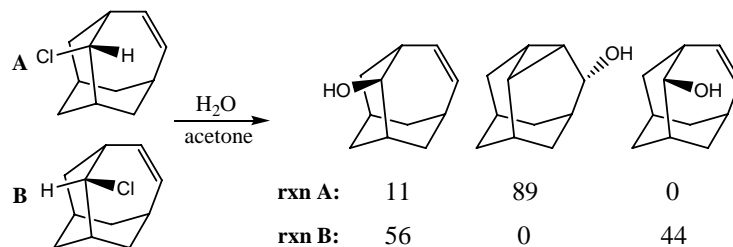


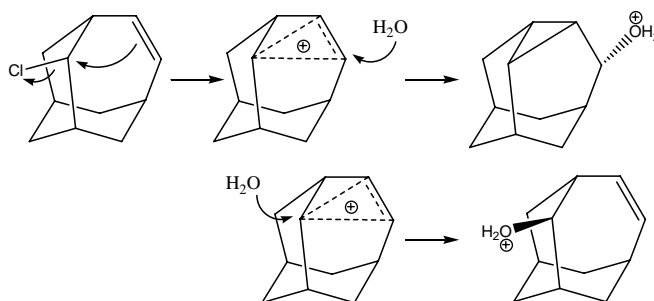
Ch 144A, Fall 2007
Homework Set Answer Key

1. (10 points)

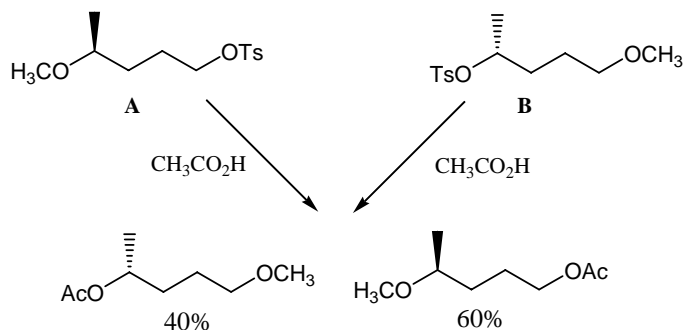
(a) Explain the different product ratios for reactions **A** and **B**.



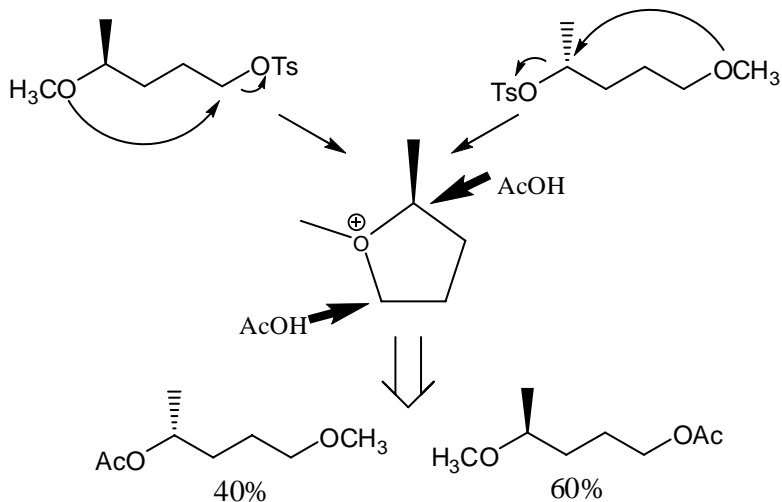
The only difference in the starting material of reactions **A** and **B** is the stereochemistry at the carbon with the Cl leaving group. In case **A** the pi bond is situated to the back of the leaving group and therefore can assist in Cl leaving as seen in part (a) forming a nonclassical carbocation. In case **B** the Cl is on the same side as the pi bond, thus the bond can not assist the leaving group and a traditional carbocation is formed. The carbocation has an essentially planar geometry so the nucleophilic solvent (H_2O) can add to either side, giving both diastereomers in ~50:50 yield.



(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.



Lone pair assistance is the primary concern here. In each case the methoxy group can assist in the tosylate leaving forming a common 5-member ring intermediate. Acetic acid can attack either of the carbon atoms α to the Oxygen and on the ring, thus reopening the ring. After deprotonation, this gives the two products.



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.

(a) Label the X and Y axis with a phrase descriptive of the structural change taking place.

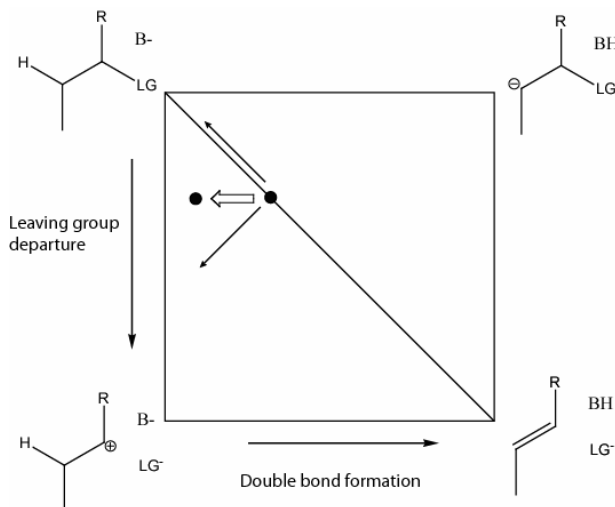
X = Extent of Double bond formation

Y = Extent of Leaving Group departure

(b) How would the transition state change if the leaving group changes from OH to OTs?

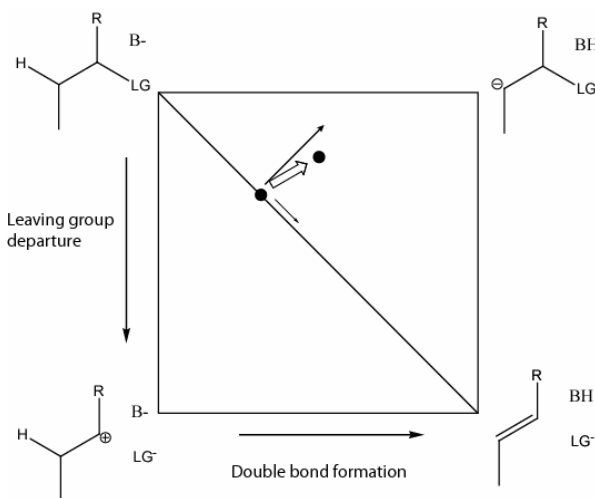
Draw vectors on plot (b) to answer this question.

If the leaving group changes from OH to OTs, this decreases the energy of LG⁻ so we expect the lower two corners to decrease in energy. Following our normal rules we get a shift in the TS as shown below. This shift suggests that for the new reaction (with an OTs) leaving group, there is less double bond character in the TS than in the original reaction.

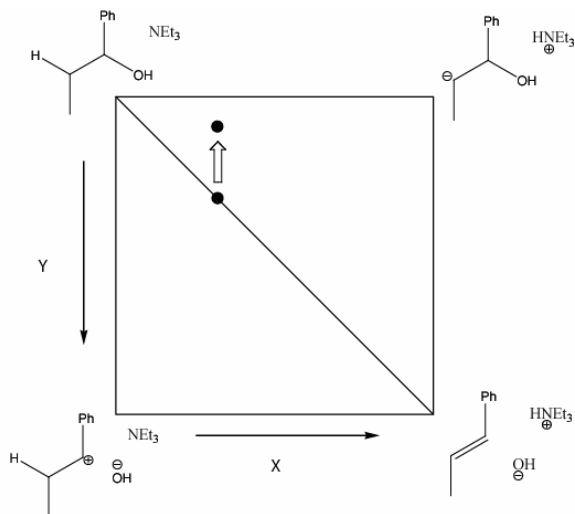


(c) How would the transition state change if R is changed from Ph to CH₃? Draw vectors on plot (c) to answer this question.

If R is changed from Ph to CH₃ the primary change is an increase in energy of the carbocation, which will no longer be resonance stabilized. The alkene product also increases in energy a little as it will no longer be part of a conjugated system. We move toward the higher energy corner along the diagonal (Hammett), however, this vector is small as the energy has only changed slightly. We move toward the lower energy corner perpendicular to the diagonal, as shown. This vector is large as the loss of resonance stabilization is quite large for the carbocation. This shift suggests that in the new TS there is more bonding between the carbon and LG than in the original reaction and there is more double bond character than in the original reaction.



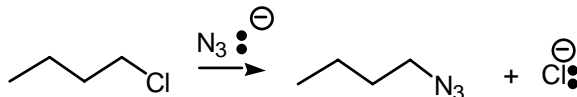
(d) Consider plot (d). Suggest a change in reactants that would lead to the new transition state shown.



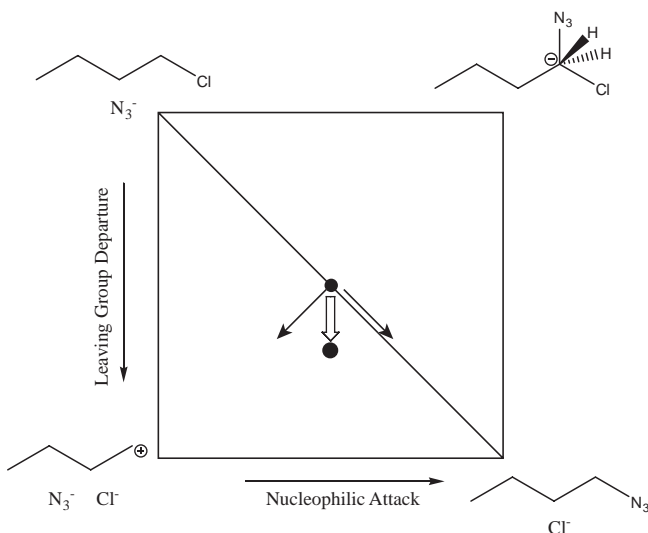
If we increase the strength of the base, we will destabilize the left side of the plot and stabilize the right side of the plot. One example might be using LDA as the base instead of NEt_3 .

3. (15 points)

Use the More O'Ferrall/Jencks plot on the last page of this homework to analyze how the position of the $\text{S}_{\text{N}}2$ transition state changes for the reaction of *n*-butylchloride with azide under the following conditions. Be sure to clearly label the axes and corners.

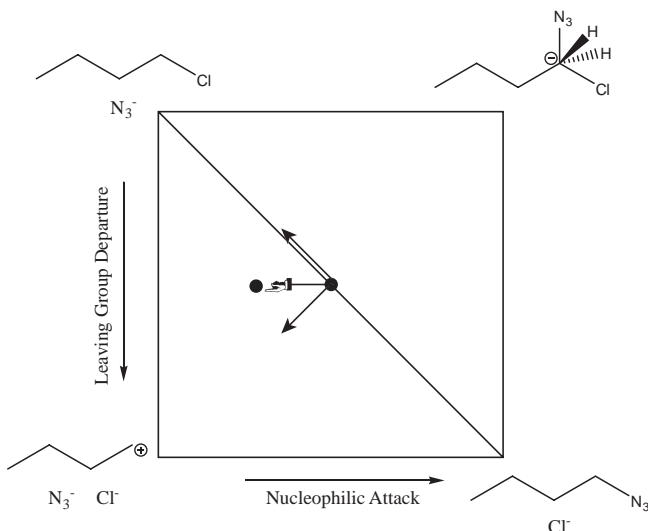


a) The nucleophile azide is changed to methanol.



When the nucleophile is changed from azide to methanol, we are stabilizing the nucleophile thus the left side of the diagram lowers in energy. The new transition state has more leaving group departure.

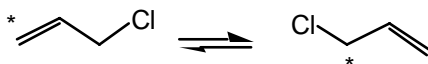
b) The leaving group chloride is changed to iodide.



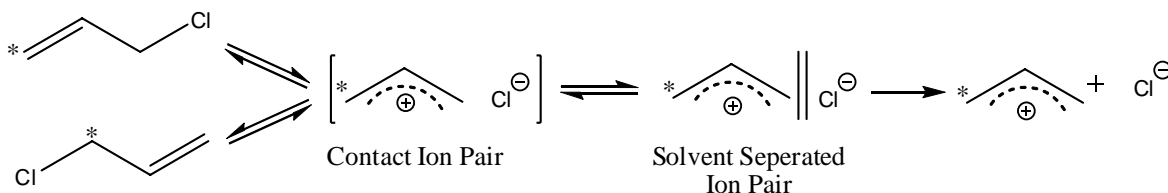
If we change the leaving group to I^- from Cl^- we stabilize the leaving group so the bottom edge lowers in energy. The new transition state has less nucleophilic attack.

4. (10 points)

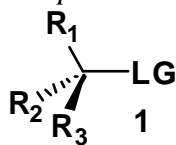
(a) During the $\text{S}_{\text{N}}1$ solvolysis of allyl chloride, some scrambling of the position of the chloride often occurs. The extent of scrambling has no dependence upon the concentration of added chloride salts. Why is this?



The scrambling occurs due to the equilibrium between the contact ion pair and the starting material. The **contact ion pair** lifetime is long enough for rotation to occur, thus scrambling the starting material.



(b) In the solvolysis of stereogenic structures such as **1**, stereochemical scrambling is often faster than product formation. To test whether 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?



When the stereochemical scrambling occurs faster than incorporation of radiolabelled leaving group, it means the scrambling is due to the contact ion pair.