Chemistry 3A - Spring 2000
Midterm 3

Professor Jean Fréchet

April 17, 2000

Your full signature_

Print your full name_
(Last name, First name, Middle)

Your SID_____

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

___161 Verdugo,Dawn
___171 Klopp,John
___181 Borths,Christopher
___191 Fujdala,Kyle
___111 Watkins,Gregory
___121 Blackwell,Bethany
___131 Fox,Daniel
___141 Werkema,Evan
___261 Peterka,Darcy
___271 Lee,Charles
___211 Tripp,Jennifer
___221 Padilla,Omayra

___361 Haman,Kristina
___371 Hecht,Stefan
___311 Saxon,Eliana
___321 Cook,Brian
___461 Purdy,Matthew
___471 Evans,John
___411 Holland,Andrew
___421 Duncan,Andrew
___431 Trimble,Alexander
___511 Marcaurelle,Lisa
_Y_521 Jen,Wendy
___531 Ling,Frank

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**.

A partial periodic table and data needed for calculations can be found on page **10** of the exam.

Do Not Write in this Box.

1.__	_(14)
2.__	_(14)
3.__	_(11)
4.__	_(12)
5.__	_(13)
6.__	_(14)
7._	_(10)
8.__	_(12)
Total	(100)

1. (14 points) **(a)** Draw the ^{1}H-NMR spectrum of $CH_3CH_2CH_2Cl$. In your drawing, show the appropriate location of the peaks (chemical shifts) as well as the splitting (assume that "ideal" spilling occurs). Each peak, or set of peaks, should be labeled to indicate which part of the molecule it corresponds to. Also show the peak integration as a "step" drawing.
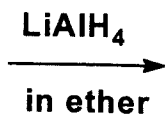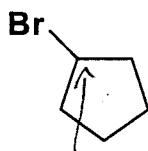
6 ppm   5   4   3   2   1   0
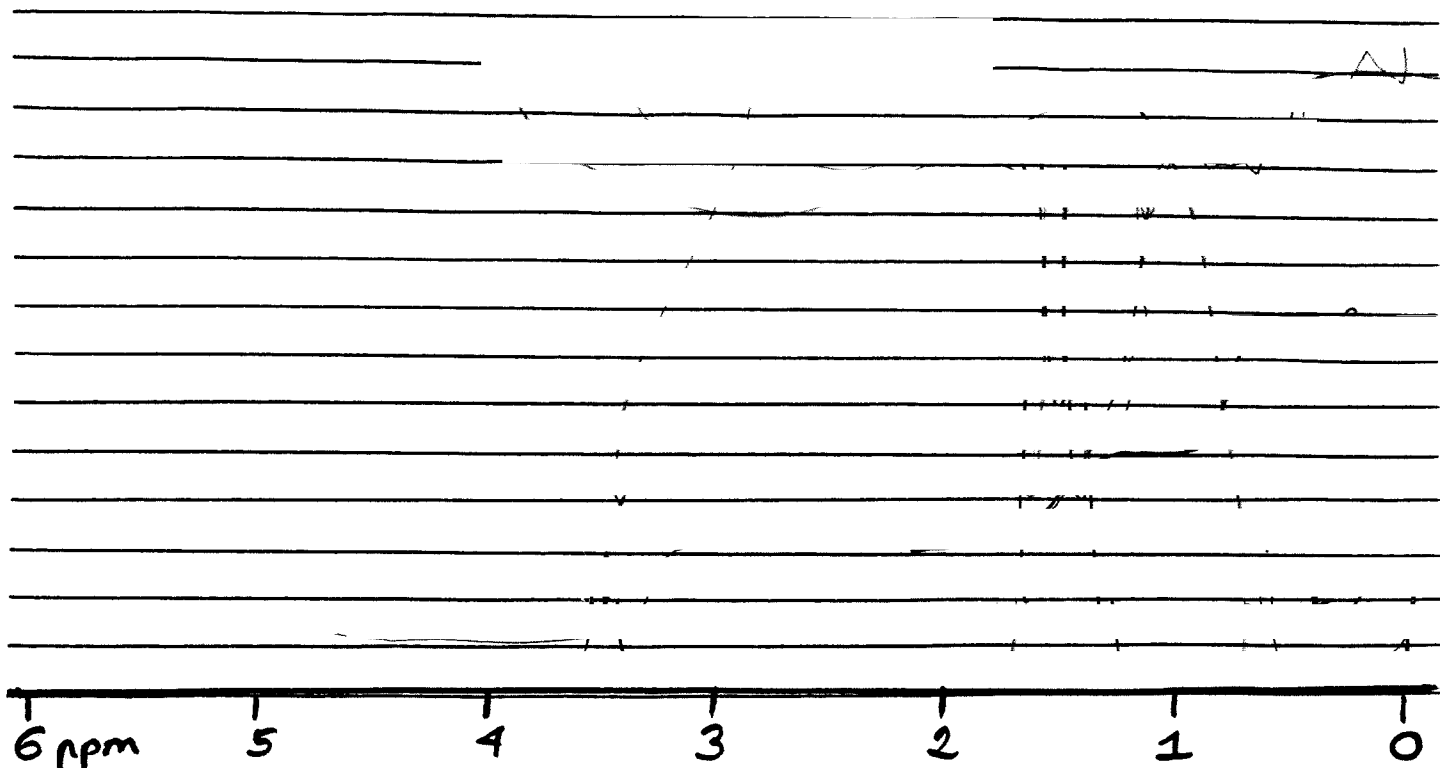
(b) How many signals would be present in the "normal" (proton decoupled) ^{13}C NMR spectrum of $CH_3CH_2CH(CH_2CH_3)_2$

Answer:

(c) Give the major product(s) of each of the following reactions.

$\xrightarrow{\begin{array}{c} H_2 \\ \hline Pt \end{array}}$

$\xrightarrow[\text{in ether}]{\text{LiAlH}_4}$
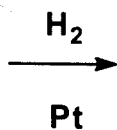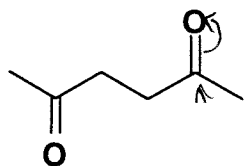
2. (14 points)

(a) Reaction of 2-bromo-2,3-dimethylbutane with strong base leads to elimination to form two isomeric alkenes **A** and **B**. Show the structure of each of these two alkenes and indicate how many peaks will be found in the ^{13}C NMR spectra of each. (b) Which reagent (used in class) would be best to produce the highest yield of the alkene with the greatest number of peaks in its ^{13}C NMR spectrum (be specific).
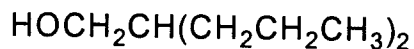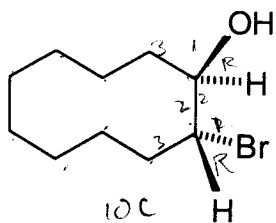
$$H_3C \quad Br$$
$$H_3C-\overset{}{\underset{H}{C}}-\overset{}{\underset{CH_3}{C}}-CH_3 \xrightarrow{\text{base}} A + B$$
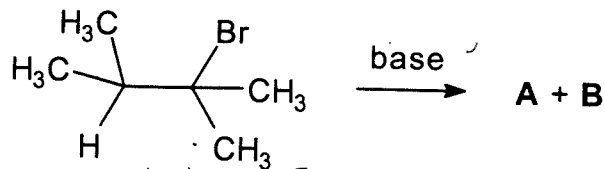
A =

Number of peaks for **A**:

B =

Number of peaks for **B**:

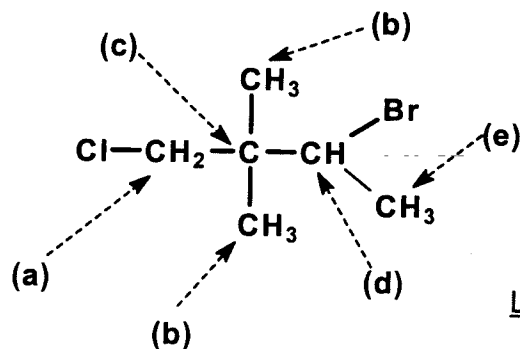**(part b)** Reagent used:

(c) Name the following according to IUPAC nomenclature. Specify <u>absolute stereochemistry</u> where appropriate.
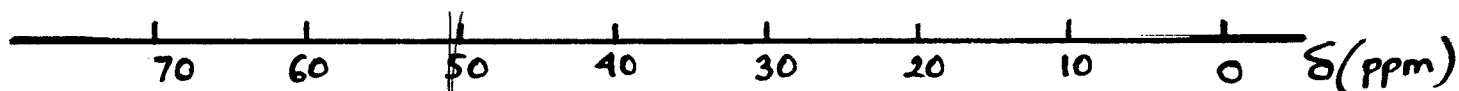
$$HOCH_2CH(CH_2CH_2CH_3)_2$$

3. (11 points)

(a) The chemical shifts for the "normal" (proton-decoupled) NMR spectrum of 3-bromo-1-chloro-2,2-dimethyl butane are given below. Sketch the DEPT-135 spectrum for this molecule.

(c) ⟍   ⟋--- (b)
       CH₃
        | Br
Cl—CH₂—C—CH ⟍   ⟋(e)
        | ⟍ CH₃
       CH₃
                    (d)
(a)   (b)

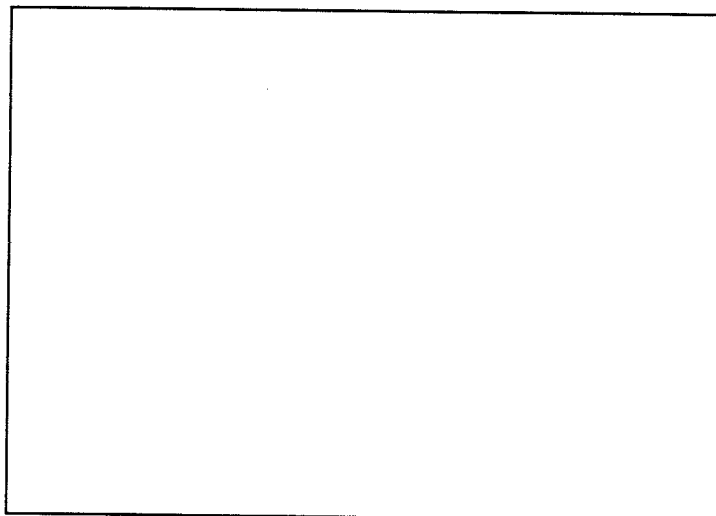**(a) 50 ppm**
(b) 15 ppm
(c) 45 ppm
(d) 40 ppm
(e) 25 ppm

Label each peak (a), (b), etc... on the spectrum to identify them

70   60   50   40   30   20   10   0 δ(ppm)

**(b)** Write a clear structure (Fischer projection) for *meso*-1,2,3,4-butanetetraol

4. (12 points). **(a)** write a clear structure (Fischer projection) for (R)-2-pentanol

**(b)** Give the expected major product of each of the following reaction sequences:

$CH_3CH_2CH_2Cl$

1) Mg, ether

2) [benzene ring]$-\overset{\overset{\displaystyle}{||}}{\underset{O}{C}}-CH_3$

3) H^+ / H_2O

$CH_3CH_2CH_2-\underset{OH}{\overset{|}{CH}}-$[cyclopentane ring]

1) CrO_3 H_2SO_4 H_2O

2) $LiAlD_4$ in ether

3) H^+ / H_2O

[epoxide with methyl groups]

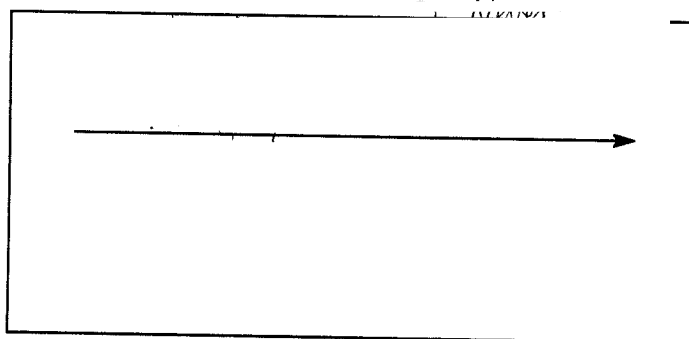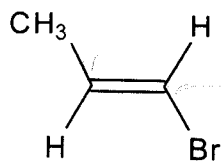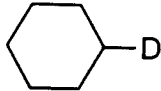1) $(CH_3)_2CHMgCl$ in ether

2) H^+ / H_2O
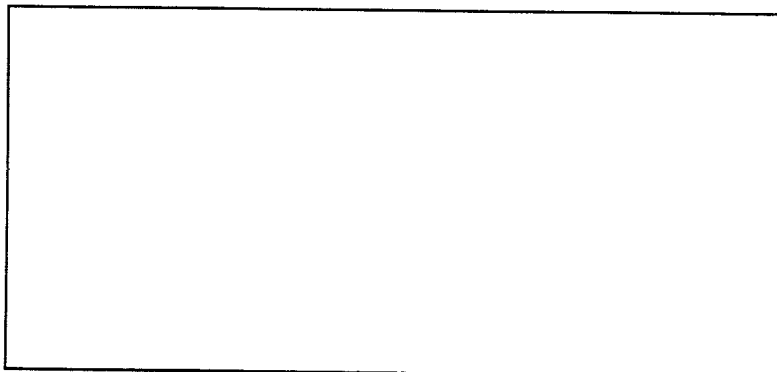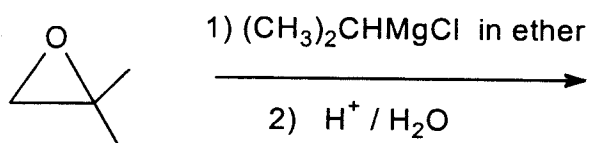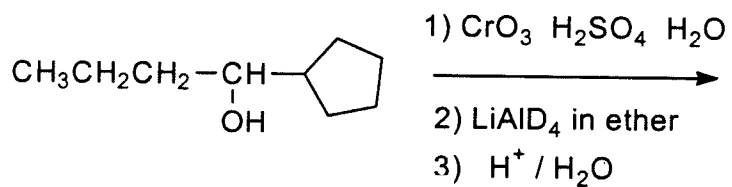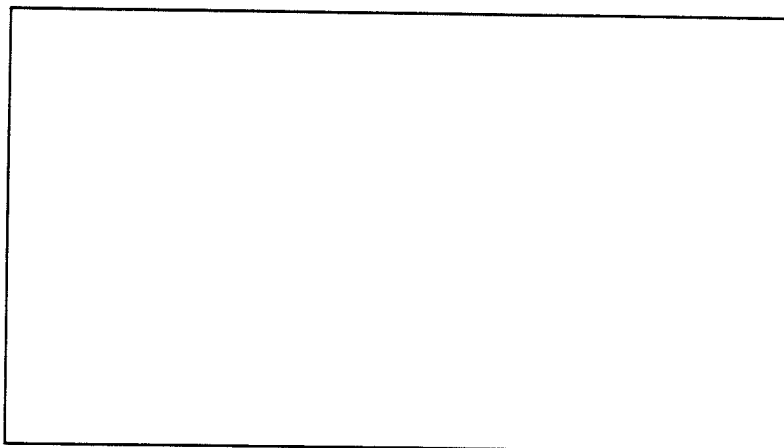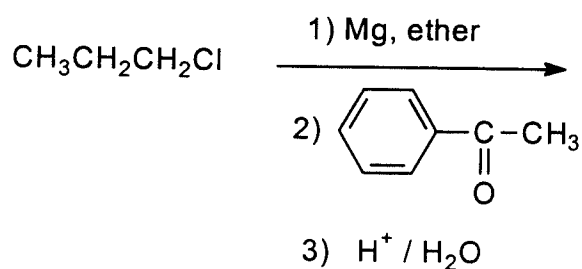
5. (13 points)

(a) Show a step-by-step mechanism (**with all curved arrows**) for the reaction below:
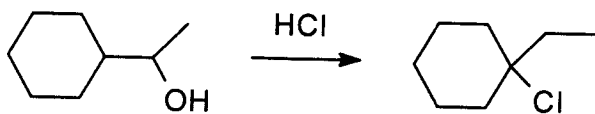
(b) Complete the reactions below showing all the missing **reagents** (and key **solvents** if appropriate). In all cases the choice of reagent must be such that the product shown is <u>the</u> major product of the reaction.
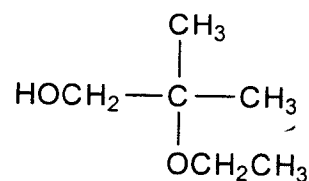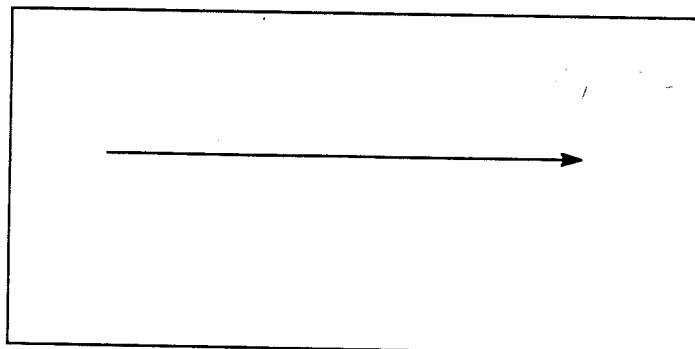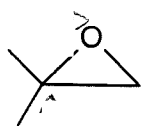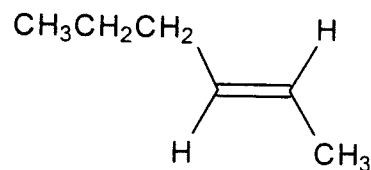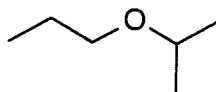
6. (14 points) **(a)** show a step by step synthesis of ⬡—D from ⬡

All reagents and also solvents, if appropriate, must be shown.

(b) propose a synthesis of $(CH_3)_2CH-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2CH_3$ from $CH_3CH_2CH_3$ and CH_3CH_3

you must show all steps and include <u>all</u> reagents and solvents as appropriate.

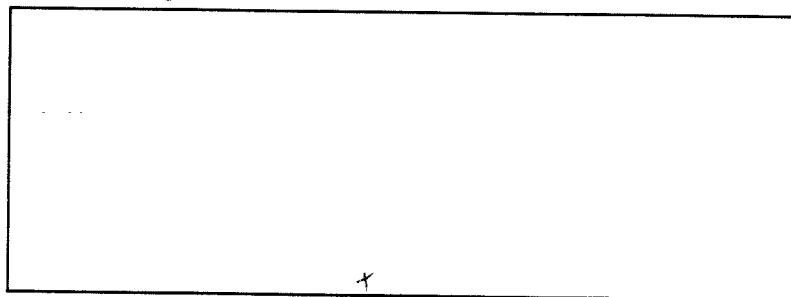**7. (10 points)** **(a)** propose a synthesis of

from 1-bromopropane
and 2-bromopropane

Show all steps, reagents, and solvents used.

(b) Write the expected major product of the following reactions:

$$CH_3CH_2CH_2CH_2OH \xrightarrow[\text{H}^+/\ H_2O]{\text{CrO}_3}$$

$$CH_3CH_2SCH_2CH_3 \xrightarrow[\text{W catalyst}]{H_2O_2\ (\text{excess})}$$

$$CH_3CH_2SCH_2CH_3 \xrightarrow{CH_3CH_2CH_2I}$$
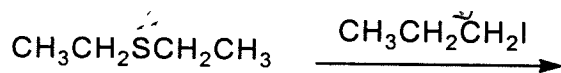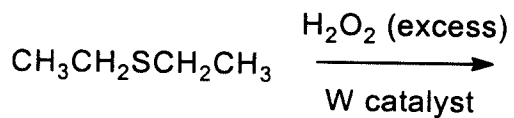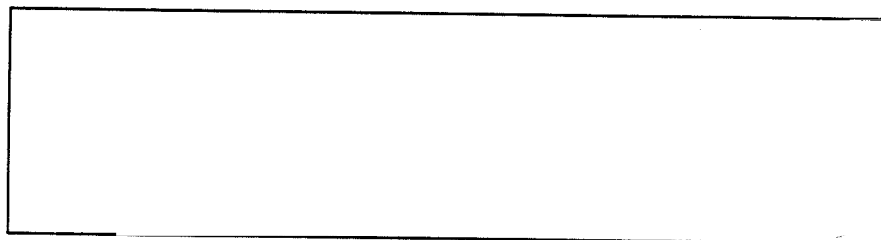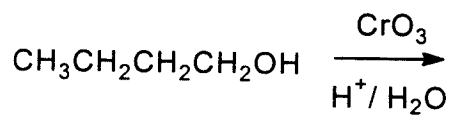
8. (12 points)
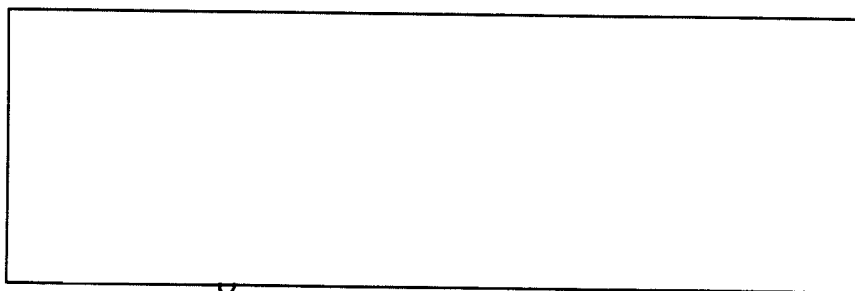
(a) Propose a step by step synthesis of the compound below starting from cyclopentanol and any compound with three C atoms or less. Show all reagents and solvents where appropriate.
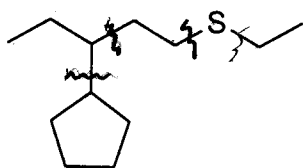
from

Note: **There are no questions to be answered on this page**, it only contains data that may be of use in solving the questions contained in this exam. Not all of the data given is needed.

Value of gas constant: $R = 2.0$ cal deg^{-1} mol^{-1}

Value of e (base for natural logarithms) $e = 2.718$

Value of absolute zero (kelvin) $= -273^{\circ}C$

Partial periodic table of the elements

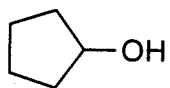| IA													O
1 **H** 1.00794	IIA						IIIA	IVA	VA	VIA	VIIA		2 **He** 4.00260
3 **Li** 6.941	4 **Be** 9.01218						5 **B** 10.811	6 **C** 12.011	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.9984		10 **Ne** 20.1797
11 **Na** 22.9898	12 **Mg** 24.3050		IB	IIB			13 **Al** 26.9815	14 **Si** 28.0855	15 **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
37 **Rb** 85.4678	38 **Sr** 87.62		47 **Ag** 107.868	48 **Cd** 112.411		49 **In** 114.82	50 **Sn** 118.710	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.904	54 **Xe** 131.29
55 **Cs** 132.905	56 **Ba** 137.327		79 **Au** 196.967	80 **Hg** 200.59		81 **Tl** 204.383	82 **Pb** 207.2	83 **Bi** 208.980	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)