from dilute alcohol. Yield 0.28 g (83%) IV, mp 190-192°C. According to [8], mp 190-191°C; according to [9], 194°C.

6-Chloroacetylindole (V, $C_{10}H_8ClNO$). Analogously to the above, 0.5 g (2.1 mmole) IIIa were hydrolyzed. Yield 0.3 g (73%) V, mp 128-129°C (from diluted alcohol). IR spectrum: 1670 (C=O), 3350 cm^{-1} (NH).

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MASS SPECTROMETRY AND STRUCTURE OF HETEROCYCLIC IONS BY COLLISIONAL ACTIVATION.

3.* DIMETHYLNITROINDOLIZINES

M. S. Bobyleva, N. S. Kulikov, and S. I. Bobrovskii

UDC 543.51:547.759

The fragmentation of isomeric dimethylnitroindolizines due to electron impact was studied by collisional activation and high resolution mass spectroscopy. The $[M - OH]^+$ ion which is formed as a result of the ortho-effect was found to have a variable structure. In the case of 2,8-dimethyl-1-nitroindolizine, one of the main fragmentation processes of $[M - OH]^+$ is the elimination of an H_2O molecule.

Recently, dissociation by collisional activation (DCA) has been widely applied for study of the structure of ions and their fragmentation processes. Basic aspects of the DCA method and its possibilities for identification of organic compounds have been reviewed by Levsen [2] and Holmes [3]. This method has been widely used for studying the structure of ions which are formed in the gas phase and the fragmentation of indole [4], pyrazine [5], piperidine [6], benzimidazole and indazole [7], and quinoline and isoquinoline [8] due to electron impact. However, disregarding the great possibilities of this method for the analysis of isomers, efforts toward the application of DCA for the study of the ortho-effect of substituents in a series of hetarenes are practically absent.

We studied the fragmentation features of isomeric monomethylnitroindolizines due to electron impact; in particular, using DCA it was shown that the $[M - OH]^+$ ion, which is formed as a result of the ortho-effect during decomposition of 2-methyl-3- and 1-nitroindolizines, has a variable structure [9].

*For Communication 2, see [1].

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 331-336, March, 1989. Original article submitted July 28, 1987.

0009-3122/89/2503-0274 $12.50

TABLE 1. Mass Spectra of Dimethylnitroindolizines

Compound	Peak intensities, % of TIC
I	51 (1,3), 63 (1,1), 65 (2,0), 77 (1,5), 78 (2,0), 89 (1,0), 91 (2,1), 92 (5,6), 103 (0,9), 104 (0,8), 105 (5,2), 115 (3,8), 116 (1,4), 117 (2,1), 118 (2,1), 119 (2,0), 128 (2,1), 129 (0,8), 130 (1,1), 131 (0,8), 142 (2,5), 143 (3,0), 144 (2,4), 145 (10,1), 146 (1,4), 155 (0,8), 156 (0,7), 157 (0,8), 159 (1,1), 160 (2,5), 173 (8,7), 174 (1,8), 189 (2,4), 190 (14,0), 191 (1,6)
II	51 (2,2), 63 (1,1), 65 (3,2), 77 (2,3), 78 (0,9), 89 (1,7), 91 (0,9), 92 (2,4), 102 (0,9), 103 (0,9), 104 (0,6), 106 (1,1), 115 (4,4), 116 (2,6), 117 (6,9), 118 (2,6), 119 (0,8), 128 (1,8), 129 (1,1), 130 (2,6), 131 (1,2), 132 (1,4), 142 (3,3), 143 (6,2), 144 (2,6), 145 (1,8), 146 (0,4), 157 (1,4), 158 (1,5), 160 (3,9), 161 (0,9), 173 (6,2), 174 (1,2), 190 (15,0), 191 (1,7)
III	63 (0,8), 65 (1,8), 77 (1,6), 78 (2,0), 89 (1,1), 91 (1,3), 103 (1,7), 104 (0,8), 105 (0,4), 106 (0,8), 115 (4,9), 116 (1,6), 117 (2,6), 118 (1,7), 128 (2,2), 129 (1,4), 130 (0,8), 131 (0,5), 142 (4,2), 143 (15,5), 144 (8,2), 145 (2,6), 146 (0,9), 160 (0,4), 173 (15,3), 174 (2,8), 190 (15,8), 191 (1,8)
IV	51 (1,3), 63 (0,9), 65 (1,8), 77 (1,8), 78 (2,0), 89 (1,3), 91 (1,6), 103 (1,3), 104 (0,9), 105 (0,9), 106 (0,4), 115 (3,8), 116 (2,0), 117 (3,3), 118 (3,2), 119 (0,6), 120 (0,8), 128 (2,6), 129 (1,6), 130 (1,6), 142 (6,0), 143 (8,7), 144 (8,7), 145 (3,8), 146 (1,1), 157 (1,1), 158 (3,2), 159 (1,3), 160 (1,1), 173 (10,3), 174 (0,9), 190 (22,4), 191 (1,8)
V	63 (1,5), 65 (1,2), 77 (2,0), 78 (0,7), 79 (0,9), 89 (1,5), 91 (2,1), 102 (0,7), 103 (1,1), 104 (1,1), 105 (0,9), 106 (0,5), 115 (6,0), 116 (2,2), 117 (4,4), 118 (2,4), 127 (1,1), 128 (2,8), 129 (1,2), 130 (1,1), 131 (1,2), 132 (0,9), 141 (1,4), 142 (5,2), 143 (8,3), 144 (5,8), 145 (4,0), 146 (2,2), 159 (0,9), 160 (0,7), 173 (6,0), 174 (1,1), 190 (15,4), 191 (2,2)
VI	43 (1,1), 51 (1,3), 58 (1,7), 63 (1,1), 65 (1,3), 69 (1,9), 77 (1,3), 89 (1,1), 91 (1,5), 115 (6,6), 116 (1,9), 117 (1,3), 128 (1,9), 129 (1,7), 131 (1,1), 132 (1,5), 142 (4,9), 143 (13,8), 144 (13,8), 145 (2,6), 160 (0,6), 189 (7,5), 190 (21,5), 191 (2,6)
VII	58 (1,6), 77 (2,0), 102 (0,8), 103 (1,9), 104 (1,1), 105 (1,4) 115 (5,0), 116 (1,6), 117 (3,0), 118 (1,1), 128 (2,5), 132 (1,4), 142 (3,0), 143 (8,5), 144 (21,4), 145 (1,9), 160 (1,6), 167 (1,9), 190 (28,1), 191 (1,9)

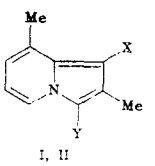
TABLE 2. Intensities, % of TIC, of Characteristic Fragment Ions in Mass Spectra of Dimethylnitroindolizines

Compound	W_M*	$[M-OH]^+$ 173	$[M-NO_2]^+$ 144	$[M-NO]^+$ 160	$[C_{10}H_9N]^+$ 143	$[C_9H_9N_2]^+$ 145**
I	14,0	8,7	2,4	2,5	3,0	10,1
II	15,0	6,2	2,6	3,9	6,2	1,8
III	15,8	15,3	8,2	0,4	15,5	2,6
IV	22,4	10,3	8,7	1,1	8,7	3,8
V	15,4	6,0	5,8	0,7	8,3	4,0
VI	21,5	—	13,8	0,6	13,8	1,1
VII	28,1	—	21,4	1,6	8,5	—

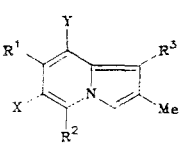
*W_M is the stability of the molecule to electron impact.

**For VI and VII, the intensity is given accounting for isotopic abundance.

In this work the electron impact mass spectra of dimethylnitroindolizines I-VII, which are homologs of the 2-methyl-1-, -3-, -6-, and -8-nitroindolizines which were studied earlier, are obtained.



I, II



III–VII

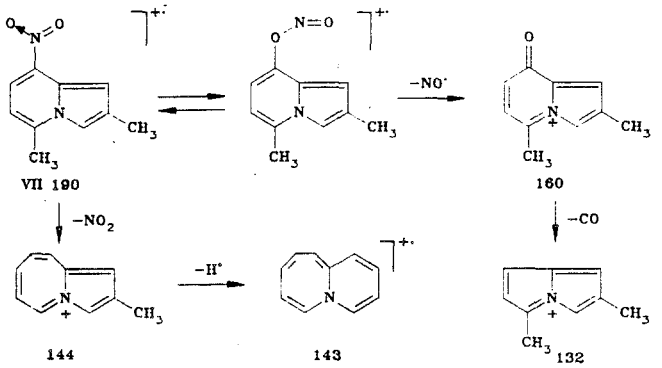
I, III, V, VI X=NO_2; II, IV, VII Y=NO_2; III, IV R^1=Me; V, VII R^2=Me; VI R^3=Me; unassigned X, Y, R^1, R^2, R^3=H

Study of unstable decomposition by DCA and calculation of elemental composition by high resolution mass spectra allow the initial fragmentation pathways of I-VII to be found. For them, as for nitrohetarenes in general [10], processes in which the nitro group participates are characteristic: a) loss of the nitro group, b) dissociation of the NO radical as a result of nitro-nitrito rearrangement, and c) dissociation of a OH radical as a result of the ortho-effect. Loss of a nitro group is the dominant fragmentation pathway only for VI and VII which do not contain a methyl group in the position ortho to it. Special attention was given to the study of the structure and fragmentation features of the stable ions $[M - OH]^+$ (the formation of these ions in the mass spectra of III-V as a result of the ortho-effect was briefly mentioned in [11]). DCA has not been used earlier for studying either the fragmentation of indolizines or the ortho-effect.

Mass spectra of I-VII are given in Table 1, the intensities of the main fragment ions relative to the total ion current (TIC) are given in Table 2. Mechanisms of fragmentation and hypothetical structures of the ions are given in Schemes 1-5. Introduction of a second methyl group into the nitroindolizine molecule increases the stability to electron impact (see [1]); an analogous trend is observed in the case of methylindolizines which do not contain a nitro group [12].

A specific feature of the fragmentation of I-VII is the formation of $[C_{10}H_9N]^+$ ions (143),* the peaks of which are rather intense (Tables 1 and 2). Two fragmentation pathways which are not characteristic for monomethylnitroindolizines, the elimination of a hydrogen atom by $[M - NO_2]^+$ ions or the elimination of a NO radical by $[M - OH]^+$ ions, lead to the formation of these ions which can be assigned the structure of the pyridoazepine cation. The first of these pathways is possible only for VI and VII (see Scheme 1), while in the case of I-V, in which the methyl and nitro groups are located in ortho positions, the second pathway dominates (Scheme 2).

Scheme 1

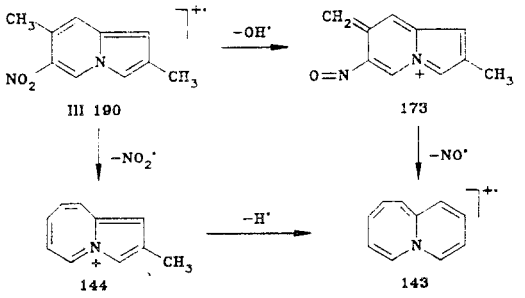


The presence of $[M - NO]^+$ (160) fragments in the mass spectra of I-VII is related to the nitro-nitrito rearrangement in the molecular ions. The nitro-nitrito rearrangement for VII is given as an example in Scheme 1; for I-VI this process proceeds analogously, therefore, in Schemes 2-5 this fragmentation pathway is not shown. It follows from Table 2 that the probability of isomerization is higher when the nitro group is in the pyrrole ring, or the 3 or 1 position. The reason for this is probably the stability of the cations which are formed (see Scheme 2 on top of following page).

The ortho-effect which determines the elimination of the HO· radical is observed during decomposition of isomers I-V and for II-IV the $[M - OH]^+$ peaks are of maximal intensity. Analysis of the DCA spectra of these ions (Table 3) and also the spectra of their metastable decomposition showed that the structure of the $[M - OH]^+$ ions varies. The contributions of the main concurrent fragmentation pathways for these ions, elimination of CO (145), NO· (143), H_2O (155), and CH_3· (158), differ markedly. Thus, in the DCA spectrum of the $[M - OH]^+$ ions of III, the base peak corresponds to the (143) ions which are formed as a result of elimination of the NO radical. For IV, loss of a CO molecule (145) and a CH_3 radical

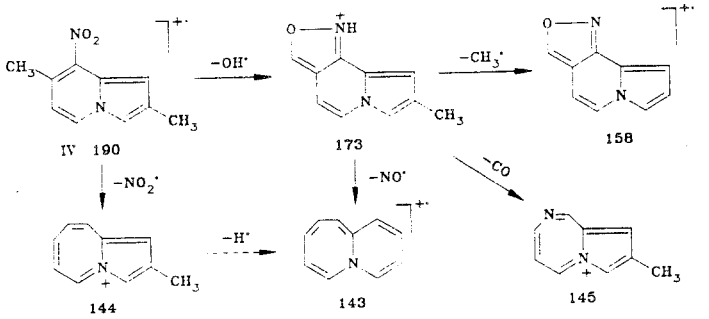
*In the text, Schemes, and Tables, the numbers which denote ions are in units of m/z.

Scheme 2



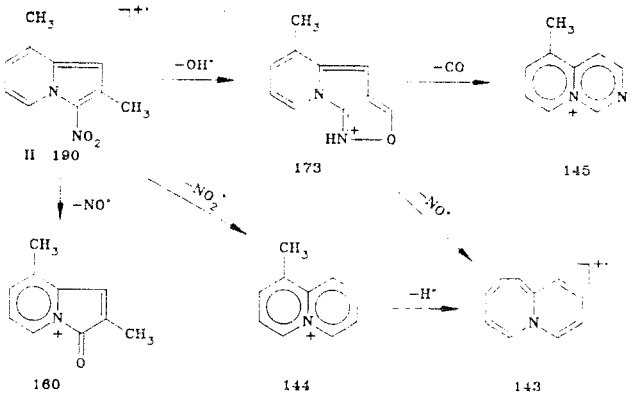
(158) are the main fragmentation pathways, and for I, the loss of CO is most characteristic. Fragmentation of the $[M - OH]^+$ ions which are formed as a result of the ortho-effect from the molecular ions of II is less selective and the elimination of CO (145) and NO· (143) dominate.

Scheme 3



The 119 ions which are observed in the DCA spectra of I-IV are probably formed as a result of elimination of HC≡C–CH=O (or simultaneously CO and C_2H_2) by $[M - OH]^+$ ions. Thus, the intensity of the $[M - OH, -C_3H_2O]^+$ ions is higher for the 1-nitrosubstituted (I) isomer than for the 3-isomer (II) (and also isomers III and IV), as in the DCA spectra of the $[M - OH]^+$ ions of the lower homologs 2-methyl-1- and 3-nitroindolizine [1].

Scheme 4



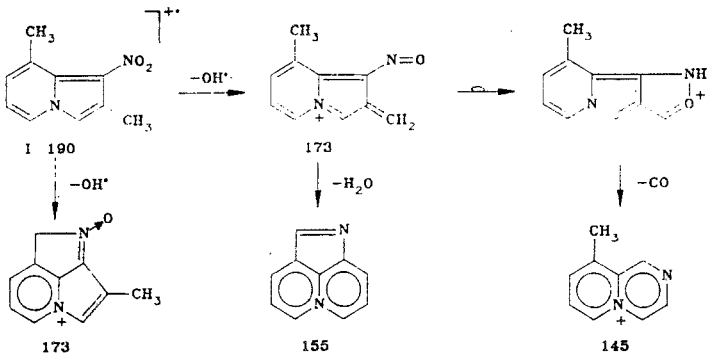
The elimination of a H_2O molecule by $[M - OH]^+$ ions during decomposition of 2,8-dimethyl-1-nitroindolizine (I) is of special interest. This fragmentation process is undoubtedly explained by the presence of a methyl group in the peri position to the nitro group. Thus, the structure of the 173 ions which are formed as a result of ortho- or peri-elimination of a HO radical can in principle be different (Scheme 5). The $[M - OH]^+$ ions, which are formed as a result of the ortho-effect without participation by the peri-located methyl

TABLE 3. DCA Spectra of $[M - OH]^+$ (173) Ions

m/z	Peak intensity, % of TIC				m/z	Peak intensity, % of TIC			
	I	II	III	IV		I	II	III	IV
102	1	2	1	2	141	1	3	2	1
103	2	2	1	2	142	2	6	10	3
104	4	3	1	2	143	4	12	58	5
115	2	4	3	1	144	7	5	5	3
116	2	6	2	2	145	32	13	2	19
117	4	8	2	2	146	7	5	1	7
118	3	6	2	5	155	10	3	0,5	2
119	5	2	0,5	2	156	3	3	0,5	3
128	1	4	4	2	157	2	3	0,5	2
129	1	2	2	4	158	4	4	2	28
130	1	1	0,5	3					

group while the dissociation of a H_2O molecule with formation of the (155) ion requires the participation of a second methyl group, probably undergo elimination of a CO molecule with formation of the very intense (145) ion. Note that a double ortho-effect was described earlier in elimination of HOD during mass spectral fragmentation of 1-D-3-methyl-2-nitroindazole [13].

Scheme 5



Thus, the relative positions of nitro and methyl groups substantially affect the fragmentation of isomeric dimethylnitroindolizines. Using DCA it was shown that the $[M - OH]^+$ ions which are formed as a result of the ortho-effect have variable structure and do not undergo isomerization processes and that the DCA spectra of these ions can be used for identification.

EXPERIMENTAL

The dimethylnitroindolizines I, II, VI [14], and III-V, and VII [15] were synthesized by methods described earlier. Mass spectra and DCA spectra were obtained on a MAT-212 mass spectrometer using direct sample introduction into the ion source. The ionization electron energy was 70 eV, acceleration potential was 3 kV, ionization chamber temperature was 200-250°C, and the resolving power was 1000 and 10000. The DCA spectra were registered in the first zero-field region of the mass spectrometer using scanning at a constant ratio of electrostatic potential and magnetic field with a rate of 6 amu/sec. Helium was used as neutral gas. The coefficient of parent ion production was 0.5-0.6.

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SYNTHESIS OF 4-NITROSOPYRAZOLES FROM N-SUBSTITUTED N-NITROSOHYDRAZINES

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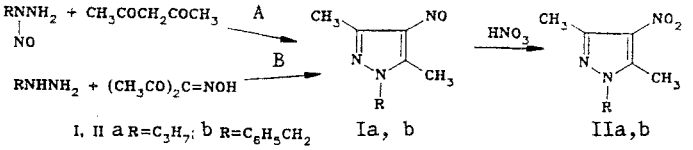
UDC 547.773

Reaction of N-nitrososubstituted propyl- and benzylhydrazines with acetylacetone gives the corresponding 4-nitrosopyrazoles.

The reaction of nitrosohydrazines, $RN(NO)NH_2$ with carbonyl compounds is known to form N-nitrosohydrazones [1, p. 70].

Study of the reaction of N-nitrososubstituted propyl- and benzylhydrazines with acetylacetone showed that besides the expected hydrazones, 1-propyl- and 1-benzyl-3,5-dimethyl-4-nitrosopyrazoles (Ia, b) are formed. The structure of Ia, b was confirmed by physicochemical and spectral properties identical to those of characteristic nitrosopyrazoles obtained by known methods from isonitrosoacetylacetone and propyl- or benzylhydrazine by analogy to the synthesis of 3,5-dimethyl-4-nitroso-1-phenylpyrazole [2].



Nitrosopyrazoles Ia, b are yellow liquids and a mixture of monomeric and dimeric forms. The monomeric forms of Ia, b could not be separated although for some nitrosopyrazoles the monomeric forms have been obtained [3, p. 236]. The structure of the reaction products of nitrosohydrazines with acetylacetone also was confirmed by oxidation with nitric acid of Ia to 3,5-dimethyl-4-nitro-1-propylpyrazole (IIa) by the method of [2].

Formation of nitrosopyrazoles from nitrosohydrazines and acetylacetone can be viewed as a result of intramolecular 1,4-migration of the nitroso group in the nitrosohydrazone which is formed in the initial step. The possibility of such rearrangement was shown earlier for the reaction of isonitrosopyrazolones from nitrosohydrazines and acetoacetic ester

Siberian Technological Institute, Krasnoyarsk 660000. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 337-339, March, 1989. Original article submitted May 20, 1987; revision submitted June 28, 1988.