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Synthesis of alkyl perfluoroalkanedithiocarboxylates and some aspects of their reactivity in cycloaddition reactions

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Summary — A new method for the synthesis of the title compounds is proposed. The starting fluorinated compounds are commercially available trifluoroethanol and higher homologues, which were transformed in three steps into (2,2-dichloroperfluoroalkyl) alkylsulfides. The last step consisted in a substitution of chlorine by sulfur by treatment with zinc sulfide. The source of zinc sulfide is crucial and the possible role of catalytic impurities was investigated. These dithioesters are excellent dienophiles. Some cycloaddition reactions with 2,3-dimethylbuta-1,3-diene and 1-(trimethylsilyloxy)buta-1,3-diene are reported.

perfluorinated dithioester / polyfluorinated sulfide / cycloaddition / tetrahydrothiopyran

Résumé — Synthèse de perfluoroalcanedithiocarboxylates d'alkyle et quelques aspects de leur réactivité dans des réactions de cycloaddition. Une nouvelle méthode de synthèse de perfluoroalkanedithiocarboxylates d'alkyle est décrite, à partir de composés commerciaux. Le trifluoroéthanol ou les homologues superieurs sont transformés en trois étapes en (2,2-dichloroperfluoroalkyl) alkylsulfures. La dernière étape consiste en une substitution des atomes de chlore par le soufre par traitement au sulfure de zinc. La source de sulfure de zinc s'est revelee determinante et le rôle catalytique d'impuretés a été étudié. Ces dithioesters sont d'excellents diénophiles, comme illustré dans des réactions avec le 2,3-diméthylbutadiène et le 1-(triméthylsilyloxy)buta-1,3-diene.

dithioester perfluoré / sulfure polyfluoré / cycloaddition / tetrahydrothiopyrane

Introduction

Derivatives of thiocarboxylic acids are versatile intermediates in organic synthesis [1]. Perfluoroanalogues are scarcely used, due to the lack of a convenient method of preparation [2, 3]. In contrast to their hydrogenated analogues [4] perfluorodithioesters were shown to react very easily in 4 + 2 cycloaddition with dienes [2, 3]. One of us recently reported a new method to prepare such dithioesters by reaction of zinc sulfide with 1,1-dichloroperfluoroalkyl sulfide, obtained by chlorination of a perfluoroaldehyde dithioacetal [5]. We report in this paper a new and general approach to the synthesis of alkyl perfluoroalkanedithiocarboxylates which uses 1,1-dihydroperfluoroalcohol as starting material. Some cycloadditions of these dithioesters, especially with dienoxysilanes, will also be described.

Results and discussion

Preparation of dithioesters

The first steps of this synthesis are described in figure 1. Tosylation of the starting alcohol **1** [6] gave **2** which reacted with the thiol in basic medium to give the sulfide **3** [7]. α-Chlorination of **3** with sulfuryl chloride gave the α,α-dichloro sulfide **4**. The overall yield of these three steps was in the range of 55% and the process worked with trifluoroethanol and higher homologues as well.

$$R_FCH_2OH \xrightarrow{TsCl} R_FCH_2OTs$$

1 **2**

$$\xrightarrow[KOH,\ DMSO]{RSH} R_FCH_2SR \xrightarrow{SO_2Cl_2} R_FCCl_2SR$$

3a–3f **4a–4f**

Fig 1. Preparation of 1,1-dichloroperfluoroalkyl sulfides (for the definition of a–f, see table I).

The main problem encountered in the synthesis of dithioesters **5** was the substitution of chlorine by sulfur (table I), which was strongly dependent on the origin of the zinc sulfide used. Sulfides **4a–f** did not react with pure ZnS (99.99% from Aldrich) under the conditions described in a preliminary report [3]. In contrast, the

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Cl/S exchange took place when zinc sulfide was prepared according to a reported procedure [8]: addition of ammonium hydroxide to an aqueous solution of zinc chloride, filtration of the residual suspension, addition of Na_2S to the filtrate for precipitation of ZnS. Hence the prepared ZnS contained some impurities that act as a catalyst. Some experiments were carried out in order to get some information about the nature of this catalyst. Addition of 5–10% of $ZnCl_2$ to the 'pure ZnS' did not allow any reaction to start, indicating that the activation of the α,α-dichloro sulfide was not a simple Lewis acid catalysis by some starting zinc chloride remaining in the solid. As mentioned above, the 'prepared ZnS' was obtained by a procedure in which the first step is the elimination of some insoluble material by treating aqueous $ZnCl_2$ with ammonium hydroxide. In order to assess its possible catalytic ability, 10% of this solid was added to the 'pure ZnS' and the mixture was introduced in an acetonitrile solution of the sulfide **4** and warmed. **4** was completely converted under reflux and the course of the reaction was very similar to the one with the 'prepared ZnS'. This catalyst was not identified, but according to microanalysis and atomic absorption measurements after careful drying in vacuum, the composition $ZnO_{1.6}Cl_{0.45}N_{0.4}H_{2.2}$ could be proposed. Some carbonyl analogue of **5** was present as a by-product. It is interesting to notice that the amount of this by-product strongly decreased when the reaction was carried out with the excess ZnS recovered from the first experiment. Although we have no satisfactory interpretation of these observations, we can assume a similar substitution of chlorine with zinc oxide present in the reagent.

Table I. Preparation of the perfluorodithioesters.

$$\underset{\textbf{4a–4f}}{R_FCCl_2SR} + ZnS \xrightarrow[\Delta]{CH_3CN} \underset{\textbf{5a–5f}}{R_FCS_2R}$$

	R_F	*R*	*Reaction time (h)*	*Yield (%)*
a	CF_3	Et	5	[a]
b	CF_3	Bn	8	50
c	C_3F_7	Et	3	49
d	C_3F_7	Pr	3	51
e	C_3F_7	Bn	8	76
f	$H(CF_2)_4$	Pr	3	70

[a] Not determined (codistilled with the solvent).

The exchange step was faster with long perfluoroalkylated sulfides. On the other hand, for a given R_F, we observed a faster reaction for alkyl (Et, Pr) than for benzyl sulfides. Aryl sulfides did not react under the same conditions.

The substitution of chlorine was also strongly dependent on the oxidation state of sulfur in the substrate. For example, the sulfoxide **6** prepared by oxidation of

$$\underset{\textbf{4a}}{CF_3CCl_2SEt} \xrightarrow[TFA]{H_2O_2} \underset{\textbf{6}}{CF_3CCl_2S(O)Et}$$

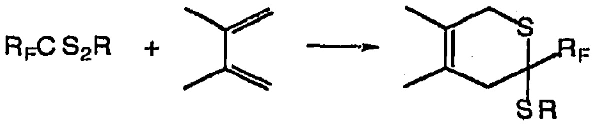
$$\xrightarrow[\times]{ZnS} CF_3C(S)S(O)Et$$

4a was completely recovered after several hours of treatment with ZnS in the same conditions.

The dithioesters **5a–f** are thermally stable, distillable red liquids which exhibit, besides a strong UV absorption, a wide absorption band at 495 μm (CH_3CN, $\varepsilon = 22$). The thiocarbonyl carbon atom gives a characteristic resonance signal at 211–212 ppm as a triplet. The trifluoromethyl compound **5a** could not be separated from acetonitrile by distillation, but it was trapped in situ by dienes (see below). According to the boiling points observed for the higher homologues (**5c**: 95 °C; **5d**: 100 °C) compound **4a** seems to be much more volatile than reported earlier [2a].

Reaction of dithioesters 5 with dienes

The easy cycloaddition reaction of dithioesters **5** with dienes constitutes a convenient access to fluorinated derivatives of thiopyran, which hydrogenated analogues were intensively studied [9]. Compounds **5** reacted efficiently with 2,3-dimethylbutadiene to lead to the thiopyran **7** (fig 2). The dithioesters **5b** and **5c** reacted at room temperature without solvent, as reported in a preliminary account [3], whereas the trifluoromethyl analogue **5a**, obtained as a solution in acetonitrile, was converted into the corresponding thiopyran **7a** by simply adding the diene to the solution.



5a, b, c

7a $R_F = CF_3$, R = Et
7b $R_F = CF_3$, R = Bn
7c $R_F = C_3F_7$, R = Et

Fig 2. Cycloadditions with 2,3-dimethylbuta-1,3-diene.

The reaction with 1-(trimethylsilyloxy)buta-1,3-diene was carried out under similar conditions. The regio- and stereoselectivity depended on the structure of the dithioester (fig 4). The trifluoromethyl compound **5b** was converted into a mixture of two regioisomers, each being obtained as a mixture of two diastereomers. According to the ^{19}F NMR data, the reaction proceeded without noticeable selectivity (2.5:1; 2.3:3.2). The separation of this mixture was difficult. Only one of the isomers was isolated as a pure material by silica gel chromatography, whereas the remaining material partially decomposed. We assume that the latter was essentially the regioisomer **8** with a hemithioketal-type structure, less stable to hydrolysis. Hence the structure **9** (stereochemistry undetermined) was assigned to the isolated compound and was in agreement with the spectral data.

Interestingly, the long *F*-alkyl dithioester **5f** reacted more regio- and stereoselectively with the siloxydiene. The ^{19}F NMR spectrum of the crude product revealed that one of the four possible isomers, **11**, was formed in more than 60% relative yield. We attempted to isolate this compound by distillation but a retro-Diels–Alder

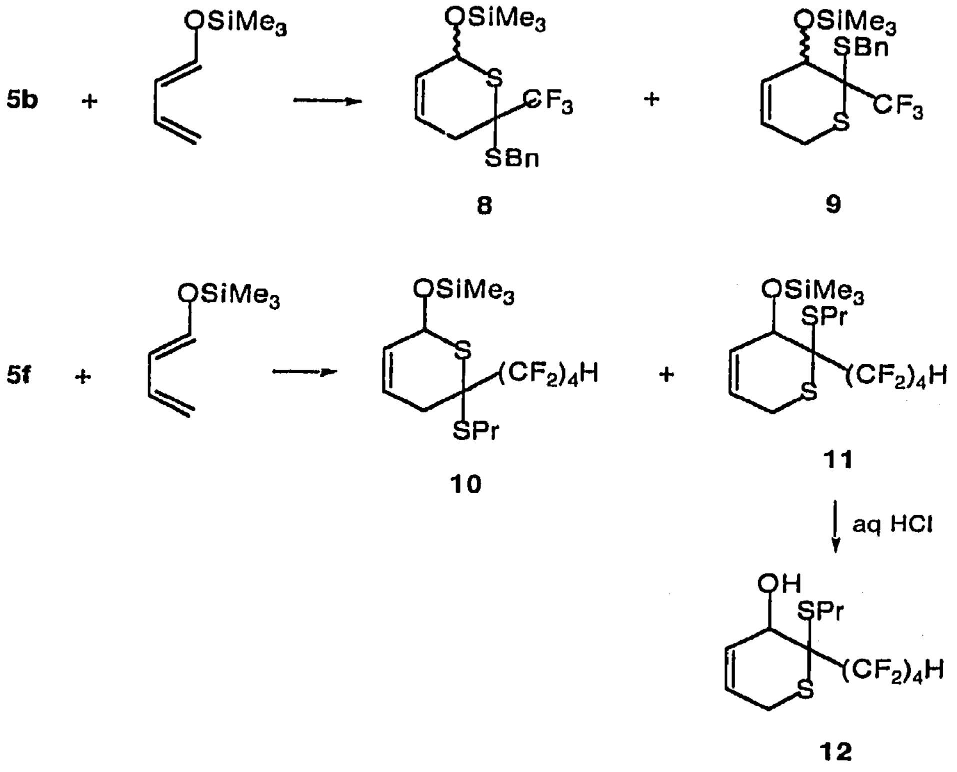


Fig 3. Cycloaddition reactions with 1-(trimethylsilyloxy)buta-1,3-diene.

reaction occurred at temperatures above 100 °C giving back the starting dithioester. This major cycloadduct **11** was isolated by chromatography together with the corresponding desilylated compound **12**. **11** was completely converted into **12** by hydrolysis with dilute hydrochloric acid. As mentioned above, the stability of this compound on silica gel as well as in acidic medium involves the regioisomeric structure **11** rather than the hemithioketalic structure **10**. Structure **12** (stereochemistry undetermined) was in complete agreement with spectral data.

Conclusion

A new and general methodology for the synthesis of alkyl perfluorodithiocarboxylates is now available. Further examples of synthetic uses in [4 + 2] cycloaddition illustrate the high reactivity of these compounds. Other aspects of their reactivity are reported elsewhere [10].

Experimental section

All reactions were carried out in an efficient hood, under an inert atmosphere (argon). Silicagel Merck (Kieselgel 60, 0.040–0.063 mm) was used for chromatographic separations. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker AC 250 at 250.13, 62.90 and 235.36 MHz respectively. Chemical shifts are given from tetramethylsilane (^{1}H, ^{13}C) and $CFCl_3$ (^{19}F) as internal standards. Elemental analyses were performed with a Perkin–Elmer CHN 2400 apparatus. The starting perfluoroalkylmethanol was purchased from Aldrich and Fluorochem.

1,1-Dihydropolyfluoroalkyl sulfides 3: general procedure

Compounds **3** were synthesized according to the method reported in [7].

- *Ethyl (2,2,2-trifluoroethyl) sulfide 3a*

Yield 73%. Bp 74–75 °C.

^{1}H NMR: δ 1.30 (t, J = 7 Hz, CH_3); 2.70 (q, J = 7 Hz, CH_2); 3.09 (q, 2H, J_{HF} = 12 Hz, CH_2CF_3).

^{13}C NMR: δ 14.1 (CH_3); 27.1 (CH_2CH_3); 33.7 (q, J = 32 Hz, CH_2CF_3); 121.7 (q, J = 270 Hz, CF_3).

^{19}F NMR: δ −67.1 (t, J = 12 Hz, CF_3).

Anal calc for $C_4H_7F_3S$: C, 33.33; H, 4.89. Found: C, 33.21; H, 4.75.

- *Benzyl (2,2,2-trifluoroethyl) sulfide 3b*

Yield 68%. Bp 50 °C (0.1 mbar).

^{1}H NMR: δ 2.88 (q, J_{HF} = 10 Hz, CH_2); 3.81 (s, CH_2); 7.30 (m, C_6H_5).

^{19}F NMR: δ −66.3 (t, J = 10 Hz, CF_3).

Anal calc for $C_9H_9F_3S$: C, 52.42; H, 4.40. Found: C, 52.36; H, 4.36.

- *Ethyl (2,2,3,3,4,4,4-heptafluorobutyl) sulfide 3c*

Yield 68%. Bp 75–77 °C (0.1 mbar).

^{1}H NMR: δ 1.30 (t, $J = 7$ Hz, CH_3); 3.10 (tt, $J_{HF} = 23$ Hz, $J_{HF} = 1.5$ Hz, CH_2CF_2); 3.50 (q, $J = 7$ Hz, CH_2).

^{19}F NMR: δ −81.2 (tm, $J_{FF} = 11.5$ Hz, CF_3); −127.8 (m, CF_2); −144.7 (tm, $J_{HF} = 23$ Hz, CF_2).

- *(2,2,3,3,4,4,4-Heptafluorobutyl) propyl sulfide* **3d**

Yield 63%. Bp 91–92 °C.

^{1}H NMR: δ 0.95 (t, $J = 7$ Hz, CH_3); 1.60 (sext, $J = 7$ Hz, CH_2); 2.50 (t, $J = 7$ Hz, CH_2); 3.10 (t, 2H, $J_{HF} = 18$ Hz, CF_2CH_2).

^{19}F NMR: δ −81.2 (tm, $J_{FF} = 11.5$ Hz, CF_3); −114.7 (tm, $J_{HF} = 18$ Hz, CF_2); −127.80 (m, CF_2).

- *Benzyl (2,2,3,3,4,4,4-heptafluorobutyl) sulfide* **3e**

Yield 68%. Bp 80–82 °C (0.15 mbar).

^{1}H NMR: δ 2.9 (t, $J_{HF} = 18.5$ Hz, CH_2); 3.9 (s, CH_2); 7.3 (m, C_6H_5).

^{19}F NMR: δ −81.1 (t, $J_{FF} = 11$ Hz, CF_3); −114.1 (tm, $J_{HF} = 18.5$ Hz, CF_2); −127.8 (m, CF_2).

- *(2,2,3,3,4,4,5,5-Octafluoropentyl) propyl sulfide* **3f**

Yield 60%. Bp 158–160 °C.

^{1}H NMR: δ 0.95 (t, $J = 7$ Hz, CH_3); 1.61 (sext, $J = 7$ Hz, CH_2); 2.52 (t, $J = 7$ Hz, CH_2); 3.09 (t, $J_{HF} = 18$ Hz, CH_2CF_2); 6 (tt, $J_{HF} = 50.0$ Hz, $J_{FF} = 5$ Hz, CF_2H).

^{19}F NMR: δ −113.9 (tm, $J_{HF} = 18$ Hz, CF_2CH_2); −125.4 (m, CF_2); −130.3 (m, CF_2); −137.7 (dm, $J_{HF} = 50.0$ Hz, CF_2H).

(1,1-Dichloropolyfluoroalkyl) alkyl sulfides 4: general procedure

SO_2Cl_2 (0.02 mol) in CH_2Cl_2 (10 mL) was slowly added, at room temperature to a solution of sulfide **3** (0.01 mol) in CH_2Cl_2 (20 mL). The mixture was stirred 2 h at room temperature, the solvent was evaporated in vacuo (10–20 mm Hg) and the resulting sulfide **4** was distilled.

- *(1,1-Dichloro-2,2,2-trifluoroethyl) ethyl sulfide* **4a**

Yield 90%. Bp 122 °C.

^{1}H NMR: δ 1.31 (t, $J = 7$ Hz, CH_3); 3.09 (q, $J = 7$ Hz, CH_2).

^{19}F NMR: δ −77.8 (s, CF_3).

Anal calc for $C_4H_5Cl_2F_3S$: C, 22.55; H, 2.36. Found: C, 22.59; H, 2.70.

- *Benzyl (1,1-dichloro-2,2,2-trifluoroethyl) sulfide* **4b** *[7]*

Yield 85%. Bp 70–72 °C (0.1 mbar).

^{1}H NMR: δ 4.21 (s, CH_2); 7.30 (m, C_6H_5).

^{19}F NMR: δ −77.4 (s, CF_3).

- *(1,1-Dichloro-2,2,3,3,4,4,4-heptafluorobutyl) ethyl sulfide* **4c**

Yield 83%. Bp 30 °C (0.1 mbar).

^{1}H NMR: δ 1.31 (t, $J = 7$ Hz, CH_3); 3.15 (q, $J = 7$ Hz, CH_2).

^{19}F NMR: δ −81.6 (t, $J_{FF} = 11.5$ Hz, CF_3); −107.2 (tm, $J_{FF} = 11.5$ Hz, CF_2–Cl_2); −120.3 (m, CF_2).

- *(1,1-Dichloro-2,2,3,3,4,4,4-heptafluorobutyl) propyl sulfide* **4d**

Yield 88%. Bp 60 °C (0.2 mbar).

^{1}H NMR: δ 1.1 (t, $J = 7$ Hz, CH_3); 1.8 (sext, $J = 7$ Hz, CH_2); 3.3 (t, $J = 7$ Hz, CH_2).

^{19}F NMR: δ −81.6 (t, $J_{FF} = 11.5$ Hz, CF_3); −107.2 (tm, $J_{FF} = 11.5$ Hz, CF_2–CCl_2); −120.3 (m, CF_2).

Anal calc for $C_7H_7Cl_2F_7S$: C, 25.70; H, 2.16. Found: C, 25.60; H, 1.93.

- *Benzyl (1,1-dichloro-2,2,3,3,4,4,4-heptafluorobutyl) sulfide* **4e**

Yield 80%. Bp 90 °C (0.2 mbar).

^{1}H NMR: δ 4.30 (s, CH_2); 7.35 (m, C_6H_5).

^{19}F NMR: δ −81.6 (t, $J_{FF} = 11.5$ Hz, CF_3); −106.9 (tm, $J_{FF} = 11.5$ Hz, CF_2); −120.3 (m, CF_2).

- *(1,1-Dichloro-2,2,3,3,4,4,5,5-octafluoropentyl) propyl sulfide* **(4f)** *[5, 6]*

Yield 86%. Bp 60 °C (0.4 mbar).

^{1}H NMR: δ 1.09 (t, $J = 7$ Hz, CH_3); 2.10 (s, $J = 7$ Hz, CH_2); 3.07 (t, $J = 7$ Hz, CH_2).

^{19}F NMR: δ −106.6 (t, $J_{FF} = 9.5$ Hz, CF_2–CCl_2); −117.7 (m, CF_2); −130.2 (m, CF_2); −137.3 (dm, $J_{HF} = 52$ Hz, CF_2).

Alkyl perfluoroalkanedithiocarboxylates 5: general procedure

A mixture of sulfide **4** (0.01 mol) and zinc sulfide (0.2 mol) in acetonitrile (20 mL) was refluxed for 3 h, (sulfides **5c,d,f**), 5 h (**5a**), 8 h (**5b,e**). The mixture was cooled to room temperature and filtered, acetonitrile distilled at atmospheric pressure and the residue fractionated at atmospheric pressure (esters (**5a,e,d**)) or in vacuo.

- *Ethyl trifluorodithioacetate* **5a**

Distilled at 80 °C together with acetonitrile.

^{19}F NMR: δ −65.6 (s, CF_3).

- *Benzyl trifluorodithioacetate* **5b**

Yield 50%. Bp 67–68 °C (0.1 mbar).

^{1}H NMR: δ 4.42 (s, CH_2); 7.30 (m, C_6H_5).

^{13}C NMR: δ 44.3 (CH_2); 118.1 (q, $J = 280$ Hz, CF_3); 128.2; 128.40; 129.0; 132.7 (C_6H_5); 211.3 (t, $J = 35.5$ Hz, $C{=}S$).

^{19}F NMR: δ −65.6 (s, CF_3).

Anal calc for $C_9H_7F_3S_2$: C, 45.75; H, 2.99. Found: C, 44.12; H, 2.32.

- *Ethyl perfluorobutanedithioate* **5c**

Yield 49%. Bp 95 °C.

^{1}H NMR: δ 1.35 (t, $J = 7$ Hz, CH_3); 3.30 (q, $J = 7$ Hz, CH_2).

^{19}F NMR: δ −80.7.(t, $J_{FF} = 11.5$ Hz, CF_3); −104.0 (t, $J_{FF} = 11.5$ Hz, CF_2); −124.7 (m, CF_2).

Anal calc for $C_6H_5F_7S_2$: C, 26.28; H, 1.84. Found: C, 26.56; H, 1.58.

- *Propyl perfluorobutanedithioate* **5d**

Yield 51%. Bp 100 °C (0.1 mbar).

^{1}H NMR: δ 1.05 (t, $J = 7$ Hz, CH_3); 1.78 (sext, $J = 7$ Hz, CH_2); 3.25 (t, $J = 7$ Hz, CH_2).

^{19}F NMR: δ −80.7 (t, $J_{FF} = 11$ Hz, CF_3); −103.9 (t, $J_{FF} = 11$ Hz, CF_2); −124.6 (m, CF_2).

Anal calc for $C_7H_7F_7S_2$: C, 29.17; H, 2.45. Found: C, 29.45; H, 2.10.

- *Benzyl perfluorobutanedithioate* **5e**

Yield 76%. Bp 90 °C (0.1 mbar).

^{1}H NMR: δ 4.45 (s, CH_2); 7.30 (m, C_6H_5).

^{13}C NMR: δ 41.8 (CH_2); 104.0–121.0 (m, $CF_2CF_2CF_3$); 128.1; 129.0; 130.1; 132.7 (C_6H_5), 211.3 (t, J = 25.5 Hz, C=S).

^{19}F NMR: δ −80.6 (t, J = 11 Hz, CF_3); −103.9 (tm, J = 11 Hz, CF_2); −124.5 (m, CF_2).

Anal calc for $C_{11}H_7F_7S_2$: C, 39.29; H, 2.09. Found: C, 39.37; H, 1.72.

- *Propyl ω-H-perfluoropentanedithioate* **5f** *[3]*

Yield 70%. Bp 68–70 °C (0.4 mbar).

^{1}H and ^{19}F NMR: see [3].

^{13}C NMR: δ 13.4 (CH_3); 20.0 (CH_2); 36.2 (CH_2); 107.8 (tt, CHF_2, J = 255 Hz, J = 30.5 Hz); 105.0–119.0 (m, $CF_2CF_2CF_2$); 212.5 (t, C=S, J = 25 Hz).

(1,1-Dichloro-2,2,2-trifluoroethyl) ethyl sulfoxide **6**

Hydrogen peroxide (3mL, 30% solution in H_2O) was added to a solution of the sulfide **4a** (0.01 mol) in CF_3COOH (10 mL) at 0 °C. The mixture was stirred for 1 h at room temperature, diluted with H_2O (200 mL) and extracted with diethyl ether (3 x 25 mL). The ethereal solution was dried over sodium sulfate, the ether was evaporated and the sulfoxide **6** was distilled in vacuo.

Yield 40%. Bp 40 °C (0.1 mbar).

^{1}H NMR: δ 1.50 (t, J = 7 Hz, CH_3); 3.20 (dq, J = 14.5 Hz, J = 7.5 Hz, CH_AH_B); 3.11 (dq, J = 14.5 Hz, J = 7.5 Hz, CH_AH_B).

^{19}F NMR: δ −73.7 (s, CF_3).

Cycloaddition of dithiocarboxylates **5** *with dienes: general procedure*

A mixture of dithiocarboxylates **5** (0.01 mol) and the diene (0.015 mol) was stirred for 10 h at room temperature and distilled in vacuo. In the case of 1-(trimethylsilyloxy)-butadiene, the excess of diene was evaporated and the crude reaction mixture was purified by chromatography on silica gel (petroleum ether/CH_2Cl_2, 4:1).

- *2-(Ethylsulfanyl)-4,5-dimethyl-2-(trifluoromethyl)-3,6-dihydro-2H-thiopyran* **7a** *[2]*

Yield 85%. Bp 45 °C (0.1 mbar).

^{1}H NMR: δ 1.25 (t, J = 7 Hz, CH_3); 1.70 (s, CH_3); 1.79 (s, CH_3); 2.20 (d, J = 18.5 Hz, CH_AH_B); 2.75 (d, J = 18.5 Hz, CH_AH_B); 2.78 (q, J = 7 Hz, CH_2CH_3); 2.91 (d, J = 15.5 Hz, CH_AH_B–S); 3.30 (d, J = 15.5 Hz, CH_AH_B–S).

^{13}C NMR: δ 13.7 (CH_3); 18.9 (CH_3); 19.9 (CH_3); 25.3 (CH_2); 30.0 (CH_2–S); 37.3 (CH_2); 58.9 (q, J = 28 Hz, C–CF_3); 123.1 (C=); 123.9 (C=); 126.8 (q, J = 282 Hz, CF_3).

^{19}F NMR: δ −73.6 (s, CF_3).

- *2-(Benzylsulfanyl)-4,5-dimethyl-2-(trifluoromethyl)-3,6-dihydro-2H-thiopyran* **7b**

Yield 75%. Bp 58 °C (0.2 mbar).

^{1}H NMR: δ 1.69 (s, CH_3); 1.78 (s, CH_3); 2.21 (d, J = 19.0 Hz, CH_AH_B); 2.78 (d, J = 19.0 Hz, CH_AH_B); 2.90 (d, J = 15.0 Hz, CH_AH_B–S); 3.30 (d, J = 15.0 Hz, CH_AH_B–S); 4.30 (s, CH_2); 7.30 (m, C_6H_5).

^{19}F NMR: δ −73.5 (s, CF_3).

Anal calc for $C_{15}H_{17}F_3S_2$: C, 56.58; H, 5.38. Found: C, 56.49; H, 5.21.

- *2-(Ethylsulfanyl)-4,5-dimethyl-2-perfluoropropyl-3,6-dihydro-2H-thiopyran* **7c**

Yield 72%. Bp 70 °C (0.1 mbar).

^{1}H NMR: δ 1.21 (t, J = 7.0 Hz, CH_3); 1.71 (s, CH_3); 1.80 (s, CH_3); 2.30 (d, J = 18.5 Hz, CH_AH_B); 2.85 (d, J = 18.5 Hz, CH_AH_B); 2.79 (q, J = 7.0 Hz, CH_2); 2.90 (d, J = 17 Hz, CH_AH_B–S); 3.30 (d, J = 17 Hz, CH_AH_B–S).

^{19}F NMR: δ −81.5 (t, J_{FF} = 12.0 Hz, CF_3); −107.1 (dt, J_{FF} = 280 Hz, J_{FF} = 12 Hz, CF_AF_B C–S); −109.0 (dt, J_{FF} = 280 Hz, J_{FF} = 12 Hz, CF_AF_BC–S); −120.0 (dm, J_{FF} = 286 Hz, CF_AF_B); −122.8 (dm, J_{FF} = 286 Hz, CF_AF_B).

Anal calc for $C_{12}H_{15}F_7S_2$: C, 40.45; H, 4.24. Found: C, 40.73; H, 3.79.

2-(Benzylsulfanyl)-2-(trifluoromethyl)-6-(trimethylsilyloxy)-3,6-dihydro-2H-thiopyran **8** *and 2-(benzylsulfanyl)-2-(trifluoromethyl)-3-(trimethylsilyloxy)-3,6-dihydro-2H-thiopyran* **9**

Yield 42%. Bp 70 °C (0.2 mbar).

^{1}H NMR: δ 0.10 (s, $SiMe_3$); 0.18 (s, $SiMe_3$); 2.30–3.30 (m, CH_2); 4.10 (s, CH_2); 5.00 (m, CH), 5.50–6.00 (m, CH=CH).

^{19}F NMR: δ −66.6 (s, CF_3); −68.8 (s, CF_3); −73.0 (s, CF_3); −73.8 (s, CF_3) (relative intensity: 2.5:1; 2.3:3.2).

Anal calc for $C_{15}H_{21}F_3OS_2Si$: C, 50.76; H, 5.59. Found: C, 50.06; H, 5.30.

- *Compound* **9** *(after chromatographic separation)*

Yield 10%.

^{1}H NMR (double homonuclear resonance): δ 0.10 (s, $SiMe_3$); 2.86 (ddm, J = 17 Hz, J = 4 Hz, CH_AH_B); 3.33 (dq, J = 17 Hz, J = 2.5 Hz, CH_AH_B); 5.00 (m, CH–OSi); 4.00 (s, CH_2), 5.42 (dq, J = 12.5 Hz, J = 2.5 Hz, CH=); 5.78 (ddt, J = 12.5 Hz, J = 4.5 Hz, J = 2.5 Hz, CH=).

^{13}C NMR: δ 0.02 ($SiMe_3$); 24.9 (CH_2); 35.4 (CH_2); 62.9 (q, J = 25 Hz, C–CF_3); 69.5 (C–OSi); 123.9 (s, C_{Ar}); 127.5 (s, C_{Ar}); 128.7 (s, CH=); 129.4 (s, CH=); 131.3 (s, C_{Ar}); 137.0 (s, C_{Ar}–CH_2).

^{19}F NMR: δ −68.8 (s, CF_3).

2-(Propylsulfanyl)-2-(ω-H-perfluorobutyl)-3,6-dihydro-2H-thiopyran-3-ol **12**

Yield 30%.

^{1}H NMR (double homonuclear resonance): δ 1.00 (t, J = 7 Hz, CH_3); 1.61 (sext, J = 7 Hz, CH_2); 2.50 (s, OH); 2.81 (t, J = 7 Hz, CH_2); 2.95 (dd, 1H, J = 18.5 Hz, J = 5.0 Hz, CH_AH_B); 3.40 (d, J = 18.5 Hz, CH_AH_B); 4.22 (d, J = 5.0 Hz, CH–OH); 5.85 (dm, J = 10.5 Hz, CH=); 5.98 (ddd, J = 10.5 Hz, J = 5.0 Hz, J = 1.5 Hz, CH=); 6.06 (tt, J_{HF} = 52.0 Hz, J = 5.5 Hz, CF_2H).

^{13}C NMR: δ 14.8 (CH_3); 22.2 (CH_2); 24.2 (CH_2); 32.9 (CH_2); 64.5 (t, J = 17.5 Hz, C–CF_2); 64.6 (C–OH); 108.2 (tt, J = 265.0 Hz, J = 29.5 Hz, CF_2H); 125.4 (CH=); 128.1 (CH=).

^{19}F NMR: δ −98.5 (d, J_{FF} = 292 Hz, CF_AF_B); −101.5 (d, J_{FF} = 292 Hz, CF_AF_B); −116.3 (d, J_{FF} = 290 Hz, CF_AF_B), −121.3 (d, J_{FF} = 290 Hz, CF_AF_B); −130.8 (m, CF_2); −137.5 (dm, J_{HF} = 52 Hz, CF_2H).

Anal calc for $C_{12}H_{14}F_8OS_2$: C, 36.92; H, 3.61. Found: C, 37.42; H, 3.69.

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