

**Chemistry 225**  
**Final Examination**

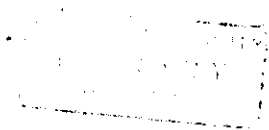
Time: 2 hr.

February 12, 1999  
M.J.Haddadin

Family Name: \_\_\_\_\_  
First Name: \_\_\_\_\_

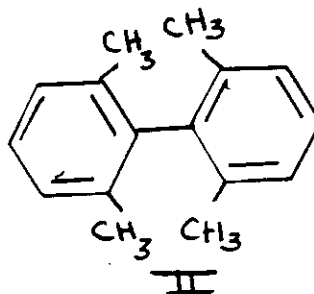
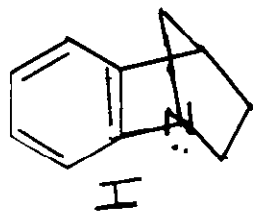
- 10- 1.
- 20- 2.
- 10- 3.
- 10- 4.
- 10- 5.
- 10- 6.
- 10- 7.
- 10- 8.
- 10- 9.

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100



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1.a) Which of the following compounds has a U.V. spectrum that resembles that of each of I and II.

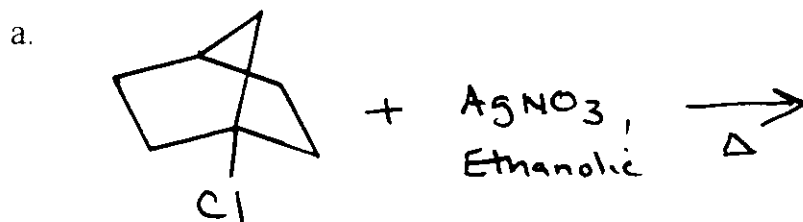


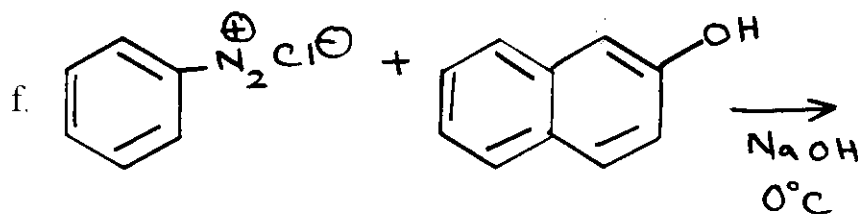
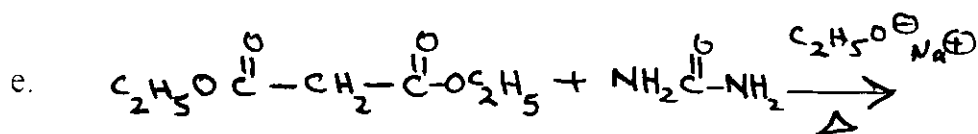
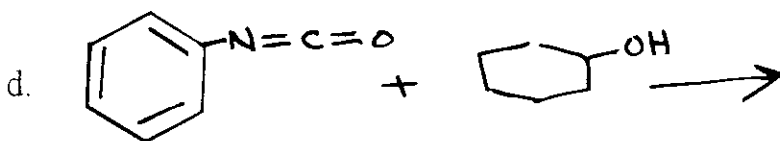
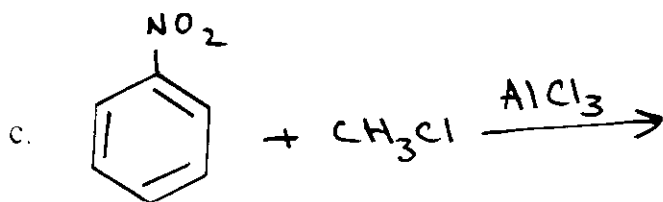
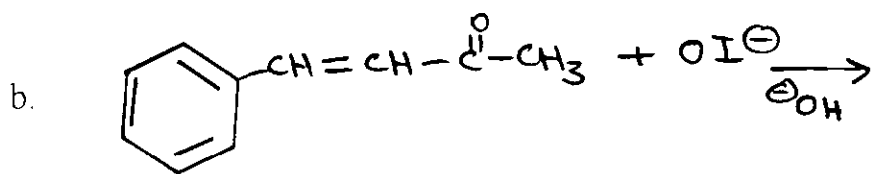
Answer:

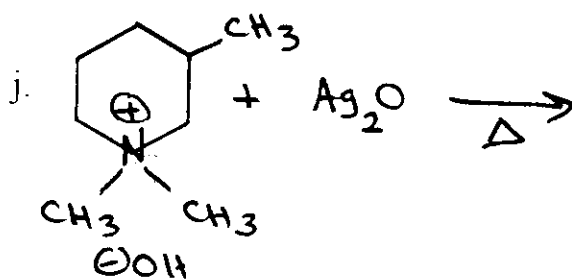
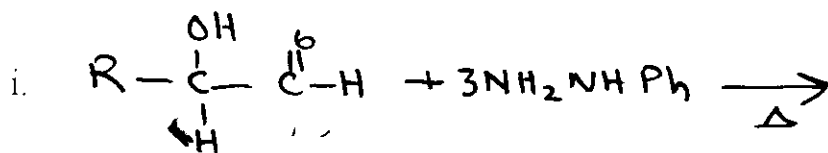
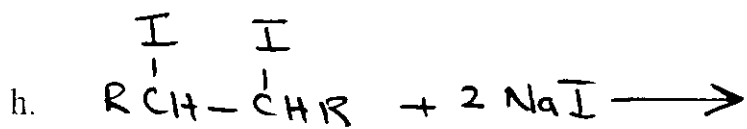
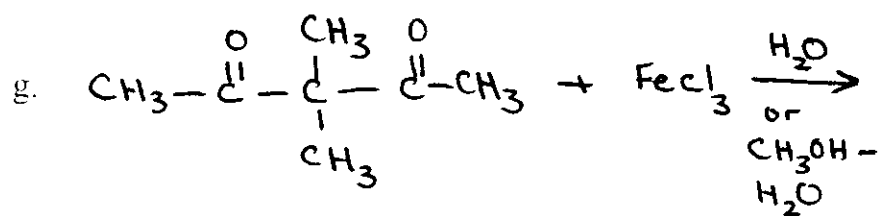
Benzene (1), N.N-Dimethylaniline(2), 1,3,5-trimetylbenzene (3), Biphenyl (4), none of (1), (2), (3) or (4).

b) Briefly, explain the reason(s) for your choice in part 1. A.

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

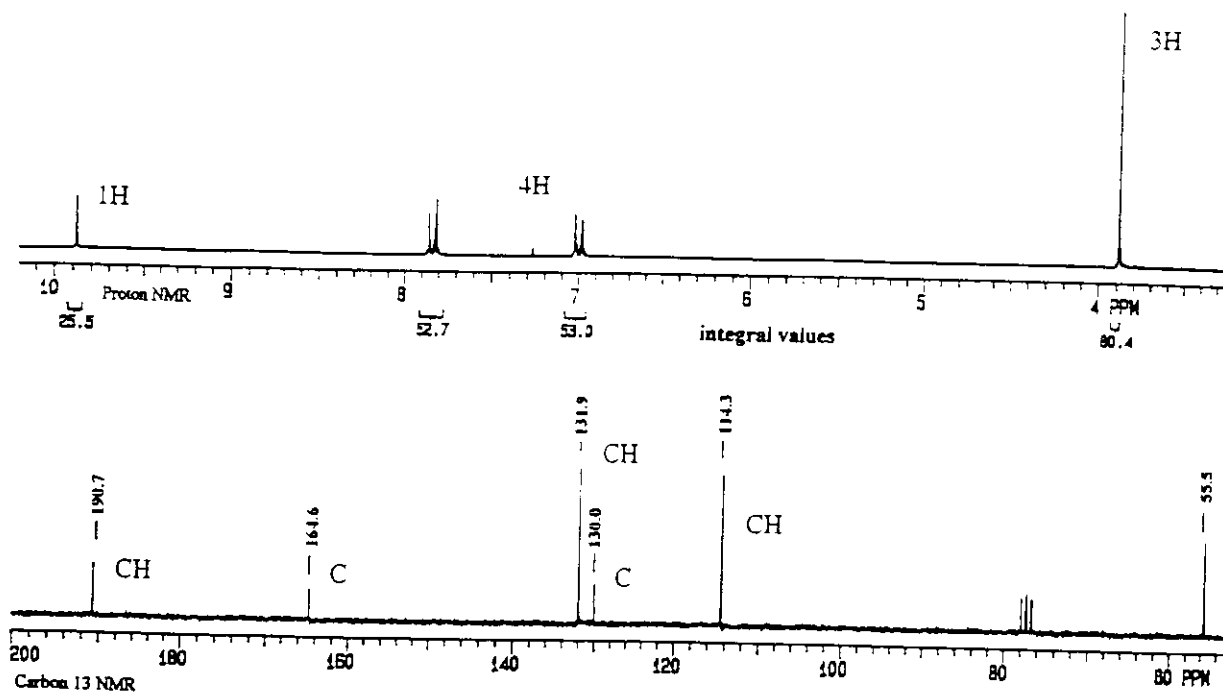






Identify the structure of each of the compounds in questions 3,4,5,6,7,8,9. IR,  $^1\text{H}$ NMR,  $^{13}\text{C}$ NMR tables are attached.

3. A compound has a molecular formula of  $C_8H_8O_2$ . This compound is water insoluble but gives a positive 2,4-dinitrophenylhydrazine test and a positive Tollens test. IR spectrum and both the  $^1H$  and  $^{13}C$  NMR spectra for this compound are below. Deduce the structure of this compound and assign all NMR signals an important IR signals. Write reactions for the positive chemical tests.



$^1H$  NMR (top) and  $^{13}C$  NMR (bottom) spectra for Problem 4. Spectra courtesy of R. To Sunbelt R&T, Inc., Tulsa, Oklahoma.

4. A compound (I) containing carbon, hydrogen, nitrogen, and oxygen was insoluble in dilute alkalis and acids. When heated for some time with hydrochloric acid, compound I yielded a solid acid (II) having a neutralization equivalent of  $180 \pm 1$ . If compound I was oxidized with potassium dichromate and sulfuric acid, it yielded a solid, nitrogen-containing acid (III) with a neutralization equivalent of  $166 \pm 1$ . Compound I reacted with benzaldehyde in the presence of alkalis to give a benzal derivative.

If compound I was treated with tin (II) chloride and hydrogen chloride in dry ether and the resulting mixture was treated with water, a new compound (IV), whose molecular formula was  $C_3H_7N$ , resulted. Analysis showed IV to possess one active hydrogen atom. Compound IV was weakly basic and was resinified by acids.

The  $^1H$  NMR spectrum of I (60 MHz,  $CDCl_3$ ) showed signals at  $\delta$  4.25, 2H, s;  $\delta$  7.5-8.0, 3H, m;  $\delta$  8.25, 1H, d (distorted slightly). The spectrum of II (60 MHz,  $CDCl_3$  containing DMSO- $d_6$ ) showed  $\delta$  4.02, 2H, s;  $\delta$  7.3-7.65, 3H, m;  $\delta$  8.0, 1H, d (distorted);  $\delta$  11.2, 1H, bs. The spectrum of III (60 MHz,  $CDCl_3$  containing DMSO- $d_6$ ) showed  $\delta$  7.5-8.0, 4H, m;  $\delta$  12.15, 1H, s. The spectrum of IV (60 MHz,  $CDCl_3$ ) showed  $\delta$  6.38, 1H, m;  $\delta$  6.76, 1H, t (distorted);  $\delta$  6.95-7.10, 4H, m;  $\delta$  7.4-7.65, 1H, m.

5. A light yellow neutral solid (I) contained chlorine but not nitrogen. It did not react with hot alcoholic silver nitrate, acetyl chloride, or bromine in carbon tetrachloride.

It gave a precipitate with phenylhydrazine. Compound I was not attacked by cold alkalis, but when it was heated for some time with concentrated sodium hydroxide, a clear solution resulted. The distillate from this alkaline solution contained no organic compounds. Acidification of the alkaline solution with phosphoric acid gave a precipitate (II), which was removed by filtration. No organic compounds could be obtained from the filtrate by distillation or evaporation to dryness.

Compound II contained chlorine, had a neutralization equivalent of  $297 \pm 2$ , and reacted with acetic anhydride to produce a compound (III) having a neutralization equivalent of  $340 \pm 3$ . Compound III did not react with bromine water, bromine in carbon tetrachloride, or phenylhydrazine.

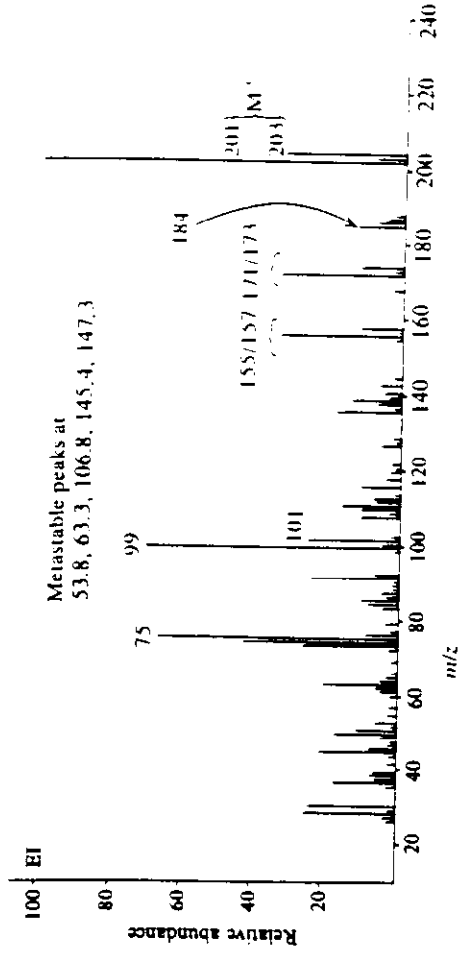
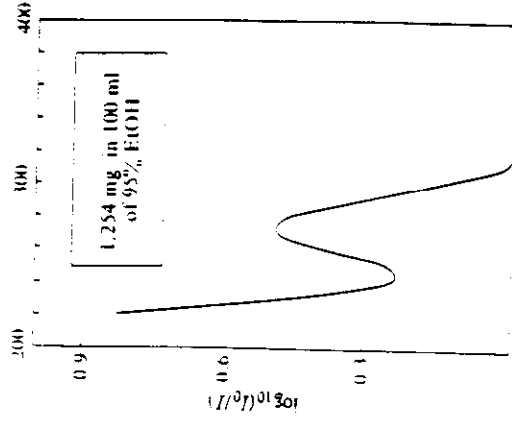
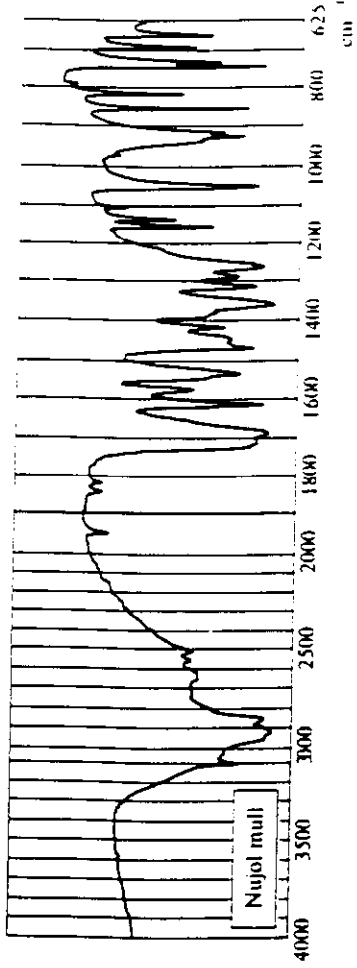
Vigorous oxidation of I with alkaline permanganate gave a very good yield of a product (IV) which contained chlorine and possessed a neutralization equivalent of  $156 \pm 1$ . No other oxidation product could be found.

Vigorous oxidation of II or III with potassium dichromate and sulfuric acid also produced IV but in very poor yield.

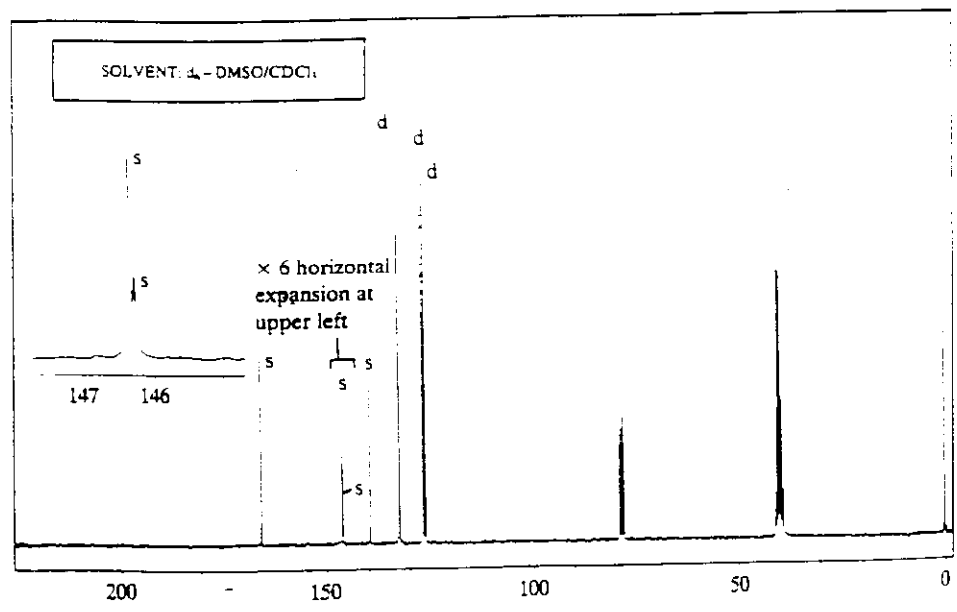
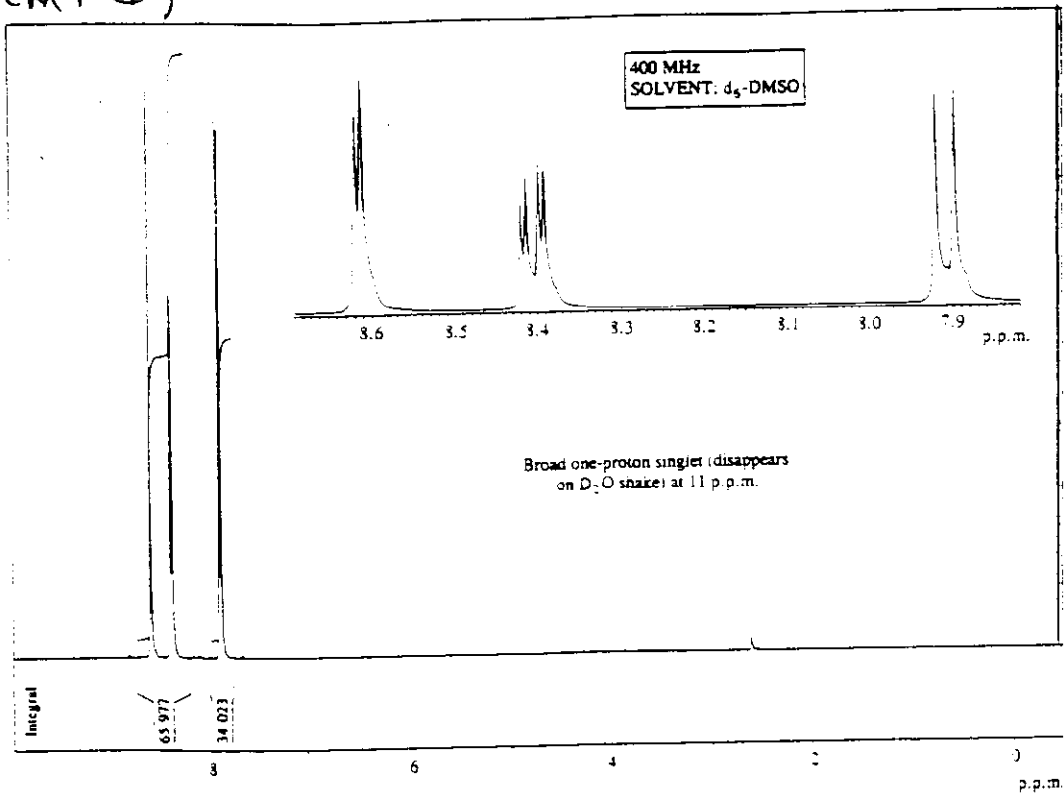
The  $^1\text{H}$  NMR spectrum of IV (60 MHz,  $\text{CDCl}_3$  plus  $\text{DMSO}-d_6$ ) showed  $\delta$  7.37, 2H, d ( $J = 9$  Hz);  $\delta$  7.45, 1H, bs;  $\delta$  7.81, 2H, d ( $J = 9$  Hz). Treatment of the solution with deuterium oxide caused the  $\delta$  7.45 signal to disappear, leaving the two doublets.



Needles m.p. 165°. Found: C, 41.7%; H, 2.0%; N, 7.0%



6. (cont'd)



7. GIVEN: IR spectrum, UV absorptions, NMR chemical shifts.  
 FIND: Identity of Compound #8

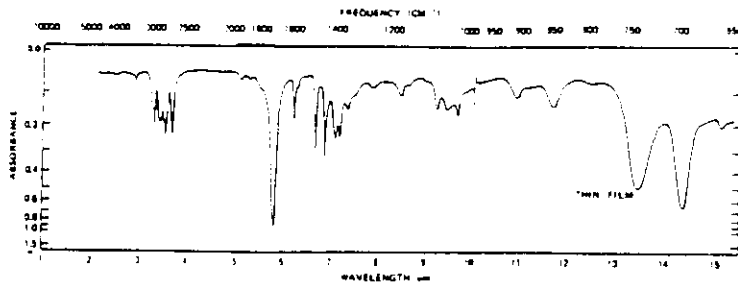


Figure 19. IR compound #8.

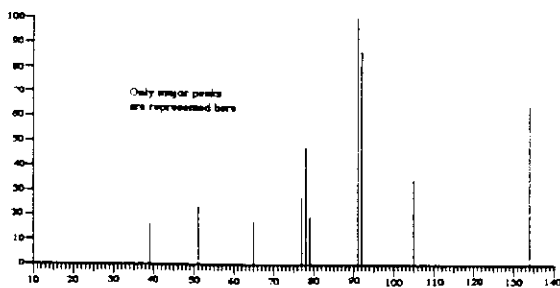


Figure 20. MS compound #8.

MS Peaks (Intensities): 91(100) 92(86) 134(64) 78(47) 105(34) 77(27) 51(23)  
 79(19) 65(17) 39(16)  
 m/e for Dominant Isotopic Species: 134.07

IR Peaks [cm<sup>-1</sup>]: 3030 2940 1720 1610 1490 1450 1410 1140 1040 740 690

UV Peaks [nm] (Absorp. Coef.): 268 264 261 258 253 247 242 208 MeOH

<sup>13</sup>C NMR Shifts [ppm]: FT 28.0 45.0 126.1 128.2 128.4 140.4 201.1 CDCl<sub>3</sub>

<sup>1</sup>H NMR Shifts [ppm]: 2.7 3.0 7.2 9.8 CDCl<sub>3</sub>

11

8.

**GIVEN:** IR spectrum, MS spectrum, m/e, UV absorptions,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shifts

**FIND:** Identity of P-9

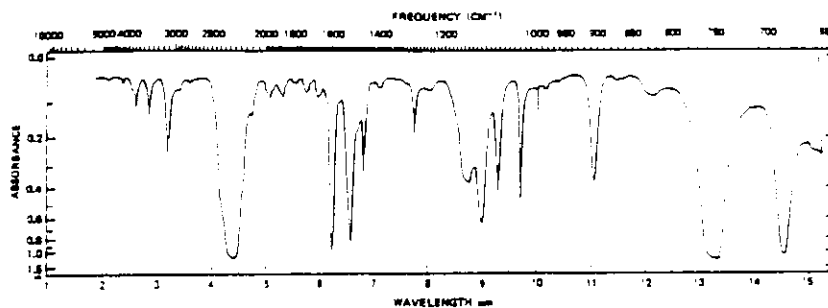


Figure 41. IR P-9.

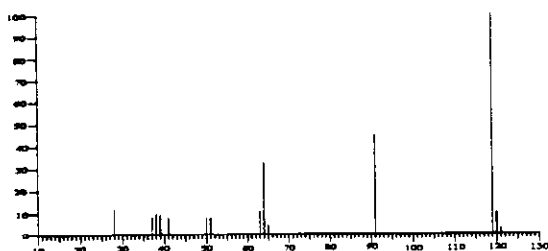


Figure 42. MS P-9.

MS Peaks (Intensities): 119(100) 91(45) 64(33) 28(12) 63(11) 120(10)  
38(10) 39(9) 51(7) 41(7)

m/e for Dominant Isotopic Species: 119.04

IR Peaks [ $\text{cm}^{-1}$ ]: 3080 2280 1600 1510 1110 750 690

UV Peaks [nm] (Absorp. Coef.): 277(468) 270(575) 263(457) 256(389)  
226(10965) hx

$^{13}\text{C}$  NMR Shifts [ppm]: FT 124.7 125.7 129.5 133.6  $\text{CDCl}_3$

$^1\text{H}$  NMR Shifts [ppm]: 7.1  $\text{CDCl}_3$

9.

GIVEN: IR spectrum,  $^1\text{H}$  NMR spectrum, MS peaks and respective intensities, m/e, UV absorptions  
FIND: Identity of P-10

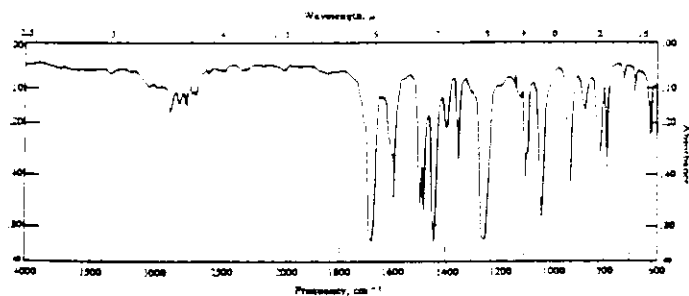


Figure 43 IR P-10.

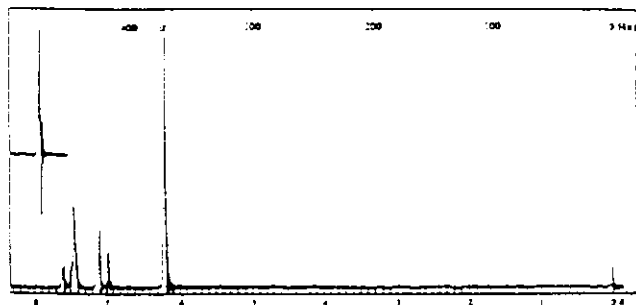


Figure 44.  $^1\text{H}$  NMR P-10.

MS Peaks (Intensities): 149(100) 150(78) 63(33) 121(27) 65(20) 38(14)  
62(13) 91(12) 39(11) 61(10)  
m/e for Dominant Isotopic Species: 150.03

IR Peaks [ $\text{cm}^{-1}$ ]: 3030 2857 1695 1613 1471 1449 1389 1351 1250 1075  
1020 926 870 800 775

UV Peaks [nm] (Absorp. Coef.): 312(8630) 272(7060) 231(16600) MeOH

$^1\text{H}$  NMR Shifts [ppm]: 6.1 7.0 7.4 7.5 9.8  $\text{CDCl}_3$

**Table 6.7 Chemical Shift Ranges for Protons<sup>a</sup> and Carbons of Organic Compounds**

Class	$\delta$ H	$\delta$ C
Alkane	$\delta$ 0.0–2.0	$\delta$ 0.0–30.0
Alkyne ( $\equiv\text{C}-\text{H}$ )	$\delta$ 2.0–3.0	$\delta$ 75–95
Monosubstituted alkane <sup>a,b</sup>	$\delta$ 2.0–5.0	$\delta$ –6.0–70.0
Alkene ( $=\text{C}-\text{H}$ )	$\delta$ 4.3–7.3	$\delta$ 100–170
Aromatic ( $=\text{C}-\text{H}$ )	$\delta$ 6.0–8.8	$\delta$ 110–150
Aldehydic ( $-\text{CH}=\text{O}$ )	$\delta$ 9.0–10.0	$\delta$ 195–205
Alcohol ( $-\text{ROH}$ )	$\delta$ 1.0–6.0 <sup>c</sup>	
Carboxylic acid ( $-\text{RCOOH}$ )	$\delta$ 10.0–13.0 <sup>c</sup>	
Phenol ( $-\text{ArOH}$ )	$\delta$ 4.0–7.5 <sup>c</sup>	
Amine ( $-\text{NH}$ )	$\delta$ 0.5–5.0 <sup>c</sup>	
Amide [ $\text{R}(\text{C}=\text{O})\text{NHR}$ ]	$\delta$ 5.0–9.0	$\delta$ 160–170
Nitrile ( $\text{R}-\text{C}\equiv\text{N}$ )		$\delta$ 105–115
Ester [ $\text{R}(\text{C}=\text{O})\text{OR}'$ ]		$\delta$ 167–174
Ketone [ $\text{R}(\text{C}=\text{O})\text{R}'$ ]		$\delta$ 200–220
Anhydride [ $(\text{RC}=\text{O})_2\text{O}$ ]		$\delta$ 167–174
<u><math>\alpha</math>-protons</u>		
Fluoride ( $\text{HC}-\text{F}$ )	$\delta$ 4.0–4.5	$\delta$ 70–80 <sup>d</sup>
Chloride ( $\text{HC}-\text{Cl}$ )	$\delta$ 3.0–4.0	$\delta$ 40–50 <sup>d</sup>
Bromide ( $\text{HC}-\text{Br}$ )	$\delta$ 2.5–4.0	$\delta$ 30–40 <sup>d</sup>
Iodide ( $\text{HC}-\text{I}$ )	$\delta$ 2.0–4.0	$\delta$ 5–15 <sup>d</sup>
Alcohol ( $\text{HC}-\text{OH}$ )	$\delta$ 3.4–4.0	$\delta$ 55–70 <sup>d</sup>
Ether ( $\text{HC}-\text{OR}$ )	$\delta$ 3.3–4.0	$\delta$ 60–80 <sup>d</sup>
Ester [ $\text{HC}-\text{O}(\text{C}=\text{O})\text{R}$ ]	$\delta$ 3.7–4.1	$\delta$ 60–70 <sup>d</sup>
Carbonyl compound ( $\text{HC}-\text{C}=\text{O}$ )	$\delta$ 2.0–2.7	$\delta$ 30–50 <sup>d</sup>

<sup>a</sup>Since chemical shifts depend upon solvent (and these data have been determined in a wide range of solvents) and other conditions, these ranges should be treated as being approximations. The carbon shifts of this table are supplemented by the carbon shifts provided on Table 6.9.

<sup>b</sup>The broad range of proton shifts for monosubstituted alkanes ( $\delta$  2.0–5.0) is subdivided at the bottom of the table ( $\alpha$ -protons). Some  $\alpha$ -carbon data are presented in this table, but a superior approach is to use Table 6.9.

<sup>c</sup>Proton shifts for such exchangeable hydrogens vary greatly since they depend greatly on concentration, solvent, and other factors which affect the exchange. Thus these ranges may not be totally reliable.