Russian Journal of Organic Chemistry, Vol. 40, No. 6, 2004, pp. 874–878. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 6, 2004, pp. 912–916.
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Dedicated to Full Member of the Russian Academy of Sciences O.N. Chupakhin on his 70th Anniversary

Synthesis of Trifluoroalkyl- and Fluoroaryl-Substituted 4,5-Dihydro-1*H*-1,2,4-triazole-5-thiones

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Received June 5, 2003

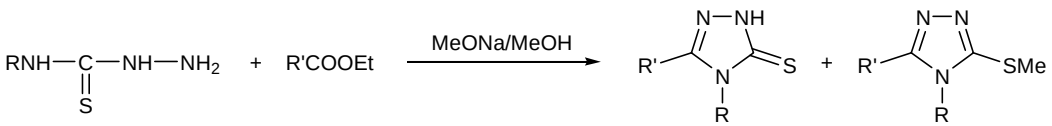
Abstract—Reactions of 4-(4-fluorophenyl)-, 4-(4-trifluoromethoxyphenyl)-, 4-(3,4-difluorophenyl)-, 4-(4-trifluoromethylphenyl)-, 4-piperidino-, and 4-(3-pyridyl)thiosemicarbazides with esters gave the corresponding 3,4-disubstituted 4,5-dihydro-1*H*-1,2,4-triazole-5-thiones and their *S*-alkyl derivatives. Analogous reactions with methyl 2,2,3,3,4,4,5,5-octafluoropentanoate and 2,2,3,3,4,4,5,5-octafluoropentanenitrile afforded, respectively, the acylation and addition products.

4,5-Dihydro-1*H*-1,2,4-triazole-5-thiones are known to exhibit biological activity. They can be synthesized by cyclization of 1-acyl-substituted thiosemicarbazides [1, 2] or by direct reaction of thiosemicarbazides with carboxylic acid esters [3]. Introduction of polyfluorinated substituents into various positions of the 1,2,4-triazole ring seems to be fairly promising, for fluorine-containing compounds are characterized by stronger biological activity as compared to nonfluorinated analogs [4].

Published data on fluorine-containing 4,5-dihydro-1*H*-1,2,4-triazole-5-thiones are very scanty. Vershilov *et al*. [5] performed condensation of fluorine-free thiosemicarbazides with a number of polyfluorinated acyl fluorides and obtained a series of compounds possessing surfactant activity, which were assigned the structure of triazole derivatives. Reactions of 2,4-disubstituted thiosemicarbazides with trifluoroacetic anhydride were reported to afford polyfluorinated 4,5-dihydro-1*H*-1,2,4-triazole-5-thiones [6]. However, no rigorous proofs for the assumed structures were given in these publications [5, 6].

In the present work we introduced fluorinated substituents into the 1,2,4-triazole ring by using as starting compounds both fluoroaryl-substituted thiosemicarbazides and fluorine-containing electrophile. For this purpose, we examined reactions of 4-(4-fluorophenyl)-, 4-(4-trifluoromethoxyphenyl)-, 4-(3,4-difluorophenyl)-, 4-(4-trifluoromethylphenyl)-, 4-piperidino-, and 4-(3-pyridyl)thiosemicarbazides **Ia**–**If** with esters derived carboxylic (**IIa**, **IIb**), hetarenecarboxylic (**IIc**, **IId**), and fluorocarboxylic acids (**IIe**) (Scheme 1).

Scheme 1.



Ia–If **IIa–IIe** **IIIa–IIIo** **IVa**, **IVb**

Ia, **IIIe**–**IIIg**, **IVa**, R = 4-FC_6H_4; **Ib**, **IIIa**–**IIIc**, R = 4-$CF_3OC_6H_4$; **Ic**, **IIId**, R = 3,4-$F_2C_6H_3$; **Id**, **IIIh**–**IIIj**, R = 4-$CF_3C_6H_4$; **Ie**, **IIIk**–**IIIm**, **IVb**, R = piperidino; **If**, **IIIn**, **IIIo**, R = 3-pyridyl; **IIa**, **IIIa**, **IIIh**, **IIIk**, R' = H; **IIb**, **IIIb**, **IIId**, **IIIi**, **IIIl**, **IIIn**, R' = Me; **IIc**, **IIIf**, R' = 3-pyridyl; **IId**, **IIIe**, R' = 2-thienyl; **IIe**, **IIIc**, **IIIg**, **IIIj**, **IIIm**, **IIIo**, **IVa**, **IVb**, R' = CF_3.

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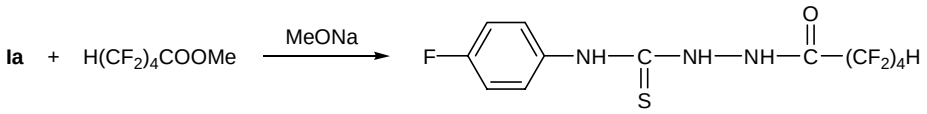
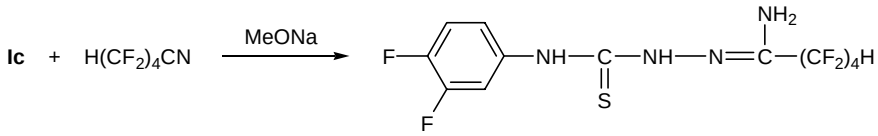
Scheme 2.



Scheme 3.



We have found that condensation of fluoroaryl-substituted thiosemicarbazides **Ia**–**Id** with esters **IIa**–**IId** leads to formation of dihydro-1,2,4-triazolethiones **IIIa**, **IIIb**, **IIId**–**IIIf**, **IIIh**, and **IIIi** containing the corresponding fluoroaryl group in position *4* of the heteroring. The reactions of ethyl trifluoroacetate (**IIe**) with fluorine-free thiosemicarbazides **Ie** and **If** gave 1,2,4-triazole-5-thiones **IIIm** and **IIIo** in which the fluoroalkyl group is located at C^3. By condensation of fluoroaryl-substituted thiosemicarbazides **Ia**–**Id** with ethyl trifluoroacetate we obtained compounds **IIIc**, **IIIg**, and **IIIj** having trifluoromethyl group on C^3 and fluoroaryl group on N^4. In addition, we were the first to reveal that the condensation with ethyl trifluoroacetate is accompanied by alkylation of the resulting heterocycles at the sulfur atom to give 5-methylsulfanyl derivatives **IV**. Compounds **IVa** and **IVb** were isolated and characterized by spectral data. The ^{1}H NMR spectra of **IVa** and **IVb** contained signals from the substituents in positions *3* and *4* of the triazole ring and a singlet at δ 2.75 ppm, which is typical of SMe group.

Presumably, the alkylation is effected by methyl trifluoroacetate.* The electron-acceptor trifluoromethyl group favors formation of trifluorocarboxylate ion which is stabilized due to the presence of sodium cation in the reaction mixture. There are published data on the use of fluorocarboxylic acid esters as alkylating agents [7].

We failed to obtain 1,2,4-triazole-5-thiones having longer polyfluoroalkyl substituents. The reaction of thiosemicarbazide **Ia** with methyl 2,2,3,3,4,4,5,5-octafluoropentanoate (**IIf**) as electrophile stopped at the stage of formation of primary acylation product (Scheme 2). Presumably, the subsequent cyclization is strongly hindered for steric reasons: attack by aryl-substituted nitrogen atom on the carbonyl group shielded by fairly bulky polyfluoroalkyl substituent becomes impossible. Our attempts to effect cyclization of 1-(2,2,3,3,4,4,5,5-octafluoropentanoyl)-4-(4-fluorophenyl)thiosemicarbazide (**V**) by prolonged heating with sodium methoxide in boiling methanol, as well as by heating in *p*-xylene, resulted in tarring. We also failed to obtain heterocyclic product by condensation of thiosemicarbazide **Ic** with polyfluorinated nitrile **VI** (Scheme 3). It might be expected that the cyclization of **VII** should be more facile than the cyclization of compound **V**. However, our numerous attempts to effect deamination of structure **VII** were unsuccessful.

Thus we have demonstated the possibility of introducing fluoroaryl and fluoroalkyl groups into dihydro-1,2,4-triazole-5-thiones, but the set of R_F groups is confined to only short trifluoromethyl substituent.

EXPERIMENTAL

The NMR spectra were recorded on Tesla BS-567A (80 MHz for ^{1}H and 75 MHz for ^{19}F) and Bruker DRX-400 (400MHz for ^{1}H and 100 MHz for ^{19}F) spectrometers using tetramethylsilane as reference (for ^{1}H). The IR spectra were measured on Specord 75-IR and Perkin–Elmer Spectrum I instruments from samples dispersed in mineral oil. The mass spectra (electron impact, 70 eV) were obtained on a MAT INCOS50 spectrometer with direct sample asdmission into the ion source.

Thiosemicarbazides **Ia**–**If** were synthesized by the procedure reported in [8].

4-(4-Fluorophenyl)thiosemicarbazide (Ia). Yield 65%, colorless crystals, mp 180–181°C (from water).

* In the reactions with ethyl trifluoroacetate, the corresponding methyl ester is formed as a result of transesterification with the solvent (methanol).

^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.7 br.s (2H, NH_2), 7.09–7.60 m (4H, C_6H_4), 9.13 s (2H, 2NH). Found, %: C 45.40; H 4.37; F 10.24. $C_7H_8FN_3S$. Calculated, %: C 45.40; H 4.40; F 10.26.

4-(4-Trifluoromethoxyphenyl)thiosemicarbazide (Ib). Yield 60%, colorless crystals, mp 124–125°C (from toluene). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.8 br.s (2H, NH_2), 7.28–7.84 m (4H, C_6H_4), 9.25 s (2H, 2NH). Found, %: C 38.12; H 2.90; F 22.67; N 16.67. $C_8H_8F_3N_3OS$. Calculated, %: C 38.25; H 3.21; F 22.69; N 16.73.

4-(3,4-Difluorophenyl)thiosemicarbazide (Ic). Yield 65%, colorless crystals, mp 173–174°C (from ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.3 br.s (1H, NH), 5.3 br.s (2H, NH_2), 7.18–8.04 m (3H, C_6H_3), 9.2 br.s (1H, NH). Found, %: C 41.45; H 3.50; F 18.70. $C_7H_7F_2N_3S$. Calculated, %: C 41.37; H 3.47; F 18.70.

4-(4-Trifluoromethylphenyl)thiosemicarbazide (Id). Yield 68%, colorless crystals, mp 162–163°C (from ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.2 br.s (2H, NH_2), 7.60–7.98 m (4H, C_6H_4), 9.40 s (2H, 2NH). Found, %: C 40.85; H 3.43; F 24.23; N 17.86. $C_7H_7F_2N_3S$. Calculated, %: C 40.70; H 3.38; F 24.23; N 17.81.

4-Piperidinothiosemicarbazide (Ie). Yield 65%, colorless crystals, mp 170–171°C (from ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.92–1.14 m (2H, CH_2), 2.29–2.49 m (4H, $2CH_2$), 2.68–2.89 m (4H, $2CH_2$), 4.7 br.s (2H, NH_2), 8.66 s (2H, 2NH). Found, %: C 41.63; H 7.80; N 32.25; S 18.36. $C_6H_{14}N_4S$. Calculated, %: C 41.35; H 8.10; N 32.15; S 18.40.

4-(3-Pyridyl)thiosemicarbazide (If). Yield 70%, colorless crystals, mp 177–178°C (from ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.2 br.s (2H, NH_2), 6.88–8.70 m (4H, C_5H_4N), 9.32 s (2H, 2NH). Found, %: C 42.75; H 4.61; N 33.01. $C_6H_8N_4S$. Calculated, %: C 42.84; H 4.79; N 33.31.

General procedure for the synthesis of compounds IIIa–IIIo, IVa, and IVb. Carboxylic acid ester **IIa**–**IIe**, 0.03 mol, was added to a solution of 0.02 mol of sodium methoxide in 10 ml of anhydrous methanol. The mixture was heated to the boiling point, a solution of 0.01 mol of thiosemicarbazide **Ia**–**If** in 5 ml of anhydrous methanol was added dropwise over a period of 1 h, and the mixture was heated for 15 h under reflux. The solvent was removed under reduced pressure, the residue was dissolved in 10 ml of boiling water, a small amount of charcoal was added, and the solution was heated for 5 min at the boiling point and filtered. After cooling, the precipitate was filtered off, reprecipitated from DMF with water, and recrystallized from hexane. We thus isolated compounds **IV**. The filtrate was cooled and acidified with concentrated hydrochloric acid to pH 2–3. The precipitate of compound **III** was filtered off and recrystallized from appropriate solvent.

4-(4-Trifluoromethoxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIIa). Yield 60%, colorless crystals, mp 178–179°C (from toluene). IR spectrum, ν, cm^{-1}: 3060, 3100, 2740 (N–H). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.58–7.85 m (4H, C_6H_4), 8.74 s (1H, HC=N), 14.0 br.s (1H, NH). Found, %: C 41.09; H 2.61; F 21.68; N15.99. $C_9H_7F_3N_3OS$. Calculated, %: C 41.22; H 2.69; F 21.73; N 16.02.

3-Methyl-4-(4-trifluoromethoxyphenyl)-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIIb). Yield 55%, light yellow crystals, mp 110–111°C (from toluene). IR spectrum, ν, cm^{-1}: 3060, 3100, 2740 (N–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.22 s (3H, CH_3), 7.26–7.52 m (4H, C_6H_4), 11.9 br.s (1H, NH). Found, %: C 43.59; H 3.01; F 20.50; N 15.24. $C_{10}H_8F_3N_3OS$. Calculated, %: C 43.64; H 2.93; F 20.71; N 15.27.

4-(4-Trifluoromethoxyphenyl)-3-trifluoromethyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIIc). Yield 58%, light yellow crystals, mp 163–164°C (from toluene). IR spectrum, ν, cm^{-1}: 3060, 3100, 2740 (N–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.37–7.98 m (4H, C_6H_4), 11.5 br.s (1H, NH). Found, %: C 36.50; H 1.50; F 34.51; N 12.69. $C_{10}H_5F_6N_3OS$. Calculated, %: C 36.48; H 1.53; F 34.62; N 12.76.

4-(3,4-Difluorophenyl)-3-methyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIId). Yield 66%, colorless crystals, mp 228–230°C (from *o*-xylene). IR spectrum, ν, cm^{-1}: 3050, 3100, 2750 (N–H). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.12 s (3H, CH_3), 7.26–7.84 m (3H, C_6H_3), 13.7 br.s (1H, NH). Found, %: C 47.75; H 2.91; F 17.00; N 18.49; S 14.07. $C_9H_7F_2N_3S$. Calculated, %: C 47.57; H 3.11; F 16.72; N 18.49; S 14.11.

4-(4-Fluorophenyl)-3-(2-thienyl)-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIIe). Yield 63%, colorless crystals, mp 218–220°C (from toluene). IR spectrum, ν, cm^{-1}: 3060, 3100, 2740 (N–H). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.23–8.18 m (7H, C_6H_4, C_4H_3S), 11.3 br.s (1H, NH). Found, %: C 52.23; H 2.46; N 15.16; S 23.27. $C_{12}H_7FN_3S_2$. Calculated, %: C 52.16; H 2.55; N 15.21; S 23.20.

4-(4-Fluorophenyl)-3-(3-pyridyl)-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIIf). Yield 41%, colorless crystals, mp 255–256°C (from hexane–chloroform, 1:10). IR spectrum, ν, cm^{-1}: 3060, 3100, 2740 (N–H). ^1H NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 7.27–8.53 m (8H, C_5H_4N, C_6H_4), 14.1 br.s (1H, NH). Found, %: C 57.25; H 3.17; F 6.88; N 20.49. $C_{13}H_9FN_4S$. Calculated, %: C 57.34; H 3.33; F 6.97; N 20.58.

4-(4-Fluorophenyl)-3-trifluoromethyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIIg). Yield 22%, colorless crystals, mp 160–161°C (from water). IR spectrum, ν, cm^{-1}: 3090, 3100, 2750 (N–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.26–7.35 m (4H, C_6H_4), 12.6 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 53.61 s (1F), 98.30 s (3F, CF_3). Mass spectrum, *m*/*z* (I_{rel}, %): 263 (100) $[M]^+$, 154 (2.39), 136 (8.00), 69 (6.83). Found, %: C 40.98; H 1.62; F 28.92; N 15.86. $C_9H_5F_4N_3S$. Calculated, %: C 41.08; H 1.92; F 28.88; N 15.97.

4-(4-Trifluoromethylphenyl)-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIIh). Yield 43%, colorless crystals, mp 185–186°C (from hexane–chloroform, 1:10). IR spectrum, ν, cm^{-1}: 3060, 3100, 2740 (N–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.78–7.85 m (4H, C_6H_4), 7.98 s (1H, HC=N), 11.8 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 98.94 s (3F, CF_3). Found, %: C 43.95; H 2.39; F 22.75; N 16.86. $C_9H_6F_3N_3S$. Calculated, %: C 44.08; H 2.47; F 23.24; N 17.14.

3-Methyl-4-(4-trifluoromethylphenyl)-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIIi). Yield 40%, colorless crystals, mp 186–187°C (from *o*-xylene). IR spectrum, ν, cm^{-1}: 3060, 3100, 2740 (N–H). ^1H NMR spectrum (DMSO-d_6–CCl_4), δ, ppm: 2.17 s (3H, CH_3), 7.56–7.99 m (4H, C_6H_4), 13.6 br.s (1H, NH). Found, %: C 46.39; H 2.97; F 22.05; N 16.26. $C_{10}H_8F_3N_3S$. Calculated, %: C 46.33; H 3.11; F 21.98; N 16.21.

3-Trifluoromethyl-4-(4-trifluoromethylphenyl)-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIIj). Yield 71%, colorless crystals, mp 173–174°C (from toluene). IR spectrum, ν, cm^{-1}: 3060, 3100, 2740 (N–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.56–7.99 m (4H, C_6H_4), 11.1 br.s (1H, NH). Found, %: C 38.40; H 1.55; F 36.28; N 13.42; S 10.19. $C_{10}H_5F_6N_3S$. Calculated, %: C 38.35; H 1.61; F 36.39; N 13.36; S 10.24.

4-Piperidino-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIIk). Yield 84%, colorless crystals, mp 192–193°C (from hexane–chloroform, 1:10). IR spectrum, ν, cm^{-1}: 3060, 3100, 2740 (N–H). ^1H NMR spectrum (acetone-d_6), δ, ppm: 1.47–1.74 m and 3.46–3.48 m (10H, $C_5H_{10}N$), 8.23 s (1H, HC=N), 12.2 br.s (1H, NH). Found, %: C 45.25; H 6.40; N 30.25. $C_7H_{12}N_4S$. Calculated, %: C 45.63; H 6.56; N 30.41.

3-Methyl-4-piperidino-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIIl). Yield 70%, colorless crystals, mp 180–181°C (from hexane–chloroform, 1:10). IR spectrum, ν, cm^{-1}: 3060, 3100, 2740 (N–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.29 s (3H, CH_3); 1.32–1.38 m, 1.57–1.81 m, 2.91–2.93 m (10H, $C_5H_{10}N$); 10.9 br.s (1H, NH). Found, %: C 48.54; H 6.99; N 28.19; S 16.08. $C_8H_{14}N_4S$. Calculated, %: C 48.46; H 7.12; N 28.26; S 16.17.

4-Piperidino-3-trifluoromethyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIIm). Yield 60%, colorless crystals, mp 178–180°C (from *o*-xylene). IR spectrum, ν, cm^{-1}: 3060, 3100, 2740 (N–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.18–1.25 m, 1.65–1.77 m, 3.13–3.15 m (10H, $C_5H_{10}N$); 9.7 br.s (1H, NH). Found, %: C 38.15; H 4.32; N 22.09; S 12.61. $C_8H_{11}F_3N_4S$. Calculated, %: C 38.09; H 4.40; N 22.21; S 12.71.

3-Methyl-4-(3-pyridyl)-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIIn). Yield 56%, colorless crystals, mp 254–255°C (from hexane–chloroform, 1:10). IR spectrum, ν, cm^{-1}: 3060, 3100, 2740 (N–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.22 s (3H, CH_3), 7.26–7.52 m (4H, C_5H_4N), 11.9 br.s (1H, NH). Found, %: C 49.84; H 4.10; N 29.21; S 16.61. $C_8H_8N_4S$. Calculated, %: C 49.98; H 4.19; N 29.14; S 16.68.

4-(3-Pyridyl)-3-trifluoromethyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione (IIIo). Yield 67%, colorless crystals, mp 226–228°C (from toluene). IR spectrum, ν, cm^{-1}: 3060, 3100, 2740 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.36–8.25 m (4H, C_5H_4N), 11.5 br.s (1H, NH). Found, %: C 38.91; H 1.92; F 22.99; N 22.58. $C_8H_5F_3N_4S$. Calculated, %: C 39.03; H 2.05; F 23.15; N 22.76.

4-(4-Fluorophenyl)-5-methylsulfanyl-3-trifluoromethyl-1,2,4-triazole (IVa). Yield 32%, colorless crystals, mp 148–149°C (from hexane). IR spectrum, ν, cm^{-1}: 1460 (C=N); 1188, 1170, 1148 (CF). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.74 s (3H, CH_3), 6.81–7.33 m (4H, C_6H_4). Found, %: C 43.18; H 2.45; N 15.05. $C_{10}H_7F_4N_3S$. Calculated, %: C 43.32; H 2.54; N 15.16.

5-Methylsulfanyl-4-piperidino-3-trifluoromethyl-1,2,4-triazole (IVb). Yield 68%, gray crystals, mp 84–85°C (from hexane). IR spectrum, ν, cm^{-1}: 1466 (C=N); 1179, 1149 (CF). ^1H NMR spectrum

($CDCl_3$), δ, ppm: 1.16–1.24 m, 1.66–1.75 m, 3.11–3.16 m (10H, $C_5H_{10}N$); 2.75 s (3H, CH_3). Found, %: C 40.48; H 4.83; F 21.31; N 20.96. $C_9H_{13}F_3N_4S$. Calculated, %: C 40.60; H 4.92; F 21.40; N 21.04.

4-(4-Fluorophenyl)-1-(2,2,3,3,4,4,5,5-octafluoropentanoyl)thiosemicarbazide (V). Yield 57%, colorless crystals, mp 108–109°C (from hexane–toluene, 4:1). IR spectrum, ν, cm^{-1}: 1690 (CONH), 3250 (N–H). ^1H NMR spectrum (acetone-d_6), δ, ppm: 6.78 t.t [1H, $(CF_2)_4H$, $^2J_{HF}$ = 51.2, $^3J_{HF}$ = 5.6 Hz], 7.04–7.59 m (4H, C_6H_4), 9.25 s (1H, NH), 9.52 s (1H, NH), 10.6 br.s (1H, NH). Found, %: C 35.11; H 2.06; N 10.15. $C_{12}H_8F_9N_3OS$. Calculated, %: C 34.88; H 1.95; N 10.17.

1-(1-Amino-2,2,3,3,4,4,5,5-octafluoropentylidene)-4-(3,4-difluorophenyl)thiosemicarbazide (VII). 2,2,3,3,4,4,5,5-Octafluoropentanenitrile (**VI**), 1.2 g (5.3 mmol), was added to a solution of 0.25 g (1.2 mmol) of thiosemicarbazide **Ic** in 15 ml of anhydrous methanol, and the mixture was left to stand for 48 h. The solvent was distilled off, and the residue was recrystallized from heptane. Yield 0.17 g (33%), colorless crystals, mp 104–105°C. IR spectrum, ν, cm^{-1}: 3318, 3355, 3430 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 5.89 s (2H, NH_2), 6.05 t.t [1H, $(CF_2)_4H$, $^2J_{HF}$ = 52.1, $^3J_{HF}$ = 5.40 Hz], 7.11–7.66 m (3H, C_6H_3), 9.10 s (1H, NH), 10.6 br.s (1H, NH). Found, %: C 33.75; H 1.84; N 13.39; S 7.26. $C_{12}H_8F_{10}N_4S$. Calculated, %: C 33.50; H 1.87; N 13.02; S 7.45.

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