EXAMINATION 2

Chemistry 3A
Professor K. Peter C. Vollhardt
April 4, 1996

Name: _____
(PRINT First name first, then Last name. Use capital letters!)

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

111	J. YANG	____	*351*	D. HOLMES	____
121	J. LOESER	____	*361*	E. CHAN	____
131	D. LARSON	____	*371*	T. LEE	____
141	I. CHOONG	____	*381*	H. CHANG	____
151	M. GOODWIN	____	*411*	J. FULLER	____
161	E. CHAN	____	*421*	B. BAXTER	____
171	J. SELL	____	*431*	J. CHIN	____
211	S. PAIKOFF	____	*441*	M. SCHULTZ	____
221	J. STAUNTON	____	*511*	D. CARROLL	____
311	J. YANG	____	*521*	D. GRAY	____
321	T. ESKER	____	*531*	J. STAUNTON	____
331	J. SELL	____	*541*	J. LOESER	____
341	T. GOUNTCHEV	____	*551*	S. KUMARASWAMY	____

Making-up an I grade ____
(If you are, please indicate which semester you previously took Chem 3A _____.)

Please write the answers you want graded in the spaces provided. Do scratch work on the backs of the pages. This test should have 12 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.	_____ (25)		
		II.	_____ (60)		
IVa.	_____	III.	_____ (30)	Va.	_____
IVb.	_____	IV.	_____ (30)	Vb.	_____
Subtotal	_____	V.	_____ (40)	Subtotal	_____
		VI.	_____ (15)		
		Total	_____ (200)		

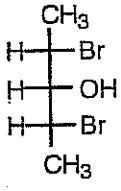
I. [25 Points]

Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary *(cis, trans, R, S, or meso).*

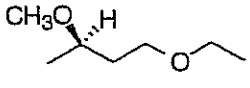
a.

(*S*)-3,3-Dimethylcyclohexanol

b.



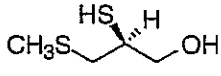
c.



d.

Trans-3-[(*cis*-2-hydroxy-cyclopropyl)methyl]cyclobutanol

e.

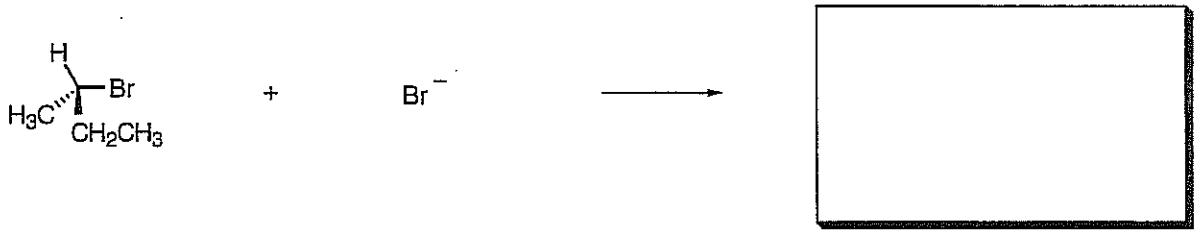


II. [60 Points]

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

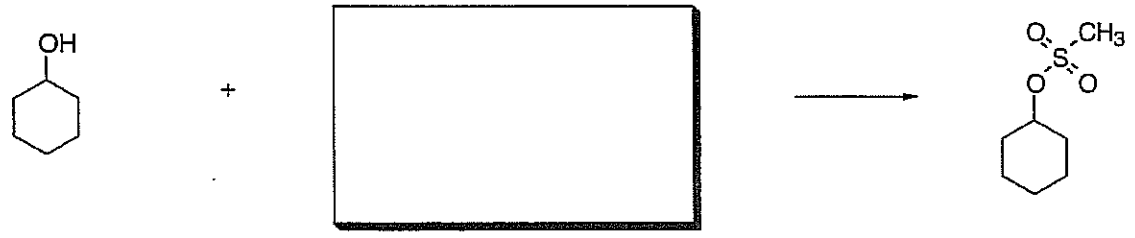
a.

b.

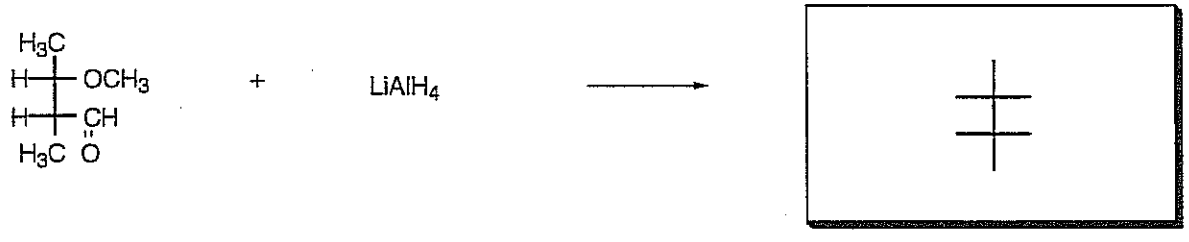


Circle one: Racemic
Optically active

c.



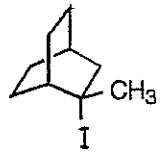
d.



e.

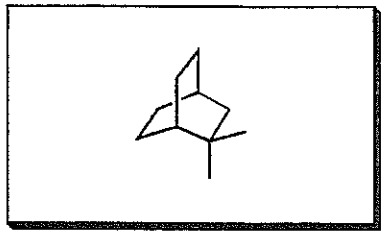
$(CH_3)_3CH$ → 1. 2. 3. → $(CH_3)_3CCH_2OH$

f.



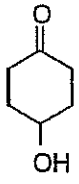
optically active

CH_3OH →



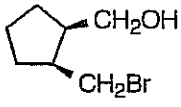
Circle one: Racemic
Optically active

g.



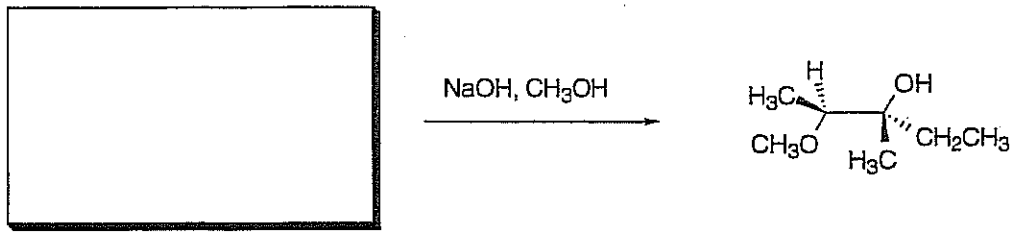
+ CH_3Li (1 equivalent) →

h.



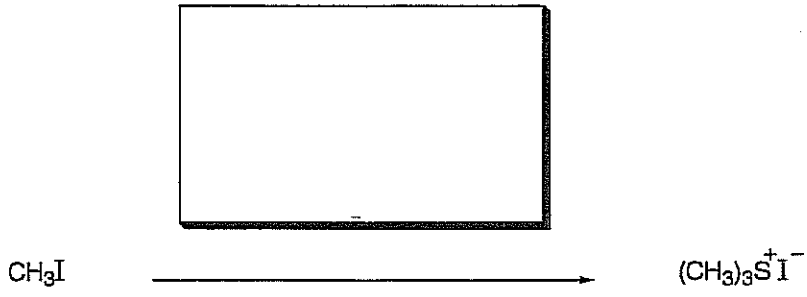
$NaOH, CH_3OH$ →

i.



an oxacyclopropane

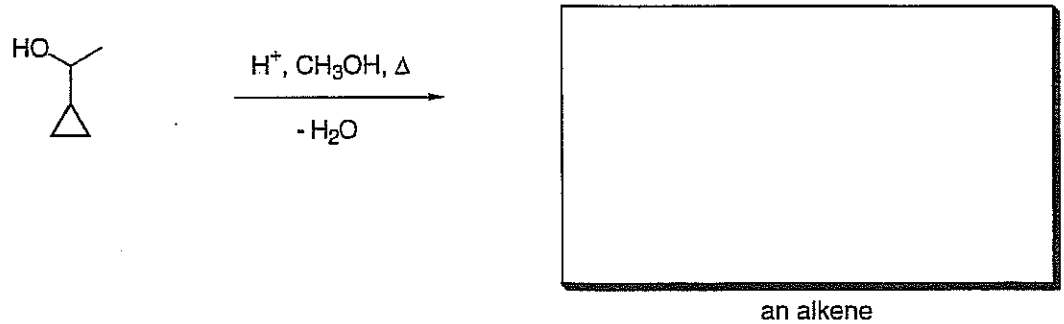
j.



III. [30 Points]

The following reactions proceed (predominantly) by S_N2, S_N1, E_2, or E_1 pathways, respectively. Give the predominant product (one only) in each case and answer the questions by circling the most applicable statement.

a.



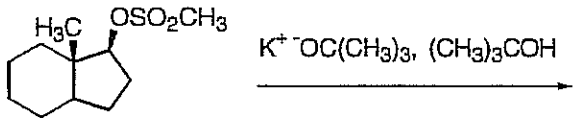
an alkene

Mechanism: S_N2 S_N1 E_2 E_1

At lower temperatures one of the following ratios will increase:

S_N2 / S_N1 S_N1 / E_1 E_2 / E_1 S_N2 / E_2

b.

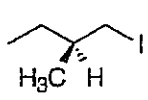


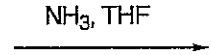
Mechanism: S_N2 S_N1 E_2 E_1

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

E_2 / E_1 S_N2 / E_2 S_N1 / E_1 E_2 / S_N2

c.



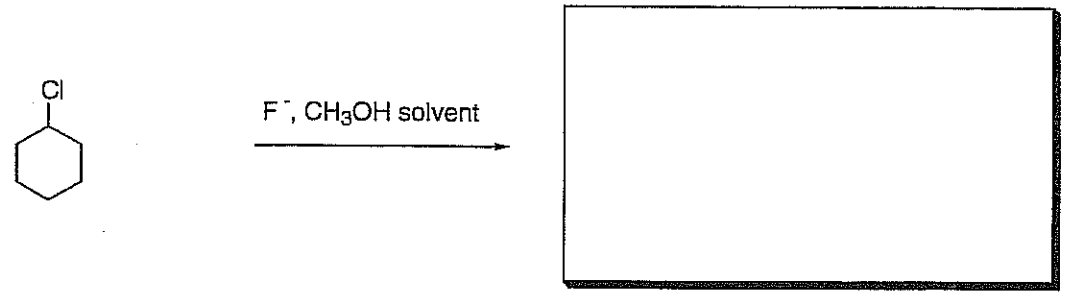


Mechanism: S_N2 S_N1 E_2 E_1

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

E_2 / S_N2 E_2 / E_1 S_N2 / S_N1 rearrangement / S_N2

d.

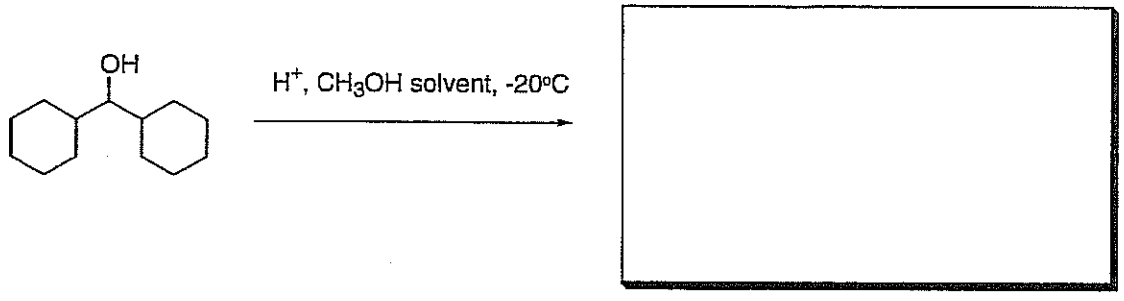


Mechanism: S_N2 S_N1 E_2 E_1

Changing the solvent to acetone will have <u>one or more</u> of the following effects (circle <u>all</u> that apply):

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

e.



Mechanism: S_N2 S_N1 E_2 E_1

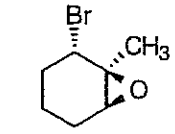
Changing the solvent to $(CH_3)_3COH$ causes <u>one</u> of the following ratios to increase:

S_N2 / S_N1 E_2 / E_1 E_1 / S_N1 S_N2 / E_2

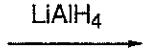
IV. [30 Points]

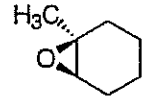
Explain the following observations by a detailed mechanism (i.e., write a scheme with structures, use arrow-pushing, etc.)

a.



optically active

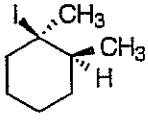




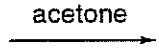
optically active

(Hint: Note the change in stereochemistry!)

b.



optically active

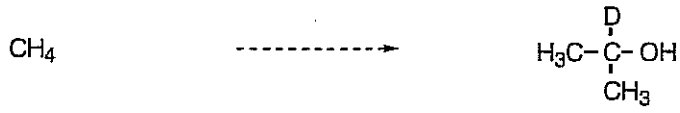


starting material, but racemic

V. **[40 Points]**

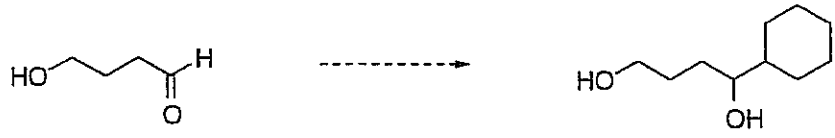
Provide a viable synthetic route from starting material to product.

a.



Only organic starting material.
You may use any required inorganic reagents.

b.



You may use any additional organic and inorganic compounds.

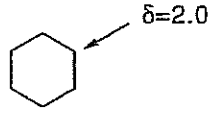
VI. [15 Points]

Chloromethoxymethane, $ClCH_2OCH_3$, and CH_3OH react slowly to give a new compound, $C_3H_8O_2$, which exhibits two sharp signals in the ^1H NMR spectrum at δ = 5.2 and 3.2 ppm, with an integrated ratio of 1:3.

a. What is the structure of this compound?

b. Assign the chemical shifts by drawing the structure again below and labeling the hydrogens as shown for cyclohexane.

Format for assigning δ values to your compound:



Answer:

c. The rate of disappearance of $ClCH_2OCH_3$ is independent of the CH_3OH concentration. Write a mechanism for this reaction.