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REACTIONS OF AZINIUM IONS.

4.* REACTIONS OF QUINOXALINIUM SALTS WITH NITROALKANES — SINGLE-STAGE PATH TO TETRAAZAHETEROCYCLES WITH BRIDGED AND FRAMEWORK STRUCTURES

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The addition of the carbanions of nitroalkanes of N-alkylquinoxalinium salts in an alcohol medium leads to dibenzo[d,k]-1,3,6,10-tetrasubstituted tricyclo[7.3.1.$0^{2,7}$]- and tetracyclo[7.3.1.$0^{2,7}0^{6,13}$]tridecanes.

The reactions of azinium ions with the carbanions of nitroalkanes take place in various ways. Thus, the N-methoxypyridinium ion adds nitroalkanes in the presence of sodium ethoxide at position 2 with subsequent opening of the pyridine ring [2]. More complex transformations were observed in the reaction of nitroalkanes with quaternary isoquinolinium salts, in which complex polycyclic systems with a framework structure are formed as a result of the successive combination of two isoquinolinium molecules [3]. In the present work we give the results from an investigation into the reactions of nitroalkanes with quaternary quinoxalinium salts, which are susceptible (unlike other azinium ions) to the formation of products from the diaddition of nucleophiles at positions 2 and 3 [4-7].

In fact, a common feature of the investigated transformations of quinoxalinium salts under the influence of trinitroalkane anions is the formation of tetrahydroquinoxalines from them as a result of the diaddition of the nucleophiles. However, the outcome of the reactions depends on the nature of the reagents, the solvent, and also the base.

When dissolved in an excess of nitroethane in the presence of diethylamine, N-methylquinoxalinium iodide (Ia) gives a high yield (87%) of the diaddition product II, melting at

*For Communication 3, see [1].

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TABLE 1. Characteristics of the Tetrahydroquinoxalines II, IIIa,d,e, and IX

Cmpd. No.	T_{mp}, °C	IR spectrum, cm^{-1}		Mass spectrum, m/z (I > 10%)	Found, %			Molecular formula	Calculated, %			Yield, %
		NH	NO_2		C	H	N		C	H	N	
II	196—197	3392	1508, 1342	—	53,5	6,3	18,8	$C_{13}H_{18}N_4O_4$	53,1	6,2	19,0	86
IIIa	217—218	—	1510, 1340	77 (12), 131 (12), 145 (62), 185 (43), 317 (100), 363 (19)	66,4	5,7	19,0	$C_{20}H_{21}N_5O_2$	66,1	5,8	19,3	37, 62
IIId	176—178	—	1500, 1345	77 (19), 130 (10), 131 (61), 159 (100), 160 (29), 185 (22), 331 (89), 332 (21), 377 (6)	66,7	6,3	19,4	$C_{21}H_{23}N_5O_2$	66,8	6,1	18,6	42
IIIe	158	—	1507, 1343	77 (11), 131 (35), 159 (82), 160 (12), 199 (44), 345 (100), 346 (37), 391 (7)	67,4	6,5	17,8	$C_{22}H_{25}N_5O_2$	67,5	6,4	17,9	44
IX	157	3392	1510, 1350	77 (13), 102 (13), 131 (12), 133 (21), 145 (100), 146 (17), 171 (43), 394 (2)	64,0	6,6	21,6	$C_{21}H_{26}N_6O_2$	64,0	6,6	21,3	55

196-197°C (Table 1). The ^1H NMR spectrum of II in deuterochloroform contains clear doublet signals for the protons of the methyl groups of the two nitroethane residues at 1.53 and 1.57 ppm, a singlet for the N-methyl protons at 2.90 ppm, a broadened signal for the NH proton at 5.82 ppm, and complex multiplets for the protons of the benzene ring (6.4-6.8 ppm, 4H) and the four methine protons in the region of 3.4-4.8 ppm. This part of the spectrum becomes significantly simplier in the transition to the 2,3-deuterated analog of II, obtained fromthe 2,3-^2H-labeled quinoxalinium ion and nitroethane (see the experimental section) and this confirms the structure of II.

The reaction of the cation Ia with nitroethane ethanol takes place differently. The polycyclic compound III, melting at 217-218°C and having the molecular formula $C_{20}H_{21}N_5O_2$ (according to mass spectrometry and elemental analysis), was isolated with a yield of 37% as the main reaction product under these conditions. By using dimethylamine as base we were able to increase the yield of III to 62% (see the experimental section). From the ^1H and ^{13}C NMR spectra of III it follows that it contains two N-methyltetrahydroquinoxaline fragments (singlets for the protons of the two N-methyl groups at 3.14 and 3.24 ppm, multiplets for the eight protons of the two benzene rings in the region of 6.5-7.5 ppm) and one nitroethane residue (a singlet for the methyl protons at 1.30 ppm) (Table 2). In view of the hydrogenated structure of the pyrazine ring and also the absence of the absorption for NH groups in the IR and ^1H NMR spectra it is possible to imagine three types of coupling of the reagents corresponding to the above-mentioned molecular composition. They can be called the 2,3 (IIIa), 2,2 (IIIb), and 3,3 (IIIc) isomers, depending on which atoms of the pyrazine ring are directly attached to the nitroethane fragment.

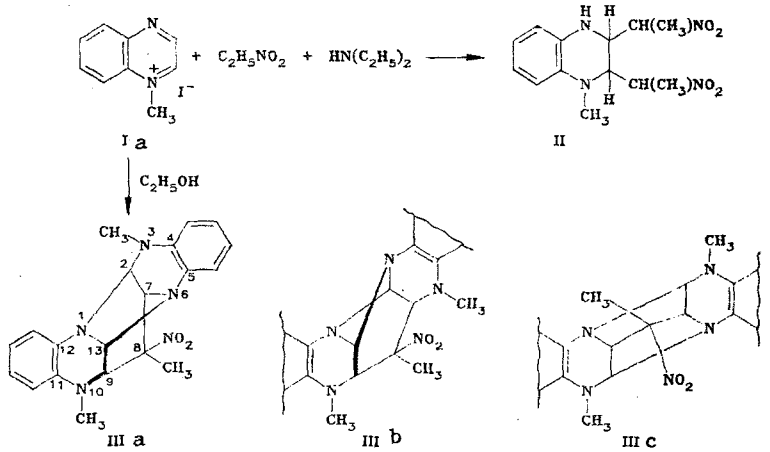


TABLE 2. ^1H and ^{13}C NMR Spectra of 8-Nitrodibenzo[d,k]-1,3,6,10-tetraazapolycyclotridecanes IIIa,d,e, and IX in Deuterochloroform

Compound	Proton chemical shifts, δ, ppm (SSCC, Hz)							
	2-H	7-H	8-H	8-CH_3	9-H	13-H	N—R	Benzene rings
IIIa	4,37, s	4,11, s	—	1,30, s	4,64, d ($^3J_{9,13}$=2,7)	4,36, d	3,14. s (3H), 3,24, s (3H) (two NCH_3)	6,5—7,4. m (8H)
IIId	4,25. s	4,00; bs	4,40, bd. ($^3J_{8,9}$=2,4; $^3J_{8,7}$=0,8)	—	4,60, dd ($^3J_{9,13}$=2,6)	4,27, d	1,0—1,5. m (6H). 3,3—3,8. m (4H) (two NC_2H_5)	6,5—7,3. m (8H)
IIIe	4,21, s	4,11, s	—	1,24, s	4,60, d ($^3J_{9,13}$=2,6)	4,19, d	1,0—1,4, s (6H). 3.4—3,7, s (4H) (two NC_2H_5)	6,5—7,3. m (8H)
IX	4,78, d d ($^3J_{2,3}$=1,6; $^3J_{2,7}$=4,5)	3,94, d d ($^3J_{7,8}$=10,5)	4,69, dd ($^3J_{8,9}$=2,7)	—	4,45, dd ($^3J_{9,13}$=1,5)	3,88, d	2,80, s (3H), 2,98, s (3H) (two NCH_3)	6,4—7,3. m (8H)

Compound	^{13}C chemical shifts, δ, ppm							
	2-C	7-C	8-C	8-CH_3	9-C	13-C	N—R	Carbon atoms of benzene rings
IIIa	64,6 ($^1J_{CH}$=162)	80,9 ($^1J_{CH}$=157)	96,2	18,0	66,0 ($^1J_{CH}$=150)	81,9 ($^1J_{CH}$=172)	37,8; 38,4 (two NCH_3)	109,5, 113,4, 117,0, 118,3, 124,7, 125,3, 125,8, 127,3, 129,7, 132,4, 136,6, 141,9
IIId	61,1*	79,8	88,5	—	63,8*	81,2	12.5 and 44.3; 13.9 and 45.6 (two NC_2H_5)	112,0, 112,9, 117,9, 118,0, 125,9, 125,9, 126,9, 127,8, 131,1, 131,9, 134,2, 140,5
IIIe	64,2 ($^1J_{CH}$=159)	77,8 ($^1J_{CH}$=152)	96,0	18,4	64,2 ($^1J_{CH}$=152)	81,5 ($^1J_{CH}$=181)	12.5 and 44.4; 13.9 and 45.5 (two NC_2H_5)	110,0, 112,6, 116,9, 117,5, 124,8, 125,6, 126,4, 127,3, 130,0, 132,2, 135,3, 140,7
IX	53,3	69,4*	88,3	—	61,7*	67,7	39,6; 40,8 (two NCH_3); 41,9 $N(CH_3)_2$	109,7, 113,4, 114,1, 116,9, 118,7, 119,5, 125,8, 125,9

*The assignment of the carbon atoms marked by asterisks may be reversed.

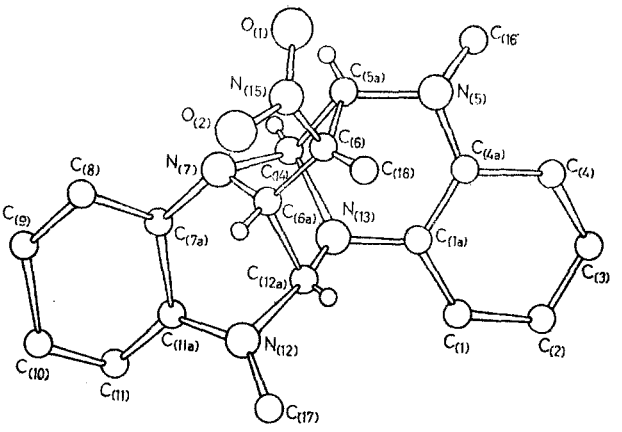


Fig. 1. The structure of compound IIIa, obtained by the reaction of N-methylquinoxalinium iodide with nitroethane and diethylamine in ethanol.

TABLE 3. Bond Lengths, d (Å), for Compound IIIa (the numbering of the atoms given in Fig. 1)

Bond	d	Bond	d	Bond	d
$C_{(1)}$—$C_{(1a)}$	1,385 (4)	$C_{(6a)}$—$N_{(7)}$	1,482 (3)	$C_{(12a)}$—$N_{(13)}$	1,489 (3)
$C_{(1)}$—$C_{(2)}$	1,379 (4)	$N_{(7)}$—$C_{(7a)}$	1,442 (3)	$C_{(12a)}$—$C_{(6a)}$	1,528 (4)
$C_{(2)}$—$C_{(3)}$	1,367 (5)	$C_{(7a)}$—$C_{(8)}$	1,375 (4)	$N_{(13)}$—$C_{(14)}$	1,478 (3)
$C_{(3)}$—$C_{(4)}$	1,388 (5)	$C_{(8)}$—$C_{(9)}$	1,406 (4)	$N_{(13)}$—$C_{(1a)}$	1,443 (3)
$C_{(4)}$—$C_{(4a)}$	1,410 (4)	$C_{(9)}$—$C_{(10)}$	1,374 (5)	$C_{(6)}$—$N_{(15)}$	1,535 (4)
$C_{(1a)}$—$C_{(4a)}$	1,405 (4)	$C_{(10)}$—$C_{(11)}$	1,392 (5)	$N_{(15)}$—$O_{(1)}$	1,215 (4)
$C_{(4a)}$—$N_{(5)}$	1,384 (4)	$C_{(11)}$—$C_{(11a)}$	1,403 (4)	$N_{(15)}$—$O_{(2)}$	1,182 (4)
$N_{(5)}$—$C_{(16)}$	1,443 (4)	$C_{(11a)}$—$C_{(7a)}$	1,414 (4)	$C_{(6)}$—$C_{(18)}$	1,498 (4)
$N_{(5)}$—$C_{(5a)}$	1,445 (3)	$C_{(11a)}$—$N_{(12)}$	1,383 (4)	$N_{(5)}$—$C_{(16)}$	1,443 (4)
$C_{(5a)}$—$C_{(6)}$	1,575 (4)	$N_{(12)}$—$C_{(17)}$	1,464 (4)	$N_{(12)}$—$C_{(17)}$	1,464 (4)
$C_{(6)}$—$C_{(6a)}$	1,535 (4)	$N_{(12)}$—$C_{(12a)}$	1,465 (4)		

TABLE 4. Bond Angles, ω (deg), for Compound IIIa (Fig. I)

Angle	ω	Angle	ω	Angle	ω
$C_{(1)}C_{(2)}C_{(3)}$	119,5 (3)	$C_{(5a)}C_{(6)}C_{(6a)}$	101,8 (2)	$N_{(7)}C_{(6a)}C_{(12a)}$	99,9 (2)
$C_{(1)}C_{(1a)}C_{(4a)}$	120,0 (3)	$C_{(5a)}C_{(6)}N_{(15)}$	109,0 (2)	$N_{(7)}C_{(14)}N_{(13)}$	103,9 (2)
$C_{(1)}C_{(1a)}N_{(13)}$	119,4 (3)	$C_{(5a)}C_{(14)}N_{(7)}$	101,3 (2)	$C_{(7a)}C_{(8)}C_{(9)}$	120,9 (3)
$C_{(1a)}C_{(1)}C_{(2)}$	120,6 (3)	$C_{(5a)}C_{(14)}N_{(13)}$	109,0 (2)	$C_{(7a)}C_{(11a)}C_{(11)}$	117,7 (3)
$C_{(1a)}C_{(4a)}N_{(5)}$	120,4 (2)	$C_{(6)}C_{(6a)}N_{(7)}$	100,7 (2)	$C_{(7a)}C_{(11a)}N_{(12)}$	120,0 (3)
$C_{(1a)}C_{(4a)}C_{(4)}$	118,7 (3)	$C_{(6)}C_{(6a)}C_{(12a)}$	112,4 (2)	$C_{(7a)}N_{(7)}C_{(14)}$	114,7 (2)
$C_{(1a)}N_{(13)}C_{(14)}$	114,4 (2)	$C_{(6)}N_{(15)}O_{(1)}$	119,1 (3)	$C_{(8)}C_{(9)}C_{(10)}$	118,2 (3)
$C_{(1a)}N_{(13)}C_{(12a)}$	116,8 (2)	$C_{(6)}N_{(15)}O_{(2)}$	118,5 (3)	$C_{(9)}C_{(10)}C_{(11)}$	122,0 (3)
$C_{(2)}C_{(3)}C_{(4)}$	121,2 (3)	$C_{(6)}C_{(5a)}C_{(14)}$	100,8 (2)	$C_{(10)}C_{(11)}C_{(11a)}$	120,2 (3)
$C_{(3)}C_{(4)}C_{(4a)}$	119,9 (3)	$C_{(6a)}C_{(6)}N_{(15)}$	106,6 (2)	$C_{(11)}C_{(11a)}N_{(12)}$	122,3 (3)
$C_{(4)}C_{(4a)}N_{(5)}$	120,9 (3)	$C_{(6a)}C_{(6)}C_{(18)}$	116,2 (3)	$C_{(11a)}C_{(7a)}C_{(8)}$	121,0 (3)
$C_{(4a)}N_{(5)}C_{(16)}$	120,9 (2)	$C_{(6a)}N_{(7)}C_{(7a)}$	110,8 (2)	$C_{(11a)}N_{(12)}C_{(12a)}$	113,5 (2)
$C_{(4a)}N_{(5)}C_{(5a)}$	119,9 (2)	$C_{(6a)}N_{(7)}C_{(14)}$	94,9 (2)	$C_{(11a)}N_{(12)}C_{(17)}$	117,2 (3)
$C_{(4a)}C_{(1a)}N_{(13)}$	120,5 (3)	$C_{(6a)}C_{(12a)}N_{(12)}$	107,4 (2)	$C_{(12a)}N_{(12)}C_{(17)}$	114,8 (2)
$N_{(5)}C_{(5a)}C_{(6)}$	115,2 (2)	$C_{(6a)}C_{(12a)}N_{(13)}$	101,7 (2)	$C_{(12a)}N_{(13)}C_{(14)}$	104,3 (2)
$N_{(5)}C_{(5a)}C_{(14)}$	112,9 (2)	$N_{(7)}C_{(7a)}C_{(8)}$	118,8 (2)	$N_{(15)}C_{(6)}C_{(18)}$	105,8 (2)
$C_{(5a)}N_{(5)}C_{(16)}$	119,1 (2)	$N_{(7)}C_{(7a)}C_{(11a)}$	120,1 (2)	$O_{(1)}N_{(15)}O_{(2)}$	122,4 (3)
$C_{(5a)}C_{(6)}C_{(18)}$	117,0 (2)				

TABLE 5. Equations for the Planes A-F in Some Planar Fragments of the Molecule of IIIa, the Projections Δ of the Atoms from These Planes, and the Angles between the Planes (Fig. 1)

A $2.105x+14.821y+4.668z-5.864=0$
B $2.206x+15.101y+4.026z-5.590=0$
C $-2.414x+10.179y+11.063z-6.751=0$
D $-2.714x+9.861y+11.170z-6.732=0$
E $-0.317x-8.109y+11.908z-7.690=0$
F $7.082x+5.488y-6.722z+0.236=0$

Plane A		Plane B		Plane C		Plane D		Plane E		Plane F	
Atom	Δ, Å	Atom	Δ, Å	Atom	Δ, Å	Atom	Δ, Å	Atom	Δ, Å	Atom	Δ, Å
$C_{(7a)}$	0,00	$C_{(6a)}$	−0,31*	$C_{(1a)}$	0,00	$C_{(1)}$	0,00	$N_{(13)}$	0,05	$C_{(5a)}$	0,02
$C_{(8)}$	0,00	$N_{(7)}$	0,00	$C_{(4a)}$	0,00	$C_{(2)}$	−0,01	$C_{(14)}$	−0,03	$C_{(14)}$	−0,01
$C_{(9)}$	0,00	$C_{(7a)}$	0,00	$N_{(5)}$	0,00	$C_{(3)}$	0,01	$N_{(7)}$	−0,81*	$N_{(7)}$	0,85*
$C_{(10)}$	−0,01	$C_{(11a)}$	0,00	$C_{(5a)}$	0,08*	$C_{(4)}$	0,00	$C_{(12a)}$	−0,05	$C_{(6)}$	−0,02
$C_{(11)}$	0,01	$N_{(12)}$	0,00	$C_{(14)}$	−0,56*	$C_{(4a)}$	−0,01	$C_{(6a)}$	0,03	$C_{(6a)}$	0,01
$C_{(11a)}$	0,00	$C_{(12a)}$	0,12*	$N_{(13)}$	0,00	$C_{(1a)}$	0,01				
		$N_{(13)}$	−1,64*								
		$C_{(14)}$	−1,32*								

Planes	Angle, deg	Planes	Angle, deg	Planes	Angle, deg
AB	2,8	*BC*	44,3	*CE*	67,3
AC	42,0	*BD*	46,6	*CF*	106,3
AD	44,3	*BE*	95,3	*DE*	66,8
AE	92,6	*BF*	63,5	*DF*	108,8
AF	65,3	*CD*	2,5	*EF*	114,2

*Atoms not involved in the calculation of the equation for the respective plane.

Since it proved impossible to determine the structure of the cyclization products III unambiguously on the basis of the ^1H and ^{13}C NMR data, we decided to use x-ray crystallographic analysis for this purpose. By this method it was established that the product has the structure of 3,8,10-trimethyl-8-nitrodibenzo[d,k]-1,3,6,10-tetraazatetracyclo [7.3.1.$0^{2,7}0^{6,13}$]-trideca-4,11-diene (IIIa).†

The structure of the molecule of compound IIIa is shown in Fig. 1, and the bond lengths and bond angles are given in Table 3 and 4. The molecule contains six condensed rings A-F. Both five-membered rings [imidazoline (E) and pyrrolidine (F)] have the envelope conformation with the $N_{(7)}$ atom projecting from the plane of the remaining four atoms of the imidazoline ring E ($C_{(6a)}$—$C_{(12a)}$—$N_{(13)}$—$C_{(14)}$) by −0.81 Å and from the plane of the pyrrolidine ring F ($C_{(14)}$—$C_{(5a)}$—$C_{(6)}$—$C_{(6a)}$) by 0.85 Å (Fig. 1). The six-membered tetrahydropyrazine rings B and C have a twisted half-chair conformation with the $C_{(12a)}$ and $C_{(6a)}$ atoms deviating from the plane of the other four atoms of ring B by 0.12 and −0.31 Å; for the $C_{(5a)}$ and $C_{(14)}$ atoms the deviations from the analogous plane of ring C amount to 0.08 and −0.56 Å respectively (Table 5). We not also that the sum of the bond angles at the nitrogen atoms $N_{(7)}$ (320.4°) and $N_{(13)}$ (335.5°) corresponds to pyramidal hybridization, whereas the configuration of the other two nitrogen atoms in the six-membered rings B and C differs; the $N_{(5)}$ nitrogen atom has the sum of the bond angles equal to 359.9°, which corresponds to a planar trigonal hybridization, while the $N_{(12)}$ nitrogen atom has 345.5° (a flattened pyramidal configuration) (Table 4). The lengths of the C—N bonds with the $N_{(5)}$ and $N_{(12)}$ atoms also differ; the $N_{(5)}$—C bonds are consistently shorter than the corresponding $N_{(12)}$—C bonds (Table 3), but the main bond lengths and bond angles in the molecule of the III as a whole agree well with standard values [9].

The data from x-ray crystallographic analysis make it possible to assign the signals in the ^1H and ^{13}C NMR spectra of IIIa. Calculation of the vicinal constants between the protons

†For the preliminary communication, see [8].

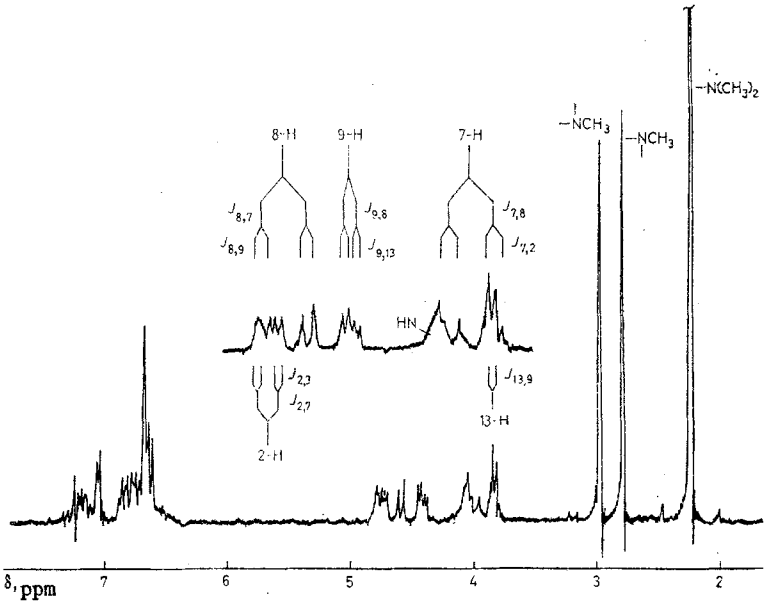


Fig. 2. The ^1H NMR spectrum in deuterochloroform for the reaction products IX obtained by the reaction of N-methylquinoxalinium iodide with nitromethane and dimethylamine in ethanol.

of the bridgehead atoms in the pyrazine rings by means of the Karplus–Conrow equation [10] showed that the experimental dihedral angles H–$C_{(6a)}$–$C_{(12a)}$–H (76°) and H–C(5a)–C(14)–H (47°) must correspond to the $^3J_{(H-H)}$, values of 0.2 and 3.2 Hz respectively. In fact, in the ^1H NMR spectrum of IIIa in deuterochloroform the protons of one pyrazine ring (9-H and 13-H) appear at 4.64 and 4.36 ppm in the form of two doublets with $^3J_{9,13}$ = 2.7 Hz, while the methine protons of the second pyrazine ring appear as broadened singlets at 4.37 and 4.11 ppm (Table 2). Thus, the x-ray data make it possible to break the signals of the methine protons down into two groups, i.e., 9-H, 13-H and 2-H, 7-H. An unambiguous assignment of the signals for these protons in the ^1H NMR spectrum of IIIa was made by comparison of the characteristics of the ^1H and ^{13}C NMR spectra, including allowance for the results from experiments with selective decoupling of the interaction of the carbon-13 nuclei with the individual protons. These experiments showed coupling between the proton with δ = 4.11 ppm and the carbon atom with the following spectral characteristics: δ = 80.9 ppm, $^1J_{(C-H)}$ = 157 Hz. Similarly it was established that the proton with δ = 4.64 ppm is coupled with the carbon atom which resonates at 66.0 ppm and has $^1J_{(C-H)}$ = 150 Hz. To judge from the $^1J_{(C-H)}$ values, the signals at 80.9 and 66.0 ppm must be assigned to the resonance of carbon atoms $C_{(9)}$ and $C_{(7)}$, coupled to one nitrogen atom, since the signals for the other two bridgehead carbon atoms [$C_{(2)}$ and $C_{(13)}$] have larger spin–spin coupling constants through one bond $^1J_{(C-H)}$ (162 and 172 Hz), which agrees with the arrangement of these CH groups between the two nitrogen atoms. On the basis of the values $^3J_{(H-H)}$ = 2.7 and $^1J_{(C-H)}$ = 150 Hz the signals with shifts $\delta_{(^1H)}$ 4.64 and $\delta_{(^{13}C)}$ 66.0 ppm were assigned to the $H_{(9)}$ and $C_{(9)}$ atoms, while the signals with $\delta_{(^1H)}$ 4.11 and $\delta_{(^{13}C)}$ 80.9 ppm were assigned to the resonance of the $H_{(7)}$ and $C_{(7)}$ atoms respectively. On account of the similar values of the chemical shifts for the 2-H and 13-H protons selective decoupling from each of them was impossible, and the assignment of the signals for the $C_{(2)}$ and $C_{(13)}$ carbon atoms was therefore made with regard to the following experimental data. First, the selective decoupling from the protons of the two N-methyl groups with chemical shifts of δ 3.14 and 3.24 ppm leads to narrowing of the signals for the α-carbon atoms in the ^{13}C NMR spectrum at 64.6 and 66.0 ppm, which makes it possible to assign the signal at δ 64.6 ppm to the resonance of the $C_{(2)}$ carbon atom (since the signal at δ 66.0 ppm had already been assigned to the $C_{(9)}$carbon atom). Second, during selective decoupling from the 9-H proton (δ 4.64 ppm), in addition to the coalesence of the signals for the $C_{(9)}$ carbon atom at 66.0 ppm into a singlet, narrowing was also observed in the lines for the signals of the $C_{(13)}$ carbon atom to a clear doublet at 81.9 ppm on account of the removal of the $^2J(C_{(13)}-H_{(9)})$ coupling. Altogether these data make it possible to assign the signals for the bridgehead carbon atoms and the protons attached to them in the ^1H and ^{13}C NMR spectra of compound IIIa (Table 2).

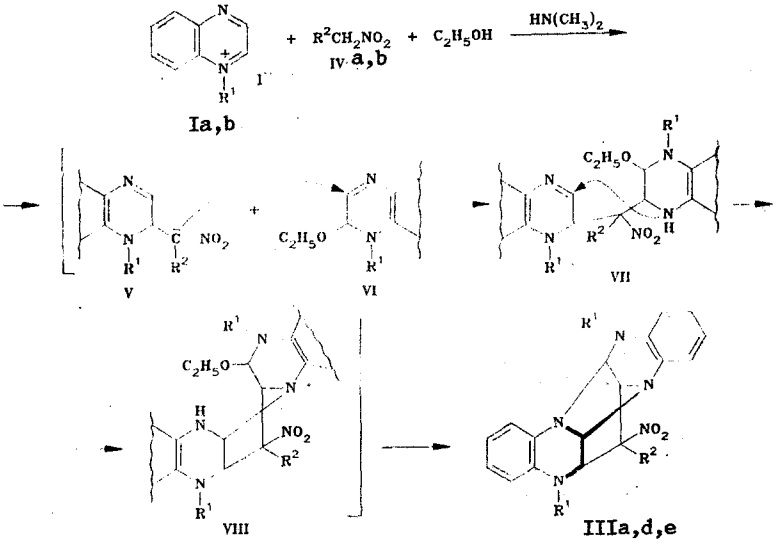
TABLE 6. Atomic Coordinates ($\times 10^4$, $\times 10^3$ for the hydrogen atoms) and the Temperature Factors $B_{eq} = 8\pi^2(U_{11}U_{22}U_{33})^{1/3}$ for Hydrogen Atoms (B_{iso} = 5.0 Å^2) (the standard deviations are given in parentheses)

Atom	x	y	z	B_{eq}
$C_{(1)}$	1599 (4)	−622 (2)	6964 (3)	4,1 (1)
$C_{(1a)}$	3356 (4)	−425 (2)	7233 (2)	3,2 (1)
$C_{(2)}$	989 (5)	−1266 (2)	7395 (3)	4,8 (1)
$C_{(3)}$	2186 (5)	−1715 (2)	8070 (3)	4,9 (1)
$C_{(4)}$	3997 (5)	−1535 (2)	8351 (2)	4,1 (1)
$C_{(4a)}$	4634 (4)	−888 (2)	7921 (2)	3,3 (1)
$N_{(5)}$	6442 (3)	−714 (1)	8161 (2)	3,6 (1)
$C_{(5a)}$	7054 (4)	−27 (2)	7747 (2)	3,0 (1)
$C_{(6)}$	6979 (4)	752 (2)	8335 (2)	3,3 (1)
$C_{(6a)}$	5819 (4)	1271 (2)	7511 (2)	3,0 (1)
$N_{(7)}$	6389 (3)	1000 (1)	6628 (2)	2,8 (1)
$C_{(7a)}$	5389 (4)	1390 (2)	5732 (2)	2,8 (1)
$C_{(8)}$	6189 (4)	1511 (2)	4970 (2)	3,3 (1)
$C_{(9)}$	5295 (5)	1917 (2)	4100 (2)	4,1 (1)
$C_{(10)}$	3596 (5)	2187 (2)	4029 (2)	4,1 (1)
$C_{(11)}$	2754 (4)	2068 (2)	4787 (2)	3,8 (1)
$C_{(11a)}$	3642 (4)	1667 (2)	5661 (2)	3,0 (1)
$N_{(12)}$	2887 (3)	1564 (1)	6456 (2)	4,0 (1)
$C_{(12a)}$	3862 (4)	1014 (2)	7204 (2)	3,1 (1)
$N_{(13)}$	3994 (3)	234 (1)	6760 (2)	2,9 (1)
$C_{(14)}$	5875 (4)	184 (2)	6715 (2)	2,8 (1)
$N_{(15)}$	8851 (4)	1120 (2)	8632 (2)	4,3 (2)
$O_{(1)}$	10155 (4)	702 (2)	8749 (2)	6,9 (2)
$O_{(2)}$	8970 (4)	1800 (2)	8772 (3)	3,6 (2)
$C_{(16)}$	7725 (5)	−1183 (2)	8872 (2)	4,7 (1)
$C_{(17)}$	936 (4)	1497 (2)	6215 (3)	4,9 (1)
$C_{(18)}$	6408 (5)	690 (2)	9283 (2)	4,8 (1)
$H_{(1)}$	77	−23	640	
$H_{(2)}$	−39	−141	713	
$H_{(3)}$	175	−223	847	
$H_{(4)}$	505	−181	894	
$H_{(5a)}$	840	−14	770	
$H_{(6a)}$	595	182	761	
$H_{(8)}$	746	124	504	
$H_{(9)}$	618	199	365	
$H_{(10)}$	286	254	342	
$H_{(11)}$	139	220	473	
$H_{(12a)}$	324	99	777	
$H_{(14)}$	602	−18	615	
$H_{(161)}$	771	−179	863	
$H_{(162)}$	750	−107	957	
$H_{(163)}$	898	−95	894	
$H_{(171)}$	67	141	690	
$H_{(172)}$	46	103	566	
$H_{(173)}$	26	204	588	
$H_{(181)}$	527	41	913	
$H_{(182)}$	620	123	957	
$H_{(183)}$	735	35	984	

The products with framework structures IIId, are formed in the reactions of N-ethylquinoxalinium iodide Ib with nitromethane and nitroethane in the presence of dimethylamine in ethanol. This follows from comparison of the characteristics of their ^1H and ^{13}C NMR spectra with the spectra of compound IIIa (Table 2). Substitution of the methyl group at the $C_{(8)}$ carbon atom by a hydrogen atom leads to the result that the signal for the 9-H proton in the ^1H NMR spectrum of compound IIId appears as a doublet of doublets at 4.60 ppm on account of interaction with the 13-H and 8-H protons. This provides a further argument in favor of the assignments of the signals in the ^1H NMR spectra for the series of compounds IIIa,d,e (Table 2).

The structure of compounds IIIa,d,e also corresponds fully to the mass-spectrometric data. In all cases the molecular ion peaks were recorded, although their intensities were low (Table 1). In the fragmentation schemes of the molecular ions it is possible clearly to trace the processes of the removal of the nitro group and also the formation of the high-intensity peaks of the quinoxalinium ions (Table 1).

From the established structure of compounds IIIa,d,e it follows that in the course of the reaction the CH-active center of the nitroalkane adds at position 2 of one molecule of the cations Ia,b and to the $C_{(3)}$ carbon atom of another quinoxalinium molecule. Since the addition of the nitroalkane at position 3 can only be realized with the formation of an intermediate having a 1,2-dihydroquinoxaline structure, the reaction mechanism can presumably be represented by the following scheme:



I a IIIa $R^1=CH_3$, I b IIId,e $R^1=C_2H_5$; III a,e,IV b $R^2=CH_3$, IIId, IVa $R^2=H$

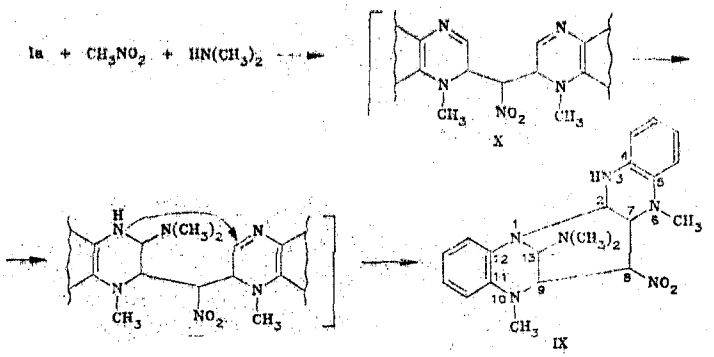
It is supposed that the two addition reactions of the carbanions of the nitroalkanes IVa, b and the ethoxide ion to the quinoxalinium ions Ia,b, leading to two types of covalent adducts (the C-adducts V and the O-adducts VI take place concurrently when the reaction is carried out in an alcohol–base medium. We recently demonstrated the formation of the dihydroquinoxalines VI in an ethanol solution in the presence of bases by ^1H NMR spectroscopy [11]. Extremely likely also is the reaction of the adducts V and VI, leading to the intermediate VII, with subsequent intramolecular cyclizations to the polycyclic compounds IIIa,d,e through the intermediates VIII. The presented mechanism makes it possible to explain the formation of compounds IIIa,d,e in ethanol solution by the participation of the covalent adducts VI of the cations Ia, b with ethanol in the cyclization and agrees well with the fact that the reactions take place in a different direction in the absence of ethanol (see the formation of compound II).

The direction of the cyclization of quinoxalinium salts with nitroalkanes does not depend only on the nature of the solvent. Smallest changes in the structure of the reagents can lead to new types of reaction products. Thus, the cation Ia in reaction with nitromethane in ethanol in the presence of dimethylamine gives a 55% yield of the polycyclic compound IX with a completely different structure compared with compound (IIIa) obtained in the reaction with nitroethane under the same conditions. On the basis of the spectral data (^1H and ^{13}C NMR spectra, mass spectra) the reaction product was assigned the structure of 6,10-dimethyl-13-dimethylamino-8-nitrodibenzo[d,k]-1,3,6,10-tetraazabicyclo[7.3.1.$0^{2,7}$] trideca-4,11-diene (IX) (Tables 1 and 2, Fig. 2).

In the tricyclic compound IX, unlike the tetracyclic product IIIa,* the nitroalkane residue was added to both tetrahydropyrazine rings at position 2, while one of the pyrazoline rings has a free NH group, which shows up clearly in the IR spectra at 3392 cm^{-1} and also in the NMR spectrum in deuterochloroform as a broadened signal at 4.08 ppm (Fig. 2). The 2-H proton also interacts with the NH proton and appears at 4.78 ppm in the form of a doublet with $^3J_{2,7}$ = 4.5 and $^3J_{2,3}$ = 1.6 Hz. It is easy to assign the remaining signals for the

*In both cases we are concerned with the skeleton of the molecules, disregarding the annellated benzene rings.

protons of the hydrogenated fragment of the molecule by subsequent analysis of the coupling between the methine protons. The 7-H, 8-H, and 9-H protons also appear in the form of double doublets at 3.94, 4.69, and 4.45 ppm respectively, while the signal of the 13-H proton appears as a doublet at 3.88 ppm with $^3J_{9,13}$ = 1.5 Hz (Table 2, Fig. 2).



It is logical to represent the formation of compound IX by a scheme involving the intermediates X and XI. The change in the type of inclusion of the nitroalkane fragment in the structure of the obtained polycyclic compound is evidently due to steric factors. In the reaction of the cation Ia with nitromethane it is possible to suppose that the product from simultaneous addition to two molecules of quinoxalinium at position 2 is formed (the intermediate X), whereas in the reaction with nitroethane 2–2 addition is difficult on account of steric hindrances on the part of the N-methyl groups, and a different type of coupling with addition of the nitromethane at positions 2 and 3 is therefore realized.

The investigated reactions of quinoxalinium salts with nitroalkanes demonstrate, on the one hand, the complexity of their mechanism and the variety of chemical transformations and, on the other, demonstrate the possibility of a new approach to the synthesis of bridged and framework tetraazapolycycloalkanes, based on simple single-stage methods and readily available reagents.

EXPERIMENTAL

The ^{1}H NMR spectra in deuterochloroform were recorded on Perkin-Elmer R-12B (60 MHz) and Bruker WH-90 (90 MHz) instruments with TMS as internal standard. The ^{13}C NMR spectra were obtained on a Bruker WH-90 spectrometer at 22.62 MHz. The ^{13}C chemical shifts were measured with reference to the signal of the solvent deuterochlorofrom (δ 77.0 ppm) and are given on the δ scale. The ^{13}C NMR spectra were recorded both with full decoupling of the spin–spin interaction between the protons and the carbons and without decoupling. For compound IIIa experiments were also carried out on the ^{13}C NMR spectra with selective decoupling between the carbons and the individual groups of protons. The IR spectra in Vaseline oil were obtained on a UR-20 spectrometer. The mass spectra were recorded on a Varian MAT-311 A instrument with direct injection into the ion source (accelerating potential 3 kV, ionization energy 70 eV, cathode emission current 1000 uA). The sample evaporation temperature was 120-170°.

The x-ray crystallographic analysis was performed on a Syntex P1 diffractometer (λCuK_α, graphite monochromator, $\theta/2\theta$ scan, 2100 reflections with $F^2 \leq 3\sigma$). The crystals of (IIIa) are monoclinic with the following unit cell parameters: a = 7.751(1), b = 17.159 (4), c = 13.855 (3) Å, β = 105.44 (2°), V = 1776 (6) Å^3, d_{calc} = 1.31 g/cm^3, z = 4, space group $P2_1/c$. The structure was interpreted by the direct method and refined by the method of least squares in anisotropic full-matrix approximation to R = 0.056 (Rw = 0.069.* The coordinates of the atoms are given in Table 6, and the bond lengths and bond angles are given in Tables 3 and 4. The equations for the planes of certain fragments of the molecules and the projection of the atoms from these planes are given in Table 5.

*The position and temperature parameters of the hydrogen atoms, revealed by the difference synthesis, were not refined.

2,3-Di(1-nitroethyl)-1-methyl-1,2,3,4-tetrahydroquinoxaline (II) (Table 1). A 2-g sample (7 mmoles) of N-methylquinoxalinium iodide was suspended in 5.5 ml (20 mmoles) of nitroethane, and 0.7 ml (7 mmoles) of diethylamine was added dropwise with stirring over 5-10 min until the initial salt had completely dissolved. The reaction solution was allowed to stand at room temperature for 2-3 h, after which the bright-yellow crysdtalsof II were separated. The yield was 1.85 g (86%); mp 196°C (from chloroform). ^{1}H NMR spectrum (in deuterochloroform), δ: 1.53 (CH_3, d, CH_3, J = 7 Hz), 1.57 (3H, d, CH_3, J = 7 Hz), 2.90 (3H, s, NCH_3), 3.4-4.8 (4CH, m, which is transformed into two quarters with centers at 4.50 and 4.60 ppm in the spectrum of the 2,3-D_2-deuterated derivative), 5.82 (1H, s, NH), 6.4-6.8 ppm (4H, m, protons of benzene ring). Electronic spectrum (in ethanol), λ_{max} (log ε): 222 (4.54), 260 (3.78), 3.10 nm (3.71).

3,8,10-Trimethyl-8-nitrodibenzo[d,k]-1,3,6,10-tetraazatetracyclo[7.3.1.$0^{2,7}0^{6,13}$]trideca-r,11-diene (IIIa). A. To a mixture of 4 g (15 mmoles) of N-methylquinoxalinium iodide and 1.1 ml (15 mmoles) of nitroethane in 20 ml of ethanol at room temperature, while stirring, we added dropwise 5 ml of a 25% solution of dimethylamine in ethanol. A solution was formed, and after 20-30 min light-yellow crystals of compound IIIa began to separate. After 1 h the precipitate was separated and recrystallized from ethanol. The yield was 1.65 g (62%); mp 217-218°C (from ethanol or acetone). If the crystals of IIIa did not separate from the reaction solution, a few drops of water were added to isolate them, and the precipitate was then separated and recrystallized twice from ethanol (the first time with charcoal).

B. To a mixture of 1 g (3.7 mmoles) of N-methylquinoxalinium iodide and 0.3 ml (3.8 mmoles) of nitroethane in 6 m of ethanol, while stirring, at room temperature we added 1.2 ml (12 mmoles) of diethylamine. A solution was formed and was left at room temperature overnight. The precipitate was separated and recrystallized from acetone, giving 0.25 g (37%) of yellowish prisms melting at 217-218°C. The characteristics of the compounds IIIa obtained by methods A (with dimethylamine) and B (with diethylamine) were fully identical (Tables 1 and 2).

3,10-Diethyl-8-nitrodibenzo[d,k]-1,3,6,10-tetraazatetracyclo[7.3.1.$0^{2,7}0^{6,13}$]trideca-4-11-diene (IIId) (Tables 1 and 2). To a mixture of 1 g (3.5 mmoles of N-ethylquinoxalinium iodide (Ib) and 0.23 ml (3.5 mmoles) of nitromethane in 10 ml of ethanol, while stirring, we added dropwise at room temperature 1.7 ml of a 33% aqueous solution of dimethylamine. The solution was left at room temperature for 3-4 h, after which the precipitate of compound IIId was separated in the form of yellow crystals. We obtained 0.3 g (46%) of the compound; mp 176-178°C (from ethanol).

3,8-Diethyl-8-methyl-8-nitrodibenzo[d,k]-1,3,6,10-tetraazatetracyclo[7.3.1.$0^{2,7}0^{6,13}$] trideca-4,11-diene (IIIe). To a mixture of 1 g (3.5 mmoles) of N-ethylquinoxalinium iodide, 0.26 ml (3.5 mmoles) of nitroethane in 6 ml of ethanol, and 1 ml of DMFA at room temperature with stirring we added dropwise 4 ml of a 7% ethanol solution of dimethylamine. The reaction solution was left at room temperature for 24 h, after which the crystals of IIIe were separated. The yield was 0.3 g (44%); mp 158°C (from ethanol).

6,10-Dimethyl-13-dimethylamino-8-nitrodibenzo[d,k]-1,3,6,10-tetraazatricyclo[7.3.1.$0^{2,7}$] trideca-4,11-diene (IX) (Tables 1 and 2). To a mixture of 4 g (15 mmoles) of N-methylquinoxalinium iodide, 0.9 ml of nitromethane (15 mmoles) in 24 ml of ethanol, and 5 ml of DMFA, at room temperature while stirring, we added 9 ml of a 7% ethanol solution of dimethylamine. The solution was kept at room temperature for 2-3 h and then in the refrigerator overnight. The precipitated compound IX was separated and recrystallized from ethanol. The yield was 1.59 g (55%); mp 157°C.

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PREPARATION OF SOME SUBSTITUTED 1,2,4-TRIAZINES

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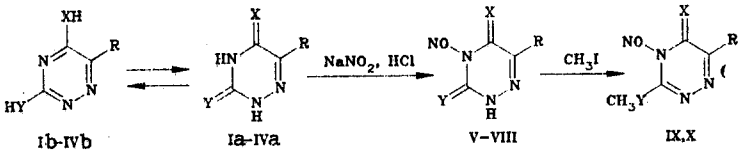
By nitrosating 6-R-1,2,4-triazine-3,5-diones(thiones) the corresponding 4-nitroso derivatives are obtained. On reacting methyl iodide with 3-thio-4-nitroso-6-R-1, 2,4-triazin-5-ones their methyl analogs are obtained. The influence of structural factors on the course of the reactions has been examined.

Interest in the chemistry of 1,2,4-triazines has been stimulated by the possibility of obtaining compounds possessing biological activity. Certain 4-substituted 1,2,4-triazin-5-ones [1], obtained by condensation of α-dicarbonyl compounds with thiocarbohydrazides [1, 2] or of hydrazine with acylhydrazones of glyoxylic acid esters [3], have found application as herbicides. Utilization of reactions for replacement of hydrogen in the triazine ring in preparing 4-substituted 1,2,4-triazin-5-ones has been little investigated except for methylation of 1,2,4-triazine-3,5-diones (thiones) by various reagents [4].

The aim of the present work was to investigate the nitrosation of 1,2,4-triazine-3,5-diones(thiones) for synthesis of the 4-nitroso derivatives.

The starting compounds — 3-thio-6-tert-butyl-1,2,4-triazin-5-one (I), 3-thio-6-phenyl-1, 2,4-triazin-5-one (II), 6-phenyl-1,2,4-triazine-3,5-dione (III), and 6-phenyl-1,2,4-triazine-3,5-dithione (IV) — were synthesized according to [5, 6]. The products were identified from the data of elemental analysis and IR spectroscopy.

On nitrosation of compounds I-IV with sodium nitrite in an acid medium, the 4-nitroso-6-R-1,2,4-triazine-3,5-diones(thiones) (V-VIII) were obtained respectively.



Ib-IVb Ia-IVa V-VIII IX,X

I—III, V—VII, IX, X X=O, IV, VIII X=S; I, II, IV—VI, VIII Y=S, III, VII Y=O, IX, X Y=—SCH_3; I, V, IX R=—$C(CH_3)_3$, II—IV, VI—VIII, X R=—C_6H_5

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