Synthesis and reactivity of fluorine-containing thiols and thioacyl halides

A. Yu. Sizov, A. N. Kovregin, R. N. Serdyuk, M. V. Vorob´ev, V. A. Porosyatnikov, A. A. Tsvetkov, D. O. Korneev, and A. F. Ermolov*

S. K. Timoshenko Military Academy of Radiation, Chemical, and Biological Defence, 13 per. Brigadirskii, 105005 Moscow, Russian Federation.
E-mail: covy@list.ru

A route to α-hydropolyfluoroalkanethiols and polyfluorothioacyl halides *via* thermal splitting of benzyl polyfluoroalkyl sulfides under the action of phosphorus pentoxide was proposed. The thiols obtained were used as starting materials for the synthesis of α-hydropolyfluoroalkanesulfenyl chlorides. The properties of the resulting F,S-containing compounds were studied.

Key words: benzyl polyfluoroalkyl sulfides, α-hydropolyfluoroalkanethiols, polyfluorothioacyl halides, α-hydropolyfluoroalkanesulfenyl chlorides, thermal splitting, phosphorus pentoxide.

Modern development of organofluorosulfur chemistry is closely related to development of new methods for the synthesis of structurally simple reagents capable of various transformations. In recent years, considerable attention has been given to the creation of F,S-containing synthons, in particular, by decomposition of sulfides containing easily leaving (*e.g.*, benzyl) groups. For instance, splitting of α-chloro- or α-bromo-containing benzyl polyfluoroethyl sulfides under the action of TiF_4 or $TiCl_4$ affords polyfluorinated thioacetyl chlorides (bromides).[1] α,β-Unsaturated benzyl polyfluoroalkenyl sulfides in the presence of strong acids such as H_2SO_4 and HSO_3F) give α,β-unsaturated thiols,[2] which in the case of α-fluoro-containing sulfides isomerize into α-hydro thioyl fluorides.[3]

Previously,[4] we have found that P_2O_5 can serve as an acidic splitting agent. In the case of benzyl perfluoroisobutenyl sulfide, the product (α-hydrohexafluoroisobutyrothioyl fluoride) is the same as in the splitting with fluorosulfonic acid, while the reaction with *tert*-butyl 1,3,3,3-tetrafluoro-2-methoxycarbonylpropenyl sulfide gives trifluoromethyl(methoxycarbonyl)thioketene resulting from dehydrofluorination of the corresponding acid fluoride. The present work was devoted to a further development of the method of thermal splitting of fluorinated benzyl sulfides in the presence of P_2O_5 with the aim of obtaining various F,S-containing reagents.

Results and Discussion

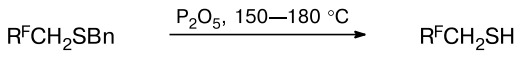
We studied benzyl α,α-dihydro-, α-hydro-, α-chloro-α-hydro-, α,α-difluoro-, α,α-dichloro-, and α,β-unsaturated α-fluoroalkyl sulfides, which in turn are precursors of polyfluorinated thiols, thioacyl halides, and sulfenyl chlorides.

Synthesis of α-hydropolyfluoroalkanethiols

α-Hydropolyfluoroalkanethiols are poorly studied, mainly because preparative access to these compounds is difficult. The major drawbacks of the known[5—7] routes to them include use of not easily accessible starting reagents, labor- and energy-consuming processes, and explosion hazard.

We developed a new method for the synthesis of these compounds. Our method involves splitting of benzyl 1,1-dihydropolyfluoroalkyl sulfides on heating with a two- or threefold molar excess of P_2O_5 (Scheme 1). According to this method, we obtained thiols **1**—**3** with primary polyfluoroalkyl groups in 80—95% yields.

Scheme 1



1—3

R^F = CF_3 (**1**), $H(CF_2)_2$ (**2**), $H(CF_2)_4$ (**3**)

The reaction mixtures were heated at 180 °C until low-boiling compounds ceased to evolve. The resulting products (>95% purity) require no additional purification. With less than two equivalents of P_2O_5, the yield of the product decreased. However, use of more than a three-

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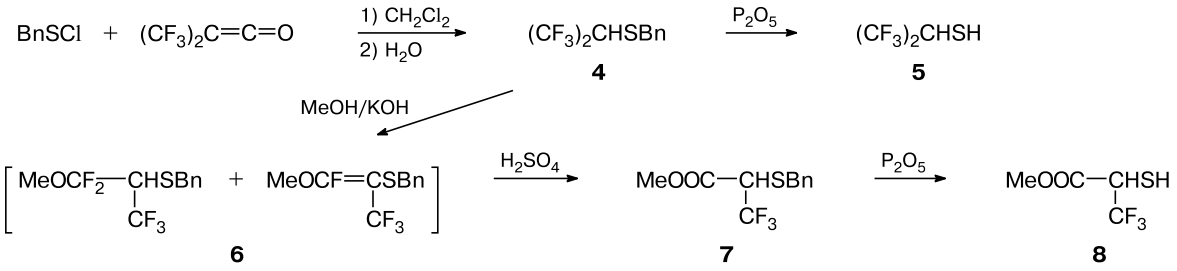
Scheme 2



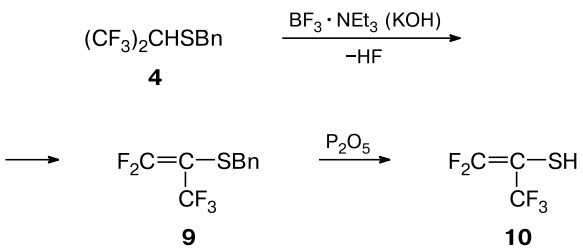
fold excess of P_2O_5 was not effective and therefore is inexpedient. We selected this temperature range because the reaction does not occur below 150 °C and should be accelerated at the final step by heating to 180 °C. The starting benzyl sulfides were prepared from polyfluoroalkyl tosylates easily accessible from commercial fluorinated alcohols.

Analogous reactions of sulfides containing secondary polyfluoroalkyl groups gave thiols **5** and **8** (Scheme 2). The starting sulfide **4** was prepared by addition of benzylsulfenyl chloride to bis(trifluoromethyl)ketene (by analogy with reactions with other sulfenyl chlorides[8,9]) followed by hydrolysis and decarboxylation. Benzyl sulfide **7** was prepared by a reaction of sulfide **4** with KOH in methanol, which yielded a mixture of addition and substitution products **6**, followed by mild acid hydrolysis. The conditions of the hydrolysis should be thoroughly met because of possible cleavage of the S—Bn bond.

Apparently, the decomposition mechanism of benzyl sulfides in heating with P_2O_5 is essentially the same as decomposition by protic acids. Two possible versions of the mechanism can be advanced. The first involves protonation of the S atom, protons coming from impurities of polyphosphoric acids in P_2O_5. It is also not improbable that such reactions start with the formation of sulfide salts with P_2O_5 as the Lewis acid, which is accompanied by insertion of P_2O_5 into the S—Bn bond, as in its reactions with ethers.[10]

Decomposition of benzyl sulfides to thiols in the presence of P_2O_5 proved to be effective for the synthesis of α,β-unsaturated thiol **10** obtained from benzyl pentafluoropropen-2-yl sulfide **9** (Scheme 3).

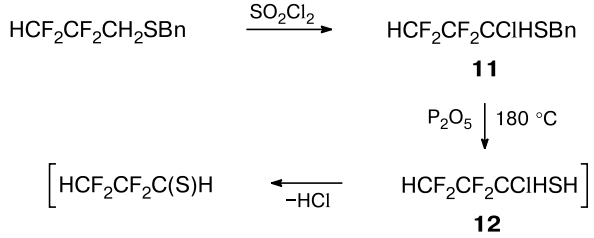
Scheme 3



Pentafluoropropene-2-thiol **10** is stable and does not isomerize into the corresponding thioketone under normal conditions, in contrast to its oxygen analog pentafluoropropen-2-ol, which on heating or in solvents easily changes into pentafluoroacetone.[11] We failed to detect pentafluorothioacetone in [4+2] cycloaddition reactions with cyclopentadiene in solutions (also in base-catalyzed reactions).

Nor was an attempted synthesis of 1-chloro-2,2,3,3-tetrafluoropropanethiol (**12**) by heating of benzyl 1-chloro-2,2,3,3-tetrafluoropropyl sulfide (**11**) with P_2O_5 successful (Scheme 4). Apparently, thiol **12** easily undergoes dehydrochlorination to give unstable, *in situ* polymerizable thioaldehyde.

Scheme 4



The starting sulfide **11** for this reaction was prepared by chlorination of benzyl 2,2,3,3-tetrafluoropropyl sulfide with an equimolar amount of sulfuryl chloride.

Thus, the developed method for the synthesis of polyfluoroalkanethiols can be undoubtedly extended to the preparation of some compounds of this class but is not suitable for thiols containing halogen atoms in the α-positions.

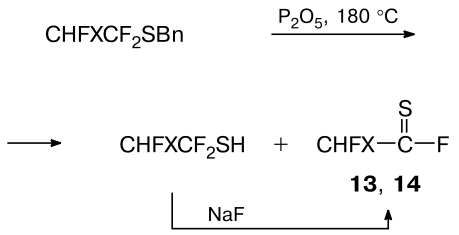
Synthesis of polyfluoroalkanethioyl halides

We found that saturated benzyl polyfluoroalkyl sulfides containing an α,α-dihalomethylene group decompose on heating with P_2O_5 to give thioyl halides.

For instance, thioacetyl fluorides **13** and **14** were obtained from α,α-difluoro-containing sulfides (Scheme 5). The reaction conditions were the same as for the decom-

position of benzyl sulfides with the α-methylene group. Small amounts of thiols were obtained as by-products. The target fluorides were purified from them by passing the vapor of the mixture over NaF.

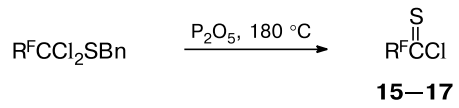
Scheme 5



X = F (**13**), Cl (**14**)

Heating of benzyl 1,1-dichloropolyfluoroalkyl sulfides with P_2O_5 proved to be a convenient laboratory route to polyfluorothioacyl chlorides (Scheme 6). Using this method, we obtained thioacyl chlorides **15**—**17** in up to 90% yields.

Scheme 6



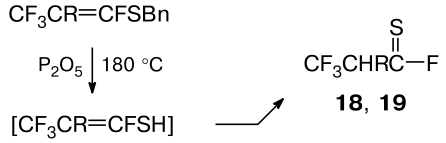
R^F = CF_3 (**15**), $H(CF_2)_2$ (**16**), $H(CF_2)_4$ (**17**)

The reactions were also carried out while heating the reaction mixture to 150 °C and then raising the temperature to 180 °C to complete the process, with simultaneous removal of the product. The resulting thioacyl chlorides **15**—**17** (≥95% purity) can be used without additional purification for subsequent transformations. The absence of even traces of thiols among the products of this reaction suggests that 1,1-dichloro thiols are less stable than 1,1-difluoro analogs.

The method we proposed have some advantages over the literature ones. For instance, we found that the decomposition of benzyl 1,1-dichloro-2,2,3,3-tetrafluoropropyl sulfide with $TiCl_4$ under the conditions specified in Ref. 1 gives thioacyl chloride **16** in 57% yield. It should be emphasized that such a yield was reached only with small amounts of reagents (10 mmol). Otherwise, the process was difficult to control (vigorous exothermic reaction with the formation of large amounts of gaseous and low-boiling destruction products, which substantially lowers the yield of the target product). According to our method, a mixture of reagents prepared by shaking them in a closed flask can be stored for a long period of time and used in portions and the decomposition can be stopped at any instant by turning the heating off and then resumed.

We extended our method proposed earlier[4] for the decomposition of α,β-unsaturated benzyl polyfluoroalkenyl sulfides by heating with P_2O_5, which affords α-hydro thioacyl fluorides, to the synthesis of acid fluorides **18** and **19** (Scheme 7).

Scheme 7



R = F (**18**), H (**19**)

Obviously, as in other cases of acid-catalyzed decomposition of benzyl polyfluoroalkenyl sulfides, the reaction proceeds through the formation of thiols followed by migration of the thiol proton to the β-carbon atom.

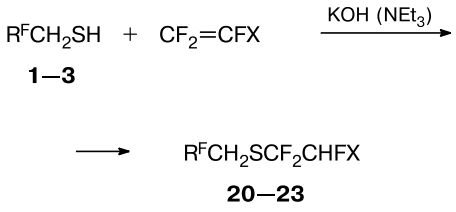
Thioacyl halides **13**—**17** are dark red liquids (unlike less intensely colored, yellowish red thioacyl fluorides **18** and **19**), have a characteristic pungent odor, slightly fume in air, and do not dimerize, at least in several hours.

Properties of the compounds obtained

The F,S-containing compounds obtained are highly reactive and can be used in various transformations.

For instance, thiols **1**—**3** easily add to tetrafluoro- and chloro(trifluoro)ethenes to give sulfides **20**—**23** (Scheme 8). Reactions are carried out in DMF and catalyzed by bases (triethylamine or KOH), giving exclusively addition products in high yields.

Scheme 8

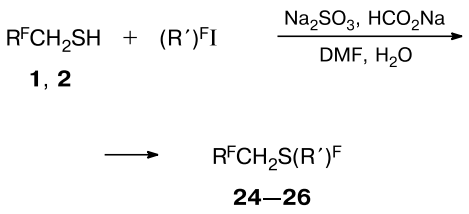


R^F = CF_3, X = F (**20**); R^F = $H(CF_2)_2$, X = F (**21**), Cl (**22**); R^F = $H(CF_2)_4$, X = F (**23**)

Alkylation of thiols **1** and **2** with perfluoroalkyl iodides under the conditions for the formation of the sulfoxylate radical anion[12] (Scheme 9) afforded the target sulfides **24**—**26** in satisfactory yields (up to 50%).

The reaction was carried out at room temperature in aqueous DMF. The radical anion $SO_3^{\bullet -}$ was generated with a mixture of sodium formate and sodium sulfite. In

Scheme 9



$R^F = CF_3$, $(R')^F = C_3F_7$ (**24**); $R^F = H(CF_2)_2$, $(R')^F = C_2F_5$ (**25**); $R^F = H(CF_2)_2$, $(R')^F = C_3F_7$ (**26**)

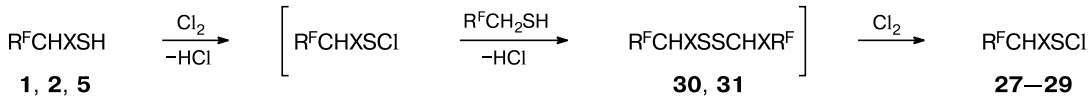
the absence of the sulfoxylate radical anion, no alkylation products were detected.

α-Hydropolyfluoroalkanethiols are known[6] to be efficient precursors of α-hydropolyfluoroalkanesulfenyl chlorides. However, a common method for the synthesis of sulfenyl chlorides by chlorinolysis of appropriate benzyl sulfides is unsuitable for α-hydro compounds, because the reaction begins with chlorination at the α-position.[13] Our method for the synthesis of α-hydropolyfluoroalkanethiols makes it possible to obtain and study such compounds. For instance, chlorination of thiols **1**, **2**, and **5** with elemental chlorine in halogen-containing solvents at room temperature gave the corresponding α-hydro sulfenyl chlorides **27**—**29** in up to 70% yields (Scheme 10).

Like halogenation of nonfluorinated thiols, this reaction proceeds in three steps through intermediate disulfides. The amount of chlorine and the reaction duration are decisive for the nature of reaction products. For instance, with a slight excess of chlorine and immediate isolation upon the mixing of the reagents, disulfides were obtained as the major products; in the case of compounds **30** and **31**, they were isolated by fractionation. In contrast, keeping of a reaction mixture with a large excess of chlorine for several hours gave considerable amounts of products with the chlorinated methylene group. The best results in the synthesis of sulfenyl chlorides **27**—**29** were attained with an approximately double excess of chlorine and a reaction time of 1—1.5 h. Various halogen-containing hydrocarbon solvents can be used; however, for isolation purposes, it proved to be most convenient to use tetrachloroethane for sulfenyl chlorides **27** and **29** and dichloromethane for sulfenyl chloride **28**.

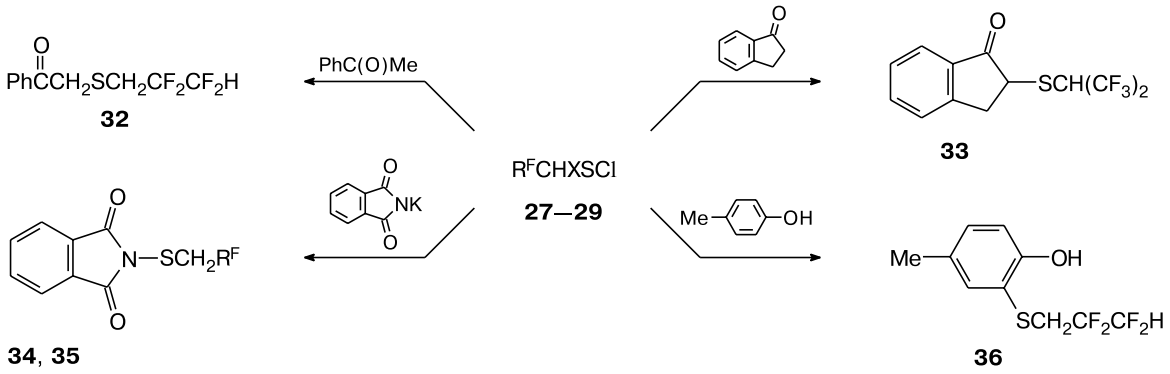
The reactivities of sulfenyl chlorides **27**—**29** were studied in some reactions. They easily sulfenylated CH acids: *e.g.*, sulfenyl chloride **28** reacted with acetophenone to give phenacyl sulfide **32**, while a reaction of sulfenyl chloride **29** with indan-1-one yielded product **33** (Scheme 11). In the former reaction, the final mixture contained a small amount of the disubstitution product (^{1}H NMR data), which was removed by fractionation. Reactions of sulfenyl chlorides **27** and **28** with potassium phthalimide gave the corresponding sulfenamides **34** and **35**, respectively. As expected, α-hydro sulfenyl chlorides are more reactive than perhalogenated analogs. For instance, sulfenyl chloride **28** reacted with *p*-cresol at the *ortho*-position even at room temperature to give sulfide **36**, while for such reac-

Scheme 10



$R^F = CF_3$, X = H (**27**, **30**); $R^F = H(CF_2)_2$ (**28**, **31**); $R^F = X = CF_3$ (**29**)

Scheme 11



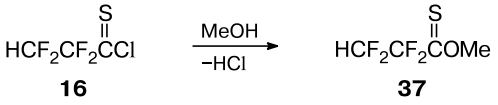
$R^F = CF_3$ (**34**), $H(CF_2)_2$ (**35**)

tions with chloroperfluoroethanesulfenyl chlorides, heating to 70 °C was required (see Ref. 14).

The properties of the thioacyl halides obtained were studied with 2,2,3,3-tetrafluoropropanethioyl chloride **16** as an example for its preparative accessibility and convenient physical characteristics (liquid with b.p. 76—78 °C), as well as for easy identification of its reaction products from ^{1}H NMR spectra (the presence of the characteristic signal for the polyfluoroalkyl proton).

The chemical properties of thioacyl chloride **16** are determined by the presence of both the thiocarbonyl group and the mobile Cl atom. Reactions of thioacyl chloride **16** with nucleophiles leave the thiocarbonyl group intact; *e.g.*, its reaction with methanol gave methyl ester **37** (Scheme 12).

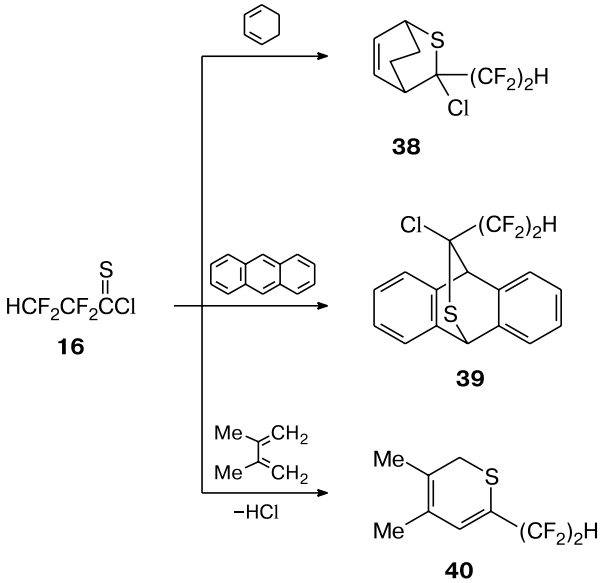
Scheme 12



16 **37**

In contrast, in reactions with various dienes, thioacyl chloride **16** acts as a reactive dienophile involving its thiocarbonyl group. For instance, compound **16** readily reacted with cyclohexa-1,3-diene, anthracene, and 2,3-dimethylbuta-1,3-diene to give cycloadducts **38**—**40** in high yields (Scheme 13).

Scheme 13



The reactions with cyclohexadiene and 2,3-dimethylbuta-1,3-diene were carried out in CH_2Cl_2 at −78 °C, while those with anthracene, in toluene at room temperature. The adduct with 2,3-dimethylbutadiene was unstable and underwent spontaneous dehydrochlorination in CH_2Cl_2 even at room temperature to give 2*H*-thiopyran **40**.

Thus, thermal decomposition of benzyl polyfluoroalkyl sulfides under the action of P_2O_5 is a convenient preparative method for the synthesis of polyfluorinated thiols and thioacyl halides. In contrast to earlier known methods, our high-yielding method involves more accessible starting reagents and simple implementation of the process. Tentative estimates of the chemical properties of the F,S-containing compounds obtained suggest that they are promising reagents for the synthesis of new compounds of various structural types.

Experimental

^{19}F NMR spectra were recorded on a Bruker AC-200F spectrometer (188.31 MHz) in $CDCl_3$. ^{1}H NMR spectra were recorded on a Bruker AC-300SF instrument (300.13 MHz) in $CDCl_3$ or DMSO-d_6. Chemical shifts δ are referenced to CF_3COOH (^{19}F, external standard) and Me_4Si (^{1}H, internal standard). The course of the reactions was monitored and the purity of the products was checked by the GC-MS method (for solutions in CH_2Cl_2 and $CHCl_3$ with concentrations of 10^{-3}—10^{-4} mg mL^{-1}) on a Hewlett—Packard 5989 B series 2 instrument fitted with an HP-5972 mass-selective detector (ionizing voltage 70 eV). The *m*/*z* values obtained for the molecular ions of all products were consistent with the calculated data. The yields, physical and spectroscopic characteristics, and elemental analysis data for the compounds obtained are given in Table 1.

The starting benzyl sulfides were prepared according to known procedures.[15—17]

Decomposition of benzyl polyfluoroalkyl sulfides under the action of phosphorus pentoxide (general procedure). A mixture of an appropriate benzyl sulfide (0.1 mol) and P_2O_5 (0.2—0.3 mol) was prepared by shaking in a closed flask and slowly heated on an oil bath at 150—180 °C; the escaping product was collected in a cooled receiver. For compounds **3** and **17**, the reaction was carried out *in vacuo* (100 Torr). Compounds **13** and **14** were additionally purified by passing their vapors through a column (length 20 cm, diameter 2 cm) packed with a blend of NaF and glasswool. This procedure was used to obtain compounds **1**—**3**, **5**, **8**, **10**, and **13**—**19**.

2,2,2-Trifluoroethanethiol (1)[18], ^{19}F NMR, δ: 11.1 (t, CF_3, J = 12 Hz); **2,2,3,3-tetrafluoropropane-1-thiol (2)**, ^{19}F NMR, δ: −59.2 (dm, 2 F, CF_2H, J = 52 Hz); −39.5 (m, 2 F, CF_2); **2,2,3,3,4,4,5,5-octafluoropentanethiol (3)**;[6] **1,1,1,3,3,3-hexafluoropropane-2-thiol (5)**;[5] **methyl 3,3,3-trifluoro-2-mercaptopropionate (8)**; **pentafluoropropene-2-thiol (10)**, ^{19}F NMR, δ: 9.6 (dq, 1 F, J = 11 Hz, J = 3 Hz); 12.9 (dq, 1 F, J = 24 Hz, J = 5 Hz); 15.3 (q, 3 F, CF_3, J = 24 Hz, J = 11 Hz); **difluorothioacetyl fluoride (13)**;[7] **chlorofluorothioacetyl fluoride (14)**;[7] **trifluorothioacetyl chloride (15)**,[1] ^{19}F NMR, δ: 9.2 (s, CF_3); **2,2,3,3-tetrafluoropropanethioyl chloride (16)**, ^{19}F NMR, δ: −58.1 (dm, 2 F, CF_2H, J = 54 Hz); −34.5 (m, 2 F, CF_2); **2,2,3,3,4,4,5,5-octafluoropentanethioyl chloride (17)**, ^{19}F NMR, δ: −61.5 (dm, 2 F,

Table 1. Yields, physicochemical properties, elemental analysis data, and spectroscopic characteristics of the compounds obtained

Compound	Yield (%)	B.p./°C (*p*/Torr) [M.p./°C]	Found / Calculated (%) C	Found / Calculated (%) H	Molecular formula	^{1}H NMR,* δ, *J*/Hz
1[18]	95	35—36	20.73 20.69	2.74 2.60	$C_2H_3F_3S$	1.93 (t, 1 H, SH, *J* = 8); 3.15 (td, 2 H, CH_2, *J* = 12, *J* = 8)
2	90	81—82	24.30 24.33	2.68 2.72	$C_3H_4F_4S$	1.79 (t, 1 H, SH, *J* = 8); 3.54 (td, 2 H, CH_2, *J* = 19, *J* = 8); 6.04 (tt, 1 H, CHF_2, *J* = 52, *J* = 3)
3[6]	80	83—85 (60)	24.17 24.20	1.59 1.62	$C_5H_4F_8S$	2.63 (t, 1 H, SH, *J* = 8); 3.29 (tm, 2 H, CH_2, *J* = 19); 6.72 (tm, 1 H, CHF_2, *J* = 53)
4	41	73—77 (10)	43.57 43.80	2.85 2.92	$C_{10}H_8F_6S$	4.07 (s, 2 H, CH_2); 4.83 (sept, 1 H, CH, *J* = 10); 7.30 (m, 5 H, Ph)
5[5]	85	42—43	19.72 19.56	1.00 1.08	$C_3H_2F_6S$	2.33 (d, 1 H, SH, *J* =12); 3.78 (m, 1 H, CH)
7	37	99—101 (4)	49.87 50.00	4.12 4.17	$C_{11}H_{11}F_3O_2S$	3.68 (s, 3 H, Me); 3.96 (m, 2 H, CH_2); 4.33 (q, 1 H, CH, *J* = 8); 7.30 (m, 5 H, Ph)
8	54	125—127	27.46 27.59	2.79 2.88	$C_4H_5F_3O_2S$	2.61 (d, 1 H, SH, *J* = 12); 3.83 (s, 3 H, Me); 3.95 (m, 1 H, CH)
9	59	69—71 (10)	47.32 47.24	2.69 2.76	$C_{10}H_7F_5S$	3.92 (s, 2 H, CH_2); 7.25 (m, 5 H, Ph)
10	62	37—38	21.86 21.95	0.58 0.61	C_3HF_5S	2.24 (m, SH)
11	73	80—82 (5)	44.15 44.05	3.35 3.33	$C_{10}H_9ClF_4S$	3.92 (s, 2 H, CH_2); 4.62 (m, 1 H, CHCl); 6.54 (tt, 1 H, CHF_2, *J* = 53, *J* = 3)
13[7]	71	14—16	—	—	C_2HF_3S	6.0 (td, 1 H, CH, *J* = 48, *J* = 3)
14[7]	86	44—47	17.74 18.40	1.09 0.77	C_2HClF_2S	5.52 (dd, 1 H, CH, *J* = 49, *J* = 4)
15[1]	81	28—29	16.15 16.16	—	C_2ClF_3S	—
16	90	76—77	20.01 19.96	0.59 0.56	C_3HClF_4S	6.82 (tt, 1 H, CF_2H, *J* = 54, *J* = 5)
17	75	127—129	21.50 21.41	0.34 0.36	C_5HClF_8S	6.72 (tm, 1 H, CHF_2, *J* = 53)
18[3]	72	31—33	21.99 21.96	0.58 0.61	C_3HF_5S	4.5 (dq, 1 H, *J* = 42, *J* = 6)
9	59	40—42	24.75 24.66	1.47 1.38	$C_3H_2F_4S$	3.62 (m, CH_2)
20	77	90—92	22.25 22.23	1.42 1.40	$C_4H_3F_7S$	4.05 (q, 2 H, CH_2, *J* = 10); 6.77 (tm, 1 H, CHF_2, *J* = 54)
21	68	65—67 (100)	24.24 24.20	1.65 1.62	$C_5H_4F_8S$	3.78 (t, 2 H, CH_2CF_2, *J* = 17); 6.55 (tm, 1 H, CHF_2, *J* = 53); 6.72 (tm, 1 H, CHF_2, *J* = 54)
22	73	73—75 (45)	22.95 22.70	1.71 1.52	$C_5H_4ClF_7S$	3.78 (t, 2 H, CH_2CF_2, *J* = 17); 6.57 (tt, 1 H, CHF, *J* = 53, *J* = 5); 7.28 (dt, 1 H, CHCl, *J* = 49, *J* = 6)
23	57	69—71 (15)	24.32 24.15	1.22 1.16	$C_7H_4F_{12}S$	3.82 (t, 2 H, CH_2CF_2, *J* = 18); 6.61 (tm, 1 H, CHF_2, *J* = 53); 6.83 (tm, 1 H, CHF_2, *J* = 53)
24	46	84—86	21.45 21.14	0.83 0.71	$C_7H_4F_{12}S$	3.52 (q, 2 H, CH_2, *J* = 8)
25	48	66—68	22.65 22.57	1.18 1.14	$C_5H_3F_9S$	3.49 (t, 2 H, CH_2CF_2, *J* = 17); 6.01 (tt, 1 H, CHF_2, *J* = 54, *J* = 4)
26	37	94—96	22.85 22.81	1.06 0.96	$C_6H_3F_{11}S$	3.51 (t, 2 H, CH_2CF_2, *J* = 17); 5.96 (tt, 1 H, CHF_2, *J* = 54, *J* = 4)
27[6]	72	62—64	15.80 15.96	1.42 1.34	$C_2H_2ClF_3S$	2.92 (q, 2 H, CH_2, *J* = 6)
28	70	110—111	19.80 19.74	1.70 1.66	$C_3H_3ClF_4S$	2.90 (t, 2 H, CH_2, *J* = 18); 6.2 (tt, 1 H, CF_2H, *J* = 52, *J* = 5)

(*to be continued*)

Table 1 (*continued*)

Compound	Yield (%)	B.p./°C (*p*/Torr) [M.p./°C]	Found / Calculated (%) C	H	Molecular formula	^{1}H NMR,* δ, *J*/Hz
29	63	54—56	16.55 16.48	0.40 0.46	C_3HClF_6S	5.65 (pent, CHS, *J* = 9)
30[18]	51	50—52 (12)	20.96 20.87	1.62 1.75	$C_4H_4F_6S_2$	2.87 (q, 4 H, 2 CH_2, *J* = 9)
31	54	72—73 (12)	24.58 24.49	2.13 2.06	$C_6H_6F_8S_2$	3.62 (t, 4 H, 2 CH_2, *J* = 18); 6.52 (tt, 2 H, 2 CF_2H, *J* = 54, *J* = 5)
32	50	132—135 (3)	49.70 49.62	3.90 3.82	$C_{11}H_{10}F_4OS$	3.20 (t, 2 H, CH_2, *J* = 16); 4.12 (s, 1 H, CH_2); 6.25 (tm, 1 H, CF_2H, *J* = 53); 7.50 (m, 3 H, Ph); 7.95 (m, 2 H, Ph)
33	68	[63—64]	45.93 45.86	2.60 2.55	$C_{12}H_8F_6OS$	2.96, 3.78 (both m, 1 H each, CH_2); 4.17 (m, 1 H, CHC(O)); 5.40 (pent, 1 H, CHS, *J* = 8); 7.60 (m, 4 H, C_6H_4)
34	57	[120—121]	47.69 47.83	3.25 3.28	$C_{11}H_9F_3NO_2S$	3.70 (q, 2 H, SCH_2, *J* = 6); 7.90 (m, 4 H, Ph)
35	68	[91—92]	46.84 46.76	3.18 3.27	$C_{12}H_{10}F_4NO_2S$	3.68 (t, 2 H, SCH_2, *J* = 15); 6.65 (tt,1 H, CF_2H, *J* = 54, *J*′ = 5); 7.95 (m, 4 H, Ph)
36	72	70—72 (3)	47.33 47.24	3.87 3.94	$C_{10}H_{10}F_4OS$	2.30 (s, 3 H, Me); 3.49 (t, 2 H, CH_2, *J* = 18); 6.34 (tm, 1 H, CF_2H, *J* = 52); 6.65, 6.92 (both d, 1 H each, *J* = 8); 7.18 (s, 1 H)
37	63	98—101	27.15 27.28	2.21 2.29	$C_4H_4F_4OS$	4.29 (s, 3 H, OMe); 6.65 (tt, 1 H, CF_2H, *J* = 53, *J* = 5)
38	65	80—82 (3)	41.60 41.47	3.57 3.48	$C_9H_9ClF_4S$	1.70—2.60 (m, 4 H, C(7)H_2C(8)H_2); 3.40—3.65 (m, 1 H, C(4)H); 3.72—3.80 (m, 1 H, C(1)H); 6.28 (m, 1 H, CH); 6.46 (m, 1 H, CF_2H); 6.64 (m, 1 H, C(6)H)**
39	85	[76—78]	56.78 56.91	3.03 3.09	$C_{17}H_{11}ClF_4S$	5.21, 5.65 (both s, 1 H each, CH); 6.58 (tt, 1 H, CF_2H, *J* = 52, *J* = 4); 7.40 (m, 8 H, CH)
40	62	69—70 (3)	47.90 47.80	4.32 4.46	$C_9H_{10}F_4S$	1.83, 1.92 (both s, 3 H each, Me); 3.21 (s, 2 H, CH_2); 5.21 (tm, 1 H, CF_2H, *J* = 51); 6.48 (s, 1 H, CH)

* In $CDCl_3$ for compounds **1**—**3**, **5**, **8**, **10**, **13**—**19**, **24**—**30**, **38**, and **40** and in DMSO-d_6 for compounds **4**, **7**, **9**, **11**, **20**—**23**, **31**—**37**, and **39**.

** The mixture of the *exo*- and *endo*-isomers in the ratio 3 : 2.

CF_2H, *J* = 52 Hz); –54.4, –49.6, –37.5 (all m, 2 F each, CF_2); **2,3,3,3-tetrafluoropropanethioyl fluoride (18)**;[3] and **3,3,3-trifluoropropanethioyl fluoride (19)**, ^{19}F NMR, δ: 7.2 (m, 3 F, CF_3); 138.6 (m, 1 F, C(S)F).

Benzyl 1,1,1,3,3,3-hexafluoropropan-2-yl sulfide (4). α-Toluenethiol (12.4 g, 0.1 mol) was added dropwise at 5—10 °C to a stirred solution of *N*-chlorosuccinimide (13.4 g, 0.1 mol) in CH_2Cl_2 (150 mL). The mixture was kept at room temperature for 2 h and the precipitate that formed was filtered off. Bis(trifluoromethyl)ketene (18.2 g, 0.1 mol) was bubbled through the filtrate. The reaction mixture was stirred for 1 h and concentrated *in vacuo*. Water (50 mL) was added to the residue and stirring was continued at 20 °C for 1 h and then at 60 °C for 0.5 h. The mixture was washed with water and the organic layer was separated, dried over Na_2SO_4, and fractionated.

Methyl 2-benzylthio-3,3,3-trifluoropropionate (7). Sulfide **4** (13.5 g, 0.05 mol) was added dropwise at 0—5 °C to a stirred solution of KOH (6.0 g) in methanol (75 mL). The reaction mixture was kept at 20 °C for 1.5 h and then at 60 °C for 1 h and washed with water (2×100 mL). The product was extracted with ether, dried over Na_2SO_4, and fractionated, while collecting a fraction with b.p. 100—130 °C (12 Torr). The yield of a mixture of sulfides **6** was 5.5 g (GC-MS data). Concentrated H_2SO_4 (3 mL) was added dropwise at 0—5 °C. The reaction mixture was stirred at 20 °C for 30 min and poured onto ice (50 mL). The product was extracted with ether, dried over Na_2SO_4, and fractionated.

Benzyl 1,1,1,3,3-pentafluoropropen-2-yl sulfide (9). ***A.*** Sulfide **4** (3.5 g, 0.013 mol) was added dropwise at 5—10 °C to a stirred suspension of KOH (3.5 g, 0.063 mol) in ether (5 mL). The mixture was kept for 4 h, the precipitate was filtered off, and the filtrate was dried over Na_2SO_4 and fractionated.

B. A mixture of sulfide **4** (8.2 g, 0.03 mol) and $BF_3 \cdot NEt_3$ (10.2 g, 0.06 mol) was heated at 150 °C for 4 h. Volatile products were removed by heating the reaction mixture to 70 °C (3 Torr). The product was refractionated.

Benzyl 1-chloro-2,2,3,3-tetrafluoropropyl sulfide (11). Sulfuryl chloride (1.34 g, 10 mmol) in CH_2Cl_2 (5 mL) was added dropwise at room temperature to a solution of benzyl 2,2,3,3-tetrafluoropropyl sulfide (2.38 g, 10 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was kept for 12 h and concentrated *in vacuo* and the residue was fractionated.

Addition of thiols 1—3 to fluoroolefins (general procedure). An appropriate fluoroolefin (70 mmol) was bubbled through a solution of thiol **1**—**3** (50 mmol) in DMF (30 mL) containing KOH or triethylamine (0.5 mmol). The reaction mixture was

stirred for 4 h and poured into ice water. The product was extracted with CH_2Cl_2 and washed with 20% NaOH, 10% HCl, and water. The organic layer was separated, dried over Na_2SO_4, and fractionated. This procedure was used to obtain **1,1,2,2-tetrafluoroethyl 2,2,2-trifluoroethyl sulfide (20)**, **1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl sulfide (21)**, **2-chloro-1,1,2-trifluoroethyl 2,2,3,3-tetrafluoropropyl sulfide (22)**, and **1,1,2,2-tetrafluoroethyl 2,2,3,3,4,4,5,5-octafluoropentyl sulfide (23)**.

2,2,2-Trifluoroethyl 1,1,2,2,3,3,3-heptafluoropropyl sulfide (24). Sodium formate (1.36 g, 20 mmol) was added to a stirred mixture of thiol **1** (2.0 g, 17 mmol), perfluoropropyl iodide (5.1 g, 17 mmol), sodium sulfite (2.2 g, 17 mmol), DMF (17 mL), and water (5.6 mL). The mixture was stirred at 20 °C for 12 h and poured into water (100 mL). The product was extracted with tetrachloroethane, washed with 10% HCl and water, dried over Na_2SO_4, and fractionated. ^{19}F NMR, δ: −46.35, −10.24 (both m, 2 F each, CF_2); −2.27 (m, 3 F, CF_3); 10.93 (t, 3 F, CF_3, J = 8 Hz).

An analogous procedure was used to obtain compounds **25** and **26** from thiol **2** and perfluoroethyl iodide or perfluoropropyl iodide, respectively.

1,1,2,2,2-Pentafluoroethyl 2,2,3,3-tetrafluoropropyl sulfide (25). ^{19}F NMR, δ: −58.51 (m, 2 F, CF_2H); −40.37 (m, 2 F, CF_2CH_2); −15.41 (m, 2 F, CF_2S); −6.47 (m, 3 F, CF_3).

1,1,2,2,3,3,3-Heptafluoropropyl 2,2,3,3-tetrafluoropropyl sulfide (26). ^{19}F NMR, δ: −59.01 (m, 2 F, CF_2H); −48.05 (m, 2 F, $C\underline{F}_2CF_3$);−38.25 (m, 2 F, CF_2CH_2); −12.17 (m, 2 F, CF_2S); −4.25 (m, 3 F, CF_3).

2,2,2-Trifluoroethanesulfenyl chloride (27) (see Ref. 6). Dry gaseous chlorine (1.42 g, 20 mmol) was slowly bubbled at 15 °C through a solution of thiol **1** (1.16 g, 10 mmol) in tetrachloroethane (5 mL). The reaction mixture was kept for 1 h and fractionated. ^{19}F NMR, δ: 11.2 (t, CF_3, J = 6 Hz).

An analogous procedure was used to obtain **2,2,3,3-tetrafluoropropanesulfenyl chloride (28)** (with CH_2Cl_2 as a solvent) and **1,1,1,3,3,3-hexafluoropropane-2-sulfenyl chloride (29)** from thiols **2** and **5**, respectively.

Bis(2,2,2-trifluoroethyl) disulfide (30).[18] Dry chlorine (0.71 g, 10 mmol) was bubbled at room temperature through a solution of thiol **1** (1.16 g, 10 mmol) in CH_2Cl_2 (5 mL). The mixture was fractionated. ^{19}F NMR, δ: 11.5 (t, CF_3, J = 9 Hz).

Bis(2,2,3,3-tetrafluoropropyl) disulfide (31) was obtained analogously. ^{19}F NMR (DMSO-d_6), δ: −60.5 (m, 2 F, CF_2H); −39.2 (m, 2 F, CF_2).

1-Phenyl-2-(2,2,3,3-tetrafluoropropylthio)ethan-1-one (32). Sulfenyl chloride **28** (1.0 g, 5.4 mmol) was added dropwise at room temperature to a solution of acetophenone (0.65 g, 5.4 mmol) in CCl_4 (3 mL). The reaction mixture was stirred until HCl ceased to evolve (20 h) and fractionated.

2-(1,1,1,3,3,3-Hexafluoropropan-2-ylthio)indan-1-one (33). A mixture of sulfenyl chloride **29** (1.0 g, 4.5 mmol) and indan-1-one (0.6 g, 4.5 mmol) was kept for 24 h and recrystallized from hexane.

2-(2,2,2-Trifluoroethylthio)-1*H*-isoindole-1,3(2*H*)-dione (34). A solution of sulfenyl chloride **27** (1.5 g, 10 mmol) in benzene (2.5 mL) was added at 20 °C to a suspension of potassium phthalimide (1.5 g, 8 mmol) in benzene (2.5 mL). The reaction mixture was stirred for 1 h and concentrated *in vacuo*. The residue was recrystallized from benzene—light petroleum (1 : 2).

2-(2,2,3,3-Tetrafluoropropylthio)-1*H*-isoindole-1,3(2*H*)-dione (35) was obtained analogously.

4-Methyl-2-(2,2,3,3-tetrafluoropropylthio)phenol (36). A mixture of sulfenyl chloride **28** (1.0 g, 5.4 mmol) and *p*-cresol (0.6 g, 5.4 mmol) was stirred at room temperature until HCl ceased to evolve (24 h) and fractionated.

***O*-Methyl 2,2,3,3-tetrafluoropropanethioate (37).** Thioacyl chloride **16** (1.8 g, 10 mmol) was added at room temperature to stirred anhydrous methanol (5 mL). The reaction mixture was stirred for 1 h and washed with water. The product was extracted with ether and the organic layer was separated, dried over Na_2SO_4, and fractionated.

3-Chloro-3-(1,1,2,2-tetrafluoroethyl)-2-thiabicyclo[2.2.2]oct-5-ene (38). Thioacyl chloride **16** (1.8 g, 10 mmol) was added at −78 °C to a stirred solution of cyclohexa-1,3-diene (1.0 g, 12.5 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 1 h, warmed to room temperature, kept for 12 h, and fractionated. ^{19}F NMR, δ: −56.5 (m, 2 F, CF_2H); −39.4 (m, 2 F, CF_2).

16-Chloro-16-(1,1,2,2-tetrafluoroethyl)-15-thiatetracyclo[6.6.2.0.^{2,7}.0^{9,14}]hexadeca-2,4,6,9,11,13-hexaene (39). Thioacyl chloride **16** (1.8 g, 10 mmol) was added at room temperature to a stirred solution of anthracene (1.8 g, 10 mmol) in dry toluene (25 mL). The reaction mixture was kept for 12 h and concentrated *in vacuo*. The residue was recrystallized from hexane.

3,4-Dimethyl-6-(1,1,2,2-tetrafluoroethyl)-2*H*-thiopyran (40). Thioacyl chloride **16** (1.8 g, 10 mmol) in CH_2Cl_2 (5 mL) was added dropwise at −78 °C to a stirred solution of 2,3-dimethylbutadiene (0.98 g, 12 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was warmed to room temperature (evolution of HCl was observed), refluxed until HCl ceased to evolve (8 h), and fractionated.

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