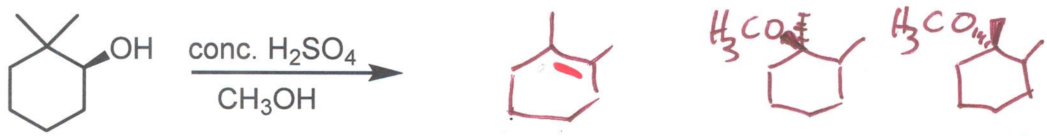
1) Predict the major product(s) in each of the following reactions. Label each as SN1, SN2, E1, or E2. (2 pts each)

a)

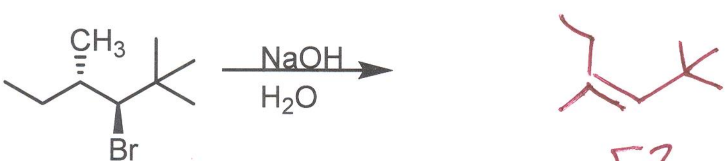


E1 SN1 SN1

b)

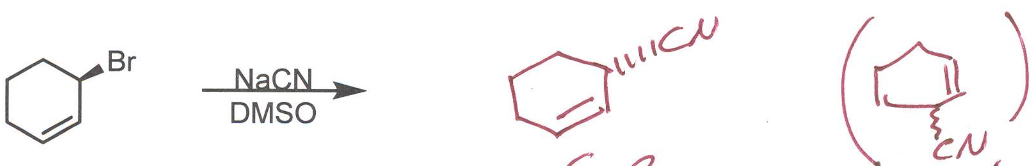
SN2

c)



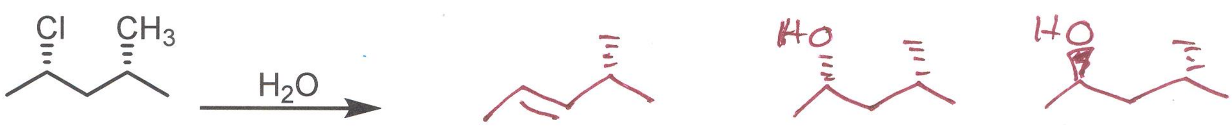
E2

d)



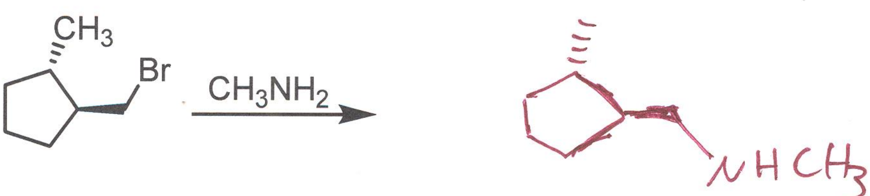
SN2 SN2' (minor)

e)



E1 SN1

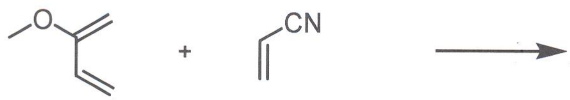
f)

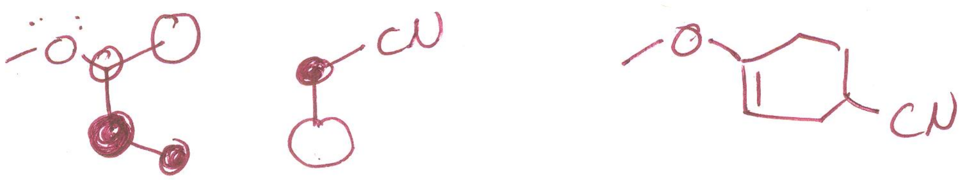


SN2

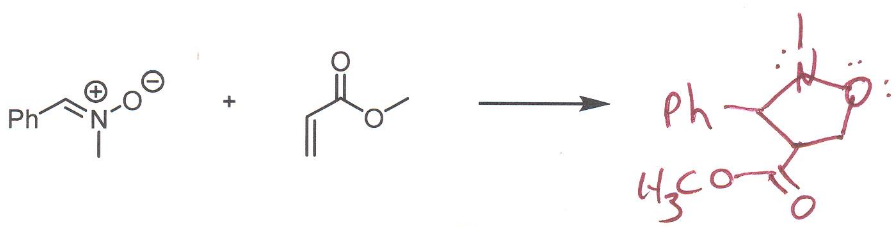
2) Draw the HOMO of the 4π-system and the LUMO of the 2π-system for each cycloaddition below. Be sure to show the relative orbital character on each atom using PMOT. Finally, draw the major product for each reaction, showing the correct regiochemistry. (~~6~~ 4 pts each)

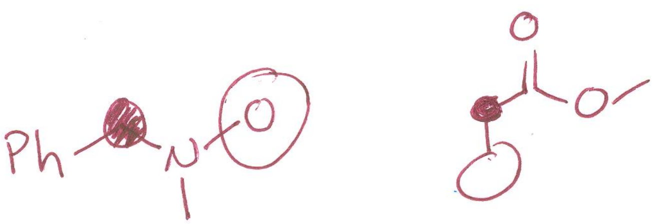
a)





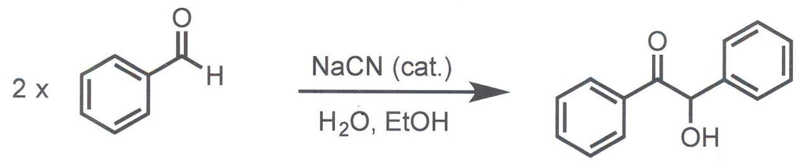
b)

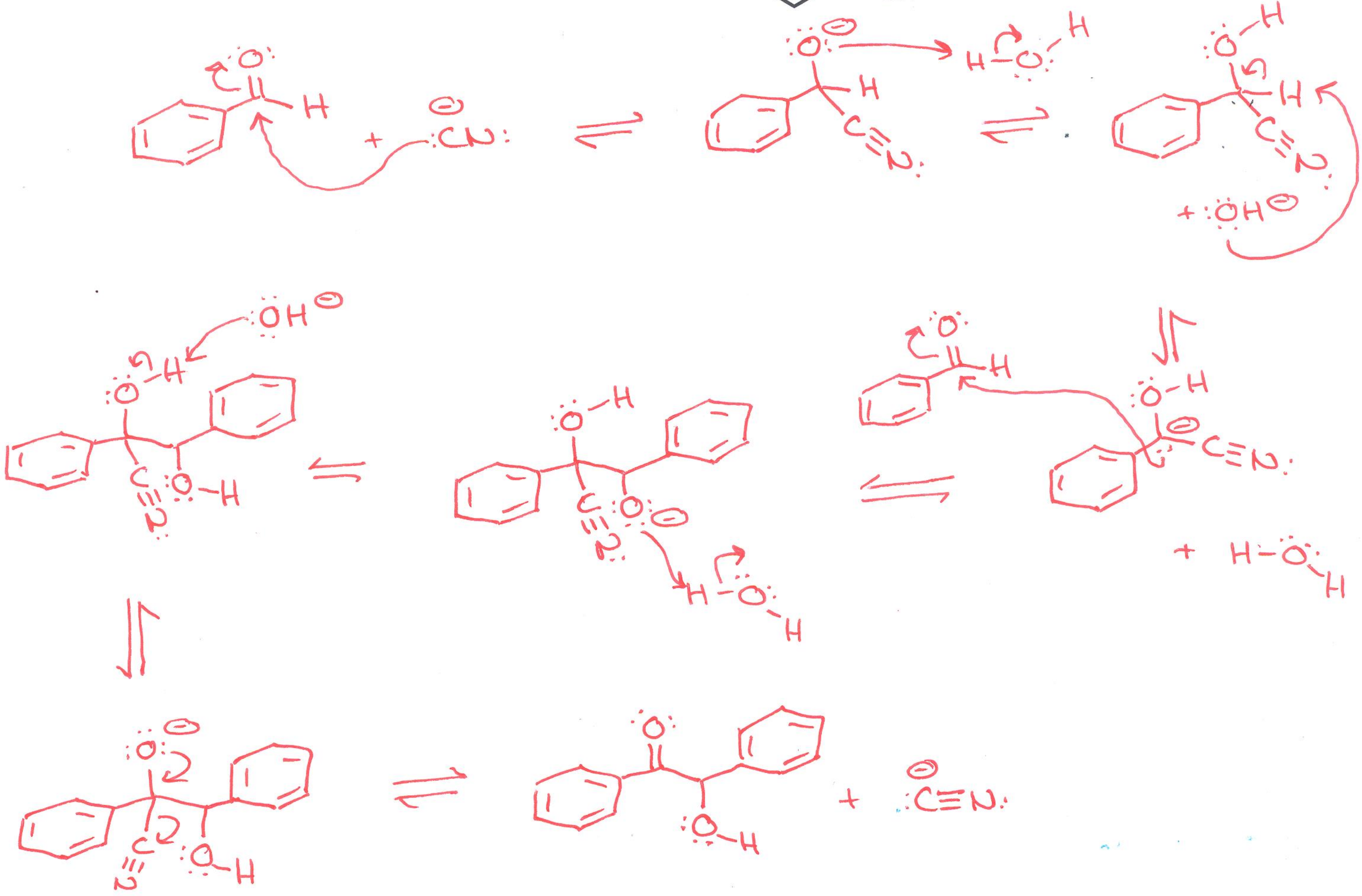




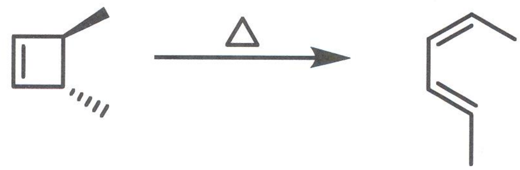
like allyl anion

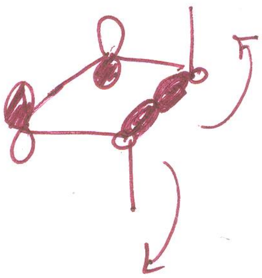
3) Provide a mechanism for the following transformation, showing all lone pairs and all arrow pushing. (7 pts)





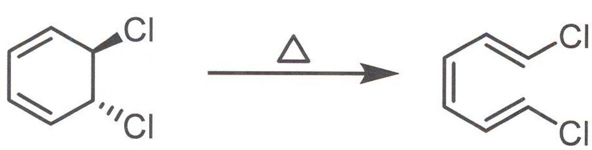
4) a) Using FMOT, show whether the following transformation is allowed or forbidden. (5 pts)

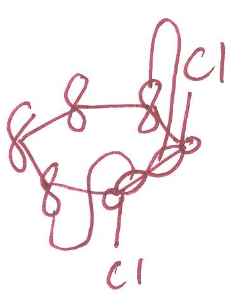




forbidden

b) Using the Woodward-Hoffman rules, show whether the following transformation is allowed or forbidden. (5 pts)



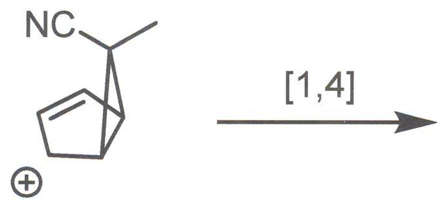


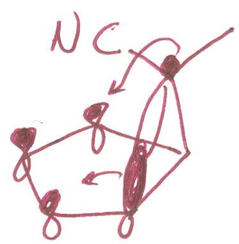
2σs

4πa

forbidden

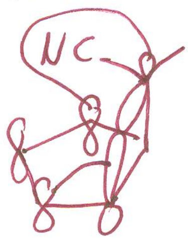
(c) Using either FMOT or the Woodward-Hoffman rules, show the allowed product of the following [1,4]-sigmatropic shift (also called a walk rearrangement). Is the stereochemistry retained or inverted? (8 pts)





inverted

W-H

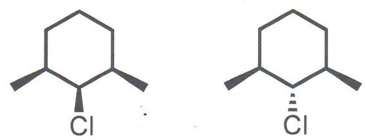


$2\sigma a$

$2\pi s$

allowed w/ inversion

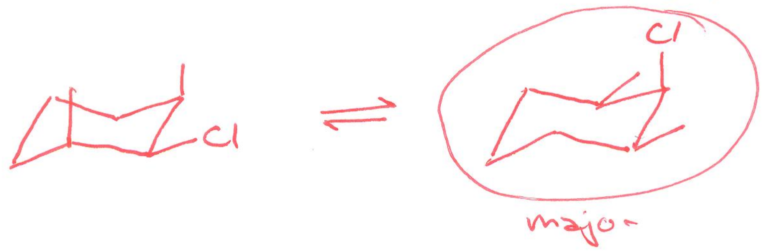
5) Consider the E2 reaction of the following molecules.



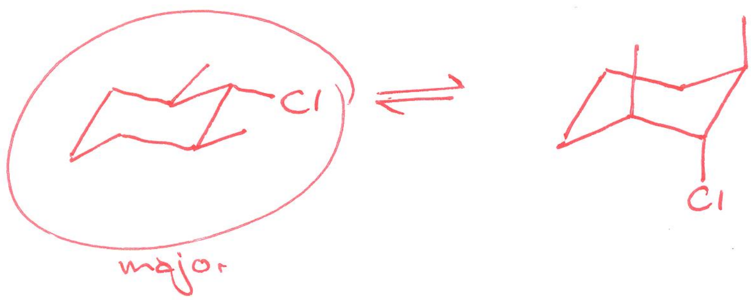
A B

all possible
a) Draw ~~the~~ chair conformations of both molecules, **A** and **B**. (4 pts)

A:



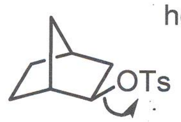
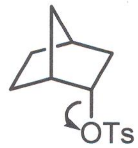
B:



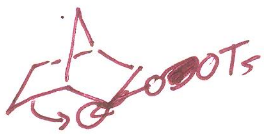
b) Based on the chair conformations you drew in part a), which molecule do you expect to undergo an E2 reaction more quickly? Why? (2 pts)

A. For B it is not possible to achieve a chair conformation where the proton being abstracted is antiperiplanar to the leaving group.

6) The reaction rates below are for the solvolysis of the following alkyl tosylates.

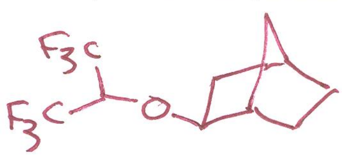
		rate at 125 °C in hexafluoroisopropanol:
A		72
B		0.21

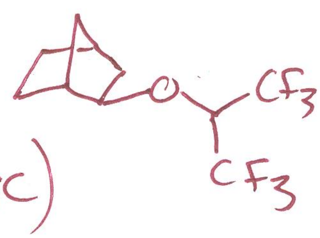
a) Explain the difference in rate between **A** and **B**. (4 pts)



better alignment with exo antibonding orbital

b) Draw the products for these reactions. Pay attention to stereochemistry. (2 pts)



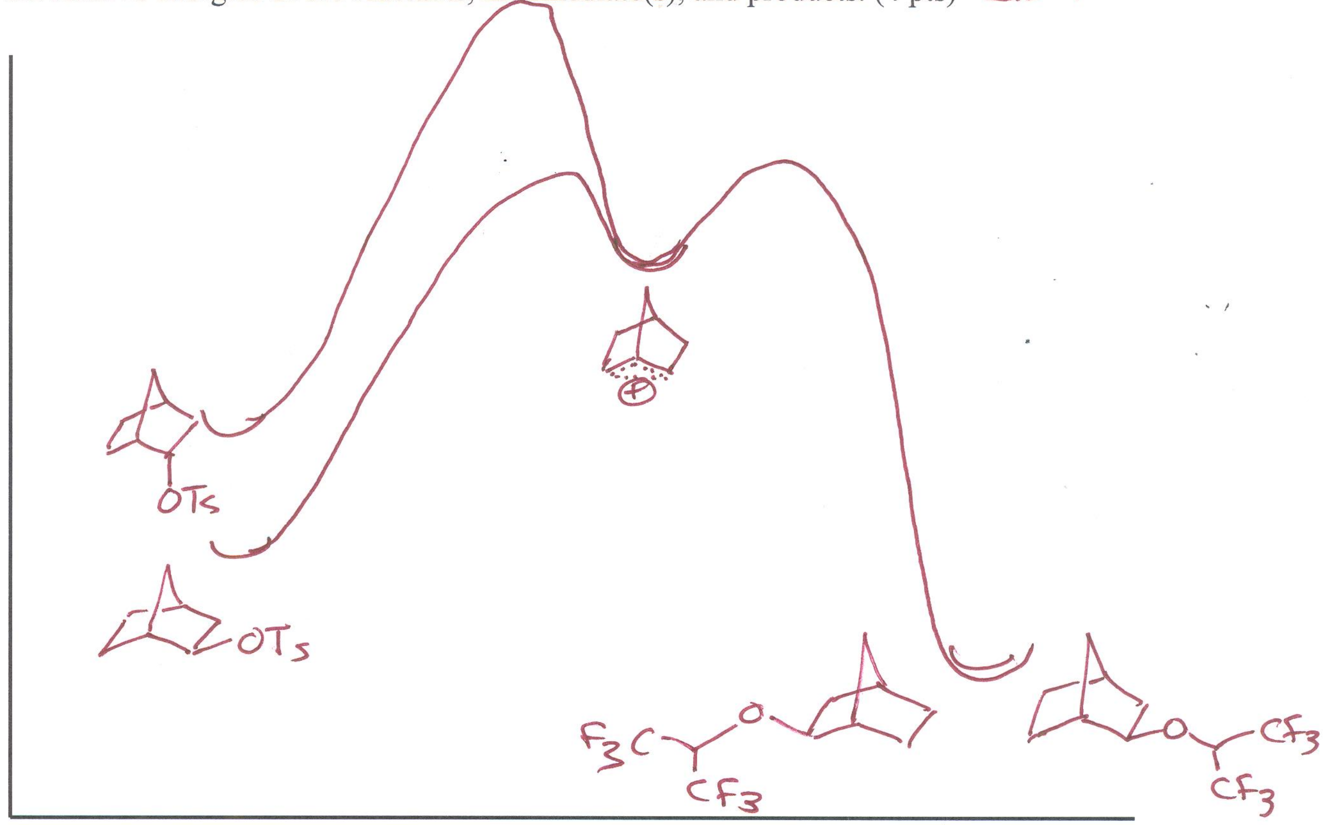


(racemic)

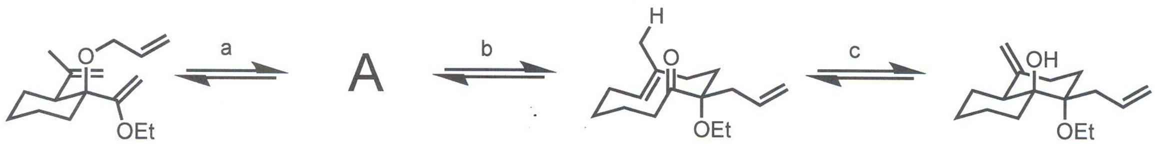
c) The product ratio for solvolysis is the same for **A** and **B**. What does this mean about the intermediate(s) formed from both reactions? (2 pts)

Common intermediate

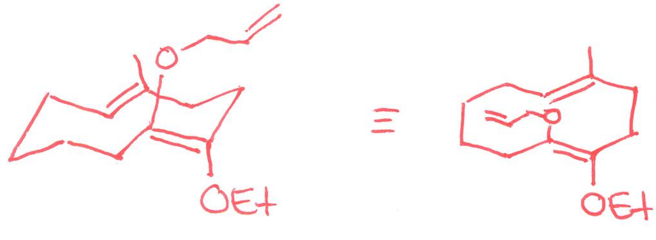
d) Draw a reaction coordinate diagram for both of these reactions on the axes below. Show the relative energies of the reactants, intermediate(s), and products. (4 pts) Label.



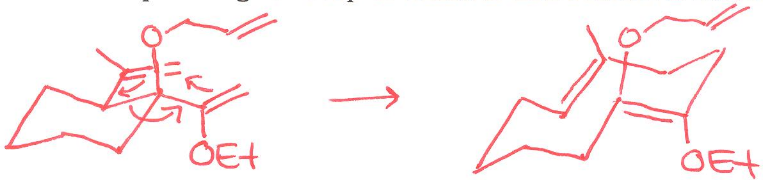
7) Consider the following three step thermal reaction sequence. Steps **a** and **b** are pericyclic reactions we learned in class. (10 pts)



a) Give the structure of intermediate A.

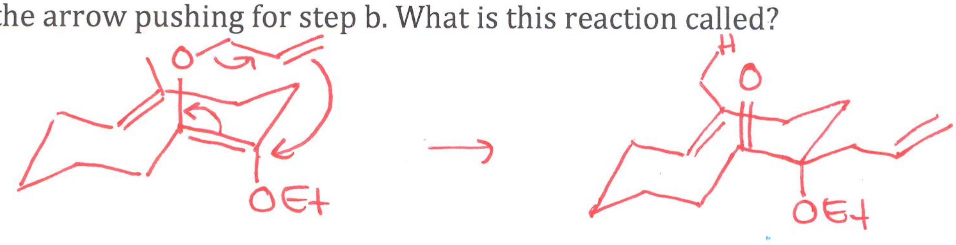


b) Give the arrow pushing for step a. What is this reaction called?



(oxa) cope

c) Give the arrow pushing for step b. What is this reaction called?



claisen

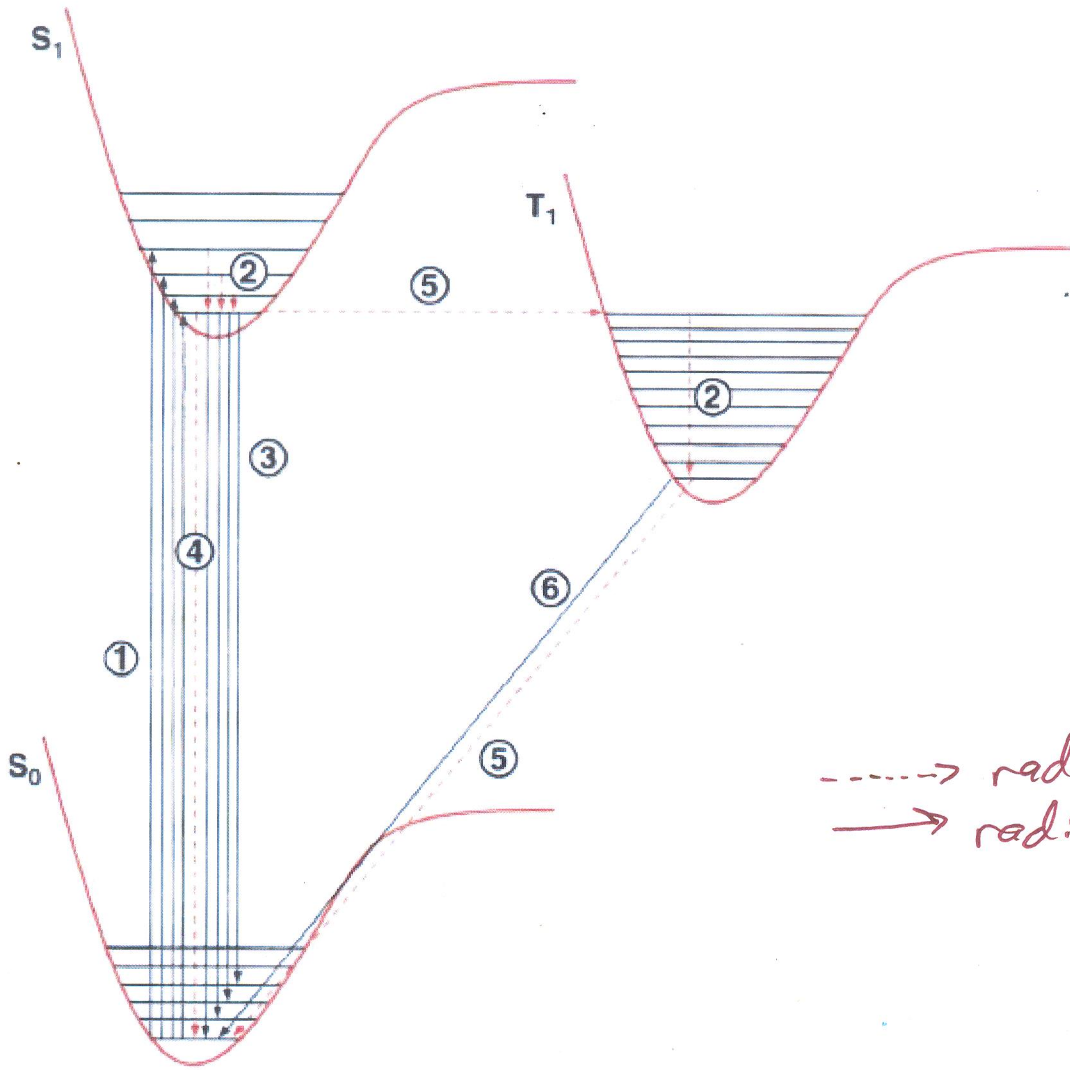
d) Step c is an example of an ene reaction, which we did not cover in class. Give the arrow pushing for this step.

→ P

e) Is the ene reaction as you drew it in d) pericyclic? Why? Why not?

Yes. It involves a cyclic array of interacting orbitals.

8) Fill in the table with the appropriate labels corresponding to the numbers on the Jablonski diagram. (6 pts)

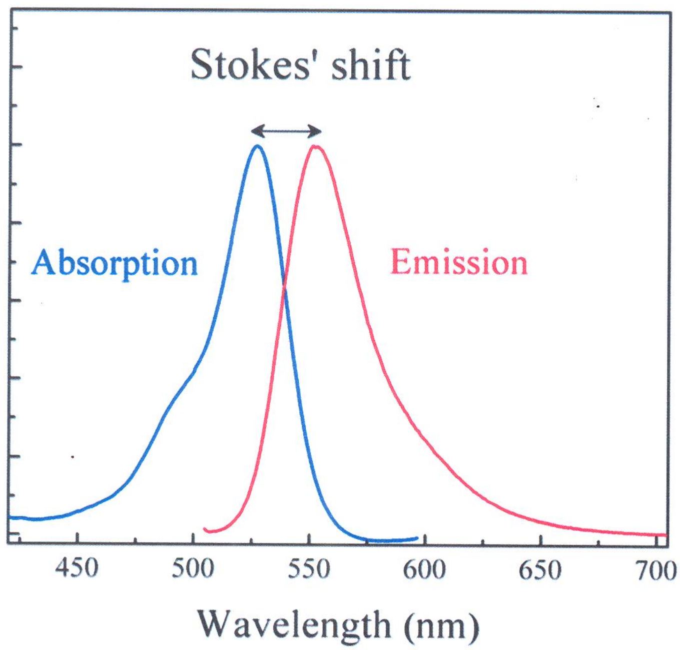


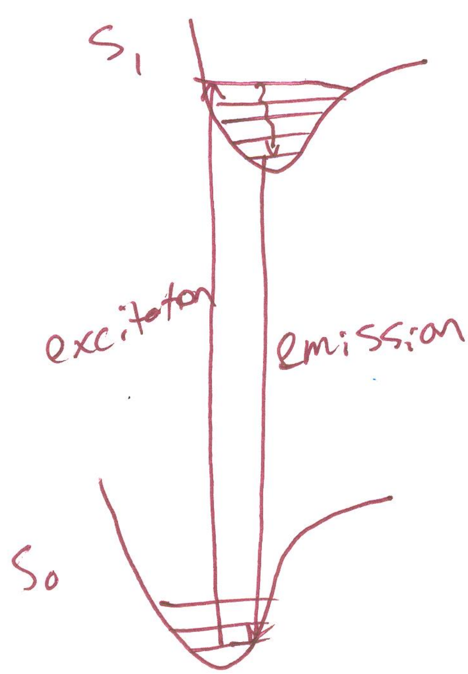
- - - - -> radiationless

⟶ radiative

1	Absorption
2	Relaxation
3	Fluorescence
4	Internal Conversion
5	Intersystem Crossing
6	Phosphorescence

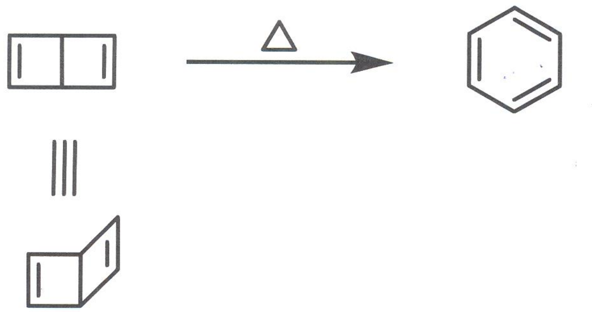
9) Explain the origin of a Stokes' shift like the one shown below. (4 pts)





Emission is ~~[illegible]~~ lower in energy so a longer wavelength. Exaggerated by larger change in geometry upon excitation.

10) Dewar benzene was proposed by James Dewar in 1867 to be an isomer of benzene. Since then Dewar benzene has been synthesized and its conversion to benzene studied. Note that Dewar benzene is not planar (shown).



a) Draw mechanistic arrows showing the transformation from Dewar benzene to benzene. How many electrons are involved in this process? (2 pts)

$4e^-$

b) Show the FMOT orbitals for this process. (4 pts)

Based upon your answer in b, is the

c) ~~Is this~~ ring-opening conrotatory or disrotatory? (2 pts)

d) Finally, is this ring-opening allowed or forbidden? (2 pts)

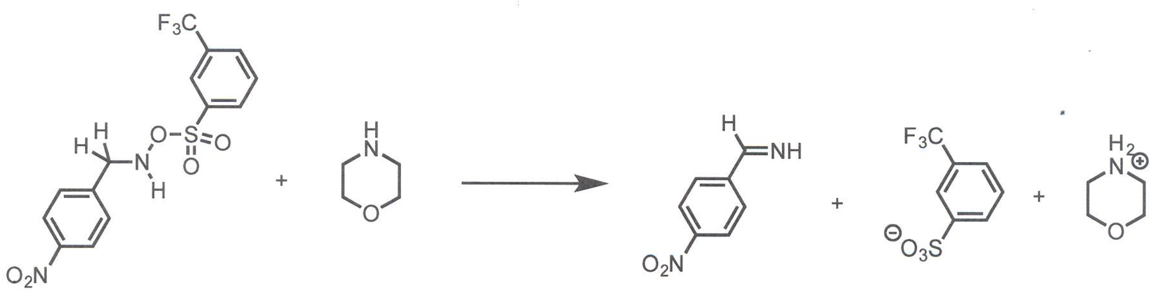
forbidden

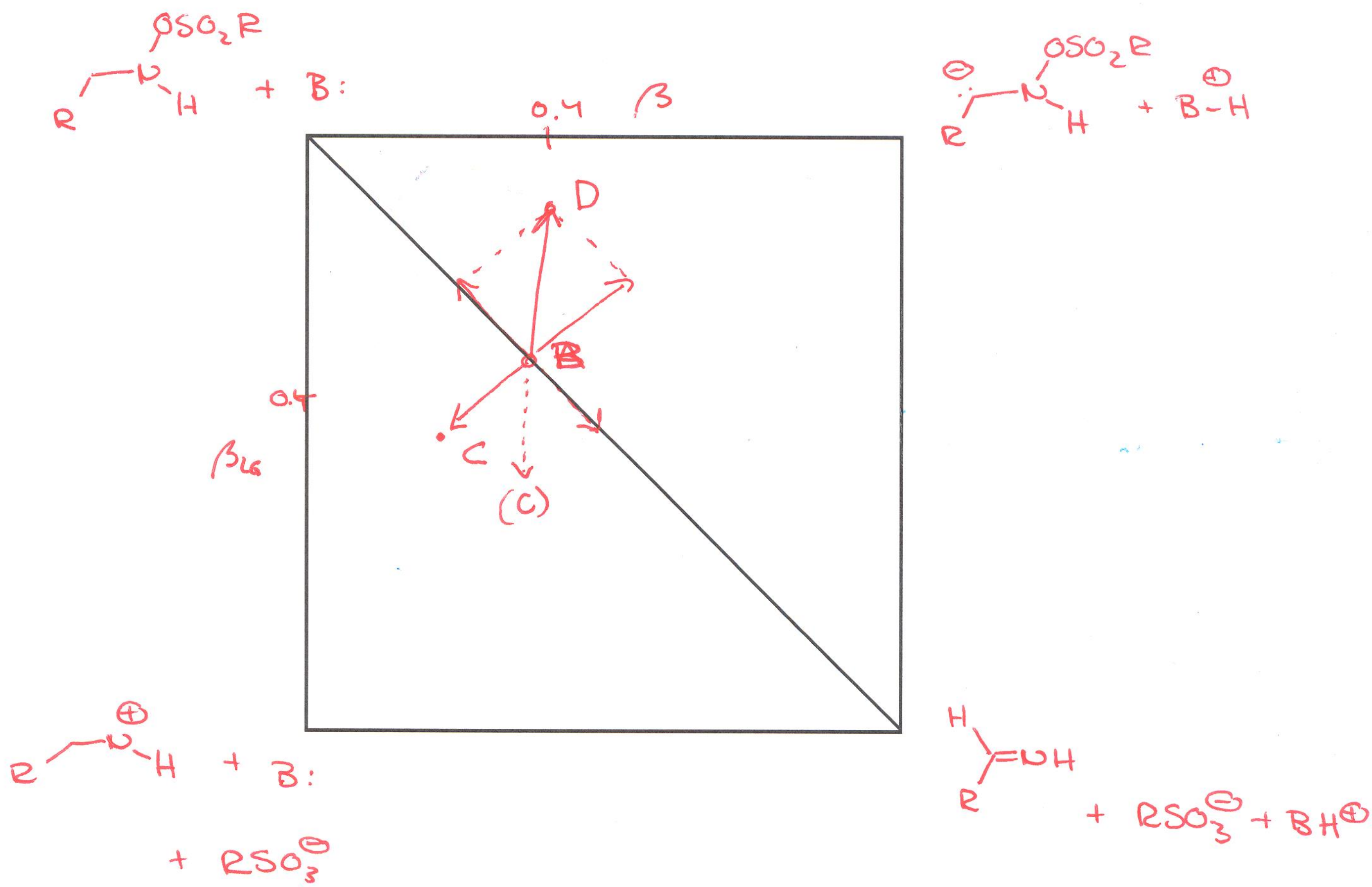
11

3) a) Draw a More O'Ferrall-Jencks plot for the base promoted elimination shown below. (6 pts)

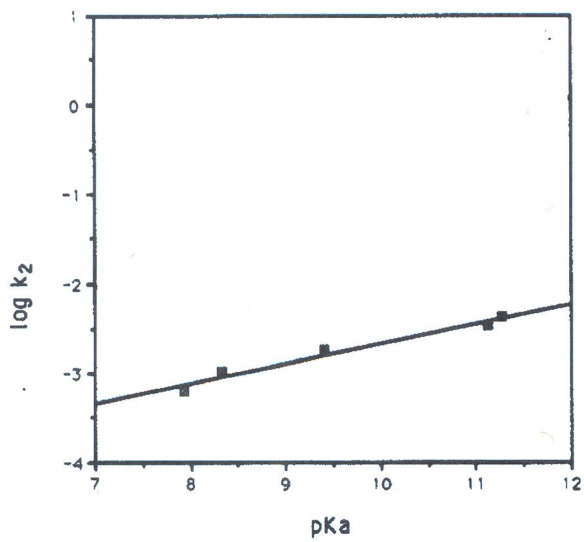
i. Draw the reactants and products corresponding to each of the possible mechanism in the corners of the plot below, with the top right corner corresponding to an E1CB mechanism.

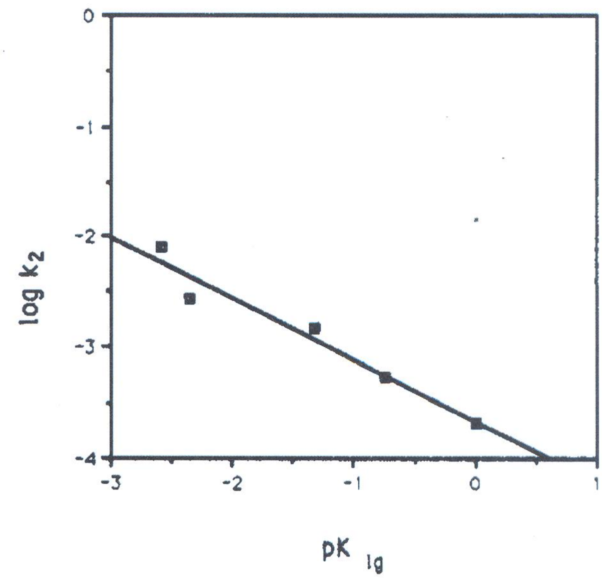
ii. Label the axes of the plot with the corresponding LFER parameter (α, β, β_{Nuc}, β_{LG}).





b) The Brønsted of the log of the second-order rate constant k_2 vs. the pK$_a$ of B-H$^+$ is given below on the left. The slope of the plot is 0.43. The plot on the right is the Brønsted plot of log(k_2) vs. pK$_a$ of the protonated leaving group. The slope of this plot is -0.41.





i. What parameter does the slope of the plot on the left correspond to? What does this parameter tell us about the transition state?

Extent of deprotonation. = β

2

ii. What parameter does the slope of the plot on the right correspond to? What does this parameter tell us about the transition state?

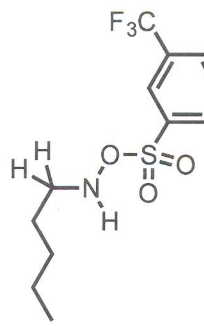
β_{LG} = extent of LG departure

2

iii. With the information extracted from the Brønsted plots, put a dot on the More O'Ferrall-Jencks plot on the previous page corresponding to the transition state of the reaction and label it as "B".

1

c) How would the transition state of the concerted elimination reaction change, if the substrate is changed to the following molecule? Show the transition state on the More O'Ferrall-Jencks plot and label it as "C". What changes in the transition state, and why does this make sense?



less stabilization of neg. charge (top right corner raised)
→ less deprotonation at T.S.
→ larger extent of LG departure

+2

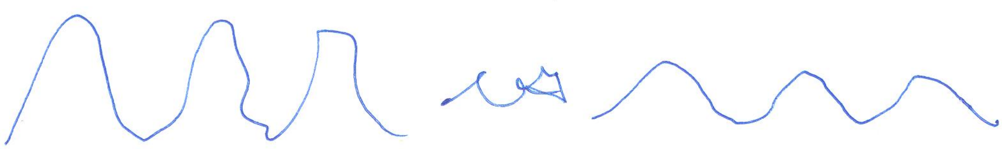
d) How would the transition state of the concerted elimination reaction change, if NaOH is used as the base? Show the transition state on the More O'Ferrall-Jencks plot and label it as "D". What changes in the transition state, and why does this make sense?

Stronger base → raise left corners
⇒ Extent of deprotonation at T.S. does not change, but less leaving group departure is required to effect that amount of proton transfer.

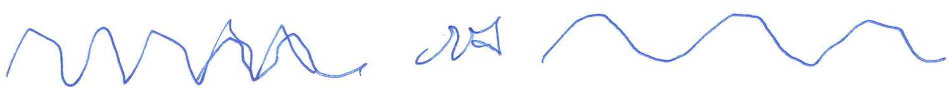
+2

12) a) Every year the Anslyn group has a splash competition at Eric's house during the group party (Yes, we know you're jealous). Two of the ways of judging who won are by looking at the waves produced. What are two indicators of the energy of these waves? Explain these two variables by drawing pictures of the waves you are imagining in the pool. (6 pts)

Amplitude



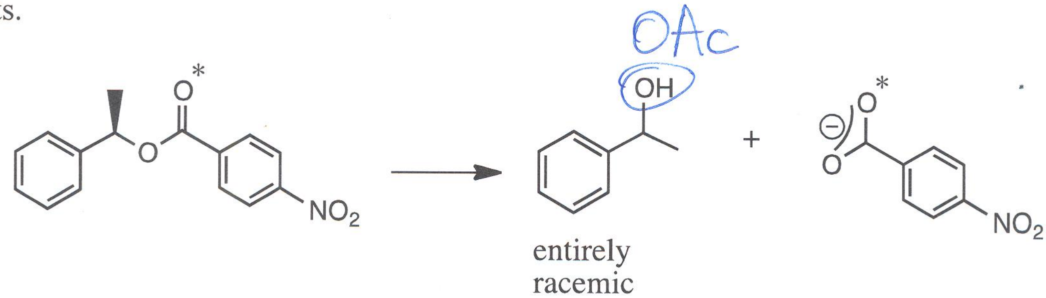
Frequency



b) Now, explain how the del-squared operator (∇^2) reveals the kinetic energy of a wave. Relate this back to your two answers from part a). (4 pts)

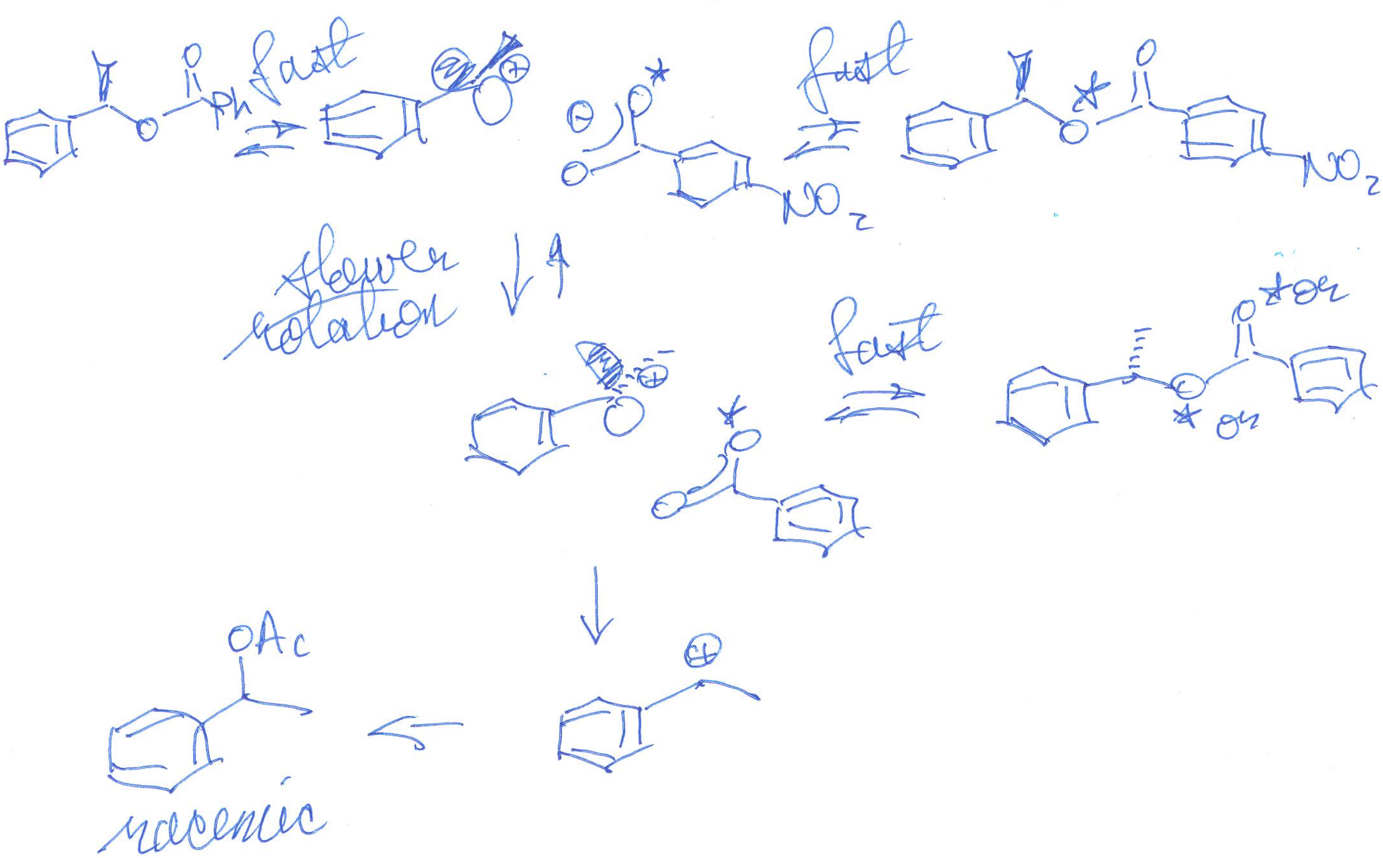
$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{z^2}$, it is a second derivative, meaning the slope of a plot of slope vs 3 dimensions. It is the rate of change of the rate of change. Which when integrated over all space gives amplitude and frequency a higher K.E.

13) Goering studied the solvolysis of the compound shown below in acetic acid to give the products shown. During his study, he examined how this reactant changed structure. The fastest change in **reactant** structure was the scrambling of the isotopic label of the carbonyl oxygen of the ester with the ether oxygen of the ester. In fact, this scrambling occurs before a significant amount of product is created. In addition, this isotopic scrambling was faster than the racemization of the stereocenter in this reactant. Yet, the reactant is completely racemized before the product is entirely formed. Combined, this means that both scrambing of the isotopic label and the stereochemistry of the starting material were faster than the actual formation of racemic products.

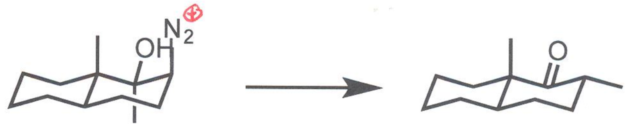


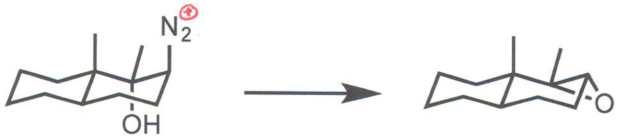
Give a chemical explanation of these observations, and draw chemical structures to support your theory. (8 pts)

The isotope scrambling occurs rapidly in a solvent cage = ion pair.

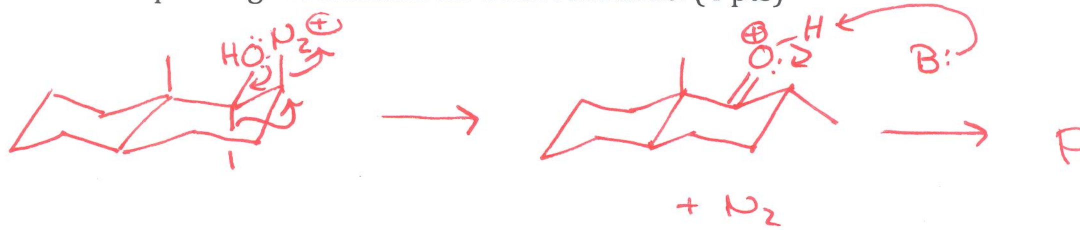


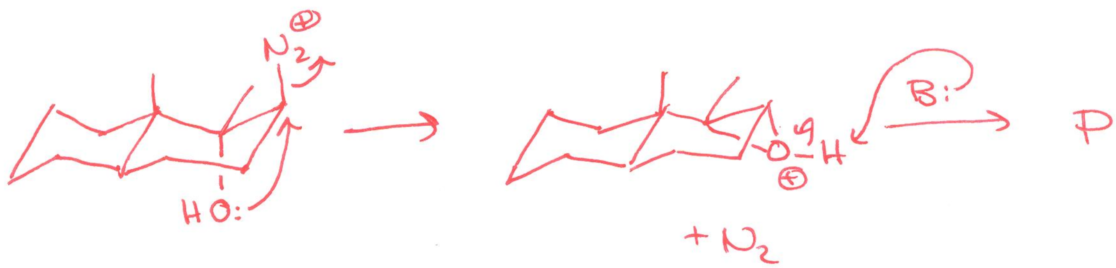
14) Consider the following two reactions.

A


B


a) Draw the arrow pushing mechanism for both reactions. (4 pts)

A


B


b) Explain why only the given product is observed in each case. (2 pts)

In A, the migrating group is antiperiplanar, OH can not achieve backside attack.

In B, the methyl group cannot migrate because it is not antiperiplanar, but the OH is and can reach over to do backside attack.