Chemistry 3A – Spring 2011
Second Midterm – April 1, 2011

Professor Carolyn Bertozzi

Your full signature__ _____

Print your full name_____
(Last Name, First Name, Middle)

Your SID_____

GSI's name or section number_____

This exam has **20** pages; **make sure that you have them all**. We will only grade answers that are in the designated spaces; please do your scratch work on the last page or the backs of pages. Write only **one** answer to each problem; multiple answers will receive **no** credit, even if one of them is correct.

Note: This examination runs for a total of 120 minutes. Please write legibly; ambiguous or illegible answers will receive **no credit**.

Do Not Write in this Box:
1._____(16)
2._____(8)
3._____(18)
4._____(9)
5._____(12)
6._____(12)
7._____(8)
8._____(12)
9._____(5)
Total_____(100)

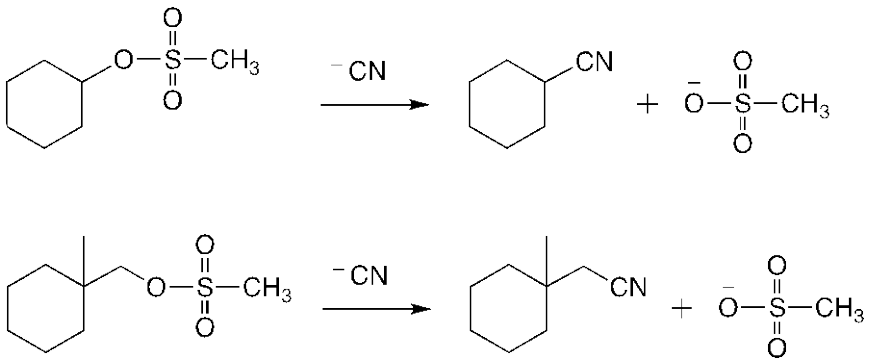
Partial Periodic Table

I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr
Rb	Sr	In	Sn	Sb	Te	I	Xe

1. [16 points]

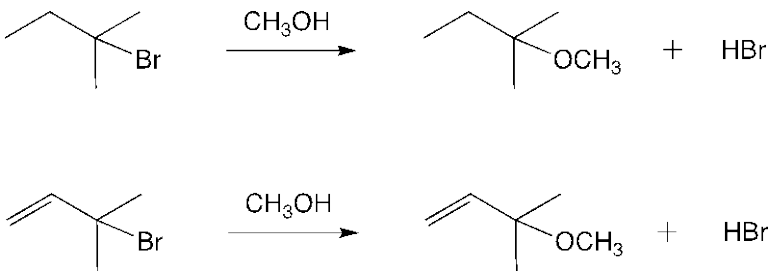
For each pair of reactions, <u>circle the one that will proceed fastest and provide a brief explanation for your choice in the space below the pair</u>. <u>Your explanation must include the reaction type</u> (i.e., S_N2, S_N1, E1 or E2).

a.



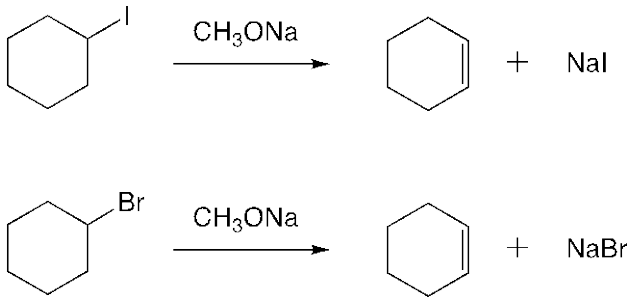
Explanation:

b.



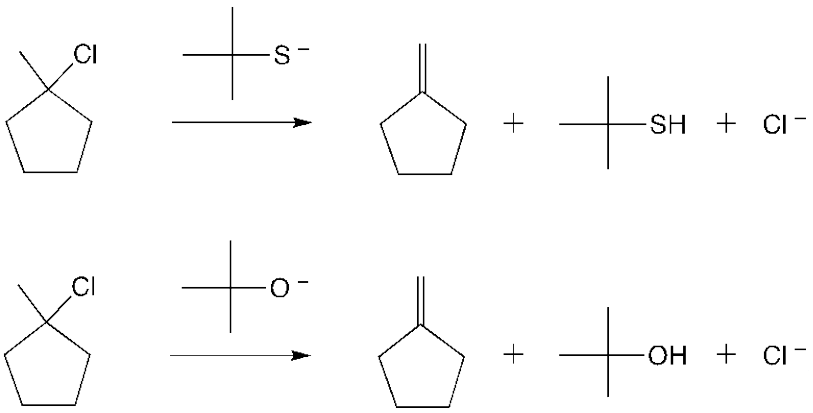
Explanation:

c.



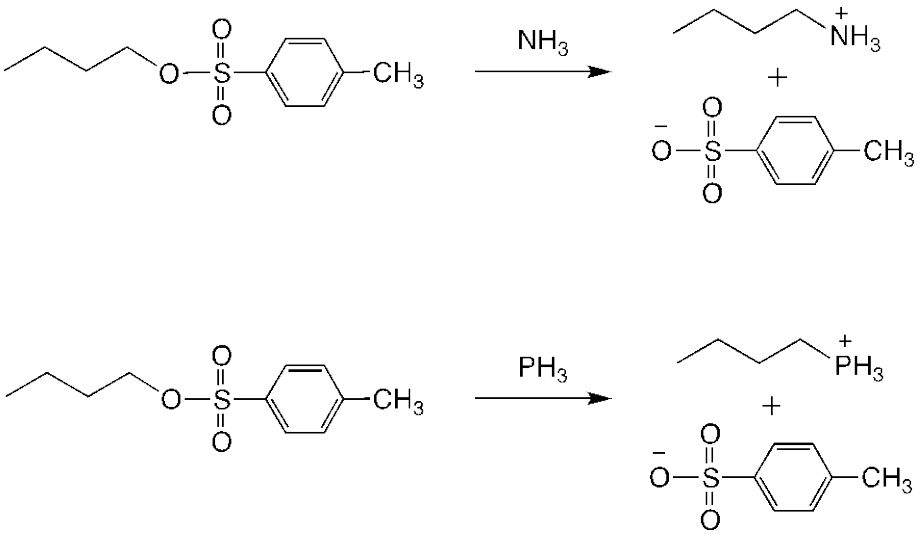
Explanation:

d.



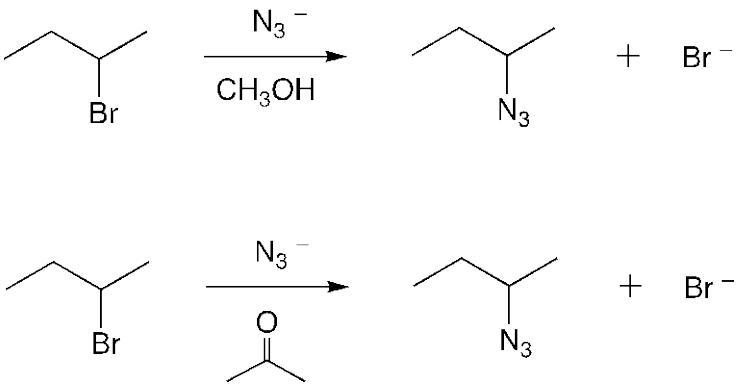
Explanation:

e.



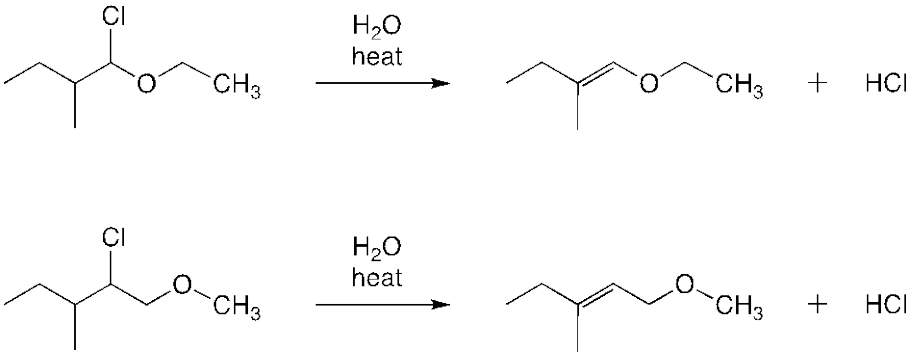
Explanation:

f.



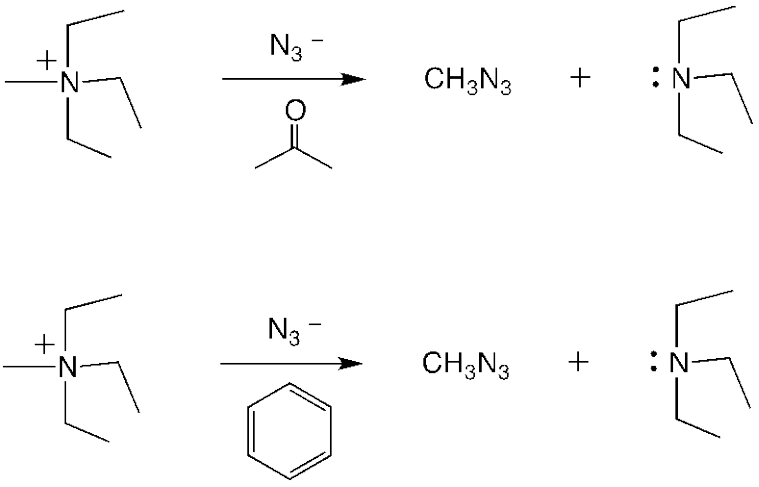
Explanation:

g.



Explanation:

h.

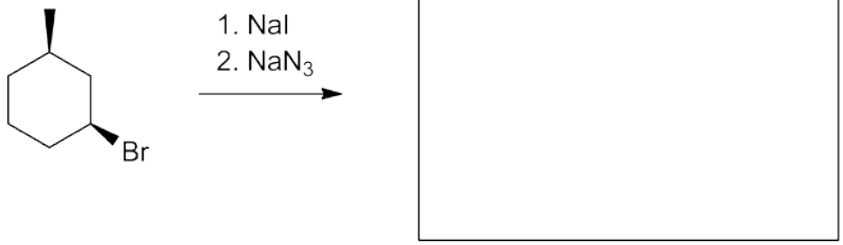


Explanation:

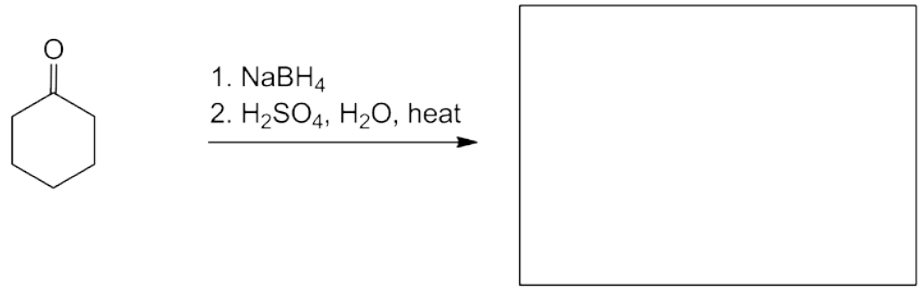
2. [8 points]

In each box, fill in the major organic product or reactant that completes the synthesis scheme. Assume workup steps are included in reactions that normally require them; they are not shown explicitly. Be sure to clearly indicate the stereochemistry of the product where relevant.

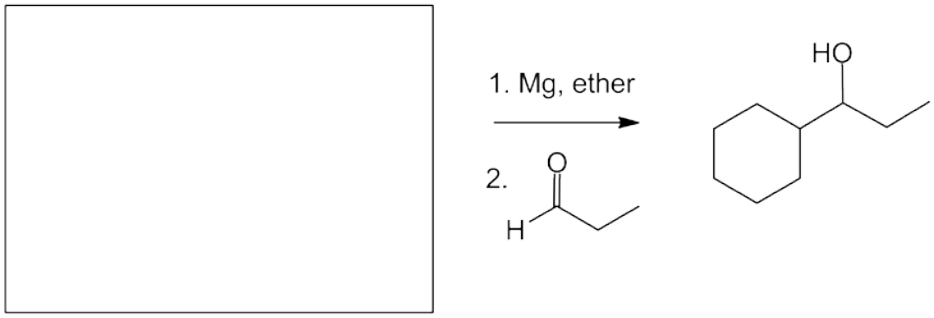
a.



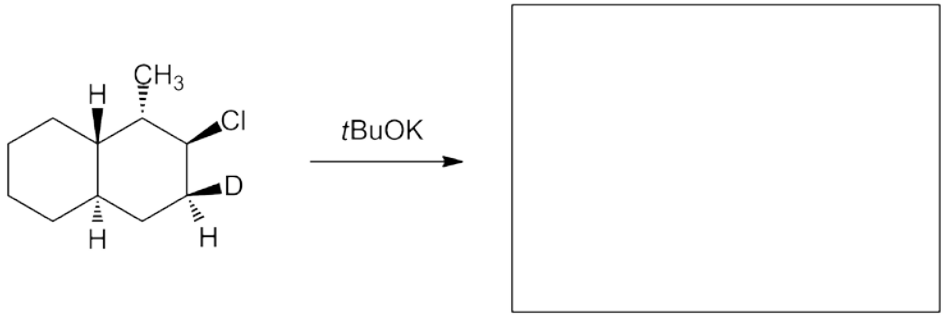
b.



c.



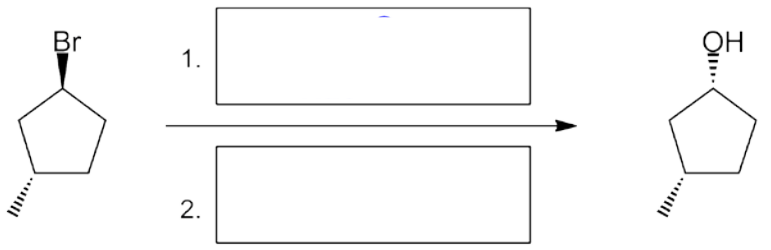
d.



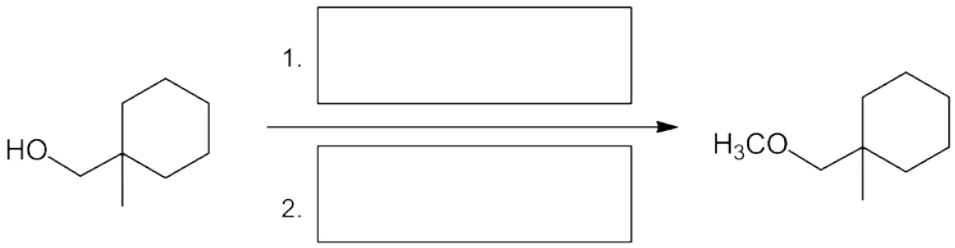
3. [18 points]

For each synthetic scheme below, add reagents to the boxes above and below each arrow that are required to convert the starting material to the given product. Each box should include reagents for just one synthetic step. Workup steps are implied and should **not** be shown in boxes.

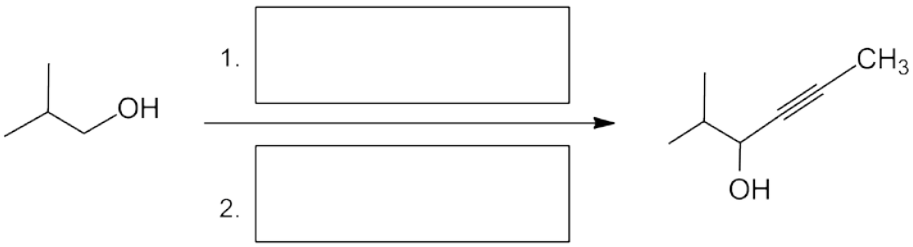
a.



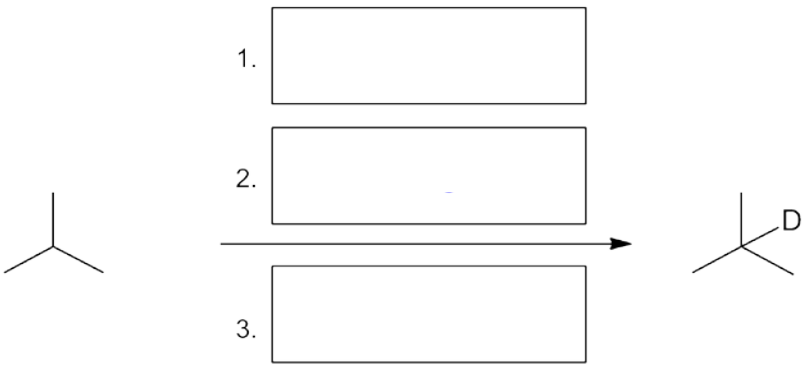
b.



c.



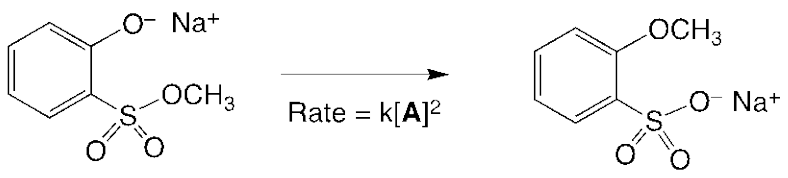
d.



4. [9 points]

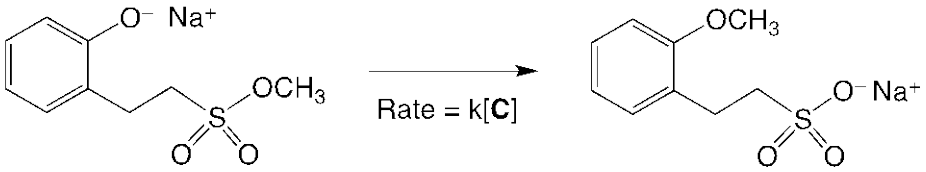
The two related reactions below display different experimental rate laws, as indicated below the arrows.

Reaction 1



A **B**

Reaction 2



C **D**

a. Using the curved-arrow notation, show a step-wise mechanism for each reaction that is consistent with its observed rate law. Be sure to show all steps leading from reactants to products.

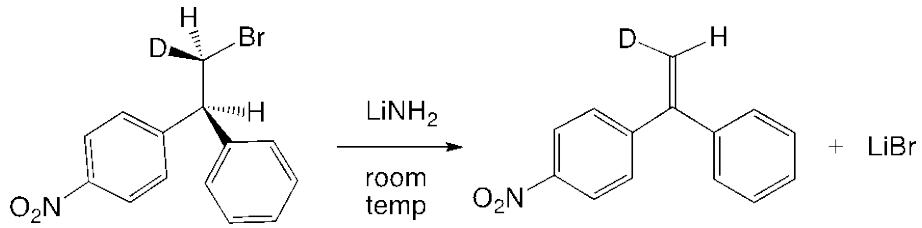
Mechanism of Reaction 1:

Mechanism of Reaction 2:

b. Provide a rationale for any differences in the two mechanisms you proposed above (Hint: Draw the transition states for the rate-determining step in each reaction).

5. [12 points]

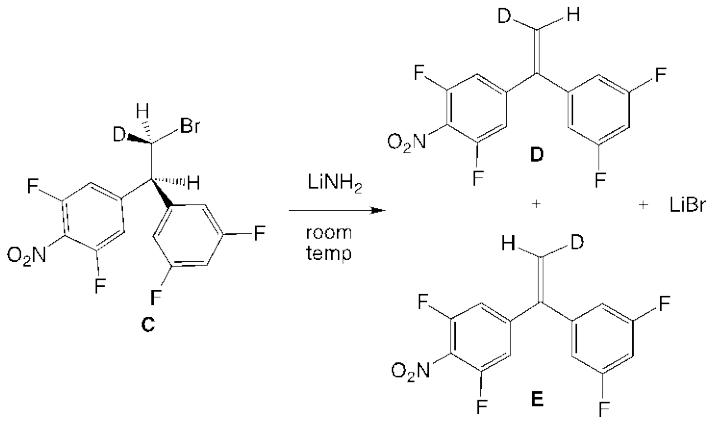
a. Reactant **A** below undergoes an E2 reaction in the presence of $LiNH_2$ to give a single alkene product **B**.



A **B**

Draw a three-dimensional structure of the transition state for the reaction that clearly indicates the relative orientations of substituents around the α– and β– carbon atoms. Explain how the stereochemistry of reactant **A** determines the stereochemistry of product **B**?

b. Compound **C** also undergoes a kind of elimination reaction in the presence of $LiNH_2$, but in this case two alkene diastereomers, **D** and **E**, are formed in roughly equal amounts.



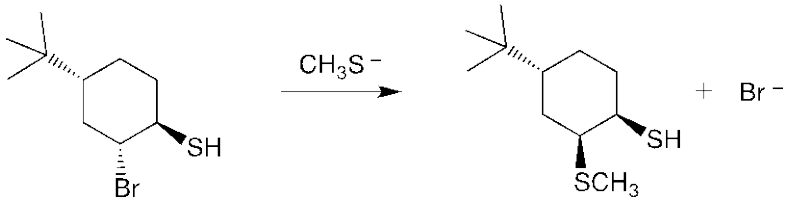
Using the curved arrow notation, <u>provide a step-wise mechanism for this reaction that explains how **C** reacts to form both products **D** and **E**</u>.

c. Why does reaction (**b**) proceed via a mechanism that is different from the conventional E2 mechanism observed in (**a**)?

6. [12 points]

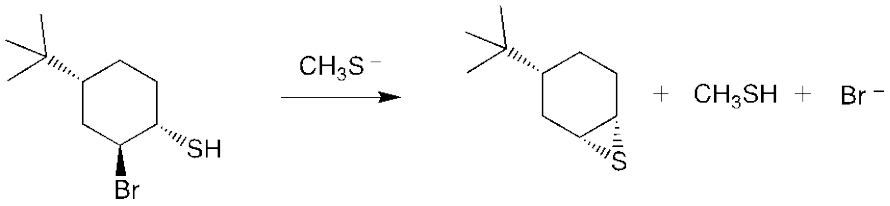
In reactions **1** and **2** below, diastereomers **A** and **C** react with CH_3S^- to give different products, **B** and **D**, respectively.

Reaction 1



A **B**

Reaction 2



C **D**

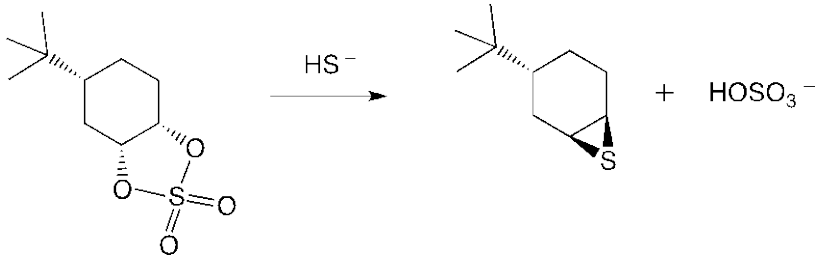
a. In the spaces provided, show step-wise mechanisms for these two transformations using the curved-arrow notation.

Mechanism of Reaction 1:

Mechanism of Reaction 2:

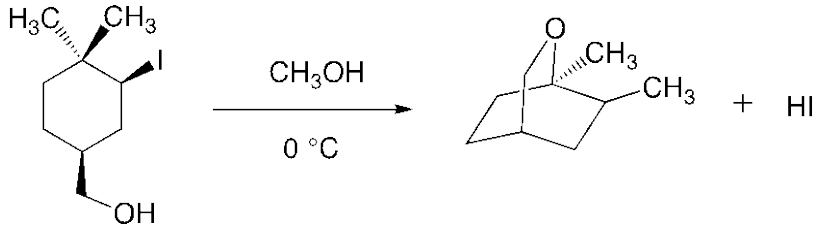
b. Using three-dimensional structural representations, explain why **A** and **C** give different products under these conditions.

c. Based on your above analysis, <u>show the best step-wise mechanism</u> for the following reaction using the curved-arrow notation.



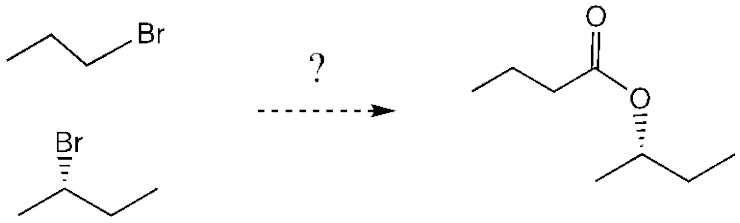
7. [8 points]

Provide a step-wise mechanism for the reaction below using the curved arrow notation:



8. [12 points]

Propose a synthesis of the compound on the right starting with the reagents on the left as well as any other necessary reagents. Be sure to show each individual step of your synthesis, the required reagents (above the arrow), and the intermediate product obtained from each step. Workup steps are implied and need not be shown explicitly.



9. [5 points]

For each of the following multiple choice questions, mark the single best answer with an **X**.

a. The Swern oxidation is often preferred to the use of PCC because:

A. ___ PCC tends to over-oxidize 1° alcohols to carboxylic acids.

B. ___ Cr^{VI} is toxic to humans and the environment.

C. ___ DMSO is a good solvent for S_N2 reactions.

D. ___ PCC reacts with water to form a flammable gas.

b. Which reagent is Nature's equivalent of $NaBH_4$?

A. ___ NADH

B. ___ $LiAlH_4$

C. ___ SAM

D. ___ NaH

c. The E1 reaction can be favored over a competing S_N1 reaction by using:

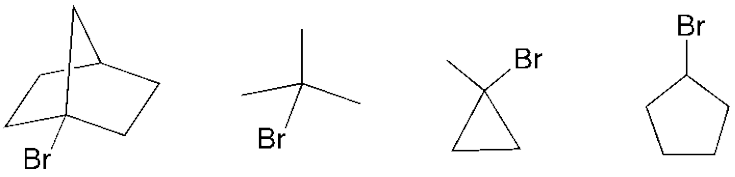
A. ___ an excellent leaving group

B. ___ a polar protic solvent

C. ___ a strong nucleophile

D. ___ high temperatures

e. Which substrate undergoes the fastest solvolysis reaction in H_2O?



A **B** **C** **D**

A. ___

B. ___

C. ___

D. ___

f. Which of the following reactions is stereospecific?

A. ___ S_N1

B. ___ Formation of an alkyllithium reagent at room temperature

C. ___ Free radical halogenation

D. ___ None of the above

BLANK PAGE