Research Methods (CHEM 251)
Synthetic Organic Chemistry Part
Final Examination

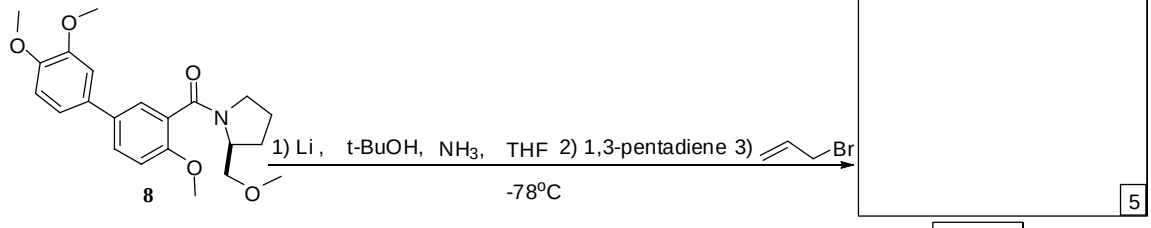
Prof. Malachowski

Due: December 16, 2005, 5 PM

Honor Code: You may take this examination while consulting your course lecture notes, lab notebook and handouts. You are not to consult any other electronic or written material during the exam. You have 1.5 consecutive hours to complete the exam. You should not discuss the exam with anyone until all students have handed in their exam. There are a total of four questions. The point values for each question are written with the question.

1. Preliminary experimentation has succeeded in the Birch-Cope sequence. It is time to increase the scale of the reaction to push intermediates ahead in an effort to make the final (+)-mesembrine product. Using your familiarity with the Birch reduction-allylation reaction and the experimental section of the class project manuscript, answer the following questions. Beware of significant figures!

a) To begin, we will need to calculate the necessary reagents and determine the appropriate glassware. Complete the reaction table below by filling in the appropriate numbers in the boxes. (0.5 pts. each) Beware of significant figures!



8

m.w. (g/mol)	385.5	6.94	74.1	17	72.1	68.1	121	
d (g/mL)	—	—	0.775	—	0.889	0.683	1.398	—
b.p. (°C)	—	—	83	-33	65-7	42	70-1	—
m.p. (°C)	—	180	23-6	-78	-108	-87	-119	—

Scale:

mmol				—	—		
equiv.	1.00	2.50		—	—	2.50	
g	1.00			—	—		
ml	—	—					—

b) What size and type of round bottom flask should you select? (4 pts.)

c) If the reaction temperature is lowered to -110°C, what problems might occur? (4 pts.)

d) Some Birch reduction reactions are conducted under an ammonia reflux. What would be the temperature of the reaction under these conditions? (4 pts.)

e) What will be the approximate concentration of **8** in the reaction? (4 pts.)

29 total pts.

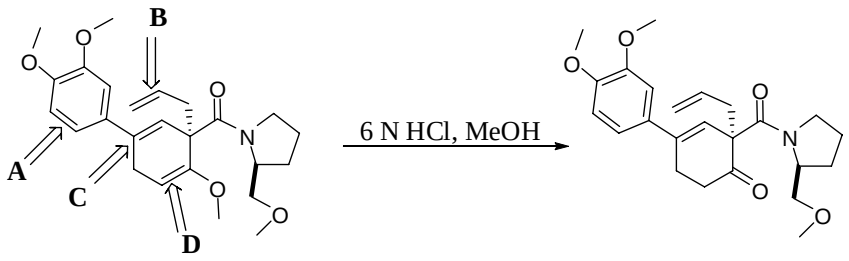
f) We have found that the stereoselectivity of the reaction can be increased if the reaction is run under more dilute conditions. What would have to be done to run the reaction under more dilute conditions? (4 pts.)

g) One common problem in the Birch reductions run in our class was over-reduction of the aromatic system. Draw one possible product of over-reduction of **8**. (4 pts.)

h) What analytical tools could be used to confirm over-reduced products and what would you look for with these tools? (6 pts.)

14 total pts.

2. In the following hydrolysis reaction, only alkene **D** reacts. Describe why alkenes **A**-**C** do not react. (15 pts.)

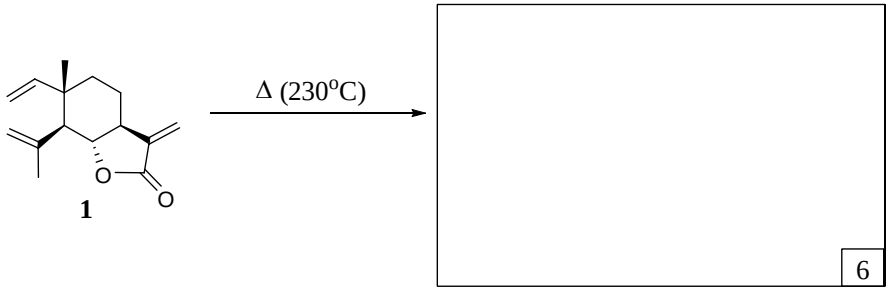


a) Why doesn't **A** react?

b) Why doesn't **B** react?

c) Why doesn't **C** react?

3. a) Show the mechanism (curved electron flow arrows) and product of the Cope rearrangement of **1**.

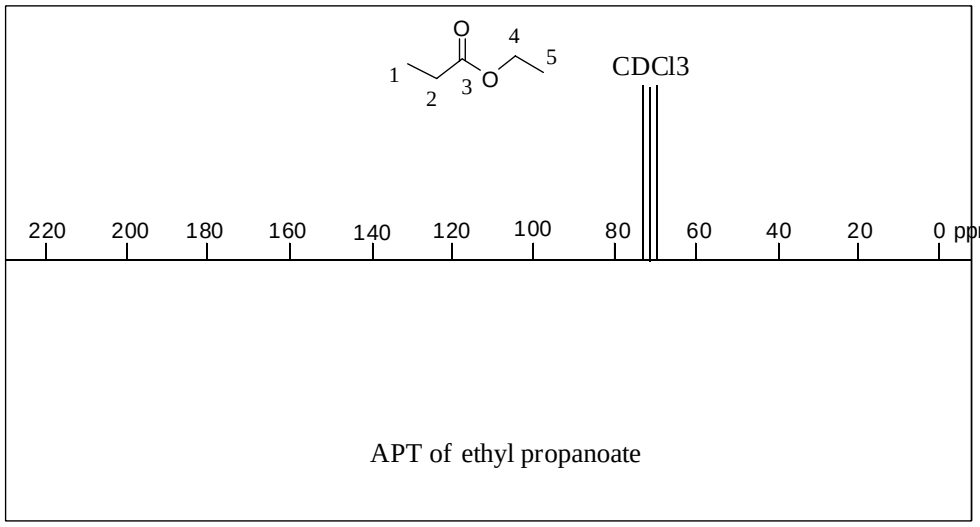


1 **2**

b) As reported in the scientific literature, this reaction affords only 33% of **2** along with 67% of **1**. Explain why this might be happening. (6 pts.)

27 total pts.

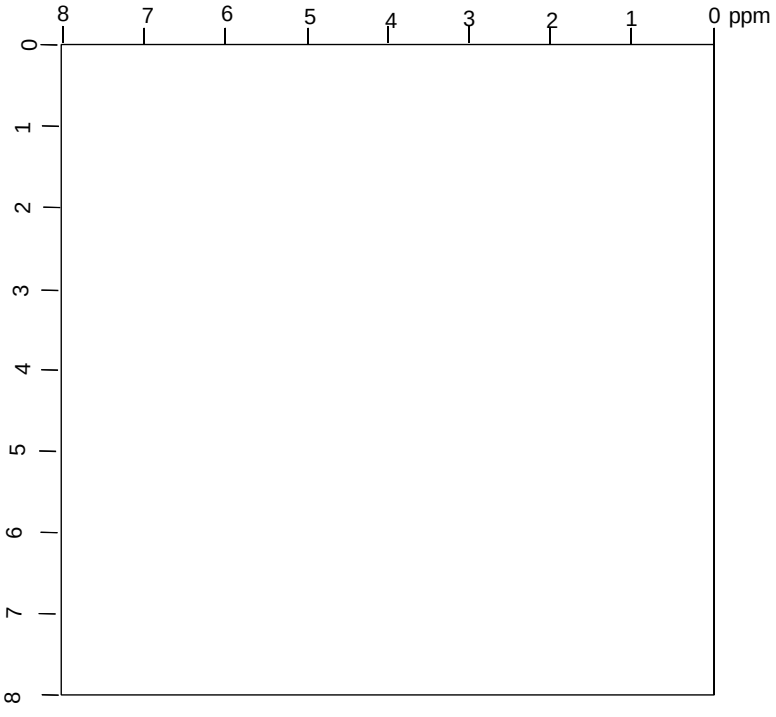
4. a) Draw the expected APT spectrum for ethyl propanoate. Label the ^{13}C signals on the spectrum with the numbering scheme in the structure below. There are chemical shift tables on page 7 of the exam that may help in answering the NMR questions. (10 pts.)



APT of ethyl propanoate

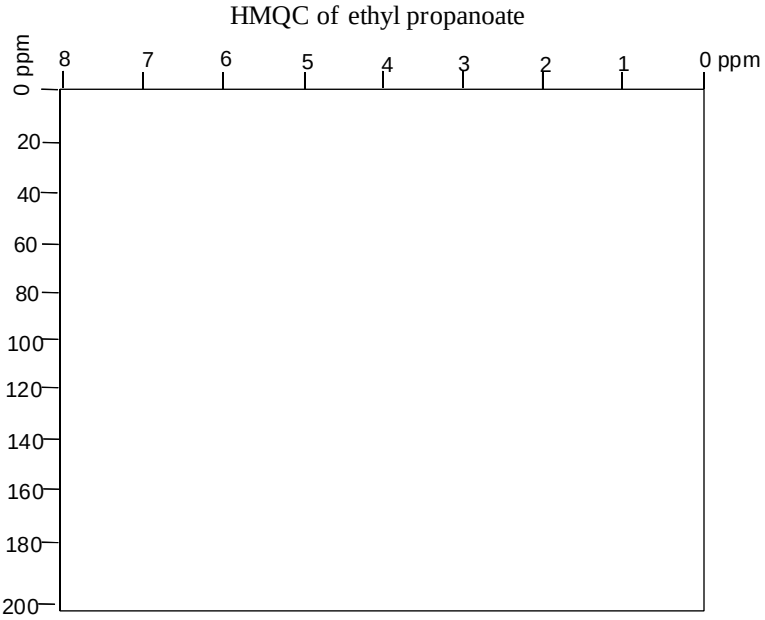
b) Draw the expected COSY spectrum for ethyl propanoate. You should place dots on the 2D spectrum in the locations where there would be signals. Label the dots on the spectrum with the numbering scheme in the structure above. You only need to label one of the two crosspeaks. You do not need to show the spectrum projections on the axes nor do you need to worry about showing peak splitting information. (10 pts.)

2D COSY NMR of ethyl propanoate



20 total pts.

c) Draw the expected HMQC spectrum for ethyl propanoate. You should place dots on the 2D spectrum in the locations where there would be signals. Label the dots on the spectrum with the numbering scheme in the structure on page 5. You do not need to show the spectrum projections on the axes nor do you need to worry about showing peak splitting information. (10 pts.)



10 total pts.