NOTES

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The Mass Spectra of *N*,*N*'-Diarylpiperazines

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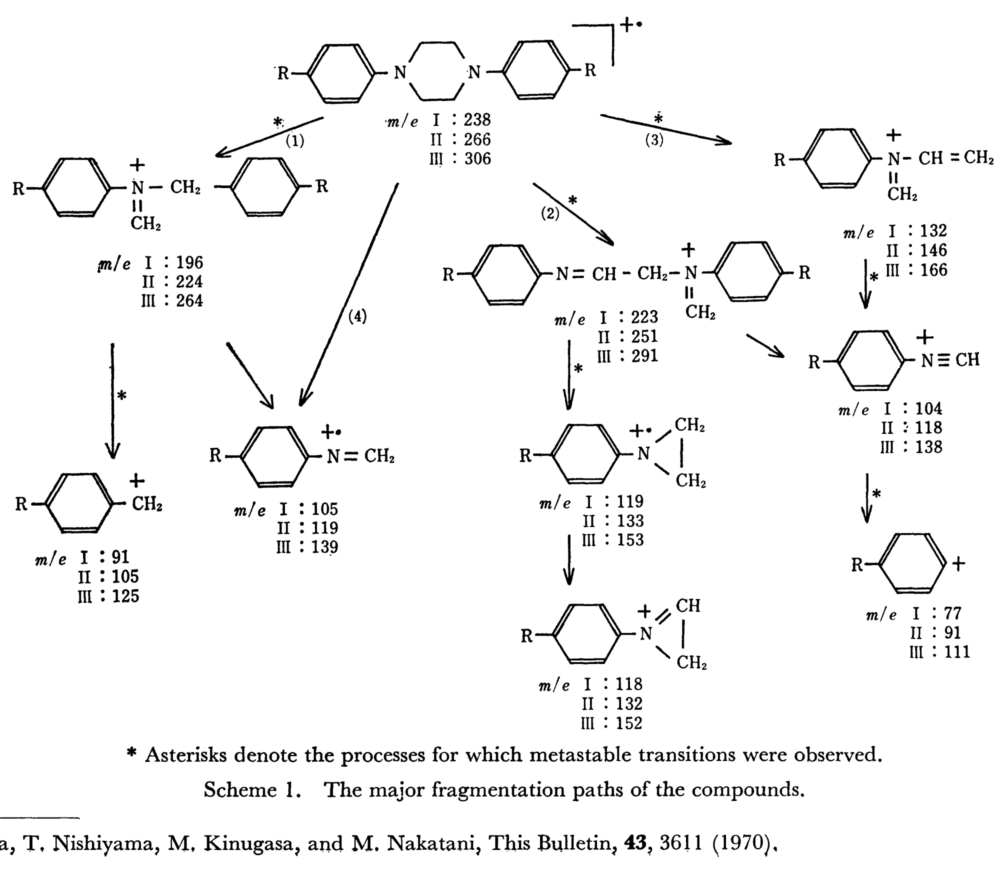
In a previous paper, we reported on the preparation of *N*,*N*'-diarylpiperazines, which have a substituent, a *p*-methyl or *p*-chloro group, on the benzene ring.[1] Mass spectrometric data will now be reported for *N*,*N*'-diphenylpiperazine (I, R=H), *N*,*N*'-di-*p*-tolylpiperazine (II, R=CH_3), and *N*,*N*'-di-*p*-chlorophenylpiperazine (III, R=Cl). By the use of metastable-ion measurements, the major fragmentation pathways of the three compounds, I, II, and III, have been deduced.

The mass spectral data of the compounds are shown

TABLE 1. MASS SPECTRAL DATA OF THE COMPOUNDS, I, II, AND III

Compound I			Compound II			Compound III		
m/e	Ion composition[a]	Rel. int. (%)	*m/e*	Ion composition	Rel. int. (%)	*m/e*	Ion composition	Rel. int. (%)
238	$C_{16}H_{18}N_2$	79	266	$C_{18}H_{22}N_2$	89	306	$C_{16}H_{16}N_2Cl_2$	57
223	$C_{15}H_{15}N_2$	14	251	$C_{17}H_{19}N_2$	26	291	$C_{15}H_{13}N_2Cl_2$	3
196	$C_{14}H_{14}N$	10	224	$C_{16}H_{18}N$	13	264	$C_{14}H_{12}NCl_2$	6
132	$C_9H_{10}N$	40	146	$C_{10}H_{12}N$	49	166	C_9H_9NCl	39
119	C_8H_9N	21	133	$C_9H_{11}N$	29	153	C_8H_8NCl	12
105	C_7H_7N	100	119	C_8H_9N	100	139	C_7H_6NCl	100
104	C_7H_6N	39	118	C_8H_8N	34	138	C_7H_5NCl	41
91	C_7H_7	19	105	C_8H_9	23	125	C_7H_6Cl	16
78	C_6H_6	11	92	C_7H_8	23	111	C_6H_4Cl	26
77	C_6H_5	53	91	C_7H_7	60			

a) The high-resolution mass spectra of these compounds gave correct composition of all ions mentioned in the table, within the error of ±5 millimass units.



* Asterisks denote the processes for which metastable transitions were observed.

Scheme 1. The major fragmentation paths of the compounds.

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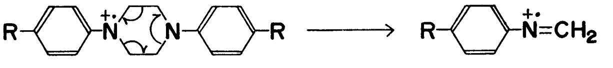
[1] F. Yamada, T. Nishiyama, M. Kinugasa, and M. Nakatani, This Bulletin, **43**, 3611 (1970).

in Table 1, while the major fragmentation paths are shown in Scheme 1.

The molecualr ions produce a prominent peak and are usually the second most abundant ion in the spectra of the compounds. The base peaks are at masses 105, 119, and 139 respectively, and are due to R–C_6H_4N-$CH_2^{+\cdot}$. These ions result from the elimination of the R–$C_6H_4\dot{C}H_2$ radical from the intermediate ion, (R–$C_6H_4)_2\overset{+}{N}CH_2CH_2$, (Path 1 in Scheme 1) or from the retro-Diels-Alder decomposition of the molecular ion (Path 4). This decomposition will be a dominating process in the formation of the R–$C_6H_4\overset{+\cdot}{N}CH_2$ ion:

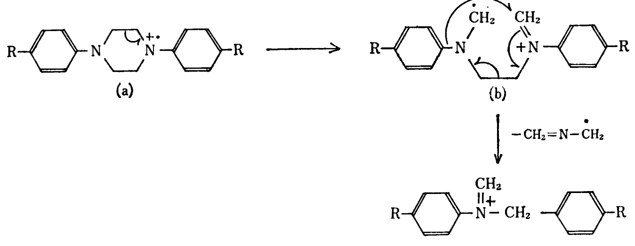


m/e 238, 266, and 306 *m/e* 105, 119, and 139

In the case of Compound I, the metastable transition indicates that the above ion can also be formed by another route, one which involves the loss of C_2H_2 from the $C_9H_9N^{+\cdot}$ ion with the mass of 131. Thus, the fragmentation pathways of I are rather more complex than those of II and III. However, all three compounds, I, II, and III, give very similar pathways, as is shown in Scheme 1.

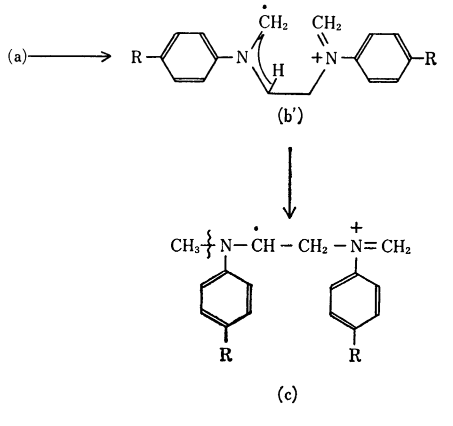
The metastable transitions and exact mass measurements indicate the following results.

Path (1), Giving m/e 196, 224, and 264. These fragments are generated directly from the molecular ion by the loss of a C_2H_4N radical. The probable fragmentation mechanism is indicated by the following diagram:



m/e 196, 224, and 264

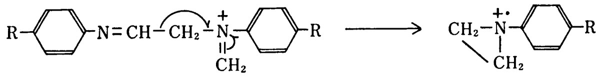
The ring cleavage of the molecular ion as in **a** and the subsequent rearrangement with the transfer of the *N*-bonded aryl group, as is shown in **b**, afforded the fragment ion.



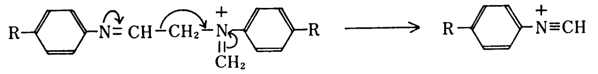
Path (2), Giving m/e 223, 251, and 291. These ions are produced from the molecular ion by the loss of the respective methyl radicals.

The rearrangement with the transfer of a hydrogen atom, as is shown in **b'**, followed by the loss of the species from **c**, gives the fragment ions.

The ions at the masses of 119, 133, and 153 can be formed by the loss of the R–C_6H_4NCH radical from *m/e* 223, 251, and 291 respectively, while the ions at *m/e* 104, 118, and 138 may also be formed by the expulsion of the R–$C_6H_4NC_2H_4$ fragment from the same point of origin. It is thought that this fragmentation process is due to a one- or two-electron shift, as is shown below:

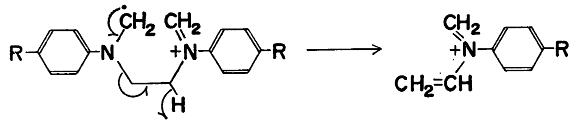


m/e 119, 133 and 153



m/e 104, 118 and 138

Path (3), Giving m/e 132, 146, and 166. These ions are produced by the loss of the R–$C_6H_4NCH_3$ radicals from the respective molecular ions.



m/e 132, 146, and 166

As has been described above, in the mass spectra of the three compounds, I, II, and III, there are four principal modes of fragmentation of the molecular ion:

(1) Aryl rearrangement (Path 1)
(2) Loss of a methyl radical (Path 2)
(3) Loss of a R–$C_6H_4NCH_3$ radical (Path 3), and
(4) retro-Dieles-Alder decomposition (Path 4).

This fragmentation behavior of the compounds resembles that of piperazine and its derivatives,[2] but the M−1 ions were not observed, as expected, in the *N,N'*-diarylpiperazines.

Experimental

The high-resolution mass spectra were obtained with a Japan Electron Optics Co., Ltd., JMS-O1SG mass spectrometer. Accurate mass values were obtained from the photoplate by means of a JMA-1C Automatic Data analyzer. The metastable-ion transitions were determined by scanning the accelerating voltage, as has been described in the literature.[3]

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[2] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco (1967), p. 321.

[3] J. H. Futrell, K. R. Ryan, and L. W. Sieck, *J. Chem. Phys.*, **43**, 1832 (1965).