

CHEMISTRY 112A FALL 2015

EXAM 2

OCTOBER 22, 2015

*Answer
Key*

NAME- WRITE BIG _____

STUDENT ID: _____

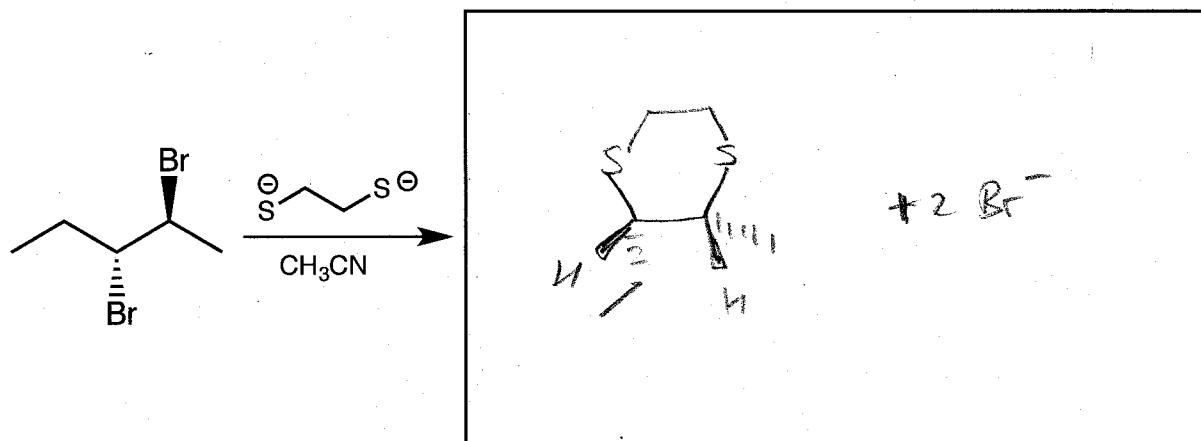
SECTION AND/OR GSI IF YOU ARE IN THE LABORATORY COURSE: _____

- You will have 75 minutes in which to work.
- **BE NEAT!** Non-legible structure drawings will not be graded.
- Only answers in the answer boxes will be graded – you can write in other places, but we only grade the answers in the boxes.
- All pages of the exam must be turned in.
- No calculators
- No stencils
- Molecular models may be used

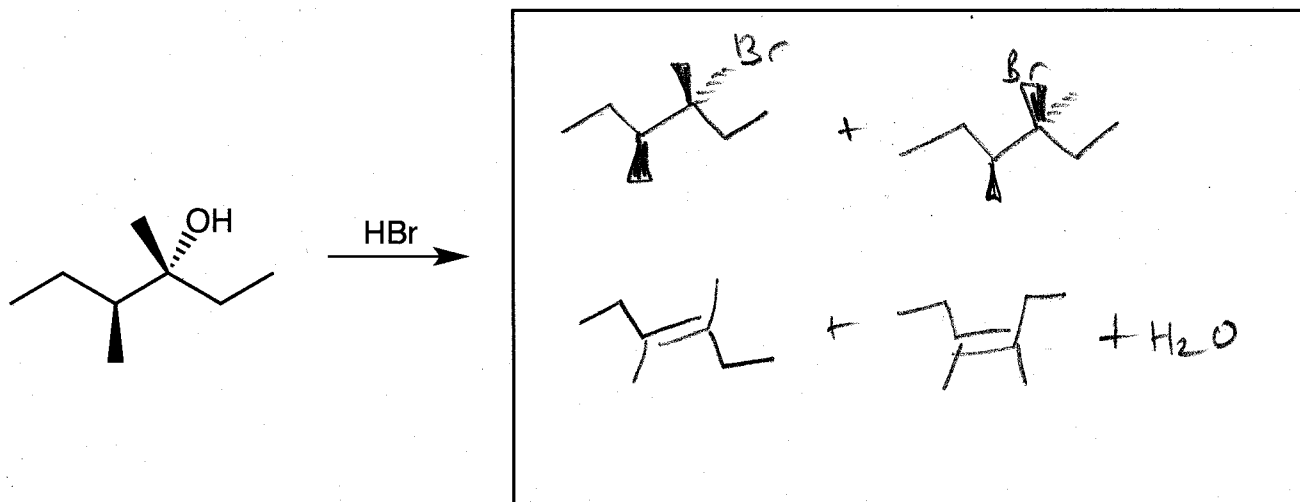
Problem	Points (Maximum)
1	24
2	24
3	14
4	12
5	16
6	30
<i>Total</i>	<i>120</i>

1. (24 points) For each reaction draw the major organic products, **including all stereoisomers**. Write NR if you think there will be no reaction.

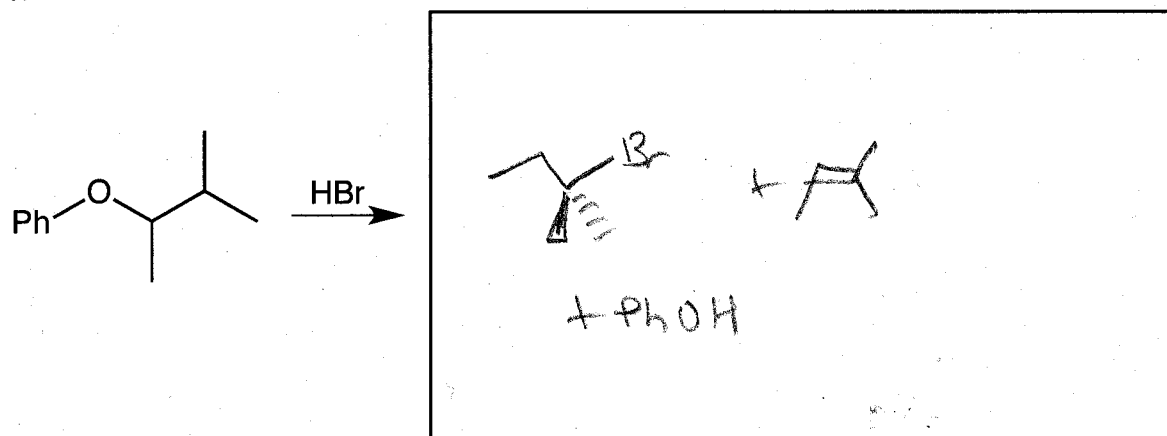
a.



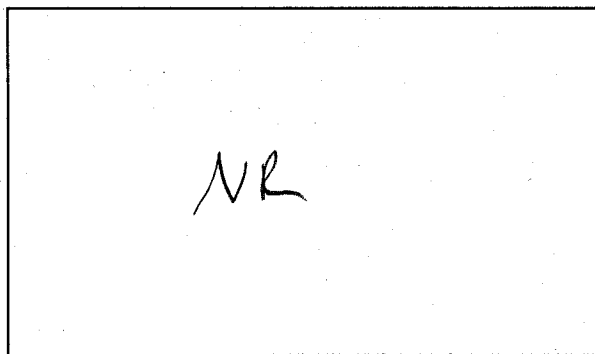
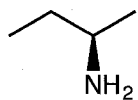
b.



c.

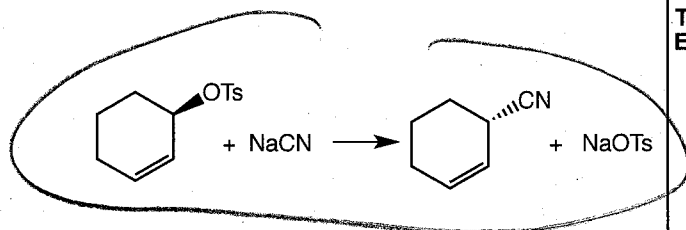


d.

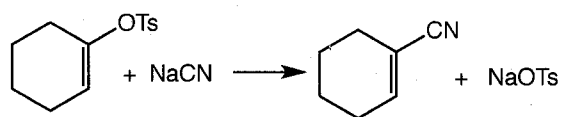


2. (24 points) Circle the reaction in the following pairs of reactions that you would expect to go faster. It is possible that one of the reactions shown in each pair does not occur at a measurable rate. Give explanations in the boxes provided.

a.



or

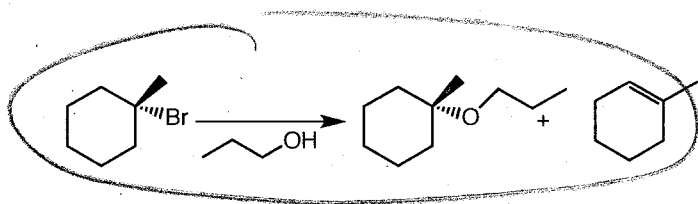


Type of mechanism: SN2

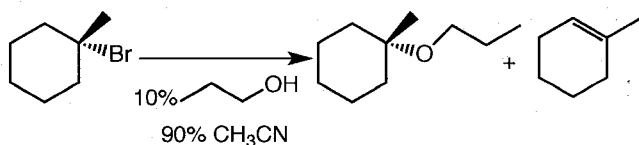
Explanation

SN2 does not occur at sp² carbons because the back side of the C-OTs bond is blocked. SN1 does not occur because carbocation at sp² carbon is unstable because greater %s makes a electronegative.

b.



or

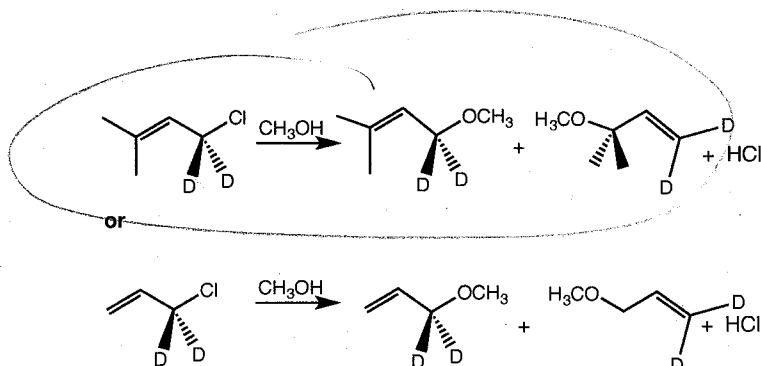


Type of mechanism: SN1/E1

Explanation

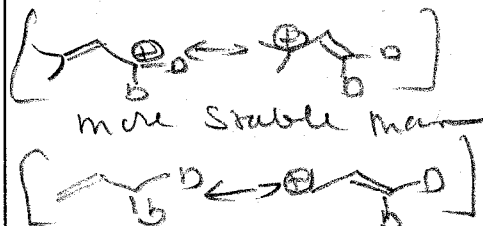
SN1/E1 is faster in polar protic solvent because T.S. is more charged than neutral starting materials. Therefore, TS is more stabilized than starting materials in polar protic solvent & rxn is faster.

c.

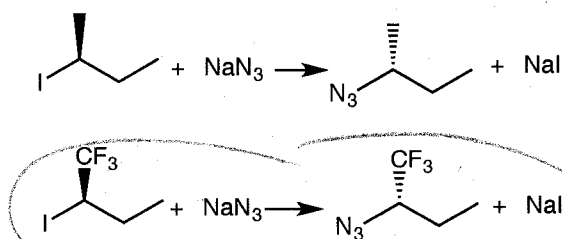


Type of mechanism: S_N1
 Explanation

Intermediate carbocation is more substituted & therefore more stable. T.S. resembles intermediate carbocation + the T.S. that forms the more stable carbocation is more stable & that reaction is faster.



d.

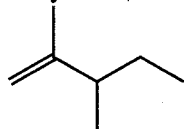


Type of mechanism: S_N2
 Explanation

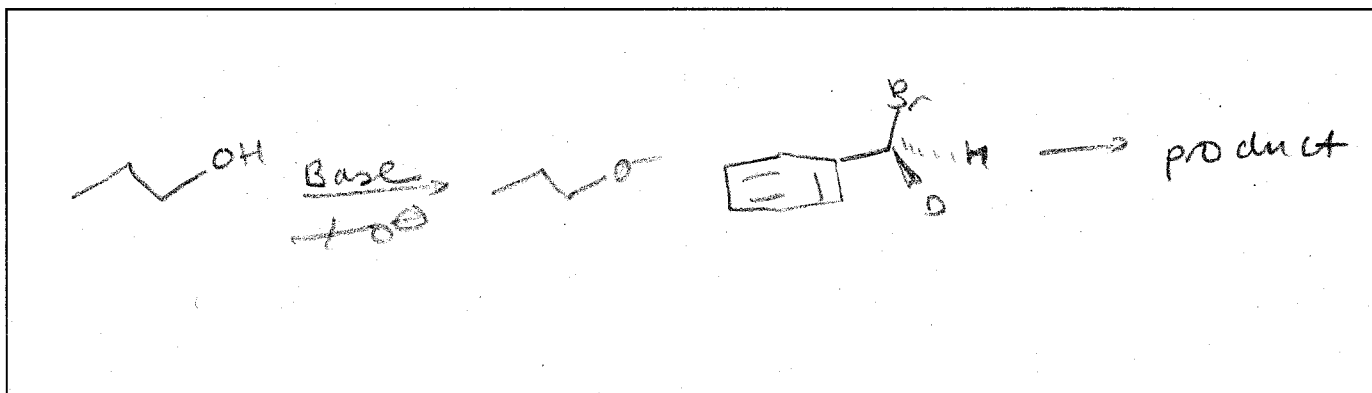
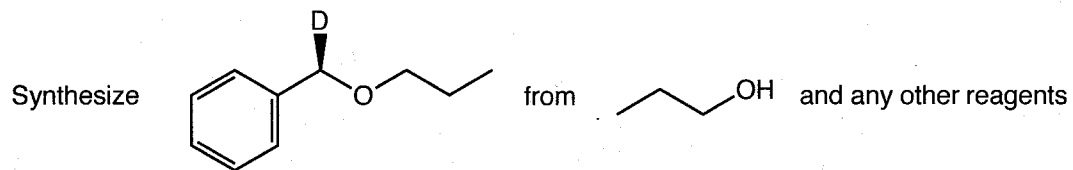
Faster because e⁻ withdrawing CF₃ makes carbon more e⁻ poor & electrophilic & therefore more reactive to nucleophile. However steric size will slow 2nd reaction down.

3. (14 points) Predict starting materials and plan synthesis.

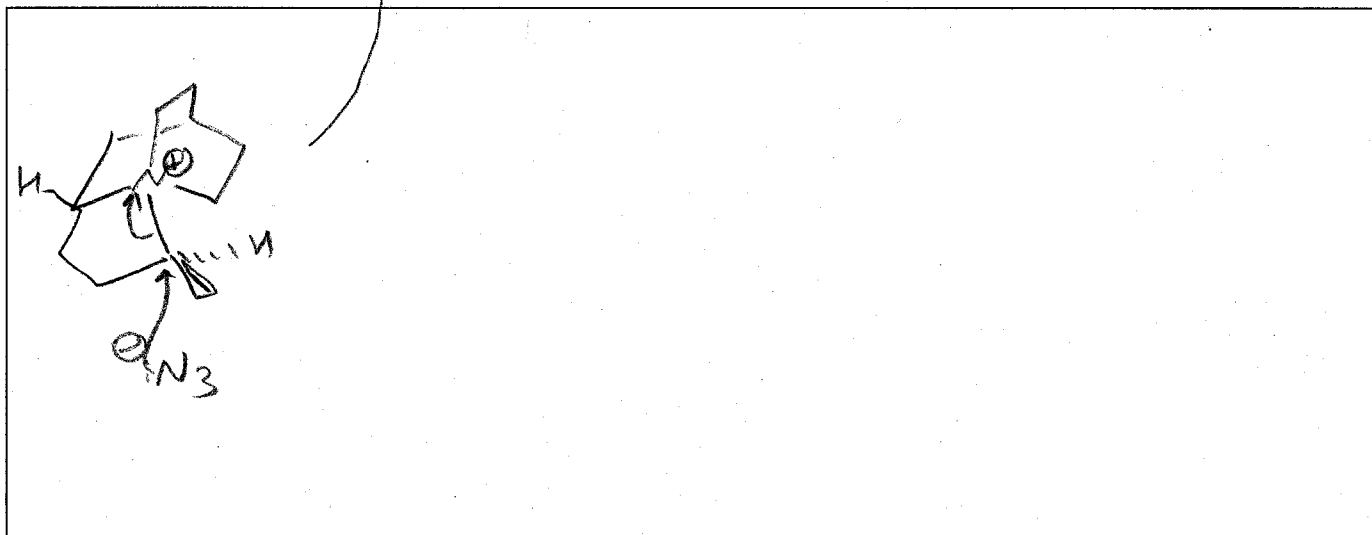
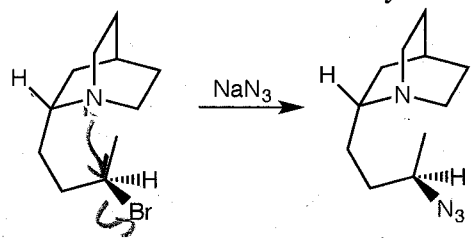
a. Synthesize the following alkene from an alkyl halide and any other reagents.



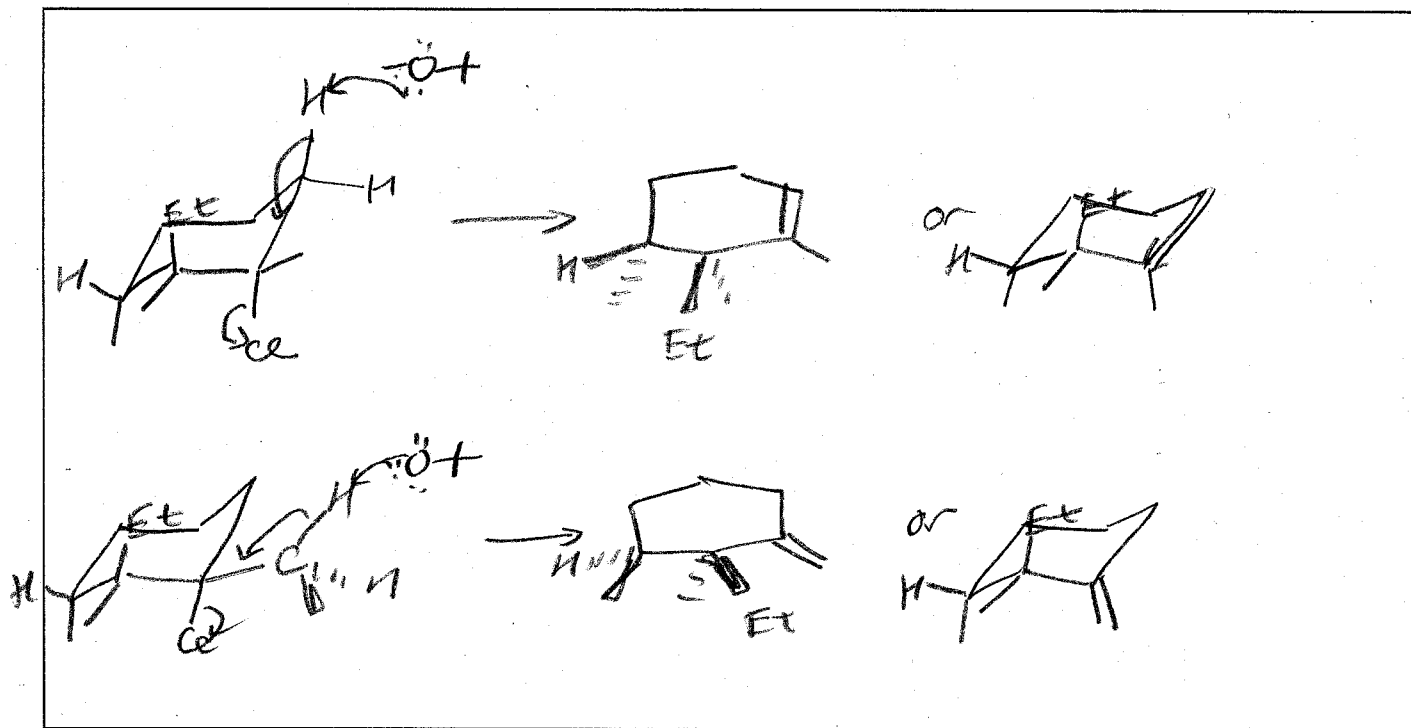
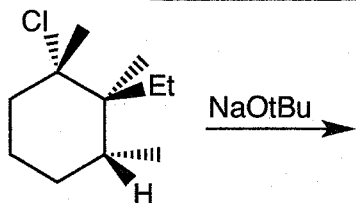
b.



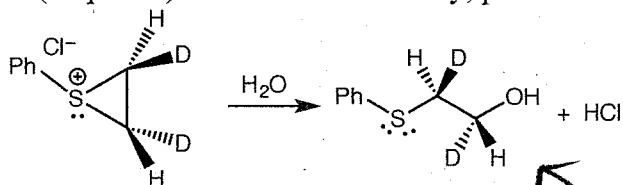
4. (12 points) Draw the mechanism of the following reaction using arrows to indicate the flow of electrons. Make sure to clearly indicate stereochemistry.



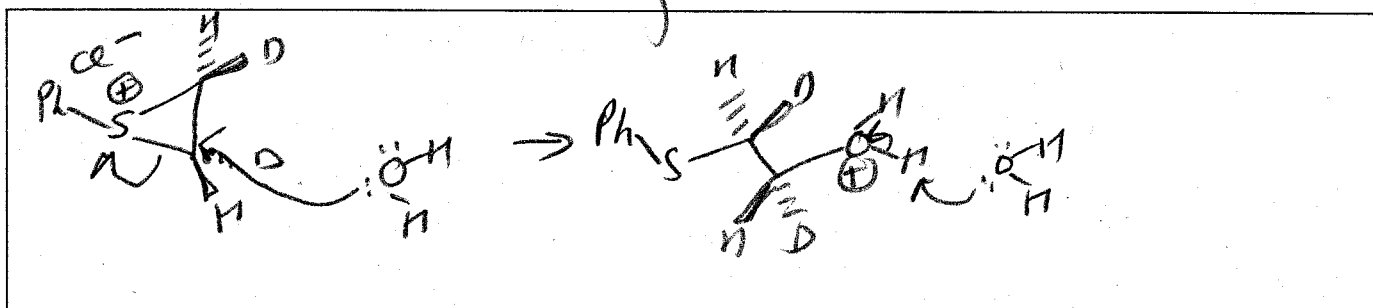
5. (16 points) Draw the mechanism of the following reaction using arrows to indicate the flow of electrons. Indicate major and minor products. Make sure to clearly indicate stereochemistry. In your mechanism draw the chair conformation of the starting material that undergoes the reaction.



6. (30 points) In lecture on Tuesday, problem 3 involved the reaction shown below.



a. Given that this is an S_N2 reaction, draw the mechanism of the reaction using arrows to indicate the flow of electrons.

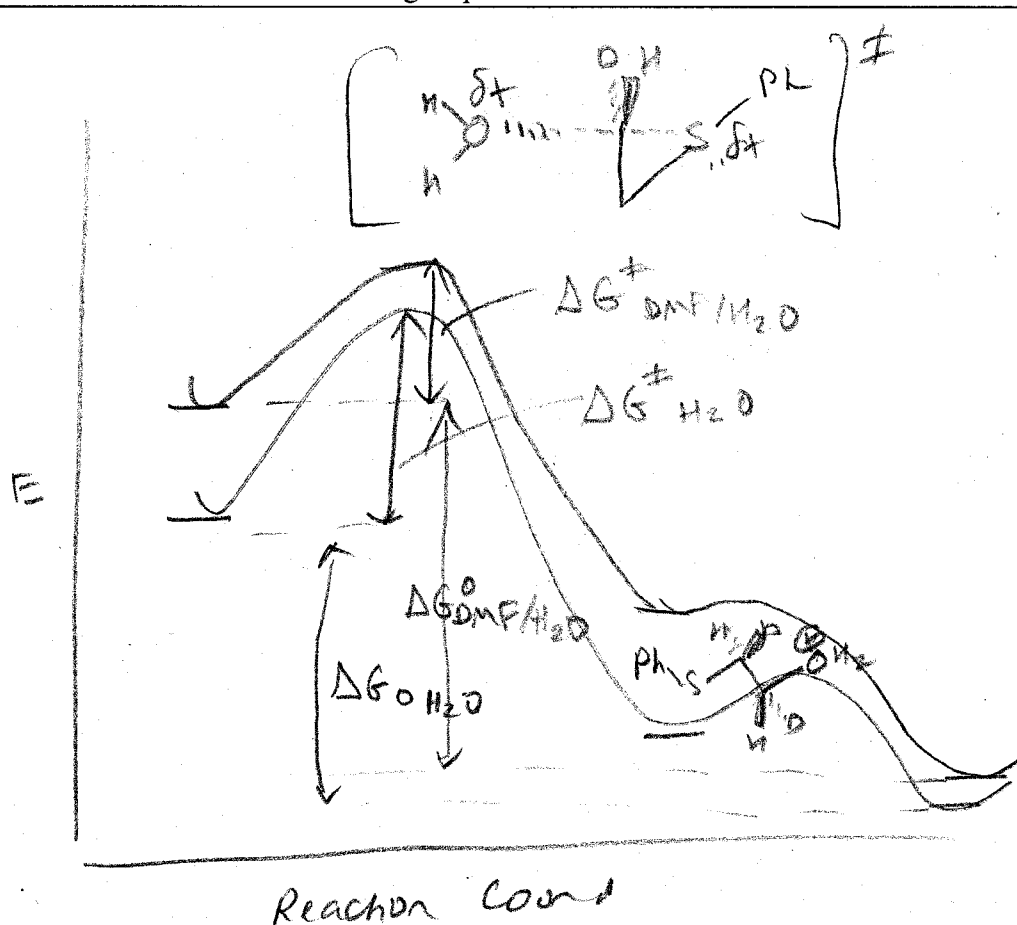


b. Would you expect this reaction to be faster or slower in a solvent containing 10% water and 90% DMF (dimethylformamide) instead of pure H₂O. Explain your answer.

Reaction will be faster in 10% H₂O & 90% DMF
 The starting materials have localized charge & this charge will be less localized in T.S. Therefore T.S. will be destabilized less than starting materials in the polar aprotic solvent & reaction will be faster
 *Note - this problem was graded based on your answer to a *

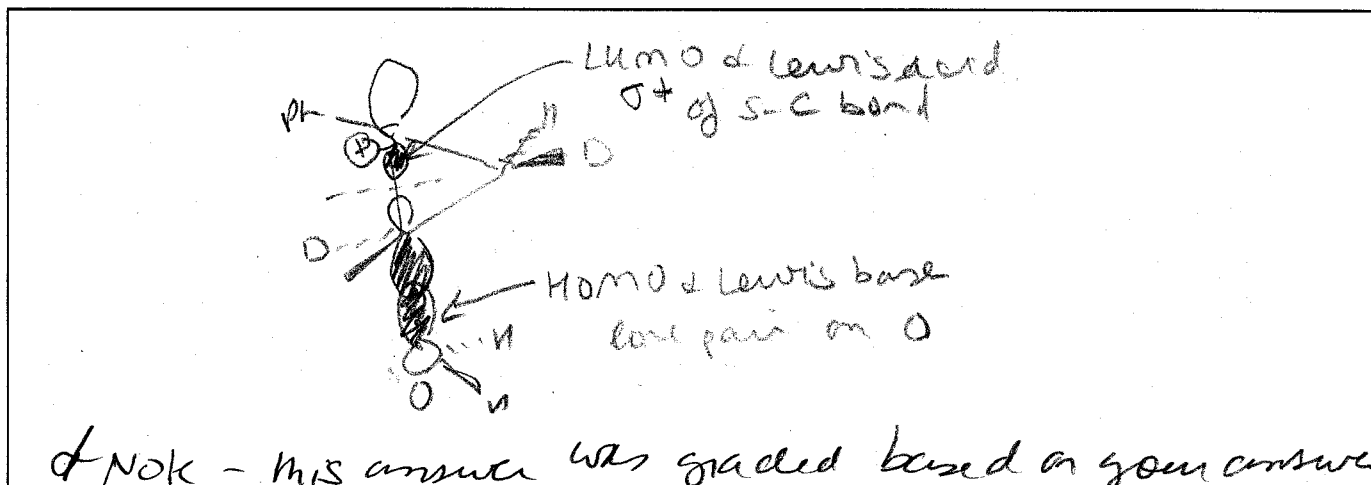
c. Draw a reaction coordinate diagram to illustrate your answer to part b. Include on one diagram the reaction performed in H₂O and the reaction performed in 10% water and 90% DMF. Include in your diagram:

- structures of all intermediates.
- a sketch the transition state at the rate determining step
- label ΔG° for reactions in both solvents
- label ΔG^\ddagger of the rate-determining step for reactions in both solvents

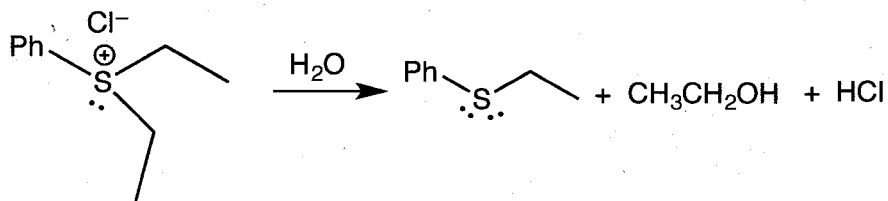


Note this answer was graded based on your answer to a & b.

d. Sketch the orbitals involved in the reaction on a line drawing of the reactants. Label the orbitals and label the Lewis Acid (LUMO) and Lewis Base (HOMO).



e. Would you expect the reaction below to be faster or slower than the one drawn at the beginning of the problem? Explain your answer.



Reaction shown here is slower.
The reaction at the beginning of this problem is faster because the ring is opened & ring strain is released in this reaction. The transition state has long partial bonds & therefore has less ring strain than starting material. As a result starting material is more destabilized than T.S. & reaction is fast compared to the reaction that does not involve release of ring strain.