Final Exam
5.13, Organic Chemistry
Professors Timothy M. Swager and Gregory C. Fu
Monday, May 19, 2003
200 Pts Possible

Name Key (printed neatly)

_____(Signature, required for credit)

MIT ID#_____

Name of recitation TA

_____

General Instructions: Make sure that your exam has 21 pages (including a periodic table, and two spectroscopy reference sheets). Write all of your answers in the spaces provided. If you run out of room, use the blank page and **indicate** this for the grader. **If in doubt as to the level of detail expected, put down more than you think is necessary.**

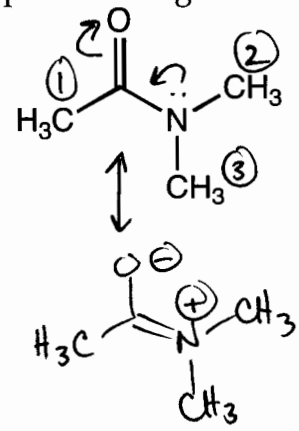
Good Luck!

1	_____	_____
2	_____	_____
3	_____	_____
4	not covered this semester	
5	_____	_____
6	_____	_____
7	_____	_____
8	_____	_____
9	_____	_____
10	_____	_____
11	_____	_____
12	_____	_____
13	_____	_____
14	_____	_____
15	not covered	this semester

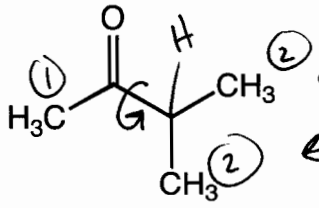
Total_____

Note: Two problems were omitted because the material was not covered this semester.

1a (6 pts) The two compounds shown below both have 3 different methyl peaks in the ^{1}H NMR. Explain the origin of the three signals for each.

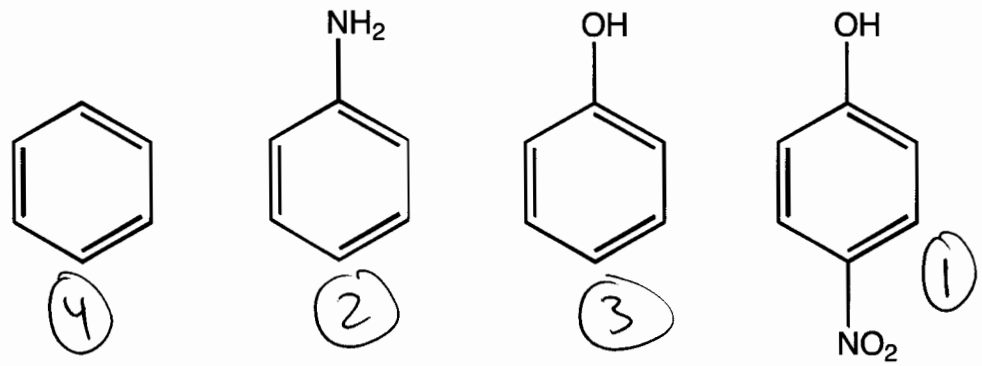


- high barrier to rotation because of resonance → distinct cis & trans methyl groups in ^{1}H NMR.

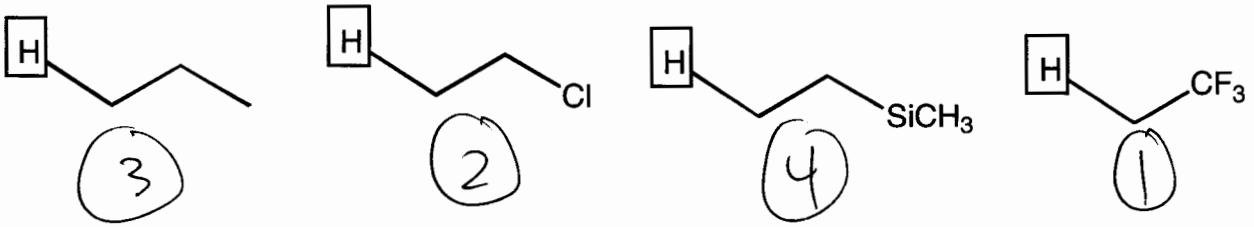


these two methyls are identical because free rotation around C-C bond. However, peak split into a doublet by adjacent H.

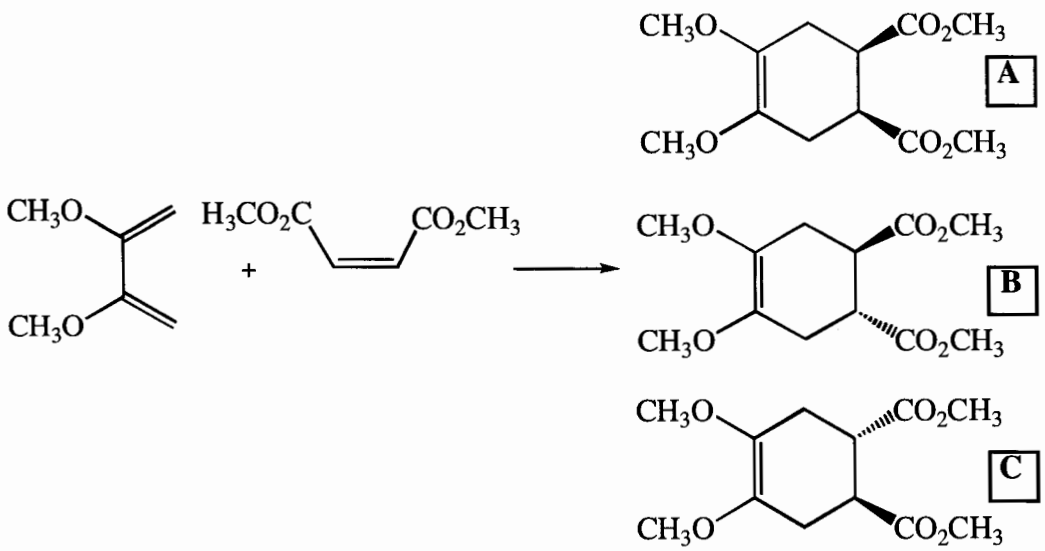
1b (4 pts) Rank-order the following chromophores in order of their absorption wavelengths. 1=Longest



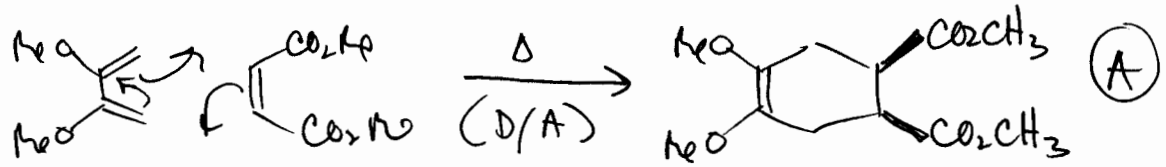
1c (4 pts) Rank-order the ^{1}H NMR shifts for the protons in the boxes. 1=furthest downfield (highest ppm)



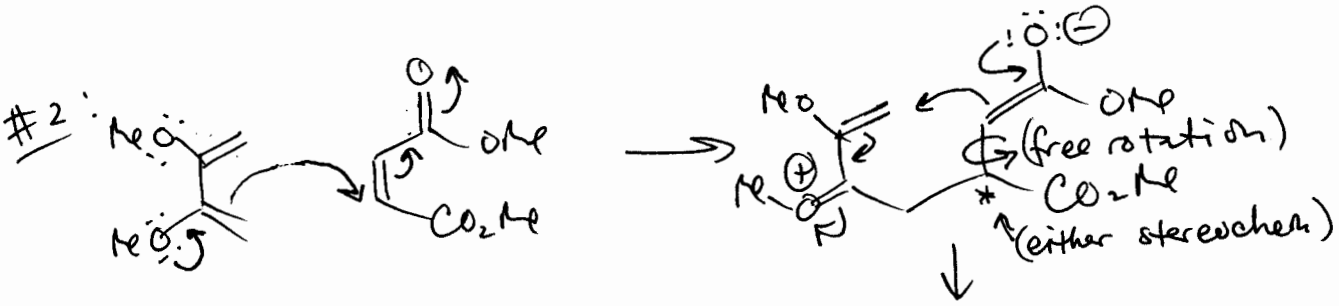
2. (15 pts) The following reaction was run in methanol at high temperature and was found to give the following products. Show the <u>two parallel mechanisms</u> that account for the products. How would you make the reaction more selective for **A**?



#1:



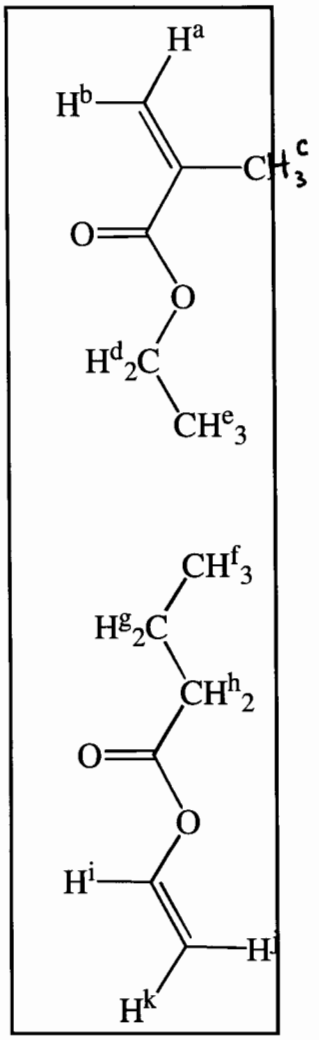
#2:

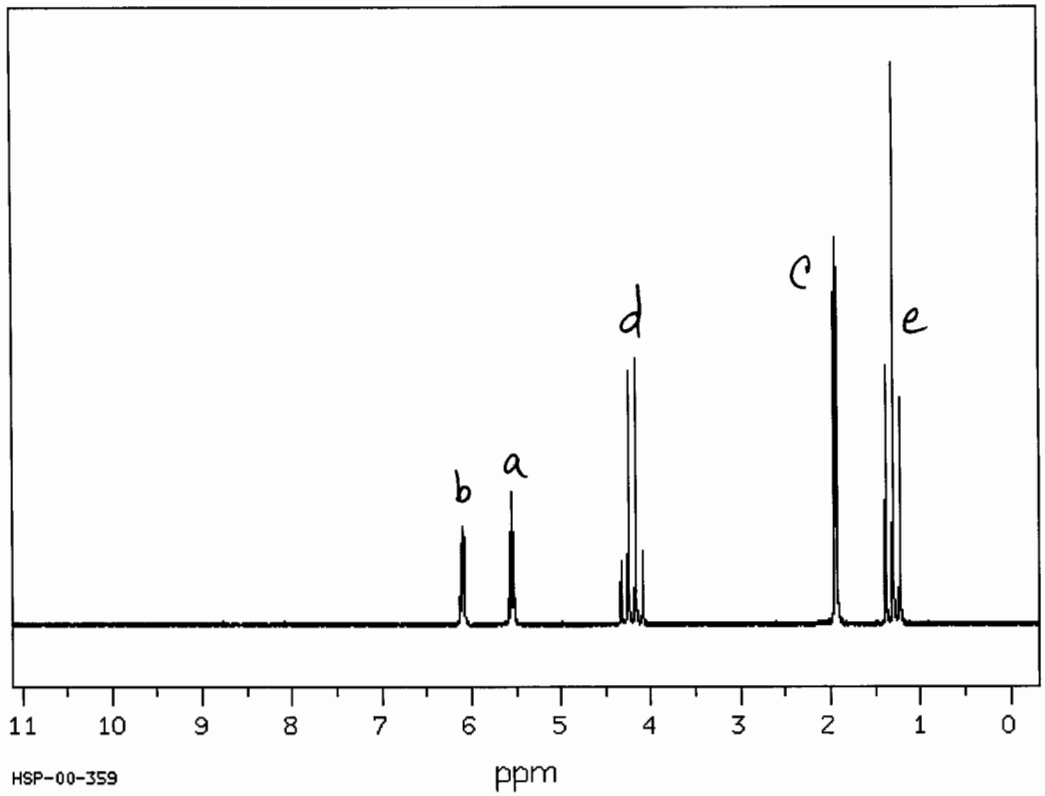


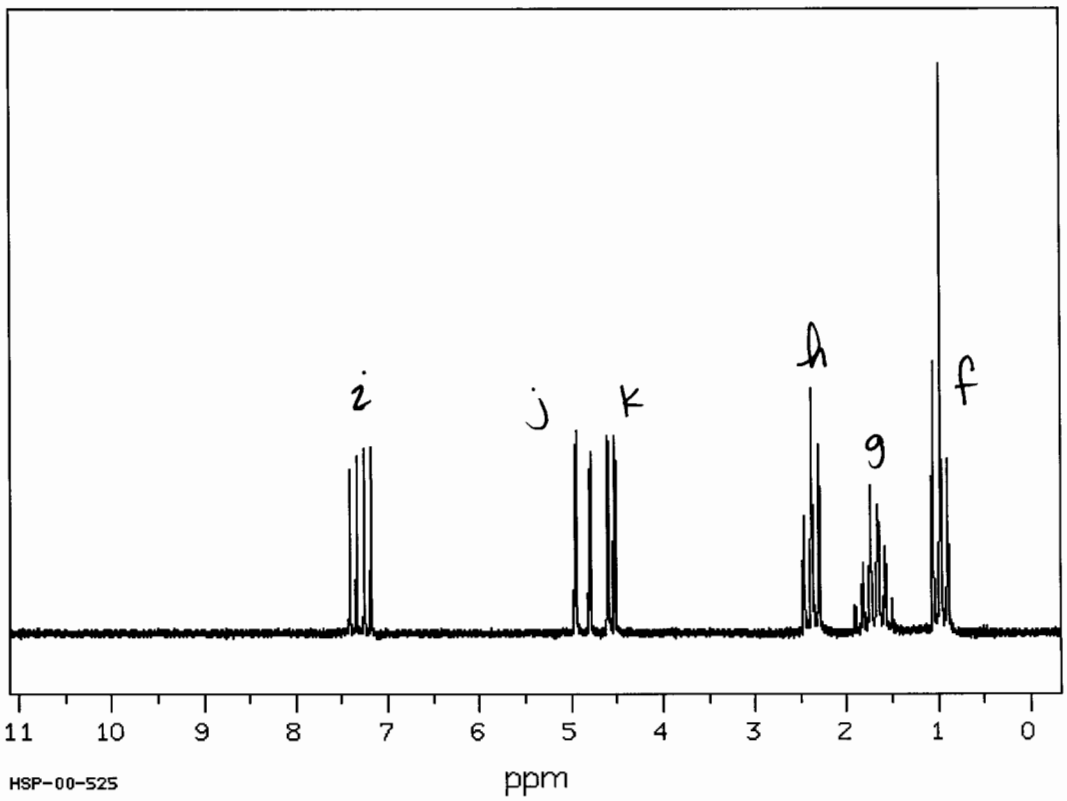
(A), (B), (C)

To select for (A), must destabilize the ionic intermediate in path #2. Switch to a less polar solvent or lower the temperature.

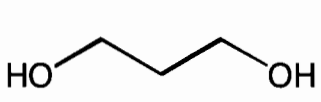
3. (14 points) The following two compounds exhibit the two ^{1}H NMR spectra shown (taken at 90mHz or 90Hz per ppm). Assign each of the proton peaks to their respective hydrogens using the given labels (a-k).



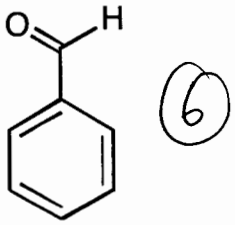




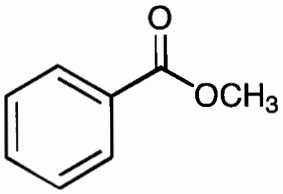
5. (21 points) The Infrared spectra for **seven** of the following **10** compounds are given on the next page. Put the number of the spectrum below the correct compound.

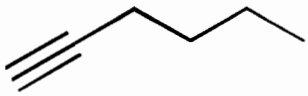


4

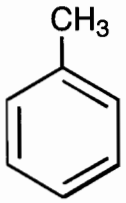


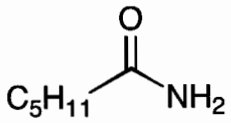
6



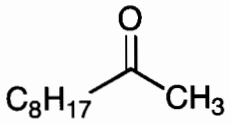


5

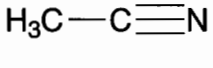




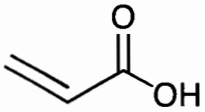
3



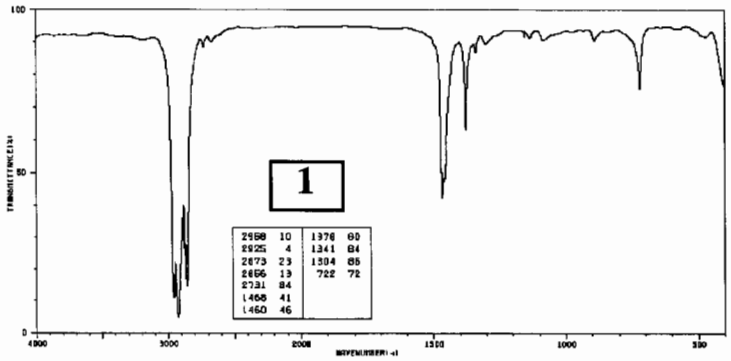
7

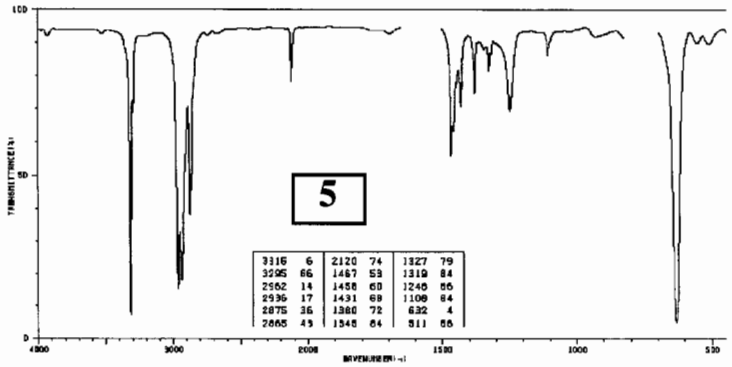


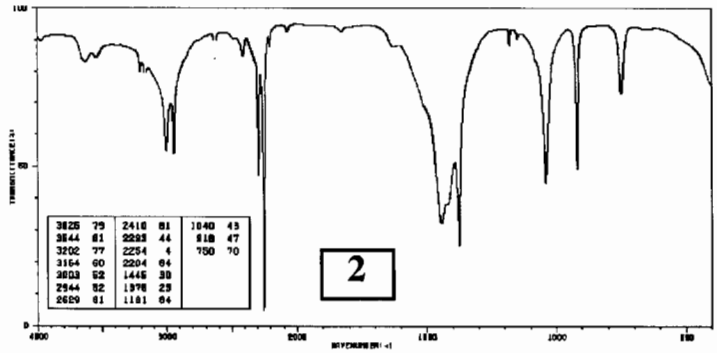
2

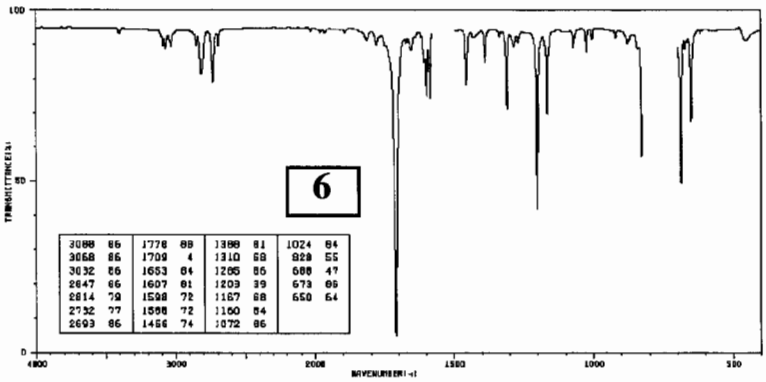


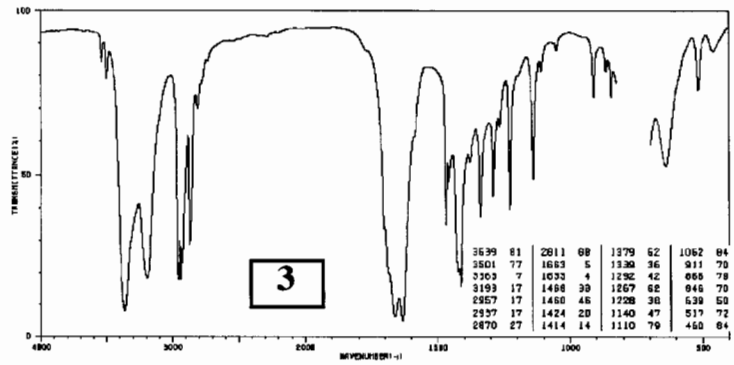
1

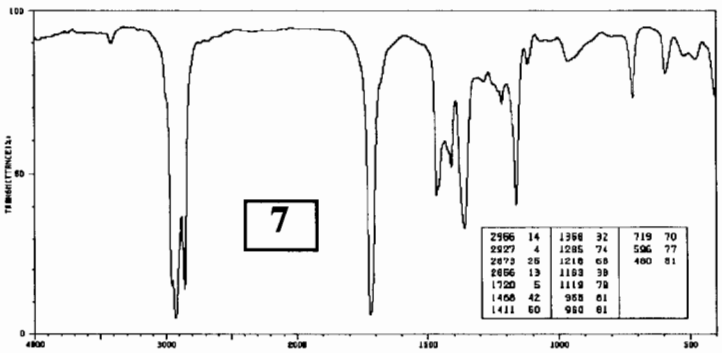

1

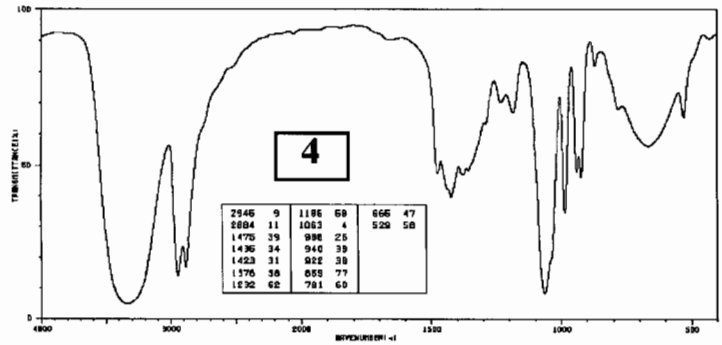

5


2

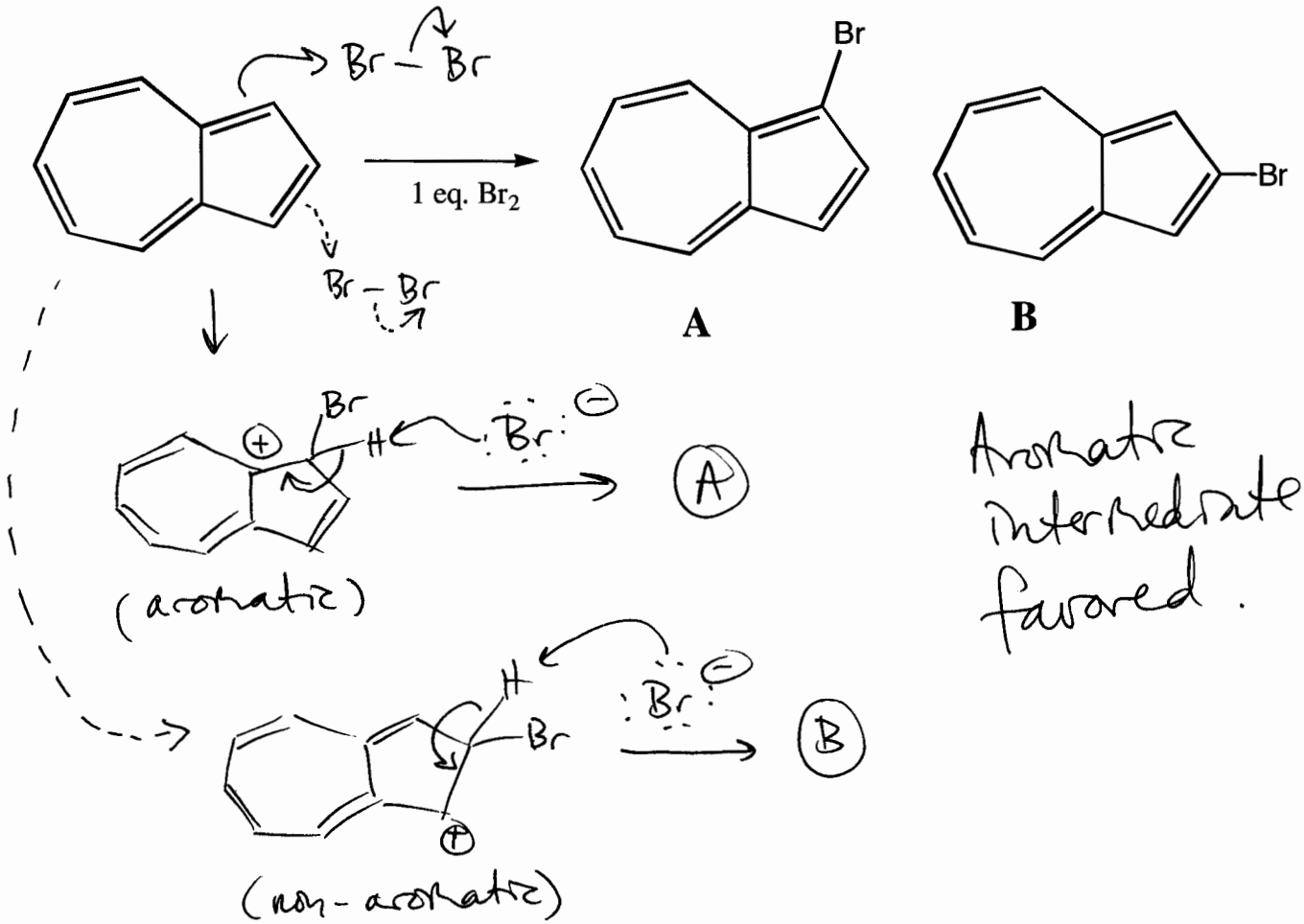

6


3

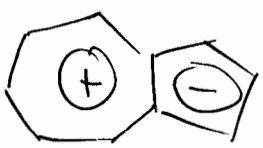

7


4

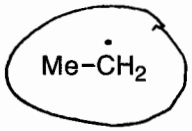
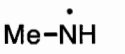
6. (12 pts) Azulene when reacted with one equivalent of Br_2 gives only Compound **A**. Provide a mechanism for this reaction and indicate why the reaction only occurs at the 5-membered ring and why Compound **B** is not formed.

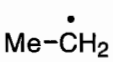
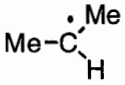
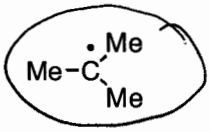


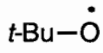
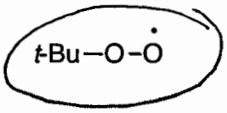
Will not react w/ 7-membered ring because it is electron-poor due to

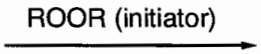
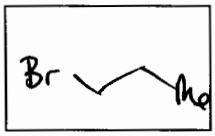


7. (2 points each, 8 points total)

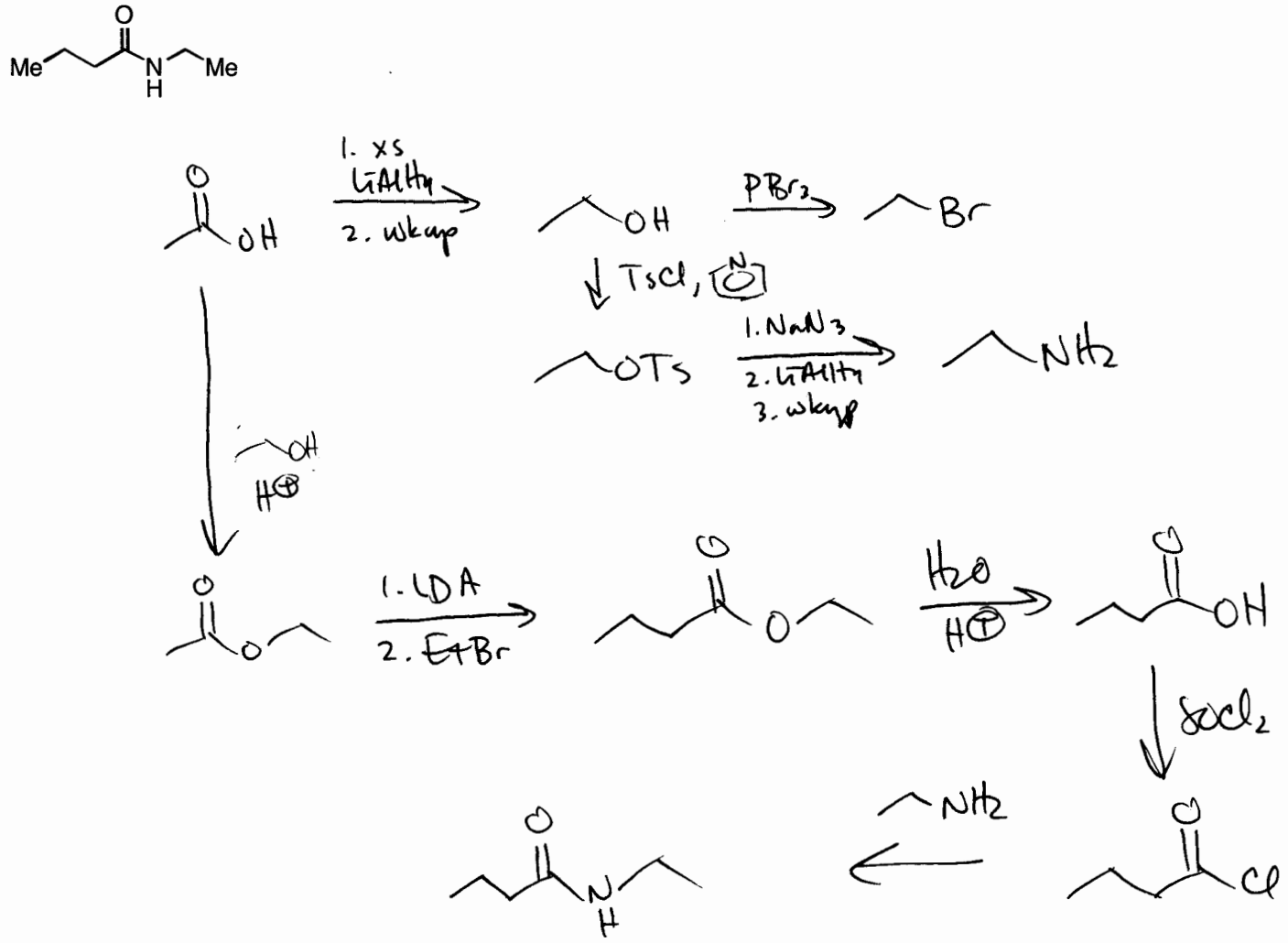
(a) The most stable radical (circle one):   

(b) The most stable radical (circle one):   

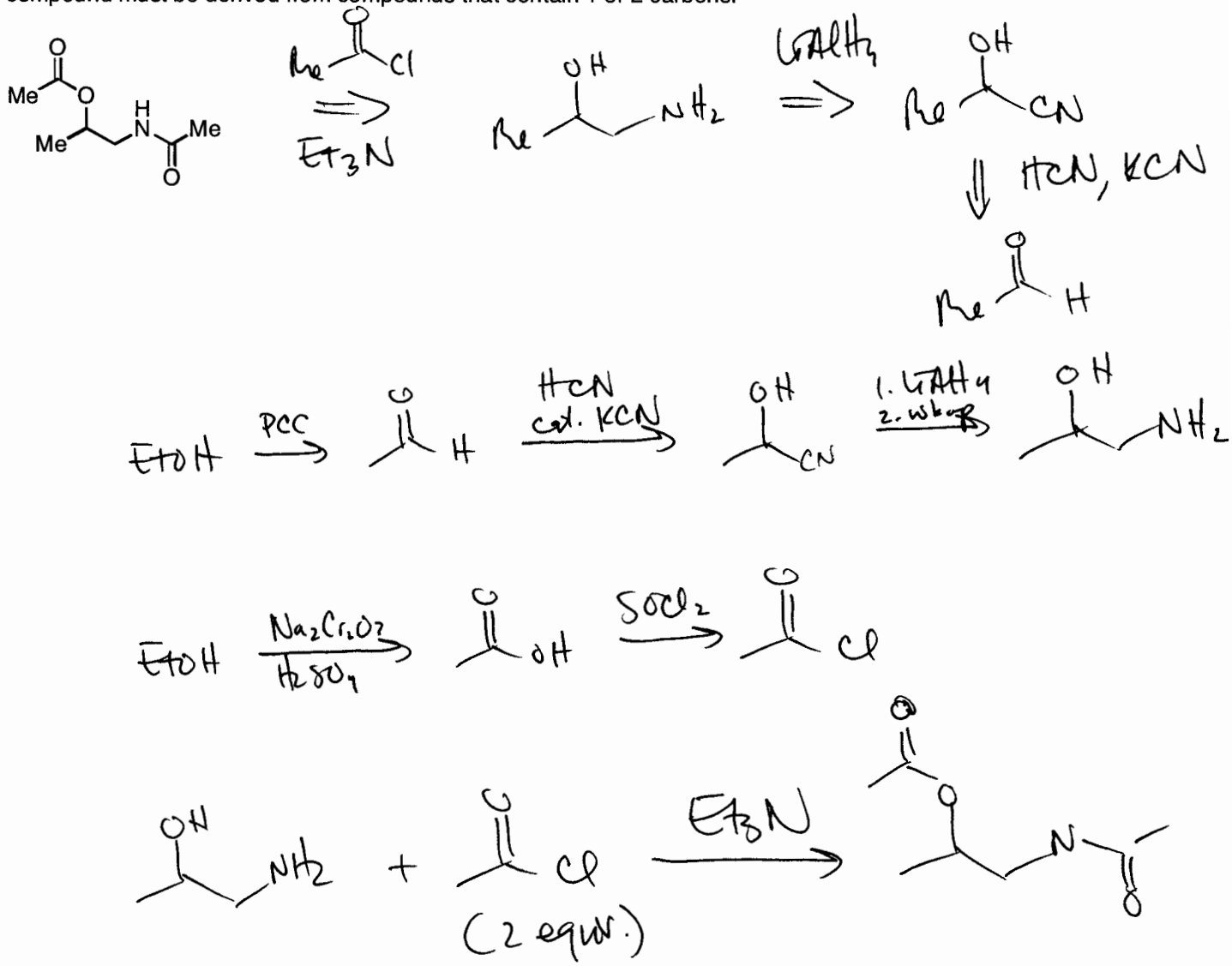
(c) The most stable radical (circle one):   

(d)  HBr  

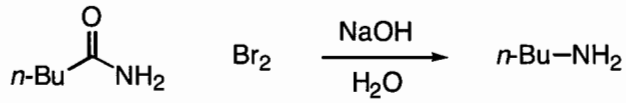
8. (12 points) Please provide a SELECTIVE synthesis of the illustrated compound. All of the carbons of this compound must be derived from acetic acid.



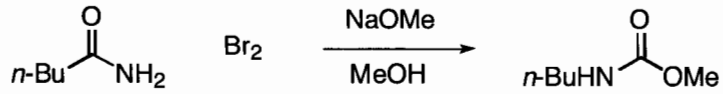
9. (12 points) Please provide a selective synthesis of the illustrated compound. All of the carbons of this compound must be derived from compounds that contain 1 or 2 carbons.



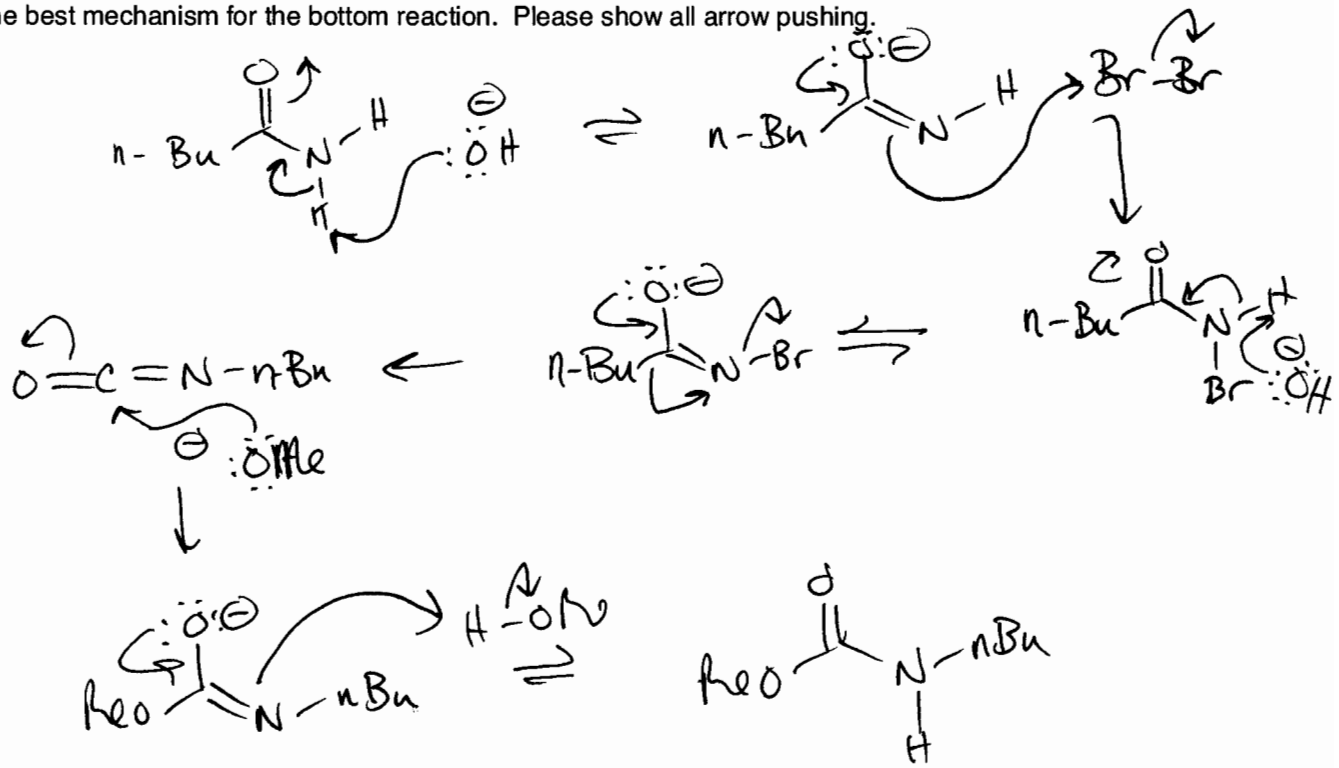
10. (10 points) In class, you learned the mechanism for the Hoffmann reaction, which generates an amine when the reaction is run in water:



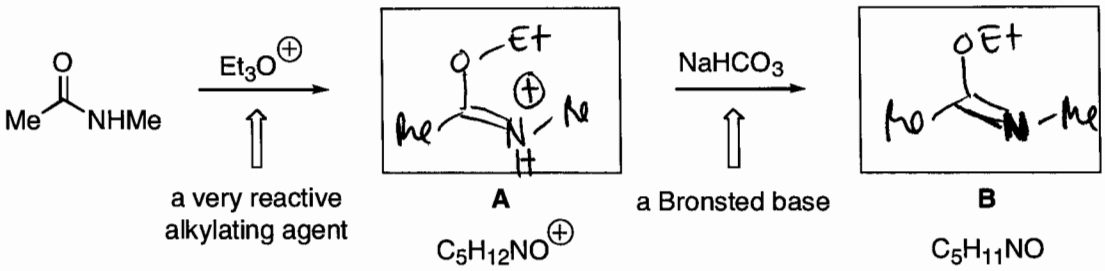
When the reaction is run in MeOH, a different product is formed:



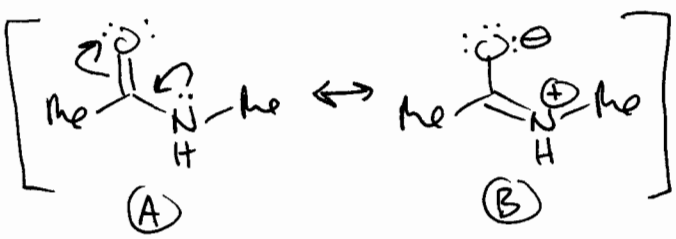
Provide the best mechanism for the bottom reaction. Please show all arrow pushing.



11. (16 points total) (a) (2 points each, 4 points total) Please identify **A** and **B**.

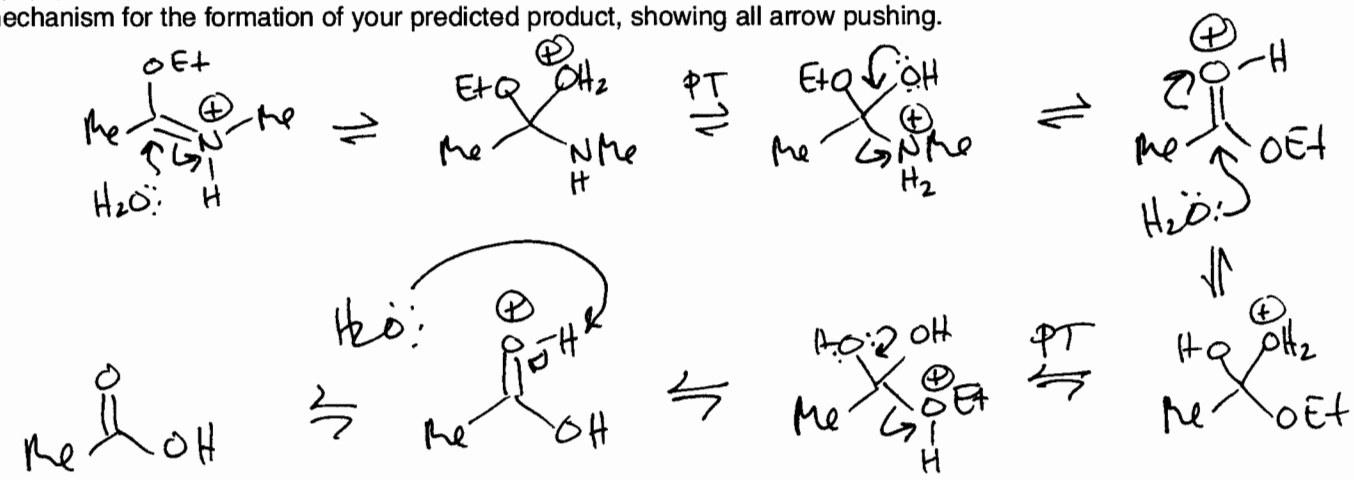


(b) (5 points) Please provide a rationale for the formation of **A**.



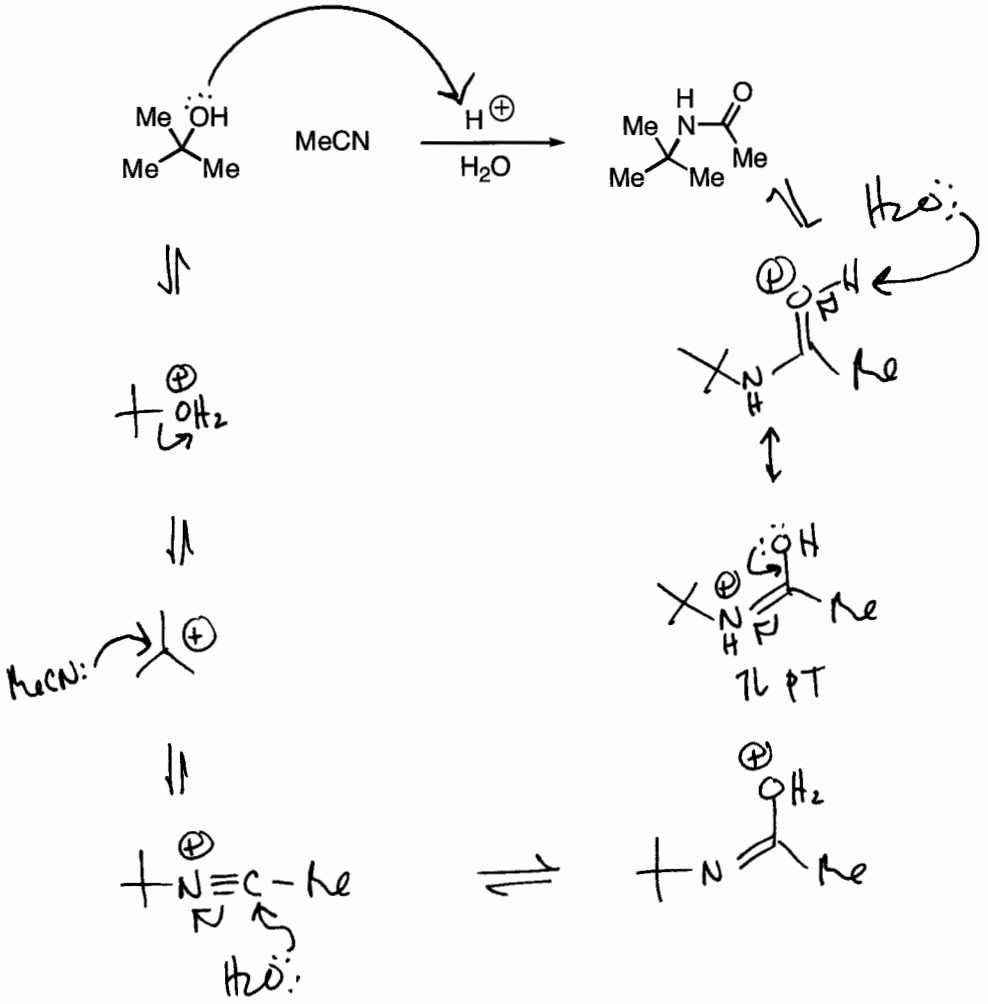
(B) is a major resonance contributor. As a result, the oxygen is more electron dense and nucleophilic than the nitrogen.

(c) (7 points) Predict the product that would be obtained if **A** is treated with aqueous acid. Draw the mechanism for the formation of your predicted product, showing all arrow pushing.

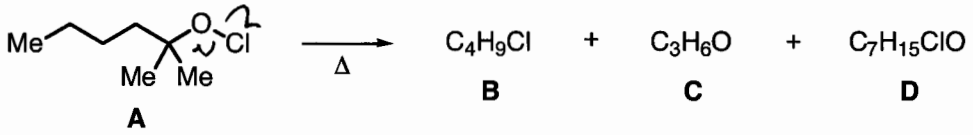


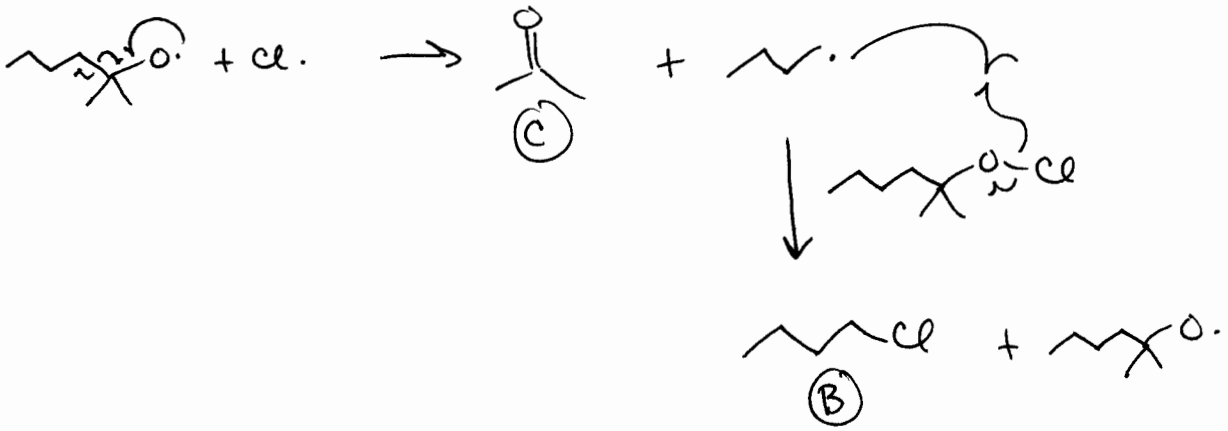
- would get ester ($Me\text{-}C(=O)\text{-}OEt$) first, followed by subsequent hydrolysis to the acid ($Me\text{-}C(=O)\text{-}OH$)

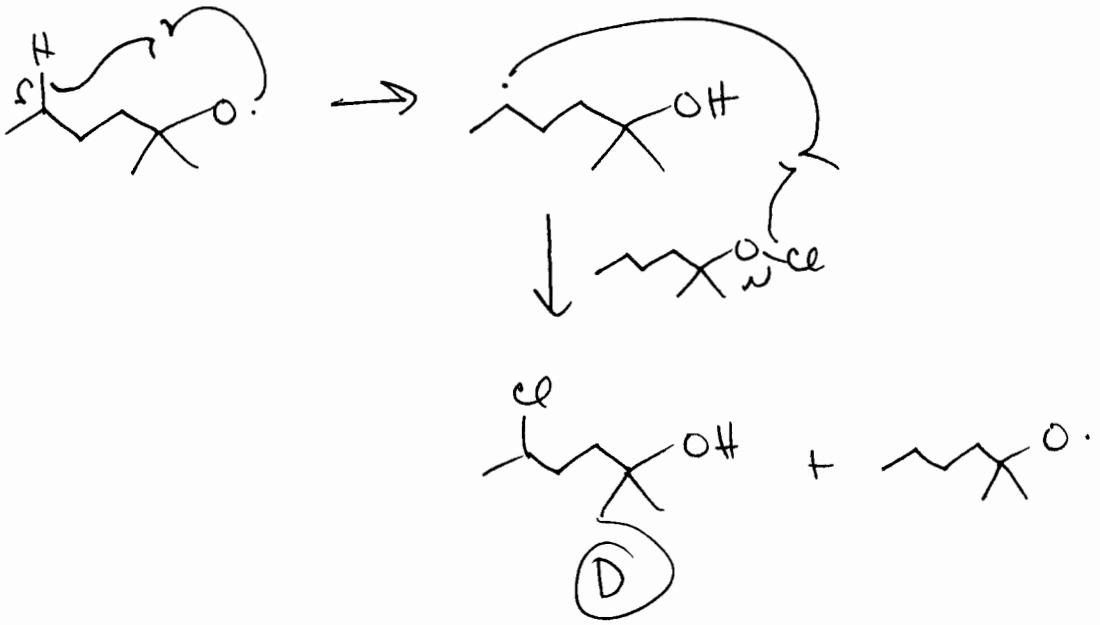
12. (12 points) Provide the best mechanism for the illustrated transformation. Please show all arrow pushing.



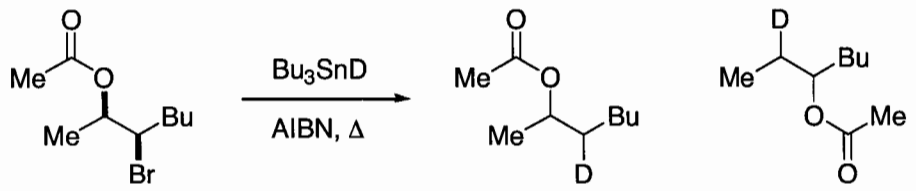
13. (10 points) Compound **A** is converted to **B**, **C**, and **D** upon heating. The reaction is accelerated by irradiation. Provide the structures of **B**, **C**, and **D**, and provide the mechanisms by which they are formed (please show all arrow pushing).







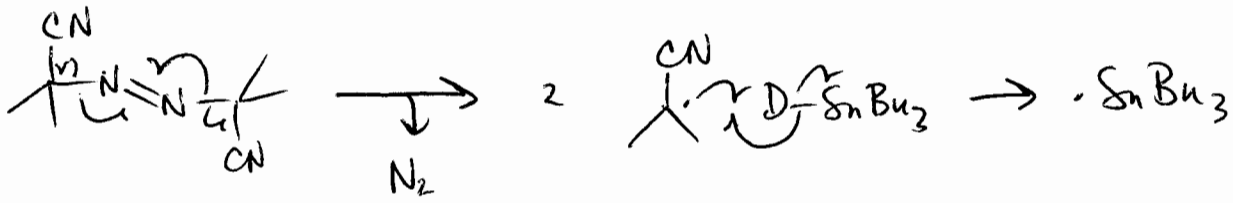
14. (20 points total) In the reduction of **A**, two products are observed, the expected reduction product (**B**) and a constitutional isomer (**C**).



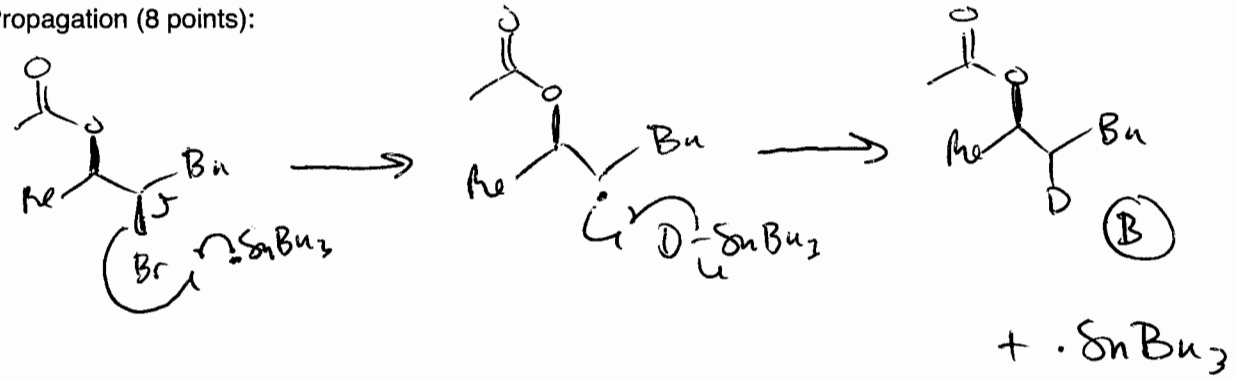
A **B** **C**

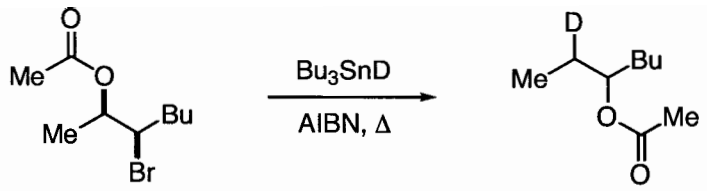
(a) (12 points total) Provide the best mechanism for the formation of **B**. Please show all arrow pushing.

Initiation (4 points):



Propagation (8 points):





A **C**

(b) (8 points) Provide the best mechanism for the formation of **C**. Please show all arrow pushing.