FINAL EXAMINATION

Chemistry 3A
Professor Carolyn Bertozzi
Professor Peter Vollhardt
December 11, 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.

161	Baryza,Jeremy	_____	311	Adronov,Alex	_____
111	Goon,Scarlett	_____	321	Mullins,Sarah	_____
121	Yeston,Jake	_____	331	Esker,Todd	_____
131	Gruneich,Jeffrey	_____	341	Shaffer,Wendy	_____
141	Richards,Steven	_____	351	Loftus,Christine	_____
151	Berglund,Timna	_____	411	Lemieux,George	_____
211	Thornton,Joel	_____	421	Essy,Blair	_____
221	Moore,Jennifer	_____	511	Staunton,Joanna	_____
361	Paisner,Sara	_____	521	Magliery,Thomas	_____
371	Tellers,David	_____	531	Marcordes,Belinda	_____

Making up an I-grade_____
(If you are, please indicate the semester during which you took Chem 3A previously_____and the professor _____.)

Please write the answers you want graded in the spaces provided. Do scratch work on the backs of the pages. This test should have 23 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

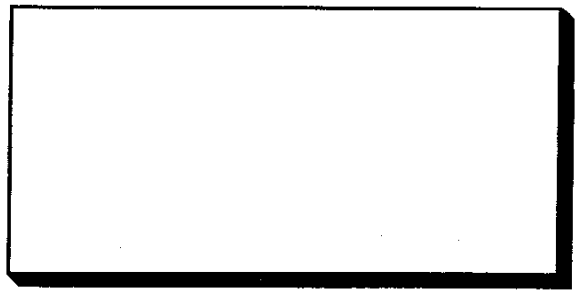
		I.	_____(30)		
		II.	_____(90)		
		III.	_____(35)		
		IV.	_____(60)		
IVa.	_____	V.	_____(45)	VIa.	_____
IVb.	_____	VI.	_____(60)	VIb.	_____
IVc.	_____	VII.	_____(80)	VIc.	_____
Total	_____	Total	_____(400)	Total	_____

I. [30 Points]

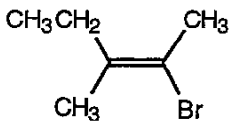
Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary (cis, trans, R, S, and E, Z). Do not forget about the alphabetical ordering of substituents.

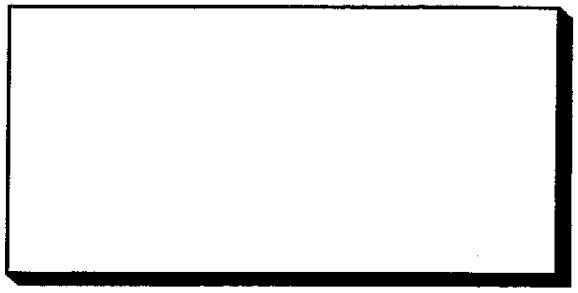
a.

(R)-1-hexen-5-yn-3-ol



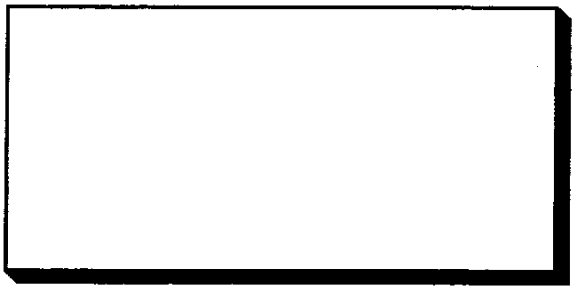
b.





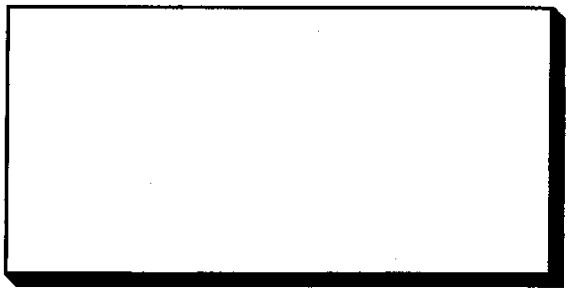
c.

Racemic



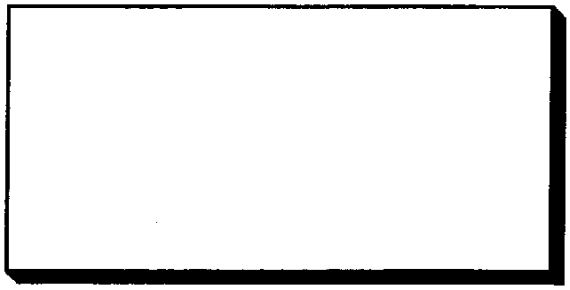
d.

(2R)-4-butyl-4-pentyl-2-propyl-1-nonanethiol



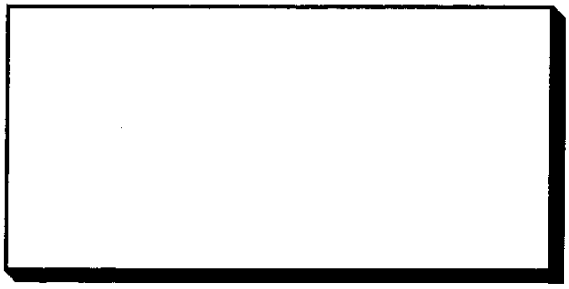
e.

cis-3,7-dimethylcycloheptene



f.

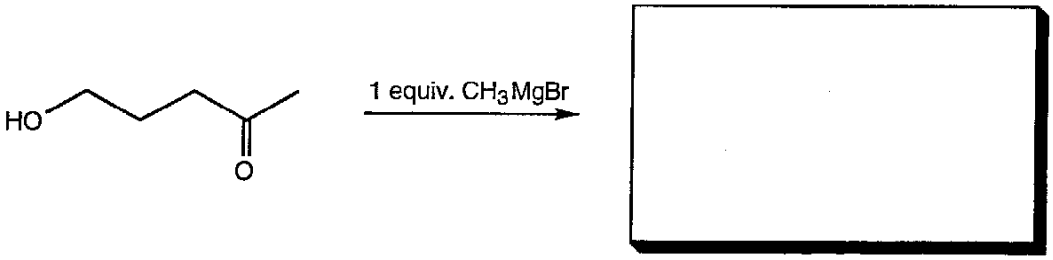
meso-3,4-dichloro-1,5-hexadiene



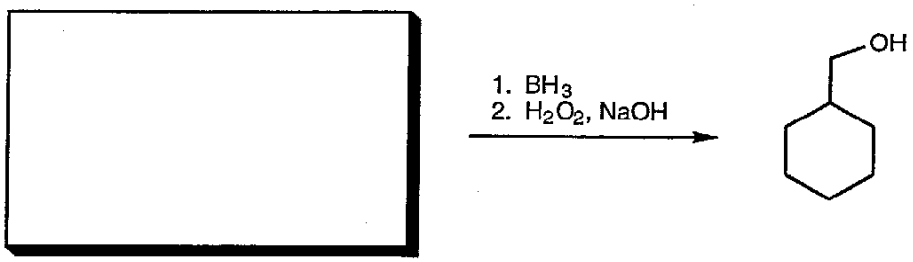
II. [90 points]

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

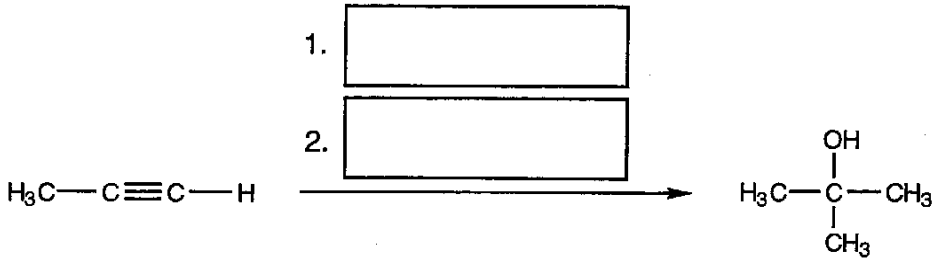
a.



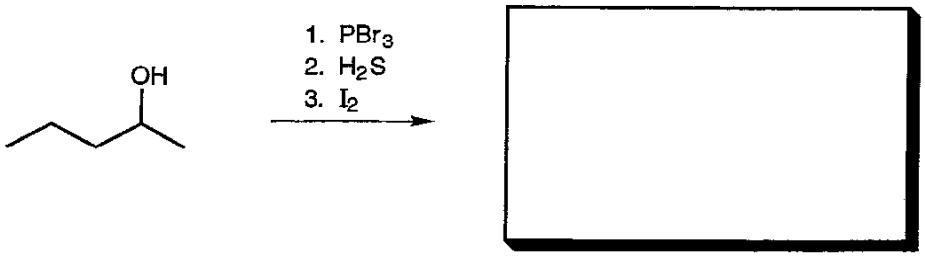
b.



c.

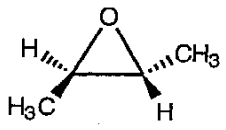


d.

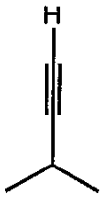


e. $H_3C-C\equiv C-CH_3$

1. [ ]
2. [ ]



f.



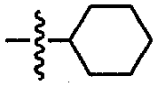
1. HBr, ROOR
2. Li
3. CuI
4. CH_3CH_2Br

[ ]

g.

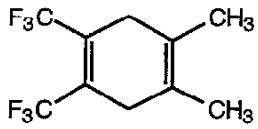
1. R_2BH
2. H_2O_2, NaOH
3. CH_3Li

R =

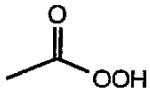


[ ]

h.

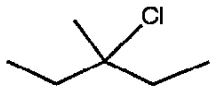


1 equiv.

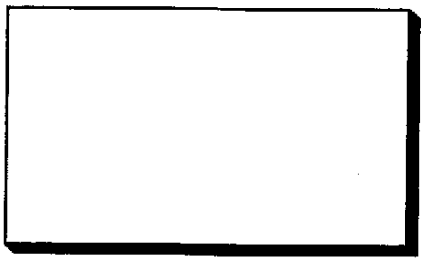


[ ]

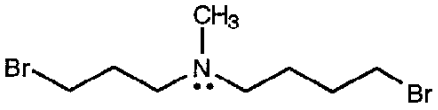
i.



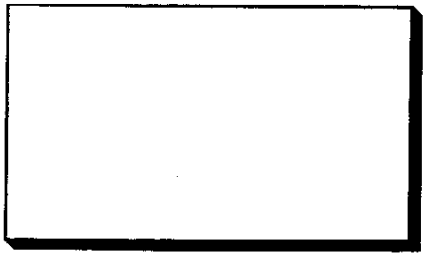
1. $(CH_3)_3CONa$
2. O_3
3. CH_3SCH_3



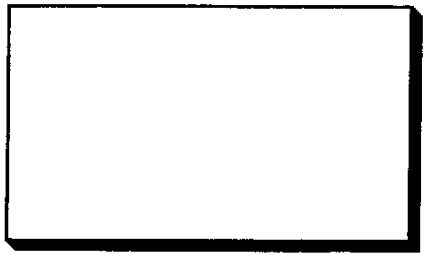
j.



Δ



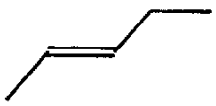
k.



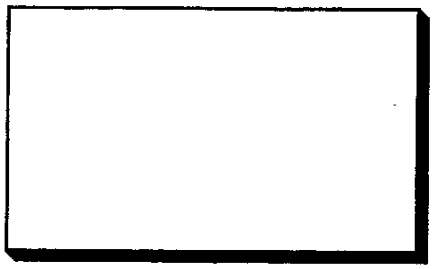
^{13}C NMR: δ 22, 29, 123, 132 ppm

1. H_2, Pd/C
2. Cl_2, hv

l.

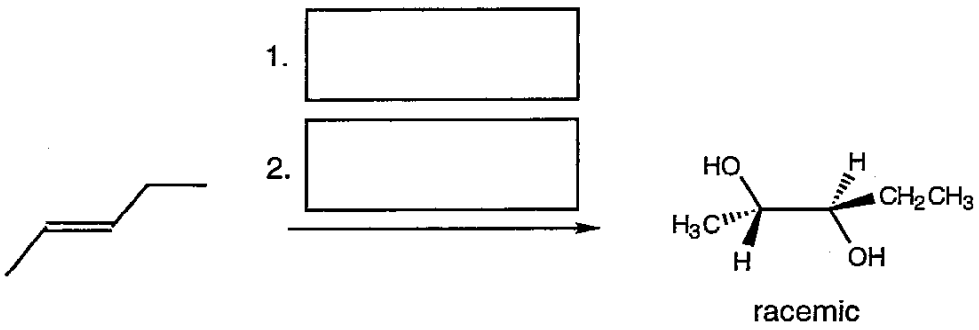


cat. OsO_4, H_2O_2



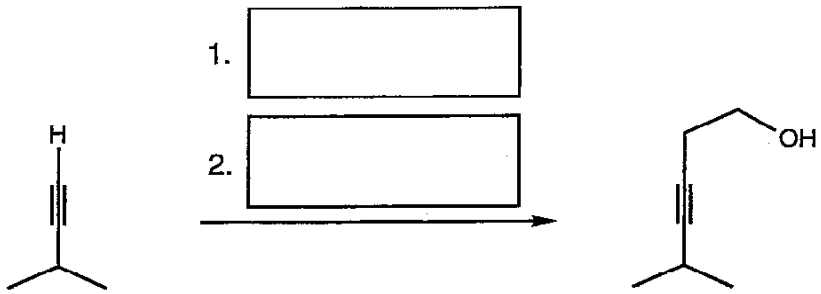
show stereochemistry!

m.

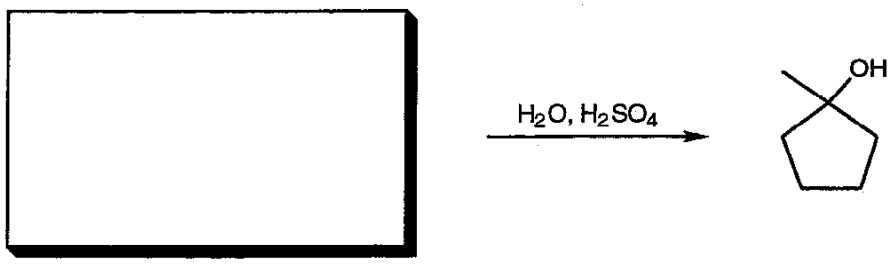


racemic

n.



o.



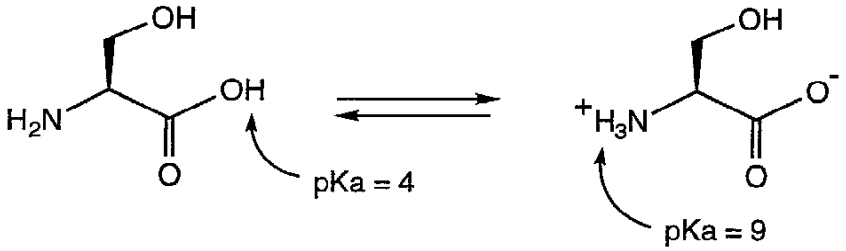
$C_6H_{12}O$

^{13}C NMR: δ 18, 25, 27, 28, 32, 65 ppm

IR: broad peak at 3200-3500 cm^{-1}

III. [35 points]

a. Amino acids such as serine (compound A, shown below) are the building blocks of proteins. Serine can undergo an internal acid-base reaction to give the charge-separated species B as illustrated in equation 1. Using the indicated pKa values, calculate the equilibrium constant K_{eq} for Equation 1. Place your answer in the box provided below. Is the Gibbs free energy ($\Delta G°$) for this reaction positive, negative or zero? (Circle one answer below).



A
(Serine)

B

(Eq. 1)

K_{eq} = ☐

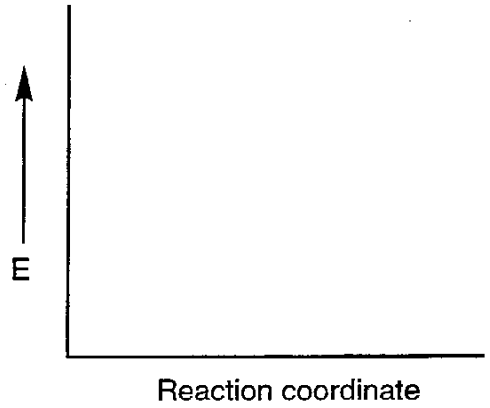
Circle one:

$\Delta G° < 0$

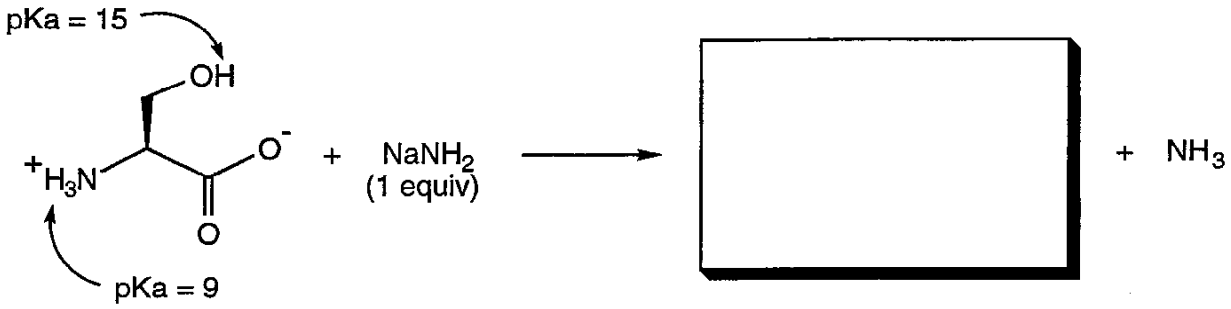
$\Delta G° > 0$

$\Delta G° = 0$

b. Indicate the relative energies of A and B on the potential energy diagram below and indicate $\Delta G°$.



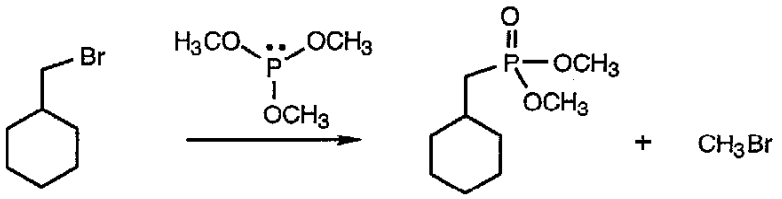
c. When serine is treated with one equivalent of sodium amide ($NaNH_2$), a favorable proton transfer reaction takes place. What is the product of the proton transfer reaction? Place your answer in the box provided below. (Hint: consider the indicated pKa's. The pKa of NH_3 is 32).



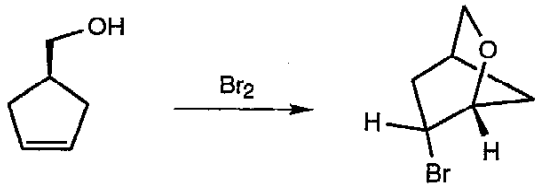
IV. [60 points]

Write detailed step-wise mechanisms for the following transformations. Use only structures and "arrow-pushing" techniques. Note: These are NOT synthetic problems. Do NOT add any other reagents.

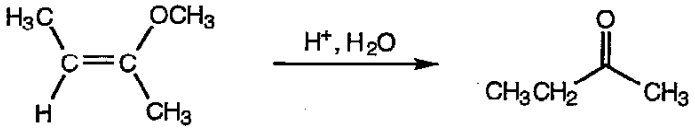
a.



b.



c.



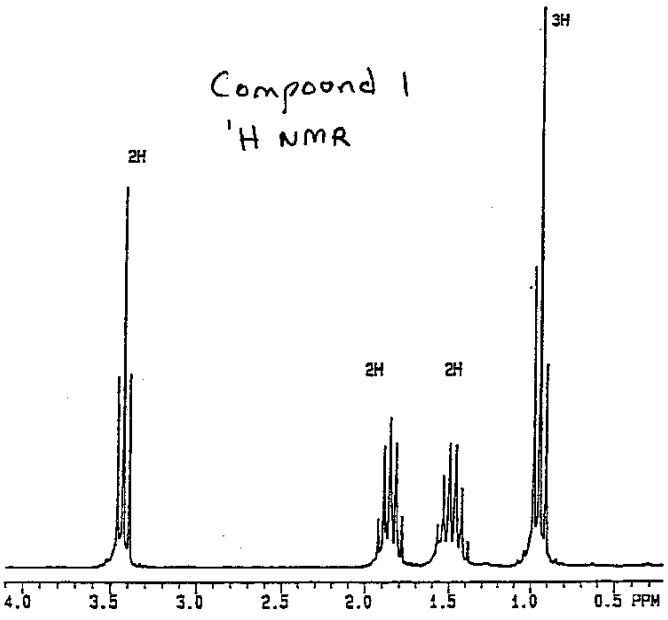
V. [45 points]

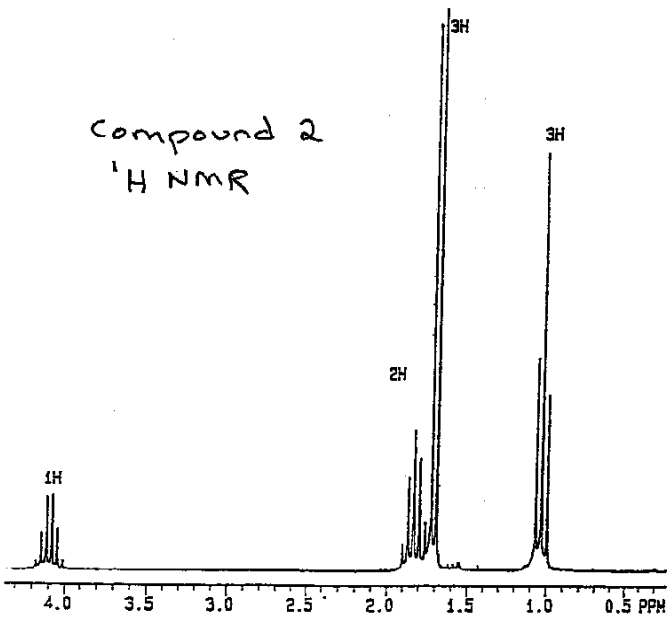
The reaction of 1-butene in an open reaction flask with HBr gives a mixture of two products, compounds 1 and 2, the NMR and IR spectra of which are shown below.

a. Provide structures for compounds 1 and 2 in the boxes provided using the information in the spectra. Make peak assignments on the ^{1}H NMR spectra for both compounds showing which protons give rise to which peaks (i.e., label the unique sets of protons a, b, c...etc. on your structures in the boxes, and label the corresponding peaks in the ^{1}H NMR spectra for compounds 1 and 2 with the same letters).

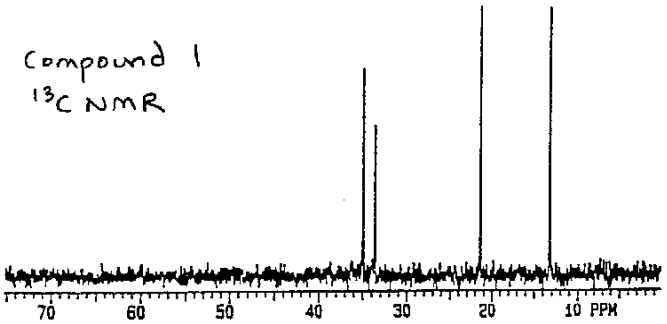
compound 1

compound 2

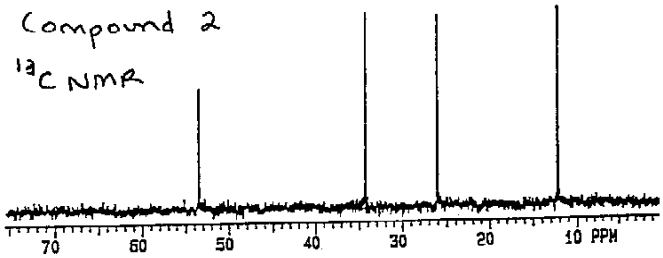


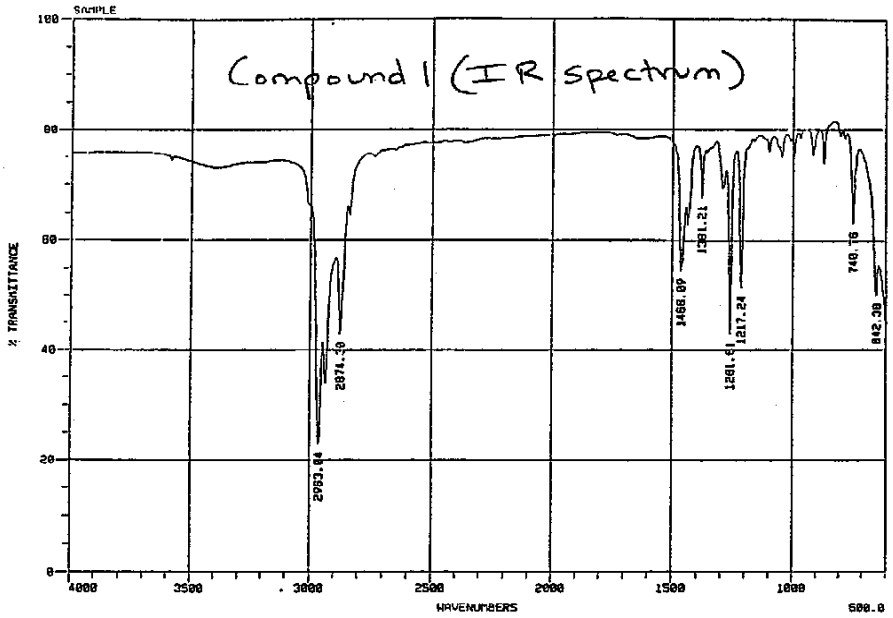


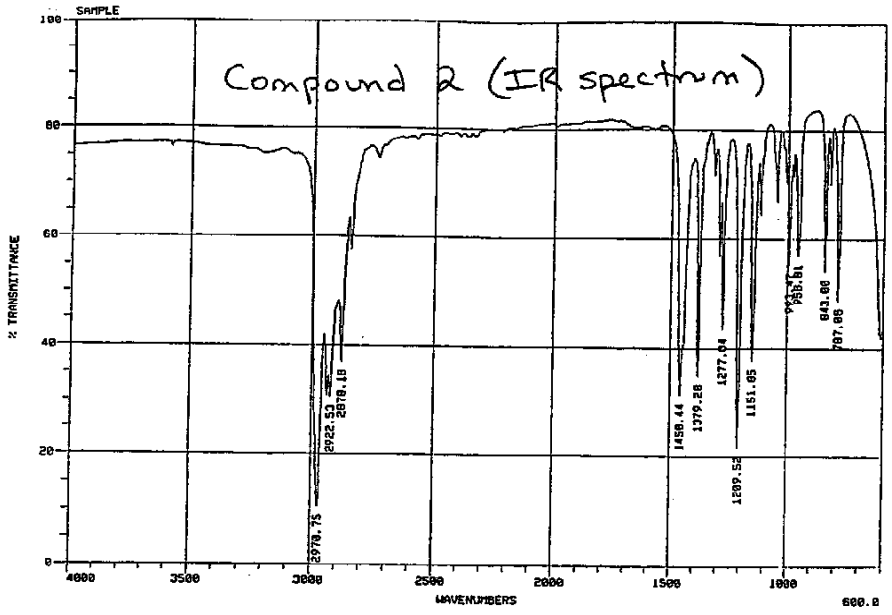
Compound 1
^{13}C NMR



Compound 2
^{13}C NMR



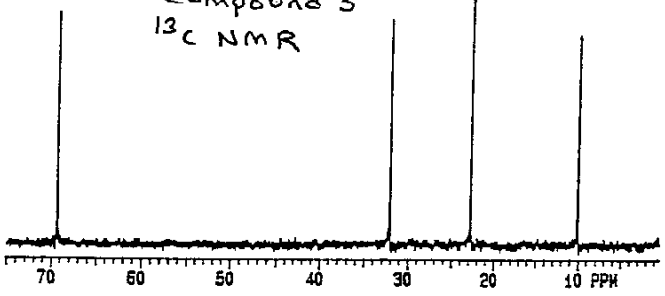




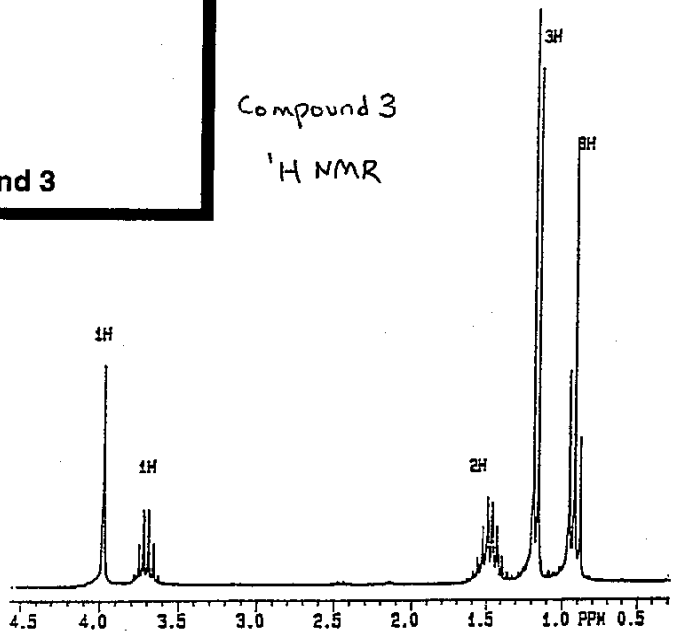
b. **When compound 2 is stored in a humid environment, it slowly converts to compound 3. Provide a structure for compound 3 in the box provided using the information in the NMR and IR spectra below. Explain your answer by identifying the characteristic peaks in the ^{1}H NMR and IR spectrum.**

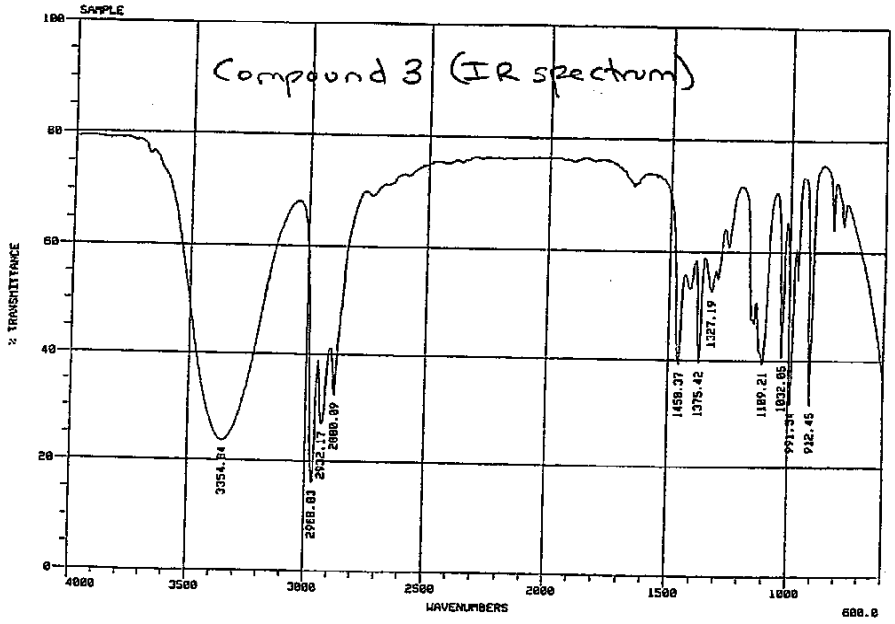
compound 3

Compound 3
^{13}C NMR



Compound 3
^{1}H NMR

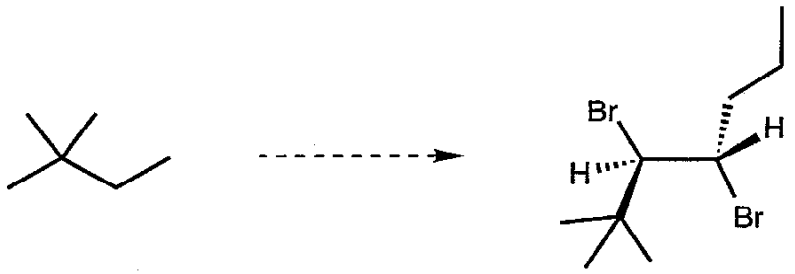




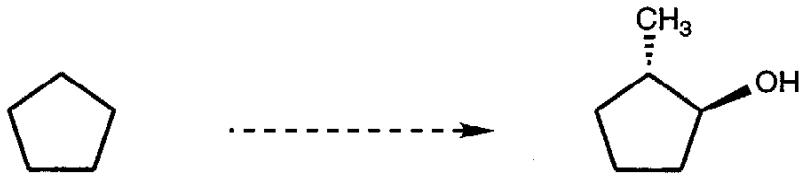
VI. [60 points]

Provide a viable synthetic route from starting material to product. Several steps are required in each case; there may be several solutions to each problem but you should use only one. It is best to work backwards first (retrosynthetically), and then formulate your synthesis in the forward direction. In addition to the starting structure, you may use any additional organic or inorganic compounds containing four carbons or less, except for problem c in which the starting structure is the only available organic starting material.

a.



b.



c.

as the only organic starting material (i.e., make all your required organic pieces from this compound).

VII. [80 Points]

Mark the answer in each of the following multiple choice problems that you deem most correct.

a. Which of the following resonance structures is the major contributor to the overall structure?

A **B**

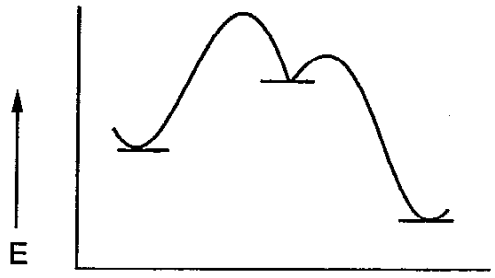
_____A, because it retains the triple bond.

_____B, because the charges are further apart.

_____A, because C, N, and B have octets.

_____B, because CH_3 stabilizes the adjacent positive charge.

b. The following potential energy diagram fits which one of the reactions shown?



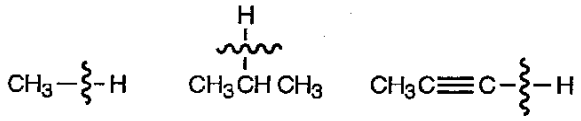
_____$(CH_3)_3CCl + H_2O$

_____$CH_3Cl + {}^-OH$

_____$(CH_3)_3CCl + (CH_3)_3CO^-$

_____$(CH_3)_3COH + N_3^-$

c.



1 2 3

The correct order of <u>increasing</u> strength of the marked bonds is: (i.e., weakest, middle, strongest)

_____1, 2, 3

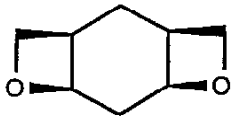
_____3, 2, 1

_____2, 1, 3

_____2, 3, 1

_____Other (specify): _____ , ____ , ____

d. **The ^{13}C NMR spectrum of A shows the following number of lines:**



A

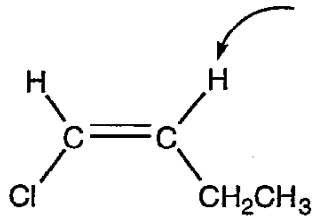
_____eight

_____four

_____five

_____three

e.



The marked hydrogen is expected to show the following splitting pattern in the ^1H NMR spectrum:

_____doublet, J_{trans} = 16 Hz

_____doublet, J_{cis} = 9 Hz

_____doublet of triplets

_____septet

f. **The heat of formation ($\Delta H°$) of CH_3CH_3 (-20.2 Kcal/mol) and CH_3CH_2OH (-66.3 Kcal/mol) differ by 46.1 Kcal/mol. Therefore, their heats of combustion will:**

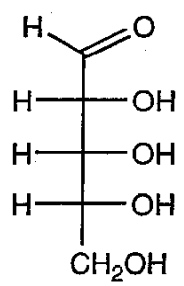
_____not be comparable because they are not isomers.

_____differ by the same amount.

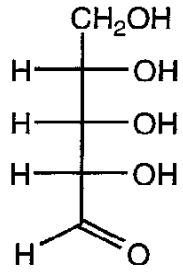
_____be -46.1 Kcal/mol.

_____be -(66.3 + 46.1) = -112.4 Kcal/mol.

g.



A



B

Compounds A and B are:

_____**diastereomers**

_____**enantiomers**

_____**identical**

_____**constitutional isomers**

h.

1 **2** **3** **4**

The order of increasing acidity of 1-4 is:

_____**1, 2, 3, 4**

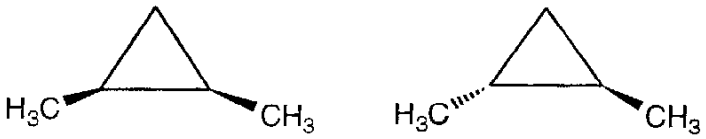
_____**4, 3, 2, 1**

_____**3, 4, 2, 1**

_____**1, 2, 4, 3**

_____**Other (specify):** _____, _____, _____, _____

i.



A B

Can you make a structural assignment of the two isomers A and B using NMR spectroscopy? (i.e., can you distinguish which is which?)

_____yes, because A has a mirror plane.

_____no, because stereoisomers have similar spectra.

_____no, because each compound has four chemically unique hydrogens with identical connectivity.

_____yes, because A has four, whereas B has only three chemically unique hydrogens.

j. The role of a catalyst is:

_____to shift the reaction equilibrium.

_____to initiate a reaction.

_____to accelerate a reaction.

_____to trap reactive intermediates.