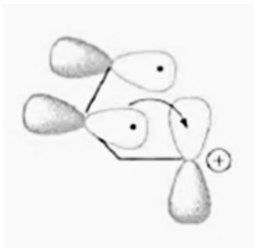
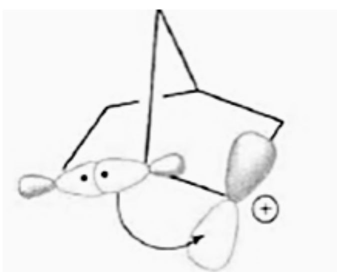
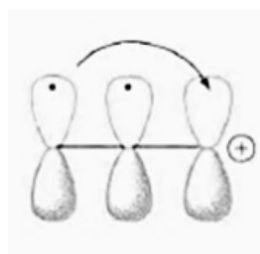
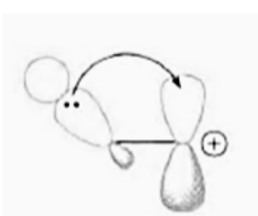
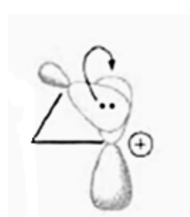
1. (6 points) Write the term that chemists use to describe the type of carbocation stabilization shown for the following examples:



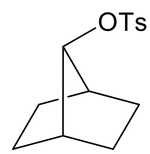




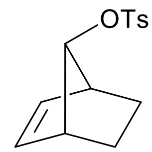




2. (8 points)
One of the following structures undergoes acetolysis 10^{11} times faster than the other.



A



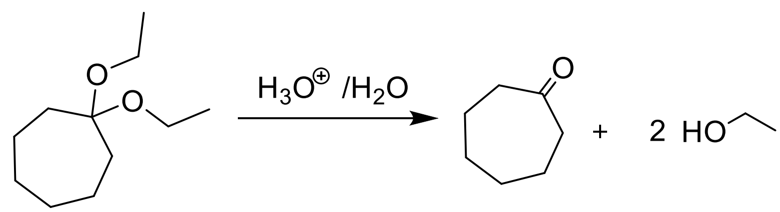
B

a) Which one is faster and why? (4 points)

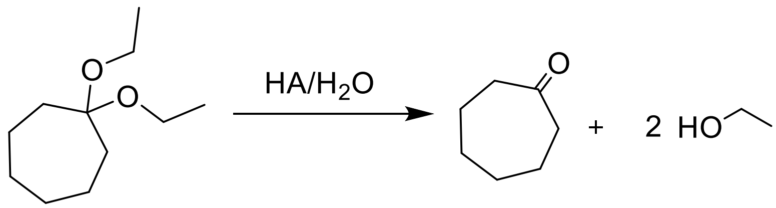
b) What stereochemistry would you expect in the products from **A**? Briefly explain your answer. (2 points)

c) What stereochemistry would you expect in the products from **B**? Briefly explain your answer. (2 points)

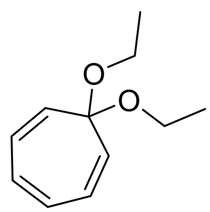
4. (29 points)
   a) Write a mechanism for the hydrolysis of the acetal following a specific acid-catalyzed route. Show all arrow pushing. (10 points)



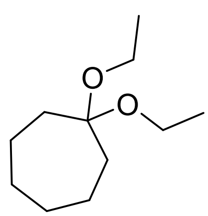
b) Now write a general acid-catalyzed mechanism for the same reaction. Show all arrow pushing. (10 points)



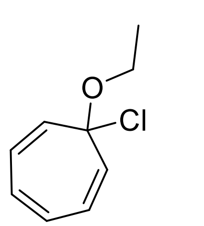
c) The hydrolysis of the following three structures either show specific acid, general acid, or no catalysis. Predict which corresponds to each mechanistic alternative and **explain** your answer. (9 points)



A



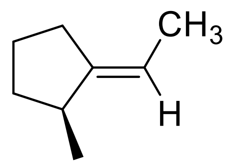
B



C

5. (13 points)

a) For an E2 reaction, draw the two different alkyl bromide regioisomers that would give the following product. Don't yet worry about showing stereochemistry. (4 points)



1 **2**

b) Draw all the possible alkene regioisomers that can be produced from the two reactants you gave in part "a". **Circle** the regioisomer that dominates and tell us which rule you used to make the prediction. (5 points)

1 $\longrightarrow$

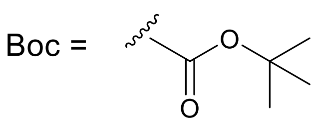
2 $\longrightarrow$

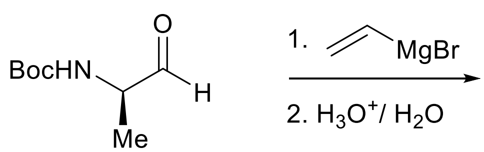
c) Now, considering the appropriate stereochemistry, draw the possible alkyl bromide stereoisomers that will give the desired alkene from part "a". (4 points)

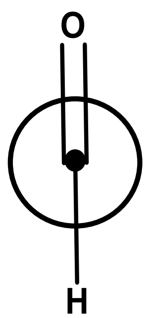
7. (10 points) Predict the preferential face of nucleophilic attack to the carbonyl carbon using the following models.

   a) Draw the preferential alcohol products of the nucleophilic addition using the Grignard reagents.
   b) Using the template given, draw a Newman projection to support your answer.

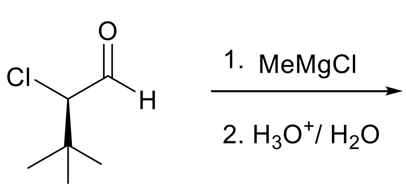
A. Felkin Ahn Model

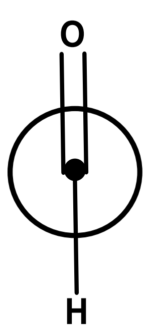






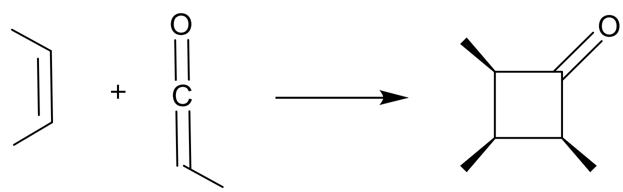
B. Cram Model



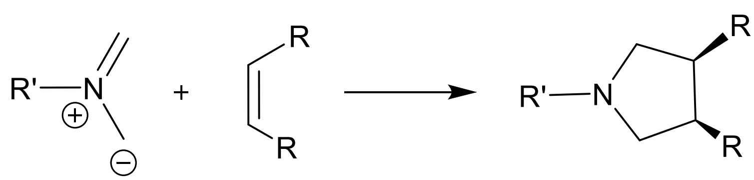


9. (8 points) The following two reactions are allowed. Label the two components appropriately to show that they obey the Woodward-Hoffman rules (i.e. σ2a, or the like).

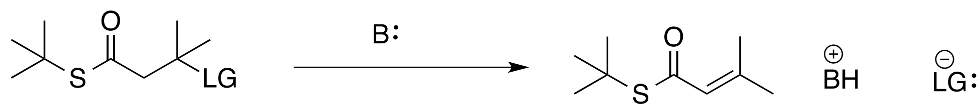
a)



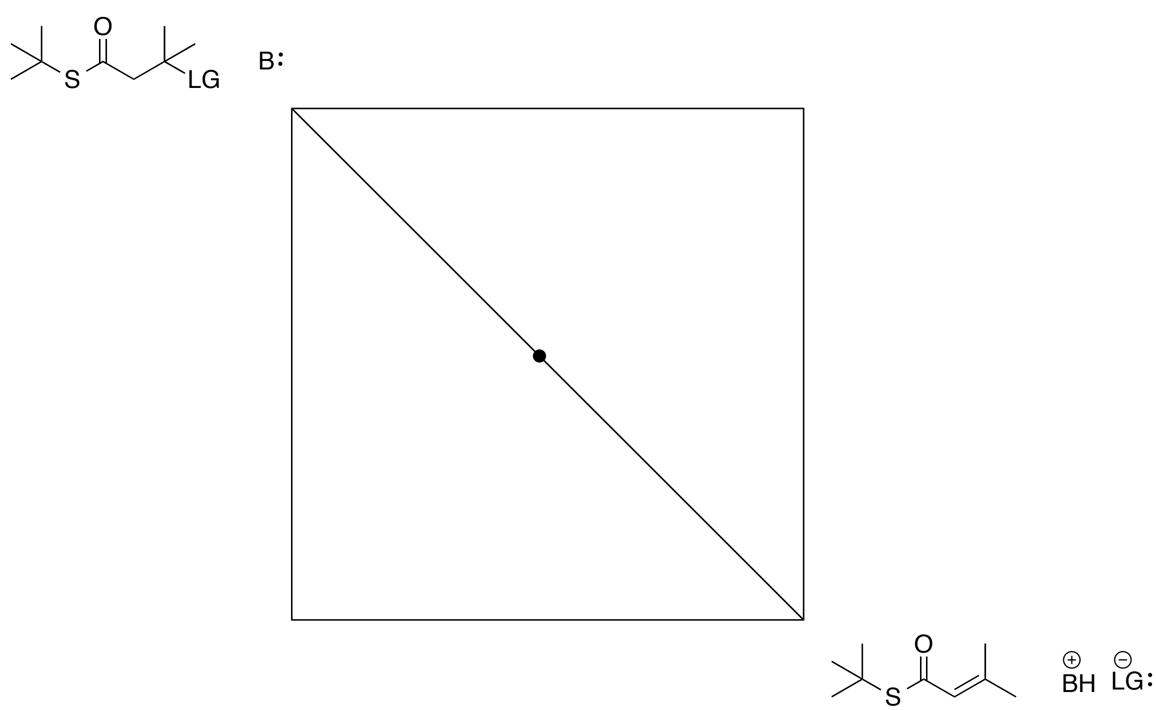
b)



6. (16 pts) For the following elimination reaction:

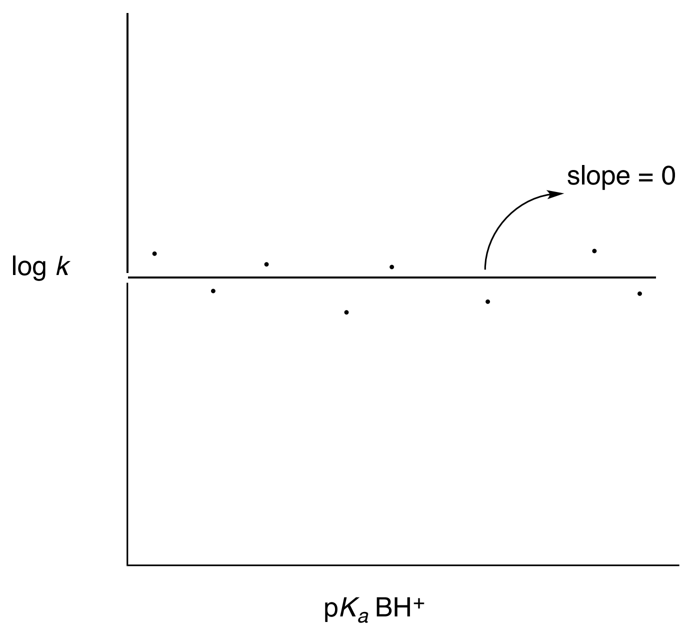


a) Fill in the corners and axes on the More O'Ferrall-Jencks plot below (4 pts):



b) What is the effect of having a better leaving group on the position of the TS in the E2 pathway? Why does this make sense? (2 pts)

Suppose the plot of log k vs. pK_a BH$^+$ of the above reaction gave a slope of zero.

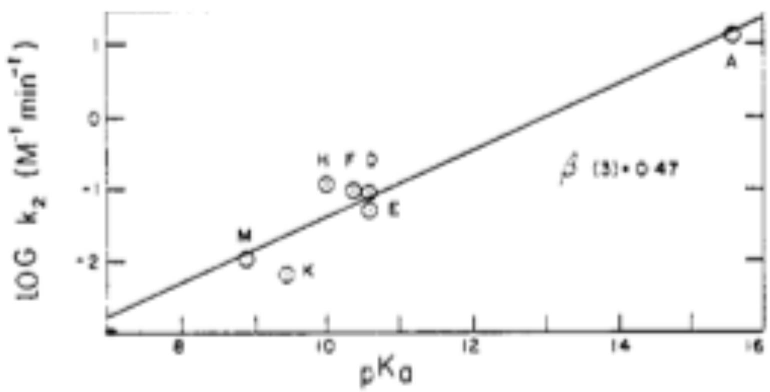


c) What is the extent of deprotonation occurring at the transition state of the rate-determining step? (2 pts)

d) What does the slope indicate about the type of base catalysis of the reaction? (2 pts)

e) Which reaction mechanism, E1, E2, or $E1_{CB}$ would give a slope of zero and kinetic dependence upon the base inasmuch as it only sets the solution's pH? (2pts)

However, when the experiment is actually performed, a plot of log k vs. p*Ka* BH^+ does **not** give a slope of zero. Instead, β=0.47, as shown below:

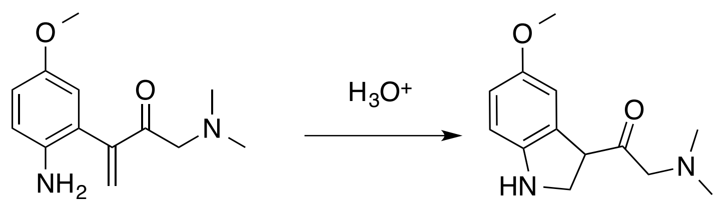


f) What effect does using a stronger base have on the extent of deprotonation at the transition state of the rate-determining step? (2 pts)

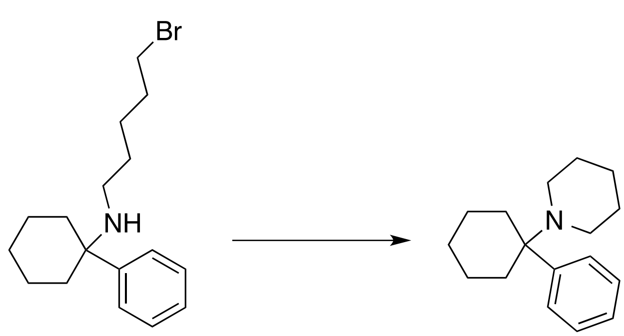
g) What effect does using a stronger base have on the rate of the elimination reaction? (2 pts)

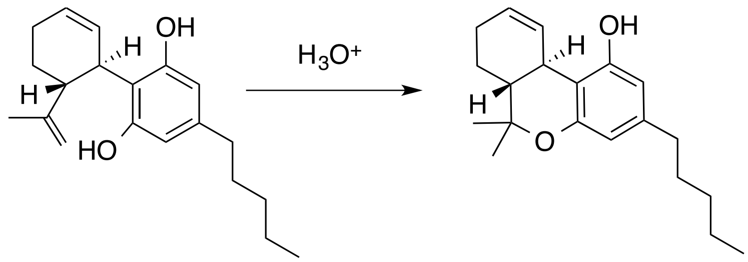
8. (6 pts, 2 each) Name the following cyclization reactions with the appropriate prefixes (number-endo/exo) and suffices (dig, trig, tet) and use Baldwin's table to determine whether or not each reaction is favored.

a)



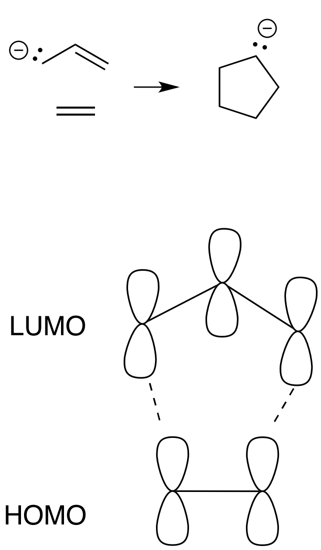
b)

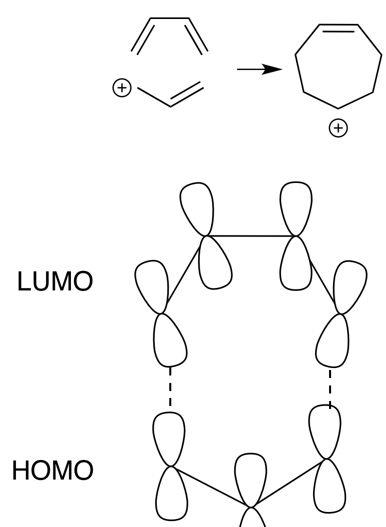


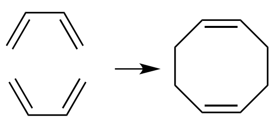
c) 

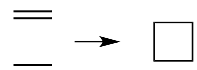
	Exo			Endo	
Ring size	dig	trig	tet	dig	trig
3	unfav	fav	fav	fav	unfav
4	unfav	fav	fav	fav	unfav
5	fav	fav	fav	fav	unfav
6	fav	fav	fav	fav	fav
7	fav	fav	fav	fav	fav

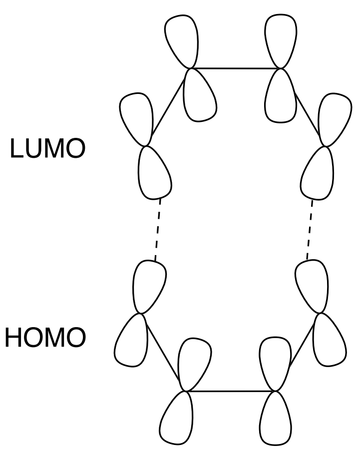
10. (8 pts, 2 each) Use frontier molecular orbital theory (FMOT) to fill in the orbitals for the reactions below. Indicate whether the reaction is allowed or forbidden in the geometry shown.

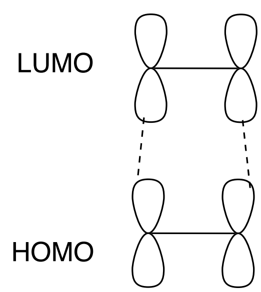




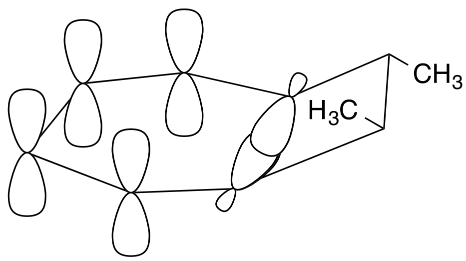


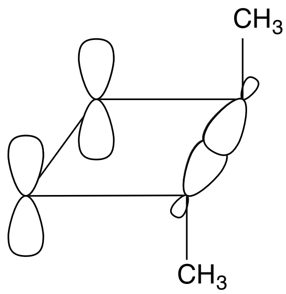




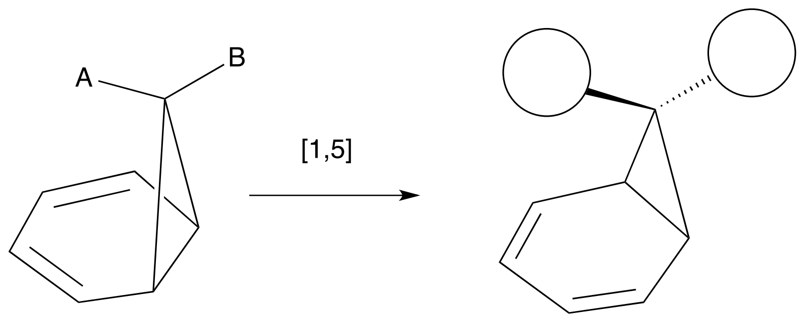


11. (8 pts, 4 each) For the following electrocyclic ring opening reactions fill in the orbitals below that make the reaction allowed. Describe the orbital movements as conrotatory or disrotatory for each reaction. Finally, draw the allowed product with correct stereochemistry


CH3
H3C



12. (8 pts) The cyclopropyl ring shown below can "walk" around the cyclohexyldiene ring by a series of [1,5] sigmatropic shifts.



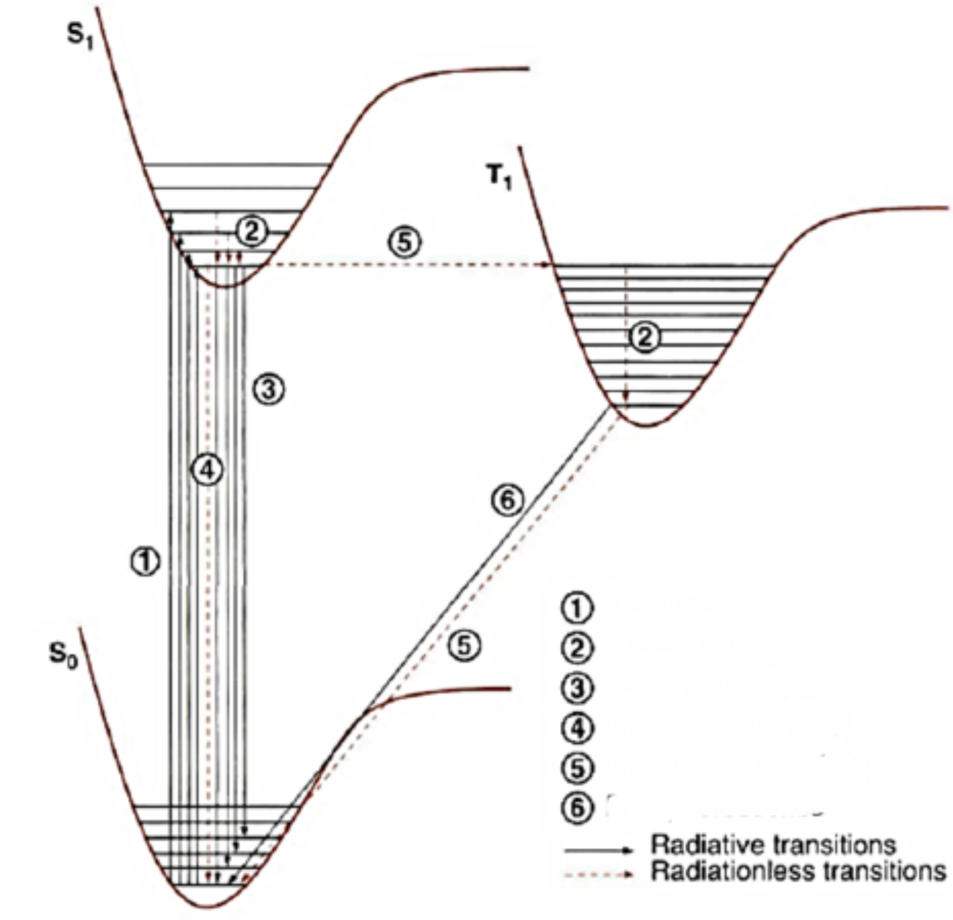
a) Draw the frontier molecular orbitals that control the sigmatropic shift shown above. (4 pts)

b) Determine the orientation of A and B after the shown sigmatropic shift, and fill in the appropriate letters on the product structure above. (2 pts)

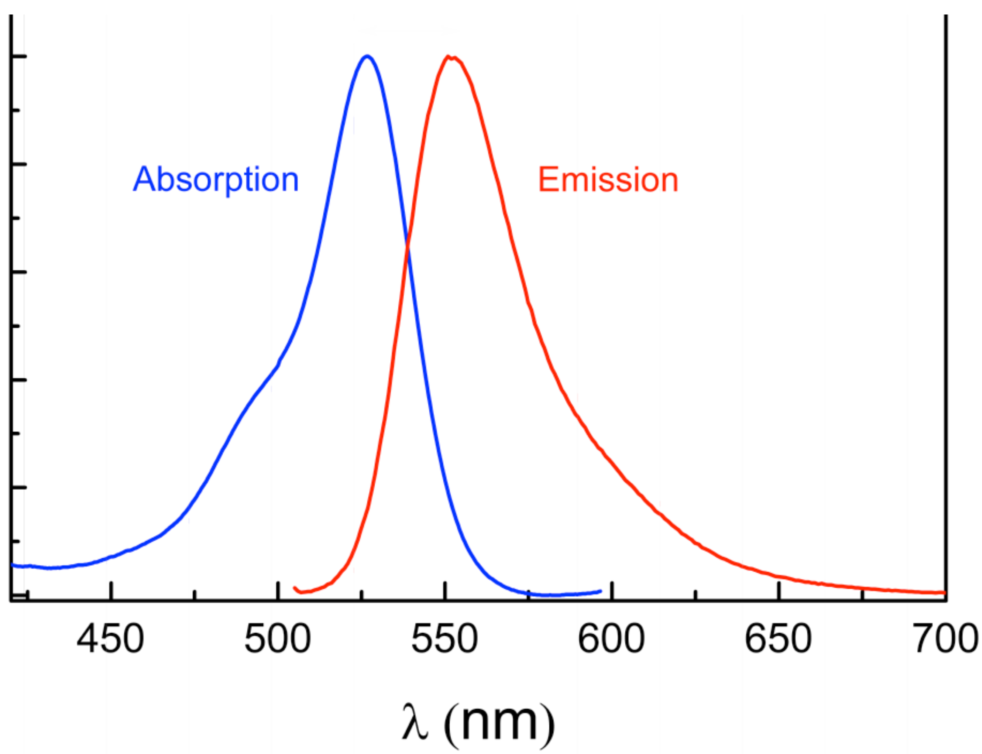
c) Is the result from part b surprising? Why or why not? (2 pts)

13. (11 pts)

a) Write the name of the labeled transitions next to each number shown on the following Jablonski diagram (6 pts):



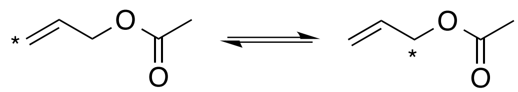
A certain fluorophore gave the following absorbance and fluorescence spectra:



b) Indicate the Stokes' shift on the above absorption/emission spectrum. (1 pt)

c) Using only S_0 and S_1, draw a Jablonski diagram below that shows the transitions that give rise to the different absorption and emission maxima. Label your diagram with "absorption" and "emission". (4 pts)

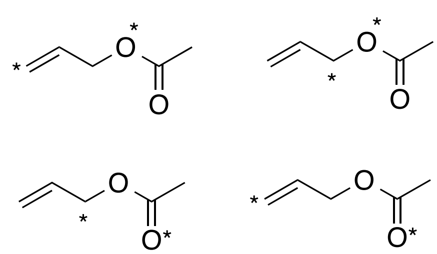
3. (9 pts) S_N1 solvolysis of this ^{13}C isotopically labeled allyl derivative results in scrambling of the starting material.



a) Draw the step(s) in the solvolysis that lead(s) to ^{13}C scrambling. (2 pts)

b) Explain why it is observed that extent of scrambling is NOT dependent on the concentration of any added sodium acetate. (2 pts)

If the oxygen is ^{18}O isotopically labeled, then the starting material can be scrambled as follows:



c) Draw the step(s) in the solvolysis that lead(s) to ^{18}O scrambling. (3 pts)

d) Which isotopic scrambling would you predict occurs faster? (2 pts)