ISSN 1070-4280 Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 2, pp. 261–265. © Pleiades Publishing, Inc. 2006.
Original Russian Text © I.N. Fesun, V.M. Timoshenko, Yu.G. Shermolovich, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, no. 2, pp. 272–276.

Synthesis of 3-Imino and 3-Ylideno Derivatives of 4-Fluoro-5-polyfluoroalkyl-1,2-dithiolenes

I.N. Fesun, V.M. Timoshenko, and Yu.G. Shermolovich

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev, 02094 Ukraine
e-mail: sherm@bpci.kiev.ua

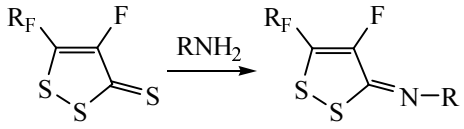
Received November 26, 2004

Abstract—Reactions of 4-fluoro-5-polyfluoroalkyl-1,2-dithiol-3-thiones with hydroxylamine and hydrazines occur with replacement of the thiocarbonyl by imino group affording oximes and hydrazones respectively. *N*-Alkyl- and *N*-aryl-3-imino-1,2-dithiolenes formed in reactions of 3-chlorothio-1,2-dithiolium salts with primary alkyl- or arylamines. 3-Chlorothio-1,2-dithiolium salts react with compounds possessing an active methylene group yielding 3-ylideno derivatives of 1,2-dithiolenes.

DOI: 10.1134/S1070428002120187

We have reported on the synthesis of 4-fluoro-5-polyfluoroalkyl-1,2-dithiol-3-thiones **I** and their cycloaddition [1] and chlorination [2] reactions. Here we describe the reactions of dithiolthiones **I** with compounds containing an amine function, and with compounds possessing a methylene group proceeding through the substitution of the exocyclic sulfur atom.

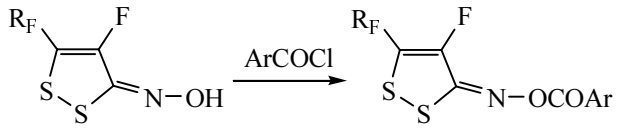
1,2-Dithiol-3-thiones are known to undergo like thioketones the condensation with hydrazines and hydroxylamine [3]. Fluoro-containing dithiolthiones **I** also enter into these reactions furnishing oximes **IIa** and **IIb** and hydrazones **III** and **IV**.



Ia, Ib **IIa, IIb, III, IV**

I, $R_F = CF_3$ (**a**), HCF_2CF_2 (**b**); **II**, R = OH, $R_F = CF_3$ (**a**), HCF_2CF_2 (**b**); **III**, $R = NH_2$, $R_F = HCF_2CF_2$; **IV**, R = NHPh, $R_F = HCF_2CF_2$.

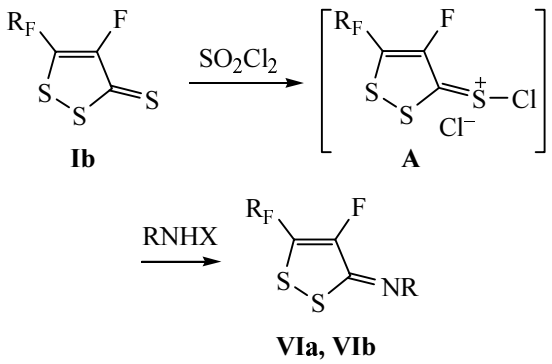
Oximes **IIa** and **IIb** were acylated with aroyl chlorides yielding O-acylated derivatives **Va** and **Vb**.



IIa, IIb **Va, Vb**

Attempting to prepare acyl derivatives of hydrazone **IV** we found that the addition of triethylamine to compound **IV** caused its dehydrofluorination. In the ^{19}F NMR spectrum of the reaction mixture appeared a signal belonging to triethylamine hydrofluoride at –150 ppm and very broad signals from the reaction products thus revealing more complex transformations. When the reaction was carried out in the presence of triethylamine at the molar reagents ratio dithiolthione **Ib** : phenylhydrazine : triethylamine 1:3:5 the signals from the fluorine atoms of the tetrafluoroethyl fragment disappeared. Apparently here the difluoromethylene groups are one after another converted into phenylhydrazone groups like in the process we have previously described for reactions of polyfluoroalkyl sulfones with phenylhydrazine [4]. However we failed to isolate from the reaction mixture and characterize individual products.

It is known that dithiolthiones react wuth primary amines to give 3-imino-1,2-dithiolene and/or their isomers isothiazole-3-thiones [5]. Fluoro-containing dithiolthiones



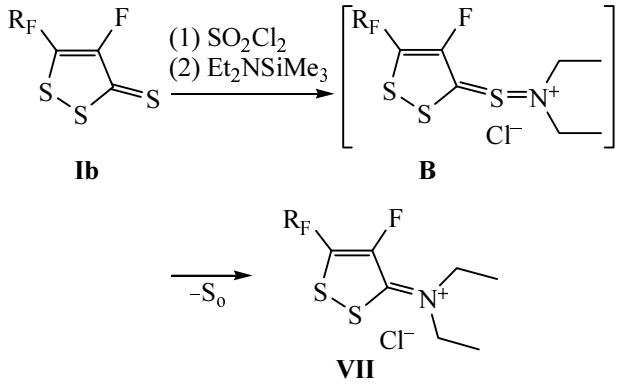
Ib **A**

VIa, VIb

VI, R = *t*-Bu (**a**), *p*-BrC_6H_4 (**b**); $R_F = HCF_2CF_2$; X = H, $SiMe_3$

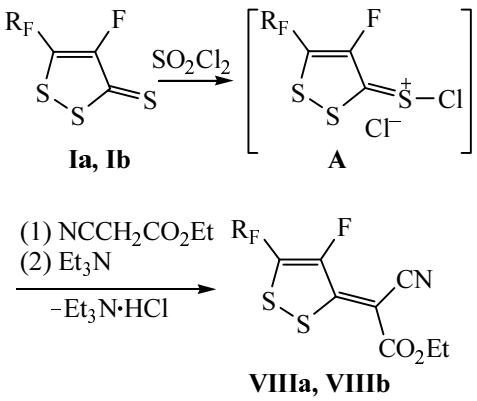
I in reactions with equimolar amounts of primary amines afforded mixtures of products. We found a more selective procedure for preparation of 3-imino derivatives of 1,2-dithiolenes **VIa** and **VIb** consisting in treating with primary alkyl- and arylamines or their monosilylated derivatives 3-chlorothio-1,2-dithiolium salts **A** formed on addition to thione **I** of an equimolar amount of sulfuryl chloride [2]. Therewith the yield of imines **VIa** and **VIb** from silylated amines was somewhat higher.

Silylated secondary amines also react under similar conditions. The reaction between salt **A** and silylated diethylamine afforded a stable crystalline salt **VII**. Here apparently first formed unstable sulfinimide **B** that on decomposition gave iminium salt **VII**. The formation of the intermadiate **B** is suggested by appearance of dark color of the reaction mixture that quickly disappears even at low temperature.



Ib **B** **VII**

In the ^{1}H and ^{13}C NMR spectra of compound **VII** two sets of signals from nonequivalent ethyl groups are observed indicating hindered rotation around the double C=N bond and consequently a significant contribution from the structure with a positive charge localized on a nitrogen.



Ia, Ib **A** **VIIIa, VIIIb**

Salts **A** in the presence of triethylamine react also with compounds possessing an active methylene group as we have shown by preparation of ylidenes **VIIIa** and **VIIIb** from ethyl cyanoacetate.

The ^{1}H and ^{19}F NMR spectra of compounds **VIII** contain a single set of signals corresponding to the only geometrical isomer; however the available data are not sufficient for unambiguously assigning its geometry.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer UR-20. NMR spectra were registered on a spectrometer Varian VXR-300 at operating frequencies 299.943 (^{1}H), 282.203 (^{19}F), and 75.429 (^{13}C) MHz from solutions in $CDCl_3$ and DMSO-d_6, internal references TMS (δ_H and δ_C 0.00 ppm) and hexafluorobenzene (δ_F –162.9 ppm). Mass spectra were taken on a MKh-1321 instrument. The column chromatography was carried out on silica gel Merck 60 (40–63 μm). The reaction progress was monitored by ^{19}F NMR spectroscopy. The solvents were dried by standard procedures.

4-Fluoro-5-trifluoromethyl-1,2-dithiolene 3-oxime (IIa). A mixture of 0.44 g (2.0 mmol) of dithiolthione **Ia**, 0.32 g (4.6 mmol) of hydroxylamine hydrochloride, and 0.54 g (4.0 mmol) of sodium acetate trihydrate in 15 ml of ethanol was heated at reflux for 20 min. On cooling the reaction mixture was poured into 30 ml of water, extracted with dichloromethane (2 × 30 ml), the combined extracts were dried on Na_2SO_4, and evaporated. The residue was extracted with hot hexane (3×20 ml), and the hexane was evaporated from combined extracts. On crystallization from hexane the yield was 0.27 g (63%), mp 92–94°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.81 br.s (1H, OH). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –59.63 d (3F, CF_3, $^4J_{FF}$ 12.2 Hz), –120.95 q (1F, C^{4}F, $^4J_{FF}$ 12.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 219 (24) $[M]^+$, 203 (13) $[M–O]^+$, 188 (16) $[M–NOH]^+$, 69 (100) $[CF_3]^+$. Found, %: N 6.30; S 29.19. $C_5H_2F_5NOS_2$. Calculated, %: N 6.39; S 29.26.

4-Fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiolene 3-oxime (IIb) was prepared like compound **IIa** from 0.50 g (2.0 mmol) of dithiolthione **Ib**, 0.32 g (4.6 mmol) of hydroxylamine hydrochloride, and 0.54 g (4.0 mmol) of sodium acetate trihydrate. Yield 0.32 g (65%), mp 105–106°C (from hexane). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 9.30 br.s (1H, OH), 6.03 t.t (1H, HCF_2, $^2J_{HF}$ 51.3, $^3J_{HF}$ 2.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 145.69 d (C=N, $^2J_{CF}$ 17.6 Hz), 145.81 d.t (C^{4}F, J_{CF} 283.9, $^3J_{CF}$ 5.5 Hz), 122.29 t.d (C^5, $^2J_{CF}$ 29.9, $^2J_{CF}$ 15.7 Hz), 113.00 t.t.d (CF_2, J_{CF} 253.3, $^2J_{CF}$ 30.3, $^3J_{CF}$ 3.9 Hz), 109.19 t.t.d (HCF_2, J_{CF} 253.6, $^2J_{CF}$ 38.9,

$^5J_{CF}$ 3.0 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –110.79 s (2F, CF_2), –121.92 m (1F, C^{4}F), –135.76 d (2F, HCF_2, $^2J_{HF}$ 51.3 Hz). Mass spectrum, *m/z* (I_{rel}, %): 251 (100) [*M*]$^+$, 200 (30) [*M*–HCF_2]$^+$, 101 (14) [HCF_2CF_2]$^+$, 51 (19) [HCF_2]$^+$. Found, %: N 5.53; S 25.21. $C_5H_2F_5NOS_2$. Calculated, %: N 5.59; S 25.53.

4-Fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiolene 3-hydrazone (III) was prepared like compound **IIa** from 0.50 g (2.0 mmol) of dithiolthione **Ib**, 0.60 g (4.6 mmol) of hydrazine sulfate, and 0.82 g (6.0 mmol) of sodium acetate trihydrate. Heating at reflux for 6 h. The residue was purified by column chromatography on SiO_2, eluent chloroform, R_f 0.3 (TLC: Silufol UV-254, development in iodine vapor). Red crystals. Yield 0.32 g (64%), mp 58–60°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.03 t.t.d (1H, HCF_2, $^2J_{HF}$ 53.3, $^3J_{HF}$ 3.4, $^5J_{HF}$ 0.9 Hz), 5.20 br.s (2H, NH_2). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –110.99 s (2F, CF_2), –121.51 m (1F, C^{4}F), –136.01 d (2F, HCF_2, $^2J_{HF}$ 53.3 Hz). Mass spectrum, *m/z* (I_{rel}, %): 250 (100) [*M*]$^+$, 101 (24) [HCF_2CF_2]$^+$, 51 (33) [HCF_2]$^+$. Found, %: N 11.05; S 25.33. $C_5H_3F_5N_2S_2$. Calculated, %: N 11.20; S 25.65.

4-Fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiolene 3-phenylhydrazone (IV). A mixture of 0.50 g (2.0 mmol) of dithiolthione **Ib** and 0.42 g (4.2 mmol) of phenylhydrazine in 20 ml of benzene was heated at reflux for 24 h. On cooling the solvent was evaporated, 20 ml of anhydrous ethyl ether was added to the residue, the insoluble impurities were filtered off, the filtrate was evaporated, and the residue was crystallized from hexane. Yield 0.55 g (81%), mp 81–82°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.97–7.29 (5H, Ph), 6.42 s (1H, NH), 6.04 t.t.d (1H, HCF_2, $^2J_{HF}$ 53.2, $^3J_{HF}$ 3.4, $^3J_{HF}$ 0.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 148.80 d.t (C^{4}F, J_{CF} 283.9, $^3J_{CF}$ 6.0 Hz), 144.38 s (C–NH), 135.15 d (C=N, $^2J_{CF}$ 18.1 Hz), 129.43 s (*m*-Ph), 122.16 s (*n*-Ph), 114.22 s (*o*-Ph), 116.81 t.d (C^5, $^2J_{CF}$ 29.3, $^2J_{CF}$ 17.7 Hz), 113.18 t.t.d (CF_2, J_{CF} 252.6, $^2J_{CF}$ 30.0, $^3J_{CF}$ 4.2 Hz), 109.20 t.t.d (HCF_2, J_{CF} 253.6, $^2J_{CF}$ 39.0, $^3J_{CF}$ 3.2 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –110.77 m (2F, CF_2), –120.40 quint. (1F, C^{4}F), –136.03 d.m (2F, HCF_2, $^2J_{HF}$ 53.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 326 (88) [*M*]$^+$, 92 (100) [PhNH]$^+$, 77 (47) [Ph]$^+$. Found, %: N 8.73; S 19.12. $C_{11}H_7CN_2F_5S_2$. Calculated, %: N 8.58; S 19.65.

4-Fluoro-5-trifluoromethyl-1,2-dithiolene 3-[*O*-(4-bromobenzoyl)]oxime (Va). To a mixture of 0.44 g (2.00 mmol) of oxime **IIa** and 0.30 ml (2.2 mmol) of triethylamine in 20 ml of dry benzene was added dropwise a solution of 0.46 g (2.1 mmol) of *p*-bromobenzoyl chloride in 10 ml of anhydrous benzene, and the mixture was stirred for 1 h. The precipitate was filtered off, the filtrate was washed with water (2×30 ml), the organic layer was separated, dried with Na_2SO_4, and evaporated. The residue was crystallized from ethanol. Yield 0.72 g (90%), mp 206–208°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.91 and 7.84 (4H, Ar). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –56.75 d (3F, CF_3, $^4J_{FF}$ 12.2 Hz), –116.83 q (1F, C^{4}F, $^4J_{FF}$ 12.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 402 (5) [*M*]$^+$, 202 (32) [*M* – BrC_6H_4COO]$^+$, 184 (94) [BrC_6H_4CO]$^+$, 156 (21) [BrC_6H_4]$^+$, 69 (13) [CF_3]$^+$, 64 (100) [S_2]$^+$. Found, %: Br 19.76; N 3.45; S 15.81. $C_{12}H_5BrF_5NO_2S_2$. Calculated, %: Br 19.87; N 3.48; S 15.94.

4-Fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiolene 3-[O-(4- bromobenzoyl)]oxime (Vb) was obtained similarly to compound **Va** from 0.50 g (2.0 mmol) of oxime **IIb**, 0.3 ml (2.2 mmol) of triethylamine, and 0.46 g (2.1 mmol) of *p*-bromobenzoyl chloride. Yield 0.79 g (91%), mp 212–213°C (from ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.92 and 7.85 (4H, Ar), 6.98 t (1H, HCF_2, $^2J_{HF}$ 51.9 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 160.91 s (C=O), 158.39 d (C=N, $^2J_{CF}$ 16.1 Hz), 144.01 d.t (C^{4}F, J_{CF} 284.0, $^3J_{CF}$ 5.1 Hz), 132.20, 131.04 (*m*-Ar, *o*-Ar), 128.40, 126.35 (*p*-Ar, C CO), 125.89 t.d (C^5, $^2J_{CF}$ 27.9, $^2J_{CF}$ 16.1 Hz), 112.94 t.t.d (CF_2, J_{CF} 253.8, $^2J_{CF}$ 30.1, $^3J_{CF}$ 3.6 Hz), 109.06 t.t.d (HCF_2, J_{CF} 252.1, $^2J_{CF}$ 37.3, $^3J_{CF}$ 2.9 Hz). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –109.85 C (2F, CF_2), –117.73 m (1F, C^{4}F), –135.52 d (2F, HCF_2, $^2J_{HF}$ 51.9 Hz). Mass spectrum, *m/z* (I_{rel}, %): 434 (6) [*M*]$^+$, 235 (10) [*M* – BrC_6H_4COO]$^+$, 184 (100) [BrC_6H_4CO]$^+$, 156 (22) [BrC_6H_4]$^+$. Found, %: Br 18.36; N 3.19; S 14.38. $C_{12}H_5BrF_5NO_2S_2$. Calculated, %: Br 18.40; N 3.23; S 14.77.

***N*-*tert*-Butyl-4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiolene 3-imine (VIa).** To a solution of 0.50 g (2.0 mmol) of dithiolthione **Ib** in 5 ml of dry dichloromethane was added 0.16 ml (2.05 mmol) of SO_2Cl_2. In 0.5 h the solvent was decanted, 2 ml of dichloromethane was poured to the residue and again decanted. The precipitate was dissolved in 20 ml of anhydrous THF, and at the temperature around 0°C was added dropwise a solution of 0.38 ml (1.9 mmol) of monosilylated *tert*-butylamine in 5 ml of anhydrous THF. After 10 min a solution of 0.27 ml (2.0 mmol) of anhydrous triethylamine in 5 ml of anhydrous THF was added within a period of 10 min, and the mixture was stirred for 1 h. The solvent was

evaporated, the residue was extracted with ethyl ether (3 × 20 ml), the combined extracts were evaporated. The residue was maintained in a vacuum (10–15 mm Hg) at 40°C for 1 h to afford pure imine **VIa**, yellow oily substance. Yield 0.43 g (74%). ^{1}H NMR spec-trum ($CDCl_3$), δ, ppm: 6.05 t (1H, HCF_2, $^2J_{HF}$ 53.2 Hz), 1.41 s (9H, 3 CH_3). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –111.02 s (2F, CF_2), –114.55 s (1F, C^{4}F), –135.52 d (2F, HCF_2, $^2J_{HF}$ 53.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 291 (9) $[M]^+$, 57 (100) $[C_4H_9]^+$. Found, %: N 4.68; S 22.32. $C_9H_{10}F_5NS_2$. Calculated, %: N 4.81; S 22.01.

***N*-(4-Bromophenyl)-4-fluoro-5-(1,1,2,2-tetra-fluoroethyl)-1,2-dithiolene 3-imine (VIb)** was prepar-ed in the same way as compound **VIa** from 0.50 g (2.0 mmol) of dithiolthione **Ib**, 0.16 ml (2.05 mmol) of SO_2Cl_2, and 0.98 g (5.7 mmol) of *p*-bromoaniline in the absence of triethylamine. The reaction mixture was stirred for 1 h at room temperature, then it was poured into 40 ml of water and diluted with 30 ml of dichloromethane. The organic layer was separated, washed with 20 ml of 10% hydrochloric acid, with 10 ml of water, the solvent was evaporated, and the residue was crystallized from 80% ethanol to obtain yellow crystals. Yield 0.6 g (77%), mp 52–53°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.55 d (2H, Ar), 7.05 d (2H, Ar), 6.10 t.t.d (1H, HCF_2, $^2J_{HF}$ 53.2, $^3J_{HF}$ 3.4, $^5J_{HF}$ 0.9 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –111.70 s (2F, CF_2), –118.78 quint. (1F, C^{4}F), –135.36 d (2F, HCF_2, $^2J_{HF}$ 53.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 390 (100) $[M]^+$, 156 (41) $[C_6H_4Br]^+$. Found, %: N 3.57; S 16.74. $C_{11}H_5BrF_5NS_2$. Calculated, %: N 3.59; S 16.44.

***N,N*-Diethyl-4-fluoro-5-(1,1,2,2-tetrafluoro-ethyl)-1,2-dithiolene 3-iminium chloride (VII)** was prepared in the same way as compound **VIa** from 0.50 g (2.0 mmol) of dithiolthione **Ib**, 0.16 ml (2.05 mmol) of SO_2Cl_2, and 0.36 ml (1.9 mmol) of silylated diethylamine with no triethylamine added. Reaction time was 2 h. The separated precipitate was filtered off, washed with 5 ml of THF, dried, and crystallized from a small amount of acetonitrile to obtain yellowish crystals. Yield 0.58 g (89%), mp 221–223°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.03 t.t (1H, HCF_2, $^2J_{HF}$ 51.6, $^3J_{HF}$ 3.9 Hz), 3.91 q.d (2H, CH_2, $^3J_{HH}$ 7.1, $^5J_{HF}$ 2.2 Hz), 3.83 q (2H, CH_2, $^3J_{HH}$ 7.1 Hz), 1.35 t (3H, CH_3, $^3J_{HH}$ 7.1 Hz), 1.30 t (3H, CH_3, $^3J_{HH}$ 7.1 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 170.48 d (C=N, $^2J_{CF}$ 10.5 Hz), 145.65 d.t (C^{4}F, J_{CF} 284.8, $^3J_{CF}$ 4.2 Hz), 138.71 t.d (C^5, $^2J_{CF}$ 28.5, $^2J_{CF}$ 12.6 Hz), 112.85 t.t.d (CF_2, J_{CF} 254.3, $^2J_{CF}$ 29.9, $^3J_{CF}$ 2.2 Hz), 108.87 t.t (HCF_2, J_{CF} 252.0, $^2J_{CF}$ 36.9 Hz), 52.61 c (CH_2), 49.91 d (CH_2, $^5J_{CF}$ 11.8 Hz), 13.80 d (CH_3, $^6J_{CF}$ 2.1 Hz), 9.55 s (CH_3). ^{19}F NMR spectrum (DMSO-d_6), δ, ppm: –111.41 m (2F, CF_2), –112.69 m (1F, C^{4}F), –136.12 d.m (2F, HCF_2, $^2J_{HF}$ 51.6 Hz). Mass spectrum, *m/z* (I_{rel}, %): 292 (100) $[M - Cl]^+$, 276 (18) $[M - Cl–CH_4]^+$, 262 (19) $[M - Cl–C_2H_6]^+$, 72 (14) $[NEt_2]^+$. Found, %: Cl 10.72; N 4.19; S 19.45. $C_9H_{11}ClF_5NS_2$. Calculated, %: Cl 10.81; N 4.27; S 19.56.

Ethyl cyano(4-fluoro-5-trifluoromethyl-1,2-dithiol-3-ylidene)acetate (VIIIa) was obtained similarly to compound **VIa** from 0.44 g (2.0 mmol) of dithiolthione **Ia**, 0.16 ml (2.05 mmol) of SO_2Cl_2, 0.22 ml (2.1 mmol) of a freshly distilled ethyl cyanoacetate, and 0.58 ml (4.2 mmol) of anhydrous triethylamine. The solvent was evaporated, the residue was extracted with hot hexane (5×10 ml), the combined extracts were evaporated, and the residue was crystallized from ethanol to obtain fine yellow-orange needle crystals. Yield 0.31 g (52%), mp 164–165°C. IR spectrum (KBr), ν, cm^{-1}: 1190, 1330 (CF), 1650 (C=O), 2230 (C≡N), 3020 (CH). ^{1}H NMR spec-trum ($CDCl_3$), δ, ppm: 4.40 q (2H, CH_2, $^3J_{HH}$ 7.2 Hz), 1.41 t (3H, CH_3, $^3J_{HH}$ 7.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 167.81 s (C=O), 162.64 d (=C–CF), 149.27 d.q (=C–F, J_{CF} 288.0, $^3J_{CF}$ 2.8 Hz), 130.84 q.d (=C–CF_3, $^2J_{CF}$ 40.0, $^2J_{CF}$ 17.0 Hz), 119.49 q.d (CF_3, J_{CF} 274.9, $^3J_{CF}$ 2.1 Hz), 112.81 s (C≡N), 88.38 d (=C–CN, $^3J_{CF}$ 3.2 Hz), 63.67 s (CH_2), 14.31 s (CH_3). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –59.10 d (3F, CF_3, $^4J_{FF}$ 12.2 Hz), –109.97 q (1F, =C–F, $^4J_{FF}$ 12.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 299 (100) $[M]^+$, 254 (28) $[M - OC_2H_5]^+$, 69 (37) $[CF_3]^+$. Found, %: N 4.63; S 21.48. $C_9H_8F_4NO_2S_2$. Calculated, %: N 4.68; S 21.43.

Ethyl cyano[4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiol-3-ylidene]acetate (VIIIb). was obtained similarly to compound **VIa** from 0.50 g (2.0 mmol) of dithiolthione **Ib**, 0.16 ml (2.05 mmol) SO_2Cl_2, 0.22 ml (2.1 mmol) of a freshly distilled ethyl cyanoacetate, and 0.58 ml (4.2 mmol) of anhydrous triethylamine. Yellow-orange crystals. Yield 0.42 g (64%), mp 126–128°C (from hexane). IR spectrum(KBr), ν, cm^{-1}: 1120, 1330 (CF), 1670 (C=O), 2235 (C≡N), 3030 (CH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.12 t.t (1H, HCF_2, $^2J_{HF}$ 53.1, $^3J_{HF}$ 3.1 Hz), 3.40 q (2H, CH_2, $^3J_{HH}$ 7.1 Hz), 1.40 t (3H, CH_3, $^3J_{HH}$ 7.1 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –109.60 s (2F, CF_2), –110.73 m (1F, =C–F), –135.12 d (2F, HCF_2, $^2J_{HF}$ 53.1 Hz). Mass spectrum, *m/z* (I_{rel}, %): 331 (100) $[M]^+$, 303 (86) $[M - C_2H_4]^+$, 286 (33) $[M - OC_2H_5]^+$, 259 (52) $[M - C_2H_4–COO]^+$, 232 (17) $[M$ –

$COOC_2H_5$–CN]$^+$. Found, %: N 4.18; S 19.15. $C_{10}H_6F_5NO_2S_2$. Calculated, %: N 4.23; S 19.36.

REFERENCES

1. Timoshenko, V. M., Bouillon, J.-P., Shermolovich, Yu. G., and Portella, C., *Tetrahedron Lett*., 2002, vol. 43, p. 5809.
2. Fesun, I.N., Timoshenko, V.M., Chernega, A.N., and Shermolovich, Yu.G., *Zh. Org. Khim.,* 2005, no. 350/04.
3. Vasil'eva, T.P., Lin'kova, M.G., and Kil'disheva, O.V., *Usp. Khim.,* 1976, vol. 45, p. 1269.
4. Timoshenko, V.M., Nikolin, Ya.V., Kolesnik, N.P., and Shermolovich, Yu.G., *Zh. Org. Khim*., 2001, vol. 37, p. 666.
5. Pedersen, C.T., *Adv. Heterocycl. Chem.,* 1982, vol. 31, p. 63.