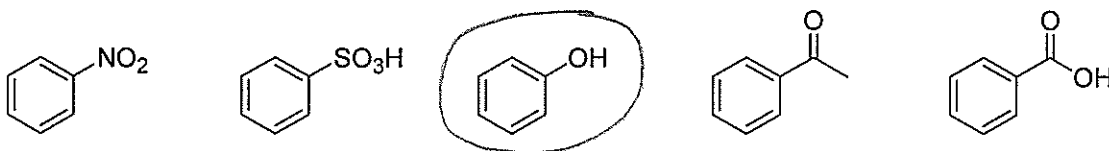


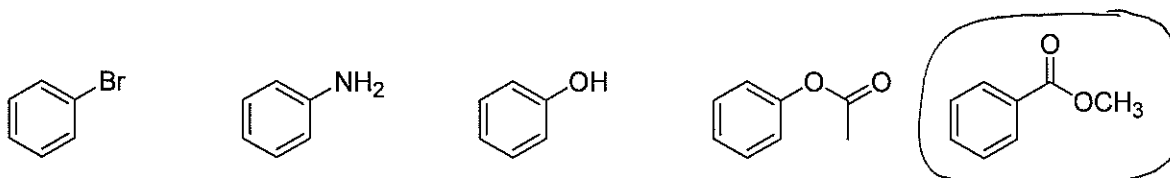
Key - 3331 Exam 1
Summer 09
Munger

1. Circle the best answer for each question. (20 pts)

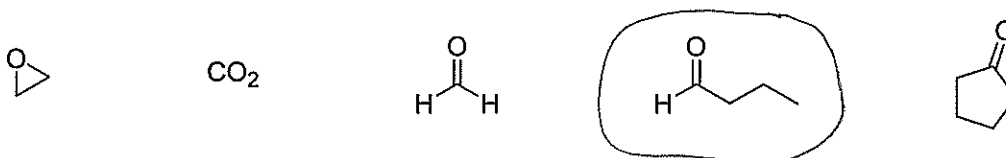
1a. Which of the following substituted benzenes is activated towards electrophilic aromatic substitution?



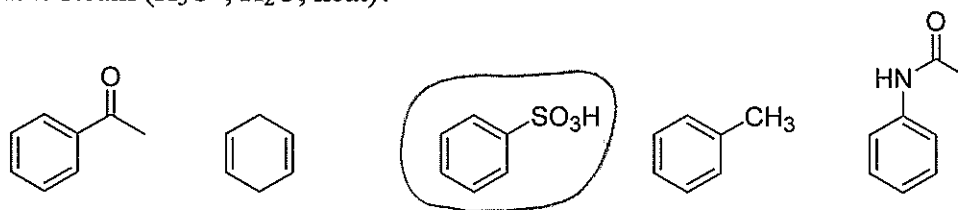
1b. Which of the following substituted benzenes will **not** undergo a Friedel-Crafts alkylation?



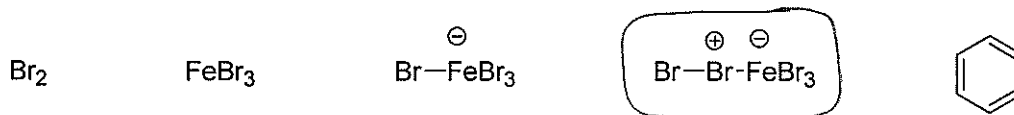
1c. Which of these compounds, when reacted with a Grignard reagent followed by aqueous workup, will produce a secondary alcohol?



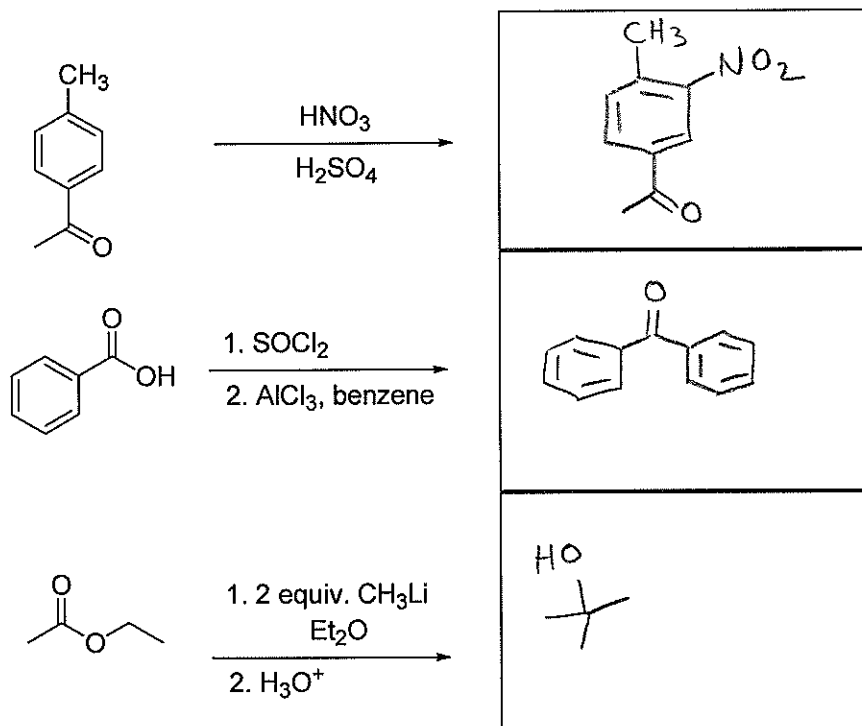
1d. Which of the following compounds can be converted to benzene when treated with acidic steam (H_3O^+ , H_2O , heat)?



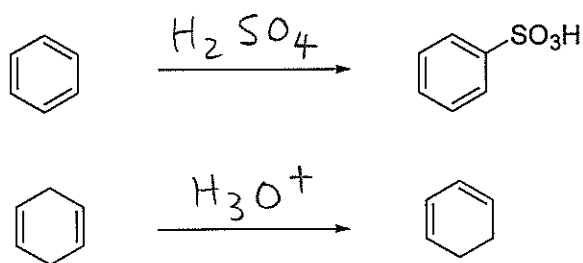
1e. What is the electrophile in the bromination of benzene?



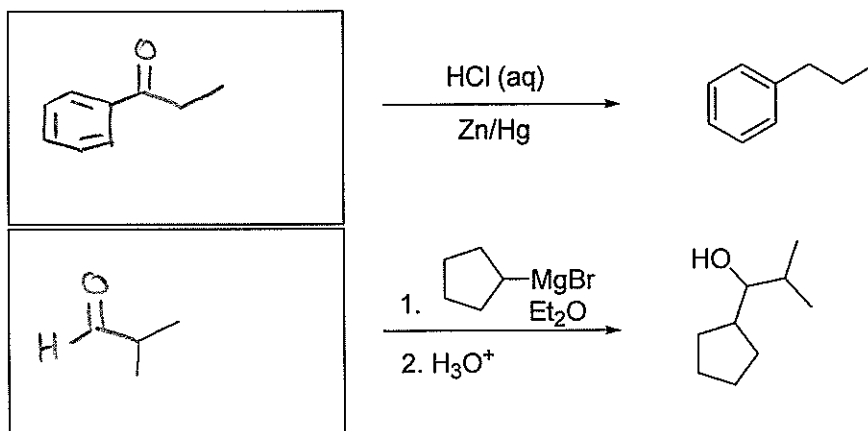
2a. Provide the major organic product for each of the transformations shown here. (9pts)



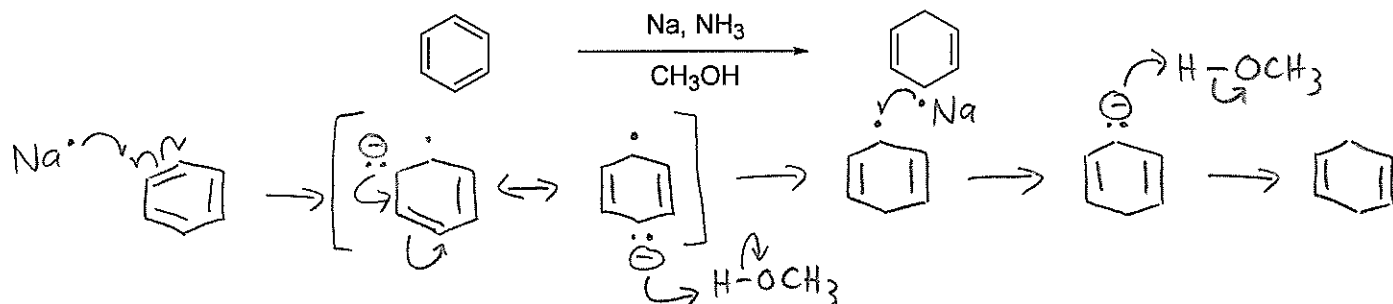
2b. Provide the missing reagents to accomplish each of the transformations shown here. (6 pts)



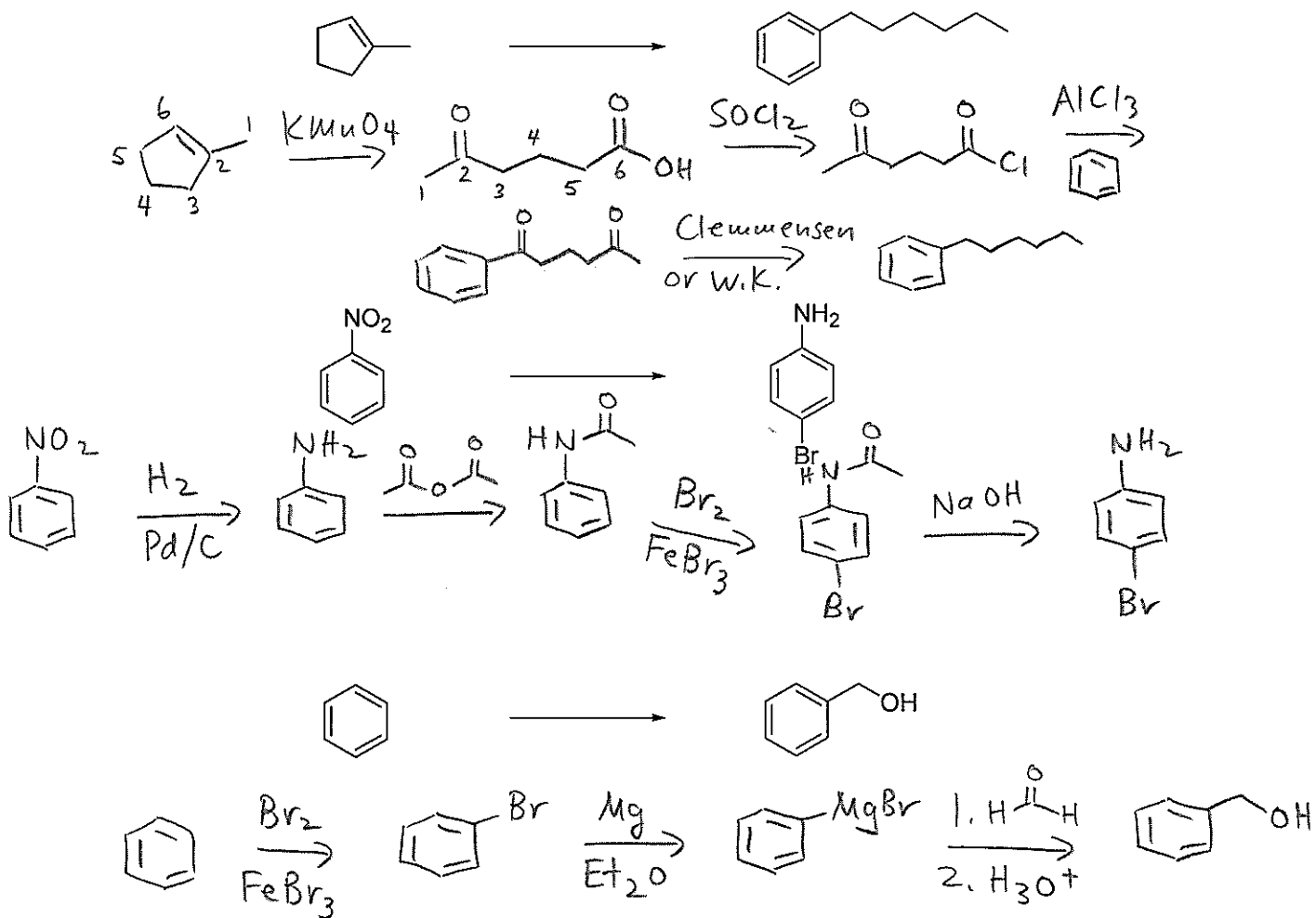
2c. Provide the missing starting material for the transformations shown here. (6 pts)



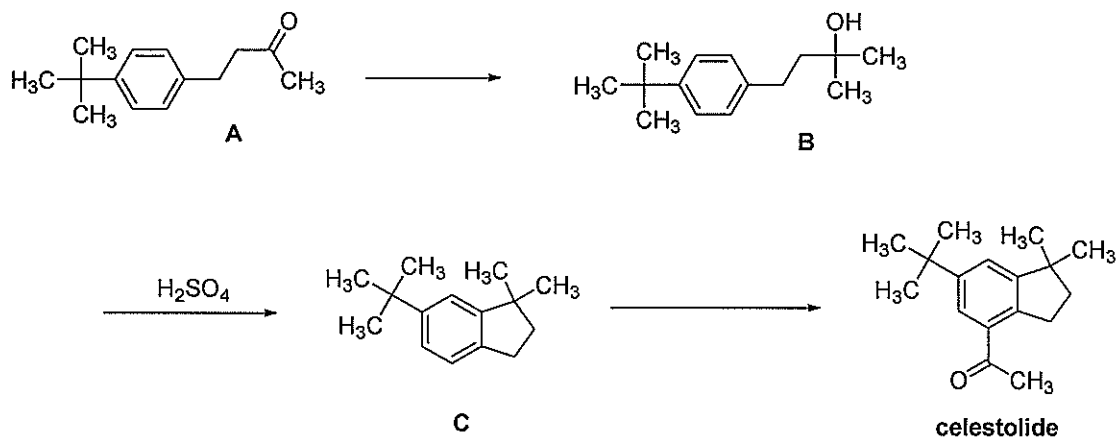
3a. Draw a mechanism for the transformation shown here. Include all necessary single electrons and lone pairs, curved arrows, and non-zero formal charges for full credit. (10 pts)



3b. Design a multi-step synthesis for **any two of the following three transformations**. Provide the reagents needed for each step and the product of each step. Do not draw any mechanisms. If you simply write a list of reagents without showing the product of each step, you will not receive full credit. (16 pts)

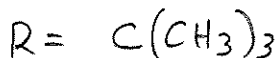
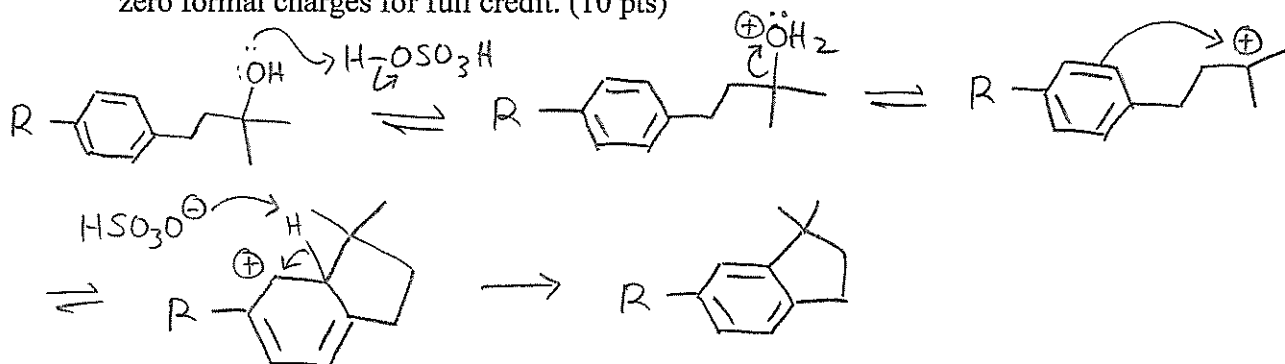


4. A compound called *celestolide* is a perfuming agent with a musky odor. Part of the synthesis of celestolide is shown here:

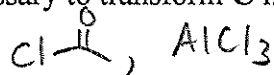


4a. Indicate the reagent(s) necessary to transform **A** into **B** (2 pts):
 1. MeLi or MeMgBr
 2. H₃O⁺

4b. Intermediate **B** reacts with sulfuric acid to produce **C**. Draw a mechanism to show how **B** is transformed into **C**. Include all necessary electrons, curved arrows, and non-zero formal charges for full credit. (10 pts)



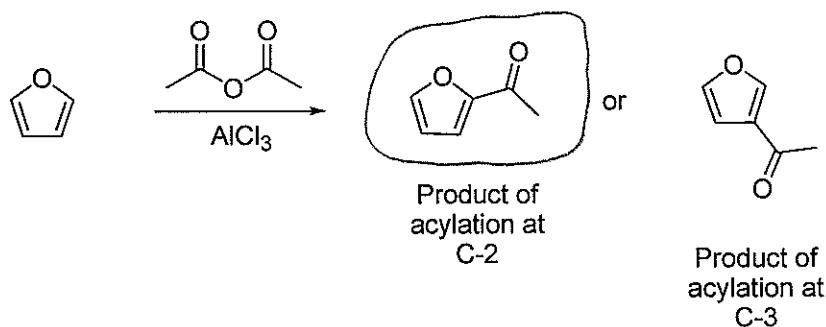
4c. Indicate the reagent(s) necessary to transform **C** into celestolide. (2 pts)



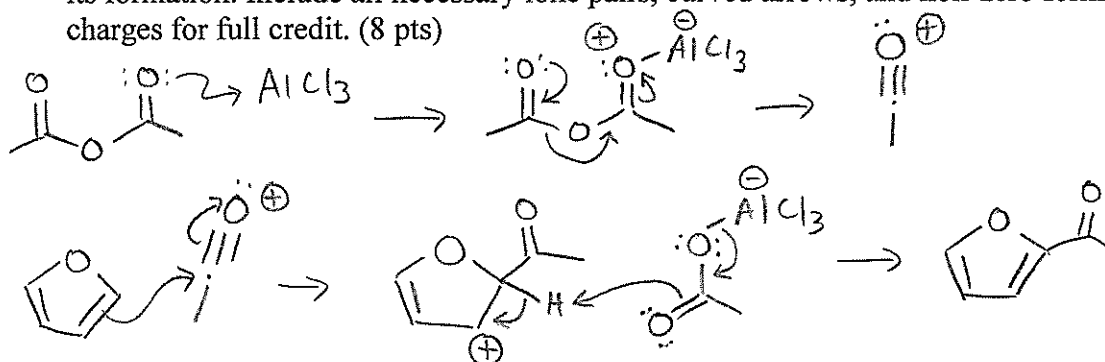
4d. Explain the regiochemistry of the reaction that transforms **C** into celestolide. Why does the carbonyl group attach at that position and not at the others available? (3 pts)

It has the least amount of steric hindrance

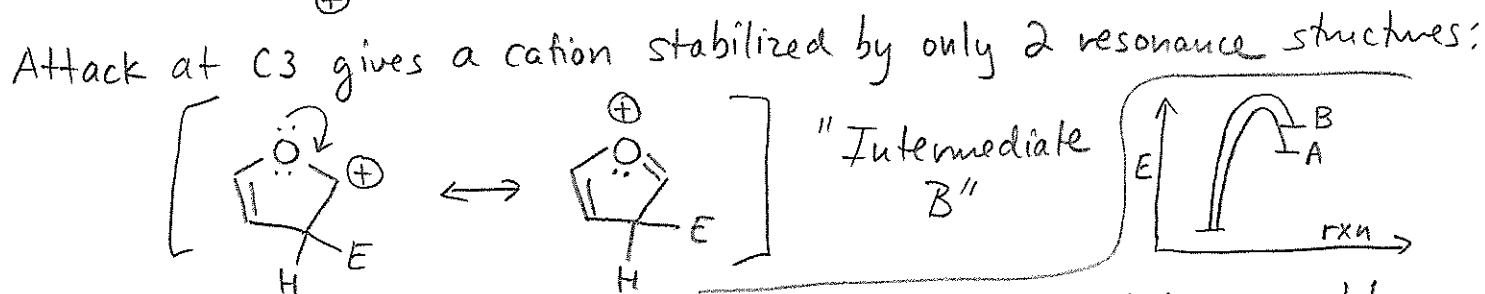
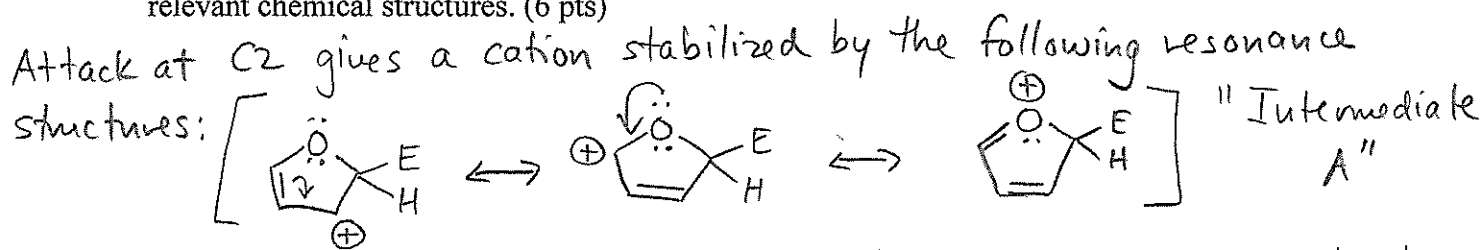
5. The acylation of furan occurs under typical Friedel-Crafts acylation conditions. The acyl group can either attach at C-2 or C-3:



5a. Which is the major product? **Circle it above (2 pts)**, and draw a mechanism for its formation. Include all necessary lone pairs, curved arrows, and non-zero formal charges for full credit. (8 pts)



5b. Use the Hammond postulate to explain why the product you chose is favored over the other possible product of the reaction shown above. Support your answer by drawing relevant chemical structures. (6 pts)



Thus, since this step is endothermic, the transition state resembles the product of the step, and factors that stabilize these products also stabilize the transition states leading to them. The transition state leading to "A" is lower in energy than that leading to "B", so path A has a lower E_a and is favored in the reaction.