Fragmentation of *o***-Nitrodiarylamines on Electron Impact: Formation of Carbazole Radical Cations**

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The HO' fragment eliminated on electron impact (EI) from the molecular ions of *o*-nitrodiarylamines contains either the amine or the aryl hydrogen. Moreover, 2-phenylamino-3-nitropyridine loses H' from the phenyl group. As confirmed by collision-activated dissociation mass-analysed ion kinetic energy spectra, the fragmentation of such compounds involves the formation of carbazole radical cations. Such a process was not observed for the corresponding *o*-aminodiarylamines.

INTRODUCTION

Diarylamines lose two hydrogen atoms on electron impact (EI) to give the respective carbazole radical cation.¹ Dibenzofurans² and thiophenes³ are formed with o-nitro-substituted diaryl ethers and sulphides expel HNO₂. Formation of the respective aza heterocycles was suggested to take place in EI-induced fragmentation of 2- and 4-phenylamino-3-nitropyridines.⁴ It was proved recently⁵ that N-(o-nitrophenyl)-p-aminobenzoic acid loses successively HO' and NO' under similar conditions to form the respective carbazole carboxylic acid radical cation.

In this work, some new *o*-nitrodi(hetero)arylamines and their deutero analogues were prepared and their EI-induced fragmentation was investigated. Collision techniques were used to confirm the structure⁴ of the product of NHO₂ elimination from the molecular ions of the compounds under study. The formation of carbazole ions from *o*-nitroarylamine molecular ions is analogous to the Pschorr reaction.^{6,7}

RESULTS AND DISCUSSION

The loss of HNO₂ from 2- and 4-phenylamino-3-nitropyridine on EI can be a one- or a two-step process.⁴ This paper discusses the EI-induced formation of carbazole radical cations from a series of nitrodiarylamines $(1-12; R^1 = O)$ (Scheme 1).



Scheme 1. Structures of compounds. Some amino-substituted diarylamines (13–17; $R^1 = H$) were included to study similar cyclization processes.

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Table 1. Characteristic EI-induced (70 eV) fragmentation of nitrodiarylamines 1-17 [m/z and relative intensities (% of base peak) in parentheses]

No.ª	M+	M + 1	M – 1	M – 2	M - 15	M-16	M – 17	M – 30	M – 46	M – 47
1	214	215	213	212	199	198	197	184	168	167
	(98)	(12)	(<1)	(<1)	(<1)	(2)	(15)	(2)	(25)	(100)
2	215	216	214	``	200	199	198	185	169	168
	(100)	(10)	(49)		(<1)	(<1)	(6)	(2)	(27)	(74)
3	264	265	263	_	249	248	247	234	218	217
	(100)	(14)	(<1)		(<1)	(1)	(8)	(1)	(40)	(67)
4 ^b	215	216	214	213	200	199	198	185	169	168
	(81)	(11)	(81)	(3)	(<1)	(2)	(9)	(4)	(18)	(100)
5	216	217	215	214	201	200	199	186	170	169
	(69)	(6)	(100)	(22)	(<1)	(<1)	(2)	(1)	(11)	(49)
6	229	230	228		214	213	212	199	183	182
	(20)	(3)	(6)		(<1)	(<1)	(5)	(<1)	(12)	(15)
7	257	258	256		242	241	240	227	211	210
	(31)	(5)	(<1)		(100)	(<1)	(2)	(2)	(18)	(17)
8	258	259	257	_	243	242		228	212	211
	(37)	(5)	(8)		(100)	(17)		(2)	(13)	(10)
9	265	266	264	263	250	249	248	235	219	218
	(58)	(9)	(19)	(<1)	(<1)	(3)	(20)	(1)	(19)	(100)
10	216	217	215	_	_	200	199	186	170	169
	(6)	(1)	(<1)			(<1)	(<1)	(<1)	(100)	(10)
11 ^b	215	216	214	213	200	199	198	185	169	168
	(100)	(21)	(2)	(<1)	(<1)	(1)	(17)	(2)	(19)	(27)
12	265	266	264	263	250	249	248	235	219	218
	(100)	(14)	(11)	(<1)	(<1)	(2)	(15)	(2)	(32)	(75)
13	184	185	183	182	169	168	167	154	138	137
	(100)	(9)	(37)	(12)	(29)	(3)	(3)	(1)	(<1)	(<1)
14	185	186	184	183	170	169	168	155	139	—
	(61)	(5)	(100)	(6)	(1)	(2)	(2)	(<1)	(<1)	
15	235	236	234	233	220	219	218	205	189	188
	(96)	(16)	(100)	(14)	(11)	(25)	(8)	(4)	(<1)	(<1)
16	185	186	184	183	170	169	168	155	139	138
	(20)	(2)	(9)	(2)	(7)	(1)	(<1)	(<1)	(<1)	(<1)
17	185	186	184	183	170	169	168	155	139	
	(100)	(12)	(33)	(9)	(20)	(2)	(1)	(<1)	(<1)	
" The	formulae c	of the ion	s of <i>m/z</i> 26	55, 264, 2	257, 248, 2	242, 235,	229, 220-	214, 211,	210, 185-	-182 and

170–167 (relative intensity >3%) were confirmed by accurate mass measurement.

^b Data from Ref. 4.

The complete mass spectral data for compounds 1-19 are given in Tables 1 and 2. The primary fragmentation pattern of 7 is shown in Scheme 2 as an example. Secondary processes for the compounds studied will not be discussed here. Compounds 4 and 11 have been considered previously.⁴



Nitrodiarylamine molecular ions expel the same fragments, as observed previously^{4,8} (see also Table 1 and Scheme 2) but their molecular ions are very stable. However, this is not the case for 2-mesitylaminopyridine (7), 2-(methylphenylamino)pyridine (6) and, particularly, 2-(2-pyridylamino)-3-nitropyridine (10).

The same exceptions are observed for $[M - 47]^{+}$ resulting from elimination of HNO₂ from the molecular ions. The effect of an aza nitrogen atom in the nitro-substituted ring on the relative abundance of that ion depends on the substituent.

The ions $[M - 1]^+$ have low abundances in the spectra of all the compounds except 4. Most spectra show small peaks of $[M - 17]^+$ and $[M - NO]^+$. The $[M - 46]^+$ ion has a medium relative abundance. Only for 10 the elimination of NO₂[•] is abundant, and this gives rise to the base peak in the spectrum.

A carbazole ion may be the product of direct expulsion of HNO_2 or of three other two-step eliminations, i.e. (i) HO' and NO', (ii) NO' and HO' and (iii) H' and NO₂', from the molecular ions of 4 and 11.⁴ To prove the structure of the ion $[M - HNO_2]^{+*}$, the collision-activated decomposition mass analysed ion kinetic

No.ª.b								Remaining	peaks ^c							
1	181 (9) 78	180 (26) 77	179 (3) 76	170 (4) 65	169 (30) 64	166 (20) 63	157 (5) 52	156 (3) 51 (21)	154 (3) 50	140 (9)	139 (12)	132 (3)	129 (4)	128 (3)	115 (5)	84 (4)
2	(3) 197 (11) 90 (4) 51	(21) 182 (5) 85 (4) 50	(3) 181 (6) 84 (8)	(4) 180 (26) 83 (5)	(3) 170 (13) 81 (5)	(8) 167 (49) 77 (22)	(4) 166 (12) 71 (7)	(21) 157 (4) 70 (3)	(7) 141 (4) 69 (9)	140 (9) 65 (5)	139 (8) 64 (5)	129 (3) 63 (7)	115 (4) 57 (11)	97 (4) 55 (7)	95 (3) 53 (3)	91 (3) 52 (5)
3	(25) 231 (7) 108 (5)	(7) 230 (20) 101 (4)	229 (4) 96 (4)	220 (4) 95 (3)	219 (26) 77 (8)	216 (30) 75 (5)	215 (6) 63 (6)	214 (5) 51 (5)	204 (4) 50 (3)	190 (6)	189 (8)	131 (3)	127 (12)	126 (7)	115 (9)	109 (8)
5	198 (6) 57 (4)	171 (3) 55 (3)	168 (51) 53 (3)	142 (5) 52 (4)	141 (7) 51 (22)	140 (5) 50 (6)	116 (5)	115 [´] (7)	114 (4)	85 (7)	78 (6)	77 (23)	69 (4)	65 (5)	64 (4)	63 (3)
6	184 (11)	181 (4)	156 (44)	107 (100)	106 (8) 209	105 (8)	94 (5)	195	10/	102	193	192	191	168	167	117
,	243 (12) 115 (4)	(10) (104 (3)	224 (3) 103 (4)	212 (7) 91 (10)	209 (31) 79 (4)	(8) 78 (5)	(38) 77 (9)	(19) 65 (5)	(6) 53 (3)	(3) 51 (5)	(3)	(4)	(5)	(5)	(4)	(3)
8	244 (11) 105	227 (7) 104	226 (6) 103	224 (3) 98	213 (5) 97	210 (19) 91	209 (27) 79	208 (4) 78	198 (5) 77	197 (30) 65	196 (15) 57	195 (10) 55 (2)	194 (5) 53	182 (4)	168 (3)	115 (3)
9	(5) 232 (4) 77 (6)	(3) 231 (8) 75 (4)	(4) 220 (7) 63 (3)	(3) 217 (11) 51 (4)	(4) 216 (4)	(11) 191 (8)	(3) 190 (8)	(5) 164 (4)	(7) 140 (3)	(4) 127 (13)	(4) 126 (7)	(3) 115 (5)	(3) 110 (5)	109 (8)	101 (4)	96 (4)
10	171 (9)	79 (4)	78 (25)	52 (6)	51 (12)	205	102	101	100	165	164	162	140	120	121	120
12	232 (5) 127 (16)	231 (15) 126 (9)	220 (18) 115 (9)	(13) (13) (6)	(4) 109 (8)	205 (4) 101 (5)	(5) 96 (7)	(11) 83 (4)	(11) 82 (4)	(5) 77 (8)	(6) 75 (5)	(4) 63 (4)	(4) 51 (5)	(3) 50 (3)	(3)	(3)
13 14	181 (5) 93	170 (3) 92	166 (3) 82	118 (4) 81	107 (5) 77	92 (6) 66	91 (7) 55 (7)	80 (9) 54	77 (6) 51	65 (6)	53 (3)	52 (4)	51 (7)			
15	(4) 232 (5) 78 (5)	(5) 225 (5) 77 (4)	(5) 217 (5) 75 (4)	(4) 154 (4) 66 (4)	(7) 140 (3) 65 (4)	(3) 128 (5) 63 (4)	(7) 127 (13) 55 (8)	(5) 126 (5) 54 (7)	(4) 118 (5) 53 (3)	117 (7) 52 (5)	115 (8) 51 (4)	109 (5)	93 (4)	91 (19)	89 (3)	81 (6)
16° 17 18	93 (5) 168 (14)	92 (6) 167 (100)	81 (7) 166 (26)	78 (5) 140 (9)	77 (11) 139 (14)	66 (11) 89 (4)	65 (4) 83 (10)	55 (3) 76 (4)	54 (9) 70 (5)	53 (5) 69 (5)	52 (6) 63 (4)	51 (9)	50 (3)			
19	169 (10)	168 (100)	167 [´] (6)	141 (9)	140 (14)	115 (3)	114 (8)	113 (5)	88 (3)	84 (9)	70 (3)	63 (5)				

Table 2. Additional peaks in the EI mass spectra (70 eV) of nitrodiarylamines 1–17, carbazole 18 and α-carboline 19 [m/z and relative intensities (% of base peak) in parentheses]

^a Complete spectra of compounds 4 and 11 are given in Ref. 4.

^b The formulae of the ions of m/z 243, 231, 230, 220, 219, 217, 216, 209, 196, 195, 191, 189, 183, 180, 169–166, 156, 140, 127 and 107 (relative intensity >3%) were confirmed by accurate mass measurement.

^c lons below m/z 50 and lower than 3% are not included. ^d No peaks >3% below m/z 170 in the spectrum.

energy (CAD-MIKE) spectra of the ions of m/z 167 of 1

and m/z 168 of 4 and also of carbazole ions, 18, and α -carboline ions, 19, were recorded. The elemental compositions for the respective ions, as determined by the high-resolution technique, are $C_{12}H_9N$ (167.07251; cal-

culated 167.07345) and $C_{11}H_8N_2$ (168.06782; calculated 168.06870), respectively. The structures of the ions [M -47]^{+•} formed from [1]^{+•} and [4]^{+•} can be clearly proved by comparing their spectra with those of 18 and 19 (see Figs 1 and 2).

Figure 1. CAD-MIKE spectra of ions at (a) m/z 167 of 1 and (b) M⁺⁺, m/z 167 of 18.

The fragmentation patterns of 1 and 4 (see also Ref. 4) are similar. However, H[•] is not eliminated from the molecular ion of the former. The relative abundances of the respective ions in the spectrum of the naphthylamino derivative 3 resemble those observed for 1 but a noticeable drop in the relative abundance of $[M - 47]^{+*}$ is observed. In comparison with the spectrum of 4, the relative abundances of the ions M^{+*} , $[M - 1]^+$ and $[M - 47]^{+*}$ for 6 and 10 are much lower. Replacing of the phenyl ring in 4 by the pyridyl group also results in a decrease in the relative abundances of the ions $[M - 17]^+$ and $[M - 30]^+$. On the other hand, the relative abundance of the ion $[M - 46]^+$ increases, and it forms the base peak for 10.

The spectrum of 2-(2,4,6-trimethylphenylamino)-3nitropyridine (7) was recorded to show how substituents



Figure 2. CAD-MIKE spectra of ions at (a) m/z 168 of 4 and (b) M⁺⁺, m/z 168 of 19.

other than hydrogen in an *ortho* position on the phenyl ring affect the fragmentation. The methyl groups present in 7 were expected to preclude the formation of a carbazole radical cation. Unfortunately, of all the primary fragment, CH_3 , is eliminated most easily from $[7]^+$. The effectiveness of the process is comparable to that of elimination of H[•] from $[4]^{+\bullet}$. Hence the carboline cation can be formed from 7 provided that the *o*rather than *p*-methyl was eliminated; $[7]^{+\bullet}$ does not expel H[•] and the elimination of HNO₂ and HO[•] is less effective than in $[4]^{+\bullet}$.

Replacing phenyl with 1-naphthyl in 1, 4 and 11 affords 3, 9 and 12, respectively. This does not alter the fragmentation routes. Hence, the relative abundances of both M^{+*} and $[M - 1]^+$ are decreased and that of $[M - 47]^{+*}$ is increased when the naphthylamino substituent is present in position 2 on the pyridine ring. The relative abundances of the ions $[M - 1]^+$, $[M - 46]^+$ and $[M - 47]^{+*}$ are higher in the spectrum of 12 as compared with 11.

Deuterium labelling can be used to detect the origin of the hydrogen atom expelled with the fragments. Hence derivatives 2, 5 and 8 were obtained and their spectra recorded. Although the degree of deuteration was low, the following seems clear: (i) $[M - 1]^+$ is a result of the expulsion of H[•] originating mainly from the phenyl ring of 4; (ii) HO[•] ejected from $[1]^{+*}$ and $[4]^{+*}$ contains either the amine or the aryl hydrogen atom (see also Ref. 8); (iii) it is impossible to state the origin of the hydrogen atom expelled with HNO₂ since the same ion $[M - 47]^{+*}$ is also a product of three other twostep eliminations from M^{+*}.

As shown by the similar abundances of the ion $[M - HNO_2 - H]^+$ in the spectra of 4 and 6, the hydrogen atom eliminated from $[M - 47]^{+}$ is not the 'pyrrole' one.

Aminodiarylamines are useful starting materials in the syntheses of carbazoles.^{7,9} It was therefore interesting to check whether elimination of NH_3 from the vicinally amino-substituted diarylamine molecular ions leads to the respective cyclization products. As seen in Table 1, elimination of NH_3 from $[13]^+ - [17]^+$ is not abundant in general. In most spectra the intensity of the molecular ion peak is high. Usually these molecular ions lose H[•] easily; the other fragments eliminated are NH and NH_2° .

CONCLUSION

Electron impact-induced elimination of HNO_2 by one- or two-step processes takes place for all *o*-nitrodiarylamines studied. Very similar CAD-MIKE spectra of the ions $[M - 47]^{+*}$ formed and those of the respective (aza)carbazole molecular ions prove the cyclic structure of the elimination product ions. *o*-Aminodiarylamines do not lose NH₃ to form similar carbazole radical cations.

The labelling studies show that the ion $[M - 1]^+$ is a result of the expulsion of aryl hydrogen atom. The HO' fragment ejected from the molecular ions contains either the amine or the aryl hydrogen.



EXPERIMENTAL

2-Aminodiphenylamine (13) and carbazole (18) are commercial products. They were recrystallized or vacuum sublimed, respectively, before use. Compounds 4 and 11 have been prepared previously.⁴ The other compounds were prepared according to known procedures: $1,^{10}$ m.p. 74–75 °C (from 95% ethanol); $6,^7$ m.p. 73.5–75 °C (from methanol); $9,^{11}$ m.p. 153.5–154 °C (from benzene); $10,^{12}$ m.p. 119–121 °C (from water); $12,^{11}$ m.p. 179.5– 181 °C (from benzene). α-Carboline (19) was obtained from 2-bromopyridine and o-phenylenediamine;^{13,14} 213-216 °C (from ethanol). Two known m.p. procedures^{15,16} were modified for the preparation of 3. Both gave a product of m.p. 158-160 °C (from 80% acetone). Compound 7 was synthesized by heating 2chloro-3-nitropyridine with a slight excess of 2,4,6-trimethylaniline at 155 °C for 3 h. The product, freed from the steam volatile substances, had m.p. 156-156.5 °C (from ethanol); yield, 62%.

Phenyldiaminopyridines 14, 16 and 17 are the products of the reduction of the respective nitrophenylaminopyridines or their N-oxides with

iron-acetic acid.^{17,18} The naphthylamino derivative 15 was obtained similarly from 9; m.p. 162-164 °C (from benzene).

The purity of all compounds was checked by thinlayer chromatography. Correct IR and ¹H and ¹³C NMR spectra and C, H and N analyses were obtained for all the compounds studied.

Vacuum evaporation of the solvent from solutions containing 50 mg of 1, 4 or 7 in 0.6 ml of hot methanol- d_1 was repeated three times to give deuterated analogues of nitrodiarylamines, i.e. 2, 5 and 8, respectively. During evaporation, P2O5 protection against water was used.

The mass spectra (low- and high-resolution and metastable transitions) were recorded as described previously.¹⁹ The CAD-MIKE spectra were measured using an AMD-604 spectrometer (AMD Intectra, Germany) with an accelerating voltage of 8 kV and helium as a collision gas. The collision cell pressure was adjusted to reduce the molecular ion intensity to 50% of its starting value. The sharp peaks appearing at m/z 83.8 in the spectra represent the doubly charged (aza) carbazole ions.

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