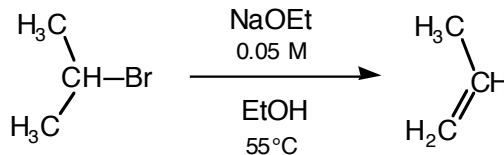


Chemistry 124 Fifth Examination
February 3, 2010

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.

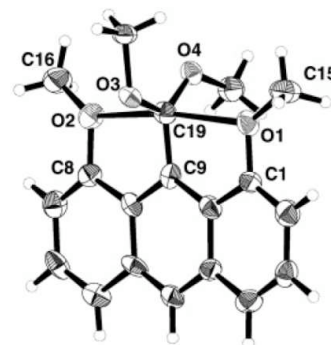
1. (8 min) Influences on the rate of this elimination reaction:
- A) Using $(\text{CD}_3)_2\text{CHBr}$ instead of *i*-PrBr slows the rate about 7-fold
 - B) Using of *i*-PrI instead of *i*-PrBr increases the rate
 - C) Increasing $[\text{NaOEt}]$ to 0.1 M doubles the rate



Consider the following five possible profiles for the reaction, four of which have a carbon cation or a carbon anion intermediate. Put an **X** in the box for each mechanism that **IS consistent** with each of the three observations above.

Mechanism					
(A) D for H	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
(B) I for Br	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
(C) 0.1M NaOEt	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

2. (5 min) Explain the main logical error that was made when the structure of the ion illustrated on the right was used to “prove” that a trivalent carbon cation with two adjacent nucleophiles should be considered pentavalent.



- 3.** (5 min) **Draw three lines** to connect each radical in the second column with the corresponding dissociation energy (kcal/mole) in the first column for its bond to the H atom.

Then **explain the size of the other two** values relative to that for the H-CH₃ bond.

<u>BDE_{H-R}</u>	<u>R</u>
88.8	CH ₃
105.0	CH=CH ₂
110.7	CH ₂ -CH=CH ₂

- 4.** (2 min) Explain the source of the stabilization called “hydrogen bonding”.
- 5.** (4 min) Why is cyclopropyl bromide so much slower to react in S_N2 substitution reactions than cyclopentyl bromide?

6. (4 min) List six factors that can be important in determining the pK_a for an organic acid (just name, no explanation)

A.

B.

C.

D.

E.

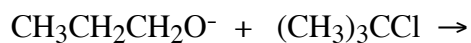
F.

7. (6 min) Fill in the table by drawing two pairs of related acids with their pK_a 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 what their relative pK_a s teach about relevant factors you listed question 6.

PAIR I	
Structure	pK_a
1	
2	
Lesson(s):	

PAIR II	
Structure	pK_a
1	
2	
Lesson(s):	

8. (2 min) Show the **principal product(s)** from the following reaction. (No mechanism necessary)



9. (2 min) Show **reagent(s)** for accomplishing the following conversion in a practical manner. (No mechanism necessary).



10. (3 min) What is done **to make radioactive fluoride a more reactive nucleophile**, so that a fluorinated analogue of glucose can be prepared rapidly for use in PET scanning.

11. (3 min) Suppose you found that quadrupling the concentration of a reagent only doubles its reaction rate. How might this be explained?

- 12.** (6 min) C-H bond dissociation energies are often used to support the contention that more substituted free radicals are more stable (t-Bu > i-Pr > Et > CH₃ in stability). Explain briefly how other data casts doubt on this interpretation.