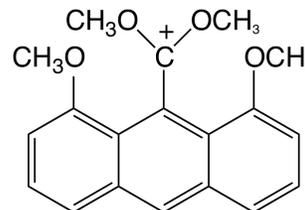
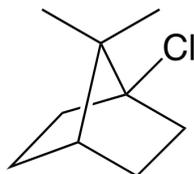
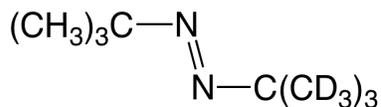


Chemistry 125 Fifth Examination
February 4, 2011

Name _____

The exam budgets 50 minutes, but you may have 60 minutes to finish it. Good answers can fit in the space provided.
Question values correspond to allotted time. Don't waste too much time on cheap questions.

1. (10 min) The following molecules were carefully designed to answer particular questions about reaction mechanisms.



CIRCLE ONE (ONE ONLY) of the molecules and **explain**

- (A) What question(s) it was designed to answer.
- (B) What features of the molecule were relevant to the experimental design.
- (C) What answer study of this molecule provided to the question(s) in part A.

- 2.** (5 min) It is frequently said that the stability order of carbon radicals is tertiary > secondary > primary.
- A.** What evidence supports this contention?
- B.** What experimental and computational evidence shows that there is more to this series than simply “radical stability”?
- 3.** (2.5 min) What is curious about the hydrogen bond in the hydrated hydroxide ion (H_3O_2^-)?
- 4.** (2.5 min) Why is HBr the only hydrogen halide that undergoes free-radical addition to alkenes?

5. (2 min) List four factors that can be important in determining the **pKa** for an organic acid (just name, no explanation)
- A.
 - B.
 - C.
 - D.

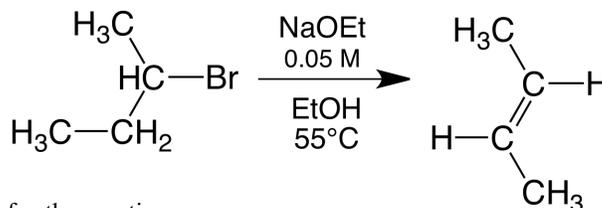
6. (6 min) Fill in the table by drawing two pairs of related acids **with their pKa values** (if you wish, one acid can appear in both pairs, in which case you would have a series of three acids), and **explain** below how their relative pKa values relate to factors you listed question 5.

PAIR I	
Structure	pK _a
1	
2	
Explanation:	

PAIR II	
Structure	pK _a
1	
2	
Explanation:	

7. Consider these influences on the rate of this elimination reaction:

- A) Increasing $[\text{NaOEt}]$ to 0.1 M doubles the rate
 B) Using of *i*-PrI instead of *i*-PrBr increases the rate
 C) Using $(\text{CD}_3)_2\text{CHBr}$ instead of *i*-PrBr slows the rate about 7-fold

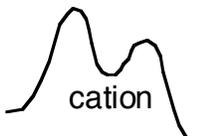
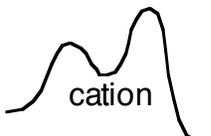
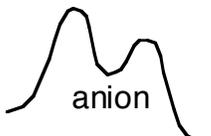
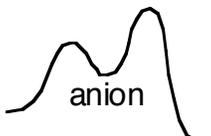


A. (7.5 min) Below are five possible reaction coordinate diagrams for the reaction.

The first two involve initial loss of bromide with formation a carbon cation intermediate.

The second two involve initial abstraction of a proton by ethoxide with formation of a carbon anion intermediate.

Put an **X** in the box for each mechanism that **IS consistent** with the corresponding experimental observation (A-C) above.

Mechanism					
(A) 0.1M NaOEt					
(B) I for Br					
(C) D for H					

B. (1.5 min) This elimination is said to follow “Saytzeff Rule” regiochemistry. What would have been the product if it had followed the “Hoffman Rule”?

[Just draw the structure, no explanation necessary]

C. (3 min) **Explain** which mechanism (or pair of mechanisms) in part A would be most strongly favored by using a more polar solvent (*e.g.* water containing only enough EtOH to achieve dissolution).

D. (10 min) Assuming that this is an **E2** reaction, **draw as accurate a diagram as you are able** showing the starting 2-bromobutane and ethoxide molecules **properly situated in space** for reaction. Include **carefully drawn curved arrows** showing electron pair shifts. Clearly **show the proper conformation** of the 2-bromobutane.

Draw your diagram **on the back of this page**.