YOUR NAME: Irika Sinha

Chemistry 346 Final Examination

Winter 2019

Professor Hopkins

1.	15	/15
2.	12	/15
3.	08	/12
4.	06	/~~8~~6
5.	04	/8
6.	10	/10
7.	04	/7
8.	08	/8
9.	02	/10

Good!

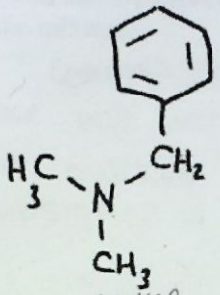
Total: 69 /93

You are responsible for confirming that this examination contains **17** pages, including the cover sheet.

This is a closed-book and closed-notes exam.

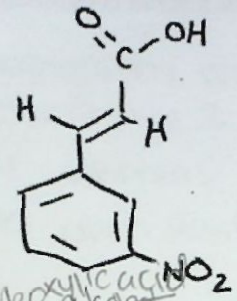
Submission of this exam for grading constitutes confirmation that the work herein is your own.

1. (15 points) Assume you are provided a 4 g sample of a mixture composed 1:1:1:1 by weight of the following four organic compounds that have the indicated physical properties:



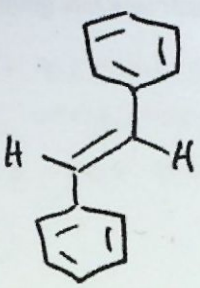
amine

1



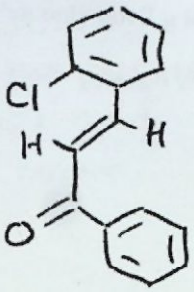
carboxylic acid

2



neutral

3



neutral

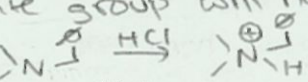
4

	1	2	3	4
m.p. (°C)	-75	202-204	122-124	49-52
b.p. (°C)	183-184	(high)	305-307	(high)

a. Describe a very simple procedure which would separate substance **1** from the remaining three substances (**2-4**). [You do not need to isolate or purify **1**, just separate it from the other three substances.] State briefly why you believe this will work.

- Dissolve the mixture in diethyl ether & add to separatory funnel
- Add 1M HCl in 5mL aliquot - ensure aqueous layer is acidic
- collect acidic aq. layer
- add 5mL HCl (1M) aliquot & ensure aq. layer is acidic
- collect & combine acid extracts.

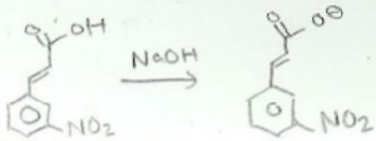
This will work because the addition of HCl will protonate substance 1, causing it to drop into the aqueous layer because it will be water soluble due to its charged nature. It will remain in a acidic aqueous layer and be present in collected acid extracts. None of the other substances will become aqueous in the presence of HCl: substance 2's nitrate group will not protonate b/c the nitrogen isn't positively charged.



b. Assume the procedure in (a) removed **1** from the original mixture. Describe a very simple procedure which would separate substance **2** from the remaining two substances (**3**, **4**). [You do not need to isolate or purify **2**, just separate it from the other two substances.] State briefly why you believe this will work.

- Add 6M NaOH and then 5mL 1M NaOH aliquot
- Ensure the aqueous layer is basic & collect it
- Add 5mL aliquot of 1 NaOH & ensure aqueous layer is basic
- collect & combine base extracts

This will work because NaOH will deprotonate substance 2, causing it to be water soluble & part of the aqueous layer. It will remain in the aqueous layer if the layer is basic, and will be present in the collected base extracts. None of the other substance will become ~~water soluble~~ aqueous in the presence of base.



c. Assume the procedures in (a) and (b) removed **1** and **2** from the original mixture. Describe a procedure that would separate **3** from **4**. State briefly why you believe this will work. Bear in mind that selective crystallization is never a sure thing and also that you've only got 2 g total of the mixture.

Column chromatography with hexane as the mobile phase will work. Substance 3 is very nonpolar and will quickly elute whereas the far more polar substance 4 elutes much slower.

5

column chromatography is a purification method dependent on differences in polarity.

2. (15 points) Answer the questions below.

a. How would you go about removing a very small amount of water from 15 mL of 4-methyl-1-cyclohexene?

Add anhydrous $MgSO_4$ to the liquid in order to dehydrate it.

✓

b. How would you cause a water-insoluble amine to precipitate from an aqueous solution of the amine hydrochloride salt?

Add NaOH to the solution to neutralize the acid and make the aqueous solution basic. The amine will be deprotonated and become part of the organic layer.

✓

c. How would you increase the rate a which a desired organic compound elutes through a silica gel chromatography column presently being eluted with 10% ethyl acetate in hexanes?

change the concentration of the mobile phase/solvent. Generally making it more polar (increasing the ratio of ethyl acetate to hexane) should make everything elute faster.

✓

d. Why in loading the compounds to be separated onto a silica gel chromatography column does one use the least polar solvent in which the compounds will dissolve?

compounds need to be dissolved in a solvent to move through the stationary phase. ~~Hexane~~ Solids cannot elute or move through the column.

0/3

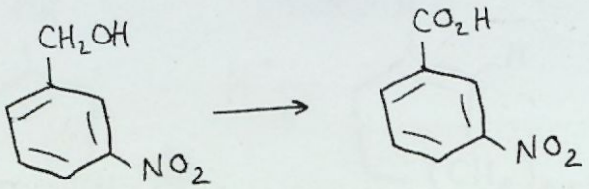
e. What was the purpose of the drying tube in the Grignard experiment? Be specific concerning what chemical reaction was being suppressed.

The drying tube prevented water from entering the flask and reacting with the extremely reactive Grignard reagent.

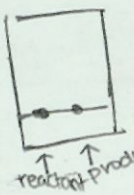
$R-MgBr + H_2O \rightarrow R-H + OH$

3

3. (12 points) You have attempted the reaction below, and obtained a pure crystalline product that is either recovered starting alcohol (a crystalline compound that is available to you), or the indicated *previously unknown* carboxylic acid (so no literature data and no authentic sample are available to you). Describe **four different** and convenient methods by which you could unequivocally distinguish which one of these two is your product. You may use *any methods available in the CHEM 346 lab*. A given spectroscopic technique (e.g., IR) may be used only once. Be sure to tell in each case specifically how you would interpret your observations; the last few pages of this exam should be helpful.



a. TLC



Spot a TLC plate with the product and starting material and then place the TLC plate in the mobile phase/solvent and allow elution. Measure Rf values for each spot after TLC is finished. If the Rf values are equal, they are likely the same product. If the spots are have different Rf values, they are likely different compounds.

b. IR spectroscopy

The reactant and a carboxylic acid would have slightly different peaks in an IR spectrum. While both contain benzene C-N, N=O, and C-C stretch peaks, the reactant will only have a broad alcohol peak around 3200 cm-1 while a carboxylic acid will have both a broad alcohol peak from 3300-2500cm-1 and a C=O peak from 1725-1700 cm-1. If the carboxylic acid peak is present, the product is not alcohol.

c. NMR spectroscopy

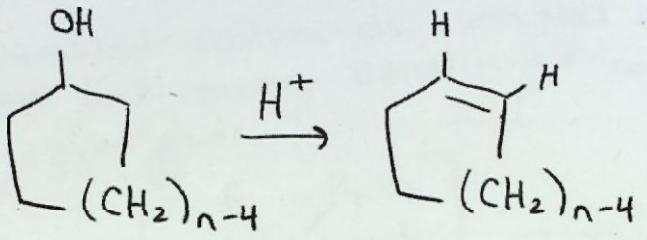
starting alcohol- would have peak envelope for 2H at ~3.5ppm and an alcohol singlet (broad) from 0.5-5ppm

carboxylic acid- would not have 2H peak envelope at ~3.5ppm, would have carboxylic acid hydrogen ~~envelope~~ singlet at >11.0ppm.

d. Melting Point Analysis

Since the literature melting point value of the starting value is likely known, the melting point range of the product should be measured. If it is the same as that of the starting alcohol, the compounds are likely the same.

4. (6 points) For a study you hope to undertake, you need to prepare several grams of each of the four cycloalkenes of ring sizes 5-8 indicated below, in each case 95+% pure. You are contemplating using the acid catalyzed dehydration/distillation method you used in class this quarter. Below are tabulated the known boiling points at atmospheric pressure of the alcohols and alkenes.



n (ring size)	b.p. alcohol (°C)	b.p. alkene (°C)
5	139-140	44-46
6	160-161	83
7	185	112-114
8	210	145-146

a. If you use a simple distillation apparatus, given the data above, do you believe the problem of contamination of the distillate (the product alkene) with the starting alcohol will get worse or better as you progress from the smaller to larger ring sizes? Why?

The contamination will get worse as ring size increases. This is because the difference in the boiling points of the alkene and alcohol decreases as ring size increases, meaning that, eventually they may boil at the same temperature.

✓

b. What specific change would you make to the simple distillation apparatus to enhance your likelihood of obtaining pure cycloalkene?

change it from a simple distillation set-up to a fractional distillation set-up by changing the column.

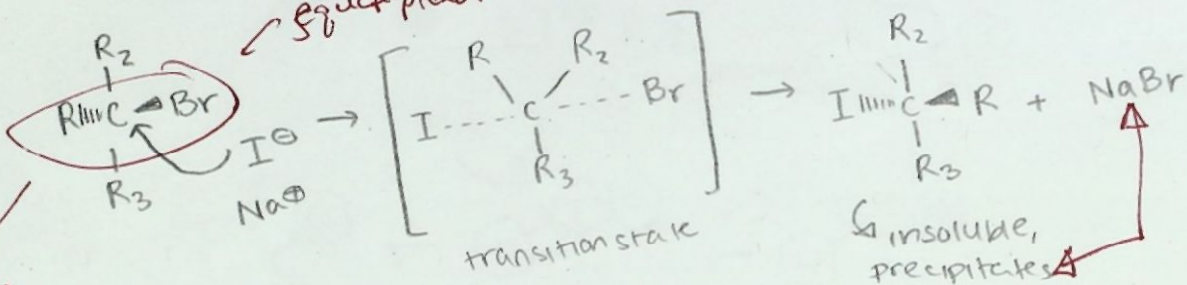
✓

5. (8 points) For either **one** of the two reaction types (S_N1 or S_N2) you studied in lab this quarter, briefly describe the specific starting materials you combined (reagents, solvents, etc.), the chemical mechanism that led to the appearance of a precipitate (the structure of the precipitate, of course), and why the rate of appearance of the precipitate could be used as an indication of the rate of the S_N1 or S_N2 reaction you were studying.

S_N2:

Mixed brominated compounds with NaI in acetone to complete an S_N2 reaction between the compound and $I^\ominus$.

reaction:



never draw chiral center flat way

If the S_N2 reaction successfully proceeded, the iodinated substance precipitated due to insolubility.

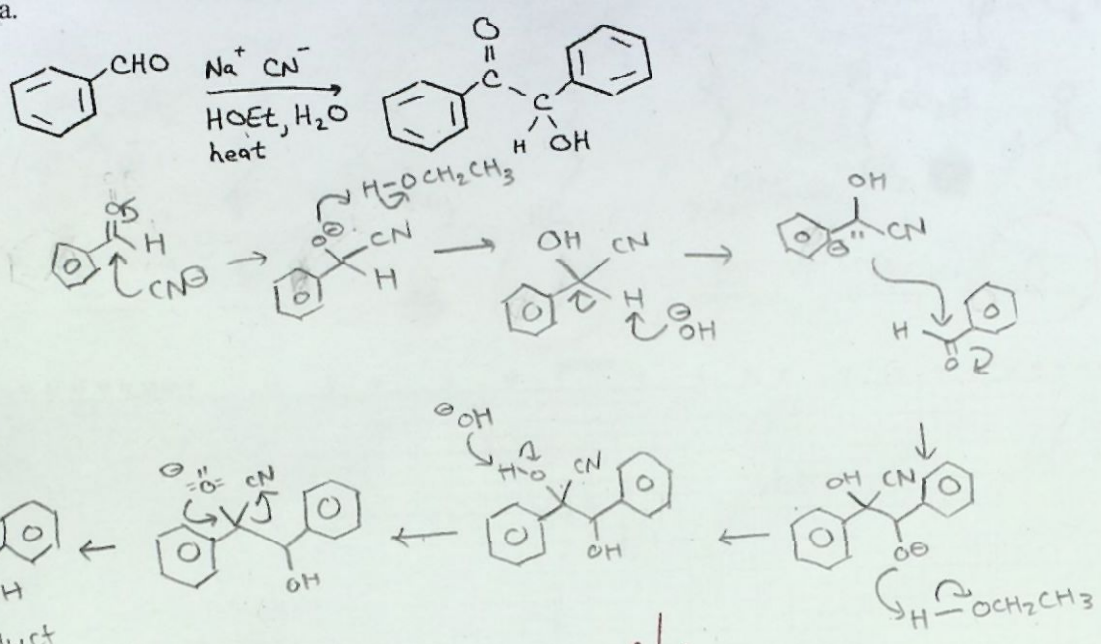
no.

The rate of appearance of the precipitate can be used as the rate of reaction because the formation of the precipitate is the fast step in the reaction and the time it takes in comparison to the time to form a stable transition state is negligible. The formation of the transition state is the rate-determining and, therefore, slow step.

4/8

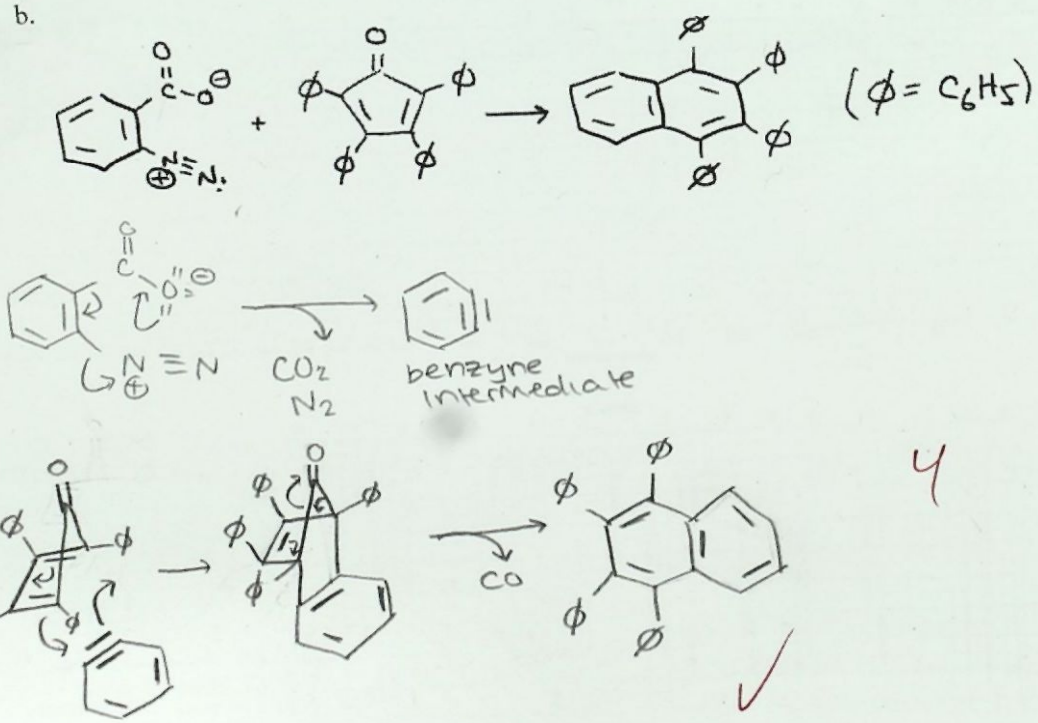
6. (10 points) Write a stepwise, electron-pushing mechanism to account for each of the following transformations.

a.



6/6

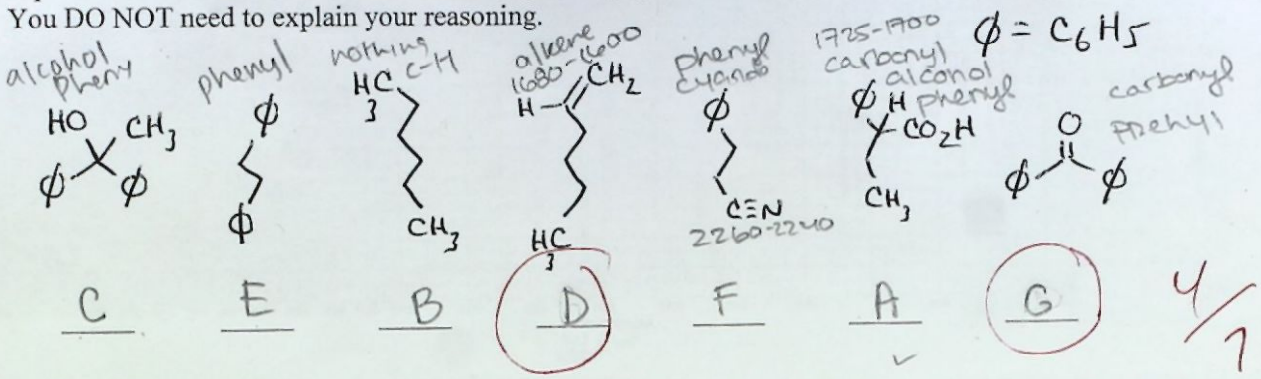
b.



4

✓

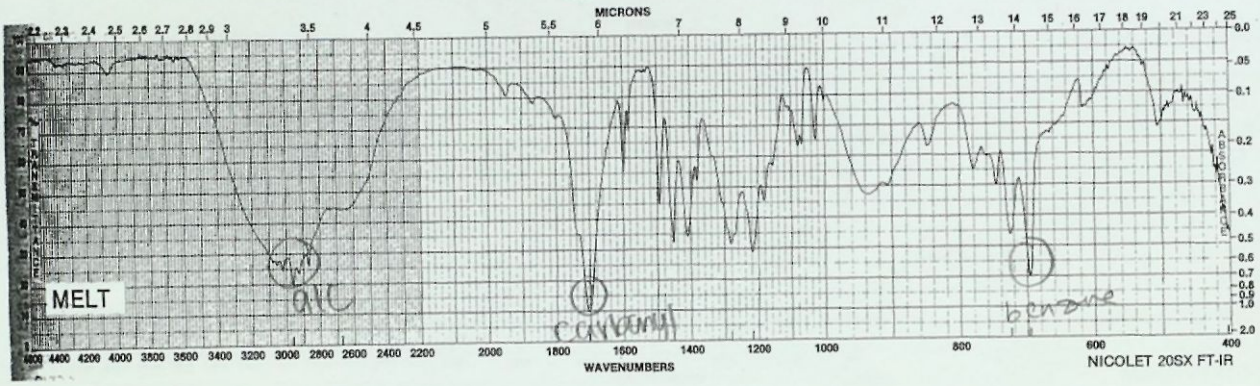
7. (7 points) Match the seven IR spectra A-G on this and the following page to the seven compounds depicted below. Write the letter of the corresponding spectrum on the line under each compound. You DO NOT need to explain your reasoning.



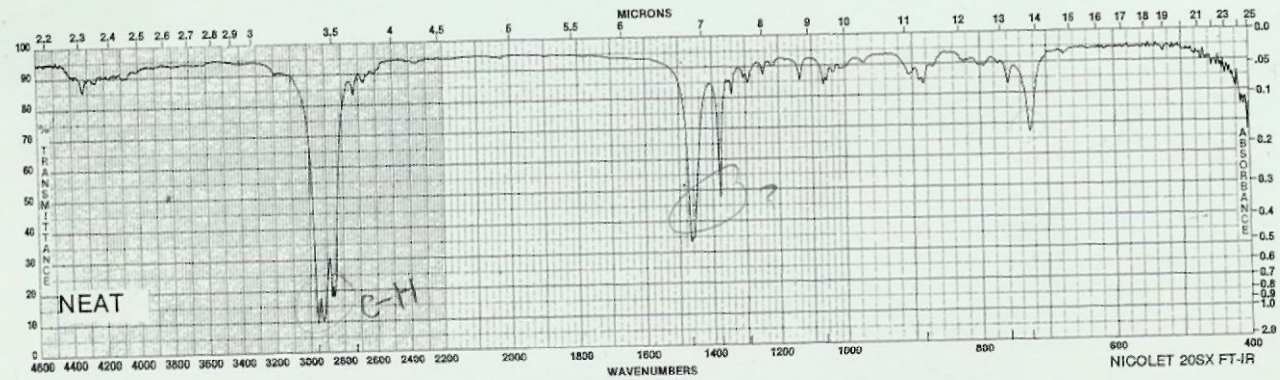
C E B D F A G

4/7

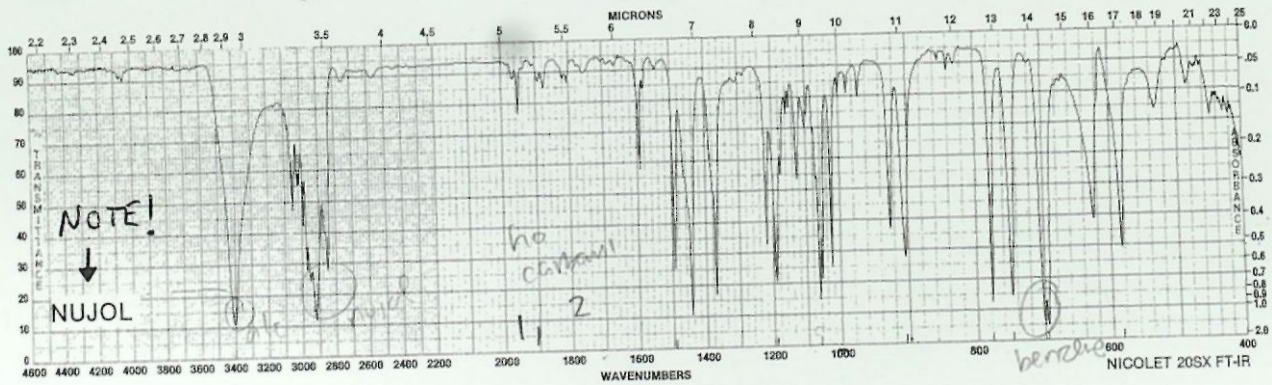
A



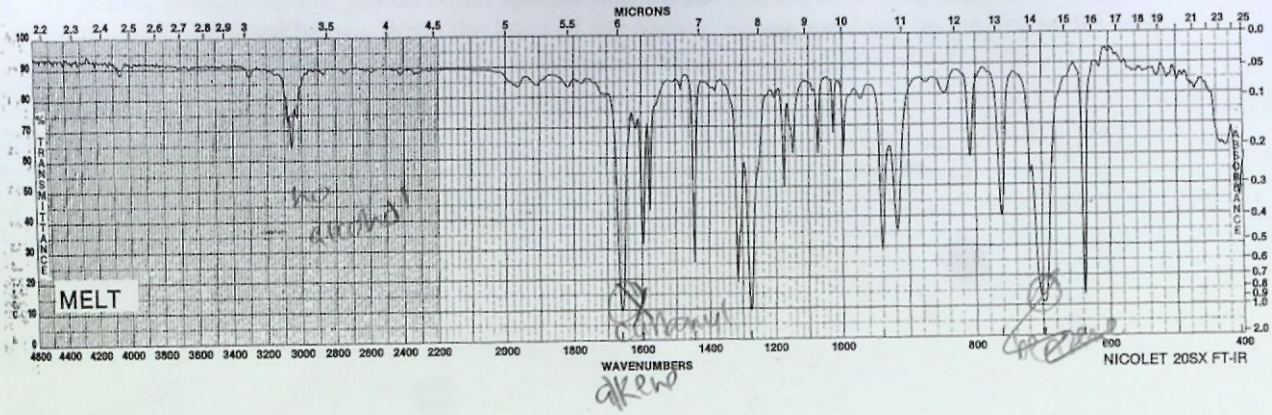
B



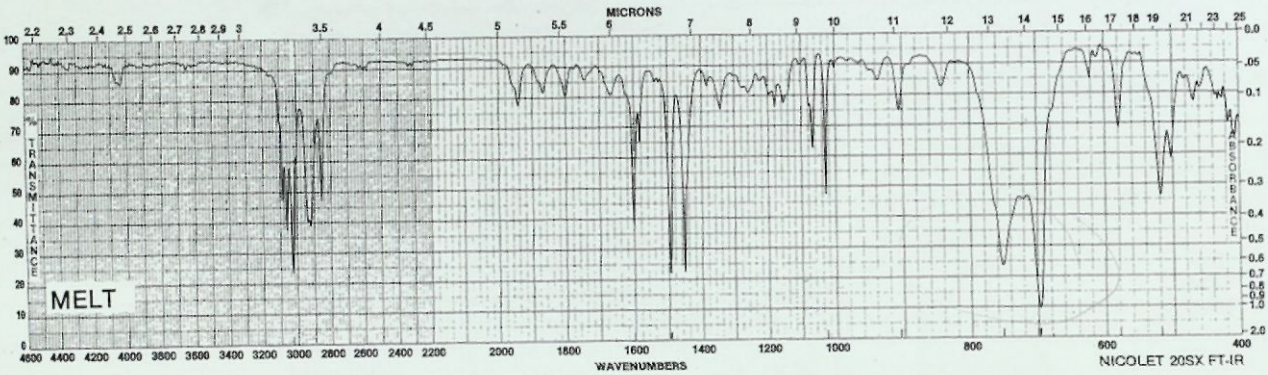
C



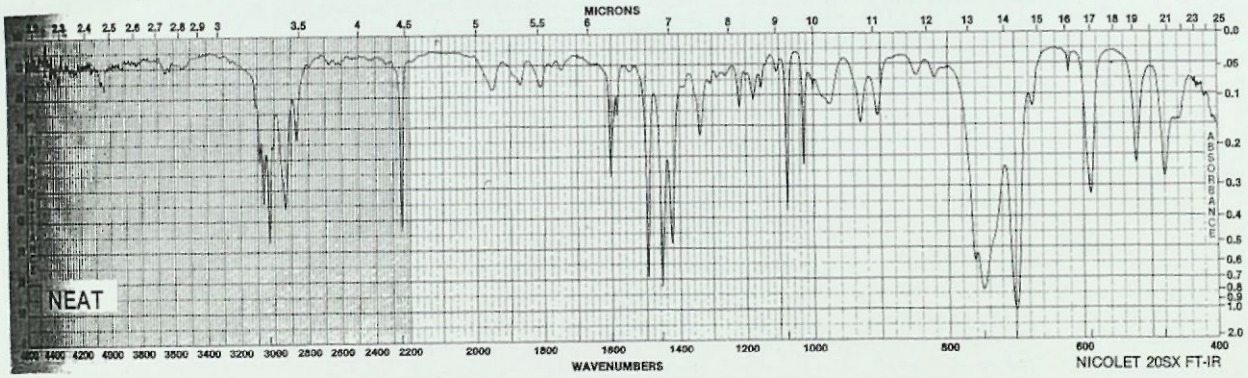
D


MICRONS
MELT
%TRANSMITTANCE
ABSORBANCE
WAVENUMBERS
NICOLET 20SX FT-IR

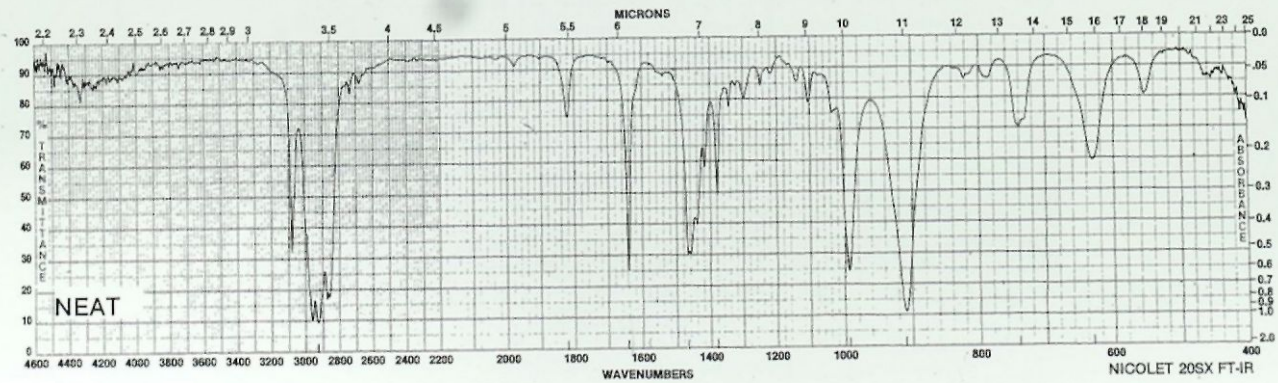
E


MICRONS
MELT
%TRANSMITTANCE
ABSORBANCE
WAVENUMBERS
NICOLET 20SX FT-IR

F

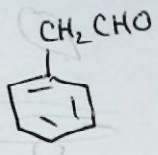

MICRONS
NEAT
ABSORBANCE
WAVENUMBERS
NICOLET 20SX FT-IR

G

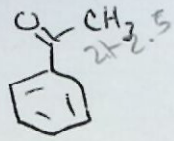

MICRONS
NEAT
%TRANSMITTANCE
ABSORBANCE
WAVENUMBERS
NICOLET 20SX FT-IR

8. (8 points) Match the four proton NMR spectra H-K on this and the following page to the four compounds depicted below. Write the letter of the corresponding spectrum on the line under each compound. You DO NOT need to explain your reasoning.

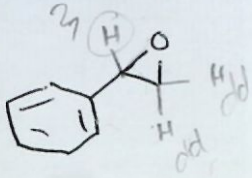
J



I

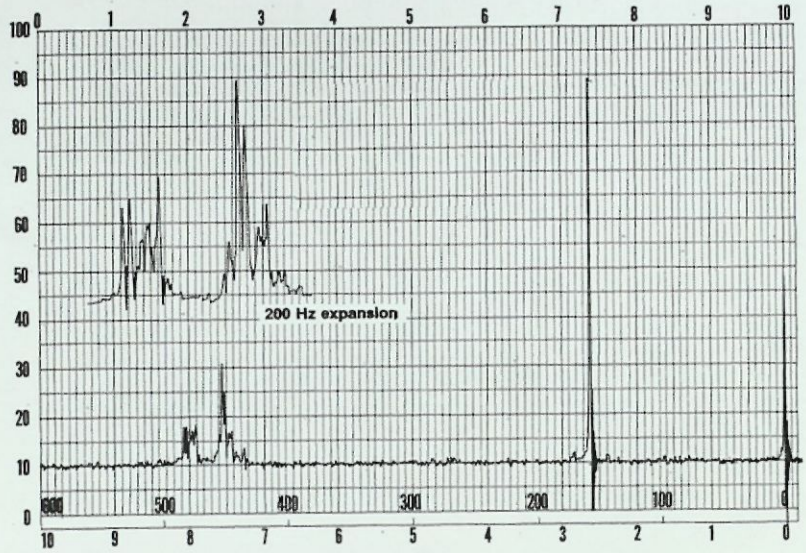


H

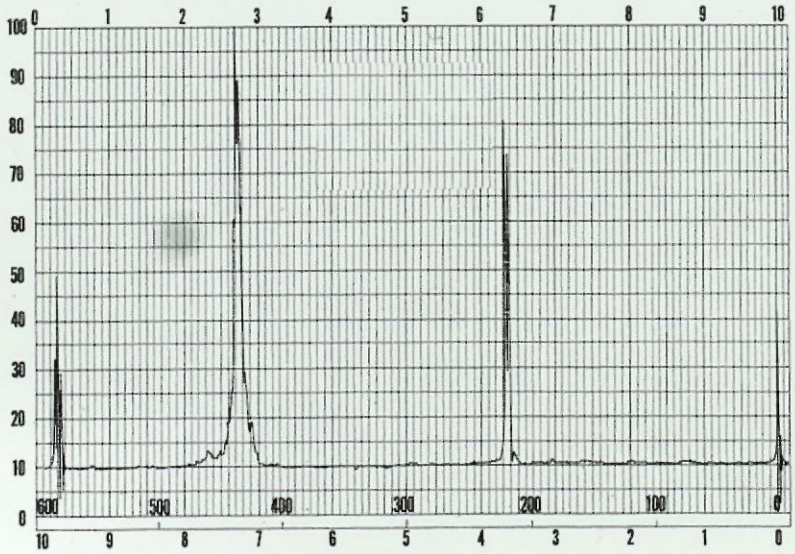


K

H



I



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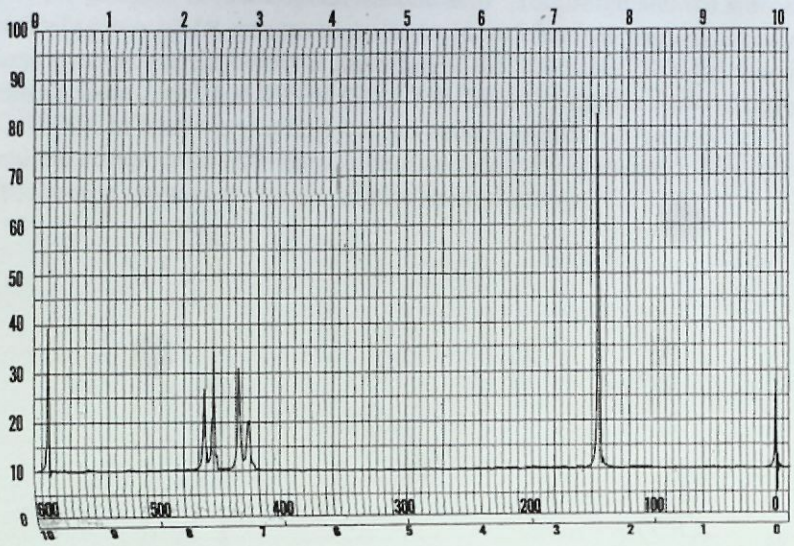
100
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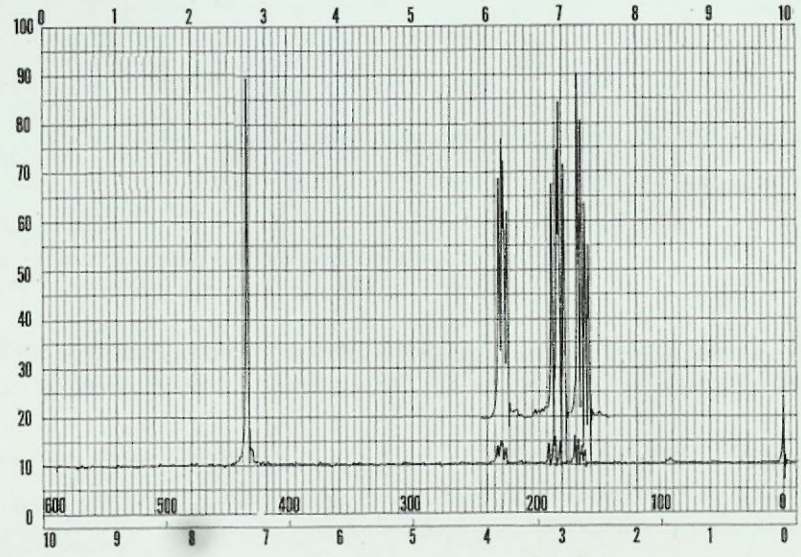
0 1 2 3 4 5 6 7 8 9 10
600 500 400 300 200 100 0
10 9 8 7 6 5 4 3 2 1 0

K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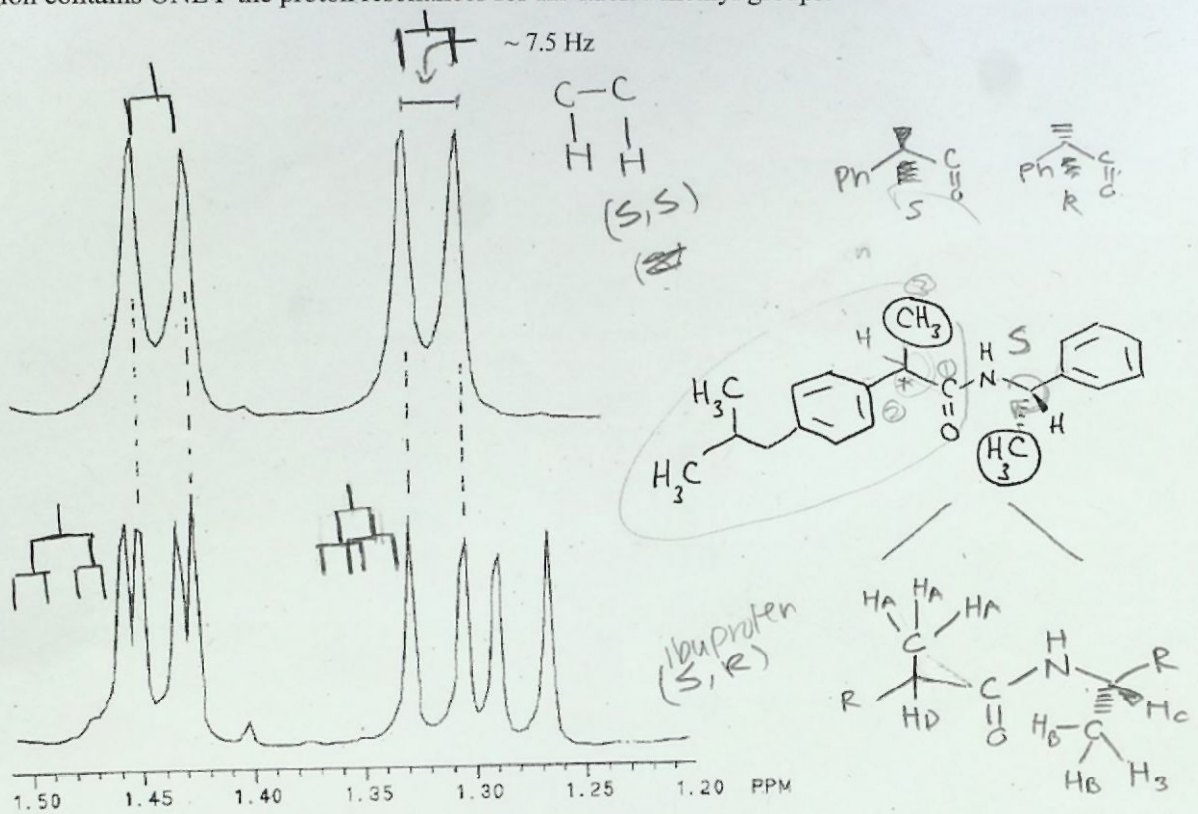
0 1 2 3 4 5 6 7 8 9 10
600 500 400 300 200 100 0
10 9 8 7 6 5 4 3 2 1 0

9. *(10 points)* Ibuprofen is an over-the-counter analgesic. The Aldrich Chemical Company sells a substance they call "(S)-(+)-4-isobutyl-α-methylphenylacetic acid". Ibuprofen and the substance from Aldrich afford identical proton NMR spectra in deuteriochloroform (not shown), identical IR spectra, and identical mass spectra. Shown below is a portion of the 300 MHz ^{1}H NMR spectrum of either the substance available from Aldrich (UPPER SPECTRUM) or ibuprofen from analgesic tablets (LOWER SPECTRUM), in both cases *after* each has been coupled to (S)-(-)-1-phenylethylamine to yield the compounds with the covalent connectivity illustrated. This spectral region contains ONLY the proton resonances for the circled methyl groups.



a. Explain the origin of the four lines in the top spectrum and eight lines in the bottom spectrum.

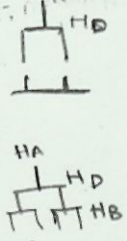
It is due to the fact that the molecules are diastereomers and couple differently.

Top: (S,S) because it is the Aldrich product. For (S,S) the methyl groups point in opposite directions and the hydrogens do not couple with each other. Each methyl hydrogen is split by the single neighboring hydrogen, which leads to a doublet.

2/8

Bottom: The molecule is (S,S) and both methyl groups point the same direction. As a result each methyl hydrogen is split into a doublet by the neighboring hydrogen, and then into another doublet by the hydrogens of the other methyl group. As a result, each methyl hydrogen shows up as a doublet of a doublet.

ex:



b. Based upon your answer to part a, what would you predict would be the observed sign and magnitude of the specific optical rotation for the ibuprofen contained in an analgesic tablet? Why?

Sign: (-) → opposite of Aldrich product

Magnitude: cannot be determined. Same as the Aldrich product, but is experimentally, not theoretically determined.

0/2

Enantiomers have the same magnitude for optical rotation but opposite signs.