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Hetrocyclic Thiones and Their Analogs in Reactions of 1,3-Dipolar Addition: VI.* Reactions of Thiazoline-2-thione with Nitrile Imines

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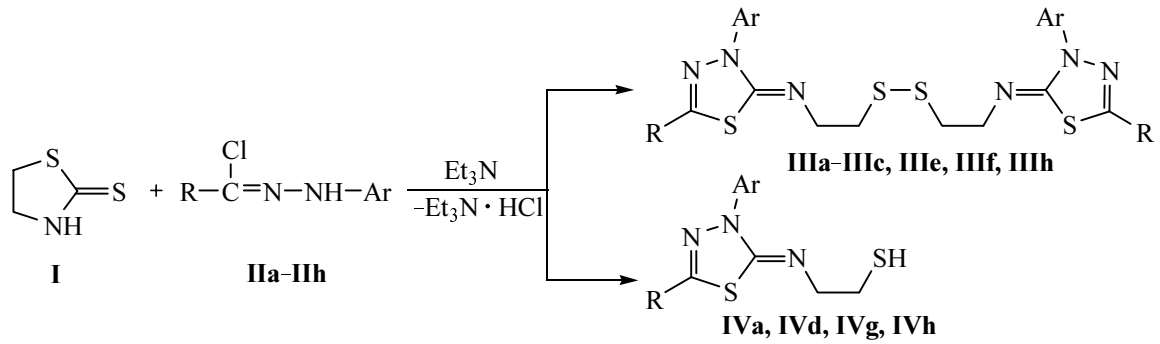
Abstract—Reactions of thiazoline-2-thione with C,N-disubstituted nitrile imines were investigated. The reaction products are substituted 2-(1,3,4-thiadiazol-2-ylideneamino)ethanethiols and bis[2-(1,3,4-thiadiazol-2-ylideneamino)ethyl] disulfides. The reaction of thiazoline-2-thione with a double excess of nitrile imine did not considerably change the process route. The structure of compounds obtained was proved by X-ray diffraction analysis. A presumable scheme is given describing the formation of compounds obtained.

The reactivity of compounds containing in the molecule N=C–SH or NH–C=S moiety is quite versatile [2–6]. The thione-thiol tautomerism existing in compounds of this structure makes them capable to react with C 1,3-dipolar systems at different reaction centers. Consequently these compounds in reactions with 1,3-dipolar reagents can form both products of N- or S-substitution, and also products of 1,3-dipolar cycloaddition. It is known however [7, 8] that reactions of some of these compounds with hydrazonoyl chlorides in the presence of triethylamine give rise to products of decomposition of intermediate unstable adducts having spiro structure.

We formerly demonstrated [9, 10] that reaction of benzothiazole-2-thione with C,N-disubstituted nitrile imines proceeded through formation of intermediate spiro compound where both C–S were labile, and the cleavage of any of these bonds was reversible.

Here we report the results obtained in investigation of the reaction between thiazoline-2-thione and C,N-disubstituted nitrile imines. Nitrile imines were prepared *in situ* by treating with triethylamine appropriate hydrazonoyl chlorides **IIa–IIi**.

We established that the reaction of thiazoline-2-thione (**I**) with nitrile imines afforded substituted bis[2-(1,3,4-thiadiazol-2-ylideneamino)ethyl] disulfides **IIIa–c**, **IIIe**, **IIIf**, and **IIIh**, and 2-(1,3,4-thiadiazol-2-ylideneamino)-ethanethiols **IVa**, **IVd**, **IVg**, and **IVh**.



R = $CH_3C(O)$, Ar = C_6H_5 (**a**), $CH_3OC_6H_4$ (**b**); R = $CH_3OC(O)$, Ar = C_6H_5 (**c**), *n*-$CH_3OC_6H_4$ (**d**); R = $C_2H_5OC(O)$, Ar = C_6H_5 (**e**), *p*-$CH_3C_6H_4$ (**f**), *m*-ClC_6H_4 (**g**), R = C_6H_5, Ar = C_6H_5 (**h**).

For communication V, see [1].

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The compounds obtained are crystalline solids; compounds **IVa**, **IVd**, **IVg**, and **IVh** are unstable in air, and compounds **IIIa–c**, **IIIe**, **IIIf**, and **IIIh** remain unchanged in air for a long time.

In the ^{1}H NMR spectra of thiols **IVa**, **IVd**, **IVg**, and **IVh** a doublet of triplets at δ 2.8 ppm corresponds to SCH_2 group, and triplet in the region δ 3.4 ppm belongs to NCH_2 group from the CH_2CH_2 structure, and also appears a triplet in the region δ 1.8–2.4 ppm from the proton of the thiol SH group.

The ^{13}C NMR spectra of isolated compounds **IVa**, **IVd**, **IVg**, and **IVh** are consistent with the assumed structure of these substances. The signals from carbon atoms located in positions *2* and *5* of the thiadiazole ring appear in the regions δ 136–139 (C^2) and 153–154 ppm (C^5). The carbon signals from the CH_2CH_2 group are observed at δ 60 (NCH_2) and 24 ppm (SCH_2).

The formation of substituted thiols **IVa**, **IVd**, **IVg**, and **IVh** was also proved by the mass spectrometry. In the mass spectra of the compounds were registered molecular ion peaks and peaks arising by cleavage of a CH_2SH group from the molecular ion. Further fragmentation followed a complicated pattern.

In the ^{1}H NMR spectra of substituted disulfides **IIIa–IIIc**, **IIIe**, **IIIf**, and **IIIh** in contrast to the spectra of compounds **IVa**, **IVd**, **IVg**, and **IVh** the signals of the CH_2CH_2 group appear as two triplets in the region δ 2.9 (SCH_2) and 3.5 ppm (NCH_2).

In the ^{13}C NMR spectra of synthesized disulfides **IIIa–IIIc**, **IIIe**, **IIIf**, and **IIIh** carbon atoms in positions *2,2'* and *5,5'* of thiadiazole rings give rise to signals in the same region δ 137–146 (C^2), 154 ppm (C^5) as the resonances of the same atoms in the spectra of thiols **IVa**, **IVd**, **IVg**, and **IVh**.

The chemical sift δ 56 ppm (NCH_2) in the CH_2CH_2 group is virtually the same as that of the similar atom in the spectra of thiols **IVa**, **IVd**, **IVg**, and **IVh**. However the position of the signal from the carbon atom in this group linked to sulfur (SCH_2) considerably differs from the corresponding signal from the atom in the (SCH_2) group in thiols **IVa**, **IVd**, **IVg**, and **IVh** (δ 38 and 24 ppm respectively). The rest signals in the ^{13}C NMR spectra of disulfides are consistent with the assumed structure.

The formation of disulfides **IIIa–IIIc**, **IIIe**, **IIIf**, and **IIIh** was also proved by the mass spectrometry. In the mass spectra of the compounds were registered peaks of ions arising from the fragmentation of the molecule due to the rupture of the S–CH_2 bond. Further fragmentation followed a complicated pattern.

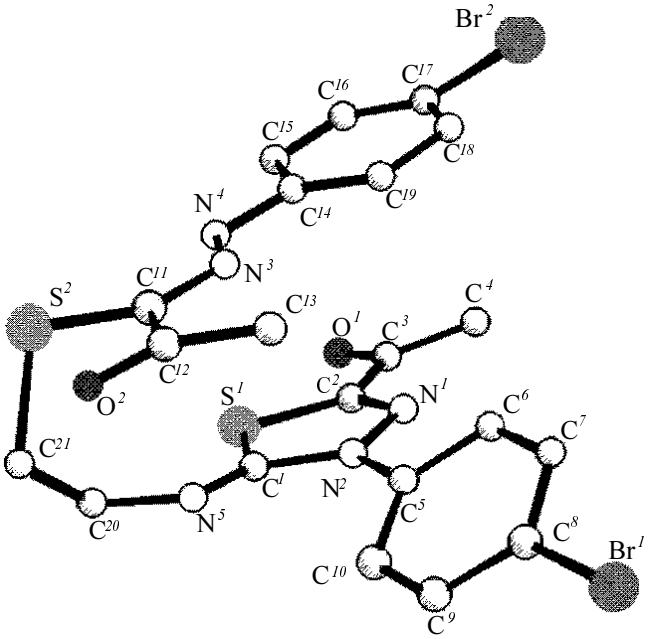


Fig. 1. Structure of the molecule of bis{2-[3-(4-methylphenyl)-5-ethoxycarbonyl-1,3,4-thiadiazol-2-ylideneamino]-ethyl}disulfide (**IIIf**) according to X-ray diffraction analysis. Hydrogen atoms are not shown.

The structure of bis[2-(1,3,4-thiadiazol-2-ylideneamino)ethyl] disulfides **IIIa–IIIc**, **IIIe**, **IIIf**, and **IIIh** was proved by X-ray diffraction analysis carried out on a single crystal of disulfide **IIIf**.

A perspective drawing of the molecule of bis[2-(1,3,4-thiadiazol-2-ylideneamino)ethyl] disulfide (**IIIf**) is shown on Fig. 1. (In all descriptions of results obtained by X-ray diffraction analysis the numbering of atoms is the same as on the figure). The X-ray diffraction study revealed that the molecule possesses a symmetry axis C_2. Therefore the second part of the molecule is obtained from the first part by rotation of the latter through 180° around the twofold symmetry axis. Consequently the bond lengths and bond angles in the second part of the molecule are absolutely the same as in the first part. The torsion angle $C^7S^2S^{2A}C^{7A}$ is equal to –113.9°. The torsion angles $N^3C^6C^7S^2$ and $N^{3A}C^{6A}C^{7A}S^{2A}$ are equal and amount to 60.9°. The thiadiazole ring is pseudoaromatic (maximum deviations of atoms from the ring plane are 0.0102 Å), the N^3 atom is located virtually in the plane of the ring (deviation of N^3 atom from the plane is –0.0426 Å). The angle between the planes of the thiadiazole and phenyl rings in the symmetrically independent part of the molecule equals to 8.8° not preventing the conjugation between these rings. The conjugation between thiadiazole ring and the ethoxycarbonyl group hardly exists for they are located

Table 1. Bond lengths *d* (Å) and bond angles ω (deg) in the molecule of bis{2-[3-(4-methylphenyl)-5-ethoxycarbonyl-1,3,4-thiadiazol-2-ylideneamino]ethyl} disulfide (**IIIf**)[a]

Bond	*d*	Bond	*d*
S^1–C^2	1.729(4)	N^1–C^8	1.437(4)
S^1–C^1	1.771(4)	N^2–C^2	1.285(5)
S^2–C^7	1.804(5)	N^3–C^1	1.268(4)
S^2–S^2	2.032(3)	N^3–C^6	1.447(5)
O^1–C^3	1.184(4)	C^2–C^3	1.485(5)
O^2–C^3	1.323(5)	C^4–C^5	1.421(11)
O^2–C^4	1.454(6)	C^6–C^7	1.512(6)
N^1–N^2	1.363(4)	C^{11}–C^{14}	1.510(6)
N^1–C^1	1.400(4)		
Angle	**ω**	**Angle**	**ω**
$C^2S^1C^1$	88.48(18)	$N^2C^2S^1$	116.9(3)
$C^7S^2S^2$	103.71(19)	$C^3C^2S^1$	122.9(3)
$C^3O^2C^4$	117.9(4)	$O^1C^3O^2$	125.6(4)
$N^2N^1C^1$	116.3(3)	$O^1C^3C^2$	125.5(4)
$N^2N^1C^8$	116.2(3)	$O^2C^3C^2$	109.0(4)
$C^1N^1C^8$	127.4(3)	$C^5C^4O^2$	109.8(6)
$C^2N^2N^1$	110.9(3)	$N^3C^6C^7$	111.4(4)
$C^1N^3C^6$	116.8(3)	$C^6C^7S^2$	117.0(3)
$N^3C^1N^1$	125.2(3)	$C^{13}C^8N^1$	119.0(3)
$N^3C^1S^1$	127.3(3)	$C^9C^8N^1$	121.5(3)
$N^1C^1S^1$	107.5(2)	$C^{10}C^{11}C^{14}$	121.9(4)
$N^2C^2C^3$	120.2(3)	$C^{12}C^{11}C^{14}$	120.8(4)

[a] Bond lengths and bond angles in the benzene ring are of standard values and are not presented in the table.

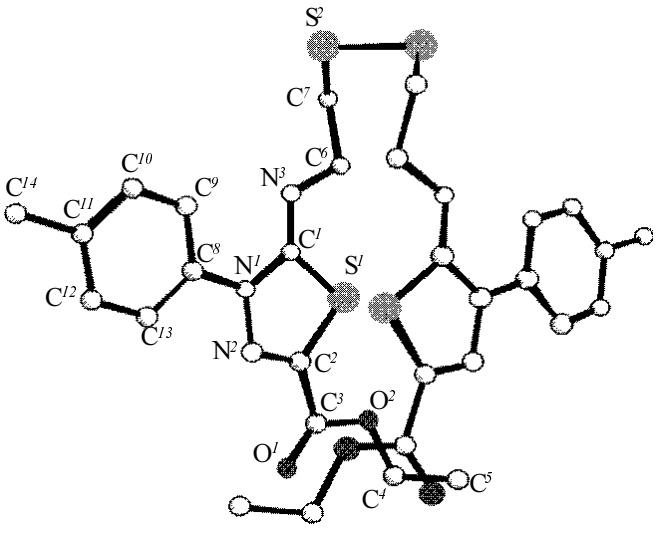
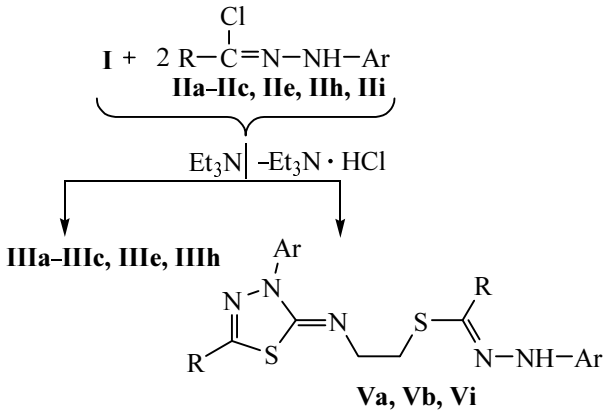


Fig. 2. Structure of the molecule of 2-[5-acetyl-7-(4-bromophenyl)-4-thia-1,6,7-triaza-5-heptenylidene]-5-acetyl-3-(4-bromophenyl)-1,3,4-thiadiazoline (**Vi**) according to X-ray diffraction analysis. Hydrogen atoms are not shown.



II, R = $CH_3C(O)$, Ar = *n*-BrC_6H_4 (**i**); **V**, R = $CH_3C(O)$, Ar = C_6H_5 (**a**), $CH_3OC_6H_4$ (**b**), *n*-BrC_6H_4 (**i**).

at an angle of 22.8°. The bond lengths and bond angles are given in Table 1.

In order to prevent thiols dimerization we attempted to acetylate them with excess nitrile imine.

It turned out however that the reaction carried out with the double amount of hydrazonoyl chlorides gave rise predominantly to disulfides **IIIc**, **IIIe**, and **IIIh**. Only the reaction with excess C-acetyl-N-arylnitrile imine afforded substituted 2-(7-aryl-5-acetyl-4-thia-1,6,7-triaza-5-heptenylidene)-1,3,4-thiazolidines, hydrazones **Va**, **Vb**, and **Vi**; therewith the corresponding disulfides **IIIa** and **IIIb** also formed.

The synthesized hydrazones **Va**, **Vb**, and **Vi** are crystalline solids stable at long storage in air.

In the ^{1}H NMR spectra of hydrazones **Va**, **Vb**, and **Vi** the signals of the CH_2CH_2 group appear as two triplets in the same region δ 2.9 (SCH_2) and 3.5 ppm (NCH_2) as in the spectra of above described disulfides **III**. The proton signal of the hydrazide moiety is seen in the region δ 10.0 ppm.

In the ^{13}C NMR spectra of synthesized compounds **Va**, **Vb**, and **Vi** carbon atoms in positions *2* and *5* of thiadiazole rings give rise to signals at δ 141–145 (C^2) and 154 ppm (C^5). The chemical sifts δ 59 ppm (NCH_2) and 33 ppm (SCH_2) from the CH_2CH_2 group are virtually the same as those of the similar atoms in the spectra of thiols **IVa**, **IVd**, **IVg**, and **IVh** and disulfides **IIIa–IIIc**, **IIIe**, **IIIf**, and **IIIh** above described. The rest signals in the ^{13}C NMR spectra of compounds **Va**, **Vb**, and **Vi** also are consistent with the assumed structure.

The formation of compounds **Va**, **Vb**, and **Vi** was also proved by the mass spectrometry.

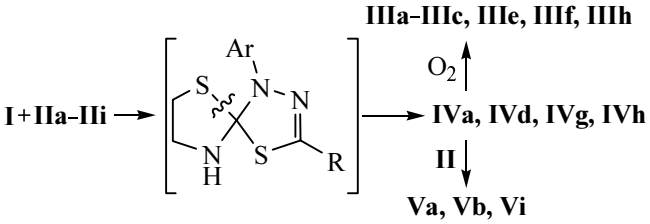
The structure of substituted hydrazones **Va**, **Vb**, and **Vi** was proved by X-ray diffraction study carried out on a single crystal of hydrazone **Vi**.

The perspective drawing of the molecule of 2-[5-acetyl-7-(4-bromophenyl)-4-thia-1,6,7-triaza-5-heptenylidene]-5-acetyl-3-(4-bromophenyl)-1,3,4-thiadiazoline (**Vi**) is presented on Fig. 2. The X-ray diffraction study demonstrated that the thiadiazole ring is planar (maximum deviations of atoms from the ring plane are 0.0227 Å). However the N^5 atom somewhat deviates from this plane (0.1430 Å). Presumably the acetyl group $C^4C^3O^1$ is involved into the conjugation with the thiadiazole ring for the angle between their planes amounts to 8.6°. The conjugation between the thiadiazole and phenyl rings is lacking since the angle between the respective planes is –28.3°. The intramolecular hydrogen bond between atoms O^2 and $H_N{}^4$ does not form because the hydrazide fragment is present in the *Z*-conformation. A conjugation exists between the acetyl group $O^2C^{12}C^{13}$ and the double bond C^{11}=N^3 for the angle between their planes is 4.4°. A conjugation is possible between the lone electron pair of the atom N^4 and the benzene ring C^{14}–C^{19} (deviation of the atom N^4 from the ring C^{14}–C^{19} plane equals to 0.0076 Å).

The bond lengths and bond angles are given in Table 2.

We believe that the reaction of 1,3-thiazoline-2-thione with C,N-disubstituted nitrile imines like that of the benzothiazole-2-thione proceeds via a stage of formation of intermediate unstable spiro compounds.

Then in the formed thiazolespirothiadiazoles an opening of the least stable thiazole ring occurs giving rise to substituted thiols **IVa**, **IVd**, **IVg**, and **IVh**. The latter suffer dimerization effected by the air oxygen to afford the corresponding disulfides **IIIa–c**, **IIIe**, **IIIf**, and **IIIh**. The formation of disulfides **IIIa–c**, **IIIe**, **IIIf**, and **IIIh** in reaction of the thiazolinethione with a double excess of nitrile imine evidences the low reactivity of thiols **IV** under given conditions.



Thus reasoning from the structures of reaction products formed from thiazoline-2-thione and C,N-disubstituted nitrile imines we believe that the process starts by giving rise to unstable spiro compounds that decompose via the rupture of a C–S bond of the thiazole ring. The use of a double amount of nitrile imine does not essentially affect the course of the reaction.

Table 2. Bond lengths *d* (Å) and bond angles ω (deg) in the molecule of 2-[5-acetyl-7-(4-bromophenyl)-4-thia-1,6,7-triaza-5-heptenylidene]-5-acetyl-3-(4-bromophenyl)-1,3,4-thiadiazoline (**Vi**)[a]

Bond	*d*	Bond	*d*
Br–C^8	1.874(12)	N^2–C^5	1.417(13)
Br^2–C^{17}	1.899(12)	N^3–C^{11}	1.278(12)
S^1–C^2	1.739(14)	N^3–N^4	1.333(10)
S^1–C^1	1.765(12)	C^2–C^3	1.490(16)
S^2–C^{11}	1.774(11)	C^3–C^4	1.439(18)
S^2–C^{21}	1.818(14)	C^{11}–C^{12}	1.481(16)
O^1–C^3	1.204(14)	C^{12}–C^{13}	1.454(15)
O^2–C^{12}	1.232(13)	C^{20}–C^{21}	1.517(18)
N^1–C^2	1.275(14)	N^5–C^1	1.263(15)
N^1–N^2	1.353(11)	N^5–C^{20}	1.444(16)
N^2–C^1	1.414(16)	N^4–C^{14}	1.394(12)
Angle	**ω**	**Angle**	**ω**
$C^2S^1C^1$	88.3(8)	$C^{10}C^5N^2$	121.2(11)
$C^{11}S^2C^{21}$	104.9(6)	$C^6C^5N^2$	117.8(11)
$C^2N^1N^2$	112.0(10)	$C^7C^6C^5$	118.8(12)
$N^1N^2C^1$	115.3(10)	$C^8C^7C^6$	120.4(13)
$N^1N^2C^5$	118.3(10)	$C^9C^8Br^1$	119.4(10)
$C^1N^2C^5$	126.3(9)	$C^7C^8Br^1$	120.6(10)
$C^{11}N^3N^4$	118.9(9)	$N^3C^{11}C^{12}$	115.7(11)
$N^3N^4C^{14}$	118.5(9)	$N^3C^{11}S^2$	123.9(9)
$C^1N^5C^{20}$	118.4(12)	$C^{12}C^{11}S^2$	120.4(10)
$N^5C^1N^2$	121.6(11)	$O^2C^{12}C^{13}$	120.8(12)
$N^5C^1S^1$	130.8(13)	$O^2C^{12}C^{11}$	118.1(12)
$N^2C^1S^1$	107.6(10)	$C^{13}C^{12}C^{11}$	121.1(13)
$N^1C^2C^3$	122.7(14)	$C^{19}C^{14}N^4$	122.3(10)
$N^1C^2S^1$	116.4(10)	$C^{19}C^{14}C^{15}$	120.0(11)
$C^3C^2S^1$	120.8(11)	$N^4C^{14}C^{15}$	117.6(10)
$O^1C^3C^4$	125.2(14)	$C^{16}C^{17}Br^2$	121.6(10)
$O^1C^3C^2$	118.0(13)	$C^{18}C^{17}Br^2$	117.9(10)
$C^4C^3C^2$	116.7(13)	$N^5C^{20}C^{21}$	110.6(12)
$C^{10}C^5C^6$	120.9(12)	$C^{20}C^{21}S^2$	113.6(9)

[a] Bond lengths and bond angles in the benzene ring are of standard values and are not presented in the table.

EXPERIMENTAL

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

X-ray diffraction study on single crystals of bis{2-[3-(4-methylphenyl)-5-ethoxycarbonyl-1,3,4-thiadiazol-2-

ylideneamino]ethyl}disulfide (**IIIf**) was performed on an automatic diffractometer Enraf-Nonius CAD-4 (MoK_α-radiation, β-filter, Θ/2Θ-scanning, $2.08 \le \Theta \le 24.97°$). Monoclinic crystals, $C_{14}H_{16}N_3O_2S_2$, *a* 14.131(3), *b* 18.687(4), *c* 13.145(3) Å, β 117.71(3)°, *V* 3073.0(12) Å^3, space group C2/*c*, *Z* 8, d_{calc} 1.394 g/cm^3. The structure was solved by the direct method [5551 reflection with $\sigma > 3\sigma$ (I)] in full-matrix approximation, anisotropic for atoms C, N, O, S, and isotropic for hydrogen atoms, till *R* 0.0242, R_W 0.0664 (no correction for extinction was done). The crystallographic coordinates of nonhydrogen and hydrogen atoms and their equivalent thermal factors are available from the authors.

X-ray diffraction study on single crystals of 2-[5-acetyl-7-(4-bromophenyl)-4-thia-1,6,7-triaza-5-heptenylidene]-5-acetyl-3-(4-bromophenyl)-1,3,4-thiadiazoline (**Vi**)) was performed on an automatic diffractometer Enraf-Nonius CAD-4 (MoK_α-radiation, β-filter, Θ/2Θ-scanning, $2.14 \le \Theta \le 24.61°$). Orthorhombic crystals, $C_{21}H_{19}Br_2N_5O_2S_2$, *a* 13.136(3), *b* 13.727(3), *c* 27.483 (5) Å, *V* 4955.7(18) Å^3, space group *PbCa*, *Z* 8, d_{calc} 1.621 g/cm^3. The structure was solved by the direct method [715 reflections with $\sigma > 3\sigma$ (I)] in full-matrix approximation, anisotropic for atoms C, N, O, S, and isotropic for hydrogen atoms, till *R* 0.0309, R_W 0.0800 (no correction for extinction was done). The crystallographic coordinates of nonhydrogen and hydrogen atoms and their equivalent thermal factors are available from the authors.

Nitrile imines were generated *in situ* by treating with the triethylamine the corresponding hydrazonoyl chlorides [11].

General procedure for reaction between thiazoline-2-thion and C-aryl(acetyl, methoxycarbonyl, ethoxycarbonyl)-N-arylnitrile imines. To a solution of 8 mmol of thiazoline-2-thione in 50 ml of anhydrous toluene was added in succession 8 mmol of an appropriate hydrazonoyl chloride and 8.8 mmol of anhydrous triethylamine. The reaction mixture was stored at room temperature for 48 h. The precipitate of triethylamine hydrochloride (yield 75–90%) was filtered off, the filtrate was evaporated under reduced pressure, and the oily residue was crystallized by grinding with ether. In reactions affording a mixture of 2-(1,3,4-thiadiazol-2-ylideneamino)ethanethiol and bis[2-(1,3,4-thiadiazol-2-ylideneamino)ethyl] disulfide the products were separated by fractional crystallization from ether. The isolated compounds were recrystallized from acetonitrile. Thus we obtained substituted thiols **IVa**, **IVd**, **IVg**, and **IVh** and disulfides **IIIa–c**, **IIIe**, **IIIf**, and **IIIh**.

Bis[2-(5-acetyl-3-phenyl-1,3,4-thiadiazol-2-ylideneamino)ethyl]disulfide (IIIa). Yield 56%, mp 95–96°C. ^{1}H NMR spectrum, δ, ppm: 2.56 s [3H, $CH_3C(O)$], 7.35–7.90 m (5H, C_6H_5), 3.40 t (2H, NCH_2), 3.00 t (2H, SCH_2). ^{13}C NMR spectrum, d, ppm: 146.42 (C^2, $C^{2'}$), 154.71 (C^5, $C^{5'}$), 56.35 (NCH_2), 38.72 (SCH_2), 189.17 [$CH_3\underline{C}(O)$], 24.71 [$\underline{C}H_3C(O)$], 122.51, 126.89, 128.76, 138.56 (C_6H_5). Mass spectrum, *m/z* (I_{rel}, %): 311 (100) $[C_{12}H_{12}N_3OS_3]^+$, 246 (40) $[C_{12}H_{12}N_3OS]^+$, 178 (35) $[C_9H_{10}N_2S]^+$, 131 (55) $[C_4H_5NS_2]^+$, 118 (35) $[C_3H_4NS_2]^+$, 91 (45) $[C_6H_5N]^+$, 77 (25) $[C_6H_5]^+$, 43 (25) $[C_2H_3O]^+$. Found, %: C 51.23; H 4.63; N 15.20; S 23.43. $C_{24}H_{24}N_6O_2S_4$. Calculated, %: C 51.78; H 4.35; N 15.09; S 23.04.

2-(5-Acetyl-3-phenyl-1,3,4-thiadiazol-2-ylideneamino)ethanethiol (IVa). Yield 31%, mp 63–64°C. ^{1}H NMR spectrum, δ, ppm: 2.6 s [3H, $CH_3C(O)$], 7.30–7.92 m (5H, C_6H_5), 3.30 t (2H, NCH_2), 2.79 t (2H, SCH_2), 1.92 t (1H, SH). ^{13}C NMR spectrum, δ, ppm: 138.60 (C^2, $C^{2'}$), 154.58 (C^5, $C^{5'}$), 60.60 (NCH_2), 24.82 (SCH_2), 189.20 [$CH_3\underline{C}(O)$], 24.71 [$\underline{C}H_3C(O)$], 122.60, 126.88, 128.79, 146.41 (C_6H_5). Mass spectrum, *m/z* (I_{rel}, %): 279 (20) $[M]^+$, 232 (50) $[M - CH_2SH]^+$, 178 (35) $[C_9H_{10}N_2S]^+$, 131 (40) $[C_4H_5NS_2]^+$, 91 (70) $[C_6H_5N]^+$, 77 (50) $[C_6H_5]^+$, 43 (100) $[C_2H_3O]^+$. Found, %: C 51.62; H 4.83; N 14.96; S 23.04. $C_{12}H_{13}N_3OS_2$. Calculated, %: C 51.59; H 4.69; N 15.04; S 22.95.

Bis{2-[5-acetyl-3-(4-methoxyphenyl)-1,3,4-thiadiazol-2-ylideneamino]ethyl} disulfide (IIIb). Yield 30%, mp 105–106°C. ^{1}H NMR spectrum, δ, ppm: 2.50 C [3H, $CH_3C(O)$], 6.95–7.73 m (4H, C_6H_4), 3.81 s (3H, CH_3O), 3.36 t (2H, NCH_2), 2.94 t (2H, SCH_2). ^{13}C NMR spectrum, δ, ppm: 145.75 (C^2, $C^{2'}$), 154.98 (C^5, $C^{5'}$), 56.27 (NCH_2), 38.73 (SCH_2), 189.01 [$CH_3\underline{C}(O)$], 24.64 [$\underline{C}H_3C(O)$], 55.30 (CH_3O), 113.84, 124.47, 131.47, 157.93 (C_6H_4). Mass spectrum, *m/z* (I_{rel}, %): 341 (50) $[C_{13}H_{14}N_3O_2S_3]^+$, 276 (30) $[C_{13}H_{14}N_3O_2S]^+$, 178 (10) $[C_9H_{10}N_2S]^+$, 131 (25) $[C_4H_5NS_2]^+$, 118 (10) $[C_3H_4NS_2]^+$, 91 (15) $[C_6H_5N]^+$, 77 (10) $[C_6H_5]^+$, 43 (35) $[C_2H_3O]^+$. Found, %: C 50.91; H 4.90; N 13.59; S 20.60. $C_{26}H_{28}N_6O_4S_4$. Calculated, %: C 50.63; H 4.58; N 13.63; S 20.79.

Bis[2-(5-methoxycarbonyl-3-phenyl-1,3,4-thiadiazol-2-ylideneamino)ethyl] disulfide (IIIc). Yield 62%, mp 98–99°C. ^{1}H NMR spectrum, δ, ppm: 3.92 s [3H, $CH_3OC(O)$], 7.25–7.89 m (5H, C_6H_5), 3.38 t (2H, NCH_2), 2.97 t (2H, SCH_2). ^{13}C NMR spectrum, δ, ppm: 138.52 (C^2, $C^{2'}$), 154.18 (C^5, $C^{5'}$), 56.36 (NCH_2), 38.79 (SCH_2), 158.26 [$CH_3O\underline{C}(O)$], 53.33 [$\underline{C}H_3OC(O)$], 122.44, 126.82, 128.73, 137.62 (C_6H_5). Mass spectrum,

m/z (I_{rel}, %): 326 (65) $[C_{12}H_{12}N_3O_2S_3]^+$, 262 (30) $[C_{12}H_{12}N_3O_2S]^+$, 178 (20) $[C_9H_{10}N_2S]^+$, 131 (25) $[C_4H_5NS_2]^+$, 118 (15) $[C_3H_4NS_2]^+$, 91 (100) $[C_6H_5N]^+$, 77 (70) $[C_6H_5]^+$, 59 (35) $[C_2H_3O_2]^+$. Found, %:

C 48.57; H 4.04; N 14.10; S 21.80. $C_{24}H_{24}N_6O_4S_4$. Calculated, %: C 48.96; H 4.11; N 14.27; S 21.78.

2-(5-Methoxycarbonyl-3-(4-methoxyphenyl)-1,3,4-thiadiazol-2-ylideneamino)ethanethiol (IVd). Yield 68%, mp 119–120°C. ^{1}H NMR spectrum, δ, ppm: 3.95 s [3H, $CH_3OC(O)$], 6.95–7.75 m (4H, C_6H_4), 3.85 s (3H, CH_3O), 3.30 t (2H, NCH_2), 2.80 t (2H, SCH_2), 1.84 t (1H, SH). ^{13}C NMR spectrum, δ, ppm: 136.86 (C^2, $C^{2'}$), 154.46 (C^5, $C^{5'}$), 60.45 (NCH_2), 24.80 (SCH_2), 158.00 [$CH_3O\underline{C}(O)$], 53.28 [$\underline{C}H_3OC(O)$], 55.33 (CH_3O), 113.92, 124.80, 131.40, 158.42 (C_6H_4). Mass spectrum, *m/z* (I_{rel}, %): 325 (20) $[M]^+$, 278 (30) $[M - CH_2SH]^+$, 206 (20) $[C_{10}H_{10}N_2O_3]^+$, 186 (25) $[C_6H_7N_3O_2S]^+$, 121 (95) $[C_7H_7ON]^+$, 106 (20) $[C_7H_7O]^+$, 59 (20) $[C_2H_3O_2]^+$. Found, %: C 47.53; H 4.72; N 12.89; S 19.95. $C_{13}H_{15}N_3O_3S_2$. Calculated, %: C 47.98; H 4.65; N 12.91; S 19.71.

Bis[2-(3-phenyl-5-ethoxycarbonyl-1,3,4-thiadiazol-2-ylideneamino)ethyl] disulfide (IIIe). Yield 65%, mp 78–79°C. ^{1}H NMR spectrum, δ, ppm: 1.37 t [3H, $C\underline{H}_3CH_2OC(O)$], 4.38 q [2H, $CH_3C\underline{H}_2OC(O)$], 7.27–7.87 m (5H, C_6H_5), 3.38 t [(2H, NCH_2], 2.97 t [2H, SCH_2]. ^{13}C NMR spectrum, δ, ppm: 137.85 (C^2, $C^{2'}$), 154.25 (C^5, $C^{5'}$), 56.35 (NCH_2), 38.82 (SCH_2), 157.78 [$CH_3CH_2O\underline{C}(O)$], 62.57 [$CH_3\underline{C}H_2OC(O)$], 13.83 [$\underline{C}H_3CH_2OC(O)$], 122.58, 126.85, 128.73, 138.54 (C_6H_5). Mass spectrum, *m/z* (I_{rel}, %): 341 (50) $[C_{13}H_{15}N_3O_2S_3]^+$, 276 (30) $[C_{13}H_{14}N_3O_2S]^+$, 178 (30) $[C_9H_{10}N_2S]^+$, 131 (50) $[C_4H_5NS_2]^+$, 118 (20) $[C_3H_4NS_2]^+$, 91 (100) $[C_6H_5N]^+$, 77 (60) $[C_6H_5]^+$. Found, %: C 50.97; H 4.75; N 13.75; S 20.68. $C_{26}H_{28}N_6O_4S_4$. Calculated, %: C 50.63; H 4.58; N 13.63; S 20.78.

Bis{2-[3-(4-methylphenyl)-5-ethoxycarbonyl-1,3,4-thiadiazol-2-ylideneamino]ethyl} disulfide (IIIf). Yield 84%, mp 123–124°C. ^{1}H NMR spectrum, δ, ppm: 1.37 t [3H, $C\underline{H}_3CH_2OC(O)$], 4.38 q [2H, $CH_3C\underline{H}_2OC(O)$], 7.19–7.73 m (4H, C_6H_4), 2.36 s (3H, CH_3), 3.36 t (2H, NCH_2), 2.96 t (2H, SCH_2). ^{13}C NMR spectrum, δ, ppm: 137.43 (C^2, $C^{2'}$), 154.37 (C^5, $C^{5'}$), 56.25 (NCH_2), 38.89 (SCH_2), 157.77 [$CH_3CH_2O\underline{C}(O)$], 62.47 [$CH_3\underline{C}H_2OC(O)$], 13.84 [$\underline{C}H_3CH_2OC(O)$], 20.49 ($CH_3$), 122.56, 129.07, 136.12, 136.32 (C_6H_4). Mass spectrum, *m/z* (I_{rel}, %): 355 (85) $[C_{14}H_{17}N_3O_2S_3]^+$, 290 (100) $[C_{14}H_{16}N_3O_2S]^+$, 178 (5) $[C_9H_{10}N_2S]^+$, 131 (25) $[C_4H_5NS_2]^+$, 118 (35) $[C_3H_4NS_2]^+$, 105 (70) $[C_7H_7N]^+$, 91 (45) $[C_7H_7]^+$. Found, %: C 52.66, H 5.19; N 12.72; S 20.07. $C_{26}H_{32}N_6O_4S_4$. Calculated, %: C 52.15; H 5.00; N 13.03; S 19.90.

2-[3-(3-Chlorophenyl)-5-ethoxycarbonyl-1,3,4-thiadiazol-2-ylideneamino]ethanethiol (IVg). Yield 75%, mp 67–68°C. ^{1}H NMR spectrum, δ, ppm: 1.31 t [3H, $C\underline{H}_3CH_2OC(O)$], 4.37 q [2H, $CH_3C\underline{H}_2OC(O)$], 7.32–8.02 m (4H, C_6H_4), 3.27 t (2H, NCH_2), 2.77 t (2H, SCH_2), 2.35 t (1H, SH). ^{13}C NMR spectrum, δ, ppm: 139.77 (C^2, $C^{2'}$), 153.77 (C^5, $C^{5'}$), 60.49 (NCH_2), 24.78 (SCH_2), 157.69 [$CH_3CH_2O\underline{C}(O)$], 62.73 [$CH_3\underline{C}H_2OC(O)$], 13.84 [$\underline{C}H_3CH_2OC(O)$], 120.41, 121.52, 126.34, 130.45, 132.97, 138.74 (C_6H_4). Mass spectrum, *m/z* (I_{rel}, %): 343 (20) $[M]^+$, 296 (70) $[M - CH_2SH]^+$, 268 (20) $[C_{11}H_9ClN_2O_2S]^+$, 212 (15) $[C_9H_9ClN_2S]^+$, 125 (95) $[C_6H_4ClN]^+$, 111 (50) $[C_6H_4Cl]^+$, 73 (10) $[C_3H_5O_2]^+$. Found, %: C 46.03; H 4.50; N 12.29; S 19.02. $C_{13}H_{14}ClN_3O_2S_2$. Calculated, %: C 45.54; H 4.10; N 12.22; S 18.73.

Bis[2-(3,5-diphenyl-1,3,4-thiadiazol-2-ylideneamino)ethyl] disulfide (IIIh). Yield 62%, mp 135–136°C. ^{1}H NMR spectrum, δ, ppm: 7.17–8.04 m (10H, C_6H_5), 3.49 t (2H, NCH_2), 3.05 t (2H, SCH_2). ^{13}C NMR spectrum, δ, ppm: 145.66 (C^2, $C^{2'}$), 153.97 (C^5, $C^{5'}$), 56.83 (NCH_2), 38.99 (SCH_2), 121.27, 125.28, 125,67, 128.45, 129.02, 129.75, 130.51, 139.51 (C_6H_5). Mass spectrum, *m/z* (I_{rel}, %): 345 (30) $[C_{16}H_{15}N_3S_3]^+$, 280 (20) $[C_{16}H_{14}N_3S]^+$, 178 (20) $[C_9H_{10}N_2S]^+$, 131 (5) $[C_4H_5NS_2]^+$, 118 (5) $[C_3H_4NS_2]^+$, 91 (100) $[C_6H_5N]^+$, 77 (40) $[C_6H_5]^+$. Found, %: C 61.12; H 4.57; N 13.59; S 20.27. $C_{32}H_{28}N_6S_4$. Calculated, %: C 61.51; H 4.52; N 13.45; S 20.53.

2-(3,5-Diphenyl-1,3,4-thiadiazol-2-ylideneamino)ethanethiol (IVh). Yield 28%, mp 117–118°C. ^{1}H NMR spectrum δ, ppm: 7.25–8.15 m (10H, C_6H_5), 3.37 t (2H, NCH_2), 2.87 t (2H, SCH_2), 2.20 t (1H, SH). Mass spectrum, *m/z* (I_{rel}, %): 313 (20) $[M]^+$, 267 (30) $[M - CH_2SH]^+$, 194 (25) $[C_{13}H_{10}N_2]^+$, 136 (20) $[C_7H_6NS]^+$, 91 (70) $[C_6H_5N]^+$, 77 (50) $[C_6H_5]^+$. Found, %: C 60.98; H 4.75; N 13.15; S 20.60. $C_{16}H_{15}N_3S_2$. Calculated, %: C 61.31; H 4.82; N 13.41; S 20.46.

General procedure for reaction between thiazoline-2-thion and a double amount of C-aryl(acetyl, methoxycarbonyl, ethoxycarbonyl)-*N*-arylnitrile imines. To a solution of 8 mmol of thiazoline-2-thione in 50 ml of anhydrous toluene was added in succession 16 mmol of an appropriate hydrazonoyl chloride and 16 mmol of anhydrous triethylamine. The reaction mixture

was stored at room temperature for a week. Then the precipitate of triethylamine hydrochloride (yield 80–90%) was filtered off, the filtrate was evaporated under reduced pressure, and the tarry oily residue was crystallized by grinding with ether.

In reactions with C-aryl(methoxycarbonyl, ethoxycarbonyl)-*N*-phenylnitrile imines the products were exclusively the previously described bis[2-(1,3,4-thiadiazol-2-ylideneamino)ethyl] disulfides **IIIc**, **IIIf**, and **IIIh**.

The mixture of crystals obtained in reactions with C-acetyl-*N*-arylnitrile imines were subjected to column chromatography on silica gel (eluent chloroform), for the TLC tests revealed alongside the presence of the disulfides also the corresponding ethanethiohydrazones. The compounds obtained were recrystallized from a mixture of acetonitrile and chloroform, 5:2.

We isolated substituted bis[2-(1,3,4-thiadiazol-2-ylideneamino)ethyl] disulfides **IIIa**, **IIIb**, **IIId**, **IIIf**, **IIIi**, and 2-(7-aryl-5-acetyl-4-thia-1,6,7-triaza-5-heptenylidene)-1,3,4-thiadiazolines **Va, Vb,** and **Vi**.

2-(5-Acetyl-7-phenyl-4-thia-1,6,7-triaza-5-heptenylidene)-1,3,4-thiadiazoline (Va). Yield 59%, mp 147–148°C. ^{1}H NMR spectrum, δ, ppm: 2.12 s, 2.31 s [6H, $CH_3C(O)$], 6.96–7.80 m (10H, C_6H_5), 3.35 t (2H, NCH_2), 3.17 t (2H, SCH_2), 10.22 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 154.34 (C^2), 142.50 (C^5), 138.60 (C^S), 59.62 (NCH_2), 33.26 (SCH_2), 192.57, 188.90 [$CH_3\underline{C}(O)$], 24.48, 24.94 [$\underline{C}H_3C(O)$], 114.43, 122.17, 122.39, 126.66, 128.67, 128.94, 133.25, 146.09 (C_6H_5). Mass spectrum, *m/z* (I_{rel}, %): 439 (20) $[M]^+$, 232 (20) $[C_{11}H_{10}N_3OS]^+$, 220 (50) $[C_{10}H_{10}N_3OS]^+$, 118 (35) $[C_3H_4NS_2]^+$, 91 (45) $[C_6H_5N]^+$, 77 (25) $[C_6H_5]^+$, 43 (100) $[C_2H_3O]^+$. Found, %: C 57.01; H 4.32; N 15.87; S 14.79. $C_{21}H_{21}N_5O_2S_2$. Calculated, %: C 57.38; H 4.82; N 15.93; S 14.59.

2-[5-Acetyl-7-(4-methoxyphenyl)-4-thia-1,6,7-triaza-5-heptenylidene]-1,3,4-thiadiazoline (Vb). Yield 50%, mp 101–102°C. ^{1}H NMR spectrum, δ, ppm: 2.36 C [6H, $CH_3C(O)$], 6.77–7.69 m (8H, C_6H_4), 3.75 s (6H, CH_3O), 3.28 t (2H, NCH_2), 3.11 t (2H, SCH_2), 10.00 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 154.59 (C^2), 145.47 (C^5), 136.22 (C^S), 59.27 (NCH_2), 33.19 (SCH_2), 192.34, 188.79 [$CH_3\underline{C}(O)$], 24.39, 24.92 [$\underline{C}H_3C(O)$], 113.79, 114.28, 115.67, 124.43, 131.51, 131.63, 154.93, 157.85 (C_6H_4). Mass spectrum, *m/z* (I_{rel}, %): 499 (35) $[M]^+$, 262 (30) $[C_{10}H_{15}N_3O_2S]^+$, 250 (70) $[C_{11}H_{15}N_2O_2S]^+$, 118 (5) $[C_3H_4NS_2]^+$, 122 (60) $[C_7H_7ON]^+$, 107 (20) $[C_7H_7O]^+$, 43 (60) $[C_2H_3O]^+$. Found, %: C 54.97; H 5.35; N 14.07; S 13.14. $C_{23}H_{25}N_5O_4S_2$. Calculated, %: C 55.29; H 5.04; N 14.02; S 12.84.

2-[5-Acetyl-7-(4-bromophenyl)-4-thia-1,6,7-triaza-5-heptenylidene]-1,3,4-thiadiazoline (Vi). Yield 71%, mp 169–170°C. ^{1}H NMR spectrum, δ, ppm: 2.17 s, 2.39 s [6H, $CH_3C(O)$], 7.15–7.82 m (8H, C_6H_4), 3.37 t (2H, NCH_2), 3.20 t (2H, SCH_2), 10.19 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 154.04 (C^2), 141.80 (C^5), 137.85 (C^S), 59.33 (NCH_2), 33.40 (SCH_2), 191.96, 188.13 [$CH_3\underline{C}(O)$], 24.27, 24.86 [$\underline{C}H_3C(O)$], 113.71, 116.20, 118.80, 123.53, 131.26, 131.35, 134.05, 146.52 (C_6H_4). Mass spectrum, *m/z* (I_{rel}, %): 597 (20) $[M]^+$, 300 (30) $[C_{10}H_9BrN_3OS]^+$, 196 (20) $[C_7H_4BrN_2]^+$, 118 (5) $[C_3H_4NS_2]^+$, 171 (35) $[C_6H_4BrN]^+$, 156 (70) $[C_6H_4Br]^+$, 43 (100) $[C_2H_3O]^+$. Found, %: C 42.35; H 3.23; N 11.37; S 11.00. $C_{21}H_{19}BrN_5O_2S_2$. Calculated, %: C 42.23; H 3.21; N 11.72; S 10.74.

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