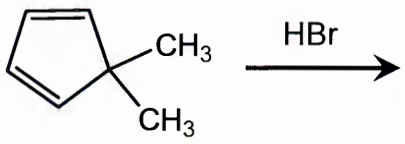
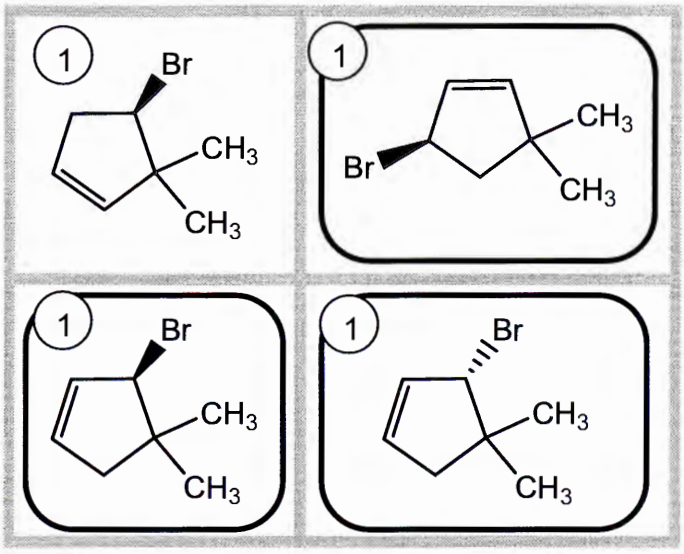
1. (10 pts) For each reaction shown below, **circle all possible products** (including minor ones). Keep in mind that, for each reaction, you might circle one, multiple, or no products.

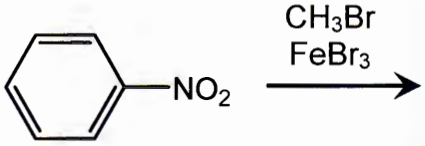




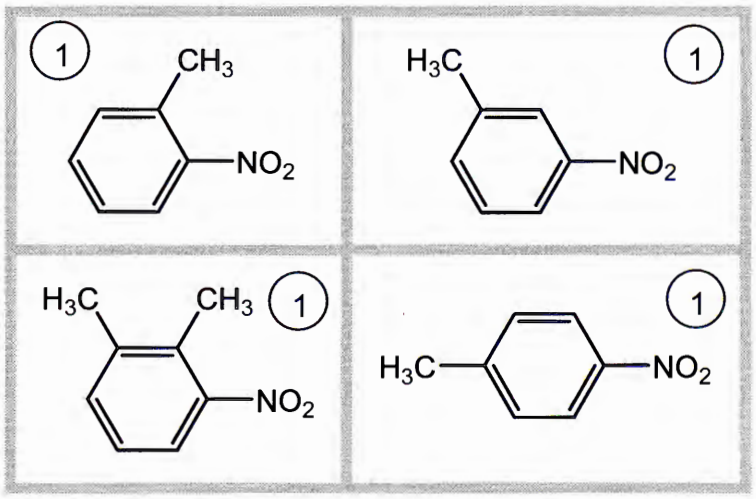
(1) *for each correct box-- either circling correctly, or correctly leaving the box alone.*

\+ (1) *for perfect answer (all 4 correct).*

So, 5 points total on each problem.

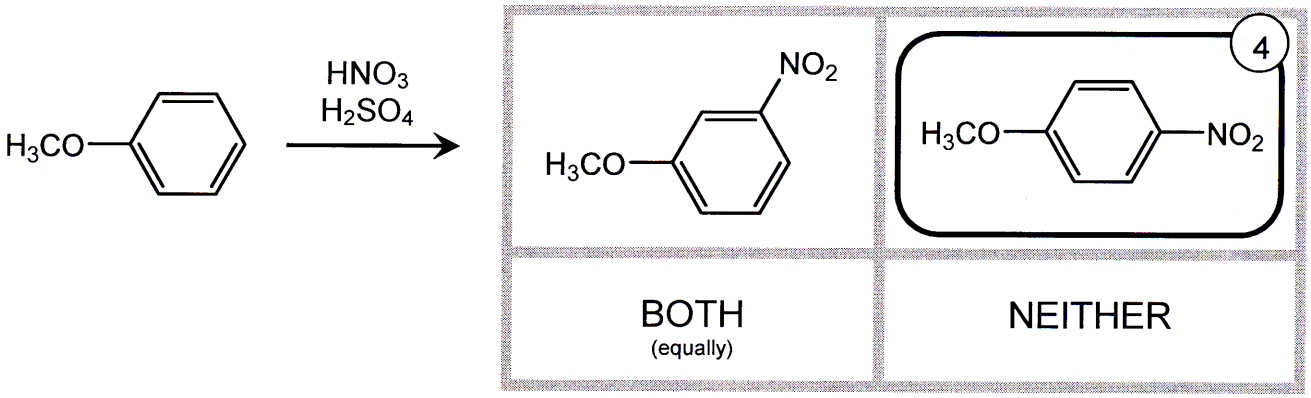


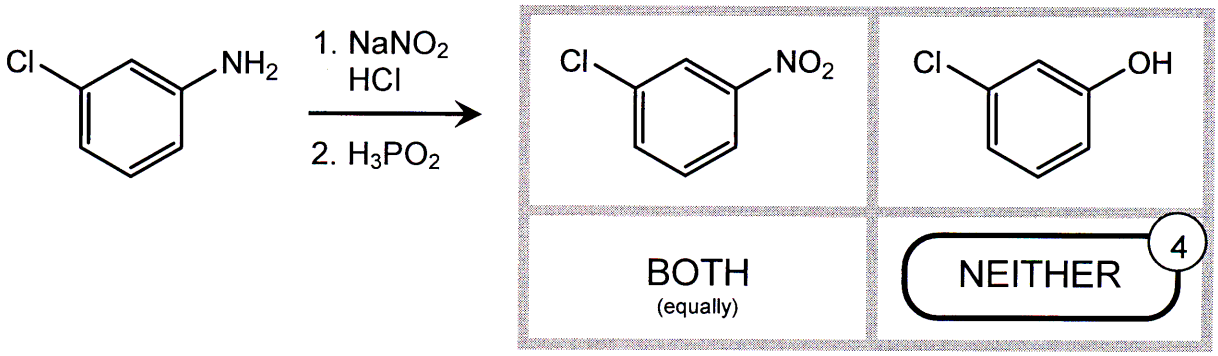
(NONE CIRCLED)

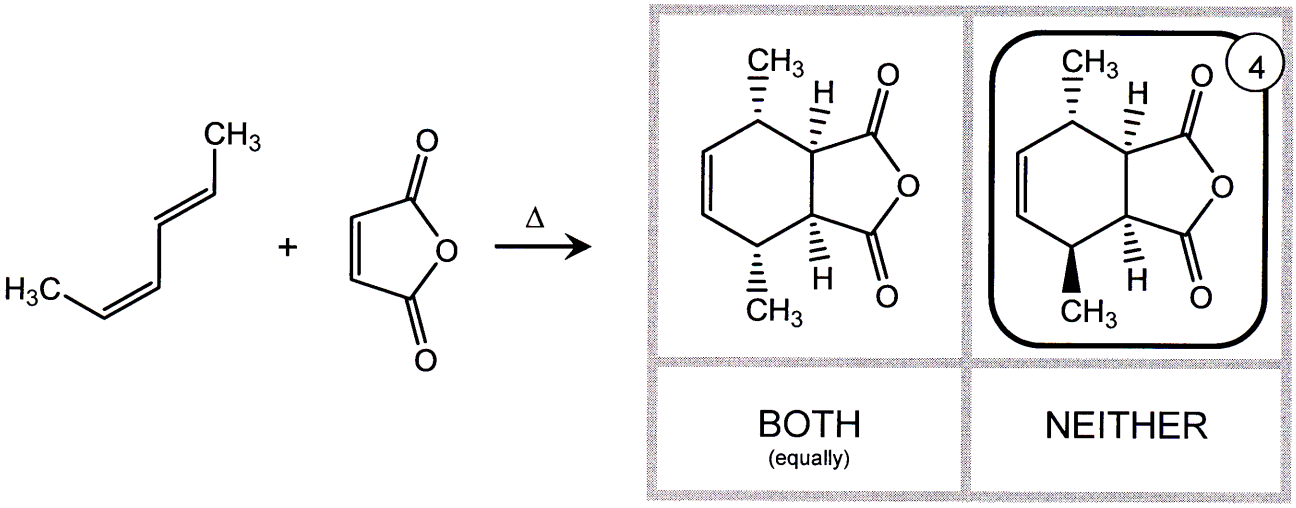


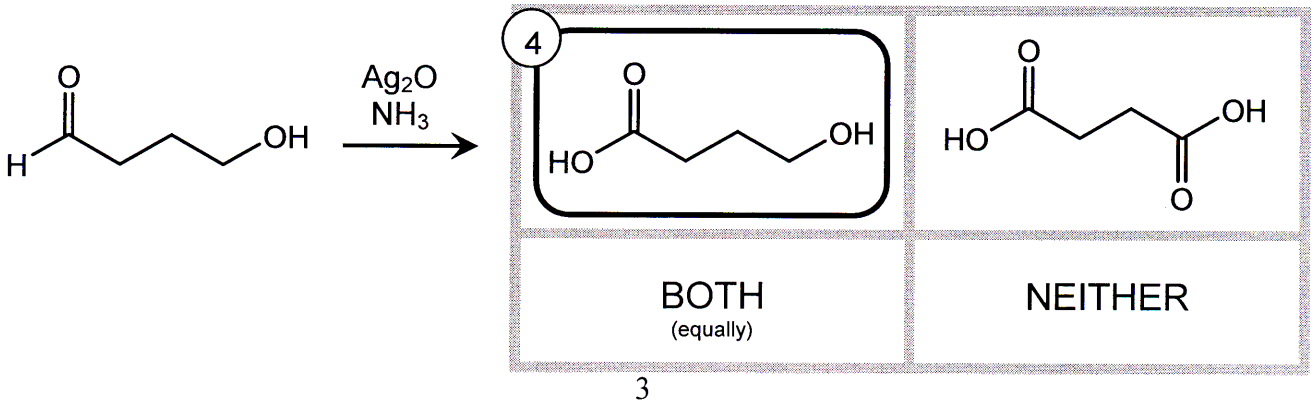
Friedel-Crafts alkylation fails on deactivated aromatics. No products are observed.

2. (16 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.**

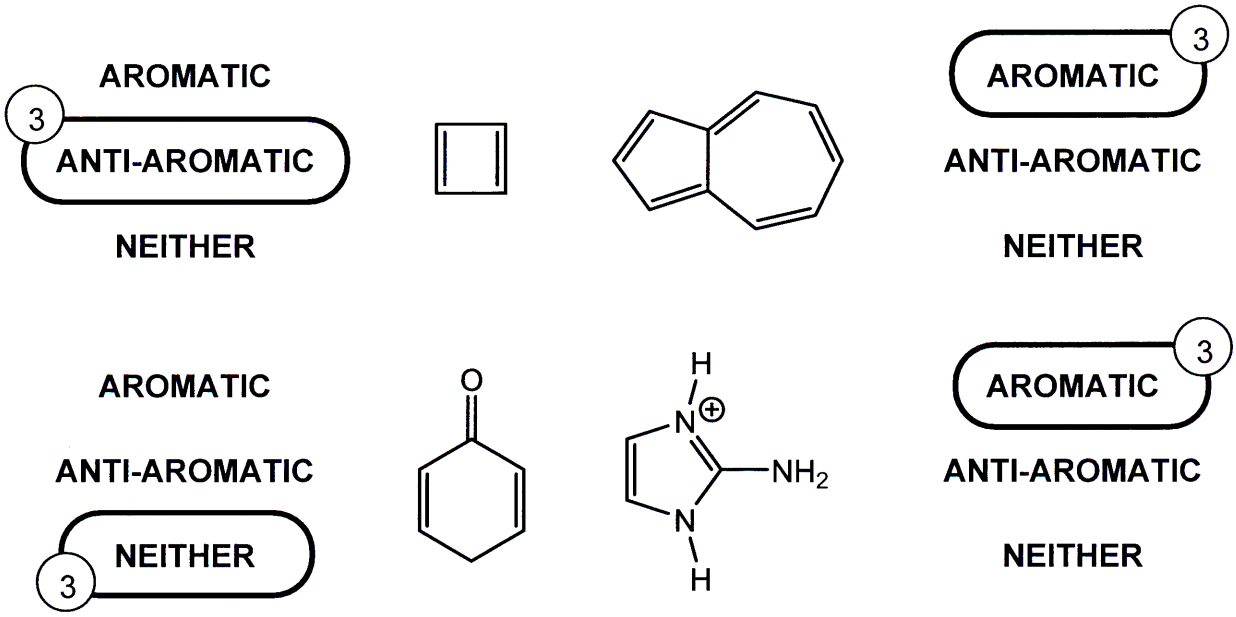




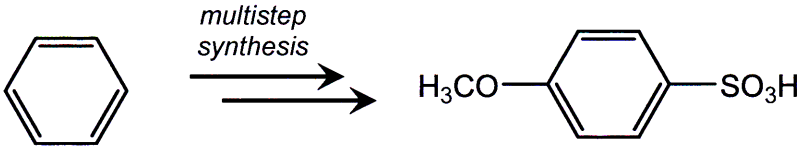


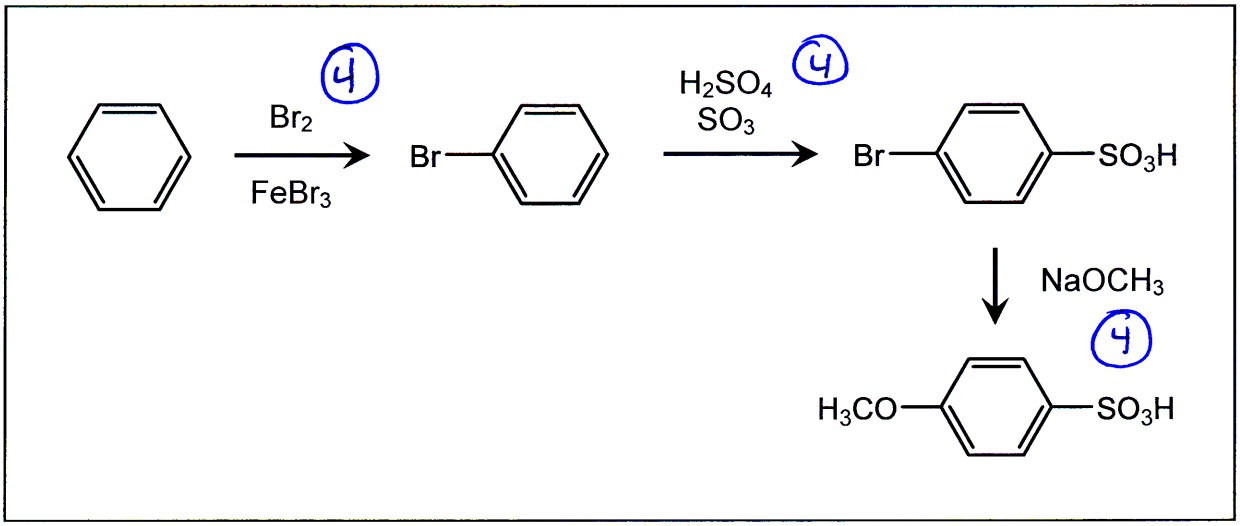


3. (12 pts) For each of the molecules below, circle whether the molecule is aromatic, anti-aromatic, or neither.

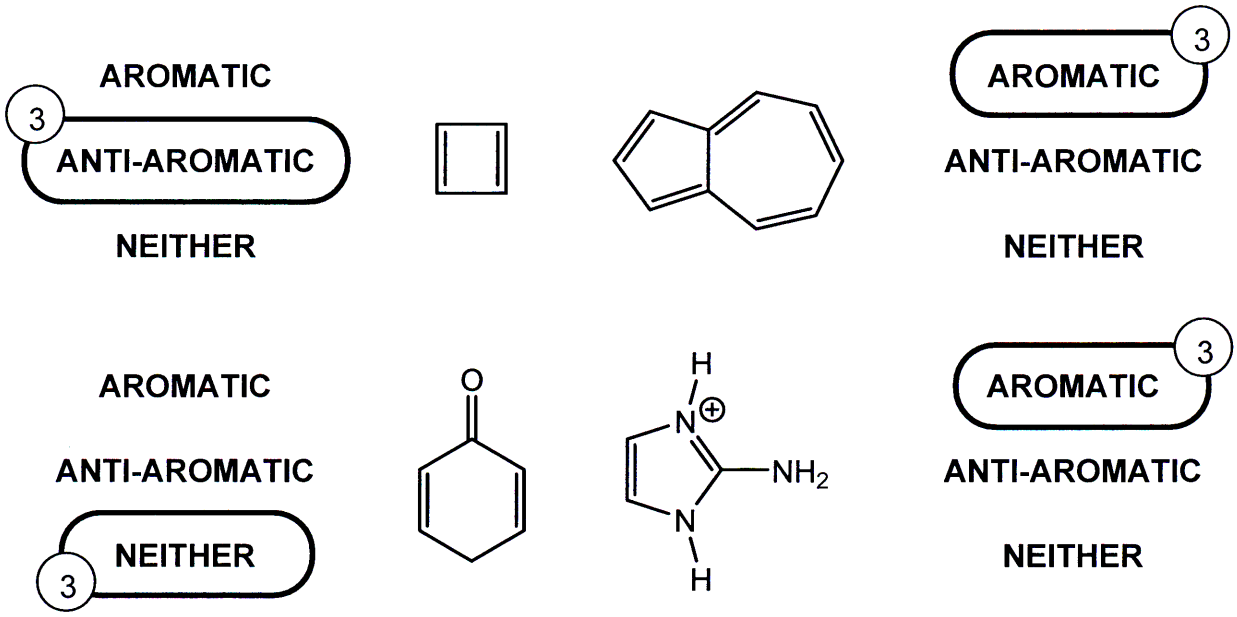


4. (12 pts) **Propose a multistep synthesis** of the product shown below, starting from benzene. You may use any reagents and reactions we've learned about in class and/or in the text. You might discover multiple answers to this problem; draw only your best (one) synthetic route. Feel free to draw an incomplete route—we will give you partial credit where we can.

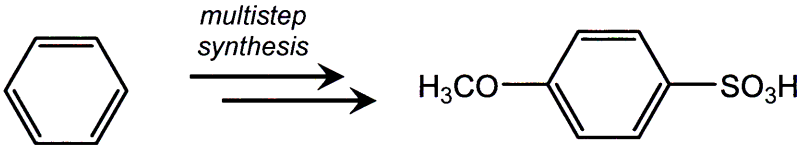


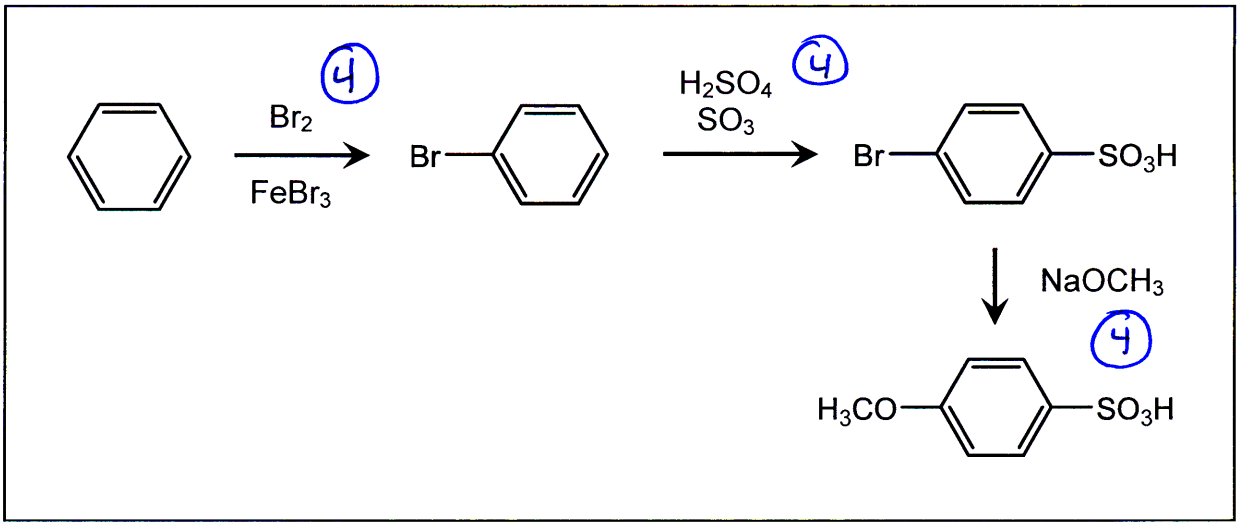


3. (12 pts) For each of the molecules below, circle whether the molecule is aromatic, anti-aromatic, or neither.



4. (12 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:

Each task is judged separately, and does not require that the synthesis makes sense, or that other tasks are correct.

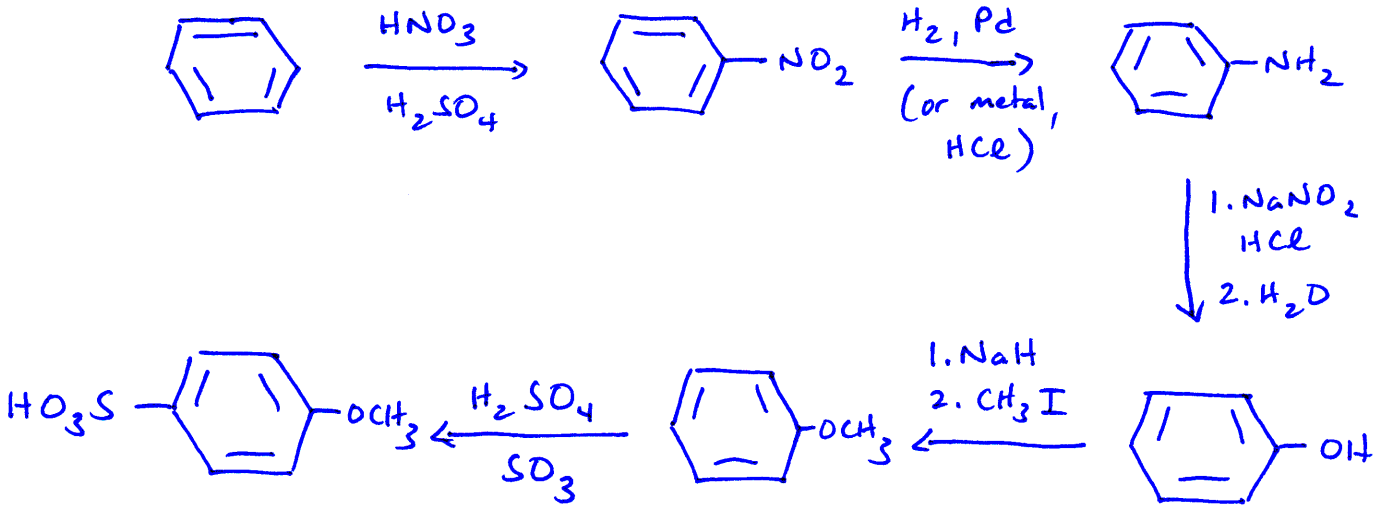
-1 point for each minor, trivial error in structures or reagents; if error propagates, points are taken off only for initial error.

-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.

ALTERNATE:



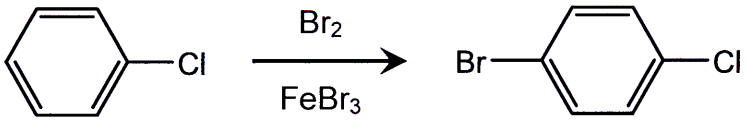
TASKS: (4) POINTS EACH.

1. INTRODUCE A TRANSFORMABLE GROUP (-Br OR $-NO_2$).
   2 POINTS PARTIAL IF REGIOCHEMISTRY IS WRONG, BUT GROUP IS CORRECT.

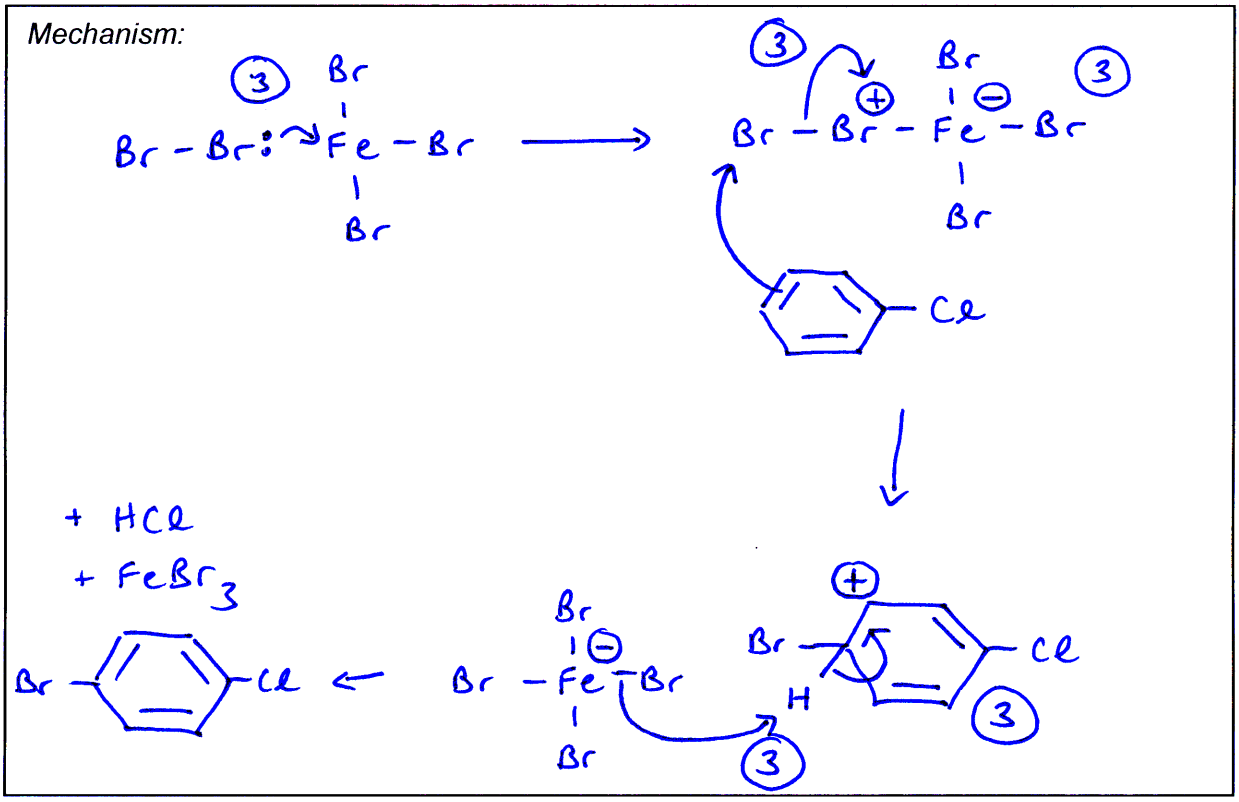
2. INTRODUCE $-SO_3H$.
   2 POINTS PARTIAL IF REGIOCHEM. IS WRONG.

3. TRANSFORM GROUP INTO $-OCH_3$.
   - IF NUCLEOPHILIC AROMATIC SUBSTITUTION, MUST HAVE π-ACCEPTOR IN PARA-POSITION.

5. (15 pts) **Draw a mechanism** (using "electron pushing") for the electrophilic aromatic substitution 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.)



Mechanism:



Rubric:

3 points for each set of pushed electron arrows.

3 points for each 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.

Things that have left for good (like HBr and $FeBr_3$ in the last step) and spectators 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.

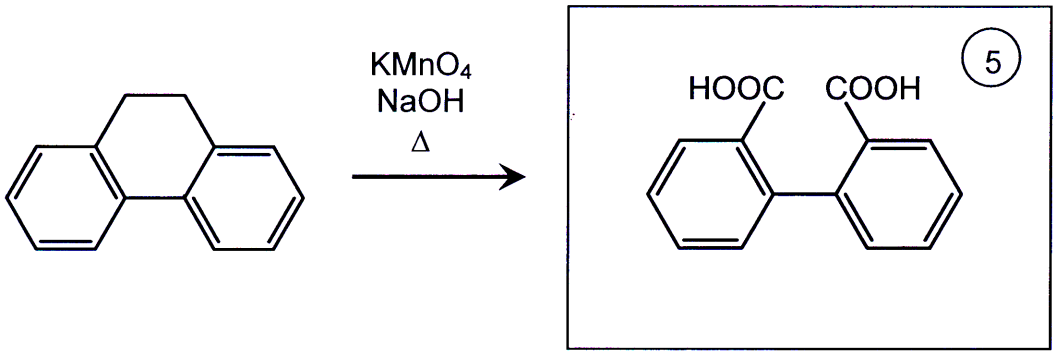
-2 points, for each arrow in each step, for errors in drawing arrows, unless the step has only one arrow. Arrow must start at an electron pair, and end at nucleus where electrons will newly interact. Can only lose points if you get them.

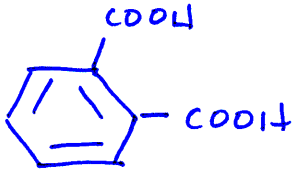
-1 point for each minor error in charge, valency, structure, etc.; if error propagates, points are taken off only for initial error.

-2 points for each use of a generic or incorrect acid/nucleophile/base. For example, in the last step you couldn't invoke H_2O or base other than $FeBr_4^-$ that you may have used in other problems.

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.

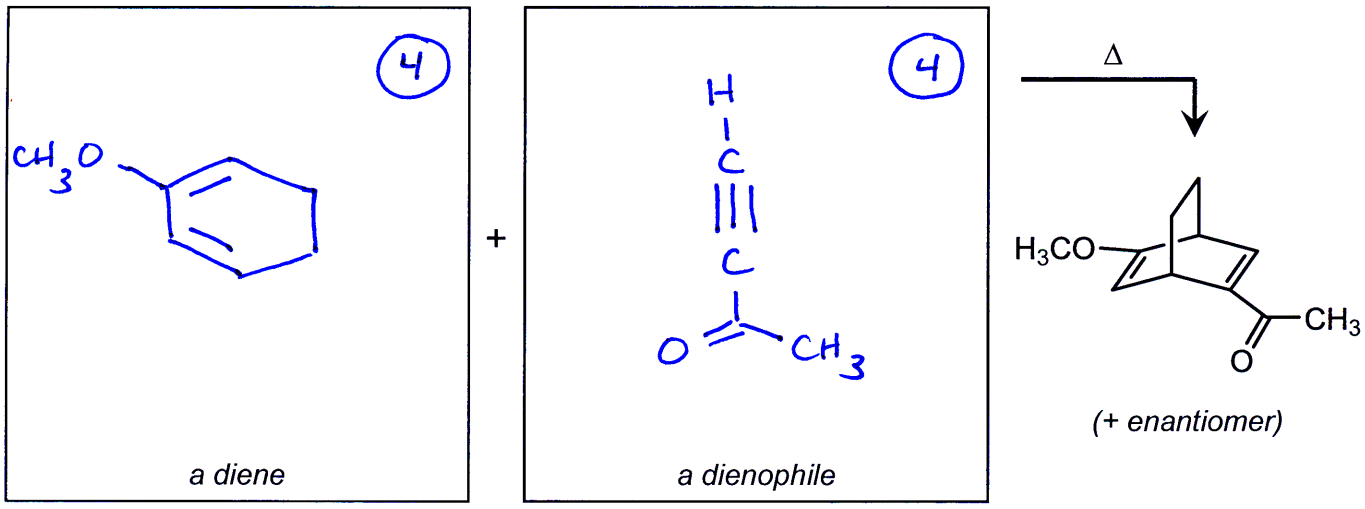
6. (18 pts) For each of the reactions below, fill in the empty box corresponding to reactants or products. Give only one answer in each box. For reactions that you expect to yield multiple products, give the major product. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note "+ enantiomer".



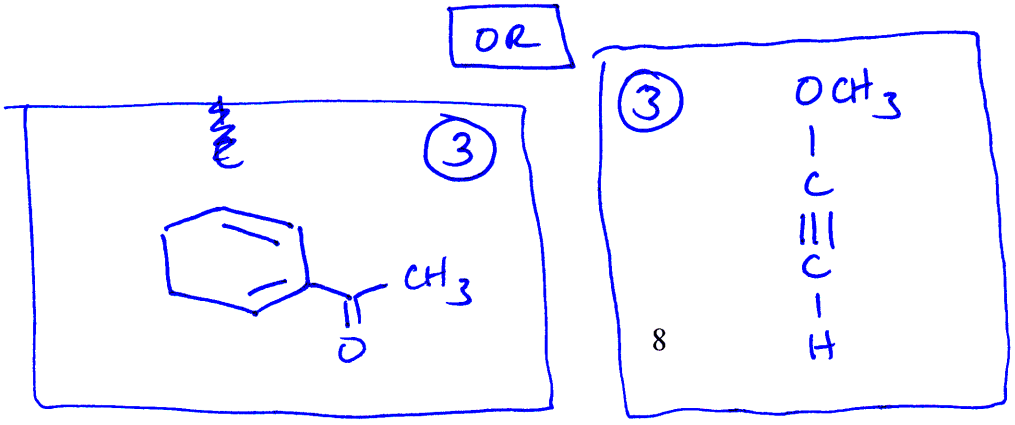
(3) PARTIAL FOR 

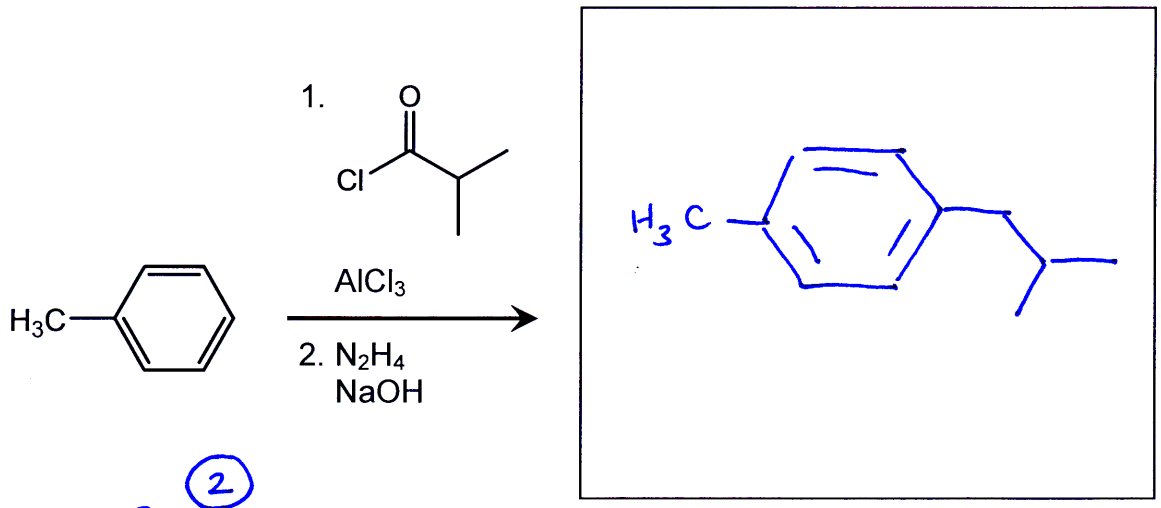
(1) FOR ANY -COOH OXIDATION PRODUCT.

-2 FOR EACH TRIVIAL ERROR IN STRUCTURE, CHARGE, ETC.

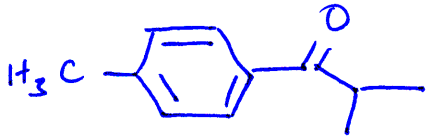


OR

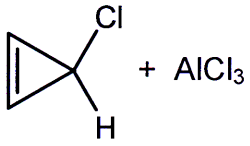




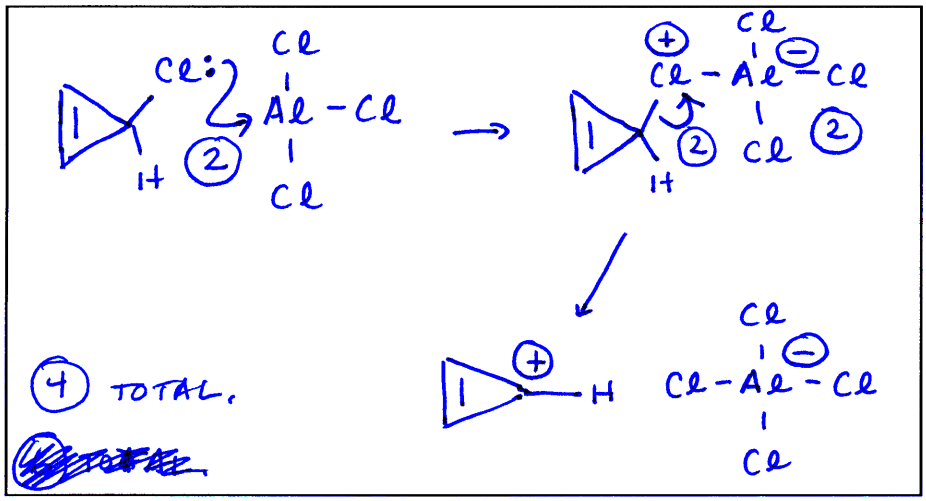
(2) PARTIAL FOR

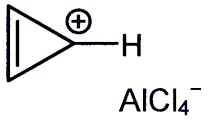


7. (17 pts) When cyclopropyl chloride (shown at right) is combined with $AlCl_3$, the result is a stable organic salt of cyclopropenyl cation ($\mathbf{C_3H_3^+}$).



a. In the box below, draw a mechanism (using "electron pushing") that illustrates the formation of $\mathbf{C_3H_3^+}$.





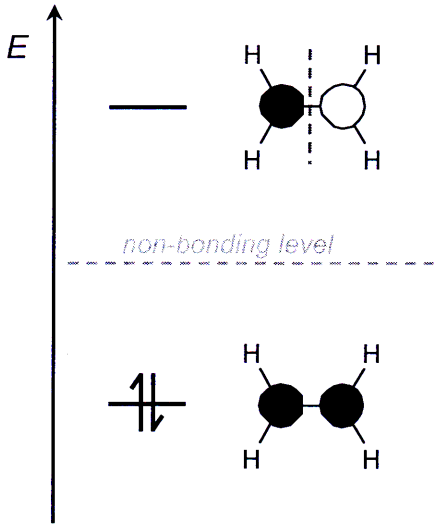
(1) PER PUSHED ARROW;

(2) FOR INTERMEDIATE.

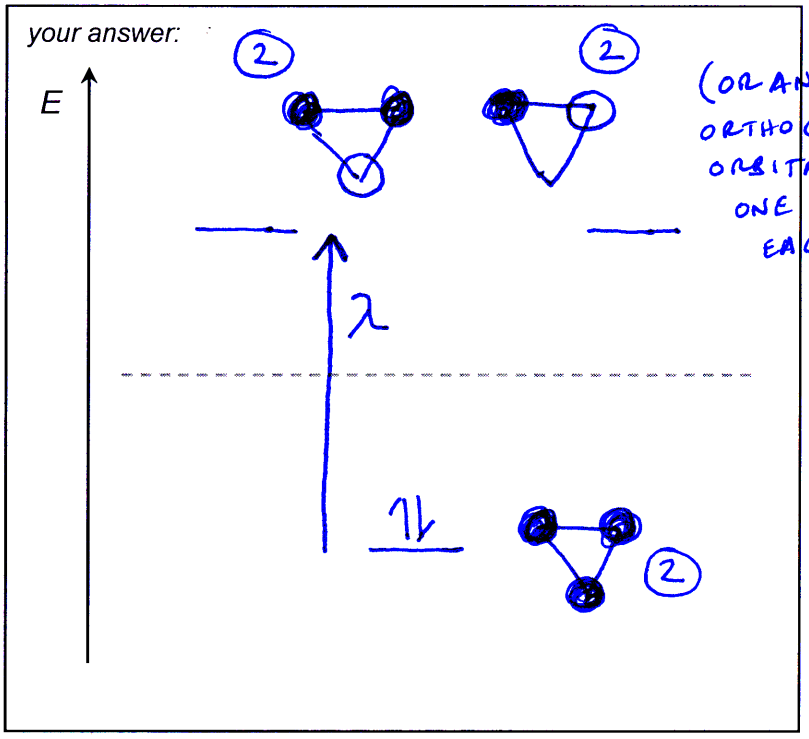
b. In the box below, draw a molecular orbital diagram for the conjugated π system in $C_3H_3^+$. In your diagram, make sure to:

- 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.

example of answer format (for C_2H_4):



your answer:



c. On your diagram above, draw a vertical arrow to illustrate an electronic transition that could be observed as an absorption peak in the UV/vis spectrum of $C_3H_3^+$. Label the arrow "λ".

(2) FOR EACH ORBITAL DRAWING. (6 TOTAL.)
(2) FOR INVERTED TRIANGLE OF 3 ORBITALS.
(2) FOR FILLING W/ 2 e^-.
(1) FOR λ ARROW FROM HOMO → LUMO.

d. Is $C_3H_3^+$ **AROMATIC** (2), **ANTIAROMATIC**, or **NON-AROMATIC** ?

(Circle one.)