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A facile one-pot synthesis of 1,1-bis(alkylmercapto)-2-perfluoroalkylsulphonyl ethylenes and the structure of $CF_3SO_2CH{=}\overline{CS(CH_2)_3S}$

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Abstract

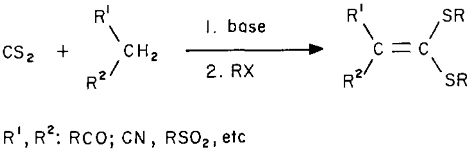
1,1-Bis(alkylmercapto)-2-perfluoroalkylsulphonyl ethylenes, $R_FSO_2CH{=}C(SR)_2$ and $R_FSO_2CH{=}\overline{CS(CH_2)_nS}$, have been prepared by the condensation of carbon disulphide and methyl perfluoroalkylsulphone, $R_FSO_2CH_3$, with subsequent alkylation. The X-ray structure analysis of $CF_3SO_2CH{=}\overline{CS(CH_2)_3S}$ is presented.

Introduction

Ketene dithioacetals and their derivatives are versatile compounds and easily accessible [1]. In particular, functionalised ketene dithioacetals are widly used in organic synthesis, since they can serve as useful intermediates and undergo many organic transformations [2]. They are generally prepared by the base-induced condensation of activated methylene compounds with carbon disulphide followed by alkylation of the dithiolate anion [1, 3]. In these reactions a hindered base such as sodium 2,6-di(t-butyl)-4-methylphenoxide, potassium t-butyloxide or lithium dialkylamide is used [4] (see Scheme 1).

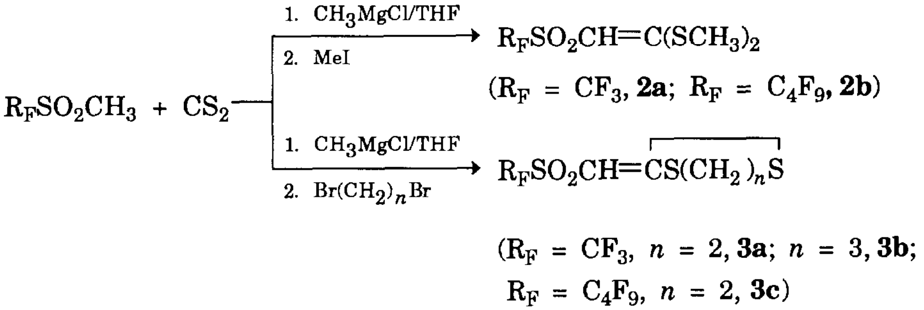
Results and discussion

We report here the use of methylmagnesium chloride, CH_3MgCl, as a base for the condensation of CS_2 and $R_FSO_2CH_3$ to prepare the title compounds, $R_FSO_2CH{=}C(SMe_2)_2$ (**2**) and $R_FSO_2CH{=}\overline{CS(CH_2)_nS}$ (**3**). To the best of our knowledge, these compounds have not been reported to date.



Scheme 1.

0022-1139/93/$6.00



$$R_FSO_2CH_3 + CS_2 \xrightarrow[2.\ MeI]{1.\ CH_3MgCl/THF} R_FSO_2CH{=}C(SCH_3)_2 \quad (2)$$

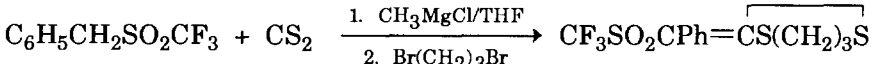
$$(R_F = CF_3, \mathbf{2a};\ R_F = C_4F_9, \mathbf{2b})$$

$$R_FSO_2CH_3 + CS_2 \xrightarrow[2.\ Br(CH_2)_nBr]{1.\ CH_3MgCl/THF} R_FSO_2CH{=}\overline{CS(CH_2)_nS} \quad (3)$$

$$(R_F = CF_3,\ n = 2, \mathbf{3a};\ n = 3, \mathbf{3b};$$
$$R_F = C_4F_9,\ n = 2, \mathbf{3c})$$

Methyl perfluoroalkylsulphone (**1**) was deprotonated by means of 2 equiv. of Grignard reagent. The methane formed was spontaneously evolved. Reaction of the resulting carbanion with excess carbon disulphide gave a dithiolate, which was alkylated by MeI or $Br(CH_2)_nBr$ to form the expected products **2** or **3**. The yields of **2** or **3** were 73–78%.

Under similar reaction conditions, benzyl trifluoromethylsulphone, $C_6H_5CH_2SO_2CF_3$ (**4**), can also react with CS_2 and then be alkylated by $Br(CH_2)_3Br$ to give $CF_3SO_2CPh{=}\overline{CS(CH_2)_3S}$, (**5**). The yield, however, was only 25% which may be explained by the lower reactivity of the $CF_3SO_2\bar{C}HC_6H_5$ anion due to steric hindrance and resonance stability.



$$C_6H_5CH_2SO_2CF_3 + CS_2 \xrightarrow[2.\ Br(CH_2)_3Br]{1.\ CH_3MgCl/THF} CF_3SO_2CPh{=}\overline{CS(CH_2)_3S}$$

(**4**) (**5**)

The results obtained are summarised in Table 1. All these new products were characterised by microanalysis, IR, NMR and mass spectrometry. They were stable and could be stored in a closed flask at room temperature without decomposition.

Recrystallisation of products **2** and **3** from acetone and acetonitrile (1:1) gave fine yellow crystals. X-Ray structural analysis of **3b** (see Fig. 1) showed that O(1), S(1), C(1), C(3), S(2) and S(3) are planar. The bond distances C(1)–S(1), C(3)–S(2) and C(3)–S(3) (respectively, 1.711(5), 1.741(4) and

TABLE 1

Preparation of compounds **2**, **3** and **5**

Substrate **1**	RX	Products **2** or **3**	Yield (%)[a]	M.p. (°C)
1a	MeI	**2a**	76	76
1a	$Br(CH_2)_2Br$	**3a**	78	86
1a	$Br(CH_2)_3Br$	**3b**	75	88
1b	MeI	**2b**	73	91–93
1b	$Br(CH_2)_2Br$	**3c**	75	93
4	$Br(CH_2)_3Br$	**5**	25	126–128

[a] Isolated yield based on **1** or **4**.

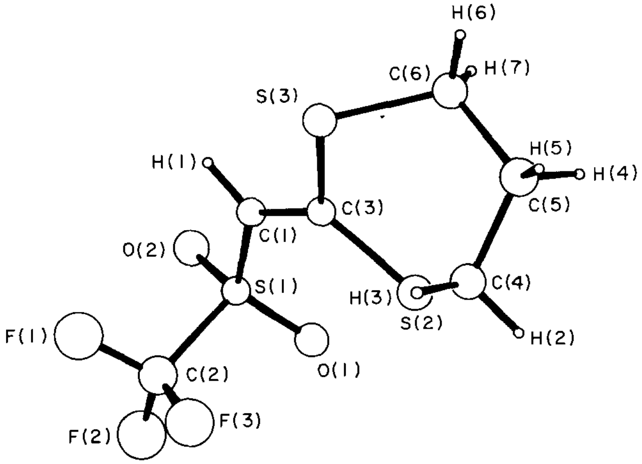
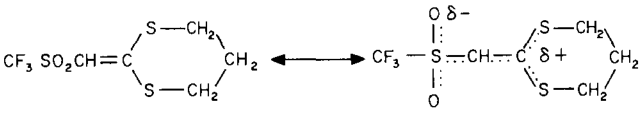


Fig. 1. The structure of compound **3b**.



Scheme 2.

1.743(4) Å) are shorter than those of C(2)–S(1), C(4)–S(2) and C(6)–S(3) (1.823(7), 1.804(5) and 1.814(5) Å). The normal C–S bond length is 1.81 Å [5]. From these data, we propose a delocalised structure for compound **3a**, (see Scheme 2).

In conclusion, the present method provides a facile synthesis of 1,1-bis(alkylmercapto)-2-perfluoroalkylsulphonyl ethylenes.

Experimental

Melting points were measured on a Thiele apparatus and are reported uncorrected. THF was purified before use. ^{1}H NMR and ^{19}NMR spectra were recorded on a Varian 360L instrument using Me$_4$Si and CF$_3$Cl as internal and external standards, respectively. IR spectra were obtained with an IR-440 Shimadzu spectrophotometer. Low-resolution mass spectra were obtained on a Finnigan GC–MS 4021 instrument. Methyl perfluoroalkylsulphone (**1**) and benzyl trifluoromethylsulphone (**4**) were prepared according to literature methods [6].

The general synthetic procedure was as follows. Methylmagnesium chloride in THF (1 N, 20 ml) was injected into a solution of CF$_3$SO$_2$CH$_3$ (1.48 g, 0.01 mol) in dry THF (10 ml) at 0 °C; after stirring for 2 h, CS$_2$ (1.52 g, 0.02 mol) was added using a syringe at 0 °C. The reaction mixture was warmed to 20 °C, then stirred for 4 h. MeI (3 g, 0.021 mol) was added and the mixture stirred for another 4 h. The solvent was evaporated and the residue was sublimed under vacuum to give crude product **2a** (2 g, yield 76%). Recrystallization from $(CH_3)_2CO$ and CH_3CN (1:1) gave pure **2a**.

1,1-Di(methylmercapto)-2-trifluoromethylsulphonyl ethylene, $CF_3SO_2CH=C(SCH_3)_2$ (**2a**): IR (KCl) (cm^{-1}): 3075 (m); 2998 (w); 2990 (w); 1646 (w); 1460 (s); 1427 (m); 1342 (s); 1320 (m); 1263 (m); 1196 (s); 983 (m); 923 (m); 845 (m); 697 (s); 582 (s); 505 (s). ^1H NMR, $(CD_3)_2CO$, 60 MHz, δ: 5.84 (s, 1H); 2.72 (s, 3H); 2.65 (s, 3H) ppm. ^{19}F NMR δ: -79.3 (s, 3F) ppm. MS(*m/z*) (EI): 253 (M+H, 8.3); 252 (M^+, 22.7); 238 ($M+H-CH_3$, or M^+-O, 3.4); 183 (M^+-CF_3, 42.4); 119 ($M^+-CF_3SO_2$, 20.6); 104 ($M^+-CF_3SO_2-CH_3$, 100); 89 ($SO_2CH=C^+$, 18.4); 73 ($SOCH=C^+$, 41.5); 69 (CF_3^+, 36.1); 47 (SCH_3^+, 12.7). Analysis: $C_5H_7F_3O_2S_3$ requires: C, 23.81; H, 2.78; F, 22.62%. Found: C, 23.95; H, 2.80; F, 22.38%.

(1,3-Dithiolane-2-ylidene)methyltrifluoromethylsulphone, $CF_3SO_2CH=\overline{CS(CH_2)_2S}$ (**3a**): IR (cm^{-1}): 3044 (m); 2941 (w); 1670 (w); 1486 (s); 1480 (s); 1338 (s); 1325 (s); 1286 (s); 1327 (s); 1198 (vs); 1151 (s); 1116 (vs); 928 (s); 841 (s); 711 (s); 590 (s); 508 (s). ^1H NMR δ: 6.54 (s, 1H); 3.74 (s, 4H) ppm. ^{19}F NMR δ: -79.6 (s, 3F) ppm. MS(*m/z*) (EI): 250 (M^+, 14.5); 181 (M^+-CF_3, 67.0); 133 ($CF_3SO_2^+$, 2.6); 117 ($M^+-CF_3SO_2$ or CF_3SO^+, 4.5); 89 ($SO_2CH=C^+$, 100); 77 (SO_2CH^+, 1.7); 69 (CF_3^+, 14.1); 45 (SCH^+, 51.0). MS(*m/z*) (CI): 251 (M+H, 100); 250 (M^+, 47.0); 181 (M^+-CF_3, 30.0); 167 ($M^+-CF_3-CH_2$, 10.1); 165 (M^+-CF_3-O, 5.8); 133 ($CF_3SO_2^+$, 1.8); 118 (CF_3SOH^+, 22.8); 117 (CF_3SO^+ or $M^+-CF_3SO_2$, 1.7). Analysis: $C_5H_5F_3O_2S_3$ requires: C, 24.00; H, 2.00; F, 22.80%. Found: C, 23.95; H, 2.40; F, 22.78%.

(1,3-Dithiolcyclohexylidene)methyltrifluoromethylsulphone, CF_3SO_2-$CH=\overline{CS(CH_2)_3S}$ (**3b**): IR (cm^{-1}): 3020 (w); 2880 (w); 1642 (w); 1464 (s); 1418 (s); 1340 (vs); 1239 (m); 1184 (vs); 1108 (s); 930 (s); 820 (s); 728 (m); 591 (s); 558 (m); 505 (s). ^1H NMR δ: 6.43 (s, 1H); 3.23 (m, 4H); 2.33 (m, 2H) ppm. ^{19}F NMR δ: -79.0 ppm. MS(*M/z*) (EI): 265 (M+H, 23.91); 264 (M^+, 68.01); 195 (M^+-CF_3, 98.4); 179 (M^+-CF_3-O, 5.2); 133 ($CF_3SO_2^+$, 3.0); 131 ($M^+-CF_3SO_2^+$, 31.1); 121 ($SO_2CH=C=S^+$, 4.6); 89 ($SO_2CH=C^+$, 54.9); 73 ($SOCH=C^+$, 21.9); 69 (CF_3^+, 46.0); 45 (SCH^+, 100). Analysis: $C_6H_7F_3O_2S$ requires: C, 27.27; H, 2.65; F, 21.57%. Found: C, 27.18; H, 2.39; F, 21.19%.

1,1-Bis(methylmercapto)-2-perfluorobutanesulphonyl ethylene, C_4F_9-$SO_2CH=C(SCH_3)_2$ (**2b**): IR (cm^{-1}): 3042 (m); 2993 (w); 2990 (w); 1645 (w); 1459 (s); 1430 (m); 1340 (s); 1320 (m); 1200–1100 (vs); 985 (m); 850 (m); 700 (s); 585 (s); 502 (s). ^1H NMR δ: 2.75 (s, 3H); 2.68 (s, 3H); 5.85 (s, 1H) ppm. ^{19}F NMR δ: -79.3 (s, 3F); -108.4 (m, 4F); -120.0 (m, 2F); -124.2 (m, 2F) ppm. MS(*m/z*) (EI): 403 (M+H, 4.83); 402 (M^+, 12.33); 387 (M^+-CH_3, 4.13); 386 (M^+-O, 2.76); 267 ($C_4F_9SO^+$, 3.46); 219 ($C_4F_9^+$, 7.63); 119 ($M^+-C_4F_9SO_2$ or $C_2F_3^+$, 46.79); 104 (M^+--$C_4F_9-SO_2-CH_3$, 100); 89 ($SO_2CH=C^+$, 17.38); 69 (CF_3^+, 44.10); 47 (SCH_3^+, 18.29). Analysis: $C_8H_7F_9O_2S_3$ requires: C, 23.88; H, 1.74; F, 42.54%. Found: C, 23.73; H, 1.68; F, 43.01%.

(1,3-Dithiolane-2-ylidene)methylperfluorobutylsulphone, $C_4F_9SO_2CH{=}\overline{CS(CH_2)_2S}$ (**3c**): ^1H NMR δ: 3.70 (s, 4H); 6.44 (s, 1H) ppm. ^{19}F NMR δ: -79.5 (s, 3F); -108.5 (m, 2F); -120.0 (m, 2F); -124.3 (s, 2F) ppm. Analysis: $C_8H_5F_9O_2S_3$ requires: C, 24.00; H, 1.25; F, 42.75%. Found: C, 24.13; H, 1.38; F, 41.98%.

(1,3-Dithiocyclohexylidenephenyl)methyltrifluoromethylsuphone, $CF_3SO_2CC_6H_5{=}\overline{CS(CH_2)_3S}$ (**5**): IR (cm^{-1}): 3020 (w); 2900 (w); 2850 (w); 1600 (w); 1490 (m); 1450 (m); 1350 (s); 1200 (vs); 1105 (s); 1030 (m); 950 (m); 760 (s); 695 (s); 640 (m); 580 (m); 520 (m). ^1H NMR δ: 2.15 (m, 2H); 3.03 (m, 4H); 7.2–7.5 (m, 5H) ppm. ^{19}F NMR δ: -78.8 (s, 3F) ppm. MS(m/z) (EI): 341 (M+H, 1.39); 3.40 (M^+, 3.40); 312 ($M^+ - C_2H_2$, 0.93); 298 ($M^+ - C_3H_6$, 1.41); 254 ($M^+ - CSC_3H_6$, 2.24); 238 ($CF_3SOCC_6H_5{=}S$, 0.25); 223 ($M^+ - CF_3SO$, 0.86); 207 ($M^+ - CF_3SO_2$, 7.37); 180 ($M^+ - CF_3SO_2 - C_2H_3$, 100); 178 ($M^+ - C_6H_5 - CF_3O$, 27.83); 165 ($M^+ - CF_3SO_2 - C_3H_6$ or $CF_3 - SO_2S$, 16.69); 121 ($C_6H_5CS^+$, 4.74); 77 ($C_6H_5{}^+$, 0.90). Analysis: $C_{12}H_{11}F_3O_2S_3$ requires: C, 42.35; H, 3.24; F, 16.76%. Found: C, 42.07; H, 3.04; F, 16.97%.

Crystal data

$C_6H_7O_2F_3S_3$, $M = 264.31$, monoclinic; space group $P2_1/c$; $a = 11.247(1)$ Å, $b = 8.957(1)$ Å, $c = 11.271(7)$ Å, $\beta = 113.13(2)$, $V = 1044.2$ Å^3, $Z = 4$; $D_c = 1.681$ g cm^{-3}, $F(000) = 536$, $\mu(MoK\alpha) = 6.96$ cm^{-1}; crystal dimensions $0.2 \times 0.2 \times 0.1$ mm. Intensity data were collected at 20 °C with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated MOKα radiation. 2087 unique reflections were measured in the range $2° < 2\theta < 50$ with $0 < h < 14$, $0 < k < 11$, $-14 < l < 14$. LP and absorption corrections were applied to the intensity data. The structure was solved by direct methods using MULTAN 11/82. The positions of the H atoms were defined via geometric calculation. All positional parameters and anisotropic thermal parameters for non-H atoms were refined by a full-matrix least-squares technique. Final R, Rw and S values were 0.038, 0.049, 1.15, respectively, for 1492 observed reflections ($F^2 > 3\sigma(F^2)$). All computations were performed on a MICROVAX II computer with SDP, MULTAN 11/82 and ORTEP programs. Scattering factors were

TABLE 2

Compound **3b**: bond distances in Ångstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S(1)	O(1)	1.426(4)[a]	S(3)	C(6)	1.814(5)	C(4)	H(2)	0.950(4)
S(1)	O(2)	1.428(3)	F(1)	C(2)	1.315(7)	C(4)	H(3)	0.950(6)
S(1)	C(1)	1.711(5)	F(2)	C(2)	1.310(7)	C(5)	C(6)	1.533(7)
S(1)	C(2)	1.823(7)	F(3)	C(2)	1.299(7)	C(5)	H(4)	0.950(5)
S(2)	C(3)	1.741(4)	C(1)	C(3)	1.342(6)	C(5)	H(5)	0.950(5)
S(2)	C(4)	1.804(5)	C(1)	H(1)	0.951(4)	C(6)	H(6)	0.951(5)
S(3)	C(3)	1.743(4)	C(4)	C(5)	1.527(7)	C(6)	H(7)	0.951(5)

[a] Numbers in parentheses are estimated standard deviations for the last digits.

TABLE 3

Compound **3b** bond angles in degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O(1)	S(1)	O(2)	120.0(2)[a]	S(1)	C(2)	F(3)	111.0(4)	C(4)	C(5)	C(6)	113.5(4)
O(1)	S(1)	C(1)	112.6(3)	F(1)	C(2)	F(2)	108.6(5)	C(4)	C(5)	H(4)	108.5(5)
O(1)	S(1)	C(2)	104.6(3)	F(1)	C(2)	F(3)	108.9(6)	C(4)	C(5)	H(5)	108.5(5)
O(2)	S(1)	C(1)	109.2(3)	F(2)	C(2)	F(3)	108.0(5)	C(6)	C(5)	H(4)	108.4(5)
O(2)	S(1)	C(2)	104.3(3)	S(2)	C(3)	S(3)	118.3(3)	C(6)	C(5)	H(5)	108.4(5)
C(1)	S(1)	C(2)	104.6(3)	S(2)	C(3)	C(1)	125.1(3)	H(4)	C(5)	H(5)	109.5(5)
C(3)	S(2)	C(4)	101.2(2)	S(3)	C(3)	C(1)	116.6(3)	S(3)	C(6)	C(5)	115.2(3)
C(3)	S(3)	C(6)	101.9(2)	S(2)	C(4)	C(5)	113.0(3)	S(3)	C(6)	H(6)	108.0(4)
S(1)	C(1)	C(3)	125.5(3)	S(2)	C(4)	H(2)	108.6(4)	S(3)	C(6)	H(7)	108.0(4)
S(1)	C(1)	H(1)	117.3(4)	S(2)	C(4)	H(3)	108.6(4)	C(5)	C(6)	H(6)	108.0(4)
C(3)	C(1)	H(1)	117.3(4)	C(5)	C(4)	H(2)	108.6(5)	C(5)	C(6)	H(7)	108.0(4)
S(1)	C(2)	F(1)	110.0(4)	C(5)	C(4)	H(3)	108.6(4)	H(6)	C(6)	H(7)	109.5(5)
S(1)	C(2)	F(2)	110.5(5)	H(2)	C(4)	H(3)	109.4(5)				

[a] Numbers in parentheses are estimated standard deviations for the last digits.

TABLE 4

Compound **3b**: positional parameters and their estimated standard deviations

Atom	x	y	z	$B(\text{Å}^2)^a$
S(1)	0.2327(1)	0.3715(1)	0.7651(1)	3.57(2)
S(2)	0.2884(1)	0.0559(2)	0.6380(1)	4.44(3)
S(3)	0.3225(1)	−0.0821(2)	0.8909(1)	3.89(2)
F(1)	0.0235(3)	0.3726(6)	0.8087(3)	9.2(1)
F(2)	0.0141(4)	0.5074(5)	0.6495(4)	9.5(1)
F(3)	0.0023(4)	0.2728(5)	0.6304(4)	9.3(1)
O(1)	0.2564(3)	0.3742(4)	0.6498(3)	4.77(8)
O(2)	0.2785(4)	0.4903(4)	0.8564(3)	5.47(9)
C(1)	0.2734(4)	0.2044(5)	0.8444(4)	3.33(9)
C(2)	0.0573(5)	0.3811(7)	0.7097(6)	5.9(2)
C(3)	0.2924(4)	0.0759(5)	0.7931(3)	2.96(9)
C(4)	0.2651(5)	−0.1428(6)	0.6146(4)	4.2(1)
C(5)	0.3824(5)	−0.2329(6)	0.7008(5)	4.6(1)
C(6)	0.4353(5)	−0.1844(6)	0.8426(5)	4.3(1)
H(1)	0.283	0.202	0.932	4.3*
H(2)	0.248	−0.165	0.527	5.5*
H(3)	0.193	−0.171	0.633	5.5*
H(4)	0.449	−0.221	0.670	6.0*
H(5)	0.358	−0.335	0.696	6.0*
H(6)	0.461	−0.272	0.895	5.6*
H(7)	0.509	−0.123	0.858	5.6*

[a] Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a2B(1,1)+b2B(2,2)+c2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

taken from *International Tables for X-Ray Crystallography* (1974). Full details of the crystallographic data thus obtained are given in Tables 2–4.

Acknowledgement

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