MASS-SPECTROMETRIC BEHAVIOR OF ISOMERIC NITRO- AND NITROAMINOINDOLIZINES AND INDOLES

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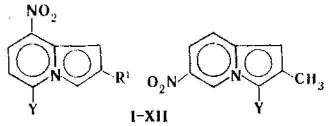
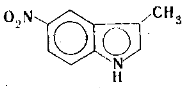
Peaks of $[M - NO]^+$ and $[M - NO_2]^+$ ions are characteristic for the mass spectra of nitroindolizines, whereas peaks of ions of the indole type, viz., $[M - HCN]^+$ and $[M - H, - HCN]^+$ (for alkylindoles), are not characteristic. In the mass spectra of nitroindoles the latter ions give more intense peaks, while the loss of a nitro group or its rearrangement is a considerably less significant process. When a dialkylamino group is introduced in the nitroindolizine molecule, the primary processes in the fragmentation of such compounds are due to fragmentation of the alkylamino group.

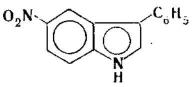
We have previously shown [1-3] that nitroindoles that contain a nitro group in the benzene ring undergo fragmentation similar to the fragmentation of nitroarenes under the influence of electron impact [4]. The introduction of an electron-donor substituent (a methoxy group) in the molecule affected the character of the fragmentation when it was in the ortho position relative to the nitro group [3]. Ions that are characteristic for the dissociative ionization of indole derivatives were virtually absent in the mass spectra of nitromethoxyindoles. It seemed of interest to us to examine the behavior of nitro- and nitroaminoindolizines as compared with nitroindoles. The latter are formed in a number of cases in processes involving the isomerizational recyclization of some nitroindolizines via the scheme of the Kost–Sagitullin rearrangement [5, 6]. As models for the study we selected nitro- and nitroaminoindolizines I-XII, as well as nitroindoles XIII-XVI.



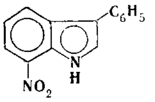
I-XII



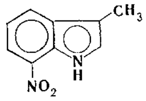
XIII



XVI



XIV



XV

I $R^1=CH_3$, $Y=H$; II $R^1=C_6H_5$, $Y=H$; III $R^1=CH_3$, Y = pyrrolidyl; IV $R^1=C_6H_5$, Y = pyrrolidyl; V $R^1=C_6H_5$, Y = piperidyl; VI $R^1=C_6H_5$, Y = morpholyl; VII $R^1=C_6H_5$, $Y=NH{-}C_4H_9\text{-n}$; VIII $R^1=C_6H_5$, $Y=NH{-}CH(CH_3)C_2H_5$; IX $R^1=C_6H_5$, $Y=NH{-}C(CH_3)_3$; X $R^1=C_6H_5$, $Y=H$; XI $R^1=C(CH_3)_3$, $Y=H$; XII $R^1=CH_3$, $Y=COCH_3$

The mass spectra of these compounds are presented in Table 1, while the intensities of the types of principal characteristic ions are given in Table 2. It is apparent from these data that replacement in the nitroindolizine molecule of the methyl group in the 2 position (I) by a phenyl residue (II) halves the stability of the molecule with respect to electron impact. Similar phenomena can be observed when one compares the W_M values (III and IV). This is evidently associated with the electron-acceptor properties of the benzene ring with respect to the pyrrole fragment of the indolizine molecule. Shifting the nitro group in the nitroindolizine molecule from the 4 position to the 6 position (I) markedly increases the stability of the molecular ion (M^+) of this compound; this is probably associated with the absence of direct conjugation of the electron-acceptor nitro group in the 4 position with the electron-donor pyrrole ring. It should be noted that the stability of the M^+ ion of 5-nitro-3-phenylindole (XVI), which is formed in the recyclization of nitroindolizine X, decreases sharply. Similar character in the change in the W_M value on passing from indolizines to indoles can be observed when one compares I and XIII. However, it should be noted that the molecular ions of 7-nitroindoles (XIV and XV) are always more stable than those of the other isomers. A change in the character of the amino

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TABLE 1. Mass Spectra of I-XVI*

Compound	m/z (relative intensity, %)
I	176 (100), 131 (10), 130 (89), 129 (6), 128 (12), 118 (11), 77 (40), 146 (5), 117 (4), 103 (46)
II	238 (100), 192 (51), 191 (56), 165 (16), 149 (11), 137 (11), 111 (11), 109 (11), 95 (17), 85 (25)
III	245 (100), 217 (30), 202 (21), 199 (4), 176 (54), 171 (5), 170 (6), 169 (3), 143 (7), 130 (10), 118 (5)
IV	307 (100), 277 (47), 260 (5), 237 (76), 231 (18), 204 (10), 192 (15), 191 (13), 190 (12), 165 (13)
V	321 (100), 291 (42), 275 (9), 265 (10), 252 (16), 237 (58), 219 (11), 192 (27), 191 (21), 190 (19)
VI	323 (100), 293 (14), 265 (26), 237 (26), 219 (9), 192 (16), 191 (16), 190 (16), 165 (16), 99 (10), 81 (7)
VII	309 (50), 293 (20), 277 (18), 263 (5), 253 (100), 236 (11), 235 (8), 234 (30), 207 (25), 180 (18)
VIII	309 (22), 291 (12), 263 (31), 252 (33), 207 (100), 206 (45), 205 (40), 204 (25), 180 (22), 152 (13)
IX	309 (42), 253 (100), 207 (19), 206 (13), 205 (8), 180 (8), 111 (7), 97 (18), 85 (18), 71 (38)
X	238 (100), 192 (45), 191 (16), 180 (5), 165 (11), 164 (4), 163 (5), 139 (4), 115 (5), 63 (4)
XI	218 (100), 203 (97), 172 (10), 171 (8), 157 (57), 144 (11), 130 (10), 129 128 (5), 115 (9)
XII	218 (100), 203 (97), 172 (10), 171 (8), 157 (57), 144 (11), 130 (10), 129 (14), 128 (11), 112 (14)
XIII	176 (100), 130 (75), 129 (16), 103 (18), 97 (8), 85 (9), 83 (12), 77 (20), 71 (30), 69 (32)
XIV	238 (100), 192 (36), 191 (15), 165 (32), 164 (8), 163 (7), 128 (6), 95 (4), 94 (4), 78 (3)
XV	176 (100), 175 (46), 130 (65), 129 (27), 128 (12), 118 (5), 103 (31), 102 (13), 101 (4), 77 (27)
XVI	238 (100), 192 (31), 191 (11), 165 (61), 164 (11), 163 (10), 136 (7), 111 (6), 107 (11), 97 (13)

*The molecular-ion peak and the 10 most intense peaks are presented.

TABLE 2. Intensities of the Peaks of the Principal Characteristic Ions in the Mass Spectra of I-XVI

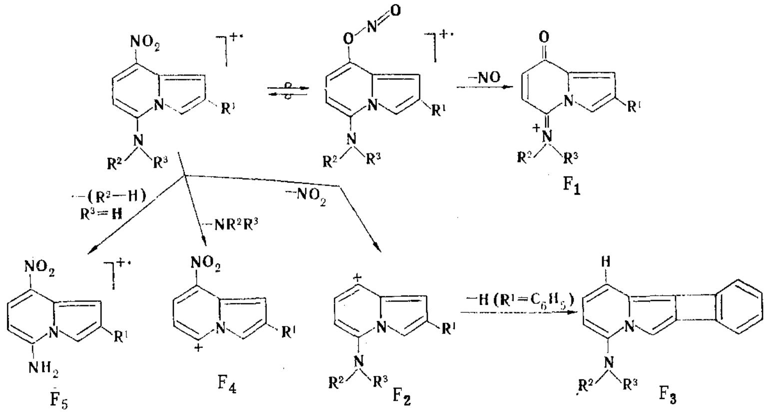
Compound	W_M	$[M-CH_3]^+$	F_1	F_2	F_3	F_4	F_5	I_{F_2}/I_{F_1}
I	25,7	—	1,2	20,7	1,4	—	—	17
II	12,3	—	0,7	5,7	6,3	—	—	8
III	31,6	0,09	0,35	1,1	0,02	16,0	—	3,0
IV	20,3	—	8,2	0,5	0,9	13,2	—	0,06
V	15,8	—	5,5	1,2	0,4	7,6	—	0,2
VI	16,2	—	2,0	0,7	—	3,8	—	0,35
VII	10,6	1,2	0,4	0,8	0,8	0,7	17,9	2,0
VIII	3,3	—	0,4	3,7	0,6	0,4	4,2	9,0
IX	8,8	0,1	0,2 (1,0)*	3,5	2,4	0,9	18,5	17,0
X	42,7	—	0,2	17,3	6,2	—	—	86,0
XI	12,7	17,5	—	1,3		—	—	—
XII	20,6	18,0	0,2	1,9	1,4	—	—	6,0
XIII	19,7	17,6	0,5	0,9	—	—	—	1,8
XIV	36,0	—	0,3	11,5	4,8	—	—	35,0
XV	27,6	—	0,1	16,2	6,7	—	—	162,0
XVI	28,9	—	0,7	8,2	2,8	—	—	12,0

*The $[M - C_4H_8, - R]^+$ ions.

group in nitroaminoindolizines IV-IX also has an appreciable effect on the stabilities of their M^+ ions: the W_M value decreases on passing from heterocyclic amines (IV-VI) to aliphatic amines (VII-IX).

The principal pathways of fragmentation of the molecular ions of nitroindolizines I, II, X, and XII and nitroindoles XIV and XVI are characterized by splitting out of the nitro group as a whole with the formation of an F_2 ion (see the scheme given below), while nitro-nitrite rearrangement of M^+ takes place to a small extent (in most cases $I_{[M-NO_2]^+}/I_{[M-NO]^+} \gg 1$).

This ratio is much less than one in the mass spectra of IV-VI, which contain a phenyl substituent in the 2 position and the residue of a heterocyclic amine in the 4 position. The increase in the fraction of isomerized molecular ion in this case is evidently explained by the smaller volume of the amine residue, which promotes stabilization of the positive charge in the ion. The overall intensities of the molecular-ion and F_1-F_3 ion peaks in the mass spectra of nitroindoles (XII-XVI) and nitroindolizines that do not contain an amino group (I, II, X)



range from 30 to 60%. However, additional fragmentation pathways associated with the fragmentation of a given substituent ($[M - CH_3]^+$ ions) appear in the dissociative ionization of alkyl- or acetyl-substituted nitroindolizines (XI and XII). The loss by M^+ of an amino group as a whole (typical for III and VI) or splitting out of the alkyl grouping attached to the nitrogen atom in the form of an olefin molecule (the F_5 ion) are characteristic pathways for the fragmentation of nitroaminoindolizines (III-IX), in addition to the pathways mentioned above. The elementary compositions of the resulting principal fragment ions are confirmed by the high-resolution mass spectra (IX). The intensities of the peaks of the indicated characteristic ions together with the intensity of M^+ generally constitute more than half of the total ion current.

Thus the mass-spectral behavior of nitroindolizines, as well as nitroaminoindolizines, differs from the fragmentation of nitroindoles that contain electron-donor substituents in the benzene ring; this is probably associated with the greater electron unsaturation of the six-membered ring of indolizine as compared with the benzene ring of indole.

EXPERIMENTAL

The mass spectra were obtained with an MKh-1303 spectrometer at an ionization energy of 50 eV with direct introduction of the samples into the ion source. The high-resolution mass spectra were recorded with a JMS 01-SG-2 spectrometer at an ionization energy of 70 eV.

We have previously described [7, 8] the synthesis of the compounds investigated in this research.

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