Chemistry 116 Sec. A (8:00-8:50)
Exam No. 4
"Substitution and Elimination"
December 1, 2000

Instructions: You have until 8:55 a.m. to complete the exam. At that time, I will request that all remaining test takers cease writing, turn their exams over, and pass them to their rightmost isle. If you finish before 8:50 a.m. you may turn in the exam at the front of the room prior to leaving. If you finish within the final 5 min. of class, please turn your exam over and remain seated until I call for the remaining exams to be turned in. *In fairness to all, anyone still working on the exam after "time" is called will receive a grade of zero!*

Be sure to read the instructions for each question. It may be helpful to skim the entire exam and solve the easier questions first.

Exam Agreement: I, _____, have read and agree to
(Please print)
abide by the instructions above. On my honor, I have neither given nor accepted any help during this exam.

Signature: _____

College: _____

1. For each pair shown below, circle the structure that best fits the description and provide an explanation for your selection. *Note:* some explanations may require illustrations to receive full credit. (7 points each)

Best solvent for an E1 reaction?

$(CH_3CH_2)_2NH$ (δ^- on N, δ^+ on H) vs. CH_3CH_2OH (δ^- on O, δ^+ on H)

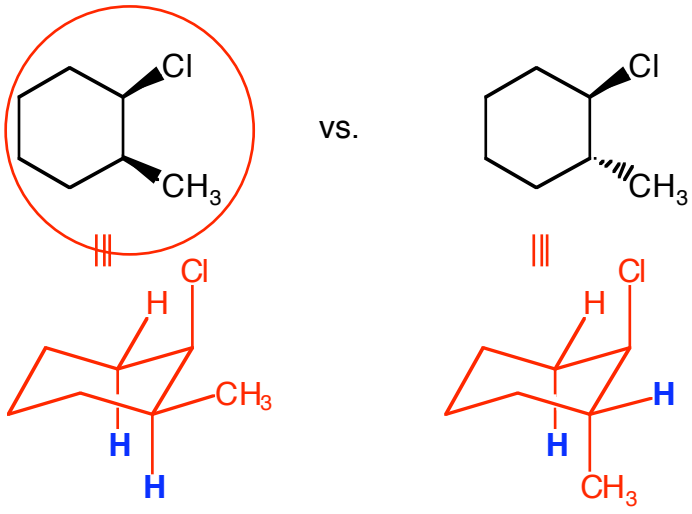
Oxygen is more electronegative than nitrogen. Thus, oxygen induces a larger dipole on the hydrogen attached to it than nitrogen does. The greater polarity of this bond makes CH_3CH_2OH a more polar solvent and better able to stabilize the cation and anion that will be formed in the E1 reaction. This stability lowers the energy of the intermediates and thus (according to Hammond's Postulate) will decrease the energy of the transition state. This, in turn, lowers the activation energy and speeds up the E1 reaction.

Solvent that makes NaCN a stronger nucleophile?

DMF vs. CH_3OH

CH_3OH is a polar protic solvent. It possesses both a partially positive end and a partially negative end. These two partially charged ends will allow it to solvate both the cation (Na^+) and the anion (^-CN) of NaCN. DMF, on the other hand, is a prolar aprotic solvent. It only possesses a partially negative end, which can only solvate the cation (Na^+). An anion (such as the nucleophile, ^-CN) that is not solvated is less stable than one that is solvated. Since ^-CN is less stable in DMF, it is more reactive and thus a stronger nucleophile.

Gives the faster E2 reaction?

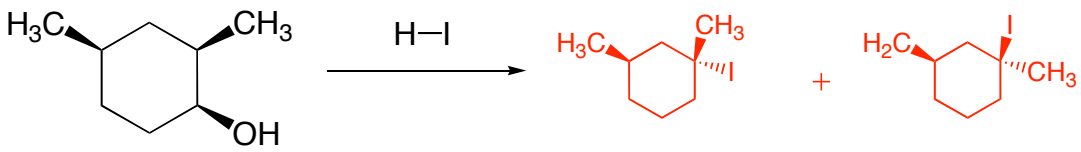


The alkyl chloride on the left possesses two anti-coplanar β-protons while the other alkyl chloride only possesses one anti-coplanar β-proton. Therefore, the one on the left is twice as likely to react with a base than the one on the right.

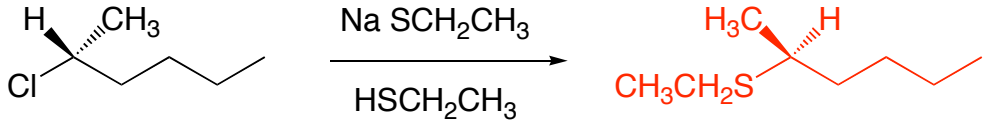
2. Draw the **major product** of each of the following reactions. For partial credit, indicate whether it is an E1, E2, S_N1, or S_N2 reaction on the line provided. *Be sure to include stereochemistry in your answers where appropriate*. (6 points each)

Type of Reaction

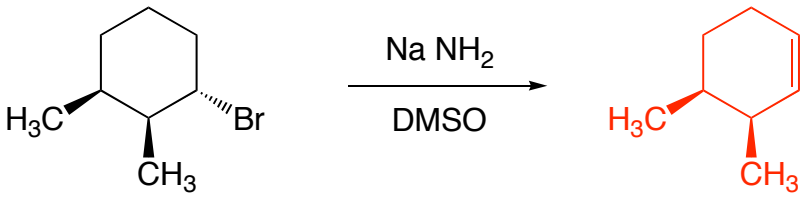
S_N1 (a)



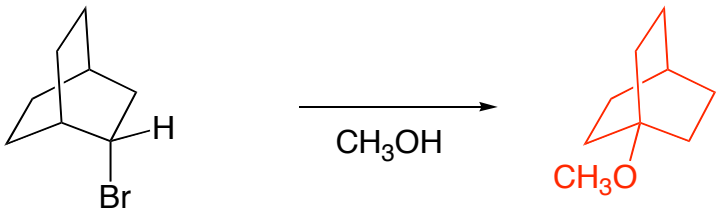
S_N2 (b)



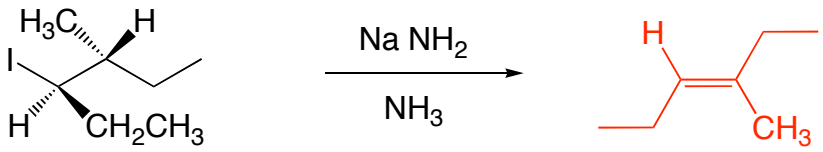
E2 (c)



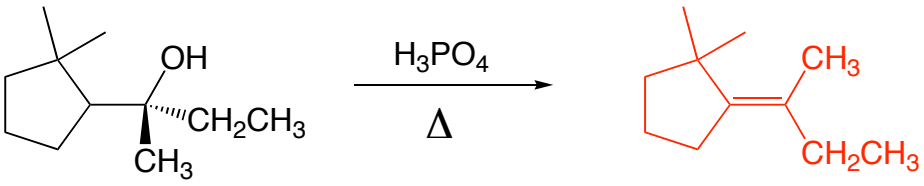
S_N1 (d)



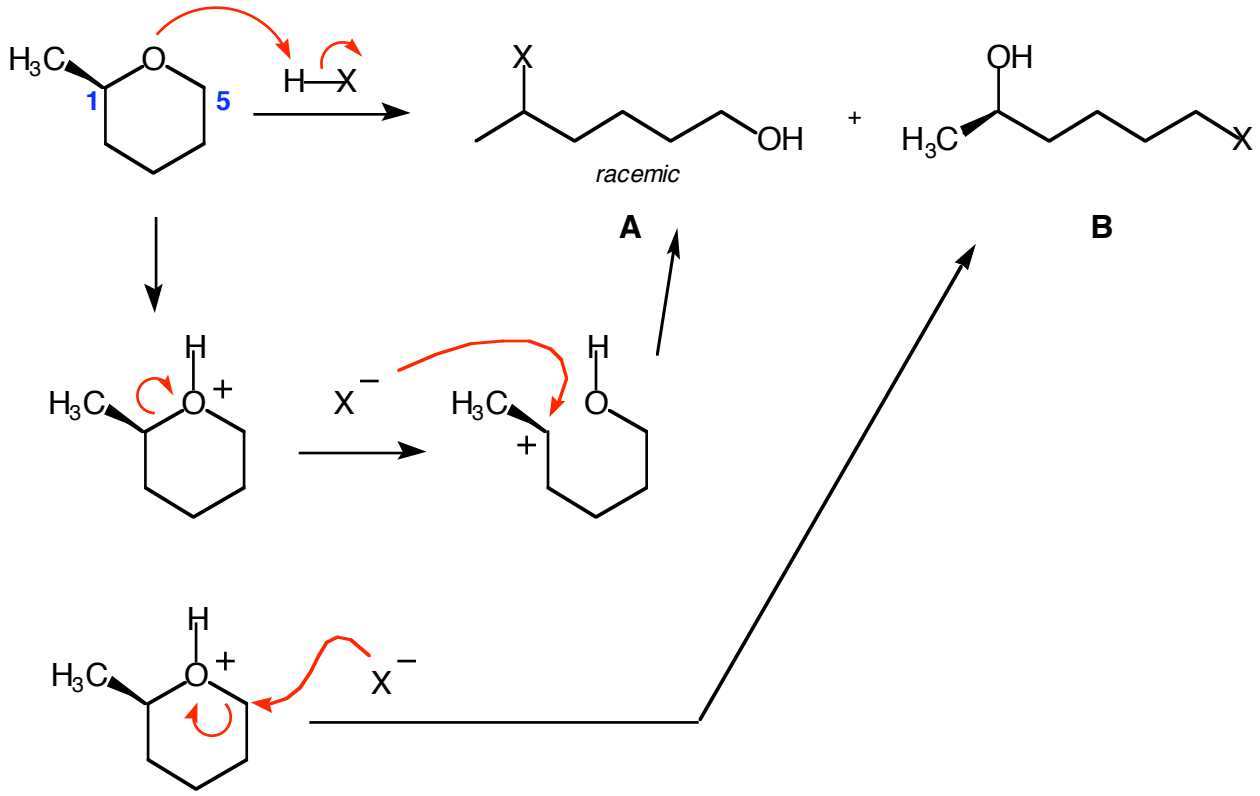
E2 (e)



E1 (f)



3. When the ether shown below is reacted with HX, two sets of products are obtained. Provide mechanisms that account for the formation of the products and answer the questions that follow: (8 points)



a) What will happen to the ratio of **A**:**B** if H-Cl is used instead of H-Br? (6 points)

The nucleophile does not affect the rate of a SN1 reaction, the reaction leading to A. The reaction leading to B is a SN2 reaction. The strength of the nucleophile is very important in an SN2 reaction. Since Cl anion is a weaker nucleophile in water than Br anion, we would expect the amount of B to *decrease* if HCl is used versus when HBr is used.

b) Is it possible to obtain **B** as a racemic mixture or **A** as a single enantiomer? Why or why not? (5 points)

B will never be racenic because the only stereocenter in the product never takes part in the reaction mechanism!

The carbon leading to A is a secondary carbon (C_1). Secondary carbon's *can* undergo SN2 reactions. If conditions could be adjusted to favor an SN2 reaction, then A would be formed via backside attack only; it would therefore be a single enantiomer.

4. (Choose 2 out of 3) Propose a synthesis (sequence of reactions) that will accomplish each of the following transformations. *Be sure to include the products of each step*. Clearly indicate which two you wish for me to grade. If no indication is made, I will grade the first two. (12 points each)