in the presence of DBr is shifted to 430 cm^{-1}; the corresponding shift of this band is considerably smaller in the case of AD^+Cl^- (Fig. 2). The electronic structure of the acridinium ion evidently experiences more profound perturbations in the case of complexing with HBr than in the case of complexing with HCl.

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CYCLIZATION PROCESSES IN THE FRAGMENTATION OF THE MOLECULAR IONS OF N-(AZA-9-FLUORENYLIDENE)AMINES

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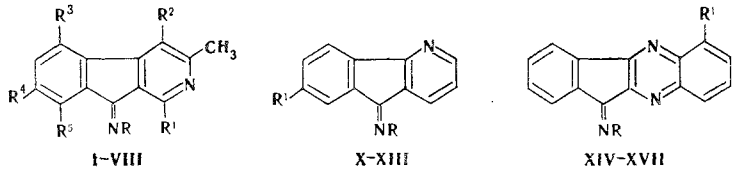
The dissociative ionization of 17 Schiff bases obtained from 2(4)-azafluorenones and linear benzo-1,4-diazafluorenone was investigated. The intensities of the $[M - H]^+$ and $[M - CH_3]^+$ ion peaks depend on the structures of the ketone and imine parts of the molecules and are determined by the possibility of the occurrence of cyclization processes with the participation of their structural elements. The fragmentation of the investigated azomethines is also accompanied by the elimination of an NR particle and a hydrocarbon R radical by the molecular ions. This process takes place most easily when a cyclohexyl substituent is present in the imine fragment. In contrast to previously investigated azomethines, the loss of an HCN molecule by the M^+ ion occurs without participation of the exocyclic nitrogen atom.

Research on the dissociative ionization of a new group of azomethines of the heterocyclic type, viz., N-(aza-9-fluorenylidene)amines, was begun in [1]. It was proposed that the anomalously high intensities of the peaks of some fragments in their mass spectra can be explained by cyclization processes during elimination of H and CH_3 radicals by the molecular ions. To ascertain the dependence of the direction of cyclization on the position and number of ring nitrogen atoms and on the position of the substituents in the azafluorenylidene and aryl(cyclohexyl)imine fragments of azomethines of this type we investigated the dissociative ionization of methyl-substituted and unsubstituted azomethines, viz., derivatives of 2-azafluorenes (I-VIII), N-(1,4,7-trimethyl-2-aza-9-fluoroenylidene)mesidine (IX), 4-azafluorenones (X-XIII), and 5,11-diazabenzo[b]fluorenes (XIV-XVII) (Table 1).



I-VIII X-XIII XIV-XVII

I $R=C_6H_5$, $R^1—R^5=H$; II $R=C_6H_5$, $R^4=CH_3$, $R^1—R^3$, $R^5=H$; III $R=o\text{-}CH_3C_6H_4$, $R^1—R^5=H$; IV $R=m\text{-}CH_3C_6H_4$, $R^1—R^5=H$; V $R=p\text{-}CH_3C_6H_4$, $R^1—R^5=H$; VI $R=p\text{-}CH_3C_6H_4$, $R^1=CH_3$, $R^1—R^5=H$; VII $R=p\text{-}CH_3C_6H_4$, R^3, $R^5=CH_3$, R^2, $R^4=H$; VIII R= 2-fluorenyl, $R^1—R^5=H$; X R=2- fluorenyl, $R^1=H$; XI R=2-naphthyl, $R^1=H$; XII 2- pyridyl, $R^1=H$; XIII $R=C_6H_4$, $R^1=CH_3$; XIV $R=C_6H_5$, $R^1=H$; XV $R=m\text{-}CH_3C_6H_4$, $R^1=H$; XVI $R=C_6H_4$, $R^1=H$; XVII $R=C_4H_6$, $R^1=H$

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TABLE 1. Mass Spectra of I-XVII*

m/e values (relative intensities of the ion peaks in percent of the maximum peak)

N-(3-Methyl-2-aza-9-fluorenylidene) (I): 271 (19.8), 270 (100), 269 (48.2), 268 (6,4), 267 (2,4), 255 (5,1), 254 (1,3), 253 (1,2), 243 (0,5), 242 (1,4), 241 (1,2), 229 (1,4), 228 (3,1), 227 (2,1), 205 (1,2), 180 (0,7), 179 (1,3), 138 (2,8), 77 (5,5), 76 (1,9)

N-(3,7-Dimethyl-2-aza-9-fluorenylidene)aniline (II): 285 (21,3), 284 (100), 283 (50,4), 282 (7,6), 281 (3,4), 269 (14,5), 268 (5,2), 267 (4,0), 266 (2,3), 257 (0,6), 256 (1,2), 255 (1,7), 254 (2,0), 253 (1,3), 243 (1,3), 242 (3,0), 241 (3,7), 240 (1,9), 228 (1,2), 227 (1,9), 207 (0,3), 194 (2,3), 193 (1,1), 181 (0,2), 153 (1,2), 152 (3,8), 151 (2,5), 77 (2,5)

N-(3-Methyl-2-aza-9-fluorenylidene)-o-toluidine (III): 285 (20,1), 284 (100), 283 (91,2), 282 (14,3), 281 (14,4), 270 (1,3), 269 (19,1), 268 (11,1), 267 (7,2), 266 (2,0), 257 (0,9), 256 (1,8), 255 (2,4), 254 (3,2), 253 (1,1), 243 (2,0), 242 (5,1), 241 (5,0), 240 (1,4), 180 (3,8), 91 (1,9)

N-(3-Methyl-2-aza-9-fluorenylidene)-m-toluidine (IV): 285 (21,7), 284 (100), 283 (20,1), 282 (6,5), 281 (1,8), 269 (10,2), 268 (4,0), 267 (3,3), 257 (0,8), 256 (1,9), 255 (2,4), 254 (2,6), 253 (1,7), 242 (1,8), 241 (1,9), 180 (1,6), 91 (2,3), 89 (1,3)

N-(3-Methyl-2-aza-9-fluorenylidene)-p-toluidine (V): 285 (20,3), 284 (100), 283 (35,3), 282 (2,8), 281 (4,8), 269 (11,2), 268 (4,0), 267 (3,5), 266 (2,3), 257 (0,9), 256 (2,2), 255 (2,3), 254 (2,4), 253 (1,5), 243 (1,2), 242 (2,5), 241 (2,9), 240 (2,2), 228 (1,4), 227 (1,7), 205 (2,4), 180 (3,5), 179 (1,5), 167 (0,4), 152 (1,6), 151 (2,3), 91 (3,3), 89 (1,5)

N-(1,3-Dimethyl-2-aza-9-fluorenylidene)-p-toluidine (VI): 299 (23,1), 298 (100), 297 (61,7), 296 (8,5), 295 (2,8), 284 (12,1), 283 (50,4), 282 (12,5), 281 (9,0), 280 (6,2), 279 (3,5), 270 (1,4), 269 (4,2), 268 (9,4), 267 (8,3), 266 (4,2), 257 (1,4), 256 (4,1), 255 (5,5), 254 (6,0), 253 (2,8), 252 (2,1), 241 (2,0), 207 (0,4), 206 (0,7), 194 (1,1), 193 (0,8), 181 (1,4), 180 (2,4), 179 (1,1), 154 (1,1), 153 (2,4), 152 (5,0), 151 (4,8), 91 (3,5), 89 (3,3)

N-(3,5,8-Trimethyl-2-aza-9-fluorenylidene)-p-toluidine (VII): 313 (23,5), 312 (100), 311 (33,0), 310 (4,0), 309 (1,3), 298 (7,9), 297 (32,3), 296 (16,1), 295 (12,2), 294 (2,1), 285 (1,2), 284 (2,7), 283 (4,5), 282 (6,0), 281 (2,1), 271 (0,4), 221 (0,3), 91 (1,5)

N-(3-Methyl-2-aza-9-fluorenylidene)-2-aminofluorene (VIII): 359 (25,4), 358 (100), 357 (14,4), 356 (3,2), 355 (1,1), 343 (2,1), 342 (1,8), 331 (0,3), 330 (0,7), 317 (0,7), 316 (1,2), 315 (1,3), 314 (1,4), 194 (0,4), 193 (0,5), 180 (4,6), 179 (4,1), 178 (4,3), 167 (2,3), 166 (3,8), 165 (19,3), 164 (8,4), 163 (4,2)

N-(1,4,7-Trimethyl-2-aza-9-fluorenylidene)mesidine (IX): 341 (19,6), 340 (93,0), 339 (11,2), 338 (1,6), 326 (27,2), 325 (100), 324 (8,5), 323 (6,1), 322 (1,9), 313 (0,7), 312 (1,0), 311 (3,7), 310 (1,1), 309 (11,0), 308 (3,7), 307 (1,6), 283 (1,9), 282 (2,1), 281 (1,0), 208 (0,5), 207 (0,5), 153 (2,1), 152 (2,4), 151 (1,0), 120 (4,2), 119 (1,6), 91 (1,2)

N-(7-Methyl-4-aza-9-fluorenylidene)-2-aminofluorene (X): 359 (25,9), 358 (100), 357 (8,1), 356 (2,7), 355 (1,3), 343 (2,3), 342 (2,2), 341 (1,5), 331 (0,4), 330 (0,7), 194 (0,4), 193 (0,6), 180 (2,7), 179 (6,9), 178 (4,5), 167 (0,6), 166 (2,5), 165 (11,2), 164 (5,8), 163 (3,0), 153 (1,3), 152 (2,7)

N-(7-Methyl-4-aza-9-fluorenylidene)-2-naphthylamine (XI): 321 (25,4), 320 (100), 319 (32,1), 318 (5,5), 317 (4,1), 306 (1,1), 305 (13,0), 304 (3,4), 303 (3,1), 293 (0,9), 292 (1,9), 291 (1,7), 278 (1,1), 277 (1,4), 193 (0,5), 192 (0,8), 191 (0,4), 180 (0,3), 179 (0,3), 178 (0,6), 167 (0,3), 166 (0,5), 127 (2,5), 126 (1,9), 125 (0,5), 115 (1,3)

N-(7-Methyl-4-aza-9-fluorenylidene)-2-aminopyridine (XII): 272 (25,8), 271 (100), 270 (10,9), 269 (5,7), 268 (1,4), 257 (1,2), 256 (8,3), 244 (0,9), 243 (1,7), 242 (1,9), 193 (0,6), 192 (1,4), 179 (0,6), 178 (1,4), 177 (1,1), 167 (1,2), 166 (1,4), 153 (1,4), 152 (3,3), 151 (1,5), 150 (3,1), 149 (1,2), 141 (1,5), 140 (7,4), 139 (6,7), 90 (1,4), 89 (4,3), 87 (3,8), 86 (2,1), 79 (2,3), 78 (15,5), 77 (2,9)

N-(7-Methyl-4-aza-9-fluorenylidene)cyclohexylamine (XIII): 277 (23,2), 276 (100), 275 (50,4), 274 (3,2), 261 (57,4), 260 (1,2), 249 (2,1), 248 (10,0), 247 (31,7), 246 (2,0), 245 (1,9), 236 (2,4), 233 (70,8), 232 (7,6), 231 (5,2), 230 (5,4), 223 (1,6), 222 (9,8), 221 (30,5), 220 (12,7), 219 (29,3), 218 (17,6), 217 (5,8), 209 (3,9), 208 (17,6), 207 (10,7), 206 (11,0), 205 (19,5), 204 (6,1), 196 (3,8), 195 (19,5), 194 (46,4), 193 (31,7), 192 (18,3), 191 (18,5), 190 (3,0), 181 (7,1), 180 (19,5), 179 (25,6), 178 (8,2), 176 (2,3), 168 (1,1), 167 (2,0), 166 (3,3), 155 (2,1), 154 (1,8), 153 (4,8), 152 (9,8), 151 (9,6), 150 (3,7), 143 (1,0), 142 (1,3), 141 (4,9), 140 (5,6), 139 (4,6), 89 (2,4), 88 (1,0), 87 (1,6), 84 (1,6), 83 (4,1), 82 (2,0)

N-(2,3-Benzo-1,4-diaza-9-fluorenylidene)aniline (XIV): 308 (17,2), 307 (72,8), 306 (100), 305 (6,7), 304 (1,4), 280 (0,6), 279 (1,2), 231 (0,5), 230 (2,2), 229 (0,2), 217 (3,4), 216 (0,9), 215 (0,9), 205 (1,1), 204 (0,7), 203 (1,3), 77 (8,1), 76 (3,1), 75 (1,8)

N-(2,3-Benzo-1,4-diaza-9-fluorenylidene)-m-toluidine (XV): 322 (22,6), 321 (100), 320 (85,1), 319 (9,0), 318 (3,9), 307 (9,2), 306 (39,4), 305 (1,9), 304 (2,0), 294 (0,9), 293 (2,1), 292 (1,7), 231 (0,9), 230 (2,4), 229 (0,5), 218 (2,5), 217 (6,7), 216 (1,3), 215 (2,4), 204 (1,2), 203 (1,0), 142 (1,4), 141 (10,0), 129 (1,3), 91 (7,0)

N-(2,3-Benzo-1,4-diaza-9-fluorenylidene)cyclohexylamine (XVI): 314 (25,7), 313 (100), 312 (3,9), 285 (1,7), 284 (3,9), 272 (1,3), 271 (1,7), 270 (7,4), 269 (1,3), 268 (1,1), 258 (2,0), 257 (3,5), 256 (10,9), 255 (1,7), 245 (2,6), 244 (3,5), 243 (3,9), 242 (1,3), 233 (7,0), 232 (39,2), 231 (20,0), 230 (4,8), 229 (1,7), 219 (3,9), 218 (19,6), 217 (13,0), 216 (5,6), 215 (5,2), 214 (3,3), 204 (3,5), 190 (4,4), 189 (2,4), 188 (1,7), 177 (1,3), 169 (1,3), 156 (1,1), 155 (3,5), 149 (1,3), 142 (1,7), 141 (5,2), 130 (0,6), 129 (4,4), 128 (1,7), 115 (1,3), 114 (1,7), 102 (3,5), 101 (6,1), 98 (2,2), 97 (1,3), 96 (3,5), 95 (1,1), 83 (2,2), 82 (1,3), 81 (2,2), 77 (4,8), 76 (5,6), 69 (2,6)

TABLE 1. (continued)

N-(1-Methylquinoxolino[2,3-a]-6-indenylidene)cyclohexylamine (XVII): 328 (27,2), 327 (100), 326 (4,1), 325 (1,1), 312 (0,9), 311 (0,3), 300 (0,6), 299 (1,5), 298 (4,0), 286 (1,1), 285 (2,0), 284 (7,1), 283 (1,5), 272 (1,7), 271 (1,9), 270 (9,5), 269 (2,4), 259 (2,3), 258 (3,2), 257 (3,1), 247 (5,9), 246 (32,0), 245 (20,9), 244 (9,9), 243 (4,0), 233 (3,3), 232 (15,3), 231 (10,1), 230 (4,0), 229 (7,8), 219 (1,2), 218 (1,3), 217 (1,1), 91 (1,4), 90 (2,3), 89 (4,6), 83 (0,8)

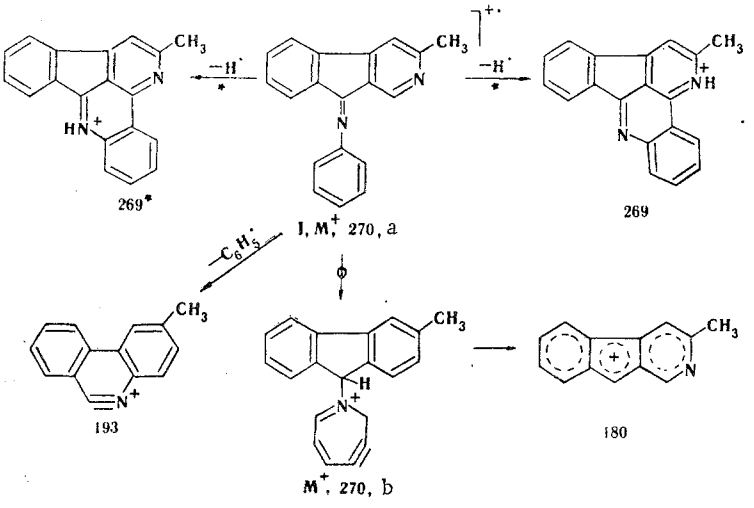
*The intensities of peaks >1% relative to the maximum peak, as well as of the peaks of all of the ions discussed in the text, are indicated.

An anlysis of the mass spectra of these compounds confirmed the assumption that the ions formed in the fragmentation of the series of substances undergo cyclization with the ejection of $H^{\bullet}$ and $CH_3^{\bullet}$ radicals, which also explains the increased relative intensities of the $[M - H]^+$ and $[M - CH_3]^+$ ion peaks. The direction of cyclization is determined by the structure of the azomethine.

High intensity of the $[M - H]^+$ ion peak is observed only for I-III and VI in the series of azomethines, viz., 2-azafluorene derivatives I-VII and IX (Table 2).

The cyclization processes that lead to the intense $[M - H]^+$ ion peaks in the fragmentation of I and II are evidently accompanied by fastening of the o-carbon atom of the imine fragment to the azafluorene ring (Scheme 1) with simultaneous migration of the hydrogen atom attached to the o-carbon atom to the endocyclic or exocyclic nitrogen atom. This ensures coplanarity of the $[M - H]^+$ ion and leads to conjugation of the imine and azafluoroenylidene fragments in the indicated ion, the stability of which is also increased due to the development of a quaternized nitrogen atom [2].

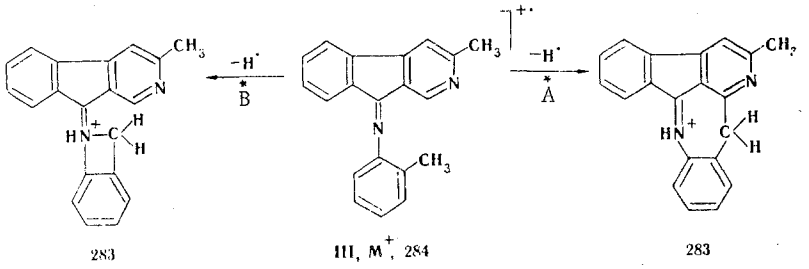
Scheme 1



The cyclization processes in the case of the appearance of the $[M - H]^+$ ion take place with a higher probability for III and VI as compared with the dissociative ionization of azomethines I and II. This is evidently associated with the different direction of cyclization in the fragmentation of the molecular ions of III and VI, which can eliminate a hydrogen atom via two pathways (Schemes 2 and 3, Pathways A and B). The ease of cyclization in this case is due to the higher lability of the hydrogen atom of the methyl group as compared with the aromatic hydrogen atom. Of the two alternative cyclization pathways indicated in Schemes 2 and 3, the formation of a seven-membered ring is preferred. In the case of III (Scheme 2) both cyclization pathways can lead to partial conjugation in the $[M - H]^+$ ion of the azafluorenylidene fragment with the o-phenylene grouping (Pathway A involving the formation of a seven-membered ring, and Pathway B involving the formation of a four-membered ring). However, in the fragmentation of the molecular ion of azomethine VI (Scheme 3) the indicated conjugation, which leads to stabilization of the $[M - H]^+$ ion, is realized only via Pathway A.

*The numbers that characterize the ions in all of the schemes are the mass-to-charge ratios.

Scheme 2

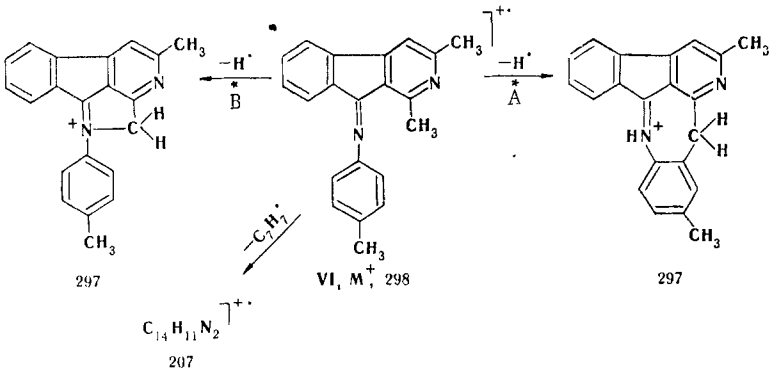


283 III, M^+, 284 283

On the basis of a comparison of the intensities of the $[M - H]^+$ ion peaks of azomethines VI (61.7%) and VII (33%) it may be concluded that cyclization occurs primarily with the participation of the methyl group in the pyridine ring rather than in the benzene ring of the azafluorenylidene fragment.

Cyclization processes with the splitting out of a hydrogen atom evidently do not take place for IV, V, and IX, which contain a CH_3 group in the meta or para position of the imine fragment. In the case of azomethine IV the intensity of the $[M - H]^+$ ion peak is virtually equal to the intensity of this peak in the mass spectrum of 3-methyl-2-azafluorene. The certain increase in the intensity of the $[M - H]^+$ ion peak in the fragmentation of V and VII as compared with IV is probably explained by the formation of an $[M - H]^+$ fragment, which has a p-quinoid structure [3].

Scheme 3



297 VI, M^+, 298 297

$C_{14}H_{11}N_2$

207

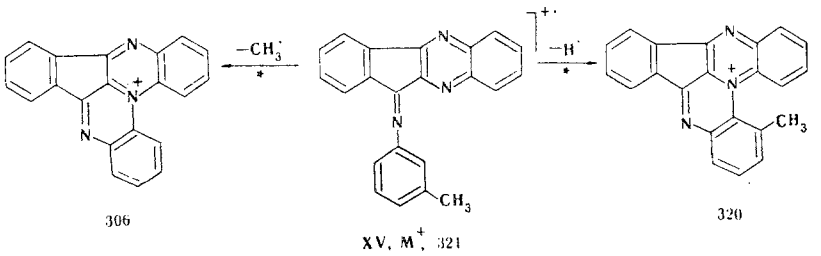
Replacement of the N-aryl group by a 2-fluorenyl group (azomethines VIII and X) excludes cyclization with splitting out of a hydrogen atom, evidently as a consequence of the mutual repulsion of the N-fluorenyl and azafluorene rings. This assumption is confirmed by the significant increase (by a factor of approximately six) in the intensity of the peak of the $[M - H]^+$ fragment in the mass spectrum of XI. Steric hindrance to the formation of a six-membered ring is considerably smaller in this compound.

When a nitrogen atom is present in the imine fragment as in XII, cyclization during the formation of the $[M - H]^+$ ion is not observed. Consequently, as demonstrated by the fragmentation of IV, V, and XII, the probability of the occurrence of cyclization depends not only on the topology of the molecule but also on the peculiarities of the electronic structure of the imine fragment.

The probability that cyclization occurs during dissociative ionization increases markedly on passing to azomethines of the azafluorene series to the analogous derivatives of 5,11-diazabenzo[b]fluorene (XIV and XV). This fact is probably due to the possibility of a one-step mechanism for the formation of a six-membered ring in the $[M - H]^+$ ion (without migration of a hydrogen atom to the exocyclic nitrogen atom, Scheme 4).

Conjugation of the imine fragment with, respectively, the azafluorenylidene and 5,11-diazabenzo[b]fluorenylidene fragments is excluded in the case of XVII, XVI, and XVII, which have an N-cyclohexylamine fragment. However, a considerably higher-intensity $[M - H]^+$ ion peak as compared with the mass spectra of XVI and XVII is observed in the mass spectrum of XIII. This fact is evidently due to the relatively greater increase in the π-electron energy

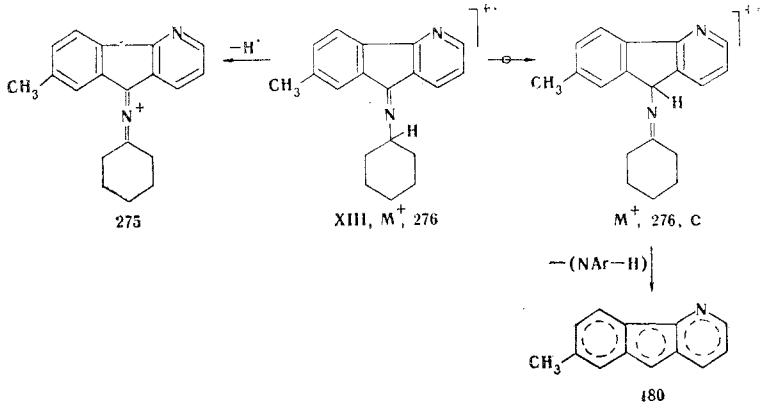
Scheme 4



306 XV, M^+, 321 320

of the $[M - H]^+$ ion in the formation of a quaternized nitrogen atom in the case of fragmentation of XIII (Scheme 5) than in the $[M - H]^+$ ion for azomethines XVI and XVII.

Scheme 5



275 XIII, M^+, 276 M^+, 276, C 180

The second pathway of fragmentation of the investigated methyl-substituted azomethines, which is due to the elimination of a CH_3 radical, is also evidently accompanied in a number of cases by cyclization of the imine and azafluorenylidene fragments during the formation of $[M - CH_3]^+$ ions. This may explain the anomalously high intensities of the indicated ions in the mass spectra of VI, VII, IX, and XV. In the fragmentation of VI and VII the facile loss of a methyl group is due to the formation of a six-membered ring in the $[M - CH_3]^+$ ion. This process, like the formation of the $[M - H]^+$ ion, takes place with higher probability in the case of participation of the pyridine ring rather than the benzene ring of the azafluorene ring; this follows from a comparison of the intensities of the peaks of $[M - CH_3]^+$ fragments in the mass specta of these azomethines. The probability of cyclization with splitting out of a methyl group from the imine fragment is determined by its position in the latter, as well as

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 Azomethines I-XVII

Compound	W_M	$[M-H]^+$	$[M-CH_3]^+$	$[M-HCN]^+$	$[M-R]^+$	R	$[M-(NAr-H)]^+$
I	0,31	48,2	5,1	0,5	—	5,5	0,7
II	0,29	50,4	14,5	0,6	0,3	2,5	2,3
III	0,25	91,2	19,1	0,9	—	1,9	3,8
IV	0,34	20,1	10,2	0,8	—	2,3	1,6
V	0,31	35,3	11,2	0,9	—	3,3	3,5
VI	0,24	61,7	50,4	—	0,4	3,5	1,1
VII	0,29	33,0	32,3	1,2	0,3	1,5	—
VIII	0,32	14,4	2,1	0,3	0,5	19,3	4,6
IX	0,17	11,2	100,0	0,6	—	4,2	0,5
X	0,31	8,1	2,3	0,4	0,6	11,2	2,7
XI	0,29	32,1	13,0	0,9	0,5	2,5	0,3
XII	0,26	10,9	8,3	0,9	0,6	15,5	0,6
XIII	0,13	50,4	57,3	2,1	31,7	4,1	19,5
XIV	0,31	100,0	—	0,6	2,2	8,1	3,4
XV	0,20	85,1	39,4	0,9	2,4	7,0	6,7
XVI	0,23	3,9	—	—	4,8	2,2	13,0
XVII	0,25	4,1	0,9	3,6	9,9	0,8	10,1

by the character of the azafluorenylidene radical. Thus the elimination of an o-methyl radical (azomethine III) is accompanied by the formation of a six-membered ring in the $[M - CH_3]^+$ ion. The possibility of the formation of a new ring in the formation of $[M - CH_3]^+$ ions is excluded in the case of azomethines with methyl groups in the imine fragment in the meta or para positions (IV and V, Table 2). However, cyclization evidently occurs in the case of XV, which contains an m-methyl group in the imine fragment; this can be explained by randomization of the hydrogen atoms in the N-phenyl group of the $[M - CH_3]^+$ ion (Scheme 4), which leads to the development of a free valence on the o-carbon atom, and by one-step cyclization of the latter at the nitrogen atom of the diazobenzofluorenylidene fragment.

The maximum value of the $[M - CH_3]^+$ ion peak in the mass spectrum of IX is primarily explained by steric interaction of the methyl groups in its molecular ion, which promotes detachment of a $CH_3^{\cdot}$ radical with the subsequent formation of a seven-membered ring, as in the case of the formation of an $[M - H]^+$ fragment, which is shown in Schemes 2 and 3.

The presence of a cyclohexyl group in the imine fragment (azomethines XIII, XVI, and XVII, Table 2) is responsible for a different dependence of the intensity of the $[M - CH_3]^+$ ion peak on the character of the azafluorene fragment. The high intensity of the $[M - CH_3]^+$ ion peak in the mass spectrum of N-(7-methyl-4-aza-9-fluorenylidene)cyclohexylamine (XIII) is evidently associated with cleavage of the cyclohexyl ring [4]. This process is not observed in the fragmentation of XVI and XVII, which contain a benzodiazafluorenyl ring. This fact, like the formation of an $[M - H]^+$ ion in the fragmentation of XIII, XVI, and XVII, can be explained by the relatively large increase in the π-electron energy in the $[M - CH_3]^+$ ion as compared with XVI and XVII, in which a quaternized nitrogen atom is formed as a result of cleavage of the C'_1—C'_2 bond of the cyclohexyl ring.

A characteristic pathway of fragmentation of the investigated compounds is also splitting out of a hydrocarbon radical of the imine fragment, which is probably accompanied by the formation of a six-membered ring due to the inclusion of a nitrogen atom in the five-membered ring (Schemes 1 and 3). For substances that contain an aromatic grouping in the imine fragment this process takes place with primary localization of the positive charge on the hydrocarbon grouping (Table 2); the probability of cleavage of the C—N bond depends on the character of both fragments.

A distinctive peculiarity of the dissociative ionization of the investigated azomethines consists in the elimination of an imine fragment by the molecular ions, which is accompanied by migration of hydrogen to the azafluorenylidene system. The formation of ions of the $[M - (NAr - H)]^+$ type is confirmed by data from the high-resolution mass spectra of I (with precise mass 180.1399 and empirical formula $C_{13}H_{10}N$) and II (with precise mass 194.1580 and empirical formula $C_{14}H_{12}N$). Since cleavage of the C=N bond in the M^+ ion is unlikely, the appearance of these fragments is evidently due to isomerization of some of the molecules from form *a* to form **b** (Scheme 1); in contrast to the elimination of an aryl group, the positive charge is localized on the principal part of the molecule. The presence of a cyclohexyl substituent (azomethines XIII, XVI, and XVII) markedly increases the probability of splitting out of an imine fragment. This fact can be explained by the existence of some of the molecular ions in form **c** (scheme 5), in which the possibility of conjugation between both structural fragments is absent; this is also responsible for the more facile cleavage of the C—N bond, which leads to the formation of a completely conjugated azafluorenyl ion ($[M - C_6H_{11}]^+$).

The fragmentation of the investigated substances also includes the elimination of an HCN molecule by the molecular ions; this is confirmed by data from the high-resolution mass spectra for I and II. In contrast to the dissociative ionization of mononuclear imines [5, 6], this process is associated with splitting out of an HCN molecule from the pyridine ring rather than from a structural fragment that includes an exocyclic azomethine bond. The absence of $[M - HCN]^+$ ion peaks in the mass spectrum of VI and the formation of $[M - RCN]^+$ and $[M - HCN]^+$ ions, respectively, in the fragmentation of I and II serve to confirm this.

EXPERIMENTAL

The mass spectra of I-XVII were obtained with an MKh-1303 mass spectrometer with a system for the direct introduction of samples into the ion source at an ionizing voltage of 70 V and an admission temperature of 40-70°C. The precise masses were measured with a JMS-01 SG-2 spectrometer with an automatic system for information processing.

Compounds I-XVII were synthesized by the methods in [7-9], and their purity and individuality were monitored by thin-layer chromatography. The structures of the substances were established on the basis of data from the IR, UV, and PMR spectra.

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REACTION OF 2,4,6-TRIALKYLPYRIMIDINE 1,3-DIOXIDES WITH ELECTROPHILIC REAGENTS

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The nitrosation of 2,4,6-trimethylpyrimidine 1,3-dioxide and the bromination of 2,4,6-trimethyl- and 2-ethyl-4,6-dimethylpyrimidine 1,3-dioxides take place primarily at the methyl groups in the 4 and 6 positions of the heteroring. In the reaction of 2,4,6-trimethylpyrimidine 1,3-dioxide with phosphorus oxychloride chlorine is incorporated in the methyl group in the 2 position of the heteroring, while in the reaction with acetic anhydride an acetoxy group is incorporated in the methyl group in the 2 position and in the 5 position of the heteroring, whereas in the case of tosyl chloride a tosyloxy group is incorporated in the 5 position of the heteroring.

Pyrimidine 1,3-dioxides have relatively recently become accessible [1, 2], and virtually no study has been devoted to their chemical properties [3]. The reaction of N-oxides of alkyl-substituted azines with electrophilic reagents takes place both with retention of the oxygen atom of the N-oxide group, as, for example, in halogenation and nitrosation, and with the loss of the oxygen atom of this group, as, for example, in acetoxylation and halogenation with phosphorus oxychloride [4]. In the present research we studied the reactions of 2,4,6-trialkylpyrimidine 1,3-dioxides (Ia, b) with alkyl nitrites, bromine, phosphorus oxychloride, acetic anhydride, and tosyl chloride.

The nitrosation of 1,3-dioxide Ia with ethyl or amyl nitrite in an acidic medium (cf. [5]) led to the formation of 4-oximidomethyl-2,6-dimethylpyrimidine 1,3-dioxide (II). The nonequivalence of the protons of the two methyl groups (2.39 and 2.62 ppm) in the PMR spectrum of II (Table 1) and the coincidence of their chemical shifts with the shifts of the protons of the corresponding methyl groups in starting 1,3-dioxide Ia (2.31 ppm for 4,6-CH_3, and 2.62 ppm for 2-CH_3 [2]) indicate that nitrosation took place at the methyl group in the 4 position

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