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Preliminary Note

A new procedure for the synthesis of alkyl perfluoroalkanedithiocarboxylates

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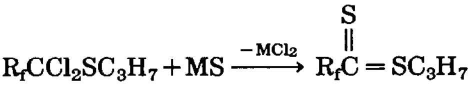
Abstract

Alkyl perfluoroalkanedithiocarboxylates have been synthesized from 1,1-dichloroperfluoroalkyl propyl sulfides by reaction with zinc sulfide or cadmium sulfide.

Dithiocarboxylates are well-known reactive compounds used wisely in organic syntheses [1, 2]. Much less is known about the properties of perfluoroalkanedithiocarboxylates and the possibilities for their synthetic application; this may be connected with a lack of convenient methods for their synthesis [3].

We have found a convenient procedure for the synthesis of propyl perfluoroalkanedithiocarboxylates (I) by reaction of 1,1-dichloroperfluoroalkyl propyl sulfides (II) with zinc sulfide or cadmium sulfide:



$$\underset{\textbf{(II)}}{R_fCCl_2SC_3H_7} + MS \xrightarrow{-MCl_2} \underset{\textbf{(I)}}{R_f\overset{\overset{S}{\|}}{C} = SC_3H_7}$$

(a) $R_f = H(CF_2)_4$; (b) $R_f = CF_3(CF_2)_3$: M = Zn, Cd

Compounds (II) have been prepared in good yield by chlorination of the dithioacetals of perfluorinated aliphatic aldehydes (III) [4].

$$\underset{\textbf{(III)}}{R_fCH(SC_3H_7)_2} + Cl_2 \longrightarrow \underset{\textbf{(II)}}{R_fCCl_2SC_3H_7}$$

The esters (I) are red, foul-smelling liquids.

The presence of an electron-withdrawing perfluoro group allows ready reaction to occur between dithiocarboxylates and dienes [5]. The compounds **Ia,b** react with 2,3-dimethylbutadiene even at ambient temperature to give the thiaines **IVa,b**.

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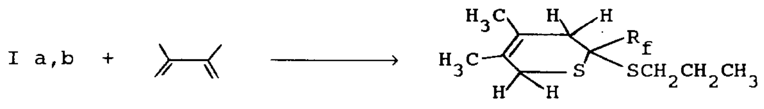
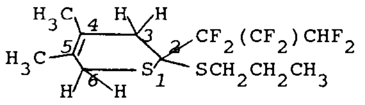


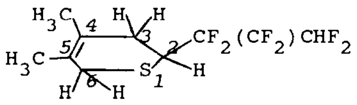
(a) $R_f = H(CF_2)_4$; (b) $R_f = CF_3(CF_2)_3$

(IV)

The structure of compound **IVa** has been confirmed by ^{1}H and ^{13}C NMR spectral data (in $CDCl_3$ solution using a Gemini 200 MHz spectrometer, the chemical shifts quoted being from internal TMS). In the ^{13}C NMR spectrum, four signals associated with CH_2 carbon atom nuclei were observed. Two of these (22.50 and 33.70 ppm) were assigned to the carbon atoms of the $SCH_2CH_2CH_3$ moiety, on the basis of the two-dimensional ^{13}C–^{1}H chemical shift correlation spectrum (HETCOR) [6] (Fig. 1); the respective proton signals possess characteristic multiplicity. The respective methylene ^{13}C signals (29.91 and 37.56 ppm) were assigned to $C\mathit{CH}_2S$ and $C\mathit{CH}_2C$ carbon atoms, respectively, on the basis of NMR spectral data for the model compound **V** [7].



(IVa)



(V)

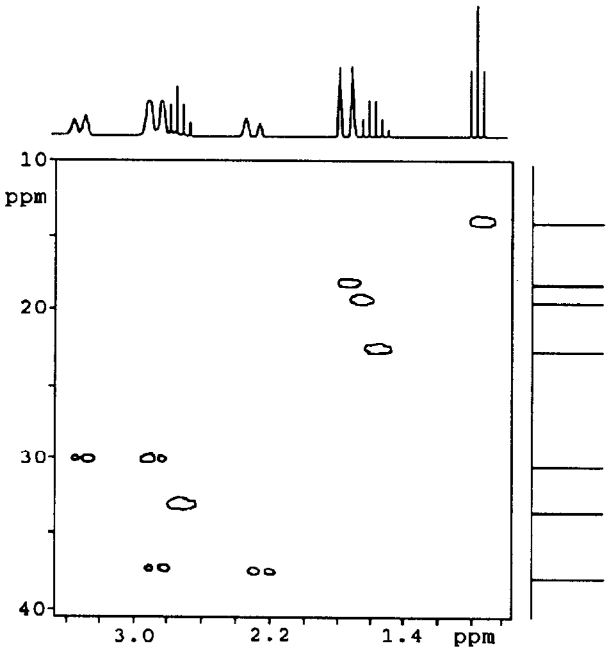


Fig. 1. The HETCOR spectrum of the compound **IVa**.

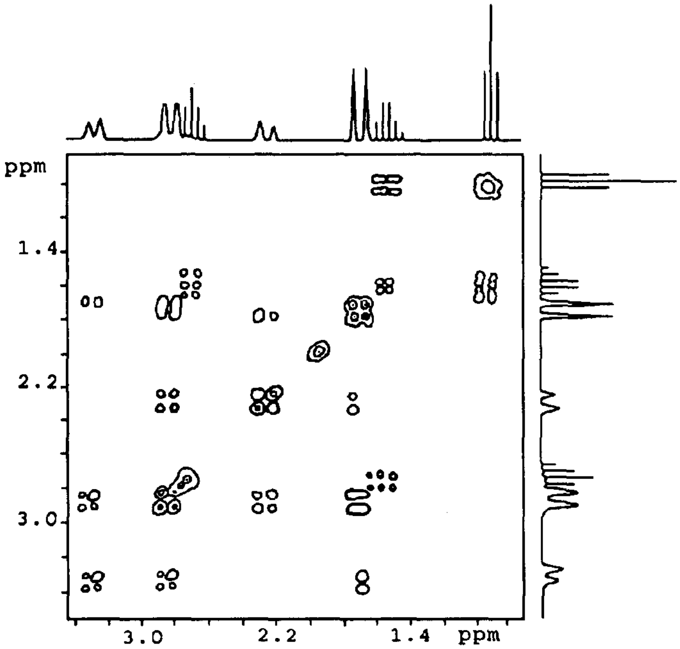


Fig. 2. The COSY spectrum of the compound **IVa**.

In the NMR spectrum of compound **V** the ring methylene carbon chemical shifts (δ_C) are very close to each other (30.72 and 30.89 ppm). The strongest effect arising from replacing the SPr substituent in compound **IVa** by a hydrogen should be observed for the C-3 atom (in the present case this should correspond to shielding of 6.7 ppm); on the other hand, this replacement has virtually no influence on the δ_C value for C-6 (a high-field shift of 0.8 ppm). The signals from the ring methylene protons of compound **V** are AB and ABX spin multiplets with broadened components, due to long-range spin–spin interactions between the methylene protons and the ^1H and ^{19}F nuclei. Analysis of the COSY ^1H spectrum [6] from compound **V** reveals that the C^3H_2 moiety protons are shielded to a greater extent ($\delta H_A = 2.40$, $\delta H_B = 2.48$ ppm) than the C^6H_2 ones ($\delta H_A = 3.03$, $\delta H_B = 3.25$ ppm). Similar positions for the methylene multiplets are also observed in the ^1H NMR spectrum of compound **IVa** ($\delta H_A = 2.29$, $\delta H_B = 2.87$ for C^2H_2 and $\delta H_A = 2.87$, $\delta H_B = 3.33$ ppm for C^6H_2). The signals have been assigned on the basis of the HETCOR NMR spectrum data. The assignment of the ^1H and ^{13}C NMR signals is based on the cross peak analysis of the COSY ^1H NMR spectra (Fig. 2).

In a typical experiment, a mixture of the sulfide **IIa,b** (26.5 mmol), and zinc or cadmium sulfide (79.5 mmol) was refluxed in acetonitrile (100 ml) for 6 h. The mixture was cooled to 20 °C and filtered, acetonitrile distilled off at atmospheric pressure and the residue fractionated *in vacuo*. The yield of the esters **Ia,b** was 70–75%.

Propyl ω-H-perfluorodithiovalerate (Ia), b.p., 49–51 °C (0.05mmHg) ^{1}H NMR ($CDCl_3$, TMS): δ 1.06 (t, 3H, $J=7.4$ Hz, CH_3), 1.76 (sextet, 2H, $J=7.4$ Hz, CH_2), 3.28 (t, 2H, $J=7.4$ Hz, CH_2), 6.09 (tt, 1H, $J=52.0$, 5.0 Hz, CHF_2) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ -138.00 (d, 2F, $J=52.0$ Hz, CF_2H), -130.03 (m), -124.44 (m), -103.38 (m) ppm. Analysis: Found: C, 29.89; H, 2.71; S, 19.89%. $C_8H_8F_8S_2$ requires C, 30.00; H, 2.76; S, 20.02%.

Propyl perfluorodithiovalerate (Ib), b.p., 65–67 °C (12 mmHg). ^{1}H NMR ($CDCl_3$, TMS): δ 1.06 (t, 3H, $J=7.4$ Hz, CH_3), 1.76 (sextet, 2H, $J=7.4$ Hz, CH_2), 3.28 (t, 2H, $J=7.4$ Hz, CH_2) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ -126.46 (m), -121.54 (m), -103.84 (m), -81.92 (m) ppm. Analysis: Found: C, 29.22; H, 2.14; F, 50.60; S, 18.90%. $C_8H_7F_9S_2$ requires C, 28.40; H, 2.08; F, 50.54; S, 18.95%.

4,5-Dimethyl-2-propylthio-2-ω-H-perfluorobutyl-3H,6H-thiaine (IVa). 17.2 mmol of the ester **Ia** and 35.4 mmol of dimethylbutadiene were mixed; the mixture was allowed to stand for 24 h at ambient temperature and was then distilled *in vacuo*. The yield of the thiaine **IV** was 79%; b.p., 90–92 °C (0.06 mmHg). ^{1}H NMR spectrum ($CDCl_3$, TMS): δ 1.00 (t, 3H, $J=7.4$ Hz, CH_3), 1.60 (sextet, 2H, $J=7.4$ Hz, CH_2), 1.71 (s, 3H, CH_3), 1.78 (s, 3H, CH_3), 2.29, 2.87 (AB, 2H, $J=16.0$ Hz, CH_2), 2.87, 3.39 (AB, 2H, $J=16.0$ Hz, CH_2), 2.75 (t, 2H, $J=7.4$ Hz, CH_2), 6.06 (tt, 1H, $J=52.2$, 5.64 Hz, CHF_2) ppm. ^{13}C NMR ($CDCl_3$, TMS): δ 13.84 (s), 19.14 (s), 20.17 (s), 22.50 (s), 29.91 (s), 33.77 (s), 37.56 (s), 61.29 (s), 92–102 (m), 123.35 (s), 124.33 (s) ppm. Analysis: Found: C, 41.77; H, 4.3; F, 38.24; S, 15.96%. $C_{14}H_{18}F_8S_2$ requires C, 41.78; H, 4.50; F, 37.75; S, 15.93%.

4,5-Dimethyl-2-propylthio-2-perfluorobutyl-3H,6H-thiaine (IVb). Obtained similarly to compound **IVa** Yield, 65%; b.p., 75–76 °C (0.04 mmHg). ^{1}H NMR ($CDCl_3$, TMS): δ 1.00 (t, 3H, $J=7.2$ Hz, CH_3), 1.60 (sextet, 2H, $J=7.2$ Hz, CH_2), 1.71 (s, 3H, CH_3), 1.78 (s, 3H, CH_3), 2.29, 2.87 (AB, 2H, $J=16.0$ Hz, CH_2), 2.75 (t, 2H, $J=7.20$ Hz, CH_2), 2.87, 3.32 (AB, 2H, $J=16.0$ Hz, CH_2) ppm. ^{19}F NMR ($CDCl_3$, $CFCl_3$): δ 126.92 (m, 2F), -120.30, -117.19 (AB, 2F, $J=291.8$ Hz), -109.31, -107.30 (AB, 2F, $J=280.5$ Hz), -81.79 (s, 3F) ppm. Analysis: Found: C, 39.87; H, 3.91; F, 40.23; S, 15.58%. $C_{14}H_{17}F_9S_2$ requires C, 39.99; H, 4.07; F, 40.67; S 15.25%.

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References

1 A. Thuillier, *Phosphorus Sulfur, 23* (1985) 253.
2 N. M. Yousif, U. Pedersen, B. Yde and S. O. Lawesson, *Tetrahedron, 40* (1984) 2663.
3 W. J. Middleton, E. G. Howard and W. H. Sharkey, *J. Org. Chem., 30* (1965) 1375.

4 L. N. Markovski, E. I. Slusarenko, V. M. Timoshenko, E. I. Kaminskaja, A. G. Kirilenko and Yu. G. Shermolovich, *Zh. Org. Khim.*, *26* (1991), in press.

5 W. J. Middleton, *J. Org. Chem.*, *30* (1965) 1390.

6 A. E. Derome, *Modern NMR Techniques for Chemistry Research*, Pergamon, Oxford, 1987.

7 Yu. G. Shermolovich, E. I. Slusarenko and L. N. Markovski, *Zh. Org. Khim.*, *24* (1989) 1931.