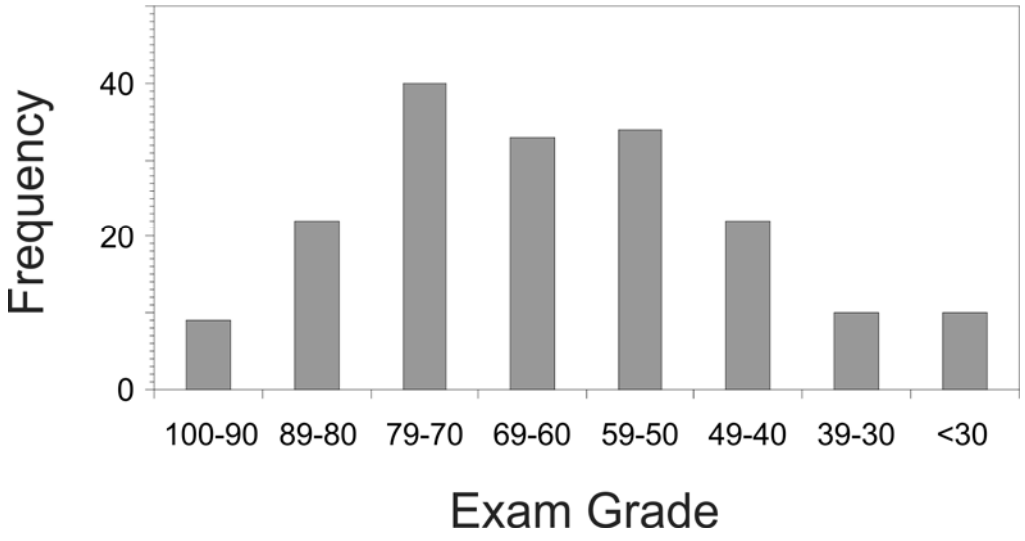
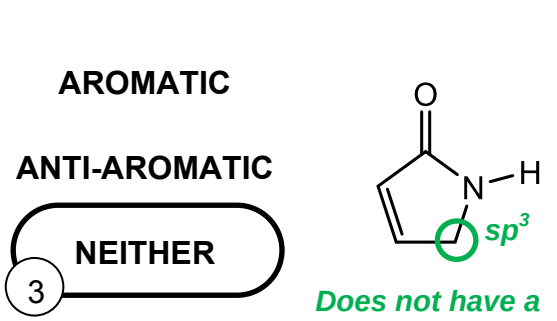
Exam 1
Answer Key

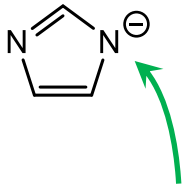
Exam 1 Mean:	63
Exam 1 Median:	64
Exam 1 St. Dev.:	19

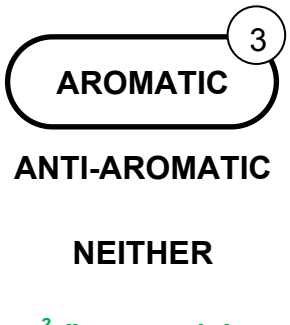


1. (12 pts) For each of the following molecules, circle whether the molecule is aromatic, anti-aromatic, or neither.

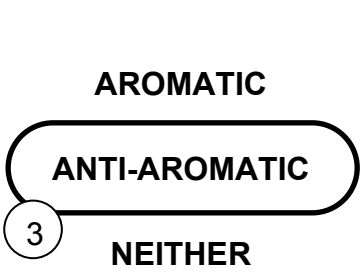


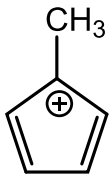
Does not have a complete cycle of p orbitals.



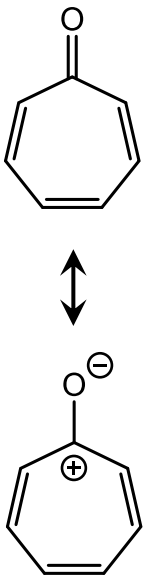


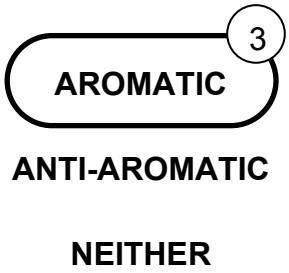
This N hybridizes sp^2 (because it has at least one lone pair, and is adjacent to a multiple bond), and puts a lone pair into a p orbital. 6 π electrons means aromatic.





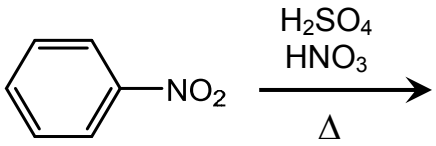
4 π electrons.

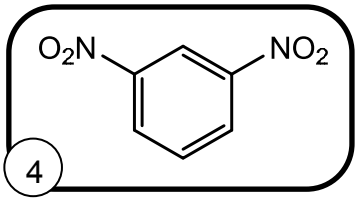




Has an aromatic resonance structure. So is aromatic.

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 <u>equally</u>, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

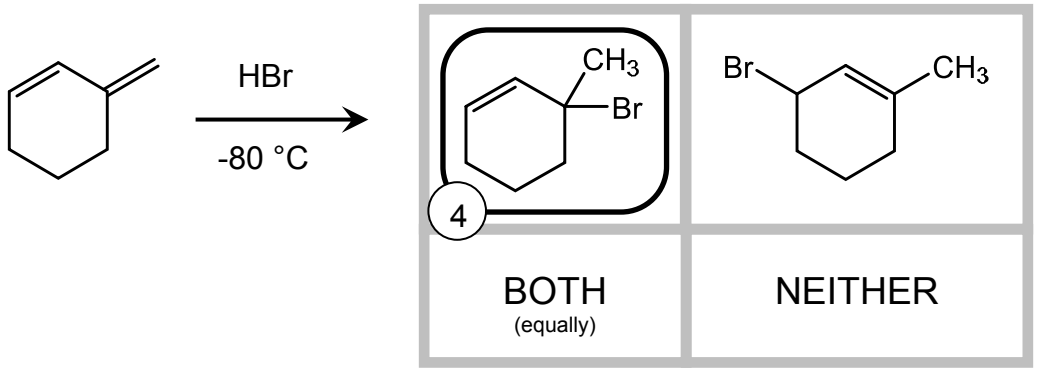




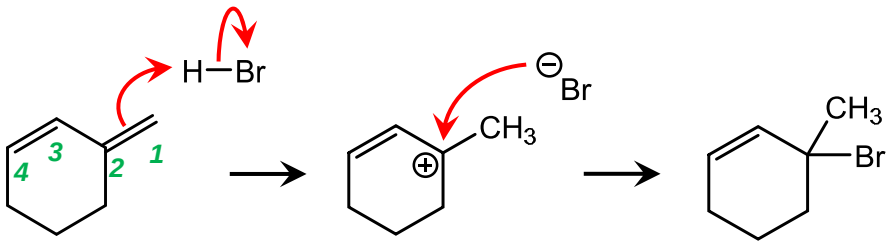
BOTH (equally)

NEITHER

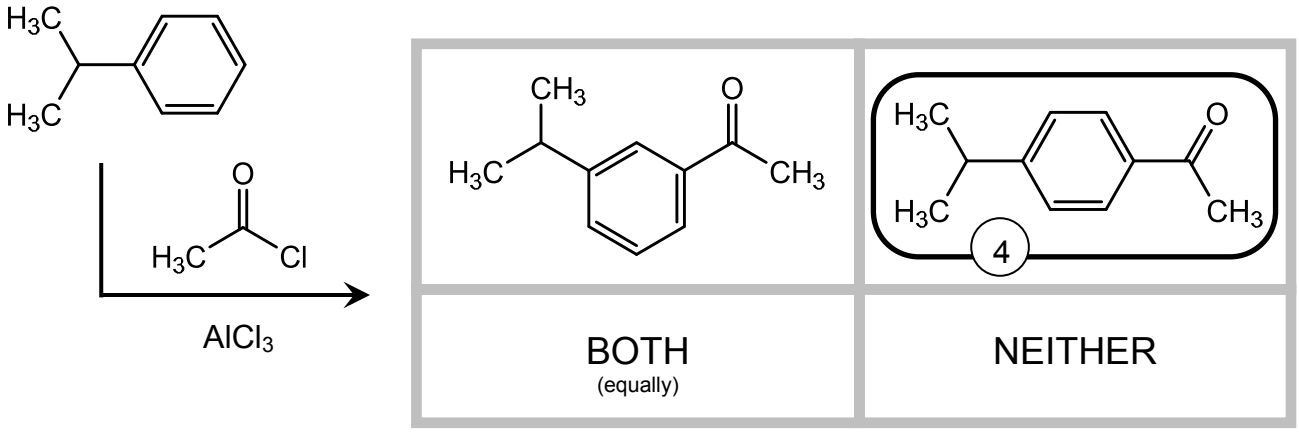
Electrophilic aromatic nitration. The $-NO_2$ group is a *meta*-director, so the product is *meta*-disubstituted. This reaction doesn't happen very easily, and requires heat.



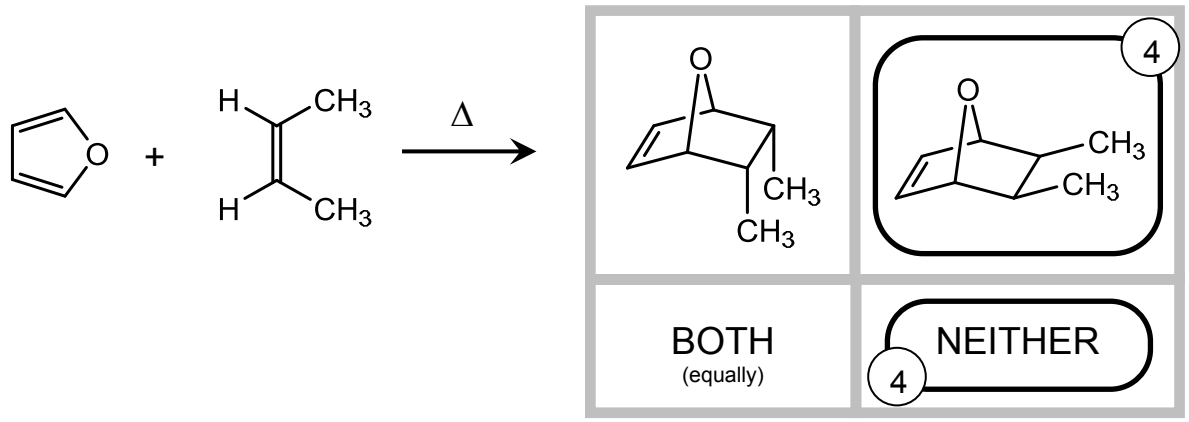
This problem asks you to distinguish between 1,2-addition and 1-4-addition of HBr to the diene starting material. At low temperatures, 1,2-addition is favored, and yields the kinetic product:



Proton adds preferentially to form most substituted cation. Then, at low temperature (kinetic conditions), addition happens 1,2.

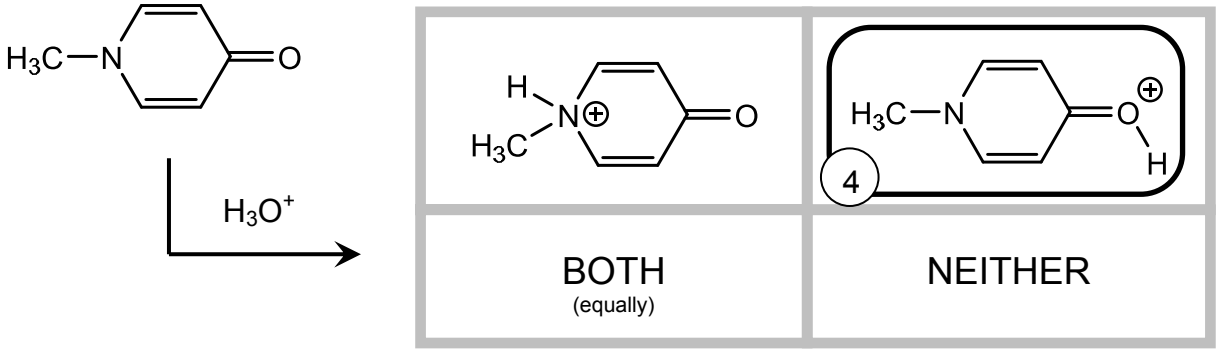


Friedel-Crafts acylation. Alkyl groups are *ortho*-/*para*-directors, and in this case, because the alkyl group is pretty large, the *para*-product will probably be favored over *ortho*-substitution (not shown). In any case, the *para*-product will certainly be favored over the *meta*-one.



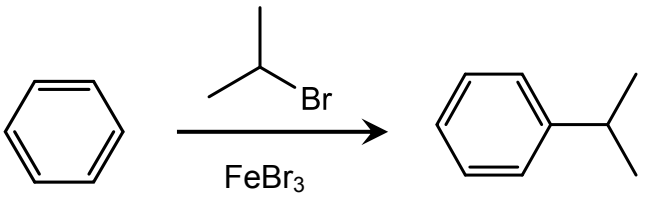
This problem was a little more complicated than I first imagined. ***Assuming that the two starting materials react,*** the product will be the molecule on the right; the methyl groups are not π-substituents, so they will want to orient themselves *exo* (away) with respect to the diene. That leads to the second product.

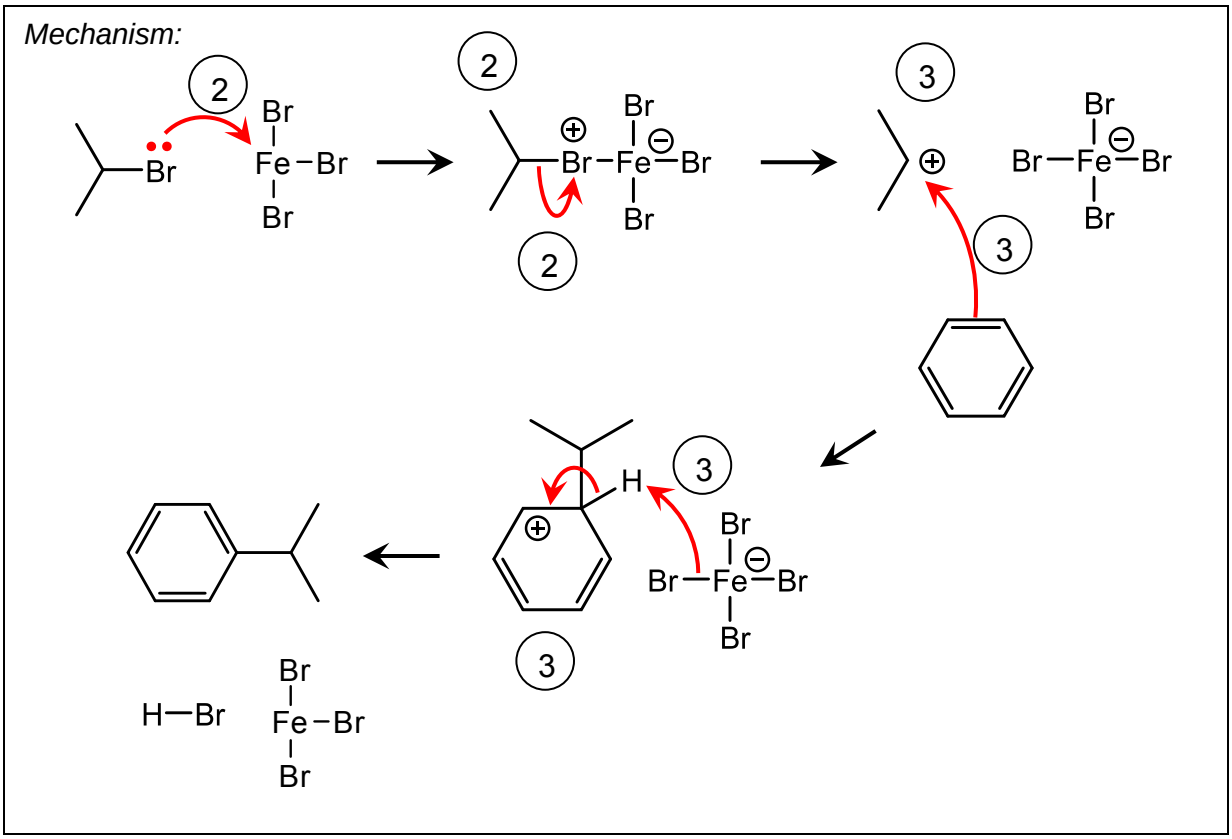
But do the starting materials react? Tthe first starting material, furan, is aromatic. (And the product is not.) That makes furan very choosy about electrophiles it will react with. In general, it will only combine with the most electron-deficient dienophiles, and our reactant on the right is not one of those. So the actual answer is "NEITHER"—no reaction would actually occur here. But that was trickier than I expected, so we accepted either answer.



Out of the two products, the second one is aromatic (because it has an aromatic resonance structure) but the first is not (because an sp^3-hybridized nitrogen breaks the cycle of *p*-orbitals).

3. (18 pts) **Draw a mechanism** (using "electron pushing") for each of the reactions 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.)





Rubric:

3 points for each electron-pushing step.
3 points for each intermediate/set of intermediates.
EXCEPTION: 6 points total for getting to isopropyl carbocation.

Overall notes:

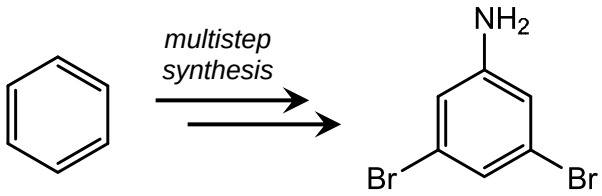
Overall, the minimum score for each step is zero; errors in a step cannot earn you negative points that count against another, correct step.
Things that have left for good (e.g., HBr) and spectators may be omitted.
-2 points, for each arrow in each step, for errors in drawing arrows. Arrow must start 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.

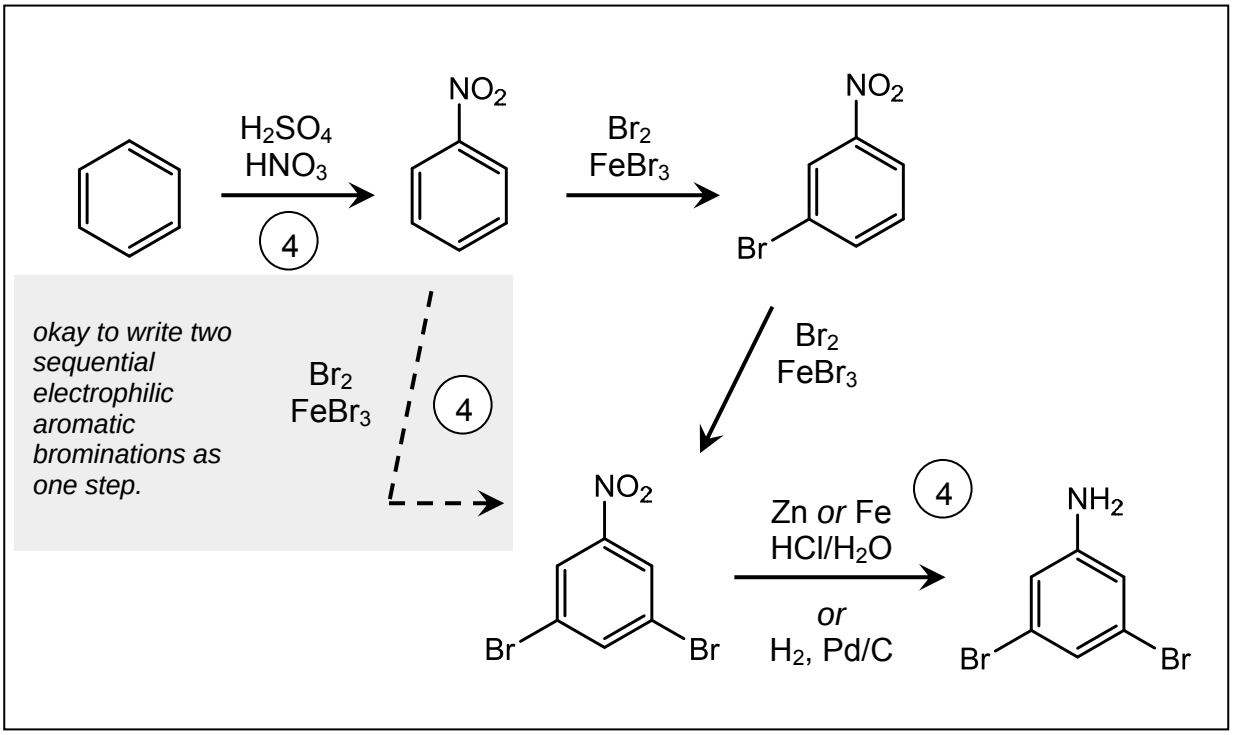
-2 points for each use of a generic or incorrect nucleophile/base. For example, in the last step you couldn't invoke ⁻OH or any other base you may have used in other problems.

-2 points for forming a complex between starting material and $FeBr_3$ <u>without then progressing to cation</u>. This doesn't happen, because starting material is 2°.

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.

4. (12 pts) On the following page, p**ropose a multistep synthesis** of the product shown, 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.





<u>Rubric:</u>

This synthesis requires three tasks, listed below. Each task is judged separately, and does not require that the synthesis makes sense, or that other tasks are correct. However, you may lose points if a correct step is out of order.

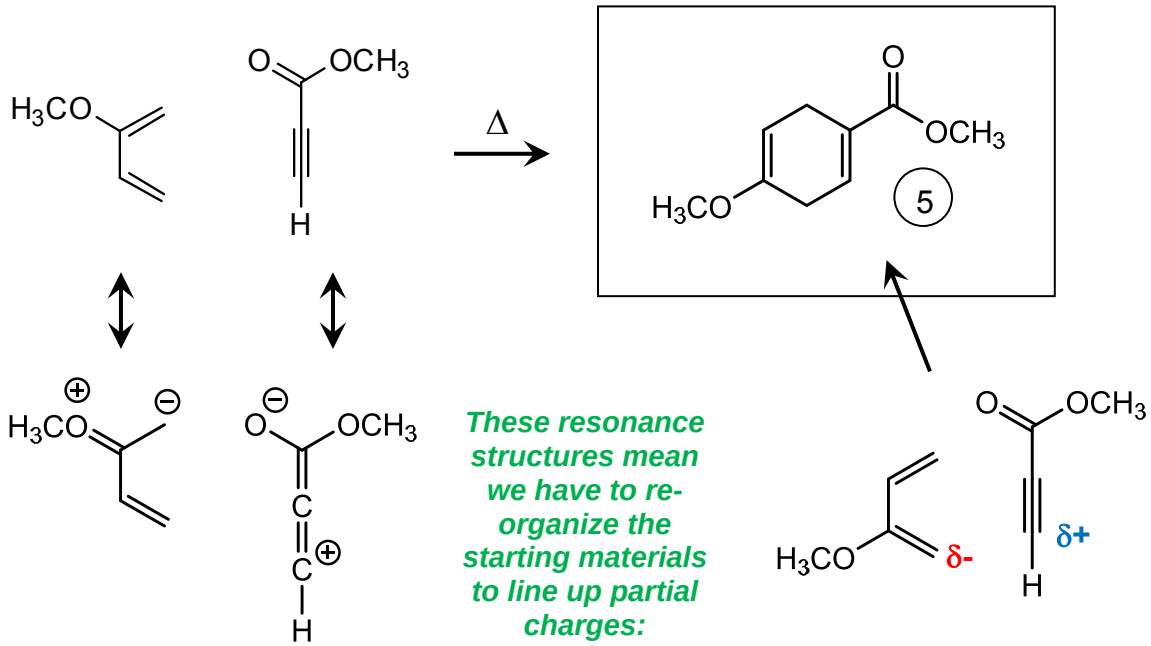
-1 point for each minor error in structures or reagents; if error propagates, points are taken off only for initial error.
-2 points if step reagents are incorrect, but reaction could otherwise be accomplished with correct reagents.

1. Electrophilic nitration (*4 points*).
2 points partial for not doing this step first. Any other order won't place nitro group in the correct regiochemistry.

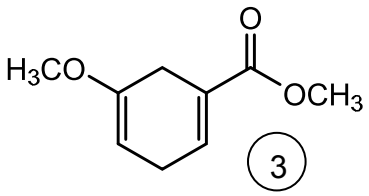
2. Double electrophilic bromination (*4 points*).
Full credit for illustrating this either stepwise or as one step.
2 points partial for not doing this step second. Any other order won't place groups in the correct regiochemistry.

3. Reduce $-NO_2$ to $-NH_2$ (*4 points*).
2 points partial for not doing this step at the end. If the molecule has an $-NH_2$ group in it at any other time, it will activate & ortho-/para-direct other reactions.

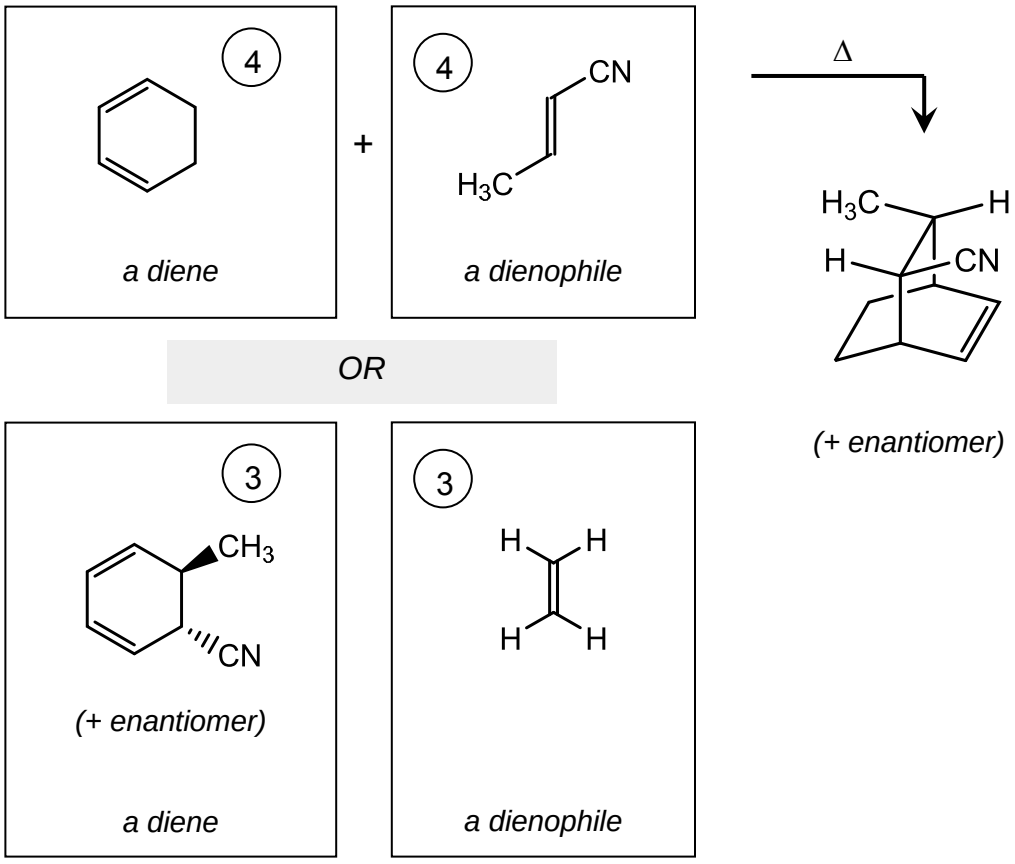
5. (23 pts) For each of the reactions below, fill in the empty box corresponding to reactants or products. Give only one answer in each box. For reactions that you expect to yield multiple products, give the major product. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note "+ enantiomer".



Rubric for this part:
5 points for correct structure.
3 points partial for opposite regiochemistry.

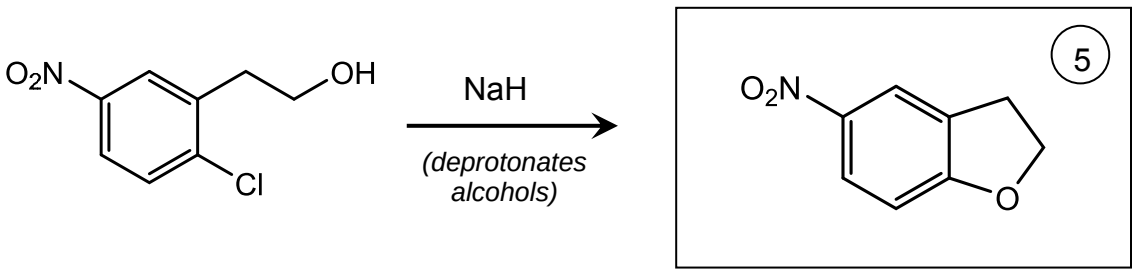


-2 points for each clearly trivial structure mistake. (E.g., omitting double bonds in ring.) By "trivial", I mean your intent must be clear—it must be obvious that you meant to write the correct answer, but you accidentally made a minor change that keeps your intent clear.



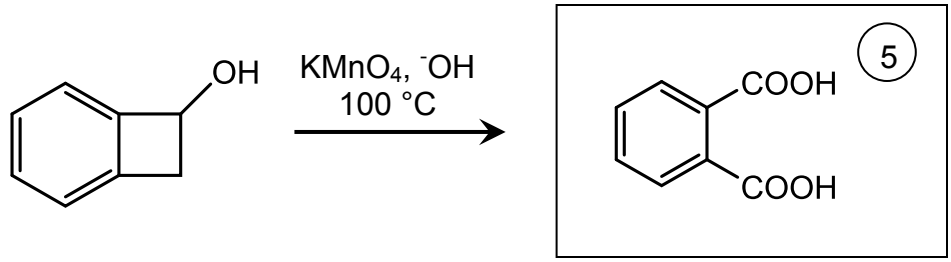
You could get from either of these pairs of reactants to the product via electron pushing, but the dienophile in the second pair is much less reactive, and maybe even unreactive, because it doesn't have an electron-withdrawing substituent attached to it. (And electron-poor dienophiles are the most reactive in Diels-Alder reactions.) We gave partial credit for this pair.

Rubric for this part:
4 points for each correct structure.
3 points partial (each) for choosing diene/dienophile pair that isn't activated.
1 point partial for any open- or close-structure diene.
2 points partial for cis- instead of trans-dienophile.
-1 point each if you put the diene in the dienophile box and vice versa.
-2 points for each clearly trivial structure mistake.



Deprotonating the alcohol forms an alkoxide that can perform an intramolecular nucleophilic aromatic substitution:

Rubric for this part:
5 points for correct structure.
1 point partial for alkoxide (just deprotonating alcohol).
-2 points for each clearly trivial structure mistake. This includes omitting a carbon from chain. It doesn't include omitting –OH group.



$KMnO_4$ converts every benzylic carbon that has a C-O or C-H bond to a –COOH group, and breaks/gets rid of all other bonds in the process.

Rubric for this part:
5 points for correct structure.
2 points partial for any product with at least one carboxylic acid in it.
-2 points for each clearly trivial structure mistake.

6. (15 pts) For the conjugated π-orbital system in 1,3-cyclohexadiene,
   a) How many molecular orbitals describe the conjugated π-system? (Answer in the box on the right.)
   b) Draw all of these molecular orbitals on the energy diagram below. Draw both the shapes of the orbitals (as viewed from the top) and their energies, and fill the orbitals with the appropriate number of electrons. Then, to the right of the HOMO and LUMO orbitals, write "HOMO" and "LUMO".

1,3-cyclohexadiene

4	2
# of π MO's	

This question asks us to draw a molecular orbital diagram of a conjugated π system. To solve the problem, we have to ask some basic questions first:

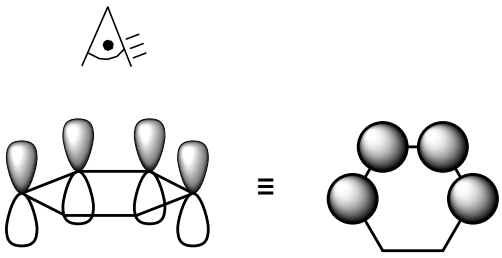
i. **Is the conjugated system of *p* orbitals linear or cyclic?** This molecule is a ring, but it doesn't have sp^2-hybridized carbons all the way around the ring; there are two sp^3-hybridized carbons at the bottom. This is a <u>linear</u> system.

ii. **How many *p* orbitals are there?** Four sp^2-hybridized carbons, so four *p* orbitals. This gives us the answer in the box above, because the number of molecular orbitals in a conjugated π system is equal to the number of *p* orbitals that combine to create it.

iii. **How many π electrons are there?** This is a different question than (ii); sometimes the answer to (ii) and (iii) will be the same, sometimes not. Our conjugated system has two double bonds containing a total of four π electrons.

This means we need to draw a molecular orbital diagram for a *linear* system of 4 molecular orbitals that contains 4 electrons. To do this:

- On the energy diagram, draw four, evenly spaced energy levels, symmetrically arranged about the non-bonding level.
- Each energy level corresponds to a MO shape that is a combination of the four atomic *p* orbitals, in which the mathematical phase of each orbital lobe is either matched or mismatched with its neighbor. The bottom-most, lowest-energy orbital has all of its component *p* orbitals in-phase (matched). All of the orbital interactions in this lowest-energy orbital are bonding.

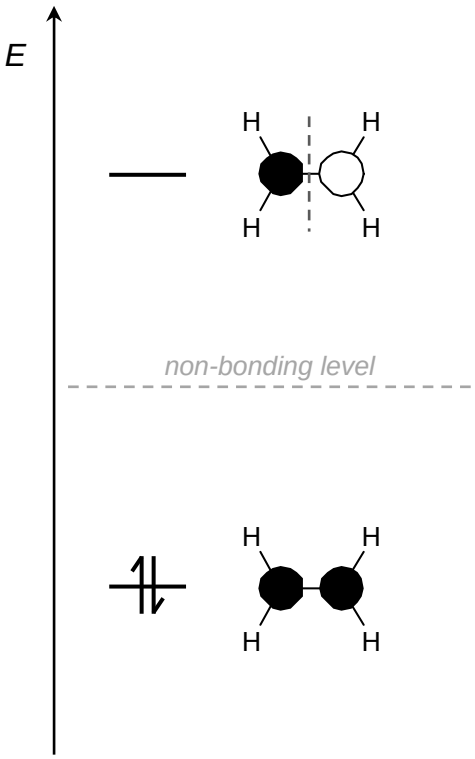


- Higher-energy orbitals have nodes that represent mismatched phase between neighbors. Each level above the first has one more node. Here, we have three

more energy levels with one, two, and three nodes; each set of nodes is distributed symmetrically about the set of *p* orbital components.

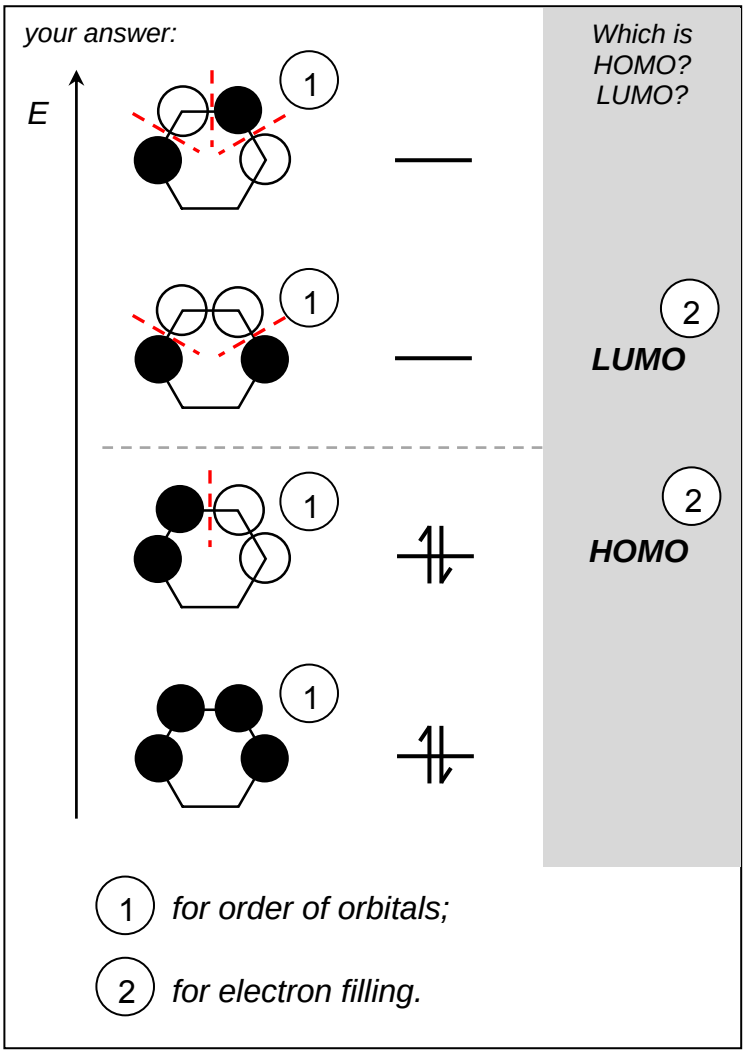
So, mapping what we know onto the energy diagram:

example of answer format (for C_2H_4):



I've drawn nodes on the orbitals as red dashed lines, but you didn't have to.

your answer:



Your orbitals did not have to be drawn on a 6-membered ring backbone, but they do have to look like mine (or their opposites, with white/black switched).

I've filled this diagram with the 4 π electrons, using the Aufbau principle you learned in General Chemistry, from the bottom up. The HOMO (Highest Occupied Molecular Orbital) is the highest-energy orbital that has electrons in it, and the LUMO (Lowest Unoccupied Molecular Orbital) is the lowest-energy orbital that is empty of electrons.

Rubric for this part:

1 point for each correct orbital shape. *(4 points total.)*

The arrangement of orbitals did not have to be correct to receive these points, but the shape of the orbital did.

I've drawn my orbitals from a top-down perspective, but you could also draw them looking from the side if you like.

-1 point for each incorrect orbital shape beyond four. (So, if you drew 8 molecular orbitals, even if 4 of them were correct, the other 4 cancel them out.)

1 point for each correct orbital ordering. (Not an inverted polygon.)

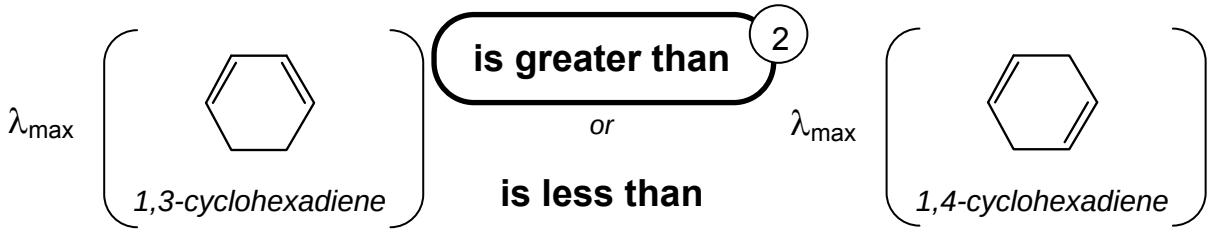
You only got these points if you drew 4 orbitals.

2 points for filling your (any) orbital diagram with 4 electrons, from the bottom up.

2 points for correctly identifying the HOMO in your diagram.

2 points for correctly identifying the LUMO.

c) Both 1,3-cyclohexadiene and 1,4-cyclohexadiene absorb UV light. Which of the two molecules absorbs at longer wavelengths (has a greater λ_{max})?



(circle one)

λ_{max} is determined by the energy difference between the HOMO and LUMO orbitals in a molecule; the smaller the "HOMO-LUMO gap", the larger λ_{max} is. Conjugation moves these orbitals closer together, and makes λ_{max} greater. (This is why, for example, colored clothing dyes are highly conjugate molecules; the small HOMO-LUMO gaps in these molecules shifts their λ_{max} values from the UV into visible wavelengths.