CHEM 3A. MIDTERM 3. SPRING 2001 FRECHET

Chemistry 3A - Spring 2001
Midterm 3

Professor Jean Fréchet

April 18, 2001

Your full signature

Print your full name (Last name, First name, middle)

Your SID

Name of your GSI/TA

Please check the section number and name of your GSI/TA:

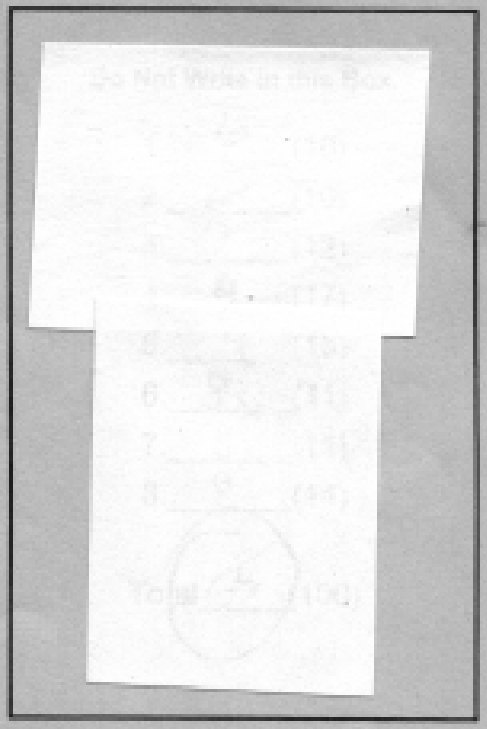
___161 Padilla-De Jesus,Omayra
___171 Fox,Daniel
___181 Furuta,Paul
___191 Ling,Frank
___111 Cordaro,Joseph
___121 Le,Scheherazade
___131 Thalji,Reema
___141 Catherine Seeley
___261 Peterka,Darcy
___271 Miljanic,Ognjen
___211 Dertz,Emily
___221 Simon,Matthew
___361 Barry,David
___371 Miljanic,Ognjen
___311 Sivamani,Raja
___321 Li, Ben
___461 Huang,Alan
___471 Liang,Catherine
___411 Phillips,Scott
___421 Saxon,Eliana
___431 Osterhout,Robin
___561 Merolle,Mauro
___511 Klopp,John
___521 Wu,Sarah
___531 Rao,Vikas

If you are making up an I-grade, indicate the semester you took 3A_____ and the Professor_____.

This exam has **10** 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 backs of the exam pages. Write only **one** answer to each problem; multiple answers will receive **no** credit, even if one of them is correct.

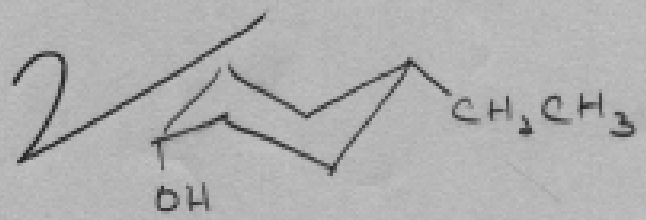
Note: This examination runs for a total of 90 minutes. No questions will be answered by proctors after the exam begins. Please write legibly; ambiguous or messy answers will receive **no credit**.



1. (10 Points). Name or draw the structure of the following molecules as appropriate.

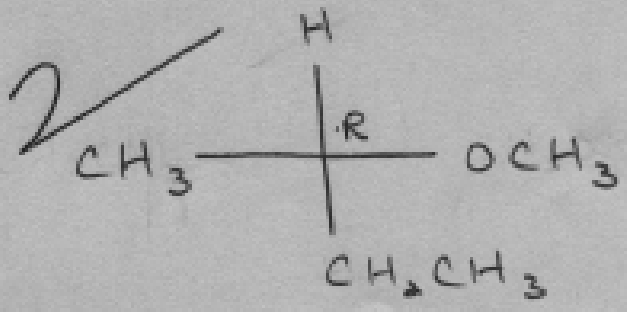
(a) cis-4-ethylcyclohexanol

(show in chair form)



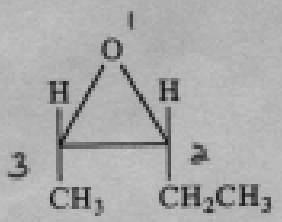
(b) (R)-2-methoxybutane

(show in Fischer Projection)



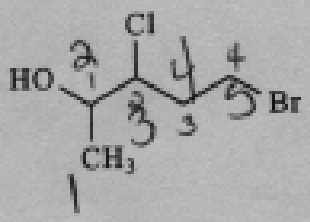
$CH_3CH(OCH_3)CH_2CH_3$

(c)



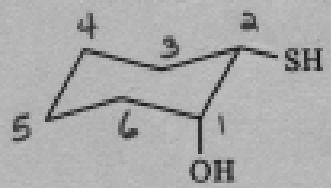
2-ethyl-3-methyl-oxacyclopropane

(d)



4-bromo-2-chloro-1-methylbutanol

(e)



cis 2-mercapto cyclohexanol

2. (10 Points). (a) Rank the following in order of INCREASING pKa

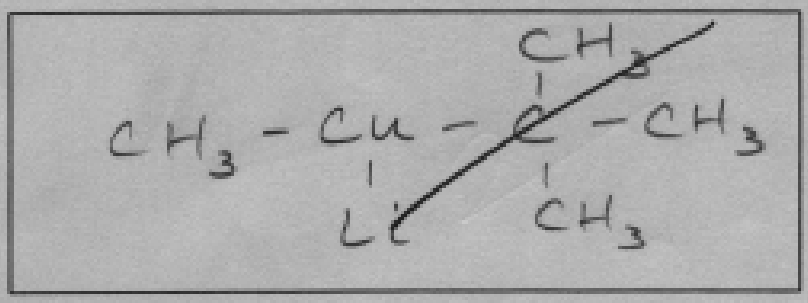
CH_3CH_2SH $(CH_3)_3COH$ H_2O

Answer: CH_3CH_2SH $(CH_3)_3COH$ H_2O

Lowest pKa Highest pKa

(b) Write the structure of a GILMAN reagent containing a butyl group

Answer:



(c) Explain in one sentence why alcohols have a higher boiling point than the corresponding thiols

Alcohols experience hydrogen bonding while thiols do not

2

(d) Name two functional groups found in the odorant compounds that constitute GARLIC.

sulfides $R-S-R'$ thiol and sulfonate or sulfoxides or disulfides or sulfinic acid

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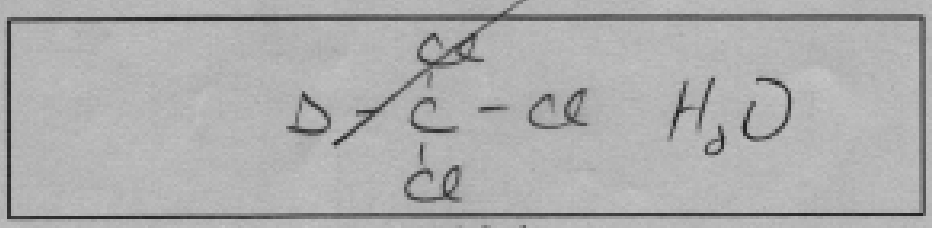
(e) Write the structure of the molecule responsible for most of the signal in Magnetic Resonnce Imaging (MRI)



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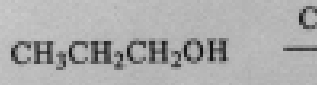
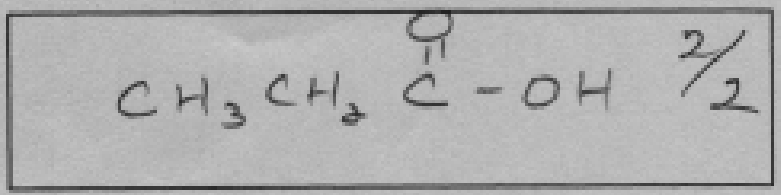
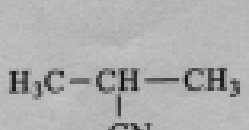
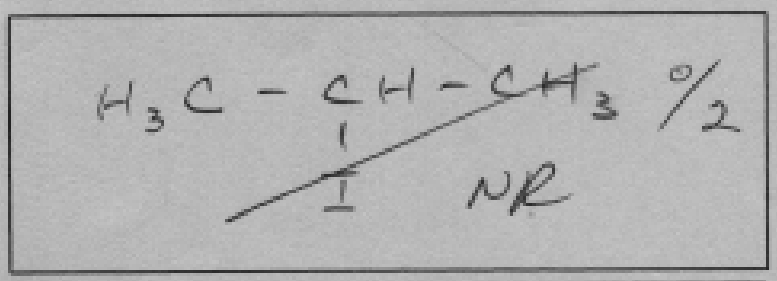
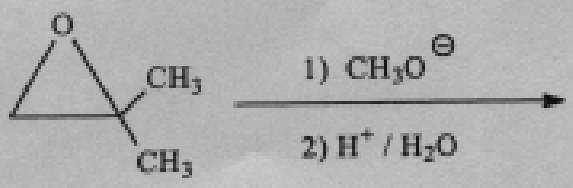
3. (12 Points). Complete the reactions below showing the structure of the major product (with stereochemistry where appropriate). If no reaction occurs write "NR".

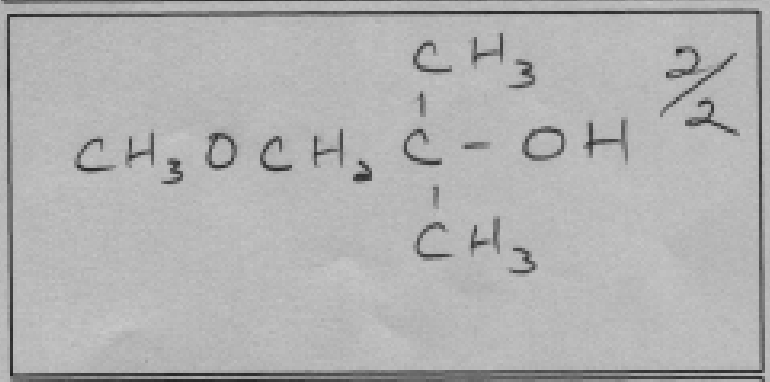


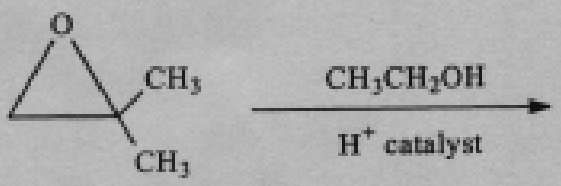


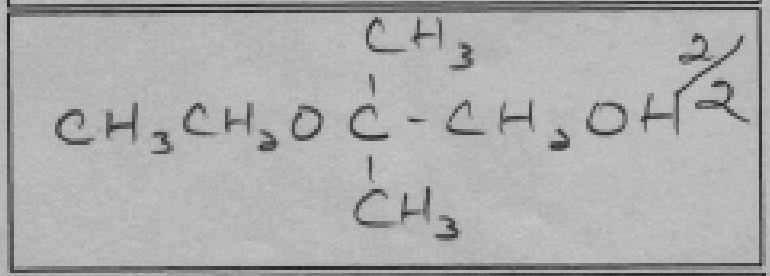


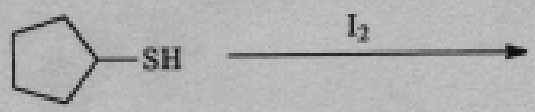


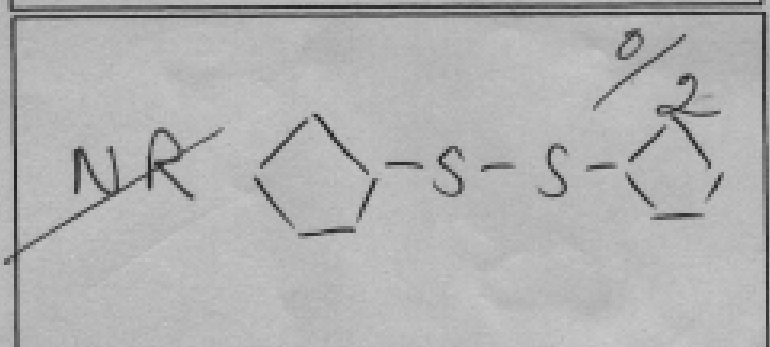


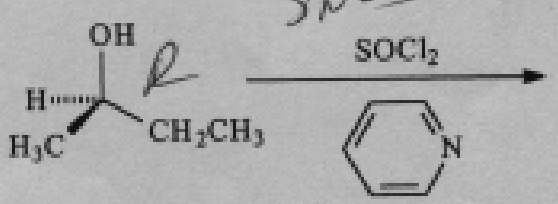




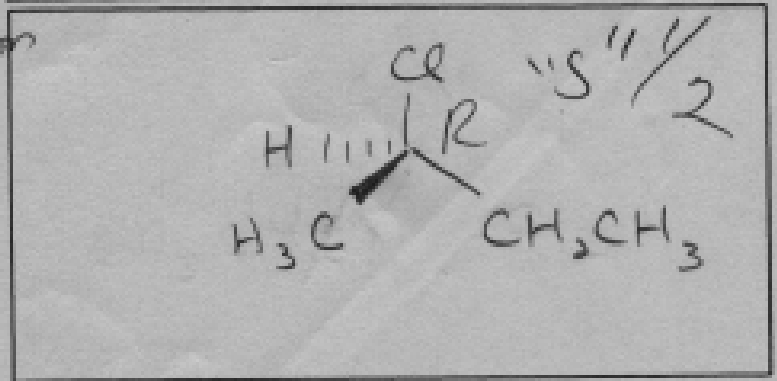




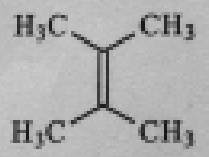




SN2 inversion

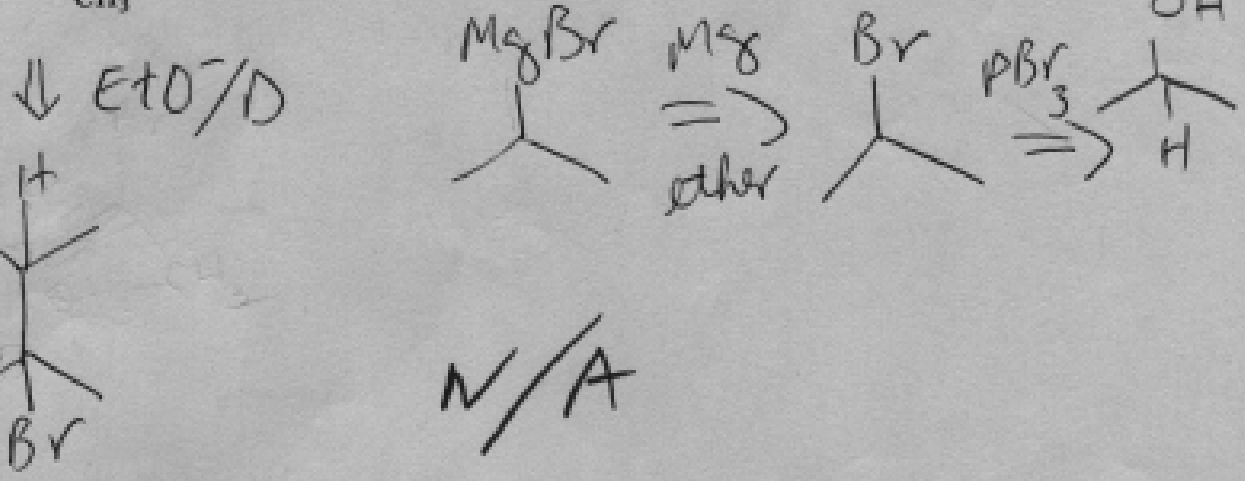


4. (17 Points). (a) Show a step by step synthesis of the compound below starting from $CH_3CHOHCH_3$

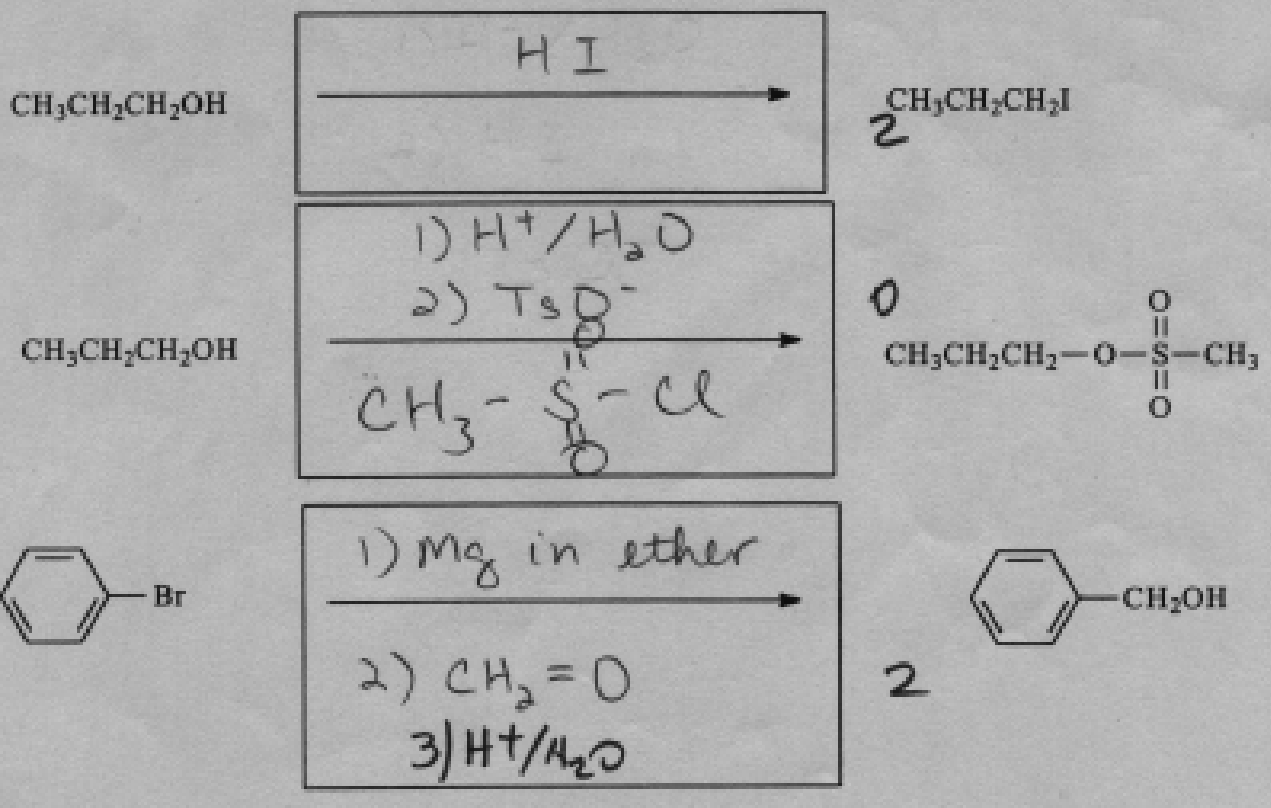


(only source of carbon)

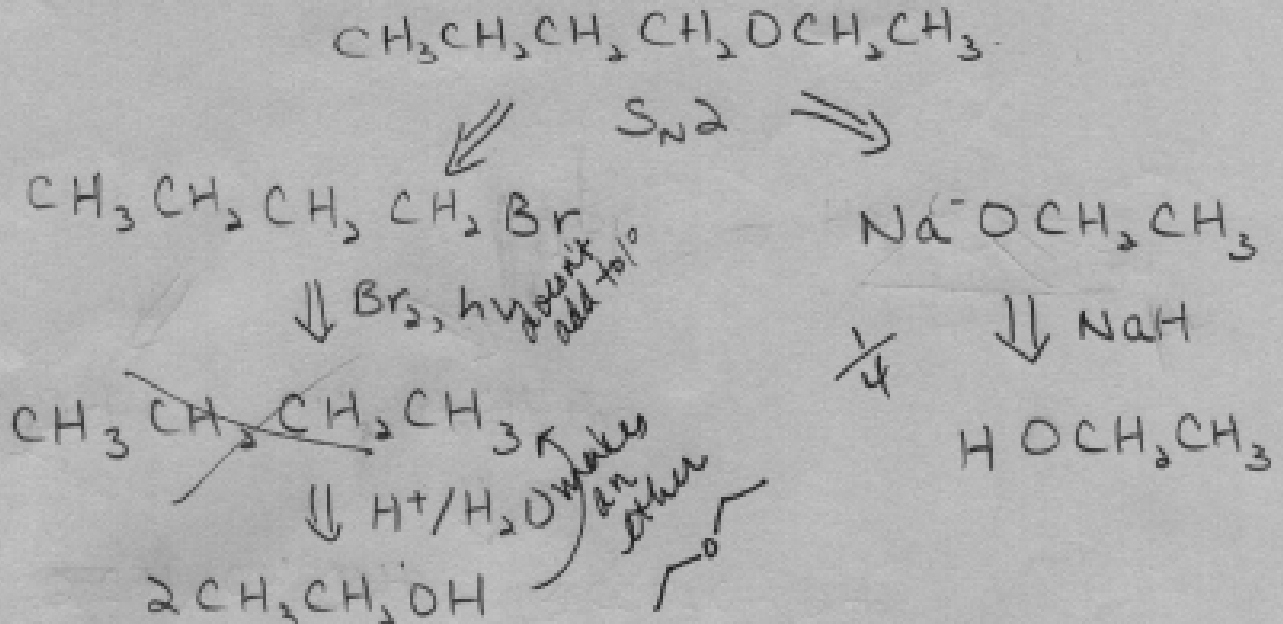
elimination



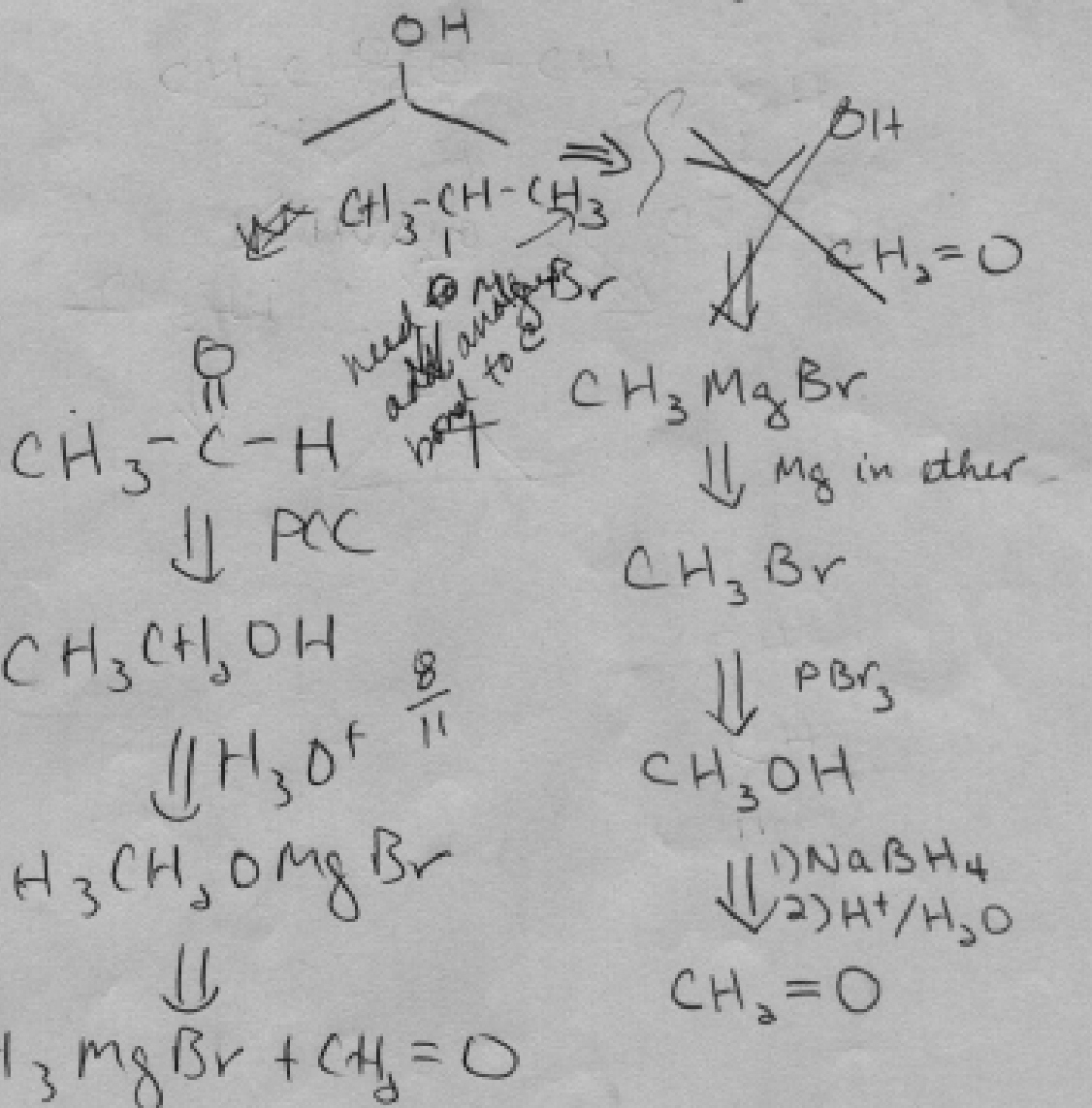
(b) Complete the reactions below showing the missing reagents (note that several steps may be required)



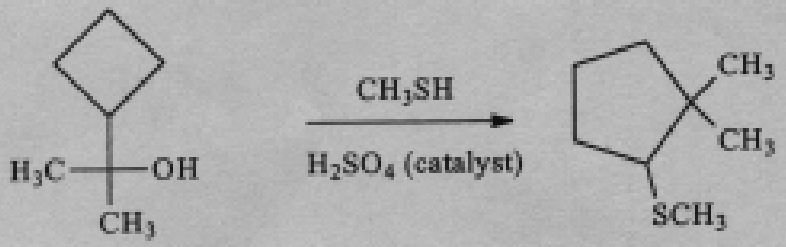
5. **(15 Points)** (a) Propose a step by step synthesis of $CH_3CH_2CH_2CH_2OCH_2CH_3$ from any starting material containing 3 carbon atoms or less

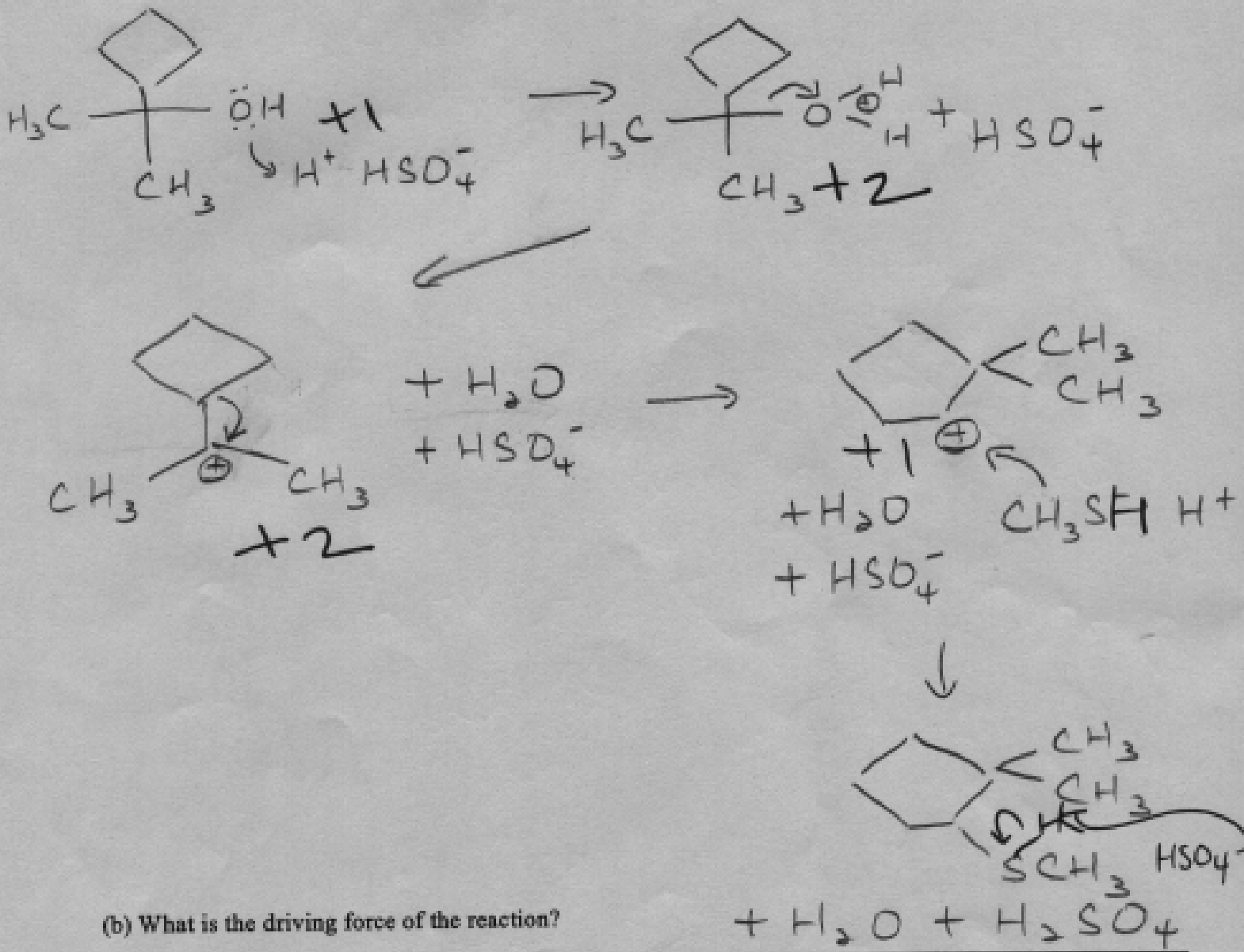


(b) Propose a step by step synthesis of $CH_3CHOHCH_3$ from $CH_2{=}O$ (only source of C)



6. (11 Points). (a) Show a step-by step mechanism for the following reaction:

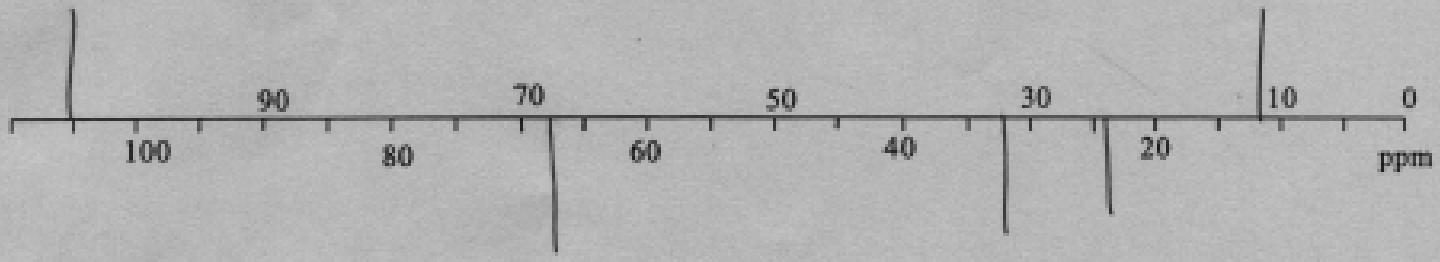


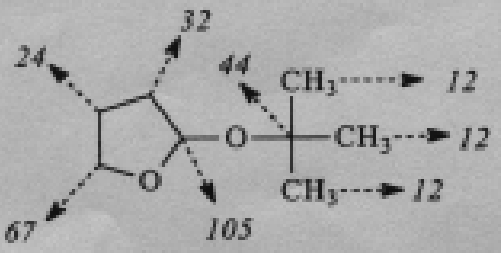


(b) What is the driving force of the reaction?

Answer (one sentence): +2 The driving force is the energy released by the breaking of the ring due to ring strain.

7. (11 Points). (a) Draw the DEPT-135 ^{13}C-NMR spectrum for the molecule below for which the ^{13}C "normal" decoupled chemical shifts are given.





CH 105

CH$_2$ 24, 32, 67

CH$_3$ 12

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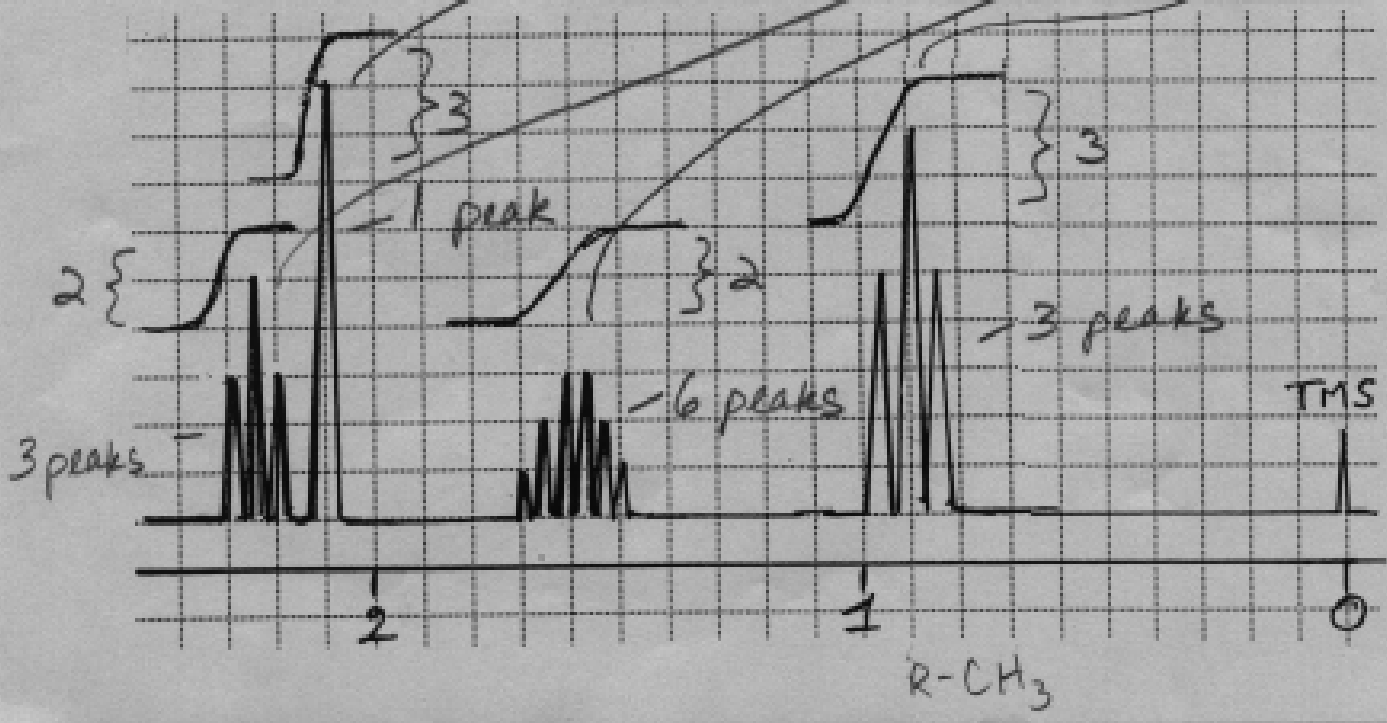
(b) What is the structure of the compound $C_5H_{10}O$ whose ^{1}H NMR spectrum is shown below. Write a clear structure and provide a peak assignment using arrows to indicate which peak (or set of peaks) corresponds to each set of protons.

Answer: $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$



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8. (14 Points). (a) A **saturated** *cyclic* compound A with the formula $C_7H_{13}Br$ reacts with NaOH in an elimination reaction to afford an **unsaturated** *cyclic* hydrocarbon B with the formula C_7H_{12}.
The NMR data for both A and B are given below.

Compound A

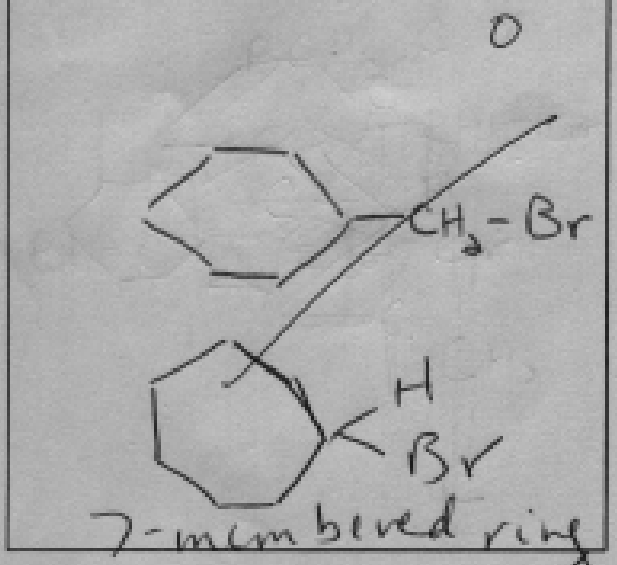
"Normal" decoupled ^{13}C NMR (δ in ppm): four peaks only at 25; 28; 40; 56 ppm.
DEPT-90 spectrum: one peak only at 56 ppm. CH
DEPT-135 spectrum: one positive peak at 56; three negative peaks at 25, 28, and 40 ppm.

Compound B CH2

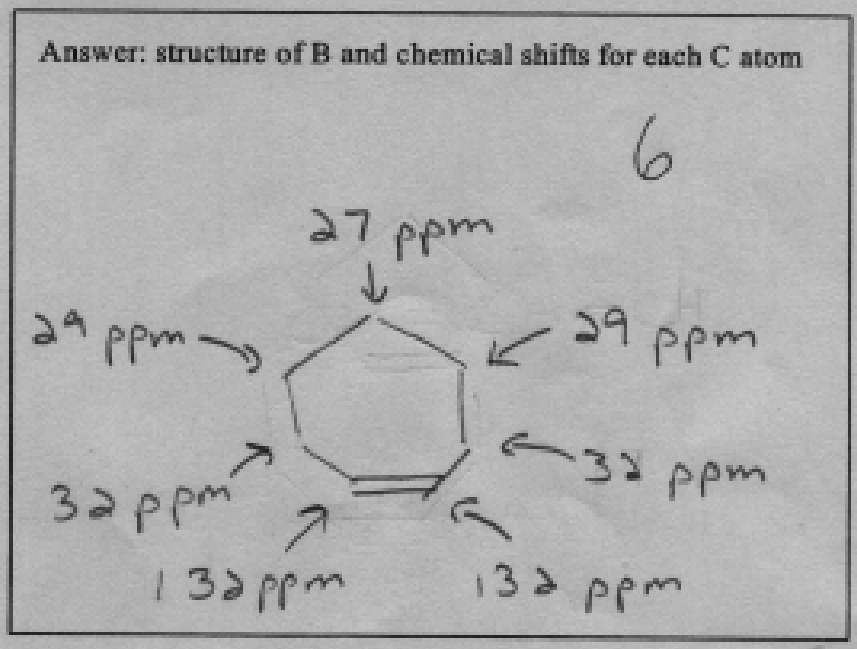
"Normal" decoupled ^{13}C NMR (δ in ppm): four peaks only at 27; 29; 32; 132 ppm.
DEPT-90 spectrum: one peak only at 132 ppm. CH
DEPT-135 spectrum: one positive peak at 132 ppm; and three negative peaks at 27, 29, and 32 ppm.

Show clear structures for both A and B and *in the case of B* write the chemical shift next to each C atom CH

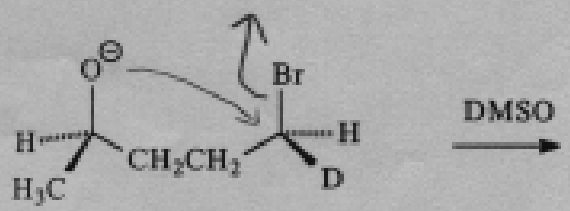
Answer: Structure of A

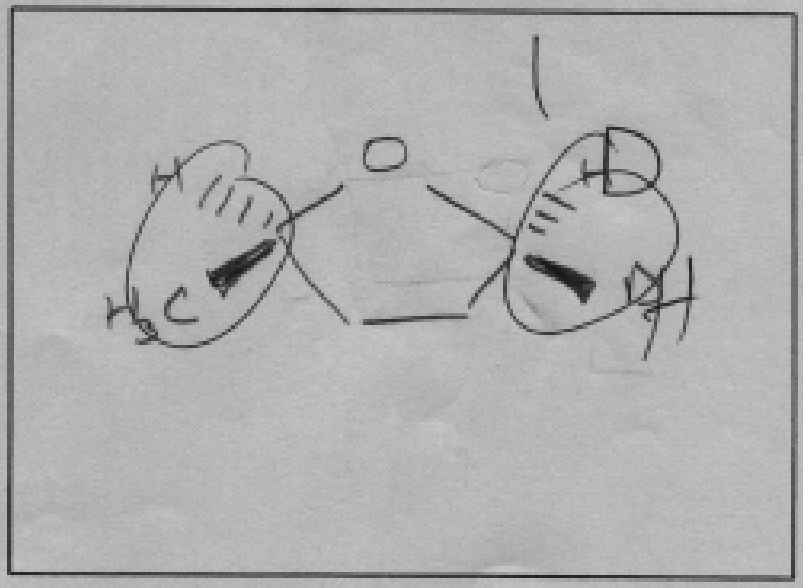


Answer: structure of B and chemical shifts for each C atom



(b) Write a clear stereochemical structure for the product of the reaction below. What is the kinetic order of the reaction?





Kinetic order = 1 1

Note: **There are no questions to be answered on this page,**
Not all of the data provided may be needed

Typical ^{1}H NMR chemical shifts

R-CH_3	0.7-1.3
R-CH_2-R'	1.2-1.6
R_3CH	1.4-1.8
R-CH_2-O-R'	3.3-3.9
R-CH_2Cl	3.4-3.7
R_2CHCl	3.9-4.4
RO-CH_2Cl	5.2-5.6
$CH_3-\overset{\overset{O}{\|}}{C}-R$	2.0-2.4

Typical ^{13}C NMR chemical shifts

R-CH_3	5-25
R-CH_2-R'	25-35
R_3CH	35-55
R_4C	30-45
R-CH_2-O-R'	50-90
R-CH_2Cl	25-50
R-COOH	170-180
R-CH=CH-R'	100-150
$CH_3-\overset{\overset{O}{\|}}{C}-R$	170-220

Rules for DEPT ^{13}C NMR

DEPT-90 reveals signals of C atoms bound to one hydrogen (CH) only.

DEPT-135 produces normal (positive) signals for CH and CH_3, no signals for quaternary carbons, and negative absorptions for CH_2

Partial periodic table of the elements

IA	IIA	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.00794							2 He 4.00260
3 Li 6.941	4 Be 9.01218	5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050	13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80

IB IIB