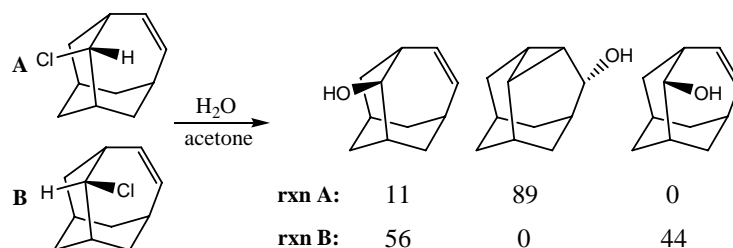


Ch 144A, Fall 2007
Homework Set
Due Tuesday, Dec. 4, 10 AM, Rom 359 Crellin

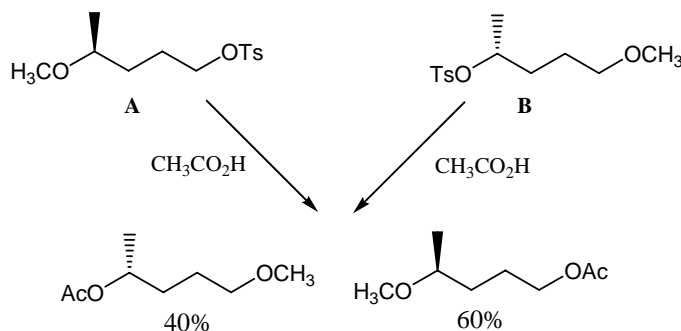
Homework Policy: This homework is to be done individually. No collaboration or consultation with other students is permitted. You may consult your class notes and the textbook. *Searching the internet, consulting the primary chemical literature, or perusing the textbook Solutions Manual for clues or answers, as well as consulting problem sets or exams from past years is forbidden.*

1. (10 points)

(a) Explain the different product ratios for reactions **A** and **B**.



(b) Explain the observations shown below. Compound **A** reacts with acetic acid to give two products in a 40:60 mixture. Compound **B** reacts with acetic acid to give the same products in the same ratio.

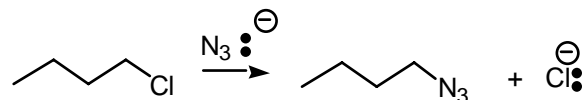


2. (15 points) A More O'Ferrall Jencks plot for elimination reactions is shown on the last pages of this homework set. Use these plots to answer the following questions. You will need to hand in the pages with the plots when you hand in your homework.

- Label the X and Y axis with a phrase descriptive of the structural change taking place.
- How would the transition state change if the leaving group changes from OH to OTs? Draw vectors on plot (b) to answer this question.
- How would the transition state change if R is changed from Ph to CH₃? Draw vectors on plot (c) to answer this question.
- Consider plot (d). Suggest a change in reactants that would lead to the new transition state shown.

3. (15 points)

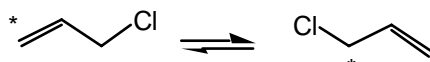
Use the More O'Ferrall/Jencks plot on the last page of this homework to analyze how the position of the S_N2 transition state changes for the reaction of n-butylchloride with azide under the following conditions. Be sure to clearly label the axes and corners.



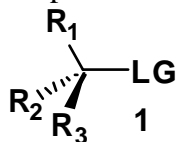
- a) The nucleophile azide is changed to methanol.
- b) The leaving group chloride is changed to iodide.

4. (10 points)

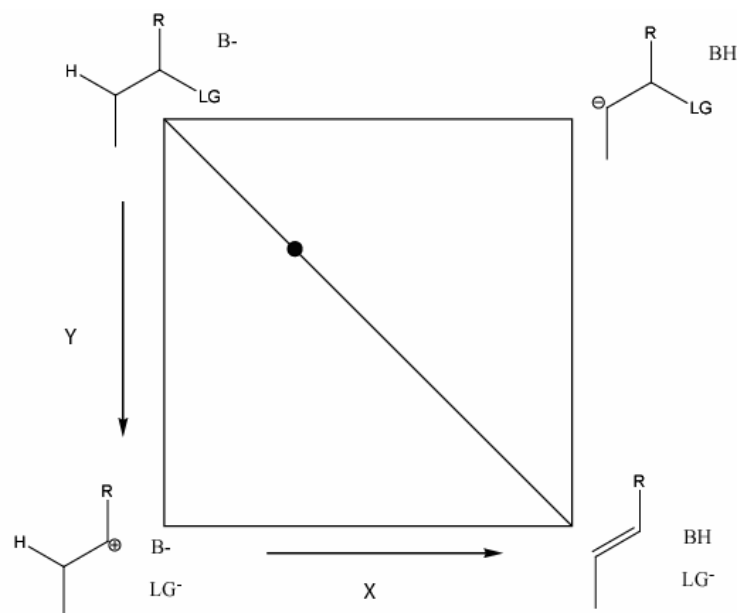
(a) During the S_N1 solvolysis of allyl chloride, some scrambling of the position of the chloride often occurs. The extent of scrambling has no dependence upon the concentration of added chloride salts. Why is this?



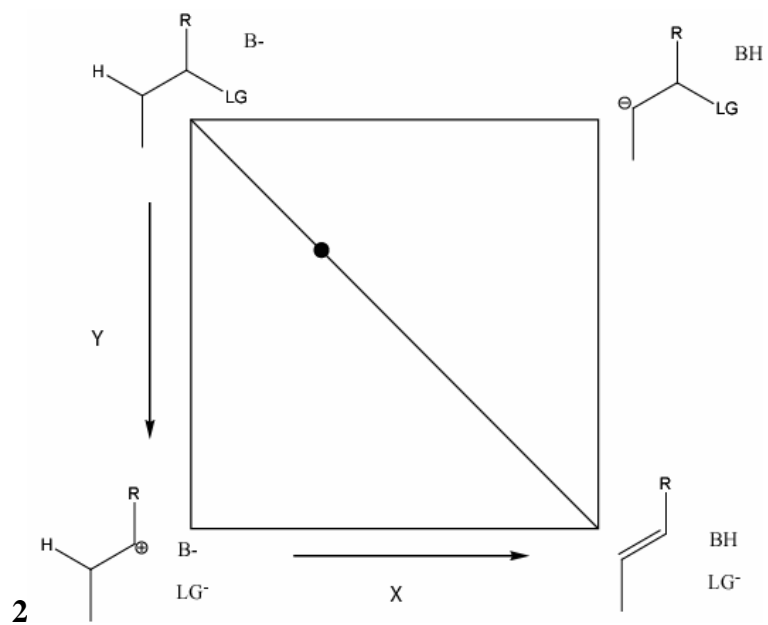
(b) In the solvolysis of stereogenic structures such as **1**, stereochemical scrambling is often faster than product formation. To test whether the such scrambling occurs within a contact ion pair or via reaction of the carbenium ion with free leaving group, radiolabeled leaving groups can be added to the reaction. What does it mean when the reactant undergoes stereochemical scrambling faster than incorporation of radiolabeled leaving group?



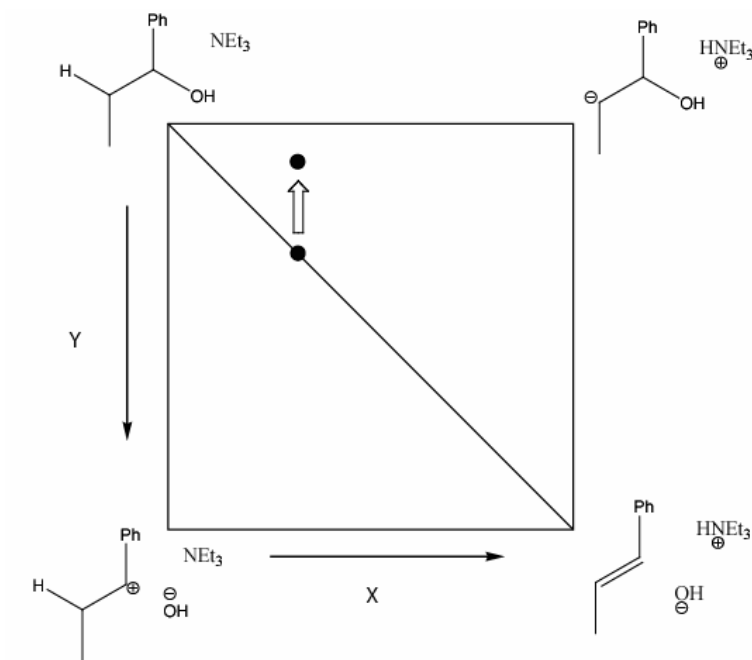
2b



2c



2d



#3

