

MASS-SPECTROMETRIC STUDY OF NITRO DERIVATIVES  
OF 2(4)-AZAFLUORENES AND 2(4)-AZAFLUORENONES

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The dissociative ionization of 13 nitro derivatives of 2(4)-azafluorenes and 2(4)-azafluorenones was investigated. The introduction of an electron-acceptor nitro group into the molecule markedly reduces the stability of the molecular ions and suppresses the fragmentation pathways that are characteristic for azafluorenes. Nitro-nitrite rearrangement proceeds more readily in nitro-substituted 4-azafluorenes than in nitro-substituted 2-azafluorenes. A characteristic feature of the fragmentation of azafluorenes that do not contain nitro and methyl groups in a vicinal orientation is elimination of a OH particle by the molecular ions. It was established by deuterium labeling that in this case the formation of an  $[M - OH]^+$  ion is due to the presence of a methylene group attached to the C<sub>9</sub> atom in the molecule.

The literature on the mass-spectrometric behavior of polycondensed heterocyclic compounds [1] does not contain data pertaining to the problem of the mutual effect of the azafluorene ring and the nitro group on the formation of ions that are characteristic for the fragmentation of nitro derivatives of the heteroaromatic series [2]. To solve this problem and to continue our study of the mass-spectral behavior of azafluorene systems [3] in the present research we studied the dissociative ionization of isomeric (with respect to the position of the nitrogen atom) nitro-substituted azafluorenes and azafluorenones, as well as their hydrocarbon analogs, viz., 2-nitrofluorene (I), 7-nitro-3-methyl- and 6-nitro-3,7-dimethyl-2-azafluorenes (II, III), 7-nitro-, 7-nitro-1-methyl- and 6-nitro-3,7-dimethyl-4-azafluorenes (IV-VI), 2-nitrofluorenone (VII), 7-nitro-3-methyl- and 6-nitro-3,7-dimethyl-4-azafluorenones (VIII, IX), and 7-nitro-, 7-nitro-1-methyl-, and 6-nitro-7-methyl-4-azafluorenones (X-XII), as well as 2-nitro-9,9-D<sub>2</sub>-fluorene (XIII). Intense peaks of molecular ions are observed in the mass spectra of I-XIII (Tables 1 and 2). However, their stabilities ( $W_M$ ) are appreciably lower than the stabilities of the  $M^+$  ions of 2(4)-azafluorenes, which is typical for heteroaromatic nitro derivatives [4, 5]. The  $W_M$  values are approximately identical in the case of the dissociative ionization of 2-nitrofluorene (I) and nitroazafluorenes that do not contain a methyl substituent in the ortho position relative to the nitro group, whereas the  $W_M$  values increase by a factor of ~1.5 on passing to their keto derivatives (VII, VIII, X, and XI). The stabilizing effect of the keto group was also previously observed during a study of the fragmentation of 2(4)-azafluorenes [3]. The molecular ions of azafluorenones that contain a nitro group in the ortho position relative to the methyl group (III, VI, IX, and XII; Table 2) have the lowest  $W_M$  values. As a result of the "ortho effect" of these substituents, the  $W_M$  values for azafluorenes decrease by a factor of 1.7-2, as compared with a factor of four to five in the case of azafluorenones.

The introduction of an electron-acceptor nitro group changes the mass-spectral behavior of fluorenes and azafluorenes substantially. Thus the mass spectra of nitro compounds I-XIII do not contain the peaks of doubly charged molecular ions ( $M^{2+}$ ), and the intensities of the  $[M - H]^+$  and  $[M - CH_3]^+$  ion peaks decrease sharply, whereas in the case of keto derivatives VII-XII virtually no formation of the indicated fragments is observed. Elimination by the  $M^+$  ion of a CO molecule, which was the dominant process in the fragmentation of azafluorenones [3], is not observed in the dissociative ionization of nitro-substituted azafluorenones VII-XII. The indicated peculiarities can be explained by both the electron-

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TABLE 1. Mass Spectra of I-XII Obtained at 70 eV

Com-pound	m/e values (relative intensities of the ion peaks in percent of the maximum peak)*
1	2
I	212 (14,1), 211 (87,2), 195 (7,2), 194 (33,6), 181 (10,8), 180 (3,6), 166 (16,2), 165 (100), 164 (42,1), 163 (27,6), 153 (6,6), 152 (8,4), 139 (8,7), 115 (6,2), 87 (3,4), 63 (5,4)
II	227 (15,2), 226 (99,3), 210 (6,8), 209 (28,5), 196 (7,7), 195 (3,3), 181 (17,8), 180 (100), 179 (33,1), 178 (10,5), 177 (4,1), 168 (6,8), 167 (4,1), 166 (6,0), 165 (5,4), 164 (4,7), 154 (3,8), 153 (10,5), 152 (27,8), 151 (12,1), 150 (4,9), 141 (4,5), 140 (4,5), 139 (10,1), 138 (6,1), 137 (3,2), 127 (6,0), 126 (4,7), 113 (4,3), 63 (7,1)
III	241 (13,7), 240 (84,2), 224 (17,1), 223 (100), 210 (9,7), 209 (8,6), 208 (4,1), 196 (9,1), 195 (51,8), 194 (60,3), 193 (22,9), 192 (10,8), 191 (5,1), 190 (3,4), 182 (5,1), 181 (6,3), 180 (8,6), 179 (11,4), 178 (8,6), 177 (5,1), 163 (3,4), 168 (12,6), 167 (9,7), 166 (8,6), 165 (20,0), 164 (5,7), 163 (4,6), 155 (4,6), 154 (4,6), 153 (8,1), 152 (23,4), 151 (10,8), 150 (5,1), 149 (3,4), 141 (8,0), 140 (4,9), 139 (8,6), 128 (3,4), 127 (5,1), 126 (4,0), 115 (5,7), 77 (3,9), 76 (4,0), 75 (4,0), 63 (5,7), 57 (5,7), 55 (5,1), 51 (4,0)
IV	213 (15,5), 212 (100), 196 (4,5), 195 (21,5), 182 (12,8), 181 (4,1), 167 (14,7), 166 (84,9), 165 (31,3), 164 (14,0), 155 (3,0), 154 (11,7), 153 (3,11), 141 (5,3), 140 (18,5), 139 (19,6), 138 (7,5), 137 (3,8), 127 (4,1), 116 (3,8), 113 (4,9), 89 (3,8), 87 (4,1), 63 (6,0)
V	227 (13,6), 226 (100), 210 (4,3), 209 (15,6), 196 (14,3), 195 (3,9), 181 (4,3), 180 (74,1), 179 (27,3), 178 (12,3), 177 (3,9), 168 (8,4), 167 (5,8), 166 (6,5), 165 (4,5), 164 (5,2), 154 (4,5), 153 (8,4), 152 (20,8), 151 (9,1), 150 (3,9), 141 (3,9), 141 (3,9), 140 (3,9), 139 (5,2), 127 (5,8), 126 (3,9), 113 (3,2), 77 (7,1), 76 (7,1), 76 (5,8), 75 (4,5), 63 (5,2), 57 (3,2)
VI	227 (10,8), 226 (69,3), 210 (18,3), 209 (100), 196 (5,3), 182 (16,0), 181 (81,8), 180 (39,6), 179 (31,4), 178 (27,2), 177 (6,8), 168 (6,0), 167 (10,2), 166 (5,9), 165 (3,1), 164 (3,8), 155 (5,8), 154 (23,6), 153 (15,6), 152 (35,8), 151 (16,4), 150 (5,8), 141 (7,8), 140 (4,9), 139 (4,2), 128 (4,3), 127 (8,8), 126 (5,6), 77 (10,1), 76 (7,1), 75 (5,1), 63 (8,8)
VII	226 (17,1), 225 (100), 196 (6,5), 195 (33,2), 180 (5,1), 179 (24,3), 167 (10,4), 155 (4,6), 152 (11,2), 151 (68,3), 150 (27,2), 149 (5,7), 141 (10,3), 139 (12,2), 125 (5,1), 99 (3,6), 98 (4,1), 87 (3,1), 76 (3,0), 75 (3,0), 74 (9,8), 71 (3,1), 69 (8,0)
VIII	241 (15,5), 240 (100), 210 (8,7), 195 (8,0), 194 (46,1), 182 (8,1), 167 (4,2), 166 (27,1), 165 (3,2), 164 (5,2), 154 (7,7), 152 (3,2), 140 (8,4), 139 (3,9), 137 (2,5), 126 (4,5), 125 (24,1), 113 (5,2), 99 (6,8), 87 (4,2), 75 (8,7), 74 (5,8), 63 (5,8)
IX	255 (12,9), 254 (76,1), 238 (18,0), 237 (100), 225 (4,0), 224 (16,9), 223 (4,7), 210 (20,3), 209 (98,2), 208 (32,1), 207 (6,9), 206 (3,1), 196 (6,9), 195 (8,7), 194 (3,0), 193 (3,8), 183 (3,0), 182 (20,3), 181 (54,2), 180 (20,4), 179 (18,4), 178 (16,4), 177 (7,8), 169 (4,4), 168 (9,1), 167 (9,1), 166 (8,9), 165 (6,7), 164 (13,6), 155 (8,2), 154 (8,7), 153 (24,0), 152 (51,9), 151 (26,1), 150 (11,8), 149 (3,0), 142 (3,3), 141 (15,9), 140 (24,2), 139 (64,2), 138 (26,1), 137 (14,3), 130 (3,1), 129 (3,3), 128 (11,6), 127 (36,2), 126 (22,1), 125 (9,1), 124 (3,0), 123 (3,0), 115 (9,3), 114 (4,9), 113 (11,8), 112 (4,2), 111 (5,3), 110 (3,1), 89 (12,2), 88 (8,4), 87 (14,7), 86 (9,5), 77 (12,9), 76 (9,1), 75 (14,4), 74 (10,0), 64 (4,4), 63 (2,4), 62 (9,8), 61 (2,2), 57 (3,0), 55 (4,2), 51 (11,2)
X	227 (13,6), 226 (100), 216 (15,3), 196 (15,3), 181 (4,5), 180 (26,8), 168 (10,1), 153 (5,3), 152 (47,7), 151 (6,8), 140 (9,1), 126 (4,9), 125 (14,5), 101 (3,6), 99 (5,7), 98 (3,2), 77 (4,0), 76 (4,9), 75 (8,5), 74 (5,0), 51 (3,6)
XI	241 (19,4), 240 (100), 211 (7,2), 210 (23,3), 195 (18,4), 194 (41,8), 182 (10,4), 167 (4,2), 166 (25,7), 165 (5,4), 154 (7,8), 141 (3,3), 140 (14,9), 139 (16,7), 138 (4,5), 127 (3,3), 113 (3,4), 89 (3,0), 63 (3,4)
XII	241 (8,3), 240 (45,2), 224 (16,5), 223 (100), 211 (8,7), 210 (19,9), 209 (6,7), 196 (10,8), 195 (53,9), 194 (25,3), 193 (4,1), 182 (7,1), 181 (6,6), 168 (8,7), 167 (27,4), 166 (22,4), 165 (16,6), 164 (10,9), 155 (3,3), 154 (6,6), 153 (4,1), 152 (3,3), 141 (6,6), 140 (20,2), 139 (21,6), 138 (8,3), 137 (5,0), 127 (8,7), 126 (3,3), 115 (3,1), 114 (3,3), 113 (5,4), 111 (3,2), 99 (3,3), 98 (3,6), 97 (3,7), 89 (4,1), 88 (4,0), 87 (4,6), 86 (3,3), 85 (4,1), 75 (3,5), 74 (3,4), 73 (3,3), 63 (5,2), 62 (3,4), 57 (7,7), 56 (3,1), 55 (5,8), 51 (3,9)
XIII	214 (12,1), 213 (77,8), 212 (17,3), 197 (6,9), 196 (24,5), 195 (18,7), 184 (4,3), 183 (15,8), 182 (7,2), 181 (4,7), 180 (5,0), 179 (6,6), 178 (3,1), 177 (4,3), 176 (4,6), 168 (15,8), 167 (100), 166 (50,4), 165 (36,3), 164 (20,1), 163 (8,3), 155 (10,1), 154 (11,5), 153 (8,6), 152 (7,2), 151 (18,7), 150 (10,0), 149 (9,1), 141 (9,3), 140 (8,6), 139 (8,6), 138 (3,7), 88 (5,1), 87 (8,6), 86 (3,6), 85 (4,3), 77 (5,5), 76 (4,9), 75 (8,6), 74 (9,8), 71 (6,1), 69 (8,6), 65 (3,9), 64 (5,7), 63 (6,9), 62 (4,3), 57 (10,0), 56 (4,9), 55 (9,1)

\*The ion peaks with intensities  $\geq 3\%$  are presented.

TABLE 2. Stabilities of the Molecular Ions ( $W_M$ ) and Relative Intensities of the Peaks of the Characteristic Fragments (in percent of the maximum peak) in the Mass Spectra of Nitro Derivatives of 2- and 4-Azafluorenes

Compound	Ionization energy, eV	$M^+$	$W_M$	$[M-OH]^+$	$[M-NO]^+$	$[M-NO_2]^+$	$[M-OH, -CO]^+$	$[M-NO, -CO]^+$
I	70	87,2	18	33,6	10,8	100	—	6,6
	20	100	—	25,9	9,2	66,6	—	3,9
II	70	99,3	—	28,5	7,7	100	—	6,8
	20	100	14	26,3	7,1	66,3	—	—
III	70	84,2	—	100	9,7	60,3	51,8	5,1
	20	100	10	65,5	13,2	13,2	11,2	—
IV	70	100	—	21,5	12,8	84,9	—	11,7
	20	100	19	7,5	7,0	14,	—	—
V	70	100	—	15,6	14,3	74,1	—	8,4
	20	100	20	8,8	10,2	17,0	—	—
VI	70	69,3	—	100	5,3	39,6	81,8	6,0
	20	98,4	9	100	11,3	23,4	63,6	—
VII	70	100	—	—	33,2	24,3	—	10,4
	20	100	22	—	28,9	17,8	3,4	6,8
VIII	70	100	—	—	8,7	46,1	—	8,1
	20	100	25	—	6,3	8,5	—	1,7
IX	70	76,1	—	—	16,9	32,1	98,2	6,9
	20	100	6	100	16,2	—	21,1	—
X	70	100	—	92,5	15,3	26,8	—	10,1
	20	100	29	—	9,8	2,0	—	—
XI	70	100	—	—	23,3	41,8	—	10,4
	20	100	27	—	8,1	8,3	—	—
XII	70	45,2	6	100	19,9	25,3	53,9	7,1
	20	68,3	—	100	16,1	11,2	45,3	3,9
XIII	70	77,8	—	24,5	15,8	100	—	10,1
				18,7*				

\*This is the intensity of the  $[M-OD]^+$  ion peak.

acceptor properties of the nitro group and by the development of new energetically more favorable fragmentation pathways.

The principal process in the fragmentation of the investigated nitro derivatives that do not contain a methyl substituent in the ortho position relative to the nitro group is elimination of a  $NO_2$  particle by the molecular ions (Table 2). The ratios of the intensities of the  $[M-NO_2]^+$  and  $M^+$  ion peaks ( $I[M-NO_2]^+/I[M^+] = A$ ) are presented in Table 3. The A values for 2-nitrofluorene (I) and azafluorenes II, IV, and V are appreciably lower than in the case of the previously studied nitrobenzene ( $A \sim 2.1$ ) and m- and p-nitrotoluenes ( $A \sim 1.4$ ) [5]. This fact can be explained by the increase in the stabilities of the molecular ions of compounds of the azafluorene series due to their more condensed structure. It should be noted that the A ratio also decreases on passing from nitrofluorene I to azafluorene derivatives II, IV, and V; this change is most significant in the case of 4-azafluorenes IV and V. A more pronounced decrease in the A values is observed in the low-voltage (20 eV) mass spectra for IV and V (Table 2). The dependence indicated for the A values is in good agreement with the probability (Z) of nitro-nitrite rearrangement, which is determined by the ratio of the intensities of the peaks of the  $[M-NO]^+$  and  $[M-NO_2]^+$  ions (Table 3) in the molecular ions of the investigated substances. In fact, the Z value on passing from nitro-substituted 2-azafluorene II to 4-azafluorene derivatives IV and V increases by a factor of approximately two, whereas the A value decreases in this series of compounds by a factor of  $\sim 1.4$ . It must be noted that when the ionizing-electron energy is lowered to 20 eV, the A values for nitro-substituted fluorene I and 2-azafluorene II decrease slightly (by a factor of  $\sim 1.5$ ), whereas in the case of 4-azafluorene derivatives IV

TABLE 3. A and Z Values Obtained from the Mass Spectra of I-XII at Various Electron Energies

	Elec- tron energy eV	Compounds											
		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
$A = I_{[M-NO_2]^+} / I_M$	70	1,1	1,0	0,7	0,8	0,7	0,6	0,2	0,5	0,4	0,3	0,4	0,5
	20	0,66	0,66	0,13	0,15	0,17	0,24	0,18	0,08	0,0	0,02	0,08	0,16
$Z = I_{[M-NO]^+} / I_{[M-NO_2]^+}$	70	0,11	0,08	0,16	0,15	0,19	0,13	1,37	0,19	0,53	0,57	0,56	0,79
	20	0,14	0,11	1,0	0,5	0,60	0,48	1,62	0,74	—	4,9	0,98	1,44

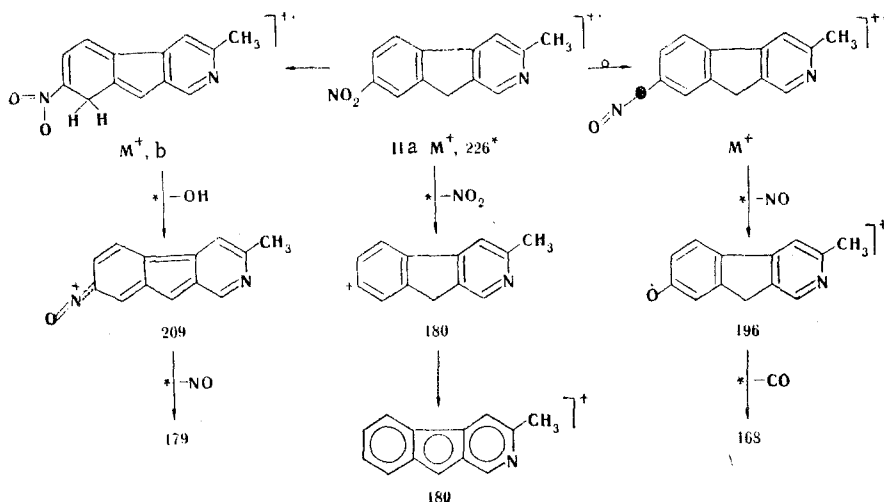
and V they decrease by a factor of four to five. At the same time, when the ionizing voltage is lowered, the probability of nitro-nitrite rearrangement (Z) in I and II increases by a factor of  $\sim 1.4$ , while the Z value for IV and V increases by a factor greater than three (Table 3). These data confirm the dependence of the probability of nitro-nitrite rearrangement on the position of the nitrogen atom in the azafluorene ring and constitute evidence for more facile rearrangement for 4-azafluorenes than for 2-azafluorenes.

In the fragmentation of keto derivatives VII, VIII, X, and XI the probability of detachment of an  $NO_2$  radical decreases markedly, and the position of the nitrogen atom affects this process to a considerably greater extent than in the case of the dissociative ionization of nitro-substituted 2- and 4-azafluorenes. This fact can be explained not only by an increase in the stability of the molecular ions as a consequence of the presence of a carbonyl group in the C<sub>9</sub> position (which is responsible for the increase in the  $\pi$ -electron energy in the molecular ions) but also by an increase in the probability of nitro-nitrite rearrangement (Table 3, the Z value).

High-intensity  $[M - OH, -CO]^+$  ion peaks are formed in addition to the intense peak of an  $[M - 46]^+$  fragment in the mass spectra of substances that contain nitro and methyl substituents in the corresponding positions (III, VI, IX, and XII) (Table 2). A measurement of the precise mass of the  $[M - 46]^+$  fragment in the mass spectra of III, VI, and IX indicates the elimination of an  $NO_2$  particle by the molecular ions of these compounds rather than the alternative loss of a hydrogen atom by the  $[M - OH, -CO]^+$  ion.

Despite the absence in nitrofluorene I and nitro-substituted 2- and 4-azafluorenes II, IV, and V of vicinal nitro and methyl substituents, a characteristic feature of their fragmentation is the formation of intense  $[M - OH]^+$  ion peaks. The nitro group in the indicated compounds is located in the benzene ring, and since  $[M - OH]^+$  ions are not formed in the mass spectra of nitrobenzene and m- and p-nitrotoluenes, one should have expected the absence of an  $[M - OH]^+$  fragment in the mass spectra of I, II, IV, and V. The elimination of a hydroxy group in the fragmentation of these substances can be explained by isomerization of their molecular ions from the a form to the b form (Scheme 1), i.e., by migration of a hydrogen atom from the methylene group to various positions of the azafluorene ring, including the ortho position relative to the nitro group, as evidenced by the absence of an  $[M - OH]^+$  fragment in the mass spectra of keto derivatives VII, VIII, X, and XI. This is also confirmed by the formation in the case of deuterio analog XIII, in addition to the  $[M - OH]^+$  ion, of an  $[M - OD]^+$  fragment, which constitutes evidence for randomization of the hydrogen atoms of the methylene group and the fluorene ring. The latter process was also previously observed in the dissociative ionization of fluorenes [7] and azafluorenes [8]. This randomization model, which is due to migration of the methylene group along the azafluorene ring, is in good agreement with the mechanism for the formation of the  $[M - OH]^+$  ion in the mass spectra of m- and p-nitrophenyl(phenyl)methanes [9], which suggests the presence in the ortho position to the nitro group of a hydrogen atom attached to an  $sp^3$ -hybridized carbon atom. However, it should be noted that the development of the latter is explained in [9] by cyclization of the  $\alpha$ -carbon atoms of the benzene rings rather than by randomization of the hydrogen atoms of the methylene group and the phenyl ring. A different mechanism for the formation of an  $sp^3$ -hybridized carbon atom in the fragmentation of nitro-diphenylmethanes and nitrofluorenes is confirmed by the significant difference in the in-

Scheme 1



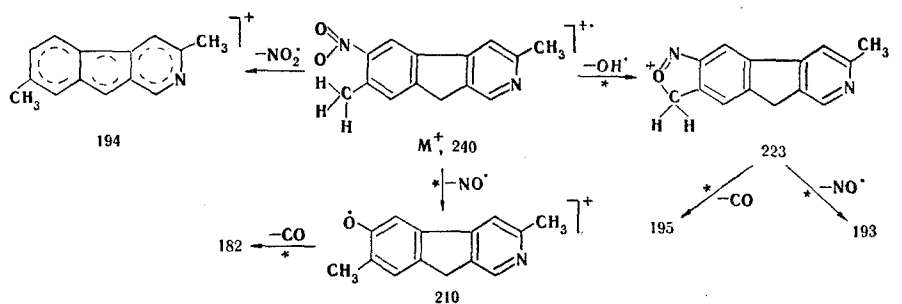
\*The numbers in Schemes 1 and 2 are the mass-to-charge ratios.

tensities of the peaks of the  $[M - OH]^+$  ions in the mass spectra of these compounds ( $\sim 8$  and 15-30%, respectively).

When the ionizing voltage is lowered to 20 V, the intensity of the  $[M - OH]^+$  ion in the mass spectra of nitro-substituted fluorene I and 2-azafluorene II remains virtually unchanged, whereas in the fragmentation of nitro derivatives of 4-azafluorenes IV and V its value decreases by a factor of 2.5-3 (Table 2). This fact is evidently due to the higher energy of isomerization of the molecular ions of 4-azafluorenes from the a form to the b form as compared with 2-azafluorenes. This conclusion is in agreement with the lower probability of splitting out of a OH radical in the mass spectra of 4-azafluorenes obtained at 70 eV (Table 2).

As expected, the intensity of the peak of the  $[M - OH]^+$  ion is maximal in the mass spectra of compounds that contain methyl and nitro groups in the ortho position (III, VI, IX, and XII) as a result of the "ortho effect." The fragmentation of these compounds in the case of 6-nitro-3,7-dimethyl-2-azafluorene (III) is presented in Scheme 2.

Scheme 2



Further fragmentation of the  $[M - OH]^+$  ions due to ejection of a CO molecule is observed only in the case of substances with vicinally oriented methyl and nitro substituents and consists in the ejection of a CO molecule (Scheme 2), and this constitutes evidence for the absence of a bond between the oxygen atom of the nitro group and one of the carbon atoms of the aromatic ring in the  $[M - OH]^+$  ion of I, II, IV, and V (Scheme 1).

#### EXPERIMENTAL

Mononitro derivatives I-XII were obtained by nitration of the corresponding 2(4)-azafluorenes and the corresponding ketones with a mixture of nitric and sulfuric acids [10]. The deuteration of 2-nitrofluorene was carried out by refluxing it in an excess amount of a 0.03 N solution of  $CH_3ONa$  in  $CH_3OD$ . The purity and individuality of the substances were monitored by thin-layer chromatography (TLC) and data from the IR, UV, and PMR spectra.

The mass spectra were obtained with an MKh-1303 spectrometer with a system for direct introduction of the substances into the ion source at ionizing voltages of 70 and 20 V and injection temperatures of 30-50°C. The precise masses of the individual fragments were measured with an MS-30 spectrometer.

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#### REACTION OF 2-METHYLENE-3-OXOQUINUCLIDINE WITH WATER, ALCOHOLS, AND ORGANIC ACIDS

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2-Methylene-3-oxoquinuclidine (I) reacts with alcohols without acidic or alkaline catalysts to give 2-alkoxymethyl-3-oxoquinuclidines. In the case of protonation of I by weak acids (benzoic and barbituric acids) water molecules do not add to the double bond. Condensed heterocyclic systems that include the quinuclidine ring were obtained on the basis of 2-hydroxymethyl-3-hydroxy- $\Delta^2$ -dehydroquinuclidine.

According to the data in [1], the 2-methylene-3-oxoquinuclidine (I) base has moderate reactivity: It does not add alcohols and water to the methylene group in the absence of a catalyst. At the same time, it has been noted [2] that unsaturated ketone I reacts with water to give an addition product that has the 2-hydroxymethyl-3-hydroxy- $\Delta^2$ -dehydroquinuclidine (II) structure.

Continuing our study of the reactivity of 2-methylene-3-oxoquinuclidine (I) we studied the reaction of I with alcohols, water, and some organic acids. We found that unsaturated ketone I without the addition of acidic or alkaline catalysts is capable of forming addition products with lower alcohols, viz., 2-alkoxymethyl-3-oxoquinuclidines (III). The reactions take place at 20°C with time and depend substantially on the nucleophilicity of the alcohol. Of the four alcohols studied, viz., methanol, ethanol, isopropyl alcohol, and n-butyl alcohol, methanol adds most readily, while isopropyl alcohol adds with the greatest difficulty. The course of the reaction was monitored by means of gas-liquid chromatography (GLC). A mixture of I and the corresponding alcohol (40 equivalents each) was maintained at 20°C for four days; addition was observed only for methanol (IIIa:I = 0.44). In the course of the next

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