Russian Journal of Organic Chemistry, Vol. 40, No. 8, 2004, pp. 1175–1180. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 8, 2004, pp. 1222–1227.

Heterocyclic Thiones and Their Analogs in Reactions of 1,3-Dipolar Cycloaddition: III.* Reaction of Benzothiazole-2-thione with a Double Excess of Nitrilimine

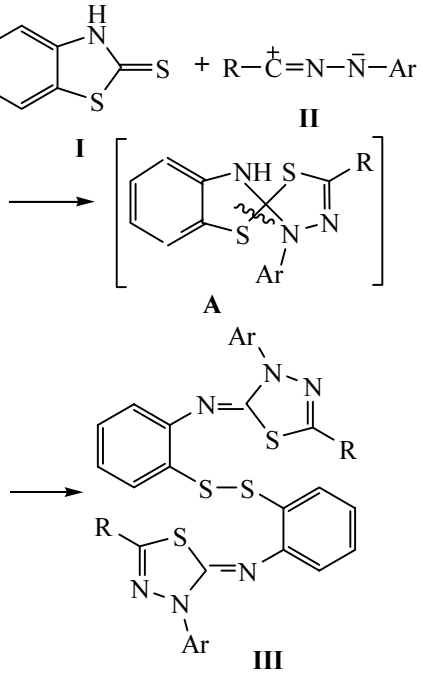
O.V. Firsova[1], T.S. Dolgushina[1], B.A. Polukeev[2], V.E. Zavodnik[3], A.I. Stash[3], V.K. Bel'skii[3], and V.A. Galishev[1]

[1]*St. Petersburg State Technological Institute,St. Petersburg, 198013Russia*
e-mail: tanya@orgchem.spb.ru, vlad@orgchem.spb.ru
[2]*Closed Joint-stock Company "Vekton", St. Petersburg*
[3]*State Scientific Center of Russian FederationKarpov Physicochemical Research Institute, Moscow, Russia*

Received May 21, 2003

Abstract—Main products of reaction between benzothiazole-2-thione and a double excess of nitrilimine are substituted 1-aryl-1-(1,3-benzothiazol-2-yl)-2-(2,3-dihydro-1,3,4-thiadiazol-2-yl)hydrazines. In the first step presumably forms a spiro compound via 1,3-dipolar cycloaddition of nitrilimine molecule to the C=S bond of the benzothiazolethione. The second nitrilimine molecule adds to the new C=S bond of the intermediate product arising by the rupture of C–S bond in the thiadiazole ring of the spiro compound.

We showed in the preceding study [1] that in reaction of equimolar amounts of benzothiazole-2-thione and C,N-disubstituted nitrilimine formed bis{2-[1,3,4-thiadiazol-2-ylideneamino]phenyl} disulfide (**III**) as a prevailing reaction product The reaction was presumed to start as a 1,3-dipolar cycloaddition of the nitrilimine across the exocyclic thione group of the benzothiazole-2-thione. The C–S bond rupture in the thiazole ring in the arising spiro compound **A** followed by dimerization would afford the final reaction product **III**.

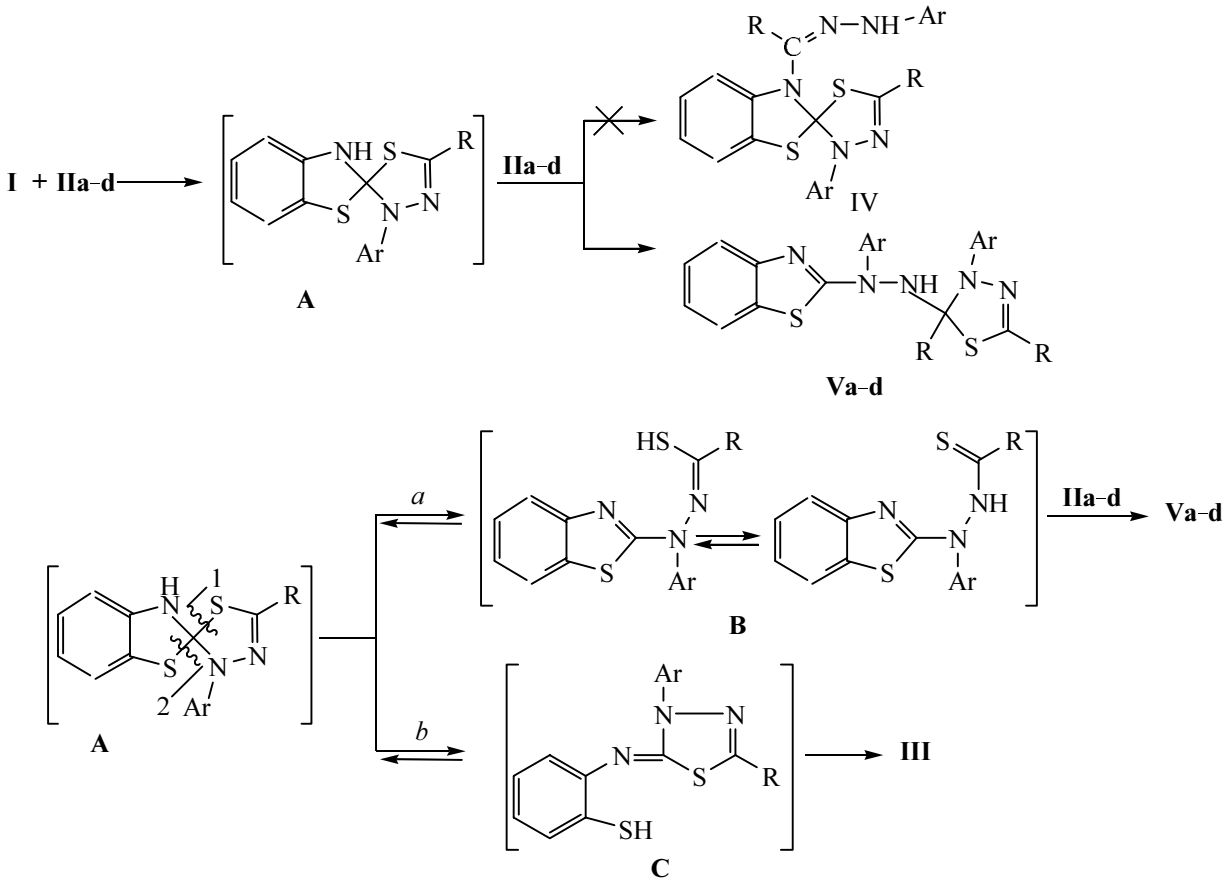


We report here on the study of reaction between benzothiazole-2-thione and a double excess of nitrilimine. Nitrilimines **IIa–d** were generated *in situ* by treating appropriate hydrazonoyl chlorides with triethylamine. It was expected that excess nitrilimine **II** would stabilize the primarily arising spiro compound **A** by substitution of the hydrogen attached to nitrogen atom affording compound **IV**.

We established that compound **IV** did not form in any of reactions performed, and the main products of this process were 1-aryl-1-(1,3-benzothiazol-2-yl)-2-(2,3-dihydro-1,3,4-thiadiazol-2-yl)hydrazines (**Va–d**).

The reaction probably commenced as 1,3-dipolar cycloaddition of nitrilimine to the exocyclic C=S bond of the thione form of benzothiazole-2-thione. Then in the primarily formed benzothiazolespirothiadiazole **A** a cleavage of the C–S bond occurred in the thiadiazole ring (path *a*) in contrast to reaction of equimolar amounts of reagents where the opening of a thiazole ring was observed (path *b*). The arising intermediate compound **B** can exist as two tautomers, in thione or thiol forms.

* For communication II see [1].



Apparently the second nitrilimine molecule enters into 1,3-dipolar cycloaddition involving the C=S bond of the thione form of intermediate compound **B.** As a result form 1-aryl-1-(1,3-benzothiazol-2-yl)-2-(2,3-dihydro-1,3,4-thiadiazol-2-yl)hydrazines (**Va–d**).

We believe that in the spiro compound **A** both C–S bonds are labile, and the rupture of any of them is reversible. In the presence of excess nitrilimine the equilibrium is displaced toward formation of intermediate compound **B** for it is consumed by irreversible cyclization at the C=S bond. In the absence of nitrilimine compound **B** cannot be stabilized, and gradually under the action of air oxygen a dimerization takes place of intermediate compound **C** yielding irreversibly disulfide **III**. In the presence of nitrilimine the rate of reaction *a* is considerably higher for the C=S is involved into cycliza-tion significantly faster than dimerization of sulfide **C** occurs. This assumption is supported by the fact that in the reaction mixture were detected by TLC very small quantities of bis{2-[1,3,4-thiadiazol-2-ylideneamino]-phenyl} disulfides (**III**).

Compounds **Va–d** obtained are crystalline solids stable in air at long storage. Their ^{1}H NMR spectra contain signals characteristic of substituents at the carbon and nitrogen of nitrilimine, and also appears the singlet from the hydrogen of the hydrazo group. The ^{13}C NMR spectra of compounds **Va–d** are consistent with assumed structures of these substances

The formation of 1-aryl-1-(1,3-benzothiazol-2-yl)-2-(2,3-dihydro-1,3,4-thiadiazol-2-yl)hydrazines (**Va–d**) is also supported by the measurement of their mass spectra. In the mass spectra of the compound are commonly seen molecular ion peaks, the fragmentation starts either by the cleavage of a C–N bond with the formation of a fragment ion of the corresponding thiadiazole ring (for compounds **Va, b**), or by the rupture of an N–N bond (for compounds **Vc, d**) with fixing of both fragment ions.

The structure of compounds **Va, d** was proved by X-ray diffraction analysis. The general view of molecules **Va** and **Vd** is given on Figs.1 and 2. (In description of the results of X-ray study the numeration of atoms corresponds to that given on figures).

The X-ray diffraction study shows that in molecule **Va** lacked an intramolecular hydrogen bond between atoms O^1 and H_{N^1} is lacking: the distance between these atoms was 2.25 Å. Thiadiazole ring in this molecule is

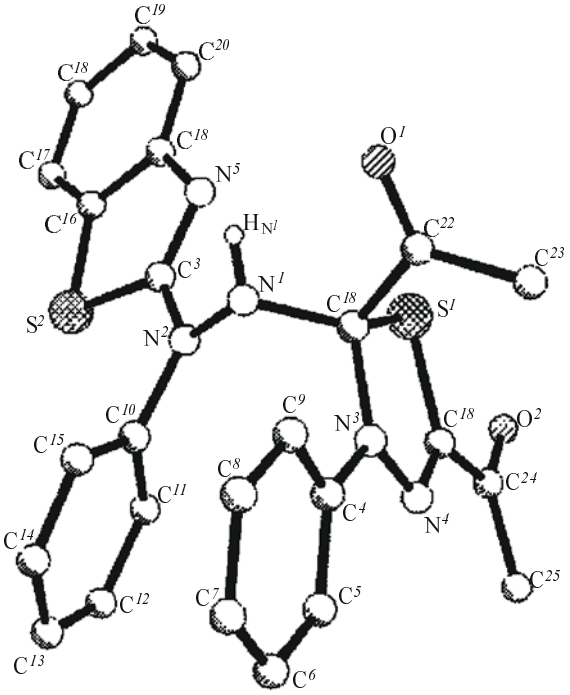


Fig. 1. Structure of a molecule of 2-(2,5-diacetyl-3-phenyl-2,3-dihydro-1,3,4-thiadiazol-2-yl)-1-(1,3-benzothiazol-2-yl)-1-phenylhydrazine (**Va**) according to X-ray diffraction study. Hydrogen atom is shown only at N^1.

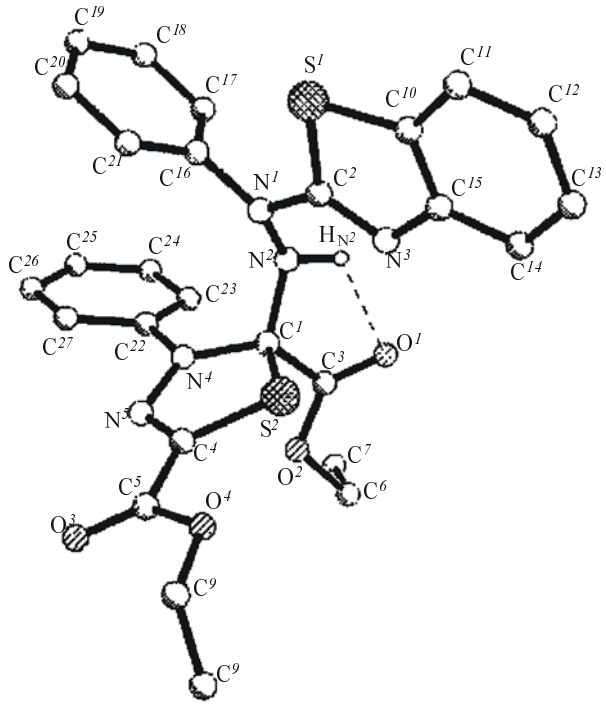


Fig. 2. Structure of a molecule of 1-(1,3-benzothiazol-2-yl)-1-phenyl-2-(2,5-diethoxycarbonyl-3-phenyl-2,3-dihydro-1,3,4-thiadiazol-2-yl)hydrazine (**Vd**) according to X-ray diffraction study. Only the hydrogen atom involved into a hydrogen bond is shown.

Table 1. Bond lengths (d, Å) and bond angles (ω, deg) in the molecule of 2-(2,5-diacetyl-3-phenyl-2,3-dihydro-1,3,4-thiadiazol-2-yl)-1-(1,3-benzothiazol-2-yl-1-phenylhydrazine (**Va**)[a]

Bond	d	Bond	d
S^1–C^2	1.738(2)	N^4–C^2	1.287(3)
S^1–C^1	1.850(2)	N^5–C^3	1.289(3)
S^2–C^{16}	1.744(2)	N^5–C^{21}	1.393(3)
S^2–C^3	1.762(2)	C^1–C^{22}	1.547(3)
O^1–C^{22}	1.200(3)	C^2–C^{24}	1.469(3)
O^2–C^{24}	1.214(3)	C^{16}–C^{17}	1.388(3)
N^1–N^2	1.399(3)	C^{16}–C^{21}	1.392(3)
N^1–C^1	1.435(3)	C^{17}–C^{18}	1.370(4)
N^2–C^3	1.367(3)	C^{18}–C^{19}	1.377(4)
N^2–C^{10}	1.432(3)	C^{19}–C^{20}	1.378(4)
N^3–N^4	1.350(2)	C^{20}–C^{21}	1.392(3)
N^3–C^4	1.417(2)	C^{22}–C^{23}	1.485(4)
N^3–C^1	1.478(3)	C^{24}–C^{25}	1.490(4)
Angle	ω	Angle	ω
$C^2S^1C^1$	89.80(9)	$N^5C^3S^2$	117.40(16)
$C^{16}S^2C^3$	87.53(11)	$N^2C^3S^2$	119.34(17)
$N^2N^1C^1$	115.11(18)	$C^9C^4N^3$	120.81(19)
$C^3N^2N^1$	117.53(18)	$C^5C^4N^3$	119.59(19)
$C^3N^2C^{10}$	124.21(18)	$C^{11}C^{10}N^2$	119.0(2)
$N^1N^2C^{10}$	116.02(16)	$C^{15}C^{10}N^2$	120.9(2)
$N^4N^3C^4$	118.31(16)	$C^{17}C^{16}C^{21}$	121.8(2)
$N^4N^3C^1$	118.37(15)	$C^{17}C^{16}S^2$	128.2(2)
$C^4N^3C^1$	122.94(16)	$C^{21}C^{16}S^2$	109.96(16)
$C^2N^4N^3$	111.85(17)	$C^{18}C^{17}C^{16}$	117.8(3)
$C^3N^5C^{21}$	109.45(19)	$C^{17}C^{18}C^{19}$	121.2(3)
$N^1C^1N^3$	110.77(17)	$C^{18}C^{19}C^{20}$	121.4(3)
$N^1C^1C^{22}$	107.83(17)	$C^{19}C^{20}C^{21}$	118.5(3)
$N^3C^1C^{22}$	112.72(17)	$C^{20}C^{21}C^{16}$	119.3(2)
$N^1C^1S^1$	116.84(14)	$C^{20}C^{21}N^5$	125.1(2)
$N^3C^1S^1$	102.52(13)	$C^{16}C^{21}N^5$	115.6(2)
$C^{22}C^1S^1$	106.16(13)	$O^1C^{22}C^{23}$	123.6(2)
$N^4C^2C^{24}$	123.3(2)	$O^1C^{22}C^1$	118.9(2)
$N^4C^2S^1$	117.43(16)	$C^{23}C^{22}C^1$	117.5(2)
$C^{24}C^2S^1$	119.31(16)	$O^2C^{24}C^2$	118.0(2)
$N^5C^3N^2$	123.2(2)	$O^2C^{24}C^{25}$	122.9(2)

[a] Here and hereinafter the bond lengths and bond angles in the benzene rings have standard values and therefore are not included in the tables.

Table 2. Bond lengths (*d*, Å) and bond angles (ω, deg) in the molecule of 1-(1,3-benzothiazol-2-yl)-1-phenyl-2-(2,5-diethoxycarbonyl-3-phenyl-2,3-dihydro-1,3,4-thiadiazol-2-yl)hydrazine (**Vd**)

Bond	*d*	Bond	*d*
S^1–C^{10}	1.739(4)	N^3–C^{15}	1.399(5)
S^1–C^2	1.755(3)	N^4–N^5	1.358(4)
S^2–C^4	1.744(4)	N^4–C^{22}	1.420(5)
S^2–C^1	1.861(4)	N^4–C^1	1.464(4)
O^1–C^3	1.193(4)	N^5–C^4	1.282(4)
O^2–C^3	1.304(5)	C^1–C^3	1.535(5)
O^2–C^6	1.485(6)	C^4–C^5	1.466(5)
O^3–C^5	1.198(4)	C^6–C^7	1.414(8)
O^4–C^5	1.337(5)	C^8–C^9	1.487(7)
O^4–C^8	1.467(5)	C^{10}–C^{15}	1.385(5)
N^1–C^2	1.364(4)	C^{10}–C^{11}	1.394(5)
N^1–N^2	1.407(4)	C^{11}–C^{12}	1.371(6)
N^1–C^{16}	1.441(5)	C^{12}–C^{13}	1.380(6)
N^2–C^1	1.433(4)	C^{13}–C^{14}	1.386(6)
N^3–C^2	1.291(4)	C^{14}–C^{15}	1.385(5)
Angle	**ω**	**Angle**	**ω**
$C^{10}S^1C^2$	88.04(17)	$O^2C^3C^1$	111.1(3)
$C^4S^2C^1$	89.07(16)	$N^5C^4C^5$	121.2(3)
$C^3O^2C^6$	116.4(3)	$N^5C^4S^2$	117.1(3)
$C^5O^4C^8$	118.2(3)	$C^5C^4S^2$	121.5(3)
$C^2N^1N^2$	115.9(3)	$O^3C^5O^4$	125.0(4)
$C^2N^1C^{16}$	121.4(3)	$O^3C^5C^4$	125.2(4)
$N^2N^1C^{16}$	115.8(3)	$O^4C^5C^4$	109.8(3)
$N^1N^2C^1$	115.2(3)	$C^7C^6O^2$	105.4(6)
$C^2N^3C^{15}$	109.8(3)	$O^4C^8C^9$	109.3(4)
$N^5N^4C^{22}$	118.0(3)	$C^{15}C^{10}C^{11}$	121.5(4)
$N^5N^4C^1$	118.0(3)	$C^{15}C^{10}S^1$	110.1(3)
$C^{22}N^4C^1$	123.8(3)	$C^{11}C^{10}S^1$	128.4(3)
$C^4N^5N^4$	111.9(3)	$C^{12}C^{11}C^{10}$	117.8(4)
$N^2C^1N^4$	111.8(3)	$C^{11}C^{12}C^{13}$	121.2(4)
$N^2C^1C^3$	105.8(3)	$C^{12}C^{13}C^{14}$	121.1(4)
$N^4C^1C^3$	114.3(3)	$C^{15}C^{14}C^{13}$	118.4(4)
$N^2C^1S^2$	116.4(2)	$C^{10}C^{15}C^{14}$	120.0(3)
$N^4C^1S^2$	102.3(2)	$C^{10}C^{15}N^3$	115.3(3)
$C^3C^1S^2$	106.4(3)	$C^{14}C^{15}N^3$	124.7(3)
$N^3C^2N^1$	122.8(3)	$C^{17}C^{16}N^1$	120.5(3)
$N^3C^2S^1$	116.8(3)	$C^{21}C^{16}N^1$	118.7(3)
$N^1C^2S^1$	120.4(3)	$C^{27}C^{22}N^4$	118.4(4)
$O^1C^3O^2$	126.3(4)	$C^{23}C^{22}N^4$	121.3(4)
$O^1C^3C^1$	122.5(3)		

planar (maximum deviation of atoms from the plane was 0.004 Å). A common conjugation system presumably exists between the lone electron pair of N^3 atom, electrons of the double bond N^4=C^2, and of carbonyl group C^{24}=O^2 (the angle between the planes of acetyl group $O^2C^{24}C^{25}$ and thiadiazole ring amounts to 2.3°). Benzene ring C^4–C^9 is excluded from this conjugation system (the angle between the planes of thiadiazole ring and C^4–C^9 ring is 17.9°). Bond lengths and bond angles are given in Table 1.

The X-ray analysis of crystals **Vd** showed the presence of a weak intramolecular hydrogen bond between atoms O^1 and H_{N^2}. Parameters of the hydrogen bond are as follows: N^2–H_{N^2} 0.903, O^1–H_{N^2} 2.13, O^1–N^2 2.64 Å, angle $N^2H_{N^2}O^1$ 114.8°. The ring $H_{N^2}N^2C^1C^3O^1$ formed by the hydrogen bond $O^1 \leq \Theta \leq H_{N^2}$ is not planar (maximum deviation of atoms from this ring plane is 0.099 Å). Thiadiazole ring is not quite planar (maximum deviation of atoms from the plane $C^1N^4N^5C^4S^2$ is 0.02 Å). A common conjugation system presumably exists between the carboxylate group $C^5O^3O^4$, double bond N^5=C^4, and lone electron pair on the atom N^4 for the angle between the planes $N^4N^5C^4$ and $C^5O^3O^4$ equals to 1.4°. The benzene ring C^{22}–C^{27} does not take part in this conjugation since the angle between the planes $N^4N^5C^4S^2C^1$ and C^{22}–C^{27} amounts to 153.5°. Bond lengths and bond angles are given in Table 2.

Thus we established that reaction of benzothiazole-2-thione with a double excess of C,N-disubstituted nitrilimines started with 1,3-dipolar cycloaddition to the exocyclic C=S bond, then the arising unstable spiro compound readily underwent a cleavage of the C–S bond in the thiadiazole ring, the second molecule of nitrilimine added to the formed C=S bond giving substituted 1-aryl-1-(1,3-benzothiazol-2-yl)-2-(2,3-dihydro-1,3,4-thiadiazol-2-yl)hydrazines (**Va–d**).

EXPERIMENTAL

^{1}H NMR spectra (500 MHz) and ^{13}C NMR spectra (125 MHz) were registered from 20% solutions of compounds in DMSO-d_6 on spectrometer Bruker AM-500. Mass spectra were recorded on MKh-1321 instrument, at vaporizer temperature 120°C, ionizing chamber temperature 200°C, ionizing electrons energy 70 eV.

X-ray diffraction analysis of crystals **Va** was performed on automatic diffractometer Enraf-Nonius CAD-4 (MoK_α-radiation, β-filter, θ/2θ-scanning, 1.67 ≤

$\Theta \le 24.97°$Å Triclinic crystals, *a* 9.092(2), *b* 10.684(2), *c* 12.519(3) , α 95.91(3), β 100.95(3), γ 93.94(3)°, *V* 1182.7(4) Å^3, space group *P* 1, *Z* 2, d_{calc} 1.369 g/cm^3. The structure was solved by the direct method [2686 reflections with $\sigma > 3\sigma$ (I)] in a full-matrix anisotropic approximation for atoms O, N, C, and S, and in isotropic approximation for hydrogen atoms till R 0.0280, R_W 0.0779 (no correction for extinction was introduced).

X-ray diffraction analysis of crystals **Va** was performed on automatic diffractometer Enraf-Nonius CAD-4 (MoK_α-radiation, β-filter, θ/2θ-scanning, $1.57 \le \Theta \le 24.92°$). Monoclinic crystals, *a* 10.071(2), *b* 10.468(2), *c* 26.225(5) Å, β 97.69(3)°, *V* 2739.9(9) Å, space group $P2_1/n$, *Z* 4, d_{calc} 1.328 g/cm^3. The structure was solved by the direct method [2107 reflections with $\sigma > 3\sigma$ (I)] in full-matrix anisotropic approximation for atoms O, N, C, and S, and in isotropic approximation for hydrogen atoms till R 0.0327, R_W 0.0900 (no correction for extinction was introduced).

Crystallographic coordinates of nonhydrogen and hydrogen atoms and their equivalent thermal factors are available from the authors.

Reaction of benzothiazole-2-thione with C-(acetyl, methoxycarbonyl, ethoxycarbonyl)-N-phenyl-nitrilimines. To a solution of 8 mmol of benzothiazole-2-thione in 50 ml of anhydrous toluene was added in succession 16 mmol of an appropriate hydrazonoyl chloride and 16.5 mmol of anhydrous triethylamine. The reaction mixture was heated at reflux for 3 h. On cooling the precipitate of triethylamine hydrochloride (yield 75–90%) was filtered off, the filtrate wasevaporated under reduced pressure, and the oily residue was crystallized by grinding with ether. Compounds **Va–d** obtained were recrystallized from an appropriate solvent. In crystalline compounds **Va, d** an impurity of bis{2-[1,3,4-thiadiazol-2-ylideneamino]-phenyl} disulfides (**III**) was detected by TLC, therefore the compounds were subjected to additional purification by chromatography on silica gel (eluent chloroform).

2-(2,5-Diacetyl-3-phenyl-2,3-dihydro-1,3,4-thiadiazol-2-yl)-1-(1,3-benzothiazol-2-yl)-1-phenylhydrazine (Va). Yield 50%, mp 195–196°C (from acetone). ^{1}H NMR spectrum, δ, ppm: 2.43 s, 2.46 s [6H, $CH_3C(O)$], 6.74–7.64 m (14H, C_6H_5), 8.40 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 24.15, 24.89 [$\underline{CH}_3C(O)$], 95.39 (C^2), 115.55, 125.09, 126.63, 127.91, 128.27, 128.74, 139.81 (NC_6H_5), 119.33, 121.03, 122.83, 125.75, 131.34, 140.91 (C_6H_4), 152.02 (C^9), 171.25 (C^1), 189.95, 197.27 [$CH_3\underline{C}(O)$]. Mass spectrum, *m/z* (I_{rel}, %): 487 (5) $[M]^+$, 247 (100) $[C_{12}H_{11}N_2O_2S]^+$, 226 (10) $[C_{13}H_{10}N_2S]^+$, 205 (30) $[C_{10}H_9N_2OS]^+$, 77 (15) $[C_6H_5]^+$.Found, %: C 61.73; H 4.47; N 14.23. $C_{25}H_{21}N_5O_2S_2$. Calculated, %: C 61.52; H 4.34; N 14.36.

2-(2,5-Diacetyl-3-*m*-chlorophenyl-2,3-dihydro-1,3,4-thiadiazol-2-yl)-1-(1,3-benzothiazol-2-yl)-1-*m*-chlorophenylhydrazine (Vb). Yield 65%, mp 202–203°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 2.46 s, 2.49 s [6H, $CH_3C(O)$], 6.75–7.67 m (12H, C_6H_4), 8.85 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 25.04, 25.24 [$\underline{CH}_3C(O)$], 95.39 (C^2), 115.39, 124.44, 125.45, 126.67, 129.25, 130.18, 132.55, 133.77, 140.27, 140.77 (NC_6H_4Cl-*m*), 119.57, 121.12, 122.75, 125.81, 131.42, 141.91 (C_6H_4), 151.96 (C^9), 171.13 (C^1), 189.97, 196.72 [$CH_3\underline{C}(O)$]. Mass spectrum, *m/z* (I_{rel}, %): 556 (5) $[M]^+$, 281 (100) $[C_{12}H_{10}ClN_2O_2S]^+$, 259 (20) $[C_{13}H_8ClN_2S]^+$, 239 (45) $[C_{10}H_7N_2OS]^+$. Found, %: C 53.84; H 3.42; N 12.72; S 11.66. $C_{25}H_{19}Cl_2N_5O_2S_2$. Calculated, %: C 53.96; H 3.44; N 12.74; S 11.52.

1-(1,3-Benzothiazol-2-yl)-1-*p*-bromophenyl-2-(2,5-dimethoxycarbonyl-3-*p*-bromophenyl-2,3-dihydro-1,3,4-thiadiazol-2-yl)hydrazine (Vc). Yield 68%, mp 181–182°C (from acetone). ^{1}H NMR spectrum, δ, ppm: 3.83 s, 3.89 s [6H, $CH_3OC(O)$], 6.77–7.68 m (12H, C_6H_4), 8.73 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 54.72, 53.12 [$\underline{CH}_3OC(O)$], 98.72 (C^2), 114.52, 117.32, 119.71, 127.63, 130.92, 131.27, 139.19 (NC_6H_4Br-*p*), 119.58, 121.28, 122.32, 125.92, 131.49, 140.41 (C_6H_4), 151.89 (C^9), 159.14, 166.04 [$CH_3O\underline{C}(O)$], 171.18 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 373 (10) $[C_{12}H_{11}BrN_3O_4S]^+$, 359 (40) $[C_{12}H_{11}BrN_2O_4S]^+$, 357 (50) $[C_{12}H_{11}BrN_3O_3S]^+$, 304 (50) $[C_{13}H_8BrN_2S]^+$. Found, %: C 44.35; H 2.88; N 9.63; S 9.99. $C_{25}H_{19}Br_2N_5O_4S_2$. Calculated, %: C 44.33; H 2.83; N 10.34; S 9.47.

1-(1,3-Benzothiazol-2-yl)-2-(2,5-diethoxycarbonyl-3-phenyl-2,3-dihydro-1,3,4-thiadiazol-2-yl)-1-phenylhydrazine (Vd). Yield 59%, mp 146–147°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.36 t, 1.15 t [6H, $\underline{CH}_3CH_2OC(O)$], 4.34 q, 4.28 q [4H, $CH_3\underline{CH}_2OC(O)$], 6.89–7.62 m (14H, C_6H_5), 8.19 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 13.93, 13.37 [$\underline{CH}_3CH_2OC(O)$], 62.05, 63.54 [$CH_3\underline{CH}_2OC(O)$], 98.99 ($C^2$), 115.78, 125.20, 125.83, 126.78, 128.12, 128.49,

140.25 (NC_6H_5), 119.43, 121.18, 122.13, 122.67, 131.45, 141.46 (C_6H_5), 151.95 (C^9), 158.98, 165.81 [$CH_3CH_2OC(O)$], 171.21 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 547 (5) $[M]^+$, 308 (100) $[C_{14}H_{16}N_2O_4S]^+$, 225 (30) $[C_{13}H_9N_2S]^+$, 77 (50) $[C_6H_5]^+$. Found, %: C 59.51; H 4.44; N 13.14; S 11.96. $C_{27}H_{25}N_5O_4S_2$. Calculated, %: C 59.22; H 4.56; N 12.79; S 11.69.

The study was carried out under financial support of the Russian Foundation for Basic Research (grants nos. 00-03-32578 and-03-32919).

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