in heptane and water. IR spectrum: 1620 (C=C, C=N) and 1560 cm^{-1} (NO_2). UV spectrum, λ_{max} (log ε): 218 (4.1), 346 (4.2), and 432 nm (3.5). PMR spectrum ($CDCl_3$): 8.53 (1H, s, 2-H), 8.50 (1H, s, 6-H), 7.19 (1H, d, 4α), 5.19 (1H, d, 4β), and 3.01 ppm (6H, s, Me). Found: C 39.7; H 3.7; Br 29.4; N 15.6%. $C_9H_{10}BrN_3O_2$. Calculated: C 39.7; H 3.7; Br 29.4; N 15.4%.

4-Bromo-6-azaindole (V). A mixture of 0.75 g (2.8 mmole) of vinylpyridine IV and 1.0 g (18 mmole) of iron filings in 6 ml (105 mmole) of glacial acetic acid was refluxed for 40 min, after which the unchanged filings were removed by filtration, and the filtrate was diluted with 20 ml of water. The resulting solution was made alkaline to pH 8-9 with potassium carbonate and extracted with chloroform. The extract was dried with magnesium sulfate and vacuum evaporated to give 0.36 g (67%) of 4-bromo-6-azaindole (V) as yellowish crystals with mp 188-189°C (from benzene). The product was insoluble in heptane and water but soluble in ether, benzene, and chloroform and very soluble in acetone, ethyl acetate, alcohols, and hot benzene. IR spectrum: 1600 and 1550 cm^{-1} (C=C and C=N). UV spectrum, λ_{max} (log ε): 375 nm (3.7). PMR spectrum [d_6-DMSO-CCl_4 (1:1)]: 11.81 (1H, s, NH), 8.67 (1H, s, 7-H), 8.12 (1H, s, 5-H), 7.55 (1H, m, 2-H), and 6.44 ppm (1H, m, 3-H). Found: C 42.8; H 2.6; Br 40.3; N 14.2%. $C_7H_5BrN_2$. Calculated: C 42.7; H 2.6; Br 40.6; N 14.2%.

LITERATURE CITED

1. A. A. Prokopov and L. N. Yakhontov, Khim. Geterotsikl. Soedin., No. 4, 496 (1978).
2. A. A. Prokopov, L. F. Linberg, T. F. Vlasova, Yu. N. Sheinker, and L. N. Yakhontov, Khim. Geterotsikl. Soedin., No. 4, 492 (1978).
3. E. Koenigs and A. Fulde, Ber., 60, 2106 (1927).
4. O. Bremer, Ann., 529, 290 (1937).

MASS-SPECTROMETRIC STUDY OF 2- AND 4-AZAFLUORENONES

P. I. Zakharov, V. P. Zvolinskii, V. K. Shevtsov,
V. G. Pleshakov, T. S. Seitembetov, A. V. Varlamov,
G. A. Vasil'ev, and N. S. Prostakov

UDC 543.51:547.836

A mass-spectrometric study of 2- and 4-azafluorenones and their mono- and polymethyl derivatives showed that the presence of a methyl group in the benzene ring leads to a sharp increase in the relative intensity of the $[M - H]^+$ ion peak. In contrast to the fragmentation of 2- and 4-azafluorenes, the mass spectra of monomethyl-substituted compounds do not contain an $[M - CH_3]^+$ fragment; this is probably associated with expansion of the pyridine or benzene ring to a seven-membered ring in the step involving the formation of the molecular ion due to inclusion of the methyl group. The intensity of the $[M - CO]^+$ ion peak in the mass spectra of the 4-azafluorenones is higher by a factor of two with respect to the 2-azafluorenone isomers, and the $[M - HCN]^+$ and $[M - H, -HCN]^+$ ion peaks observed in the mass spectra of 2-azafluorenones are absent in them.

We have previously investigated the dissociative ionization of 2- and 4-azafluorenes and their derivatives [1, 2]. In the present research we examined the behavior of 2- and 4-azafluorenones under the influence of electron impact in order to ascertain the dependence of their fragmentation on the position of the nitrogen atom and on the character, position, and number of substituents in the azafluorenone ring. To solve this problem we investigated the mass spectra of compounds of this series (Table 1)(see scheme on page 81).

As in the case of 2- and 4-azafluorenes, the molecular-ion peak is the most intense peak in the mass spectra of I-XVI. The molecular ions (M^+) of unsubstituted 4- and 2-azafluorenones I and II have the highest stabilities (W_M) (Table 2). The presence of a methyl

---

Patrice Lumumba International-Friendship University, Moscow 117923. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 89-95, January, 1979. Original article submitted October 21, 1977; revision submitted June 19, 1978.

0009-3122/79/1501-0078$07.50

TABLE 1. Mass Spectra of 2- and 4-Azafluorenones I-XVI

Compound	m/e values (relative intensities of the ion peaks in percent of the maximum peak)*
1	2
I	182 (12,8); 181 (100); 180 (1,8); 154 (6,5); 153 (52,0); 152 (1,0); 127 (11,7); 126 (17,9); 125 (1,7); 102 (1,0); 100 (1,5); 99 (1,6); 98 (1,1); 77 (2,2); 76 (2,5); 75 (2,1); 74 (1,8); 63 (2,3); 51 (1,9)
II	182 (13,1); 181 (100); 180 (2,8); 154 (10,1); 153 (25,2); 152 (4,6); 151 (1,5); 126 (2,3); 125 (5,2); 101 (1,2); 100 (2,8); 99 (3,7); 98 (2,8); 77 (4,0); 76 (5,2); 75 (4,1); 74 (4,1); 63 (6,2); 62 (1,9); 51 (2,2)
III	196 (14,7); 195 (100); 194 (1,8); 168 (1,1); 167 (8,2); 166 (9,1); 165 (2,2); 164 (1,4); 141 (2,0); 140 (8,7); 139 (9,0); 138 (2,1); 137 (1,0); 127 (1,4); 126 (1,1); 125 (1,8); 115 (1,6); 114 (2,9); 113 (2,7); 102 (2,0); 101 (1,3); 100 (1,1); 99 (1,7); 98 (1,5); 89 (1,9); 88 (1,8); 87 (2,3); 86 (1,4); 77 (1,5); 76 (2,4); 75 (2,3); 74 (2,7); 70 (1,2); 69 (1,0); 64 (1,6); 63 (4,5); 66 (2,2); 51 (2,6)
IV	196 (15,1); 195 (100); 194 (15,1); 168 (7,0); 167 (53,8); 166 (19); 165 (4,1); 164 (2,2); 141 (3,0); 140 (12,0); 139 (15,5); 138 (2,2); 137 (1,0); 127 (1,2); 115 (1,8); 114 (2,2); 113 (2,3); 99 (1,0); 90 (1,1); 89 (2,4); 88 (1,2); 87 (2,1); 86 (2,0); 84 (1,0); 83 (1,2); 76 (1,0); 75 (2,2); 74 (2,1); 71 (1,1); 70 (1,5); 69 (1,5); 64 (1,0); 63 (3,4); 62 (2,2); 51 (4,0)
V	196 (15,2); 195 (100); 194 (5,3); 168 (5,1); 167 (39,0); 166 (17); 165 (3,5); 164 (2,4); 140 (10,1); 139 (14,4); 138 (2,1); 137 (1,2); 127 (1,2); 126 (1,2); 116 (1,8); 115 (2,4); 114 (2,5); 113 (2,4); 99 (1,2); 98 (1,5); 89 (2,4); 88 (1,2); 87 (2,1); 86 (2,0); 83 (1,3); 77 (1,0); 76 (1,2); 75 (1,7); 74 (1,7); 70 (1,9); 69 (1,7); 63 (3,5); 62 (1,7); 51 (1,9)
VI	196 (15,1); 195 (100); 194 (1,6); 168 (3,2); 167 (4,1); 166 (5,4); 141 (1,2); 140 (8,1); 139 (11,3); 138 (1,4); 127 (1,9); 126 (6,1); 125 (2,7); 115 (1,0); 114 (1,2): 113 (1,5); 101 (1,1); 100 (1,4); 99 (1,9); 98 (1,7); 89 (1,1); 88 (1,1); 87 (2,4); 86 (1,6); 77 (1,6); 76 (3,5); 75 (4,0); 74 (4,0); 70 (1,4); 69 (1,0); 63 (5,4); 62 (1,9); 51 (2,2)
VII	210 (16,1); 209 (100); 208 (3,1); 182 (1,2); 181 (5,4); 180 (6,6); 168 (1,6); 167 (1,4); 166 (2,6); 165 (1,4); 164 (1,6); 154 (1,6); 153 (4,0); 152 (5,2); 151 (2,0); 141 (1,4); 140 (5,4); 139 (11,1); 138 (1,6); 137 (1,0); 128 (1,0); 127 (1,6); 126 (1,4); 115 (1,8); 114 (1,6); 113 (2,1); 99 (1,2); 98 (1,0); 91 (1,1); 90 (2,1); 89 (2,0); 88 (1,2); 87 (1,8); 86 (1,1); 77 (2,0); 76 (4,1); 75 (2,0); 74 (1,6); 71 (1,2); 69 (1,4); 64 (1,2); 63 (3,1); 62 (2,1); 57 (1,6); 56 (1,2); 55 (1,4)
VIII	210 (16,2); 209 (100); 208 (7,5); 207 (1,0); 194 (2,2); 182 (1,5); 181 (7,8); 180 (13,5); 179 (1,8); 178 (1,4); 168 (1,0); 167 (5,5); 166 (7,2); 165 (2,0); 164 (2,6); 153 (6,5); 152 (8,3); 151 (4,0); 150 (1,4); 141 (2,3); 140 (8,6); 139 (15,0); 138 (2,0); 137 (1,1); 128 (1,4); 127 (2,6); 126 (1,9); 115 (2,3); 114 (1,7); 113 (2,6); 100 (1,1); 99 (1,1); 91 (1,1); 90 (2,3); 89 (3,1); 88 (1,4); 87 (2,6); 86 (1,7); 77 (2,6); 76 (3,8); 75 (3,1); 74 (2,3); 69 (1,1); 65 (1,1); 64 (2,0); 63 (4,6); 62 (2,3); 51 (2,6)
IX	224 (18,1); 223 (100); 222 (7,4); 221 (1,5); 208 (4,3); 196 (2,1); 195 (8,1); 194 (11,8); 193 (2,5); 192 (1,0); 182 (1,4); 181 (5,0); 180 (8,7); 179 (1,9); 178 (1,9); 177 (1,2); 168 (1,7); 167 (3,1); 166 (2,8); 165 (7,4); 164 (1,9); 163 (1,6); 154 (2,2); 153 (8,1); 152 (16,7); 151 (4,0); 150 (1,4); 149 (1,2); 141 (1,5); 140 (2,5); 139 (3,5); 128 (2,3); 127 (2,5); 126 (1,5); 115 (3,4); 113 (1,0); 112 (1,2); 102 (1,2); 97 (3,2); 90 (2,4); 89 (2,6); 88 (1,2); 87 (1,6); 84 (1,2); 83 (2,8); 82 (3,4); 81 (1,1); 77 (3,1); 76 (4,3); 75 (2,5); 74 (1,5); 70 (1,3); 65 (1,3); 64 (1,4); 63 (4,1); 62 (1,5); 52 (1,6); 51 (3,1)
X	224 (18,1); 223 (100); 222 (10,1); 208 (9,8); 196 (2,6); 195 (8,6); 194 (12,5); 193 (11,6); 182 (1,3); 181 (6,1); 180 10,5); 179 (2,2); 178 (2,1); 177 (1,1); 168 (2,1); 167 (3,6); 166 (3,3); 165 (7,5); 164 (1,6); 163 (1,3); 155 (1,3); 154 (2,3); 153 (8,2); 152 (13,3); 151 (4,1); 150 (1,3); 141 (4,6); 140 (5,3); 139 (3,6); 128 (2,0); 127 (2,0); 126 (1,2); 115 (3,6); 98 (1,0); 97 (2,9); 89 (1,6); 87 (1,3); 84 (1,4); 83 (1,8); 82 (2,1); 76 (2,1); 75 (2,6); 74 (1,1); 70 (1,0); 69 (1,3); 63 (2,6); 51 (2,1)
XI	272 (20,0); 271 (100); 270 (76,1); 269 (9,0); 257 (4,8); 256 (25,0); 243 (3,8); 242 (5,2); 241 (8,6); 240 (6,0); 227 (2,3); 226 (6,1); 225 (1,9); 224 (1,0); 216 (1,2); 214 (4,5); 213 (2,1); 212 (2,5); 203 (1,1); 202 (3,3); 201 (4,1); 200 (5,2); 199 (1,2); 189 (1,6); 176 (1,5); 175 (1,4); 174 (1,0); 164 (1,0); 163 (1,2); 151 (1,1); 150 (1,2); 149 (1,1); 141 (2,3); 140 (1,1); 139 (2,3); 126 (1,1); 125 (1,0); 121 (2,5); 115 (1,9); 114 (2,3); 113 (1,3); 102 (1,7); 101 (2,5); 100 (2,8); 99 (1,1); 88 (2,5); 87 (1,5); 77 (1,5); 76 (1,3); 75 (1,9); 74 (1,1); 69 (1,5); 63 (1,4); 51 (1,5)
XII	272 (20,9); 271 (100); 270 (17,2); 269 (3,1); 256 (2,2); 243 (3,0); 242 (4,1); 241 (9,1); 240 (3,1); 227 (1,8); 226 (3,0); 216 (1,5); 215 (7,5); 214 (2,2); 213 (2,2); 202 (1,0); 201 (1,6); 201 (1,0), 189 (1,5); 188 (1,0); 166 (1,0); 165 (1,5); 164 (1,5); 141 (1,4); 140 (4,5); 139 (7,5); 127 (1,4); 126 (1,8); 125 (2,8); 121 (3,0); 115 (2,9); 114 (3,1); 113 (2,9); 103 (1,3); 102 (4,5); 101 (1,8); 100 (1,6); 99 (1,7); 88 (1,8); 87 (1,5); 86 (1,5); 84 (3,1); 77 (2,9); 76 (2,9); 75 (3,0); 74 (2,6); 63 (3,0); 51 (2,9)

TABLE 1 (continued)

1	2
XIII	272 (20,4); 271 (100); 270 (49,2); 269 (6,0); 256 (10,1); 255 (10,1); 243 (1,3); 242 (2,0); 241 (3,4); 240 (3,7); 228 (1,3); 227 (3,3); 226 (1,3); 225 (1,0); 214 (2,6); 213 (1,6); 212 (2,0); 202 (2,0); 201 (2,3); 200 (3,3); 189 (1,1); 139 (2,0); 115 (1,0); 114 (1,3); 113 (1,0); 101 (1,3); 100 (1,6); 89 (1,0); 88 (1,3); 87 (1,0); 77 (1,0); 76 (1,1); 75 (1,2); 63 (1,2); 51 (1,3)
XIV	258 (19,5); 257 (100); 256 (21,6); 255 (2,0); 229 (5,5); 228 (10,8); 227 (8,8); 226 (2,4); 203 (1,4); 202 (3,0); 201 (3,7); 200 (2,9); 152 (1,9); 151 (1,0); 127 (1,5); 126 (4,8); 125 (2,0); 115 (1,2); 114 (5.1); 113 (1,5); 102 (4,6); 101 (3,4); 100 (2,7); 99 (1,5); 88 (1,4); 87 (1,5); 77 (1,7); 76 (2,7); 75 (2,2); 74 (1,7); 63 (1,4); 51 (1,9)
XV	334 (23,9); 333 (100); 332 (38,5); 331 (4,6); 330 (1,6); 305 (1,6); 304 (4,6); 303 (4,0); 302 (4,6); 301 (2,4); 278 (1,0); 277 (1,8); 276 (2,6); 257 (1,1); 256 (5,0); 255 (3,2); 254 (1,3); 228 (1,2); 227 (2,7); 226 (1,4); 225 (1,0); 216 (1,1); 215 (2,4); 202 (1,2); 201 (3,2); 200 (2,8); 199 (3,6); 189 (1,0); 165 (1,8); 158 (1,6); 157 (1,8); 155 (2,2); 152 (3,4); 151 (4,6); 150 (1,6); 126 (1,0); 125 (1,1); 102 (1,1); 101 (1,0); 100 (1,1); 77 (1,4); 76 (1,0); 75 (1,0); 57 (1,0)
XVI	334 (24,5); 333 (100); 332 (33,0); 331 (1,5); 305 (1,1); 304 (2,1); 303 (4,4); 302 (4,9); 301 (2,1); 277 (2,5); 276 (2,4); 257 (1,0); 256 (4,6); 255 (5,4); 254 (1,0); 228 (1,3); 227 (4,0); 226 (1,3); 225 (1,1); 215 (1,6); 203 (1,3); 202 (3,0); 201 (2,7); 200 (4,5); 199 (1,3); 176 (1,0); 175 (1,0); 152 (1,9); 151 (5,0); 150 (2,0); 149 (1,1); 139 (1,9); 138 (3,4); 137 (1,6); 126 (1,6); 125 (1,8); 113 (1,0); 101 (1,0); 100 (1,4); 77 (2,4); 76 (1,2); 75 (1,3); 63 (1,5); 57 (1,5); 51 (2,1)

---

*The ions with peak intensities >1% of the maximum peak are presented in the table.

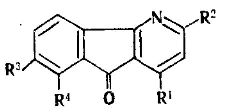
TABLE 2. Stabilities of the Molecular Ions (W_M) and Intensities of the Peaks of the Principal Characteristic Fragments (in percent of the maximum peak) in the Mass Spectra of 2- and 4-Azafluorenones

Compound	W_M	M^{++}	$[M-H]^+$	$[M-CH_3]^+$	$[M-HCN]^+$	$[M-CH_3CN]^+$	$[M-CO]^+$	$[M-CO, -H]^+$ or $[M-H, -CO]^+$	$[M-C_6H_5]^+$	$[M-CO, -HCN]^+$
I	0,47	1,8	1,8	—	—	—	52,0	1,0	—	2,1
II	0,48	1,4	2,8	—	10,1	—	25,2*	4,6	—	2,3
III	0,46	1,3	1,8	—	—	—	8,2	9,1	—	8,7
IV	0,48	2,9	15,1	—	—	—	53,8	19,0	—	12.0
V	0,45	3,1	5,3	—	—	—	39,0	17,0	—	10,1
VI	0,36	2,0	1,6	—	3,2	—	4,1	5,4	—	8,1
VII	0,36	2.9	3,1	0,8	1,2	1,6	5,4	6,6	—	1,6
VIII	0,36	1,5	7,5	2,2	1,5	1,0	7,8	13,5	—	0,9
IX	0.29	3,0	7,4	4,3	2,1	1,4	8,1	11,8	—	1,7
X	0,29	2,8	10,1	9,8	2,6	1,3	8,6	12,5	—	2,1
XI	0,32	7,5	76,1	25,0	—	—	3,8	5,2	—	1,2
XII	0,35	7,0	17,2	2,2	—	—	3,0	4,1	—	1,5
XIII	0,37	7,2	49,2	10,1	—	1,2	1,3	2,0	—	2,0
XIV	0,36	3,8	21,6	—	—	—	5,5	10.8	—	3,0
XV	0,30	11,1	38,5	—	—	—	1,6	4,6	1,1	1,0
XVI	0,28	13,0	33,0	—	—	—	1,1	2,1	4,6	0,8

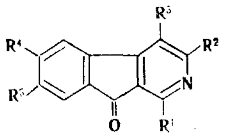
---

*A different value (58.4%) of the intensity of the peak of this ion is indicated in [10]. The value presented in Table 2 was reproduced with an accuracy of ±6% in the mass spectra of 2-azafluorene that we obtained with different types of spectrometers (MKh-1303, MKh-1309, LKV-9000, and MS-30).

group in the 4-azafluorenone ring of III-V has virtually no effect on the W_M value, while the introduction of a methyl group in the 2-azafluorenone molecules (VI) lowers the stability of M^+ appreciably. At the same time, the stabilities of the molecular ions remain virtually unchanged on passing from monomethyl-substituted 2-azafluorenone VI to dimethyl- and trimethyl-substituted ketones VII-X. The presence of phenyl substituents in XI-XVI reduces the W_M values sharply. The relative intensities of the peaks of the doubly charged M^{2+} ions of unsubstituted azafluorenones I and II are approximately identical (Table 2) and are com-



I, III–V, XI, XII, XIV, XV



II, VI–X, XIII, XVI

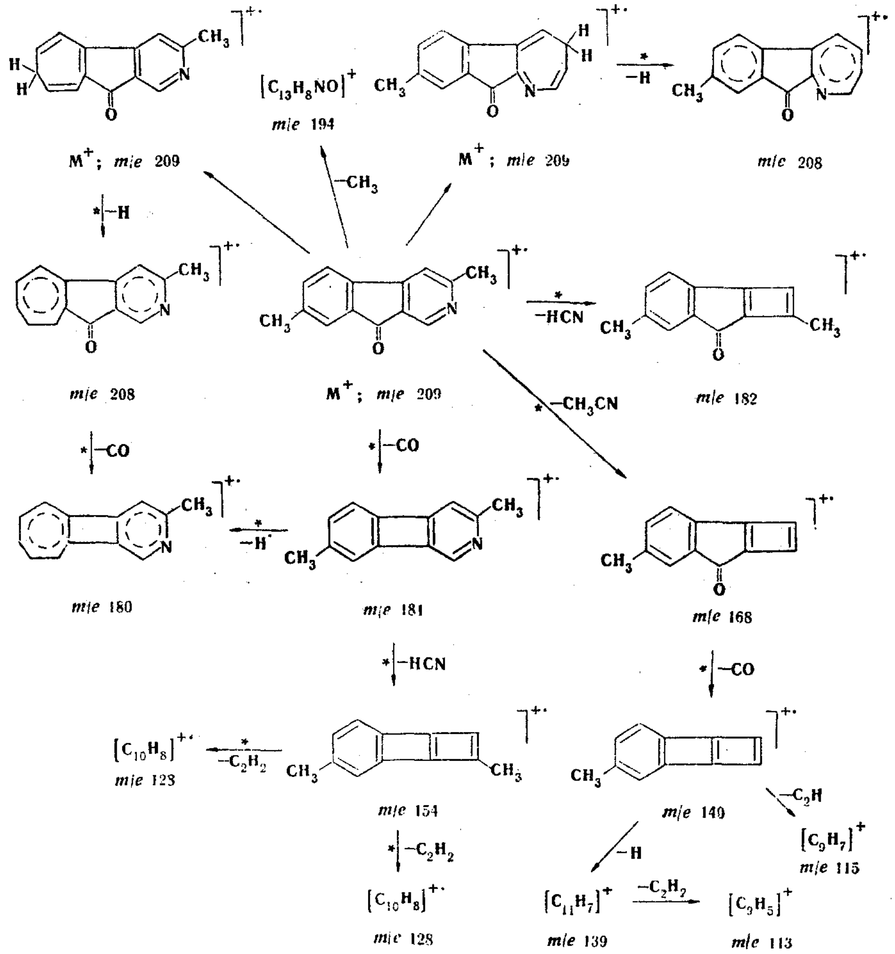
I $R^{1-4}=H$; III $R^1=CH_3$, $R^{2,3,4}=H$; IV $R^3=CH_3$, $R^{1,2,4}=H$; V $R^4=CH_3$, $R^{1-3}=H$; XI $R^1=C_6H_5$, $R^2=CH_3$, $R^{3,4}=H$; XII $R^1=CH_3$, $R^2=C_6H_5$, $R^{3,4}=H$; XIV $R^2=C_6H_5$, $R^{1,3,4}=H$; XV $R^{1,2}=C_6H_5$, $R^{3,4}=H$

II $R^{1-5}=H$; VI $R^2=CH_3$, $R^{1,3,4,5}=H$; VII $R^{1,2}=CH_3$, $R^{3,4,5}=H$; VIII $R^{2,5}=CH_3$, $R^{1,3,4}=H$; IX $R^{1,3,4}=CH_3$, $R^{2,5}=H$; X $R^{1,3,5}=CH_3$, $R^{2,4}=H$; XIII $R^1=C_6H_5$, $R^2=CH_3$, $R^{3-5}=H$; XVI $R^{1,2}=C_6H_5$, $R^{3,4,5}=H$

parable to the values observed for III and VI, which contain a methyl group in the pyridine ring. The methyl group in the benzene ring of 4-azafluorenones IV and V increases the relative intensity of the M^{2+} ion peak by a factor of more than 1.5. The presence of one or two phenyl substituents in the pyridine ring increases the intensity of the peak of the doubly charged M^{2+} ion by a factor of two to eight.

A low-intensity $[M - H]^+$ ion peak, the formation of which can be explained by elimination of a hydrogen atom from the ortho position of the pyridine ring, is observed in the mass spectra of unsubstituted 2- and 4-azafluorenones I and II. The intensity of the $[M - H]^+$ ion peak increases sharply in the fragmentation of methyl derivatives IV, V, and VII-X, while the presence of a methyl group in the pyridine ring of the III and VI molecules has virtually no effect on its relative magnitude. The elimination of a hydrogen atom from the methyl group bonded to the six-membered aromatic or heteroaromatic ring is accompanied by ring expansion to a seven-membered ring [4, 5]. The above-noted fact consequently constitutes evidence in favor of the easier formation of a hydrotropylium ring as compared with a hydroazatropylium ring.

Scheme



We will demonstrate below that this process evidently takes place via the step involving the formation of a molecular ion (see the scheme). The presence of a CH_3 group in the 7 or 8 position of the 4-azafluorenone ring (IV and V) leads to $[M - H]^+$ ion peaks with markedly different relative intensities (Table 2). The relative intensity of the $[M - H]^+$ ion peak in the mass spectrum of ketone IV is higher by a factor of almost three than in the spectrum of V, and this makes it possible to reliably distinguish between these structural isomers. The presence of one or two phenyl groups in the pyridine ring of the azafluorenones (XI-XVI) is responsible for the sharp increase in the intensity of the peak of the $[M - H]^+$ fragment. In the case of XII-XVI this fact can be explained by cyclization of the ortho carbon atom of the α-phenyl group at the nitrogen atom of the pyridine ring. However, in the case of the fragmentation of ketone XI, which does not contain an α-phenyl group, the relative intensity of the $[M - H]^+$ ion peak is higher by a factor of two than in the mass spectra of XII-XVI. This fact is probably a distinctive feature of the dissociative ionization of 4-azafluorenones that contain a methyl substituent in the α position relative to the nitrogen atom, since a similar effect is not observed in the fragmentation of the similarly constructed XIII.

The mass spectra of monomethyl-substituted 4- and 2-azafluorenones III-VI do not contain the peak of an $[M - CH_3]^+$ fragment; this is a characteristic feature of their fragmentation as compared with the dissociative ionization of monomethyl-substituted 2- and 4-azafluorenes [1, 2]. An increase in the number of methyl groups in the azafluorene ring leads to the appearance of an $[M - CH_3]^+$ ion (Table 2 and the scheme above). This makes it possible to assume that the expansion of the pyridine or benzene ring to a seven-membered ring with the inclusion of the carbon atom of the methyl group in it occurs in the step involving the formation of the molecular ion. The introduction of a phenyl group in the pyridine ring of the azafluorenone system increases the relative intensity of the $[M - CH_3]^+$ ion peak considerably only in the case of 4-azafluorenone XI (Table 2). However, the increased intensity of the $[M - CH_3]^+$ ion peak in the mass spectrum of XI is probably due to the presence of a methyl group in the α position of 4-azafluorenone XI rather than to the effect of the phenyl substituent.

The formation of an $[M - C_6H_5]^+$ fragment is not observed when there is one phenyl substituent in the pyridine ring of XI-XIV, whereas in the mass spectra of diphenyl-substituted XV and XVI the peak of this ion has appreciable intensity, and its formation is confirmed by the metastable ion $m^* \approx 196.8$ (Table 2).

A peculiarity of the dissociative ionization of 4-azafluorenones in contrast to 4-azafluorenes [2] is the absence of $[M - HCN]^+$ and $[M - H, -HCN]^+$ fragments, although metastable ions corresponding to $M^+ \rightarrow [M - HCN]^+$ and $[M - H]^+ \rightarrow [M - H, -HCN]^+$ transitions are formed in the fragmentation of these compounds. Peaks of $[M - HCN]^+$ and $[M - H, -HCN]^+$ ions and peaks of metastable ions that confirm their genetic relationship are observed in the mass spectra of the isomeric 2-azafluorenones. The compositions of the fragment ions were established by means of the high-resolution mass spectra (Table 3 and the scheme above).

A general feature of the dissociative ionization of I-XVI is the elimination of a CO molecule by their molecular ions; in this case the intensity of the resulting $[M - CO]^+$ fragment depends on both the position of the nitrogen atom in the azafluorenone ring and on the position and character of the substituent in the benzene or pyridine ring. It is apparent from a comparison of the mass spectra of the isomeric 4- and 2-azafluorenones (Table 2) that the presence of a nitrogen atom in the 4 position increases the relative intensity of the peak of the $[M - CO]^+$ fragment by a factor of two. These data indicate the higher stability of the $[M - CO]^+$ ion in the case of 4-azafluorenones as compared with 2-azafluorenones, which is also confirmed by the formation of a metastable peak with a flat apex ($E = 0.3$ eV) [6] for the $M^+ \rightarrow [M - CO]^+$ transition in the mass spectrum of unsubstituted 4-azafluorenone II.

There is an appreciable difference in the fragmentation of I-XVI with respect to the probability of the formation of $[M - H, -CO]^+$ and $[M - CO, -H]^+$ ions; this is due to the position of the nitrogen atom in the azafluorenone ring and the presence of a substituent in its pyridine or benzene ring. Thus in the mass spectrum of 2-azafluorenone II the relative intensity of the $[M - H, -CO]^+$ ion peak with m/e 152 (the $[M - H]^+ \rightarrow [M - H, -CO]^+$ transition, $m^* \approx 128.4$) is lower by a factor of 4.6 than in the spectrum of 4-azafluorenone I (Table 2). This can be explained by the fact that the $[M - CO]^+ - H^\cdot$ process makes a substantial contribution to the formation of $[M - HCO]^+$ ions in the case of II; this is in good

TABLE 3. Data from the High-Resolution Mass Spectra of II, III, VII, X, and XV in the Region of Medium m/e Values

Compound	Masses		Ionic composition	Compound	Masses		Ionic composition
	observed	calc.			observed	calc.	
II	154,0415	.0419	$C_{11}H_6O$	VII	181,0660	.0653	$C_{13}H_9O$
	153,0573	.0577	$C_{11}H_7N$		168,0570	.0575	$C_{12}H_8O$
	152,0498	.0499	$C_{11}H_6N$		154,0779	.0782	$C_{12}H_{10}$
	126,0466	.0469	$C_{10}H_6$		153,0700	.0704	$C_{12}H_9$
	125,0398	.0391	$C_{10}H_5$		140,0628	.0625	$C_{11}H_8$
	101,0386	.0391	C_8H_5		115,0545	.0547	C_9H_7
	99,0240	.0234	C_8H_3	X	196,0880	.0888	$C_{14}H_{12}O$
	98,0160	.0156	C_8H_2		195,1050	.1048	$C_{14}H_{13}N$
III	167,0728	.0734	$C_{12}H_9N$		194,0960	.0969	$C_{14}H_{12}N$
	166,0660	.0656	$C_{12}H_8O$		182,727	.0731	$C_{13}H_{10}O$
	140,0628	.0625	$C_{11}H_8$		181,0648	.0653	$C_{13}H_9O$
	139,0550	.0547	$C_{11}H_7$		168,0943	.0939	$C_{13}H_{12}$
	127,0552	.0547	$C_{10}H_7$		154,0780	.0782	$C_{12}H_{10}$
	126,0470	.0469	$C_{10}H_6$	XV	305,1195	.0204	$C_{23}H_{15}N$
	115,0542	.0547	C_9H_7		304,1118	.1127	$C_{23}H_{14}N$
					278,1086	.1096	$C_{22}H_{14}$
					256,0769	.0763	$C_{18}H_{10}O$

agreement with the stability of the $[M - CO]^+$ ion in the mass spectra of I and II. The primary formation of an $[M - CO, -H]^+$ ion with m/e 166 ($m^* \approx 165$) rather than an $[M - H, -CO]^+$ fragment is observed in the case of the fragmentation of monomethyl-substituted 4- and 2-azafluorenones III-VI. The intensity of the $[M - CO, -H]^+$ ion peak is higher than the intensity of the peak of the $[M - CO]^+$ parent fragment when there is a CH_3 group in the pyridine ring rather than in the benzene ring of the azafluorenone system (III and VI, Table 2). This result can be explained by the partial formation of an ion with m/e 166 in the case of III and VI from the $[M - H]^+$ ions, for which the corresponding metastable ion constitutes unambiguous evidence. The metastable ion corresponding to this process is absent in the mass spectra of IV and V, which contain a methyl group in the benzene ring.

Two processes, $[M - CO]^+ - H^\bullet$ and $[M - H]^+ - CO$, are observed in the fragmentation of polymethyl-substituted azafluorenones VII-X, as evidenced by the corresponding metastable ion peaks (see the scheme above). However, a metastable transition is observed only for the process $[M - H]^+ \rightarrow [M - HCO]^+$ in the case of the fragmentation of 2- and 4-azafluorenones that contain a phenyl group in the pyridine ring of the azafluorenone system (X-XVI).

A peculiarity of the dissociative ionization of unsubstituted 4- and 2-azafluorenones I and II is the formation of $[M - CO, -CN]^+$ ions (Table 3); this process is not observed in the mass spectra of substituted 2- and 4-azafluorenones III-XVI. At the same time, the peak of the $[M - CO, -HCN]^+$ fragment is present in the mass spectra of both unsubstituted and monomethyl-, polymethyl-, and polyphenyl-substituted 2- and 4-azafluorenones. In the case of III-VI and VIII-X the formation of this fragment is easily explained by the successive elimination of CO and HCN molecules. However, the appearance of the $[M - CO, -HCN]$ fragment in the mass spectra of VII, XI, and XIII (Table 3) is evidently due to expansion of the pyridine ring to a hydroazatropylium ring. In the case of 1,3-dimethyl-substituted 2-azafluorenone VII the loss of an HCN molecule is possible from both the M^+ ion and the $[M - CO]^+$ ion, while loss of an HCN molecule is possible only from the $[M - CO]^+$ ion in the case of monophenyl-substituted III-VI (Tables 2 and 3). The formation of an $[M - CO, -HCN]^+$ fragment in the fragmentation of diphenyl-substituted azafluorenones XV and XVI (Tables 2 and 3) constitutes evidence for the occurrence of complex rearrangement processes in the step involving the formation of an $[M - CO]^+$ ion. The subsequent fragmentation of ions that do not contain a nitrogen atom in the mass spectra of I-XVI proceeds through ejection of C_2H_2, C_3H_3, and C_4H_4 particles.

EXPERIMENTAL

The mass spectra of I-XVI were measured with an MKh-1303 spectrometer with direct introduction of the samples into the ion source at ionizing voltages of 20 and 70 V and 30°C. The high-resolution mass spectra were obtained with a JMS-01SG-2 spectrometer with an automatic system for information processing. Compounds I-XI, XIII, XV, and XVI were synthesized by the methods described in [7-9]. Compounds XII-XIV were obtained for the first time by the method in [8]: XII had mp 132-133°C (from heptane-ethyl acetate) and was obtained in 48% yield, and XIV had mp 146-147°C (from heptane-ethyl acetate) and was obtained in 59% yield. The purity and individuality of the compounds were monitored by thin-layer chromatography and the IR, UV, and PMR spectral data.

LITERATURE CITED

1. V. P. Zvolinskii, P. I. Zakharov, V. K. Shevtsov, V. K. Pleshakov, A. V. Varlamov, G. A. Vasil'ev, K. I. Furnaris, and N. S. Prostakov, Khim. Geterotsikl. Soedin., No. 1, 101 (1977).
2. V. P. Zvolinskii, P. I. Zakharov, V. K. Shevtsov, A. V. Varlamov, V. G. Pleshakov, G. A. Vasil'ev, and N. S. Prostakov, Khim. Geterotsikl. Soedin., No. 2, 246 (1978).
3. M. Marx and C. Djerassi, J. Amer. Chem. Soc., 90, 678 (1968).
4. F. W. McLafferty and J. Winkler, J. Amer. Chem. Soc., 96, 5182 (1977).
5. P. B. Terent'ev, R. A. Kheml'nitskii, I. S. Khromov, A. N. Kost, I. P. Gloriozov, and M. Islam, Zh. Org. Khim., 6, 606 (1970).
6. R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Zester, Metastable Ions, Amsterdam (1973), p. 60.
7. N. S. Prostakov, V. G. Pleshakov, T. S. Seitembetov, D. A. Fesenko, L. Olubazho Onasan'ya, Zh. Org. Khim., 13, 1484 (1977).
8. N. S. Prostakov, A. V. Varlamov, G. A. Vasil'ev, O. G. Kesarev, and G. A. Urbina, Khim. Geterotsikl. Soedin., No. 1, 124 (1977).

9. N. S. Prostakov, A. A. Obynochnyi, L. A. Gaivoronskaya, L. M. Kirillova, and V. P. Zvolinskii, Khim. Geterotsikl. Soedin., No. 12, 1664 (1972).
10. C. Mayor and C. Wentrup, J. Amer. Chem. Soc., 24, 7467 (1975).

SYNTHESIS OF SUBSTITUTED 3-BENZOYL-1,2,3,4-TETRAHYDROPYRIDINES BY THE ADDITION OF PRIMARY AMINES TO 1,3,5-TRIPHENYL-2-METHYLIDENE-1,5-PENTANEDIONE*

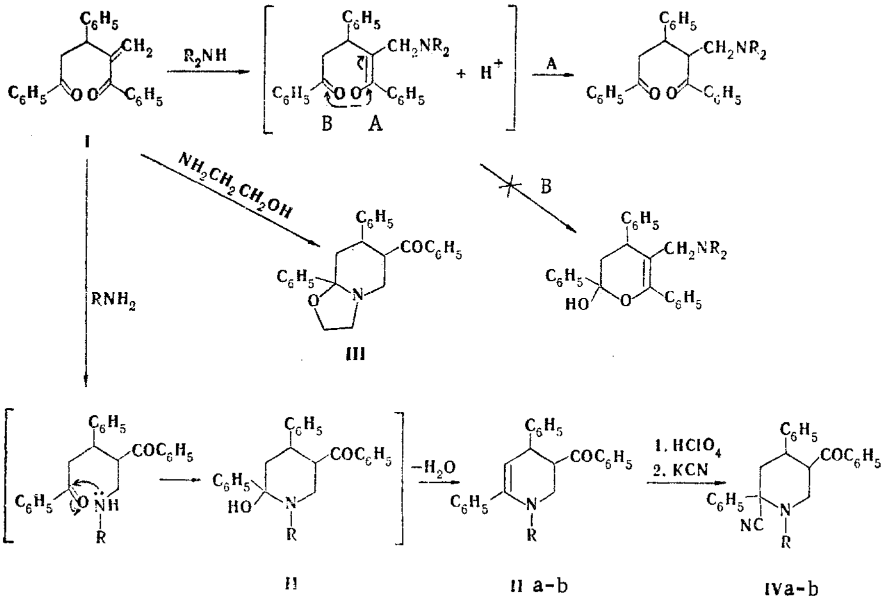
G. V. Pavel' and M. N. Tilichenko

UDC 547.442.5'233'824

1,3,5-Triphenyl-2-methylidene-1,5-pentanedione adds methyl- and cyclohexylamines to give, respectively, 1-methyl- and 1-cyclohexyl-3-benzoyl-4,6-diphenyl-1,2,3,4-tetrahydropyridines; 1-aza-3-benzoyl-4,6-diphenyl-7-oxabicyclo[4.3.0]nonane is obtained with ethanolamine.

Only secondary amines have been added to aryl-aliphatic α-methylidene-1,5-diketones [2]; in this case, of the two possible reaction pathways A and B, only pathway A was observed. The electrophilicity of the carbon atom of the aryl-aliphatic carbonyl group is evidently insufficient for the realization of pathway B. Thus reaction via pathway B proceeds successfully in the case of semicyclic α-methylidene-1,5-diketones, in which the more electrophilic alicyclic carbonyl group acts as a source of enolate ion [3]. The nucleophilicity of the nitrogen atom in the $-CH_2NR_2$ fragment is higher than that of the enol oxygen atom, but this cannot lead to a valence-saturated stable N,O-hemiacetal of the II form, as in the addition of a primary amine.

It therefore seemed of interest to test primary amines — methylamine, cyclohexaylamine, and ethanolamine — in the reaction with ketone I. As a result, we obtained 1-methyl- and 1-cyclohexyl-3-benzoyl-4,6-diphenyl-1,2,3,4-tetrahydropyridines (IIa,b) and 1-aza-3-benzoyl-4,6-diphenyl-7-oxabicyclo[4.3.0]nonane (III) in good yields.



II, IV a R=CH_3; b R=cyclo-C_6H_{11}

---

*Communication 33 from the series "Reactions of 1,5-Diketones." See [1] for communication 32.

Far Eastern State University, Vladivostok 690600. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 96-97, January, 1979. Original article submitted April 4,1978.

0009-3122/79/1501-0085$07.50