FINAL EXAMINATION

Chemistry 3A
Professor K. Peter C. Vollhardt
May 13, 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.

111	J. YANG	______
121	J. LOESER	______
131	D. LARSON	______
141	I. CHOONG	______
151	M. GOODWIN	______
161	E. CHAN	______
171	J. SELL	______
211	S. PAIKOFF	______
221	J. STAUNTON	______
311	J. YANG	______
321	T. ESKER	______
331	J. SELL	______
341	T. GOUNTCHEV	______
351	D. HOLMES	______
361	E. CHAN	______
371	T. LEE	______
381	H. CHANG	______
411	J. FULLER	______
421	B. BAXTER	______
431	J. CHIN	______
441	M. SCHULTZ	______
511	D. CARROLL	______
521	D. GRAY	______
531	J. STAUNTON	______
541	J. LOESER	______
551	S. KUMARASWAMY	______

Making-up an I grade ______

(If you are, please indicate which semester you previously took Chem 3A ________________.)

Please write the answer you want graded in the space provided. Do scratch work on the back 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!** Grades will be posted on Friday, May 17, outside 305 Latimer Hall (Lab Q). **Good Luck!**

DO NOT WRITE IN THIS SPACE

IVa. ____________
IVb. ____________
IVc. ____________
Subtotal ____________

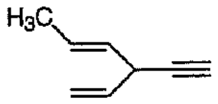
I. ____________ (30)
II. ____________ (90)
III. ____________ (30)
IV. ____________ (60)
V. ____________ (50)
VI. ____________ (60)
VII. ____________ (80)
Total ____________ (400)

VIa. ____________
VIb. ____________
VIc. ____________
Subtotal ____________

I. [30 Points]

Provide the IUPAC name or draw the structure, as appropriate, of the following molecules. Remember the priority of functional groups in choosing names, indicate the correct stereochemistry (e.g. R, S, and E, Z), and do not forget about the alphabetical ordering of substitutents!

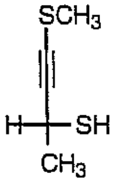
a.



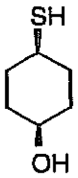
b.

(Z)-4-Chloro-3-methyl-3-penten-1-ol

c.



d.



e.

(S)-1-Bromo-2,4-dimethoxycyclopentene

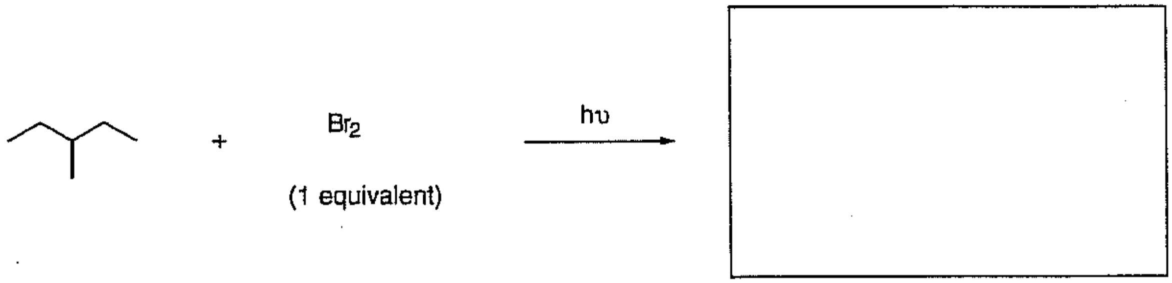
f.

meso-2,3-Dibromobutane
(Draw in a Fischer Projection)

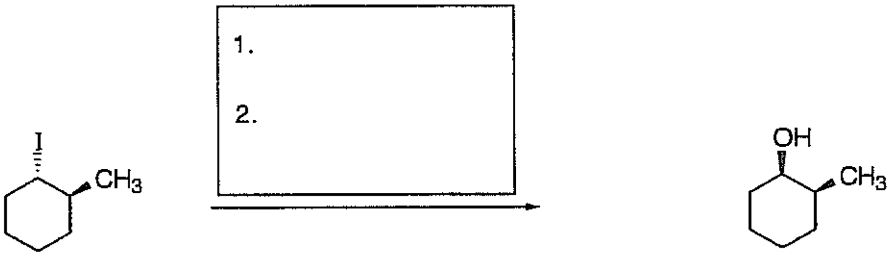
II. **[90 Points]**

Add the missing components (starting materials, reagents, or products) of the following reactions in the boxes provided. Aqueous work-up (when required) is assumed to be part of a step. It is not part of any answer.

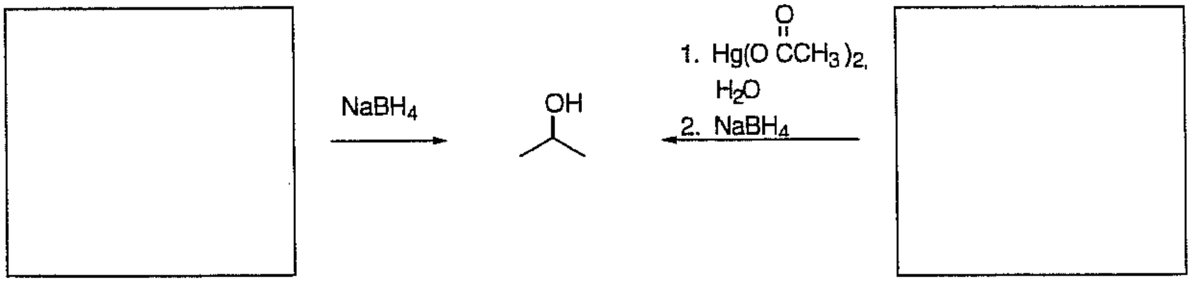
a.



b.



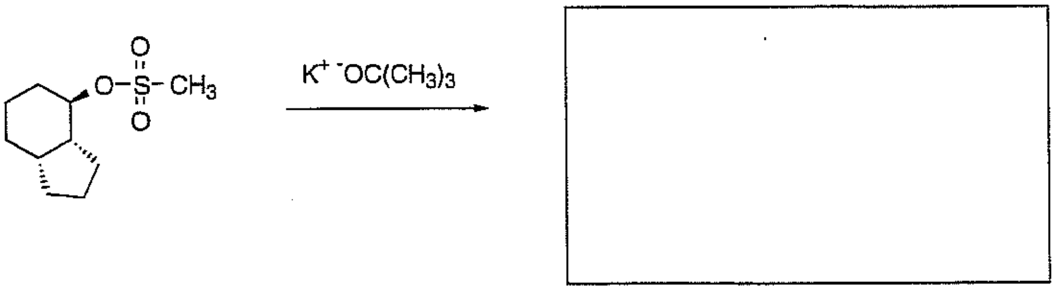
c.



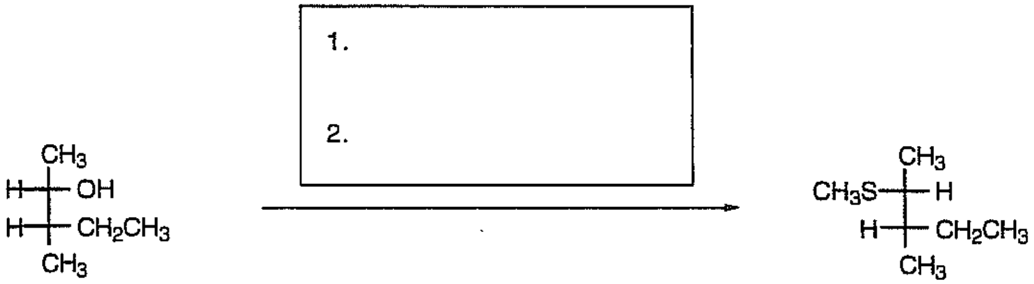
^1H NMR: $\delta = 2.01(s)$

^{13}C NMR: $\delta = 19.4$, 115.9, 133.4 ppm

d.

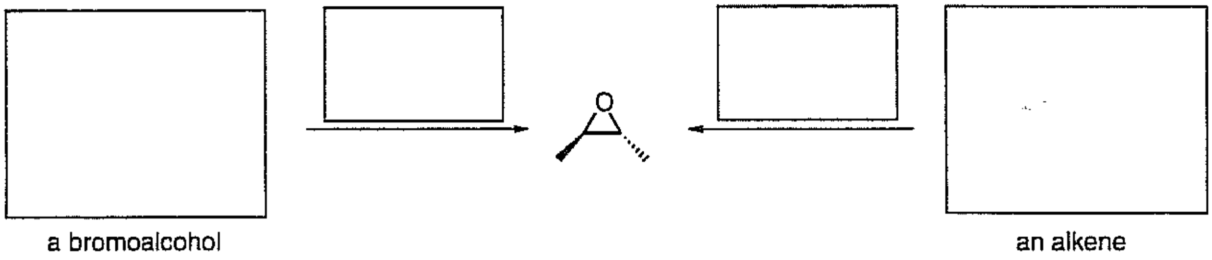


e.



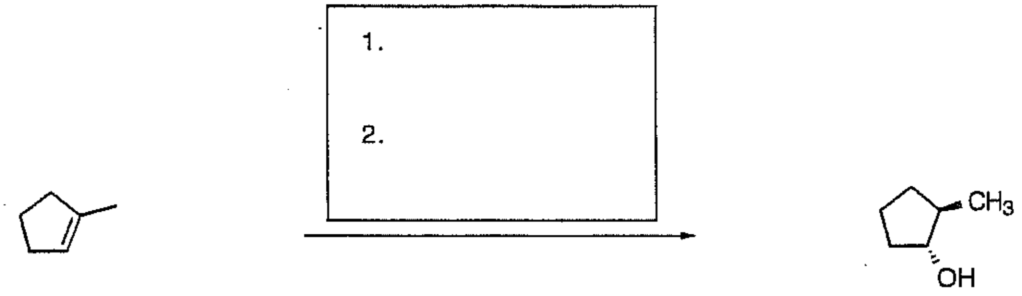
1.
2.
CH3
H
OH
H
CH2CH3
CH3
CH3
CH3S
H
H
CH2CH3
CH3

f.



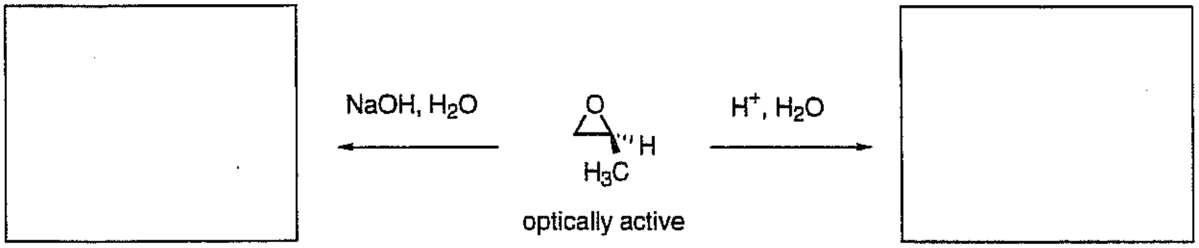
O
a bromoalcohol
an alkene

g.



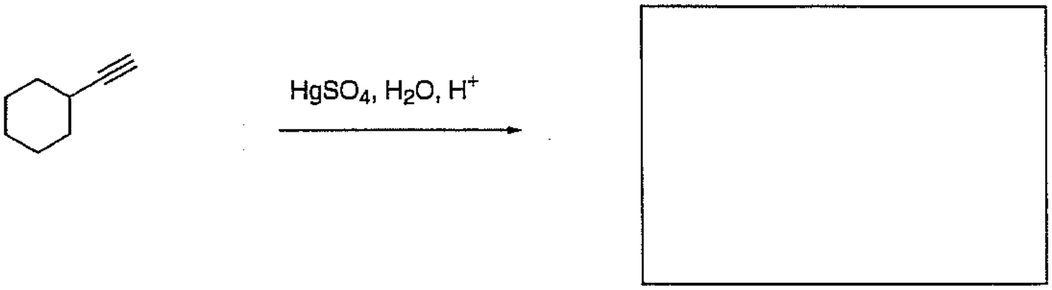
1.
2.
CH3
OH

h.



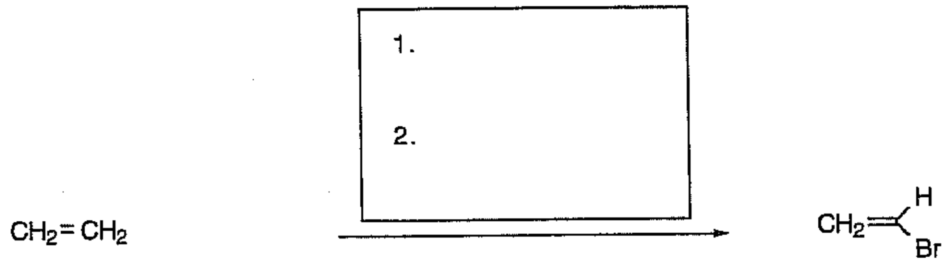
NaOH, H2O
O
H
H3C
optically active
H+, H2O

i.



HgSO4, H2O, H+

j.



k.

$$\boxed{} \xrightarrow[\text{2. } H_2\text{, Pt}]{\text{1. } O_3} \boxed{}$$

$C_7H_{10}O$

^{13}C NMR : 3 $C_{sp}2$ signals, 2 $C_{sp}3$ signals

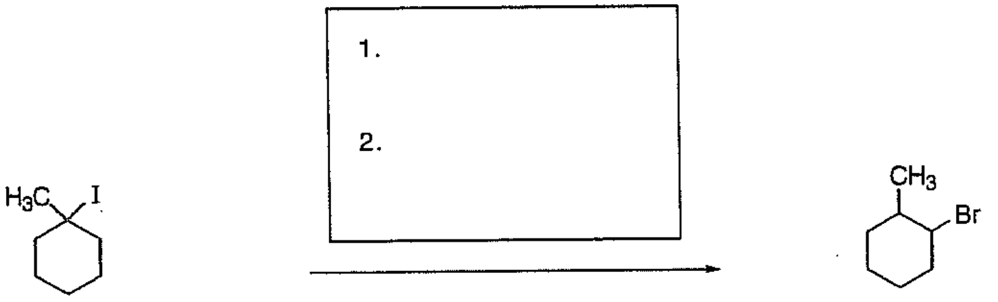
^{1}H NMR : $\delta = 5.5$ (2H), 1.9 (4H), 2.1 (4H)

$C_6H_8O_2$

^{13}C NMR : 1 $C_{sp}2$ signal, 1 $C_{sp}3$ signal

1H NMR : $\delta = 2.0$ singlet

l.



mixture of cis and trans

III. **[30 Points]**

The hydrogenation of alkenes to alkanes requires a transition metal catalyst to proceed at reasonable rates. One could also conceive of a free-radical-initiated chain mechanism. An example would be the peroxide-initiated hydrogenation of propene.

a. Write the two propagation steps for the radical chain reaction:

Step 1

Step 2

b.

ΔH°_f ($CH_3CH = CH_2$) = 5 kcal mol^{-1}

ΔH°_f ($CH_3CH_2CH_3$) = -25 kcal mol^{-1}

Given the above ΔH°_f data, calculate the heat of hydrogenation of propene.

$\Delta H^\circ =$

c. Considering the following data (in addition to those given in b), estimate the ΔH° values for the two propagation steps and recalculate the ΔH° for the overall reaction from these values.

DH° H-H 104 kcal mol^{-1}

ΔH°_f  + 21 kcal mol^{-1}

Step 1 $\Delta H^\circ =$

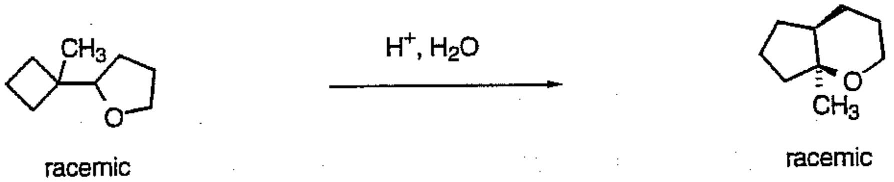
Step 2 $\Delta H^\circ =$

ΔH° (hydrogenation) =

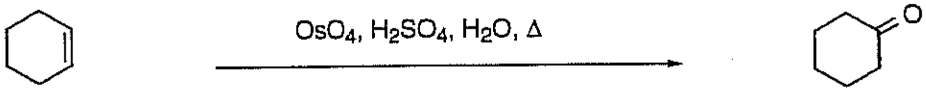
IV. **[60 Points]**

Write detailed step-wise mechanisms for the following transformations. Use only structures and "arrow-pushing" techniques. Note: These are <u>not</u> synthetic problems. Do not <u>add</u> any reagents! What you see is what you have!

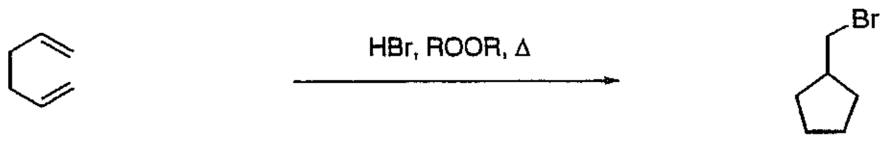
a.



b.



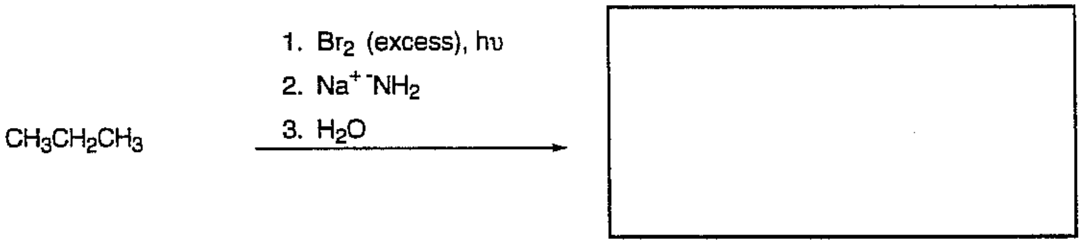
c.



Hint: Remember the free radical polymerization of alkenes.

V. **[50 Points]**

Free radical bromination of propane with excess bromine, followed by treatment with Na+ ⁻NH2 and aqueous work-up, gave a mixture of compounds. Fractional distillation furnished a colorless liquid A, C_3H_3Br, b.p. 89°C, exhibiting the spectra shown.

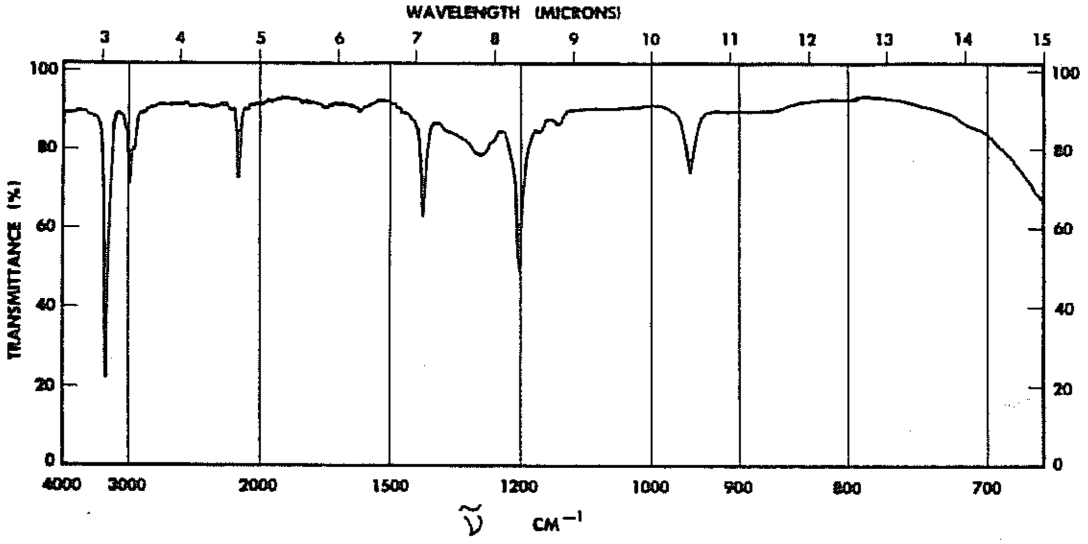


A

a. Write the structure of **A** in the box above, after analyzing the spectral data.

b. Interpret the spectral data as requested in the spaces provided.

1. IR Spectrum.



IR Spectrum

State whether the indicated funtionality is absent or present (circle the correct statement) and provide the expected or observed position of the corresponding peak in the spectrum.

C_{sp^3}-H present / absent at cm^{-1}

C_{sp^2}-H present / absent at cm^{-1}

C_{sp} -H present / absent at cm^{-1}

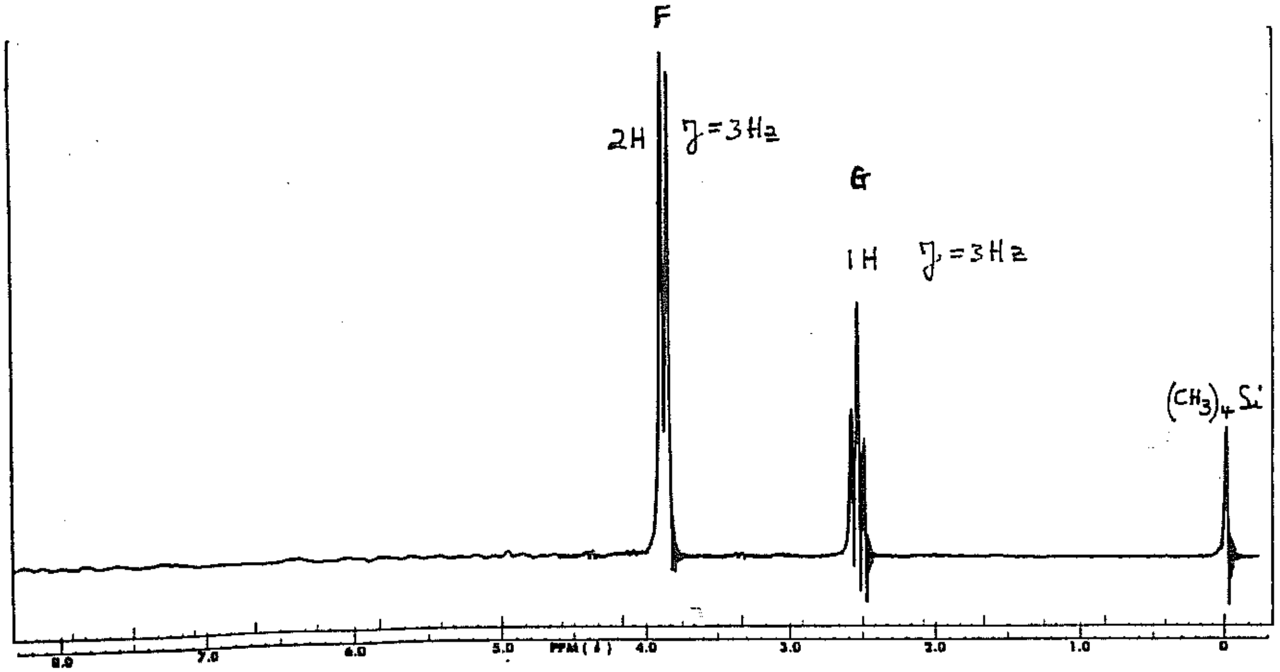
C≡C present / absent at cm^{-1}

O-H present / absent at cm^{-1}

2. ^{13}C NMR Spectrum $\delta = 82.0$(**D**), 73.8(**E**), 21.3(**F**)ppm.

Draw your suggested structure for **A** in the box, and label the carbon atoms **D**, **E**, and **F** giving rise to the corresponding signals in the spectrum. Note: make an arbitrary choice between the assignments for **D**, **E**.

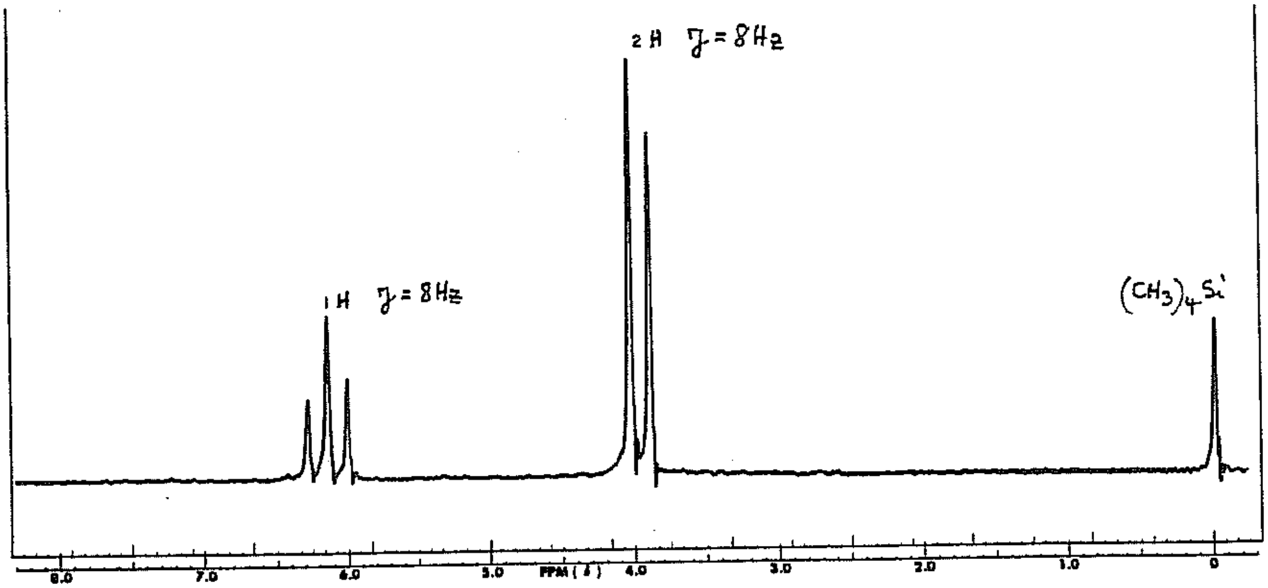
3. ^{1}H NMR Spectrum



NMR Spectrun

Draw your suggestion for **A** in the box, and label the hydrogens **F** and **G** giving rise to the corresponding signals in the spectrum.

c. The residue of the distillation resulting in **A** contained (among other products) a liquid **B**, $C_3H_3Br_3$, the ^1H NMR Spectrum of which is shown below:



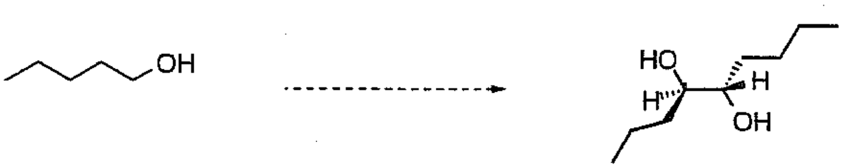
What is **B** ?

B

VI. [60 Points]

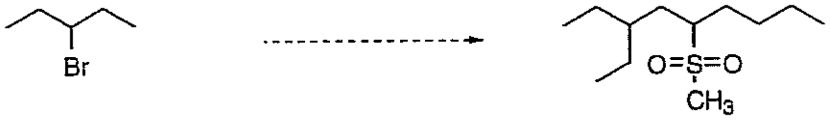
Show synthetic connections (reagents, intermediates; no mechanisms!) between the following starting materials and the final products. Note: several steps are required in each case; there may be several solutions to each problem, but you should use only one; it is best to work backwards (retrosynthetically), to enable you to dissect the products into less complex precursors; in addition to the starting structure, you may use any organic and organometallic reagents containing four carbons or less.

a.



b.

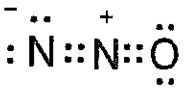
c.



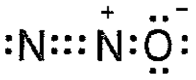
VII. **[80 Points]**

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

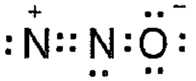
a. The best resonance structure for N_2O is:

______ 

$:\overset{-\,\cdot\cdot}{N}::\overset{+}{N}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}$

______ 

$:N:::\overset{+}{N}:\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{O}}:$

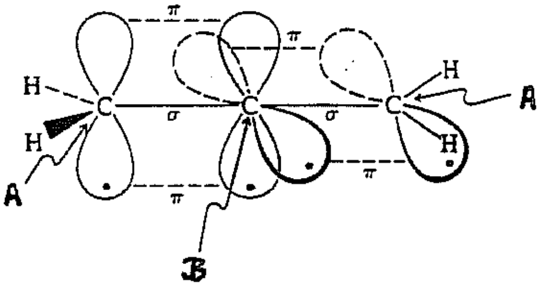
______ 

$:\overset{+}{N}::\underset{\cdot\cdot}{N}:\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{O}}:$

______ 

$:\overset{\cdot\cdot}{N}:\underset{\cdot\cdot}{N}::O\vdots$

b. Allene, $H_2C{=}C{=}CH_2$, has the orbital arrangement shown below:



The hybridization at carbons **A** and **B** is, respectively:

______ $\mathbf{A}_{sp}\ \mathbf{B}_{sp^2}$

______ $\mathbf{A}_{sp^3}\ \mathbf{B}_{sp}$

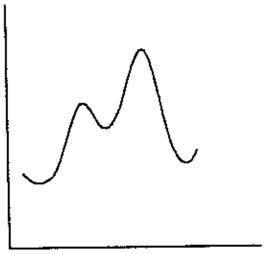
______ $\mathbf{A}_{sp^2}\ \mathbf{B}_{sp}$

______ $\mathbf{A}_{sp^2}\ \mathbf{B}_{sp^2}$

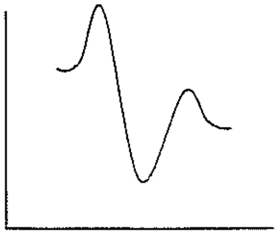
c. The reaction proflie for the following reaction is: .

$$(CH_3)_3CI \quad + \quad Cl^- \xrightarrow{\text{acetone}} (CH_3)_3CCl \quad + \quad I^-$$

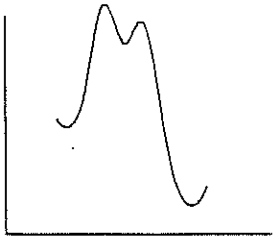
______



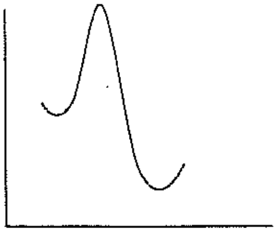
______



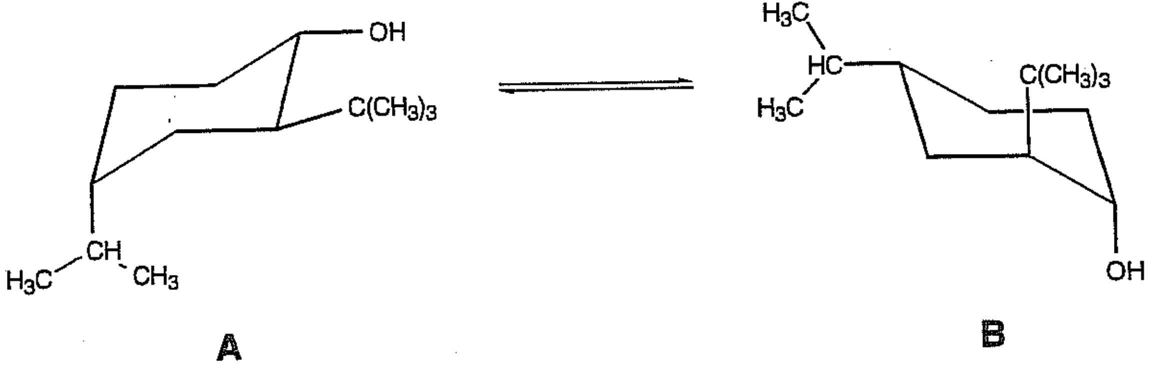
______



______



d. Consider the following conformational equilibrium and the $\Delta G°$ values for axial - equatorial conversion of the given group in substituted cyclohexane:



$\Delta°G(\text{axial} \rightarrow \text{equatorial, kcal mol}^{-1})$:		
	HO	-0.9
	$(CH_3)_3C$	-5.0
	$(CH_3)_2CH$	-2.2

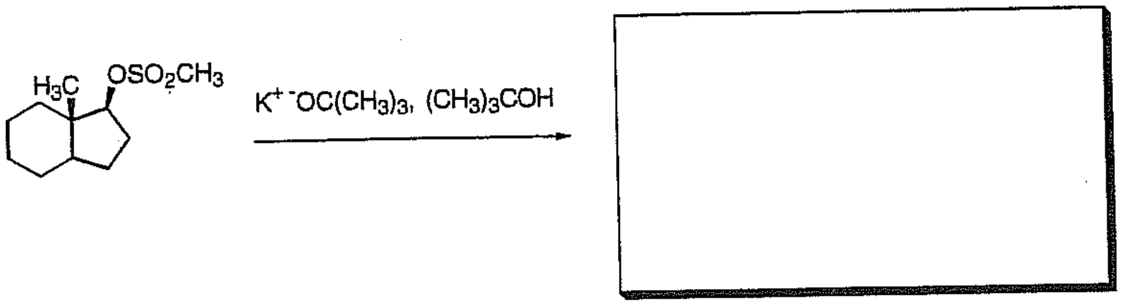
_____ **A** is more stable than **B** by 5 kcal mole^{-1}

_____ **A** is more stable than **B** by 3.7 kcal mole^{-1}

_____ **A** is more stable than **B** by 8.1 kcal mole^{-1}

_____ **A** is less stable than **B** by 2.8 kcal mole^{-1}

e. Draw the product of the following reaction and circle the appropriate entry below the scheme.

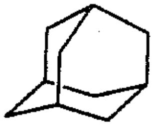


Mechanism: SN2 SN1 E2 E1

Changing the alkoxide to $CH_3O^-K^+$ causes <u>one</u> of the following ratios to increase:

E2 / E1 SN2 / E2 SN1 / E1 E2 / SN2

f. The structure of adamantane is shown below:



adamantane

The number of ^{13}C NMR signals observed for this hydrocarbon is:

______ one

______ two

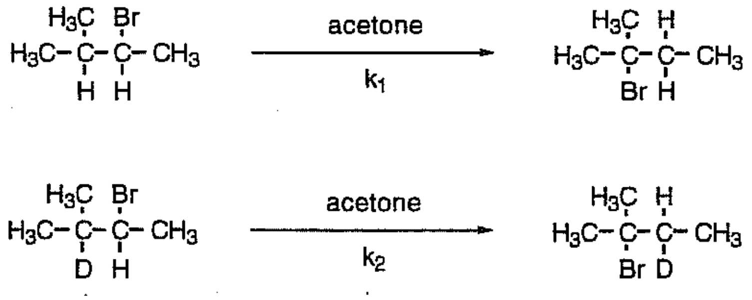
______ six

______ nine

g. Indicate the correct pK_a sequence for the following compounds:

	CH_3OH	NH_3	$HC \equiv CH$	$H_2C = CH_2$
______	0	16	30	50
______	15.5	35	25	44
______	7	12	18.5	32
______	14	0	16	20

h. Consider the relative rates of the following rearrangements:



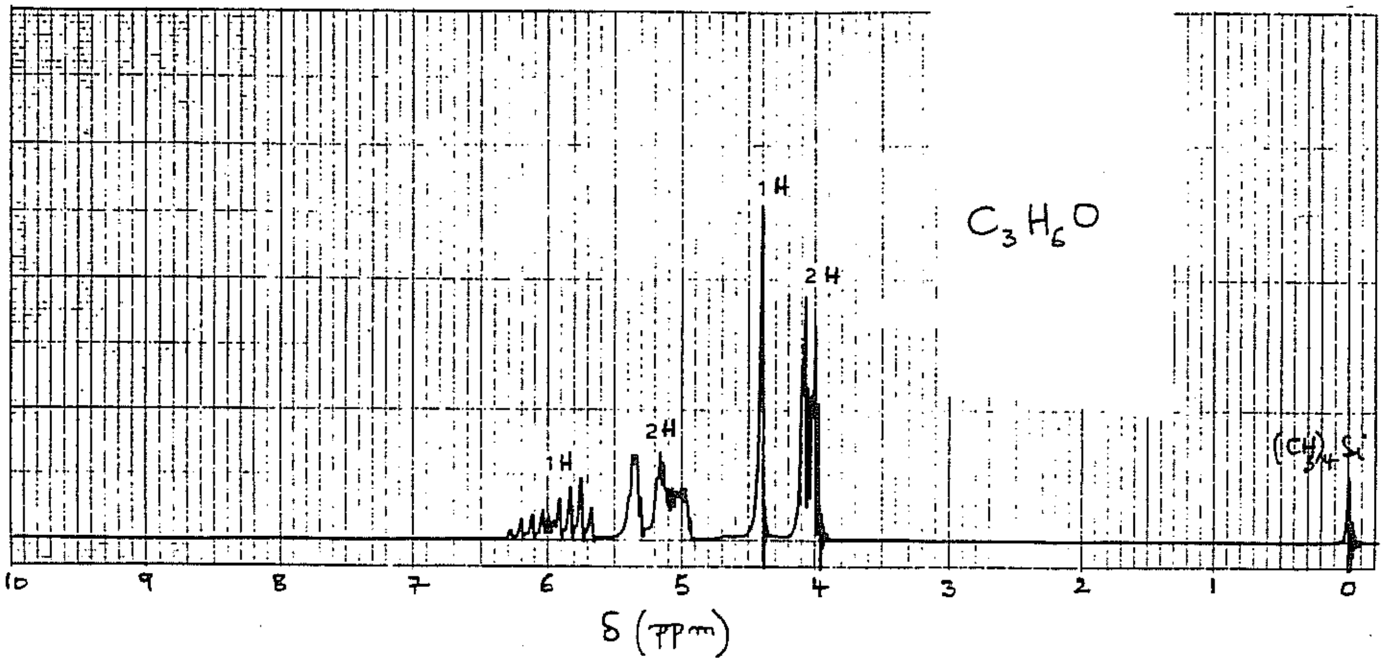
_____ $k_1 = k_2$

_____ $k_1 > k_2$

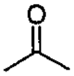
_____ $k_1 < k_2$

_____ $k_1 = 0,\ k_2 = 4-6$

i. A compound, C_3H_6O, exhibits the ^1H NMR spectrum shown:

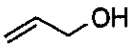


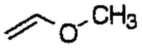
Which isomer of C_3H_6O fits the spectrum?

____ 

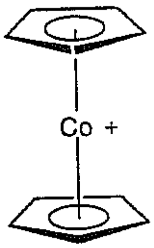
____ 

____ 

____ 

____ 

j. Cobalt has nine valence electrons. In the cobaltocinium ion **A**, cobalt has an electron shell of:



A

____ 18 electrons

____ 16 electrons

____ 14 electrons

____ 20 electrons