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# Thermal reactions of hexafluorobutadiene and hexafluorocyclobutene with elemental sulphur

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## Abstract

Hexafluorobuta-1,3-diene and hexafluorocyclobutene interact with elemental sulphur under conditions of mutual conversion ($\geqslant$280 °C) to give the same products, hexafluoro-3,6-dihydro-1,2-dithiine (**1**), hexafluorothiolene-3 (**2**) and hexafluorothiolanethione (**3**). The product composition and ratio depend on the reaction conditions.

Dithiine **1** and thiolene **2** were formed in competitive reactions. Their thermal stability and the retrocycloaddition reaction of dithiine **1** have been studied. The latter reaction results in thiolene **2** in addition to the formation of hexafluorocyclobutene. This is consistent with a stepwise mechanism for the retrocycloaddition as well as the cycloaddition reaction.

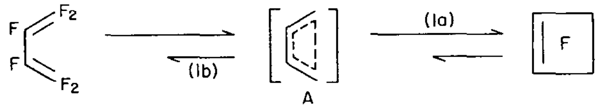
## Introduction

In recent years, the search for anti-AIDS medicines has stimulated an interest in both natural and synthetic disulphides as potential antiviral and anticancer agents. Multistep methods of elemental sulphur ($S_2$) generation for the synthesis of six-membered cyclic disulphides via Diels–Alder reactions have been worked out and synthetic ability of $S_2$ has been studied. Some disulphides from non-fluorinated dienes have been prepared since 1984 [1].

It was of interest to try hexafluorobutadiene (FB) in such a cycloaddition reaction. For this purpose we chose to study the interaction of FB with elemental sulphur, including $S_2$.

## Results and discussion

FB is known to differ from its hydrogen analogue through the non-planarity of its molecule in the ground state [2]. However, this does not prevent the concerted thermal isomerisation of FB to perfluorocyclobutadiene (FCB) (reaction (1) [3]).



(1)

Reaction (1) is reversible. At 200–300 °C, the equilibrium is shifted almost completely to formation of the cyclic isomer [3], whereas the reverse reaction (1b) is only noticeable under more drastic conditions [3, 4].

In this work we have assumed that reactions (1a) and (1b) proceeded via a planar or nearly planar transition state A capable of participating in competitive reactions during diene synthesis. As a dienophile for such a reaction, we have assumed the use of elemental sulphur ($S_2$), generated by the pyrolysis of sulphur ($S_8$) ($\geqslant$500 °C) [5, 6].

In an open system at 500 °C, FB and FCB react with elemental sulphur to form dithiine **1** and thiolene **2** [7] together with a slight admixture of thiolanethione **3** [8] and FB dimers [9] [reactions (2a) and (2b)]. The low conversions of FB (*c*. 9%) and FCB (*c*. 7%) observed (see Table 1) may be explained by several reasons. They are: (i) the short contact time of the reactants; (ii) the low partial pressure of $S_2$ in $S_8$ vapours [6]; (iii) a shift in equilibrium (1) towards the formation of FCB; and (iii) decomposition of dithiine **1** leading to the formation of sulphur and FCB (as will be shown later). The repeated procedure allows the products to be obtained on a preparative scale, but results in the loss of starting FB and FCB, probably as a result of the accumulation of non-volatile products (cf. ref. 10).

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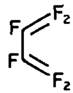
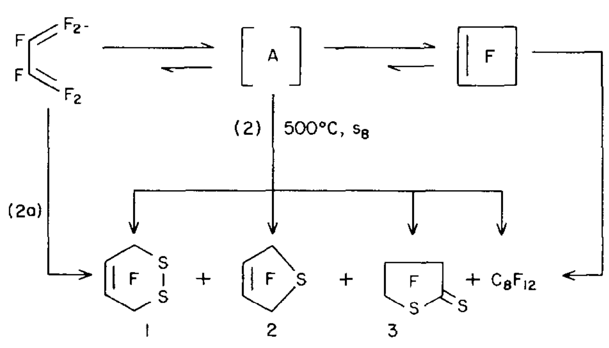
TABLE 1. Reactions of *F*-butadiene and *F*-cyclobutene with elementary sulphur in an open system and under autogenic pressure conditions

| Reaction No. | Reagents (g) | | | Temperature (°C) | | | Reaction time (min) [h] | Unchanged starting material (g) | Mixture of products (g) |
|---|---|---|---|---|---|---|---|---|---|
| | $S_8$ |  |  | Oven No. 1 | Oven No. 2 | Ampoule | | | |
| 2a | 108 | 31 | - | 380 | 520 | - | 30 | 28.0 | 2.6 |
| 2aa | 25 | 24.5 | - | 425 | 250 | - | 20 | 18.8 | 4.4 |
| 2b | 108 | - | 28 | 420 | 540 | - | 20 | 26.0 | 0.8 |
| 2bb[a] | 25 | - | 28.8 | 425 | 250 | - | - | 2.9 | 18.1 |
| 3a | 7.1 | 8.5 | - | - | - | 280 | [30] | 0.5 | 6.0 |
| 3aa | 3.5 | 4.7 | - | - | - | 200 | [6] | 3.0 | 1.2 |
| 3b | 4.7 | - | 10.3 | - | - | 280 | [30] | 8.9 | 0.5 |
| 4a | 32 | 23.5 | - | 280 | 150 | - | 25 | 20.0 | 2.3 |
| 4b | 6.4 | - | 7.8 | 280 | 310 | - | 10 | 5.7 | 1.0 |

[a] After the 11-fold procedure.

[b] Individual amounts: **4**, 10.1 mol% (14%); **5**, 1.1 mol% (2.5%).

[c] After the three-fold procedure.

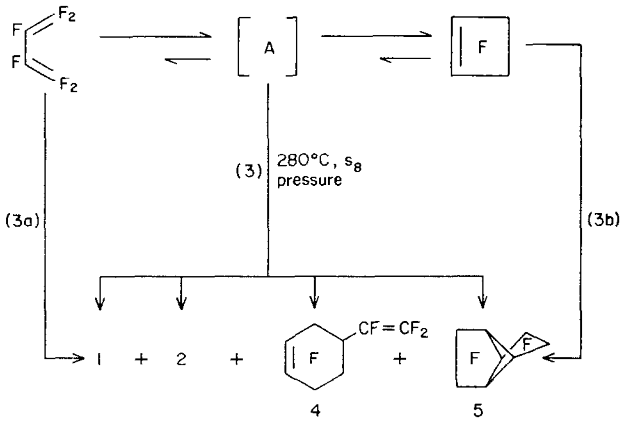


2a: 6 1 traces traces
2b: 5.6 : 1 : 0.4 0

It should be noted that in similar reactions non-fluorinated dienes form thiophenes and hydrogen sulphide [11], hexachlorobutadiene gives perchlorothiophene and $S_2Cl_2$ [12], while the reaction of tetrafluoroethene with boiling sulphur results in the formation of five- and six-membered polysulphides, $C_2F_4S_n$ ($n = 3$, 4) [13].

Since the unknown dithiine **1** was claimed earlier as a hypothetical product of the reaction between FB and elemental sulphur in a closed system [14], we have investigated their interaction [eqn (3a)] under autogenic pressure (280 °C, cf. ref. 14). This resulted in the formation of thiolene **2** and FB dimers [9] as the main products, and dithiine **1** as a negligible impurity.

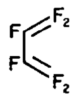
Fractional distillation and GC–MS analysis of the mixture arising from reaction (3a) allowed detection in addition of traces of $C_4F_6S_3$, $C_8F_{12}S_n$ ($n = 1$, 2) and $C_{12}F_{18}S$, demonstrating the competitive formation of FB dimers and trimers [9], followed by their reaction with elemental sulphur.

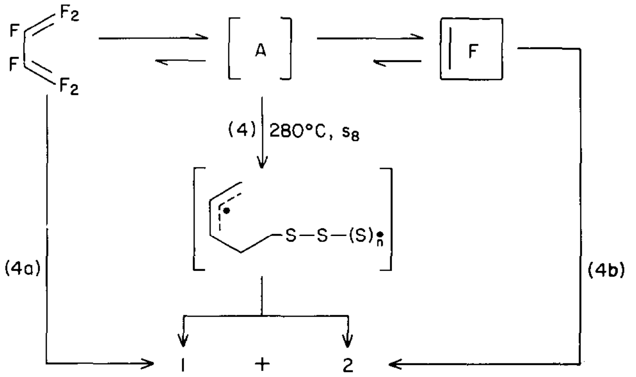


3a: 1 : 36 : 5.6 : 0.6
3b: 1 : 3 : 0 : 0

Thiolene **2** had been obtained previously from FB and $S_2Cl_2$ in 28% yield [15] and in the thermal reaction (300 °C) of FCB with elemental sulphur (and $I_2$ as a catalyst) in 23% yield [16]. We have found that a similar non-catalytic reaction (3b) gives dithiine **1** and thiolene **2** in negligible yields (see Table 1).

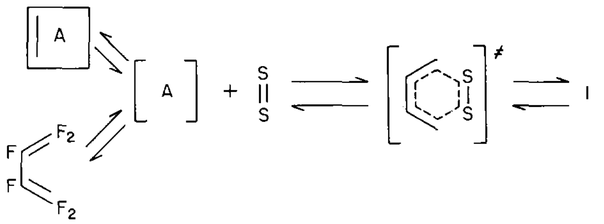
The results obtained with reactions (2) and (3) have confirmed one of our initial assumptions concerning the ability of transition state A to take part in cycloaddition reactions. Thus, reactions (2a) and (2b) give products with exactly the same composition, which is evidence of a common mechanism, and that transition state A participates in the transformations of both FB (2a) and FCB (2b). The same is also true of reactions (3a) and (3b).

| Composition of mixture of products (mol%) | | | | | | Conversion (%) | Yield (%) ($^{19}$F NMR analysis) | | | | 1:2 ratio (mol) |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | **1** | **2** | **3** | **4+5** | | **1** | **2** | **3** | **4+5** | |
| 0 | 13.2 | 64.9 | 10.7 | 0 | 0 | 9 | 63.9 | 10.9 | 0 | 0 | 6:1 |
| 8.4 | 56.9 | 31.7 | 3.0 | 0 | 0 | 9.3 | 53.6 | 5.0 | 0 | 0 | 10.6:1 |
| 0 | 7.1 | 71.6 | 12.2 | 5.4 | 0 | 7 | 22.3 | 4.0 | 1.7 | 0 | 5.6:1 |
| 0.5 | 84 | 13.0 | 2.5 | 0 | 0 | 40 | 19.5 | 3.8 | 0 | 0 | 5.1:1 |
| 0 | 21 | 1.8 | 64.7 | 0 | 11.2[b] | 87 | 1.3 | 45.5 | 0 | 16.5[b] | 1:35 |
| 59.5 | – | 0 | 9.6 | 0 | 30.9 | 24.7 | 0 | 7.5 | 0 | 48.1 | – |
| 0 | 63.4 | 9.1 | 27.5 | 0 | 0 | 9.7 | 4.1 | 12.6 | 0 | 0 | 1:3 |
| 18.9 | 30.0 | 42.4 | 8.7 | 0 | 0 | 10.8 | 33.1 | 6.8 | 0 | 0 | 4.9:1 |
| 0 | 87.8 | 8.0 | 4.2 | 0 | 0 | 16[c] | 6.2 | 2.9 | 0 | 0 | 2:1 |

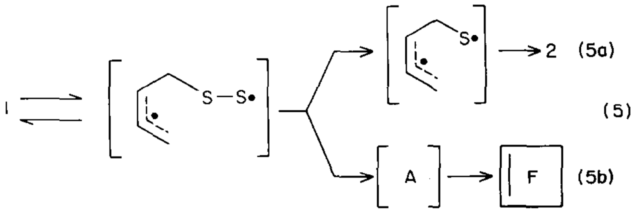


4a: 4.9 : 1
4b: 2 : 1

The second assumption, i.e. that concerning participation of the $S_2$ molecule in the formation of dithiine **1**, has not been confirmed. Although dithiine **1** is formally the [2+4]-cycloadduct of FB and $S_2$, its formation in the open system was shown to be possible under conditions which excluded the presence of $S_2$ molecules [280 °C, reaction (4)]. This fact, and the ability of sulphur to provide some linear radicals when heated (≥180 °C) [17], have led us to consider reactions (2)–(4) as stepwise radical processes. In addition, the retro-cycloaddition reaction of dithiine **1** also indicates the stepwise nature of the cycloaddition reactions. Because of the principle of microscopic reversibility, direct concerted reaction presupposes concerted retroreaction leading to the formation of only FCB (FB) in the case of dithiine **1**;



whereas the observed thermal decomposition of dithiine **1** leads to the formation of thiolene **2** together with FCB [reaction (5)].



The ratio of products arising from reaction (5) depends on the temperature (see the Experimental section), whereas the formation of thiolene **2** is observed even under the conditions prevailing in reaction (2) which rules out the concerted reaction of FB with elemental sulphur ($S_2$) at 500 °C.

The ability of dithiine **1** to provide thiolene **2** on heating makes the primary formation of the latter doubtful in reaction (2) [but not in reactions (3) and (4), see below], whereas it does not exclude such a possibility as part of a competitive stepwise process (a concerted cheletropic reaction with sulphur atoms is impossible because such atoms are not detected in sulphur vapour up to 1200 °C [5]).

The arguments in favour of the primary formation of thiolene **2** in a closed system [reaction (3a)] are (a) the stability of dithiine **1** at 280 °C (see Table 2) and (b) the absence of dithiine **1** under conditions where its absolute stability is guaranteed [reaction (3aa), Table 1]. The stability of dithiine **1** at 280 °C in the open system (see Table 2) provides evidence of the primary formation of thiolene **2** in reaction (4).

Since dithiine **1** is not formed by the interaction of sulphur vapour with thiolene **2** [reaction (6), see Experimental section], we may consider dithiine **1** as a primary product and the reactions $C_4F_6 \rightarrow \mathbf{1}$ and $C_4F_6 \rightarrow \mathbf{2}$ as competitive processes.

The mode of formation of thiolanethione **3** [8, 10] in reaction (2) remains unclear. The absence of compound **3** from amongst the products of reaction (4) indicates its secondary formation at higher temperatures. We have studied dithiine **1** and thiolene **2** as possible sources of thiolanethione **3** and have found that retroreaction (5) takes place instead of the expected isomerisation, i.e. $\mathbf{1} \rightarrow \mathbf{3}$, at 500 °C. Our attempts to carry out reaction (6) have also failed. Thiolene **2** proved to be stable at 500 °C and did not react with sulphur vapour.

$$\mathbf{2} \overset{500\ ^\circ\mathrm{C},\ S_8}{\not\longrightarrow} \mathbf{3} \qquad (6)$$

The results obtained indicate that a certain non-volatile product which is unstable at 500 °C is the source of thiolanethione **3**. Unpublished data by Ingland, given in ref. 8, indicate such a possibility.

Hence, the present work considers only those processes concerned with the formation of volatile products. On the basis of the data obtained, the following conclusions may be drawn:

1. Thermal reactions of FB and FCB with elemental sulphur proceed by a stepwise mechanism.
2. Dithiine **1** and thiolene **2** are the primary products of two competitive reactions. At the same time, when the temperature is above 280 °C, at least part of thiolene **2** can arise from the retroreaction of dithiine **1**.
3. The temperature and pressure of the reaction determine the ratio of these competitive processes. The effect of temperature in an open system leads to a reduction in the proportion of dithiine **1** as the temperature diminishes. At a similar temperature (280 °C), the effect of pressure is such as to allow both competitive reactions to proceed in an open system, but in almost complete suppression of the process $C_4F_6 \rightarrow \mathbf{1}$ under autogenic pressure conditions.

## Experimental

Mass spectra were recorded on a VG 7070E spectrometer, ionising electron energy 70 eV. These are given as *m/z* (intensity, %) [tentative assignment]. IR spectra were measured from 400 to 4000 $cm^{-1}$ as a thin layer on a UR-20 spectrophotometer. Raman spectra were measured from 10 to 4000 $cm^{-1}$ on a Ramanor HG-2S spectrometer using a 100 mW $Ar^+$ laser excited via the 5145 Å band. $^{19}F$ NMR spectra were recorded in dichloromethane on a Bruker AC-200F spectrometer (working frequence 188.3 MHz). Chemical shifts (in parts per million) are quoted relative to external trifluoroacetic acid. Preparative GLC [Tzvet 4-67 chromatograph with catharometer detector, 4000×13 mm column containing dioctylphthalate (25%) on Chromaton W with helium as the carrier gas at temperatures of 50, 100 and 150 °C] was used for the separation and purification of the products obtained.

### *Reactions in an open system. Reactions of hexafluoro-1,3-butadiene (2a,2aa,4a) and hexafluorocyclobutene (2b,2bb,4b) with elemental sulphur*

*Standard procedure*

A sample of sulphur (99.9% pure) was introduced into the apparatus shown in Fig. 1. Using a nitrogen stream, Ovens 1 and 2 were heated to the corresponding temperature (see Table 1). Then FB or FCB was allowed to interact with sulphur vapour in a nitrogen stream and the reaction products from the trap and the collector were combined. Unreacted FB or FCB was removed by recondensation (b.p. 5–10 °C). The residue was analysed by $^{19}F$ NMR and GC–MS methods (see Table 1).

### *Reactions (3a,3aa,3b) under autogenic pressure*

These were carried out in a stainless-steel bomb. The reaction conditions, composition and yields of products are listed in Table 1.

### *Reaction of hexafluoro-1,3-butadiene with elemental sulphur (3a)*

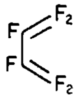
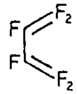
Sulphur (7.1 g) and FB (8.5 g) were heated at 280 °C in a stainless-steel bomb for 30 h. The coloured liquid (8.9 g) obtained was distilled affording: (a) hexafluorocyclobutene (b.p. 5–10 °C), yield, 0.5 g; (b) a mixture of products (composition listed in Table 1) (b.p. 43–110 °C), yield, 6.0 g; (c) a mixture containing dimer **4** together with traces of $C_4F_6S_3$, $C_8F_{12}S_n$ ($n = 1$, 2) and $C_{12}F_{18}S$ (HLC, mass spectrum, $^{19}F$ NMR spectrum) (b.p. 35–75 °C/2 mmHg), yield, 0.6 g; and ($\alpha$) 1.8 g of a dark solid residue. Distillation of fraction (b) afforded thiolene **2** (4.0 g, 41.8%, b.p. 43–44 °C) and dimer **4** (1.4 g, 17.5%, b.p. 98–100 °C).

### *Thermal stability of dithiine 1. Reaction (5)*

*A. Reactions in an open system*

A mixture (0.8 g) of dithiine **1** and thiolanethione **3** was boiling and its vapour passing through a vertical

TABLE 2 . Thermal conversion of hexafluoro-3,6-dihydro-1,2-dithiine (1) in an open system and under autogenic pressure conditions

| Reaction type | Temperature (°C) | Reaction time (h) | 1:3 ratio in starting mixture | Solid residue (g) | Mixture of products (g) | Composition of mixture of products (mol%) (NMR analysis) | | | | | Conversion (%) | Yield (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **1** | **2** | **3** |  |  | | **2** | **3** |  |  | 2 :  (mol.) |
| A | 280 | – | 97:3 | 0.1 | 0.6 | 97.9 | 0 | 2.1 | 0 | 0 | 25 | 0 | 0 | 0 | 0 | – |
| | 500 | – | 89:11 | 0.1 | 0.6 | 29.8 | 15.2 | 15.3 | 37.5 | 2.1 | 70 | 21.5 | 4 | 54.5 | 3.1 | 1:2.4 |
| B | 280 | 6 | 100:0 | – | 0.1 | 94.2 | 3.1 | 0 | 2.7 | 0 | 4.2 | 3.2 | 0 | 2.1 | 0 | 1.1:1 |
| | 300 | 4 | 100:0 | – | 0.1 | 50.0 | 29.4 | 0 | 20.6 | 0 | 49.2 | 34.7 | 0 | 17.0 | 0 | 1.4:1 |

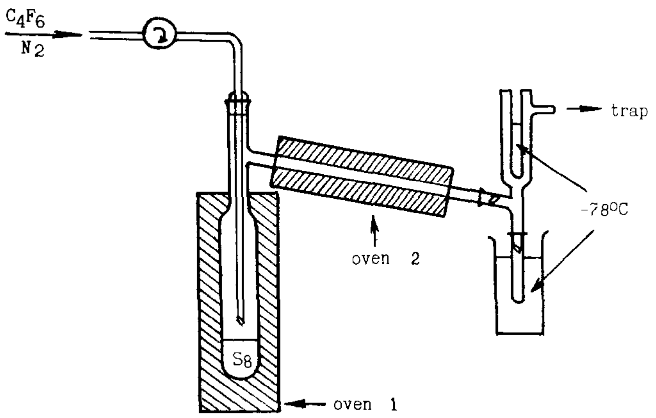


Fig. 1. Apparatus for open system reactions of *F*-butadiene and *F*-cyclobutene with elemental sulphur.

tube (20 cm) heated to a corresponding temperature. The reaction conditions, composition and yields of the products are listed in Table 2.

*B. Reactions under autogenic pressure*

Dithiine **1** (0.1 g), contained in a sealed NMR ampoule, was placed inside a thick-walled ampoule containing dichloromethane as a source of counter-pressure. The ampoule was sealed and heated in the oven. According to $^{19}F$ NMR data, dithiine **1** remained unchanged after heating for 30 h at 100 °C, 28 h at 150 °C, 6 h at 200 °C and 6 h at 250 °C. The results obtained at higher temperatures are given in Table 2.

*Thermal stability of thiolene 2. Reaction (6)*

The vapour of thiolene **2** (0.7 g) was passed over boiling sulphur (2.0 g) (450 °C) and then, in a mixture with sulphur vapours, through a vertical tube (20 cm) heated to 500 °C. Thiolene **2** (0.7 g) containing *c*. 0.3% carbon disulphide and *c*. 1.3% hexafluorocyclobutene (GLC, mass spectrum, $^{19}F$ NMR spectrum) was obtained. Dithiine **1** and thiolanethione **3** were not found in the reaction products.

*Preparation of hexafluoro-3,6-dihydro-1,2-dithiine (1)*

This was isolated from the mixture of products arising from reaction (2a). Compound **1**: b.p. 99 °C. MS: 226 (38) $[M]^+$; 207 (3.7) $[M-F]^+$; 162 (34) $[M-S_2]^+$; 157 (9) $[M-CF_3]^+$; 144 (2) $[M-CF_2S]^+$; 125 (2.5) $[M-CF_3-S]^+$; 113 (3) $[M-C_2F_3S]^+$; 112 (6.5) $[M-S_2-CF_2]^+$; 94 (7) $[M-F-C_2F_3S]^+$; 69 (4.5) $[CF_3]^+$; 64 (100) $[S_2]^+$; 63 (18) $[CFS]^+$. IR ($\nu$, $cm^{-1}$): 1729 (s); 1834 (w). Raman ($\nu$, $cm^{-1}$): 1731 (s) (p*). $^{19}F$ NMR $-\delta$: 12.7 (m, $CF_2$); 68.6 (m, CF) ppm, 2:1 intensity ratio. UV (EtOH, $\lambda_{max}$ mm): 274 ($\epsilon$ 214). Analysis: Found: C, 21.08; F, 50.54; S, 28.45%. $C_4F_6S_2$ requires: C, 21.24; F, 50.44; S, 28.32%.

*Preparation of hexafluorothiolene-3 (2)*

This was prepared in reaction (3a). Compound **2**: b.p. 43–44 °C (lit. value 40–42 °C [7]). MS: 194 (100) $[M]^+$; 175 (62)+$[M-F]^+$; 144 (100) $[M-CF_2]^+$; 131 (100) $[M-CFS]^+$; 125 (83) $[M-CF_3]^+$; 112 (43) $[M-CF_2S]^+$; 100 (18) $[C_2F_4]^+$; 94 (49) $[M-2CF_2]^+$; 93 (84) $[M-CF_3-S]^+$; 87 (19) $[C_3FS]^+$; 82 (8) $[CF_2S]^+$; 69 (30) $[CF_3]^+$; 63 (68) $[CFS]^+$. IR ($\nu$, $cm^{-1}$): 1782 (m). $^{19}F$ NMR $-\delta$: 4.2 (m $CF_2$); 70.2 (m, CF) ppm, 2:1 intensity ratio.

*Preparation of hexafluorothiolanethione-2 (3)*

This was not isolated in an individual state. It was obtained in reaction (2b) as an impurity with dithiine **1**. Compound **3**: MS (GLC)†: 226 (100) $[M]^+$; 207 (2.6) $[M-F]^+$; 157 (2) $[M-CF_3]^+$; 150 (56.5) $[M-CS_2]^+$; 131 (9) $[M-F-CS_2]^+$; 100 (94) $[M-CS_2-CF_2]^+$; 94 (20) $[M-C_2F_4S]^+$; 76 (60) $[CS_2]^+$; 69 (10) $[CF_3]^+$; 63 (16) $[CFS]^+$. $^{19}F$ NMR $-\delta$: 17.0 (m); 34.3 (m); 55.8 (m, $CF_2$) ppm, 1:1:1 intensity ratio.

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*Polarised.

†OV-101 filled capillary column (25 m).