*CHEM 112B*
*Spring 2015*

*Instructor: Felix Fischer*

# Midterm Examination II

*Thursday, April 2, 2015*

| | |
|---|---|
| Name: | |
| Student ID: | |
| GSI: | |

| | | |
|---|---|---|
| (1) | | 8 points |
| (2) | | 8 points |
| (3) | | 16 points |
| (4) | | 12 points |
| (5) | | 20 points |
| (6) | | 16 points |
| (7) | | 20 points |
| Total | | 100 points |

YOUR EXAM SHOULD HAVE **14** PAGES

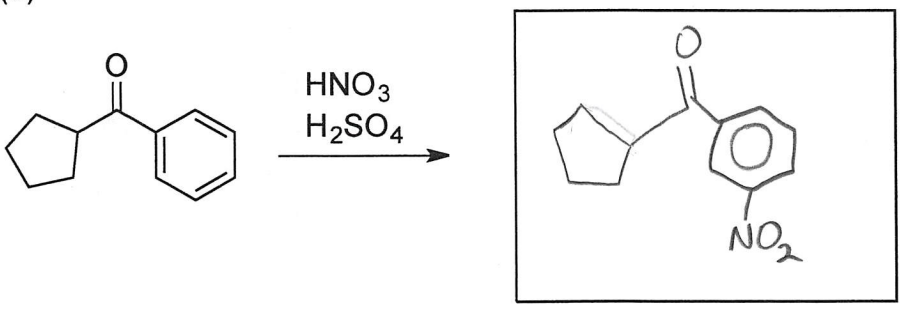
**NOTE 1:** PLEASE START BY WRITING YOUR NAME AND STUDENT ID ON THE COVER PAGE AND YOUR INITIALS ON THE TOP RIGHT OF EACH OF THE OTHER PAGES.

**NOTE 2:** PLEASE WRITE ALL ANSWERS IN THE SPACES PROVIDED. ONLY THESE WILL BE GRADED. IF YOU NEED MORE SPACE USE THE THREE SCRATCH PAPERS PROVIDED ON PAGE 12–14. PLEASE LEAVE A NOTE ON THE RESPECTIVE PAGE OF THE EXAM IF YOU WRITE AN ANSWER ON THE SCRATCH PAPER.

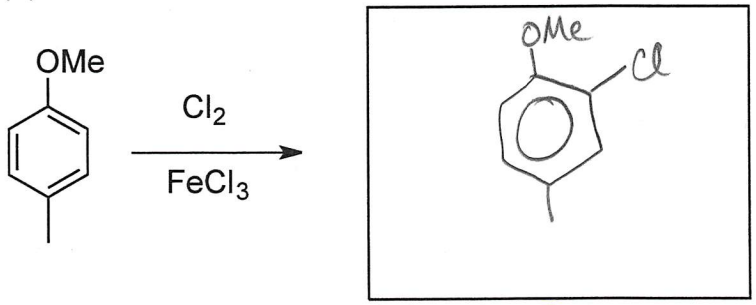
**NOTE 3:** PLEASE WRITE AND DRAW CLEARLY.

1) (8 points) Predict the major product of the following reactions.

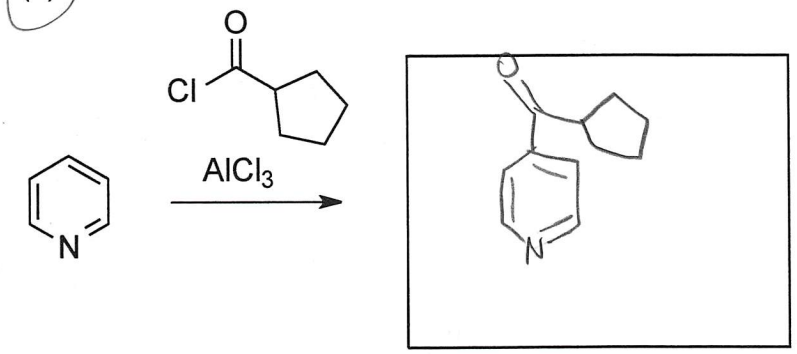
(a)



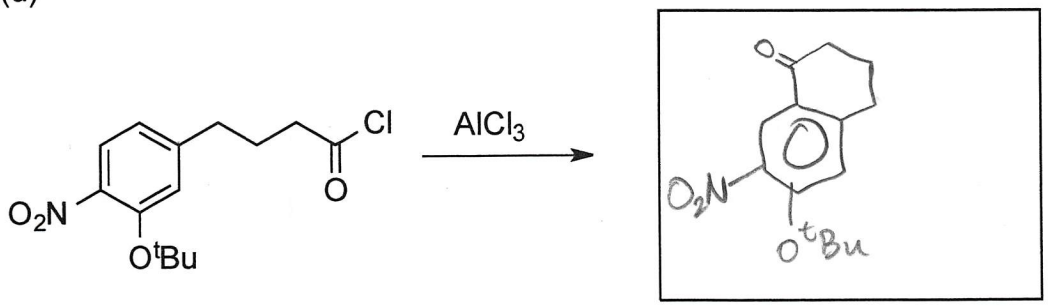

(b)




(c)

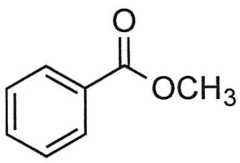



(d)

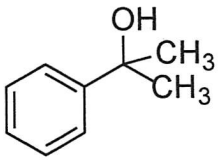


2) (8 points) Indicate how the following compounds could be prepared from the given starting materials. In some cases you might need more than one reagent/reaction step.

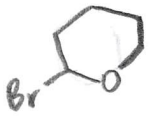
(a)

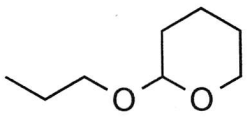


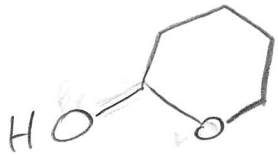

1. $H_3CMgBr$, ether
2. $HCl$, $H_2O$



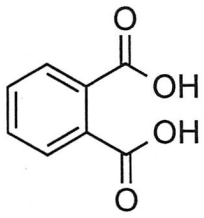

(b)


1. NaH
2. 

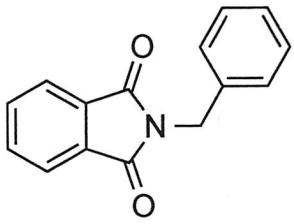



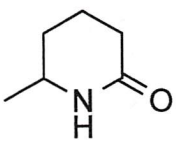

(c)



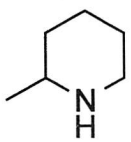

1. $PCl_3$ (2 eq)
2. $H_2N$—Ph (2 eq)




(d)

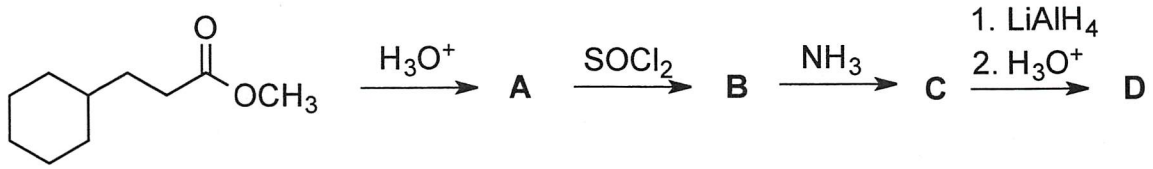



1. $LiAlH_4$, ether
2. $HCl$, $H_2O$

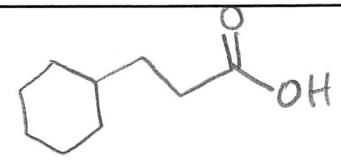


3) (16 points) Draw the major intermediates/products (**A–H**) for each of the following sequences of reactions.

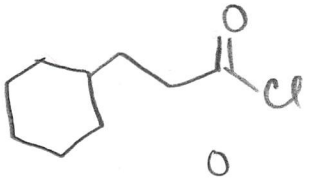
a)



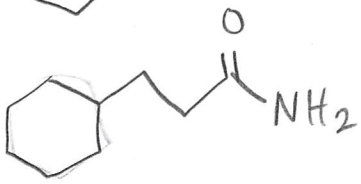

A:




B:

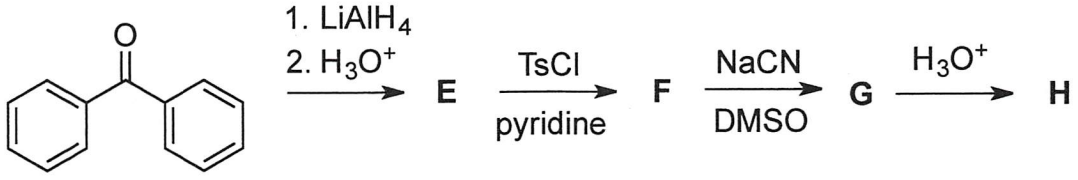


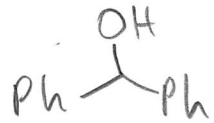

C:

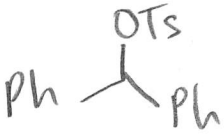


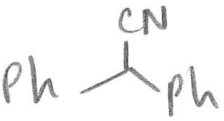

D:

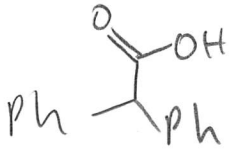
b)

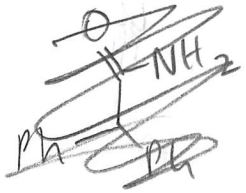



E: 

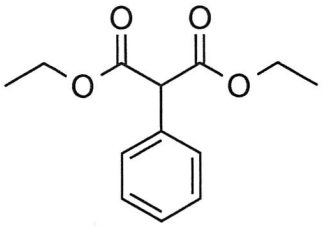
F: 

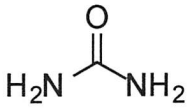
G: 

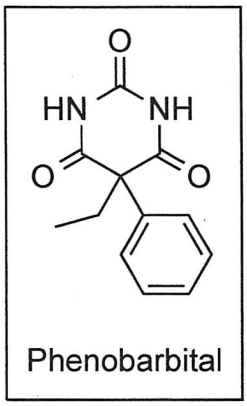
H: 



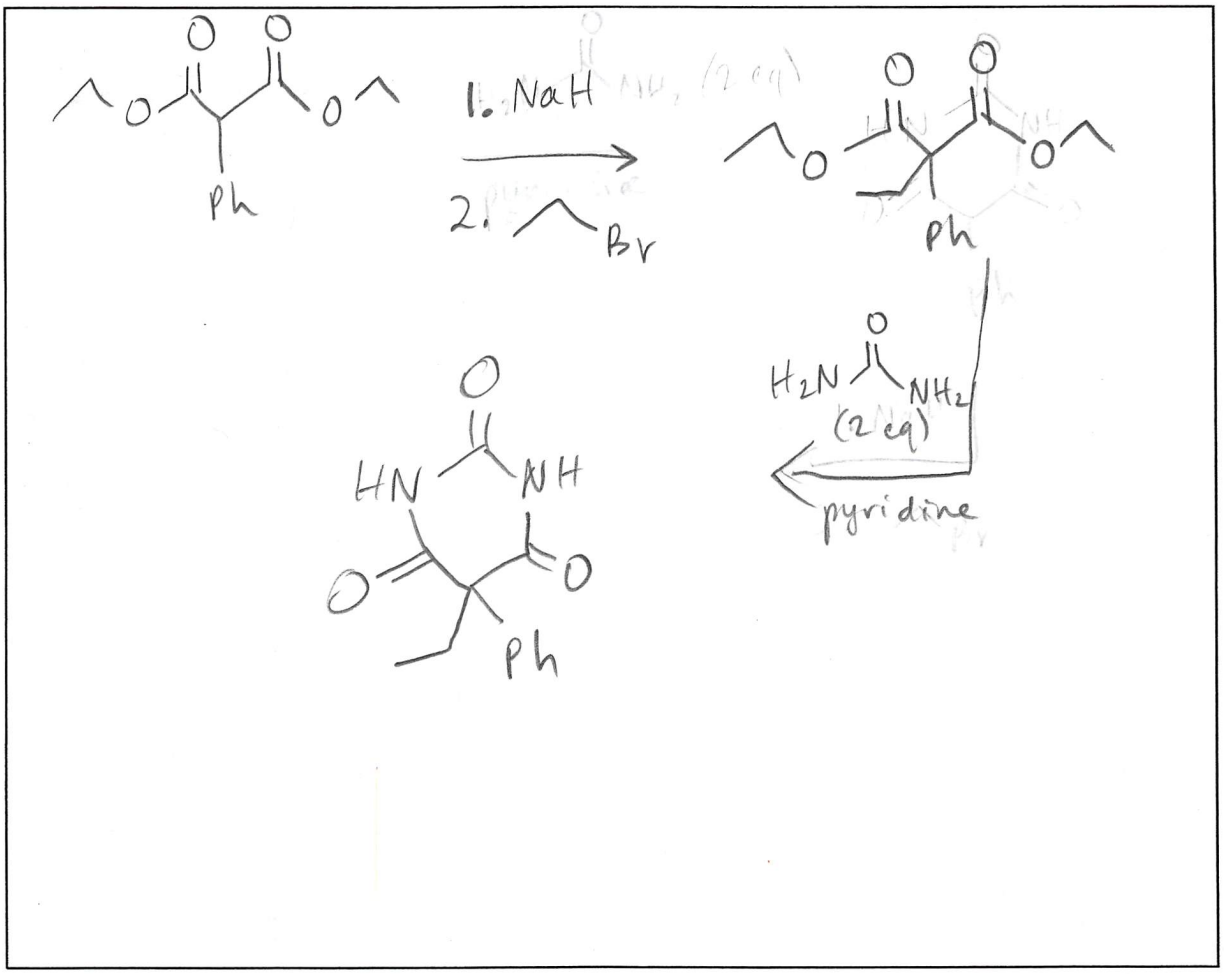
4) (12 points) Barbiturates are fast-acting sedatives for anesthesia and have been widely used as anti-seizure medication. Propose a synthesis of Phenobarbital starting from diethyl phenylmalonate, urea, and any other reagent of your choice (2 or less carbon atoms). Provide the reagents for each step. You do not need to include arrow-pushing mechanisms.





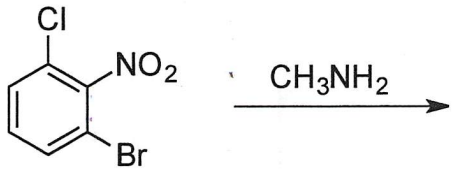


Phenobarbital

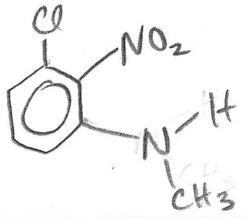


5) (20 points) Identify the products of the following reactions. Draw a <u>detailed curved arrow mechanism</u> that leads to the major product. Clearly indicate resonance structures, and charges in the intermediates

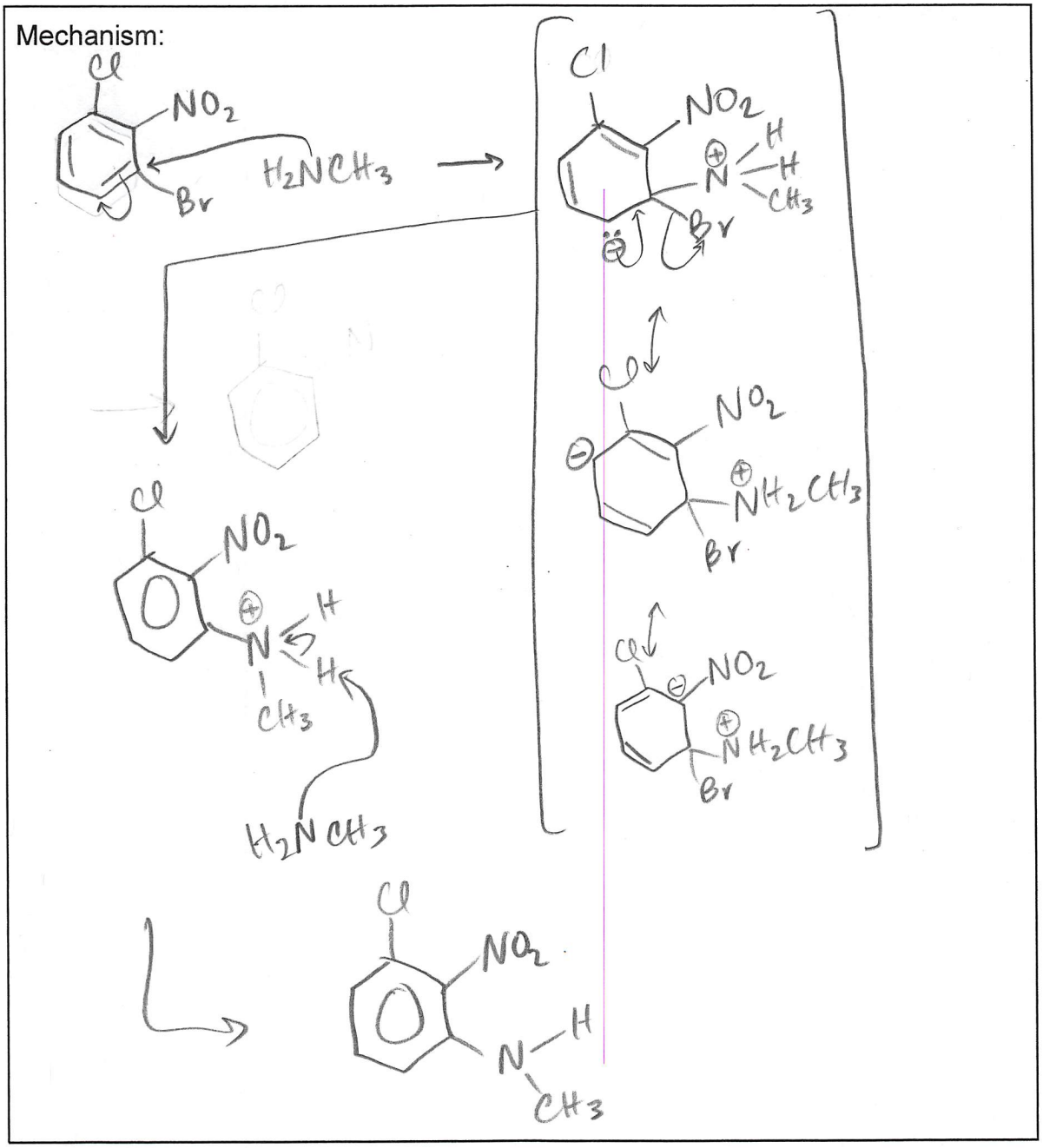
(a)



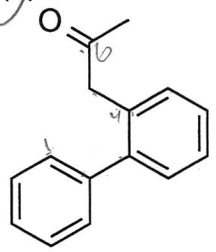

Product:



Mechanism:

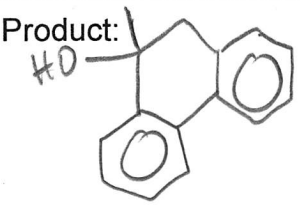


(b)

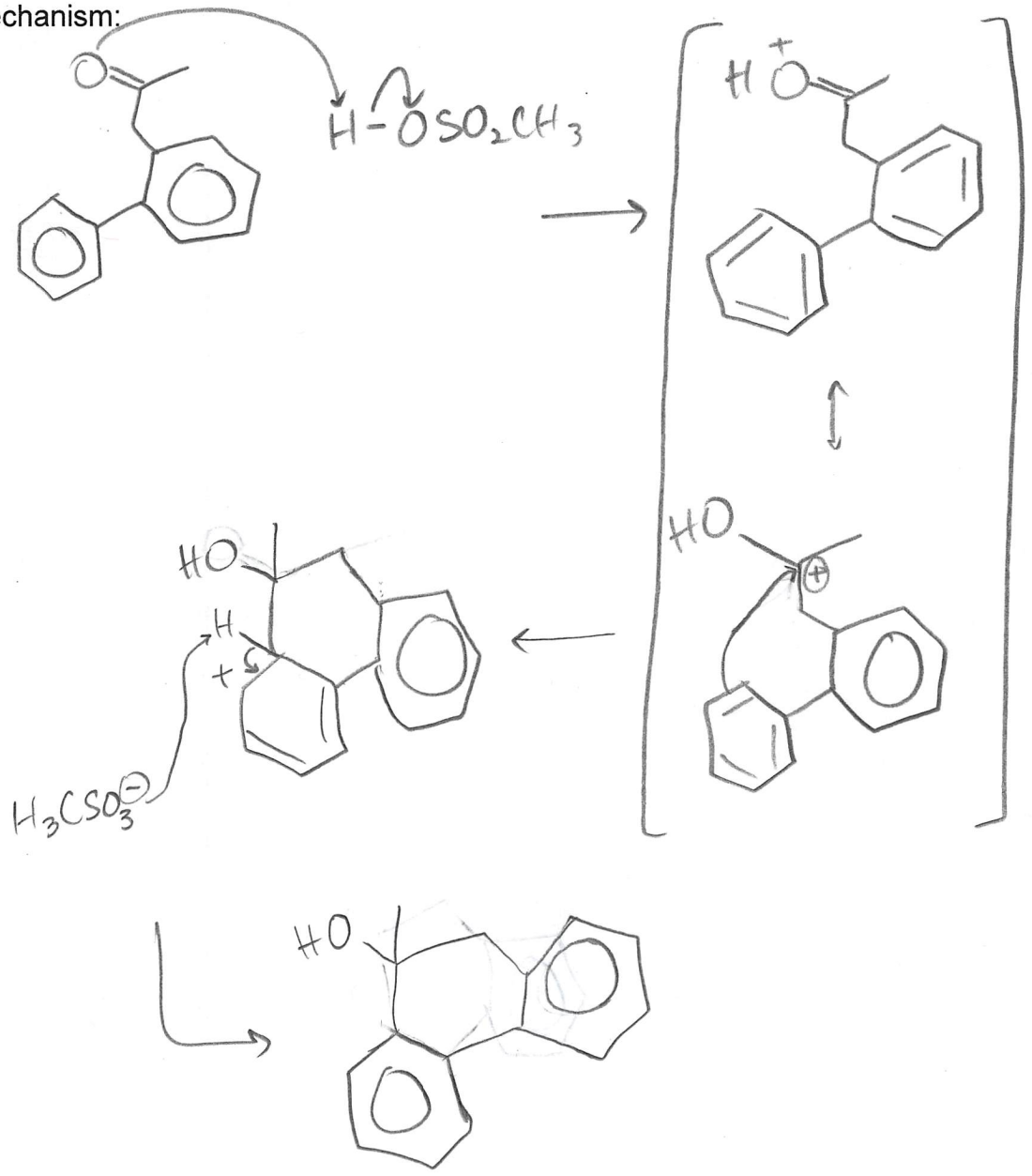


$CH_3SO_3H^*$

Product:

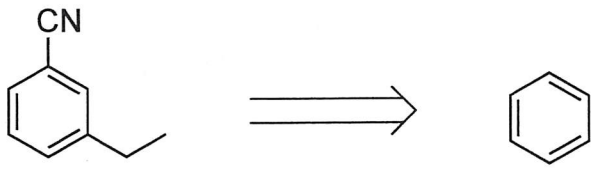


Mechanism:

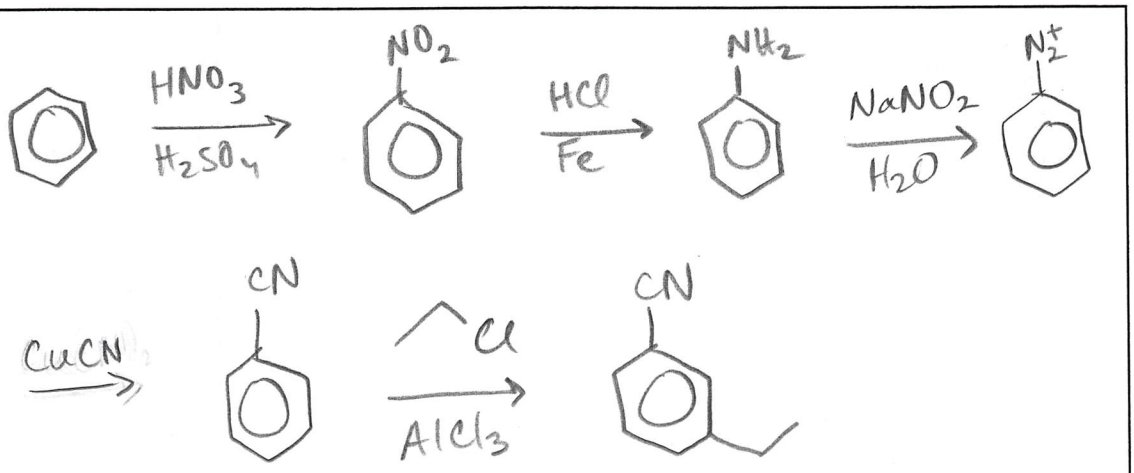



*hint*: * is a strong acid that is soluble in organic solvents

6) (16 points) Propose a reasonable synthesis of 3-ethylbenzonitrile starting from benzene and any other inorganic or organic reagent with two or less carbon atoms.

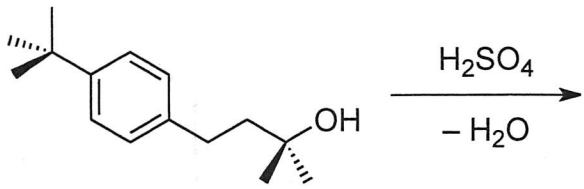



3-ethylbenzonitrile

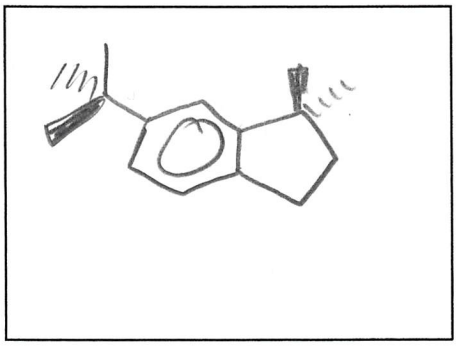


7) (20 points) Celestolide (**C** on the next page) is a perfuming agent that can be synthesized in two steps from **A**.

(a) Give a detailed curved arrow mechanism for the formation of **B** and **C**. Follow the three basic steps of electrophilic aromatic substitutions.

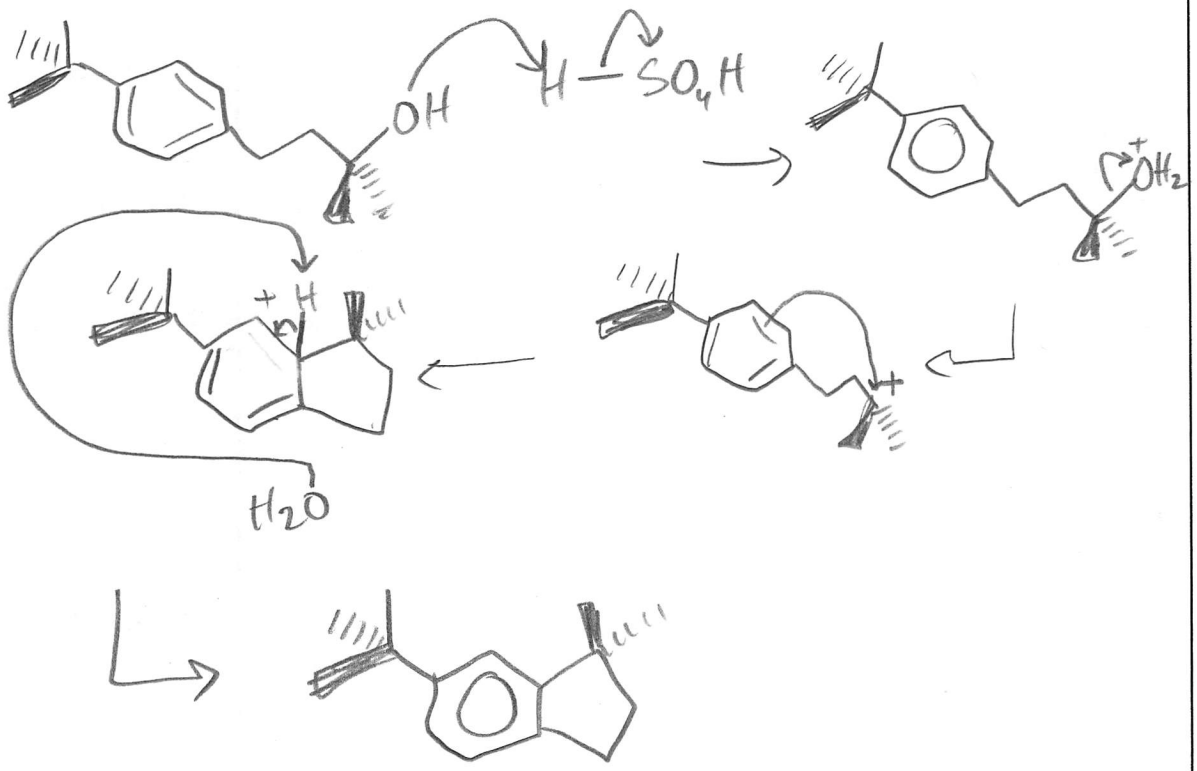


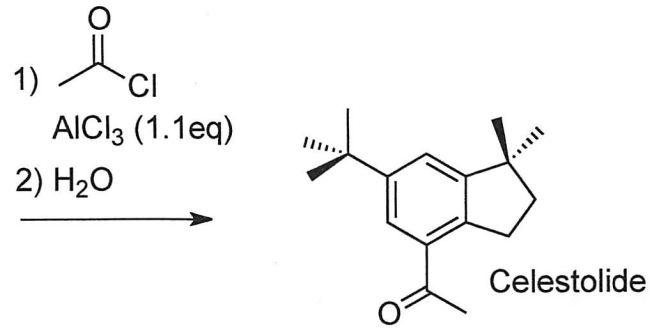

**A**



**B**

Mechanism:



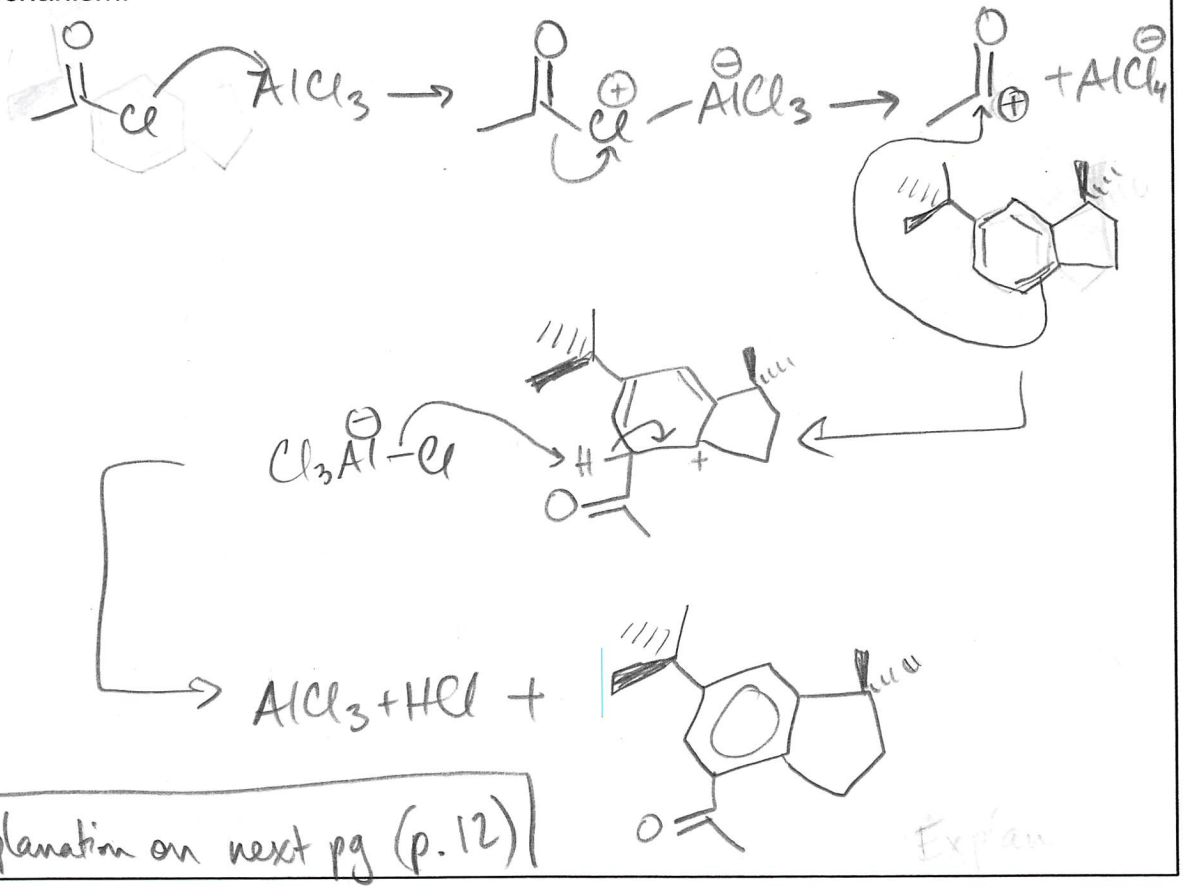



**B**

Celestolide

**C**

Mechanism:

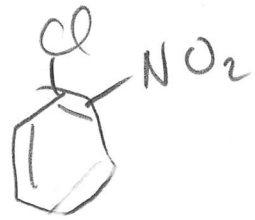


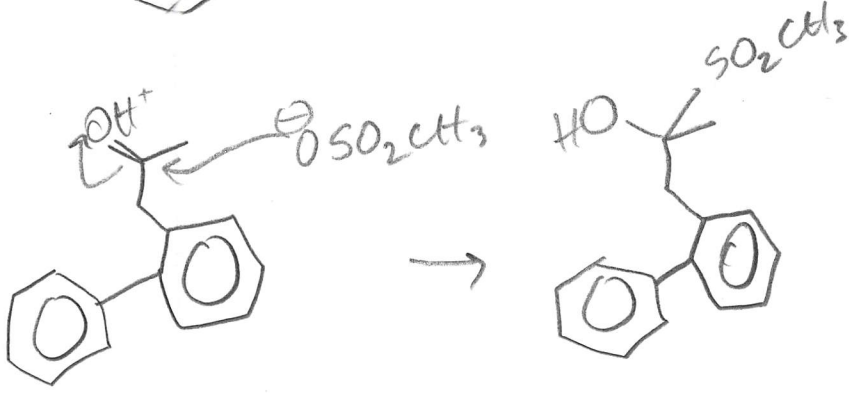

(b) Give a short explanation (less than 20 words) for the regioselectivity of the Friedel-Crafts acylation reaction in the second step.

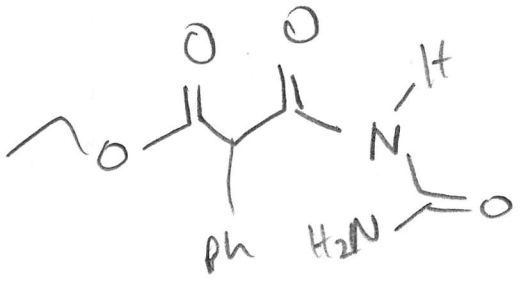
Scratch Paper:

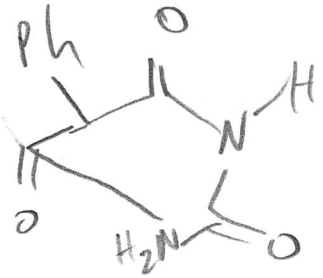
b) Every substituent is mildly activating to a similar degree, so the major product is the one with the least steric strain.

Scratch Paper:









Scratch Paper: