

Massachusetts Institute of Technology
Organic Chemistry 5.13

Tuesday, April 24, 2001

Prof. Timothy F. Jamison
Prof. Stephen L. Buchwald

Hour Exam #3

Name

SOLUTIONS

(please both **print** and **sign** your name)

Recitation Instructor

Directions: Closed book exam, no books, notebooks, notes, etc. allowed. Calculators are not allowed. However, molecular model sets are permitted.

Please read through the entire exam before beginning, in order to make sure that you have all the pages and in order to gauge the relative difficulty of each question. Budget your time accordingly.

Show all of your work if you wish to receive partial credit.

You should have **10** pages total: **7** exam pages including this page, **1** page of reference information, and **2** blank pages for scratchwork.

Question:

Grader:

1. _____ / 12 points

2. _____ / 18 points

3. _____ / 15 points

4. _____ / 20 points

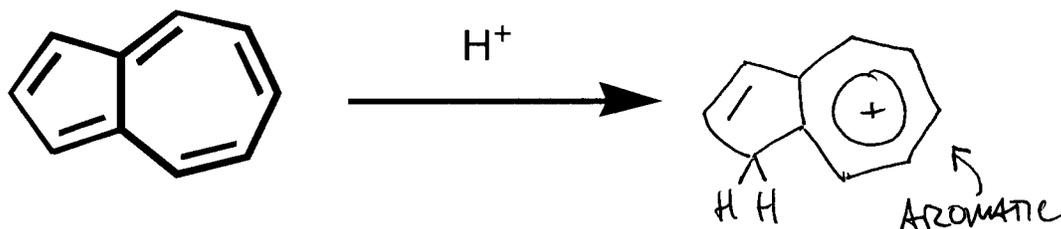
5. _____ / 20 points

6. _____ / 15 points

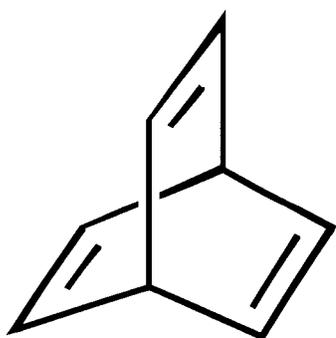
Total: _____ / 100 points

1. (12 points total)

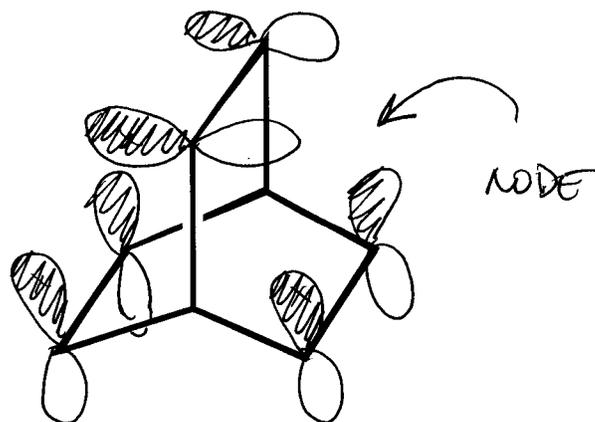
- (a) **5 points.** Draw the structure of the protonated form of azulene and briefly justify your prediction.



- (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

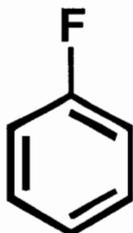


draw an atomic orbital
representation of the π -system

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

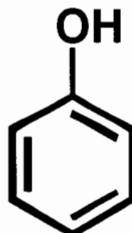
2. (18 points total)

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.



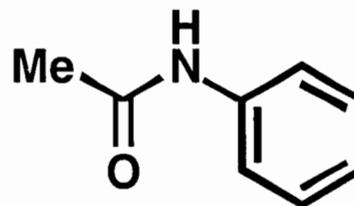
faster

slower



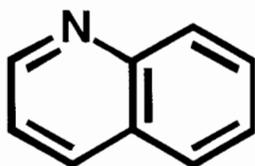
faster

slower



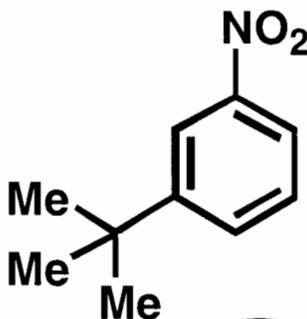
faster

slower



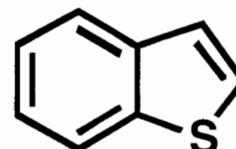
faster

slower



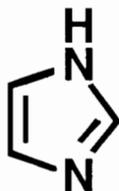
faster

slower



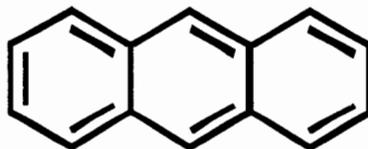
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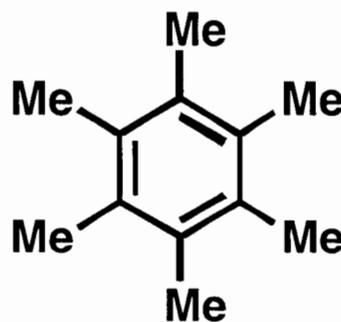
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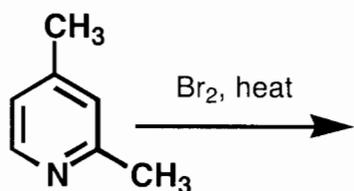
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slower

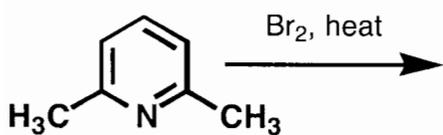
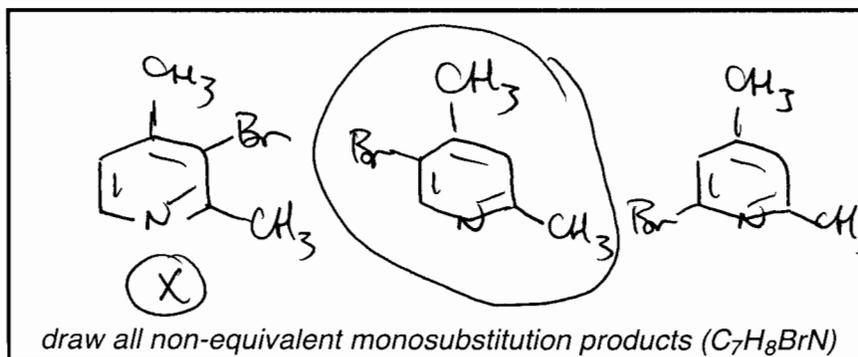
Actually, not at all since Me groups would have to leave as methyl cations. However, does react quickly with certain "E⁺" (electrophile) to form a semi-stable ionic species: [(CH₃)₆(Ph)E]⁺

3. (15 points)

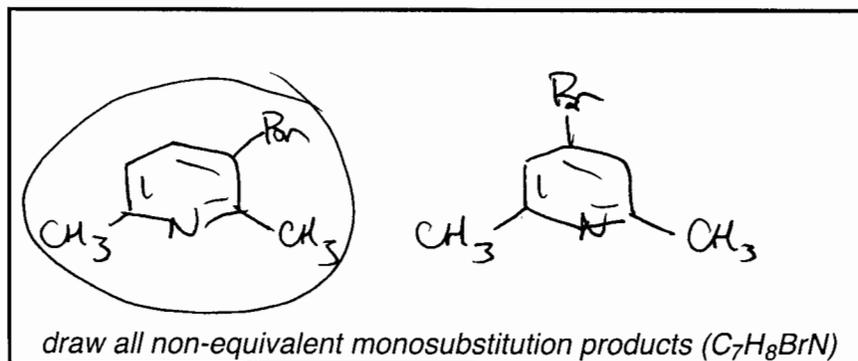
- (a) For **both** of the reactions below, draw the structure of **all non-equivalent electrophilic aromatic monosubstitution products**, whether or not they are actually formed in the reaction.
 (b) Next, for **each case**, **circle** the major product.
 (c) Finally, which reaction would you expect to be **more selective**? That is, which reaction will form the greater percentage of its major product? Explain.



reaction A



reaction B

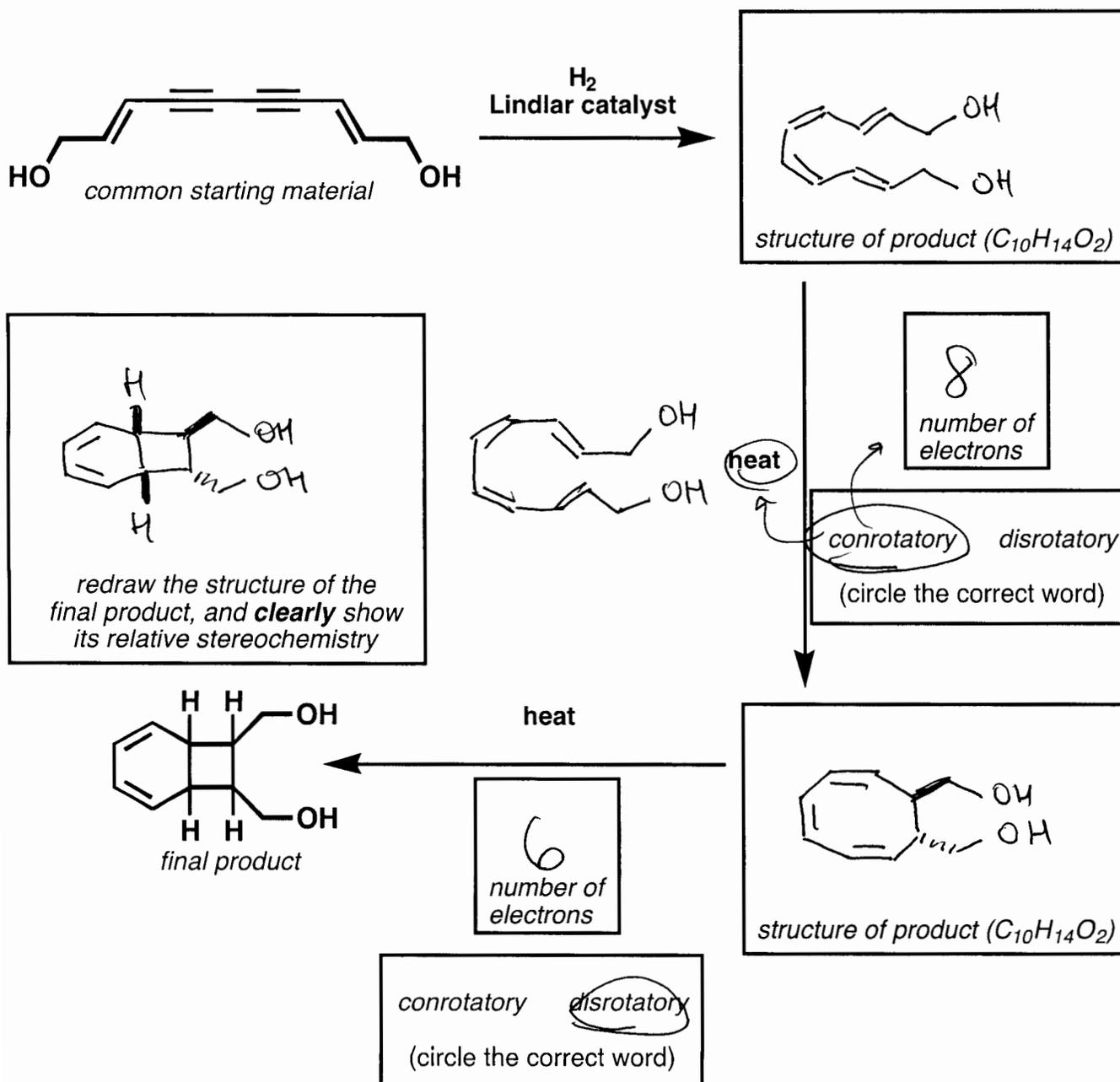


Which is the **more selective** reaction (reaction **A** or reaction **B**)? Explain.

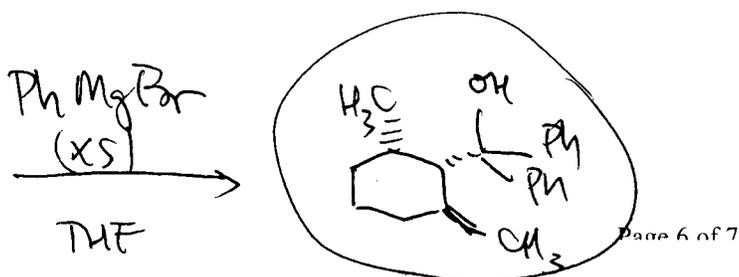
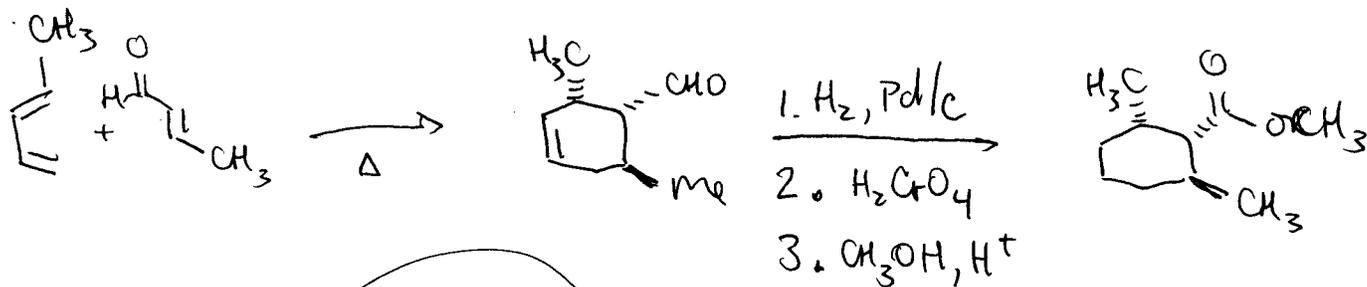
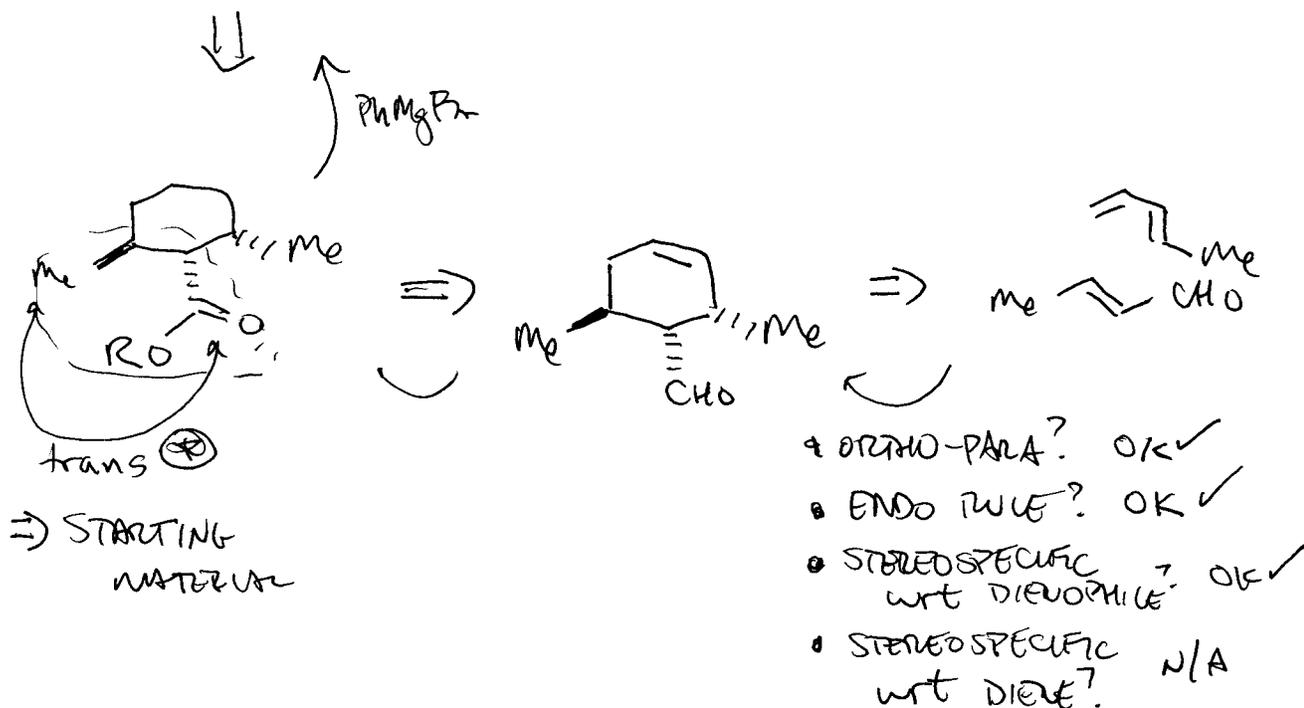
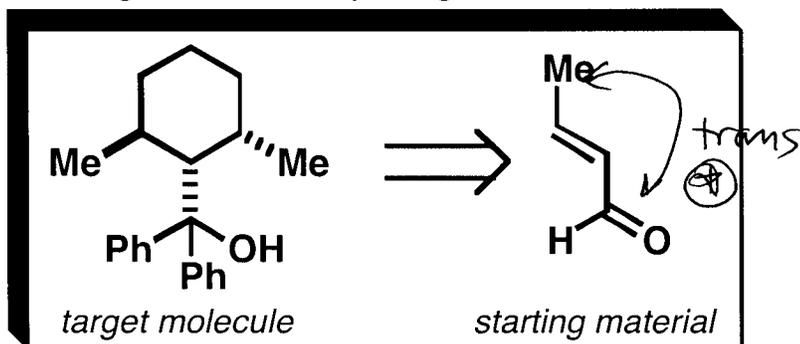
B. IN A, BOTH CIRCLED PRODUCT AND X WILL FORM. IN B, ONLY CIRCLED PRODUCT WILL FORM.

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).



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.



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

