Reduction of the Ylide IIa. A solution of 0.05 g (0.16 mmole) of compound IIa in 10 ml ethanol with 0.2 ml hydrazine hydrate is refluxed for 5 min in the presence of 0.05 g of 0.2% Pd on carbon. After hot filtration dilution of the filtrate with water gives 0.037 g (74%) 1-amino-2-morpholinomethyl-9,10-anthraquinone, identified by comparison with a sample prepared according to [9].

The photolytic conversion Ia → IIa is followed spectrophotometrically by recording the UV spectra of the solution of compound Ia ($5 \cdot 10^{-5}$ M) in toluene at given time intervals after irradiation with an OI-18 lamp in a 1-cm cell through a WK-38 light filter ($\lambda_{pass} > 370$ nm). Under these conditions full conversion Ia → IIa is achieved after 0.5 h.

The thermolysis of the azide Ia is followed spectrophotometrically by taking samples from the boiling solution of Ia in m-xylene, with a final concentration of the product Ia of $5 \cdot 10^{-5}$ M. The decomposition of the azide Ia is completed after 0.5 h.

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CYCLIZATION OF N-ALKYLAMMONIUM CATIONS WITH BIFUNCTIONAL NUCLEOPHILES. 17.* ANNELATION OF IMIDAZOLE AND 1,2,4-TRIAZINE RINGS WITH PYRAZINES VIA THE REACTIONS OF THIOSEMICARBAZIDES WITH PYRAZINIUM SALTS

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1- and 4-mono- as well as 1,4-disubstituted thiosemicarbazies undergo cyclization reactions upon treatment with N-alkylpyrazinium and quinoxalinium salts to give N-aminosubstituted imidazo[4,5-b]pyrazines and imidazo[4,5-b]quinoxalines, respectively. Thiosemicarbazides containing substituents in the 2-position react with N-alkylquinoxaline salts to give 1,2,4-triazino[5,6-b]quinoxalines after cyclization.

In previous papers [2-4] we have reported that cyclization of quaternary N-alkylquinoxalinium salts with bifunctional nucleophiles containing a thioamide functional group, R—C(=S)-NH_2, results in the formation of a variety of heterocyclic derivatives, depending on the nature of the substituents and on the reaction conditions. For example, treatment of salts of the N-alkylquinoxalinium ions I with thiobenz- and thioacetamides gives thiazolo[4,5-b]-quinoxalines [2]; in the same way, reaction with phenylthioureas produces imidazo[4,5-b]quinoxalines [3]. The course of these types of cyclization reactions are governed not only by

*For communication No. 16, see [1].

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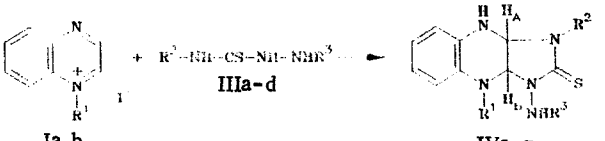
TABLE 1. ^{1}H-NMR Spectra of Imidazo[4,5-b]quinoxalines IVa-g and VI, and Imidazo[4,5-b]pyrazine V

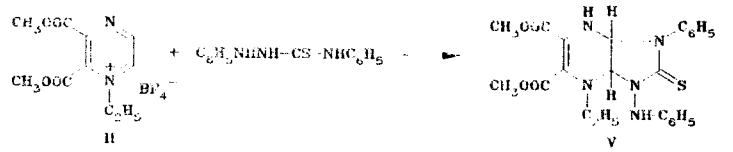
Compound	Proton chemical shifts, δ, ppm (in DMSO-D_6)					$^3J(H_A-H_B)$, Hz
	H_A, br d*	H_B, d	R^1	benzene ring	R^2, R^3	
IVa	5,16†	5,16†	2,81 s (3H)	6,5—6,7 m (4H)	8,88 br.s (1H, NH), 4,33 br.s (2H, NH_2)	—
IVb	5,17	5,29	2,9—3,7 m (2H), 1,12 t (3H)	6,5—7,0 m (4H)	8,82 br.s (1H, NH), 4,46 br.s (2H, NH_2)	9,0
IVc	5,82	5,41	3,18 s (3H)	6,3—6,8 m (4H)	7,1—7,6 m (5H), 4,80 br.s (2H, NH_2)	9,5
IVd	5,78	5,52	3,3—3,9 m (2H), 1,18 t (3H)	6,4—7,0 m (4H)	7,1—7,8 m (5H), 4,83 br.s (2H, NH_2)	9,2
IVe	5,38†	5,38†	2,84 s (3H)	6,6—7,0 m (4H)	8,08 br.s (1H, NH), 9,98 br.s (1H, NH)& 7,0—7,6 m (5H)	—
IVf	5,76	5,65	2,98 s (3H)	6,3—6,8 m (4H)	6,8—7,3 m (10H), 8,46 br.s (1H, NH)	9,8
IVg	5,93	5,63	3,03 s (3H)	6,4—6,8 m (4H)	7,1—7,8 m (5H), 1,91 s (3H, $COCH_3$)‡	9,0
V	5,83	5,52	3,0—3,7 m (2H), 0,92 t (3H)	3,68 s (3H, $COOCH_3$), 3,77 s (3H, $COOCH_3$)	6,6—7,5 m (10H), 8,22 br.s (1H, NH)	8,0
VI	5,90	5,38	2,84 s (3H)	6,4—7,0 m (4H)	7,1—7,8 m (5H), 9,30 br.s (1H, NH)	9,2

*The H_A proton doublet appears broadened as a result of its interaction with the NH group proton.
†The H_A and H_B protons give rise to one unresolved signal. The orientation of the imidazole ring in compounds IVa and IVe is assumed to be the same as in the other imidazo[4,5-b]quinoxalines IVb-d, f, and g.
‡The NH group proton is masked by the multiplet due to the aromatic protons.

kinetic considerations, but also by thermodynamic factors concerning the stabilities of the cyclization products [4]. For these reasons, thiazolo[4,5-b]quinoxalines isomerize to regioisomeric cycloadducts rather than to derivatives of pyrrolo[2,3-b]quinoxalines; it has also been demonstrated that thiazolo[4,5-b]quinoxalines are converted to imidazo[4,5-b]quinoxaline-2-tione derivatives upon treatment with phenylthioureas [4].

In the present paper we describe the cyclization reactions of N-alkylquinoxalinium cations (Ia,b) and 2,3-dimethoxycarbonyl-N-ethylpyrazinium ion (II) with yet another type of polyfunctional nucleophile containing a thioamide functional group, namely thiosemicarbazides, which can, in principle, react as either 1,3- or 1,4-dinucleophiles; as a consequence, a variety of combinations are possible for the N- and S-reactive centers which participate in the cyclization processes.





Ia, IVa,c,e—g R^1=CH_3; Ib, IVb,d R^1=C_2H_5; IIIa,c, IVa,b,e R^2=H; IIIb,d IVc,d,f,g R^2=C_6H_5; IIIa,b, IVa-d R^3=H; IIIc,d, IVe,f R^3=C_6H_5; IVg R^3=$COCH_3$

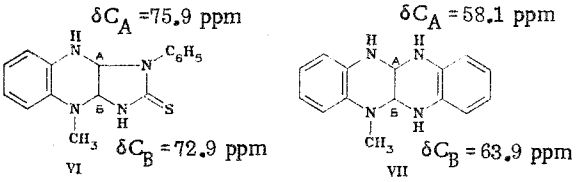
We have found that the unsubstituted thiosemicarbazide IIIa, as well as its 1- and 4-mono- and 1,4-disubstituted derivatives IIIb-d, exhibit the properties of N,N'-dinucleophiles

in their reactions with the cations Ia,b and II; the cyclization products formed in this way are the N-aminosubstituted imidazo[4,5-b]quinoxaline-2-thiones IVa-f and imidazo[4,5-b]-pyrazine-2-thione V, respectively (Tables 1-3).

The conclusions concerning both the formation of the imidazole ring system as well as its orientation were reached on the basis of the ^{1}H- and ^{13}C-NMR spectra of compounds IVa-g. ^{1}H-NMR spectral analysis of the compounds IVb-d revealed that the values of the vicinal coupling constants $^3J(H_A-H_B)$ were all in the range 9.0-9.8 Hz (Table 1); this is consistent with annelation of the five-membered imidazole ring and a cis-orientation of the H_A and H_B hydrogen atoms [3, 5]. The regiochemistry of the annelation fragment could be determined from the effects of the R^2 and R^3 substituents on the chemical shifts of the H_A and H_B protons (Table 1). Replacement of the R^2 = H group (IVa,b) with R^2 = C_6H_5 (IVc,d) resulted in a sharp displacement of the H_A proton signal toward weaker field, by 0.66 and 0.61 ppm, respectively; the H_B proton signal, on the other hand, undergoes a much smaller downfield shift of 0.25 and 0.23 ppm, respectively (Table 1). Substitution of a hydrogen atom on the free amino group with a phenyl group (R^3 = C_6H_5) exerts a much weaker influence on the chemical shifts of the H_A and H_B proton signals. Thus, the transition from compound IVa to IVe is marked by an 0.22 ppm downfield shift of both the H_A and H_B chemical shifts; for the pair of compounds IVc and IVf, the chemical shift difference for the H_B proton signals is 0.24 ppm (Table 1).

The N-amino group is easily discerned in the ^{1}H-NMR spectra of compounds IVa-d; it gives rise to a broad singlet with an intensity corresponding to two proton atoms (Table 1). The presence of the N-amino group in compound IVc was also verified by acetylation with acetic anhydride to give compound IVg. In the ^{1}H-NMR spectrum of compound IVg the H_B proton signal is shifted 0.22 ppm downfield, whereas the H_A proton signal is shifted only 0.11 ppm (Table 1).

The ^{1}H-NMR spectral characteristics of compounds IVa-g, in particular the chemical shift values and the vicinal coupling constants $^3J(H_A-H_B)$, are in excellent agreement with those found for 3-phenyl-9-methyl-2,3,3a,4,9,9a-hexahydro-1H-imidazo[4,5-b]quinoxaline-2-thione (VI) [3, 5], which serves as a close structural analog of the hydrogenated imidazo 4,5-b - quinoxaline nucleus (Table 1).



^{13}C-NMR spectral analysis of compounds IVc,e,f also verified the conclusions concerning the structures of the cyclization products (Table 2). It is known that the chemical shifts of the C_A and C_B ring junction carbon atom signals are affected significantly by the electronegativity of the heteroatoms immediately bound to them as well as by their three-dimensional arrangement, i.e., by the size of the annelated ring fragment [6]. Comparison of the structures of compounds VI and VII, which are illustrated above, reveals that for a given selection of heteroatoms around the ring junction carbon atoms, the C_A and C_B chemical shift values are shifted substantially toward higher field upon replacement of the five-membered imidazole ring with the six-membered pyrazine ring system.

All of the ^{13}C-NMR spectral data for compounds IVc,e,f, namely the chemical shifts of the C_A and C_B carbon atom signals, in the region 72-79 ppm, the $^1J(C-H)$ coupling constants (165-168 Hz), as well as the δ values for the carbon atom in the C=S group in the imidazole ring (180-183 ppm) (Table 2), are very similar to those observed for the model compound imidazo 4,5-b quinoxaline VI [3, 5]; all of these data indicate that reaction with the thiosemicarbazides IIIa-d results in annelation of an imidazole ring, not a 1,2,4-triazine ring system. Signal assignments for the ^{13}C-NMR spectrum of compound IVc were made on the basis of a spectrum obtained in the absence of spin-spin proton decoupling; under these conditions, C_B appeared at 78.6 ppm as a doublet of quartets as a result of interaction with the N-methyl group protons, $^3J(C_B-HNCH_3)$ = about 3 Hz (Table 2).

TABLE 2. ^{13}C-NMR Spectra of Imidazo[4,5-b]quinoxalines IVc,e,f and VI

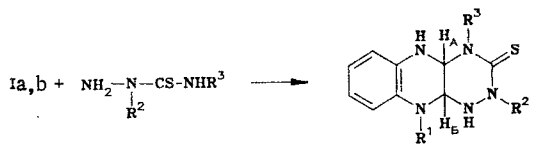
Compound	Carbon atom chemical shifts, δ, ppm; J, Hz (in DMSO-D_6)				
	C_A	C_B	N—CH_3	C=S	aromatic carbon atoms
IVc	72,6; $^1J_{(CH)}$=165	78,6; $^1J_{(CH)}$=168	37,5	180,9	113,2; 114,6; 119,7; 119,9; 126,9; 128,0; 129,0; 134,3; 135,8; 138,3
IVd	71,3*	72,9*	35,0	182,3	112,4; 112,8; 115,0; 118,9; 119,4; 119,7; 128,5; 133,9; 135,2; 147,9
IVf	72,7*	77,0*	37,1	182,0	112,7; 113,4; 114,8; 119,0; 119,9; 120,0; 127,2; 128,3; 128,6; 128,9; 133,9; 135,4; 138,0; 147,3
VI [5]	75,9; $^1J_{(CH)}$=166	72,9; $^1J_{(CH)}$=166	34,9	180,5	112,8; 115,4; 119,7; 120,5; 127,3; 128,6; 129,0; 133,7; 136,4; 137,9

*The assignments for these carbon atom signals can be inverted.

TABLE 3. Properties of Imidazo[4,5-b]quinoxalines IVa-g, Imidazo[4,5-b]pyrazine V, and 1,2,4-Triazino[5,6-b]quinoxalines IXa-c

Compound	mp, °C (dec)	Found, %				Molecular formula	Calc., %				Yield, %
		C	H	N	S		C	H	N	S	
IVa	168—170	51,2	5,7	—	13,3	$C_{10}H_{13}N_5S$	51,2	5,7	—	13,6	90
IVb	151—152	53,2	6,0	27,6	12,9	$C_{11}H_{15}N_5S$	53,0	6,1	28,1	13,9	95
IVc	185—186	61,4	5,5	—	10,2	$C_{16}H_{17}N_5S$	61,7	5,5	—	10,3	70
IVd	158—159	62,5	6,0	21,7	9,7	$C_{17}H_{19}N_5S$	62,7	5,9	21,5	9,9	65
IVe	175—176	61,5	5,5	22,2	10,2	$C_{16}H_{17}N_6S$	61,7	5,5	22,5	10,3	94
IVf	197—199	68,3	5,7	18,3	8,1	$C_{22}H_{21}N_6S$	68,2	5,5	18,1	8,3	90
IVg	169—170	61,2	5,4	19,8	9,1	$C_{18}H_{19}N_5OS$	61,2	5,6	1,6	9,1	88
V	188—189	58,8	5,2	15,2	7,3	$C_{23}H_{25}N_5O_4S$	59,1	5,4	15,0	6,9	90
IXa	173—175	53,3	6,0	27,5	12,8	$C_{11}H_{15}N_5S$	53,0	6,1	28,1	12,8	90
IXb	170—171	55,0	6,5	26,6	12,0	$C_{12}H_{17}N_5S$	54,7	6,5	26,6	12,2	65
IXc	152—154	68,6	5,9	17,5	8,0	$C_{23}H_{23}N_5S$	68,8	5,8	17,4	8,0	70

Cyclization of the salts Ia,b with the 2-substituted thiosemicarbazides VIIIa,b proceeds along a different course; the 1,2,4-triazino[5,6-b]quinoxaline-3-thiones IXa-c* are generated during these reactions (Tables 3-5).



VIIIa, IX a,b R^2=CH_3, R^3=H; IXa R^1=CH_3; b R^1=C_2H_5; VIIIb, IXc R^2=$CH_2C_6H_5$, R^3=C_6H_5; IXc R^1=CH_3

The ^{1}H and ^{13}C-NMR spectra of the 1,2,4-triazino[5,6-b]quinoxalines IXa-c differ significantly from those of the imidazo[4,5-b]quinoxalines IVa-g, particularly with respect to the chemical shift values of the carbon bridgehead atoms C_A and C_B and the H_A and H_B protons, as well as with respect to the magnitude of the spin-spin coupling constant between H_A and H_B (see Tables 4 and 5). For the 1,2,4-triazinoquinoxalines the H_A and H_B proton resonances appear at characteristically higher field (4.4-5.1 ppm); this is also true of the ^{13}C signals of the C_A and C_B carbon atoms, which appear in the region 58-65 ppm. These values may be

*For the initial preliminary communication, see [7].

TABLE 4. ^{1}H-NMR Spectra of the 1,2,4-Triazino[5,6-b]quinoxalines IXa-c and Quinoxalino[2,3-b]quinoxaline VII

Compound	Proton chemical shifts, δ, ppm (in DMSO-D_6)					$^3J(H_A-H_B)$, Hz
	H_A	H_B	N—R^1	benzene ring	R^2, R^3	
IXa	4,45	4,45	2,88 s (3H)	6,53 s (4H)	3,37 s (3H), 6,01 br.s (NH)	—
IXb	4,39 br.m	4,61 br.d	3,1—3,7 m (2H) 1,08 t (3H)	6,55 s (4H)	3,38 s (3H), 5,99 br.s (NH)	4,0
IXc	5,10 d.d	4,48 d.d	2,73 s (3H)	6,3—6,6 m (4H)	6,8—7,6 m (10H)	4,5
VII	4,69 m	4,46 m	2,90 s (3H)	6,2—6,7 m(8H)	—	2,7

TABLE 5. ^{13}C-NMR Spectra of the 1,2,4-Triazino[5,6-b]-quinoxalines IXa-c and Quinoxalino[2,3-b]quinoxaline VII

Compound	Carbon atom chemical shifts, δ, ppm; J, Hz (in DMSO-D_6)				
	C_A	C_B	N—R^1	C=S	aromatic carbon atoms
IXa	59,0	65,3	35,8 (N—CH_3)	173,2	111,8; 112,4; 117,3; 118,8; 130,3; 133,0
IXb	58,7	63,3	12,1 and 42,0 (N—C_2H_5)	172,9	111,8; 113,1; 117,6; 118,2; 128,8; 132,8
IXc	66,5 $^1J_{(CH)}=161$	66,5 $^1J_{(CH)}=161$	34,7 (N—CH_3)	178,3	111,5; 114,1; 117,9; 119,5; 127,1; 128,1; 128,6; 129,2; 129,9; 134,7; 137,7; 143,3
VII	58,1	63,9	35,4 (N—CH_3)	—	111,6; 112,6; 113,4; 113,7; 117,3; 117,5; 118,1; 130,9; 131,5; 132,6; 132,8

compared with those found for the imidazo[4,5-b]quinoxalines IVa-g, which occur at 5.1-6.0 and 72-79 ppm, respectively. We would like to point out that the ^{1}H and ^{13}C chemical shift values for the 1,2,4-triazino[5,6-b]quinoxalines IXa-c are in excellent agreement with those described in the literature for 6-methyl-5,5a,6,11,11a,12-hexahydroquinoxalino[2,3-b]quinoxaline (VII) [8], which has been selected as a model compound which is structually analogous to the bridged fragment present in compound IX (see Tables 4 and 5). The chemical shift displacement toward higher field appears to be characteristic of the transition from a five-membered ring annelated with a pyrazine ring to a six-membered ring containing the same selection of heteroatoms in the bridge (annelated) fragment [5]. The chemical shift values are markedly different not only for the bridgehead carbon atom C_A and C_B, but also for the δ carbon atoms at the C=S bonds in the imidazo[4,5-b]quinoxaline-2-thiones IV (180-183 ppm) and in the 1,2,4-triazino[5,6-b]quinoxaline-3-thiones IX (172-178 ppm). The latter values are in excellent agreement with the known ^{13}C-NMR spectral data for 1,2,4-triazino-3-thiones [9]. The sharp decrease which is observed for the $^3J(H_A-H_B)$ vicinal coupling constants upon the transition from the imidazo[4,5-b]quinoxalines IVa-g (9.0-9.8 Hz) to the 1,2,4-triazino-[5,6-b]quinoxalines IXa-c (4.0-4.5 Hz) may be attributed to the dramatic change in the geometry of the annelated ring fragment.

The orientation of the triazine ring relative to the N-methylpyrazine ring in compounds IXa-c was established on the basis of the effects of substituents on the chemical shift values of the H_A and H_B protons, as well as on the multiplicity patterns of the H_A and H_B proton signals (Table 4). If the triazine ring had occupied the reverse orientation, the H_B proton signal for compound IXc would have appeared as a doublet; in fact, the protons attached to both bridgehead positions interact with the protons of the neighboring NH groups and thus appear as doublets of doublets (Table 4).

We have demonstrated that the use of thiosemicarbazides in cyclization reactions with pyrazine salts permits the straightforward annelation synthesis of pyrazine, imidazole, as well as 1,2,4-triazine ring systems. In contrast to the imidazo[4,5-b]quinoxaline and imidazo[4,5-b]pyrazine derivatives, for which synthetic methods have appeared both in monographs [10] as well as in a series of research papers [3, 11-13], the condensed 1,2,4-triazino[5,6-b]quinoxaline system has not been mentioned previously, either in monographs [10, 14] or in

original research papers. Our communications concerning the synthesis of pyrazino[2,3-e]-1,2,4-triazine [15], the formation of 1,2,4-triazino[5,6-b]quinoxaline derivatives as reaction products in the course of thermolysis of 1,3-diaryl-5-(3-chloro-2-quinoxalinyl)formazines [16], as well as our published method for the preparation of hydrogenated 1,2,4-triazino[5,6-b]quinoxalines appear to be the first studies of this class of condensed heterocyclic ring systems.

EXPERIMENTAL

^{1}H-NMR spectra were recorded on a Perkin–Elmer R-12B spectrometer at 60 MHz for DMSO-D_6 solutions containing HMDS as internal standard (δ = 0.05 ppm). ^{13}C-NMR spectra were obtained on a Varian FT-80A spectrometer at 20 MHz for solutions in DMSO-D_6. ^{13}C chemical shifts were measured relative to solvent signals (δ = 39.7 ppm) and are reported on the δ scale.

The quaternary quinoxalinium salts Ia,b were prepared by dissolving the base in a threefold excess of the alkyl halide at room temperature followed by separation of the crystalline salt derivatives. The method described previously [17] was adapted for the synthesis of the quinoxaline from o-phenylenediamine and 40% aqueous glyoxal. The fluoroborate salt of N-ethyl-2,3-dimethoxycarbonylpyrazine (II) was obtained according to [3]. The thiosemicarbazides IIIa-d were of chemically pure grade. 2-Methylthiosemicarbazide VIIIa was prepared according to [18], 2-benzyl-4-phenylthiosemicarbazide (VIIIb) according to [19]. The model compounds, namely 3-phenyl-9-methyl-2,3,3a,4,9,9a-hexahydro-1H-imidazo[4,5-b]quinoxaline-2-thione (VI) [3] and 6-methyl-5,5a,6,11,11a,12-hexahydro-1H-quinoxalino[2,3-b]quinoxaline (VII) [8], were synthesized as described previously.

9-Methyl-3-phenyl-1-phenylamino-2,3,3a,4,9,9a-hexahydro-1H-imidazo[4,5-b]quinoxaline-2-thione (IVf). A suspension of 2.5 g (9.1 mmole) of N-methylquinoxalinium iodide (Ia) and 2.2 g (9.1 mmole) of 1,4-diphenylthiosemicarbazide (IIIf) in 5 ml of ethanol was treated with stirring with 2.5 ml of diethylamine, and then the reaction mixture was maintained at 40-50°C until all of the reagents had dissolved; the reaction mixture was allowed to stand at room temperature for 1 h. The precipitate of compound IVf was removed by filtration, washed with ethanol, and recrystallized from acetone. Yield 3.25 g (90%), mp 197-199°C (Table 3).

Compounds IVa-e were prepared in an analogous manner from the appropriate thiosemicarbazides and N-alkylquinoxalinium salts (Tables 1-3).

9-Methyl-3-phenyl-1-(N-acetylamino)-2,3,3a,4,9,9a-hexahydro-1H-imidazo[4,5-b]quinoxaline-2-thione (IVg). A suspension of 1 g (3.2 mmole) of 9-methyl-3-phenyl-1-amino-2,3,3a,4,9,9a-hexahydro-1H-imidazo[4,5-b]quinoxaline-2-thione (IVc) in 10 ml of acetic anhydride was treated with 5 ml of acetone and the mixture was heated until all of the reagents had dissolved (15-20 min). The reaction mixture was then cooled and poured onto 50 g of crushed ice. After standing for 1 day the precipitate due to compound IVg was separated by filtration, and recrystallized from a 5:1 mixture of ethanol and acetone. Yield 1 g (88%), mp 169-170°C (Tables 1-3).

7-Ethyl-3-phenyl-1-phenylamino-5,6-dimethoxycarbonyl-2,3,3a,4,7,7a-hexahydro-1H-imidazo-[4,5-b]pyrazine-2-thione (V). A suspension of 0.5 g of the fluoroborate II (1.6 mmole) and 0.38 g (1.6 mmole) of 1,4-diphenylthiosemicarbazide IIId in 2.5 ml of ethanol was treated with 0.5 ml of diethylamine. The mixture was heated at 40-50°C until all of the reagents had dissolved (15-20 min), cooled, and poured onto 20 g of crushed ice. The precipitate due to compound V was removed by filtration and recrystallized from a mixture of ethanol and acetone, 5:1. Yield 0.65 g (90%), mp 188-189°C (Tables 1 and 3).

10-Methyl-2-benzyl-4-phenyl-1,2,3,4,4a,5,10,10a-octahydro-1,2,4-triazino[5,6-b]quinoxaline-3-thione (IXc). A suspension of 1 g (3.9 mmole) of compound VIIIb and 1.06 g (3.9 mmole) of N-methylquinoxalinium iodide (Ia) in 2 ml of ethanol was treated with stirring with 1 ml of diethylamine at room temperature. After 15 min the reagents had dissolved completely and the reaction mixture was treated with 10 ml of ethanol; the resulting precipitate of IXc was filtered, washed with ethanol, and recrystallized from ethanol. Yield 1.1 g (70%), mp 152-154°C (Tables 3-5).

Compounds IXa,b were prepared in an analogous manner from salts Ia,b and 2-methylthiosemicarbazide VIIIa.

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