CHEMISTRY 12A FALL 2017

EXAM 2

Answer Key

OCTOBER 19, 2017

NAME- WRITE BIG _____

STUDENT ID: _____

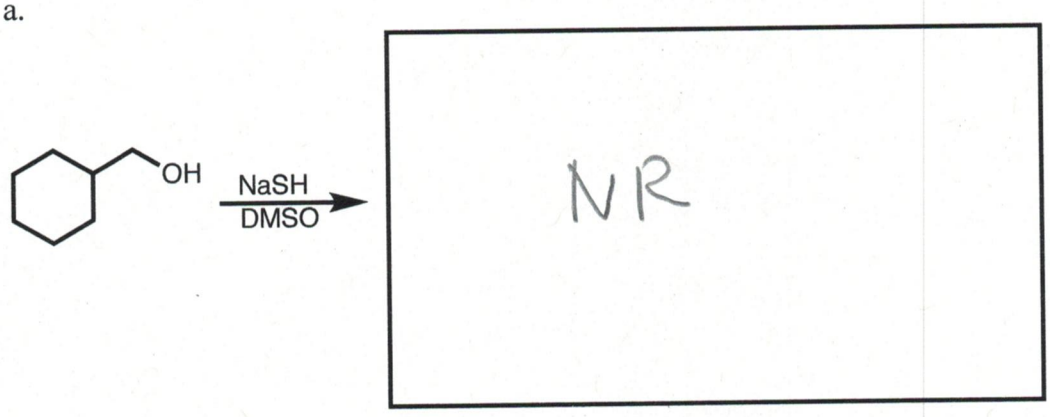
SECTION AND/OR GSI IF YOU ARE IN THE LABORATORY COURSE: _____

- **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**

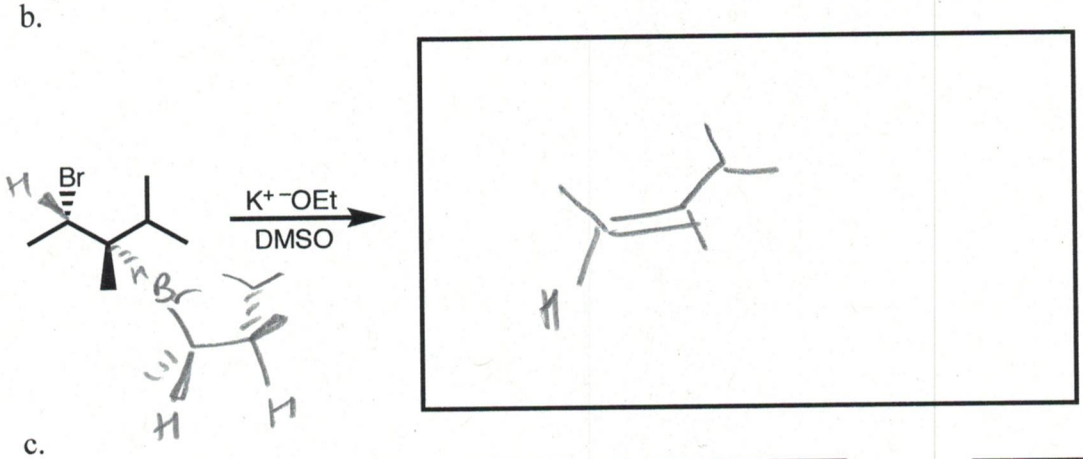
Problem	Points (Maximum)
1	21
2	20
3	18
4	10
5	15
6	12
7	18
8	6
Total	*120*

1. (21 points) For each reaction draw the major organic products, **including all stereoisomers**. Write NR if you think there will be no reaction.

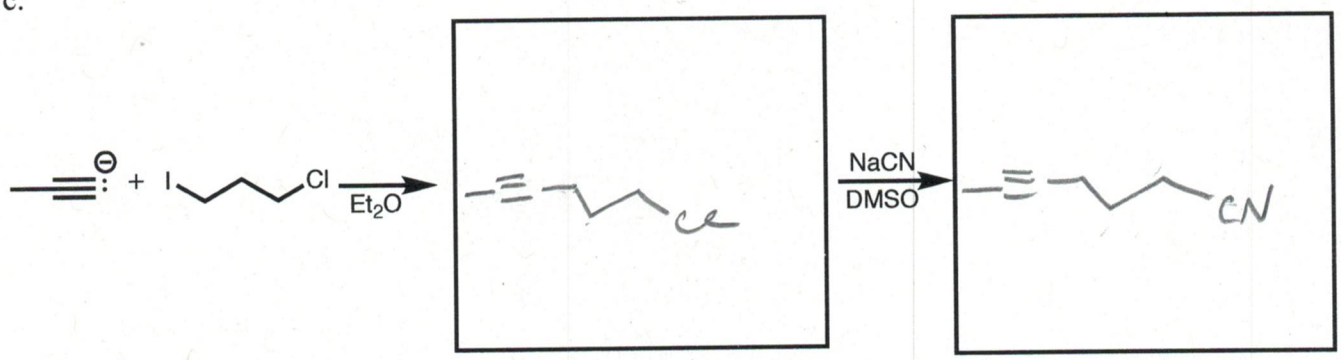
a.



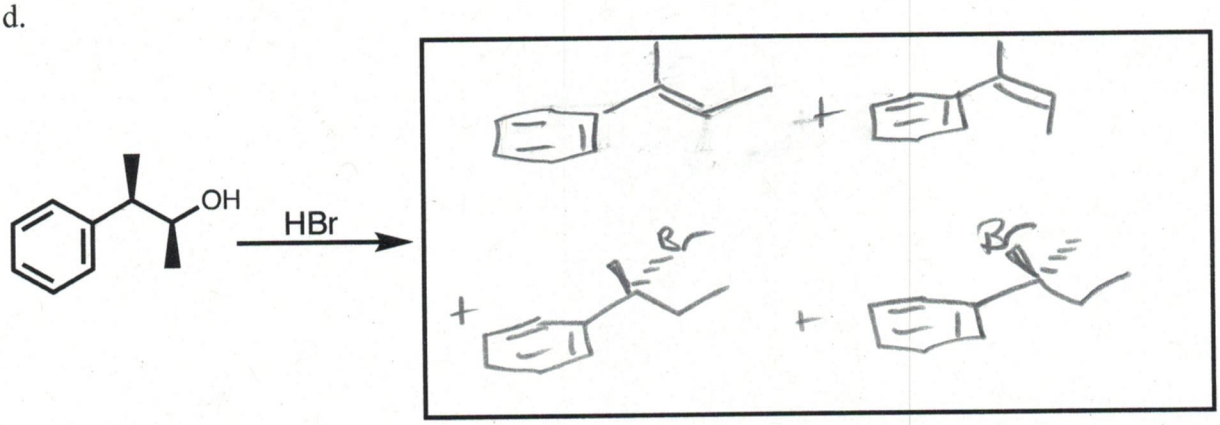
b.



c.

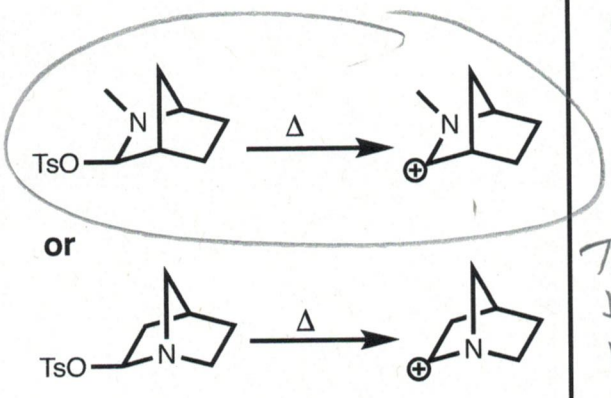


d.



2. (20 points) **Circle** the reaction in the following pairs of reactions that you would expect to go faster. It is possible that both reactions have the same rate. It is possible that one of the reactions shown in each pair does not occur at a measurable rate. You may disregard any other products besides the ones pictured that may form under the reaction conditions. Give explanations in the boxes provided.

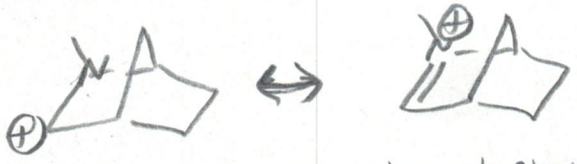
a.



(Δ means heat)

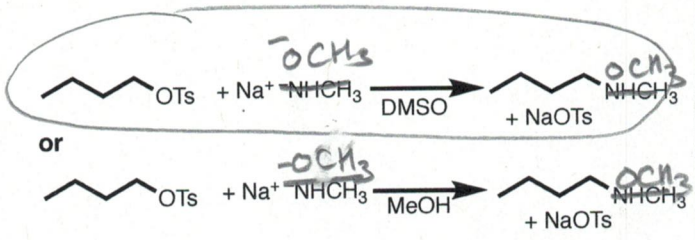
Explanation

Carbocation stabilized by resonance



The other carbocation is not stabilized by resonance because no double bond at bridgehead. Lone pair on N is perpindicular to empty p orbital

b.

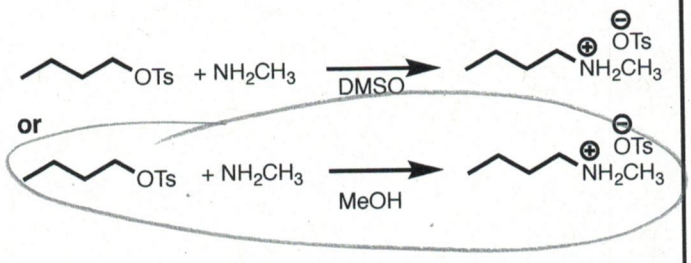


Explanation

SN2

Charge is more dispersed in T.S than in starting material. Therefore, more solvating solvent (MeOH) stabilizes starting materials more than T.S. & reaction is slowed

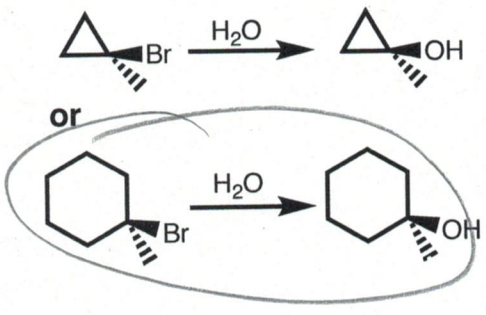
c.



Explanation

T.S. is more charged than starting materials. Therefore, T.S. is stabilized more than starting material in more solvating solvent (MeOH)

d.



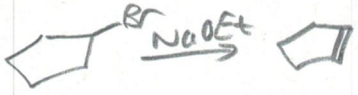
Explanation

SN1 mechanism RDS forms carbocation. Hammond postulate says T.S. looks like carbocation

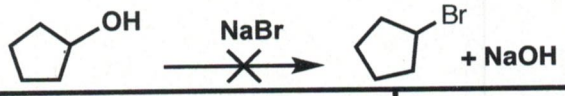
is more strained than 
Br because sp^2 hybridization prefers 120° angles while sp^3 has 109.5° angles. This makes energy difference between starting material & T.S. (which resembles carbocation) greater & rxn slower

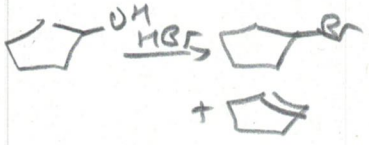
3. (18 points) The following reactions would not occur as written. i. What product would actually be made? ii. Why was the desired product not formed? iii. How could you change either the substrate **OR** reaction conditions to give the desired product?

a.

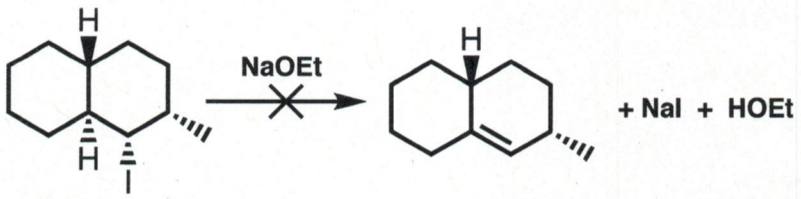
What product is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Explain in 1 sentence)	How could substrate **or** reaction be changed to give desired product? Draw your revised reaction.
	NaSH is a strong nucleophile & weak base	 Use strong base.

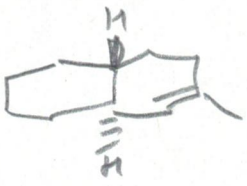
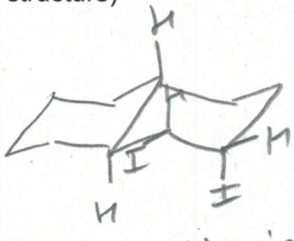
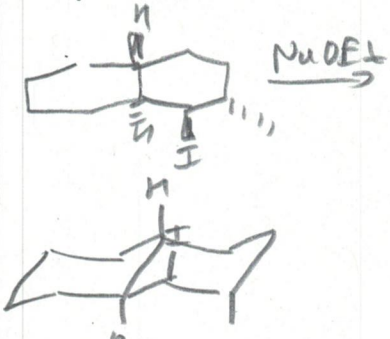
b.



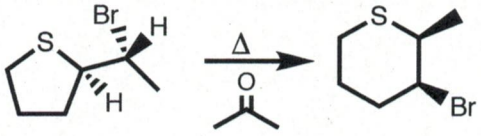
What product is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed?	How could substrate **or** reaction be changed to give desired product? Draw your revised reaction.
NR	No leaving group	Protonate OH to make a good leaving group 

c.

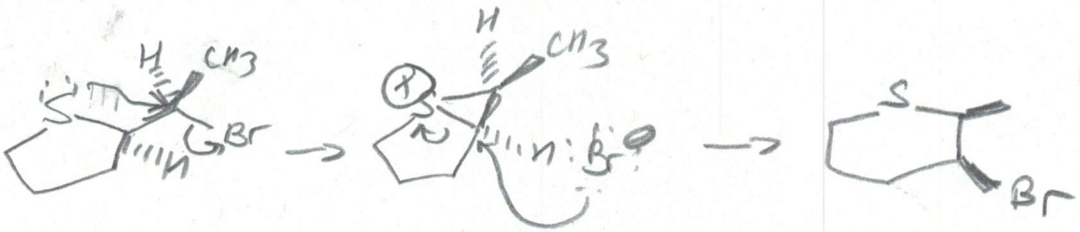


What product is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Explain in 1 sentence and include a **drawing** of a relevant chair structure)	How could substrate **or** reaction be changed to give desired product? Draw your revised reaction.
NR or slow 	 No H antiperiplanar to I & no ring flip possible.	 Now H & I are antiperiplanar

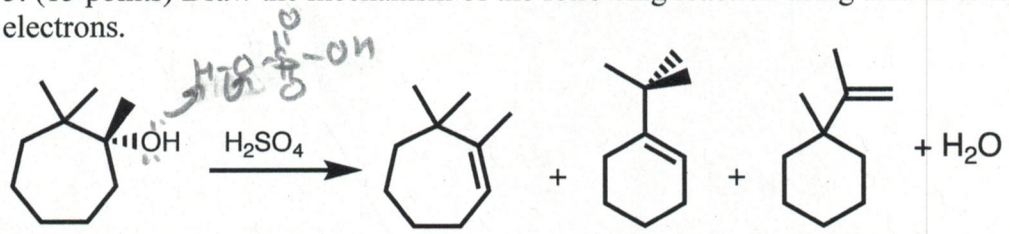
4. (10 points) Draw the mechanism of the following reaction using arrows to indicate the flow of electrons. Make sure to clearly indicate stereochemistry.

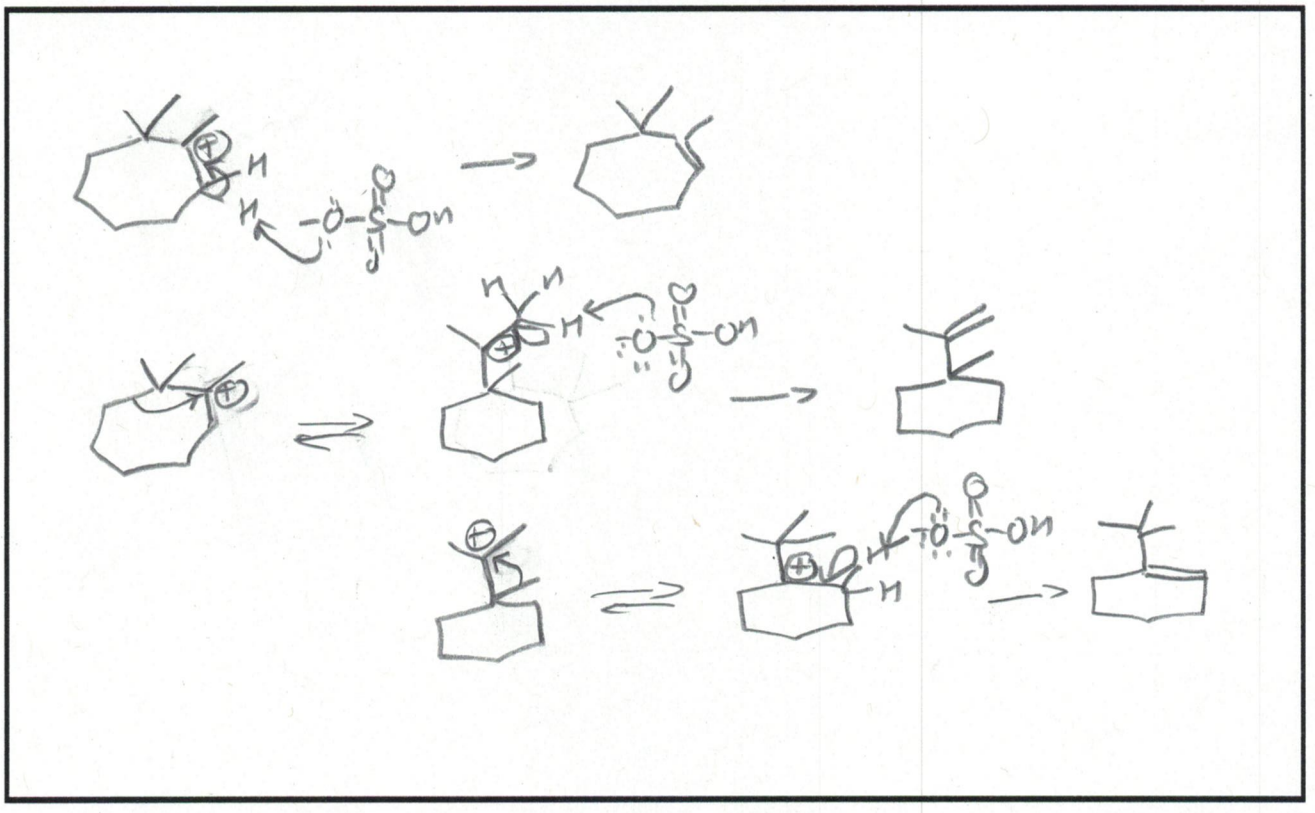


(Δ means heat)



5. (15 points) Draw the mechanism of the following reaction using arrows to indicate the flow of electrons.





6. (12 points) Consider the carbocations shown below.

a. Order the carbocations from least to most stable. Explain your reasoning.

least stable
2° carbocation
less hyperconjugation
w/ C-H or C-C bonds
possible

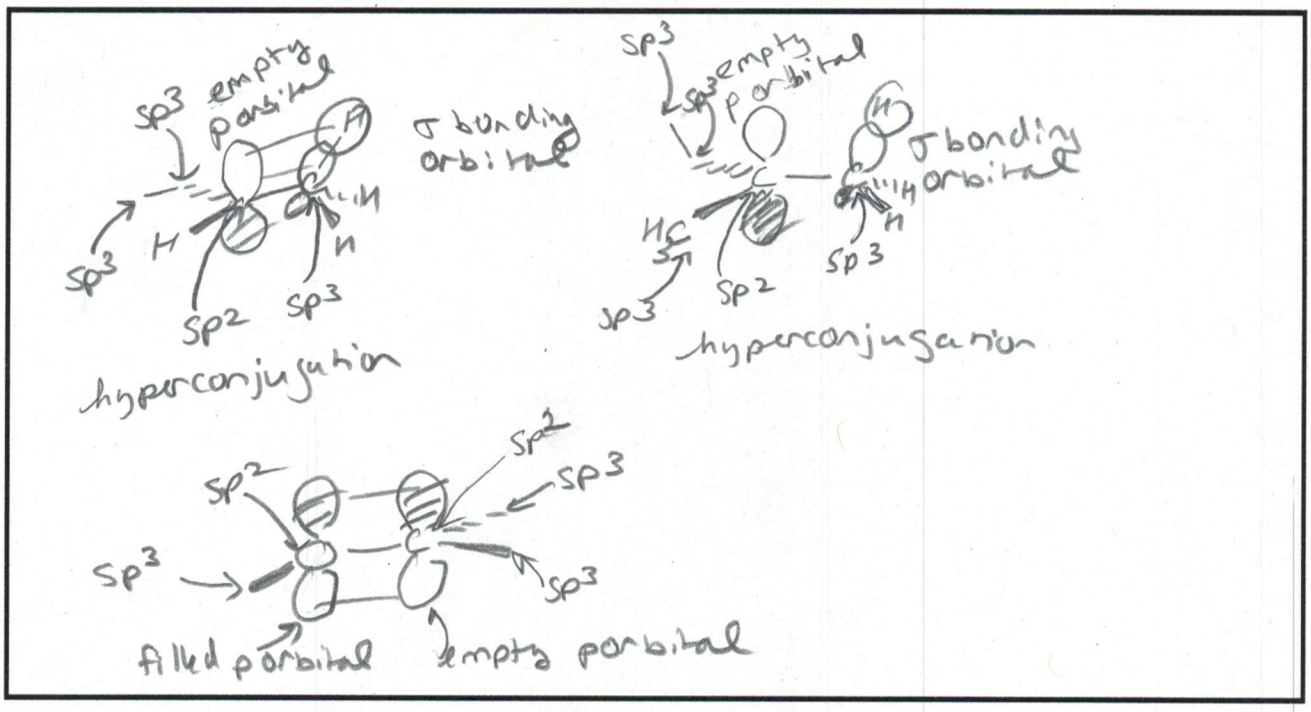
most stable because
of resonance to form
a structure w/ full
octet on all atoms

b. For each carbocation from part a of this question:

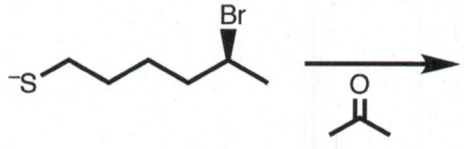
i. Draw a sketch of one example of the most important set of orbital interactions involved in stabilizing each carbocation.

ii. Label each orbital you draw.

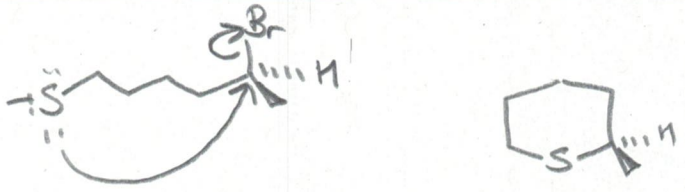
i. Label the hybridization of all non-hydrogen atoms in the three molecules.



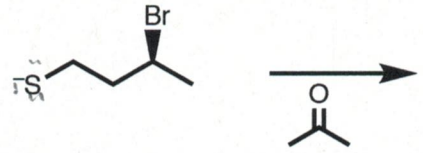
7. (18 points) Consider the reaction shown below:

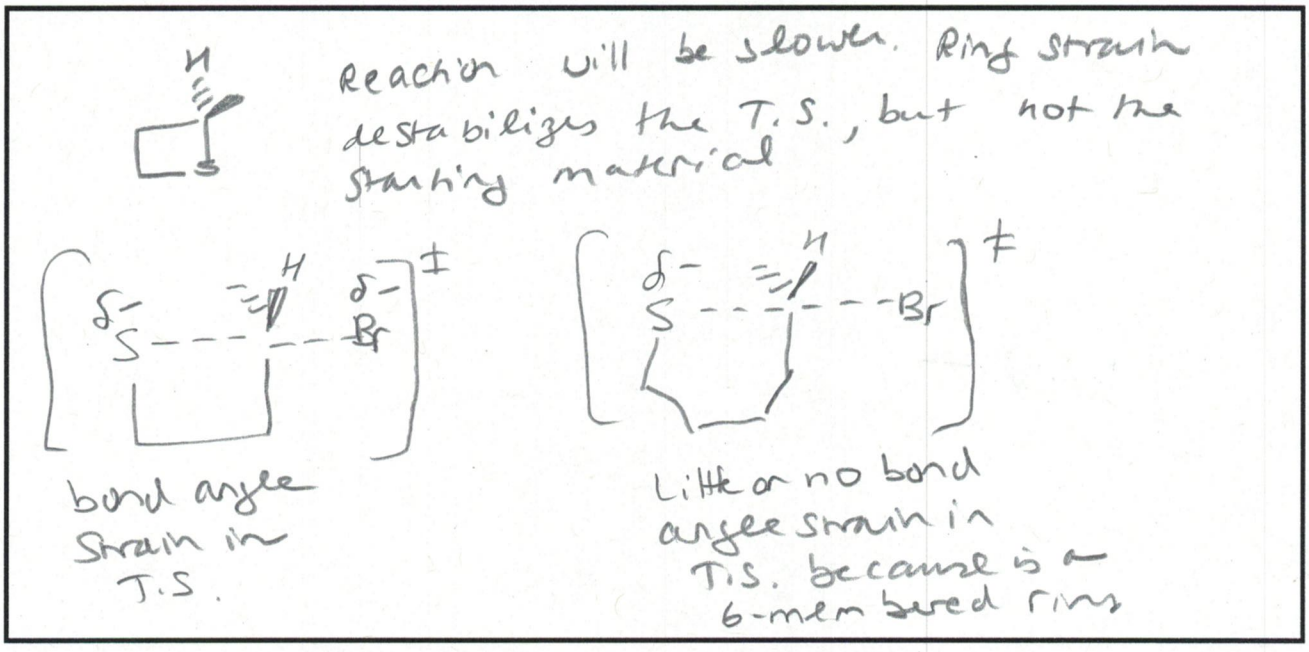


a. Draw the mechanism of this reaction using arrows to show the flow of electrons.

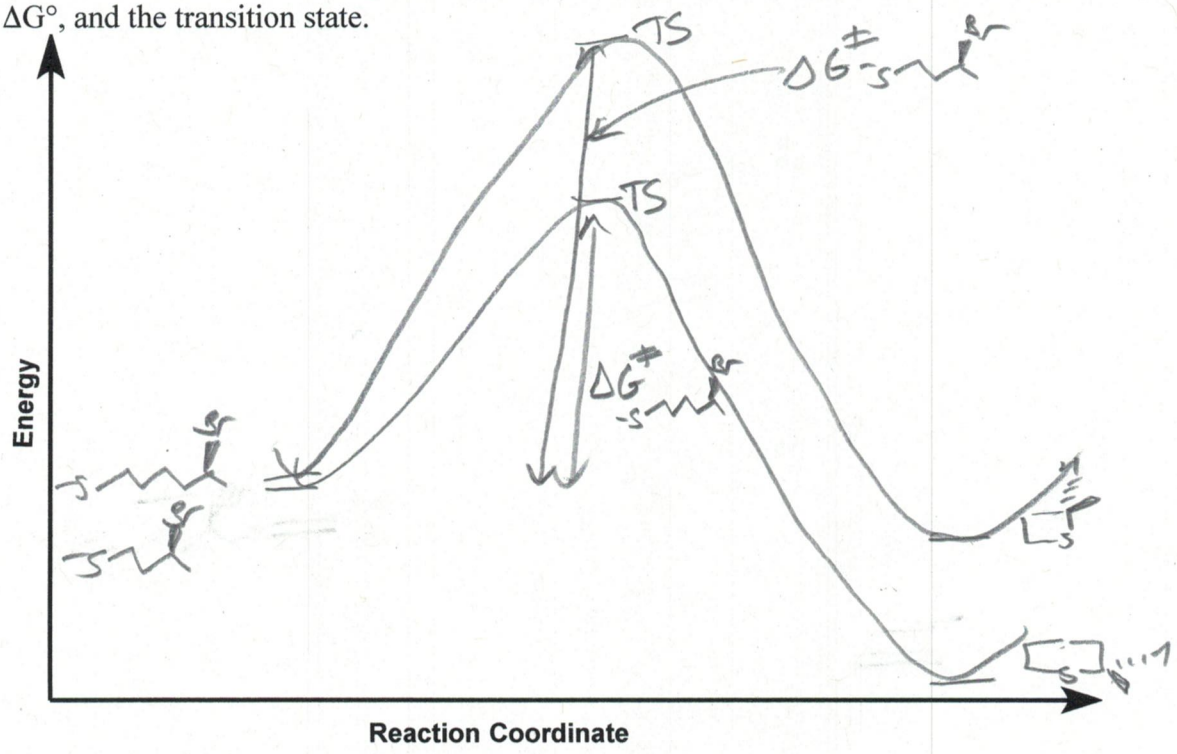


b. Draw the product of the following reaction. Will this reaction be faster or slower than the one drawn at the beginning of this problem? Explain your answer. As part of your explanation, include sketches of the transition state structure for both reactions.

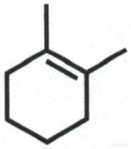
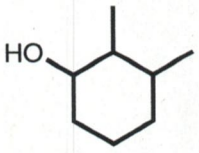




c. Draw a reaction coordinate energy diagram showing both reactions from parts a and b of this question. Assume the starting materials for the two reactions have similar stability. Label the $\Delta G^{\ddagger}$, and $\Delta G°$, and the transition state.



8. (6 points)

Synthesize  from  and any other reagents.