CHEM 3311, Fall 2011
Professor Walba
Third Hour Exam
November 17, 2011

scores:

1) 20

2) 20

3) 20

4) 20

5) 20

100

CU Honor Code Pledge: On my honor, as a University of Colorado at Boulder Student, I have neither given nor received unauthorized assistance.

Key

Name (printed): _____

Signature: _____

Recitation TA Name: _____

Recitation day and time: _____

This is a closed-book exam. The use of notes, calculators, scratch paper, or cell phones will not be allowed during the exam. You may use models brought in a clear ziplock bag. Please put all you answers on the test. Use the backs of the pages for scratch.

PLEASE read the questions very carefully!

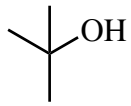
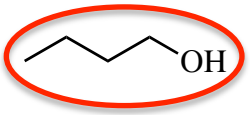
Partial Periodic Table

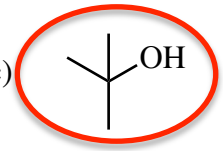
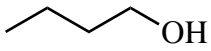
1A							8A
1 H	2A						2 He
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
						35 Br	
						53 I	

Printed Name:_____

1 (20 pts) A) For the following pairs of compounds (in solvent or the gas phase as indicated), circle the stronger acid.

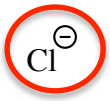
a) CH_3SO_3H CF_3SO_3H In any solvent

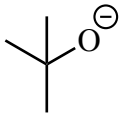
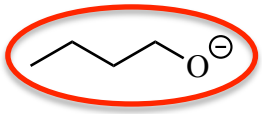
b)   In H_2O

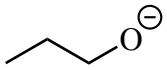
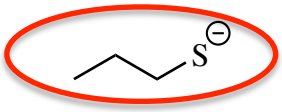
c)   In the gas phase

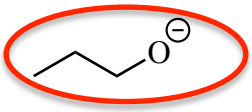
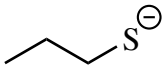
B) For the following pairs of compounds (in the indicated solvent), circle the stronger nucleophile.

d)   In ethanol

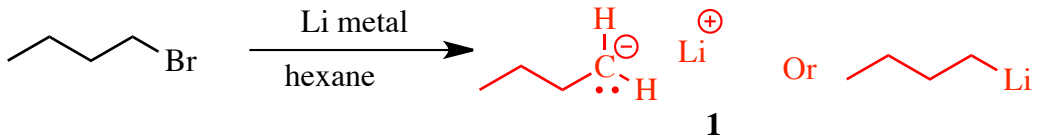
e)   In DMF

f)   In any solvent

g)   In propanol

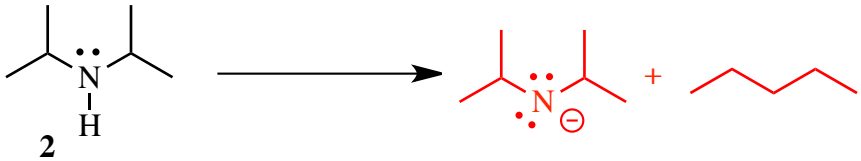
h)   In DMF

C) Carefully draw a valid valence bond structure for the compound formed in the reaction (i) below (compound **1**). For this question, include both ions if an ionic compound is formed.

i) 

1

Carefully draw a valid valence bond structures for the two compounds formed when **1** reacts with diisopropyl amine (**2**).

j) **1** + 

2

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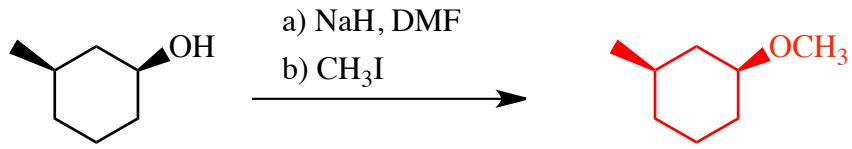
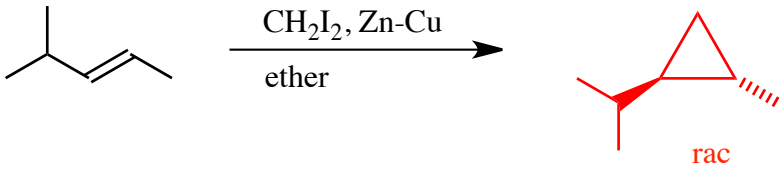
2) (20 pts) Give the single major product for each of the following reactions, carefully showing stereochemistry using wedges and dashes. If a racemate is formed, show only one enantiomer and label it "rac." Assume chiral starting materials are single pure enantiomers unless they are labeled "rac."

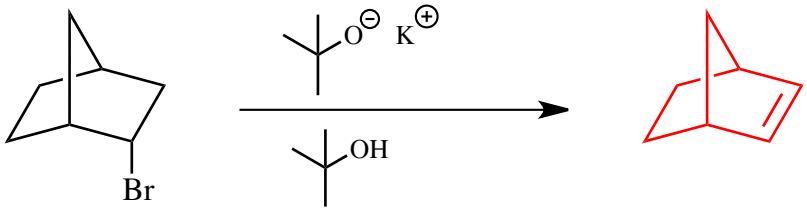
a)



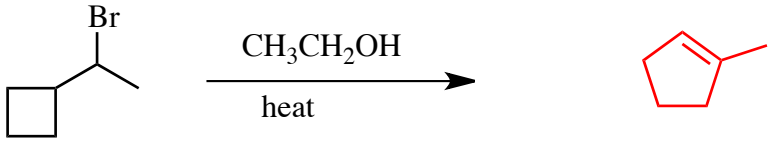
b)



c)



d)



For part d) give the major product of **elimination**

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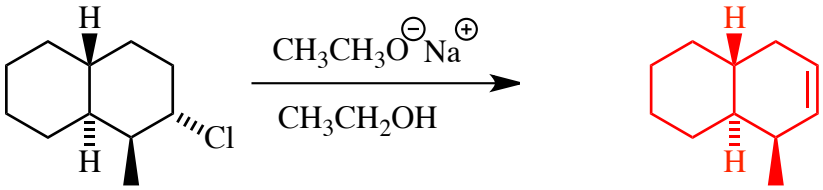
e)



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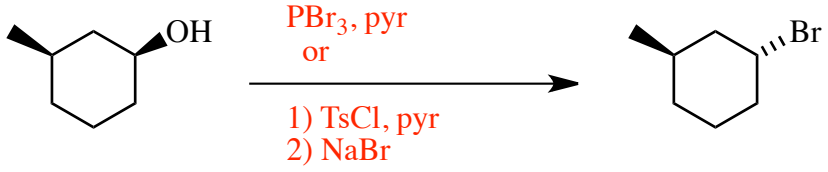
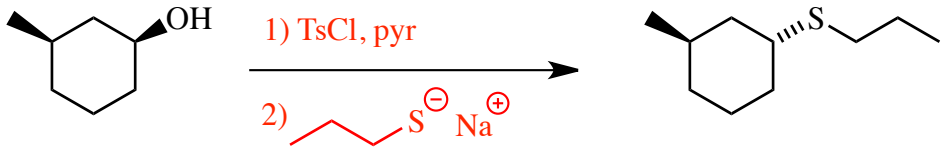
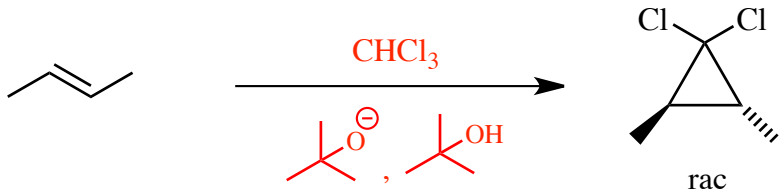
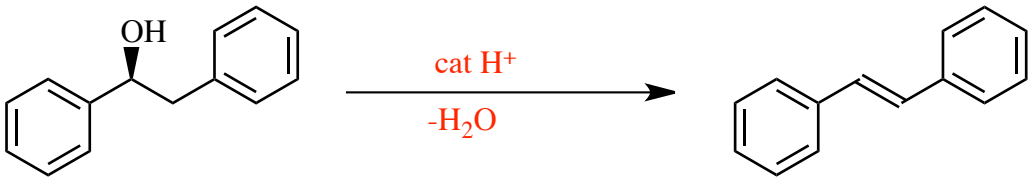
3) 20 pts) Propose reagents for accomplishing each of the following reactions. Make your reaction efficient (i.e. the target product should be the major product). If the solvent is important to obtain the product, then include the solvent along with the reagents. The reagent can be an organic ion – you don't need to show how it was made. Assume chiral starting materials and products are single pure enantiomers unless they are labeled "rac."

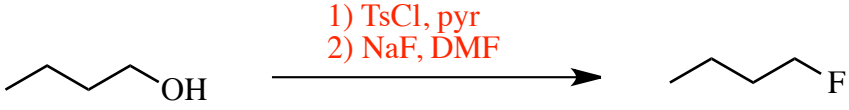
a) 

b) 

c) 

rac

d) 

e) 

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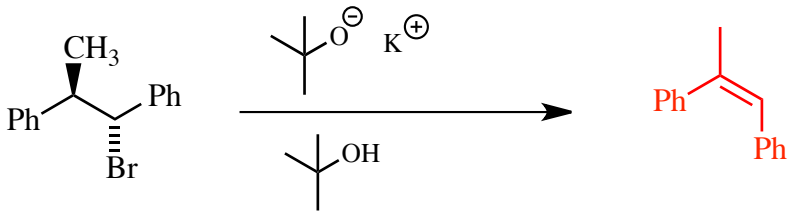
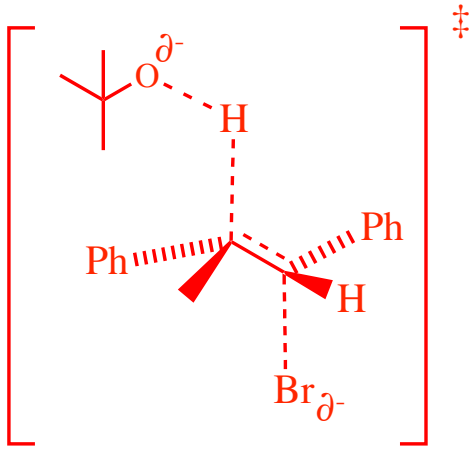
4) (20 pts) a) Give the single major product of the following reaction, clearly showing the stereochemistry of the product (the "Ph" groups are phenyl groups - benzene rings connected to the indicated carbons). Please use the Ph abbreviation in the structure of your product.



b) Carefully draw the rate determining transition state for the reaction in part a) above.



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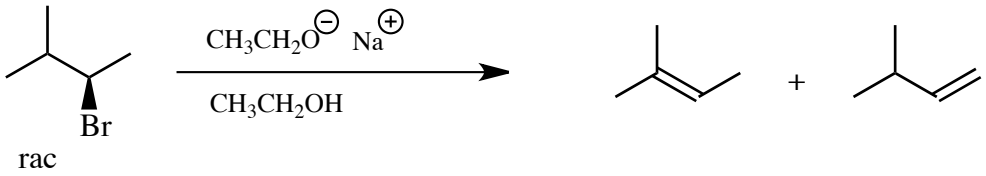
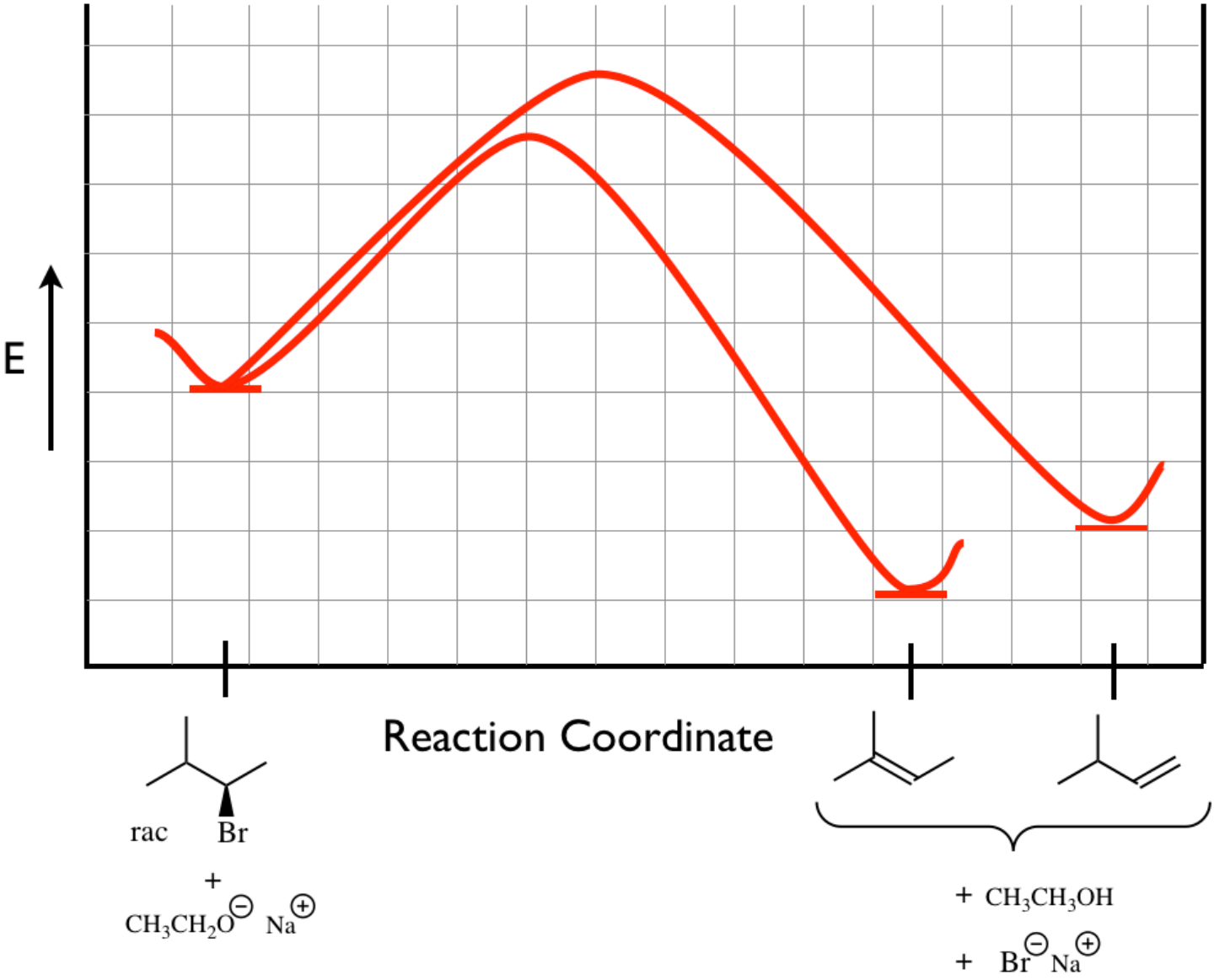
4) –continued-

c) The following reaction produces the two products of elimination, as indicated.



Complete the energy diagram for this reaction.



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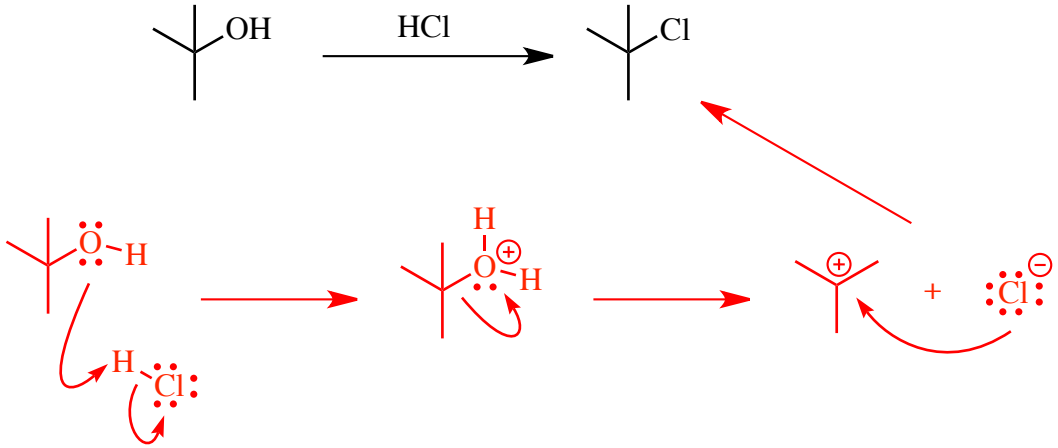
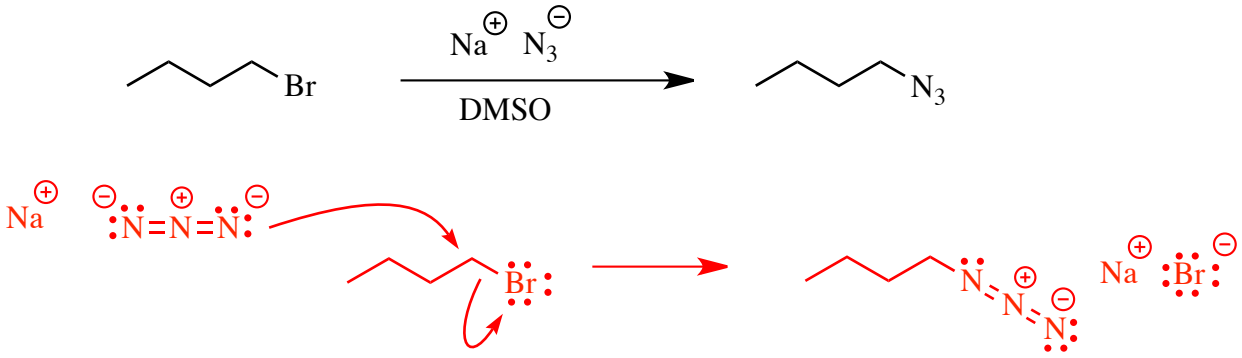
5) (20 pts) Propose arrow-pushing mechanisms for each of the following transformations. Show **all** intermediates in your mechanisms, but do not show transition states. Be sure structures are complete, valid valence bond structures, **including all lone pairs**. Indicate the stereochemistry of your intermediates using wedges and dashes if appropriate.

a)



b) NOTE: Be sure to show valid valence bond structures for all of the starting materials and products (N_3^- is NOT a valence bond structure).



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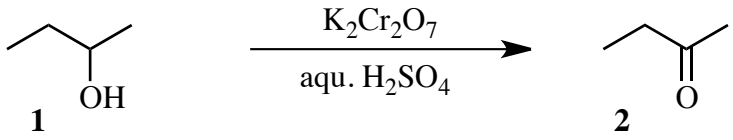
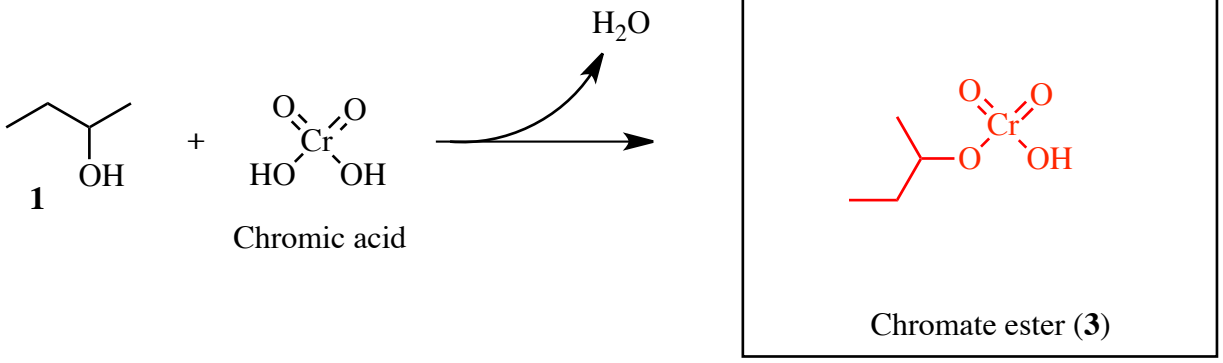
5) -continued-

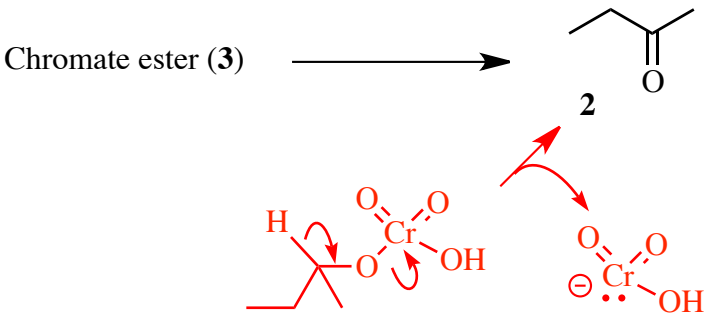
c) Potassium dichromate ($K_2Cr_2O_7$) in aqueous sulfuric acid reacts with 2-butanol (**1**) to give the ketone **2** in high yield.



The actual Cr(VI) oxidizing agent in the solution is chromic acid, which reacts with the alcohol **1** to give a reactive chromate ester **3**. Give the structure of the chromic acid ester (an H_2O molecule is lost from the starting materials in this transformation).



Propose an arrow-pushing mechanism for conversion of the chromate ester **3** to the ketone product (**2**). Be sure structures are complete, valid valence bond structures, **including all lone pairs**. Please show the structure of the initially-formed Cr species from this transformation, and don't worry about what happens to it.



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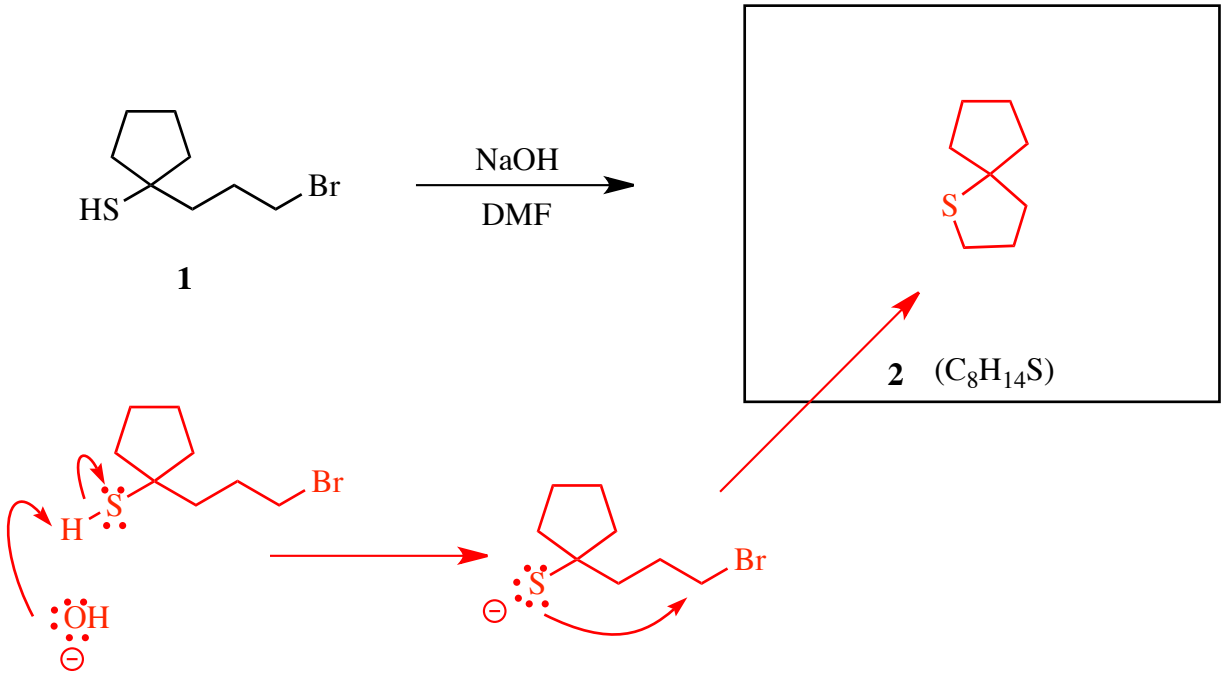
5) –continued-

d) When the bromothiol **1** is treated with sodium hydroxide (NaOH) in dimethylformamide (DMF), product **2** is formed in very high yield. Product **2** has molecular formula $C_8H_{14}S$, which means there is no OH group in the product, and spectroscopy shows it has **NO DOUBLE BOND**.

Give the structure for product **2**, and propose an arrow-pushing mechanism for its formation. Show **all** intermediates in your mechanisms, but do not show transition states. Be sure structures are complete, valid valence bond structures, **including all lone pairs**.



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