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Heterocyclic Thiones and Their Analogs in 1,3-Dipolar Cycloaddition: VII.* Reaction of 4-Methyl-1,3-thiazole-2(3*H*)-thiones with Nitrile Imines

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Abstract—Reactions of 4-methyl-1,3-thiazole-2(3*H*)-thiones with various C,N-disubstituted nitrile imines occurred by the common [3+2]-cycloaddition scheme leading to the formation in general of stable spiro compounds. In reactions of *o*-nitrophenylnitrile imines acyclic compounds were the main products.

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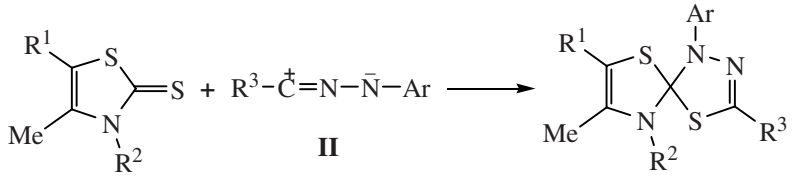
Reactions of versatile cyclic thiocarbonyl compounds with nitrile imines resulted in substituted thiadiazoles of spiro structure [2–4]. The decomposition and further transformations of spiro compounds are known for nitrile imines addition at the exocyclic C=S bond in the 1,3,4-oxathiadiazole-2(3*H*)-thiones and benzothiazole-2-thione [5–9].

1,3-Dipolar cycloaddition of nitrile imines to 1,3-thiazole-2(3*H*)-thiones was not studied before. We recently reported on reactions of 4-methyl-1,3-thiazole-2(3*H*)-thiones with some nitrile imines [10]. Here we consider in detail the reactions of these compounds with various C,N-disubstituted nitrile imines generated *in situ* by treating with triethylamine corresponding hydrazonoyl chlorides. The reactions occurred by the common [3+2]-cycloaddition scheme leading to the formation in the majority of cases of stable spiro compounds **III**.

Compounds obtained are solid crystalline substances. In the ^{1}H NMR spectra of compounds **IIIa–IIIr** appear signals characteristic of substituents at the carbon and nitrogen atoms of nitrile imine, and also the signals of the substituents of the 1,3-thiazoline ring.

In the ^{13}C NMR spectra of compounds **IIIa–IIIr** the signals of spiro carbon atoms linked to four hetero atoms are observed at δ 109–118 ppm. In the region δ 144–147 ppm signals appeared belonging to the carbon in the position *2* of thiadiazole ring, and C^7 and C^8 atoms of the thiazole ring give rise to signals in the region δ 113–117 and 135–141 ppm respectively. The other signals in the ^{13}C NMR spectra are also consistent with

Scheme 1.



I **IIIa – IIIn**

R^1 = MeOC(O) (**a, d, f,** g), EtOC(O) (**b, c, l–r**), Ac (**e, h–j**); R^2 = Me (**a, b**), Bn (**d, e**), Ph (**f–r**); R^3= Ac (**c, d, f, i, n, o**), R^3 = MeOC(O) (**b, e, h, l, m**), EtOC(O) (**a, g, j, k, p, q, r**); Ar = C_6H_4Br-*p* (**a, e**), C_6H_4Me-*p* (**b, d, j, l, q**), $C_6H_4NO_2$-*p* (**c, f**), C_6H_4Cl-*p* (**g**), Ph (**h, i, m, n, p**), C_6H_4OMe-*p* (**k**), C_6H_4Me-*o* (**o**), C_6H_4Cl-*o* (**r**).

*For Communication VI, see [1].

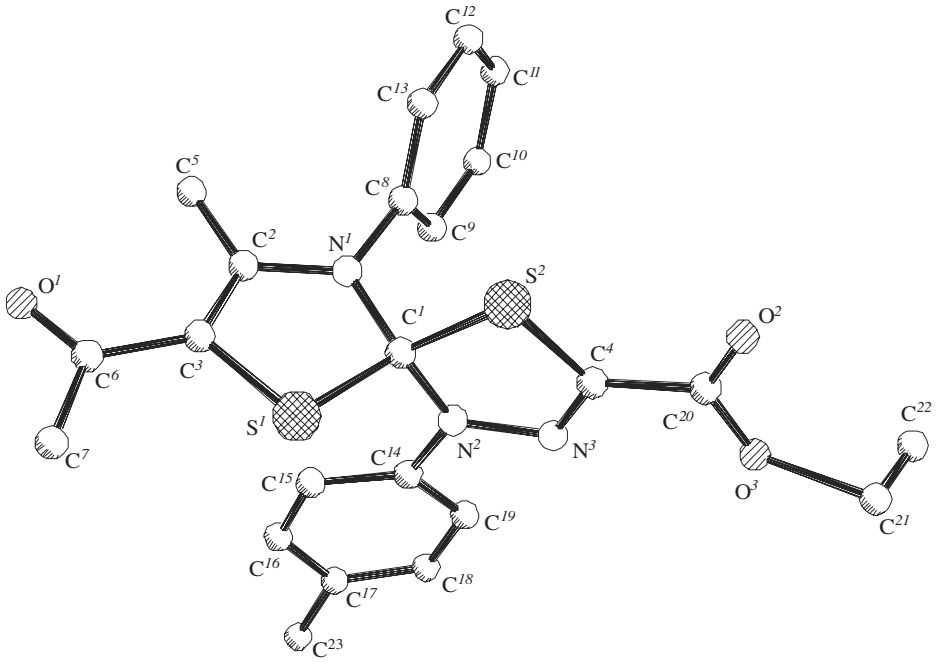


Fig. 1. Structure of the molecule of 7-acetyl-8-methyl-1-(4-methylphenyl)-9-phenyl-3-ethoxycarbonyl-4,6-dithia-1,2,9-triazaspiro[4.4]nona-2,7-diene (**IIIj**) according to X-ray diffraction study.

the assumed structure of compounds obtained. The formation of substituted 4,6-dithia-1,2,9-triazaspiro-[4.4]nona-2,7-dienes **IIIa–IIIr** was also confirmed by their mass spectra. The mass spectra of these compounds contained the peaks of the corresponding molecular ions. The main fragmentation direction of the molecular ions was a recyclic decomposition of the thiadiazole ring with ejection of the nitrile imine ion. Further fragmentation was complicated.

The structure of spiro compounds obtained was confirmed by X-ray diffraction study of crystals of 7-acetyl-8-methyl-1-(4-methylphenyl)-9-phenyl-3-ethoxycarbonyl-4,6-dithia-1,2,9-triazaspiro[4.4]nona-2,7-diene (**III**j) (Fig. 1, Table 1) (everywhere in describing the results of X-ray diffraction analysis the numbering of atoms is the same as on the figure). The X-ray diffraction analysis showed that the thiazole ($S^1C^1N^1C^2C^3$) and thiadiazole ($S^2C^4N^3N^2C^1$) rings are planar, the maximum deviations of atoms from the planes $S^1C^1N^1C^2C^3$ and $S^2C^4N^3N^2C^1$ amount to 0.0344 and 0.0048 Å respectively. The angle between these planes is 86.2 deg. A conjugation of the acetyl group with the thiazole ring is possible in the molecule for they are located virtually in the same plane,the angle between these planes is 2.1 deg.

The substitutents in the benzene ring of nitrile imine do not affect as a rule the structure of the reaction products, but when a benzene ring attached to nitrile

Table 1. Bond lengths *d* (Å) and bond angles ω (deg) in the molecule of 7-acetyl-8-methyl-1-(4-methylphenyl)-9-phenyl-3-ethoxycarbonyl-4,6-dithia-1,2,9-triazaspiro[4.4]nona-2,7-diene (**IIIj**)

Bond	*d*	Angle	ω
S^1–C^3	1.782(5)	$N^3N^2C^{14}$	116.2(3)
S^1–C^1	1.843(4)	$N^3N^2C^1$	118.4(3)
S^2–C^4	1.721(5)	$C^{14}N^2C^1$	125.2(3)
S^2–C^1	1.842(4)	$C^4N^3N^2$	111.7(3)
O^1–C^6	1.230(6)	$N^2C^1N^1$	112.4(3)
O^2–C^{20}	1.194(6)	$N^2C^1S^2$	102.4(3)
O^3–C^{20}	1.306(7)	$N^1C^1S^2$	114.5(3)
O^3–C^{21}	1.683(11)	$N^2C^1S^1$	116.1(3)
N^1–C^2	1.388(5)	$N^1C^1S^1$	103.8(3)
N^1–C^8	1.442(5)	$S^2C^1S^1$	107.9(2)
N^1-C^1	1.459(5)	$C^3C^2N^1$	114.4(4)
N^2-N^3	1.362(5)	$C^3C^2C^5$	127.3(4)
N^2–C^{14}	1.433(5)	$N^1C^2C^5$	118.3(4)
N^2–C^1	1.455(5)	$C^2C^3C^6$	128.5(5)
N^3–C^4	1.282(5)	$C^2C^3S^1$	111.9(3)
C^2–C^3	1.341(6)	$C^6C^3S^1$	119.5(4)
C^2–C^5	1.496(6)	$N^3C^4C^{20}$	123.3(5)
C^3–C^6	1.457(7)	$N^3C^4S^2$	117.0(3)
C^4–C^{20}	1.489(6)	$C^{20}C^4S^2$	119.6(4)
C^6–C^7	1.476(8)	$O^1C^6C^3$	121.7(5)
C^{21}–C^{22}	1.187(12)	$O^1C^6C^7$	119.8(6)

Table 1. (Contd.).

Angle	ω	Angle	ω
$C^3S^1C^1$	92.1(2)	$C^{15}C^{14}N^2$	123.0(4)
$C^4S^2C^1$	90.4(2)	$C^{19}C^{14}N^2$	118.8(4)
$C^{20}O^3C^{21}$	119.8(5)	$O^2C^{20}O^3$	126.4(5)
$C^2N^1C^8$	122.9(3)	$O^2C^{20}C^4$	119.7(6)
$C^2N^1C^1$	117.3(3)	$O^3C^{20}C^4$	113.8(5)
$C^8N^1C^1$	119.7(3)	$C^{22}C^{21}O^3$	93.0(9)

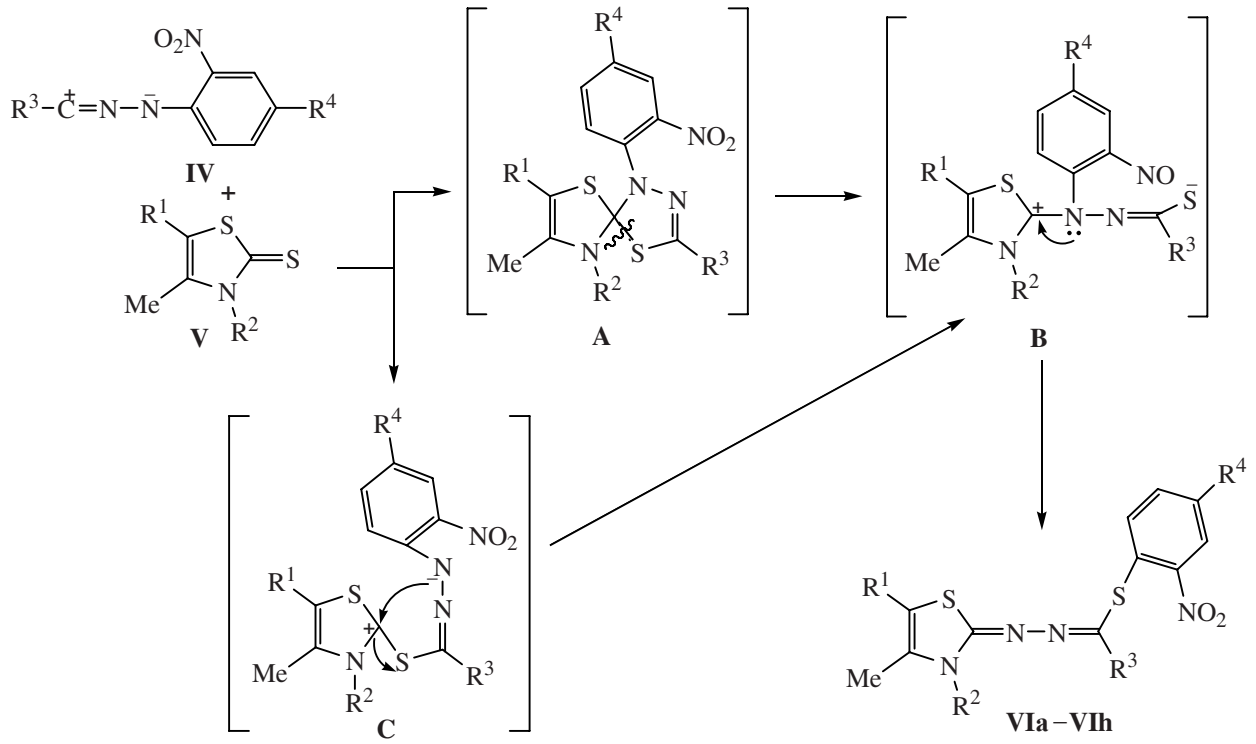
imine nitrogen contains a nitro group in the *ortho* position, the reaction takes an uncommon route providing acyclic compounds **VI** as main products. Usually the *ortho*-nitro substituted nitrile imines react with the exocyclic C=S bond giving stable spiro compounds [11]. It is known from the literature that in some events the *ortho*-substituents in the benzene ring of the nitrile imine hamper the cycloaddition to the double bond. For instance, in the reaction of benzothiazole-2(3*H*)-thione with C-ethoxycarbonyl-*N*-arylnitrile imines with a *ortho*-substituent in the benzene ring products of nucleophilic substitution of chlorine in the hydrazonoyl chloride of the thiol form of initial reagent were obtained [8].

We presume that the reaction can take two routes.

In the first case the arising spiro compound **A** proves to be unstable and suffers further transformations. Evidently the decomposition starts by the rupture of the C–S bond in the thiadiazole ring; as a result forms a bipolar ion **B**. The stabilization of the bipolar ion occurs by a migration of *ortho*-nitrophenyl moiety to the sulfur atom.

The second route begins with an electrophilic attack on the sulfur atom leading to a bipolar ion **C**, then the negatively charged nitrogen attacks the positively charged carbon with a simultaneous cleavage of the C–S bond and the formation of bipolar ion **B**. In the third stage a nucleophilic attack occurs on the most electrophilic atom of the aromatic ring. The rupture of the C–N bond is facilitated by the positive charge on the contiguous carbon atom.

The crucial importance for the change in the reaction route is the presence of a nitro group just in the *ortho*-position. The presence of other substituents, even donor ones, in the *ortho*-nitro substituted benzene ring of nitrile imine does not affect the reaction direction. At the *para*-position of the nitro group the C–S bond does not suffer



R^1 = Ac (**a, d, e**), EtOC(O) (**b, c, g, h**), MeOC(O) (f); R^2 = Me (**a–c**), Ph (**d–h**); R^3 = Me (**b**), Ac (**g**), MeOC(O) (**c, d**), EtOC(O) (**a, e, f, h**); R^4 = OMe (**a**), NO_2 (**b**), H (**c–h**).

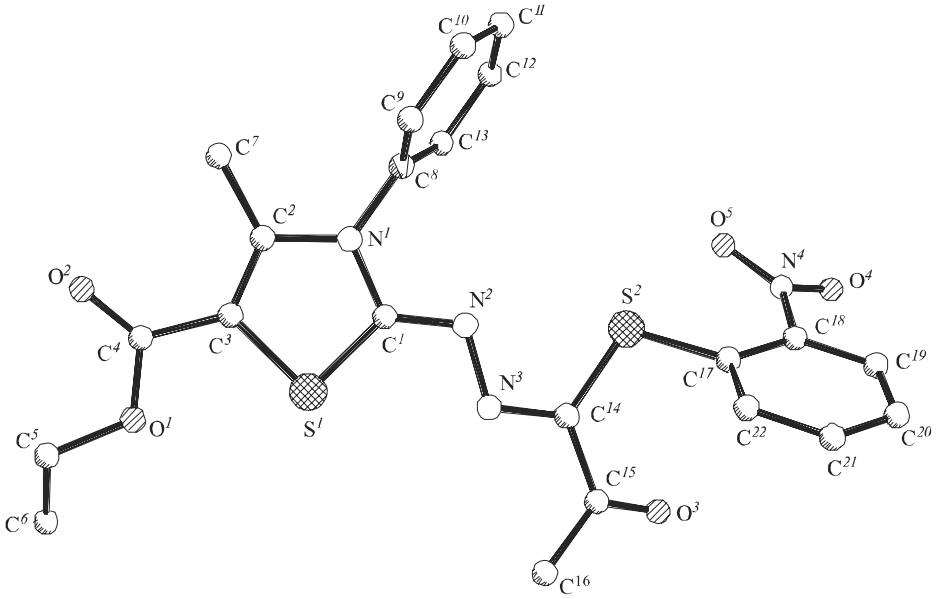


Fig. 2. Structure of the of 1-[acetyl(2-nitrophenylsulfanyl)methylene]-2-[4-methyl-3-phenyl-5-ethoxycarbonyl-1,3-thiazole-2(3*H*)-ylidene]hydrazine (**VIg**) according to X-ray diffraction analysis.

rupture, and a stable spiro compound is obtained. It is presumable that the field effect of the nitro group causes the loosening of bonds at the spiro center, and the cleavage of the C–S bond in the thiadiazole ring favors just the migration of the *ortho*-nitro substituted ring but not the methyl or phenyl group.

The structure of products was established from ^{1}H and ^{13}C NMR and mass spectra and was confirmed by X-ray diffraction analysis. ^{1}H NMR spectra of isolated compounds **VIa–VIh** are in agreement with the assumed structures. In the ^{13}C NMR spectra of these compounds lacked the signal characteristic of the spiro carbon of 3,4,7,8,9-substituted-4,6-dithia-1,2,9-triazaspiro[4.4]-nona-2,7-dienes, but appeared a signal in the region 170–172 ppm from the carbon in the acyclic chain attached to sulfur and nitrogen. The other signals are also consistent with the assumed structure. In the mass spectra of compounds **VId–VIh** the peaks of their molecular ions appeared; subsequent fragmentaion of the molecular ions occurred with the rupture of the C–S bond and ejection of the thiophenyl fragment. Further fragmentation was complicated like that with compounds **IIIa–IIIr**.

The structure of hydrazines obtained was confirmed by X-ray diffraction analysis on crystals of 1-[acetyl(2-nitrophenylsulfanyl)methylene]-2-[4-methyl-3-phenyl-5-ethoxycarbonyl-1,3-thiazol-2(3*H*)-ylidene]hydrazine (**VIg**) (Fig. 2, Table 2).

The X-ray diffraction analysis showed that the thiazole ring is planar (the maximum deviation of atoms from the plane was 0.0122 Å). It is presumable that the ethoxycarbonyl group is involved into the conjugation with the thiazole ring, for the angle between their planes is 7.1 deg, and the conjugtion of phenyl and thiazole rings is lacking since the angle between their planes is 76.9 deg. A conjugation might also exist between the thiazole ring and the thiohydrazine chain because the molecule is virtually planar (maximum deviation of atoms from the plane of 2-thiahydrazothiazole is 0.0122 Å).

EXPERIMENTAL

^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were registered on a spectrometer Bruker AM-500 from 1–5% solutions of compounds in DMSO-d_6 or $CDCl_3$. Mass spectra were recorded on a Kratos MS-890 instrument, vaporizer temperature 120°C, ion source temperature 200°C, ionizing energy 70 eV. Reaction progress was monitored by TLC on Silufol UV-254 plates, development under UV irradiation.

X-ray diffraction study of crystals of spiro compound **IIIj** was carried out on an automatic diffractometer CAD-4 (Mo*K*-radiation, β-filter, θ/2θ-scanning, $2.28 \le \theta \le 24.97$ deg). Crystals orthorhombic. $C_{23}H_{23}N_3O_3S_2$. *a* 16.006(3) Å, α 90 deg, *b* 7.869(2) Å, β 90 deg, *c* 17.852(4) Å, γ 90 deg, *V* 2248.5(9) Å^3; space group Pna2(1), *Z* 4, d_{calc} 1.394 g/cm^3. The structure was solved

Table 2. Bond lengths *d* (Å) and bond angles ω (deg) in the molecule of 1-[acetyl(2-nitrophenylsulfanyl)methylene]-2-[4-methyl-3-phenyl-5-ethoxycarbonyl-1,3-thiazole-2(3*H*)-ylidene]hydrazine (**VIg**)

Bond	*d*	Angle	ω
S^1–C^1	1.738(2)	$O^5N^4O^4$	123.1(3)
S^1–C^3	1.761(2)	$O^5N^4C^{18}$	119.0(2)
S^2–C^{17}	1.758(2)	$O^4N^4C^{18}$	117.8(3)
S^2–C^{14}	1.771(2)	$N^2C^1N^1$	120.10(17)
O^1–C^4	1.333(3)	$N^2C^1S^1$	129.51(15)
O^1–C^5	1.460(3)	$N^1C^1S^1$	110.38(13)
O^2–C^4	1.206(2)	$C^3C^2N^1$	112.31(16)
O^3–C^{15}	1.208(2)	$C^3C^2C^7$	129.08(18)
O^4–N^4	1.235(3)	$N^1C^2C^7$	118.60(18)
O^5–N^4	1.217(3)	$C^2C^3C^4$	127.04(18)
N^1–C^1	1.372(2)	$C^2C^3S^1$	112.26(14)
N^1–C^2	1.393(2)	$C^4C^3S^1$	120.56(15)
N^1–C^8	1.445(2)	$O^2C^4O^1$	124.60(18)
N^2–C^1	1.298(2)	$O^2C^4C^3$	125.24(19)
N^2–N^3	1.379(2)	$O^1C^4C^3$	110.14(17)
N^3–C^{14}	1.290(2)	$O^1C^5C^6$	108.7(2)
N^4–C^{18}	1.459(4)	$C^9C^8C^{13}$	121.2(2)
C^2–C^3	1.343(3)	$C^9C^8N^1$	119.80(18)
C^2–C^7	1.491(3)	$C^{13}C^8N^1$	119.0(2)
C^3–C^4	1.471(3)	$N^3C^{14}C^{15}$	117.06(17)
C^5–C^6	1.472(4)	$N^3C^{14}S^2$	119.53(15)
C^{14}–C^{15}	1.502(3)	$C^{15}C^{14}S^2$	122.40(14)
C^{15}–C^{16}	1.497(3)	$O^3C^{15}C^{16}$	122.2(2)
Angle	ω	$O^3C^{15}C^{14}$	120.81(19)
$C^1S^1C^3$	90.19(10)	$C^{16}C^{15}C^{14}$	117.01(19)
$C^{17}S^2C^{14}$	102.56(10)	$C^{22}C^{17}C^{18}$	116.8(2)
$C^4O^1C^5$	117.65(18)	$C^{22}C^{17}S^2$	120.07(17)
$C^1N^1C^2$	114.77(16)	$C^{18}C^{17}S^2$	123.11(19)
$C^1N^1C^8$	120.37(15)	$C^{19}C^{18}C^{17}$	121.6(3)
$C^2N^1C^8$	124.81(15)	$C^{19}C^{18}N^4$	117.5(3)
$C^1N^2N^3$	111.96(16)	$C^{17}C^{18}N^4$	120.8(2)
$C^{14}N^3N^2$	113.03(16)		

by the direct method [2343 reflections with $I > 2\sigma(I)$] in a full-matrix approximation, anisotropic for atoms O, N, C, S and isotropic for hydrogen, till R 0.0344, R_W 0.08 (no correction for extinction was introduced).

X-ray diffraction study of crystals of substituted hydrazine **VIg** was carried out on an automatic diffractometer CAD-4 (MoK-radiation, β-filter, θ/2θ-scanning, $1.73 \le \theta \le 24.97$ deg). Crystals triclinic. $C_{22}H_{20}N_4O_5S_2$. a 9.102(2) Å, α 65.98(3) deg., b 10.945(2) Å, β 88.92(3) deg, c 12.914(3) Å, γ 76.13(3) deg, V 1136.3(4) Å^3; space group P-1, Z 2, d_{calc} 1.416 g/cm^3. The structure was solved by the direct method [2940 reflections with $I > 2\sigma(I)$] in a full-matrix approximation, anisotropic for atoms O, N, C, S and isotropic for hydrogen, till R 0.0327, R_W 0.0876 (no correction for extinction was introduced). The crystallographic coordinates of nonhydrogen and hydro-gen atoms and their equivalent temperature factors are available from the authors.

Initial 1,3-thiazole-2-thiones were synthesized by a reaction of ammonium salts of N-phenyl-, N-benzyl, and N-methyldithiocarbamic acids with methyl and ethyl α-chloroacetoacetates or with 3-chloroacetylacetone [12]. Nitrile imines were generated in situ by treating with triethylamine appropriate hydrazonoyl chlorides **II** and **IV** [13].

Reaction of 4-methyl-1,3-thiazole-2-thione with hydrazonoyl chlorides. To a mixture of 4 mmol of 1,3-thiazole-2-thione (**I**) or **V** and 4 mmol of an appropriate hydrazonoyl chloride **II** or **IV** in 15–20 ml of dichloromethane was added 20 ml of 2-propanol and 1 ml (7 mmol) of triethylamine. The reaction mixture was left overnight at room temperature. Then the solution was concentrated, the separated precipitate was filtered off, washed with 50% 2-propanol, and recrystallized from acetone or acetonitrile.

1-(4-Bromophenyl)-8,9-dimethyl-7-methoxycarbonyl-3-ethoxycarbonyl-4,6-dithia-1,2,9-triazaspiro[4.4]nona-2,7-diene (IIIa). Yield 74%, mp 144–146°C (from acetone). ^{1}H NMR spectrum, δ, ppm: 1.36 t [3H, C$\underline{H}_3$CH$_2$OC(O)], 2.37 s (3H, CH$_3$), 2.87 s (3H, CH$_3$N), 3.66 s [3H, CH$_3$OC(O)], 4.32 q [2H, CH$_3$C$\underline{H}_2$OC(O)], 7.15–7.46 m (4H$_{arom}$). ^{13}C NMR spectrum, δ, ppm: 13.00 [$\underline{C}$H$_3$CH$_2$OC(O)], 13.91 (CH$_3$), 29.71 (CH$_3$N), 51.04 [$\underline{C}$H$_3$OC(O)], 61.99 [CH$_3\underline{C}$H$_2$OC(O)], 116.63 (C^5), 117.31 (C^7), 139.05 (C^8), 146.93 (C^2), 159.15 [CH$_3$O$\underline{C}$(O)], 162.44 [CH$_3$CH$_2$O$\underline{C}$(O)], 120.28, 131.75, 134.11 (Ar). Mass spectrum, m/z (I_{rel}, %): 472 (10) [M]$^+$, 203 (100) [$C_7H_9NO_2S_2$]$^+$. Found, %: C 43.51; H 4.01; N 8.73. $C_{17}H_{18}BrN_3O_4S_2$. Calculated, %: C 43.23; H 3.84; N 8.90. M 472.38.

8,9-Dimethyl-1-(4-methylphenyl)-3-methoxycarbonyl-7-ethoxycarbonyl-4,6-dithia-1,2,9-triazaspiro[4.4]nona-2,7-diene (IIIb). Yield 80%, mp 115–117°C (from a mixture acetone–acetonitrile).^{1}H NMR spectrum, δ, ppm: 1.24 t [3H, C$\underline{H}_3$CH$_2$OC(O)], 2.31 s

(3H, CH_3), 2.34 s (3H, $C_6H_4C\underline{H}_3$-*p*), 2.87 s (3H, CH_3N), 3.85 C [3H, $CH_3OC(O)$], 4.11 q [2H, $CH_3C\underline{H}_2OC(O)$], 7.05–7.25 m ($4H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 12.89 [$\underline{C}H_3CH_2OC(O)$], 13.87 ($CH_3$), 20.26 ($C_6H_4\underline{C}H_3$-*p*), 29.35 ($CH_3N$), 52.42 [$\underline{C}H_3OC(O)$], 59.76 [$CH_3\underline{C}H_2OC(O)$], 117.58 ($C^5$), 118.70 ($C^7$), 137.25 ($C^8$), 145.29 ($C^2$), 160.24 [$CH_3O\underline{C}(O)$], 162.78 [$CH_3CH_2O\underline{C}(O)$], 129.11, 132.16, 133.86 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 407 (25) $[M]^+$, 217 (30) $[C_8H_{11}NO_2S_2]^+$. Found, %: C 53.13; H 5.00; N 10.25. $C_{18}H_{21}N_3O_4S_2$. Calculated, %: C 53.05; H 5.19; N 10.31. *M* 407.51.

3-Acetyl-8,9-dimethyl-1-(4-nitrophenyl)-7-ethoxycarbonyl-4,6-dithia-1,2,9-triazaspiro[4.4]-nona-2,7-diene (IIIc). Yield 93%, mp 160–162°C (from acetonitrile). ^1H NMR spectrum, δ, ppm: 1.26 t [3H, $C\underline{H}_3CH_2OC(O)$], 2.37 s (3H, CH_3), 2.54 s [3H, $CH_3C(O)$], 2.60 s (3H, CH_3N), 4.28 q [2H, $CH_3C\underline{H}_2OC(O)$], 7.35–8.21 m ($4H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 12.89 [$\underline{C}H_3CH_2OC(O)$], 13.85 ($CH_3$), 24.80 [$\underline{C}H_3C(O)$], 29.29 ($CH_3N$), 69.14 [$CH_3\underline{C}H_2OC(O)$], 116.42 ($C^5$), 116.62 ($C^7$), 145.07 ($C^8$), 145.48 ($C^2$), 162.45 [$CH_3CH_2O\underline{C}(O)$], 190.73 [$CH_3\underline{C}(O)$], 124.53, 142.70 144.58 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 422 (15) $[M]^+$, 217 (100) $[C_8H_{11}NO_2S_2]^+$. Found, %: C 48.56; H 4.31; N 12.97. $C_{17}H_{18}N_4O_5S_2$. Calculated, %: C 48.33; H 4.29; N 13.26. *M* 422.48.

3-Acetyl-9-benzyl-8-methyl-1-(4-methylphenyl)-7-methoxycarbonyl-4,6-dithia-1,2,9-triazaspiro-[4.4]nona-2,7-diene (IIId). Yield 83%, mp 138–140°C (from acetonitrile). ^1H NMR spectrum, δ, ppm: 2.13 s (3H, CH_3), 2.35 s [3H, $CH_3C(O)$], 2.50 s (3H, $C_6H_4C\underline{H}_3$-*p*), 3.64 s [3H, $CH_3OC(O)$], 4.58 s (2H, $C_6H_5C\underline{H}_2N$), 7.15–7.31 m ($9H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 13.48 (CH_3), 20.38 ($C_6H_4\underline{C}H_3$-*p*), 24.80 [$\underline{C}H_3C(O)$], 47.13 ($C_6H_5\underline{C}H_2N$), 51.15 [$\underline{C}H_3OC(O)$], 116.18 (C^5), 120.61 (C^7), 141.36 (C^8), 147.29 (C^2), 162.48 [$CH_3O\underline{C}(O)$], 190.87 [$CH_3\underline{C}(O)$], 126.13, 127.11, 128.42, 129.44, 134.94, 136.51, 137.19 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 453 (5) $[M]^+$, 279 (25) $[C_{13}H_{13}NO_2S_2]^+$. Found, %: C 61.35; H 5.95; N 8.91. $C_{23}H_{23}N_3O_3S_2$. Calculated, %: C 60.90; H 5.11; N 9.26. *M* 453.59.

7-Acetyl-9-benzyl-1-(4-bromophenyl)-8-methyl-3-methoxycarbonyl-4,6-dithia-1,2,9-triazaspiro-[4.4]nona-2,7-diene (IIIe). Yield 98%, mp 114–116°C (from acetonitrile). ^1H NMR spectrum, δ, ppm: 2.18 s [3H, $CH_3C(O)$], 2.20 s (3H, CH_3), 3.82 s [3H, $CH_3OC(O)$], 4.59 s (2H, $C_6H_5C\underline{H}_2N$), 7.16–7.46 m ($9H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 14.51 (CH_3), 29.57 [$\underline{C}H_3C(O)$], 47.40 ($C_6H_5\underline{C}H_2N$), 52.86 [$\underline{C}H_3OC(O)$], 108.50 (C^5), 115.51 (C^7), 138.92 (C^8), 145.60 (C^2), 159.56 [$CH_3O\underline{C}(O)$], 188.26 [$CH_3\underline{C}(O)$], 117.08, 121.26, 126.22, 127.16, 128.39, 131.74, 133.51, 136.11 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 518 (20) $[M]^+$, 263 (30) $[C_{13}H_{13}NOS_2]^+$. Found, %: C 50.73; H 4.11; N 8.02. $C_{22}H_{20}BrN_3O_3S_2$. Calculated, %: C 50.97; H 3.89; N 8.10. *M* 518.46.

3-Acetyl-8-methyl-7-methoxycarbonyl-1-(4-nitrophenyl)-9-phenyl-4,6-dithia-1,2,9-triazaspiro[4.4]nona-2,7-diene (IIIf). Yield 78%, mp 168–170°C (from acetonitrile). ^1H NMR spectrum, δ, ppm: 2.05 s (3H, CH_3), 2.29 s [3H, $CH_3C(O)$], 3.73 s [3H, $CH_3OC(O)$], 6.65–8.33 m ($9H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 14.31 (CH_3), 24.38 [$\underline{C}H_3C(O)$], 51.22 [$\underline{C}H_3OC(O)$], 114.35 (C^5), 117.99 (C^7), 145.67 (C^8), 146.93 (C^2), 163.01 [$CH_3O\underline{C}(O)$], 190.73 [$CH_3\underline{C}(O)$], 125.26, 129.70, 130.02, 135.74, 143.53, 145.14 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 471 (100) $[M]^+$, 266 (30) $[C_{12}H_{12}NO_2S_2]^+$. Found, %: C 53.43; H 4.03; N 11.70. $C_{21}H_{18}N_4O_5S_2$. Calculated, %: C 53.61; H 3.86; N 11.91. *M* 470.53.

8-Methyl-7-methoxycarbonyl-9-phenyl-1-(4-chlorophenyl)-3-ethoxycarbonyl-4,6-dithia-1,2,9-triazaspiro[4.4]nona-2,7-diene (IIIg). Yield 89%, mp 173–174°C (from acetonitrile). ^1H NMR spectrum, δ, ppm: 1.27 t [3H, $C\underline{H}_3CH_2OC(O)$], 2.05 sC (3H, CH_3), 3.37 sC [3H, $CH_3OC(O)$], 4.18 q [2H, $CH_3C\underline{H}_2OC(O)$], 7.29–7.41 m ($9H_{arom}$). ^{13}C NMR spectrum, δ, ppm 13.78 [$\underline{C}H_3CH_2OC(O)$], 14.48 ($CH_3$), 51.31 [$\underline{C}H_3OC(O)$], 61.90 [$CH_3\underline{C}H_2OC(O)$], 114.23 ($C^5$), 119.18 ($C^7$), 138.57 ($C^8$), 145.93 ($C^2$), 158.77 [$CH_3O\underline{C}(O)$], 162.48 [$CH_3CH_2O\underline{C}(O)$], 128.18, 128.97, 129.26, 129.52, 130.48, 133.64, 135.10 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 490 (100) $[M]^+$, 265 (40) $[C_{12}H_{11}NO_2S_2]^+$. Found, %: C 54.11; H 3.91; N 8.91. $C_{22}H_{20}ClN_3O_4S_2$. Calculated, %: C 53.93; H 4.11; N 8.58. *M* 490.00.

7-Acetyl-8-methyl-3-methoxycarbonyl-1,9-diphenyl-4,6-dithia-1,2,9-triazaspiro[4.4]nona-2,7-diene (IIIh). Yield 74%, mp 161–163°C (from acetonitrile). ^1H NMR spectrum, δ, ppm: 2.05 s (3H, CH_3), 2.25 s [3H, $CH_3C(O)$], 3.75 s [3H, $CH_3OC(O)$], 7.18–7.45 m ($10H_{arom}$). ^{13}C NMR spectrum, δ, m.d: 15.58 (CH_3), 29.58 [$\underline{C}H_3C(O)$], 52.81 [$\underline{C}H_3OC(O)$], 109.63 (C^5), 113.24 (C^7), 137.74 (C^8), 144.36 (C^2), 159.41 [$CH_3O\underline{C}(O)$], 188.82 [$CH_3\underline{C}(O)$], 117.82, 123.99, 129.16, 129.34, 129.64, 132.51, 135.27 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 425 (30) $[M]^+$, 316 (45) $[C_{15}H_{14}N_3O_3S]^+$, 249 (70) $[C_{12}H_{11}NOS_2]^+$, 250 (15) $[C_{12}H_{12}NOS_2]^+$. Found, %: C 59.47; H 4.44; N 9.79. $C_{21}H_{19}N_3O_3S_2$.

Calculated, %: C 59.28; H 4.50; N 9.87. *M* 425.53.

3,7-Diacetyl-8-methyl-1,9-diphenyl-4,6-dithia-1,2,9-triazaspiro[4.4]nona-2,7-diene (IIIi). Yield 71%, mp 155–157°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 2.05 s (3H, CH_3), 2.24 s, 2.35 s [6H, $CH_3C(O)$], 7.2–7.45 m ($10H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 15.51 (CH_3), 24.55, 29.54 [$\underline{C}H_3C(O)$], 109.50 (C^5), 112.96 (C^7), 141.66 (C^8), 144.29 (C^2), 188.57, 190.17 [$CH_3\underline{C}(O)$], 117.99, 124.15, 129.09, 129.19, 129.50, 131.68, 135.27, 139.65 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 409 (5) $[M]^+$, 250 (15) $[C_{12}H_{12}NOS_2]^+$. Found, %: C 61.88; H 5.02; N 10.24. $C_{21}H_{19}N_3O_2S_2$. Calculated, %: C 61.59; H 4.68; N 10.26. *M* 409.53.

7-Acetyl-8-methyl-1-(4-methylphenyl)-9-phenyl-3-ethoxycarbonyl-4,6-dithia-1,2,9-triazaspiro-[4.4]nona-2,7-diene (IIIj). Yield 75%, mp 170–172°C (from acetone). ^{1}H NMR spectrum, δ, ppm: 1.25 t [3H, $C\underline{H}_3CH_2OC(O)$], 2.05 (3H, $C_6H_4C\underline{H}_3$-*p*), 2.25 s (3H, CH_3), 2.35 s [3H, $C\underline{H}_3C(O)$], 4.20 q [2H, $CH_3C\underline{H}_2OC(O)$], 7.1–7.45 m ($9H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 13.81 [$\underline{C}H_3CH_2OC(O)$], 15.51 ($CH_3$), 20.25 ($C_6H_4\underline{C}H_3$-*p*), 29.54 [$\underline{C}H_3C(O)$], 61.72 [$CH_3\underline{C}H_2OC(O)$], 109.33 ($C^5$), 113.30 ($C^7$), 137.42 ($C^8$), 144.12 ($C^2$), 158.97 [$CH_3CH_2O\underline{C}(O)$], 188.56 [$CH_3\underline{C}(O)$], 117.89, 129.24, 129.50, 132.24, 133.15, 135.35 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 453 (30) $[M]^+$, 249 (30) $[C_{12}H_{11}NOS_2]^+$, 250 (10) $[C_{12}H_{12}NOS_2]^+$, 204 (5) $[C_{11}H_{12}N_2O_2]^+$. Found, %: C 60.57; H 5.11; N 9.51. $C_{23}H_{23}N_3O_3S_2$. Calculated, %: C 60.90; H 5.11; N 9.26. *M* 453.59.

7-Acetyl-8-methyl-1-(4-methoxyphenyl)-9-phenyl-3-ethoxycarbonyl-4,6-dithia-1,2,9-triazaspiro-[4.4]nona-2,7-diene (IIIk). Yield 96%, mp 181–182°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.25 t [3H, $C\underline{H}_3CH_2OC(O)$], 2.05 s (3H, CH_3), 2.25 s [3H, $CH_3C(O)$], 3.82 s (3H, $C_6H_4OC\underline{H}_3$-*p*) 4.17 q [2H, $CH_3C\underline{H}_2OC(O)$], 6.92–7.43 m ($9H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 12.91 [$\underline{C}H_3CH_2OC(O)$], 13.81 ($CH_3$), 29.57 [$\underline{C}H_3C(O)$], 51.14 ($C_6H_4O\underline{C}H_3$), 61.63 [$CH_3\underline{C}H_2OC(O)$], 109.26 ($C^5$), 113.48 ($C^7$), 135.47 ($C^8$), 144.02 ($C^2$), 159.01 [$CH_3CH_2O\underline{C}(O)$], 188.51 [$CH_3\underline{C}(O)$], 114.23, 119.78, 129.23, 129.44, 130.30, 131.70, 133.07, 156.18 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 470 (100) $[M]^+$, 338 (32) $[C_{19}H_{18}N_2O_2S]^+$. Found, %: C 59.01; H 4.93; N 8.85. $C_{23}H_{23}N_3O_4S_2$. Calculated, %: C 58.83; H 4.94; N 8.95. *M* 469.59.

8-Methyl-1-(4-methylphenyl)-3-methoxycarbonyl-9-phenyl-7-ethoxycarbonyl-4,6-dithia-1,2,9-triazaspiro[4.4]nona-2,7-diene (IIIl). Yield 64%, mp 165–167°C (from a mixture 2-PrOH–acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.30 t [3H, $C\underline{H}_3CH_2OC(O)$], 2.05 s (3H, $C\underline{H}_3C_6H_4$), 2.25 s (3H, CH_3), 3.82 s [3H, $CH_3OC(O)$], 4.17 q [2H, $CH_3C\underline{H}_2OC(O)$], 6.92–7.43 m (9H, Ar). ^{13}C NMR spectrum, δ, ppm: 14.15 [$\underline{C}H_3CH_2OC(O)$], 14.48 ($CH_3$), 20.25 ($\underline{C}H_3C_6H_4$), 52.65 [$\underline{C}H_3OC(O)$], 59.96 [$CH_3\underline{C}H_2OC(O)$], 114.34 ($C^5$), 117.81 ($C^7$), 137.42 ($C^8$), 145.55 ($C^2$), 159.45 [$CH_3O\underline{C}(O)$], 162.21 [$CH_3CH_2O\underline{C}(O)$], 129.23, 129.44, 129.54, 131.30, 131.20, 133.20, 135.27 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 469 (40) $[M]^+$, 346 (70) $[C_{16}H_{16}N_3O_4S]^+$, 279 (60) $[C_{13}H_{13}NO_2S_2]^+$, 190 (10) $[C_{10}H_{10}N_2O_2]^+$. Found, %: C 59.20; H 4.60; N 8.94. $C_{23}H_{23}N_3O_4S_2$. Calculated, %: C 58.83; H 4.94; N 8.95. *M* 469.59.

8-Methyl-3-methoxycarbonyl-1,9-diphenyl-7-ethoxycarbonyl-4,6-dithia-1,2,9-triazaspiro[4.4]-nona-2,7-diene (IIIm). Yield 70%, mp 144–145°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.20 t [3H, $C\underline{H}_3CH_2OC(O)$], 2.05 s (3H, CH_3), 3.70 s [3H, $CH_3OC(O)$], 4.15 q [2H, $CH_3C\underline{H}_2OC(O)$], 7.05–7.45 m ($10H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 14.17 [$\underline{C}H_3CH_2OC(O)$], 14.51 ($CH_3$), 52.79 [$\underline{C}H_3OC(O)$], 60.06 [$CH_3\underline{C}H_2OC(O)$], 114.35 ($C^5$), 117.80 ($C^7$), 139.79 ($C^8$), 145.79 ($C^2$), 159.45 [$CH_3O\underline{C}(O)$], 162.26 [$CH_3CH_2O\underline{C}(O)$], 124.01, 129.16, 129.27, 129.51, 130.41, 132.64, 135.22 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 455 (62) $[M]^+$, 346 (74) $[C_{16}H_{16}N_3O_4S]^+$, 279 (100) $[C_{13}H_{13}NO_2S_2]^+$, 280 (20) $[C_{13}H_{14}NO_2S_2]^+$. Found, %: C 57.99; H 4.66; N 9.11. $C_{22}H_{21}N_3O_4S_2$. Calculated, %: C 58.00; H 4.65; N 9.22. *M* 455.56.

3-Acetyl-8-methyl-1,9-diphenyl-7-ethoxycarbonyl-4,6-dithia-1,2,9-triazaspiro[4.4]nona-2,7-diene (IIIn). Yield 90%, mp 136.5–138°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.28 t [3H, $C\underline{H}_3CH_2OC(O)$], 2.05 s (3H, $C_6H_5C\underline{H}_3$), 2.35 s (3H, CH_3), 3.73 s [3H, $CH_3OC(O)$], 4.20 q [2H, $CH_3C\underline{H}_2OC(O)$], 7.10–7.41 m ($9H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 14.17 [$\underline{C}H_3CH_2OC(O)$], 14.53 ($CH_3$), 24.60 [$\underline{C}H_3C(O)$], 60.05 [$CH_3\underline{C}H_2OC(O)$], 113.95 ($C^5$), 118.01 ($C^7$), 141.79 ($C^8$), 145.86 ($C^2$), 162.25 [$CH_3CH_2O\underline{C}(O)$], 190.49 [$CH_3\underline{C}(O)$], 124.26, 129.20, 129.47, 135.20, 139.68 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 279 (32) $[C_{13}H_{13}NO_2S_2]^+$, 280 (5) $[C_{13}H_{14}NO_2S_2]^+$. Found, %: C 60.49; H 4.58; N 9.37. $C_{22}H_{21}N_3O_3S_2$. Calculated, %: C 60.12; H 4.82; N 9.56. *M* 439.56.

3-Acetyl-8-methyl-1-(2-methylphenyl)-9-phenyl-7-ethoxycarbonyl-4,6-dithia-1,2,9-triazaspiro-[4.4]nona-2,7-diene (IIIo). Yield 88%, mp 152–154°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.19 t

[3H, C$\underline{H}_3$CH$_2$OC(O)], 2.08 s (3H, C$_6$H$_5$C$\underline{H}_3$), 2.17 s (3H, CH$_3$), 2.23 s [3H, CH$_3$C(O)], 4.05 q [2H, CH$_3$C$\underline{H}_2$OC(O)], 7.29–7.51 m (9H, Ar). ^{13}C NMR spectrum, δ, m.d: 14.14 [$\underline{C}$H$_3$CH$_2$OC(O)], 14.93 (CH$_3$), 18.85 ($\underline{C}$H$_3$C$_6$H$_4$), 24.51 [$\underline{C}$H$_3$C(O)], 59.83 [CH$_3\underline{C}$H$_2$OC(O)], 113.75 (C^5), 124.91 (C^7), 140.06 (C^8), 145.38 (C^2), 162.06 [CH$_3$CH$_2$O$\underline{C}$(O)], 190.18 [CH$_3\underline{C}$(O)], 126.70, 128.17, 129.02, 129.24, 129.79, 131.64, 136.54, 138.67 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 454 (100) [*M*]$^+$, 280 (75) [C$_{13}$H$_{14}$NO$_2$S$_2$]$^+$. Found, %: C 61.15; H 5.22; N 9.01. C$_{23}$H$_{23}$N$_3$O$_3$S$_2$. Calculated, %: C 60.90; H 5.11; N 9.26. *M* 453.59.

8-Methyl-1,9-diphenyl-3,7-bis(ethoxycarbonyl)-4,6-dithia-1,2,9-triazaspiro[4.4]nona-2,7-diene (IIIp). Yield 53%, mp 134–135°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.25 d.t [6H, C$\underline{H}_3$CH$_2$OC(O)], 2.05 s (3H, CH$_3$), 4.15 d.q [4H, CH$_3$C$\underline{H}_2$OC(O)], 7.10–7.45 m (10H$_{arom}$). ^{13}C NMR spectrum, δ, ppm: 13.80, 14.15 [$\underline{C}$H$_3$CH$_2$OC(O)], 14.48 (CH$_3$), 59.98, 61.81 [CH$_3\underline{C}$H$_2$OC(O)], 114.28 (C^5), 117.78 (C^7), 139.84 (C^8), 145.60 (C^2), 158.95, 162.19 [CH$_3$CH$_2$O$\underline{C}$(O)], 123.90, 129.02, 129.20, 129.43, 130.29, 132.88, 135.27 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 469 (20) [*M*]$^+$, 360 (25) [C$_{17}$H$_{18}$N$_3$O$_4$S]$^+$, 279 (48) [C$_{13}$H$_{13}$NO$_2$S$_2$]$^+$, 278 (30) [C$_{13}$H$_{12}$NO$_2$S$_2$]$^+$. Haθdε-νO, %: C 58.57; H 4.63; N 8.65. C$_{23}$H$_{23}$N$_3$O$_4$S$_2$. Calculated, %: C 58.83; H 4.94; N 8.95. *M* 469.59.

8-Methyl-1-(4-methylphenyl)-9-phenyl-3,7-bis(ethoxycarbonyl)-4,6-dithia-1,2,9-triazaspiro-[4.4]nona-2,7-diene (IIIq). Yield 98%, mp 147–148.5°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.28 d.t [6H, C$\underline{H}_3$CH$_2$OC(O)], 2.03 s (3H, CH$_3$), 2.37 s (3H, C$\underline{H}_3$C$_6$H$_4$), 4.17 d.q [4H, CH$_3$C$\underline{H}_2$OC(O)], 7.20–7.41 m (9H, Ar). ^{13}C NMR spectrum, δ, ppm: 13.81, 14.17 [$\underline{C}$H$_3$CH$_2$OC(O)], 14.51 (CH$_3$), 60.01, 61.83 [CH$_3\underline{C}$H$_2$OC(O)], 114.31 (C^5), 117.88 (C^7), 137.45 (C^8), 145.67 (C^2), 159.05, 162.26 [CH$_3$CH$_2$O$\underline{C}$(O)], 129.24, 129.46, 129.59, 132.40, 133.27, 135.30 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 484 (100) [*M*]$^+$, 280 (10) [C$_{13}$H$_{14}$NO$_2$S$_2$]$^+$, 205 (5) [C$_{11}$H$_{13}$N$_2$O$_2$]$^+$. Found, %: C 60.00; H 5.15; N 8.49. C$_{24}$H$_{25}$N$_3$O$_4$S$_2$. Calculated, %: C 59.61; H 5.21; N 8.69. *M* 483.61.

8-Methyl-1-phenyl-4-(4-chlorophenyl)-3,7-bis(ethoxycarbonyl)-4,6-dithia-1,2,9-triazaspiro-[4.4]nona-2,7-diene (IIIr). Yield 74%, mp 149–150°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.20 d.t [6H, C$\underline{H}_3$CH$_2$OC(O)], 2.07 s (3H, CH$_3$), 4.04 q, 4.14 q [4H, CH$_3$C$\underline{H}_2$OC(O)], 7.41–7.65 m (9H, Ar). ^{13}C NMR spectrum, δ, ppm: 13.74, 13.95 [$\underline{C}$H$_3$CH$_2$OC(O)], 14.92 (CH$_3$), 59.89, 61.74 [CH$_3\underline{C}$H$_2$OC(O)], 115.32 (C^5), 126.81 (C^7), 137.42 (C^8), 144.61 (C^2), 159.55, 162.72 [CH$_3$CH$_2$O$\underline{C}$(O)], 127.71, 128.65, 129.08, 129.44, 130.60, 134.10, 134.38, 136.74 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 504 (50) [*M*]$^+$, 280 (100) [C$_{13}$H$_{14}$NO$_2$S$_2$]$^+$. Found, %: C 54.64; H 4.67; N 8.30. C$_{23}$H$_{22}$ClN$_3$O$_4$S$_2$. Calculated, %: C 54.81; H 4.40; N 8.34. *M* 504.03.

2-[5-Acetyl-3,4-dimethyl-1,3-thiazol-2(3*H*)-ylidene]-1-[4-methoxy-2-nitrophenylsulfanyl-(ethoxycarbonyl)methylene]hydrazine (VIa). Yield 84%, mp 161–161.5°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.10 t [3H, C$\underline{H}_3$CH$_2$OC(O)], 2.32 s (3H, CH$_3$), 2.58 s [3H, CH$_3$C(O)], 3.24 s (3H, CH$_3$N), 3.82 s (3H, OCH$_3$) 4.04 q [2H, CH$_3$C$\underline{H}_2$OC(O)], 6.90–7.50 m (3H$_{arom}$). ^{13}C NMR spectrum, δ, ppm: 13.15 [$\underline{C}$H$_3$CH$_2$OC(O)], 13.64 (CH$_3$), 29.88 [$\underline{C}$H$_3$C(O)], 31.81 (CH$_3$N), 55.78 (OCH$_3$), 61.84 [CH$_3\underline{C}$H$_2$OC(O)], 109.54 (C^5), 145.07 (C^4), 151.01 (C^2), 159.12 [CH$_3$O$\underline{C}$(O)], 161.69 [CH$_3$CH$_2$O$\underline{C}$(O)], 169.87 (N=C–S), 189.10 [CH$_3\underline{C}$(O)], 114.65, 119.31, 120.29, 135.38, 145.41 (Ar). Found, %: C 48.07; H 4.70; N 12.29. C$_{18}$H$_{20}$N$_4$O$_6$S$_2$. Calculated, %: C 47.78; H 4.46; N 12.38. *M* 452.51.

2-[3,4-Dimethyl-5-ethoxycarbonyl-1,3-thiazol-2(3*H*)-ylidene]-1,2,4-dinitrophenylsulfanyl-(methyl)-methylene]hydrazine (VIb). Yield 78%, mp 188–189°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.36 t [3H, C$\underline{H}_3$CH$_2$OC(O)], 2.18 s (3H, CH$_3$) 2.30 s (3H, CH$_3$C=N), 3.25 s (3H, CH$_3$N), 4.22 q [2H, CH$_3$C$\underline{H}_2$OC(O)], 7.31–8.80 m (3H$_{arom}$). ^{13}C NMR spectrum, δ, ppm: 12.56 [$\underline{C}$H$_3$CH$_2$OC(O)], 14.07 (CH$_3$), 23.21 ($\underline{C}$H$_3$C=N), 31.27 (CH$_3$N), 60.66 [CH$_3\underline{C}$H$_2$OC(O)], 103.76 (C^5), 146.09 (C^4), 149.70 (C^2), 161.58 [CH$_3$CH$_2$O$\underline{C}$(O)], 166.90 (N=C–S), 120.02, 125.63, 136.04, 138.54, 146.28, 147.38 (Ar). Found, %: C 43.49; H 4.21; N 15.55. C$_{16}$H$_{17}$N$_5$O$_6$S$_2$. Calculated, %: C 43.73; H 3.90; N 15.94. *M* 439.471.

2-[3,4-Dimethyl-5-ethoxycarbonyl-1,3-thiazol-2(3*H*)-ylidene]-1-[methoxycarbonyl(2-nitrophenyl-sulfanyl)methylene]hydrazine (VIc). Yield 84%, mp 175–176°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.25 t [3H, C$\underline{H}_3$CH$_2$OC(O)], 2.58 s (3H, C$\underline{H}_3$), 3.26 s (3H, C$\underline{H}_3$N), 3.36 s [3H, C$\underline{H}_3$OC(O)], 4.24 q [2H, CH$_3$C$\underline{H}_2$OC(O)], 7.24–8.08 m (4H$_{arom}$). ^{13}C NMR spectrum, δ, ppm: 12.53 [$\underline{C}$H$_3$CH$_2$OC(O)], 14.02 ($\underline{C}$H$_3$), 31.83 ($\underline{C}$H$_3$N), 52.72 [$\underline{C}$H$_3$OC(O)], 60.97 [CH$_3\underline{C}$H$_2$OC(O)], 106.55 (C^5), 146.15 (C^4), 148.51 (C^2), 161.18 [CH$_3$O$\underline{C}$(O)], 162.74 [CH$_3$CH$_2$O$\underline{C}$(O)], 171.91 (N=C–S), 125.01, 126.70, 131.88, 132.40, 132.45, 140.83 (Ar).

Found, %: C 45.87; H 4.43; N 12.46. $C_{17}H_{18}N_4O_6S_2$. Calculated, %: C 46.57; H 4.14; N 12.78. *M* 438.48.

2-[5-Acetyl-4-methyl-3-phenyl-1,3-thiazol-2(3*H*)-ylidene]-1-[methoxycarbonyl(2-nitrophenylsulfanyl)methylene]hydrazine (VId). Yield 96%, mp 187–188°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 2.25 s (3H, CH_3), 2.45 s [3H, $CH_3C(O)$], 3.69 s [3H, $CH_3OC(O)$], 7.12–8.01 m (9H, Ar). ^{13}C NMR spectrum, δ, ppm: 14.39 (CH_3), 29.39 [$\underline{C}H_3C(O)$], 52.41 [$\underline{C}H_3OC(O)$], 117.36 (C^5), 141.44 (C^4), 147.69 (C^2), 162.06 [$CH_3O\underline{C}(O)$], 171.45 (N=C–S), 188.63 [$CH_3\underline{C}(O)$], 125.25, 127.38, 127.70, 129.33, 130.05, 132.11, 132.89, 135.04, 145.01 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 471 (100) $[M]^+$, 316 (35) $[C_{15}H_{14}N_3O_3S]^+$. Found, %: C 53.37; H 3.88; N 11.67. $C_{21}H_{18}N_4O_5S_2$. Calculated, %: C 53.61; H 3.86; N 11.91. *M* 470.53.

2-[5-Acetyl-4-methyl-3-phenyl-1,3-thiazol-2(3*H*)-ylidene]-1-[(2-nitrophenylsulfanyl)ethoxycarbonylmethylene]hydrazine (VIe). Yield 98%, mp 167–167.5°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.10 t [3H, $C\underline{H}_3CH_2OC(O)$], 2.25 s (3H, CH_3), 2.46 s [3H, $CH_3C(O)$], 4.04 q [2H, $CH_3C\underline{H}_2OC(O)$], 7.19–8.01 m (9H, Ar). ^{13}C NMR spectrum, δ, ppm: 13.56 [$\underline{C}H_3CH_2OC(O)$], 14.63 ($CH_3$), 26.58 [$\underline{C}H_3C(O)$], 61.76 [$CH_3\underline{C}H_2OC(O)$], 117.32 ($C^5$), 142.89 ($C^4$), 148.50 ($C^2$), 161.34 [$CH_3CH_2O\underline{C}(O)$], 171.28 (N=C–S), 189.25 [$CH_3\underline{C}(O)$], 125.45, 127.98, 128.32, 129.04, 129.56, 132.97, 133.43, 135.18, 145.51 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 485 (100) $[M]^+$, 330 (10) $[C_{16}H_{16}N_3O_3S]^+$. Found, %: C 54.72; H 4.41; N 11.43. $C_{22}H_{20}N_4O_5S_2$. Calculated, %: C 54.53; H 4.16; N 11.56. *M* 484.56.

2-[4-Methyl-5-methoxycarbonyl-3-phenyl-1,3-thiazol-2(3*H*)-ylidene]-1-[(2-nitrophenylsulfanyl)-ethoxycarbonylmethylene]hydrazine (VIf). Yield 87%, mp 215–216°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.1 t [3H, $C\underline{H}_3CH_2OC(O)$], 2.24 s (3H, CH_3), 3.82 s [3H, $CH_3OC(O)$], 4.04 q [2H, $CH_3C\underline{H}_2OC(O)$], 7.21–8.01 m ($9H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 13.55 [$C\underline{H}_3CH_2OC(O)$], 13.76 ($CH_3$), 52.25 [$\underline{C}H_3OC(O)$], 61.75 [$CH_3\underline{C}H_2OC(O)$], 105.07 ($C^5$), 142.69 ($C^4$), 148.49 ($C^2$), 161.32 [$CH_3CH_2O\underline{C}(O)$, $CH_3O\underline{C}(O)$], 171.59 (N=C–S), 125.43, 127.94, 128.31, 129.09, 129.50, 132.95, 133.43, 135.13, 147.45 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 501 (100) $[M]^+$, 346 (20) $[C_{16}H_{16}N_3O_4S]^+$, 247 (15) $[C_{12}H_{11}N_2O_2S]^+$. Found, %: C 52.58; H 4.11; N 10.97. $C_{22}H_{20}N_4O_6S_2$. Calculated, %: C 52.79; H 4.03; N 11.19. *M* 500.56.

1-[Acetyl(2-nitrophenylsulfanyl)methylene]-2-[4-methyl-3-phenyl-5-ethoxycarbonyl-1,3-thiazol-2(3*H*)-ylidene]hydrazine (VIg). Yield 70%, mp 153–155°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.36 t [3H, $C\underline{H}_3CH_2OC(O)$], 2.23 s (3H, CH_3), 2.52 s [3H, $CH_3C(O)$], 4.31 q [2H, $CH_3C\underline{H}_2OC(O)$], 7.04–7.94 m ($9H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 13.76 [$\underline{C}H_3CH_2OC(O)$], 14.12 ($CH_3$), 26.12 [$\underline{C}H_3C(O)$], 61.17 [$CH_3\underline{C}H_2OC(O)$], 106.25 ($C^5$), 146.51 ($C^4$), 147.45 ($C^2$), 160.81 [$CH_3CH_2O\underline{C}(O)$], 172.38 (N=C–S), 193.79 [$CH_3\underline{C}(O)$], 125.40, 126.84, 127.68, 129.41, 130.65, 131.81, 133.02,134.86, 146.93 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 484 (10) $[M]^+$, 330 (10) $[C_{16}H_{16}N_3O_3S]^+$, 288 (100) $[C_{14}H_{14}N_3O_2S]^+$. Found, %: C 54.99; H 4.41; N 11.58. $C_{22}H_{20}N_4O_5S_2$. Calculated, %: C 54.53; H 4.16; N 11.56. *M* 484.56.

2-[4-Methyl-3-phenyl-5-ethoxycarbonyl-1,3-thiazol-2(3*H*)-ylidene]-1-[(2-nitrophenylsulfanyl)-ethoxycarbonylmethylene]hydrazine (VIh). Yield 92%, mp 163–164°C (from acetonitrile). ^{1}H NMR spectrum, δ, ppm: 1.14, 1.36 d.t [6H, $C\underline{H}_3CH_2OC(O)$], 2.26 s (3H, CH_3), 4.06, 4.28 d.q [4H, $CH_3C\underline{H}_2OC(O)$], 7.18–7.99 m ($9H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 13.56 [$\underline{C}H_3CH_2OC(O)$], 14.05 ($CH_3$), 60.62, 61.29 [$CH_3\underline{C}H_2OC(O)$], 105.80 ($C^5$), 146.45 ($C^4$), 148.14 ($C^2$), 160.54, 161.23 [$CH_3CH_2O\underline{C}(O)$], 171.33 (N=C–S), 125.02, 127.39, 127.64, 129.21, 129.29, 130.06, 132.50, 132.61, 135.07, 142.38 (Ar). Mass spectrum, *m/z* (I_{rel}, %): 515 (100) $[M]^+$, 360 (50) $[C_{17}H_{18}N_3O_4S]^+$, 288 (25) $[C_{14}H_{14}N_3O_2S]^+$. Found, %: C 53.91; H 4.67; N 10.70. $C_{23}H_{22}N_4O_6S_2$. Calculated, %: C 53.69; H 4.31; N 10.89. *M* 514.58.

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