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CYCLIZATION OF N-ALKYLAZINIUM CATIONS WITH BISNUCLEOPHILES.
3.* endo ADDUCTS IN THE REACTION OF QUINOXALIUM SALTS WITH β-DIKETONES AND THEIR X-RAY DIFFRACTION ANALYSIS

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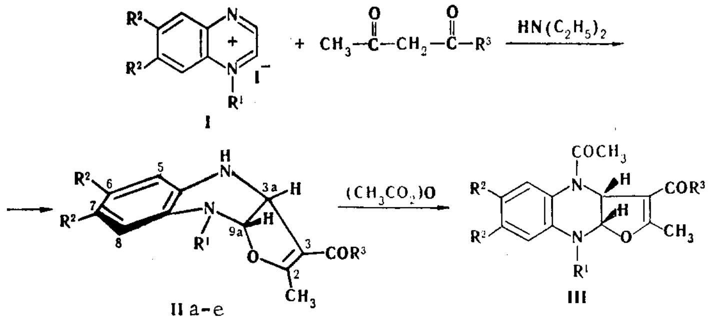
The cyclization of N-alkylquinoxalinium salts with the anions of β-dicarbonyl compounds proceeds regioselectively and stereoselectively and leads to endo-3a,4,9,9a-tetrahydrofuro[2,3-b]quinoxalines. The structure of the cycloadducts was established on the basis of the ${}^1H$ and ${}^{13}C$ NMR spectra and the results of x-ray diffraction analysis.

The meta bonding of polynitroaromatic compounds and their heterocyclic analogs by bisnuclophiles has recently become one of the effective methods for the one-step synthesis of complex and practically useful two-ring compounds [2-8]. Two-ring intermediates formed due to meta bonding have also been postulated or recorded in the course of transformations of heterocyclic systems [9, 10]. A new cyclization reaction of quinoxalinium salts with enamines of cyclic ketones that has a number of principles in common with meta-bonding reactions but differs with respect to ortho bonding of a heteroaromatic system has been reported [11, 12]. A new ortho-cyclization reaction of N-alkylquinoxalinium salts with β-diketones is described in the present paper, and its stereochemical aspects are examined.

The reaction of quinoxalinium salts I with acetylacetone and acetoacetic ester in the presence of bases (diethyl- and triethylamines) proceeds with an appreciable exothermic effect, and the reaction was therefore carried out at -50 to +20°C in ethanol. Under these conditions the reaction was complete after a few minutes and gave endo-3a,4,9,9a-tetrahydrofuro[2,3-b]quinoxalines (IIa-e) in high yields (Table 1).



I

IIa-e

III

The structure of IIa-e was established on the basis of spectral data (Tables 1 and 2). The chemical shift of the protons of the N-methyl group at δ 3.04 ppm and the narrow multiplet of aromatic protons (δ 6.4-6.9) correspond to a tetrahydroquinoxaline structure [13]. The 9a-H proton appears in the PMR spectrum of IIa as a doublet with ${}^3J_{9a,3a} = 9$ Hz. The 3a-H proton, in addition to coupling with 9a-H, has a long-range spin-spin coupling constant (SSCC) with the protons of the methyl group in the 2 position of the furan ring (${}^5J_{3a} = 0.9$ Hz) and gives a doublet of quartets with 5.04 ppm (Fig. 1).

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*See [1] for Communication 2.

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TABLE 1. endo-3a,4,9,9a-Tetrahydrofuro[2,3-b]quinoxalines IIa-e

Compound	R^1	R^2	R^3	mp,* °C (dec.)	UV spectrum (in ethanol), λ_{max}, nm (log ε)	IR spectrum, ν, cm^{-1}		Found, %			Empirical formula	Calc., %			Yield, %
						C=C, C=O	NH	C	H	N		C	H	N	
IIa†	CH_3	H	CH_3	118—120	218 (4,46), 251 (4,14), 275 (3,98)	1600—1640	3320	68,8	6,7	11,5	$C_{14}H_{16}N_2O_2$	68,8	6,6	11,5	78
IIb	C_2H_5	H	CH_3	114—115	219 (4,55), 252 (4,19), 276 (4,04)	1600—1640	3328	69,7	6,9	10,7	$C_{15}H_{18}N_2O_2$	69,7	7,0	10,8	75
IIc	CH_3	CH_3	CH_3	154—155	218 (4,55), 252 (4,17), 274 (3,99)	1620—1640	3338	70,8	7,7	10,2	$C_{16}H_{20}N_2O_2$	70,6	7,4	10,3	66
IId‡	CH_3	H	OC_2H_5	115—116	218 (4,58), 243 (4,26), 297 (3,59)	1635, 1695	3370	65,4	6,8	10,3	$C_{15}H_{18}N_2O_3$	65,7	6,6	10,2	76
IIe	C_2H_5	H	OC_2H_5	108—109	218 (4,51), 245 (4,19), 298 (3,49)	1640, 1695	3368	66,8	7,2	9,8	$C_{16}H_{20}N_2O_3$	66,7	7,0	9,7	75

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*The melting points were determined approximately at a heating rate of 5°/min. In the case of slow heating the substances decomposed at 90-100°C.

†Mass spectrum of IIa (J≥10%): 39 (14), 42 (11), 43 (100), 51 (13), 77 (21), 78 (27), 98 (12), 131 (16), 133 (30), 145 (39), 146 (20), 159 (14), 187 (13), 201 (55), 229 (14), 244 m.e. (49) mass units.

‡Mass spectrum of IId: 39 (30), 42 (19), 43 (98), 51 (19), 52 (11), 65 (17), 76 (13), 77 (35), 78 (29), 91 (13), 92 (27), 102 (12), 103 (15), 104 (11), 118 (15), 119 (14), 130 (18), 131 (44), 132 (12), 133 (12), 133 (83), 143 (11), 145 (57), 146 (23), 157 (80), 158 (13), 159 (13), 171 (29), 172 (12), 185 (53), 186 (11), 201 (36), 203 (34), 214 (40), 227 (11), 228 (72), 229 (22), 231 (100), 232 (14), 244 (12), 274 (90), 275 m.e. (16) mass units.

Hz) and gives a doublet of quartets with δ 5.04 ppm (Fig. 1). The remaining compounds IIb-e also have similar spectra (Table 2). Long-range SSCC often appear in the spectra of compounds of the furan series [14-16], and in this case their presence was established by means of double NMR. Suppression of the signal of the H_{3a} proton in the spectrum of Ia leads to merging to a singlet of the doublet signal of the methyl group at 2.07 ppm (Fig. 1). The correctness of the assignments of the signals was also confirmed in an experiment with deuterated (at C_{3a} and C_{9a}) Ia. The PMR spectrum of the product of the reaction of 2,3-d_2-N-methylquinoxalinium iodide with acetylacetone did not contain signals of protons with δ 5.04 and 5.78 ppm, whereas the protons of the methyl group of the furan ring appeared as a singlet. The NH group in IIa-e shows up distinctly in the IR and PMR spectra (Tables 1 and 2) and is also readily acetylated.

β-Dicarbonyl compounds are capable of various types of cyclizations. On the one hand, reactions of β-diketones with polynitro aromatic compounds in which they behave like biscarbanions are known [2, 3]. On the other hand, there is a possibility of participation of the enolate oxygen atom in cyclization. Thus the reaction of β-diketones with olefins leads to 3-acylfurans [15, 17]. If one takes into account the possibility of only these two types of cyclizations with the formation of two new C—N bonds or C—C and C—O bonds, as well as the different regio- and stereoorientations of the reagents, the total number of possible isomers in the reaction of salts I with acetylacetone is eight, as compared with twelve in the case of the reaction with acetoacetic ester. Moreover, no signs whatsoever of the presence of a mixture of regio- or stereoisomers were observed in the ^1H and ^{13}C NMR spectra for any of the IIa-e adducts. The only products identified in the PMR spectra of the reaction mixtures in CD_3OD recorded immediately after mixing of the reagents were also endo-furo[2,3-b]quinoxalines IIa-e. Thus the reaction under consideration is evidently stereospecific.

TABLE 2. ^1H and ^{13}C NMR Data for endo-3a,4,9,9a-Tetrahydrofuro[2,3-b]-quinoxalines IIa-e and III in Deuterochloroform

Nucleus or group of nuclei	Chemical shifts of the protons, δ, ppm, and SSCC, Hz					
	IIa	IIb	IIc	IId	IIe	III
NH	4,75	4,72	4,61	4,59	4,50	—
CH_3	2,07 d	2,09 d	2,11 d	2,06 d	2,08 d	2,06 d
COR^3	2,22 s	2,22 s	2,24 s	1,29 t 4,20 q	1,29 t 4,22 q	2,21 s
3a-H	5,04 dq	4,95 dq	5,03 dq	4,97 dq	4,93 dq	Under the aromatic proton signals
9a-H	5,78 d	5,86 d	5,77 d	5,79 d	5,91 d	5,75 d
$N—R^1$	3,04 s	1,32 t 3,46 m	3,03 s	3,03 s	1,32 t 3,47 m	3,00 s
Benzene ring	6,4—6,9 m	6,4—6,9 m	6,36 s 6,46 s	6,4—6,9 m	6,4—6,9 m	6,8—7,5 m
$^3J_{3a,9a}$	9,0	8,7	8,9	8,9	8,8	9,5
$^3J_{3a}$, methyl	0,9	0,9	0,9	1,0	0,9	1,0
	Chemical shifts of the ^{13}C nuclei, δ, ppm					
C_2	167,7	167,8	—	168,7	—	—
CH_3	15,4	15,6	—	14,3	—	—
C_3	115,8	116,0	—	104,3	—	—
COR^3	193,6, 28,8	193,6, 28,8	—	165,1, 59,3, 13,7	—	—
C_{3a}	60,0	59,6	—	59,5	—	—
C_{9a}	96,6	95,0	—	97,0	—	—
$N—R^1$	36,1	12,6, 43,2	—	36,0	—	—
Benzene ring	112,6, 114,2, 119,3, 120,6, 132,7, 135,6	112,9, 114,5, 119,2, 120,3, 131,7, 135,7	—	112,8, 114,3, 119,5, 120,7, 133,1, 135,6	—	—

On the basis of data only from the NMR spectra one could not unambiguously establish the three-dimensional structures of cycloadducts IIa-e, since the SSCC between the 3a-H and 9a-H protons ranged from 8.7 to 9.0 Hz (Table 2) and did not make it possible to form a preference for the endo or exo isomers [18]. Convincing evidence that cycloadducts II are the endo isomers was obtained by x-ray diffraction analysis. The projection of the III molecule — the acetyl derivative of IIa — on the xy plane is presented in Fig. 2. The bond lengths and angles of III, which are presented in Tables 3 and 4, lie within the range of the tabulated values. Only the C(4)—O(1) bond of the dihydrofuran ring (1.475 Å) is somewhat elongated as compared with the sum of the covalent radii (1.43 Å); however, close values for the C—O bonds have also been previously observed (for example, 1.47 [19] and 1.49 Å [20]). The tetrahydropyrazine ring has a boat conformation — the N(1) and N(2) atoms deviate 0.555 and 0.403 Å , respectively, from the plane of the four carbon atoms (Table 5). The dihderal angle between the A and B planes is 21.52°, while the dihedral angle between the B and C planes is 79.42°. Considering the similarity in the PMR spectra of IIa-e and IIIi and, particularly, the closeness of the $^3J_{3a,9a}$ constants (Table 2), it may be deemed likely that all of the compounds have the indicated structure with a cis orientation of the 3a-H and 9a-H atoms.

Two alternative cyclization pathways — stepwise and concerted — can be imagined. If the reaction is a two-step process, in conformity with the reactivities of salts I in reactions with nucleophiles [13], it should be assumed that attack by the enolate oxygen atom of the β-diketone in the 2 position occurs initially with the formation of intermediate IV and subsequent intramolecular cyclization. At the same time, the regio- and stereospecificity of the reaction may serve as arguments in favor of concerted, thermally allowed cycloaddition of the 4π electron system of the enolate anion to the aromatic pyrazine ring, which acts as a 2π component [21].

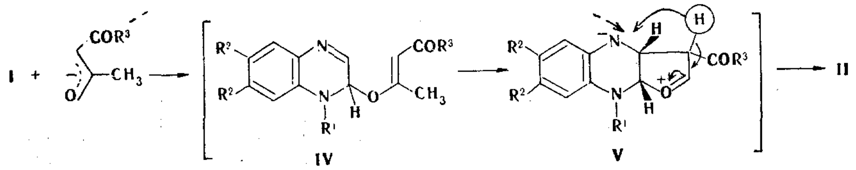

TABLE 3. Bond Lengths (d, Å) for III (the numbering of the atoms is given in Fig. 2)

Bond	d	Bond	d
O(1)—C(1)	1,368 (4)	C(2)—C(3)	1,513 (5)
O(1)—C(4)	1,475 (5)	C(2)—C(15)	1,467 (6)
O(2)—C(15)	1,220 (4)	C(3)—C(4)	1,537 (6)
O(3)—C(11)	1,242 (4)	C(5)—C(6)	1,400 (6)
N(1)—C(3)	1,461 (6)	C(5)—C(10)	1,394 (5)
N(1)—C(6)	1,441 (4)	C(6)—C(7)	1,374 (7)
N(1)—C(11)	1,369 (5)	C(7)—C(8)	1,408 (5)
N(2)—C(4)	1,436 (5)	C(8)—C(9)	1,379 (7)
N(2)—C(5)	1,398 (5)	C(9)—C(10)	1,383 (7)
N(2)—C(13)	1,462 (6)	C(11)—C(12)	1,491 (7)
C(1)—C(2)	1,330 (7)	C(15)—C(16)	1,495 (7)
C(1)—C(14)	1,482 (6)		

TABLE 4. Bond Angles (ω, deg) for III (Fig. 2)

Angle	ω	Angle	ω
C(1)O(1)C(4)	107,0 (3)	N(2)C(4)C(3)	113,2 (3)
C(3)N(1)C(6)	113,3 (3)	N(2)C(5)C(6)	117,7 (3)
C(3)N(1)C(11)	120,3 (3)	N(2)C(5)C(10)	124,3 (4)
C(6)N(1)C(11)	125,8 (3)	C(6)C(5)C(10)	117,9 (4)
C(4)N(2)C(5)	117,2 (3)	N(1)C(6)C(5)	114,6 (3)
C(4)N(2)C(13)	113,4 (3)	N(1)C(6)C(7)	122,6 (4)
C(5)N(2)C(13)	118,6 (3)	C(5)C(6)C(7)	122,7 (4)
O(1)C(1)C(2)	114,7 (4)	C(6)C(7)C(8)	118,8 (4)
O(1)C(1)C(14)	122,3 (3)	C(7)C(8)C(9)	118,8 (4)
C(2)C(1)C(14)	132,9 (4)	C(8)C(9)C(10)	122,1 (4)
C(1)C(2)C(3)	108,8 (4)	C(5)C(10)C(9)	119,7 (4)
C(1)C(2)C(15)	125,6 (4)	O(3)C(11)N(1)	120,1 (3)
C(3)C(2)C(15)	125,5 (4)	O(3)C(11)C(12)	121,0 (4)
N(1)C(3)C(2)	116,4 (3)	N(1)C(11)C(12)	118,8 (3)
N(1)C(3)C(4)	110,9 (3)	O(2)C(15)C(2)	122,9 (4)
C(2)C(3)C(4)	102,1 (3)	O(2)C(15)C(16)	119,7 (4)
O(1)C(4)N(2)	110,8 (3)	C(2)C(15)C(16)	117,4 (4)
O(1)C(4)C(3)	105,5 (3)		

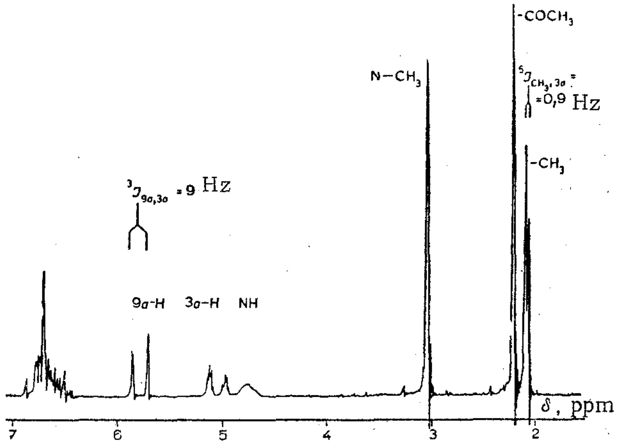

Fig. 1. PMR spectrum of IIa in deuterochloroform.

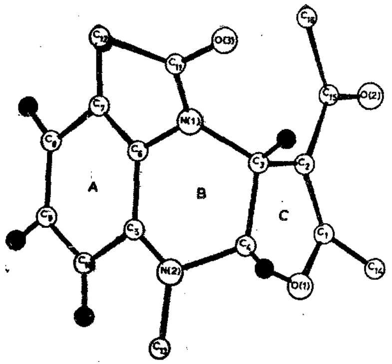

Fig. 2. Projection of the III molecule.

TABLE 5. Equations of the A-C Planes of Some Fragments of the III Molecule and Deviations (Δ, Å) of the Atoms from these Planes (Fig. 2)

$$A-0.3961x-0.7228y-0.5662z+2.2926=0$$
$$B-0.2527x-0.4994y-0.8287z+2.6412=0$$
$$C\ 0.4527x+0.5577y-0.6957z+3.5010=0$$

Plane A		Plane B		Plane C	
atom	Δ	atom	Δ	atom	Δ
C(5)*	0,0023	C(3)*	0,0666	C(1)*	0,0388
C(6)*	−0,0105	C(4)*	−0,0634	C(2)*	0,0307
C(7)*	0,0123	C(6)*	−0,0652	C(3)*	−0,0824
C(8)*	−0,0061	C(5)*	0,0637	C(4)*	0,0993
C(9)*	−0,0034	N(1)	−0,5547	O(1)*	−0,0316
C(10)*	0,0048	N(2)	−0,4030	N(1)	0,8845
N(1)	0,0201	C(11)	−1,6133	N(2)	1,3620
N(2)	−0,0839	C(13)	−0,4205	H(3)	−0,9044
				H(4)	−0,5773
				C(14)	0,0399
				C(15)	0,0300

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*These are the atoms through which the plane passes.

TABLE 6. Coordinates of the Nonhydrogen Atoms ($\times 10^4$)

Atom	x	y	z
O(1)	−5699 (4)	501 (9)	1604 (1)
O(2)	−3199 (4)	−1001 (1)	714 (1)
O(3)	147 (4)	159 (1)	3473 (1)
N(1)	−1141 (5)	575 (1)	2242 (2)
N(2)	−3753 (5)	1353 (1)	1869 (2)
C(1)	−5121 (7)	0 (2)	1244 (2)
C(2)	−3500 (7)	−152 (2)	1561 (2)
C(3)	−2781 (7)	286 (2)	2261 (2)
C(4)	−4206 (6)	771 (2)	2175 (2)
C(5)	−2642 (6)	1341 (2)	1327 (2)
C(6)	−1202 (6)	958 (1)	1528 (2)
C(7)	12 (6)	929 (2)	1060 (2)
C(8)	−161 (7)	1318 (2)	367 (2)
C(9)	−1570 (7)	1699 (2)	169 (2)
C(10)	−2808 (6)	1716 (2)	632 (2)
C(11)	206 (6)	530 (2)	2910 (2)
C(12)	1709 (7)	944 (2)	2956 (2)
C(13)	−5154 (7)	1800 (2)	1723 (3)
C(14)	−6479 (7)	−282 (2)	597 (2)
C(15)	−2600 (6)	−684 (2)	1316 (2)
C(16)	−866 (8)	−830 (2)	1828 (3)

EXPERIMENTAL

The ^{13}C NMR spectra of 30% solutions of the substances in a 10 mm ampul were recorded with a Bruker HX-90 spectrometer; the signal of $CDCl_3$ served as the control for deuterium stabilization of the spectrometer. A laboratory B-NC-12 minicomputer was used for Fourier transformation and optimization of the spectra. The following set of parameters was used: a sweep of 5000 Hz, a pulse width of 10 μsec (15 μsec for a 90° pulse), and a time between pulses of 5 sec. The PMR spectra of solutions in $CDCl_3$ were recorded with a Perkin-Elmer R-12B spectrometer (60 MHz) with tetramethylsilane as the internal standard. The IR spectra were obtained with a UR-20 spectrometer. The UV spectra were obtained with a Specord spectrophotometer. The mass spectra were recorded with a Varian Mat-311 spectrometer with direct introduction of the samples into the ion source. The recording conditions were as follows: an accelerating voltage of 3 kV, and ionization energy of 70 eV, and a cathode emission current of 300 μA.

X-Ray Diffraction Analysis. The analysis was conducted with a Syntex P1 automatic diffractometer. The crystals of III were monoclinic with a = 8.006, b = 21.69, c = 16.609 Å , $\beta = 102.69°$, space group $P2_1/_c$, z = 8 (two independent molecules), $d_{calc} = 1.399\ g/cm^3$, and $(MoK_\alpha) = 1.1\ cm^{-1}$. The intensities of 2381 reflections were measured with the automatic diffractometer.. The structure was elucidated by a direct method with the aid of the automated system of Rentgen-70 programs. The coordinates of the hydrogen atoms were revealed from differential synthesis. The structure was refined by the method of least squares within the anisotropic approximation for all of the nonhydrogen atoms (R = 0.045).

Since the bond lengths and angles in two independent molecules were virtually identical, the values for one of them are presented in Tables 3-5. The coordinates of the nonhydrogen atoms are presented in Table 6.

Quaternary Quinoxalinium Salts. These salts were obtained by quaternization of the base with alkyl halides; the method in [22] was used to obtain quinoxaline from o-phenylenediamine and 40% aqueous glyoxal.

General Method for the Preparation of endo-3a,4,9,9a-Tetrahydrofuro[2,3-b]-quinoxalines (IIa-e). A 2-ml (0.018 mole) sample of acetylacetone was added to a suspension of 2 g (0.007 mole) of N-methylquinoxalinium iodide in 7 ml of ethanol, the mixture was cooled to -50°C, and 2 ml (0.020 mole) of diethylamine was added with stirring. The reaction was carried out in such a way that the temperature of the reaction mass did not exceed 20°C. The reaction took place in 5-10 min and was virtually determined by the rate of dissolving of the starting quaternary quinoxalinium salt. The precipitated colorless crystals of endo-2,9-dimethyl-3-acetyl-3a,4,9,9a-tetrahydrofuro[2,3-b]quinoxaline (IIa) were separated and recrystallized from ethanol. The recrystallization should be carried out as fast as possible, since heating ethanol solutions of II gives rise to their irreversible transformations, in the course of which the solutions turn red. Compounds II in the crystalline state can be stored for several months without appreciable changes in their spectra (IR and PMR). Compounds IIb-e were similarly obtained. The characteristics of IIa-e and their spectral data are presented in Tables 1 and 2.

endo-2,9-Dimethyl-3,4-diacetyl-3a,4,9,9a-tetrahydrofuro[2,3-b]quinoxaline (III). A solution of 2 g of IIa in 5 ml of acetic anhydride was maintained at 50°C for 10 min, after which it was cooled and poured over ice. The precipitated III was separated and recrystallized from isopropyl alcohol to give a product with mp 181-182°C and R_f 0.70 [Silufol, isopropyl alcohol—water (4:1)]. Found: C 67.4; H 6.5; N 9.8%. $C_{16}H_{18}N_2O_3$. Calculated: C 67.1; H 6.4; N 9.8%. UV spectrum in ethanol, λ_{max} (log ε): 219 (4.37), 246 (4.17), 272 (4.00). Mass spectrum, m/z ($\geqslant$ 10%): 51 (19), 63 (12), 65 (21), 76 (13), 77 (35), 78 (10), 91 (14), 92 (27), 102 (12), 103 (13), 118 (25), 119 (13), 130 (10), 131 (15), 132 (10), 133 (51), 143 (11), 145 (33), 157 (22), 159 (54), 171 (11), 183 (19), 185 (15), 187 (15), 201 (100), 202 (13), 229 (25), 243 (84), 244 (49), 286 (37).

2,3-d_2-Quinoxaline. A mixture of 30 g of quinoxaline with 50 ml of heavy water was heated in an autoclave at 225-230°C for 40 h, after which it was cooled and extracted three times with ether. The combined extracts were dried over calcined sodium sulfate, the ether was removed by distillation, and the residue was distilled *in vacuo* and redeuterated under the same conditions with 30 ml of D_2O for 40 h. After this procedure was repeeated three times, the degree of deuteration of quinoxaline was greater than 90%.

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MASS-SPECTRAL BEHAVIOR OF 2-AZATRIPTYCENE AND ITS DERIVATIVES

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The mass-spectral behavior of 11 aromatic and partially hydrogenated 2-azatriptycenes was investigated. It was established that the principal fragmentation pathway for these compounds is the formation of $[M-nH]^{+}$ and $[M-nH]^{2+}$ ions (n = 1-6), as well as pseudoretrodiene fragmentation of the heterocyclic ring with the elimination of the atoms in the 2 and 3 positions.

The mass-spectral behavior of triptycene has been studied frequently [1-3]. It has been established that this compound upon electron impact loses one, two, three, and even four hydrogen atoms. Double charged (M^{+}, $[M-H]^{2+}$, and $[M-2H]^{2+}$) and even triply charged ions are also formed during fragmentation [1]. The facile formation of polycharged molecular or fragment ions of the $[M-H]^{n+}$, $[M-2H]^{n+}$, and $[M-3H]^{n+}$ type (n = 2, 3) is also characteristic for heteroanalogs of triptycene that contain phosphorus [4], arsenic, and antimony [5], or, simultaneously, nitrogen and phosphorus [6], or nitrogen and arsenic [7] atoms in the bridge positions of the triptycene molecule.

Up until now, the mass-spectral behavior of heteroanalogs of triptycene that contain heteroatoms in the aromatic rings has not been studied. To fill this gap we studied the mass-spectral behavior of a series of 2-azatriptycenes (III-XI). For comparison, we recorded the mass spectra of triptycene (I) itself and 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene (II).

It is apparent from an analysis of the mass spectra (Table 1) that intense molecular-ion peaks (the maximum peaks in most cases) are characteristic for all of the investigated compounds except VII. As in the mass spectrum of triptycene itself, peaks of $[M-H]^{+}$, $[M-2H]^{+}$, and $[M-3H]^{+}$ ions, as well as peaks of the corresponding doubly charged ions, were observed in the mass spectra of completely aromatic III-IX. However, whereas the intensities of the single charged fragment $[M-nH]^{+}$ (n = 1-3) are quite high (up to 42.8% of $\Sigma 100$),* the intensities of the $[M-nH]^{2+}$ ion peaks do not exceed 2.2% (see Table 2). Peaks of $[M-nH]$ ions ($n \geqslant 2$) are completely absent in the mass spectra of partially hydrogenated X and XI; the $[M-H]^{+}$ ion is also virtually absent in the mass spectrum of XI. The introduction of two nitrogen atoms in one of the aromatic rings does not lead to an appreciable change in the character of the primary fragmentation. Thus peaks of $[M-nH]^{+}$ ions (n = 1-3) are also

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*The $\Sigma 100$ symbol denotes the overall intensity of the ion peaks for m/z values from 100 to M^{+}.

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