

Chlorination and Oxidation of 4-Fluoro-5-tetrafluoroethyl-1,2-dithiole-3-thione

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Abstract—Chlorination of 4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiole-3-thione with an equimolar amount of chlorine or sulfuryl chloride gives 3-chlorosulfanyl-4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiolium chloride. The reaction of the title compound with excess chlorinating agent leads to 3,3,4,5-tetrachloro-4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiolane. By oxidation and oxidative imination of 4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiole-3-thione, the corresponding *S*-oxide and sulfimide were obtained, respectively.

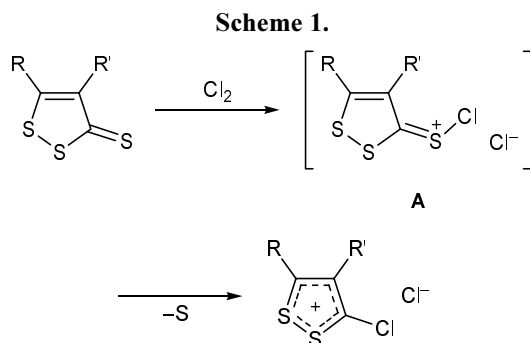
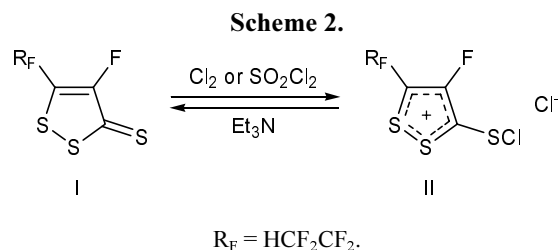
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1,2-Dithiole-3-thiones are pseudoaromatic heterocyclic compounds possessing a broad spectrum of biological activity. In addition, they are convenient synthons for the preparation of other sulfur-containing heterocyclic systems. Chemical properties of 1,2-dithiole-3-thiones have been extensively studied [1, 2]. However, among a large number of synthesized 1,2-dithiole-3-thiones, only a few fluoro- or polyfluoroalkyl-substituted representatives have been reported [3]. We recently described the synthesis and cycloaddition reactions of 4-fluoro-5-polyfluoroalkyl-1,2-dithiole-3-thiones [4]. The present communication reports on some reactions of 4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiole-3-thione (**I**) with electrophilic reagents.

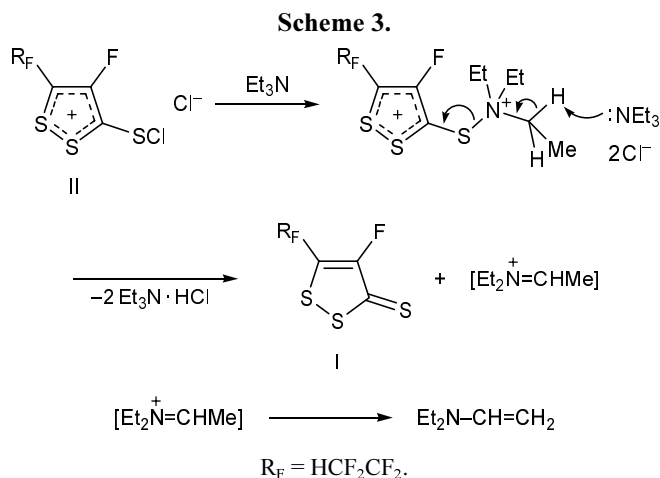
It is known that 1,2-dithiole-3-thiones are readily chlorinated to the corresponding 3-chloro-1,2-dithiolium salts under mild conditions [1, 5, 6]. Chlorine, sulfuryl chloride, oxalyl chloride, and carbonyl chloride were used as chlorinating agents, and the reactions

were carried out in acetic acid or carbon tetrachloride as solvent. The chlorination involves intermediate formation of thiolium salts **A** which readily eliminate sulfur to produce crystalline 3-chloro-1,2-dithiolium salts [**7**] (Scheme 1).

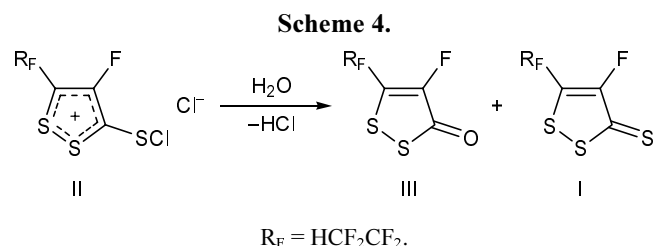
We have found that addition of an equimolar amount of chlorine or sulfuryl chloride to a solution of 4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiole-3-thione (**I**) leads to formation of 3-chlorosulfanyl-1,2-dithiolium salt **II** (Scheme 2).



The product structure as 3-chlorosulfanyl rather than 3-chloro derivative follows from the analytical data which showed the sulfur-to-chlorine ratio to be equal to 3:2. Addition of triethylamine to a solution of salt **II** in tetrahydrofuran led to dechlorination, and initial 1,2-dithiole-3-thione was isolated in a high yield. This result also supports the formation of salt **II**. The reaction with triethylamine may be interpreted by analogy with dehalogenation of arenesulfonyl halides by the action of triethylamine, which gives thiolate ion [**8**] (Scheme 3).

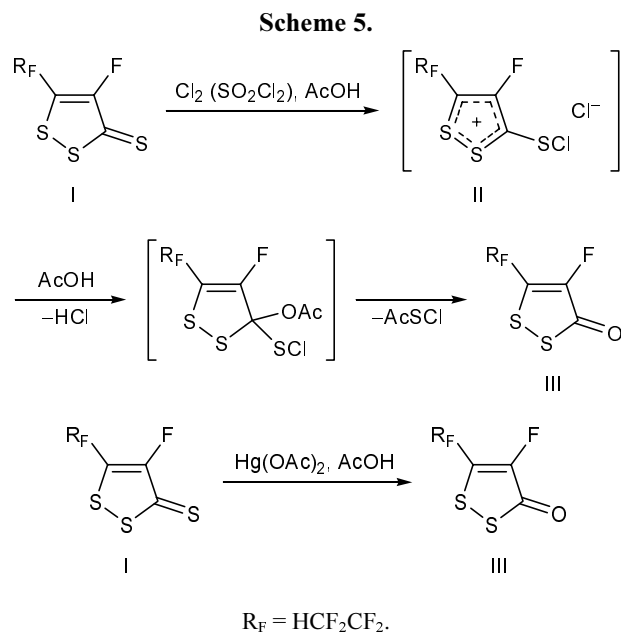


Salt **II** is a yellow high-melting crystalline substance with a sharp odor. It undergoes hydrolysis on exposure to atmospheric moisture to give 85–90% of 1,2-dithiol-3-one **III** and 10–15% of initial 1,2-dithiole-3-thione **I** (Scheme 4). Fast hydrolysis occurs on addition of water to a solution of salt **II**, and the fraction of thione **I** among the products increases to 20%.



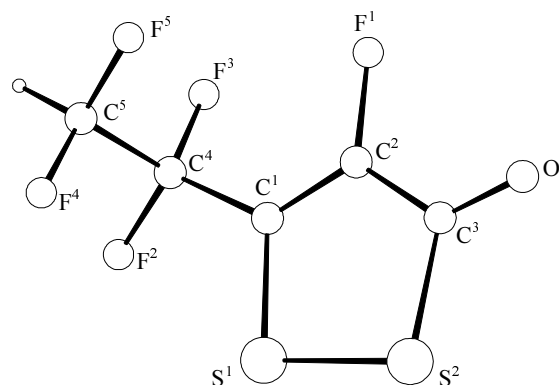
1,2-Dithiol-3-one **III** can be obtained in almost quantitative yield by chlorination of dithiolethione **I** with chlorine or sulfuryl chloride in glacial acetic acid. In these reactions, compound **III** may be formed via both partial hydrolysis of intermediate dithiolium salt **II** and reaction of the latter with acetic acid, followed by decomposition of the resulting 3-acetoxy-3-chloro-sulfanyl derivative in acid medium (Scheme 5). Compound **III** is also formed as a result of desulfurization of thione **I** by the action of mercury(II) acetate in acetic acid; this reaction is typical of such compounds.

4-Fluoro-5-(1,1,2,2-tetrafluoro)-1,2-dithiol-3-one (**III**) is a low-melting volatile crystalline substance. Its structure was proved by X-ray analysis. The general view of molecule **III** and its principal geometric parameters are given in Fig. 1. The five-membered heteroring $\text{S}^1\text{S}^2\text{C}^1\text{C}^2\text{C}^3$ is planar (deviations of atoms from the mean-square plane do not exceed 0.013 Å), and the bond lengths and bond angles therein are very

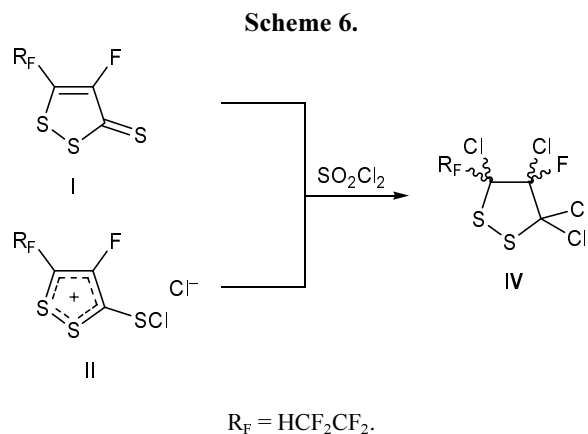


consistent with the corresponding parameters found for structurally related compounds [9].

Unlike dithiol-3-ones reported previously [10], compound **III** failed to react with chlorinating agents, such as chlorine, sulfuryl chloride, and oxalyl chloride. The S–S bond in molecule **III** was retained, and no expected ring opening products were detected. By contrast, treatment of 1,2-dithiole-3-thione **I** with excess sulfuryl chloride leads to replacement of the thiocarbonyl moiety by dichloromethylene and addition of chlorine at the endocyclic double bond to give tetrachlorodithiolane **IV** in high yield. The same product



Structure of the molecule of 4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiol-3-one (**III**) according to the X-ray diffraction data. Principal bond lengths (Å) and bond lengths (deg): S^1-S^2 2.041(3), S^1-C^1 1.735(7), S^2-C^3 1.767(9), C^1-C^2 1.348(13), C^2-C^3 1.433(13), O^1-C^3 1.222(13); $\text{S}^2\text{S}^1\text{C}^1$ 94.5(4), $\text{S}^1\text{S}^2\text{C}^3$ 97.8(4), $\text{S}^1\text{C}^1\text{C}^2$ 116.7(7), $\text{C}^1\text{C}^2\text{C}^3$ 120.6(7), $\text{S}^2\text{C}^3\text{C}^2$ 110.4(7)°.



was obtained by chlorination of salt **II** with excess sulfuryl chloride (Scheme 6).

Compound **IV** is a yellow liquid with a sharp odor. Its composition was determined on the basis of the mass-spectrometric and analytical data which showed the ratio of chlorine to sulfur atoms to be 2:1. The ^{13}C NMR spectrum of **IV** contained signals from three quaternary carbon atoms. Molecule **IV** contains two asymmetric carbon atoms, which implies the existence of diastereoisomers. In fact, two sets of signals belonging to *AB* spin systems of two stereoisomers were observed in the ^{19}F NMR spectrum, but one of these prevailed considerably (isomer ratio 95:5).

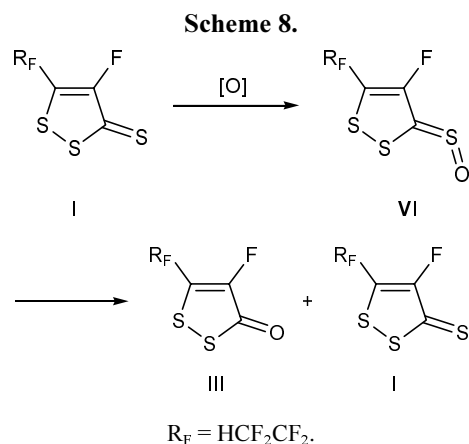
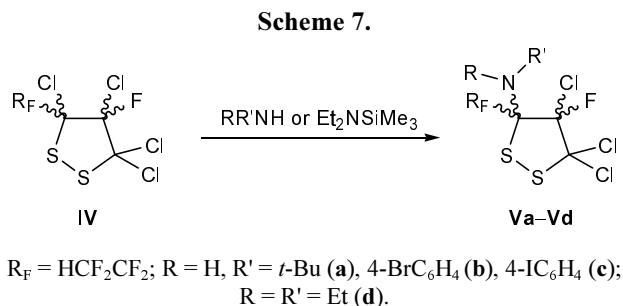
We failed to obtain compound **IV** with high selectivity by chlorination of 1,2-dithiole-3-thione with excess chlorine. The ^{19}F NMR spectrum of the reaction mixture revealed the presence of at least five products (compound **IV** among them); however, none of the components was isolated and identified. No reaction occurred between compound **I** and thionyl chloride or oxalyl chloride.

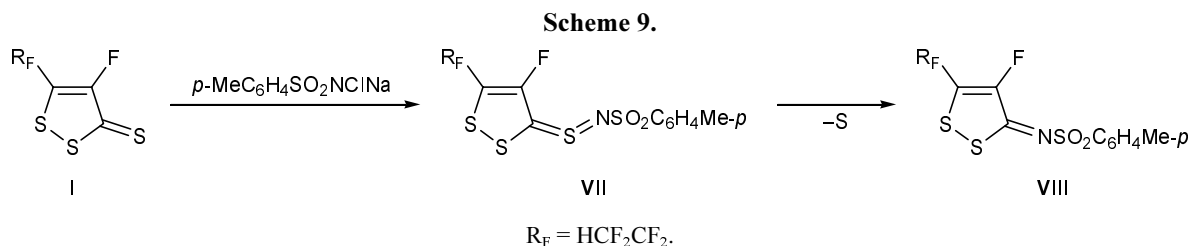
Tetrachlorodithiolane **IV** smoothly reacted with *tert*-butylamine to afford product of replacement of only one chlorine atom by the amine residue. Comparison of the ^{13}C NMR spectra of the initial compound and reaction product showed that the chemical

shift of C^5 changed most strongly (the C^5 signal is readily identified due to the presence of two $^2J_{\text{CF}}$ coupling constants). The difference in the C^5 chemical shifts attains 10 ppm, while the positions of the other carbon signals change within 1–2 ppm. Therefore, we presumed that substitution of chlorine occurs at the 5-position to give compound **Va** (Scheme 7).

Compound **IV** reacted in a similar way with aromatic amines; as a result, the corresponding 5-aryl-amino derivatives **Vb** and **Vc** were obtained. According to the NMR data, the reaction mixtures contained two stereoisomeric products at the same ratio as that found for initial tetrachlorodithiolane **IV**. After purification, it was difficult to identify the minor isomer because of its small concentration. Dithiolane **IV** also reacted with secondary amines. However, in the reaction with diethylamine, the corresponding monosubstitution product (compound **Vd**) was detected only by spectral data. Attempts to isolate it by column chromatography on silica gel led to formation of a mixture of several compounds containing (according to the ^{19}F NMR data) no desired amino derivative **Vd**. It should also be noted that our attempts to replace more than one chlorine atom in molecule **IV** by amino groups using excess *tert*-butylamine or diethyl(trimethylsilyl)amine were unsuccessful. Analysis of the reaction mixtures by ^{19}F NMR spectroscopy showed the presence of only compounds **Va** and **Vd**, respectively, even after heating in boiling benzene for 1 h.

1,2-Dithiole-3-thione **I** is readily oxidized to the corresponding *S*-oxide **VI** with *m*-chloroperoxybenzoic acid in methylene chloride (Scheme 8). The product is formed as a single isomer; in keeping with published data for structurally related compounds [11], *S*-oxide **VI** is likely to have *Z* configuration. Compound **VI** is a bright red crystalline substance, which is stable in





solution in inert solvents. On storage over a period of 48 h, crystalline *S*-oxide **VI** undergoes disproportionation to give 90% of 1,2-dithiol-3-one **III** and 10% of thione **I**; this transformation is typical of such compounds [2, 12].

1,2-Dithiole-3-thione (**I**) also undergoes oxidative imination. The reaction of **I** with Chloramine-T in methanol at -50°C yields sulfimide **VII** as a bright red crystalline substance which is stable in the crystalline state. Compound **VII** in solution eliminates sulfur to give imine **VIII** (Scheme 9). The latter is formed directly from compound **I** when the reaction with Chloramine-T is carried out at room temperature. On the whole, elimination of sulfur is typical of sulfimides like **VII** [13].

S-Oxide **VI** gave no cycloaddition products with dimethylbutadiene, ethoxyethene, and dimethyl acetylenedicarboxylate. Likewise, compound **VII** did not react with the same dienophiles at -50°C , while it decomposed to imine **VIII** at higher temperature.

EXPERIMENTAL

The NMR spectra were recorded on a Varian VXR-300 spectrometer at 299.943 (^1H), 282.203 (^{19}F), and 75.429 MHz (^{13}C) using chloroform-*d* and acetone-*d*₆ as solvents. The chemical shifts were referenced to TMS (internal, ^1H and ^{13}C) or C₆F₆ (internal, ^{19}F , $\delta_{\text{F}} -162.9$ ppm). The mass spectra (70 eV, electron impact) were run on an MKh-1321 instrument. The IR spectra were obtained on a UR-20 spectrometer. Silica gel 60 (40–63 μm , Merck) was used for column chromatography. The progress of reactions was monitored by ^{19}F NMR spectroscopy. Solvents were purified and dehydrated by standard procedures.

X-Ray analysis of a single crystal of 4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiol-3-one (III). The X-ray diffraction data were acquired from a $0.41 \times 0.56 \times 0.66$ -mm single crystal at room temperature on an Enraf-Nonius CAD-4 automatic four-circle diffractometer (CuK α irradiation, $\lambda = 1.54178$ Å, scan rate ratio $2\theta/\omega = 1.2$, $\theta_{\text{max}} = 70^{\circ}$, spherical segment $-2 \leq$

$h \leq 18$, $-2 \leq k \leq 12$, $-2 \leq l \leq 6$). Insofar as compound **III** is volatile, its crystals were placed in thin-walled Pyrex capillaries under argon. Total of 1763 reflections were measured, 835 of which were symmetry-independent. Rhombic crystals with the following unit cell parameters: $a = 14.830(4)$, $b = 10.126(2)$, $c = 5.243(4)$ Å; $V = 787.9(6)$ Å³; M 236.2; $Z = 4$; $d_{\text{calc}} = 1.99$ g/cm³; $\mu = 67.0$ cm⁻¹; $F(000) = 464.0$; space group *Pna*2₁ (no. 33). The structure was solved by the direct method and was refined by the least-squares procedure in full-matrix anisotropic approximation using CRYSTALS software package [14]. In the refinement procedure, 593 reflections with $I > 2\sigma(I)$ were used (118 refined parameters, 5.02 reflections per parameter). The H⁵ atom was localized from the geometry considerations and was included in the refinement procedure with fixed positional and thermal parameters. Chebyshev's weight scheme [15] was utilized with the following three parameters: 15.2, -7.3, and -12.5. The final divergence factors were $R = 0.059$ and $R_w = 0.066$; GOF = 1.061; residual electron density from the Fourier difference series 0.48 and -0.32 e/Å³. Absorption by the crystal was taken into account by azimuthal scanning [16]. The absolute configuration of the crystalline structure of **III** was determined according to Flack [17]; the enantiopole parameter was refined to 0.03(7) from 854 reflections with unaveraged Friedel mates. The complete set of crystallographic data for compound **III** was deposited to the Cambridge Crystallographic Data Center (entry no. CCDC 254055).

3-Chloro-4-fluorosulfanyl-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiolium chloride (II). A solution of 2 mmol of chlorine or sulfuryl chloride in 5 ml of methylene chloride was added dropwise under stirring to a solution of 0.5 g (2 mmol) of compound **I** in 10 ml of methylene chloride. After 30 min, the solvent was separated by decanting, and the precipitate was washed with 2 ml of methylene chloride and dried under reduced pressure (10–15 mm). The product was brought into further syntheses without additional purification. Yield 0.58 g (90%), mp 147–150°C (in a sealed capillary). ^1H NMR spectrum (acetone-*d*₆), δ , ppm: 6.78 t.t

(1H, HCF₂, ²J_{HF} = 52.2, ³J_{HF} = 3.8 Hz). ¹⁹F NMR spectrum (acetone-*d*₆), δ_F, ppm: -110.92 m (2F, CF₂), -114.04 br.s (1F, 4-F), -134.95 d.m (2F, HCF₂, ²J_{HF} = 52.2 Hz). Found, %: Cl 22.05; S 29.56. C₅HCl₂F₅S₃. Calculated, %: Cl 21.94; S 29.77.

Reaction of salt II with triethylamine. Triethylamine, 0.14 ml (1.0 mmol), was added under stirring to a solution of 100 mg of (0.31 mmol) of salt II in 2 ml of tetrahydrofuran, and the mixture immediately turned red. After 10 min, 5 ml of 10% hydrochloric acid and 5 ml of diethyl ether were added, and the organic layer was separated, washed with 3 ml of water, dried over Na₂SO₄, filtered, and evaporated. The residue was recrystallized from petroleum ether to obtain 68 mg (87%) of 1,2-dithiole-3-thione I.

4-Fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiole-3-one (III). *a.* A solution of 0.89 ml (0.011 mol) of SO₂Cl₂ in 3 ml of glacial acetic acid was added dropwise under stirring to a solution of 2.52 g (0.01 mol) of compound I in 10 ml of glacial acetic acid. After 20–25 min, the mixture was neutralized with a saturated aqueous solution of NaHCO₃ and extracted with chloroform (2×15 ml). The extracts were combined, dried over Na₂SO₄, filtered, and evaporated, and the residue was dried under reduced pressure (10–15 mm) without heating. Yield 2.12 g (95%).

b. A solution of 2.52 g (0.01 mol) of compound I in 3 ml of benzene was slowly added under stirring to 3.82 g (0.012 mol) of Hg(CH₃COO)₂ in 10 ml of glacial acetic acid. The mixture was heated for 6 h under reflux, neutralized with a saturated solution of NaHCO₃, and extracted with diethyl ether (2×15 ml), the extracts were combined, dried over Na₂SO₄, filtered, and evaporated, and the residue was dried under reduced pressure (10–15 mm) without heating. Yield 2.19 g (93%).

Colorless crystals, mp 29–30°C (from a small amount of hexane). IR spectrum (KBr), ν, cm⁻¹: 1040, 1115, 1230, 1330 (CF); 1670 (C=O); 2990 (CH). ¹H NMR spectrum (CDCl₃), δ, ppm: 6.09 t.t.d (1H, HCF₂, ²J_{HF} = 53.3, ³J_{HF} = 3.0, ⁵J_{HF} = 1.1 Hz). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 109.03 t.t.d (HCF₂, J_{CF} = 252.5, ²J_{CF} = 38.5, ⁴J_{CF} = 2.2 Hz), 113.21 t.t.d (CF₂, J_{CF} = 254.8, ²J_{CF} = 31.1, ³J_{CF} = 4.3 Hz), 134.56 t.d (C⁵, ²J_{CF} = 30.0, 16.0 Hz), 149.2 d.t (C⁴, J_{CF} = 284.6, ³J_{CF} = 4.2 Hz), 181.52 d (C=O, ²J_{CF} = 24.6 Hz). ¹⁹F NMR spectrum (CDCl₃), δ_F, ppm: -112.89 m (2F, CF₂), -125.15 quint (1F, 4-F), -135.32 d.m (2F, HCF₂, ²J_{HF} = 53.3 Hz). Mass spectrum, *m/z* (*I*_{rel}, %): 236 (94) [M]⁺, 185 (11) [M - HCF₂]⁺, 157 (16) [M - HCF₂ -

CO]⁺, 64 (100) [S₂]⁺. Found, %: C 25.13; H 0.48; S 27.52. C₅HF₅OS₂. Calculated, %: C 25.43; H 0.43; S 27.15.

3,3,4,5-Tetrachloro-4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiolane (IV). Sulfuryl chloride, 9.7 ml (0.12 mol), was added to a solution of 5.05 g (0.02 mol) of compound I in 5 ml of chloroform. After 1 h, the solvent and excess chlorinating agent were removed under reduced pressure (10–15 mm), 20 ml of chloroform was added to the residue, the mixture was washed with 15 ml of a saturated solution of NaHCO₃ and 10 ml of water, dried over Na₂SO₄, filtered, and evaporated, and the residue was distilled under reduced pressure. Yield 6.44 g (89%), yellowish liquid with a sharp odor, bp 58–60°C (0.06 mm). IR spectrum, ν, cm⁻¹: 650, 745 (C–Cl); 1020, 1115, 1145, 1245 (C–F).

Major isomer (95%). ¹H NMR spectrum (CDCl₃), δ, ppm: 6.30 t.d.d (1H, HCF₂, ²J_{HF} = 51.3, ³J_{HF} = 8.9, 1.8 Hz). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 67.86 t.d (C⁵, ²J_{CF} = 25.7, 24.6 Hz), 91.56 d.d (C³, ²J_{CF} = 27.8, ⁴J_{CF} = 2.9 Hz), 109.74 d.d.d.d (HCF₂, J_{CF} = 258.2, 249.5, ²J_{CF} = 34.2, 28.9 Hz), 114.41 d.d.d.d (CF₂, J_{CF} = 269.7, 264.2, ²J_{CF} = 27.8, 24.6 Hz), 117.31 d (C⁴, J_{CF} = 294.4 Hz). ¹⁹F NMR spectrum (CDCl₃), δ_F, ppm: -99.22 d.d (1F, 4-F, ⁴J_{FF} = 39.7, 18.3 Hz), -112.88 d.d.d.d (1F, CF_AF_B, J_{AB} = 276.5, ⁴J_{FF} = 39.7, ³J_{FF} = 10.6, 9.2, ³J_{HF} = 8.9 Hz), -113.98 d.d.d (1F, CF_AF_B, J_{AB} = 276.5, ⁴J_{FF} = 18.3, ³J_{FF} = 12.2 Hz), -134.89 d.d.d (1F, HCF_AF_B, J_{AB} = 304.8, ²J_{HF} = 51.3, ³J_{FF} = 9.2 Hz), -140.12 d.d.t (1F, HCF_AF_B, J_{AB} = 304.8, ²J_{HF} = 51.3, ³J_{FF} = 12.2 Hz).

Minor isomer (5%). ¹H NMR spectrum (CDCl₃), δ, ppm: 6.23 t.d.d (1H, HCF₂, ²J_{HF} = 52.3, ³J_{HF} = 7.9, 3.5 Hz). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 80.62 q (C⁵, ²J_{CF} = 26.5 Hz), 98.02 d (C³, ²J_{CF} = 28.3 Hz), 109.23 t.t.m (HCF₂, J_{CF} = 256.4, ²J_{CF} = 34.2 Hz), 114.21 t.d.d (CF₂, J_{CF} = 268.0, ²J_{CF} = 27.8, 24.2 Hz), 120.66 d (C⁴, J_{CF} = 266.0 Hz). ¹⁹F NMR spectrum (CDCl₃), δ_F, ppm: -98.44 t (1F, 4-F, ⁴J_{FF} = 30.9 Hz), -114.37 d.d.m (1F, CF_AF_B, J_{AB} = 266.6, ³J_{FF} = 27.3 Hz), -115.87 d.d.d (1F, CF_AF_B, J_{AB} = 266.6, ⁴J_{FF} = 30.9, ³J_{FF} = 10.2 Hz), -130.14 d.d.d (1F, HCF_AF_B, J_{AB} = 299.3, ²J_{HF} = 52.3, ³J_{FF} = 10.2 Hz), -140.12 d.d.t (1F, HCF_AF_B, J_{AB} = 299.3, ²J_{HF} = 52.3, ³J_{FF} = 7.0 Hz). Mass spectrum, *m/z* (*I*_{rel}, %): 360 (8) [M]⁺, 325 (7) [M - Cl]⁺, 293 (10) [M - Cl - S]⁺, 145 (100) [HCF₂CF₂CS]⁺, 31 (71) [CF]⁺. Found, %: Cl 38.70; S 18.24. C₅HCl₄F₅S₂. Calculated, %: Cl 39.18; S 17.72.

Reaction of 3,3,4,5-tetrachloro-4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiolane (IV) with amines (general procedure). A solution of 4.1 mmol of

amine in 2 ml of diethyl ether was added under stirring at room temperature to a solution of 0.50 g (2 mmol) of compound **IV** in 10 ml of diethyl ether. The progress of reactions was monitored by ^{19}F NMR spectroscopy, following disappearance of signals belonging to the initial compound. The precipitate of amine hydrochloride was filtered off, and the filtrate was washed with water (2×15 ml), dried over Na_2SO_4 , and evaporated under reduced pressure. The residue was purified as described below.

5-tert-Butylamino-3,3,4-trichloro-4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiolane (Va). Reaction time 1 h. The product was isolated by vacuum distillation. A fraction boiling in the range from 72 to 78°C (0.03 mm) was collected. Yield 0.68 g (86%), red liquid with a specific odor. ^1H NMR spectrum (CDCl_3), δ , ppm: 6.31 t.d.d (1H, HCF_2 , $^2J_{\text{HF}} = 52.4$, $^3J_{\text{HF}} = 7.7$, 4.0 Hz), 3.04 s (1H, NH), 1.19 s (9H, *t*-Bu). ^{13}C NMR spectrum (CDCl_3), δ_{C} , ppm: 30.07 s (CH_3), 55.34 s (CCH_3), 76.15 t.d (C^5 , $^2J_{\text{CF}} = 23.6$, 20.4 Hz), 92.00 d (C^3 , $^2J_{\text{CF}} = 27.8$ Hz), 109.71 d.d.d.d (HCF_2 , $J_{\text{CF}} = 257.9$, 254.7, $^2J_{\text{CF}} = 34.3$, 32.1 Hz), 115.10 d.d.d.d (CF_2 , $J_{\text{CF}} = 266.5$, 256.0, $^2J_{\text{CF}} = 28.0$, 25.6 Hz), 115.98 d.d (C^4 , $J_{\text{CF}} = 295.2$, $^3J_{\text{CF}} = 4.3$ Hz). ^{19}F NMR spectrum (CDCl_3), δ_{F} , ppm: -91.58 d.t (1F, 4-F, $^4J_{\text{FF}} = 36.7$, 18.3 Hz), -111.50 d.d (1F, CF_AF_B , $J_{AB} = 272.6$, $^4J_{\text{FF}} = 36.7$ Hz), -113.69 d.t (1F, CF_AF_B , $J_{AB} = 272.6$, $^3J_{\text{FF}} = 14.0$ Hz), -134.40 d.d.d.d (1F, HCF_AF_B , $J_{AB} = 302.8$, $^2J_{\text{HF}} = 52.4$, $^3J_{\text{FF}} = 18.3$, 14.0 Hz), -136.96 d.d.m (1F, HCF_AF_B , $J_{AB} = 302.8$, $^2J_{\text{HF}} = 52.4$ Hz). Mass spectrum, m/z (I_{rel} , %): 399 (14) [M] $^+$, 342 (14) [$M - \text{C}_4\text{H}_9$] $^+$, 145 (78) [$\text{HCF}_2\text{CF}_2\text{CS}$] $^+$, 57 (100) [C_4H_9] $^+$. Found, %: Cl 26.15; N 3.47; S 15.89. $\text{C}_9\text{H}_{11}\text{Cl}_3\text{F}_5\text{NS}_2$. Calculated, %: Cl 26.68; N 3.51; S 16.09.

5-*p*-Bromophenylamino-3,3,4-trichloro-4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiolane (Vb). Reaction time 24 h. The product was isolated by extraction from the residue with boiling hexane (2×15 ml). The extracts were combined and evaporated, and the residue was dried under reduced pressure (10–15 mm). Yield 0.67 g (68%), reddish viscous oily substance with a specific odor. ^1H NMR spectrum (CDCl_3), δ , ppm: 7.36 and 6.94 (4H, H_{arom}), 6.17 t.t (1H, HCF_2 , $^2J_{\text{HF}} = 52.8$, $^3J_{\text{HF}} = 5.5$ Hz), 5.32 s (1H, NH). ^{19}F NMR spectrum (CDCl_3), δ_{F} , ppm: -94.52 t (1F, 4-F, $^4J_{\text{FF}} = 24.2$ Hz), -111.42 d.m (1F, CF_AF_B , $J_{AB} = 278.5$ Hz), -112.69 d.m (1F, CF_AF_B , $J_{AB} = 278.5$ Hz), -133.84 d.d (1F, HCF_AF_B , $J_{AB} = 304.3$, $^2J_{\text{HF}} = 52.8$ Hz), -135.78 d.d (1F, HCF_AF_B , $J_{AB} = 304.3$, $^2J_{\text{HF}} = 52.8$ Hz). Mass spectrum, m/z (I_{rel} , %): 498 (16) [M] $^+$, 342 (12) [$M - \text{C}_6\text{H}_4\text{Br}$] $^+$, 171 (100) [$\text{NHC}_6\text{H}_4\text{Br}$] $^+$, 145 (10)

[$\text{HCF}_2\text{CF}_2\text{CS}$] $^+$. Found, %: Br+Cl 37.15; N 2.76; S 12.68. $\text{C}_{11}\text{H}_6\text{BrCl}_3\text{F}_5\text{NS}_2$. Calculated, %: Br+Cl 37.44; N 2.82; S 12.89.

3,3,4-Trichloro-4-fluoro-5-*p*-iodophenylamino-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiolane (Vc). Reaction time 7 days. The product was isolated by column chromatography on silica gel using hexane–chloroform (1:1) as eluent, R_f 0.78 (Silufol UV-254; development with iodine vapor). Yield 0.7 g (65%), dark red oily substance with a specific odor. ^1H NMR spectrum (CDCl_3), δ , ppm: 7.55 and 6.95 (4H, H_{arom}), 6.17 t.t (1H, HCF_2 , $^2J_{\text{HF}} = 52.8$, $^3J_{\text{HF}} = 5.5$ Hz), 5.31 s (1H, NH). ^{19}F NMR spectrum (CDCl_3), δ_{F} , ppm: -94.31 s (1F, 4-F), -111.37 d.d (1F, CF_AF_B , $J_{AB} = 282.4$, $^3J_{\text{FF}} = 34.7$ Hz), -113.11 d (1F, CF_AF_B , $J_{AB} = 282.4$ Hz), -133.02 d.d (1F, HCF_AF_B , $J_{AB} = 303.8$, $^2J_{\text{HF}} = 52.8$ Hz), -135.86 d.d (1F, HCF_AF_B , $J_{AB} = 303.8$, $^2J_{\text{HF}} = 52.8$ Hz). Mass spectrum, m/z (I_{rel} , %): 543 (15) [M] $^+$, 250 (100) [$M - \text{C}_6\text{H}_4\text{I} - \text{HF} - 2\text{Cl}$] $^+$, 218 (27) [$\text{NHC}_6\text{H}_4\text{I}$] $^+$, 145 (8) [$\text{HCF}_2\text{CF}_2\text{CS}$] $^+$. Found, %: Cl+I 42.45; N 2.61; S 11.59. $\text{C}_{11}\text{H}_6\text{Cl}_3\text{F}_5\text{INS}_2$. Calculated, %: Cl+I 42.83; N 2.57; S 11.78.

3,3,4-Trichloro-5-diethylamino-4-fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiolane (Vd). Reaction time 4 h. Compound **Vd** was extracted from the residue with hexane (2×15 ml); the extracts were combined and evaporated, and the residue was dried under reduced pressure (10–15). The product was a reddish viscous oily substance with a specific odor, which decomposed on attempted purification by chromatography on silica gel. ^1H NMR spectrum (CDCl_3), δ , ppm: 6.11 t.t (1H, HCF_2 , $^2J_{\text{HF}} = 52.6$, $^3J_{\text{HF}} = 5.4$ Hz), 2.73 m (4H, CH_2), 1.11 m (6H, CH_3). ^{19}F NMR spectrum (CDCl_3), δ_{F} , ppm: -92.86 d.t (1F, 4-F, $^4J_{\text{FF}} = 36.6$, 16.4 Hz), -112.03 d.d.t (1F, CF, $J_{\text{FF}} = 273.7$, $^4J_{\text{FF}} = 36.6$, $^3J_{\text{FF}} = 7.9$ Hz), -113.63 d.t (1F, CF, $J_{\text{FF}} = 273.7$, $^3J_{\text{FF}} = 11.9$ Hz), -133.40 d.d.d.d (1F, HCF, $J_{\text{FF}} = 301.5$, $^2J_{\text{HF}} = 52.6$, $^4J_{\text{FF}} = 16.4$, $^3J_{\text{FF}} = 7.9$ Hz), -137.27 d.d.d (1F, HCF, $J_{\text{FF}} = 301.5$, $^2J_{\text{HF}} = 52.6$, $^3J_{\text{FF}} = 11.9$ Hz).

4-Fluoro-5-(1,1,2,2-tetrafluoroethyl)-1,2-dithiole-3-thione S-oxide (VI). Compound **I**, 0.5 g (2 mmol), was dissolved in 10 ml of methylene chloride, and 0.54 g of 70% *m*-chloroperoxybenzoic acid was added under stirring. After 24 h, the precipitate was filtered off, 10 ml of a saturated aqueous solution of sodium hydrogen carbonate was added to the filtrate, and the mixture was vigorously stirred for 4 h. The organic layer was separated, washed with 15 ml of water, dried over Na_2SO_4 , and evaporated, and the residue was dried under reduced pressure (10–15 mm) and recryst-

tallized from hexane. Yield 0.45 g (85%), long red needles, mp 83–84°C. ¹H NMR spectrum (CDCl₃), δ, ppm: 6.05 t.t (1H, HCF₂, ²J_{HF} = 53.5, ³J_{HF} = 2.3 Hz). ¹⁹F NMR spectrum (CDCl₃), δ_F, ppm: –107.91 m (2F, CF₂), –114.13 m (1F, 4-F), –133.82 d.m (2F, HCF₂, ²J_{HF} = 53.5 Hz). Found, %: C 22.39; H 0.38; S 35.86. C₅H₅OS₃. Calculated, %: C 22.28; H 0.36; S 35.62.

N-[4-Fluoro-5-(1,1,2,2-tetrafluoroethyl)-3H-1,2-dithiol-3-ylidene-λ⁴-sulfanylidene]-4-methylbenzenesulfonamide (VII). A solution of 0.2 g (0.8 mmol) of compound I in 5 ml of anhydrous methanol was added to a solution of 0.35 g (1.43 mmol) of Chloramine-T [preliminarily dried at 40°C under reduced pressure (oil pump)] in 10 ml of anhydrous methanol, cooled to –50°C. The mixture was stirred for 0.5 h at that temperature and allowed to warm up to room temperature, and the precipitate was filtered off, washed with 10 ml of water, dried under reduced pressure (oil pump), and recrystallized from chloroform. Yield 0.3 g (89%), mp 124–127°C. ¹H NMR spectrum (CDCl₃), δ, ppm: 7.82 and 7.27 (4H, H_{arom}), 6.08 t (1H, HCF₂, ²J_{HF} = 53.5 Hz), 2.40 s (3H, CH₃). ¹⁹F NMR spectrum (CDCl₃), δ_F, ppm: –108.92 m (2F, CF₂), –112.37 m (1F, 4-F), –134.28 d (2F, HCF₂, ²J_{HF} = 53.5 Hz). Found, %: N 3.38; S 29.98. C₁₂H₈F₅NO₂S₄. Calculated, %: N 3.32; S 30.42.

N-[4-Fluoro-5-(1,1,2,2-tetrafluoroethyl)-3H-1,2-dithiol-3-ylidene]-4-methylbenzenesulfonamide (VIII). A solution of 0.2 g (0.8 mmol) of compound I in 5 ml of methylene chloride was added to a suspension of 0.35 g (1.43 mmol) of Chloramine-T [preliminarily dried at 40°C under reduced pressure (oil pump)] in 10 ml of methylene chloride. The mixture was stirred for 2 h, 15 ml of a 0.1 M solution of sodium hydroxide was added, and the mixture was vigorously stirred for 2 h. The organic phase was separated, washed with water (2×20 ml), dried over Na₂SO₄, and evaporated under reduced pressure, and the residue was recrystallized from chloroform. Yield 0.28 g (92%), mp 148–150°C. ¹H NMR spectrum (CDCl₃), δ, ppm: 7.87 and 7.34 (4H, H_{arom}), 6.08 t.d (1H, HCF₂, ²J_{HF} = 53.2, ³J_{HF} = 2.6 Hz), 2.44 s (3H, CH₃). ¹³C NMR spectrum (CDCl₃), δ_C, ppm: 169.24 d (C=N, ²J_{CF} = 15.0 Hz), 150.91 d.t (C⁴, J_{CF} = 280.2, ³J_{CF} = 4.3 Hz), 145.82 (Cⁱ), 137.75 (C^p), 134.66 t.d (C⁵, ²J_{CF} = 29.6, 15.0 Hz), 130.75 (C^m), 127.81 (C^o), 114.39 t.t.d (CF₂, J_{CF} = 253.4, ²J_{CF} = 30.0, ³J_{CF} = 4.1 Hz), 110.24 t.t.d (HCF₂, J_{CF} = 251.4, ²J_{CF} = 37.0, ³J_{CF} = 2.2 Hz), 21.56 s (CH₃). ¹⁹F NMR spectrum (CDCl₃), δ, ppm: –109.51 m (2F, CF₂), –113.59 quint

(1F, 4-F), –134.18 d.m (2F, HCF₂, ²J_{HF} = 53.2 Hz). Mass spectrum, *m/z* (*I*_{rel}, %): 389 (12) [*M*]⁺, 155 (68) [SO₂C₆H₄CH₃]⁺, 91 (100) [C₆H₄CH₃]⁺. Found, %: N 3.68; S 24.02. C₁₂H₈F₅NO₂S₃. Calculated, %: N 3.60; S 24.70.

REFERENCES

1. Pedersen, C.T., *Adv. Heterocycl. Chem.*, 1982, vol. 31, p. 63.
2. Pedersen, C.T., *Sulfur Rep.*, 1995, p. 173.
3. Bobrov, M.B., Saloutin, V.I., and Pashkevich, K.I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, p. 879; Pashkevich, K.I., Saloutin, V.I., and Bobrov, M.B., *Sulfur Lett.*, 1987, p. 93; Krokhalev, V.M., Saloutin, V.I., and Pashkevich, K.I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, p. 2266; Hodgson, R.L. and Smutny, E.J., US Patent no. 3394146, 1968; *Chem. Abstr.*, 1968, p. 67362n.
4. Timoshenko, V.M., Bouillon, J.-P., Shermolovich, Yu.G., and Portella, C., *Tetrahedron Lett.*, 2002, vol. 43, p. 5809.
5. Vasil'eva, T.P., Lin'kova, M.G., and Kil'disheva, O.V., *Usp. Khim.*, 1976, vol. 45, p. 1269.
6. Landis, P.S., *Chem. Rev.*, 1965, vol. 65, p. 237.
7. Faust, J. and Mayer, R., *Justus Liebigs Ann. Chem.*, 1965, vol. 688, p. 150.
8. Sosnovsky, G. and Krogh, J.A., *Justus Liebigs Ann. Chem.*, 1982, p. 121.
9. Barriga, S., Konstantinova, L.S., Marcos, C.F., and Rakitin, O.A., *J. Chem. Soc., Perkin Trans. 1*, 1999, p. 2237; Chin Hsuan Wei, *Acta Crystallogr., Sect. C*, 1985, vol. 41, p. 1525; Mogensen, P.K., Simonsen, O., and Wainwright, C.E., *Acta Crystallogr., Sect. C*, 1991, vol. 47, p. 1905.
10. Vasil'eva, T.P., Lin'kova, M.G., Kil'disheva, O.V., and Knunyants, I.L., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, p. 643.
11. Behringer, H. and Meinetsberger, E., *Phosphorus Sulfur*, 1981, vol. 12, p. 115.
12. Perez, M.A. and Kresze, G., *Justus Liebigs Ann. Chem.*, 1981, p. 1510.
13. Markovskii, L.N., Timoshenko, V.M., and Shermolovich, Yu.G., *Russ. J. Org. Chem.*, 1995, vol. 31, p. 139.
14. Watkin, D.J., Prout, C.K., Carruthers, J.R., and Bette-ridge, P.W., *CRYSTALS, Issue 10*, Oxford: Chemical Crystallography Laboratory, Univ. of Oxford, 1996.
15. Carruthers, J.R. and Watkin, D.J., *Acta Crystallogr., Sect. A*, 1979, vol. 35, p. 698.
16. North, A.C.T., Phillips, D.C., and Mathews, F.S., *Acta Crystallogr., Sect. A*, 1968, vol. 24, p. 351.
17. Flack, H.D., *Acta Crystallogr., Sect. A*, 1983, vol. 39, p. 876.