don’t use “B:” as a generic base.)



NO_2^+ and OSO_3H^- are generated from $\text{HNO}_3/\text{H}_2\text{SO}_4$. You do not need to draw a mechanism for the formation of NO_2^+ and OSO_3H^- —just use them.

Mechanism:



Rubric:

3 points for each arrow-pushing step.

3 points for intermediate.

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.

Spectators (e.g., OSO_3H^- in the first step) may be omitted.

Resonance is NOT a mechanistic step; it is just multiple ways of drawing the same intermediate. As a result, we did not evaluate electron-pushing that showed resonance—you can push electrons for resonance, or not, your choice. Any molecule can be represented in any resonance form. In addition, resonance does not have to be shown as an explicit “step”—it can be combined with adjacent steps, for full credit.

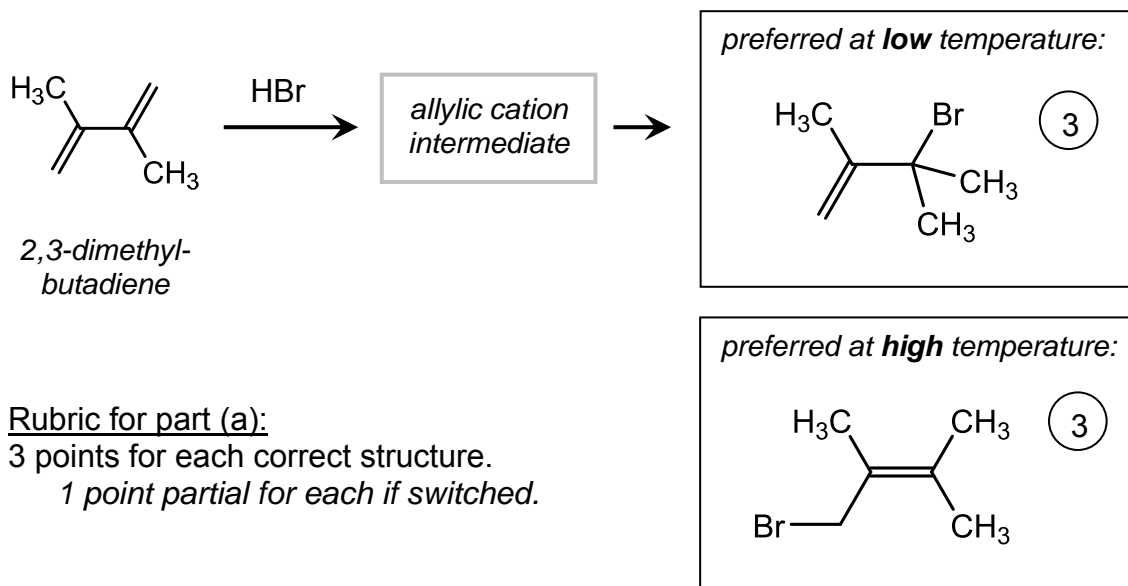
-2 points, for each arrow in each step, for errors in drawing arrows. Arrow must start at an electron pair, and end at nucleus where electrons will newly interact. Can only lose points if you get them.

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

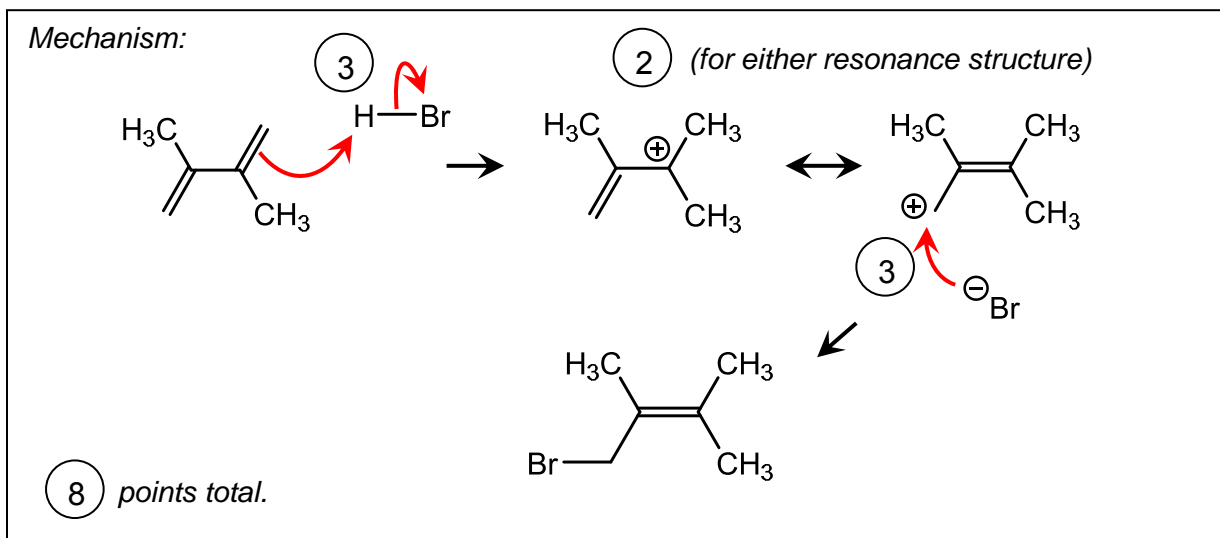
-2 points for each use of a generic or incorrect acid/nucleophile/base. For example, in the last step you couldn't invoke a base other than OSO_3H^- that you may have used in other problems. Exception: In this problem, you could also use H_2O as a base, because it is generated by $\text{HNO}_3/\text{H}_2\text{SO}_4$.

If you combine steps that can't be combined, you can get points for arrows that are in the rubric, but not for the intermediate you skipped.

6. (28 pts) 2,3-Dimethylbutadiene (the reactant below) reacts with HBr to form two different products, both of which come from one allylic cation intermediate. The preferred product depends on whether the reaction is performed at low or high temperature.
- a. In the boxes below and on the next page, draw the structures of the two products of the reaction between 2,3-dimethylbutadiene and HBr. Draw each product in the box corresponding to its preferential conditions.



- b. In the box below, **draw a mechanism** (using “electron pushing”) that shows how the **high-temperature product** is formed from 2,3-dimethylbutadiene. Make sure your mechanism shows the structure of the allylic cation intermediate.



Rubric for part (b):

3 points for each arrow-pushing step.

2 points for intermediate.

See problem 5 for mechanism rubric details.

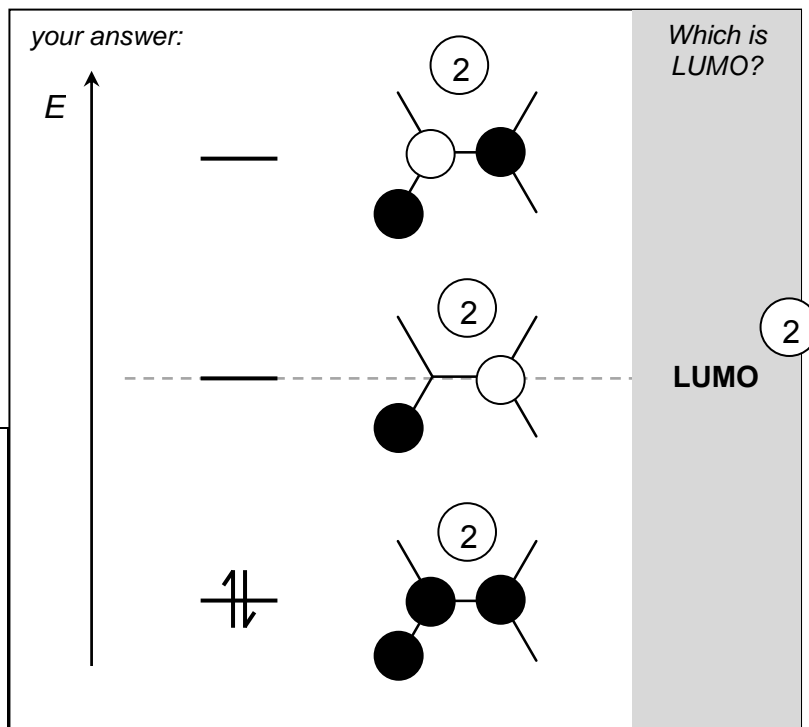
c. In the box below, draw a molecular orbital diagram for the conjugated π system in the **allylic cation intermediate**. In your diagram, make sure to:

- Draw orbital energy levels;
- Draw a molecular orbital for each energy level. Use dark and light shading to indicate the phase in each orbital lobe.
- Fill your orbitals with the appropriate number of electrons.

2 for set of 3 orbitals—one bonding, one non-bonding, one antibonding.

2 for filling orbital diagram with 2 electrons.

You did not have to draw the molecule backbone, or nodes, in your orbital structures; just the lobes was enough. You could also draw your orbitals with a side-on perspective instead of looking down from the top, as I have.



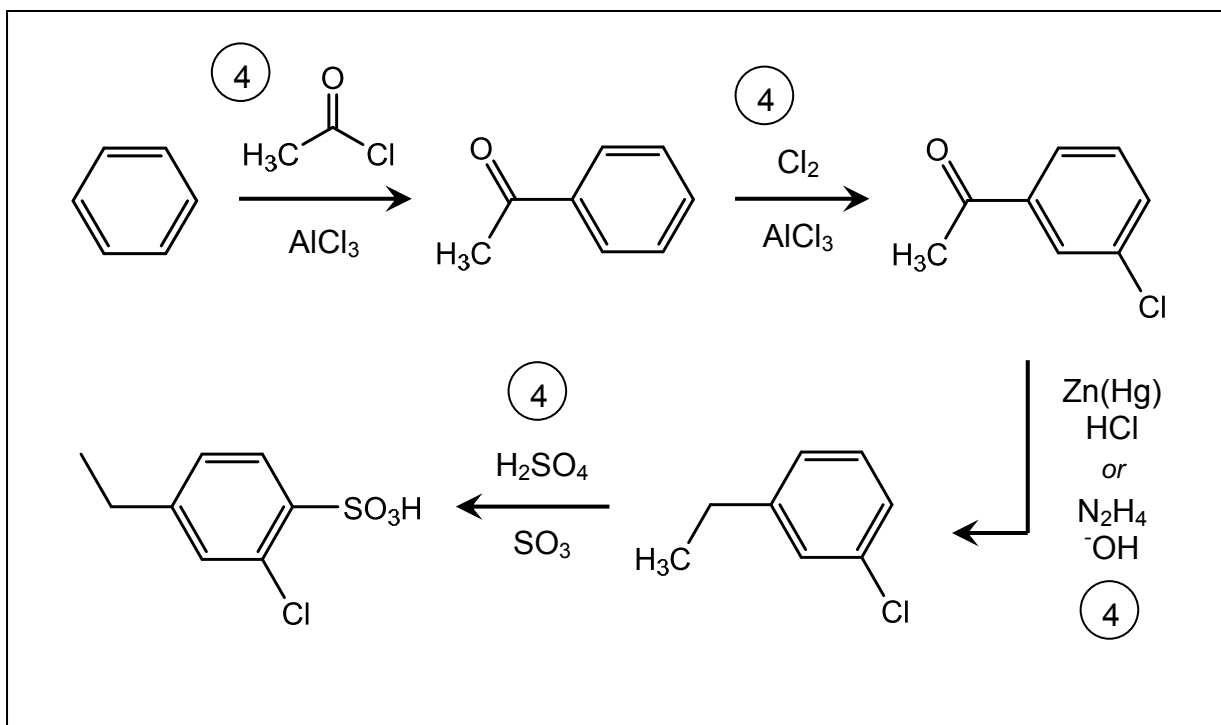
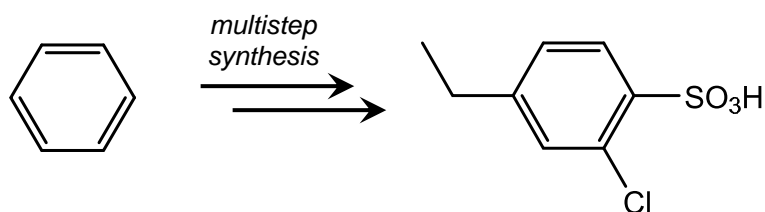
d. Which of the orbitals you drew is the LUMO? On your diagram on the previous page, write “**LUMO**” next to this orbital.

e. Would you expect $\lambda_{\max}(\text{products})$ to be $>$, $<$, or $=$ $\lambda_{\max}(2,3\text{-dimethylbutadiene})$?

(circle one)

The more conjugated double bonds a molecule has, the longer the wavelength that molecule will absorb at. The products only have one double bond, but the starting material has 2, so λ_{max} will be greater for the starting material.

7. (16 pts) **Propose a multistep synthesis** of the product shown below, starting from benzene. You may use any reagents and reactions we've learned about in class and/or in the text. You might discover multiple answers to this problem; draw only your best (one) synthetic route. Feel free to draw an incomplete route—we will give you partial credit where we can.



Rubric:

General notes:

Your synthesis was graded on tasks/steps, rather than on molecules. Each task is judged separately, and does not require that the synthesis makes sense, or that other tasks are correct.

If you combined a sequence of successful tasks or reagents into one arrow, without drawing synthetic intermediates, you can still receive full credit for completing the required tasks. *However*, if you do not draw synthetic intermediates, and any of

your sequence of tasks is incorrect, you may not receive partial credit for any subsequent steps that are ambiguous to the grader.

- 1 point for each *minor, trivial* 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.
- 2 points if reagents are correct, but product is wrong. If this happened, and you were led down an incorrect synthetic path by your mistake, you can also lose later points.

We only gave points for reagents if they connected a starting material and a product in an understandable way. So, for example, just writing a change in the starting material, by itself, isn't worth any points.

Tasks:

1. Friedel-Crafts acylation.

- 4 points for acylation at the beginning of the synthesis, or later as long as the regiochemical relationship with existing groups works.
- 2 points partial for acylation with failed regiochemistry at any point.
- 2 points partial for direct Friedel-Crafts alkylation, with correct or incorrect stereochemistry.

2. Electrophilic aromatic chlorination.

- 4 points for chlorination at the beginning of the synthesis, or later as long as the regiochemical relationship with existing groups works.
- 2 points for introducing -Cl via Sandmeyer. Unnecessarily long.
- 2 points partial for electrophilic aromatic chlorination with failed regiochemistry at any point.

3. Clemmensen or Wolff-Kischner reduction of C=O to CH₂.

- 4 points, at any point in the synthesis.

4. Electrophilic aromatic sulfonation.

- 4 points for sulfonation at the beginning of the synthesis, or later as long as the regiochemical relationship with existing groups works.
- 2 points partial for electrophilic aromatic sulfonation with failed regiochemistry at any point.