FINAL EXAMINATION

Chemistry 3A
Kim Lavoie
Peter Vollhardt
December 12, 2001

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	John Antos	361	Karl Tupper
121	Jennifer Barbarow	371	Eric Schneider
161	Dennis Leung	411	Amish Patel
171	Dan Weix	421	Jennifer Prescher
211	Scheherazade Le	511	Stephany Schuck
221	Steve Pham	521	Javier Rangel
311	David Tang	561	Lianne Beltran
321	Joshua Goldberger		

Making up an I Grade _____

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

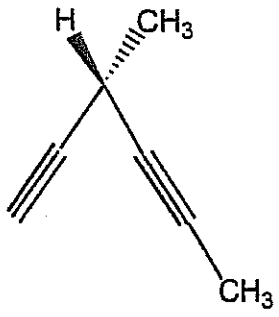
Please write the answer you wish to be graded in the spaces provided. *Do scratch work on the back of the pages.* This test should have 25 numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **read carefully over the questions (at least twice); make sure 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 Wed, December 19, outside 305 Latimer Hall (Lab Q). Good Luck!**

DO NOT WRITE IN THIS SPACE

I.	_____	(30)
II.	_____	(90)
III.	_____	(30)
IV.	_____	(50)
V.	_____	(60)
VI.	_____	(60)
VII.	_____	(80)
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!

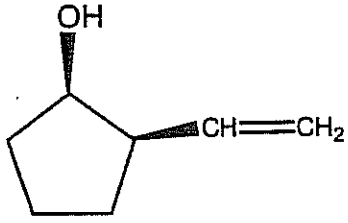
a.



b.

(*E*)-4-Ethyl-5-methyl-4-octene

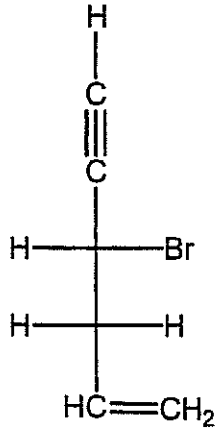
c.



d.

Trans-2-mercaptocyclohexanol

e.

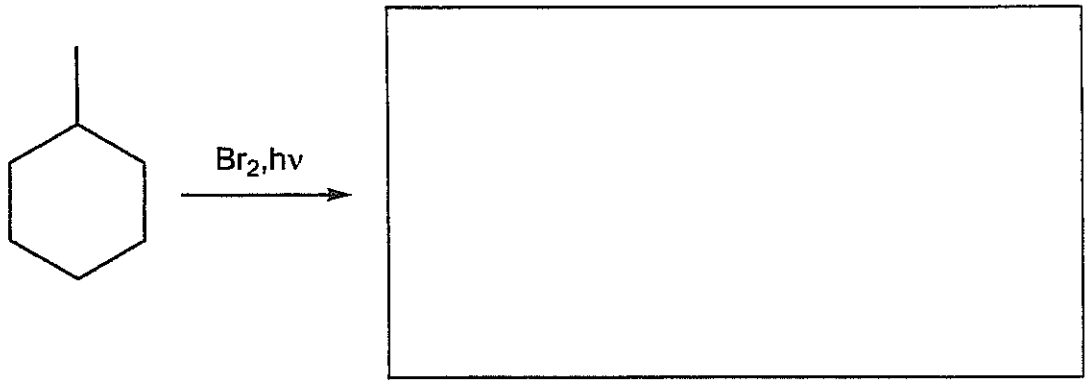


f.

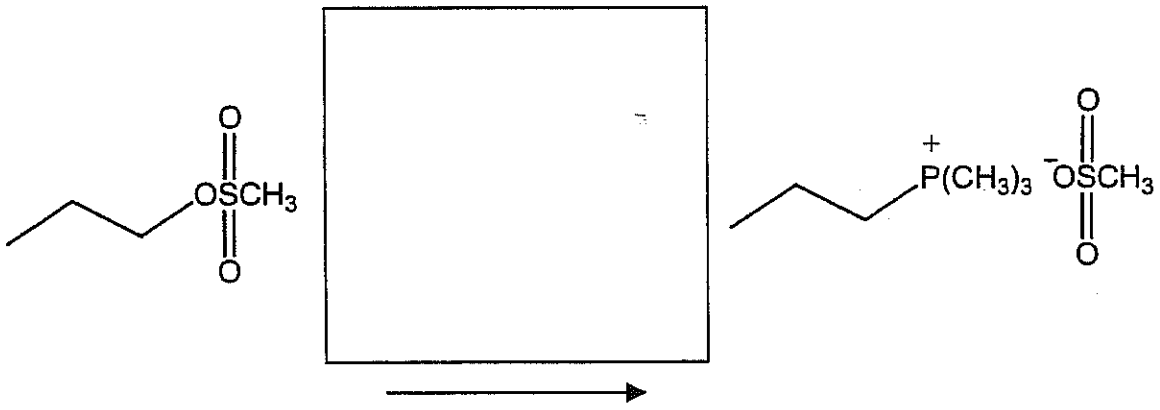
Meso-1,2,3,4-tetrachlorobutane

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.

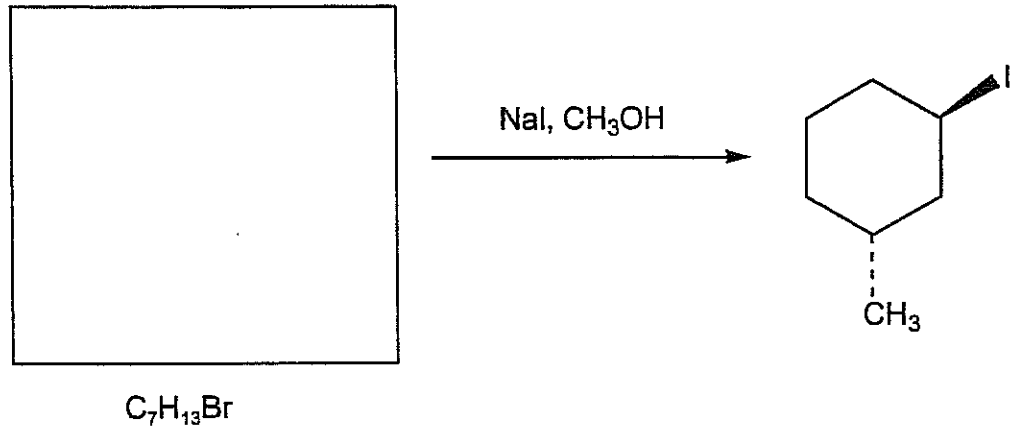
a.



b.

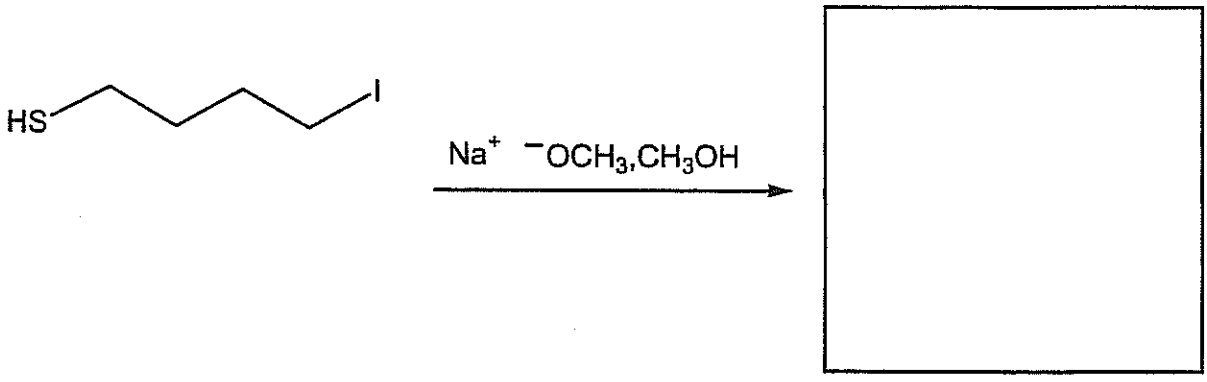


c.

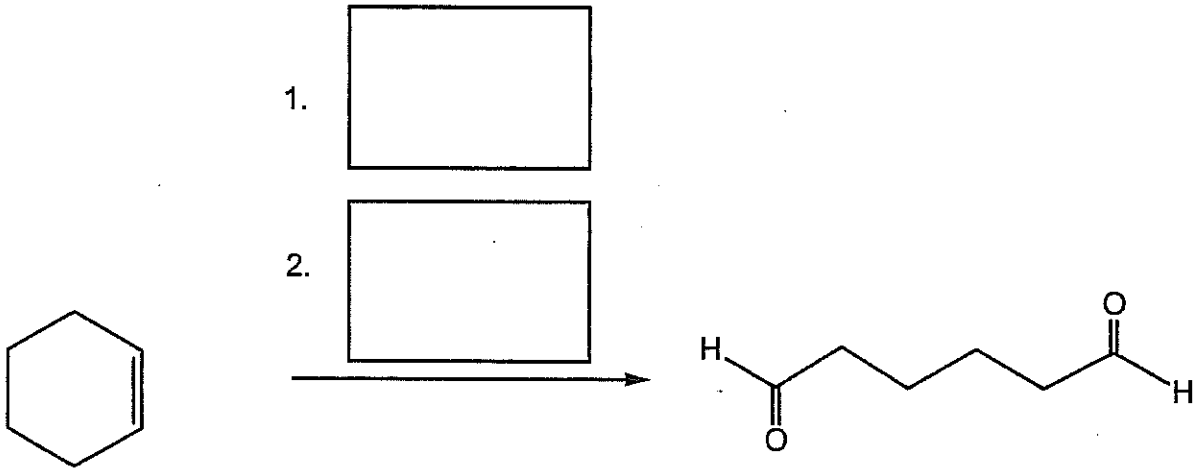


$C_7H_{13}Br$

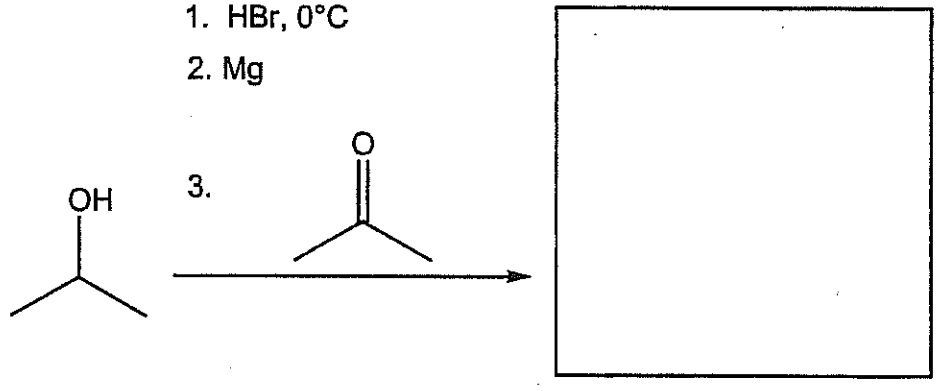
d.



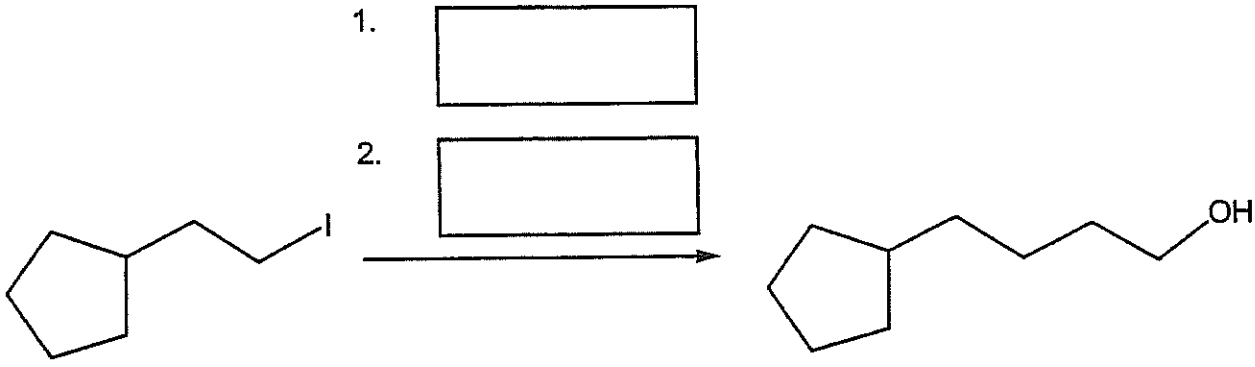
e.



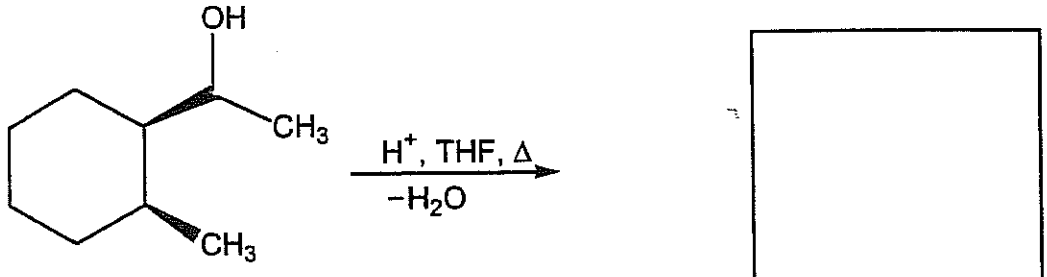
f.



g.

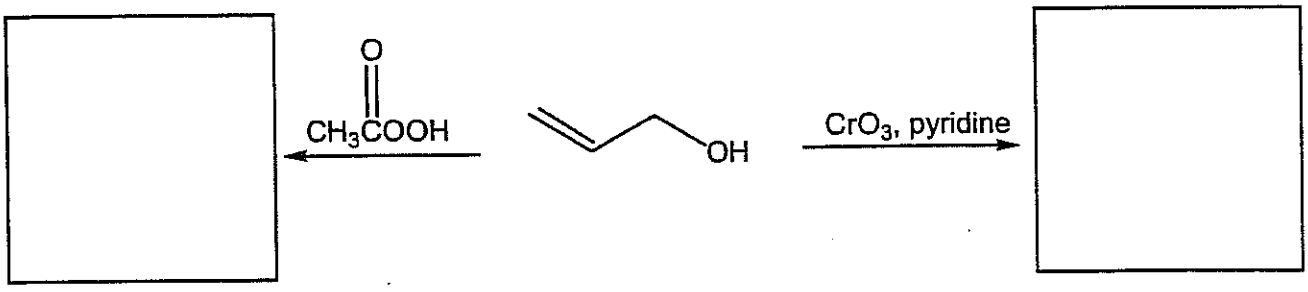


h.

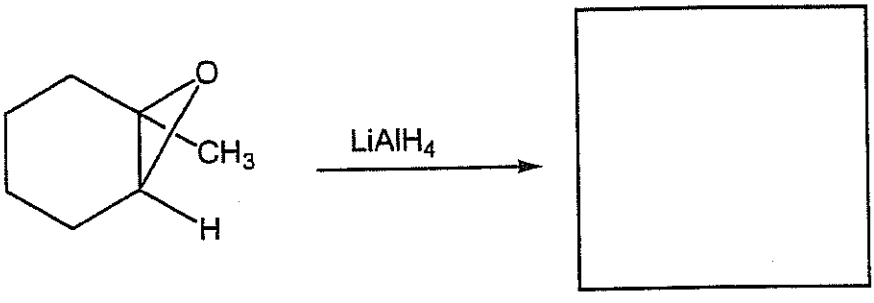


Most stable isomer

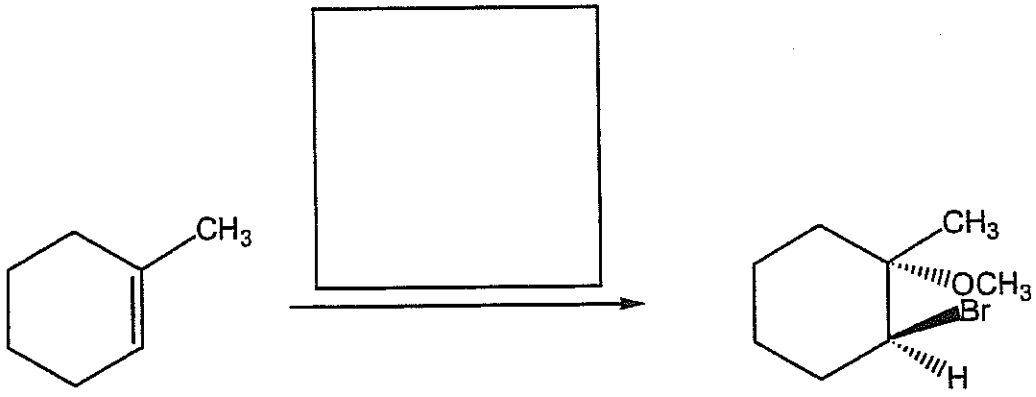
i.



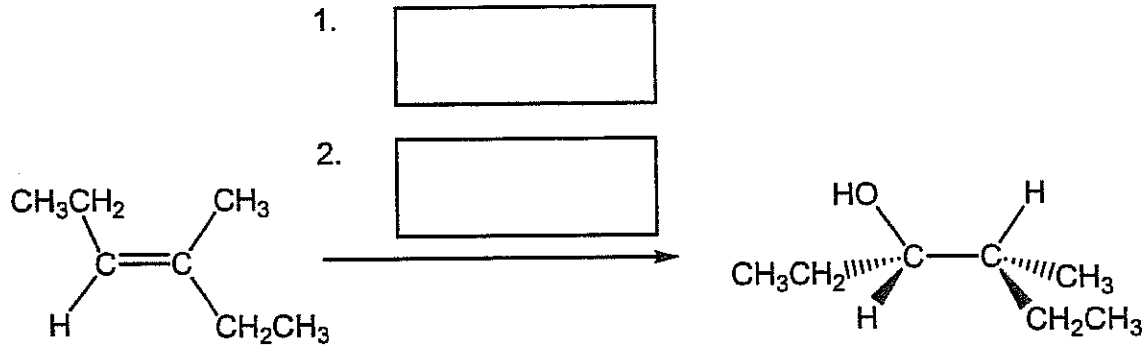
j.



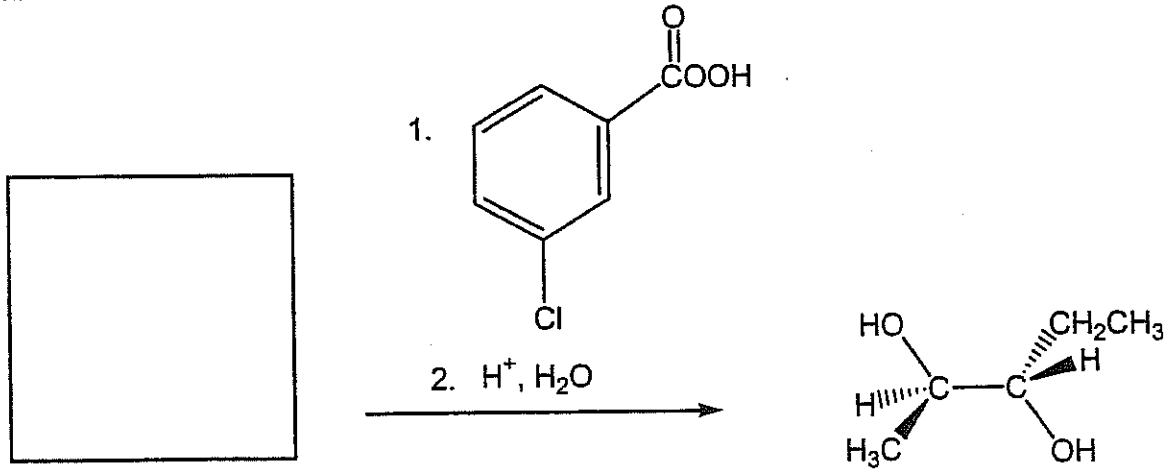
k.



l.

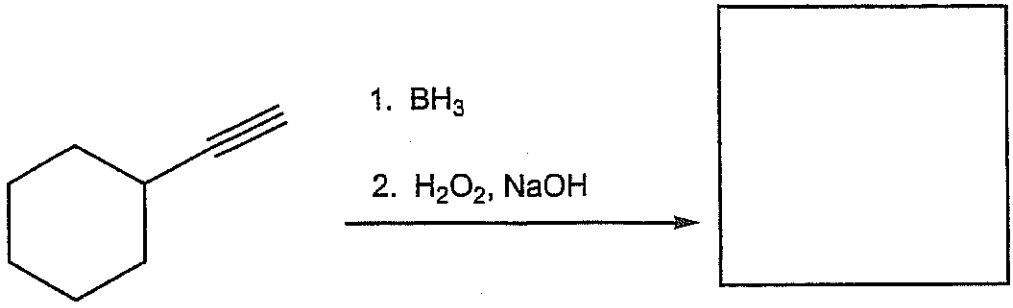


m.

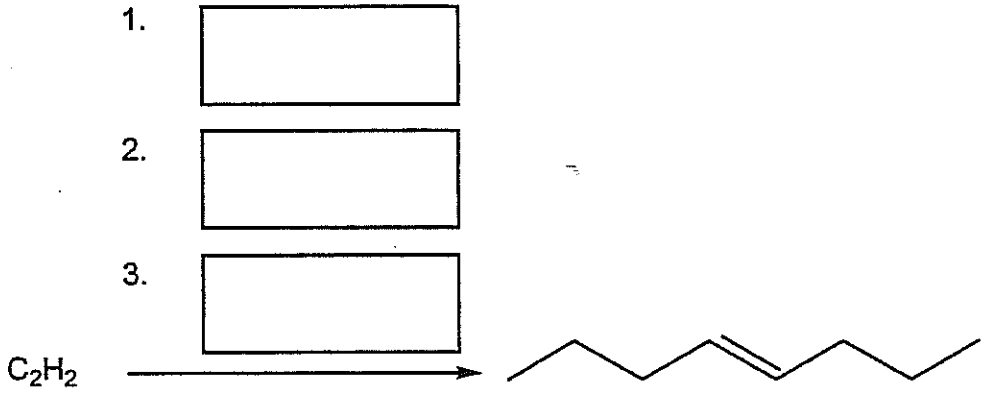


An alkene

n.



o.



III. [30 Points] Consider the anti-Markovnikov hydrohalogenation of propene.

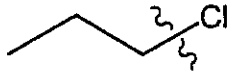
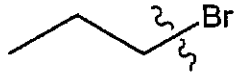
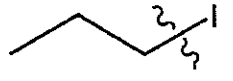
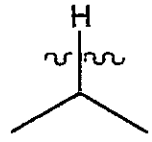
a. Formulate the propagation steps of this process:

Propagation steps.

1.

2.

b. Using the bond strength data below, estimate the $\Delta H°$ values of each propagation step for X = Cl, Br, and I.

$DH°$ (kcal mol^{-1}) :	π bond	65		81
	HCl	103		68
	HBr	87		53
	HI	71		95

$\Delta H°$ of step 1 :

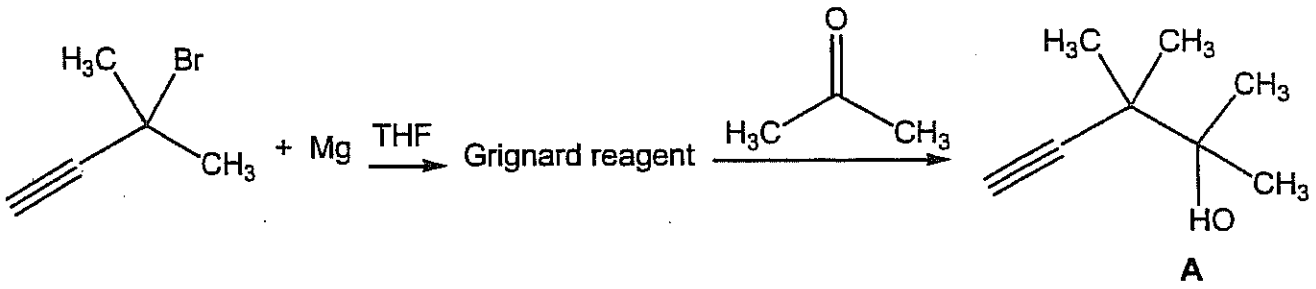
Cl :
Br:
I :

$\Delta H°$ of step 2 :

Cl :
Br:
I :

c. Under radical chain conditions, only HBr adds to propene in an anti-Markovnikov manner; HCl and HI follow the normal electrophilic, Markovnikov addition pathway. Considering your data in b., why should this be so?

IV. [50 Points] A researcher executed the following steps to prepare the alcohol A.



A

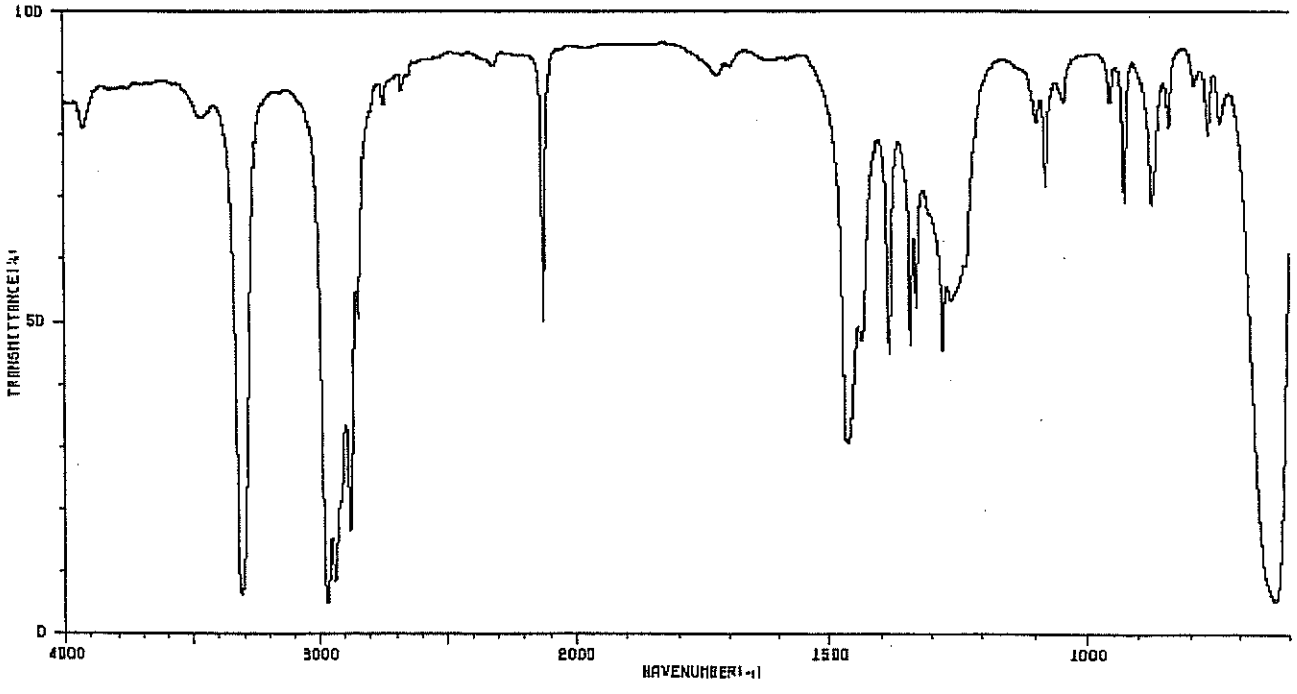
In addition to A, another compound B, C_5H_8, was obtained in small amounts, which exhibited the IR and NMR spectra shown.

a. After consideration of the spectral data, write the structure of B in the box below.

Structure of B

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

1. IR Spectrum



Considering the starting materials of the attempted synthesis, B could be an alkyne, alkene, or alcohol. Confirm or rule out these functionalities.

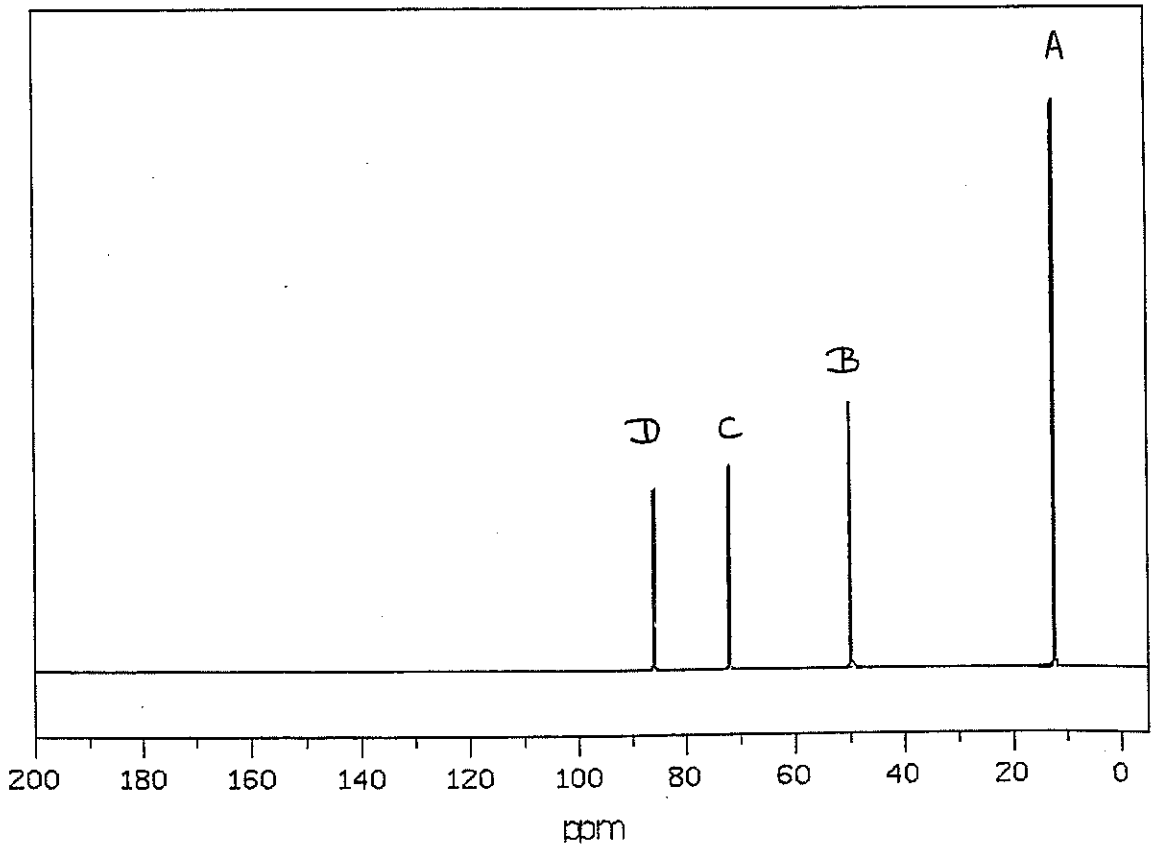
$\tilde{\nu}$ (C≡C) is : present absent at ____ cm^{-1}
(circle correct statement)

$\tilde{\nu}$ (C_{sp}–H) is present absent at ____ cm^{-1}

$\tilde{\nu}$ (C_{sp^2}–H) is : present absent at ____ cm^{-1}

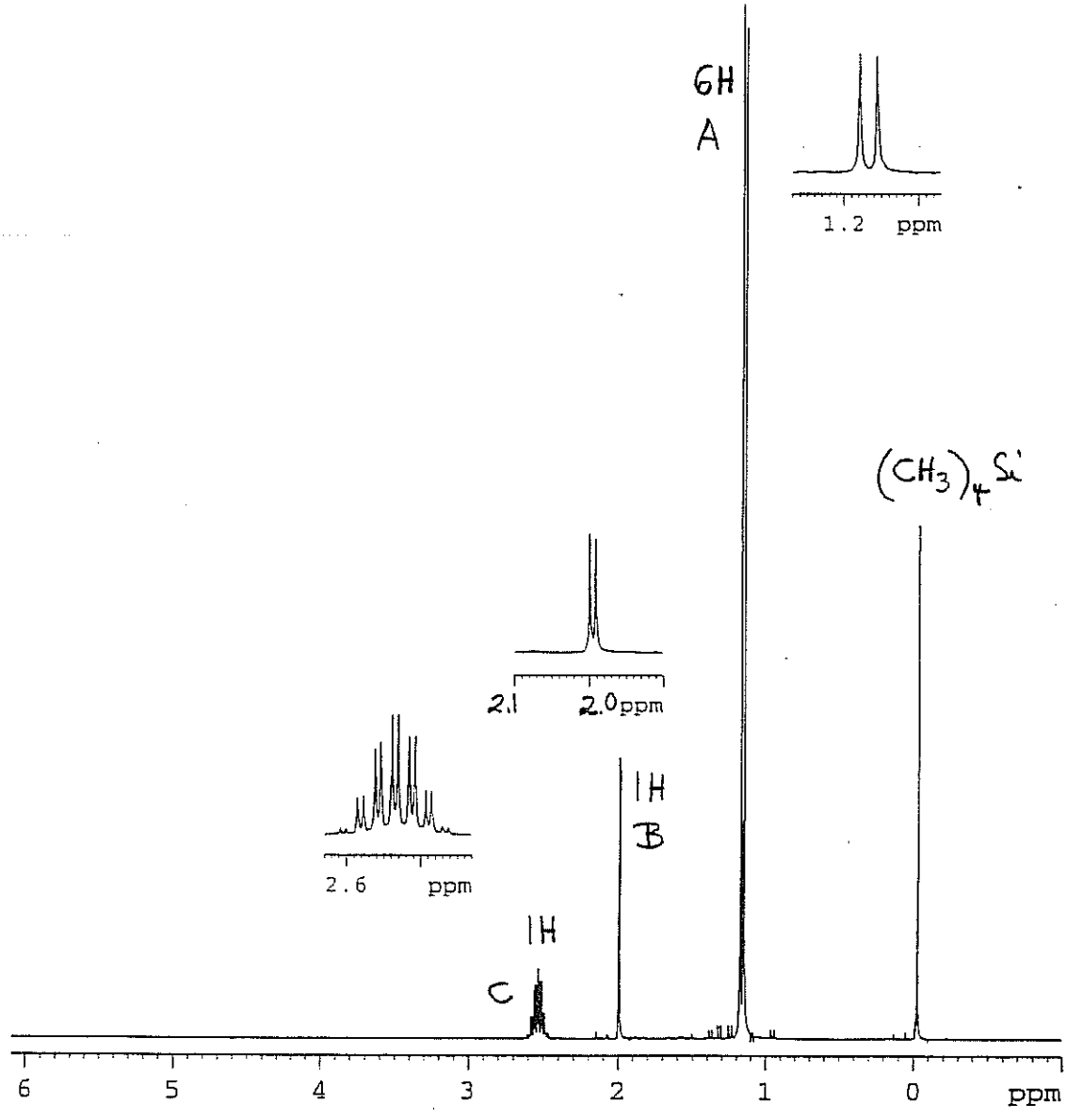
$\tilde{\nu}$ (O–H) is : present absent at ____ cm^{-1}

2. ^{13}C NMR Spectrum

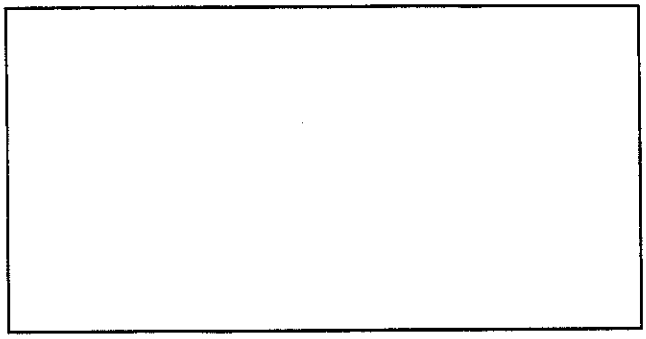


Draw your suggestion for B in the box below and label the carbon atoms A, B, C, and D giving rise to the corresponding signals in the spectrum. Note: You are allowed to make an arbitrary assignment of peaks C and D, as long as you pick the right pair of carbons in your molecule.

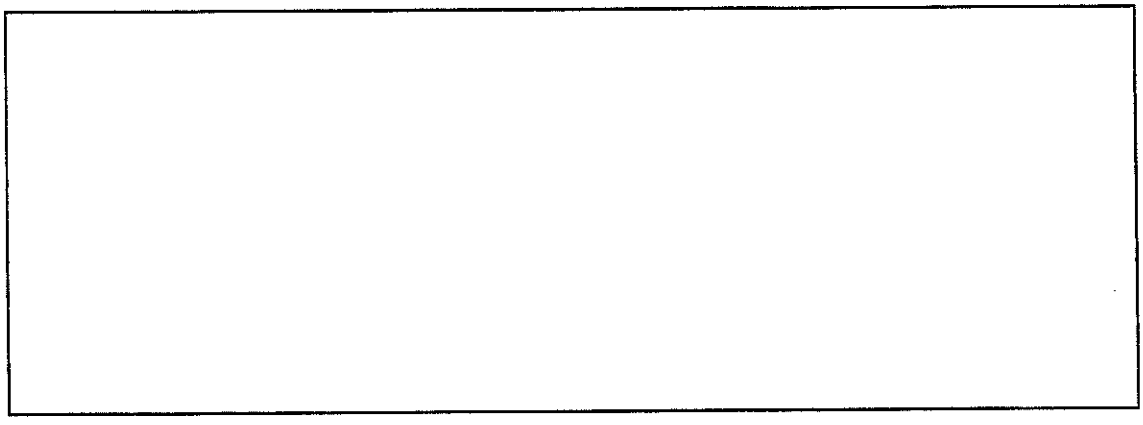
3. ^{1}H NMR Spectrum



Draw your suggestion for B in the box and label the hydrogens A, B, and C giving rise to the corresponding signals in the spectrum.

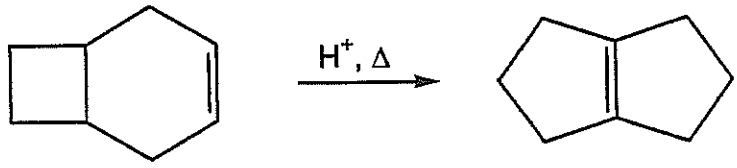


c. Provide an explanation (guess) for the formation of B.

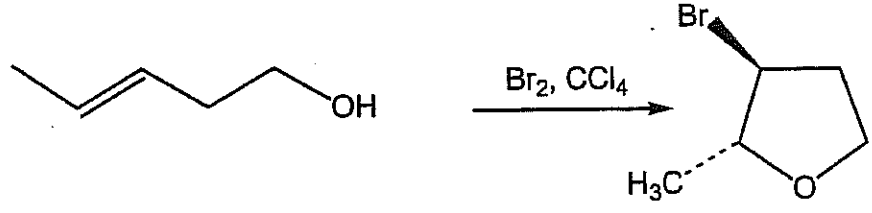


V. [60 Points] Write detailed step-wise mechanisms for the following transformations. Use only structures and "arrow-pushing" techniques. Note: These are <u>not</u> synthetic problems. Do not <u>add</u> any reagents! What you see is what you have!

a.

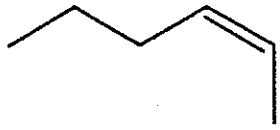


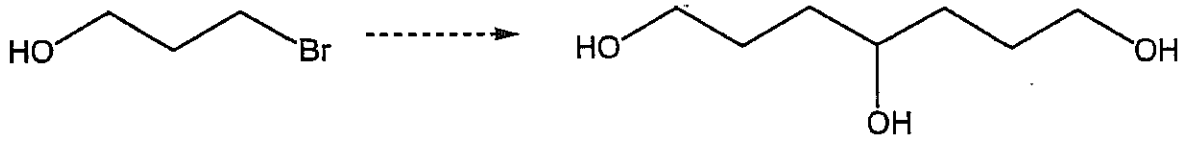
b.

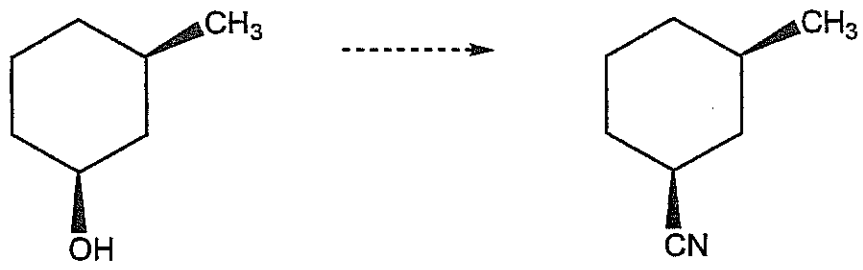


c. $CH_3OH + SOCl_2 \longrightarrow CH_3Cl + SO_2 + HCl$

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.**

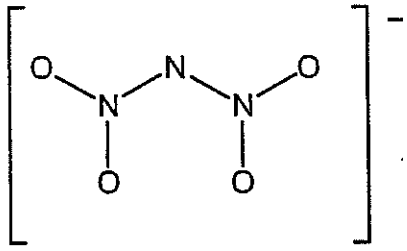
a. $(CH_3)_3CH$ ----------> 

b. 

c. 

VII. [80 Points]

a. Draw the best resonance structure for the "dinitramide" anion:

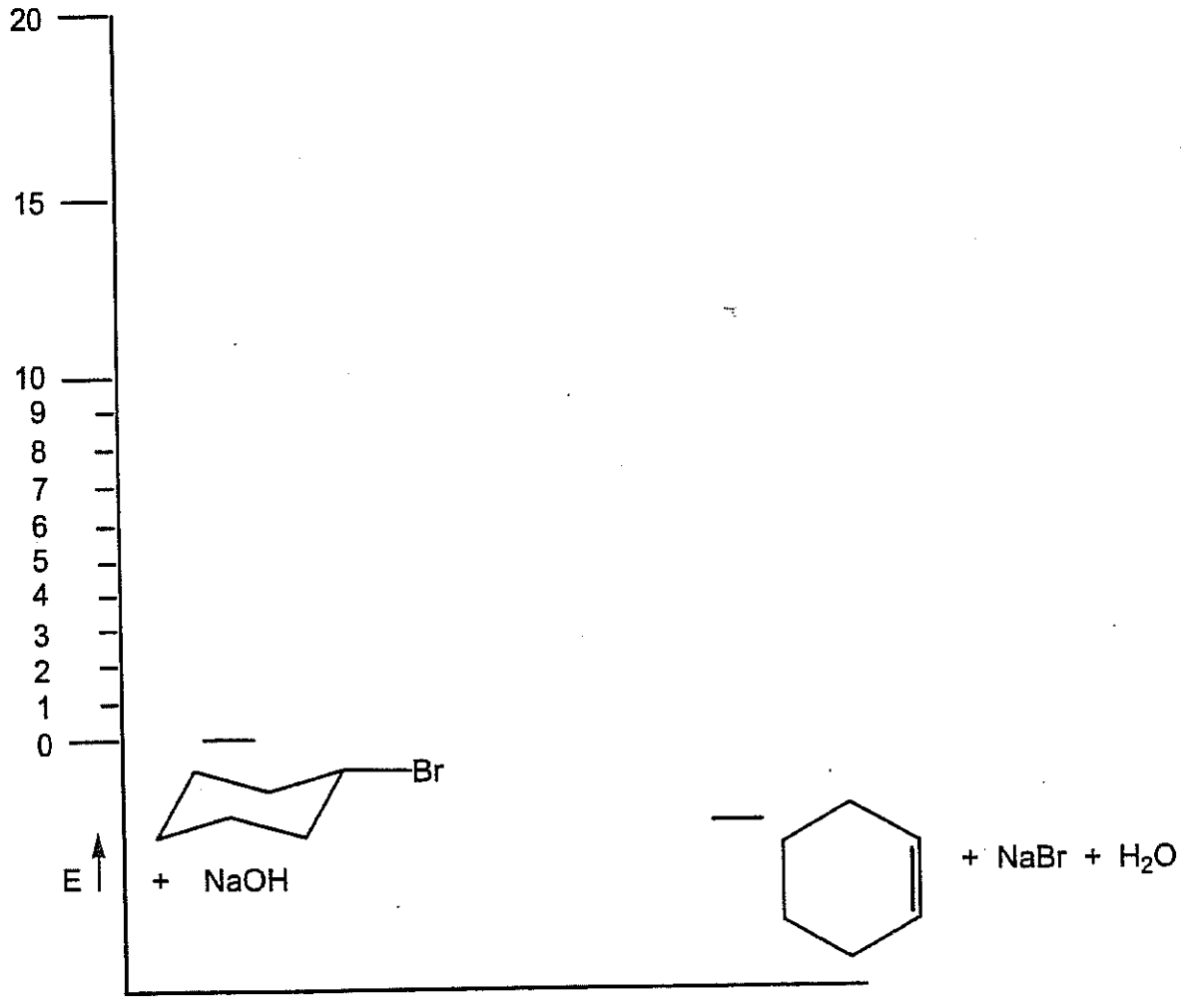


Don't forget charges!

b. Alkynyl anions, $RC{\equiv}C^-$, have a lone pair situated on the terminal carbon. What type of orbital does it occupy (e.g. sp^3, p, etc.)?

c. The mechanism fo rthe E2 reaction of bromocyclohexane with NaOH proceeds through the axial conformer [$\Delta G°$ (equatorial-axial) = 0.5 kcal mol^{-1}, E_a (equatorial-axial) = 10 kcal mol^{-1}] with an activation barrier of 19.5 kcal mol^{-1}. Draw the potential energy diagram for this process. Show clearly the position of the transition states (use the labels "TS1" and "TS2") and of the axial conformer (use the label "Ax").

Potential Energy Diagram:



d. Using key words or a short sentence, list four techniques or experiments that support the mechanism of the S_N2 reaction.

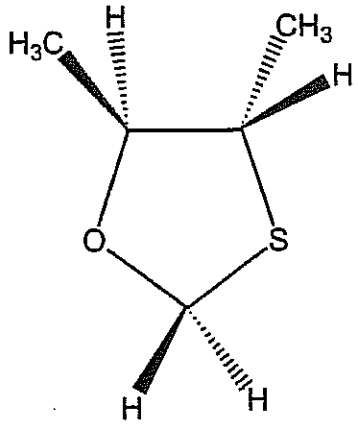
1.

2.

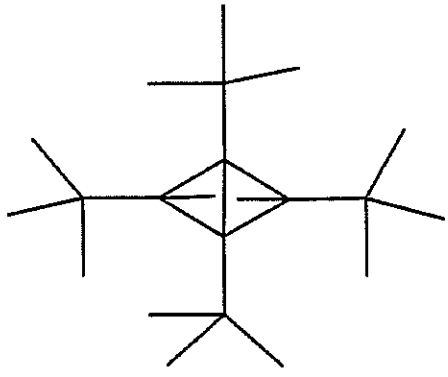
3.

4.

e. Predict the coupling patterns of all 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. Apply the sequential N+1 rule.



f. How many ^{13}C NMR peaks do you expect for tetra-*t*-butyltetrahedrane :



g. Give approximate ^{1}H NMR δ values (ppm) for the hydrogens in the two functional groups shown.

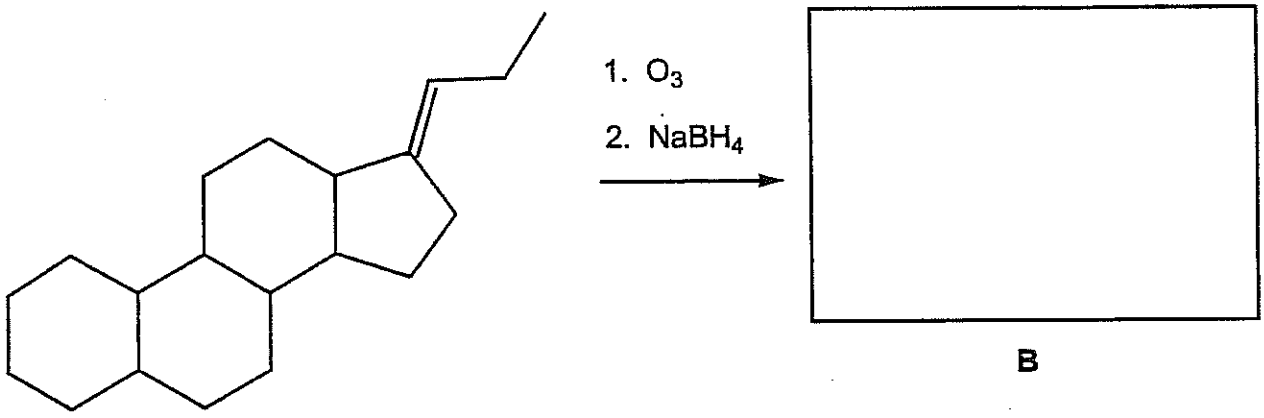
RC≡CH

δ :

$R_2C{=}CH_2$

δ :

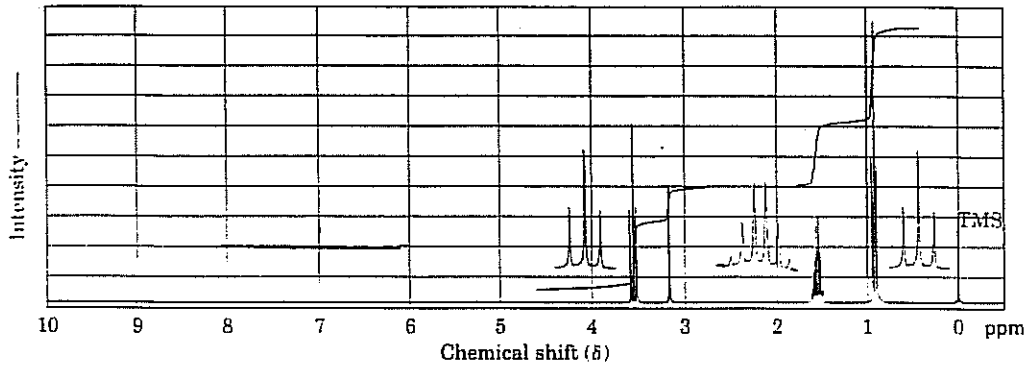
h. A researcher cleaved the alkylidene side chain of steroid A by treatment with O_3 in CH_2Cl_2, followed by $NaBH_4$ (instead of the usual Zn-CH_3COOH). Distillation of the product led to the isolation of liquid B. Assign a structure using the spectral data shown below.



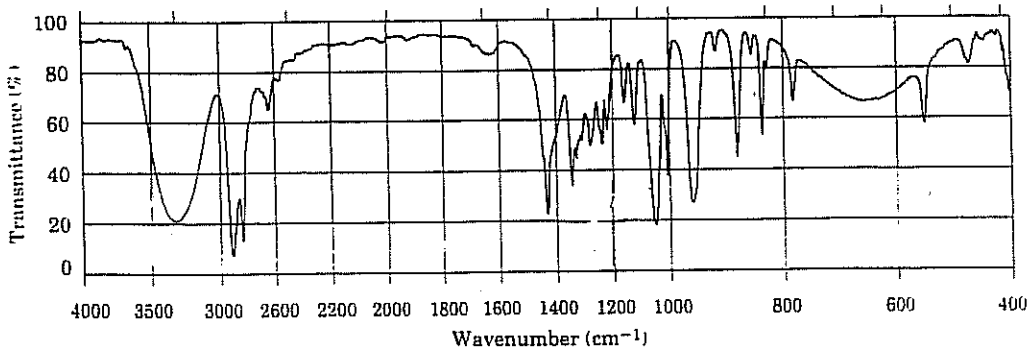
A

B

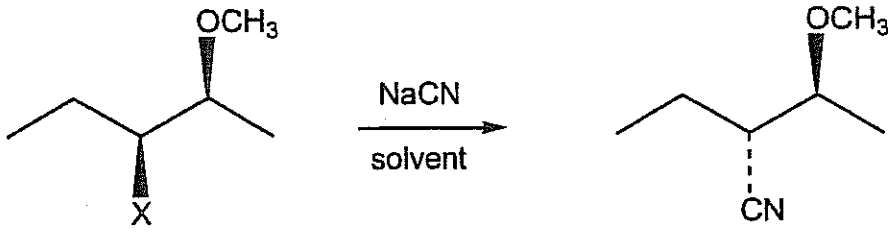
^{1}H NMR Spectrum:



IR Spectrum:



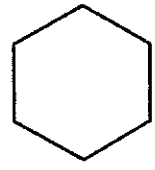
i. You want to convert A to B. Circle the best variables to accomplish this task.



A

X : F Cl – CH_3—S(=O)(=O)—O— HO—

Solvent : H_2O CH_3OH DMF



j. The rate (k_1) of the S_N2 reaction of *R*-2-iodooctane with iodide has been measured by using the radioactive isotope ^{129}I. How does k_1 relate to the rate (k_2) of loss of optical activity? Circle the correct answer.

$k_1 = k_2$ $k_1 = 2k_2$ $k_1 = ½\ k_2$

Final page of the Medical Boards

* The End *

Merry Christmas and an Excellent New Year to All of You!