

Final Exam

5.13, Organic Chemistry

Professors Timothy M. Swager and Gregory C. Fu

Monday, May 19, 2003

200 Pts Possible

Name _____ (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.**

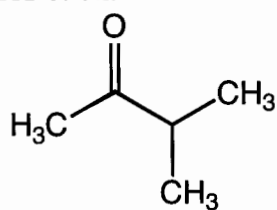
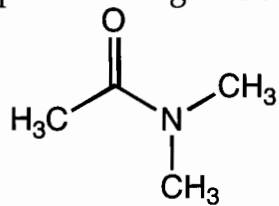
Good Luck!

1	_____	_____
2	_____	_____
3	_____	_____
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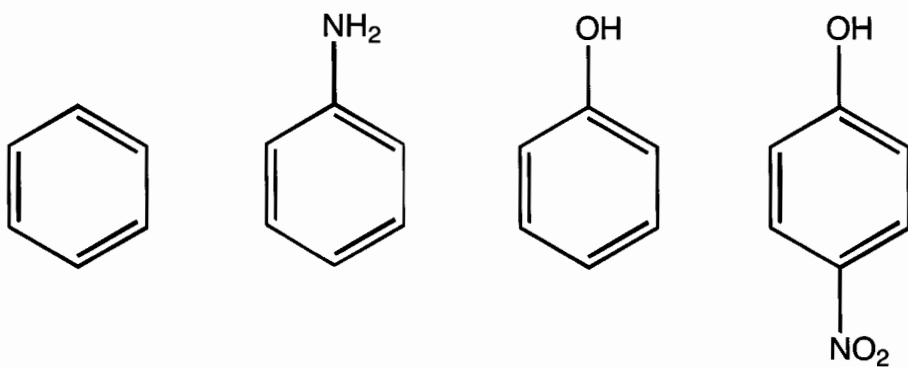
Total _____

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

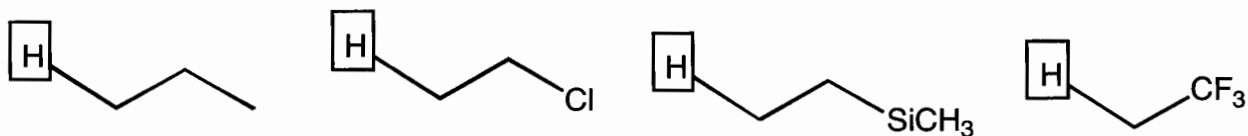
1a (6 pts) The two compounds shown below both have 3 different methyl peaks in the ^1H NMR. Explain the origin of the three signals for each.



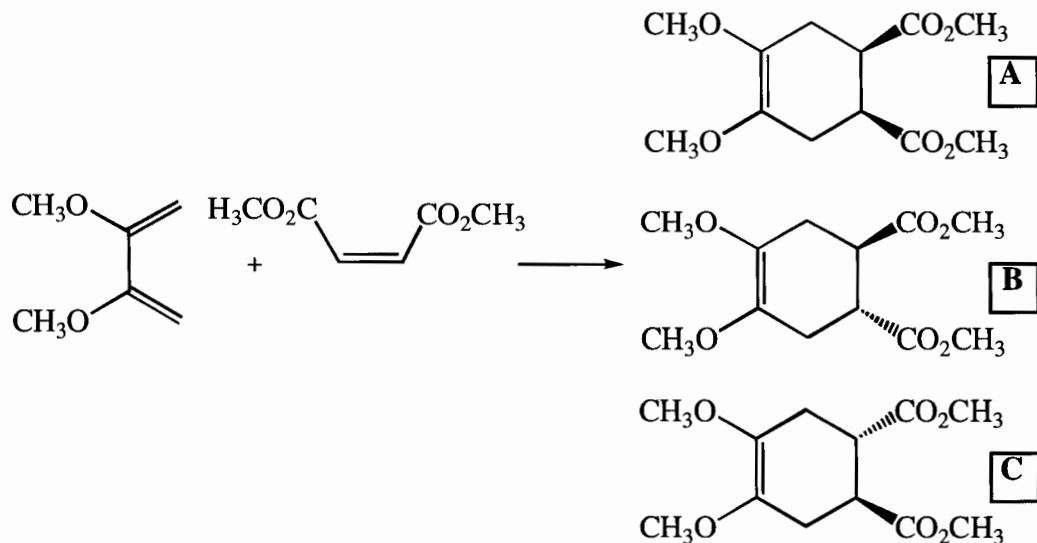
1b (4 pts) Rank-order the following chromophores in order of their absorption wavelengths. 1=Longest



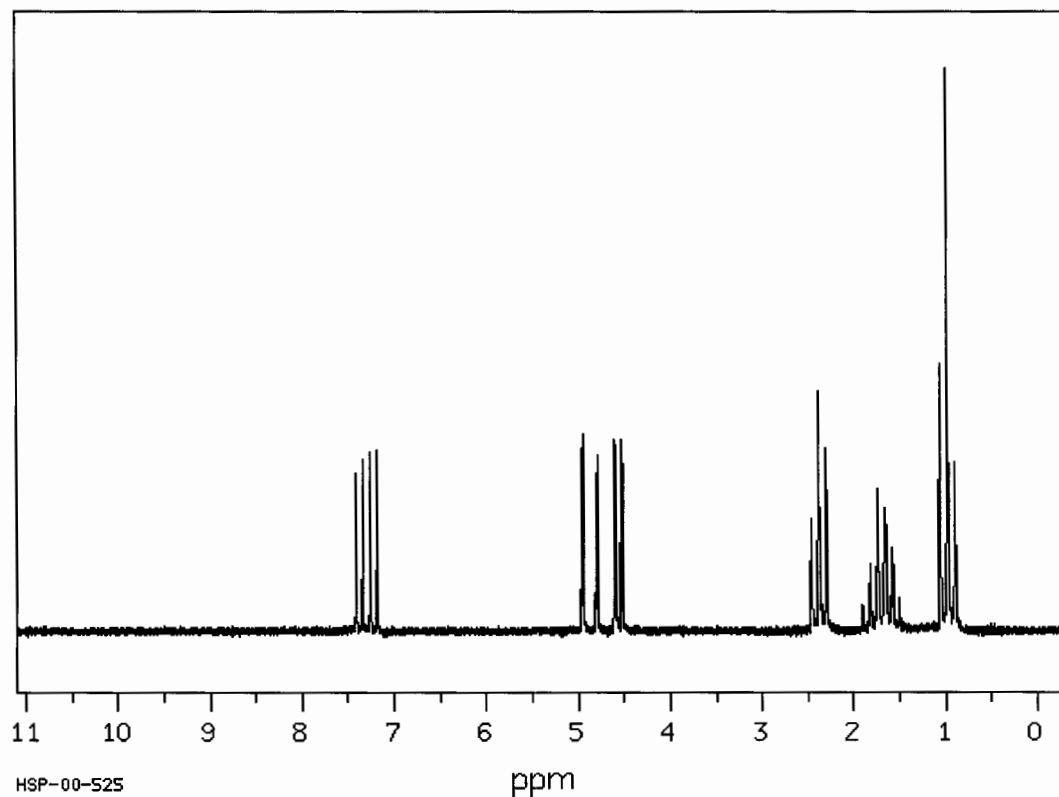
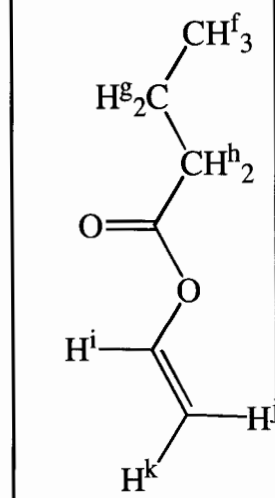
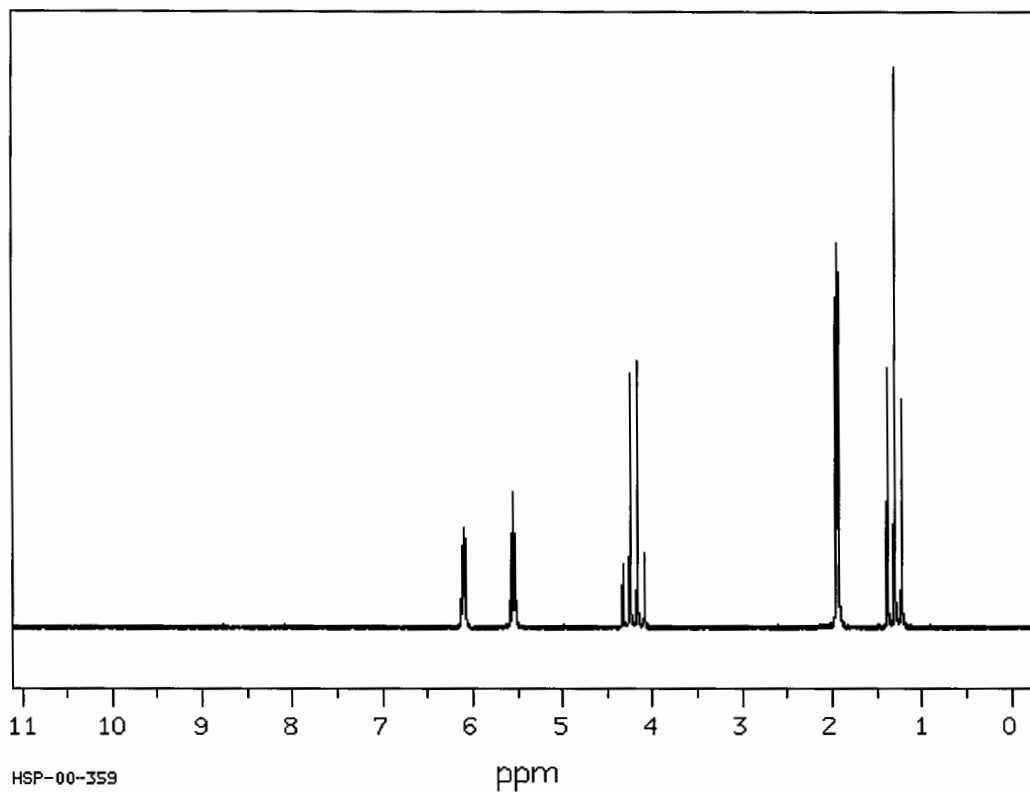
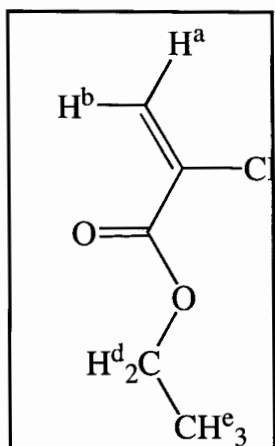
1c (4 pts) Rank-order the ^1H NMR shifts for the protons in the boxes. 1=furthest downfield (highest ppm)



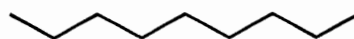
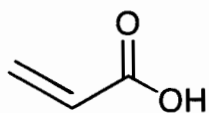
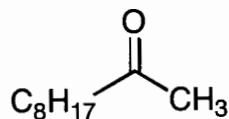
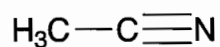
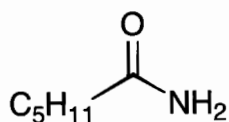
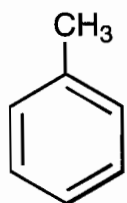
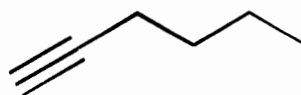
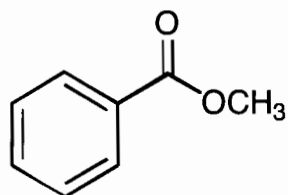
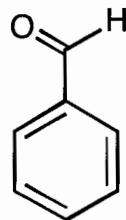
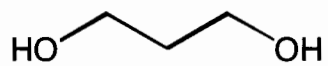
2. (15 pts) The following reaction was run in methanol at high temperature and was found to give the following products. Show the two parallel mechanisms that account for the products. How would you make the reaction more selective for A?

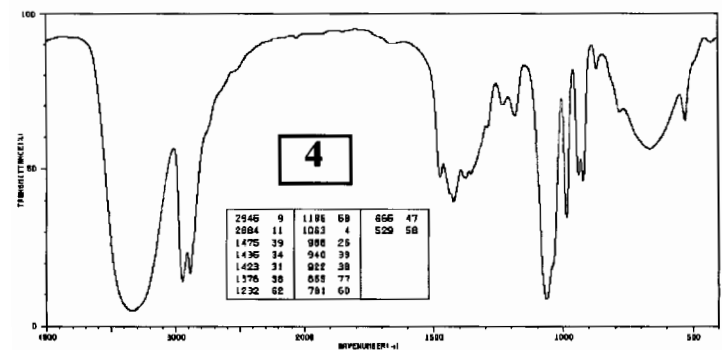
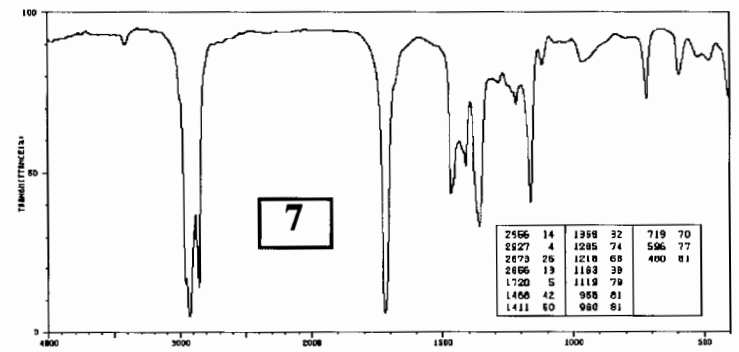
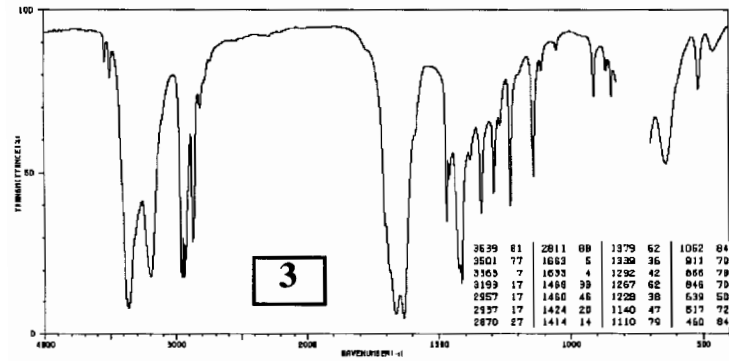
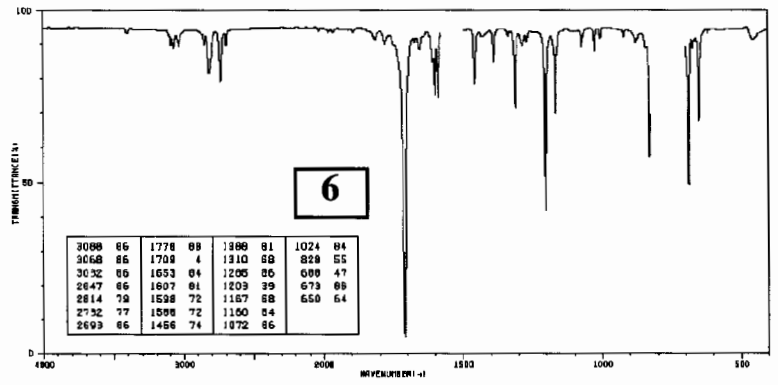
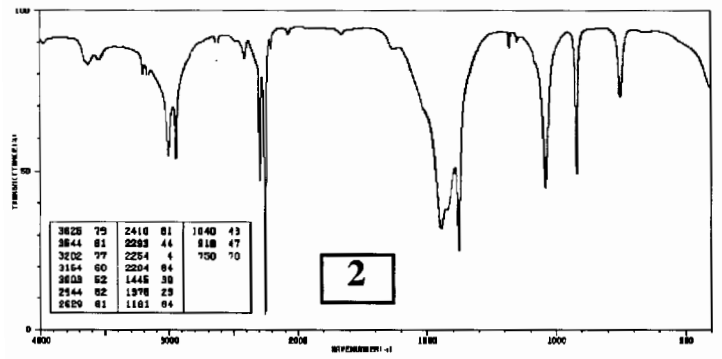
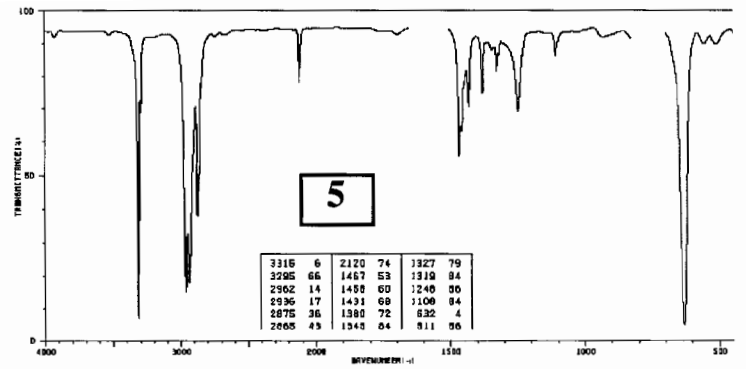
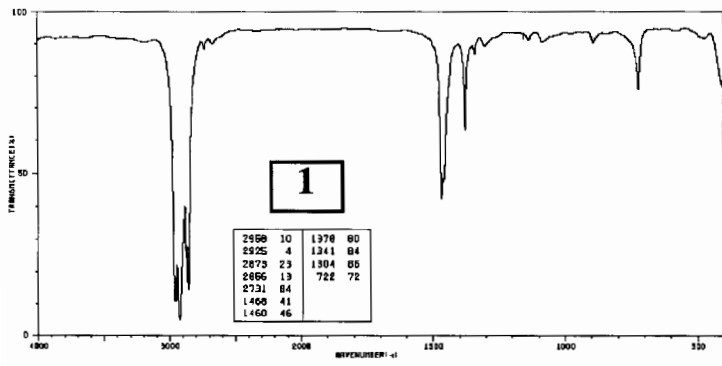


3. (14 points) The following two compounds exhibit the two ^1H NMR spectra shown (taken at 90MHz or 90Hz per ppm). Assign each of the proton peaks to their respective hydrogens using the given labels (a-k).

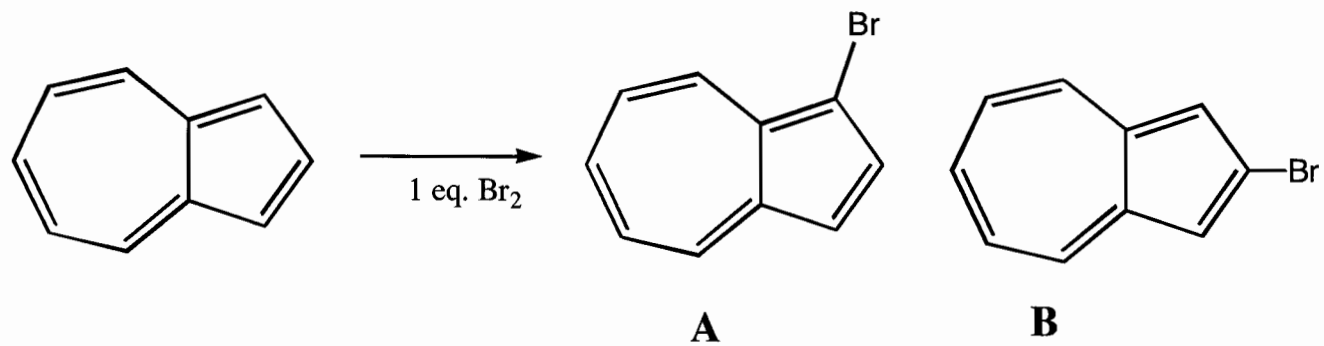


5. (21 points) The Infrared spectra for **seven** of the following **10** compounds are given on the next page. Put the number of the spectrum below the correct compound.





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.

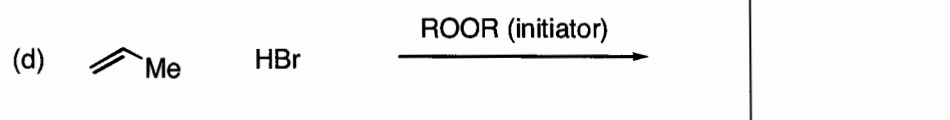


7. (2 points each, 8 points total)

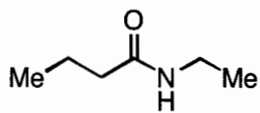
(a) The most stable radical (circle one): $\text{Me}-\dot{\text{C}}\text{H}_2$ $\text{Me}-\dot{\text{N}}\text{H}$ $\text{Me}-\dot{\text{O}}$

(b) The most stable radical (circle one): $\text{Me}-\dot{\text{C}}\text{H}_2$ $\text{Me}-\overset{\cdot}{\text{C}}\begin{matrix} \text{Me} \\ \text{H} \end{matrix}$ $\text{Me}-\overset{\cdot}{\text{C}}\begin{matrix} \text{Me} \\ \text{Me} \end{matrix}$

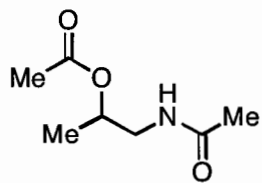
(c) The most stable radical (circle one): $t\text{-Bu}-\dot{\text{O}}$ $\text{Me}-\dot{\text{O}}$ $t\text{-Bu}-\text{O}-\dot{\text{O}}$



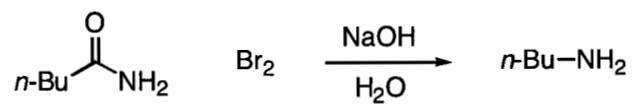
8. (12 points) Please provide a SELECTIVE synthesis of the illustrated compound. All of the carbons of this compound must be derived from acetic acid.



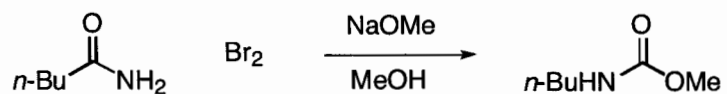
9. (12 points) Please provide a selective synthesis of the illustrated compound. All of the carbons of this compound must be derived from compounds that contain 1 or 2 carbons.



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

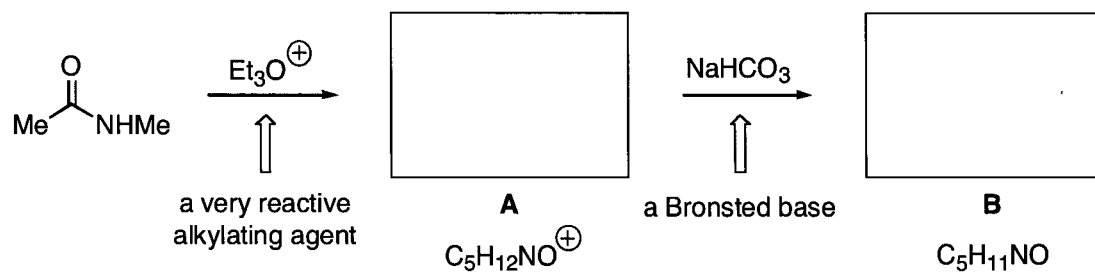


When the reaction is run in MeOH, a different product is formed:



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

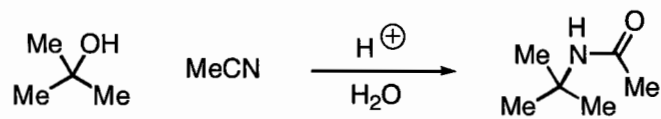
11. (16 points total) (a) (2 points each, 4 points total) Please identify **A** and **B**.



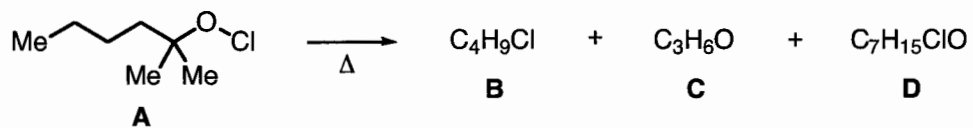
(b) (5 points) Please provide a rationale for the formation of **A**.

(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.

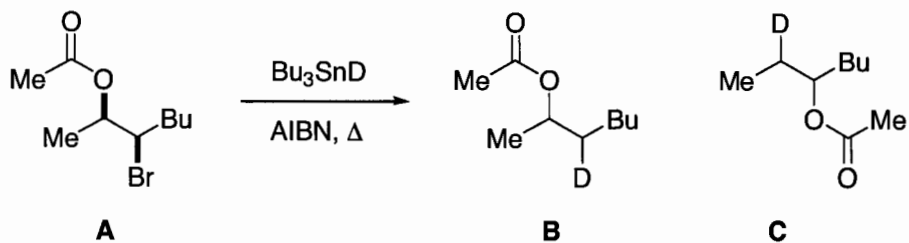
12. (12 points) Provide the best mechanism for the illustrated transformation. Please show all arrow pushing.



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).



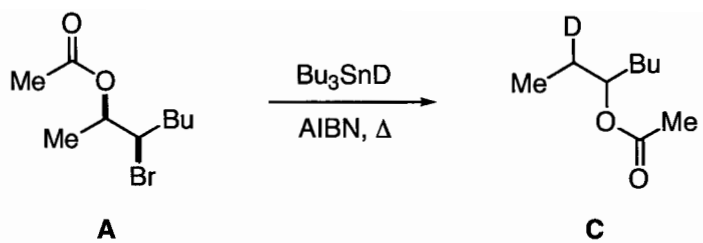
14. (20 points total) In the reduction of **A**, two products are observed, the expected reduction product (**B**) and a constitutional isomer (**C**).



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

Initiation (4 points):

Propagation (8 points):



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