1,2-Dimethyl-4-(N,N-dimethylaminobutyl)-9H-pyrido[3,4-b]indole (X). A suspension of 1.6 g (3 mmole) of IX in a saturated alcohol solution of alkali (KOH) was refluxed for 5 min, after which it was poured into water, and the resulting precipitate was removed by filtration to give 0.8 g (96%) of X with mp 174-175°C (from acetonitrile). IR spectrum: 1670 cm^{-1} (C=N). Mass spectrum, m/z (%): 42 (16), 44 (16), 58 (100), 84 (16), 142 (10), 167 (10), 209 (11), 210 (12), 223 (40), 224 (19), 235 (25), 238 (10), 251 (10), 280 (17), 295 (13). Found, %: C 77.5, H 8.4, N 14.3. $C_{19}H_{25}N_3$. Calculated, %: C 77.3, H 8.5, N 14.2.

1,9-Dimethyl-4-(N,N-dimethylaminobutyl)-9H-pyrido[3,4-b]indole Methiodide (XI). A mixture of 0.8 g (3 mmole) of X with excess methyl iodide was refluxed in 10 ml of methanol for 1 h, after which it was cooled and treated with ether. The resulting precipitate was removed by filtration and recrystallized from methanol to give 1 g (79%) of a product with mp 292-294°C. Found, %: C 54.8, H 6.7, N 9.5. $C_{20}H_{28}IN_3$. Calculated, %: C 54.9, H 6.4, N 9.6.

LITERATURE CITED

1. G. T. Tatevosyan, Anhydronium Bases of the Caroline Series [in Russian], Yerevan, Izd. Akad. Nauk Armyansk. SSR (1966), p. 964.
2. G. V. Lazur'evskii (ed.), Brevicolline — An Alkaloid from *Carex parvae* [in Russian], Shtiintsa, Kishinev (1969), p. 99.
3. H. Yamamoto, Y. Nakamura, and M. Nakao, Japanese Patent No. 4,932,558; Rev. Zh. Khim., 90240P (1975).
4. T. V. Stupnikova, A. R. Kirilash, B. P. Zemskii, N. A. Klyuev, V. I. Dulenko, and R. S. Sagitullin, Khim. Geterotsikl. Soedin., No. 2, 197 (1984).
5. Q. N. Porter and I. Baldass, Mass Spectrometry of Heterocyclic Compounds, Wiley-Interscience, New York (1971), p. 564.
6. Xu Guang-zei and Bian Ze-liang, Acta Chim. Sin., 40, 1007 (1982); Ref. Zh. Khim., No. 7, B157 (1983).

MASS-SPECTROMETRIC STUDY OF NITRO-SUBSTITUTED DIHYDROSILAAZAANTHRONES

V. K. Shevtsov, A. V. Varlamov,
Nazrul Islam, and N. S. Prostakov

UDC 543.51:547.828'819

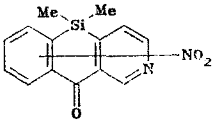
The effect of the position of the nitro group on the character of the dissociative ionization of nitro-substituted dihydrosilaazaanthrones was studied. It was established that a change in the position of the nitro group in the molecule affects not only the probability of the occurrence of monotypic fragmentations but is also responsible for the development of new pathways of the fragmentation of the molecular ions. This makes it possible to identify the isomeric nitrodihydrosilaazaanthrones from their mass spectra.

The dissociative ionization of a new type of heterocyclic compounds, viz., dihydrosilaazaanthracenes that contain various substituents in the 9 position, was studied in [1-3]. The mass-spectrometric properties of such systems with substituents in the benzene and pyridine rings had not been previously studied, since these substances were unknown until recently.

In the present research we examined the mass-spectrometric behavior of 4(5,6,7,8)-nitro-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthrones (I-V) in order to establish the principles involved in the fragmentation as a function of the position of the nitro group. The mass spectra of the investigated compounds are presented in Table 1.

Patrice Lumumba International-Friendship University, Moscow 117923. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 534-538, April, 1985. Original article submitted April 23, 1984.

TABLE 1. Mass Spectra of Mononitrodihydrosilaazaanthrones I–V



I–V

Compound	R	m/z values* (relative intensities)
I	4-NO_2	284 (83), 283 (27), 256 (58), 254 (60), 239 (100), 238 (23), 226 (48), 224 (27), 211 (50), 180 (35)
II	5-NO_2	284 (32), 283 (32), 269 (60), 256 (100), 254 (92), 239 (43), 238 (47), 224 (62), 210 (82), 180 (65)
III	6-NO_2	284 (42), 269 (100), 223 (20), 211 (5), 210 (2), 180 (9), 154 (4), 153 (5), 152 (3), 141 (3)
IV	7-NO_2	284 (51), 269 (100), 254 (3), 239 (5), 224 (5), 223 (22), 211 (4), 210 (2), 180 (8), 154 (3)
V	8-NO_2	284 (100), 269 (20), 254 (22), 239 (22), 211 (4), 224 (10), 210 (12), 180 (20), 167 (10), 166 (12)

*The ten most intense ion peaks are presented.

TABLE 2. Intensities of the Peaks (in % relative to the ion current Σ_{50}) of the Characteristic Ions in the Mass Spectra of I-V

Compound	W_M	$[M-H]^+$	$[M-CH_3]^+$	$[M-OH]^+$	$[M-CO]^+$	$[M-NO]^+$	$[M-NO_2]^+$	$[M-CH_3, -NO]^+$	$[M-CH_3, -NO_2]^+$	$[M-NO, -Si(CH_3)_2]^+$
I	4,1	1,3	1,1	0,2	2,8	2,9	1,1	4,9	0,3	0,8
II	1,8	1,8	3,5	0,6	5,8	5,4	2,7	2,5	0,4	1,9
III	10,6	—	25,4	—	—	0,5	0,5	0,9	5,5	0,7
IV	18,2	—	35,7	—	—	0,9	0,6	1,8	7,8	1,1
V	27,0	—	5,4	—	1,1	5,9	1,1	5,9	1,6	4,3

A rather intense molecular-ion peak (M^+) is observed in the mass spectra of I-V, whereas in the case of 8-nitro-substituted dihydrosilaazaanthrone V, this peak is the maximum peak (Table 2). As one should have expected [4], the introduction of a strong electron-acceptor nitro group into the dihydrosilaazaanthrone molecule destabilizes the molecule; however, the resistance of isomers I-V to fragmentation additionally depends markedly on the position of the substituent (Table 2, the W_M values). The stability of the M^+ ion is maximum for the 6- (III), 7- (IV), and 8-nitro (V) derivatives and is reduced markedly in the case of I and II, which contain a nitro group in the peri position relative to the methyl substituent. The lower W_M values in the case of I and II are associated primarily with the development of new pathways of the fragmentation of the M^+ ions due to the position of the nitro group.

The dissociative ionization of I-V is characterized by common fragmentation pathways; however, there are specific fragmentation pathways that are determined by the position of the nitro substituent. As in the fragmentation of unsubstituted dihydrosilaazaanthrone [2], the $[M-CH_3]^+$ ion peak is the maximum peak in the mass spectra of III and IV, but has significantly lower intensity in the fragmentation of the I, II, and V isomers (Table 2). The decrease in the intensity of the peak of this ion in the mass spectra of I and II can be explained by the formation of energically more favorable fragmentation pathways as a result of rearrangement of the M^+ ion due to the peri position of the nitro group relative to the methyl substituent. At the same time, in the fragmentation of the M^+ ion of V, in contrast to I and II, fragmentation pathways that compete with the splitting out of a methyl group are absent (Tables 1 and 2); however, the intensity of the $[M-CH_3]^+$ ion peak is considerably lower than in the mass spectra of III and IV. On the basis of the PMR spectrum of V it was established* that the nitro group in the 8 position is not coplanar with the three-ring framework of the

---

*The results of this investigation will be published in a separate communication.

molecule. A consequence of this is a decrease in the destabilizing effect of the nitro group as compared with III and IV, which is manifested in an increase in the W_M values due to suppression of the common fragmentation processes, particularly to a decrease in the probability of the elimination of a methyl substituent (Table 2). Disruption of the conjugation of the nitro group with the phenylene ring in V is also manifested in the formation of a significantly more intense $[M - NO_2]^+$ ion peak as compared with isomers III and IV. (The formation of intense $[M - NO_2]^+$ ion peaks in the mass spectra of I and II, as we will demonstrate below, is associated with rearrangement processes in the M^+ ions of these substances.)

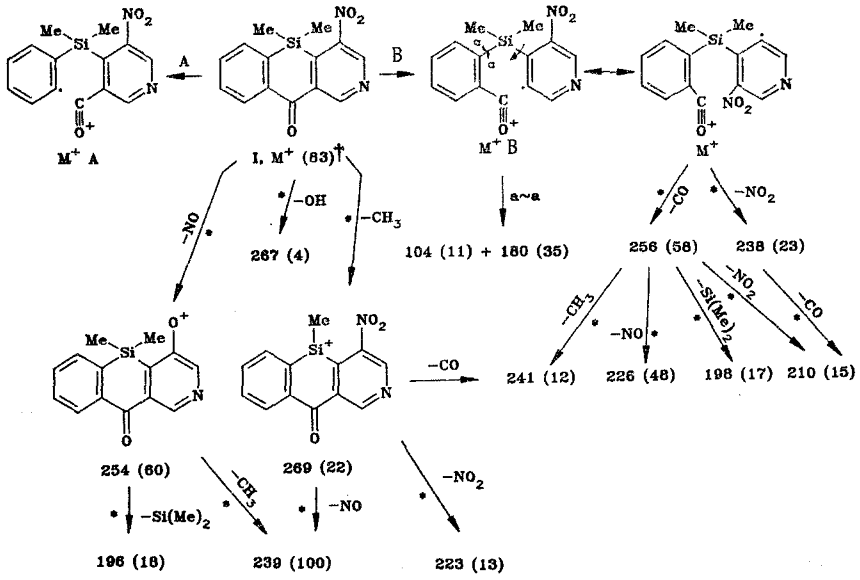
A peculiarity of the fragmentation of I-V, as in the case of most aromatic nitro derivatives, is the formation of $[M - NO_2]^+$ ions, which is due to simple cleavage of the bond in the M^+ and $[M - NO]^+$ ions formed as a result of nitro-nitrite rearrangement [5]. It is important to note that the probability of nitro-nitrite rearrangement, which is determined by the Z value ($Z = I_{[M-NO]^+}/I_{[M-NO_2]^+}$), which is considerably greater in the fragmentation of isomers I, II, and V as compared with III and IV. The increase in the fraction of M^+ ions that exist in the nitrite form in the fragmentation of V is apparently associated with the lower electron density [6] on the $C_{(8)}$ atom as compared with the $C_{(6)}$ and $C_{(7)}$ atoms. At the same time, the increased Z value in the case of I and II contradicts the well-known assumption that the interaction of the nitro group with the ortho or peri substituent suppresses nitro-nitrite rearrangement [5]. The fact noted above can be explained if one assumes that the fragmentation of isomers I and II takes place from the open forms of M^+ (A or B), which are formed through cleavage of one of the bonds of the central ring; ring opening precedes nitro-nitrite rearrangement. The structures that may be formed in the cleavage in the M^+ ion of I of the bonds of the carbonyl carbon atom with the benzene (pathway A) or pyridine (pathway B) fragment of the molecule are shown in the scheme. It should be emphasized that the pathways that lead to the formation of the open form of M^+ (see the scheme) assume localization of a part of the positive charge on the oxygen atom of the keto group and subsequent cleavage of the β bond relative to the oxygen atom [7]. In this case, in the open form of the M^+ ion (see the scheme) one may arbitrarily make a distinction between the cationic and radical centers. Of the two open forms of the M^+ ion shown in the scheme, the preferred form is the B form since, in this case, the radical center is stabilized by the electron-acceptor nitro group [8]. The existence of the M^+ ions of I and II in the open form with stabilization of the radical center of the nitro group is confirmed indirectly by the presence in the mass spectra of I and II of characteristic ions that are formed as a result of cleavage of the bond between the silicon atom and the aromatic fragment that does not contain a nitro group (see the scheme, a ~ a cleavage). Intense peaks of ions at 180 and 104 (see the scheme),* which are formed as a result of this sort of cleavage, are recorded in the mass spectra of I and II; in the case of II, cleavage of the $Si-C_{aryl}$ bond is accompanied by migration of hydrogen to the silicon-containing fragment. The proposed pathway for the formation of the indicated ions is confirmed by measurements of their precise masses (for I, M_{meas} 180.0355, $C_7H_8N_2O_2Si$, and M_{calc} 180.0355; for II, M_{meas} 180.0480, $C_8H_{10}NO_2Si$, and M_{calc} 180.0481; for M 104, in the case of I: M_{meas} 104.0262, C_6H_4CO, and M_{calc} 104.0263). The presence in the mass spectra of isomers III-V of characteristic fragments at 180 (Table 1) also constitutes evidence for the existence of part of the molecular ions of these substances in the B form.

The open form of the M^+ ion makes it possible to explain the significant differences in the fragmentation of nitro-substituted dihydrosilaazaanthrones. In fact, in the M^+ ions of I and II, as a result of rotation about the $Si-C_{aryl}$ bond, one observes the development of conformations in which the nitro substituent may exert anchimeric assistance in the elimination of a CO molecule [8], which is also responsible for the high intensities of the $[M - CO]^+$ and $[M - NO_2]^+$ ion peaks in the mass spectra of these compounds (Table 2). In the M^+ ions of III-V the manifestation of the anchimeric effect of the nitro group, even in the open form, is impossible, and the intensities of the $[M - CO]^+$ and $[M - NO_2]^+$ ion peaks in the mass spectra of these substances are therefore low (Table 2).

The formation of the open form of M^+ also leads to substantial differences in isomers I-V in the second stage of fragmentation, particularly to the formation of intense peaks of $[M - CO, -NO]^+$ and $[M - CO, -NO_2]^+$ ions in the mass spectra of I and II (scheme, Table 1) and their absence in the mass spectra of III-V. The elimination of an $Si(CH_3)_2$ particle, which is characteristic for the fragmentation of most silicon-containing aromatic compounds, is observed in the second stage of the fragmentation (scheme).

---

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



---

*Metastable transition.
†The intensities of the peaks in percent of the maximum peak are presented in parentheses.

Yet another characteristic peculiarity of the dissociative ionization of I and II, which contain a nitro group in the peri position relative to the methyl substituent, is the formation of $[M - H]^+$ and $[M - OH]^+$ ions. The appearance of the first ion is evidently due to steric interaction of the nitro and methyl groups and may be an analytical sign of their spatial proximity in the molecule. The formation of $[M - OH]^+$ ions is characteristic for nitro-substituted aromatic compounds that contain a nitro group in the ortho or peri position relative to the methyl substituent [5].

The experimental results obtained constitute evidence that the position of the nitro group in nitro-substituted dihydrosilaazaanthrones can be determined from mass-spectral data. The formation of a high-intensity $[M - CO]^+$ ion peak is characteristic for the fragmentation of 4- and 5-nitro derivatives I and II; its magnitude is maximal in the mass spectrum of II. In contrast to I-IV, the M^+ peak has the maximum intensity in the fragmentation of 8-nitro derivative V, whereas the $[M - CH_3]^+$ ion peak is the maximum peak in the mass spectra of 6- and 7-nitro derivatives III and IV; in the case of 7-nitro derivative IV, $[M - NO]^+$ and $[M - NO, -CH_3]^+$ ions, which are absent in the fragmentation of the 6-nitro derivative, are recorded in the case of 7-nitro derivative IV.

EXPERIMENTAL

The mass spectra were obtained with an MKh-1303 mass spectrometer with a system for direct introduction of the substances into the ion source; the ionizing voltage was 70 V, and the temperature at which the substance was let into the system was 40°C. The precise masses of the fragment ions were measured with an MS-30 apparatus by the method of coincidence of the peaks. We used polyphosphoric acid as the standard.

4- (I) and 6-Nitro-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthrone (III). A solution of 1.5 g (6.6 mmole) of 10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene was added to a suspension of 3.3 g (12.9 mmole) of $Cu(NO_3)_2 \cdot 3NO_2$ in 20 ml of acetic anhydride, and the mixture was heated at 70-80°C for 30 min. It was then poured over ice, and the aqueous mixture was made alkaline with ammonia. The reaction products were extracted with ether, the extract was dried with magnesium sulfate, the ether was removed by distillation, and the residue (1.3 g) was chromatographed with a column (H = 57 cm, d = 2 cm) packed with activity II aluminum oxide. Initial elution with ethyl acetate–heptane (1:5 by volume) gave 0.08 g (3%) of I, with mp 194-196°C (from heptane–ethyl acetate). Found, %: C 59.3, H 4.3, N 9.56. $C_{14}H_{12}N_2 \cdot O_3Si$. Calculated, %: C 59.1, H 4.2, N 9.8.

After this, using the same solvents (1:4), we were able to successively elute 0.4 g (24%) of 10,10-dimethyl-9,10-dihydro-10-sila-2-azanthrone and 0.33 g (16%) of nitro-substituted III with mp 204-206°C (from heptane–ethyl acetate). Found, %: C 59.4, H 4.4, N 9.4. $C_{14}H_{12}N_2O_3$. Calculated, %: C 59.1, H 4.2, N 9.8.

<u>5- (II), 7- (IV), and 8-Nitro-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthrone (V).</u> A 17-ml sample of a nitrating mixture consisting of 6 ml of nitric acid (sp. gr. 1.5 g/cm^3) and 11 ml of sulfuric acid (sp. gr. 1.84 g/cm^3) was added at 20°C in the course of 50 min to a solution of 3 g (12.5 mmole) of 10,10-dimethyl-10-sila-2-azaanthrone in 25 ml of concentrated H_2SO_4. After 1 h, the reaction mixture was poured over ice, and the aqueous mixture was made alkaline with ammonia. The reaction products were extracted with chloroform, the extract was dried with magnesium sulfate, the chloroform was removed, and the residue (3 g) was chromatographed with a column (H = 34 cm, d = 3.5 cm) packed with silica gel. Elution with ethyl acetate—heptane (1:4) gave 0.7 g (20%) of II with mp 215-217°C (from ethyl acetate). Found, %: C 59.2, H 4.47, N 9.6. $C_{14}H_{12}N_2O_3Si$. Calculated, %: C 59.1, H 4.2, N 9.8.

After this, we used the same solvents to successively elute 0.2 g (6%) of IV [mp 230-232°C (from ethyl acetate); found, %: C 59.2, H 4.4, N 9.6. $C_{14}H_{12}N_2O_3Si$. Calculated, %: C 59.1, H 4.2, N 9.8]; 0.75 g of a mixture of IV and V, and 0.17 g (4.8%) of V [mp 208-210°C (from heptane—ethyl acetate); found, %: C 59.2, H 4.5, N 9.6. $C_{14}H_{12}N_2O_3Si$. Calculated, %: C 59.1, H 4.2, N 9.8].

LITERATURE CITED

1. N. S. Prostakov, N. Saxena, P. I. Zakharov, and A. V. Valamov, J. Organomet. Chem., <u>184</u>, 167 (1980).
2. N. S. Prostakov, N. Saxena, P. I. Zakharov, A. V. Varlamov, and D. A. Fesenko, J. Organomet. Chem., <u>228</u>, 37 (1982).
3. A. V. Varlamov, V. K. Shevtsov, A. M. Klochkov, and N. S. Prostakov, Khim. Geterotsikl. Soedin., No. 8, 1071 (1984).
4. K. Levsen, Fundamental Aspects of Organic Mass Spectrometry, Verlag Chemie, Weinheip (1978), p. 312.
5. R. A. Khmel'nitskii and P. B. Terent'ev, Usp. Khim., <u>48</u>, 854 (1979).
6. O. A. Solov'ev, R. A. Khmel'nitskii, P. B. Terent'ev, N. A. Klyuev, and E. Ya. Zinchenko, Izv. Timiryazev, Sel'skokhoz. Akad., No. 3, 209 (1975).
7. L. V. Hall and W. A. Oliver, Org. Mass Spectrom., <u>2</u>, 801 (1969).
8. V. V. Takhistov, Practical Mass Spectrometry of Organic Compounds [in Russian], Izd. Leningradsk. Gosudartstv. Univ., Leningrad (1977), p. 119.

SYNTHESIS OF SPIRO COMPOUNDS WITH 3-METHYL-2-AZAFLUORENE, INDAN, PYRAZOLINE, AND CYCLOPROPANE FRAGMENTS ON THE BASIS OF 3-METHYL-9-PHENYLETHYNYL-2-AZAFLUOREN-9-OL

N. S. Prostakov, Mikhalis Makuli, N. M. Mikhailova,
Hussein Abubakr, N. D. Sergeeva, and A. A. Obynochnyi

UDC 547.678.3'772'828'
512.07

3-Methyl-9-phenylethynyl-2-azafluoren-9-ol, 3-methyl-9-phenacylidene-2-azafluorene, and spiro compounds with 2-azafluorene, indan, pyrazoline, and cyclopropane fragments were obtained starting from 3-methyl-2-azafluorenone by successive transformations. Information regarding the spatial structures of the synthesized compounds was obtained.

Continuing our research on the synthesis and study of the transformations of azafluorene derivatives, we directed our attention to the preparation of 3-methyl-9-phenylethynyl-2-azafluoren-9-ol (II) from the now accessible 3-methyl-2-azafluorenone (I). We used the Iotsich complex in the reaction.

Patrice Lumumba International-Friendship University, Moscow 117923. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 539-541, April, 1985. Original article submitted April 17, 1984.

0009-3122/85/2104-0449$09.50