FINAL EXAMINATION

Chemistry 3A
Professor K. Peter C. Vollhardt
December 11, 1995

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	Tewell,Craig	_____	331	Bruchez,Marcel	_____
121	Caylor,Chris	_____	341	Werkema,Evan	_____
131	Nitschke,Jonathan	_____	351	Sweeney,Zachary	_____
141	deForest,Sarah	_____	361	Chan,Eugene	_____
151	Wanandi,Paulus	_____	411	Barchas,Eric	_____
161	Laszlo,Chloe	_____	421	Gray,Nathanael	_____
211	Robblee,John	_____	431	Gobran,Hala	_____
221	Staunton,Joanna	_____	441	Dysard,Jeff	_____
231	Cave,John	_____	511	Furlanetto,Michael	_____
311	Fulton,Robin	_____	521	Andryski,Scott	_____
321	Golden,Jeff	_____	531	Bise,Ryan	_____
	Making-up an I grade	_____	541	Kotz,Kenneth	_____

(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 21 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, December 15, outside 305 Latimer Hall (Lab Q). **Good Luck!**

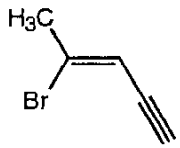
DO NOT WRITE IN THIS SPACE

		I.	_____ (30)		
IVa.	_____	II.	_____ (90)	VIa.	_____
IVb.	_____	III.	_____ (30)	VIb.	_____
IVc.	_____	IV.	_____ (60)	VIc.	_____
Subtotal	_____	V.	_____ (50)	Subtotal	_____
		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 substitutents!

a.



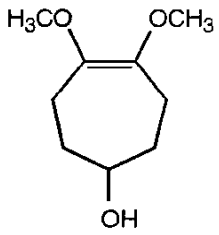
b.

1 - (2 - Propenyl)cyclohexanol

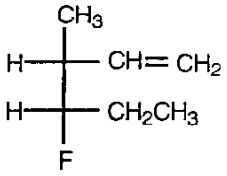
c.

1, 5, 9 - Cyclododecatriyne

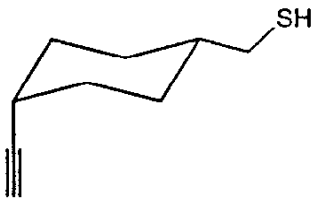
d.



e.



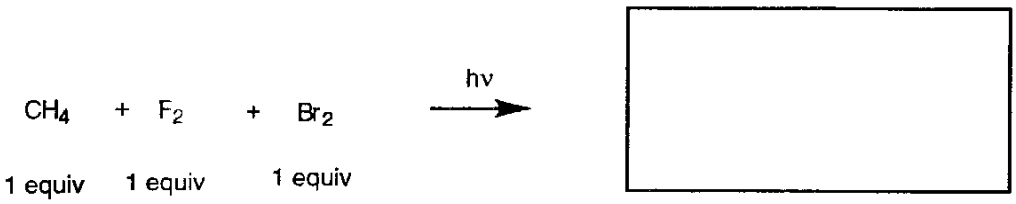
f.



II. [90 Points]

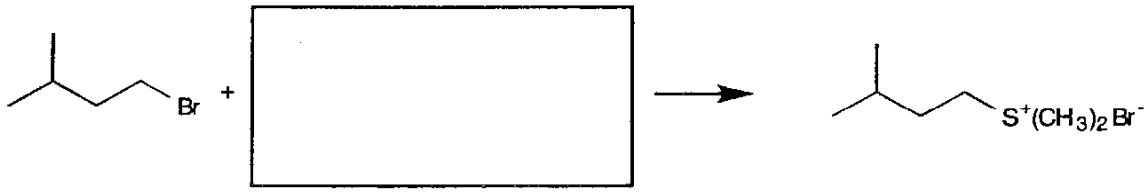
Add the missing components (starting materials, reagents, or products) of the following reactions in the boxes provided. Aqueous work-up (when required) is assumed to be part of a step. It is <u>not</u> part of any answer.

a.

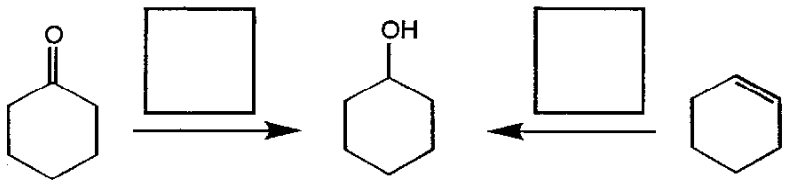


a monohalomethane

b.

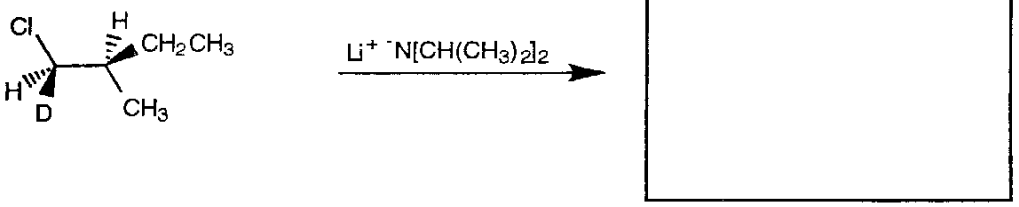


c.

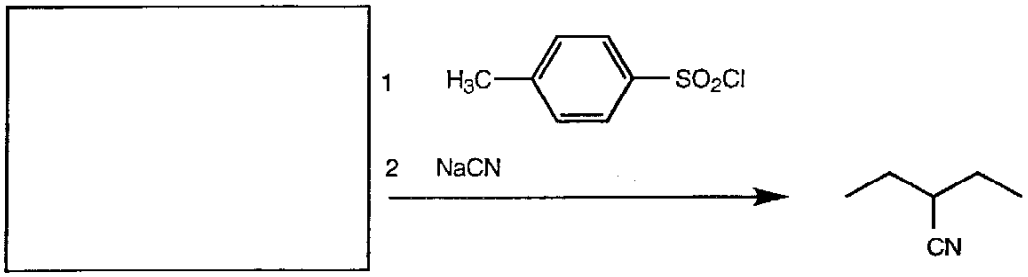


5

d.



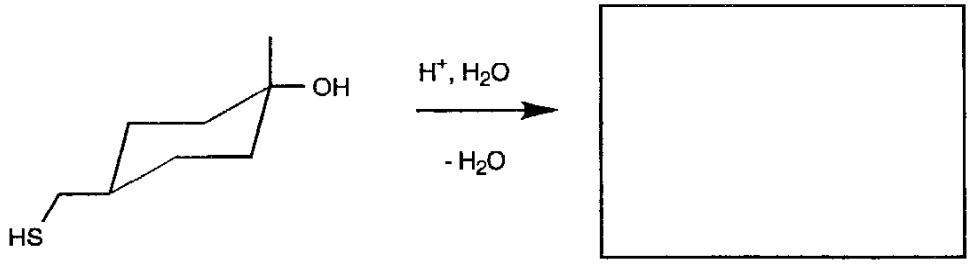
e.



$C_5H_{12}O$

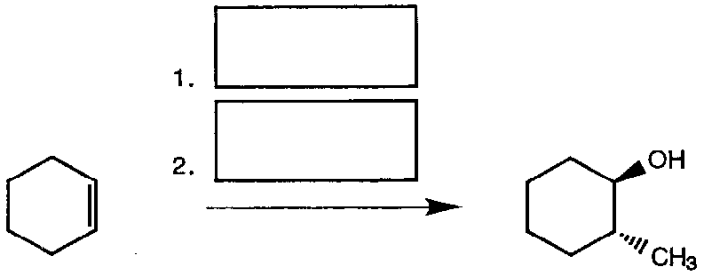
IR: $\tilde{\nu}$ = 3350 cm^{-1}

f.

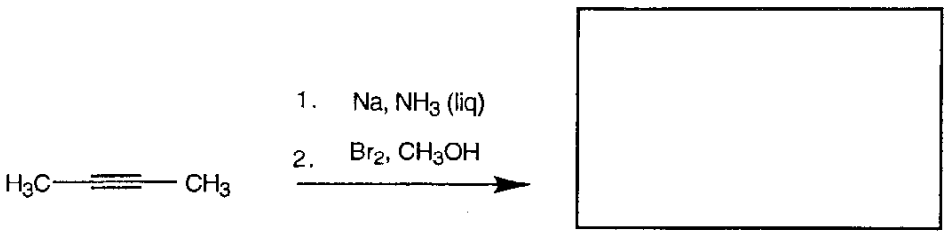


IR: no peak at 3350 cm^{-1}

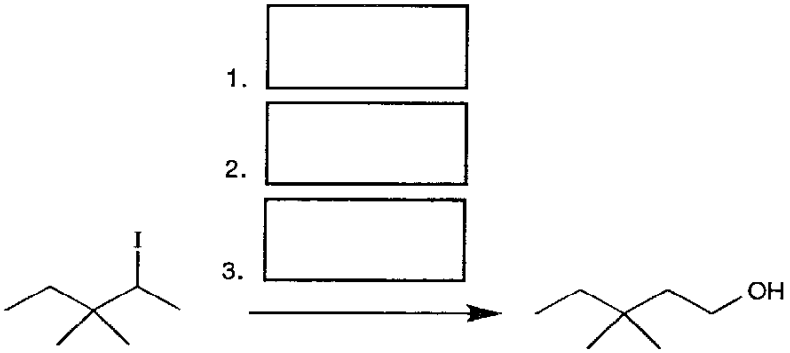
g.



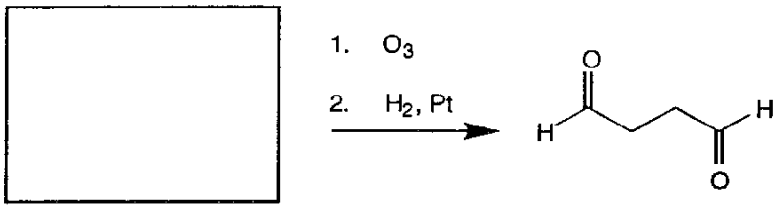
h.



i.



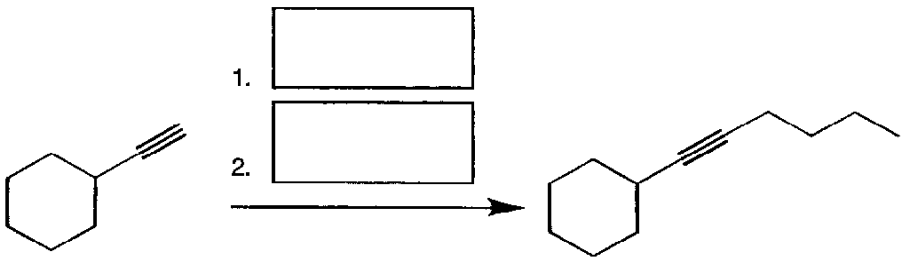
j.



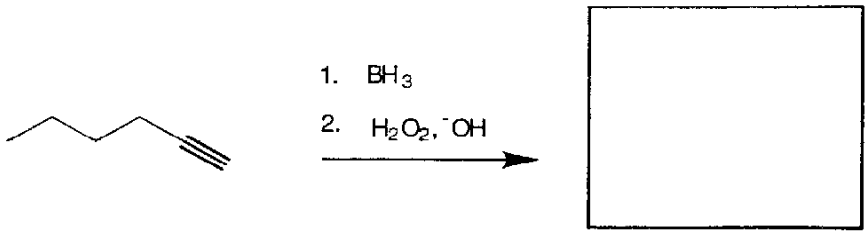
C_8H_{12} : ^{1}H NMR δ = 5.54 (m, 4 H)
2.11 (m, 8H) ppm

^{13}C NMR δ = 128.5, 28.5 ppm

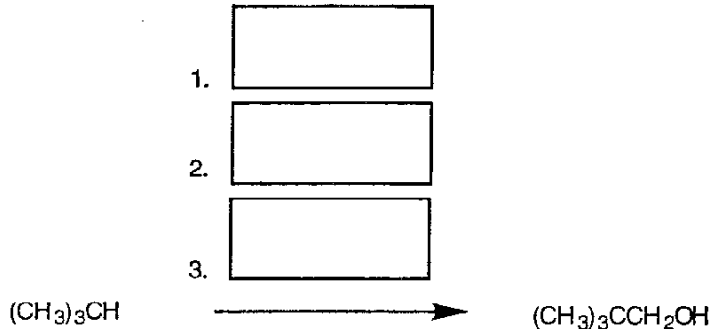
k.



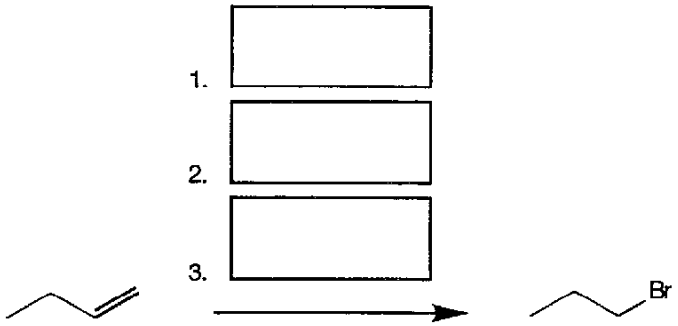
l.



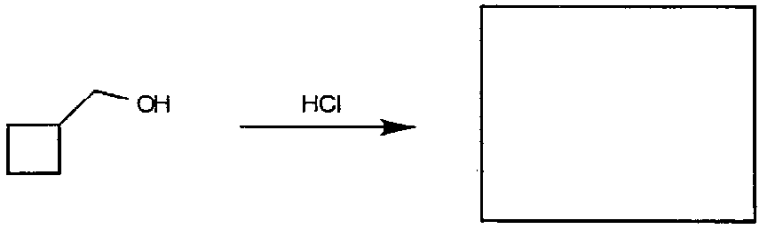
m.



n.



o.



C_5H_9Cl : ^1H NMR δ = 4.00 (m, 1 H), 1.0 - 2.0 (m, 8 H) ppm

^{13}C NMR δ = 59, 43, 26 ppm

III. [30 Points]

Treatment of ethane with bromotrichloromethane in the presence of light results in bromoethane and trichloromethane (chloroform).

$$CH_3CH_3 + BrCCl_3 \xrightarrow{h\nu,\ 20^\circ C} CH_3CH_2Br + HCCl_3 \quad \Delta H^\circ = -12 \text{ kcal mol}^{-1}$$

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

Step 1

Step 2

b. Given the ΔH^o of the reaction and the following data, calculate the bromine-carbon bond strength in $BrCCl_3$.

DH^o:	CH_3CH_2 -ξ-	H	98 kcal mole^{-1}
	CH_3CH_2 -ξ-	Br	68 kcal mole^{-1}
	Cl_3C -ξ-	H	96 kcal mole^{-1}

DH°(Br -ξ- CCl_3) :

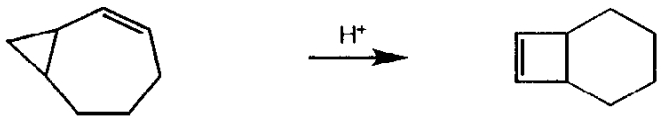
c. The dependence of rate on temperature is given by the Arrhenius equation: $k = Ae^{-E_a/RT}$. Will this reaction speed up, slow down, or proceed at the same rate at 50° C? Explain your answer.

Speed up	Slow down	Proceed at the same rate
(Circle one)		
Explain:		

IV. [60 Points]

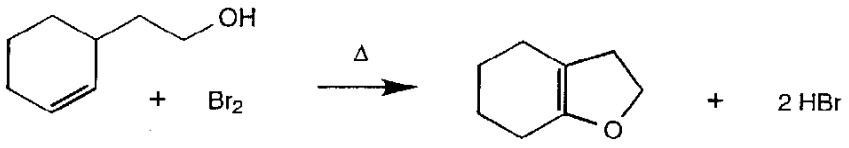
Write detailed step-wise mechanisms for the following transformations. Use only structures and "arrow-pushing" techniques.

a.

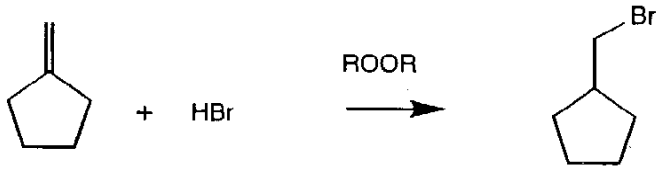


10

b.

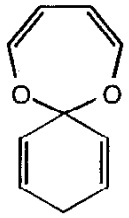


c.



V. [50 Points]

Catalytic hydrogenation of A with Lindlar's catalyst (i.e. deactivated Pd) gave several compounds, one of which, B, gave rise to the spectra depicted below.



A

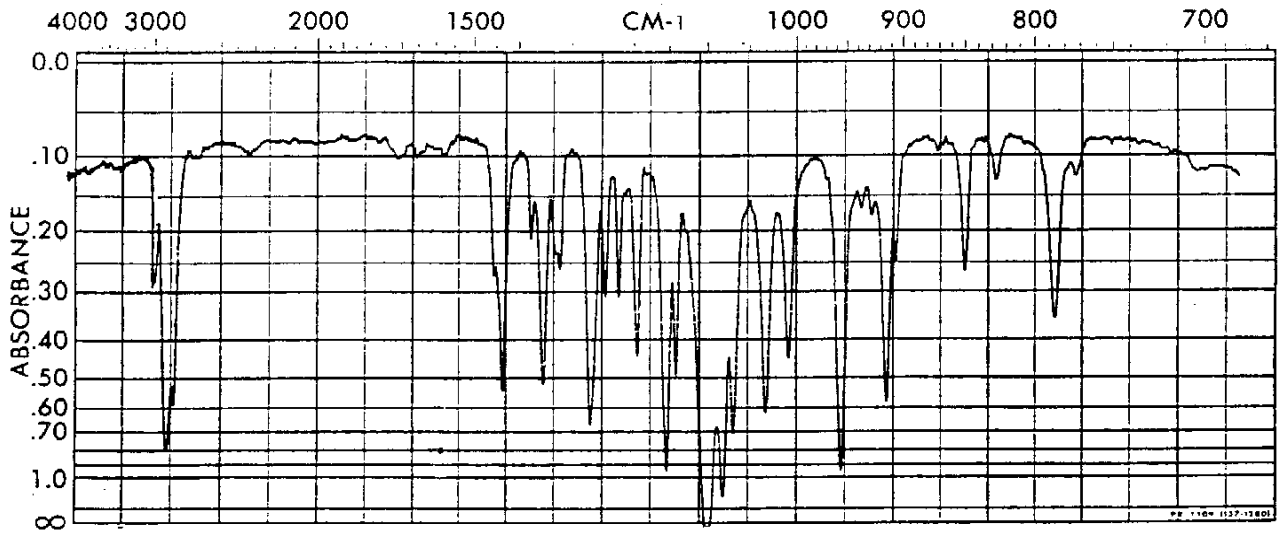
H_2, Pd (deactivated)

B $C_{10}H_{16}O_2$

a. Write the structure of **B** in the box above.

b. Interpret the spectral data as requested in the spaces provided. 12

1. IR Spectrum



Considering the oxygen functionality present in **A**, the product **B** could be an alcohol. Confirm or rule out this possibility:

Hydroxy peak is:

present / absent at _____ cm^{-1}

(circle correct statement)

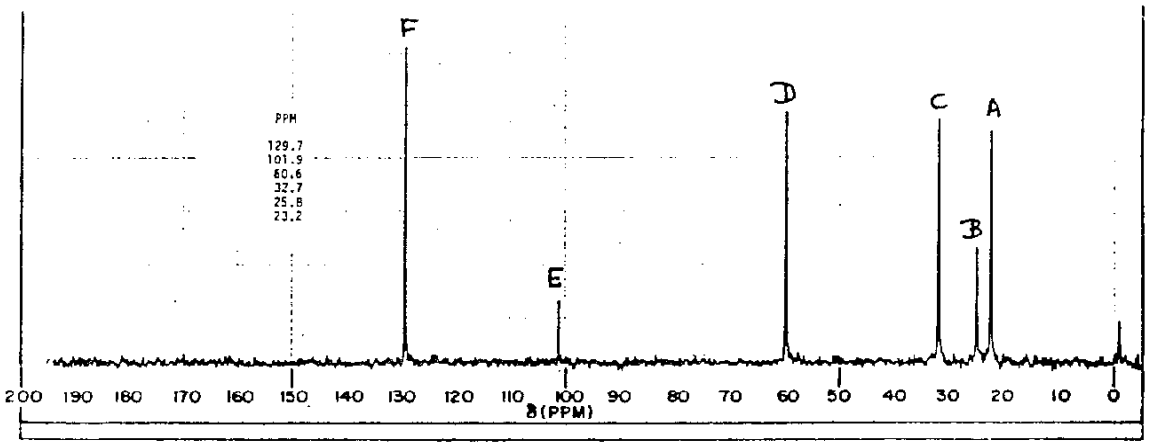
Considering the double bonds present in **A**, the product **B** could be an alkene. Confirm or rule out this possibility:

$\tilde{\nu}_{C_{sp^2}-H}$ is:

present / absent at _____ cm^{-1}

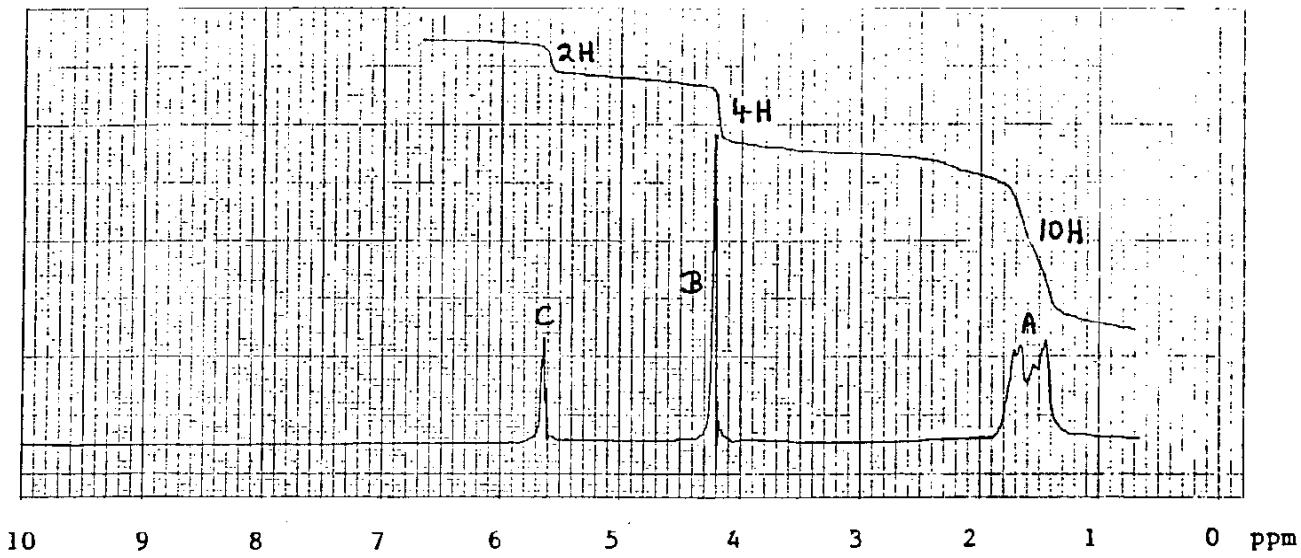
(circle correct statement)

2. ^{13}C NMR Spectrum



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

3. ^{1}H NMR Spectrum



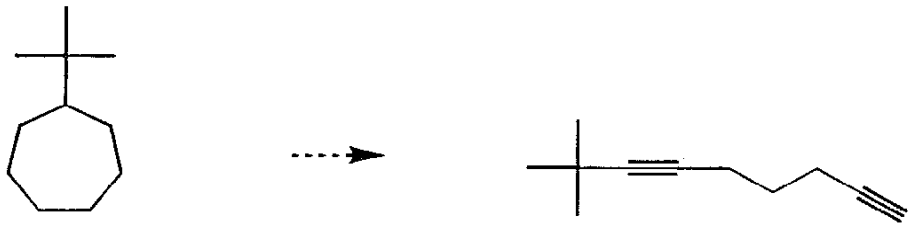
Note: $\delta = 5.63$ (quintet, $J = 4$Hz) , 4.22 (triplet, $J = 4$Hz)

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

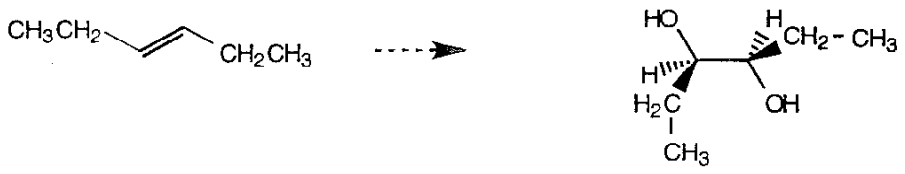
VI. [60 Points]

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.

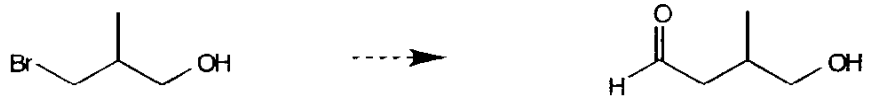
a.



b.



c.



VII. [80 Points]

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

a. The number of resonance structures for the cyclopentadienyl anion,  , is:

_____ one

_____ two

_____ three

_____ five

b. Beryllium hydride in ether solvents (R_2O) forms ether addition products of the type: $H_2Be(OR_2)_2$. In these compounds, Be is hybridized as:

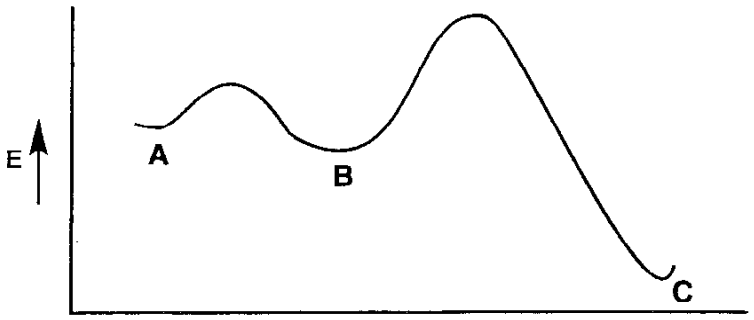
_____ sp

_____ sp^2

_____ sp^3

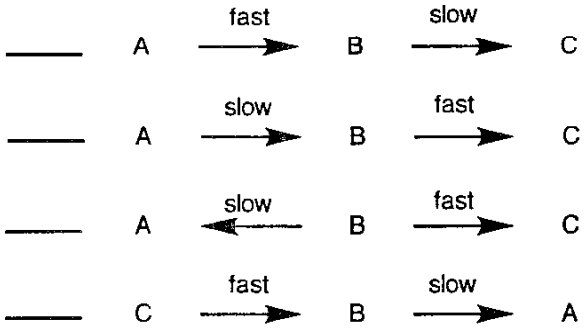
_____ not hybridized

c. Consider the following potential energy diagram.

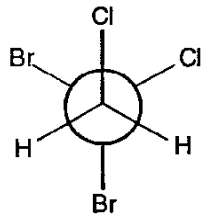


Reaction coordinate

Indicate which reaction sequence conforms best with the diagram.



d. The ^1H NMR spectrum of 1,1-dibromo-1, 2-dichloroethane at -130°C reveals the presence of the rotamer **A** by the observation of two doublets for the two hydrogens:



A

On warming to room temperature, the onset of "free rotation" will change this pattern to a:

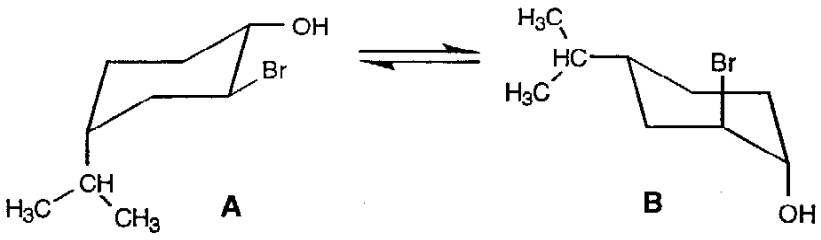
_____ singlet

_____ doublet

_____ two singlets

_____ doublet of doublets

e. Consider the following conformational equilibrium and the ΔG° values for axial - equatorial conversion of the given group in substituted cyclohexane:



$$\Delta^\circ G\left(\text{axial} \rightarrow \text{equatorial, kcal mol}^{-1}\right): \quad \begin{array}{ll} \text{HO} & -0.9 \\ \text{Br} & -0.6 \\ (CH_3)_2CH & -2.2 \end{array}$$

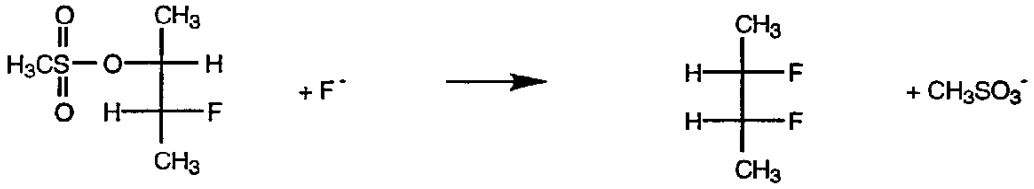
_____ **A** is more stable than **B** by 0.7 kcal mole^{-1}

_____ **A** is less stable than **B** by 0.7 kcal mole^{-1}

_____ **A** is more stable than **B** by 2.2 kcal mole^{-1}

_____ **A** is more stable than **B** by 1.9 kcal mole^{-1}

f. The optically pure starting sulfonate has a specific rotation [∝] which is monitored as it reacts with F^- by second order kinetics.



_____ [∝] goes to zero faster than the rate of disappearance of starting sulfonate

_____ [∝] goes to zero at the same rate as starting sulfonate disappears

_____ [∝] changes but never goes to zero as the reaction goes to completion

_____ [∝] stays unchanged

g. In each pair of acids shown below, circle the stronger one:

1)	$HC{\equiv}CCH_3$	$H_2C{=}CHCH_3$
2)	CH_3CH_2OH	$ClCH_2CH_2OH$
3)	$CH_3{}^{+}NH_3$	CH_3NH_2
4)	H_2S	H_2O

h. Considering what you know about the relative bond strength of C-H versus C-D, estimate the $\tilde{\nu}_{C-D}$ relative to $\tilde{\nu}_{C-H}$:

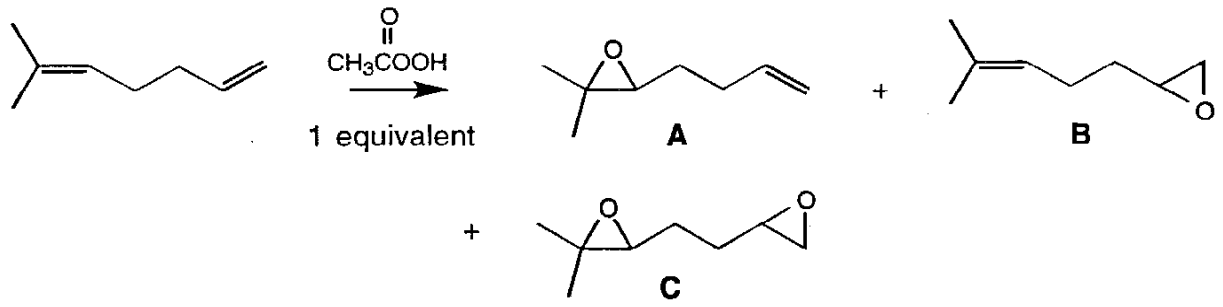
_____ $\tilde{\nu}_{C-H} = 1/2\ \tilde{\nu}_{C-D}$

_____ about the same

_____ $\tilde{\nu}_{C-D} > \tilde{\nu}_{C-H}$

_____ $\tilde{\nu}_{C-D} < \tilde{\nu}_{C-H}$

i. Consider the following oxidation and all the possible products.



What will be the observed product distribution?

_____ only **A**

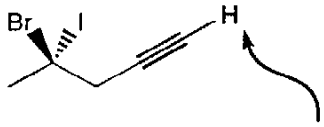
_____ **A**:**B**:**C** = 1:1:1

_____ only **B**

_____ **A**:**B**:**C** = 1:1:2

21

j. For the indicated hydrogen in compound **A,** what will be the expected ^1H NMR pattern:



_____ singlet

_____ doublet

_____ triplet, because the two hydrogens at C-3 are equivalent

_____ doublet of doublets

Hospitals to avoid

* THE END *

Merry Christmas!