EXAMINATION 2

Chemistry 3A
Kim Lavoie
Peter Vollhardt
November 6, 2001

Name:_____
[Print first name before second! Use capital letters!]

Please check the name of your TA and corresponding section number. Complete the remaining information if applicable.

111	John Antos	361	Karl Tupper
121	Jennifer Barbarow	371	Eric Schneider
161	Dennis Leung	411	Amish Patel
171	Dan Weix	421	Jennifer Prescher
211	Scheherazade Le	461	Shahed Ghoghawala
221	Steve Pham	511	Stephany Schuck
311	David Tang	521	Javier Rangel
321	Joshua Goldberger	561	Lianne Beltran

Making up an I Grade _____

(If you are, please indicate the semester during which you took previous Chem 3A previously _____).

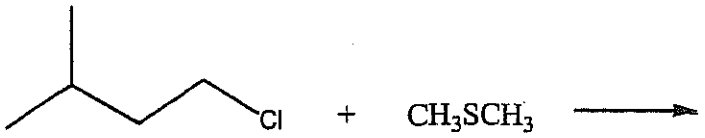
Please write the answer you wish to be graded in the spaces provided. *Do scratch work on the back of the pages.* This test should have 11 numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy structures or phrases. It is better to be pedantic in accuracy! Good Luck!**

DO NOT WRITE IN THIS SPACE

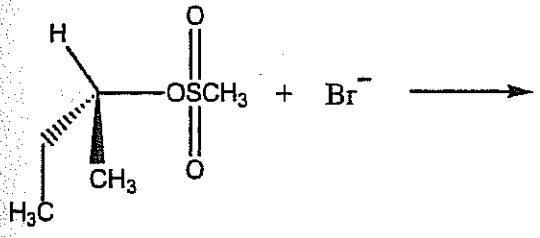
I.	_____	(60)
II.	_____	(30)
III.	_____	(30)
IV.	_____	(30)
V.	_____	(30)
VI.	_____	(20)
Total:	_____	(200)

I. [60 Points] Add the missing starting materials, reagents, or products (aqueous work-up is assumed where necessary). Don't forget stereochemistry!

a.

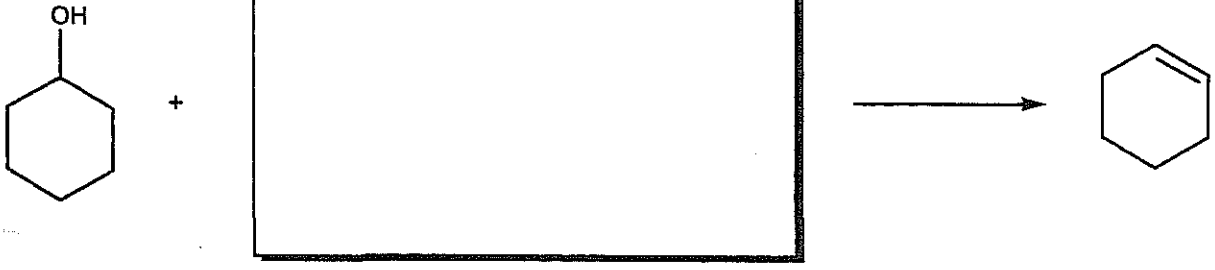


b.

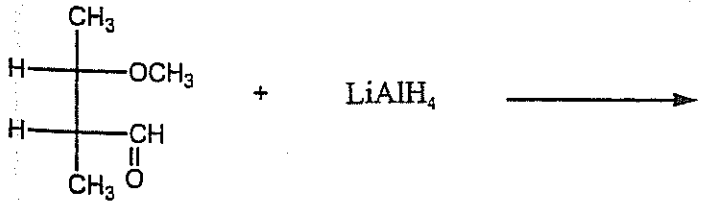


Circle one: Racemic
Optically active

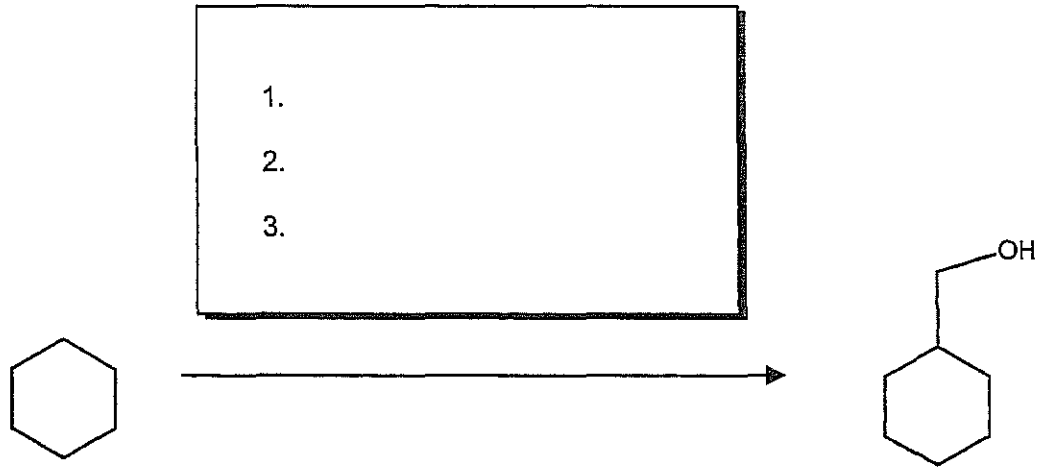
c.



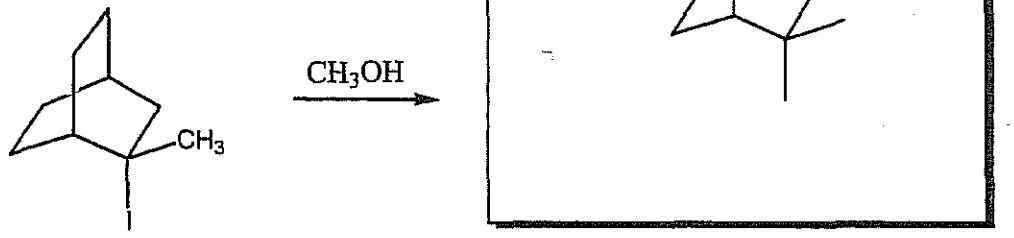
d.



e.



f.

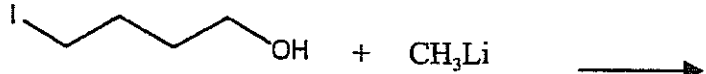


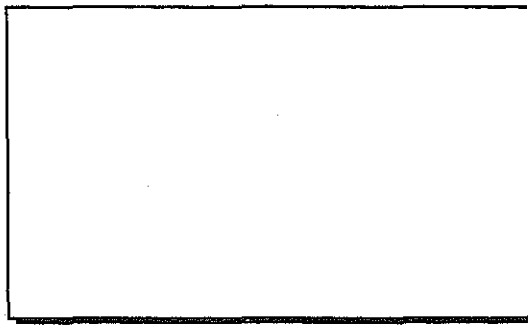
Fill in the missing substituents!

Pure enantiomer

Circle one: Racemic
Pure enantiomer

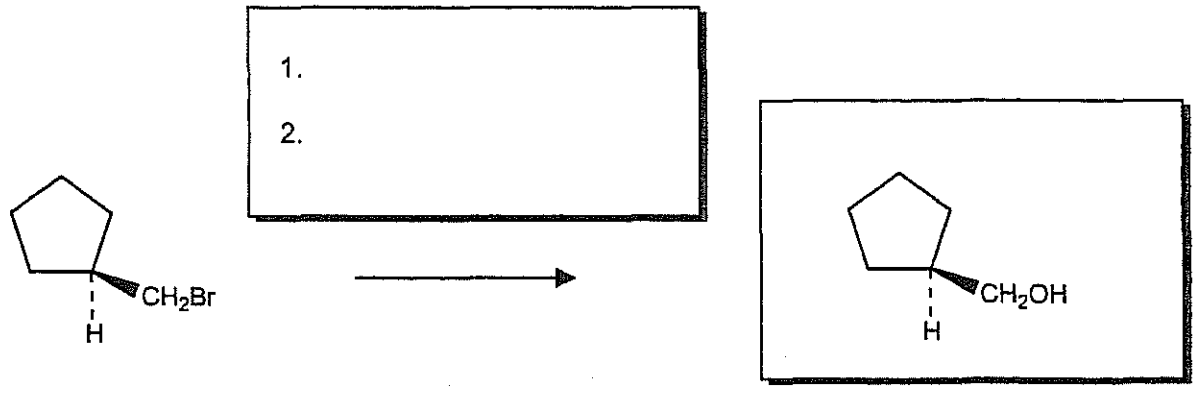
g.



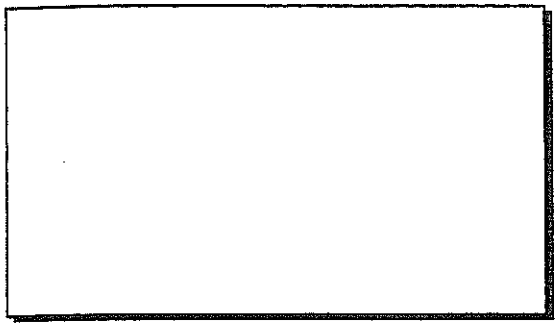


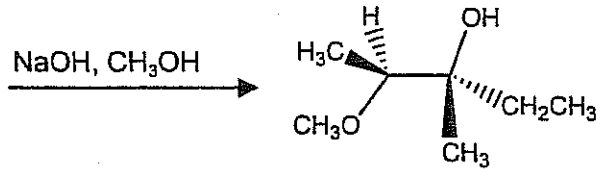
C_4H_8O

h.



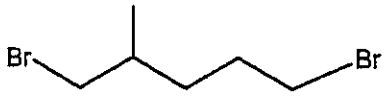
i.

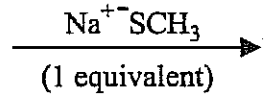


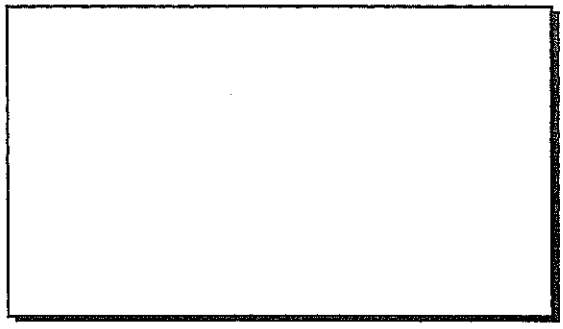


An oxacyclopropane

j.



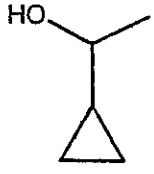


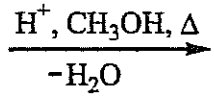


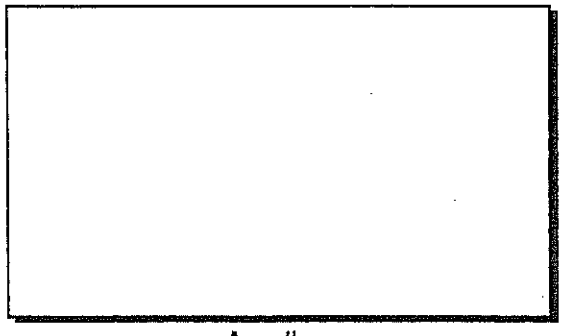
$C_7H_{15}BrS$

II. [30 Points] The following reactions proceed (predominantly) by S_N2, S_N1, E2, or E1 pathways, respectively. Give the predominant product (one only) in each case and answer the questions by circling the most applicable statement.

a.







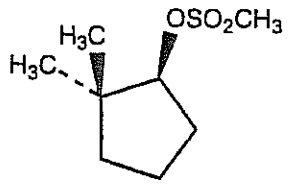
An alkene

Mechanism: S_N2 S_N1 E2 E1

At lower temperatures one of the following ratios will increase:

S_N2 / S_N1 S_N1 / E1 E2 / E1 S_N2 / E2

b.



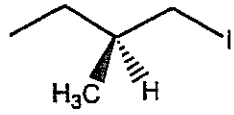
$K^{+-}OC(CH_3)_3$, $(CH_3)_3COH$

Mechanism: S_N2 S_N1 E2 E1

Changing the alkoxide to $CH_3O^-K^+$ causes <u>one</u> of the following ratios to increase:

E2 / E1 S_N2 / E2 S_N1 / E1 E2 / S_N2

c.



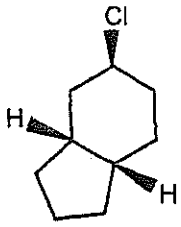
NH_3, THF

Mechanism: S_N2 S_N1 E2 E1

Changing from ammonia to lithium amide, $Li^{+-}NH_2$, causes <u>one</u> of the following ratios to increase:

E2 / S_N2 E2 / E1 S_N2 / S_N1 rearrangement / S_N2

d.



CH_3Se^-, CH_3OH solvent →

Mechanism: S_N2 S_N1 E2 E1

Changing the solvent to DMSO will have one or more of the following effects (circle all that apply):

rate increases S_N2 / S_N1 increases solvation of the $Nu:^-$ decreases

e.

$(CH_3)_3COH$ H^+, CH_3OH solvent, -20°C →

Mechanism: S_N2 S_N1 E2 E1

Changing the solvent to $(CH_3)_3COH$ causes one of the following ratios to increase:

S_N2 / S_N1 E2 / E1 E1 / S_N1 S_N2 / E2

III. [30 Points] Explain the following observations by a detailed mechanism (i.e., write a scheme with structures, use arrow-pushing, etc.)

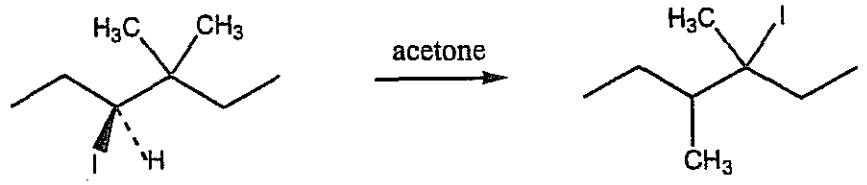
a.

optically active

optically active

(Hint: Note the change in stereochemistry!)

b.

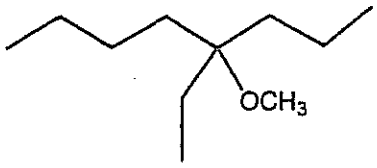


optically active

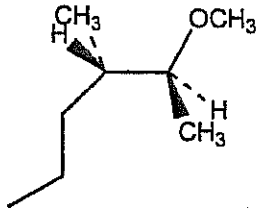
racemic

IV. [30 Points] Provide a viable synthesis of the following compounds from any starting materials containing four carbons or less. Work backwards!

a.



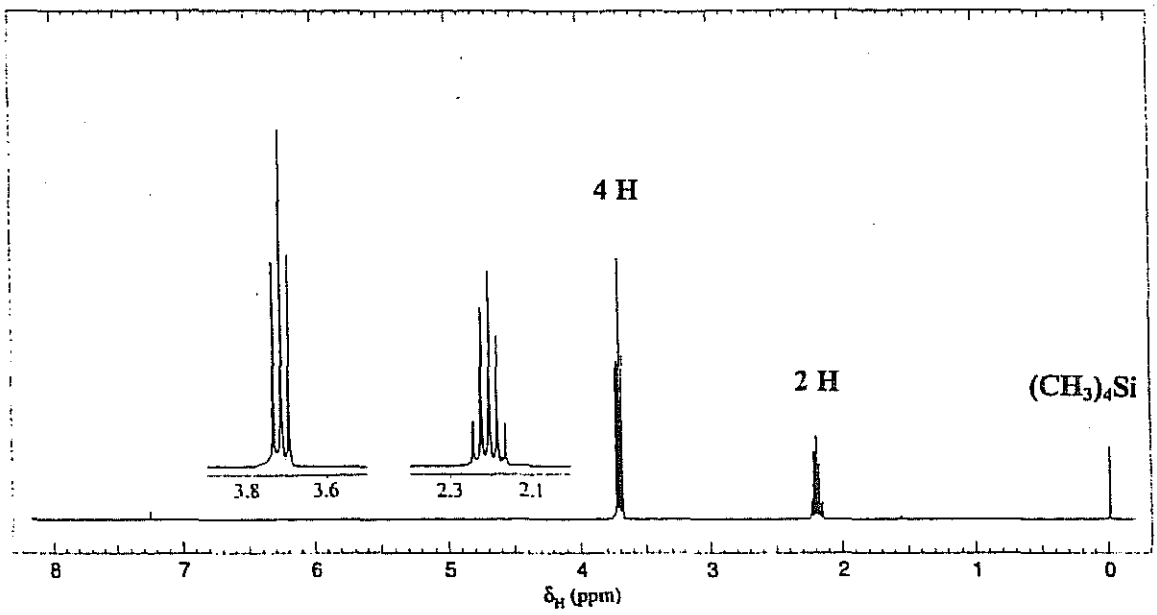
b.



(racemic)

Hint: You need to start with a defined stereoisomer of your starting material.

V. [30 Points] A researcher treated propane with Cl_2 in the presence of traces of dibenzoyl peroxide as a radical initiator. Careful separation of the product mixture revealed a minor contaminant with the ^1H NMR spectrum shown below:



a. What is the structure of this compound?

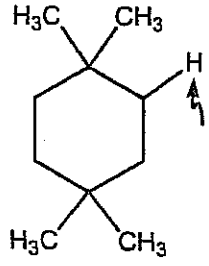
b. Assign the spectrum by labeling the hydrogens giving rise to the absorption centered at δ = 2.2 ppm with the letter "A", those at δ = 3.7 ppm with "B" in the drawing in the box above.

10

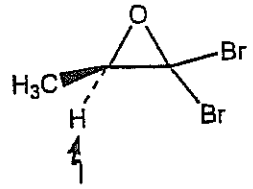
c. Explain your assignment in b.

d. Explain the multiplicity of the peaks using the $(N + 1)$ rule.

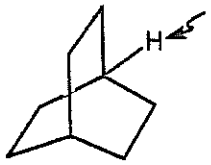
VI. [20 Points] The hydrogen highlighted by an arrow in the following compounds is expected to give rise to the circled signal pattern in the ^1H NMR spectrum:

a. 

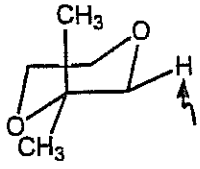
singlet doublet triplet quartet

b. 

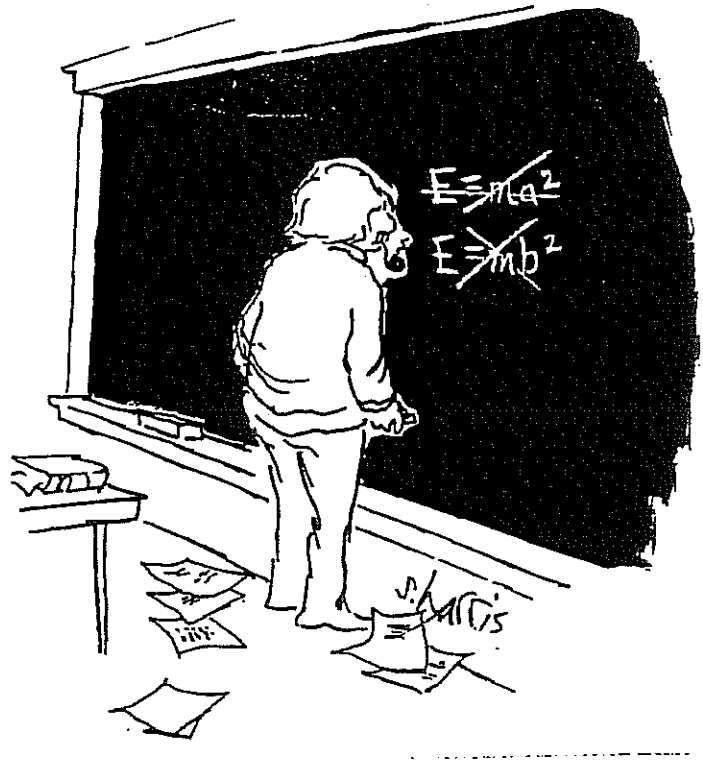
singlet doublet triplet quartet

c. 

singlet triplet quintet septet

d. 

singlet doublet doublet of doublets quartet



* The End *