

Mass Spectra of Some Phenylazopyridines and Quinolines

Ellis V. Brown

Department of Chemistry, University of Kentucky

All of the isomeric phenylazoquinolines and phenylazopyridines have been prepared and subjected to electron impact in the mass spectrometer. Fragmentation patterns of these compounds are discussed along with some of their *para*-bromo derivatives.

Relatively few papers have been published concerning the mass spectrometric behavior of quinolines and these have been limited to quinoline (1), alkylquinolines (2,3) and methoxyquinolines (4). The mass spectra of azobenzenes have been investigated (5). In this paper we wish to report the mass spectra of the isomeric phenylazoquinolines prepared by the Campbell (6) method as well as the phenylazopyridines for comparison. We have also prepared and subjected to electron impact in the mass spectrometer the four *p*-bromo derivatives of 2- and 4-phenylazopyridines and 2- and 7-phenylazoquinolines. These bromo-labelled compounds are then compared with the corresponding unbrominated azo compounds.

The Campbell (6) reaction has proved generally useful for the syntheses of phenylazo and *p*-bromophenylazoquinolines. See Table I for yields and other data. The mass spectra of the phenylazoquinolines are listed in Table II. We see that the parent ion is not 100% in any

of the three isomers and is in fact 0% in 2-phenylazoquinoline. The major peaks can be accounted for by a scheme such as shown in Figure 1. This scheme includes peaks at 77(VI), 78(V), 105(IV) and 106(III). The peaks at 50, 51 and 52 are typical of pyridine (7). The skeletal rearrangement ions (5) (I and II) at mass 155 and 154 are

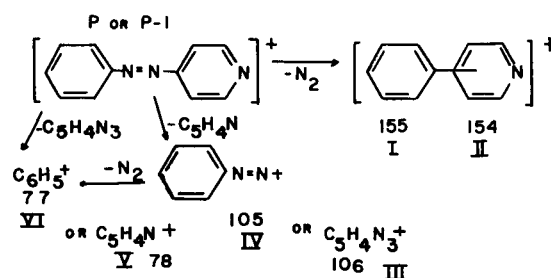


FIGURE 1

TABLE I

Phenylazoquinolines (a)

Code	Yield	M.p. °C (b)	Formula	Calcd.			Analysis		
				C	H	N	C	H	N
2-PAQ	50	92-93	C ₁₅ H ₁₁ N ₃	77.25	4.75	18.02	(c)		
3-PAQ	80	113-114	C ₁₅ H ₁₁ N ₃	77.25	4.75	18.02	77.31	4.50	18.15
4-PAQ	50	86-87	C ₁₅ H ₁₁ N ₃	77.25	4.75	18.02	(d)		
5-PAQ	60	91-92	C ₁₅ H ₁₁ N ₃	77.25	4.75	18.02	77.00	4.70	17.95
6-PAQ	80	113-114	C ₁₅ H ₁₁ N ₃	77.25	4.75	18.02	77.50	4.75	18.10
7-PAQ	90	125-126	C ₁₅ H ₁₁ N ₃	77.25	4.75	18.02	77.02	4.88	17.82
8-PAQ	50	62-63	C ₁₅ H ₁₁ N ₃	77.25	4.75	18.02	77.48	4.55	18.08
2- <i>p</i> -BrPAQ	77	164-165	C ₁₅ H ₁₀ N ₃ Br	57.70	3.21	13.46	57.30	3.23	13.53
7- <i>p</i> -BrPAQ	50	185-186	C ₁₅ H ₁₀ N ₃ Br	57.70	3.21	13.46	58.08	3.47	13.78

(a) All compounds chromatographed on alumina in toluene and recrystallized from methylcyclohexane. (b) All melting points corrected. (c) Reference 8. (d) Reference 9.

TABLE II

Mass Spectra of Phenylazopyridines
(Relative Abundances) (a)

m/e	2	3	4
184	0	9	7
183	0	63	56
155	39	2	0
154	20	13	7
106	0	5	3
105	14	42	42
93	5	0	0
88	5	0	0
79	0	5	3
78	37	49	29
77	100	100	100
69	5	0	0
65	0	6	2
64	0	9	4
63	0	5	4
62	0	2	2
58	0	23	0
52	0	8	11
51	36	56	56
50	7	53	56

(a) All peaks above 49 mass where at least one isomer was 5% or more.

TABLE III

Mass Spectra of 2- and 4-(*p*-Bromophenyl)azopyridines

2- 264(0), 263(0), 262(0), 261(0), 236(8), 235(75), 234(8), 233(75), 185(12), 183(12), 158(7), 157(88), 156(7), 155(88), 154(27), 153(5), 128(5), 127(16), 98(5), 90(9), 83(9), 74(9), 78(100), 77(9), 76(68), 75(64), 74(20), 64(12), 63(20), 62(7), 55(9), 52(27), 51(68), 50(64).

4- 264(9), 263(75), 262(9), 261(75), 186(6), 185(78), 184(6), 183(78), 158(11), 157(100), 156(11), 155(100), 127(7), 79(5), 78(36), 77(9), 76(47), 75(36), 74(9), 63(9), 52(6), 51(55), 50(36).

of high abundance only in the 2-isomer.

When we examine the mass spectra of 2- and 4-(*p*-bromophenylazo)pyridines (Table III) we find confirmation of the above analysis since we find no parent ion for the 2-isomer and 75% abundance for this ion in the case of the 4-isomer. The peaks at 77, 78 and 105 are now seen as 155, 157; 156, 158; and 183, 185. The skeletal rearrangement ion 155 is now seen as 233, 235 but is only found in the 2-isomer as before. The modest peak at 154 in the 2-isomer which doesn't appear in the 4-isomer may be the rearrangement ion less bromine.

In Table IV are listed the mass spectra of the seven phenylazoquinolines. Here can be seen the low abundance

TABLE IV

Mass Spectra of Phenylazoquinolines (Relative Abundances)

m/e	2	3	4	5	6	7	8
234	0	7	8	6	13	16	0
233	0	38	45	20	70	90	1
205	18	2	3	0	3	6	7
204	100	9	11	0	13	25	35
156	0	2	0	1	13	11	22
149	0	12	0	0	0	0	0
129	4	7	11	6	15	20	8
128	30	60	41	40	100	100	58
127	2	0	2	4	3	5	6
105	47	25	38	7	17	32	2
102	5	2	6	15	10	11	16
101	13	19	36	27	17	23	30
100	1	0	1	4	2	0	4
98	0	1	0	0	5	0	0
83	0	0	7	0	11	4	0
78	6	5	11	8	7	9	8
77	77	100	100	100	85	100	93
76	8	2	6	13	4	6	8
75	2	13	25	34	9	11	27
74	0	0	6	17	3	4	11
69	8	0	3	0	3	0	0
64	2	0	13	10	3	7	10
63	3	3	5	14	5	4	16

TABLE V

Mass Spectra of 2- and 7-(*p*-Bromophenyl)azopyridines

2- 313(4), 311(4), 285(47), 284(40), 283(50), 282(38), 245(39), 244(20), 243(17), 205(10), 204(43), 203(11), 185(13), 183(13), 173(10), 171(10), 168(10), 167(28), 166(10), 165(14), 158(6), 157(67), 156(7), 155(67), 152(10), 144(23), 127(23), 117(14), 116(8), 115(14), 114(8), 102(25), 101(68), 100(10), 98(10), 91(10), 90(15), 89(20), 88(14), 87(14), 84(6), 83(18), 81(8), 78(8), 77(67), 76(61), 75(95), 74(27), 73(8), 71(6), 70(7), 69(26), 68(7), 67(7), 66(7), 65(21), 64(19), 63(48).

7- 313(5), 311(5), 264(5), 263(40), 262(5), 261(40), 185(55), 183(55), 158(8), 157(100), 156(10), 155(100), 129(20), 128(5), 95(68), 94(100), 93(100), 92(13), 91(12), 82(5), 81(30), 80(13), 79(35), 78(32), 77(10), 69(5), 68(30), 67(10), 66(30), 65(12), 64(5).

of the parent peak in several of these compounds, notably, in the 2-isomer (0%) and the 8-isomer (1%). The skeletal rearrangement peaks (204,205) are apparent in every isomer but the 5 and are particularly high where the parent is low in most cases. We see peaks corresponding to the pyridine case, VI still 77, V now 128, IV still 105, and III now 156.

Table V gives the mass and abundances of the 2- and 7-(*p*-bromophenyl)azopyridines which can be compared with their unbrominated counterparts. The parent ions are quite low in both cases, 313 and 311. The skeletal rearrangement ions (285, 284, 283, 282) are prominent in the 2-isomer and missing in the 7-isomer. Peaks similar to Figure 1 can be seen where VI is now 157 and 155, V is 158 and 156, IV is 185 and 183, and III is 128.

EXPERIMENTAL

Melting points were determined with a Fisher-Johns block and

are corrected. Mass spectra were determined with a Hitachi Perkin-Elmer RMU-6E mass spectrometer with an ionizing potential of 70 eV and an inlet temperature (up to 230°) high enough to obtain sufficient sample for a determination.

Azo Compounds (Campbell Reaction).

Two grams of aminoquinoline were placed in a mixture of 20 ml. of 50% aqueous sodium hydroxide and 20 ml. of pyridine and warmed to 80° while adding 2 g. of nitrosobenzene over a period of 0.5 hour. After heating for an additional 0.5 hour, the solution was cooled, diluted with water and extracted with toluene. The solvent was evaporated and the residue was taken up in toluene and chromatographed over alumina. Evaporation of the toluene left the azo compound which was recrystallized from methylcyclohexane (Table I). 2-(*p*-Bromophenyl)azopyridine, m.p. 125-126°, (45%), was obtained using *p*-bromonitrosobenzene.

Anal. Calcd. for C₁₁H₈N₃Br: C, 50.38; H, 3.08; N, 16.03. Found: C, 50.42; H, 3.15; N, 15.97.

4-(*p*-Bromophenyl)azopyridine was similarly prepared, m.p. 147-148° (35%).

Anal. Calcd. for C₁₁H₈BrN₃: C, 50.38; H, 3.08; N, 16.03. Found: C, 50.60; H, 3.20. N, 16.13.

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Lexington, Kentucky 40506