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REACTIONS OF POLYHALOPYRIDINES. 16*. SYNTHESIS AND REACTIONS OF 2,3,5,6-TETRAFLUORO-4-PERFLUORO-ALKYLTHIOPYRIDINES

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*Identical reaction products, viz. 2,3,5,6-tetrafluoro-4-perfluoroalkylthiopyridines **3a-c**, were obtained on thermal decomposition of Xe(II) bisperfluoroalkylcarboxylates in the presence of mercapto-tetrafluoropyridine and bis(2,3,5,6-tetrafluoro-4-pyridyl) disulfide. Compounds **3a-c** readily interact with N-, O-, and S-containing nucleophiles, though with the first two types of reactant only with substitution of fluorine atoms in position 2 of the pyridine ring. In the latter case products are obtained both with retention of the perfluoroalkylthio group on interaction with sodium N,N-dimethyldithiocarbamate, and with total fission of that group in the case of alkali metal methanethiolate and toluenethiolate.*

Keywords: 2,3,5,6-tetrafluoro-4-perfluoroalkylthiopyridines, perfluoroalkylation of heterocyclic thiols and disulfides, nucleophilic substitution reactions.

In preliminary communications we have described the perfluoroalkylation of 4-mercapto-tetrafluoropyridine (**1**) and bis(2,3,5,6-tetrafluoro-4-pyridyl) disulfide (**2**) in the presence of bisperfluoroalkylcarboxylates of divalent xenon with the formation in both cases of identical reaction products, the 2,3,5,6-tetrafluoro-4-perfluoroalkylthiopyridines **3a-c** [2,3]. In general perfluoroalkylation occurs on thermal decomposition of the xenon compounds in the presence of thio derivatives **1** and **2**. Generation of bisperfluoroalkylcarboxylates of xenon is effected either previously (method A) or *in situ* (method B) (see Experimental). The reaction of compound **3b** with a series of nucleophilic reagents was carried out previously with the aim of studying the possibilities of this class of synthons for the synthesis of new preparations containing "superlipophilic" perfluoroalkylthio groups, which may be of considerable interest for subsequent application in pharmaceutics and agrochemistry [4].

An investigation (by TLC) has been carried out in the present work of the perfluoroalkylation of compounds **1** and **2**, and it has been established that the formation of perfluoroalkylthio derivatives **3a-c** occurs only from disulfide **2**, though the latter is generated in the reaction mixture from thiol **1** in the presence of bisperfluoroalkylxenonates obtained from 1 equiv. XeF_2 (Scheme 1). Subsequent addition of a further 2-3 equiv. of this reagent provides complete conversion into the expected compounds **3a-c**. As starting materials it is

* For Part 15 see [1].

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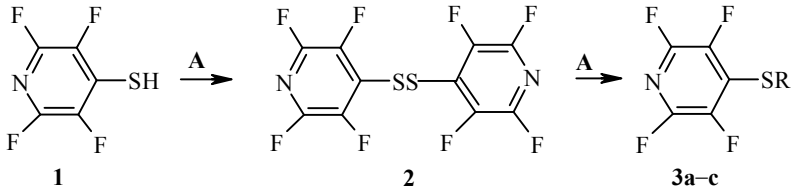
therefore possible to use both tetrafluoropyridinethiols and disulfides for this process. Methods A and B are equivalent, since the yields of the desired compounds **3a-c** are comparable, which is linked with the high solubility of the initial reactants **1** and **2** both in CH_2Cl_2 and in the perfluorocarboxylic acids. In the course of the syntheses by methods A and B the fluoro homologs **3a-c** were obtained in 41-52% yield, which is somewhat less than for 4-SCF_3-2,3,5,6-tetrafluoropyridine, synthesized previously by the interaction of trifluoromethylthiolate anion (generated previously from difluorothiophosgene and fluoride anion) with pentafluoropyridine [5]. However the advantage of the method proposed by us for the synthesis of compounds **3a-c** is its universal nature, and the possibility of obtaining a series of fluoro homologs starting from a set of standard reactants and manipulations.

Compounds **3a-c** are colorless liquids, which are characterized in the ^{19}F NMR spectra, in addition to the signals of the perfluoroalkyl groups, by the presence of two multiplets at δ -130 and -86 ppm belonging to the 3, 5 and 2, 6 fluorine atoms respectively. A stable molecular ion is observed in the mass spectra of these compounds but the main directions of mass spectral breakdown of the latter are fission of fluorine atoms, perfluoroalkyl groups, and the $CSCF_2$ fragment.

Scheme 1



1 **2** **3a–c**

3 a R = CF_3, **b** R = C_2F_5, **c** R = C_3F_7; **A** = $(RCOO)_2Xe$

The perfluoroalkylation of compound **1** may be represented as follows.

$$RSSR + (R_FCOO)_2Xe \longrightarrow RSSR^{\bullet+} + (R_FCOO)_2Xe^{\bullet-}$$

$$(R_FCOO)_2Xe^{\bullet-} \longrightarrow R_FCOO^{\bullet} + R_FCOO^{-} + Xe$$

$$R_FCOO^{\bullet} \longrightarrow R_F^{\bullet} + CO_2$$

$$RSSR^{\bullet+} \longrightarrow RS^{\bullet} + RS^{+}$$

$$RS^{\bullet} + R_F^{\bullet} \longrightarrow RSR_F$$

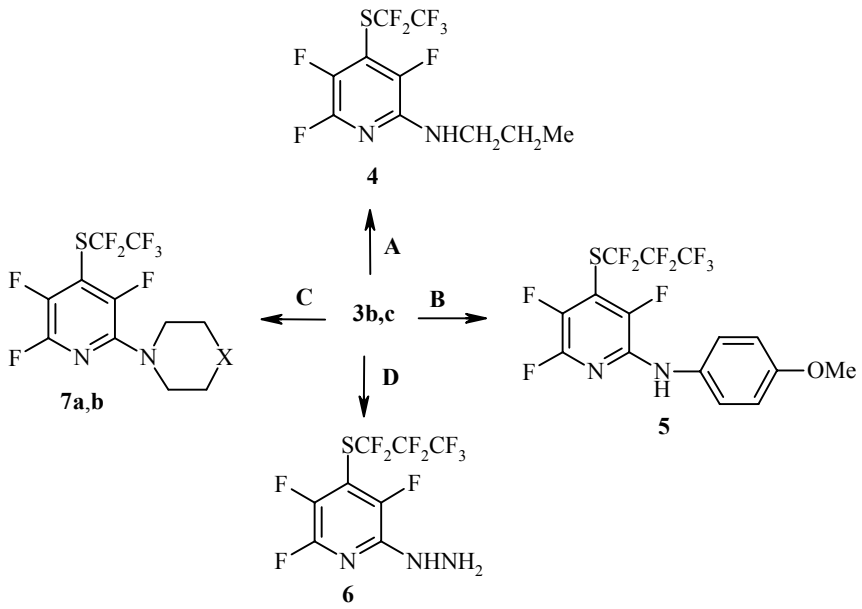
R = 2,3,5,6-tetrafluoro-4-pyridyl, $R_F = C_nF_{2n+1}$ (at n = 1-3)

The reaction may be initiated by transfer of an electron from the disulfide RSSR to the xenon bisperfluoroalkylcarboxylate molecule with the formation of a radical cation and an radical anion [6]. The latter is converted into a mixture of perfluoroalkyl radical, perfluoroalkanoate, carbon dioxide and xenon and the radical cation may decompose to two particles RS· and RS^+. Recombination of the RS· and R_F· radicals leads to the formation of the expected derivatives **3a-c**.

Compounds **3a-c** contain several mobile fluorine atoms in the pyridine ring which must display high reactivity in relation to various nucleophilic reagents. It was shown previously that in the presence of N- (aliphatic amines, cyclic secondary amines) and O- (methylate and phenolate anion) containing nucleophiles

the fluorine atom in position 2 is replaced preferentially [7]. In addition, the ready substitution of a SR (SCF_3, SC_2F_5) group in position 4 of pyridines **3a,b** by methylthio and phenylthio fragments was discovered in reactions with sulfur-containing reagents, such as sodium methanethiolate and potassium thiophenolate [4,6]. The reactivity of the fluorine homologs **3b** and **3c** in relation to a series of N- and S-containing nucleophilic reagents has been studied in the present work, in order to determine both the synthetic possibilities once again of the obtained synthons, and also the prospects for the synthesis of new compounds with potential biological activity containing "superlipophilic" perfluoroalkylthio groups.

Scheme 2

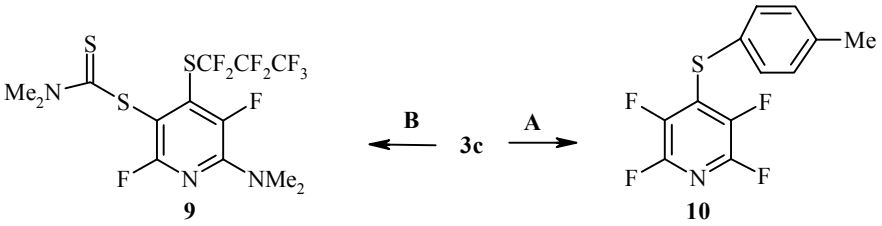


7 a X = CH_2, **b** X = O; **a C** = piperidine, **b C** = morpholine; **A** = $PrNH_2$; **B** = 4-anisidine, **D** = hydrazine hydrate

It was established that the reaction of compounds **3b** and **3c** with various N-nucleophilic reagents, such as propylamine, *p*-anisidine, hydrazine hydrate, piperidine, and morpholine (see Scheme 2), proceeds preferentially with the substitution of the fluorine atom at position 2 of the pyridine ring. Compounds, the formation of which is linked with the partial cleavage of perfluoroalkyl groups and is characteristic of the chlorine-containing analogs [8], are present in the reaction mixtures only in insignificant amounts. Compounds **4-6** and **7a,b** are characterized in their ^{19}F NMR spectra by the presence of signals of perfluoroalkyl groups, by the presence of three signals of different intensity at δ -150, -130, and -90 ppm belonging to the 5-, 3-, and 6-F fluorine atoms respectively. Intense molecular ions were observed in the mass spectra, which may decompose with cleavage of fluorine, perfluoralkyl radicals, and are also characterized by the presence of fragments linked with decomposition of the substituent in position 2.

In difference to the chloropyridine analogs [8], the pentafluoropropylthio group was retained on interaction of compound **3c** with such sulfur-containing nucleophile as sodium N,N-dimethyldithiocarbamate with the formation of compound **9**, the product of disubstitution at positions 2 and 5 of the pyridine ring (see Scheme 3). These results confirm the higher reactivity of the pyridine fluorine atoms in compounds **3a-c** in nucleophilic reactions compared with the analogous chlorine atoms, which points in favor of the occurrence of such a process of substitution in the heteroaromatic nucleus, in which fission of the bond with the leaving group does not occur at the rate determining stage. The role of the latter in this case leads to stabilization of the nascent anion due to the inductive effect, which has a maximum value for fluorine atoms in the halogen series [9].

Scheme 3

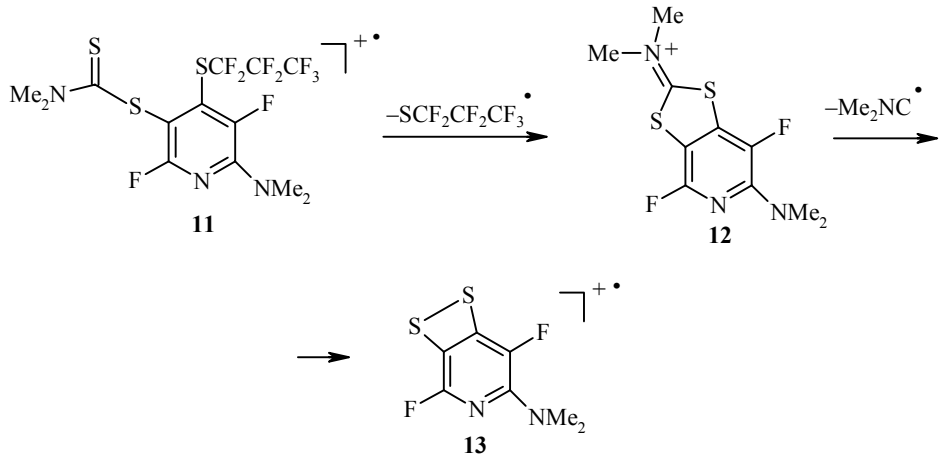


A = TolylS$^-$K$^+$/CH_3CN; **B** = $Me_2N(C{=}S)S^-Na^+\cdot 2H_2O$

The formation of disubstitution products at the pyridine ring on interaction of sodium N,N-dimethyldithiocarbamate with pentafluoropyridine and tetrafluoroisonicotinonitrile was observed previously [11]. It was also found that the dithiocarbamate group in position 2 readily sheds a molecule of CS_2 from the intermediate zwitterion [12], as a result of which an N,N-dimethylamino group is generated. In the ^{19}F NMR spectrum of compound **9**, together with three signals of the heptafluoropropyl group, two doublets are present for fluorine atoms located in positions 3 and 6 of the pyridine ring, in the *para* position relative to each other, at δ -120.98 and -61.32 ppm respectively with coupling constants $^5J_{3\text{-},6\text{-F}}$ and $^5J_{6\text{-},3\text{-F}}$ equal to 26.8 Hz. In the ^{13}C NMR spectrum the signals of the pyridine carbon atoms at positions 3 and 6 linked to the fluorine atoms are displayed at δ 146.82 ppm as a doublet of doublets with $J_{3\text{-C},3\text{-F}}$ = 254.0, $^4J_{3\text{-C},6\text{-F}}$ = 3.5 Hz and δ 157.86 ppm as a doublet with $J_{6\text{-C},6\text{-F}}$ = 234.7 Hz respectively. The methyl protons of the dimethylamino group are displayed as two singlets at 3.25 and 3.26 ppm in the ^1H NMR spectrum, and the carbon atoms at 39.9 and 40.0 ppm in the ^{13}C NMR spectrum. The N,N-dimethyldithiocarbamate group is detected by the presence in the ^1H and ^{13}C NMR spectra by a pair of singlets for the methyl groups at δ 3.54, 3.55 ppm and 41.9, 46.0 ppm respectively, and also by a signal of the carbon atom of the thiocarbonyl group at δ 195.5 ppm. The disposition of the dithiocarbamate and dimethylamino groups in the pyridine nucleus was demonstrated by analysis of the results of the mass spectral breakdown of compound **9** under electron impact. A relatively intense ion with *m/z* 276 is present in the mass spectrum of this compound, the formation of which may be linked with elimination of the heptafluoropropylthio fragment adjacent to the dithiocarbamate group from the molecular ion **11** and by the formation of the bicyclic ion **12**, which then loses a Me_2NC fragment and is converted into ion **13** (see Scheme 4). The process described is characteristic of the mass spectral breakdown of N,N-dimethyl-dithiocarbamate derivatives of polychloropyridines [12], for which extreme instability was detected for the molecular ions and exceedingly ready cleavage of the Cl atom adjacent to the dithiocarbamate group, but was not detected for the polyfluoropyridine analogs. The presence of stable molecular ions is characteristic of the latter, the decomposition of which is not linked with initial cleavage of a fluorine atom and subsequent heterocyclization [13]. The presence of the dithiocarbamate group at position 5 of the pyridine ring in compound **9** is therefore confirmed because of the ready cleavage of the heptafluoropropylthio radical as a result of intramolecular heterocyclization in the molecular ion. In the case of α-fluoro-substituted dithiocarbamate a similar process should be less probable.

As in the cases of methanethiolate and benzenethiolate [5,7] the toluenethiolate anion selectively replaces the pentafluoropropylthio group in compound **3c** with the formation of 4-(*p*-tolylthio)tetrafluoropyridine (**10**), which is then converted with an excess of reagent into the product of disubstitution at positions 2 and 4. Such a difference in the direction of the substitution process for compounds **3a-c** depending on the nature of the nucleophilic reagent may be interpreted within the framework of the HSAB principle [9], according to which the reaction of such a "soft" nucleophile as, for example, toluenethiolate anion with the "softer" leaving heptafluoropropylthio group is preferred.

Scheme 4



Signals for the heptafluoropropyl group are absent from the ^{19}F NMR spectrum of compound **10**, but a pair of multiplets for fluorine atoms is observed at -137.41 and -91.18 ppm belonging to 3-, 5- and 2-, 6-F respectively. In addition the molecular ion peak $[M]^+$ 273, I_{rel} 100% is present in the mass spectrum of compound **10**.

EXPERIMENTAL

Column chromatography was carried out on silica gel 60, 230-400 mesh (Merck) and TLC on silica gel 60 F254 (Merck) plates. The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ on Bruker AM-360 (360 MHz) or Bruker AM-500 (500 MHz) spectrometers. Internal standard was TMS or $CFCl_3$. The IR spectra were recorded on BioRad FTS-40 FT-IR and Specord M-80 instruments. Chromato-mass spectrometric analysis was carried out with a Hewlett-Packard 5890 GLC mass spectrometer (70 eV) using a capillary column (30 m) coated with HP 1 oil. The high resolution mass spectra were recorded on a VG Autospec mass spectrometer.

Perfluoroalkylation of Thiol 1 and Disulfide 2 (General Procedure). A. The initial disulfide or thiol (2.7 mmol) was added with stirring to a mixture prepared at -20°C from XeF_2 (1.4 g, 8.2 mmol), perfluoroalkylcarboxylic acid (1.2-1.8 ml, 16.4 mmol), and CH_2Cl_2 (30 ml). The reaction mixture was stirred with spontaneous heating to +5°C.

B. Xenon difluoride (1.4 g, 8.2 mmol) was added with stirring at 30°C to a mixture of the initial disulfide or thiol (2.74 mmol) in perfluoroalkylcarboxylic acid (4.2-6.0 ml, 54.8 mmol). The end of the reaction was determined in both cases by the end of gas evolution. The reaction mixture obtained by methods A or B was neutralized with Na_2CO_3 solution, extracted with chloroform, the extract was dried over Na_2SO_4, and evaporated in vacuum. The residue was chromatographed on silica gel, the eluent being light petroleum ether of bp 40-70°C.

2,3,5,6-Tetrafluoro-4-trifluoromethylthiopyridine (3a). Yield 41%, colorless oil. The ^{19}F NMR spectrum corresponded to that published previously in [2]. Mass spectrum, *m/z* (*I*, %): 251 (6) $[M]^+$, 232 (2) $[M-F]^+$, 163 (2) $[M-F-CF_3]^+$, 138 (4) $[M-F-CSCF_2]^+$, 93 (5) $[M-F-CSCF_2-NCF]^+$, 87 (7) $[M-F-CF_3-NCFCF]^+$, 69 (100) $[CF_3]^+$, 68 (33), 67 (7), 63 (6). Found: *m/z* 250.9638 $[M]^+$. C_6F_7NS. Calculated: M = 250.9640.

2,3,5,6-Tetrafluoro-4-pentafluoroethylthiopyridine (3b). Yield 40% of colorless oil. The ^{19}F NMR spectrum corresponded to that published previously in [2]. Mass spectrum, *m/z* (*I*, %): 301 (4) $[M]^+$, 232 (14) $[M-F]^+$, 138 (10) $[M-F-CSCF_2]^+$, 93 (13) $[M-F-CSCF_2-NCF]^+$, 87 (18) $[M-F-CF_3-NCFCF]^+$, 69 (100) $[CF_3]^+$, 68 (18), 63 (45). Found: *m/z* 301.9612 $[M]^+$. C_7F_9NS. Calculated: M = 301.9608.

2,3,5,6-Tetrafluoro-4-heptafluoropropylthiopyridine (3c). Yield 52% of colorless oil. The ^{19}F NMR spectrum corresponded to that published previously in [2]. Mass spectrum, *m/z* (*I*, %): 351 (1) $[M]^+$, 232 (11) $[M\text{-}C_2F_5]^+$, 138 (6) $[M\text{-}F\text{-}CSCF_2]^+$, 93 (9) $[M\text{-}F\text{-}CSCF_2\text{-}NCF]^+$, 87 (6) $[M\text{-}F\text{-}CF_3\text{-}NCFCF]^+$, 69 (100) $[CF_3]^+$, 68 (27), 63 (14) $[SCF]^+$. Found: *m/z* 350.9581 $[M]^+$. $C_8F_{11}NS$. Calculated: M = 350.9576.

Interaction of Compounds 3b,c with Nitrogen-containing Nucleophiles (General Procedure). A solution of nucleophile (5 mmol) in methanol (10 ml) was added at 20°C with stirring to a solution of compound **3b** (2.28 mmol) in methanol (10 ml). The end of the reaction was determined by the disappearance of the starting material according to TLC. The solvent was removed in vacuum, the residue was washed with water, and extracted with benzene. The extract was dried with anhydrous Na_2SO_4. The solvent was evaporated, and the residue was chromatographed on a column of silica gel with benzene as eluent.

3,5,6-Trifluoro-4-heptafluoropropylthio-2-hydrazinopyridine (6). Yield 89% of light-brown crystals; mp 80-81°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.82 (2H, br. s, NH_2); 6.28 (1H, br. s, NH). ^{19}F NMR spectrum, δ, ppm (*J*, Hz): -148.84 (1F, q, $J_{5\text{-},6\text{-}F}$ = 18.0, 5-F); -134.36 (1F, q, $J_{3\text{-},6\text{-}F}$ = 30.1, 3-F); -124.38 (2F, s, CF_2); -91.54 (1F, q, $J_{6\text{-},5\text{-}F}$ = 24.0, 6-F); -86.06 (2F, s, SCF_2); -80.58 (3F, q, *J* = 6.0, CF_3). IR spectrum (KBr), ν, cm^{-1}: 3344, 3304, 3264 (NH, NH_2). Mass spectrum, *m/z* (*I*, %): 363 (100) $[M]^+$, 346 (1) $[M\text{-}NH_3]^+$, 344 (2) $[M\text{-}F]^+$, 244 (1) $[M\text{-}C_2F_5]^+$, 225 (1) $[M\text{-}C_2H_5\text{-}F]^+$, 194 (20) $[M\text{-}C_3F_7]^+$, 177 (9) $[M\text{-}C_3F_7\text{-}NH_3]^+$, 150 (32) $[CF_2{=}CF\text{-}CF_3]^+$, 69 (34) $[CF_3]^+$. Found: *m/z* 362.9897 $[M]^+$. $C_8H_3F_{10}N_3S$. Calculated: M = 362.9888.

3,5,6-Trifluoro-4-(heptafluoropropylthio-2-(4-methoxyphenylamino)pyridine (11). Yield 75% of light-yellow crystals; mp 78-79°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.83 (3H, s, OMe); 6.52 (1H, br. s, NH); 6.93 (2H, q, *J* = 9.2, Ar); 7.46 (2H, q, *J* = 9.2, Ar). ^{19}F NMR spectrum, δ, ppm (*J*, Hz): -147.37 (1F, q, $J_{5\text{-},6\text{-}F}$ = 18.0, 5-F); -132.64 (1F, q, $J_{3\text{-},6\text{-}F}$ = 30.7, 3-F); -124.13 (2F, s, CF_2); -89.73 (1F, qq, $J_{6\text{-},5\text{-}F}$ = 23.7, $J_{6\text{-},3\text{-}F}$ = 30.5, 6-F); -85.85 (2F, s, SCF_2); -80.33 (3F, t, *J* = 9.8, CF_3). IR spectrum (KBr), ν, cm^{-1}: 3350 (NH). Mass spectrum, *m/z* (*I*, %): 454 (100) $[M]^+$, 439 (56) $[M\text{-}CH_3]^+$, 285 (14) $[M\text{-}C_3F_7]^+$, 270 (50) $[M\text{-}CH_3\text{-}C_3F_7]^+$, 253 (10) $[M\text{-}SC_3F_7]^+$, 242 (11) $[270\text{-}CO]^+$, 241 (16) $[270\text{-}HCO]^+$, 238 (4) $[M\text{-}CH_3\text{-}SC_3F_7]^+$, 209 (7) $[238\text{-}HCO]^+$, 69 (22) $[CF_3]^+$. Found: *m/z* 454.0232 $[M]^+$. $C_{15}H_8F_{10}N_2OS$. Calculated: M = 454.0198.

3,5,6-Trifluoro-4-pentafluoroethylthio-2-propylaminopyridine ($C_{10}H_8F_8N_2S$) (12). Yield 82% of a colorless oil. The data of ^1H and ^{19}F NMR spectra in $CDCl_3$ and also of the mass spectrum corresponded to those published previously in [7].

3,5,6-Trifluoro-4-pentafluoroethylthio-2-piperidylpyridine ($C_{12}H_{10}F_8N_2S$) (7a). Yield 88% of a colorless oil. The data of ^1H and ^{19}F NMR spectra in $CDCl_3$ and also of the mass spectrum corresponded to those published previously in [7].

3,5,6-Trifluoro-2-morpholinyl-4-pentafluoroethylthiopyridine ($C_{11}H_8F_8N_2OS$) (7b). Yield 86% of a colorless oil. The data of ^1H and ^{19}F NMR spectra in $CDCl_3$ and also of the mass spectrum corresponded to those published previously in [7].

Interaction of Compound 3c with Potassium *p*-Tolylthiolate. A solution of potassium *p*-tolylthiolate (0.2 g, 1.23 mmol) in CH_3CN (10 ml) was added dropwise at 20°C with stirring to compound **3c** (0.4 g, 1.14 mmol) dissolved in CH_3CN (6 ml). The stirring was continued for 1 h. The solvent was distilled off, and the residue chromatographed on a column of silica gel. Eluent benzene–heptane, 1:1. One reaction product, compound **10**, was isolated.

2,3,5,6-Tetrafluoro-4-(4-tolylthio)pyridine (10). Yield 61% of white crystals; mp 42-43°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.38 (3H, s, CH_3); 7.18 (2H, q, *J* = 8.0, Ar); 7.44 (2H, q, *J* = 8.0, Ar). ^{19}F NMR spectrum, δ, ppm: -137.41 (m, 3-, 5-F); -91.18 (m, 2-, 6-F). Mass spectrum, *m/z* (*I*, %): 273 (100) $[M]^+$, 258 (22) $[M\text{-}CH_3]^+$, 254 (12) $[M\text{-}F]^+$, 253 (14) $[M\text{-}HF]^+$, 239 (6) $[M\text{-}CH_3\text{-}F]^+$, 220 (5) $[M\text{-}CH_3\text{-}2F]^+$, 123 (6) $[TolylS]^+$, 91 (60) $[Tolyl]^+$, 65 (38) $[Tolyl\text{-}C_2H_2]^+$, 63 (16) $[Tolyl\text{-}C_2H_4]^+$. Found: *m/z* 273.0229 $[M]^+$. $C_{12}H_7F_4NS$. Calculated: M = 273.0235.

(2-Dimethylamino-3,6-difluoro-4-heptafluoropropylthio-5-pyridyl)-N,N-dimethyldithiocarbamate (9). Sodium N,N-dimethyldithiocarbamate dihydrate (0.4 g, 2.2 mmol) in acetone (10 ml) was added at 20°C with stirring to a solution of compound **3b** (0.35 g, 1.0 mmol) in acetone (10 ml). The reaction mixture acquired a yellow-brown color. Stirring was continued for 1 h. The solvent was then removed in vacuum, the residue was washed with water, extracted with chloroform, and the extract dried. The solid residue after removing the solvent was recrystallized from methanol. Light-brown crystals (0.4 g, 83%) were obtained; mp 68-69°C. ^{1}H NMR spectrum, δ, ppm: 3.25 (s); 3.26 (6H, s, NMe_2); 3.54 (s); 3.55 (6H, s, $SC(=S)NMe_2$). ^{19}F NMR spectrum, δ, ppm (*J*, Hz): -124.31 (2F, s, CF_2); -120.98 (1F, q, $J_{3-,6-F}$ = 26.8, 3-F); -86.26 (2F, br. s, SCF_2); -80.15 (3F, t, *J* = 9.2, CF_3); -61.32 (1F, q, $J_{6-,3-F}$ = 26.8, 6-F). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 39.9 (s); 40.0 (s, NMe_2); 41.9 (s); 46.0 (s, $C(=S)NMe_2$); 103.0-125.0 (m, $SCF_2CF_2CF_3$, 4-C); 130.2 (q, $J_{5-C,6-F}$ = 18.6, 5-C); 146.8 (qq, $J_{3-C,3-F}$ = 254.0, $J_{3-C,6-F}$ = 3.5, 3-C); 149.0 (qq, $J_{2-C,6-F}$ = 12.4, $J_{2-C,3-F}$ = 18.1, 2-C); 157.9 (q, $J_{6-C,6-F}$ = 234.7, 6-C); 195.5 (s, C=S). Mass spectrum, *m/z* (*I*, %): 477 (2) $[M]^+$, 308 (1) $[M-C_3F_7]^+$, 276 (6) $[M-SC_3F_7]^+$, 220 (2) $[M-SC_3F_7-Me_2NC]^+$, 191 (2), 88 (100) $[Me_2NCS]^+$. Found: *m/z* 477.0066 $[M]^+$. $C_{13}H_{12}F_9N_3S_3$. Calculated: M = 477.0050.

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