FINAL EXAMINATION

Chemistry 3A
David MacMillan
Arlyn Myers
Peter Vollhardt
May 17, 1999

Name:_____
[Print first name before second! Use capital letters!]

Please check the name of your TA and corresponding section number. Complete the remaining information if applicable.

111	Joe Ringgenberg	____	361	Ryan Smith	____
121	Polly Berseth	____	371	Kristina Haman	____
131	Jun Yin	____	381	Jocelyn Grunwell	____
141	David Nauman	____	391	Kathy Winans	____
151	Jeff Janes	____	411	David Gray	____
211	Jennifer Tripp	____	421	Sara Paisner	____
221	David Tully	____	431	Scarlett Goon	____
311	Jason Robinson	____	511	Andy Martin	____
321	Alex Adronov	____	521	Fabian Fischer	____
331	Matt Purdy	____	531	Tony Tang	____
341	Greg Watkins	____	541	Marcus Strawn	____
351	Lily Huang	____	551	Lei Wang	____
Making up an I Grade		____			

(If you are, please indicate the semester during which you took previous Chem 3A previously _____).

There is a periodic table at the end of the test. Please write the answer you wish to be graded in the spaces provided. Do scratch work on the back of the pages. This test should have 22 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 Thursday, May 20, 1 pm, outside 305 Latimer Hall (Lab Q). **Good Luck!**

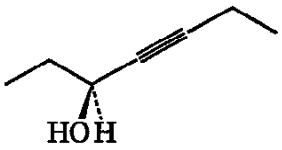
DO NOT WRITE IN THIS SPACE

I.	____	(30)
II.	____	(90)
III.	____	(40)
IV.	____	(50)
V.	____	(60)
VI.	____	(60)
VII.	____	(70)
Total:	____	(400)

I. [30 Points]

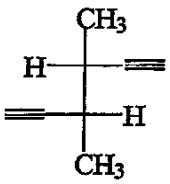
Provide the IUPAC name or draw the structure, as appropriate, of the following molecules. Remember the priority of functional groups in choosing names, indicate the correct stereochemistry (e.g. *R*, *S*, and *E*, *Z*), and do not forget about the alphabetical ordering of substituents!

a.



b. *Trans*-2 -(1-methylethenyl)cyclohexanethiol

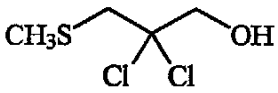
c.



3

d. (1*S*, 3*S*)-1-Ethoxy-1,3-dimethoxycyclohexane

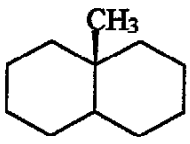
e.



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.

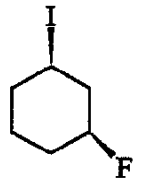
a.

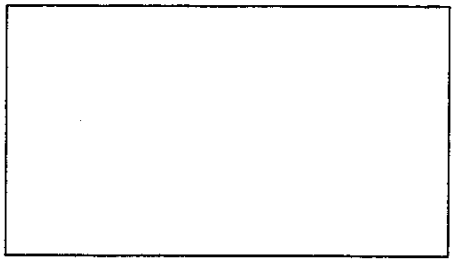


+ Br_2 $\xrightarrow{h\nu}$

bromo substituent trans to methyl

b.



+ ^{-}CN ⟶ 

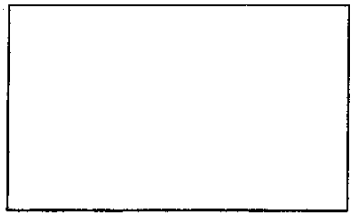
S_N2 product

c.

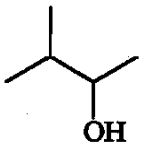
1.
2. $(CH_3)_2S$
3.

⟶ CH_3CH_2OH

d.



1.
2.

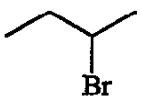
⟶ 

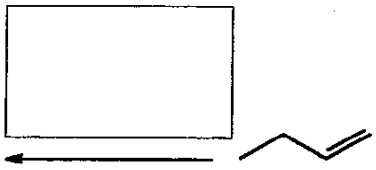
$C_4H_{10}O$

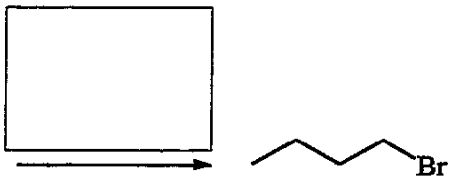
^{1}H NMR δ = 0.90 (d, 6H), 1.75 (nonet, 1H), 3.35 (d, 2H), 3.90 (br s, 1H) ppm.

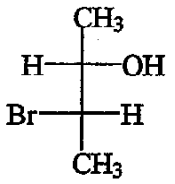
^{13}C NMR δ = 19.0, 31.1, 69.7 ppm.

e.



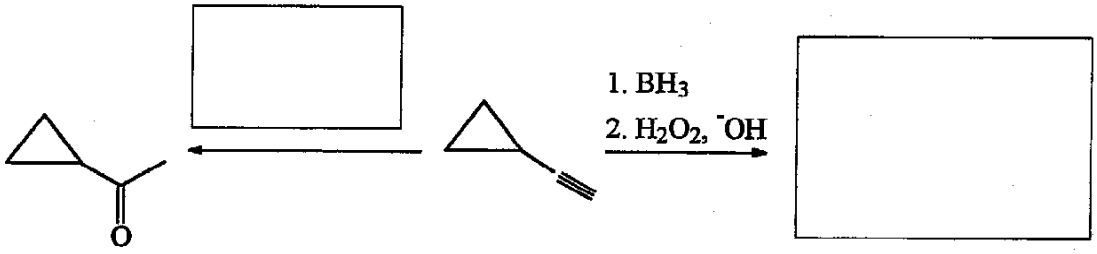




f. 

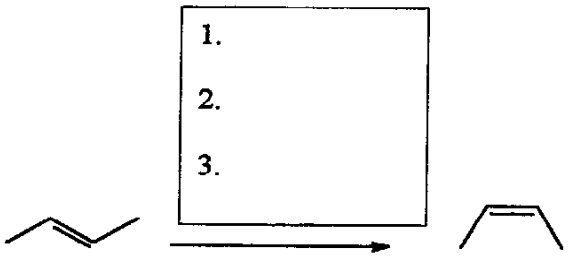
NaOH → [ ]

C_4H_8O

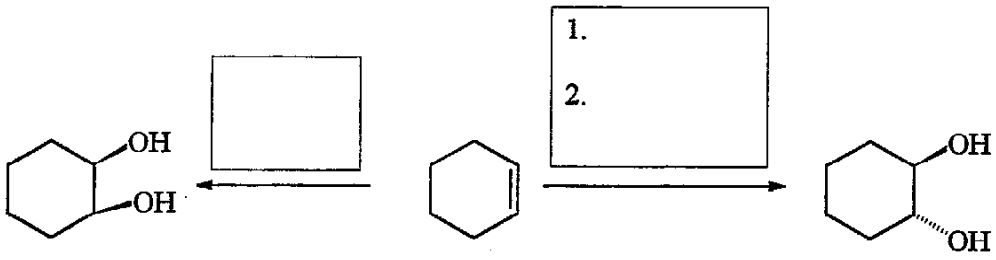
g. 

h. $H_2C{=}CH_2$ → (1. Br_2; 2. $NaOCH_3$ (1 equiv.); 3. Li; 4. CuI; 5. 

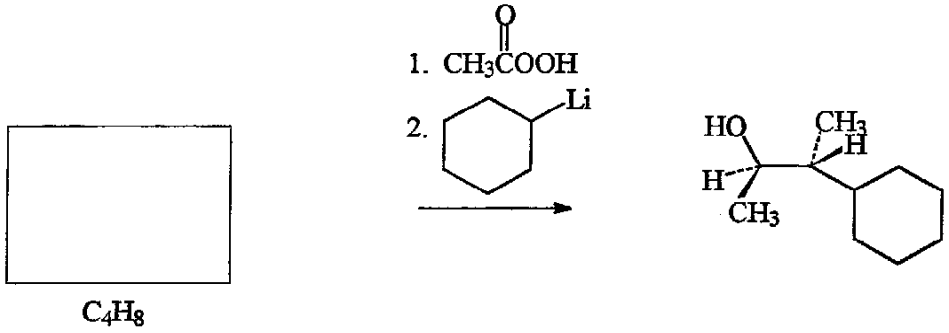
) → [ ]

i. 

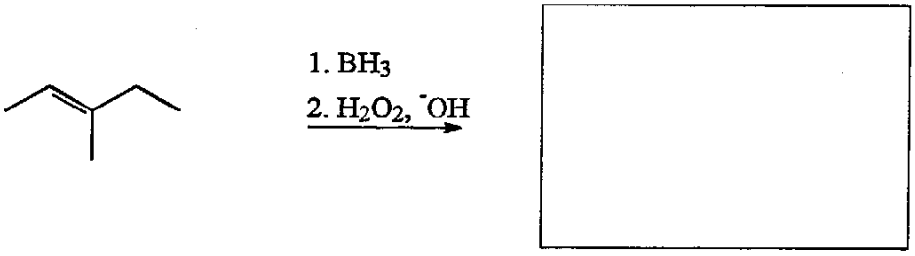
j.


OH
OH
1.
2.
OH
OH

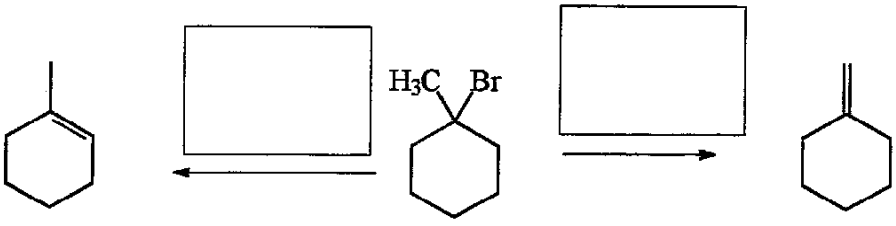
k.


C4H8
1. CH3COOH
2.
Li
HO
CH3
H
H
CH3

l.


1. BH3
2. H2O2, -OH

m.


H3C
Br

n. $CH_3C{\equiv}CH$ → (1. CH_3MgBr; 2. $CH_3CH(=O)$; 3. CH_3SO_2Cl; 4. $Na^{+-}OC(CH_3)_3$) → [ ] C_5H_6

o.  → (Br_2) → [ ] → ($Na^{+-}OCH_3$) → [ ] C_6H_8

III. [40 Points]
Tert-Butyl hypochlorite **A** is used to chlorinate hydrocarbons.

a. Calculate the $\Delta H°$ for its reaction with methane in the box provided and using the information given below. Show your work.

$$CH_4 + (CH_3)_3C{-}O{-}Cl \xrightarrow{h\nu} CH_3Cl + (CH_3)_3COH$$

A

TABLE 3-1 Bond-Dissociation Energies of Various A–B Bonds ($DH°$ in kcal mol^{-1})

	B in A–B						
A in A–B	–H	–F	–Cl	–Br	–I	–OH	$-NH_2$
H—	104	135	103	87	71	119	107
CH_3—	105	110	85	71	57	93	80
CH_3CH_2—	98	107	80	68	53	92	77
$CH_3CH_2CH_2$—	98	107	81	68	53	91	78
$(CH_3)_2CH$—	94.5	106	81	68	53	92	93
$(CH_3)_3C$—	93	110	81	67	52	93	93

Note: These numbers are being revised continually because of improved methods for their measurement. Some of the values given here may be in (small) error.

$DH°(RO{-}Cl) = 53$ kcal mol^{-1}, $DH°(RO{-}H) = 104$ kcal mol^{-1}.

$\Delta H°$:

b. Write the two propagation steps of the radical chain reaction:

Step 1

Step 2

c. Calculate the $\Delta H°$ for each step.

Step 1

$\Delta H°$:

Step 2

$\Delta H°$:

d. When methane is replaced by ethene in this reaction, addition rather than substitution takes place.

Not : $CH_2{=}CH_2 + (CH_3)_3COCl \xrightarrow{h\nu} CH_2{=}C(H)(Cl) + (CH_3)_3COH$

but : $CH_2{=}CH_2 + (CH_3)_3COCl \longrightarrow (CH_3)_3CO{-}CH_2{-}CH_2{-}Cl$

Use the data in the Table above to get some estimates of some of the relevant bond strengths, in addition to $DH°(CH_2{=}CH\text{-}H) = 110$ kcal mol^{-1}, $DH°(CH_2{=}CH\text{-}Cl) = 92$ kcal mol^{-1}, and $DH°$ (π bond) = 65 kcal mol^{-1}, to give an explanation for this finding.

IV. [50 Points]

When ethyne is bubbled through acidic butanol, a new compound **X** forms, with the spectral data shown below.

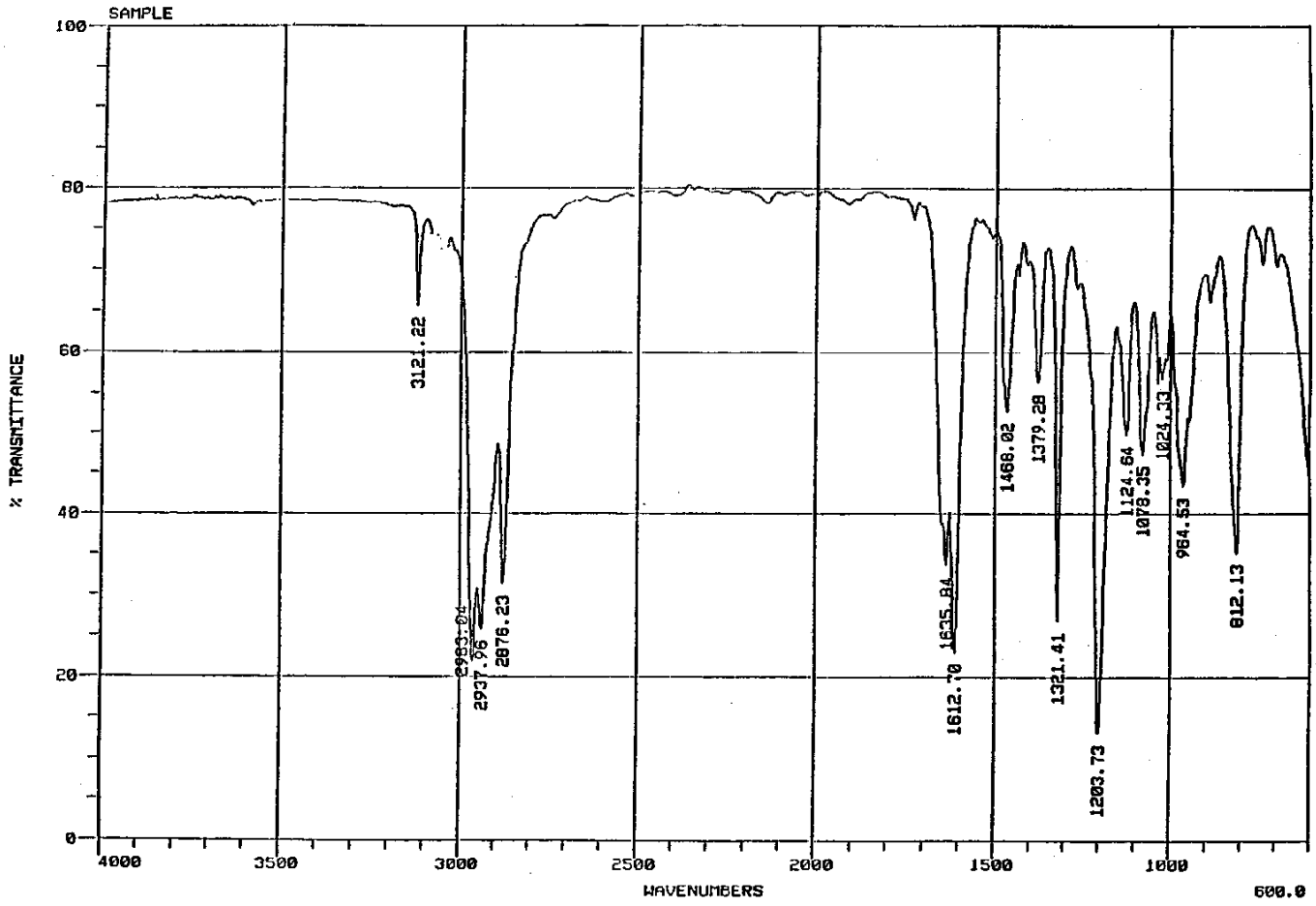
$$HC{\equiv}CH \xrightarrow{CH_3CH_2CH_2CH_2OH,\ H^+} \boxed{}$$

X $C_6H_{12}O$

a. After consideration of the spectral data below, write the structure of **X** in the box above.

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

1. IR Spectrum



Considering the starting materials, **X** could be an alkyne, alkene, or alcohol. Confirm or rule out these possibilities:

$\tilde{\nu}$ (C≡C) is :

present/absent at ____ cm^{-1}

(circle correct statement)

$\tilde{\nu}$ (C_{sp}–H) is :

present/absent at ____ cm^{-1}

(circle correct statement)

$\tilde{\nu}$ (C_{sp^2}–H) is :

present/absent at ____ cm^{-1}

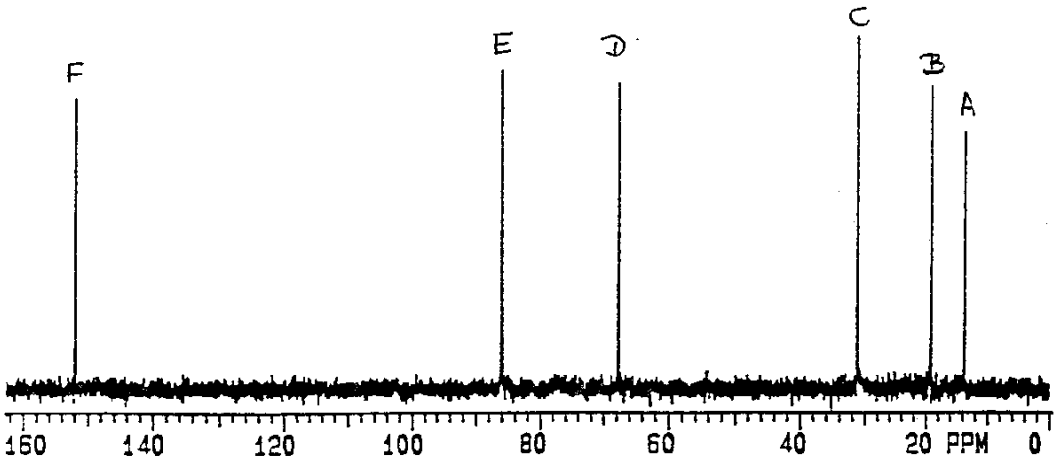
(circle correct statement)

$\tilde{\nu}$(RO–H) is :

present/absent at ____ cm^{-1}

(circle correct statement)

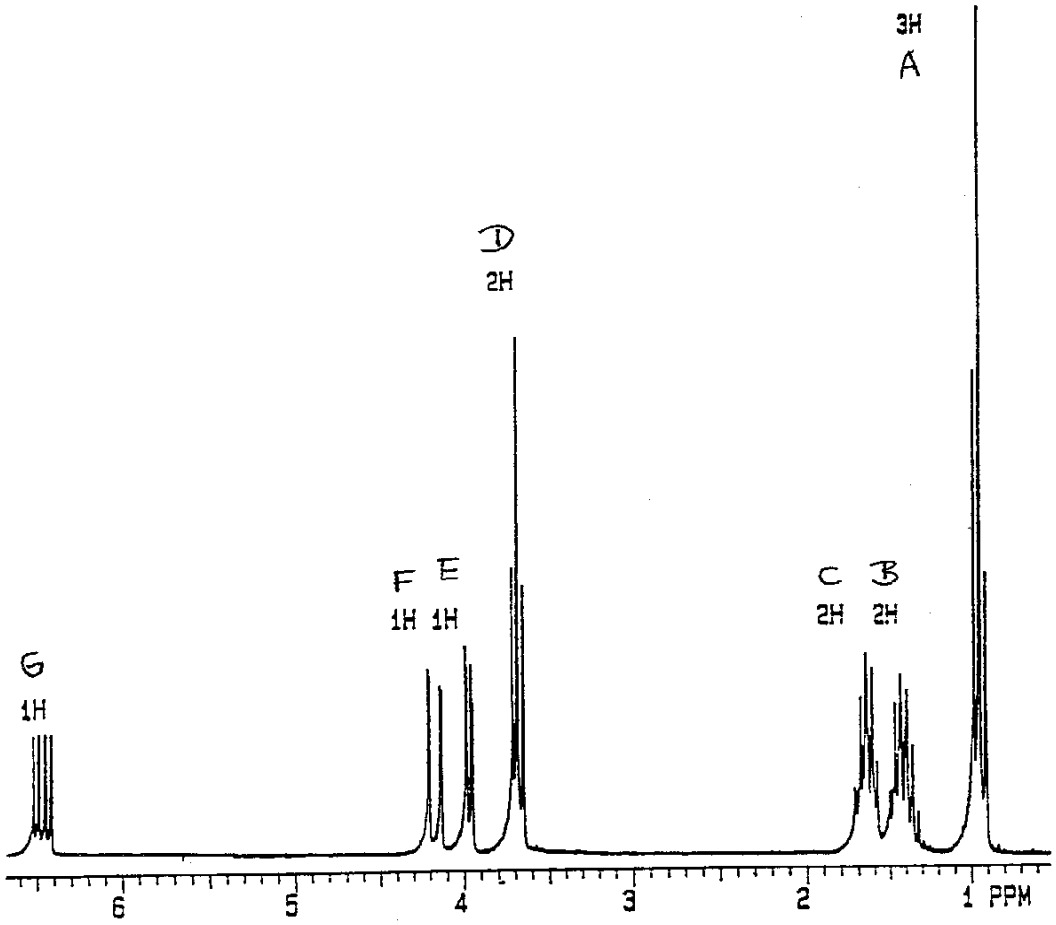
2. ^{13}C NMR Spectrum



Draw your suggestion for **X** in the box below, and label the carbon atoms A-F giving rise to corresponding signals in the spectrum.

3. ^{1}H NMR Spectrum

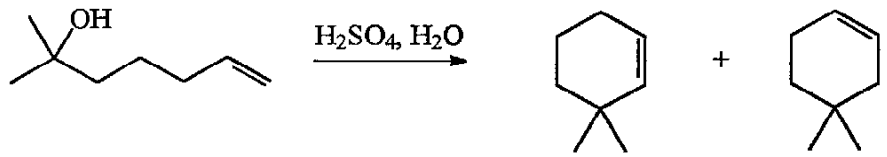
Note: E and F are actually each a dd (the second *J* is so small, 2Hz, that it is barely visible.

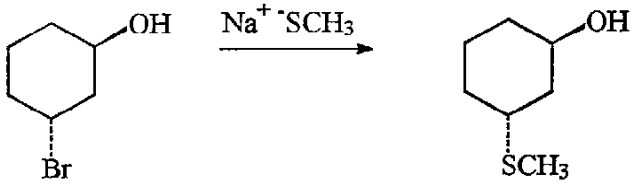


Draw your suggestion for **X** in the box and label the hydrogens A-G giving rise to the corresponding signals in the spectrum.

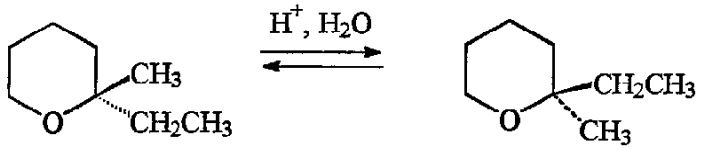
V. [60 Points]

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 reagents! What you see is what you have!

a. 

b. 

Note stereochemistry

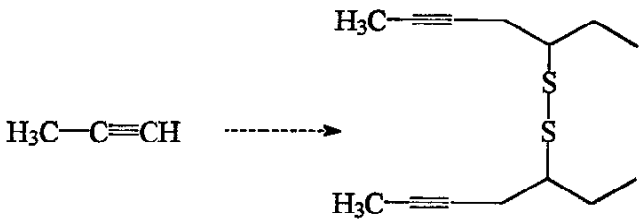
c. 

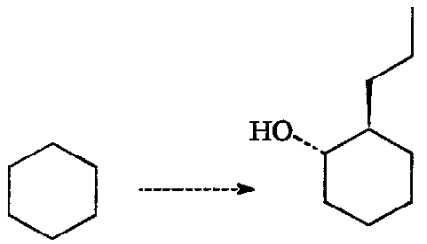
racemization

VI. [60 Points]

Show synthetic **forward connections** (reagents, intermediates; no mechanisms!) between the following starting materials and the final (racemic) 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) on the back of the exam pages, to enable you to dissect the products into less complex precursors. However, the answer to be graded should be a *forward* scheme. In addition to the starting structure, you may use any organic and organometallic reagents **containing four carbons or less.**

a.

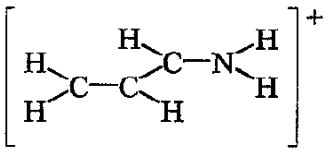


b. 

c. 

VII. [70 Points]

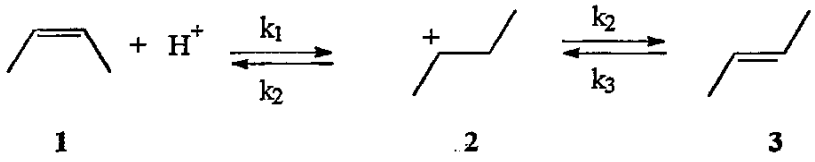
a. Draw the best resonance structure for



Indicate the position of the positive charge.

b. Nitriles, RC≡N: , have a lone pair situated on the nitrogen. What type of orbital does it occupy?

c. The mechanism for the acid-catalyzed conversion of *cis*-2-butene to *trans*-2-butene is as shown.

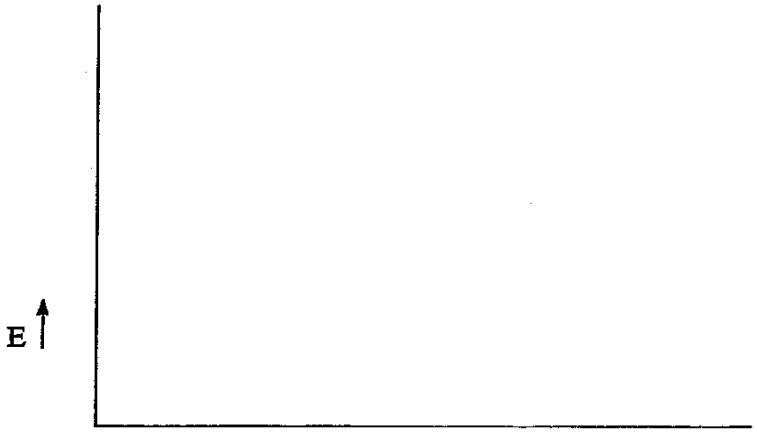


1 **2** **3**

$k_2 > k_1 > k_3$

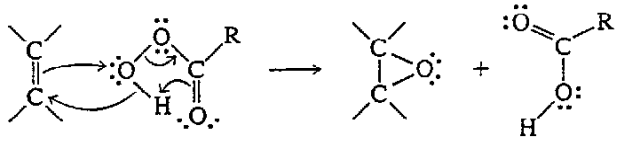
Draw the potential energy diagram for this process clearly labeled with the locations of **1**, **2**, and **3**.

Potential Energy Diagram:



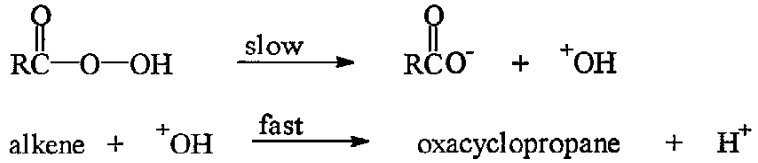
d. The mechanism of the oxacyclopropanation of alkenes by peroxycarboxylic acids proceeds in one step as shown below ("Mechanism I").

Mechanism of Oxacyclopropane Formation (Mechanism I)



An alternative mechanism ("Mechanism II") would be rate determining O–O bond heterolysis to give free HO^+ (and $R\overset{O}{\overset{\|}{C}}O^-$) which could then attack the alkene.

Alternative Mechanism (Mechanism II)



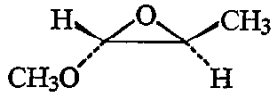
Indicate one method by which you could rule out the second mechanism.

Method:

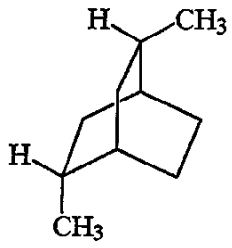
Results for Mechanism I

Results for Mechanism II

e. Predict the coupling patterns of the hydrogen signals in the ^{1}H NMR spectrum of the compound shown below. Label the hydrogens as s, d, t, q or dd, tq etc. The simplified N+1 rule does not hold here.



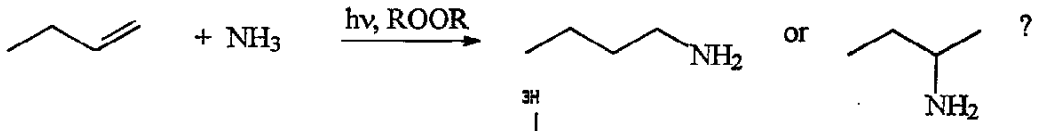
f. How many ^{13}C NMR peaks do you expect for the following compound :

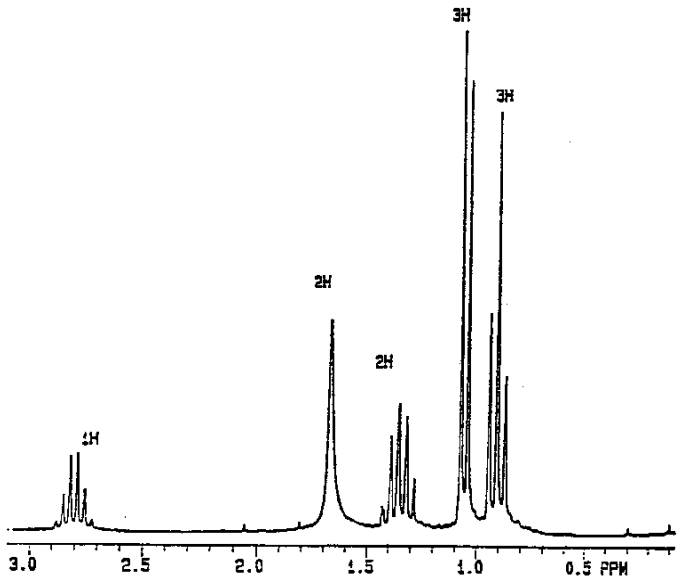


g. Give approximate p*K*a values for the two functional groups shown.

RC≡CH	ROH
p*K*a :	p*K*a :

h. A researcher attempted the free radical addition of ammonia to 1-butene. Two products of addition are in principle possible, as shown. The H NMR spectrum of the product obtained is depicted below. Circle the product to which it corresponds.

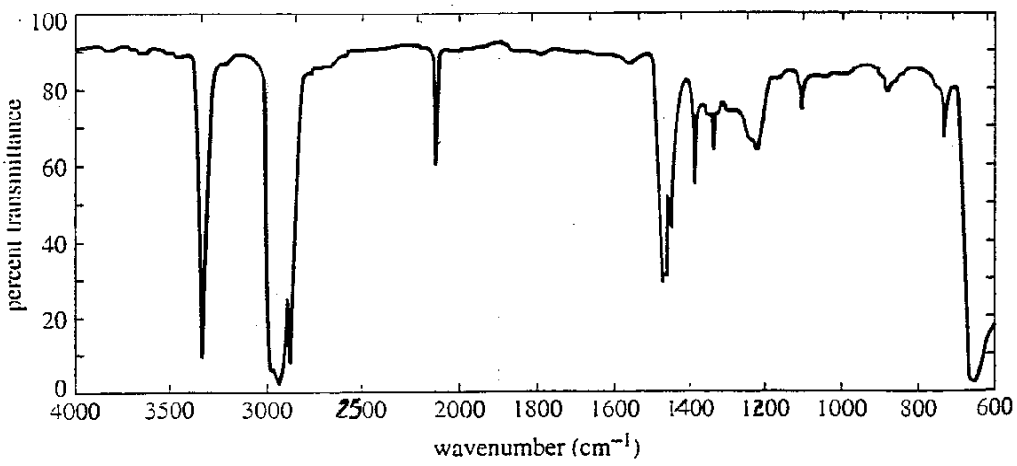




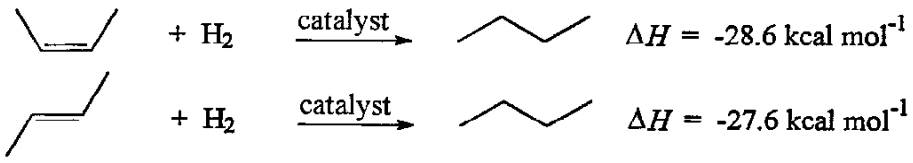
i. Octyne can exist as several isomers. Which one gives rise to the IR spectrum shown below.

Answer:

IR spectrum of an isomer of octyne :



j. Consider the following measured heats of hydrogenation :



If you were to burn the two starting alkenes to CO_2 and H_2O, which one would have a more negative ΔH_{comb}? (circle one)

Have a good summer!

TABLE 3-1 Partial Periodic Table

Period							Halogens	Noble gases
First	H^{1}							He^{2}
Second	$Li^{2.1}$	$Be^{2.2}$	$B^{2.3}$	$C^{2.4}$	$N^{2.5}$	$O^{2.6}$	$F^{2.7}$	$Ne^{2.8}$
Third	$Na^{2.8.1}$	$Mg^{2.8.2}$	$Al^{2.8.3}$	$Si^{2.8.4}$	$P^{2.8.5}$	$S^{2.8.6}$	$Cl^{2.8.7}$	$Ar^{2.8.8}$
Fourth	$K^{2.8.8.1}$						$Br^{2.8.18.7}$	$Kr^{2.8.18.8}$
Fifth							$I^{2.8.18.18.7}$	$Xe^{2.8.18.18.8}$

Note: The superscripts indicate the number of electrons in each principal shell of the atom.