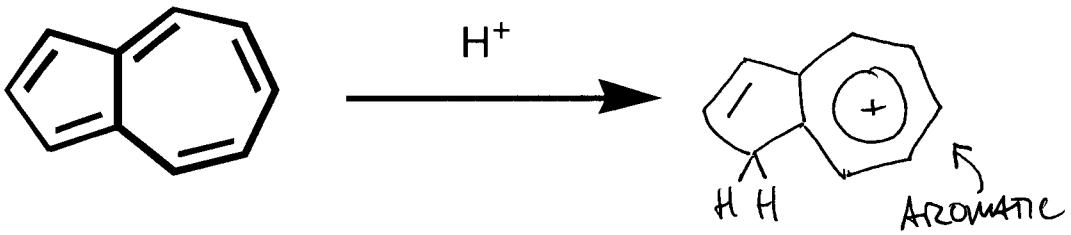
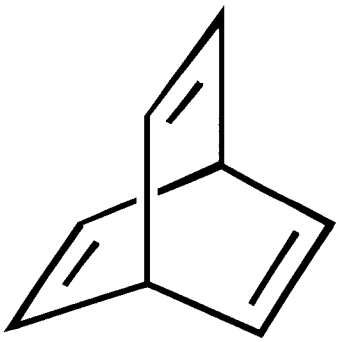
1. (12 points total)

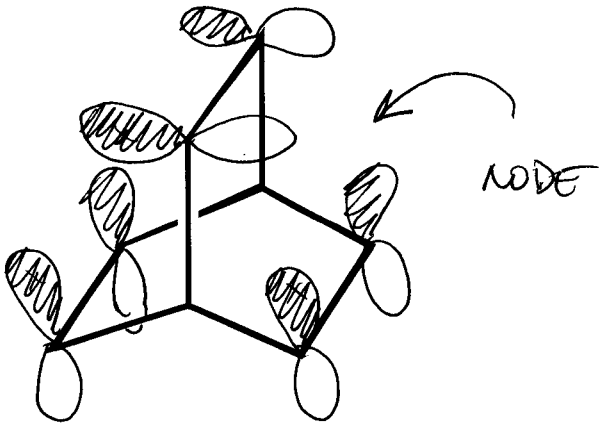
(a) **5 points**. Draw the structure of the protonated form of azulene and briefly justify your prediction.



(b) **7 points**. Barrelene is an intriguing organic molecule and was first synthesized approximately 40 years ago. Draw a three-dimensional atomic orbital representation of the π–system, using the framework given. Do you expect this molecule to show aromatic character? Use your drawing and a few appropriate words to justify your answer **in the space provided below** the structures.



barrelene

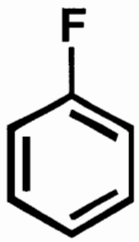


draw an atomic orbital representation of the π-system

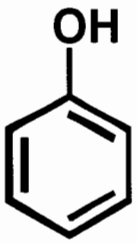
NO, NOT POSSIBLE FOR PHASES OF ALL LOBES TO LINE UP WITHOUT A NODE.

2. (18 points total)

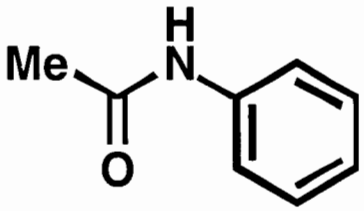
Consider the electrophilic aromatic substitution reaction between each compound below and bromine. In each case, circle the appropriate word, indicating whether the molecule shown **undergoes substitution faster or slower than benzene** would under identical conditions.



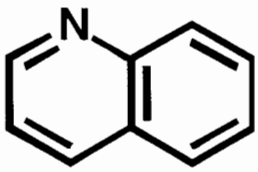
faster slower



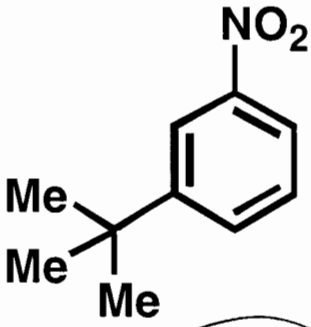
faster slower



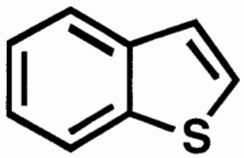
faster slower



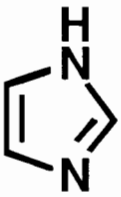
faster slower



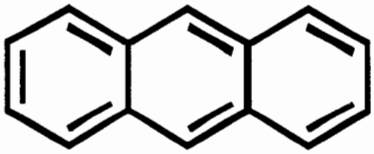
faster slower



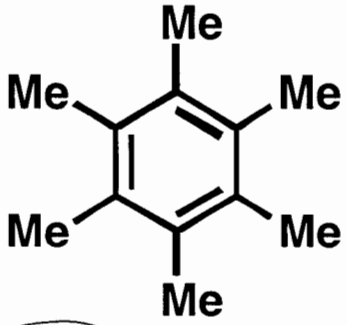
faster slower



faster slower



faster slower



faster slower

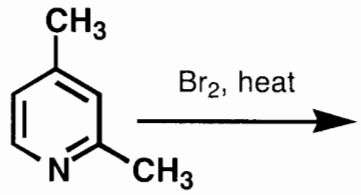
Actually, not at all since Me groups would have to leave as methyl cations. However, does react quickly with certain "E+" (electrophile) to form a semi-stable ionic species: [(CH3)6(Ph)E]+

3. (15 points)

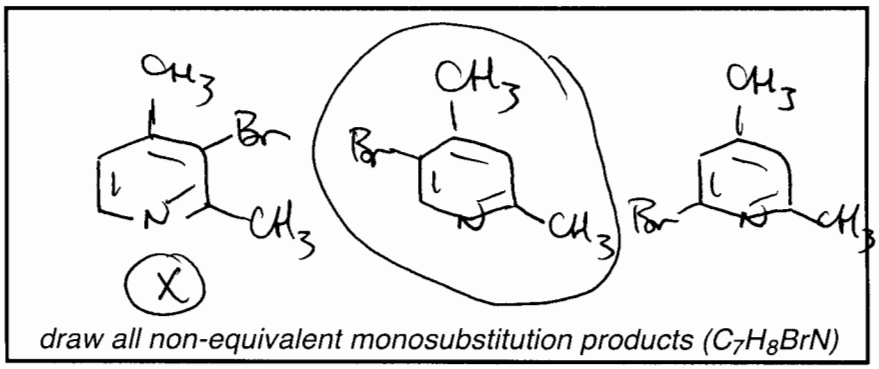
(a) For **both** of the reactions below, draw the structure of **all non-equivalent electrophilic aromatic monosubstitution products**, whether or not they are actually formed in the reaction.

(b) Next, for **each** case, **circle** the major product.

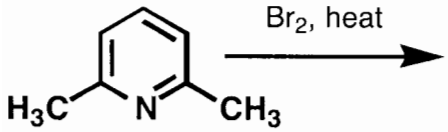
(c) Finally, which reaction would you expect to be **more selective**? That is, which reaction will form the greater percentage of its major product? Explain.



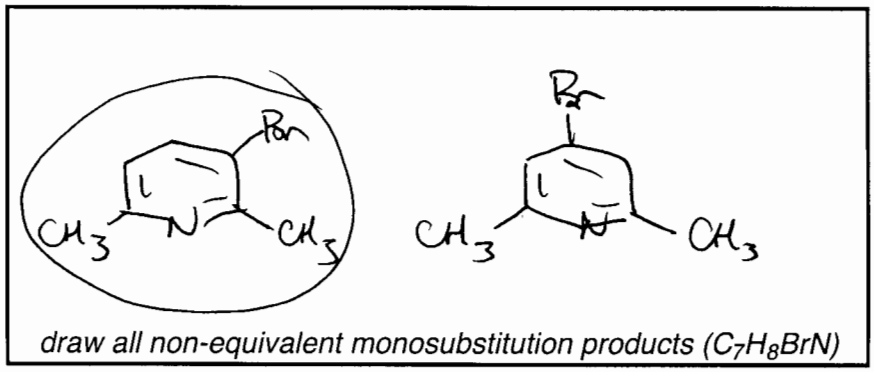
reaction A



draw all non-equivalent monosubstitution products (C_7H_8BrN)



reaction B



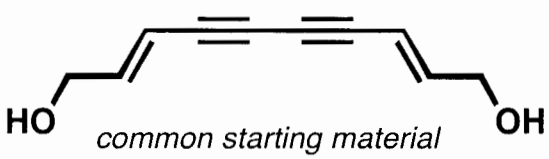
draw all non-equivalent monosubstitution products (C_7H_8BrN)

Which is the **more selective** reaction (reaction **A** or reaction **B**)? Explain.

(B) IN A, BOTH CIRCLED PRODUCT AND (X) WILL FORM. IN B, ONLY CIRCLED PRODUCT WILL FORM.

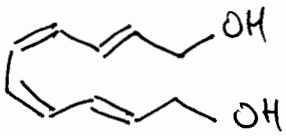
4. (20 points) K.C. Nicolaou's research group synthesized many of the endiandric acid natural products using a common starting material (the diol shown), and subjecting it to 3 reactions in sequence, 2 of which were pericyclic reactions.

Draw the structure of the two products in the boxes provided, **clearly** showing relative stereochemistry, where appropriate. Where indicated, **write the number of electrons** involved each pericyclic reaction, and indicate whether the mode of cyclization is **disrotatory or conrotatory** by **circling** the correct word. Finally, **redraw** the final product of this sequence, **clearly showing its relative stereochemistry** (All products in this sequence are formed as racemates; either correct relative stereochemistry will receive full credit).



common starting material

H_2
Lindlar catalyst



structure of product ($C_{10}H_{14}O_2$)

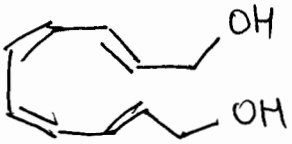
8

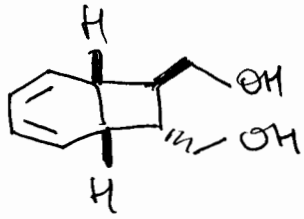
number of electrons

heat

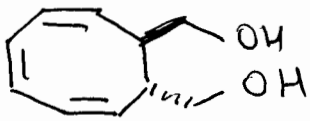
conrotatory disrotatory

(circle the correct word)





*redraw the structure of the final product, and **clearly** show its relative stereochemistry*



structure of product ($C_{10}H_{14}O_2$)

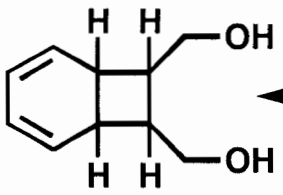
heat

6

number of electrons

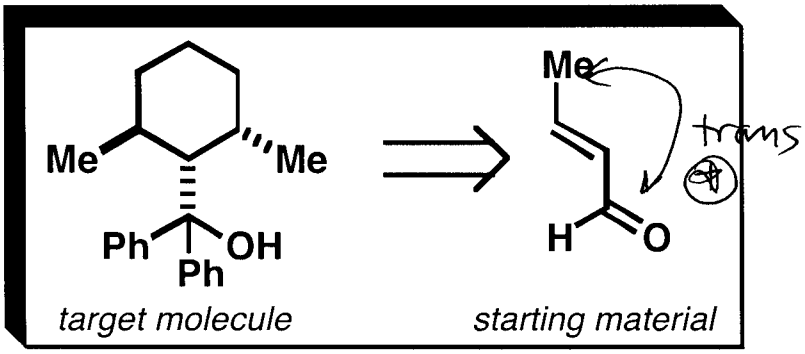
conrotatory disrotatory

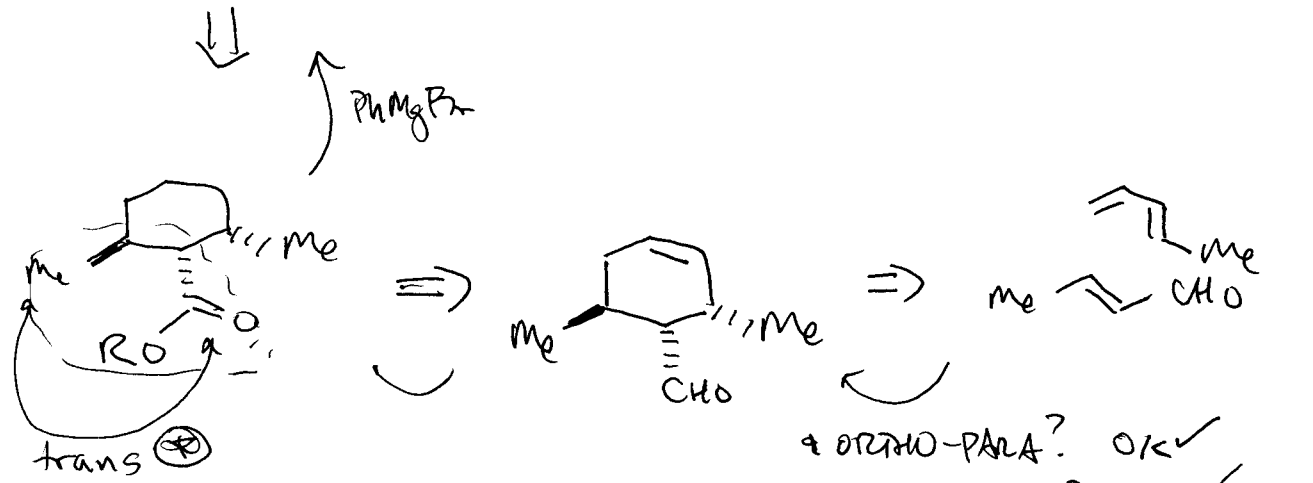
(circle the correct word)



final product

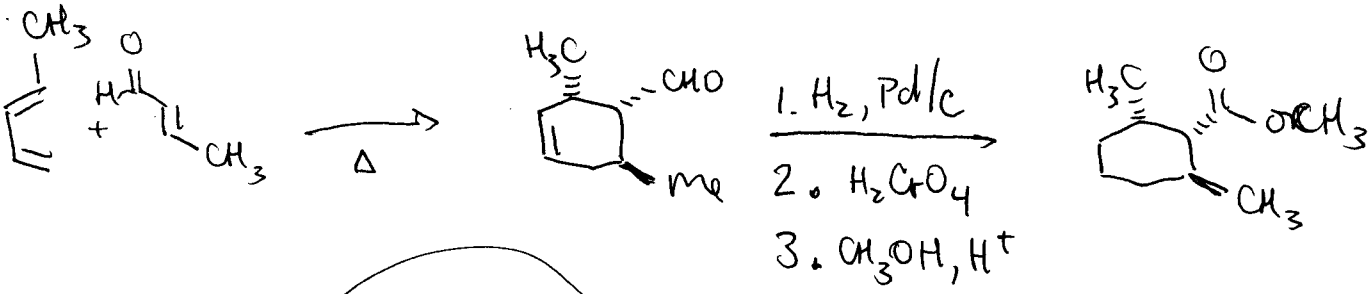
5. (20 points) In the space provided, propose an efficient synthetic route to the *target molecule* shown in the box from the *starting material* shown next to it. Assume that your "stockroom" of available reagents includes **any inorganic compounds**, **benzene**, **triphenylphosphine**, and **any** organic compound containing **3** or fewer carbon atoms. Your synthesis should provide a way to control the **relative stereochemistry** of the target molecule (but not the **absolute stereochemistry**). Write your synthesis in the **forward direction**, showing all necessary reagents and relevant reaction conditions for each step.

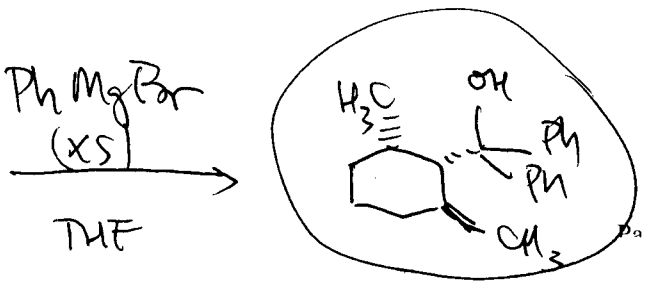




⇒ STARTING MATERIAL

- ORTHO-PARA? OK ✓
- ENDO RULE? OK ✓
- STEREOSPECIFIC wrt DIENOPHILE? OK ✓
- STEREOSPECIFIC wrt DIENE? N/A





6. (15 points) In each box provided, draw the structure of the product (or products) of each of the reactions shown.