CHEMISTRY 12A FALL 2018

EXAM 2

Answers

OCTOBER 18, 2018

NAME- WRITE BIG ________________________________

STUDENT ID: ________________

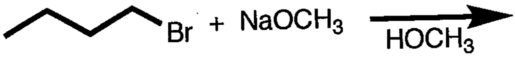
SECTION AND/OR GSI IF YOU ARE IN THE LABORATORY COURSE: ________________

- **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	20
2	20
3	12
4	16
5	22
6	22
7	8
Total	***120***

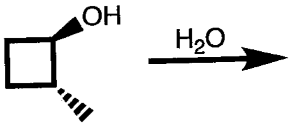
1. (20 points) For each reaction draw the major organic products, **including all stereoisomers**. Write NR if you think there will be no reaction.

a.



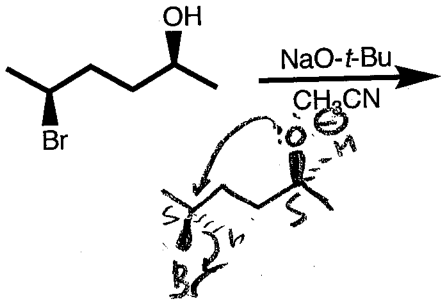
+ NaBr

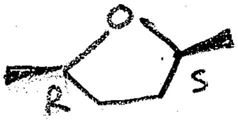
b.



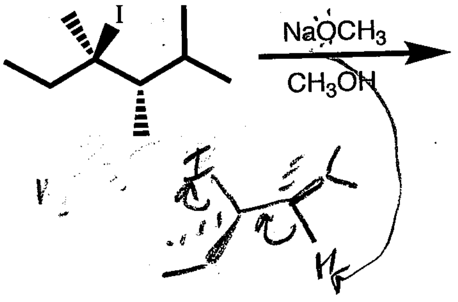
NR

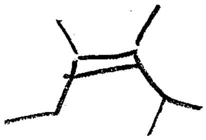
c.





d.

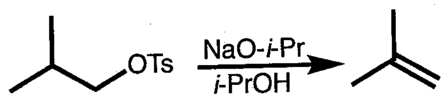




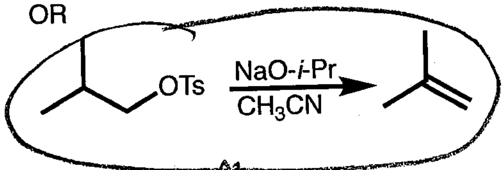
+ NaI + CH3OH

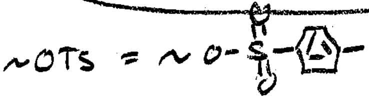
2. (20 points) **Circle** the reaction in the following pairs of reactions that you would expect to go faster. It is possible that both reactions have the same rate. It is possible that one of the reactions shown in each pair does not occur at a measurable rate. You may disregard any other products besides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

a.



OR





Type of Reaction: E2

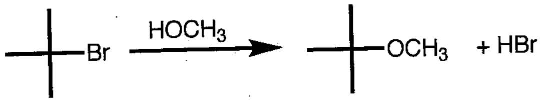
Explanation for your choice of faster reaction:

Reaction is faster in polar aprotic solvent because base is less solvated & more reactive.

Rate depends on both substrate & base.

T.S. has less localized charge than S.m & is less stabilized by solvation than is the base.

b.



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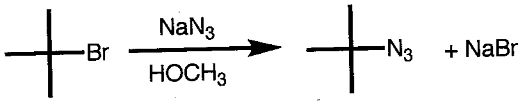
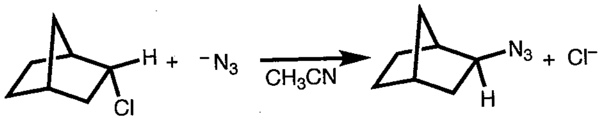


Type of Reaction: SN1

Explanation for your choice of faster reaction:

Same rate. Rate determining step does not involve nucleophile. Therefore, rate of rxn will be the same.

c.



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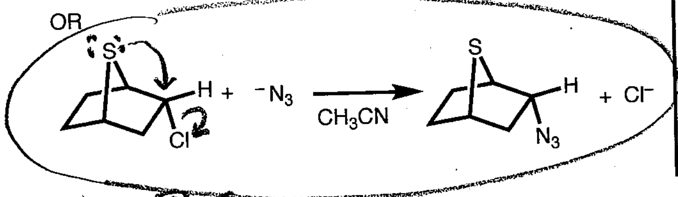
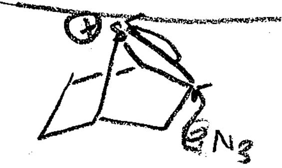
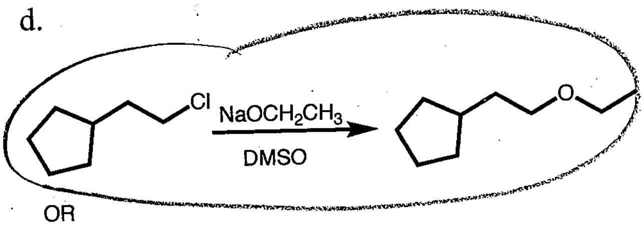




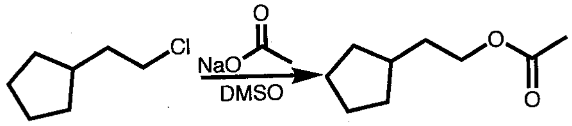
Type of Reaction: SN2

Explanation for your choice of faster reaction:

Intramolecular react w/ sulfur is fast. The positively charged sulfur is a good L.G. (pKa conj acid <<0) & reacts rapidly w/ $^{\ominus}N_3$. Sterically hindered C-Cl will react slowly w/ Nu in 1st rxn d.



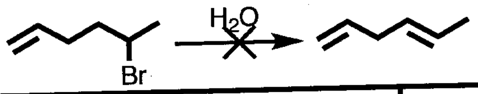
OR

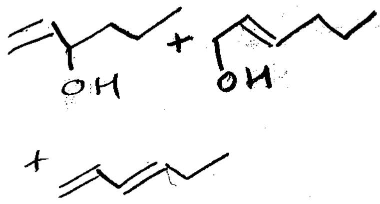
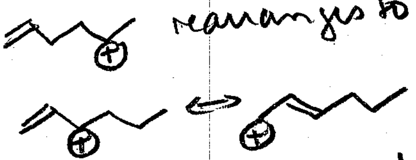
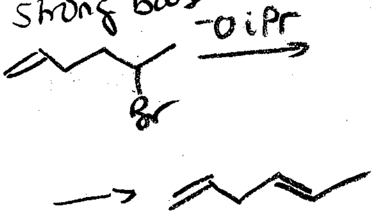


Type of Reaction: SN2
Explanation for your choice of faster reaction:
-O⌒ is a stronger base & nucleophile than -OR which is a weaker base & nucleophile due to resonance stabilization

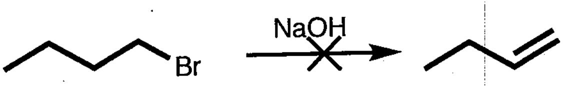
3. (12 points) The following reactions would not occur as written. i. What product or products would actually be made? ii. Why was the desired product not formed? iii. How could you change either the substrate **OR** reaction conditions to give the desired product?

a.

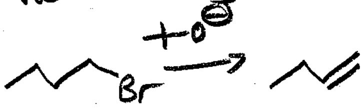


What product is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Explain in 1 sentence and include **drawings** of any relevant structures)	How could substrate **or** reaction be changed to give desired product? Draw your revised reaction.
	SN1 conditions  rearranges to which is stabilized by resonance	Use E2 conditions strong base  -OiPr

b.

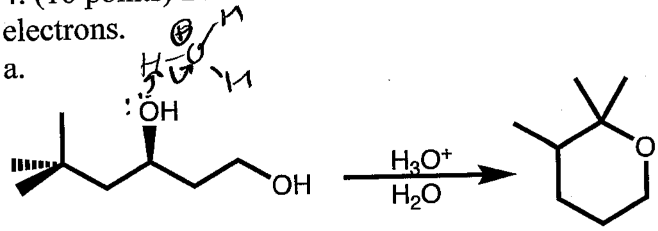


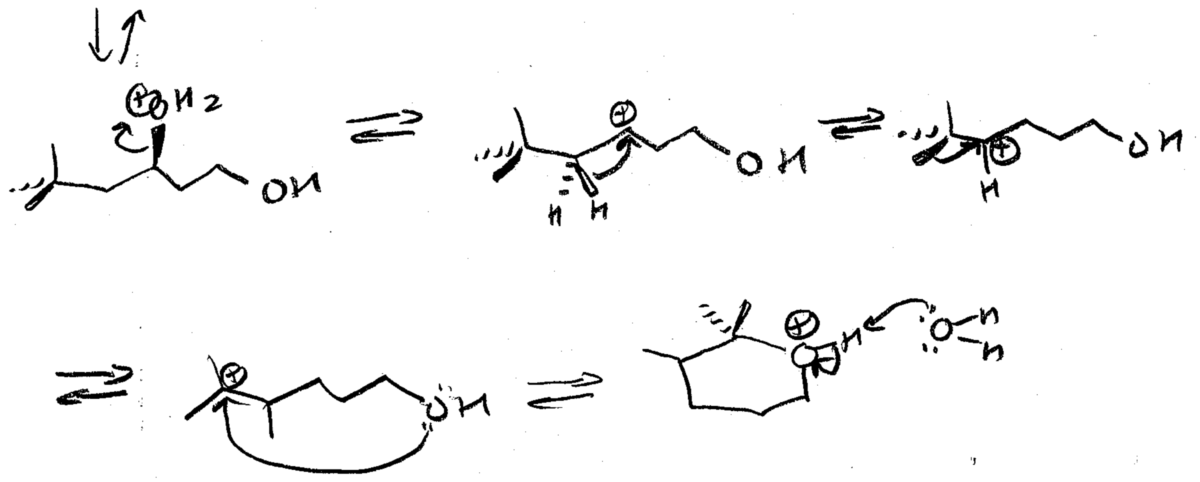
+ NaBr

What product is actually made? (Draw structure or NR for no reaction)	Why was desired product not formed? (Explain in 1 sentence and include **drawings** of any relevant structures)	How could substrate **or** reaction be changed to give desired product? Draw your revised reaction.
	SN2 w/ 1° unhindered alkyl halide & good unhindered Nu preferred.	Use bulky base  $tO^{\ominus}$

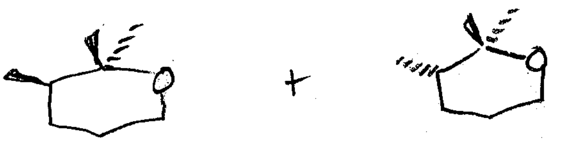
4. (16 points) Draw the mechanism of the following reaction using arrows to indicate the flow of electrons.

a.



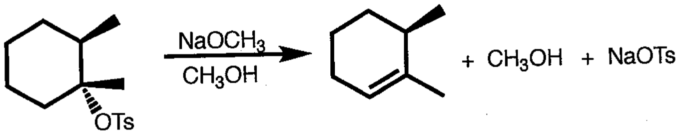


b. Draw all the stereoisomers of the products that would be formed in the reaction in part a.

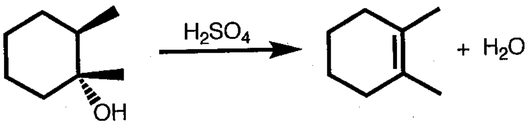


5. (22 points) Consider the two reactions shown below.

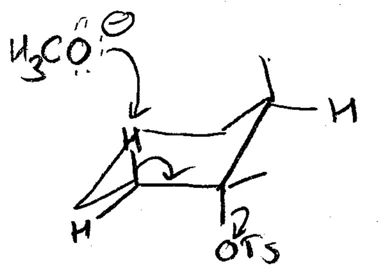
Reaction A



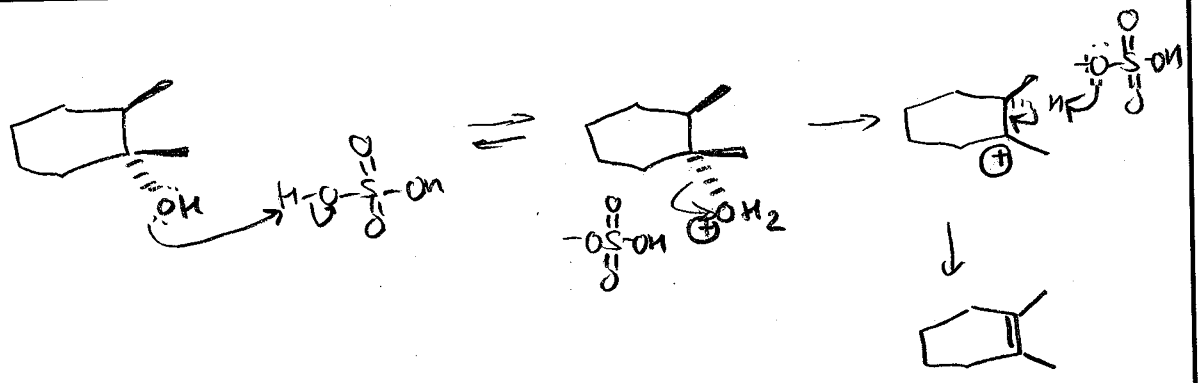
Reaction B



a. Draw the mechanism of Reaction A using arrows to show the flow of electrons.



b. Draw the mechanism of reaction B using arrows to show the flow of electrons.



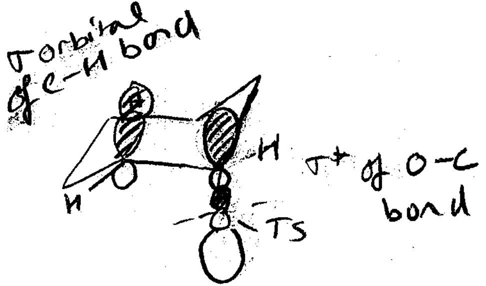
c. Why do the reactions produce different products?

i. Explain why Reaction A produces the product shown. Include a sketch and a discussion of the orbitals involved in the step that forms the alkene.

Rxn A is an E2 rxn. Therefore, the H & LG need to be anti to each other (& in the same plane). There is no anti H on the other carbon, so this alkene forms even though the other alkene is more stable.

The orbitals explain the required geometry. The C-H σ & C-O σ^* need to be in the same plane so π bond can form. They need to be anti because σ^* is largest to the back & can overlap best w/ σ orbital in this orientation

Sketch of orbitals; Label orbitals



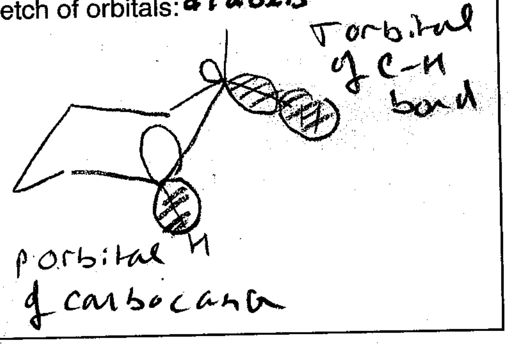
ii. Explain why Reaction B produces the product shown. Include a sketch and a discussion of the orbitals involved in the step that forms the alkene.

Rxn in B is E1 rxn.

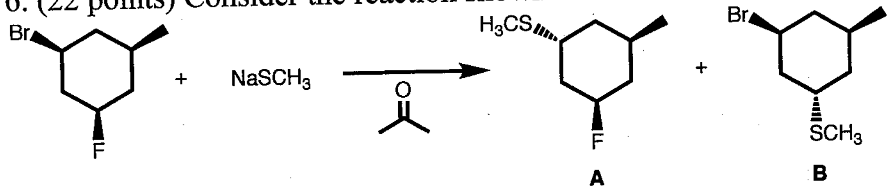
Full carbocation forms. The sp^2 hybridization distorts geometry at ring & σ orbital of C-H is able to form a π bond with empty p orbital of carbocation.

The most stable alkene is formed which is the more substituted.

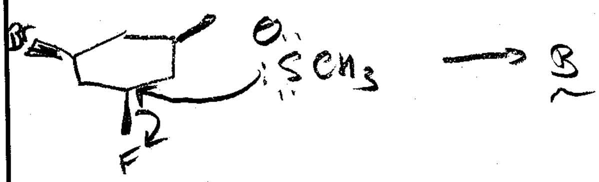
Sketch of orbitals: & labels

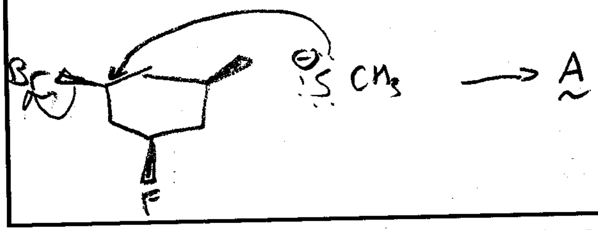


6. (22 points) Consider the reaction shown below:

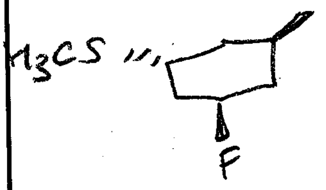


a. Draw the mechanism for the formation of each product.





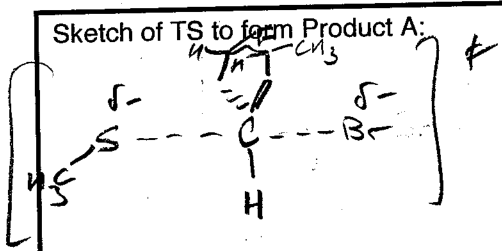
b. Which is the major product of this reaction? Explain your answer briefly. In your answer, identify the type of reaction this is.



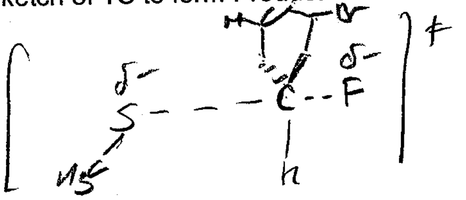
major product of rxn because F⁻ is not a good L.G. because it is too basic

c. Draw the transition state for the formation of each product. Why do the stabilities of the transition states change for the two reactions?

Sketch of TS to form Product A:



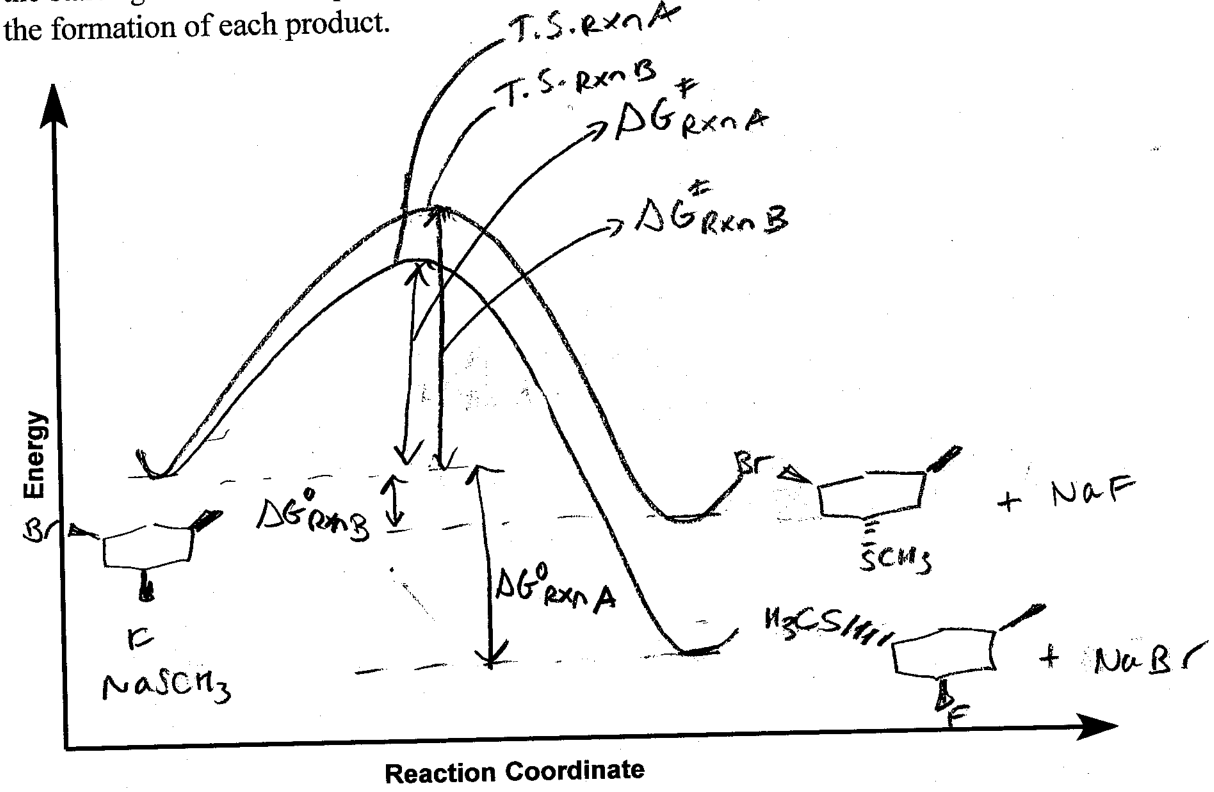
Sketch of TS to form Product B:



Are the stabilities of the two TS's different? Explain your answer.

Yes. F is less stable than Br⁻ w/ a partial bond & negative charge & so transition state on the right is less stable. F is less stable w/ negative charge because it is smaller & more basic than Br-

d. Draw a reaction coordinate energy diagram showing formation of both products. Draw structures fo the starting materials and products on your diagram. Label the ΔG‡, and ΔG°, and the transition state for the formation of each product.



7. (8 points) Synthesize the ether shown below using ethyl bromide as the only source of carbon in the product. This will require several steps.

as the only source of carbon in the product