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tert-Amino Effect Following Electron Ionization of *N,N*-Dialkyl-*o*-nitroanilines†

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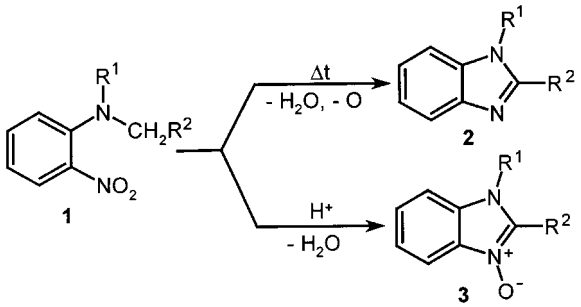
***N,N*-Dialkyl-*o*-nitroanilines undergo thermal reaction resulting in the formation of 1,2-dialkylbenzimidazoles—the process known as an example of the *tert*-amino effect. Similar processes are observed also in electron ionization spectra of these compounds. Elimination of an OH radical from the molecular ions of *N,N*-dialkyl-*o*-nitroanilines leads to several isomeric product ions depending on the substituents on the nitrogen atom. Elimination of the second OH radical yields $[M - OH - OH]^{+\cdot}$ ions, most likely with the structure of the appropriate 1-alkyl-or 1,2-dialkylbenzimidazoles. Mechanisms for these reactions are proposed.** © **1998 John Wiley & Sons, Ltd.**

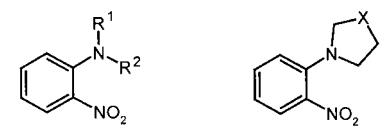
KEYWORDS: *tert*-amino effect; *ortho*-effect; fragmentation mechanisms; *N,N*-dialkyl-*o*-nitroanilines; benzimidazole derivatives

INTRODUCTION

The *tert*-amino effect, a term coined by Meth-Cohn and Sushitzky, describes the unusual reactions of tertiary anilines bearing *ortho* substituents leading to cyclization. One of the best studied groups of compounds showing different types of *tert*-amino effects are *N,N*-dialkyl-*o*-nitroanilines (**1**).[1,2] Depending on the reaction conditions, two main kinds of products are obtained: appropriately 1,2-disubstituted benzimidazoles (**2**) and their *N*-oxides (**3**).

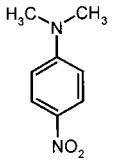


Analyzing the fragmentation pathways upon electron ionization (EI) of selected *N,N*-dialkyl-*o*-nitroanilines (**4**–**11**) we found some processes which could be rationalized in terms of the *tert*-amino effect. These processes in mass spectrometry should be classified as the examples of an *ortho* effect. Similar reactions, observed for *N*-alkyl-*o*-nitroanilines, have been described in previous papers.[3,4]



4 $R^1 = R^2 = CH_3$
5 $R^1 = R^2 = CD_3$
6 $R^1 = CH_3$, $R^2 = C_2H_5$
7 $R^1 = R^2 = C_2H_5$
11 $R^1 = R^2 = CH_2Ph$

8 X = $-CH_2-$
9 X = $-CH_2-CH_2-$
10 X = $-CH_2-O-$



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Fragmentation of *N,N*-dialkyl-*o*-nitroanilines has not previously been studied, with the exception of the work of Ramana and Vairamani,[5] who described the fragmentation of 2,4-dinitro-*N,N*-dibenzylaniline. We found that the fragmentation of **11** follows the same pattern, so this compound will not be discussed here. To make sure that the reactions we observe require an *ortho* position of the *N,N*-dialkylamino and nitro groups, we also analyzed the fragmentation of *N,N*-dimethyl-*p*-nitroaniline (**12**).

EXPERIMENTAL

Compounds **4**–**12**, 1-methylbenzimidazole, 1,2-dimethylbenzimidazole and 1-ethylbenzimidazole were prepared according to the methods described in the literature. Their purity was tested by gas chromatography/mass spectrometry.

All mass spectra were recorded on an AMD-604 double focusing mass spectrometer with BE geometry

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(AMD Intectra, Germany). Standard EI spectra were obtained with an electron energy of 70 eV, an acceleration voltage of 8 kV and an ion source temperature of 200 °C. Samples were introduced using a direct insertion probe heated, when required, from 30 to 100 °C.

Accurate mass measurements were made using the peak-matching technique for all significant peaks in the recorded spectra (see Tables 1 and 2). The resolving power was 10 000 (10% valley definition) and perfluorokerosene was used as a reference.

Fragmentation pathways were confirmed by mass-analyzed ion kinetic energy (MIKE) and B/E = constant fragment ion spectra recorded for metastable decompositions and, in some instances, also for the collisionaly induced dissociation (CID) products. MIKE spectra were recorded using a 30 s scan time. Four consecutive spectra were collected and averaged to enhance the signal-to-noise ratio and improve the accuracy of mass measurements. B/E = constant spectra were acquired using a 120 s scan time (downfield scan). A single scan gave an acceptable signal-to-noise ratio.

Both MIKE and B/E = constant spectra with CID (CID-MIKE and CID-B/E) were obtained using helium as a collision gas. The pressure in the collision chamber was set to reduce the abundance of the parent ion by 50%.

RESULTS AND DISCUSSION

General fragmentation pathways of the molecular ions of *N,N*-dialkyl-*o*-nitroanilines

The 70 eV EI mass spectra of compounds **4–10** and **12** are given in Tables 1 and 2. The fragmentation patterns

Table 1. 70 eV EI mass spectra of compounds 4–7 and 12 (m/z (relative intensity, %); elementary formula (contribution), isotope peaks not included)

4		5		6		7		12	
166(37)	$C_8H_{10}N_2O_2$	172(41)	$C_8H_4D_6N_2O_2$	180(53)	$C_9H_{12}N_2O_2$	194(29)	$C_{10}H_{14}N_2O_2$	166(100)	$C_8H_{10}N_2O_2$
165(1)	$C_8H_9N_2O_2$	154(49)	$C_8H_4D_5N_2O$	165(86)	$C_8H_9N_2O_2$	179(100)	$C_9H_{11}N_2O_2$	165(24)	$C_8H_9N_2O_2$
149(44)	$C_8H_9N_2O$	138(5)	$C_8H_4D_5N_2$(75%)	163(98)	$C_9H_{11}N_2O$	177(81)	$C_{10}H_{13}N_2O$	150(3)	$C_8H_{10}N_2O$
134(5)	C_8N_8NO(35%)		$C_8H_4D_4NO$(25%)	148(8)	$C_9H_{10}NO$(15%)	162(5)	$C_9H_{10}N_2O$	136(27)	$C_8H_{10}NO$
	$C_7H_6N_2O$(65%)	136(7)	$C_8H_4D_4N_2$(40%)		$C_8H_8N_2O$(85%)	161(3)	$C_{10}H_{13}N_2$	120(12)	$C_8H_{10}N$(90%)
133(2)	$C_8H_9N_2$		$C_7H_4D_2N_2O$(40%)	147(6)	$C_9H_{11}N_2$(85%)	160(4)	$C_{10}H_{12}N_2$		C_7H_6NO(10%)
132(3)	$C_8H_8N_2$		$C_7H_4DNO_2$(20%)		$C_8H_7N_2O$(15%)	159(4)	$C_{10}H_{11}N_2$	119(30)	C_8H_9N
121(13)	$C_7H_8N_2$	134(2)	$C_8H_4D_3N_2$	146(7)	$C_9H_{10}N_2$	151(28)	$C_7H_7N_2O$	118(9)	C_8H_8N
120(6)	$C_8H_{10}N$(30%)	126(13)	$C_7H_4D_5N_2$	145(8)	$C_9H_9N_2$	147(16)	$C_9H_{11}N_2$(90%)	117(2)	C_8H_7N
	$C_7H_8N_2$(50%)	124(12)	$C_8H_4D_5N$(85%)	135(14)	$C_8H_{11}N_2$(40%)		$C_8H_7N_2O$(10%)	108(5)	$C_7H_{10}N$
	C_7H_6NO(20%)		$C_7H_4D_4N_2$(15%)		$C_7H_7N_2O$(60%)	146(13)	$C_{10}H_{12}N$	107(2)	C_7H_9N
119(32)	C_8H_9N(35%)	123(8)	$C_8H_3D_5N$(70%)	134(20)	C_8H_8NO	145(5)	$C_9H_9N_2$	106(5)	C_7H_8N
	$C_7H_7N_2$(65%)		$C_7H_3D_4N_2$(30%)	133(33)	$C_9H_{11}N$(10%)	135(15)	$C_8H_{11}N_2$(90%)	105(15)	C_7H_7N
118(21)	C_8H_8N	122(41)	$C_8H_4D_4N$(45%)		$C_8H_9N_2$(90%)		$C_7H_7N_2O$(10%)	104(12)	C_7H_6N
107(9)	$C_6H_7N_2$		$C_7H_4D_3N_2$(55%)	132(52)	$C_9H_{10}N$	133(19)	$C_8H_9N_2$	93(4)	C_7H_9(45%)
106(6)	C_7H_8N(80%)	110(12)	$C_7H_4D_4N$(20%)	121(19)	$C_7H_9N_2$	132(13)	$C_9H_{10}N$(85%)		C_6H_7N(55%)
	$C_6H_6N_2$(20%)		$C_6H_4D_3N_2$(80%)	120(10)	$C_7H_9N_2$(80%)		$C_8H_8N_2$(15%)	92(5)	C_7H_8(45%)
105(16)	C_7H_7N	108(21)	$C_7H_4D_3N$(90%)		C_7H_6NO(20%)	121(11)	$C_7H_9N_2$(10%)		C_6H_6N(55%)
104(20)	C_7H_6N		C_6H_4DNO(10%)	119(56)	C_8H_9N(15%)		$C_6H_5N_2O$(90%)	91(11)	C_7H_7
94(15)	C_6H_8N	107(8)	$C_8H_3D_4$(10%)		$C_7H_7N_2$(85%)	119(42)	C_8H_9N(60%)	79(10)	C_6H_7(80%)
93(6)	C_7H_9(10%)		$C_7H_3D_3N$(80%)	118(32)	C_8H_8N(90%)		$C_7H_7N_2$(40%)		C_5H_5N(20%)
	C_6H_7N(70%)		C_6H_3DNO(10%)		$C_7H_6N_2$(10%)	118(13)	C_8H_8N	78(9)	C_6H_6(80%)
	C_6H_5O(20%)	106(25)	$C_7H_4D_2N$(80%)	117(10)	C_8H_7N	117(5)	C_8H_7N		C_5H_4N(20%)
92(16)	C_7H_8(50%)		C_7H_4DO(20%)	106(24)	C_7H_8N	105(39)	C_8H_9(30%)	77(22)	C_6H_5
	C_6H_6N(50%)	98(13)	$C_6H_4D_4N$	105(50)	C_8H_9(10%)		C_7H_7N(40%)	65(6)	
91(100)	C_7H_7	96(7)	$C_7H_4D_4$(30%)		C_7H_7N(80%)		$C_6H_5N_2$(30%)	63(5)	
78(10)	C_6H_6(80%)		$C_6H_4D_3N$(70%)		$C_6H_5N_2$(10%)	104(27)	C_7H_6N	42(19)	
	C_5H_4N(20%)	95(14)	$C_7H_3D_4$(70%)	104(35)	C_7H_6N	93(24)	C_6H_7N(90%)		
77(26)	C_6H_5		$C_6H_3D_3N$(30%)	94(12)	C_6H_8N(80%)		C_6H_5O(10%)		
65(9)	C_5H_5	94(100)	$C_7H_4D_3$(90%)		C_6H_6O(20%)	92(13)	C_7H_8(15%)		
63(5)	C_5H_3		$C_6H_4D_2N$(10%)	93(11)	C_6H_7N(80%)		C_6H_6N(85%)		
51(9)		82(5)			C_6H_5O(20%)	91(24)	C_7H_7(50%)		
		80(10)		92(39)	C_7H_8(50%)		C_6H_5N(50%)		
		79(8)			C_6H_6N(50%)	79(6)			
		78(19)		91(100)	C_7H_7(95%)	78(14)			
		63(5)			C_6H_5N(50%)	77(33)			
		52(6)		79(14)		75(10)			
				78(24)		65(11)			
				77(51)		51(15)			
				65(16)		43(13)			
				63(13)					
				57(8)					
				51(14)					
				43(16)					
				42(14)					

Table 2. 70 eV EI mass spectra of compounds 8–10 (*m/z* (relative intensity, %); elementary formula (contribution), isotope peaks not included)

8		9		10	
192(35)	$C_{10}H_{12}N_2O_2$	206(23)	$C_{11}H_{14}N_2O_2$	208(74)	$C_{10}H_{12}N_2O_3$
175(85)	$C_{10}H_{11}N_2O$	205(4)	$C_{11}H_{13}N_2O_2$	207(7)	$C_{10}H_{11}N_2O_3$
159(5)	$C_{10}H_{11}N_2$	189(100)	$C_{11}H_{13}N_2O$	191(100)	$C_{10}H_{11}N_2O_2$
158(10)	$C_{10}H_{10}N_2$	173(4)	$C_{11}H_{13}N_2$	178(4)	$C_9H_{10}N_2O_2$
157(12)	$C_{10}H_9N_2$	172(11)	$C_{11}H_{12}N_2$	174(39)	$C_{10}H_{10}N_2O$
145(100)	$C_{10}H_{11}N$	171(17)	$C_{11}H_{11}N_2$	173(25)	$C_{10}H_9N_2O$
144(78)	$C_{10}H_{10}N$	159(43)	$C_{11}H_{13}N$	163(10)	$C_9H_{11}N_2O$(90%)
135(6)	$C_7H_7N_2O$	158(33)	$C_{11}H_{12}N$		$C_8H_7N_2O_2$(10%)
132(6)	$C_8H_8N_2$	147(5)	$C_9H_{11}N_2$(10%)	161(19)	$C_9H_9N_2O$
131(10)	$C_8H_7N_2$		$C_8H_7N_2O$(90%)	150(12)	$C_7H_6N_2O_2$
130(7)	C_9H_8N	145(5)	$C_9H_9N_2$	147(13)	$C_9H_{11}N_2$(20%)
119(16)	$C_7H_7N_2$	144(19)	$C_{10}H_{10}N$		$C_8H_7N_2O$(80%)
118(8)	C_8H_8N(50%)	135(5)	$C_8H_{11}N_2$(10%)	145(73)	$C_9H_9N_2$
	$C_7H_6N_2$(50%)		$C_7H_7N_2O$(90%)	144(10)	$C_9H_8N_2$
117(21)	C_8H_7N	132(7)	$C_9H_{10}N$(45%)	135(35)	$C_7H_7N_2O$
105(7)			$C_8H_8N_2$(55%)	133(51)	$C_8H_9N_2$(50%)
104(36)	C_7H_6N	131(7)	C_9H_9N(55%)		$C_7H_5N_2O$(50%)
91(12)	C_7H_7		$C_8H_7N_2$(45%)	132(54)	$C_9H_{10}N$(65%)
77(23)		130(16)	C_9H_8N		$C_8H_8N_2$(30%)
65(5)		119(8)	C_8H_9N(15%)		$C_7H_4N_2O$(5%)
51(7)			$C_7H_7N_2$(80%)	131(36)	$C_8H_7N_2$(95%)
			C_7H_5NO(5%)		C_9H_9N(5%)
		118(5)	C_8H_8N(65%)	130(16)	C_9H_8N
			$C_7H_6N_2$(35%)	120(14)	C_7H_6NO
		117(6)	C_9H_9(40%)	119(97)	$C_7H_7N_2$
			C_8H_7N(60%)	118(28)	C_8H_8N(60%)
		105(7)	C_7H_7N(45%)		$C_7H_6N_2$(40%)
			$C_6H_5N_2$(55%)	117(15)	C_8H_7N
		104(18)	C_8H_8(10%)	106(45)	C_8H_8N(15%)
			C_7H_6N(90%)		C_6H_4NO(85%)
		93(11)	C_6H_7N	105(59)	C_7H_7N(20%)
		91(5)			$C_6H_5N_2$(80%)
		77(14)		104(53)	C_7H_6N(90%)
		65(4)			$C_6H_4N_2$(10%)
		51(5)		103(11)	C_8H_7(40%)
					C_7H_5N(60%)
				93(17)	
				92(43)	
				91(29)	
				79(24)	
				78(33)	
				77(84)	
				76(15)	
				75(10)	
				65(40)	
				63(11)	
				52(11)	
				51(34)	

of *N,N*-dialkyl-*o*-nitroanilines are complex and depend on the substituents on the nitrogen atom. They were studied using MIKE and *B/E* spectra recorded for metastable decompositions and, in some instances, also under CID conditions. The conclusions drawn in this work are based mainly on these spectra and results of accurate mass measurements.

Metastable ion spectra of the molecular ions of these compounds show that the only decomposition process common for all compounds under study (and also the most significant one) is the loss of the OH radical (Fig. 1).

Differences in the further fragmentation of the $[M - OH]^+$ ions indicate, however, that several isomeric structures for each of these ions should be considered. Analysis of the other primary decompositions, based on the results of the metastable ion spectra, show that they should be studied separately for two groups of *o*-nitroaniline derivatives: compounds with two alkyl groups on the nitrogen atoms (**4**, **6** and **7**) and cyclic amine derivatives (**8**–**10**).

For compounds **6** and **7**, with at least one ethyl group on the nitrogen atom, a very important fragmentation process is the elimination of $CH_3^{\cdot}$. Further fragmentation of $[M - CH_3]^+$ ion is complex, especially in the case of compound **6**. Cyclic amine derivatives **8**–**10** undergo, in addition to the $HO^{\cdot}$ elimination, two other unusual fragmentations (see below).

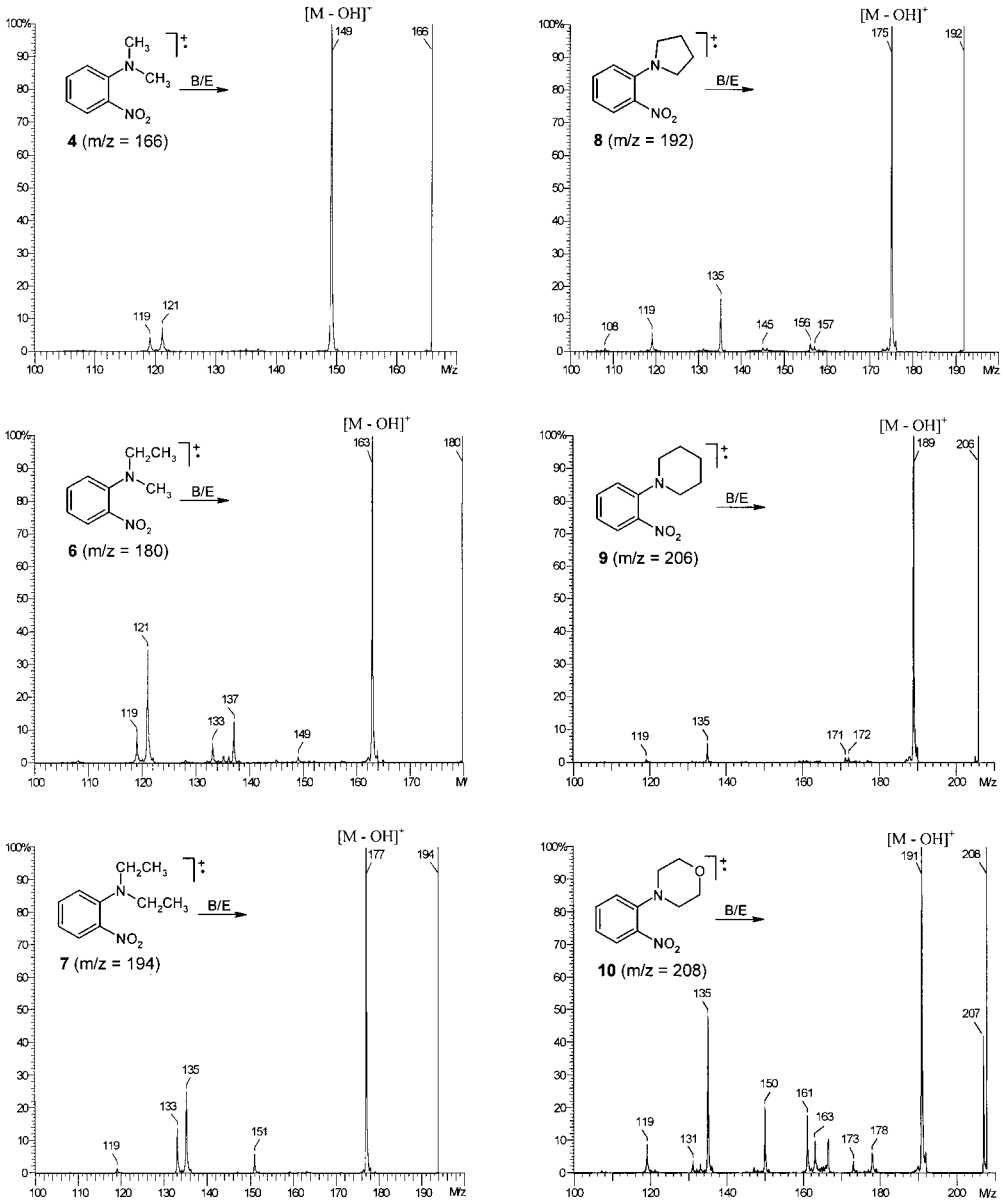
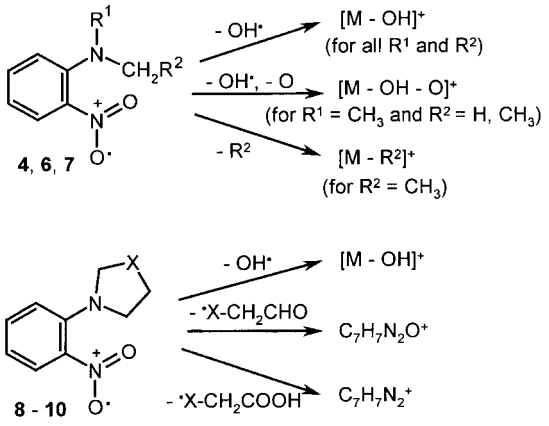
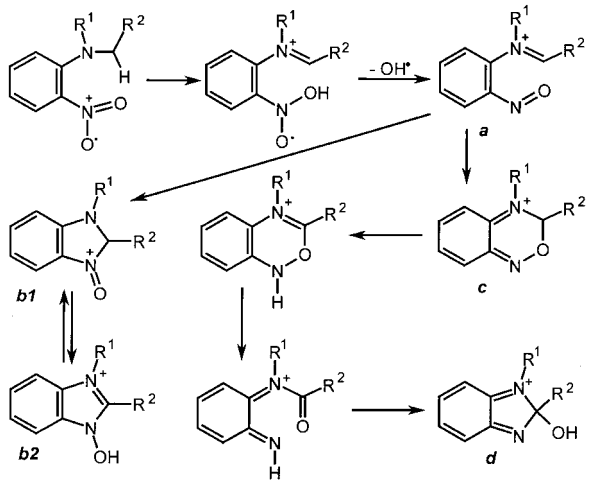


Figure 1. *B/E* = constant linked scan spectra of the molecular ions of compounds **4** and **6–10**.

The fragmentation pattern of *N,N*-dimethyl-*p*-nitroaniline (**12**) was found to be completely different to that of its *ortho* isomer **4**. The molecular ion of **12** undergoes fragmentation typical of aromatic nitro compounds, i.e.





Scheme 1. Some of the possible structures of the $[M-OH]^+$ ions resulting from the EI-induced fragmentation of *N,N*-dialkyl-*o*-nitroanilines.

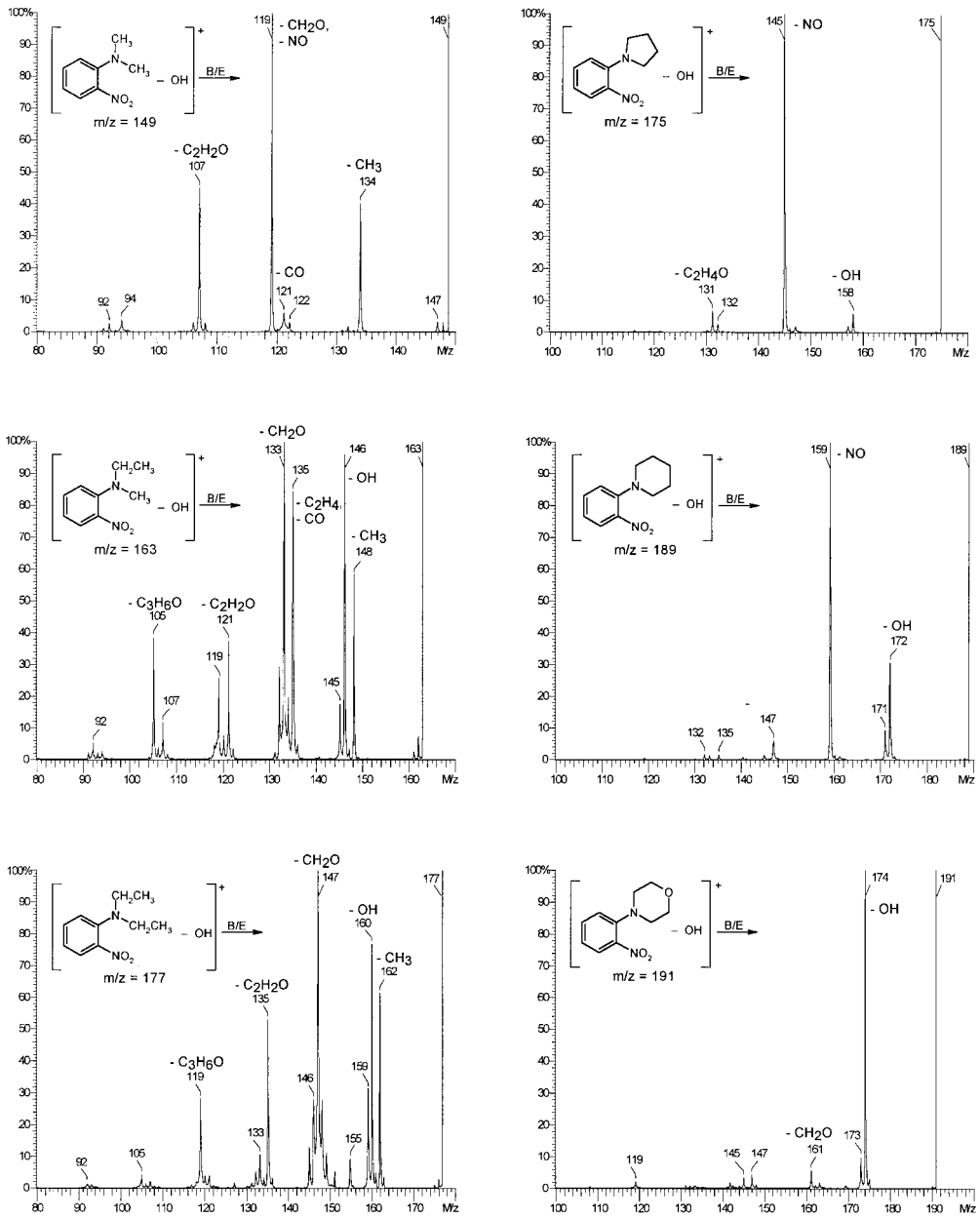


Figure 2. *B/E* = constant linked scan spectra of the $[M - OH]^+$ ions of compounds **4** and **6–10**.

losses of O, NO and NO_2 fragments (see Table 1). No elimination of HO˙ and HO_2˙ was observed.

Elimination of HO˙ from the molecular ions

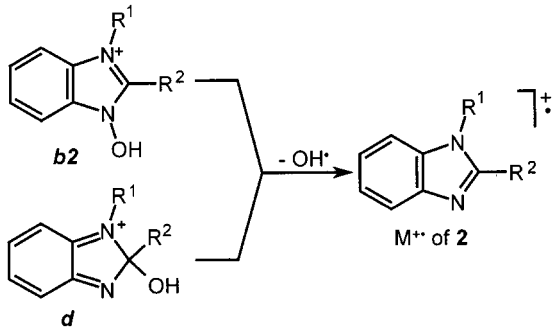
Loss of the OH radical is a major primary decomposition process for all *N,N*-dialkyl-*o*-nitroanilines studied, as proved by the metastable ion spectra (Fig. 1). The spectrum of the deuterated analog **5** shows that the hydrogen atom eliminated in the OH radical comes solely from the *N*-methyl group. Further dissociation of $[M - OH]^+$ ion (see Fig. 2) shows that several isomeric structures can exist depending on the substituents R^1 and R^2. Some possible structures with the reaction mechanisms rationalizing their formation are presented in Scheme 1.

It is reasonable that the primary product is the nitroso derivative **a** formed by the hydrogen atom transfer from carbon to oxygen atom followed by elimination of HO˙. This is supported by the elimination of the NO molecule from the $[M - OH]^+$ ion for compounds **4**, **8** and **9**. Ion **a** rearranges further to other structures, among which benzimidazole derivatives **b** and **d** seem to be most important.

Elimination of HO˙ from $[M - OH]^+$ ions

By analogy with the *tert*-amino effect, one can expect that the sequential elimination of two OH radicals from the molecular ions of *N,N*-dialkyl-*o*-nitroanilines should result in the formation of 1,2-dialkylbenzimidazoles **2**. Fragment ion spectra of the $[M - OH]^+$ ions indicate that this process is observed for all compounds studied, but with different abundances (Fig. 2).

CID-MIKE and CID-*B*/*E* linked scan spectra of the $[M - OH - OH]^{+\cdot}$ ions for compounds **4**, **6**, **8** and **9** are very similar to the published EI mass spectra of the appropriate 1-alkyl- and 1,2-dialkylbenzimidazoles.[6,7] It seems reasonable that benzimidazoles **2** are formed from the rearranged $[M - OH]^{+}$ ions with the structures **b2** or **d** (see Scheme 1).



Additional support for the formation of benzimidazole derivatives in the described reaction was obtained by measuring CID-MIKE and CID-*B*/*E* spectra for the $[M - OH - OH]^{+\cdot}$ ions for compounds **4** and **6** and comparing them with the analogous spectra of the molecular ions of the appropriate model benzimidazoles. Figure 3 presents CID-MIKE spectra for *m*/*z* 132 ion from **4** and 1-methylbenzimidazole, which are very similar. Additional peaks present in the spectrum of the $[M - OH - OH]^{+\cdot}$ ion from **4** are 'artefact peaks' as proved by comparison with the CID-*B*/*E* spectrum. A more complex situation is in the case of *N*-ethyl-*N*-methyl-*o*-nitroaniline (**6**). Sequential loss of two OH radicals from the molecular ion of **6** can result in the formation of two isomeric ions with the structure of 1,2-dimethylbenzimidazole and 1-ethylbenzimidazole.

CID-MIKE spectra for the $[M - OH - OH]^{+\cdot}$ ion from **6** (A) and molecular ions of 1,2-dimethylbenzimidazole (B) and 1-ethylbenzimidazole (C) are presented in Fig. 4. These spectra show that during fragmentation of **6** both imidazole ions are formed, but ion with the 1,2-dimethylbenzimidazole structure dominates.

Elimination of the second OH group proceeds against the 'even-electron rule.' The driving force for this reaction seems to be the resonance stabilization of the resulting benzimidazole.[8] Loss of the second OH group is most pronounced for **6**, **7**, **9** and **10** and is observed only as a minor process for **4** and **8**. Deute-

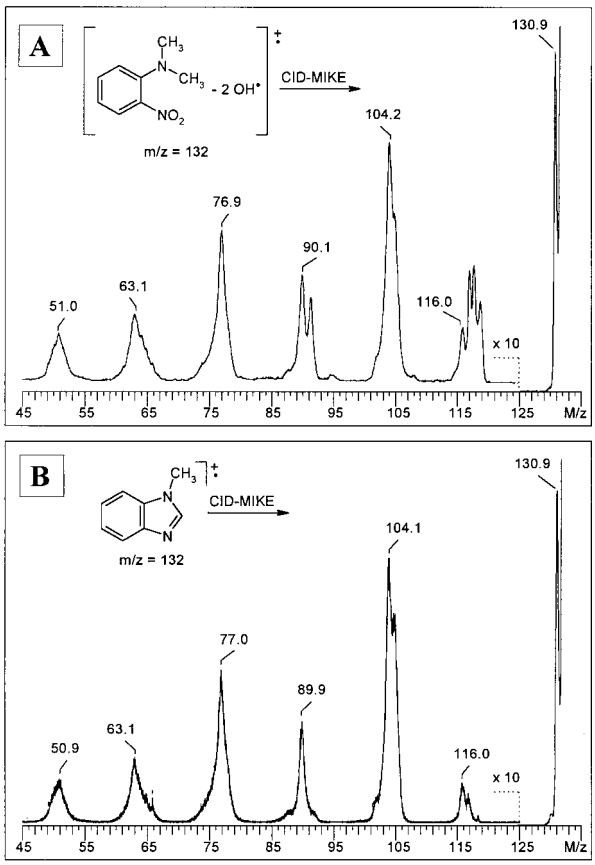


Figure 3. CID-MIKE spectra of: a) $(M - OH - OH]^{+\cdot}$ ion from **4**, b) molecular ion of 1-methylbenzimidazole. Not labeled peaks in spectrum A are artefacts as proved by *B*/*E* = constant spectrum.

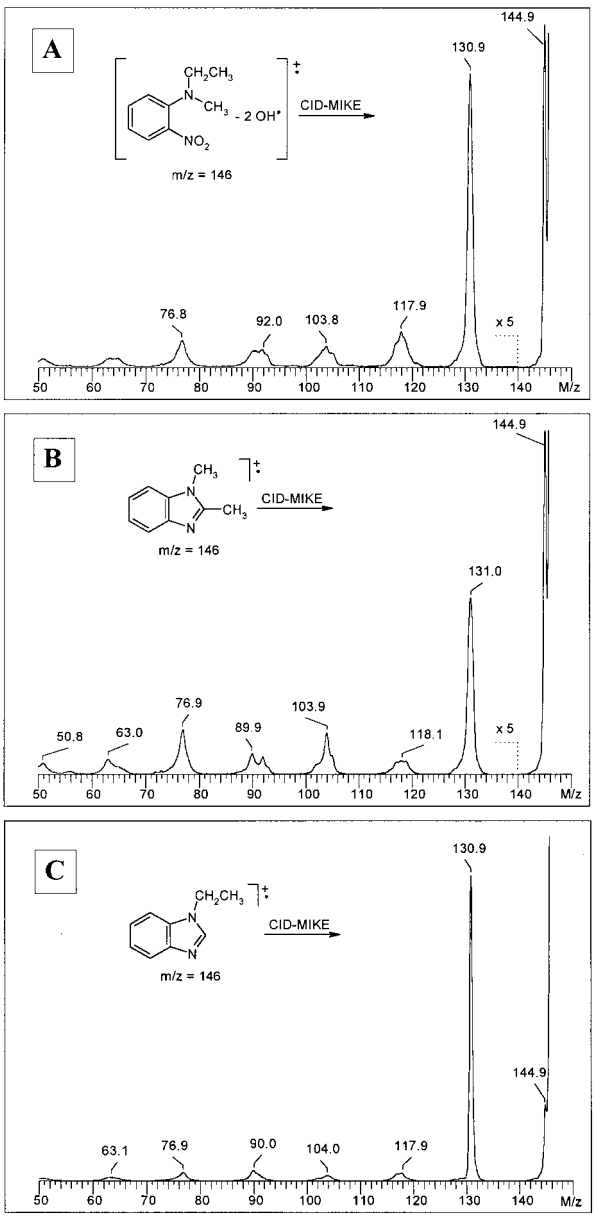
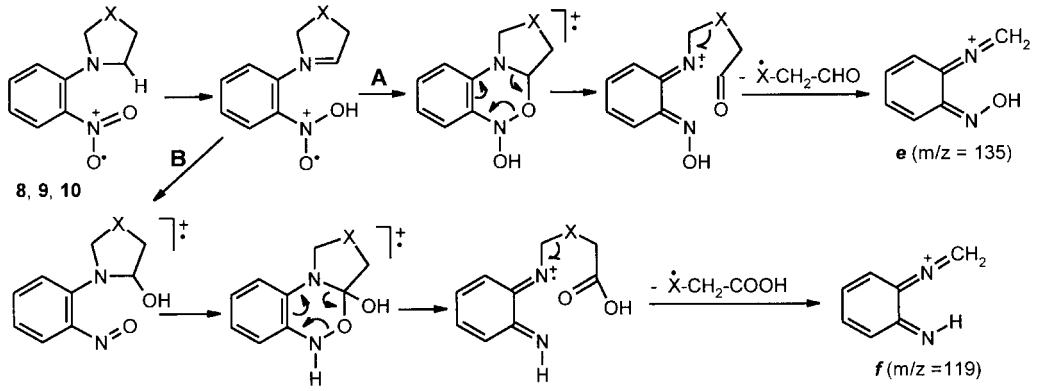
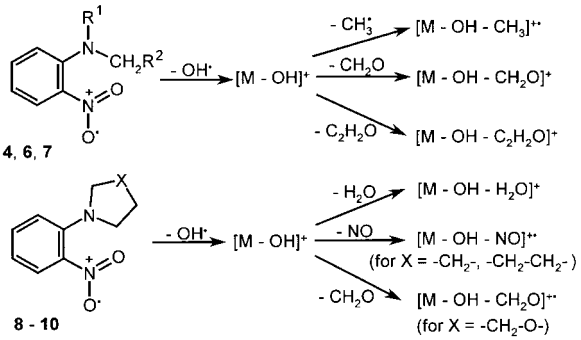


Figure 4. CID-MIKE spectra of: a) $[M - OH - OH]^{+\cdot}$ ion from **6**, b) molecular ion of 1,2-dimethylbenzimidazole, c) molecular ion of 1-ethylbenzimidazole.



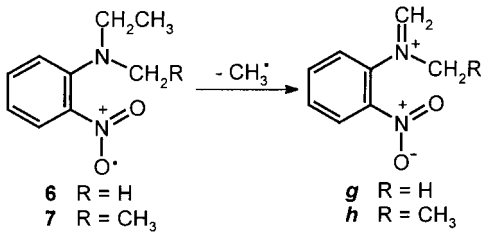
Scheme 2. Mechanism of the $^{\cdot}X-CH_2-CHO$ and $^{\cdot}X-CH_2-COOH$ elimination from the molecular ions of compounds **8**, **9** and **10**.



rium labeling shows (**5**) that again the hydrogen atom in the eliminated OH radical comes from one of the methyl groups.

Other fragmentations of $[M-OH]^+$ ions

$[M-OH]^+$ ions undergo not only HO$^{\cdot}$ elimination but also many other decomposition reactions depending on the substituents R^1 and R^2 (see Fig. 2). Compounds **4**, **6** and **7** with two alkyl chains on the nitrogen atom show complex patterns. In addition to the loss of HO$^{\cdot}$ there are three other fragmentations common to all



three compounds, i.e. losses of $CH_3^{\cdot}$, CH_2O and C_2H_2O fragments.

In the case of deuterated compound **5**, $CD_3^{\cdot}$, CD_2O and C_2D_2O fragments are eliminated, indicating that the benzene ring hydrogen atoms do not participate in these fragmentations.

$[M-OH]^+$ ions from pyrrolidine (**8**) and piperidine (**9**) derivatives decompose mainly by the loss of an NO molecule, this fragmentation being more significant than the second OH group loss. In the case of the morpholine derivative **10**, elimination of an OH radical from the $[M-OH]^+$ ion predominates. In contrast to the fragmentation of **8** and **9**, no NO elimination is observed. Instead, the $[M-OH]^+$ ion from **10** eliminates a CH_2O molecule and some other fragments.

These results indicate that the most likely candidates for the structure of the $[M-OH]^+$ ion from **10** are benzimidazole derivatives **b2** or **d** (Scheme 1). In the case of **8** and **9**, the $[M-OH]^+$ ion most likely possesses the structure **a**, which can decompose with the elimination of NO.

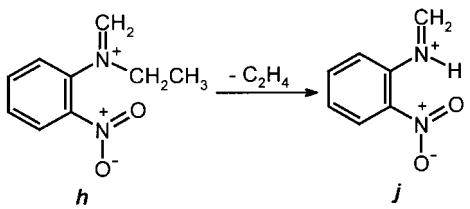
Fragmentations characteristic of the cyclic amines 8–10

The molecular ions of cyclic amine derivatives **8–10** undergo two specific fragmentations resulting in the formation of ions with *m/z* 135 (**e** in Scheme 2) and 119 (**f** in Scheme 2). In both cases fragmentation takes place in the alicyclic amine ring and is accompanied by the transfer of one or two oxygen atoms from the nitro group. Reaction mechanisms rationalizing these results are presented in Scheme 3. In both paths (A and B) the crucial step is the retro-Diels–Alder reaction followed by simple radical site induced bond cleavage.

These processes are not observed for the acyclic compounds. In the case of *N,N*-dialkyl-*o*-nitroanilines (**4**, **6** and **7**) similar mechanisms should result in the elimination of an appropriate aldehyde or carboxylic acid molecule but the peaks corresponding to these fragmentations are absent.

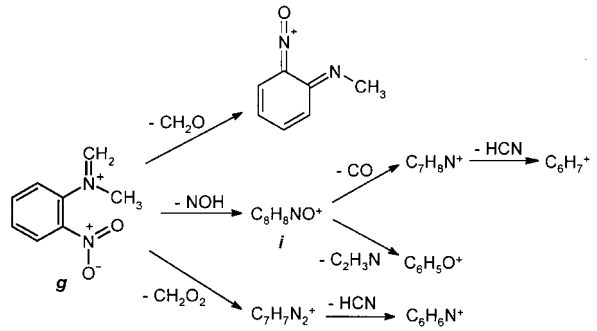
Fragmentation of $[M-CH_3]^+$ ions from compounds 6 and 7

Molecular ions of compounds **6** and **7**, having one or two ethyl groups attached to the nitrogen atom, undergo important fragmentation resulting in the loss of a methyl radical yielding immonium cations **g** and **h**, respectively.



Further decomposition of the cation **g** is complex. The main fragmentation paths are presented in Scheme 3.

Fragmentations resulting in losses of CH_2O and CH_2O_2 fragments are characteristic of this type of ion.[8]



Scheme 3. Main fragmentation paths of the methyl-methylene-(2-nitrophenyl)ammonium cation **g**.

More difficult to rationalize is the elimination of the NOH fragment, the most significant decomposition process for ion **g**. Further fragmentation of an ion **i** formed in this reaction suggests some complex rearrangements. Cation **h** undergoes fragmentation along practically one path, losing a molecule of ethylene to give ion **j**.

Fragmentation of ion **j** has been described in a previous paper.[9]

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