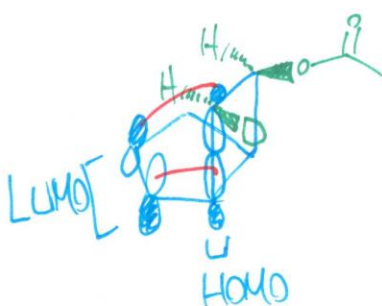
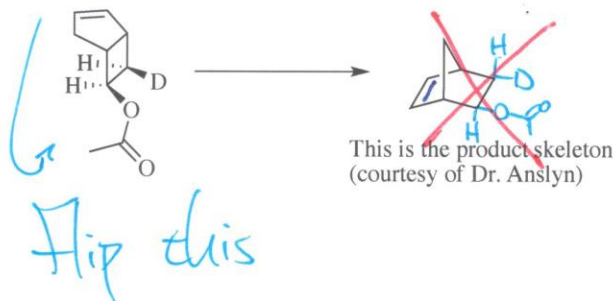


Name: Key!

Signature: _____

Page	Points	Points Possible
2		6
3		5
4		3
5		10
6		10
7		6
8		8
9		8
10		8
11		7
12		4
13		6
14		4
15		10
17		5
Total		100

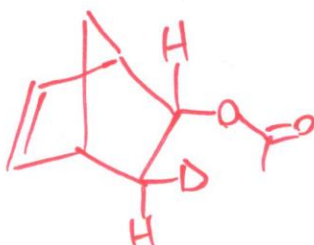
Problem 1. The molecule below undergoes a [1,3]-sigmatropic rearrangement with heating. Please draw predict the dominant product, using the skeleton given and explain your answer with Frontier Molecular Orbital Theory. Additionally, state whether the rearrangement proceeded with inversion or retention. Make sure you show all the stereocenters. (6 points)



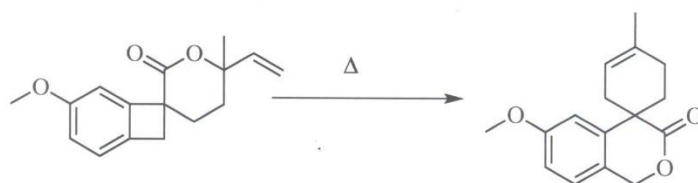
reaction proceeds with
inversion



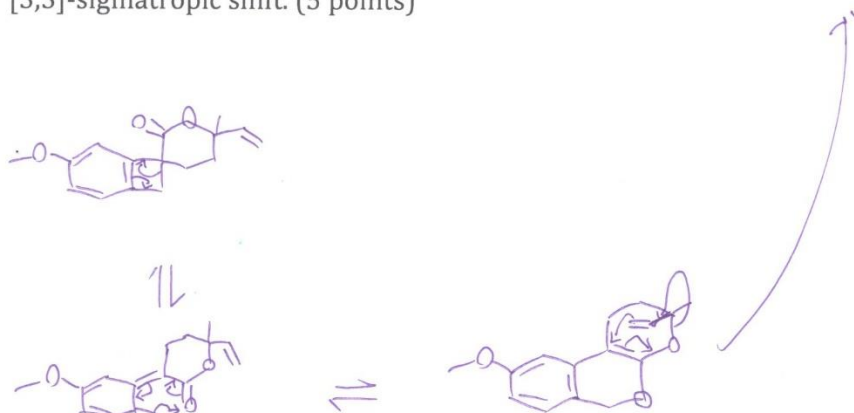
So



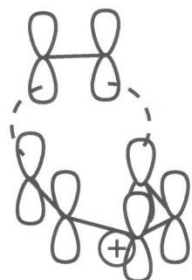
Problem 2. Provide a mechanism for the following transformation.



Courtesy of Dr. Anslyn: There are three steps in this mechanism. Start with a 4e electrocyclic ring opening, followed by a 6e electrocyclic ring closing, and end with a [3,3]-sigmatropic shift. (5 points)



Problem 3. Consider a generic [2+5] cycloaddition with pentadienyl cation and ethene under thermal conditions.



Use the Generalized Orbital Symmetry Rule (Woodward-Hoffman) to determine if the reaction is allowed or forbidden in the geometry given above. SHOW THE APPROPRIATE LABELS such as $\sigma 2a$. (3 points)

$$\pi 4s + \pi 2s$$

$$4q + 2$$

1 component $\rightarrow$ odd

allowed!

Problem 4. For the electrocyclic ring closure of butadiene to form cyclobutene under **thermal conditions**, please answer the following questions.



- a) For the allowed reaction, does the reaction proceed via a conrotatory or disrotatory process? (circle one) (1 point)

Conrotatory

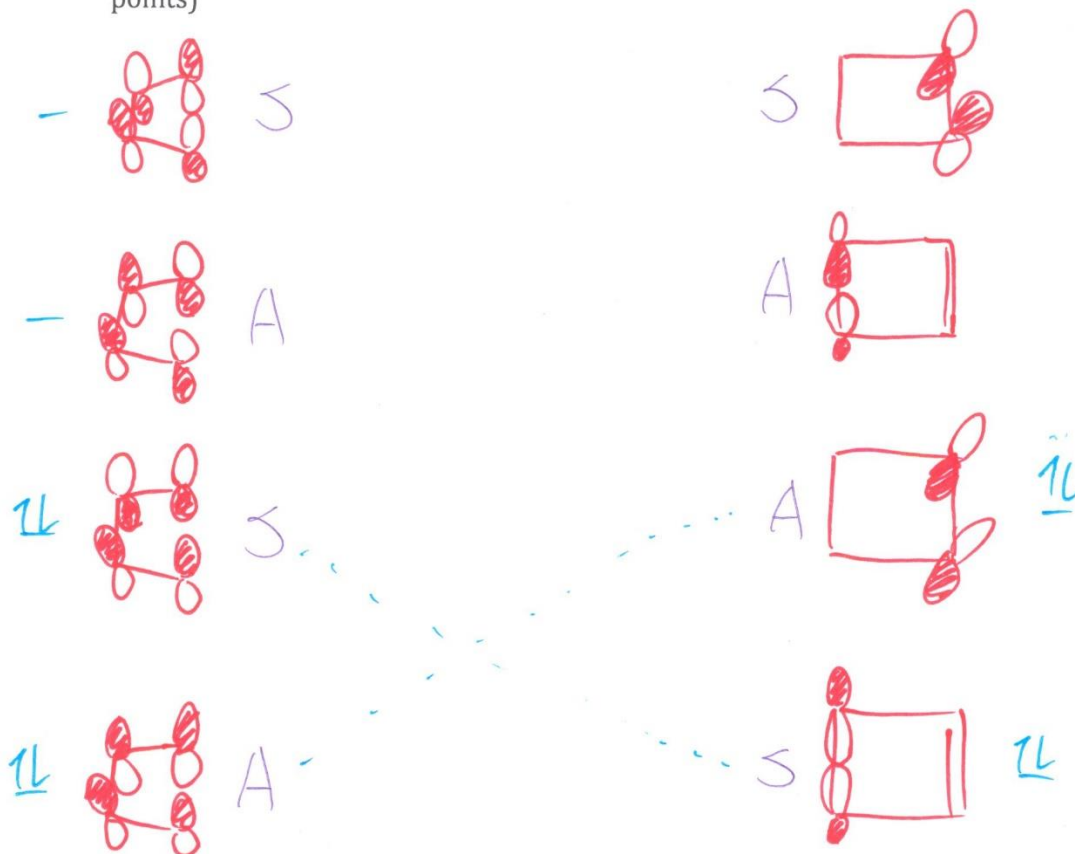
Disrotatory

- b) What symmetry element is maintained for the allowed process you identified above? (circle one) (1 point)

C_2

σ

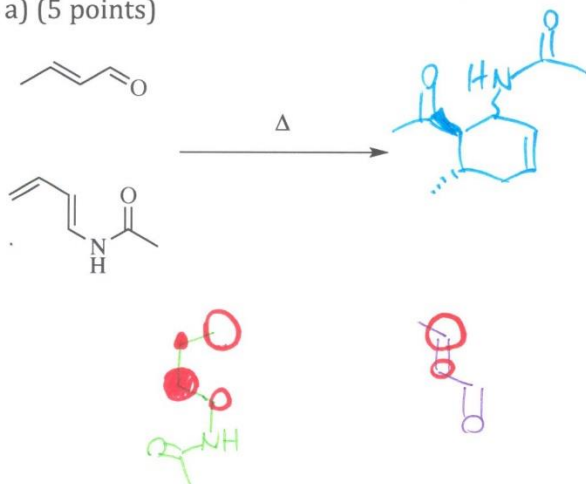
- c) Use an orbital correlation diagram to reach the same conclusion as above. (8 points)



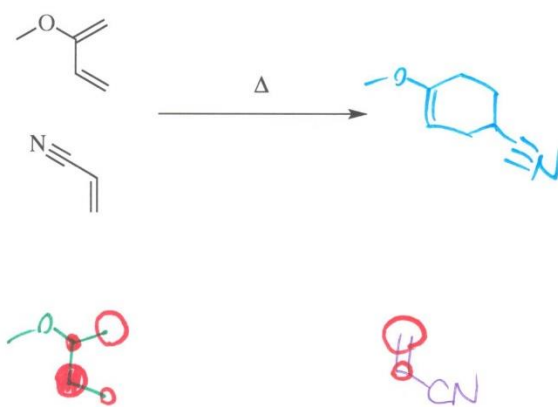
Problem 5. For the following cycloadditions,

- Please draw the LUMO of the 4 π -system and the HOMO of the other system.
- Draw the dominant product. Be sure to show stereocenter(s) when appropriate.
- For a and b, accentuate the molecular orbitals according to the resonance structures.
- For c and d, show your rationale.

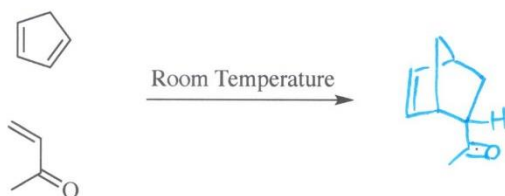
a) (5 points)



b) (5 points)

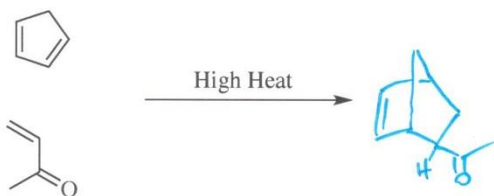


c) (3 points)



endo is preferred
under kinetic condition
due to π interaction

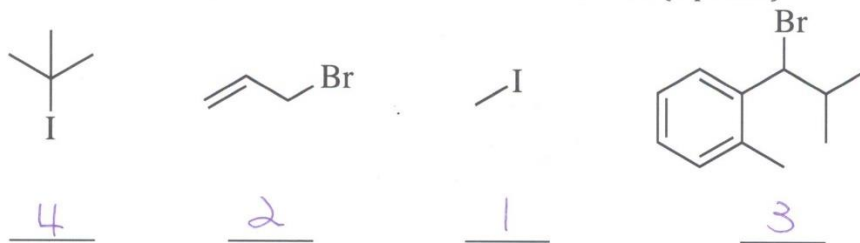
d) (3 points)



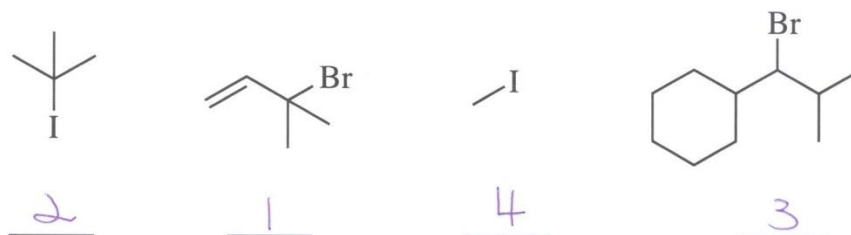
exo is the thermodynamic
product

Problem 6.

- a) Rank the following reactions in order of speed of nucleophilic attack of azide anion in acetonitrile; 1 is the fastest and 4 is the slowest. (2 points)



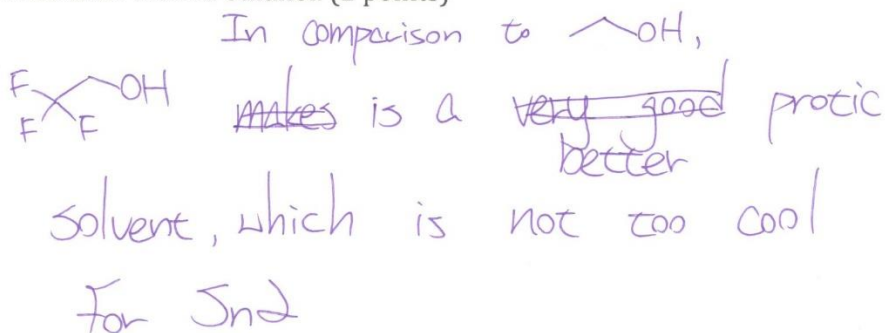
- b) Rank the following reactions in order of speed of nucleophilic attack of H₂O in (80:20) EtOH: H₂O mixture; 1 is the fastest and 4 is the slowest. (2 points)



- c) Explain why the reaction of Me₂S with bromoethane is faster in ethanol than in THF as solvent. (2 points)

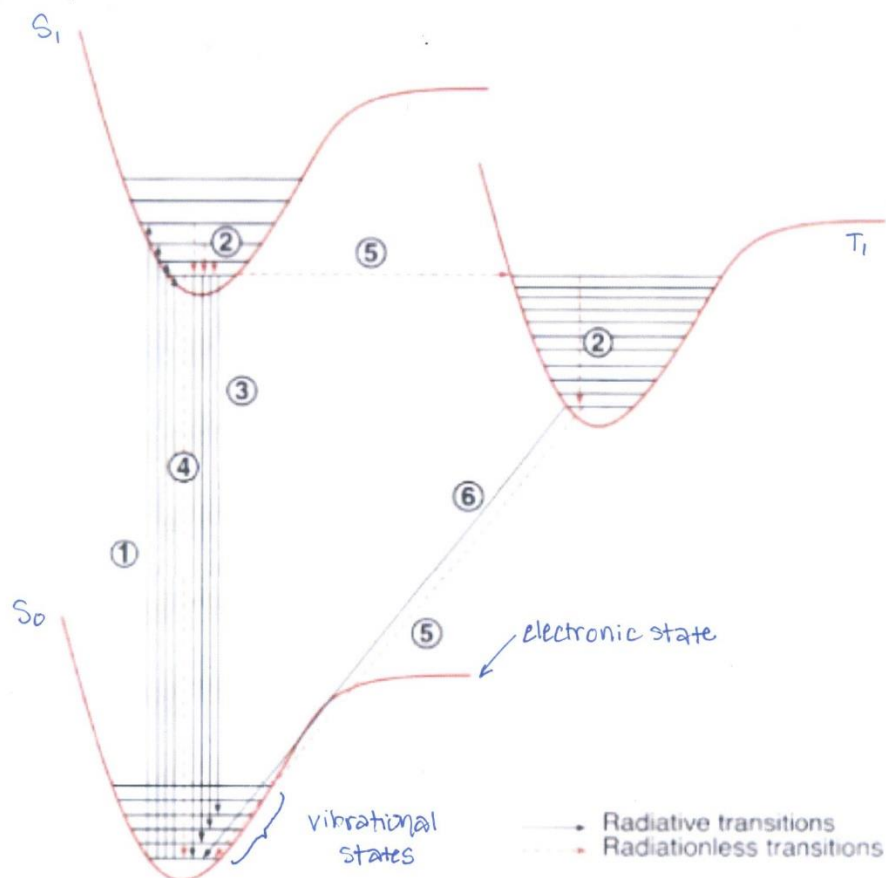


- d) Explain why the reaction of azide anion with iodomethane is slower in trifluoroethanol than in ethanol. (2 points)



Problem 7.

- a) On the Jablonski diagram below, do the following:
- Label each well appropriately (S_0 , T_0). (3 points)
 - Indicate the difference between an electronic state and a vibrational state. (2 points)

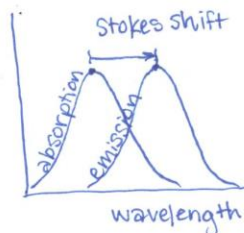
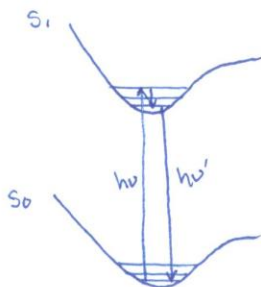


- b) Label each of the numbers as shown in the figure (3 points)

- Absorption (or excitation)
- Relaxation
- Fluorescence
- Internal conversion
- Intersystem crossing
- Phosphorescence

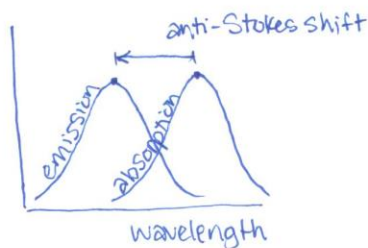
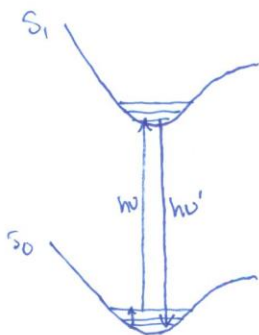
Problem 8.

- a) Draw a Jablonski diagram that illustrates how a Stokes shift arises. Draw a plot of the absorbance and fluorescence curves and show the Stokes shift on your plot. Then explain the process in words. (4 points)



A photon is absorbed and its energy excites an electron. The electron then undergoes vibrational relaxation, dissipating some energy. When that electron undergoes electronic relaxation, a photon is emitted. It now has lower energy, lower frequency, and longer wavelength.

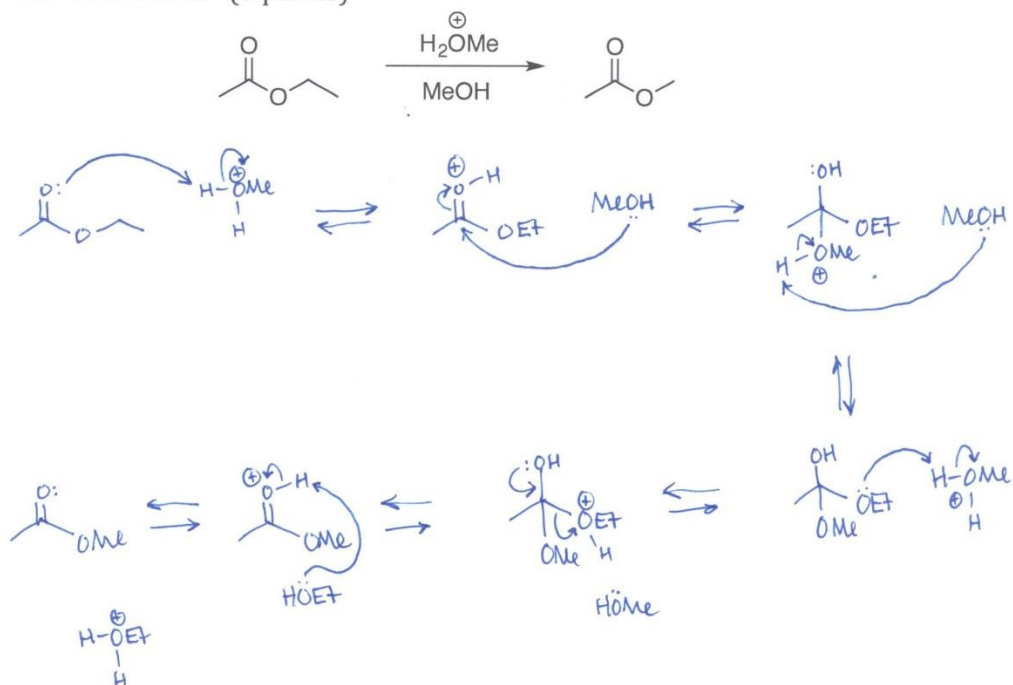
- b) Remember in class that Dr. Anslyn didn't remember how an anti-Stokes shift arose. Let's remind him! Devise a way that an anti-Stokes shift could occur, keeping in mind that they are often observed at elevated temperatures. Draw a Jablonski diagram that illustrates your suggestion. Draw a plot of the absorbance and fluorescence curves and show the anti-Stokes shift on your plot. Then explain the process in words. (4 points)



An electron is in a vibrationally excited state in the ground electronic state when it gets excited to the singlet electronic state. When it relaxes, it drops to the lowest vibrational mode as well as the ground electronic state. Thus it emits a photon with higher energy, higher frequency, and shorter wavelength.

Problem 9.

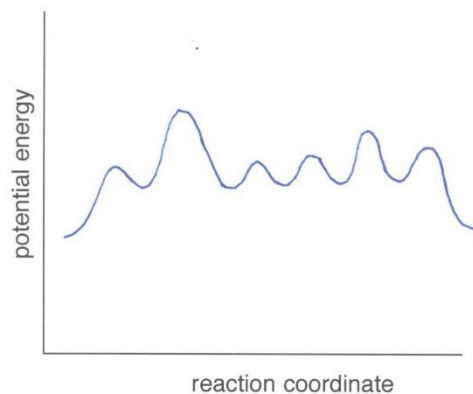
- a) Write the mechanism for the specific acid-catalyzed transesterification of ethyl acetate in methanol. (6 points)



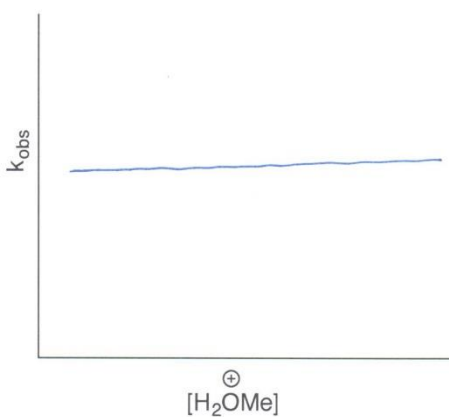
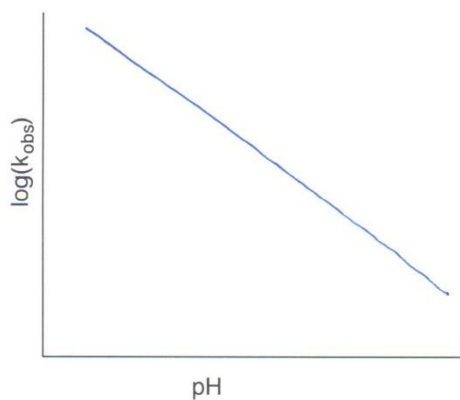
- b) In your mechanism above, is $[\text{H}_2\text{OMe}]^+$ a specific acid or a general acid? (1 point)

specific acid

- c) Draw a reaction coordinate diagram to represent your mechanism. Label each intermediate in part (a) with a letter (A,B,C...) and then label the same intermediates on your plot. (2 points)

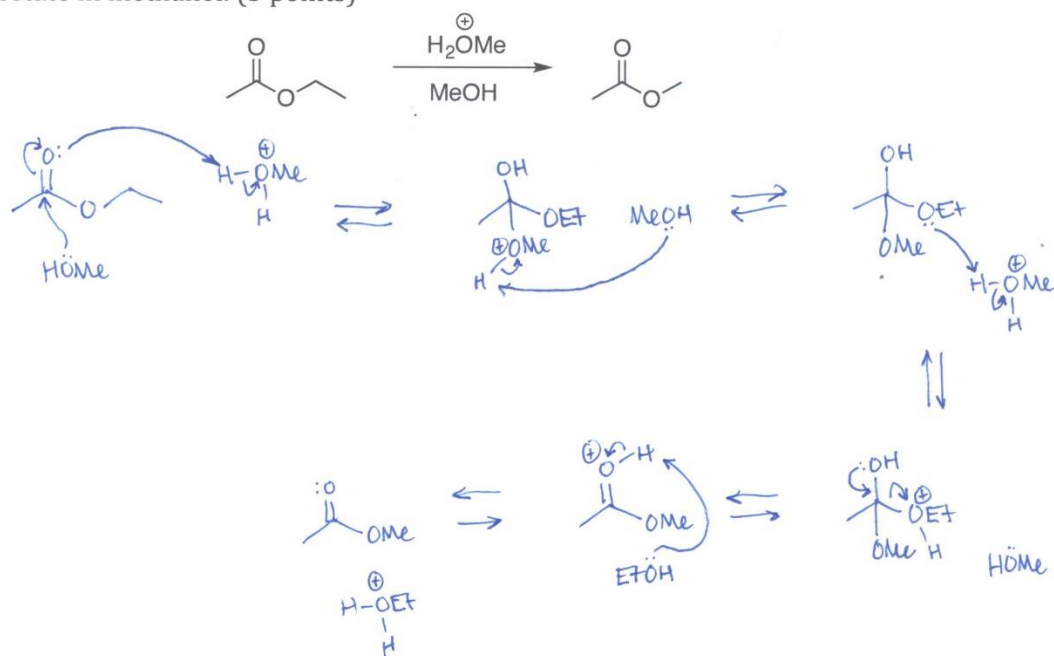


- d) Complete the following plots for specific acid catalysis. Place the pK_a of $[H_2OMe]^+$ on the pH axis, if appropriate. (2 points)



Problem 10.

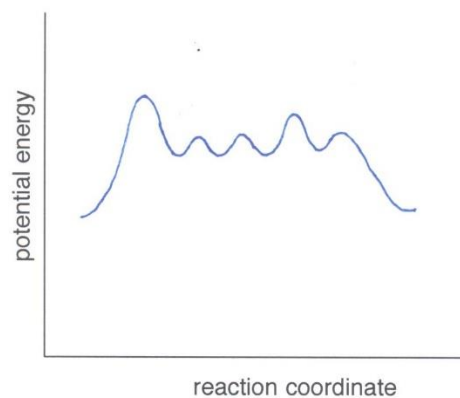
- a) Write the mechanism for the general acid-catalyzed transesterification of ethyl acetate in methanol. (5 points)



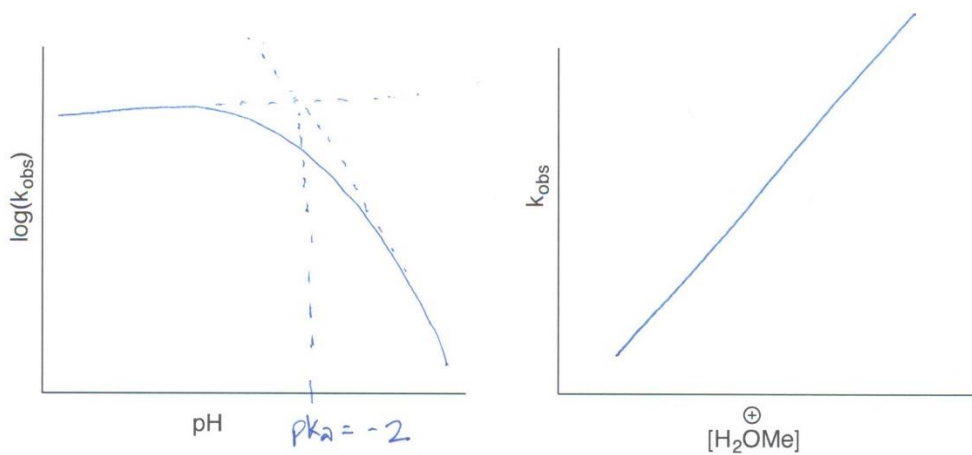
- b) In your mechanism above, is $[\text{H}_2\text{OMe}]^+$ a specific acid or a general acid? (1 point)

specific acid

- c) Draw a reaction coordinate diagram to represent your mechanism. Label each intermediate in part (a) with a letter (A,B,C...) and then label the same intermediates on your plot. (2 points)

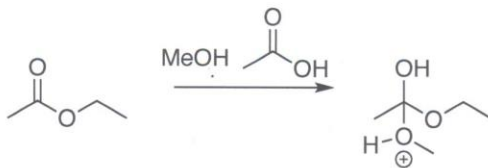


- d) Complete the following plots for general acid catalysis. Place the pK_a of $[H_2OMe]^+$ on the pH axis, if appropriate. (2 points)



Problem 11.

- a) Construct a More O'Ferrall-Jencks plot for the nucleophilic attack step of general acid-catalyzed transesterification of ethyl acetate.



- Draw the reactants and products at each corner of the plot on the next page. (2 points)
 - Label each axis. (2 points)
 - Label the pathways of specific acid catalysis, general acid catalysis, and no catalysis on the plot. (1 points)
 - Decide if this step of the reaction is exothermic or endothermic and put an initial dot on the general acid-catalyzed pathway to represent the transition state. Label the dot A. (1 point)
- b) Consider how the reaction changes when trifluoroacetic acid is used instead of acetic acid. Draw a new dot on the plot and label it B. Explain why this movement makes sense. (2 points)

Better acid, lowers the bottom two corners.



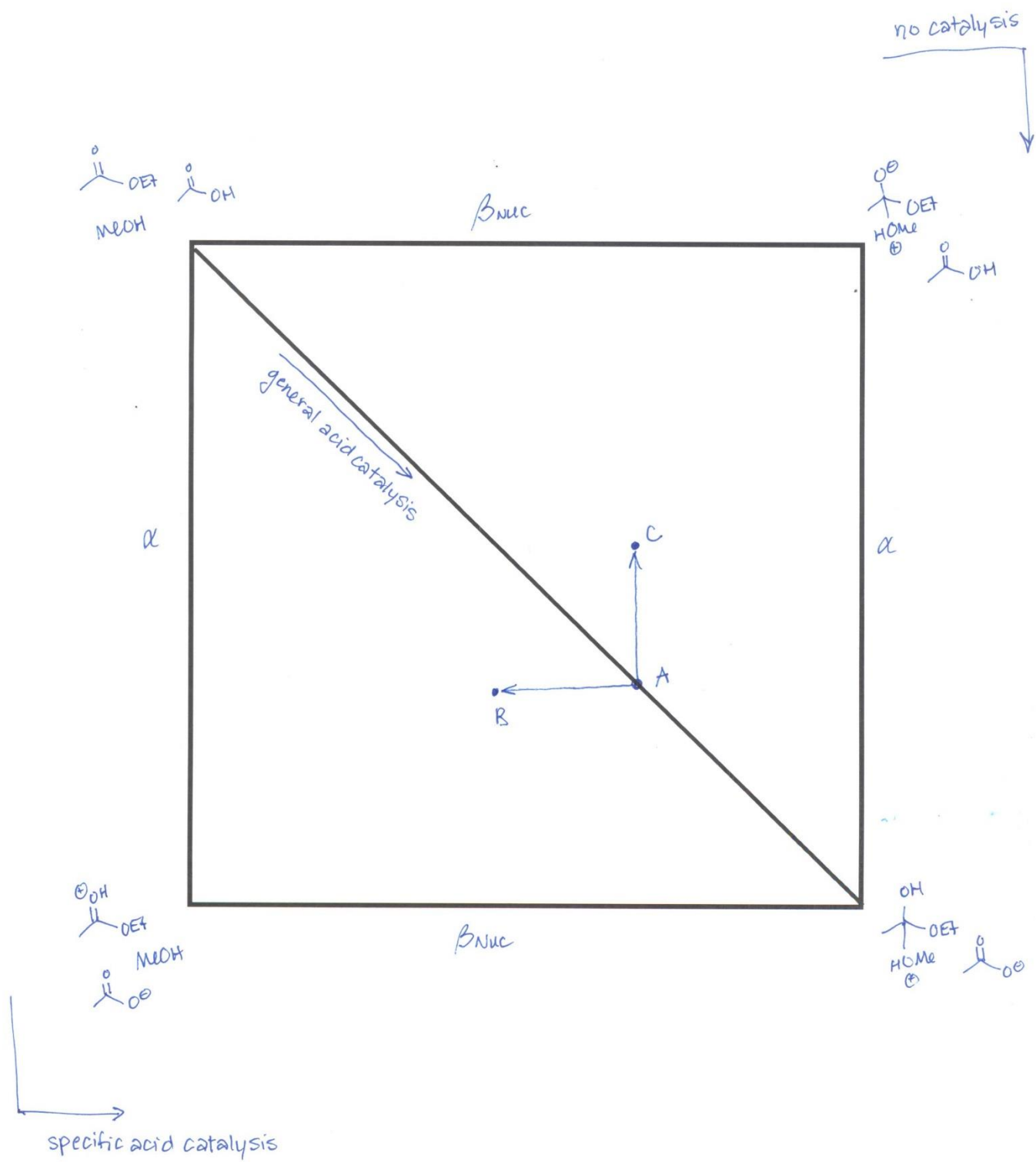
α doesn't change. β_{nuc} decreases because a lesser extent of nucleophilic attack is required for a better acid.

- c) Consider how the reaction changes when MeSH is used instead of MeOH. Draw a new dot on the plot and label it C. Explain why this movement makes sense. (2 points)

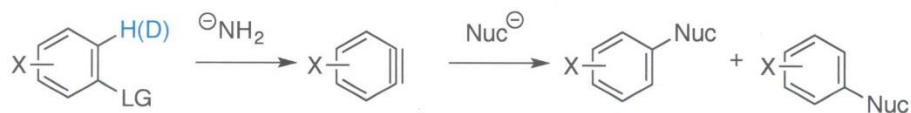
Better nucleophile, lowers the two right corners.



β_{nuc} doesn't change. α decreases because a lesser extent of protonation is required for a better nucleophile.



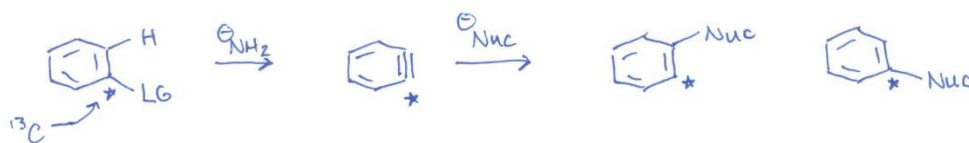
Problem 12. Consider the following reaction, which passes through a benzyne intermediate.



- a) What kind of isotope effect would you expect to observe for the blue H(D)? (1 point)

primary normal

- b) Suggest an isotope labeling experiment that would support the formation of the benzyne intermediate. Use pictures and/or words. (2 points)



The presence of both products (^{13}C NMR) would support benzyne formation.

- c) If you were to construct a Hammett plot for this reaction, would you expect a large or small ρ (rho) value? (1 point)

small ρ

- d) How would you check to make sure the benzyne intermediate is common to many different leaving groups? (1 point)

Check to see that the ratio of the two products is the same for many leaving groups.