Fused polycyclic nitrogen-containing heterocycles
15.* 1,3-Bis(4-hydroxy-4-methoxycarbonyl-3,5-diphenylthiazolidin-2-ylideneamino)-benzene in the synthesis of thiazolo[3,4-*a*]quinoxalines

V. A. Mamedov,[a] E. A. Khafizova,[a] E. A. Berdnikov,[b] Ya. A. Levin,[a] I. Kh. Rizvanov,[a] I. Bauer,[c] and W. D. Habicher[c]*

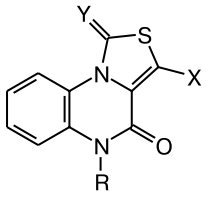
[a]*A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation. Fax: +7 (843) 273 2253. E-mail: mamedov@iopc.knc.ru*
[b]*Kazan State University, 18 ul. Kremlevskaya, 420008 Kazan, Russian Federation*
[c]*Institute of Organic Chemistry, Dresden University of Technology, 13 Mommsenstrasse, D-01062 Dresden, Germany*

Reactions of methyl chloro(phenyl)pyruvate with 1,3-bis(phenylthioureido)benzene easily afforded 1,3-bis(4-hydroxy-4-methoxycarbonyl-3,5-diphenylthiazolidin-2-ylideneamino)benzene. Reactions of the latter with 1,2-phenylenediamines gave various derivatives of thiazolo[3,4-*a*]quinoxalines, including their bisanalogs.

Key words: thiazolidines, thiazolo[3,4-*a*]quinoxalines, tautomerism, Hantzsch reaction, 1,2-phenylenediamines.

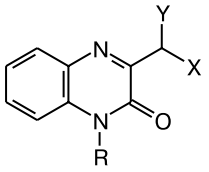
Azolo[*a*]quinoxalines and their 4,5-dihydro derivatives exhibit various biological and pharmacological properties[2—7] and are used in the synthesis of many biologically important compounds and drugs.[8—11] However, in contrast to the well-studied synthesis and properties of the imidazo[1,5-*a*]quinoxaline system, methods for the synthesis of thiazolo[3,4-*a*]quinoxalines **1** first obtained[12] as late as 1982 remain poorly investigated. Known routes to compounds of this type[12—21] are based on three different approaches.

The first approach involves replacement of the halogen atom in 3-(α-haloalkyl)quinoxalin-2-ones **2** (X = Cl, R = H, and Y = Ph or 2,4-$Cl_2C_6H_3$ and X = Br, Y = Me, and R = H or Et) by thiocyanate, thiourea, or xanthate residues. The resulting quinoxalines **2** (X = SCN, R = H, and Y = Ph or 2,4-$Cl_2C_6H_3$)[15,16] and **3** (X = NH_2, Y = NH, and Ar = Ph (see Ref. 17) and X = OMe, Y = S, and Ar = Ph or 2,4-$Cl_2C_6H_3$ (see Ref. 18)) easily undergo acid-catalyzed cyclization into thiazolo[3,4-*a*]quinoxa-



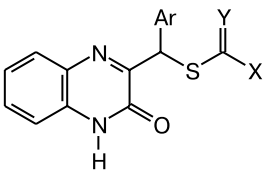
1

X = Ph; Y = NH, NPh; R = H
X = Ph, 2,4-$Cl_2C_6H_3$;
Y = S, O; R = H
X = Me; Y = NAc; R = H, Et



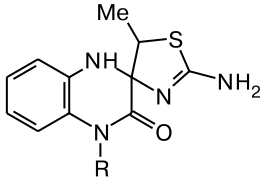
2

X = Cl, SCN; Y = Ph,
2,4-$Cl_2C_6H_3$; R = H
X = Br; Y = Me; R = H, Et



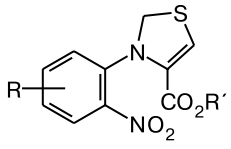
3

X = NH_2; Y = NH; Ar = Ph
X = OMe; Y = S;
Ar = Ph, 2,4-$Cl_2C_6H_3$



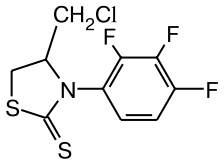
4

R = H, Et



5

R = H, 4-NO_2, 6-NO_2;
R′ = H, Me



6

* For Part 14, see Ref. 1.

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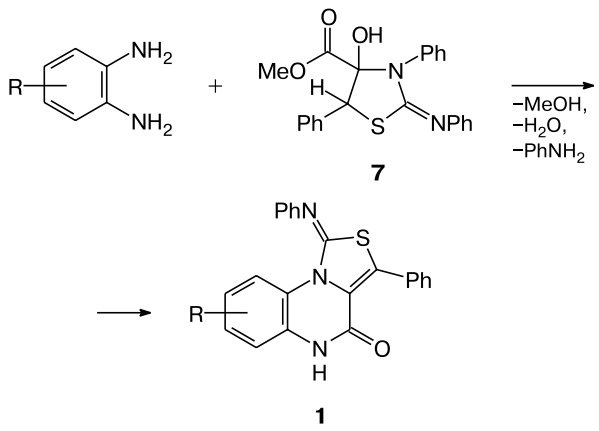
lines **1** [15–18] (except for X = Me, Y = NAc, and R = H or Et). Thioureido derivatives **4**, which predominantly exist as tautomeric spirothiazolinoquinoxalines, isomerize in acidic media to give thiazolo[3,4-*a*]quinoxalines **1** (X = Me, Y = NAc, and R = H or Et) in high yields.[19]

The second approach to the design of the thiazolo[3,4-*a*]quinoxaline system employs thiazole derivatives as starting materials, involving intramolecular reductive cyclization of 4-carboxy- or 4-methoxycarbonyl-3-(2-nitrophenyl)thiazolines **5** (R = H, 4-NO_2, or 6-NO_2; R′ = H or Me)[12,13] and amine-catalyzed intermolecular cyclization of 4-chloromethyl-3-(2,3,4-trifluorophenyl)thiazolidine-2-thione **6**.[20,21]

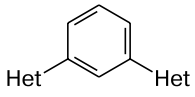
Unlike the first two approaches, according to which a thiazole molecule is annulated with the already existing quinoxaline system or *vice versa*, the third approach involves cascade annulation of the iminothiazolopyrazine system to benzene in reactions of 4-hydroxy-4-methoxycarbonyl-3,5-diphenyl-2-phenyliminothiazolidine[15,22–25] (**7**) with 1,2-phenylenediamines in boiling acetic acid (Scheme 1). The condensation affords, through elimination of methanol, water, and aniline, thiazolo[3,4-*a*]quinoxalines **1** in high yields.

Scheme 1



R = H, Me, NO_2

The present work was aimed at applying the last approach to the synthesis of bisthiazoloquinoxalines with 1,3-bis(thiazoloquinoxalinyl)benzenes as examples. These compounds can not only be biologically active but also be used as bi- and polydentate ligands or starting reagents in the synthesis of macrocycles, like other bishetaryl systems of the type **A** containing various heterocyclic fragments such as those of thiophene,[26] pyrazole,[27] 1,3,4-thiadiazole,[28] imidazole,[29] thiazole,[28,30] 1,3,4-oxadiazole,[31] 1,2,4-triazole,[32] 1,2,4-triazolo[3,2-*c*]quinazoline,[32] 1,2,4-triazolo[3,2-*a*]isoindole,[33] 10,10′-arylenebis(7*H*-benzo[*de*]-1,2,4-triazolo[5,1-*a*]isoquinolin-7-one),[33] benzoxazole,[34] indole,[35] and benzimidazole.[36]

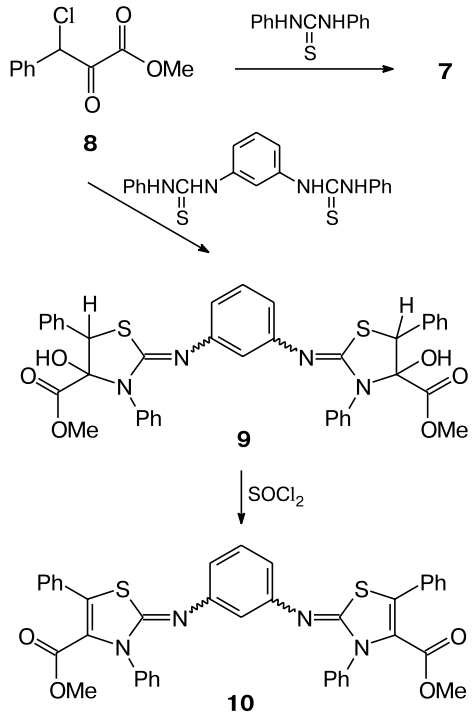


A

For this purpose, we used 1,3-bis(phenylthioureido)benzene[37] containing two *N*,*N*′-diphenylthiourea residues and methyl chloro(phenyl)pyruvate (**8**) as starting materials.

Like *N*,*N*′-diphenylthiourea,[25] its bisanalog, 1,3-bis(phenylthioureido)benzene, reacted with chloro ketone **8** to give stable bishydroxythiazolidine **9** as an intermediate in the Hantzsch reaction. The structure of compound **9** was proven by data from elemental analysis, IR spectroscopy, and mass spectrometry (Scheme 2) and confirmed by its easy and smooth dehydration with thionyl chloride into the final product of the Hantzsch bisreaction, namely, 1,3-bis[*N*,*N*′-(4-methoxycarbonyl-3,5-diphenylthiazolin-2-ylidene)]phenylenediamine (**10**).

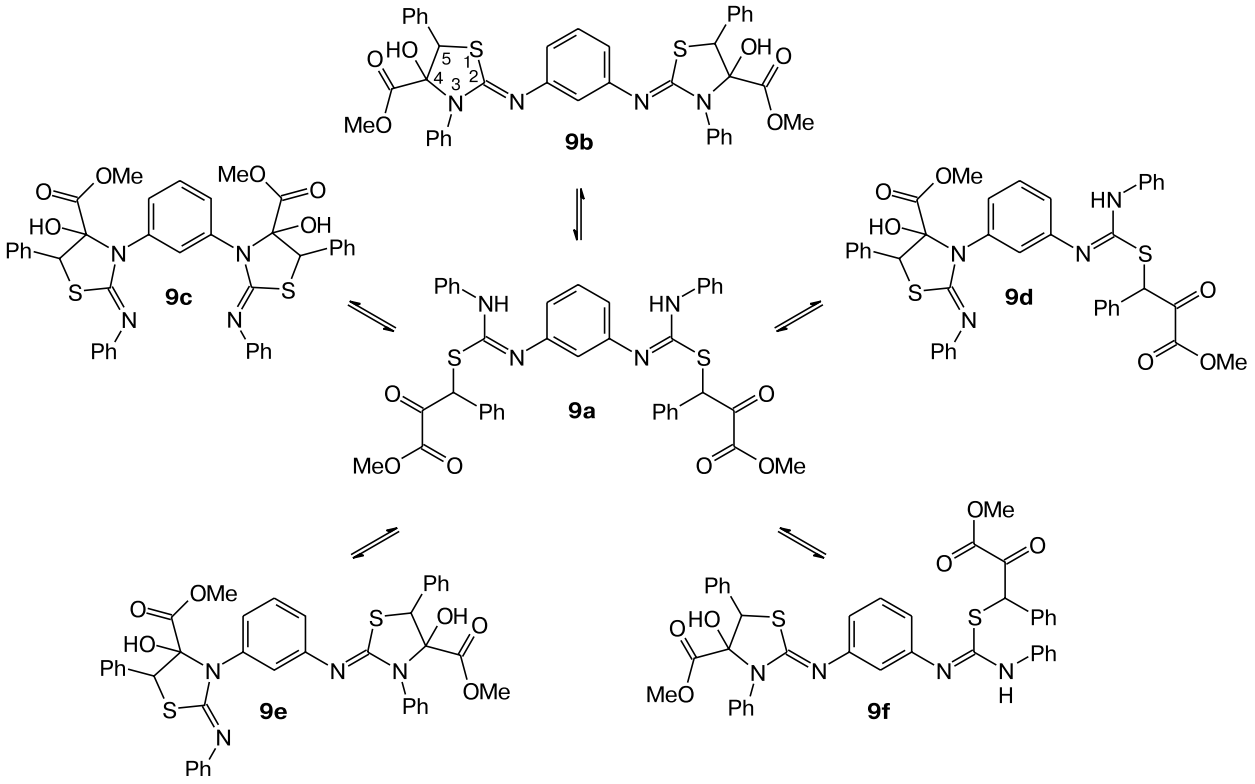
Scheme 2



The ^{1}H NMR spectrum of product **9** agrees with the bishydroxythiazolidine structure proposed for it. In contrast to its monohydroxythiazolidine prototype **7**, the ^{1}H NMR spectrum of bishydroxythiazolidine **9** shows a set of singlets for the methine and methoxy protons. The number of the singlets depends on the solvent but the ratio of the sums of their integral intensities remains constant (1 : 3).

The above complication of the ^{1}H NMR spectrum can be primarily due to the presence of four chiral centers

Scheme 3



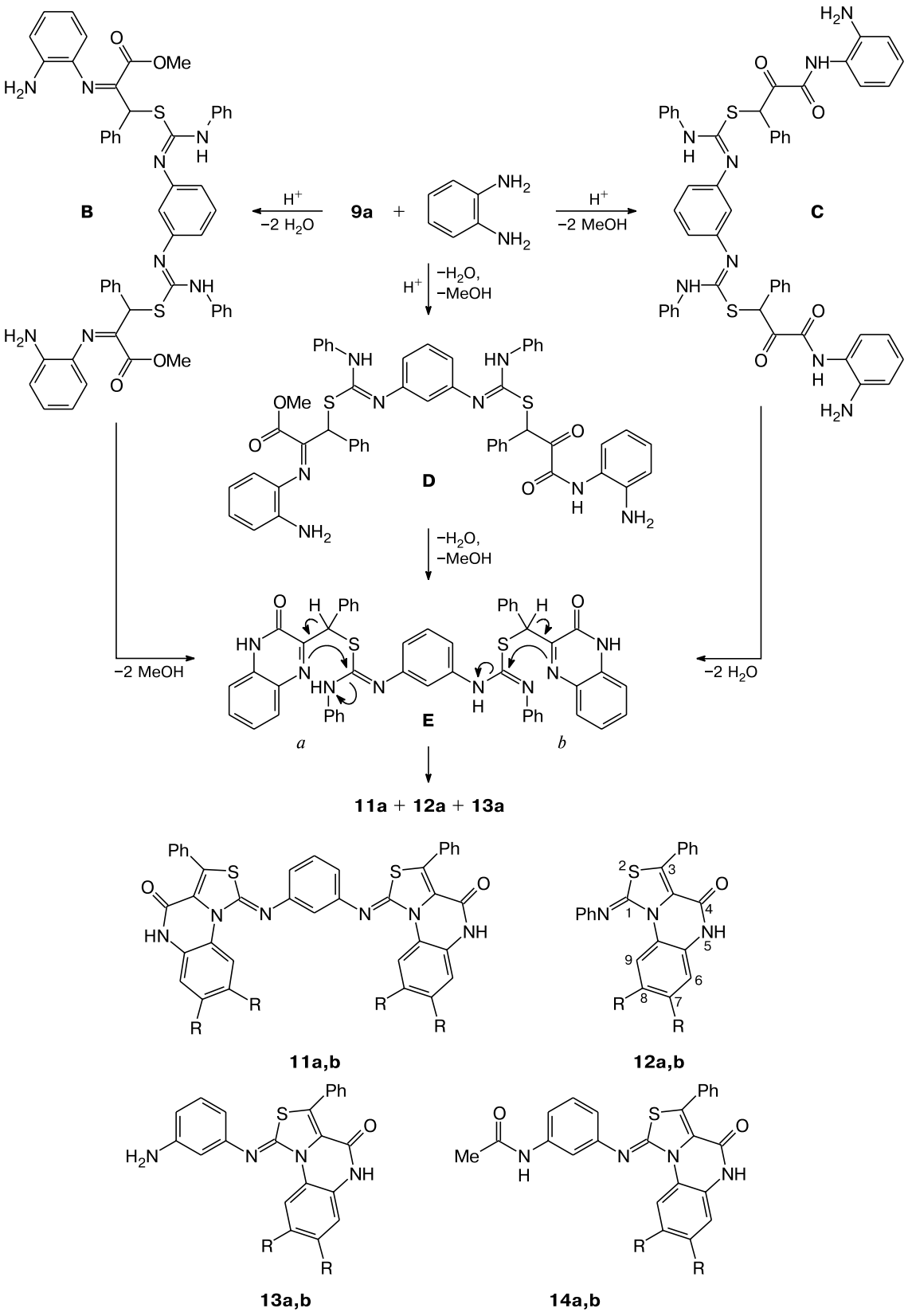
in structure **9** (two C(4) and two C(5) atoms), which gives rise to a great number of diastereomer pairs. Additional complications may result from *Z*—*E* isomerism relative to two C=N bonds and the partial existence of the hydroxythiazolidine fragments in the open-chain isothioureido form due to ring—chain tautomerism (*e.g.*, structures **9a,d,f**). Some of the resulting equilibria are shown in Scheme 3.

When carrying out the synthesis of bisthiazoloquinoxalines from bishydroxythiazolidine **9** according to the same scheme as in the synthesis of thiazoloquinoxalines **1** from monohydroxythiazolidine **7** (see Scheme 1),[23,24] the following should be kept in mind. In all tautomeric forms, compound **9** contains several types of electrophilic centers in both "halves". These are ketone, ester, and hemiaminal centers capable of reacting with 1,2-phenylenediamine in different sequential orders. The resulting intermediates can also undergo, again in different orders, further transformations leading to both the target product and other final products. For instance, different sequences of the transformations of tautomer **9a** in a reaction with 1,2-phenylenediamine can yield, through intermediates **B**, **C**, and **D**, bisthioureidobenzene **E**, which can close in an acidic medium an iminothiazoline ring *via* a nucleophilic attack of the N(4) atom of the quinoxaline system on the electrophilic C atom of the isothioureido group (Scheme 4).

For such a reaction of monohydroxythiazolidine **7**, which is the prototype of bishydroxythiazolidine **9**, the cyclization mechanism through the elimination of aniline has been considered earlier.[15] However, the case of bishydroxythiazolidine **9** is more complicated than that of its prototype **7** (see Scheme 4). For the latter, a structure analogous to **E** contain phenyl substituents at both N atoms of the isothioureido group, while in intermediate **E** derived from compound **9**, one of these N atoms is still bound to phenyl, while the other bears 3-substituted phenyl. Therefore, cyclization can be accompanied by the elimination of either aniline (pathway *a*, left-hand side of structure **E**) or *meta*-substituted aniline (pathway *b*, right-hand side). If the cyclization followed only pathway *a*, then elimination of two aniline molecules would give rise to compound **11a**. Pathway *b* would lead, through elimination of 1,3-diaminobenzene, to two molecules of thiazolo[3,4-*a*]quinoxaline **12a**. If the cyclization in different moieties of structure **E** followed pathways *a* and *b*, only one aniline molecule would be released to give thiazolo[3,4-*a*]quinoxaline **12a** and its aminophenyl analog **13a**.

These assumptions were confirmed experimentally. All final products **11a**, **12a**, and **13a** predicted for the reaction of bishydroxythiazolidine **9** with 1,2-phenylenediamine were isolated. The last product was obtained as *N*-acetyl derivative **14a** upon the acylation of

Scheme 4



R = H (**11a—14a**), Me (**11b—14b**)

1-(3-aminophenylimino)thiazolo[3,4-*a*]quinoxaline **13a** with acetic acid (solvent).

The low yield of bis(thiazolo[3,4-*a*]quinoxaline) **11a** suggests the predominant cyclization along pathway *b*. Structure **11a** was confirmed by MS data. In addition, its ^{1}H NMR spectrum shows a characteristic doublet (δ 9.40, J = 7.9 Hz) for the H(9) proton of the thiazolo[3,4-*a*]quinoxaline system[23,24] and a signal for the carbamoyl proton (δ 11.23). The major reaction product (46%) was thiazoloquinoxaline **12a**. Its spectroscopic characteristics were identical with those of the compound obtained earlier[23,24] by a reaction of methyl 4-hydroxy-3,5-diphenyl-2-phenyliminothiazolidine-4-carboxylate with 1,2-phenylenediamine. The structure of thiazolo[3,4-*a*]quinoxaline **14a** was confirmed by ^{1}H NMR data. Its spectrum contains the same signals as for compound **11a** and additional singlets at δ 9.97 and 2.20 for the NH and methyl protons, respectively, of the acetamido group.

Finally, apart from products **11a—14a**, we obtained 1,3-bisthiazoline **10** in low yield because of dehydration of compound **9**, in contrast to the reaction of 1,2-phenylenediamine with compound **7**, which affords only thiazolo[3,4-*a*]quinoxaline **12a**.[23,25]

A reaction of compound **9** with the more basic 4,5-dimethyl-1,2-phenylenediamine generally proceeds like the reaction with 1,2-phenylenediamine. The exception was that bis(thiazolo[3,4-*a*]quinoxaline) **11b** was the major product (yield 43%), while thiazoloquinoxalines **12b** and **14b** were only by-products.

Experimental

Melting points were determined on a Boetius hot stage. IR spectra were recorded on a Vector-22 FTIR spectrometer (Bruker) in Nujol (compound **9**) and in KBr pellets (**9**, **11b**, **12a**, and **14a,b**) and on a JASCO FT/IR-5000 spectrometer in the crystal (**9**, **10**, and **11a**). Mass spectra (EI) were recorded on a TRACE MS quadrupole mass spectrometer (ThermoQuest/Finnigan) (direct inlet probe, water cooling). MALDI mass spectra were recorded on a MALDI TOF DYNAMO mass spectrometer (Finnigan) with *p*-nitroaniline as a matrix. Elemental analysis was carried out on a CHN-3 analyzer. ^{1}H NMR spectra were recorded in DMSO-d_6 on Bruker DRX-500 (500.13 MHz) (for compounds **10** and **11a—14a**) and Bruker Avance-600 spectrometers (600.13 MHz) (for **9** and **11b—14b**). Chemical shifts are given on the δ scale with reference to the residual signal of DMSO as the internal standard (δ_H 2.54). Column chromatography was carried out on Silica gel 60 (0.015—0.040 mm, Merck) and Silicagel L 100/160 (Chemapol). TLC was performed with Silica gel 60 F_{254} (Merck) and Silufol plates. Methyl chloro(phenyl)pyruvate (**8**) was prepared according to a known procedure.[38]

1,3-Bis(phenylthioureido)benzene. A solution of 1,3-diaminobenzene (0.5 g, 4.6 mmol) and phenyl isothiocyanate (1.37 g, 10 mmol) in ethanol (20 mL) was stirred for 4 h. The crystals that formed were filtered off and washed with ethanol (2×10 mL). The yield was 0.46 g (92%), m.p. 189—190 °C (*cf.* Ref. 37: 160—161 °C). Found (%): C, 63.38; H, 4.69; N, 14.66; S, 16.86. $C_{20}H_{18}N_4S_2$. Calculated (%): C, 63.46; H, 4.79; N, 14.80; S, 16.94. IR (Nujol), ν/cm^{-1}: 3353, 3331, 3155, 2985, 1594, 1528, 1500, 1478, 1447, 1348, 1309, 1236, 1203, 1163, 1076, 869, 802, 761, 732, 691, 663, 627, 615. ^{1}H NMR (DMSO-d_6), δ: 7.12—7.49 (m, 13 H, 2 Ph + 3 H arom.); 7.69 (s, 1 H); 9.74, 9.88 (both s, 2 H each, 4 NH).

1,3-Bis(4-hydroxy-4-methoxycarbonyl-3,5-diphenylthiazolidin-2-ylideneamino)benzene (9). ***A.*** A mixture of 1,3-bis(phenylthioureido)benzene (0.5 g, 1.3 mmol) and sodium acetate (0.27 g, 3.3 mmol) in methanol (10 mL) was brought to boiling. A solution of methyl chloro(phenyl)pyruvate (**8**) (0.59 g, 2.8 mmol) in methanol (5 mL) was added dropwise to the resulting emulsion. The reaction mixture was refluxed for 10 min, stirred at ~20 °C for 10 h, and poured into cooled (5—10 °C) water (50 mL). The precipitate that formed was filtered off, washed with water (2×10 mL), and dried in air. Column chromatography on silica gel gave yellowish white crystals. The yield of compound **9** was 0.91 g (94%), m.p. 109—111 °C, R_f 0.49 ($CHCl_3$—AcOEt, 4 : 1). Found (%): C, 65.55; H, 4.60; N, 7.44; S, 8.72. $C_{40}H_{34}N_4O_6S_2$. Calculated (%): C, 65.74; H, 4.69; N, 7.67; S, 8.77. IR (crystal), ν/cm^{-1}: 3468, 3356, 3059, 3030, 2951, 2924, 2852, 1743 (C=O), 1631 (C=N), 1586 (C=C arom.), 1535, 1493, 1452, 1402, 1322, 1253, 1117, 1028, 1002, 832, 762, 733, 696, 633, 606, 583, 563, 496. IR (Nujol), ν/cm^{-1}: 3477 br (OH), 1743 (C=O), 1631 (C=N), 1585 (C=C arom.), 1530, 1493, 1325, 1257, 1142, 1118, 1076, 1028, 833, 765. IR (KBr), ν/cm^{-1}: 3477 br (OH), 3348 br (OH), 3059, 3029, 2951, 1743 (C=O), 1630 (C=N), 1586 (C=C arom.), 1538, 1493, 1452, 1322, 1253, 1142, 1117, 1027, 1002, 832, 762. MALDI-TOF MS, *m/z*: 731 $[MH]^+$. ^{1}H NMR (DMSO-d_6), δ: 3.12—3.23, 3.56—3.89 (s, no less than 10 and 20 lines, respectively, 6 H, 2 MeO); 5.05—5.11, 5.45—5.51 (s, no less than 7 and 8 lines, respectively, 2 H, 2 CH); 6.67—7.48 (m, 24 H, 4 Ph + 4 H arom.).

B. A solution of methyl chloro(phenyl)pyruvate (**8**) (0.59 g, 2.8 mmol) in CH_2Cl_2 (10 mL) was added dropwise at −15 to −20 °C to a mixture of 1,3-bis(phenylthioureido)benzene (0.5 g, 1.3 mmol) and sodium acetate (0.27 g, 3.3 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 3 h, warmed to ~20 °C, and washed with water (30 mL). The product was extracted with CH_2Cl_2 (2×15 mL). The extract was dried with Na_2SO_4 and concentrated *in vacuo* approximately by half to give colorless crystals. The yield was 0.29 g (58%), m.p. 114—116 °C.

The spectroscopic characteristics of compound **9** obtained according to procedures ***A*** and ***B*** were identical.

1,3-Bis(4-methoxycarbonyl-3,5-diphenylthiazolin-2-ylideneamino)benzene (10). A solution of $SOCl_2$ (1.8 mL, 20 mmol) in $CHCl_3$ (5 mL) was added dropwise to a stirred solution of compound **9** (0.8 g, 1.1 mmol) in $CHCl_3$ (10 mL). The reaction mixture was refluxed for 1 h, turning intense red. Stirring was continued at ~20 °C for an additional 20 h. The solvent and the excess of $SOCl_2$ were removed *in vacuo*. The resulting crystalline substance was washed with water (3×15 mL) and dried in air. The yield of compound **10** was 0.73 g (96%), colorless crystals, m.p. 105—107 °C, R_f 0.20 ($CHCl_3$—AcOEt, 5 : 1). Found (%): C, 68.91; H, 4.19; N, 7.89; S, 9.15. $C_{40}H_{30}N_4O_4S_2$. Calculated (%): C, 69.15; H, 4.35; N, 8.06; S, 9.23. IR, ν/cm^{-1}: 3053, 3016, 2943, 1729, 1620, 1574, 1487, 1435, 1348, 1274, 1199, 1166, 1074, 1022, 804, 759, 692, 609, 584. MALDI-TOF MS,

m/z: 695 $[MH]^+$. ^{1}H NMR (DMSO-d_6), δ: 3.46 (s, 6 H, 2 MeO); 6.98—7.57 (m, 24 H, 4 Ph + 4 H arom.).

Reaction of bishydroxythiazolidine 9 with 1,2-phenylenediamine. 1,2-Phenylenediamine (0.15 g, 1.4 mmol) was added to a solution of compound **9** (0.5 g, 0.7 mmol) in acetic acid (15 mL). The reaction mixture was refluxed for 15 min. The precipitate that formed was filtered off, washed with AcOH (2×5 mL), and dried to give compound **11a** in the analytically pure state. The filtrate was poured into water (50 mL) and the resulting solution was treated with aqueous 5% KOH to pH ~6—7. The crystals that formed were filtered off. Column chromatography in $CHCl_3$—AcOEt (10 : 1) gave products **12a**, **14a**, and **10**. The yield of the last product was 2—5%; its characteristics were identical with those of the compound **10** obtained as described above.

1,3-Bis(4-oxo-3-phenyl-1*H*,5*H*-thiazolo[3,4-*a*]quinoxalin-1-ideneamino)benzene (11a). The yield was 0.05 g (11%), yellow crystals, m.p. >360 °C, R_f 0.75 ($CHCl_3$—AcOEt, 5 : 1). Found (%): C, 69.31; H, 3.60; N, 12.83; S, 9.62. $C_{38}H_{24}N_6O_2S_2$. Calculated (%): C, 69.07; H, 3.66; N, 12.72; S, 9.70. IR, ν/cm^{-1}: 3183, 3127, 3047, 2981, 2898, 2773, 2703, 1674, 1633, 1605, 1566, 1490, 1477, 1437, 1393, 1334, 1316, 1265, 1217, 1139, 1092, 1075, 1048, 1033, 997, 962, 871, 804, 754, 740, 689, 658, 601, 551. MALDI-TOF MS, *m/z*: 661 $[MH]^+$. ^{1}H NMR (DMSO-d_6), δ: 6.82—7.44 (m, 20 H, 4 H arom. + 2 Ph + 6 H of quinoxaline); 9.40 (d, 2 H, 2 H(9), J = 7.9 Hz); 11.23 (s, 2 H, 2 NH).

3-Phenyl-1-phenylimino-1*H*-thiazolo[3,4-*a*]quinoxalin-4(5*H*)-one (12a). The yield was 0.11 g (46%), yellow crystals, m.p. 300—301 °C (*cf.* Ref. 22: m.p. 300—300.5 °C), R_f 0.59 ($CHCl_3$—AcOEt, 5 : 1). Found (%): C, 71.39; H, 4.15; N, 11.52; S, 8.47. $C_{22}H_{15}N_3OS$. Calculated (%): C, 71.52; H, 4.09; N, 11.37; S, 8.68. IR, ν/cm^{-1}: 3387, 3185, 3129, 1679, 1619, 1589, 1578, 1489, 1398, 1336, 1320, 1265, 1249, 1206, 1145, 1076, 1026, 806, 742, 690. ^{1}H NMR (DMSO-d_6), δ: 7.00—7.46 (m, 13 H, 2 Ph + 3 H of quinoxaline); 9.39 (d, 1 H, H(9), J = 7.4 Hz); 11.13 (s, 1 H, NH).

1-(3-Acetylaminophenylimino)-3-phenyl-1*H*-thiazolo[3,4-*a*]quinoxalin-4(5*H*)-one (14a). The yield was 0.012 g (4%), dark yellow crystals, m.p. 286—289 °C, R_f 0.12 ($CHCl_3$—AcOEt, 5 : 1). Found (%): C, 67.45; H, 4.15; N, 13.02; S, 7.50. $C_{24}H_{18}N_4O_2S$. Calculated (%): C, 67.59; H, 4.25; N, 13.14; S, 7.52. IR, ν/cm^{-1}: 3358, 3169, 3075, 2905, 1694, 1668, 1608, 1595, 1557, 1463, 1403, 1307, 1289, 1250, 1225, 1151, 939, 927, 875, 833, 754, 731, 689, 602, 583, 545, 467. ^{1}H NMR (DMSO-d_6), δ: 2.20 (s, 3 H, Me); 7.00—7.46 (m, 12 H, Ph + 4 H arom. + 3 H of quinoxaline); 9.41 (d, 1 H, H(9), J = 8.1 Hz); 9.97 (s, 1 H, MeCONH); 11.24 (s, 1 H, NH).

Reaction of bishydroxythiazolidine 9 with 4,5-dimethyl-1,2-phenylenediamine. A solution of compound **9** (0.5 g, 0.7 mmol) and 4,5-dimethyl-1,2-phenylenediamine (0.19 g, 1.4 mmol) in acetic acid (15 mL) was refluxed for 15 min. The precipitate that formed was filtered off and washed with AcOH (2×5 mL) to give compound **11b**. The filtrate was poured into water (30 mL) and the resulting solution was treated with aqueous 5% KOH to pH ~6—7. The crystals that formed were filtered off. Column chromatography in $CHCl_3$—MeOH (15 : 1) gave products **12b**, **14b**, and **10**.

1,3-Bis(7,8-dimethyl-4-oxo-3-phenyl-1*H*,5*H*-thiazolo[3,4-*a*]quinoxalin-1-ideneamino)benzene (11b). The yield was 0.21 g (43%), yellow crystals, m.p. >355 °C, R_f 0.78 ($CHCl_3$—MeOH, 12 : 1). Found (%): C, 70.16; H, 4.24; N, 11.38; S, 8.90. $C_{42}H_{32}N_6O_2S_2$. Calculated (%): C, 70.37; H, 4.50; N, 11.72; S, 8.94. IR, ν/cm^{-1}: 3438, 3047, 2922, 2878, 1676, 1615, 1572, 1510, 1396, 1333, 1229, 1135, 1020, 877, 754, 692, 632, 590, 454. ^{1}H NMR (DMSO-d_6), δ: 2.25, 2.26 (both s, 6 H each, 4 Me); 6.84 (s, 1 H, H(2)); 6.88 (d, 2 H, H(4), H(6), J = 7.6 Hz); 6.95 (s, 2 H, 2 H(6′)); 7.35 (dd, 4 H, 4 *m*-H_{Ph}, J = 7.54 Hz, J = 7.48 Hz); 7.40 (m, 3 H, H(5) + 2 *p*-H_{Ph}); 7.47 (d, 4 H, 4 *o*-H_{Ph}, J = 7.5 Hz); 9.24 (s, 2 H, 2 H(9′)); 11.14 (s, 2 H, 2 NH).

7,8-Dimethyl-3-phenyl-1-phenylimino-1*H*-thiazolo[3,4-*a*]-quinoxalin-4(5*H*)-one (12b). The yield was 0.05 g (15%), yellow crystals, m.p. 348—348.5 °C, R_f 0.67 ($CHCl_3$—MeOH, 12 : 1). Found (%): C, 72.35; H, 4.66; N, 10.42; S, 8.22. $C_{24}H_{19}N_3OS$. Calculated (%): C, 72.52; H, 4.82; N, 10.57; S, 8.07. IR, ν/cm^{-1}: 3443, 3195, 3048, 2969, 2937, 2878, 1684, 1612, 1576, 1514, 1485, 1442, 1389, 1337, 1216, 1148, 1020, 954, 863, 796, 773, 750, 741, 691, 633, 586, 502. ^{1}H NMR (DMSO-d_6), δ: 2.25 (s, 6 H, 2 Me); 6.96 (s, 1 H, H(6)); 7.12 (d, 2 H, 2 *o*-H_{Ph}, J = 7.8 Hz); 7.39—7.51 (m, 7 H, Ph + 2 *m*-H_{Ph}); 7.69 (d, 1 H, H arom., J = 7.8 Hz); 9.25 (s, 1 H, H(9)); 11.14 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 397 (100), 296 (35), 294 (93), 278 (32), 265 (38), 262 (29), 233 (41), 121 (79), 105 (61), 89 (21), 78 (25), 77 (80), 63 (33).

1-(3-Acetylaminophenylimino)-7,8-dimethyl-3-phenyl-1*H*-thiazolo[3,4-*a*]quinoxalin-4(5*H*)-one (14b). The yield was 0.01 g (3%), m.p. 339—341 °C, R_f 0.55 ($CHCl_3$—MeOH, 12 : 1). Found (%): C, 68.46; H, 4.69; N, 12.20; S, 6.95. $C_{26}H_{22}N_4O_2S$. Calculated (%): C, 68.70; H, 4.88; N, 12.33; S, 7.05. IR, ν/cm^{-1}: 3359, 3179, 3078, 2915, 1660, 1638, 1617, 1592, 1509, 1489, 1389, 1356, 1294, 1235, 1203, 1149, 1085, 1063, 1025, 891, 870, 815, 766, 695, 646, 625, 581, 546, 496. ^{1}H NMR (DMSO-d_6), δ: 2.19 (s, 6 H, 2 Me); 2.58 (s, 3 H, MeCONH); 6.86 (s, 1 H, H(6)); 6.99 (d, 2 H, 2 *o*-H_{Ph}, J = 7.8 Hz); 7.10 (t, 1 H, *p*-H_{Ph}, J = 6.8 Hz); 7.23 (br.s, 1 H, MeCONH); 7.30—7.37 (m, 4 H, 2 H arom. + 2 *m*-H_{Ph}); 7.69 (d, 2 H, 2 H arom., J = 7.8 Hz); 8.32 (s, 1 H, H(9)); 10.83 (s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 647 (18), 455 (12), 454 (36), 295 (19), 294 (100), 265 (9), 121 (36), 77 (9).

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