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MASS SPECTROMETRY AND STRUCTURES OF IONS OF HETEROCYCLIC COMPOUNDS ACTIVATED BY COLLISION.

2.* 2-METHYLNITROINDOLIZINES

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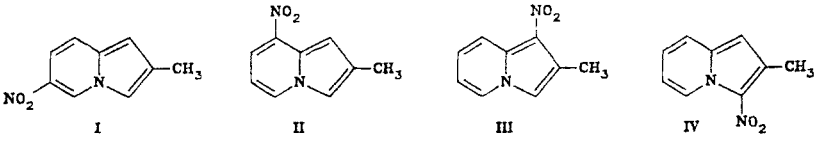
The principal pathways of the fragmentation of 2-methylnitroindolizines were investigated. The fragmentation and structures of the isomeric $[M - OH]^+$ and $[M - NO]^+$ ions formed in the fragmentation of these compounds were studied by the method of dissociative activation by collision (DAC). It was established that the stable $[M - OH]^+$ ions formed in the fragmentation of the 1- and 3-nitro isomers as a result of the "ortho effect" have different structures and that their DAC spectra can be used to determine the position of the nitro group in the molecule.

The mass spectra of 2-methyl-6-nitroindolizine and 2-methyl-8-nitroindolizine have been previously studied [2, 3]; however, only a brief communication [4] has been devoted to the fragmentation of the isomeric 1- and 3-nitro derivatives. It is known that, in addition to the common pathways of fragmentation of heterocyclic nitro compounds, there are specific fragmentation pathways that are determined by the position of the nitro group [5]. One such pathway is the formation of $[M - OH]^+$ ions in those cases in which a substituent that contains hydrogen atoms is located in the ortho position relative to the nitro group [5, 6]. In this connection it seems of interest to study the fragmentation of isomeric 2-methylnitroindolizines with nitro groups in different positions and to establish the structures of the principal fragment ions from the spectra of the products of their metastable fragmentation and dissociation activated by collision (DAC).

The following nitro derivatives of 2-methylindolizine were investigated:



I II III IV

Under the influence of electron impact these compounds form stable molecular ions $M^{+\cdot}$, the peaks of which have the maximum intensity in the mass spectra (Table 1), but their contribution to the total ion current depends on the position of the substituents in the molecule (Table 2). From the data obtained from the spectra of the metastable fragmentation of $M^{+\cdot}$ and the elementary composition of the ions determined from the high-resolution mass spectra (Table 3) one can isolate the following principal pathways of fragmentation of the molecular ions: a) splitting out of a nitro group; b) splitting out of a nitroso group; c) detachment of a hydroxyl radical. The latter process is observed only for isomers with an ortho orientation of the substituents and determines their lower stability with respect to electron impact (Table 2).

*See [1] for Communication 1.

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TABLE 1. Mass Spectra of I-IV (70 eV)

Compound	m/z (intensity, % of total ion current)
I	50 (0,9), 51 (1,9), 63 (0,9), 76 (1,5), 77 (8,8), 78 (1,2), 102 (3,4), 103 (1,2), 104 (1,9), 117 (0,9), 118 (3,2), 128 (5,2), 129 (2,1), 130 (15,5), 131 (4,2), 146 (0,8), 147 (1,2), 176 (24,6), 177 (2,7)
II	50 (1,2), 51 (4,5), 63 (1,2), 76 (1,2), 77 (8,6), 78 (1,7), 102 (2,9), 103 (10,8), 104 (2,4), 117 (1,0), 118 (2,2), 128 (4,5), 129 (1,4), 130 (18,2), 131 (2,4), 146 (1,7), 149 (1,2), 176 (23,9), 177 (2,6)
III	43 (1,6), 50 (1,6), 51 (3,1), 52 (1,1), 55 (1,1), 57 (1,3), 63 (0,8), 69 (1,9), 75 (0,8), 76 (1,5), 77 (5,8), 78 (10,1), 79 (2,4), 102 (2,1), 103 (3,6), 104 (1,3), 105 (7,8), 106 (3,7), 128 (1,3), 130 (1,9), 131 (2,3), 145 (0,8), 146 (2,6), 159 (12,0), 160 (1,5), 176 (16,2), 177 (1,5)
IV	43 (1,0), 45 (1,3), 50 (1,1), 51 (2,6), 52 (1,0), 57 (1,1), 63 (1,1), 69 (1,3), 76 (1,0), 77 (5,6), 78 (5,1), 79 (1,6), 89 (1,3), 90 (1,8), 102 (1,9), 103 (3,8), 104 (2,1), 105 (1,9), 116 (1,8), 117 (4,1), 118 (1,9), 119 (0,8), 128 (1,9), 129 (0,8), 130 (1,8), 131 (2,6), 144 (2,8), 145 (0,7), 146 (3,3), 159 (8,2), 160 (1,5), 176 (16,4), 177 (1,8)

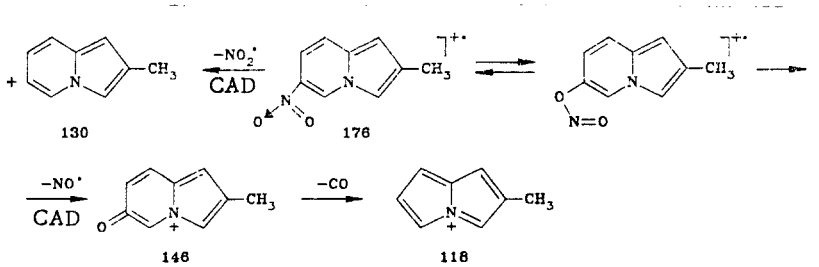
TABLE 2. Intensities (% of the total ion current) of the Peaks of the Principal Fragment Ions in the Mass Spectra of 2-Methylnitroindolizines*

Compound	W_M	$[M-OH]^+$ (159)	$[M-NO]^+$ (146)	$[M-OH-CO]^+$ (131)	$[M-NO_2]^+$ (130)	$[M-NO-CO]^+$ (118)	Z
I	24,6	—	0,8	4,2	15,5	3,2	0,05
II	23,9	—	1,7	2,4	18.2	2,2	0,09
III	16,2	12,0	2,6	2,3	1,9	—	1,4
IV	16,4	8,2	3,3	2,6	1,6	1,9	1,8

*Z is the ratio of the intensities of the ion peaks at 146 and 130; W_M is the stability of the molecule relative to electron impact.

A peculiarity of the fragmentation of methylnitroindolizines, as well as most aromatic nitro derivatives, is the formation of $[M - NO_2]^+$ ions in the case of simple cleavage of the C–N bond and $[M - NO]^+$ ions, which are formed as a result of nitro–nitrite rearrangement [5] (Scheme 1).

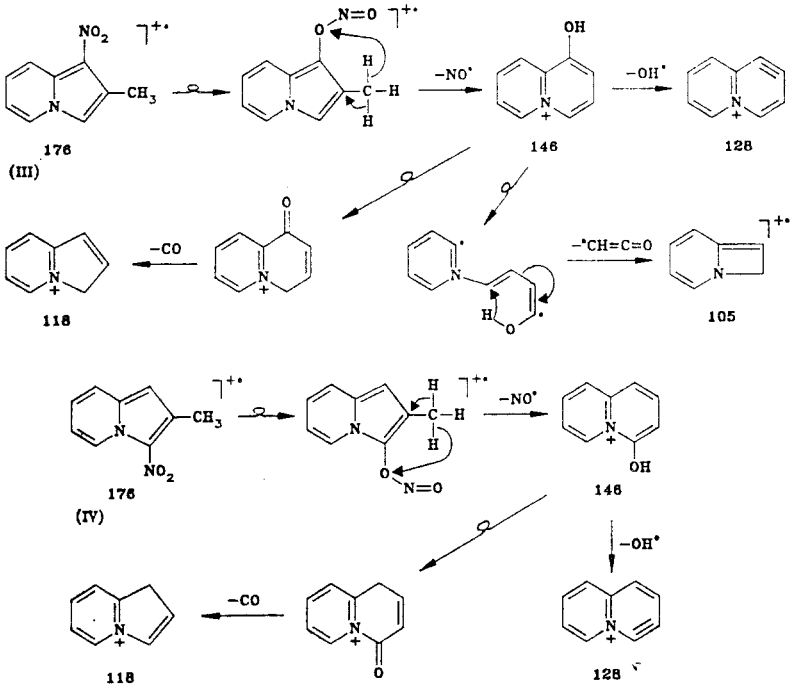
Scheme 1



The preponderance of the nonisomerized form of the molecular ion is characteristic for all of the examined compounds; the amount of the nitrite form does not exceed 4%. The contribution of the $[M - NO_2]^+$ ions to the total ion current depends to a significant extent on the position of the nitro group in the molecule. In the case of isomers with substituents located in different rings the intensity of the $[M - NO_2]^+$ ion peaks is greater by a factor of eight to nine than for isomers with an ortho orientation of the methyl and nitro groups.

It is important to note that the probability of the nitro–nitrite rearrangement, which is determined by the value $Z = I_{M-NO}/I_{M-NO_2}$, is approximately 20 times higher in the case of isomers III and IV than for isomers I and II (Table 2). This fact contradicts the previously advanced hypothesis that interaction of the nitro group with the ortho and peri substituents suppresses nitro–nitrite rearrangement [5].

Scheme 2



The detachment of an NO radical is accompanied by isomerization of M^+; in the case of I, II, and IV this is followed by the elimination of a molecule of CO with the formation of an ion at 118* (Schemes 1 and 2); this was confirmed by corresponding metastable transitions. An ion peak at 118 is absent in the mass spectrum of III (Tables 1 and 2). It follows from the DAC spectrum of the $[M - NO]^+$ ions (146) of this isomer (Table 4) that the elimination of CO occurs only in the case of their additional excitation as a result of collision with helium molecules. However, in contrast to the 3-nitro isomer, this process is less likely, and the dominating fragmentation pathway is the formation of ions at 105 (Table 4). According to the high-resolution mass spectrum (Table 3) the peak at 105 is a doublet, the two signals of which have approximately equal intensities and correspond to the $[C_7H_7N]^+$ and $[C_6H_5N_2]^+$ ions. Since the $[M - NO]^+$ ions contain only one nitrogen atom, their fragmentation in the case of isomer III is accompanied by the detachment of a C_2HO radical with the formation of $[C_7H_7N]^+$ ions. The available data are not sufficient to give an unequivocal interpretation of this interesting fact. One can only assume that the energy of activation of the elimination of a molecule of CO by $[M - NO]^+$ ions in the case of isomer III is higher

TABLE 3. Elementary Compositions of the Principal Fragment Ions of Methylnitroindolizines

Isomer	m/z	Elementary composition	Mass		Probable pathway of formation
			calc.	measured	
III, IV	159	$C_9H_7N_2O$	159,05583	159,0558	M—OH
I—IV	146	C_9H_8NO	146,06059	146,0606	M—NO
I—IV	131	$C_8H_7N_2$	131,06093	131,0617	M—OH, —CO
I—IV	130	C_9H_8N	130,06566	130,0657	M—NO_2
I, II, IV	118	C_8H_8N	118,06567	118,0658	M—NO, —CO
I, II, IV	117	C_8H_7N	117,05785	117,0582	M—NO, —CO, —H
I—IV	105	$C_6H_5N_2$	105,04526	105,0452	M—OH, —CO, —C_2H_2
III	105	C_7H_7N	105,05784	105,0578	M—NO, —C_2HO
I—IV	103	C_8H_7	103,05448	103,0553	M—NO_2, —HCN
I—IV	78	C_6H_6	78,04695	78,0461	M—NO, —HCN, —C_2H_2
I—IV	77	C_6H_5	77,03913	77,0387	M—NO, —HCN, —C_2H_3

*The numbers that characterize the ions are the m/z values.

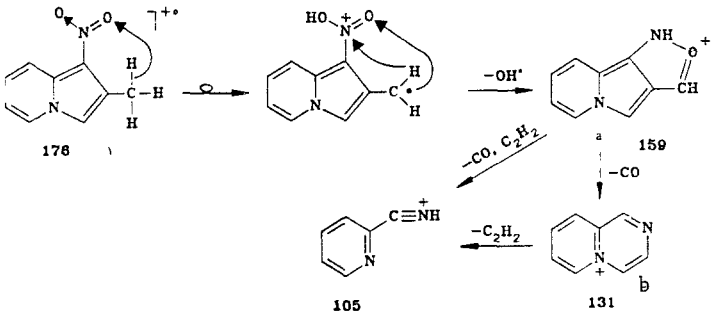
TABLE 4. DAC Spectra of the $[M - NO]^+$ and $[M - OH]^+$ Ions (intensities of the peaks I in percent of the total ion current) for III and IV

$[M-NO]^+$ (*m/z* 146)			$[M-OH]^+$ (*m/z* 159)		
m/z	III	IV	*m/z*	III	IV
78	2	—	77	12	26
105	61	—	103	12	5
106	7	—	105	50	5
117	7	—	128	10	5
118	12	67	130	5	5
128	10	33	131	12	53

than for the remaining isomers; this is evidently a consequence of the difference in the structures (and enthalpies of formation) of these ions, as well as the $[M - NO, - CO]^+$ ions (Scheme 2).

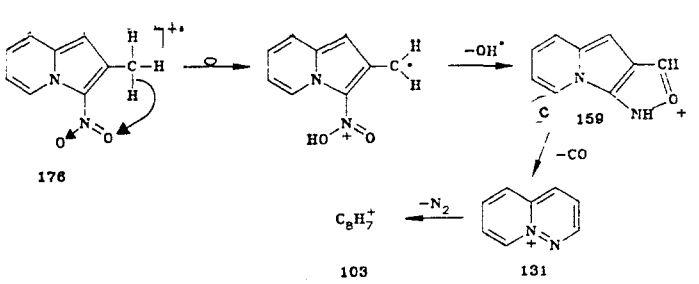
The presence of a methyl group in the ortho position relative to the nitro group in the molecules of isomers III and IV sharply changes the character of the fragmentation. An intense peak of $[M - OH]^+$ ions (159) is observed in the mass spectra of these compounds as a result of the "ortho effect." As shown in Schemes 3 and 4 transfer of a hydrogen atom of the methyl group to the oxygen atom of the nitro group precedes the detachment of a hydroxyl radical.

Scheme 3



The elimination of a molecule of CO (131) occurs in the subsequent fragmentation of the $[M - OH]^+$ *a* and b ions; in the case of the 3-nitro isomer this process predominates (Table 4). The principal product of the fragmentation of the $[M - OH]^+$ ions of III is the fragment at 105, which can be formed via both the simultaneous ejection of CO and C_2H_2 molecules and via their successive elimination through an intermediate structure (b, Scheme 3). It follows from the high-resolution mass spectra (Table 3) that in this case the component of the doublet with the elementary composition $[C_6H_5N_2]^+$ corresponds to the ion at 105 from this isomer. Activation by collision of the ion at 131, the hypothetical structure of which is presented in Scheme 4, leads to splitting out of a molecule of N_2; this confirms the ortho orientation of the nitrogen atoms in this ion.

Scheme 4



The difference in the DAC spectra of the $[M-OH]^+$ ions, as in the case of the $[M-NO]^+$ ions examined above, of isomers III and IV constitutes evidence for the significant effect of the heteroatom on the structures and stabilities of the ions formed in their subsequent fragmentation.

Thus, the mutual orientation of the methyl and nitro groups affects the fragmentation of methylnitroindolizines, and their mass spectra can be used to identify the isomers. It was demonstrated by the method of activation by collision that the isomeric $[M-OH]^+$ ions have different structures. The differences in the DAC spectra of these ions can be used to determine the position of the nitro group in the molecule as well as to identify them in mixtures by chromatographic mass spectrometry and tandem mass spectrometry.

EXPERIMENTAL

Methylnitroindolizines I-IV were synthesized by the methods in [7-9]. The mass spectra and DAC spectra were obtained with a Varian MAT-212 mass spectrometer using a system for direct introduction of the samples into the ion source. The ionizing-electron energy was 70 eV, the accelerating voltage was 3 kV, and the temperature of the ionization chamber was 200-250°C. The recording of the DAC spectra was carried out in the first fieldless range of the mass spectrometer under conditions of linked scanning at a constant ratio of the intensities of the electrical and magnetic fields at a rate of 6 amu/sec. Helium was used as the neutral gas for activation by collision. The coefficient of transmission of the beam of parent ions was 0.5-0.6.

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