Chemistry 225

Final Examination

Time: 2 1/2 hr.

February 15, 1998
M.J.Haddadin

Family Name: _____
First Name: _____

20 pt. 1.
20 pt. 2.
20 pt. 3.
20 pt. 4
30 ~~20~~ pt. 5
15 ~~30~~ pt. 6
15 ~~10~~ pt. 7.
15 ~~10~~ pt. 8.

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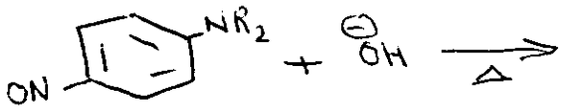
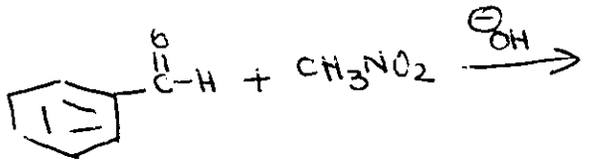
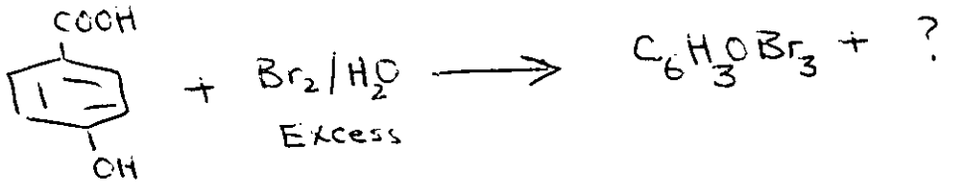
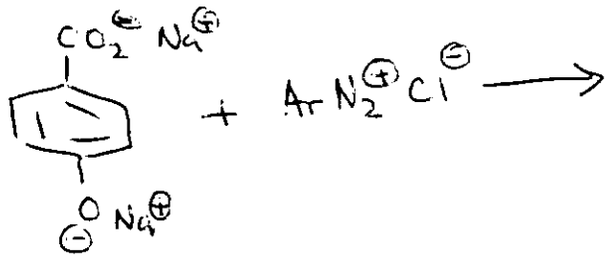
155 pt.

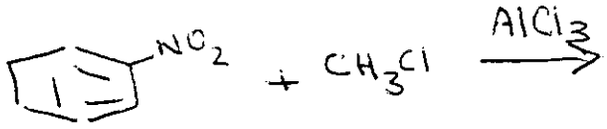
1. Give the structure of the major product(s) of each of the following reactions. If no reaction takes place, write : NO REACTION

a) 

b) 

c) 

d) 

e) 

2. Give reasonable structures for I, II, III, IV and V

A colorless liquid (I) gave no tests for halogen, nitrogen, sulfur, or metals. It was insoluble in water, dilute hydrochloric acid, dilute sodium hydroxide, and phosphoric acid, but soluble in cold concentrated sulfuric acid. It did not react with acetyl chloride or phenylhydrazine and was not affected by heating with sodium hydroxide. It was boiled with dilute phosphoric acid, and an oil (II) separated when the solution was cooled. Compound II gave a precipitate with phenylhydrazine and with sodium bisulfite solution but did not react with acetyl chloride. When II was vigorously shaken with strong alkali, a compound (III) separated from the alkaline solution. This product (III) reacted with acetyl chloride but not with phenylhydrazine. Acidification of the alkaline solution gave IV, which had a neutralization equivalent of 136 ± 1. Strong oxidation of IV gave an acid (V) with a neutralization equivalent of 82 ± 1.

The phosphoric acid solution, from which II was separated, was distilled. The distillate was saturated with potassium carbonate, and a compound (VI) was obtained. This compound reacted with sodium and acetyl chloride and gave a yellow precipitate with sodium hypoiodite. It did not react with Lucas reagent.

The nmr spectrum of II (in $CDCl_3$) showed $\delta 2.42$, 3 H, s; $\delta 7.18$, 2 H, d ($J = 8$ Hz); $\delta 7.66$, 2 H, d ($J = 8$ Hz); $\delta 9.81$, 1 H, s.

3. Identify unknowns I, II, III, IV and V in the following problem.

A compound, C_9H_7N (I), was converted by catalytic reduction into $C_9H_{11}N$ (II). When compound II was treated with an excess of methyl iodide followed by silver oxide and the reaction product was heated, a compound, $C_{11}H_{15}N$ (III), was produced. This compound was converted (a) by vigorous oxidation into $C_8H_6O_4$ (IV); (b) by treatment with ozone and hydrolysis of the reaction product into $C_{10}H_{13}ON$ (V). The ozonization product yielded $C_{20}H_{26}O_2N_2$ (VI) when heated with a dilute solution of potassium cyanide. Compound VI was converted into IV by vigorous oxidation.

Compound I (in $CDCl_3$) yielded a nmr spectrum that showed δ7.25–8.1, 5 H, m; δ8.52, 1 H, d (J = 7 Hz); δ9.26, 1 H, s.

4. The following problem is rather challenging. You may wish to postpone it until you have solved the rest of the questions. Give reasonable structures for I,II,III and IV.

A compound, $C_{10}H_6O_3$ (I), decolorized alkaline permanganate and reacted with hydroxylamine. It decomposed when distilled at ordinary pressure to give $C_9H_6O_2$ (II), a compound that yielded a monosodium derivative and was readily oxidized to $C_9H_6O_4$ (III). Compound III was an acid that, when heated with soda lime, was converted into $C_8H_6O_2$ (IV). Compound IV was decomposed by heating with dilute hydrochloric acid under pressure and yielded a weakly acidic compound having the formula $C_6H_6O_2$.

The nmr spectrum of compound IV (in $CDCl_3$) showed δ5.90, 2 H, s; δ6.83, 4 H, s (slight distortions at the bottom of this signal). The nmr spectrum of compound III (in $CDCl_3$) showed δ6.00, 2 H, s; δ6.8, 1 H, d ($J = 7$ Hz); δ7.38, 1 H, d ($J = 2$ Hz); δ7.55, 1 H, d of d ($J = 7$, 2 Hz); δ7.6, 1 H, bs. The chemical shift of the δ7.6 signal was concentration-dependent.

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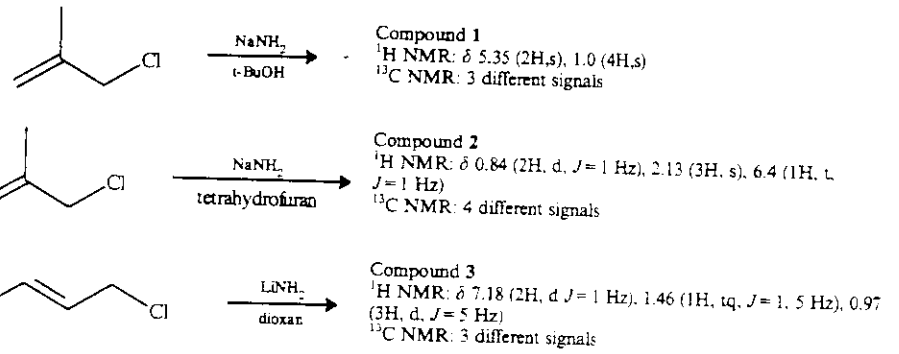
Three compounds, **1–3**, of formula C_4H_6 have been prepared by the routes shown below. Suggest structures for these isomers.

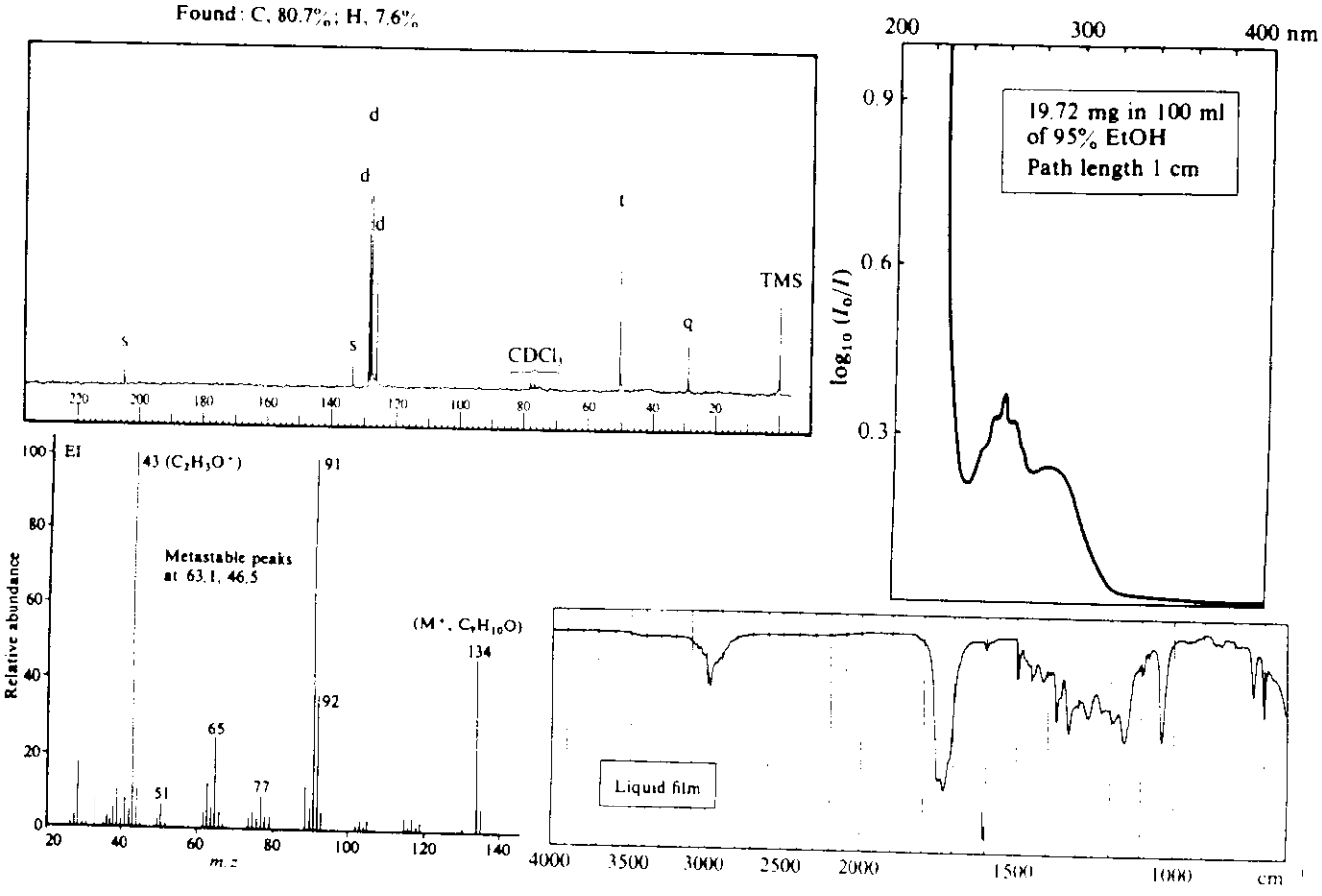


Compound **1** reacts with *m*-chloroperbenzoic acid to give compound **4**, which rearranges to compound **5** in the presence of lithium iodide. Suggest structures for compounds **4** and **5**.

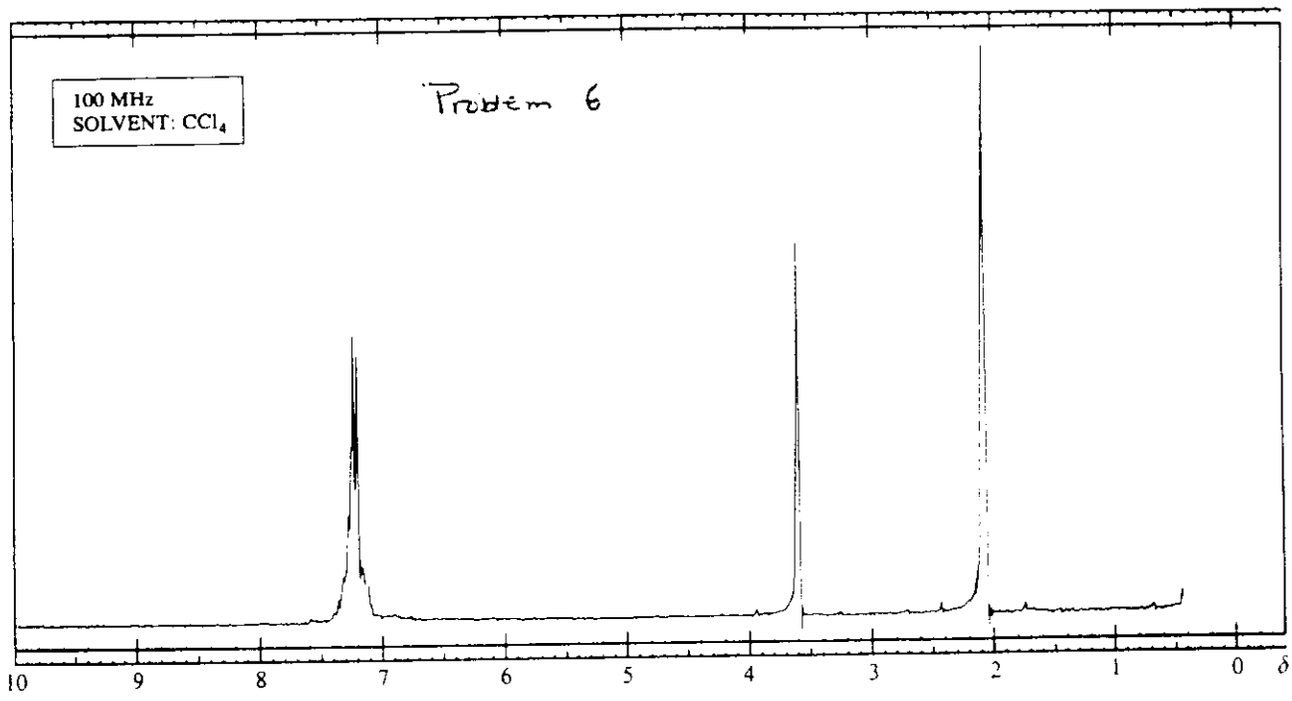
Compound **4** (C_4H_6O): IR: no strong peaks outside fingerprint
^{1}H NMR: δ 3.0 (2H, s), 0.85 (4H, AB quartet)

Compound **5** (C_4H_6O): IR: 1770 cm^{-1}
^{1}H NMR: δ 3.02 (4H, t, J = 5 Hz), 1.98 (2H, q, J = 5 Hz)

6. Give a reasonable structure for $C_9H_{10}O$ which has the following spectroscopic properties (see proton NMR on the next page).

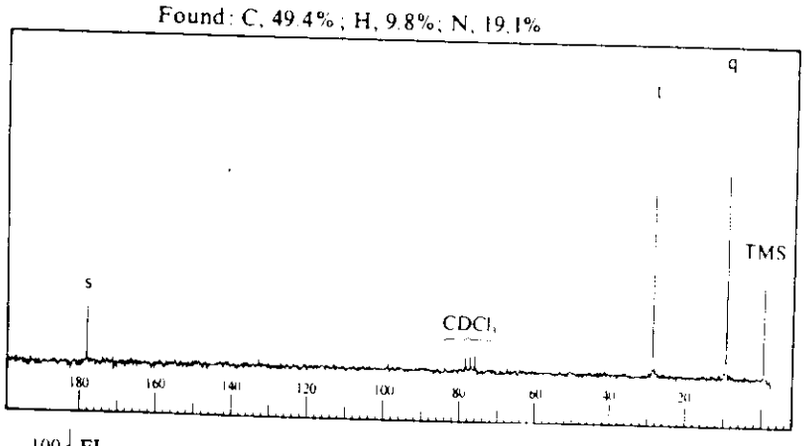


Problem 6 continued:

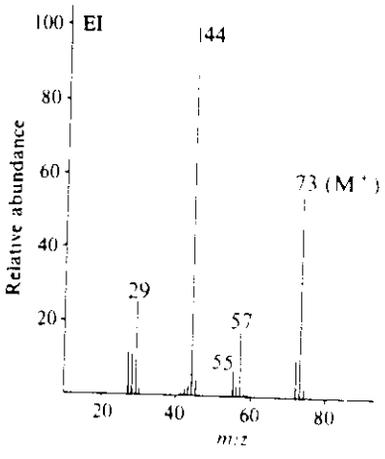


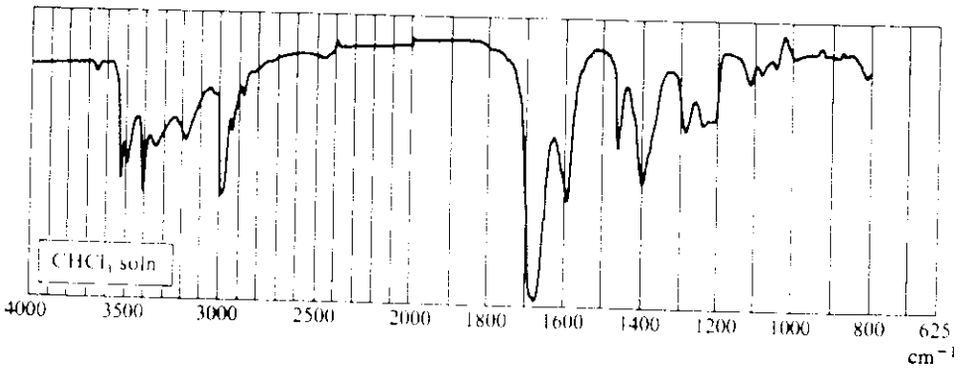
7. Give the structure of C_3H_7NO which possesses the following spectroscopic properties (see proton NMR on the next page).

Found: C, 49.4%; H, 9.8%; N, 19.1%

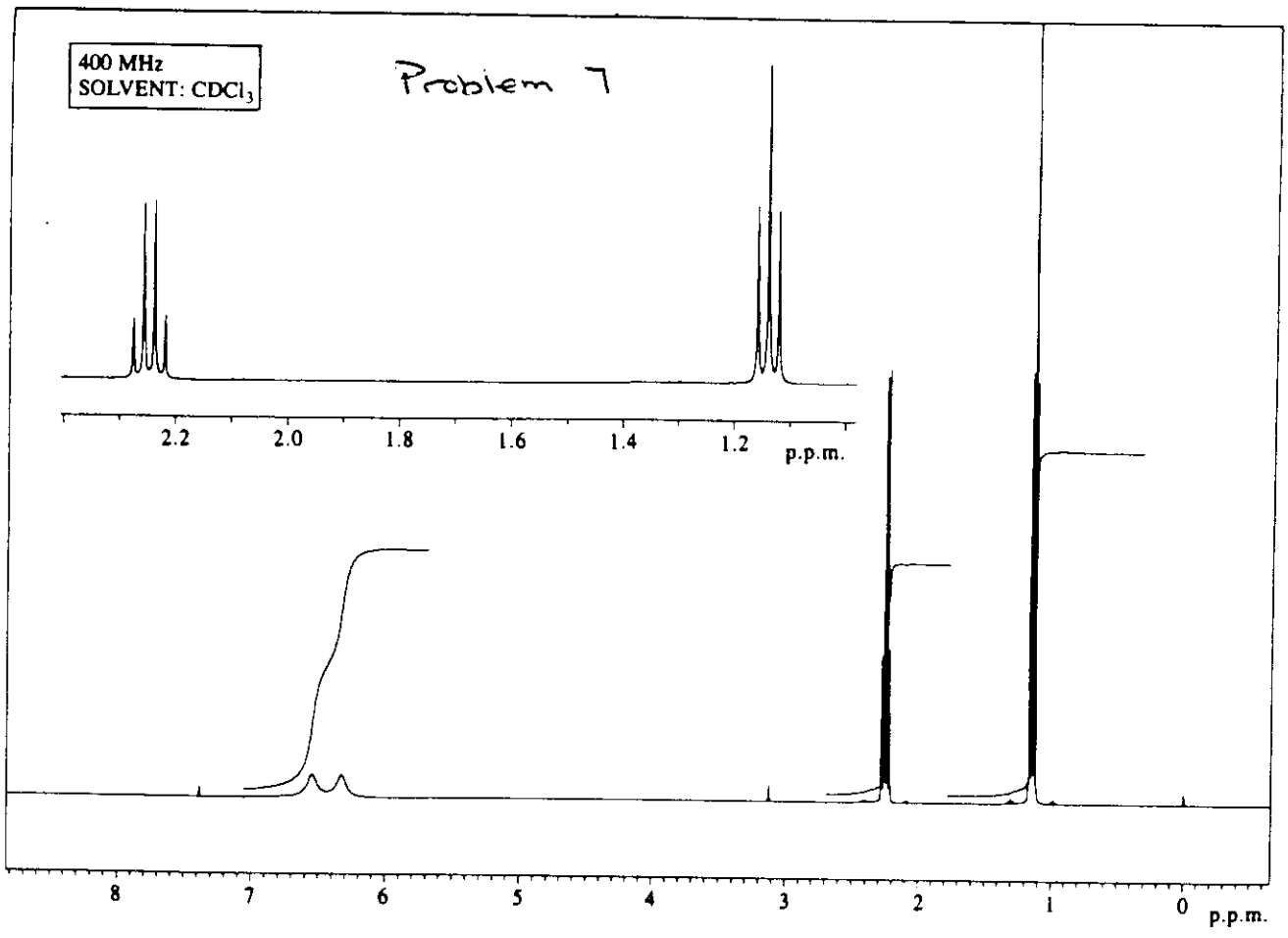


No UV maximum above 200 nm

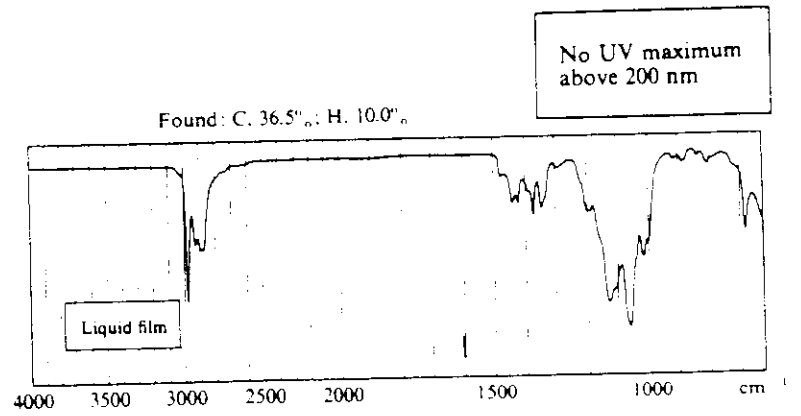


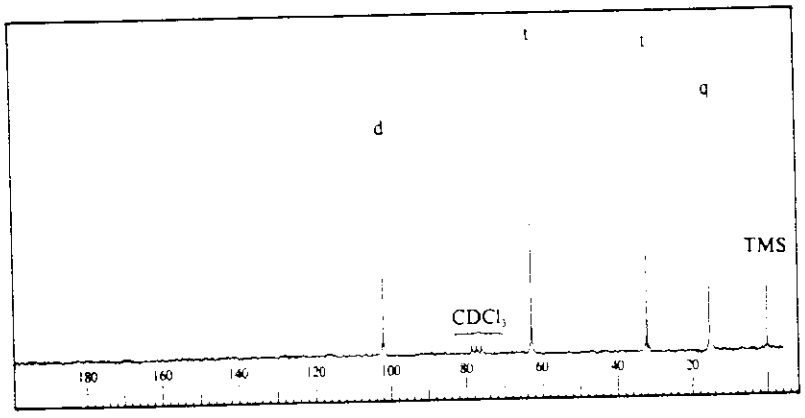


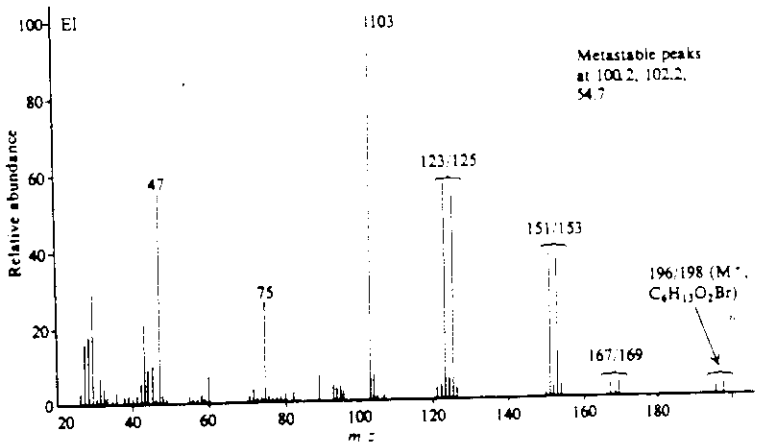
Problem 7 continued:



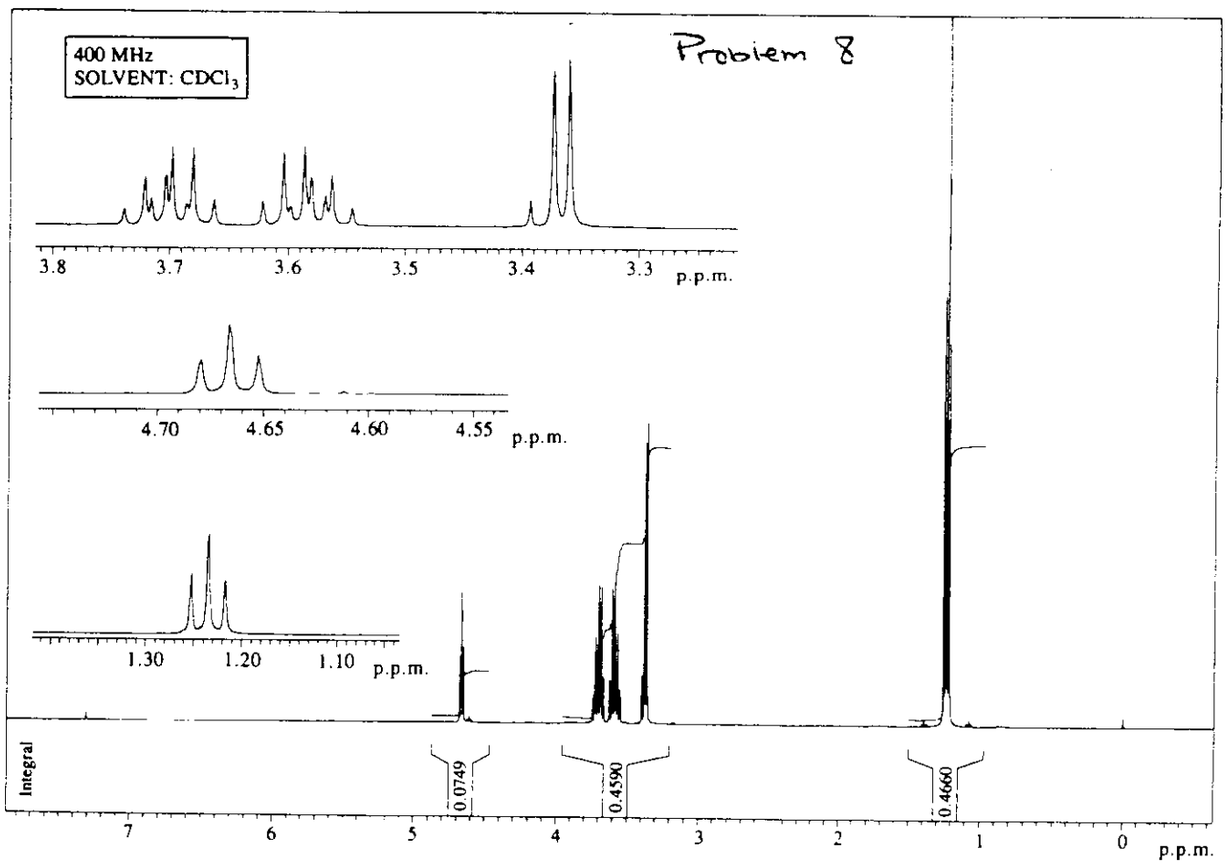
8. Give the structure of $C_6H_{13}O_2Br$ the spectroscopic data for which are shown below.







Problem 8 continued:



Approximate proton chemical shifts

TYPE OF PROTON	CHEMICAL SHIFT, δ (ppm)
1° Alkyl, RCH_3	0.8–1.0
2° Alkyl, RCH_2R	1.2–1.4
3° Alkyl, R_3CH	1.4–1.7
Allylic, $R_2C{=}C(R){-}CH_3$	1.6–1.9
Benzylic, $ArCH_3$	2.2–2.5
Alkyl chloride, RCH_2Cl	3.6–3.8
Alkyl bromide, RCH_2Br	3.4–3.6
Alkyl iodide, RCH_2I	3.1–3.3
Ether, $ROCH_2R$	3.3–3.9
Alcohol, $HOCH_2R$	3.3–4.0
Ketone, $RCCH_3$ (O)	2.1–2.6
Aldehyde, RCH (O)	9.5–9.6
Vinylic, $R_2C{=}CH_2$	4.6–5.0
Vinylic, $R_2C{=}CH(R)$	5.2–5.7
Aromatic, ArH	6.0–9.5
Acetylenic, $RC{\equiv}CH$	2.5–3.1
Alcohol hydroxyl, ROH	0.5–6.0[a]
Carboxylic, $RCOH$ (O)	10–13[a]
Phenolic, ArOH	4.5–7.7[a]
Amino, $R{-}NH_2$	1.0–5.0[a]

[a]The chemical shifts of these protons vary in different solvents and with temperature and concentration.

Approximate carbon-13 chemical shifts

TYPE OF CARBON ATOM	CHEMICAL SHIFT, δ (ppm)
1° Alkyl, RCH_3	0–40
2° Alkyl, RCH_2R	10–50
3° Alkyl, $RCHR_2$	15–50
Alkyl halide or amine, $-C(-)-X$ (X = Cl, Br, or $-N(-)-$)	10–65
Alcohol or ether, $-C(-)-O$	50–90
Alkyne, $-C{=}$	60–90
Alkene, $>C{=}$	100–170
Aryl, 	100–170
Nitriles, $-C{\equiv}N$	120–130
Amides, $-C(=O)-N(-)-$	150–180
Carboxylic acids, esters, $-C(=O)-O$	160–185
Aldehydes, ketones, $-C(=O)-$	182–215