Note: Regrades.

EXAMINATION 2
Chemistry 3A

DO NOT WRITE ON EXAM!

We have copies and any alteration will earn you trouble
P.V.

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

Peter Vollhardt
November 8, 2005

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

Section #	TA's Name	Section #	TA's Name
101	Stefan Minasian	302	Miles Carter
102	Rebecca Lalonde	311	Dan Bachovchin
103	Robin Padilla	312	Laura Miller
111	Melitta Hon	411	Sarah Bell
112	Michael Gribble	412	Dylan Domaille
113	Tabitha Clem	501	Han Sen Soo
211	Courtney Hastings	502	Nathan Shapiro
212	Philip Morganelli	511	Stavroula Hatzios
301	Cole Witham	512	Katherine Berry

Making up an I Grade _____, from Professor _____.
(Please indicate the semester during which you took previous Chem 3A: _____).

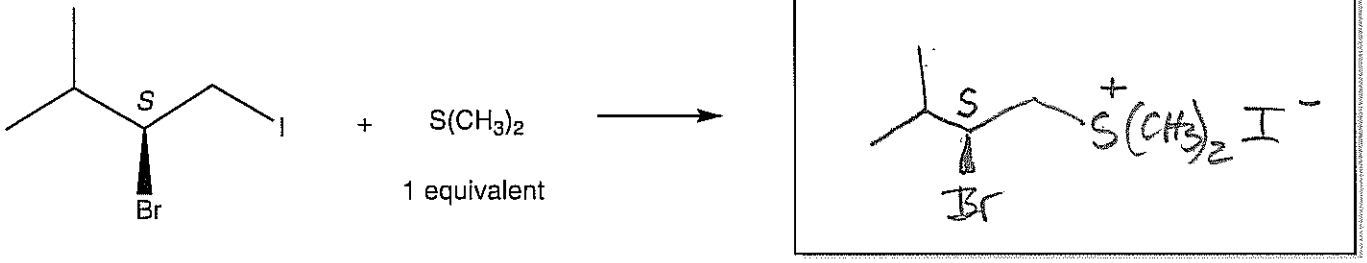
Please write the answer you wish to be graded in the spaces provided. *Do scratch work on the back of the pages.* This test should have 14 numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **read carefully over the questions (at least twice); make sure 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.	_____	**(50)**
III.	_____	**(40)**
IV.	_____	**(40)**
V.	_____	**(30)**
VI.	_____	**(30)**
Total:	_____	**(250)**

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

a.



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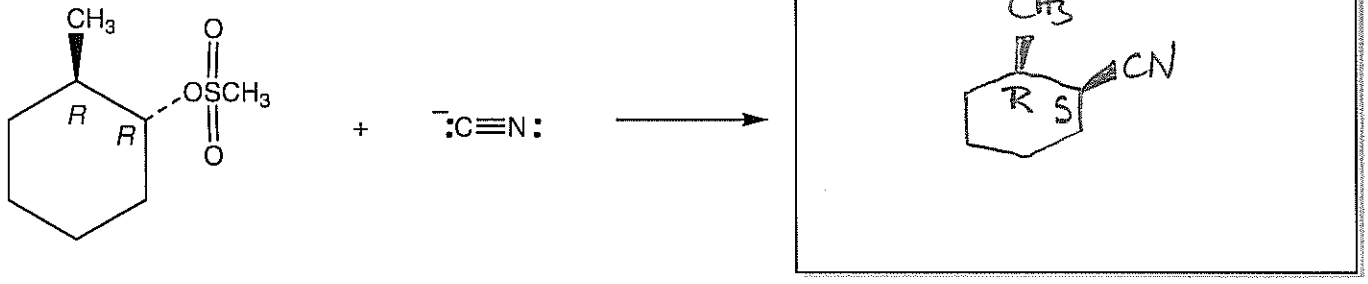
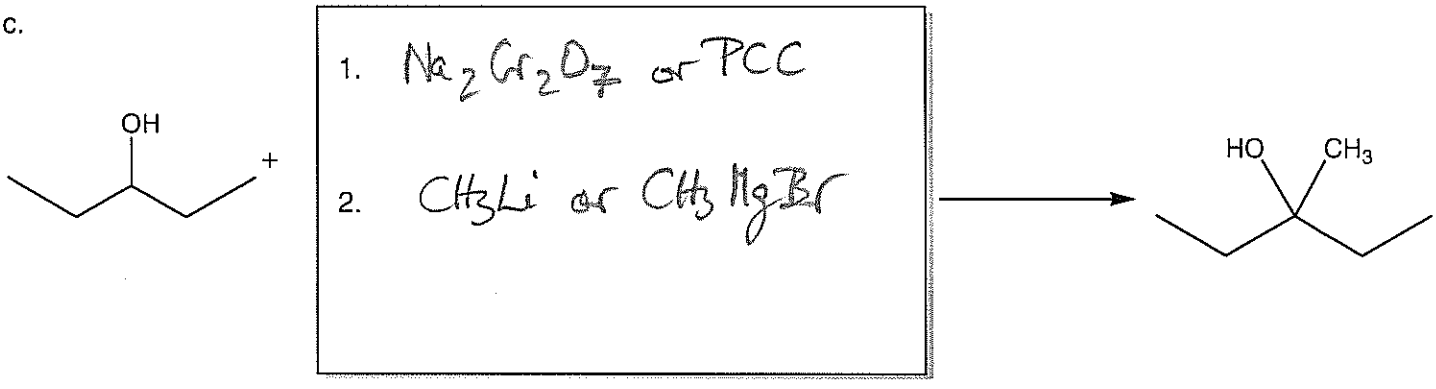
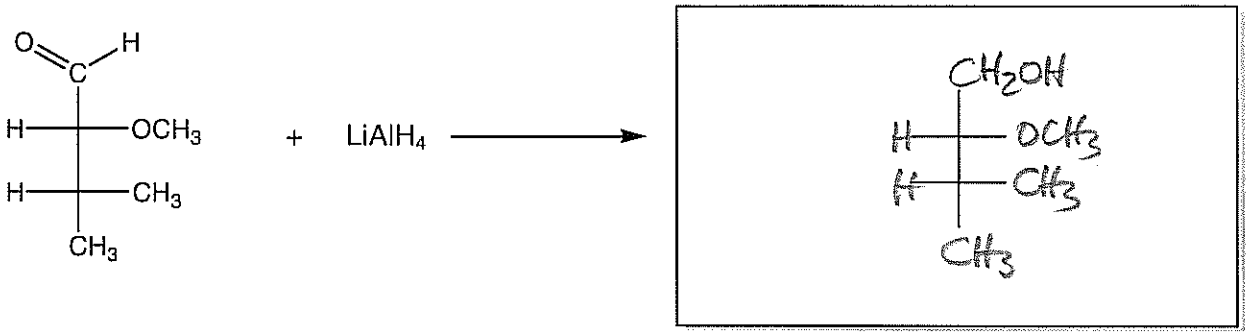


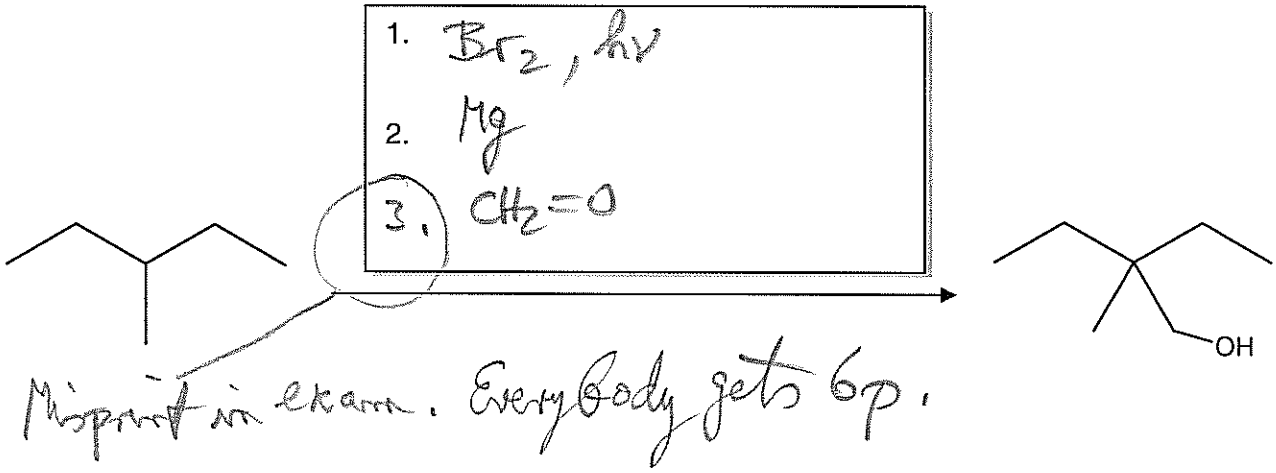
c.



d.

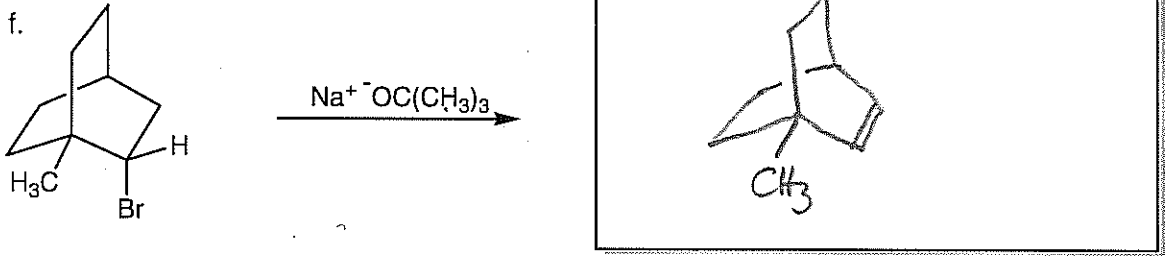


e.



Misprint in exam. Everybody gets 6p.

f.



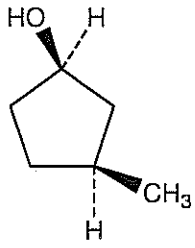
Pure enantiomer

Circle one: Racemic

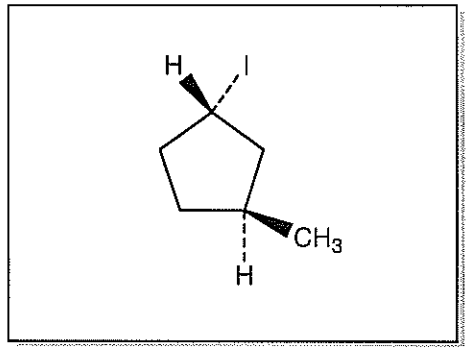
Pure enantiomer

Achiral

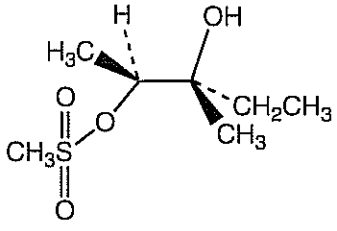
g.



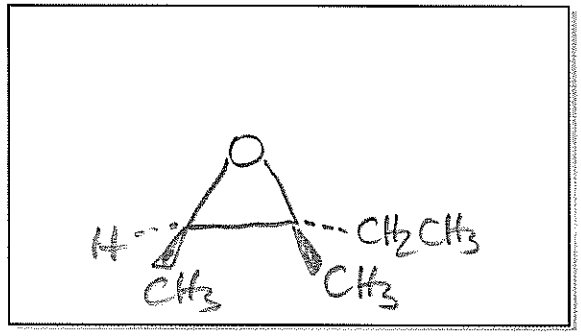
1. CH_3SO_2Cl
2. NaI



h.

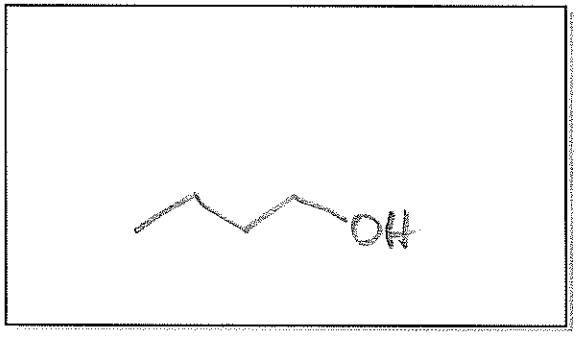


$NaOH, CH_3OH$

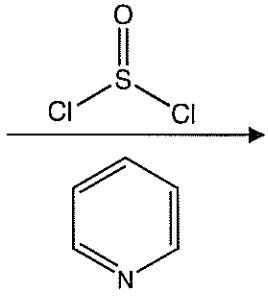


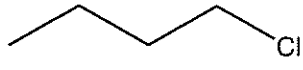
An oxacyclopropane

i.

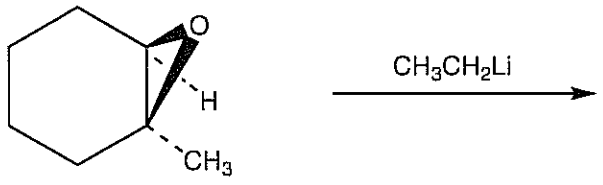


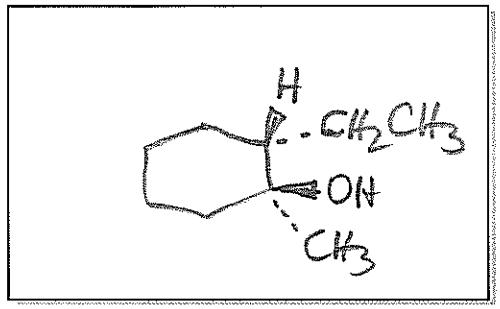
An alcohol





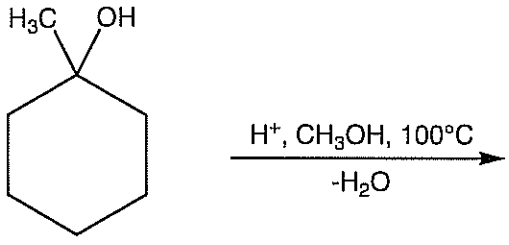
j.

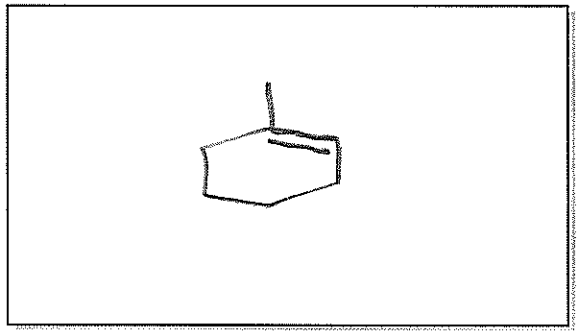




II. [50 Points] The following reactions proceed (predominantly) by S_N2, S_N1, E2, or E1 pathways, respectively. Give the major product (one only) in each case and answer the questions by ***circling*** the most applicable statement.

a.





An alkene

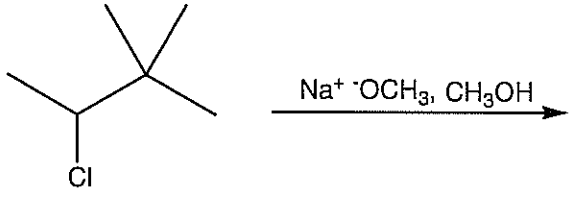
Note: Partial credit was given on the basis of your answer in the box.

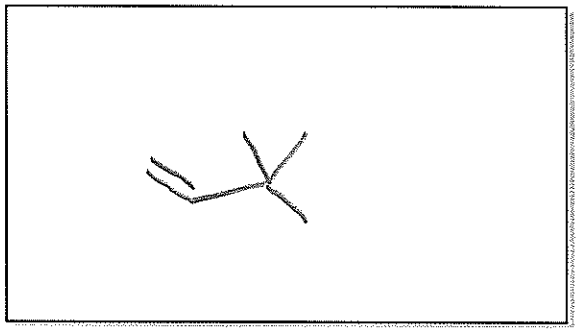
Mechanism: S_N2 S_N1 E2 (E1)

At lower temperatures one of the following ratios will increase:

S_N2 / S_N1 (S_N1 / E1) E2 / E1 S_N2 / E2

b.



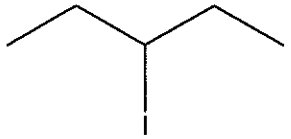


Mechanism: S_N2 S_N1 (E2) E1

Changing the alkoxide to $CH_3S^- K^+$ causes <u>one</u> of the following ratios to increase:

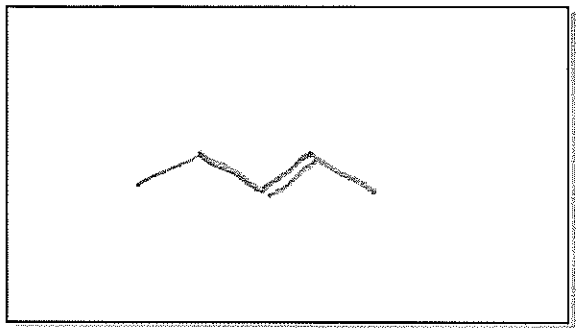
E2 / E1 (S_N2 / E2) S_N1 / E1 E2 / S_N2

c.



$Li^+ \ ^-N[CH(CH_3)_2]_2$

(LDA), THF →

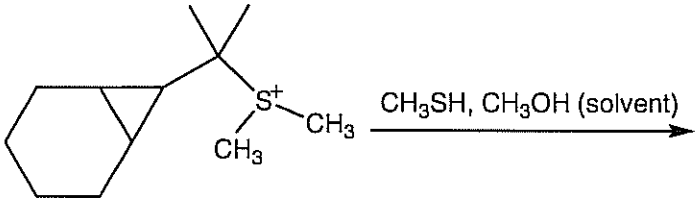


Mechanism: S_N2 S_N1 E2 E1

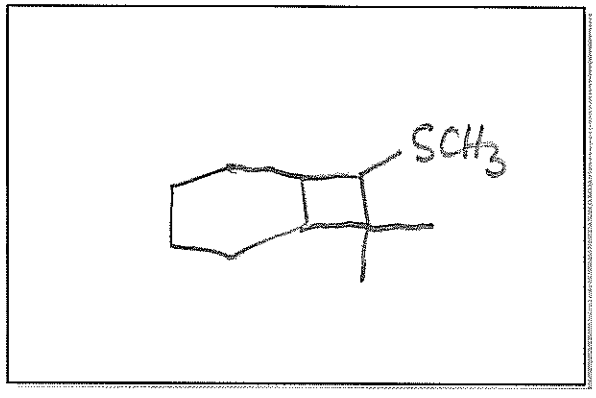
Changing the reagent from LDA to ammonia, NH_3, causes one of the following ratios to increase:

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

d.



CH_3SH, CH_3OH (solvent) →



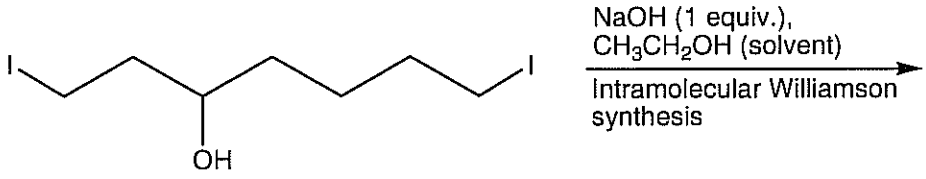
A secondary cycloalkyl methyl sulfide

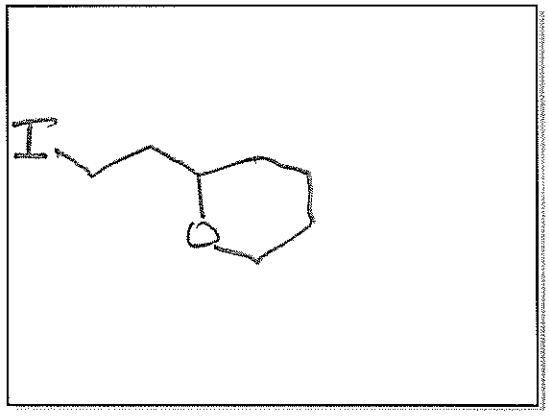
Mechanism: S_N2 S_N1 E2 E1

Changing the solvent to hexane will have one of the following effects:

rate decreases S_N2 / S_N1 increases E1/ S_N1 increases E2 / E1 increases

e.





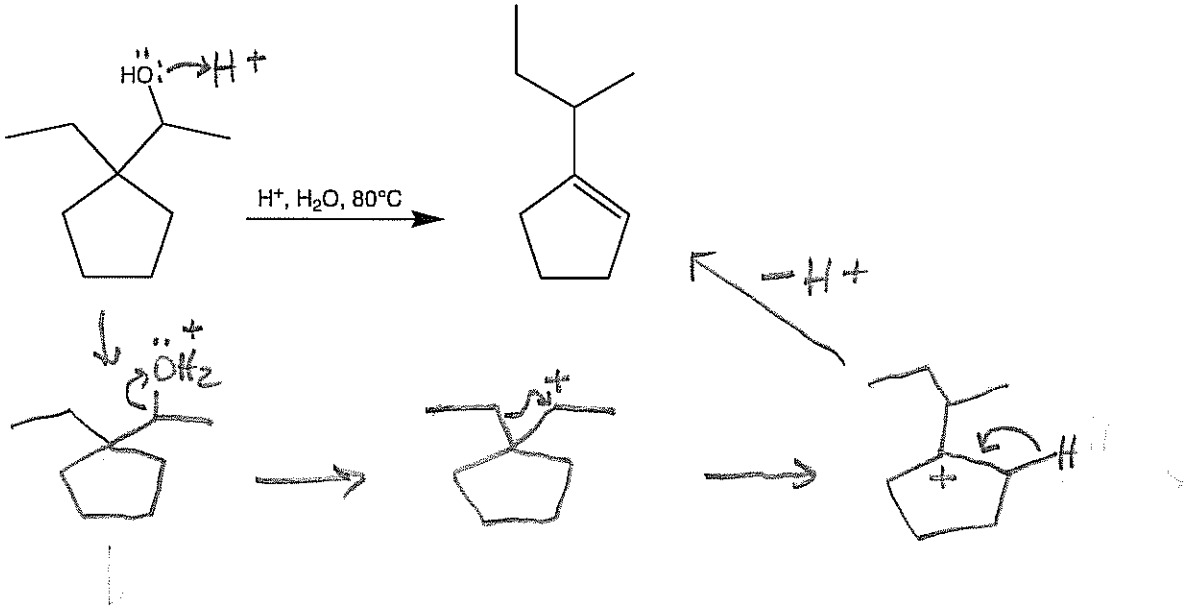
Mechanism: S_N2 S_N1 E2 E1

Changing the solvent to DMF [$CH_3\overset{\overset{O}{\|}}{C}N(CH_3)_2$] causes <u>one</u> of the following effects:

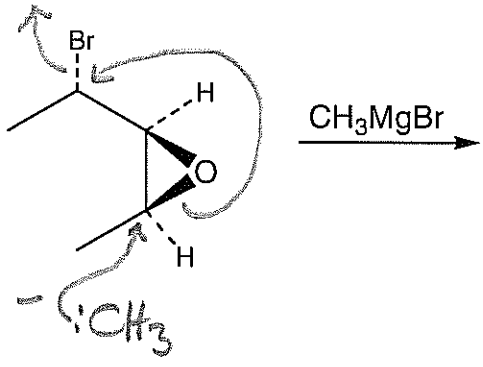
S_N2 / S_N1 increases E1 / S_N1 increases rate increases rate decreases

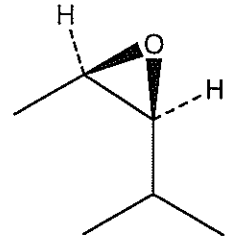
III. [40 Points] Explain the following observations by a detailed ***mechanism*** (i.e., write a scheme with structures, use ***arrow-pushing***, etc.). Do **not** *add* any reagents! This is not a synthesis!

a.



b.

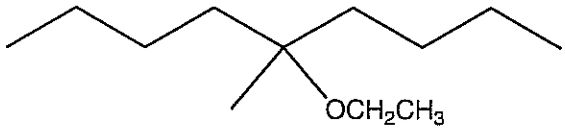


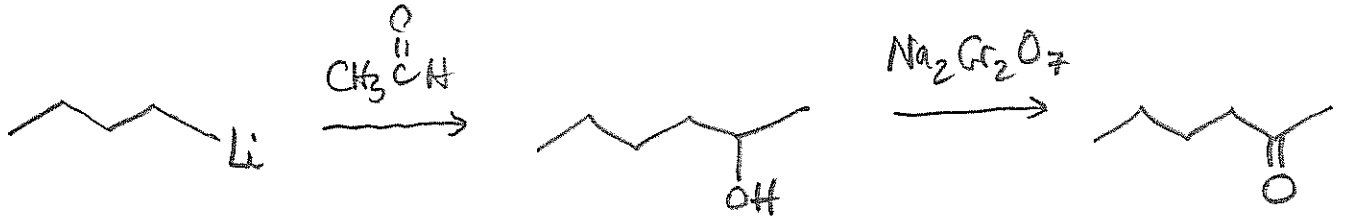


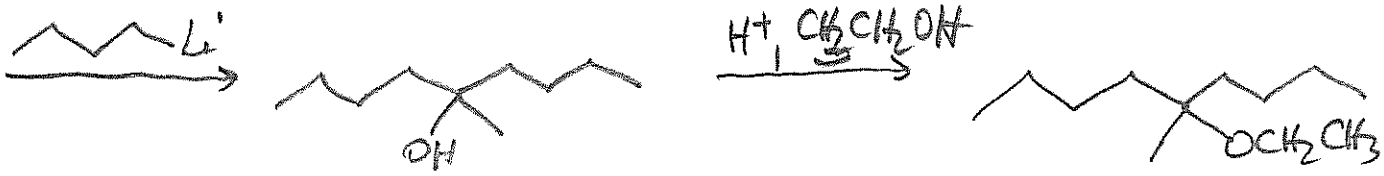
Watch stereochemistry!

IV. [40 Points]

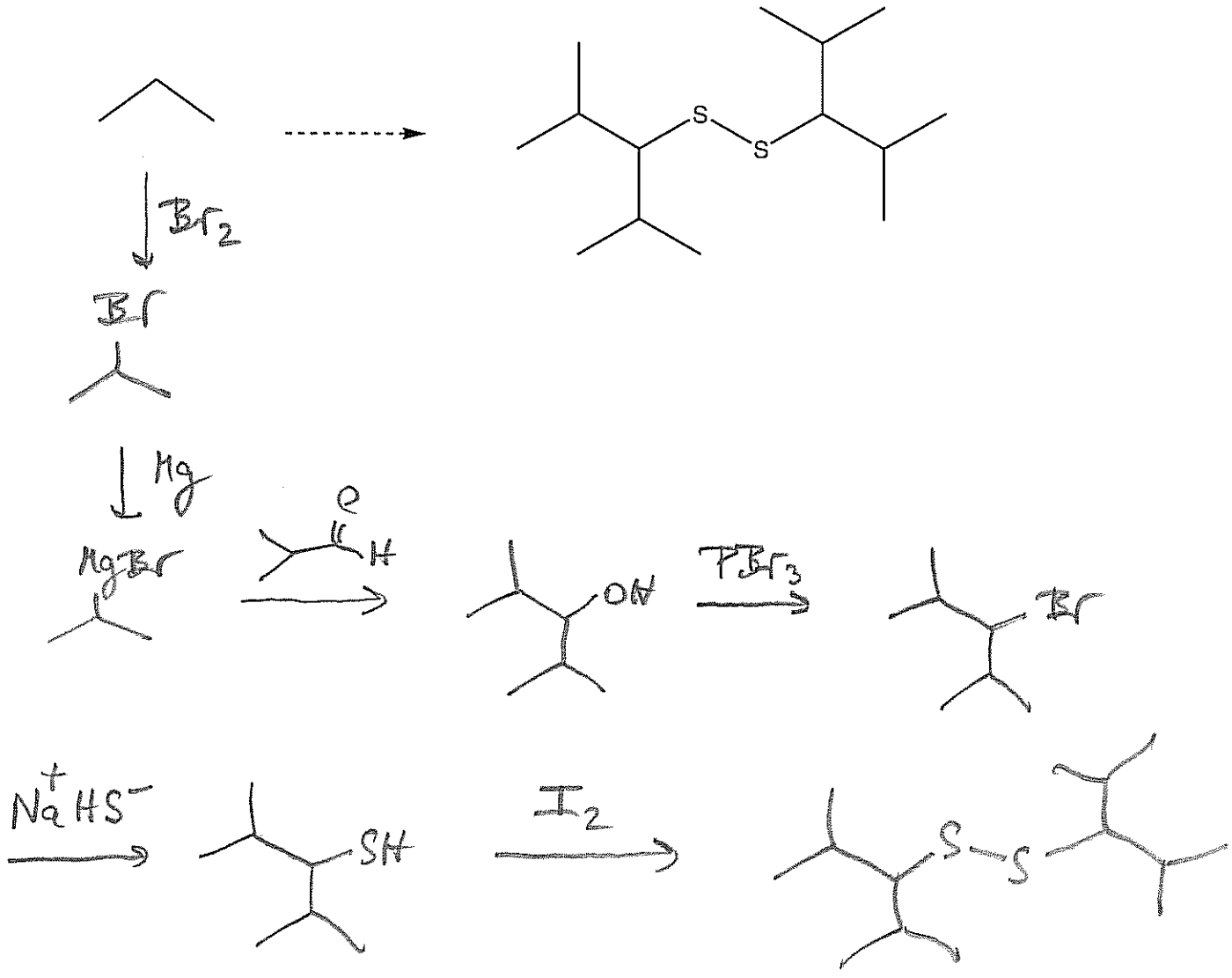
a. Provide a viable synthesis of the following compound from any starting materials containing ***four carbons or less***. Work backwards!





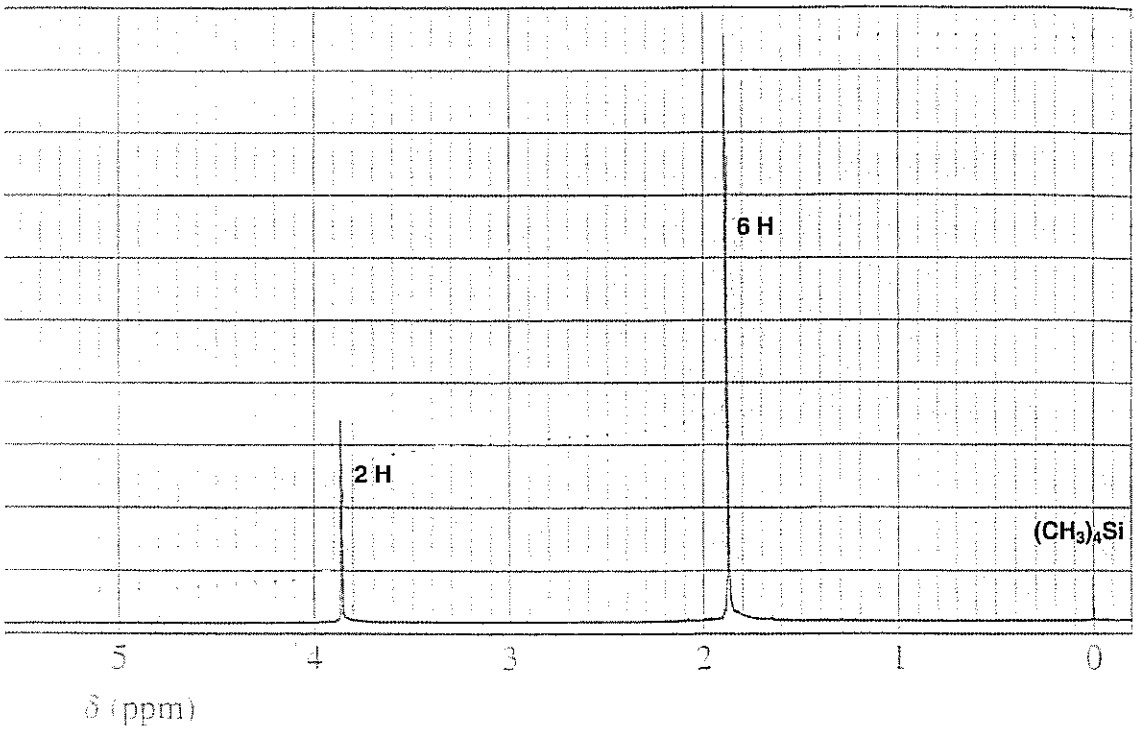


b. Provide a viable conversion of starting material to product. You may use any additional organic or inorganic compounds in your scheme.

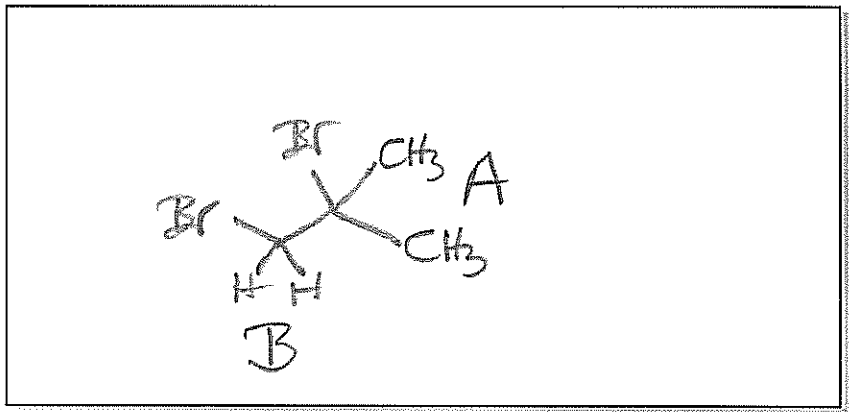


V. [30 Points]

A researcher carried out the radical bromination of 2-methylpropane, $(CH_3)_3CH$, and isolated the expected $(CH_3)_3CBr$, b.p. 82.4 ºC. However, careful distillation revealed another compound, b.p. 150 ºC, 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 = 1.90 ppm with the letter "A" and those at δ = 3.87 ppm with "B" ***in the drawing in the box above***.

c. Give ***one*** reason for your assignment in b., in ***one sentence***. Note: There are several valid answers, just pick one. If you give more, your question will not be graded.

Chemical shifts: H_B are deshielded by neighboring bromine.

Integration

VI. [30 Points] Place an ***X mark*** in the box preceding the most accurate statement. Only <u>one</u> answer is allowed.

a. Nucleophilicity in CH_3OH increases down the periodic table, because

- [ ] the nucleophilic atoms get heavier
- [ ] the basicity of the nucleophile increases
- [X] polarizability increases
- [ ] solvation is impeded by protic solvents

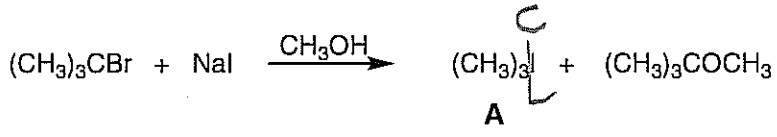
b. In ^1H NMR, the chemical shift

- [ ] decreases with increasing strength of the external magnet
- [x] increases with deshielding by electron withdrawing groups on the attached carbon
- [ ] increases with increasing strength of the external magnet
- [ ] decreases with deshielding by electron withdrawing groups on the attached carbon

c. The rate of cyclization of bromoalcohols to cyclic ethers decreases in the order (the numbers stand for the resulting ring size)

- [ ] 3, 4, 5, 6
- [ ] 4, 5, 6, 3
- [x] 3, 5, 6, 4
- [ ] 5, 6, 4, 3

d. In the reaction shown, the proportion of product **A** can be increased by

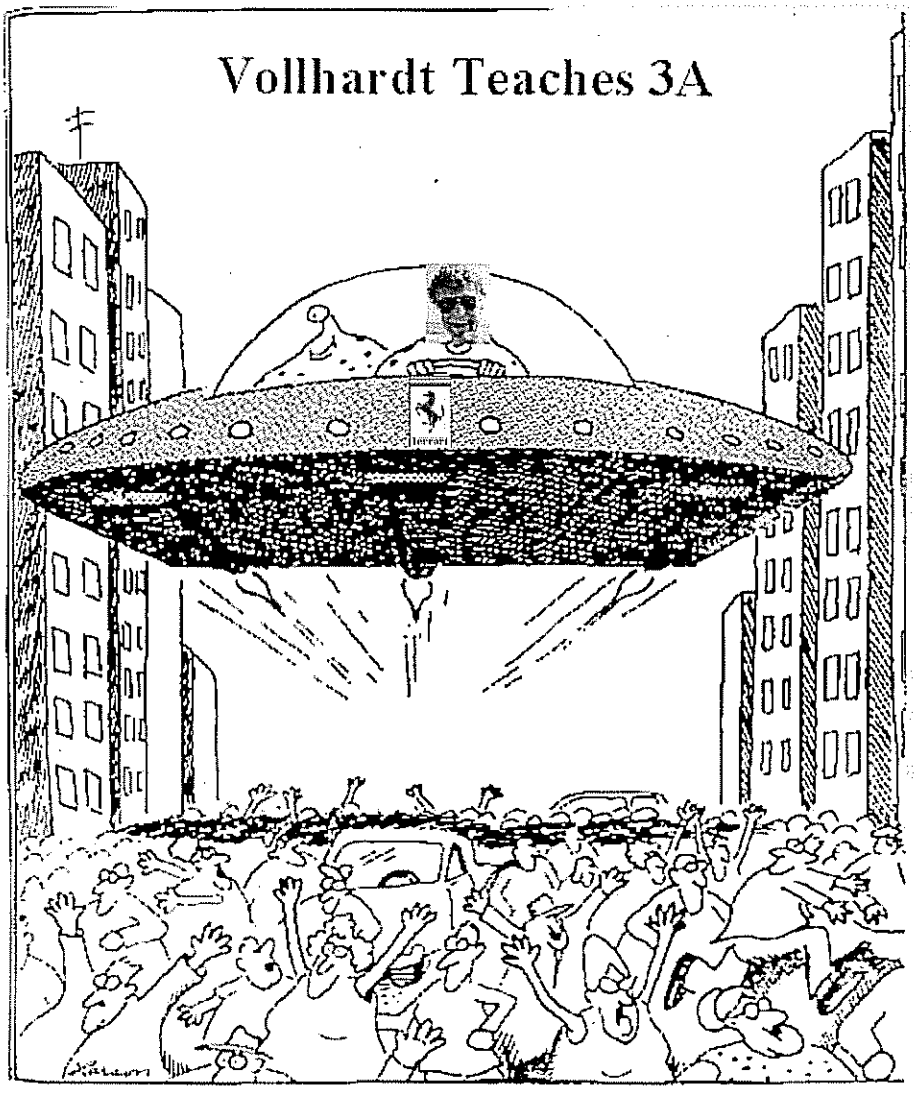


A

- [ ] heating
- [x] adding excess NaI
- [ ] changing the leaving group to methanesulfonate
- [ ] entropy

e. Carbocation stability increases with

- [x] alkyl substitution
- [ ] leaving group ability
- [ ] nucleophilicity
- [ ] hydride shifts



"Yeeeeeeeeeeha!"

* The End *