# Fused polycyclic nitrogen-containing heterocycles
## 11.* 4-Hydroxy-3,5-diphenyl-2-phenyliminothiazolidines as new key compounds in the synthesis of thiazolo[3,4-*a*]quinoxaline derivatives

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A procedure was developed for the synthesis of thiazolo[3,4-*a*]quinoxaline derivatives based on a new strategy for construction of the pyrazine ring. The key step of the process involves the reaction of 4-hydroxy-3,5-diphenyl-2-phenyliminothiazolidines with *o*-phenylenediamines.

**Key words:** Hantzsch reaction, Bodroux reaction, Phillips reaction, 4-hydroxythiazolidines, thiazolo[3,4-*a*]quinoxalines, X-ray diffraction study.

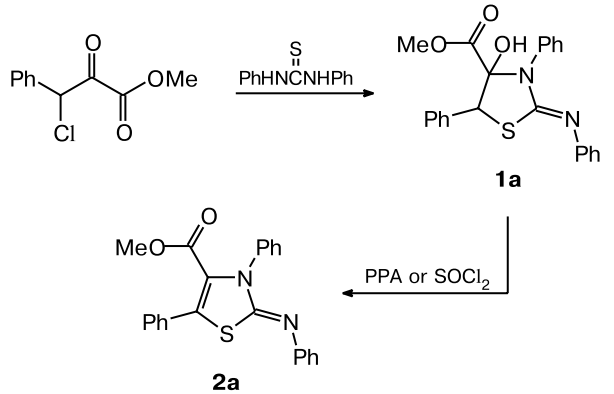
Compounds of the diazine series belong to an important class of biologically active heterocycles. Fused polycyclic heterocycles containing the 1,4-diazine fragment, such as folic acid, riboflavin, tetrahydrobiopterin, or xanthopterin, are vitally important.[2] Quinoxaline derivatives possess a wide spectrum of biological activities, such as antibacterial, antitumor, and antiviral activities, including anti-HIV activity.[3,4]

The main synthetic approaches to quinoxalines and other fused pyrazines are described in the literature.[5,6] Among various cyclizations giving rise to fused azaheterocycles, the reactions of compounds containing two nucleophilic groups with bifunctional electrophilic reagents are of particular importance. Condensation of dicarbonyl compounds with 1,2-diaminoazines[7] is a prominent example.

In the present study, we developed a new convenient procedure for the synthesis of thiazolo[3,4-*a*]quinoxaline derivatives involving condensation of potential α-dicarbonyl compounds, *viz.*, 4-hydroxy-3,5-diphenyl-2-phenyliminothiazolidines, with *o*-phenylenediamine derivatives. A known method for the synthesis of thiazolo[3,4-*a*]quinoxalines involves reduction of difficultly accessible *N*-2-nitrophenyl- and *N*-2,4-dinitrophenylthiazolidine-4-carboxylic acids.[8]

The synthetic potential of 4-hydroxythiazolidines, which are unstable intermediates in the synthesis of thiazoles by the Hantzsch reaction, has remained unexplored.[9,10] Earlier,[11,12] we have demonstrated that the reaction of methyl chloro(phenyl)pyruvate with *N*,*N*′-diphenylthiourea affords an abnormally stable intermediate of the Hantzsch reaction, *viz.*, 4-hydroxy-4-methoxycarbonyl-3,5-diphenyl-2-phenyliminothiazolidine (**1a**),

**Scheme 1**

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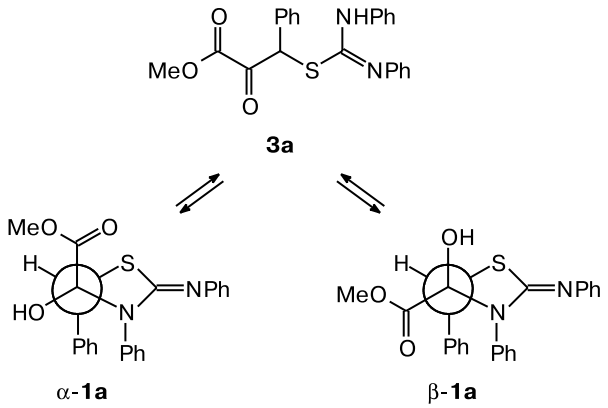
which is dehydrated only by strong dehydrating agents, such as polyphosphoric acid (PPA) or $SOCl_2$ (Scheme 1).

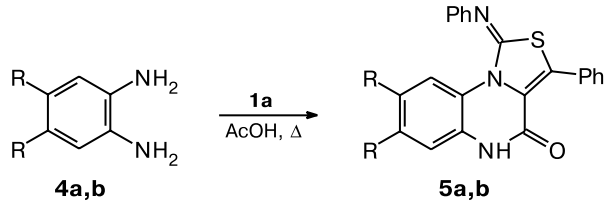
According to our data,[12] hydroxythiazolidine **1a** exists in solution as a mixture of diastereomers α-**1a** and β-**1a**, which are in equilibrium *via* open-chain isothioureido structure **3a** (Scheme 2). However, we failed to detect the latter by various spectroscopic methods.

**Scheme 2**




Earlier,[13,14] we have found that treatment of compound **1a** with *o*-phenylenediamine (**4a**) in refluxing AcOH readily results in condensation to give 4,5-dihydro-3-phenyl-1-phenyliminothiazolo[3,4-*a*]quinoxalin-4-one (**5a**) (Scheme 3).

**Scheme 3**




R = H (**a**), F (**b**)

With the aim of examining the scope of this unexpected reaction and preparing fluorinated thiazoloquinoxaline (**5b**), we carried out the reaction of hydroxythiazolidine **1a** with 4,5-difluoro-1,2-phenylenediamine (**4b**).[15] Since the nitrogen atoms in this diamine have low nucleophilicity due to the presence of strong electron-withdrawing fluorine atoms, the reaction of this compound proceeds much more slowly (under the above-described conditions, the reaction is completed in 8 h) to give compound **5b**. The structure of the latter was confirmed by the presence, in its $^1$H NMR spectrum, of a signal for the H(9) proton as a doublet of doublets with the coupling constants $^3J_{H,F} = 13.9$ Hz and $^4J_{H,F} = 8.4$ Hz along with other multiplets at δ 7.36—7.48 belonging to eleven protons (protons of two phenyl groups and the H(6) proton) and a singlet for the proton of the NH group at δ 11.21.

The structure of compound **5b** was confirmed also by X-ray diffraction analysis (Fig. 1). Compound **5b** crystal-

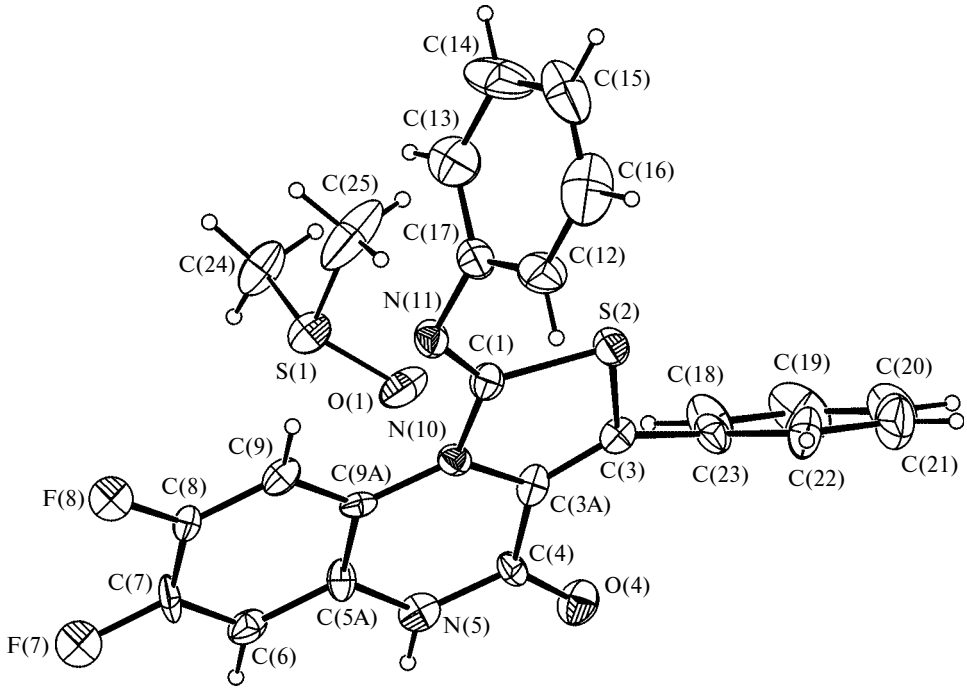



**Fig. 1.** Molecular structure of compound **5b**.

lizes as the 1 : 1 solvate with DMSO in the monoclinic system, the DMSO molecule in the crystal being disordered over two positions with occupancies of 0.7 and 0.3. It should be noted that the thiazoloquinoxaline ring in compound **5b**, as in analogous compounds studied earlier,[14] is planar (to within 0.03(3) Å). The phenyl substituents (C(12)—C(17) and C(18)—C(23)) are twisted with respect to the plane of the thiazoloquinoxaline moiety by 81.3° and 51.2°, respectively. Of intramolecular contacts, the C—H...N interaction involving the H(9) proton of the phenyl substituent and the N(11) atom ($d$(H(9)...N(11)), 2.19 Å; ∠(C(9)—H(9)...N(11)), 127°) is noteworthy. Earlier, we have demonstrated that such systems are characterized by the formation of dimers through classical hydrogen bonds, provided that the crystal contains no solvate molecules. The presence of solvates prevents the formation of dimers but favors a great diversity of intermolecular contacts.[16] Analysis of intermolecular interactions in the crystal of compound **5b** confirms the earlier observation. The molecules of this compound do not form dimers in the crystal (Fig. 2); each molecule is involved in contacts with two solvate molecules as a donor (through the bifurcated hydrogen bond, *viz.*, N(5)—H(5)...S(1) and N(5)—H(5)...O(1); $d$(H(5)...S(1)), 2.87 Å; ∠(N(5)—H(5)...S(1)), 154°; $d$(H(5)...O(1)), 1.94 Å; ∠(N(5)—H(5)...O(1)), 175°) and an acceptor (through the C(24)—H(243)...O(4′) interaction; the symmetry operation ($-1 + x$, $y$, $z$); $d$(H(243)...O(4′)), 2.57 Å; ∠(C(24)—H(243)...O(4′)), 152°). There are also strong π—π contacts in the crystal. Interaction of the electronic systems of the benzoquinoxaline fragments of the molecules related to each other by the symmetry operation ($1 - x$, $1 - y$, $-z$) results in the formation of π-dimers (the shortest distance between the planes of the rings is 3.39(2) Å, the dihedral angle is 0°). Each molecule of the π-dimer is involved in C—H...S contacts ($d$(H(15)...S(2′)), 2.86 Å; ∠(C(15)—H(15)...S(2′)), 175°; the symmetry operation ($1/2 - x$, $-1/2 + y$, $1/2 - z$)) with the molecules of the adjacent π-dimers, whose tricyclic fragments are twisted by 90°. Due to the involvement of DMSO molecules in the contacts, these chains of the molecules, which are linked through alternating π—π and C—H...S contacts, form a network of hydrogen-bonded molecules. The presence of disordered DMSO molecules indicates that the crystal contains cavities. This is also evidenced by a rather low packing coefficient of the molecules (0.67). In the crystal, hydrophobic and hydrophilic regions are localized, *viz.*, the phenyl substituents possessing hydrophobic properties form pseudolayers alternating with layers containing the hydrophilic tricyclic fragments of molecules **5b** and DMSO.

As regards the mechanism of the reaction of hydroxythiazolidine **1a** with 1,2-phenylenediamines, both linear and cyclic tautomers can give the same intermediate **A**, from which the final products **5a,b** are formed (Scheme 4). Each of the possible reaction pathways, *viz.*, amidation (path *a*), amination (path *b*), or imination (path *c*), involves various types of electrophilic substitution at the nitrogen atom of the amino group of *o*-phenylenediamines as the first step.

To elucidate which reaction route to thiazolo[3,4-*a*]quinoxalines **5** is preferable, we performed the

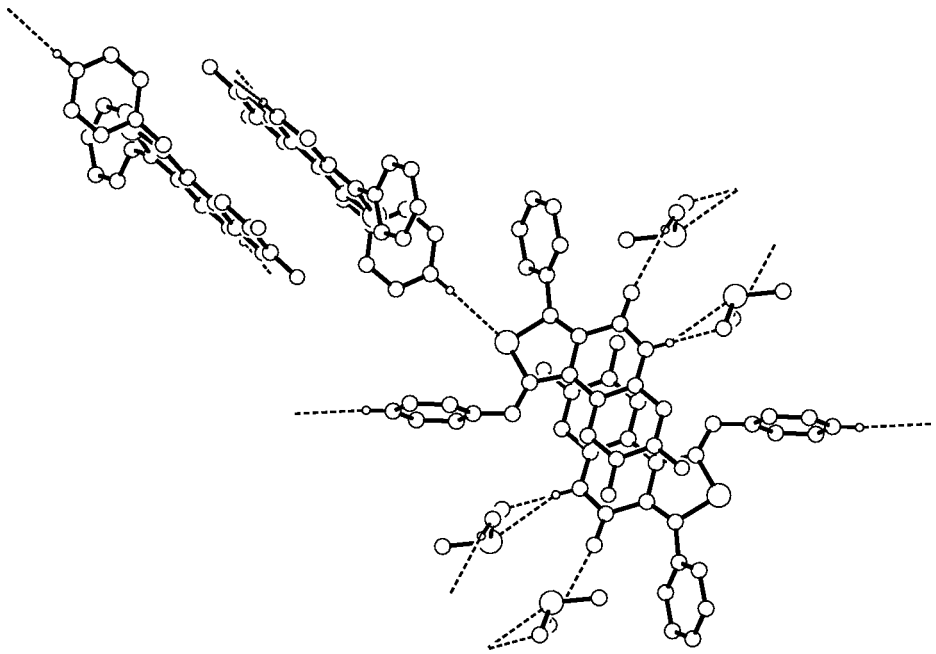
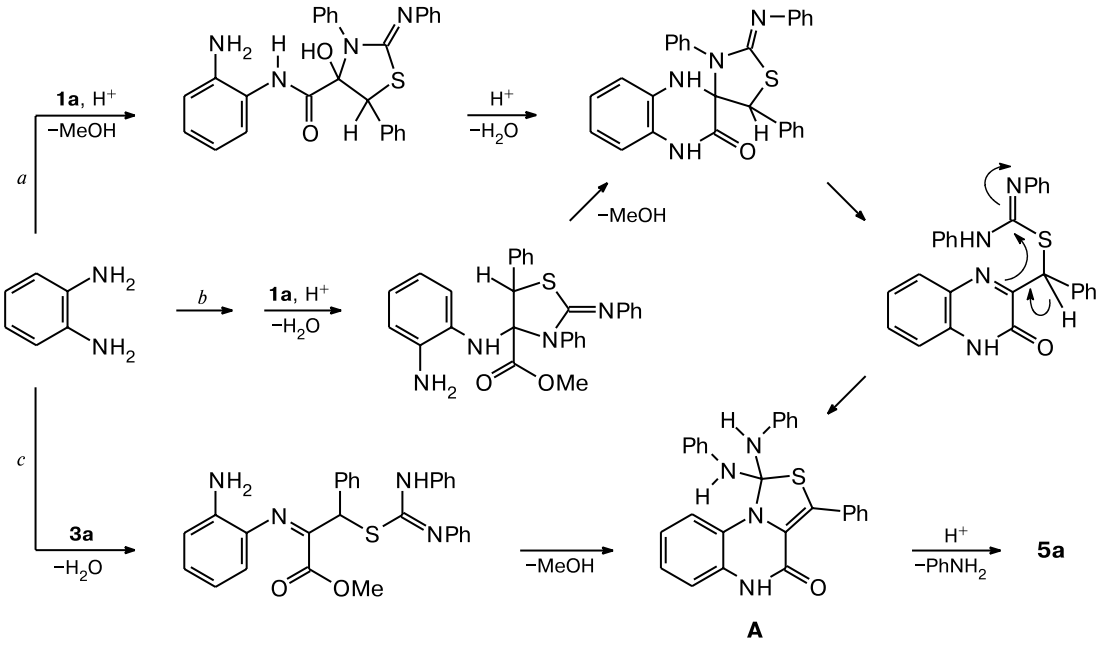


**Fig. 2.** Fragment of a hydrogen bond network in the crystal of thiazolo[3,4-*a*]quinoxaline **5b**. Only the protons involved in hydrogen bonding (dashed lines) are shown.

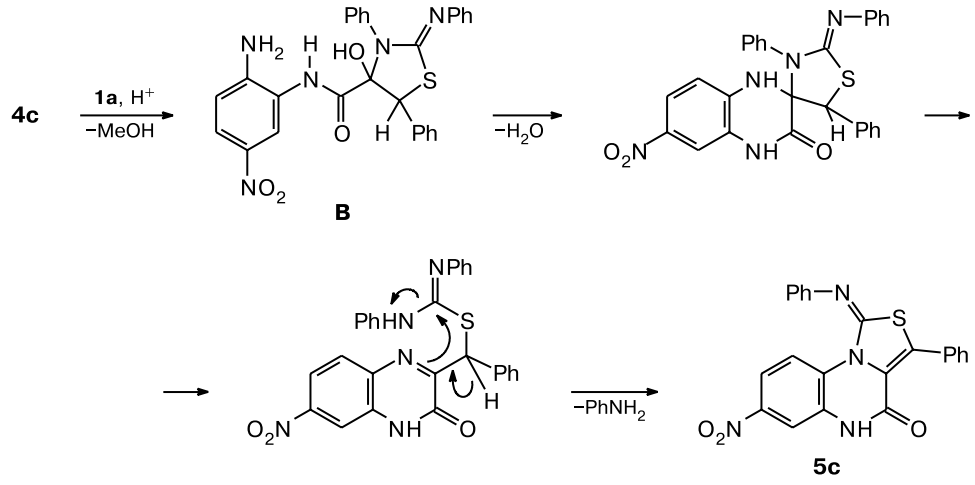
reaction of 4-hydroxythiazolidine **1a** with 4-nitro-1,2-phenylenediamine (**4c**). Depending on the reaction path, this reaction could give isomeric final products **5c** (path *a*) or **5d** (paths *b* and *c*), which differ in the position of the nitro group (Schemes 5—7).

The fact that the reaction with 4-nitro-1,2-phenylenediamine (**4c**) affords only one product is evidenced by the identity of the $^1$H NMR spectra of the crude product and the product following recrystallization from DMF (the latter spectrum contains additional signals corresponding to the solvent because of the formation of a crystal solvate). However, it is impossible to differentiate the structures **5c** and **5d** based only on the $^1$H NMR spectroscopic data. The formation of 4,5-dihydro-8-nitro-3-phenyl-1-phenyliminothiazolo[3,4-*a*]quinoxalin-4-one (**5d**) was confirmed by X-ray diffraction analysis (Fig. 3). Compound **5d**, like compound **5b**, crystallizes in the monoclinic system as a 1 : 1 solvate with DMF. The unit cell parameters of **5d** are similar to those of compound **5b**. The differences in the structure of the carbocyclic moiety of compounds **5b** and **5d** do not change substantially the geometry and the bond length distribution in the tricyclic fragment of the molecule. Even the twist angles of the phenyl substituents relative to the plane of the tricyclic

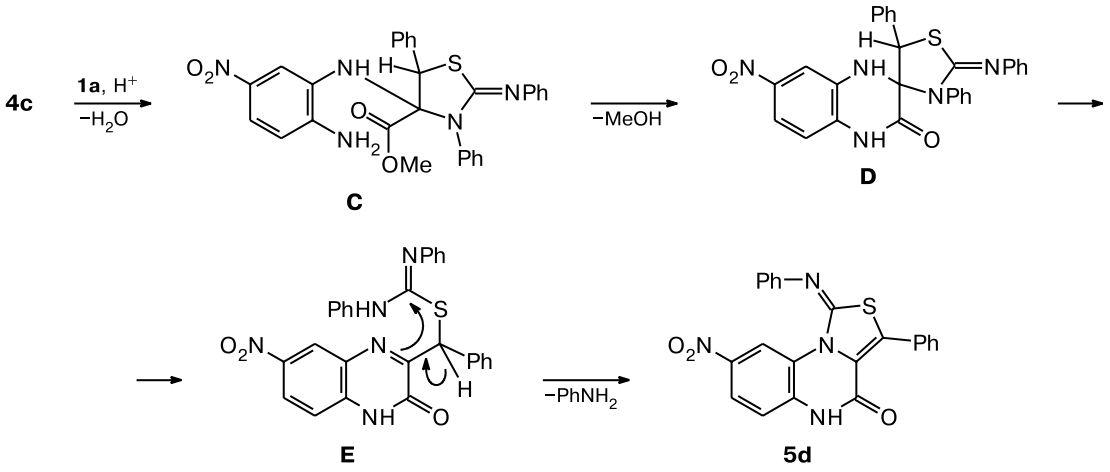
**Scheme 4**



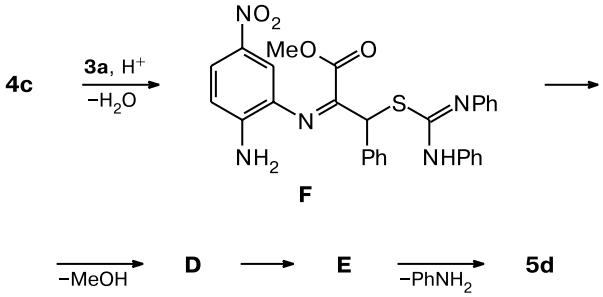

**Scheme 5**



**Scheme 6**




**Scheme 7**




fragment in **5d** (51.2° and 81.3°) are rather similar to those observed in compound **5b** (57.8° and 72.0°). The presence of the DMF solvate molecules in the crystal of compound **5d** also prevents the formation of hydrogen-bonded dimers of **5d**. However, another type of the solvent and the presence of the nitro group lead to a substantial change in the system of intermolecular contacts and the resulting supramolecular structure. The molecular and crystal structures of substituted thiazoloquinoxalines, including compound **5d**, will be described in more detail elsewhere.

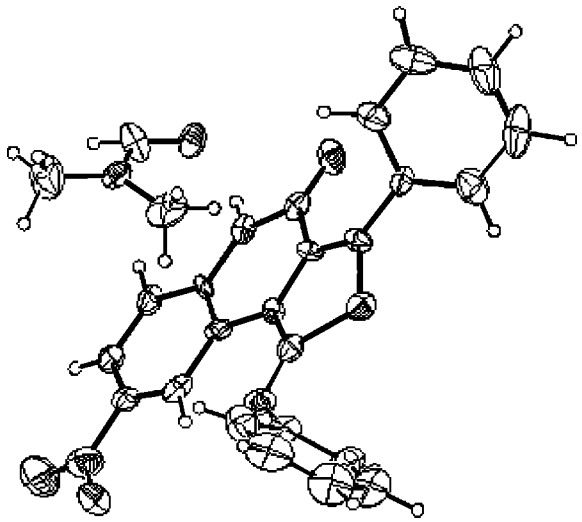


**Fig. 3.** Molecular structure of compound **5d**.

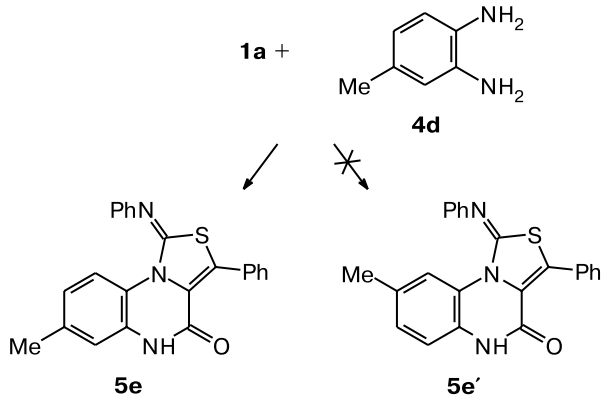
Therefore, if the hypothesis that the primary reaction involves only the 2-amino group of 4-nitro-1,2-phenylenediamine (**4c**) is correct, the fact that the reaction affords exclusively compound **5d** rules out the possibility of the path *a* (see Scheme 5). This assumption holds apparently also for other 1,2-phenylenediamines. Actually, amidation of weakly basic arylamines **4** (path *a*) seems to be less rapid and, correspondingly, less competitive compared to the formation of azomethine (path *c*). Moreover, acylation of arylamines with esters generally requires basic catalysis, for example, under conditions of metallation of the amino group in the Bodroux reaction.[17] This method was used for the acylation of 1,2-phenylenediamine (**4a**) with esters.[18] Moreover, 2-substituted benzimidazoles should easily be prepared (the Phillips reaction)[19] from the initially formed *o*-aminoacylanilides **B** (path *a*) under acidic conditions used in the reaction of 1,2-phenylenediamines (**4**) with hydroxythiazolidine **1a**. However, in no case were 2-substituted benzimidazoles detected among the reactions products of compounds **1** and **4**.

Of the other reaction routes to 8-nitrothiazolo[3,4-*a*]quinoxaline (**5d**), the path *c*, which proceeds *via* open-chain tautomer **3a** and the intermediate imine **F** (see Scheme 7), rather than the path *b*, which proceeds *via* the amine **C** (see Scheme 6), seems to be the most probable, because the formation of the structure **C** requires the unfavorable nucleophilic substitution of the hydroxy group at the sterically hindered carbon atom C(4).

Only one product was obtained in good yield in the reaction of 4-hydroxythiazolidine **1a** with 4-methyl-1,2-

phenylenediamine (**4d**) (Scheme 8). Taking into account that the substituent has the major effect on the reactivity of the *p*-amino group in diamine **4d**, we assigned the structure of 4,5-dihydro-7-methyl-3-phenyl-1-phenyliminothiazolo[3,4-*a*]quinoxalin-4-one (**5e**) to this product. Actually, the $^1$H NMR spectrum shows singlets of the methyl and carbamoyl groups and a multiplet for 12 protons (protons of two phenyl rings and two protons of the benzene ring) along with a signal for the third proton of this fragment, *viz.*, a diagnostic doublet for the H(9) proton at δ 9.27 with the vicinal coupling constant $^3J$ = 8.9 Hz. This fact indicates that the methyl group is bound to the C(7) atom (compound **5e**) rather than to C(8) (compound **5e′**), because in the latter case the signal for the H(9) proton would appear as a singlet or a doublet with a very small constant $^4J$.[20—23] This conclusion was confirmed by X-ray diffraction analysis.

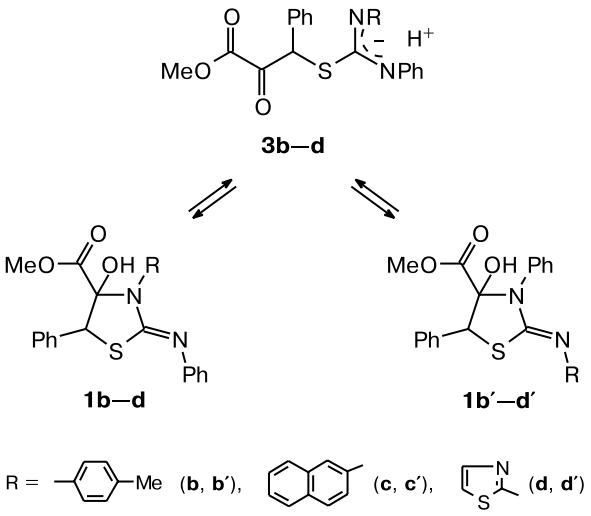
**Scheme 8**



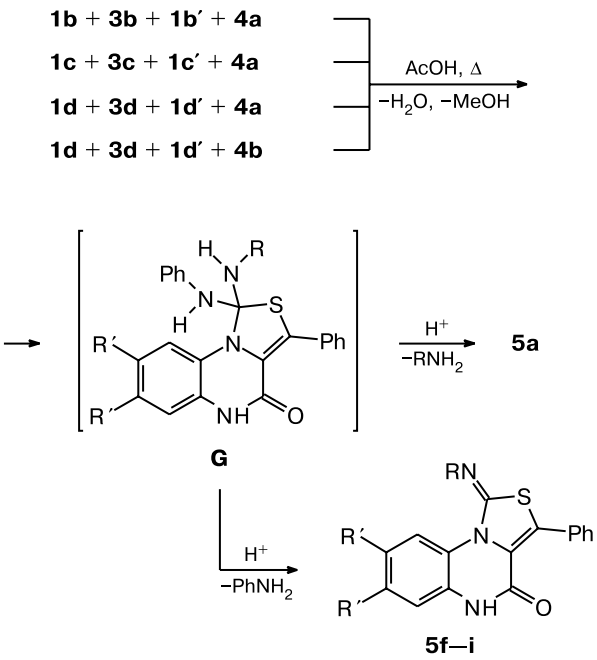

4-Hydroxythiazolidines (**1b—d**), which were synthesized from nonsymmetrical thiourea derivatives, *viz.*, *N*-phenyl-*N′*-tolyl-,[24] *N′*-2-naphthyl-*N*-phenyl-,[24] and *N*-phenyl-*N′*-(thiazol-2-yl)thioureas,[25] react with 1,2-phenylenediamine (**4a**) analogously to 4-hydroxythiazolidine **1a**, which was prepared from symmetrical *N*,*N′*-diphenylthiourea. In the general case, these hydroxythiazolidines exist as tautomeric mixtures **1b—d**+**1b′—d′**+**3b—d** (Scheme 9).

Judging from the IR and $^1$H NMR spectroscopic data, the component ratio for these mixtures depends substantially on the nature of the substituent R and the conditions of isolation and purification of the samples. The regio- and diastereomeric compositions of these mixtures are beyond the scope of the present study. Let us only note that the IR spectrum of the condensation product of *N*-phenyl-*N′*-(thiazol-2-yl)thiourea has a high-intensity absorption band of the keto group at 1764 cm$^{-1}$, which provides evidence that the mixture contained predominantly tautomer **3d**. Condensation of both cyclic and open-chain tautomers with *o*-phenylenediamine (**4a**) af-

**Scheme 9**




**Scheme 10**




| | f | g | h | i |
|---|---|---|---|---|
| R | Me | | | |
| R′ | H | H | H | F |

| Initial tautomeric mixture | 1,2-Phenylenediamine | Composition* of product (%) | | Preparative yield (%) | |
|---|---|---|---|---|---|
| **1b**+**3b**+**1b′** | **4a** | **5a** (8) | **5f** (92) | **5a** (5) | **5f** (86) |
| **1c**+**3c**+**1c′** | **4a** | **5a** (34) | **5g** (66) | **5a** (28) | **5g** (61) |
| **1d**+**3d**+**1d′** | **4a** | **5a** (4) | **5h** (96) | **5a** (0) | **5h** (94) |
| **1d**+**3d**+**1d′** | **4b** | **5b** (0) | **5i** (100) | **5b** (0) | **5i** (96) |

* Calculated from the integral intensities of the peaks of the H(9) protons in the $^1$H NMR spectra of crude products.

fords mixtures of thiazolo[3,4-*a*]quinoxalines **5a** and **5f—h** (Scheme 10). The differences in solubility of the components of these pairs allows one to separated them by fractional crystallization.

The ratio of thiazoloquinoxalines in the resulting mixture depends on the ease of elimination of $PhNH_2$ or $RNH_2$ from the same intermediate **G**. Condensation of fluorine-containing 1,2-phenylenediamine **4b** with a tautomeric mixture **1d**+**3d**+**1d´** did not afford compound **5b**.

## Experimental

The $^1$H NMR spectra were recorded on a Bruker-MCL-250 spectrometer operating at 250.13 MHz. The $^{13}$C NMR spectrum of compound **5a** was measured on a Bruker MSL-400 spectrometer operating at 100.61 MHz. The chemical shifts are given in the δ scale being measured relative to DMSO-$d_6$. The IR spectra were recorded on a UR-20 spectrometer as Nujol mulls. The melting points were determined on a Boetius hot-stage apparatus. The yields, melting points, elemental analysis data, and spectroscopic characteristics of thiazoloquinoxalines are given in Tables 1 and 2.

**4-Hydroxy-4-methoxycarbonyl-3,5-diphenyl-2-phenyliminothiazolidine (1a)** was prepared according to a known procedure.[10]

**4-Hydroxy-4-methoxycarbonyl-5-phenyl-2-phenylimino-3-(4-tolyl)thiazolidine (1b) and 4-hydroxy-4-methoxycarbonyl-3,5-diphenyl-2-(4-tolylimino)thiazolidine (1b´).** Sodium acetate (4.1 g, 0.05 mol) was added to a solution of *N*-phenyl-*N´*-*p*-tolylthiourea (4.84 g, 0.02 mol) in $CH_2Cl_2$ (100 mL). The reaction mixture was cooled to a temperature from −15 to −20 °C and then methyl chloro(phenyl)pyruvate[26] (4.2 g, 0.02 mol) was carefully added. The reaction mixture was stirred for 3 h, allowing it to gradually warm to room temperature, and then poured into water. The organic layer was separated and the aqueous layer was extracted with $CH_2Cl_2$ (3×50 mL). The extract was dried with $MgSO_4$, the solution was concentrated, and the residue was recrystallized from Pr$^i$OH. The yield of **1b**+**1b´** mixture was 3.84 g (92%). M.p. 171—174 °C. Found (%): C, 68.62; H, 5.31; N, 6.83; S, 7.45. $C_{24}H_{22}N_2O_3S$. Calculated (%): C, 68.96; H, 5.26; N, 6.70; S, 7.67. IR, ν/cm$^{-1}$: 3520, 3500 (OH); 3100—3000 (NH); 1735 (C=O); 1640 (C=N). $^1$H NMR (DMF-$d_7$), δ: 3.27 and 3.29 (both s, 3 H each, Me); 3.66 and 3.69 (both s, 3 H each, OMe); 5.47 and 5.48 (both s, 1 H each, CH); 6.50 (br.s, 2 H, 2 OH); 6.82—7.33 (m, 14 H, Ph, $C_6H_4$).

**4-Hydroxy-4-methoxycarbonyl-3-(2-naphthyl)-5-phenyl-2-phenyliminothiazolidine (1c) and 4-hydroxy-4-methoxycarbonyl-3,5-diphenyl-2-(2-naphthylimino)thiazolidine (1c´)** were prepared analogously from *N*-(2-naphthyl)-*N´*-phenylthiourea. The yield was 89%, m.p. 173—176 °C. Found (%): C, 71.05; H, 5.24; N, 6.46; S, 6.97. $C_{27}H_{22}N_2O_3S$. Calculated (%): C, 71.43; H, 4.85; N, 6.17; S, 7.06. IR, ν/cm$^{-1}$: 3505 (OH); 3120—3000 (NH); 1740 (C=O); 1630 (C=N). $^1$H NMR (DMF-$d_7$), δ: 3.67 (s, 3 H, OMe); 5.47 (s, 1 H, CH); 7.02—7.96 (m, 18 H, Ph, $C_{10}H_7$, OH).

**S-(α-Methoxalylbenzyl)-*N*-phenyl-*N´*-(thiazol-2-yl)isothiourea (3d)** was prepared analogously from *N*-phenyl-*N´*-(thiazol-2-yl)thiourea. The yield was 83%, m.p. 99—101 °C. Found (%): C, 58.18; H, 3.95; N, 10.56; S, 15.82. $C_{20}H_{17}N_3O_3S_2$. Calculated (%): C, 58.44; H, 4.14; N, 10.22; S, 15.60. IR, ν/cm$^{-1}$: 3500—3000 (NH); 1764 (C=O); 1740 (C=O); 1630 (C=N). $^1$H NMR (DMSO-$d_6$), δ: 3.64, 3.73, and 3.87 (all s (1 : 1 : 1.4), 3 H each, OMe); 5.22, 5.51, and 5.61 (all s, 1 H each, CH); 6.90—7.33 (m, Ph, $C_4SH_3$, NH, OH).

**7,8-Difluoro-4,5-dihydro-3-phenyl-1-phenyliminothiazolo[3,4-*a*]quinoxalin-4-one (5b).** A solution of 4-hydroxythiazolidine **1a** (2.02 g, 5 mmol) and 4,5-difluoro-1,2-phenylenediamine (**4b**) (0.72 g, 5 mmol) in AcOH (25 mL) was refluxed for 8 h. Cooling of the reaction mixture for 3 h afforded crystals, which were filtered off to give analytically pure compound **5b** in a yield of 1.44 g. The filtrate was concentrated *in vacuo* to isolate additionally yellow crystals of **5b** in a yield of 0.32 g. The pres-

**Table 1.** Yields, melting points, and elemental analysis data for 1-arylimino-4,5-dihydro-3-phenylthiazolo[3,4-*a*]quinoxalin-4-ones (**5a,b,d—i**)

| Compound | Yield (%) | M.p./°C (solvent) | Found / Calculated (%) | | | | Molecular formula |
|---|---|---|---|---|---|---|---|
| | | | C | H | N | S | |
| **5a** | 95 | 301—301.5 (DMSO) | 69.50 / 69.87 | 5.06 / 4.89 | 10.11 / 10.46 | 15.45 / 15.40 | $C_{22}H_{15}N_3OS \cdot Me_2SO$ |
| **5b** | 87 | 296—297 (DMF) | 65.17 / 65.24 | 3.13 / 3.21 | 10.43 / 10.37 | 8.07 / 7.92 | $C_{22}H_{13}F_2N_3OS$ |
| **5d** | 89 | 343—344 (DMF) | 61.61 / 61.77 | 4.31 / 4.38 | 14.36 / 14.53 | 6.58 / 6.73 | $C_{22}H_{14}N_4O_3S \cdot HCONMe_2$ |
| **5e** | 86 | 275—277 (DMF) | 72.06 / 71.86 | 4.44 / 4.14 | 10.97 / 10.58 | 8.36 / 8.29 | $C_{23}H_{17}N_3OS$ |
| **5f** | 94 | 257—259 (DMSO) | 72.06 / 71.87 | 4.44 / 4.16 | 10.97 / 11.12 | 8.36 / 8.19 | $C_{23}H_{17}N_3OS$ |
| **5g** | 80 | 265—270 (AcOH) | 74.81 / 74.46 | 3.21 / 4.06 | 9.87 / 10.02 | 7.71 / 7.64 | $C_{26}H_{17}N_3OS$ |
| **5h** | 76 | 345—345.5 (AcOH) | 60.61 / 60.64 | 3.25 / 3.19 | 14.50 / 14.89 | 17.41 / 17.02 | $C_{19}H_{12}N_4OS_2$ |
| **5i** | 96 | 292—293 (MeCN) | 55.21 / 55.34 | 2.35 / 2.43 | 13.42 / 13.58 | 15.73 / 15.55 | $C_{19}H_{10}F_2N_4OS_2$ |

**Table 2.** IR and $^1$H NMR spectra of 1-arylimino-4,5-dihydro-3-phenylthiazolo[3,4-*a*]quinoxalin-4-ones (**5a,b,d—i**)

| Compound | IR, ν/cm$^{-1}$ | $^1$H NMR (DMSO-d$_6$), δ, *J*/Hz |
|---|---|---|
| **5a*** | 3200—2700 (NH); 1680 (C=O); 1620 (C=N) | 7.00—7.46 (m, 13 H, 2 Ph, H(6), H(7), H(8)); 9.39 (d, 1 H, H(9), *J* = 7.4); 11.13 (br.s, 1 H, NH) |
| **5b** | 3250—2700 (NH); 1677 (C=O); 1619 (C=N) | 7.36—7.48 (m, 11 H, 2 Ph, H(6)); 9.55 (dd, 1 H, H(9), *J* = 13.9, 8.4); 11.21 (s, 1 H, NH) |
| **5d** | 3250—2600 (NH); 1680 (C=O); 1630 (C=N); 1210 (N=O) | 7.21—7.62 (m, 11 H, 2 Ph, H(6)); 8.18 (dd, 1 H, H(7), *J* = 8.9, 2.3); 10.50 (d, 1 H, H(9), *J* = 2.3); 11.69 (br.s, 1 H, NH) |
| **5e** | 3230—2600 (NH); 1665 (C=O); 1615 (C=N) | 2.40 (s, 3 H, Me); 7.02—7.59 (m, 12 H, 2 Ph, H(7), H(8)); 9.38 (d, 1 H, H(9), *J* = 8.9); 11.06 (br.s, 1 H, NH) |
| **5f** | 3220—2700 (NH); 1685 (C=O); 1635 (C=N) | 2.38 (s, 3 H, Me); 7.05—7.59 (m, 12 H, Ph, C$_6$H$_4$, H(6), H(7), H(8)); 9.37 (d, 1 H, H(9), *J* = 7.7); 11.12 (br.s,1 H, NH) |
| **5g** | 3250—2550 (NH); 1670 (C=O); 1625 (C=N) | 7.07—7.54 (m, 12 H, Ph, 4 H of naphthyl, H(6), H(7), H(8)); 7.70 (d, 1 H, H of naphthyl, *J* = 8.1); 7.93 (d, 1 H, H of naphthyl, *J* = 7.3); 8.09 (d, 1 H, H of naphthyl, *J* = 8.1); 9.60 (d, 1 H, H(9), *J* = 8.1); 11.10 (br.s, 1 H, NH) |
| **5h**** | 3220—2600 (NH); 1685 (C=O); 1610 (C=N) | 7.08—7.20 (m, 3 H, H(6), H(7), H(8)); 7.13 (d, 1 H, H(5) or H(4) of thiazole, *J* = 3.7); 7.28—7.33 (m, 3 H, 2 *m*-H$_{Ph}$, *p*-H$_{Ph}$); 7.47 (d, 1 H, H(4) or H(5) of thiazole, *J* = 3.7); 7.78 (d, 2 H, 2 *o*-H$_{Ph}$, *J* = 6.5); 8.50 (d, 1 H, H(9), *J* = 7.4); 10.83 (br.s, 1 H, NH) |
| **5i***** | 3278, 3250—2700 (NH); 1697 (C=O); 1632 (C=N) | 7.04 (dd, 1 H, H(6), $^3J_{HF}$ = 10.5, $^4J_{HF}$ = 9.2); 7.11 (d, 1 H, H(5) or H(4) of thiazole, *J* = 3.7); 7.25—7.32 (m, 3 H, 2 *m*-H$_{Ph}$, *p*-H$_{Ph}$); 7.46 (d, 1 H, H(4) or H(5) of thiazole, *J* = 3.7); 7.74—7.76 (m, 2 H, 2 *o*-H$_{Ph}$); 8.53 (dd, 1 H, H(9), $^3J_{H,F}$ = 13.1, $^4J_{H,F}$ = 8.3); 10.89 (br.s, 1 H, NH) |

* $^{13}$C NMR (100.6 MHz) of compound **5a** (DMSO-d$_6$), δ: 115.61 (dd, C(6) or C(9), *J* = 162.7 and 8.0 Hz); 118.43 (br.s, C(7) or C(8), *J* = 167.6 Hz); 121.93 (t, C(3a), *J* = 4.6 Hz); 122.50 (br.s, C(3)); 122.82 (br.s, C(8) or C(7), *J* = 160.0 Hz); 125.70 (dd, C(9) or C(6), *J* = 163.2 and 8.4 Hz); 126.21 (m, C(5a) or C(9a)); 131.42 (s, C(9a) or C(5a)); 153.25 (s, C=O); 154.60 (s, C=N); Ph: 121.17 (dt, *o*-C, *J* = 158.5 and 7.9 Hz); 124.51 (dt, *p*-C, *J* = 164.4 and 7.1 Hz); 125.46 (br.s, *ipso*-C); 128.16 (d, br.d, *m*-C, *J* = 159.9 and 7.3 Hz); 129.07 (dt, *p*-C, *J* = 160.9 and 6.3 Hz); 130.39 (dd, *m*-C, *J* = 158.8 and 8.1 Hz); 130.58 (dt, *o*-C, *J* = 161.3 and 8.1 Hz); 151.25 (t, CN, *J* = 8.4 Hz).

** The $^1$H NMR spectrum was recorded in DMF-d$_7$—CDCl$_3$ (1 : 1).

*** The $^1$H NMR spectrum was recorded in DMF-d$_7$.

ence of aniline in the filtrate was established by its transformation into *N*-benzylideneaniline, m.p. 51—53 °C.

**4,5-Dihydro-8-nitro-3-phenyl-1-phenyliminothiazolo[3,4-*a*]quinoxalin-4-one (5d) and 4,5-dihydro-7-methyl-3-phenyl-1-phenyliminothiazolo[3,4-*a*]quinoxalin-4-one (5e)** were prepared analogously by the reactions of 4-nitro- (**4c**) and 4-methyl-1,2-phenylenediamines (**4d**), respectively, with 4-hydroxythiazolidine **1a** (refluxing for 8 and 3 h). Analytically pure samples were prepared by recrystallization.

**4,5-Dihydro-3-phenyl-1-(4-tolylimino)thiazolo[3,4-*a*]quinoxalin-4-one (5f), 4,5-dihydro-1-(2-naphthylimino)-3-phenylthiazolo[3,4-*a*]quinoxalin-4-one (5g), 4,5-dihydro-3-phenyl-1-(thiazol-2′-ylimino)thiazolo[3,4-*a*]quinoxalin-4-one (5h), and 4,5-dihydro-7,8-difluoro-3-phenyl-1-(thiazol-2′-ylimino)thiazolo[3,4-*a*]quinoxalin-4-one (5i)** were synthesized analogously using the corresponding tautomeric mixtures, which were prepared from nonsymmetrical *N*-phenyl-*N*′-substituted thioureas, and isolated by recrystallization from DMSO of a crystalline substance obtained after repeated washing of the residue with a hot 1 : 1 MeOH—Pr$^i$OH mixture. The combined filtrates were concentrated and analytically pure thiazoloquinoxaline **5a** was obtained.

**X-ray diffraction study** of compound **5b** was performed on an automated four-circle Enraf-Nonius CAD-4 diffractometer. Crystals of **5b**, $C_{24}H_{19}F_2N_3O_2S_2$, are monoclinic. At 20 °C $a$ = 8.823(5), $b$ = 8.962(8), $c$ = 28.587(6) Å, β = 90.04(2)°, $V$ = 2260(2) Å$^3$, $Z$ = 4, $d_{calc}$ = 1.42 g cm$^{-3}$, space group $P21/n$. The unit cell parameters and the intensities of 2785 reflections, of which 1109 reflections were with $I \geq 2\sigma$, were measured at 20 °C (λ(Cu-Kα), graphite monochromator, ω/2θ scanning technique, θ ≤ 58.9°). The intensities of three check reflections showed no decrease in the course of X-ray data collection. Absorption was ignored (μCu 2.52 cm$^{-1}$). The structure was solved by direct methods using the SIR program[27] and refined first isotropically and then anisotropically using the SHELXL-97 [28] and WINGX [29] program packages. Subsequently, the positions of the hydrogen atoms were revealed from difference electron density maps. The contributions of the hydrogen atoms to the structure amplitudes were taken into account with fixed positional and thermal parameters. The final reliability factors were as follows: $R$ = 0.075 and $R_w$ = 0.128 based on 1109 reflections with $F^2 \geq 4\sigma$. The figures were drawn and intermolecular contacts in the crystals were calculated using the PLATON program.[30]

The X-ray diffraction data for compound **5d** were deposited with the Cambridge Structural Database (CCDC No. 181760).*

* These data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0) 1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

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