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:

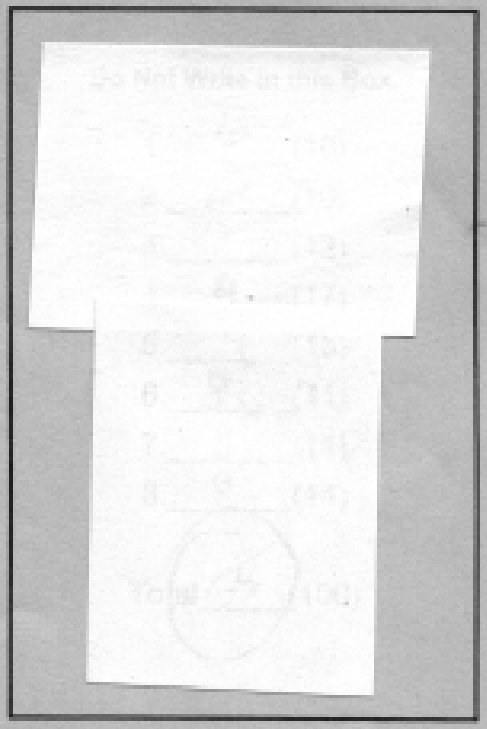
___161 Padilla-De Jesus,Omayra
___171 Fox,Daniel
___181 Furuta,Paul
___191 Ling,Frank
___111 Cordaro,Joseph
___121 Le,Scheherazade
___131 Thalji,Reema
___141 Catherine Seeley
___261 Peterka,Darcy
___271 Miljanic,Ognjen
___211 Dertz,Emily
___221 Simon,Matthew
___361 Barry,David
___371 Miljanic,Ognjen
___311 Sivamani,Raja
___321 Li, Ben
___461 Huang,Alan
X 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.

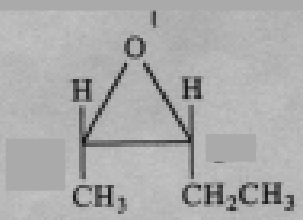
(a) cis-4-ethylcyclohexanol

(show in chair form)

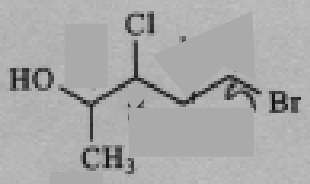
(b) (R)-2-methoxybutane

(show in Fischer Projection)

(c)



(d)



(e)

2. (10 Points). (a) Rank the following in order of INCREASING p*K*a

CH_3CH_2SH $(CH_3)_3COH$ H_2O

Answer: _____ _____ _____

Lowest p*K*a Highest p*K*a

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

Answer:

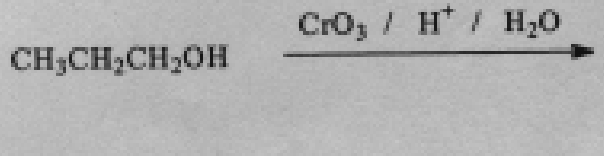
(c) Explain in one sentence why alcohols have a higher boiling point than the corresponding thiols

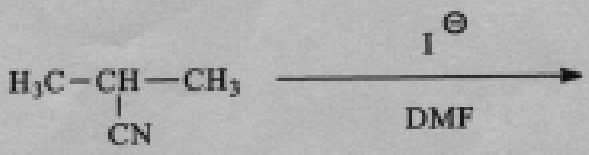
(d) Name two functional groups found in the odorant compounds that constitute GARLIC.

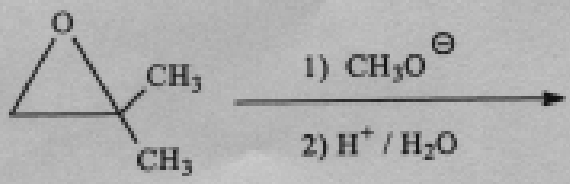
and

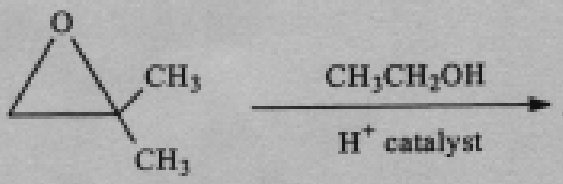
(e) Write the structure of the molecule responsible for most of the signal in Magnetic Resonnce Imaging (MRI)

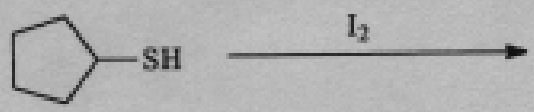
3. (12 Points). Complete the reactions below showing the structure of the major product (with stereochemistry where appropriate). If no reaction occurs write "NR".

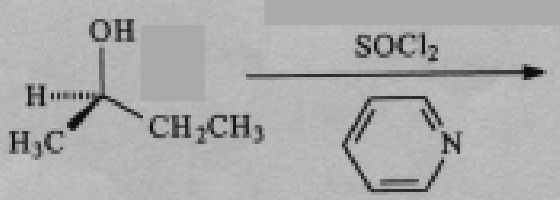




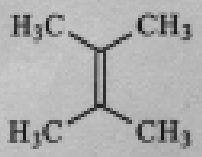




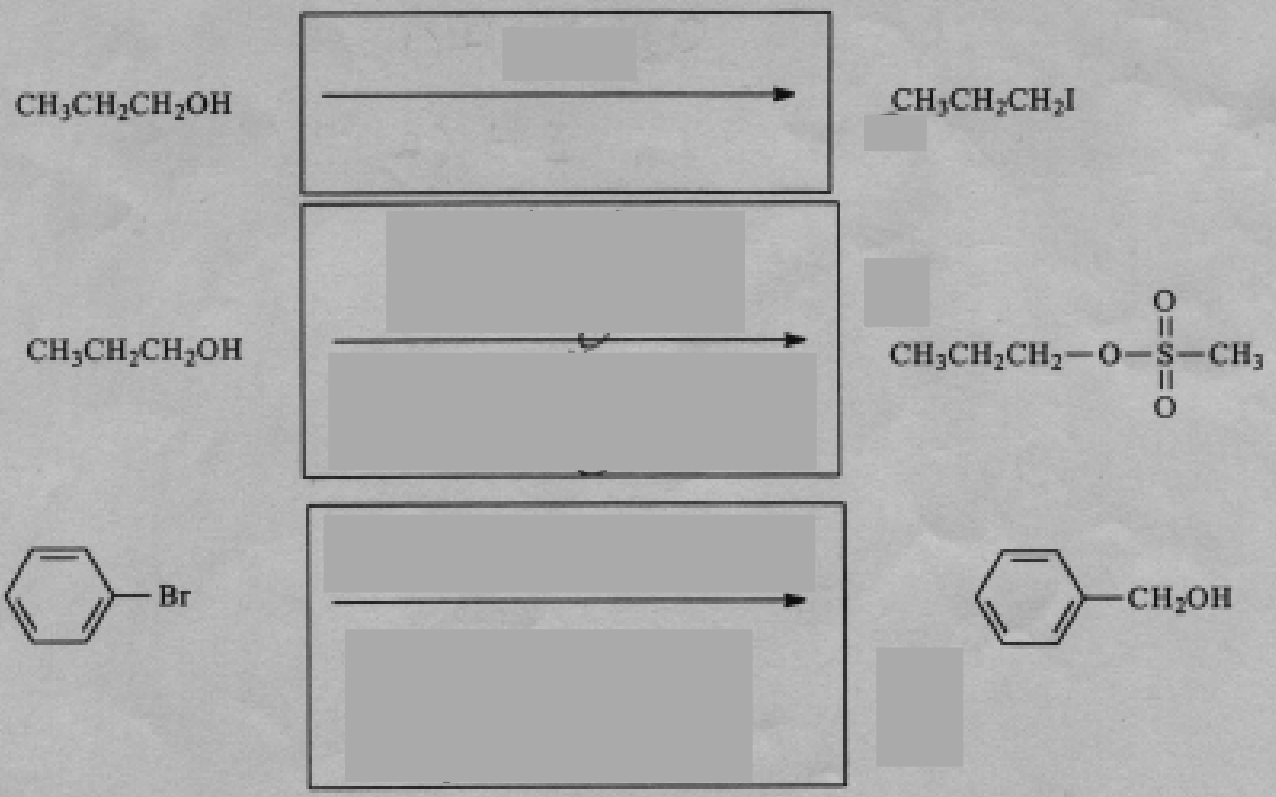




4. (17 Points). (a) Show a step by step synthesis of the compound below starting from $CH_3CHOHCH_3$



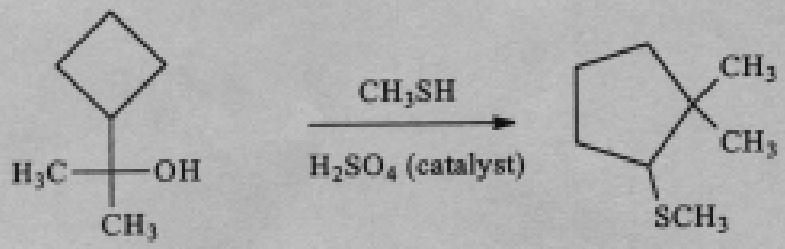
(b) Complete the reactions below showing the missing reagents (note that several steps may be required)



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 $CH_2{=}O$

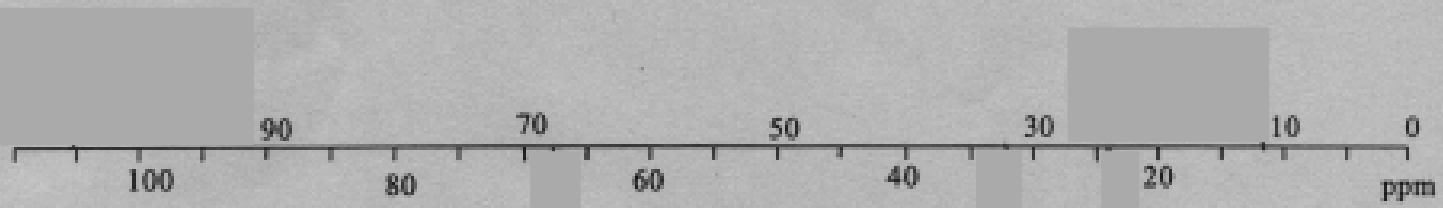
6. (11 Points). (a) Show a step-by step mechanism for the following reaction:

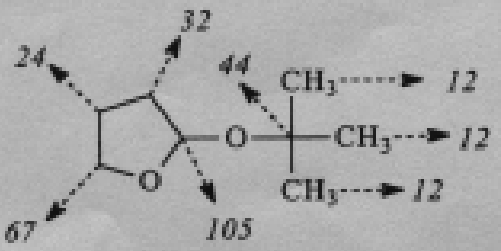


(b) What is the driving force of the reaction?

Answer (one sentence):

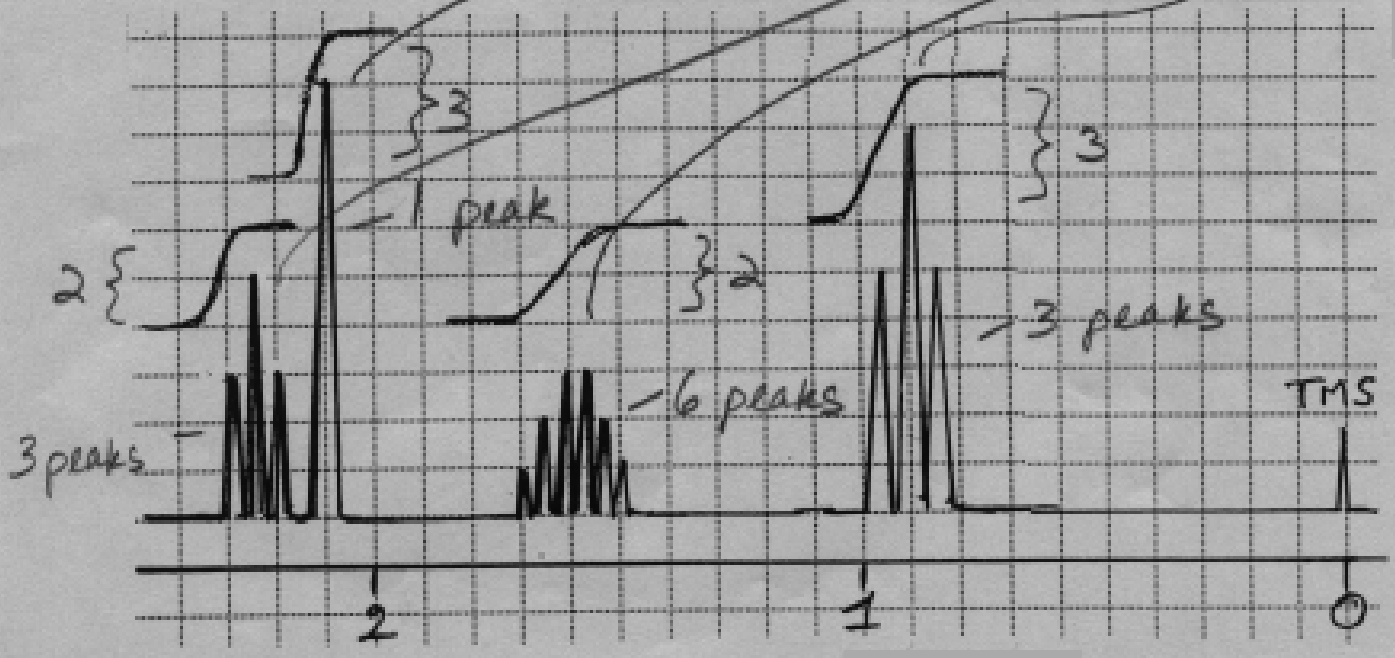
7. (11 Points). (a) Draw the DEPT-135 ^{13}C-NMR spectrum for the molecule below for which the ^{13}C "normal" decoupled chemical shifts are given.





(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:



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.
DEPT-135 spectrum: one positive peak at 56; three negative peaks at 25, 28, and 40 ppm.

Compound B

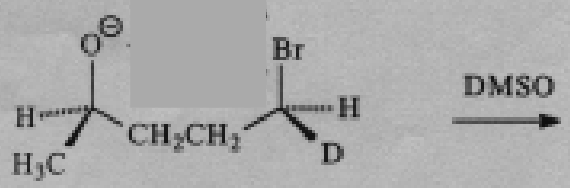
"Normal" decoupled ^{13}C NMR (δ in ppm): four peaks only at 27; 29; 32; 132 ppm.
DEPT-90 spectrum: one peak only at 132 ppm.
DEPT-135 spectrum: one positive peak at 132 ppm; and three negative peaks at 27, 29, and 32 ppm.

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

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 =

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

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

Typical ^{13}C NMR chemical shifts

$R\text{-}CH_3$	5-25
$R\text{-}CH_2\text{-}R'$	25-35
R_3CH	35-55
R_4C	30-45
$R\text{-}CH_2\text{-}O\text{-}R'$	50-90
$R\text{-}CH_2Cl$	25-50
$R\text{-}COOH$	170-180
$R\text{-}CH{=}CH\text{-}R'$	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	O
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		IB	IIB	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