EXAMINATION 1
Chemistry 3B

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

Peter Vollhardt
February 23, 2006

Please provide the following information if applicable.

Making up an I Grade _____
(If you are, please indicate the semester during which you took previous Chem 3A:

_____ _____
Semester Instructor

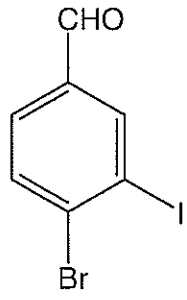
Please write the answer you wish to be graded in the spaces provided. *Do scratch work on the back of the pages.* This test should have **17** numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **Read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy structures or phrases. It is better to be pedantic in accuracy now than sorry later!** ***Good Luck!***

DO NOT WRITE IN THIS SPACE

I.	_____	**(30)**
II.	_____	**(30)**
III.	_____	**(50)**
IV.	_____	**(50)**
V.	_____	**(40)**
VI.	_____	**(30)**
VII.	_____	**(20)**
Total:	_____	**(250)**

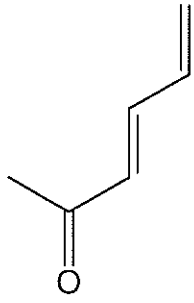
I. [30 Points] Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary (*cis*, *trans*, *R*, or *S*).

a.



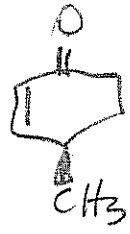
4-Bromo-3-iodo-benzaldehyde
or - benzenecarbaldehyde

b.

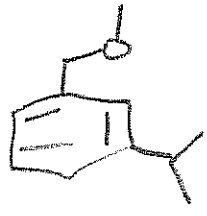


Trans-3,5-hexadien-2-one
or
Trans-hexa-3,5-dien-2-one

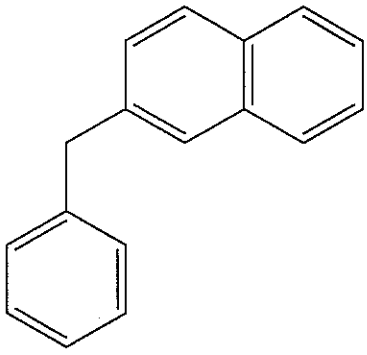
c. *R*-4-Methyl-2-cyclohexenone



d. *Meta*-(1-methylethyl)(methoxymethyl)benzene

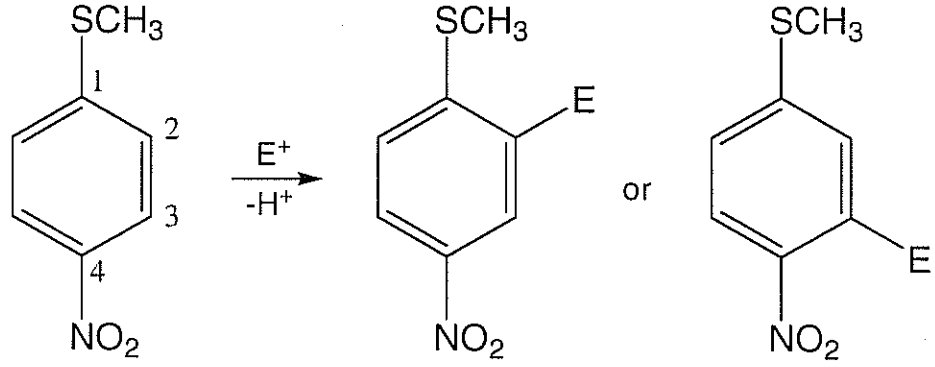


e.



2-Benzylnaphthalene
or
2-(Phenylmethyl)naphthalene

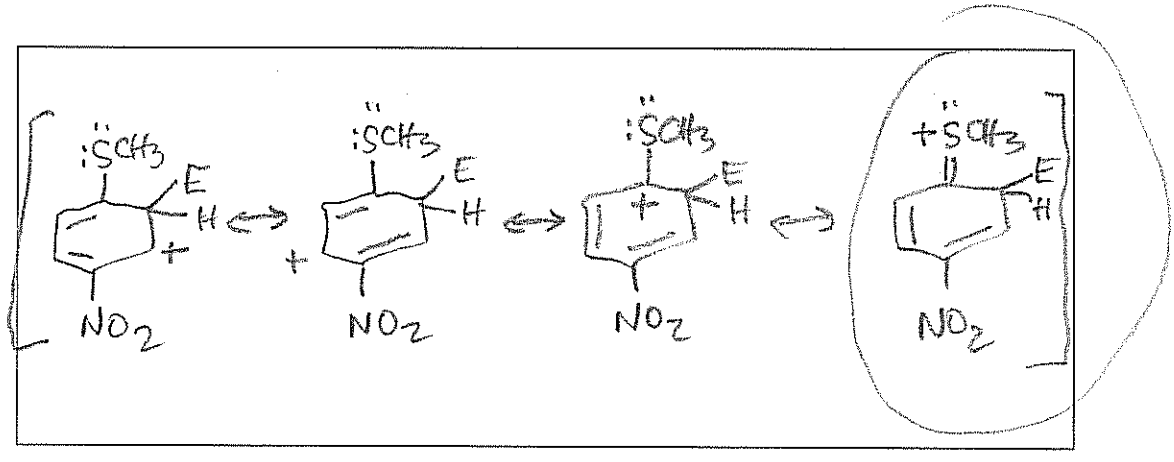
II. [30 Points] 1-Methylthio-4-nitrobenzene **A** undergoes preferential electrophilic attack by E^+ to give only one of the two products shown.



a. Which one? Mark the box below your choice with an X.

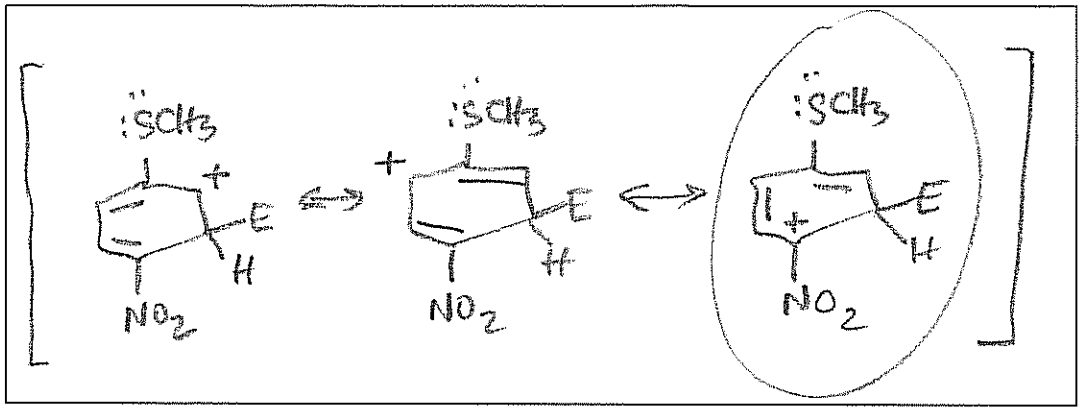
b. Write the resonance forms of the intermediate formed on attack of E^+ at:

C-2:



Four resonance forms

C-3:



Three resonance forms

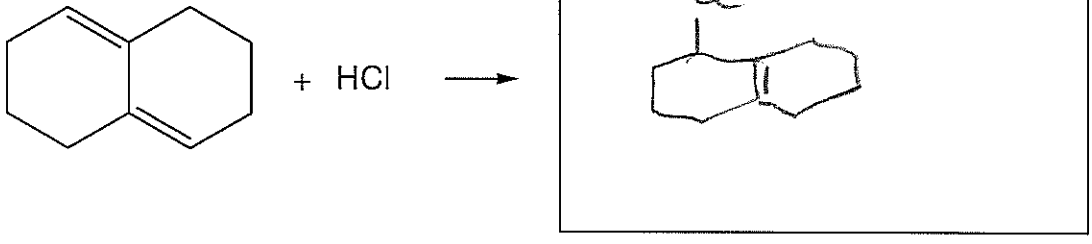
c. Circle (in your answers above):

a. the **most strongly** contributing resonance form of the attack at C-2 and

b. the **least** contributing resonance form of the attack at C-3.

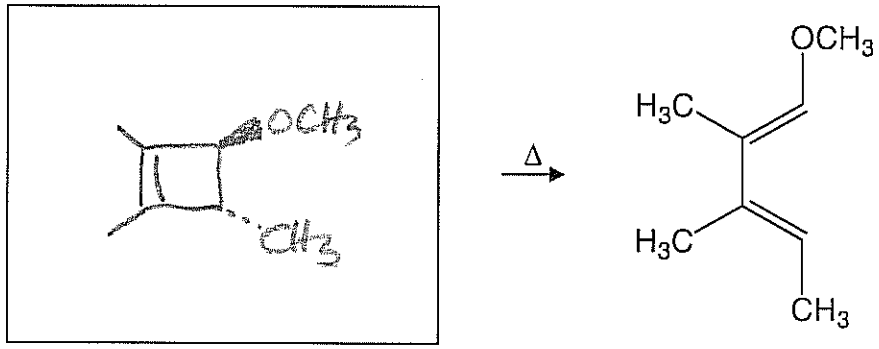
III. [50 Points] Add the missing components (starting materials, reagents, or products) of the following reactions in the boxes provided. Aqueous work-up (when required) is assumed to be part of a step. It is not part of any answer.

a.



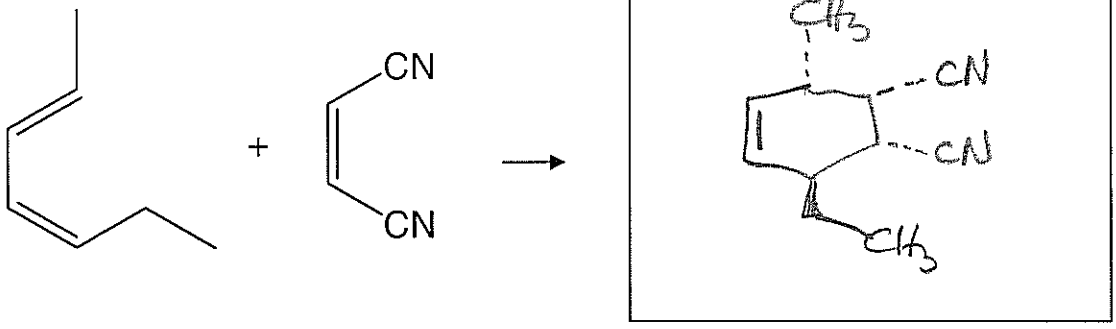
Thermodynamic product

b.

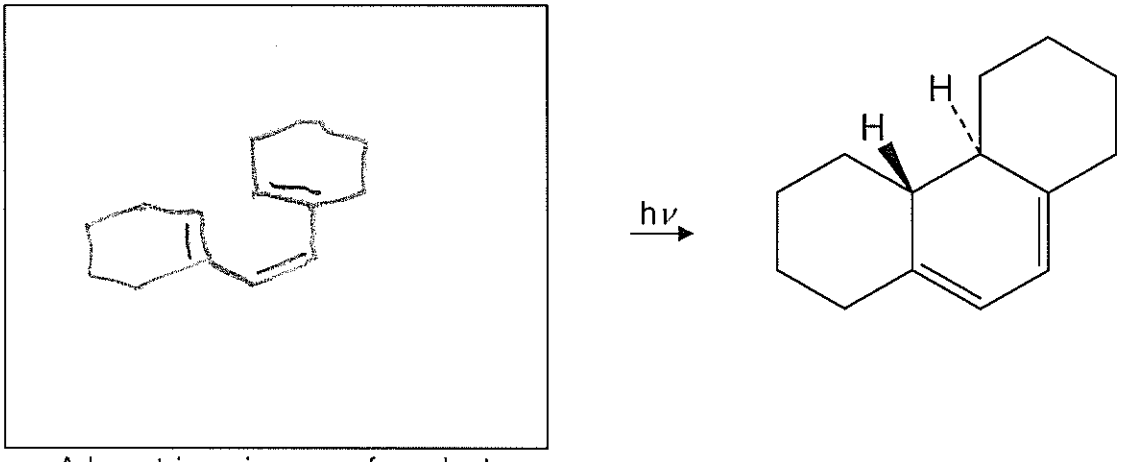


A cyclobutene

c.

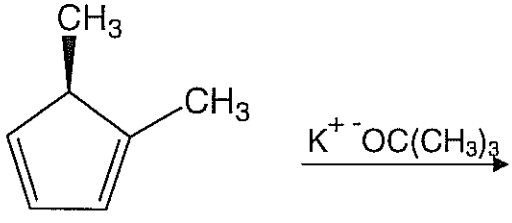


d.

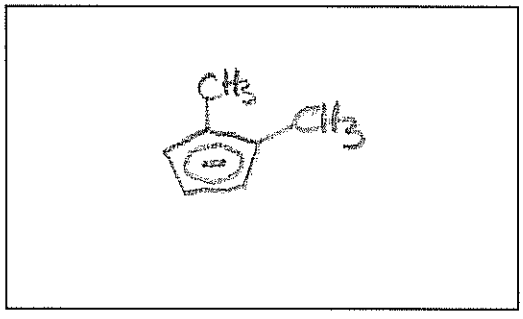


A hexatriene isomer of product.

e.

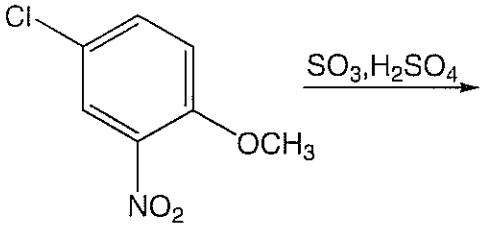


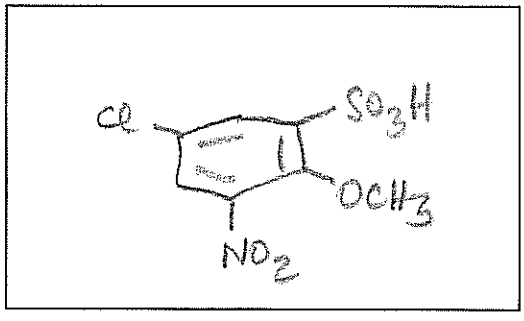
^{13}C NMR: 7 lines



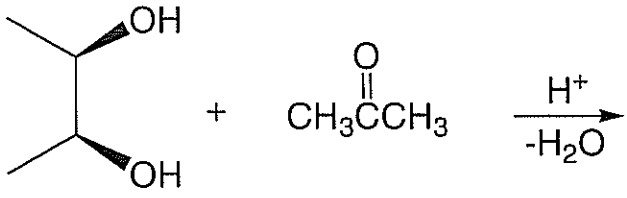
^{13}C NMR: 4 lines

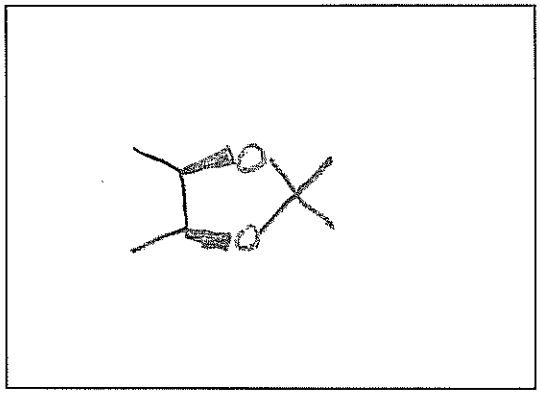
f.





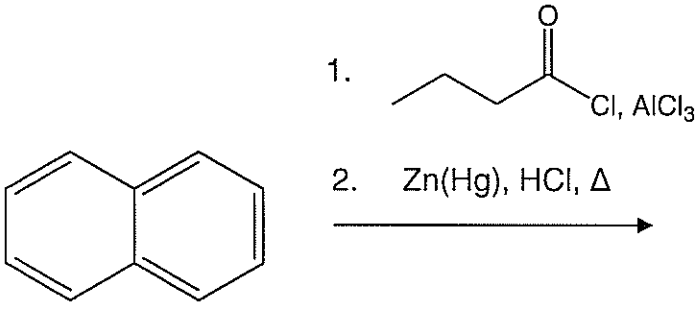
g.

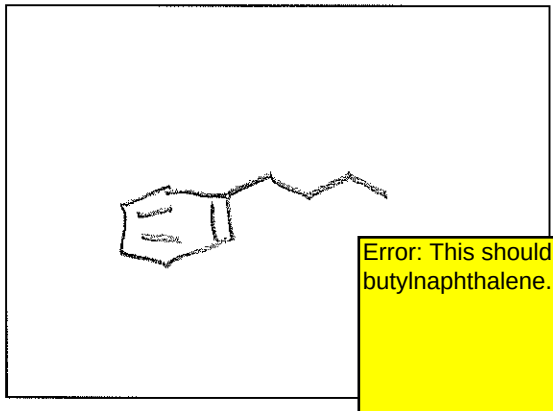




^{13}C NMR: 4 lines

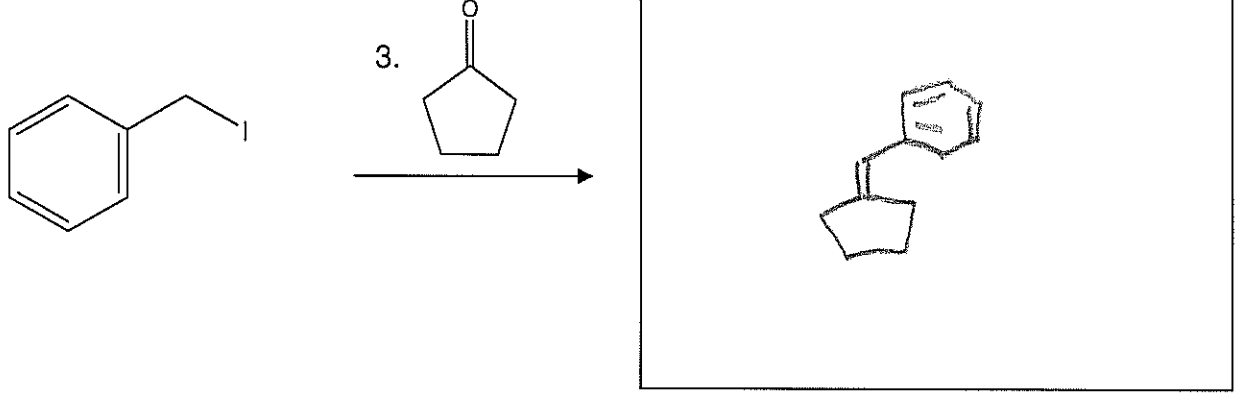
h.



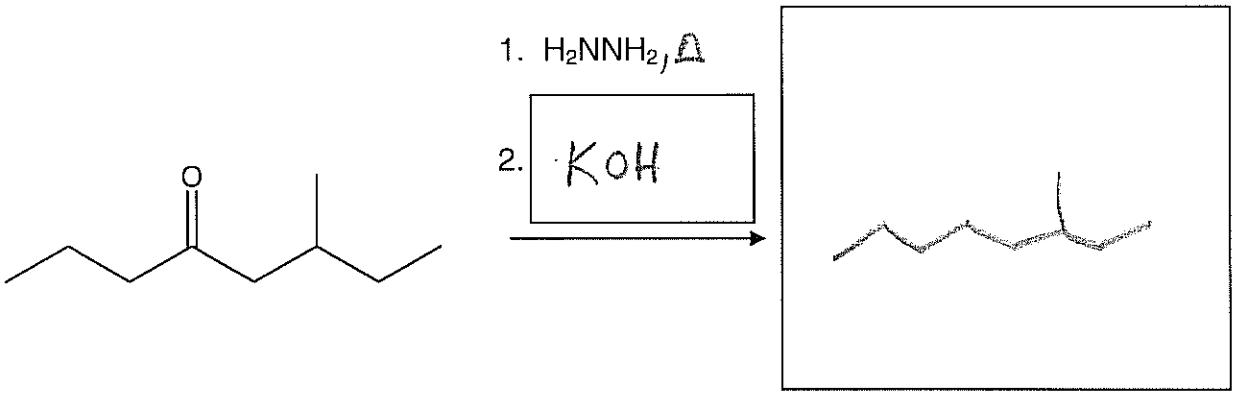


Error: This should be 1-butylnaphthalene.

i.

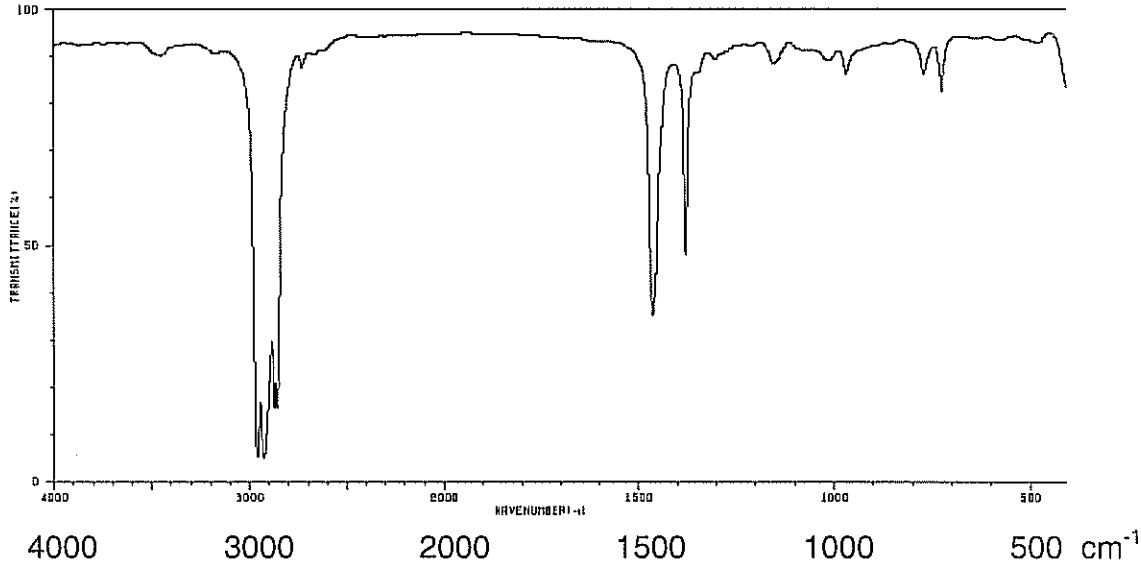


j.

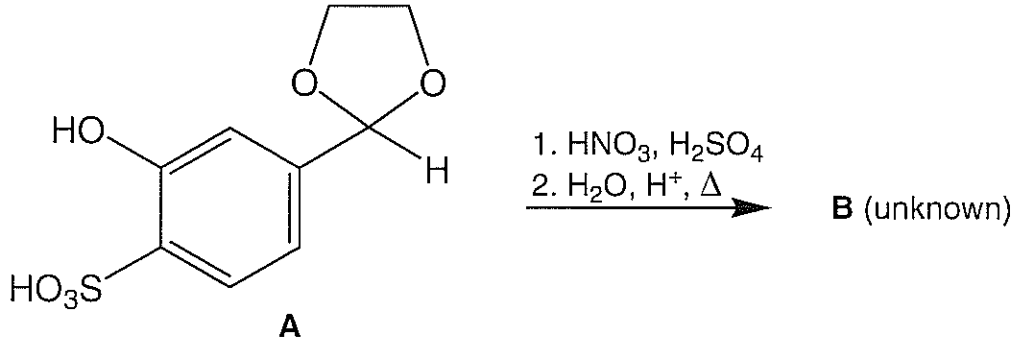


IR Spectrum of product :

A hydrocarbon

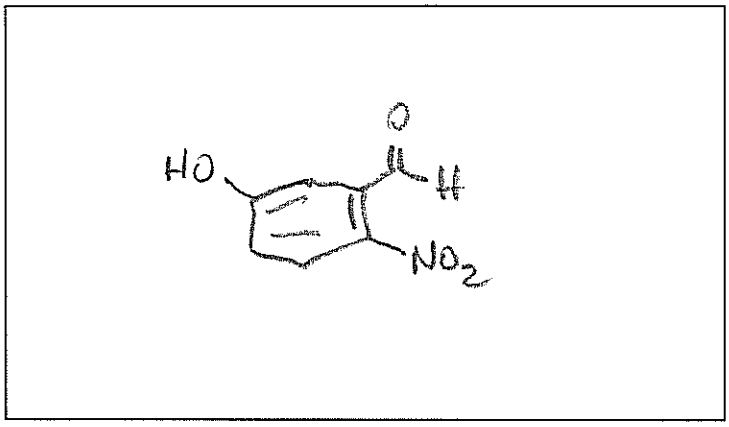


IV. [50 Points] Treatment of acetal A with conc. nitric acid and H_2SO_4 led to unknown B. The IR and NMR spectra of this product are shown below.



A

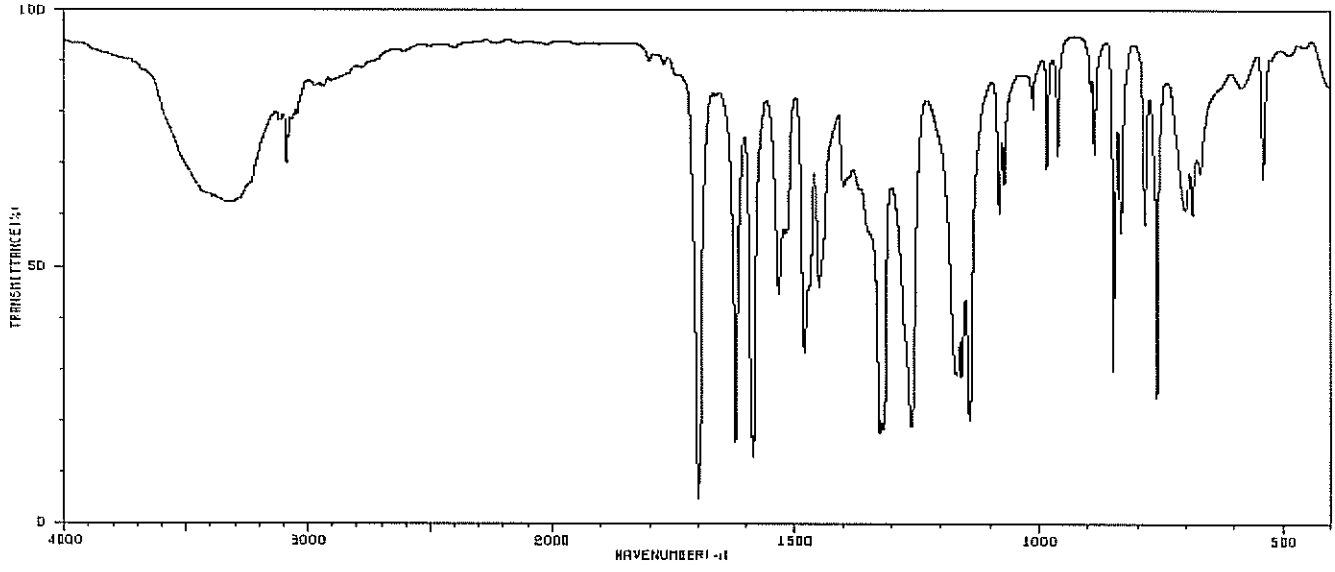
a. After consideration of the spectral data, write the structure of the product in the box below.



Structure of unknown

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

1. IR Spectrum



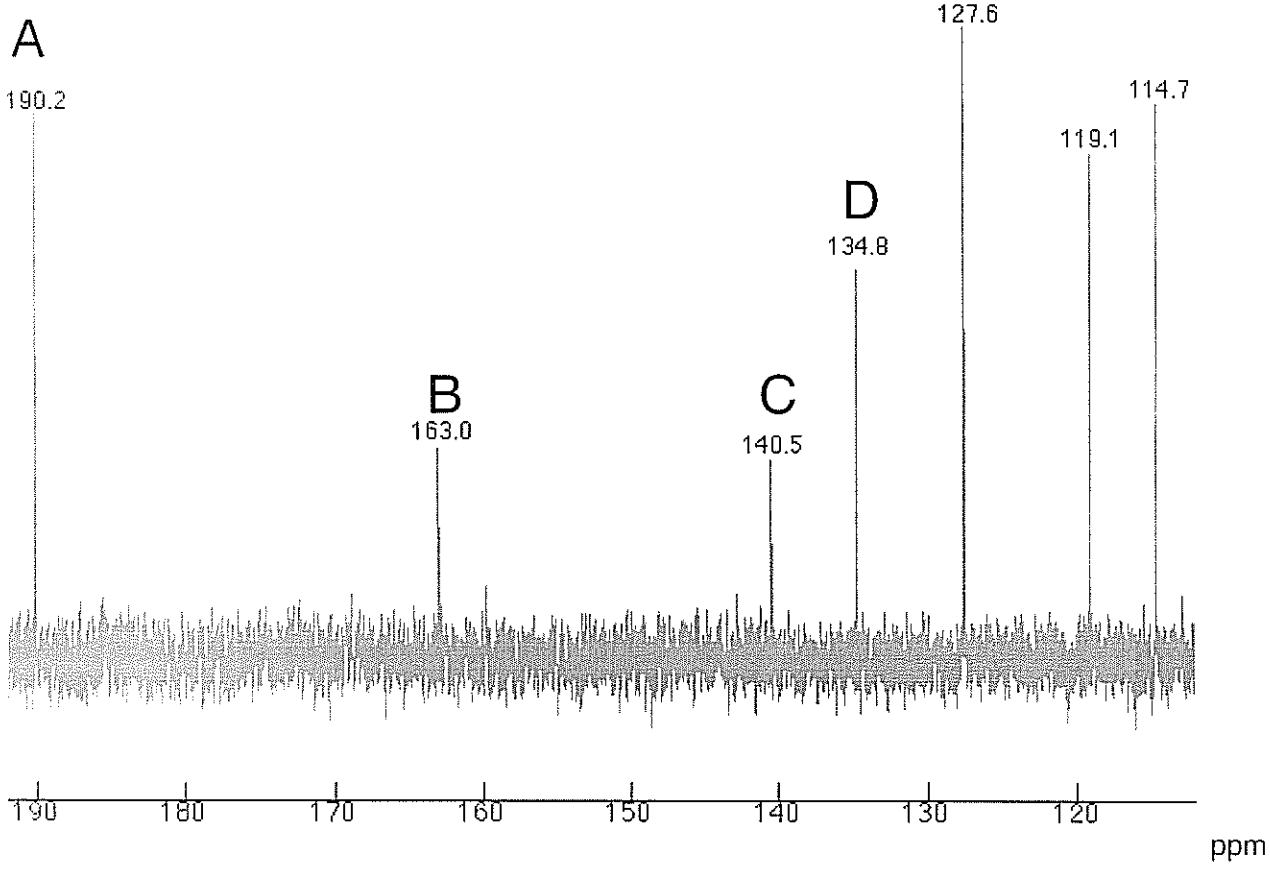
Confirm or rule out the presence or absence (circle one) of the following bonds. Enter an approximate expected stretching frequency in the box.

$\tilde{\nu}$ (C_{sp^2}–H) is: (present) absent at 3070 cm^{-1}

$\tilde{\nu}$ (O–H) is: present absent at 3300 cm^{-1}

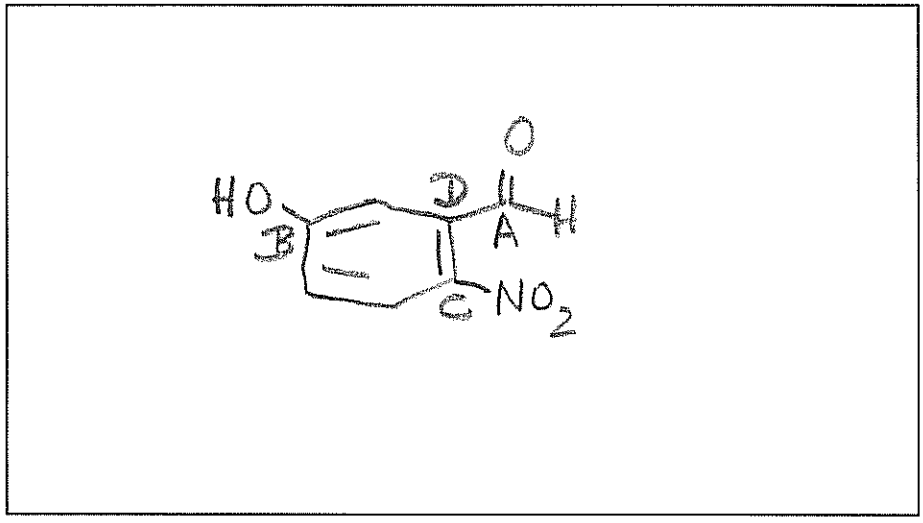
$\tilde{\nu}$ (C=O) is: present absent at 1700 cm^{-1}

2. ^{13}C NMR Spectrum (these are all single lines; ignore the seeming splitting of some).

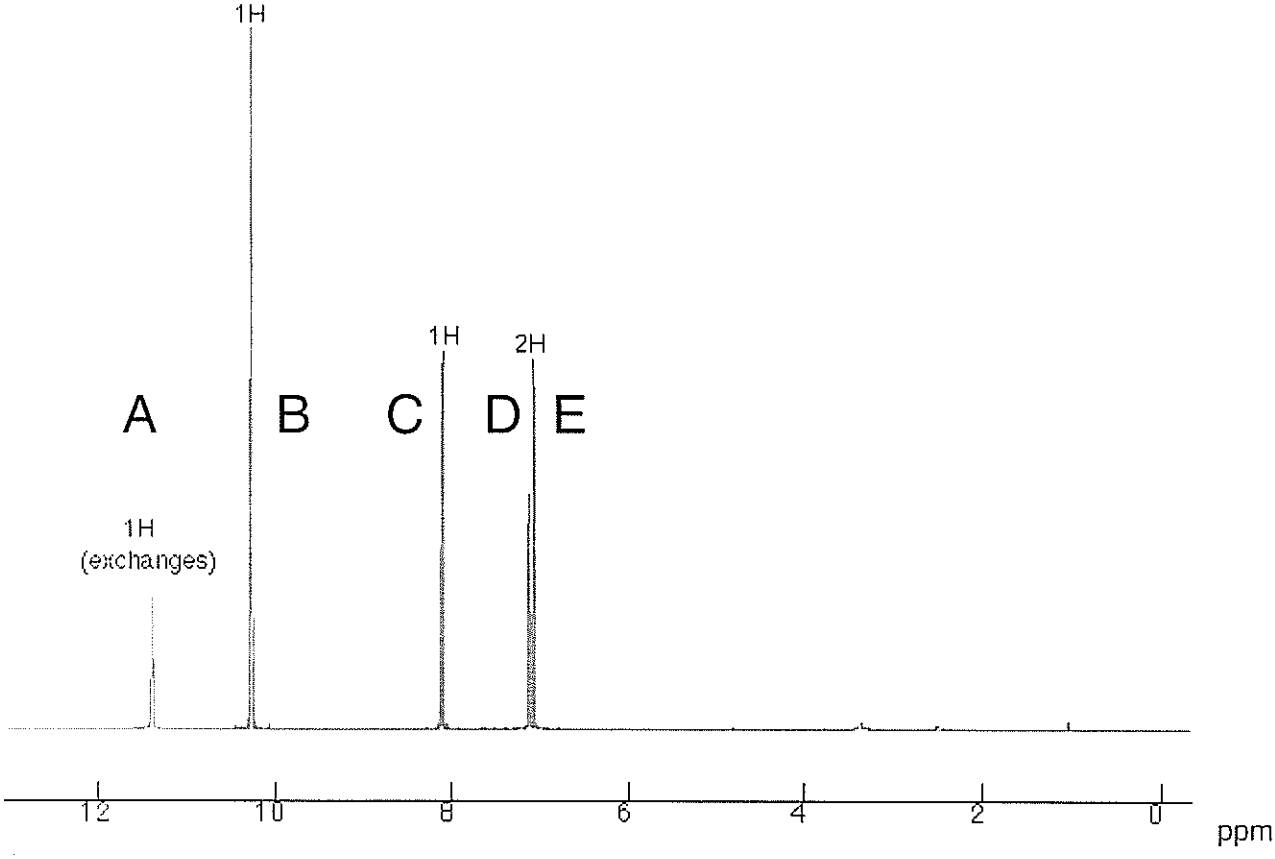


The proton-coupled spectrum leaves the singlets for B, C, and D unchanged.

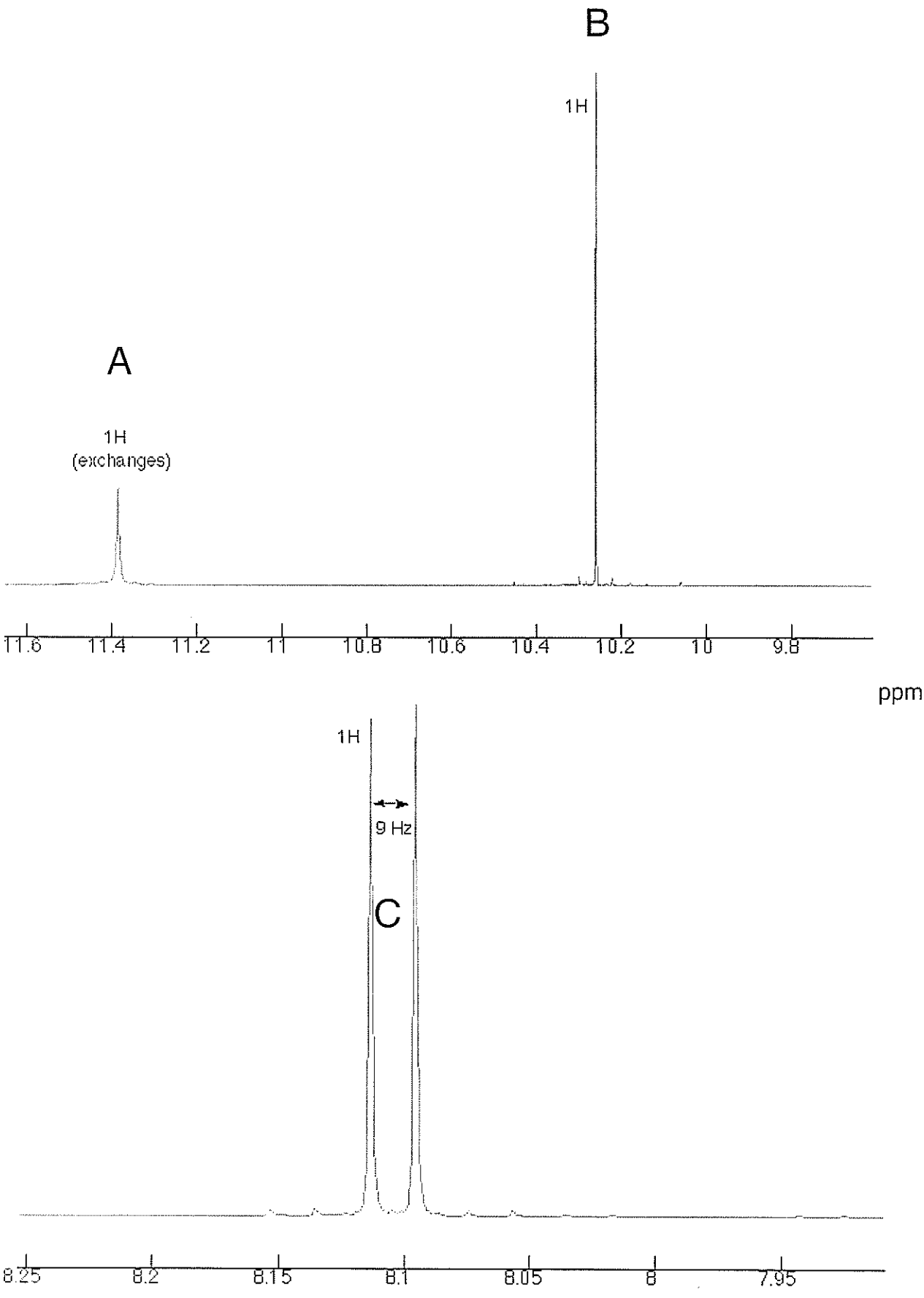
Draw your suggestion for the unknown in the box below and label the types of carbon atoms A, B, C, and D, giving rise to the corresponding signals in the spectrum. For the assignment of B, C, and D, consider that the order of chemical shifts parallels roughly the order of electronegativity of the attached atom.



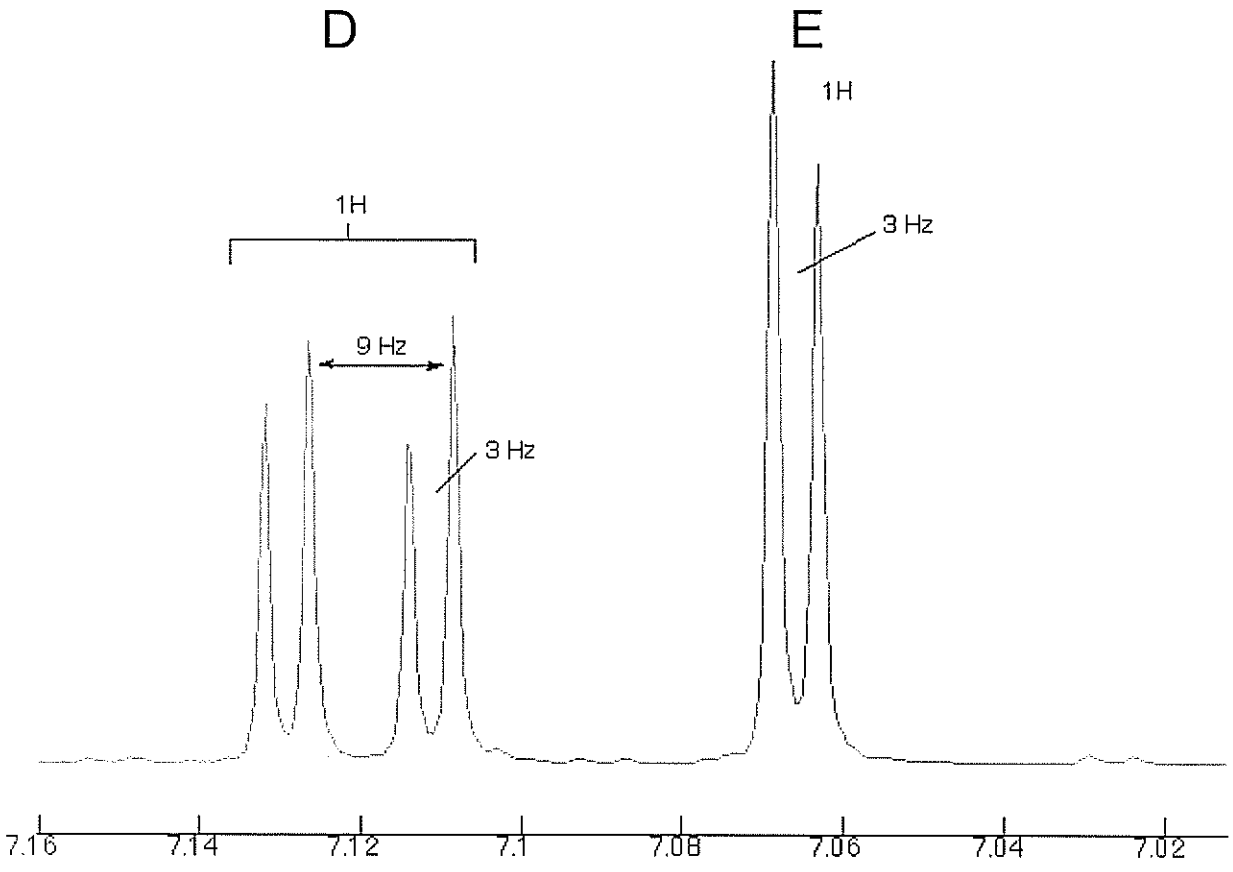
3. ^{1}H NMR Spectrum (for expanded sections, see next two pages).



The signal due to protons A disappears in D_2O solvent.

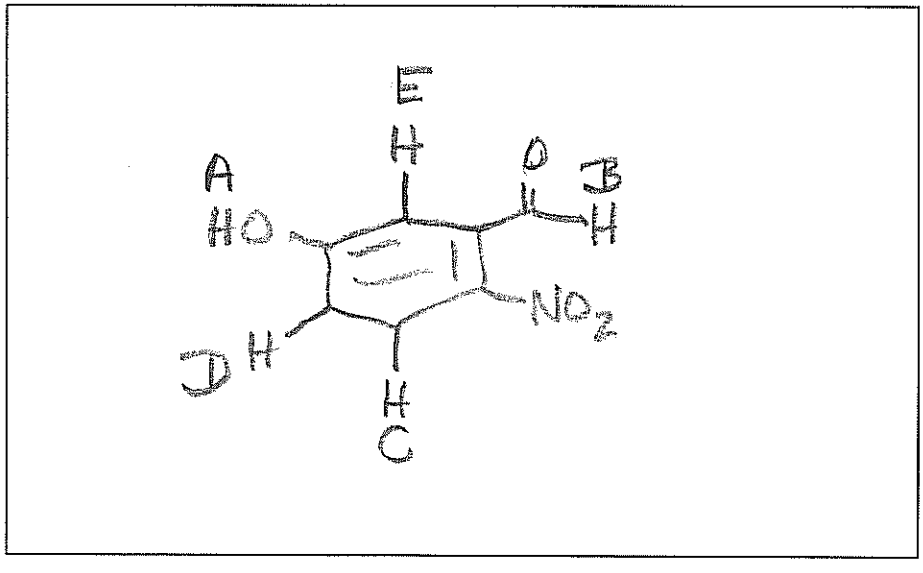

B
1H
A
1H
(exchanges)
11.6
11.4
11.2
11
10.8
10.6
10.4
10.2
10
9.8
ppm
1H
9 Hz
C
8.25
8.2
8.15
8.1
8.05
8
7.95

ppm



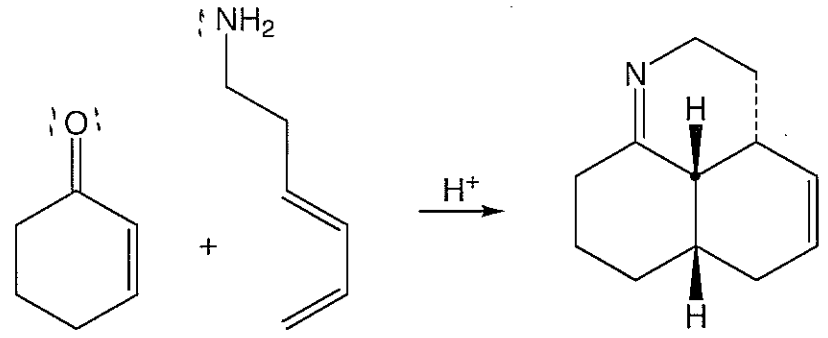
ppm

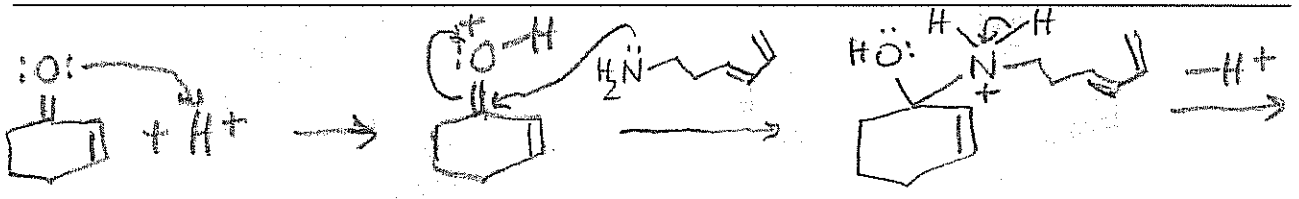
Draw your suggestion for the unknown in the box and label the hydrogens A, B, C, D, and E giving rise to the corresponding signals in the spectrum.

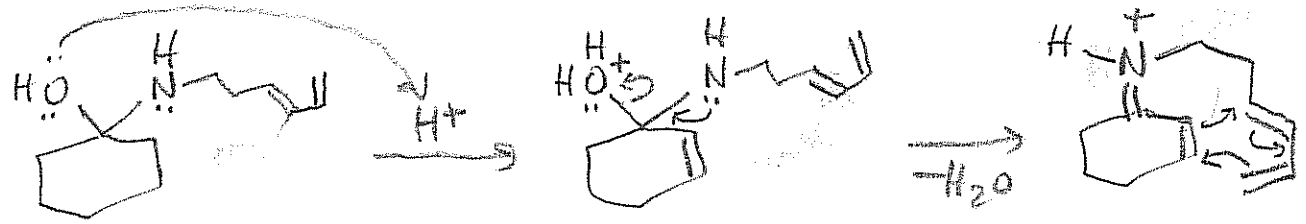


V. [40 Points] Write detailed step-wise mechanisms for the following transformations. Use only structures and "arrow-pushing" techniques. Note: These are <u>not</u> synthetic problems. Do not <u>add</u> any reagents! What you see is what you have! Work from left to right in the following spaces. There is much more space than you will need.

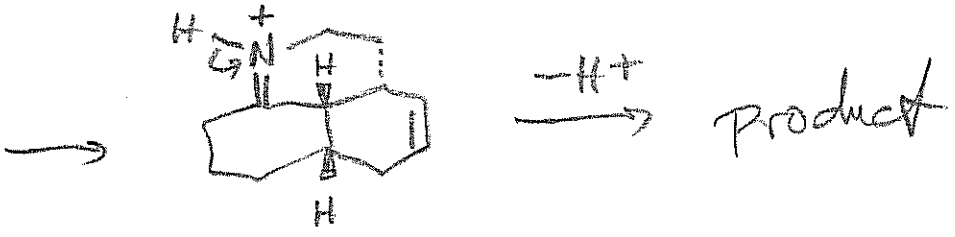
a.





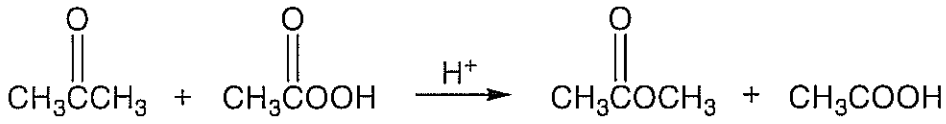


hemiaminal

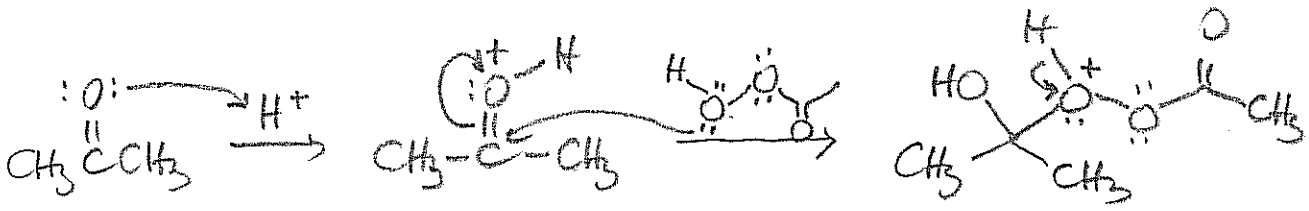


Product

b.

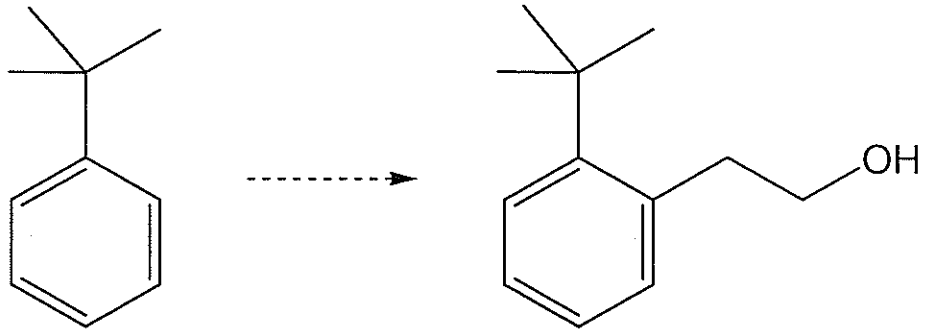


Work from left to right in the following spaces. There is much more space than you will need.

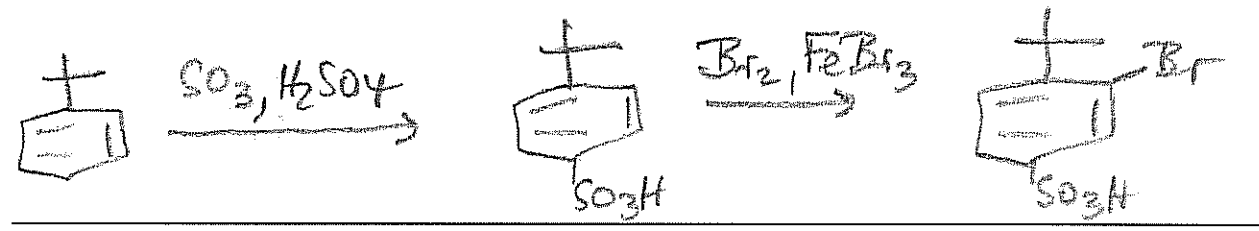


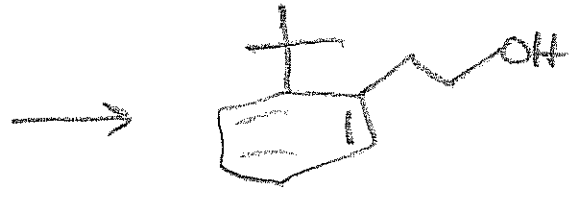
VI. [30 Points] Provide a reasonable synthetic route from starting material to product.
Note: Several steps are required, and there may be more than one solution to the problem.
Do not write mechanisms!

a. Here, you may use any additional organic or organometallic reagents to effect your conversions.

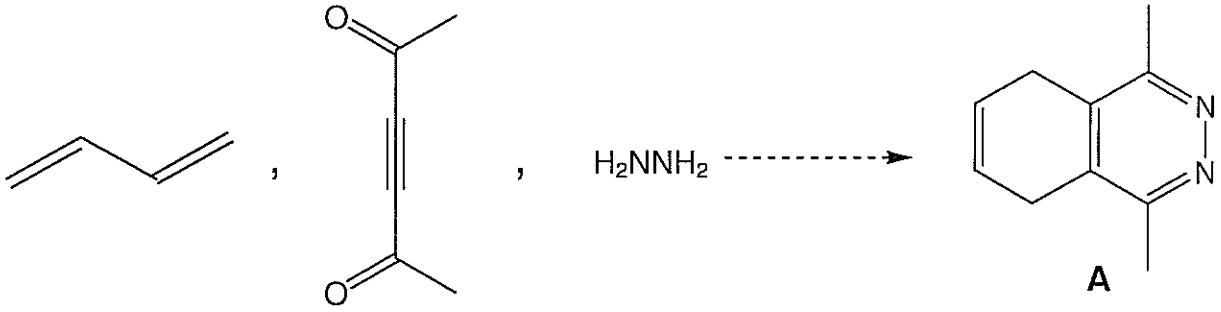


Work from left to right in the following spaces. There is much more space than you will need.



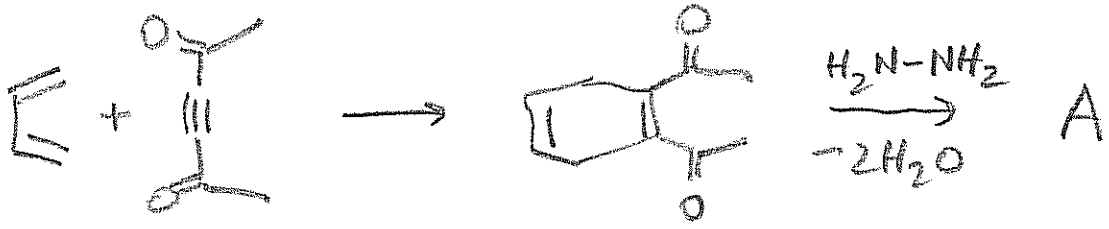


b. Synthesize compound A using only the materials shown and ***no*** additional reagents.



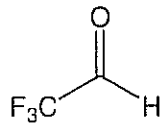
A

Work from left to right in the following spaces. There is much more space than you will need.

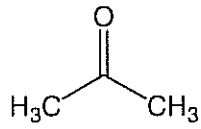


VII. [20 Points] Place an X mark in the box next to the most accurate statement.

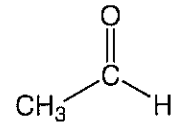
a. The equilibrium constant for hydration of **1**, **2**, and **3** increases in the order



1



2



3

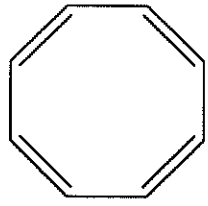
☐ **1, 2, 3**

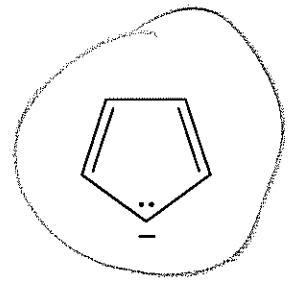
☐ **3, 2, 1**

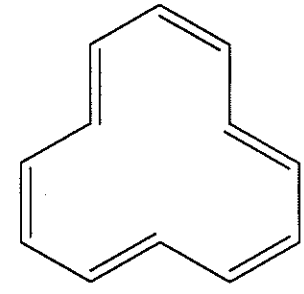
☒ **2, 3, 1**

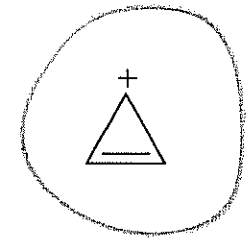
☐ **3, 1, 2**

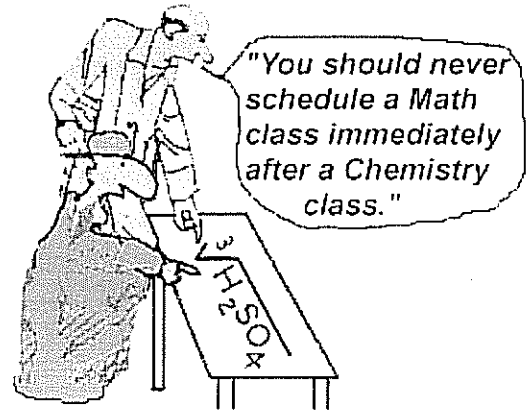
b. Circle the compounds which are aromatic











The End