

## Perfluoroalkyl Derivatives of Sulphur. Part X.<sup>1</sup> The Reaction of Polyfluoromonoiodoalkanes with Dimethyl Sulphide to give Methyl Polyfluoroalkyl Sulphides

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Polyfluoromonoiodoalkanes react photochemically with dimethyl sulphide to give as major products the corresponding methyl polyfluoroalkyl sulphides, the corresponding 1*H*-polyfluoroalkanes, 2,4-dithiapentane and trimethylsulphonium iodide. Thermal reaction of heptafluoro-1-iodopropane with dimethyl sulphide gives a higher yield of 1*H*-heptafluoropropane, at the expense of methyl heptafluoropropyl sulphide, than in the corresponding photochemical reaction. The products are explained on the basis of a free-radical mechanism.

POLYFLUOROALKYL sulphides may be prepared by a variety of methods, the more important of which include free-radical addition of fluorinated or non-fluorinated

thiols<sup>2,3</sup> and sulphenyl halides<sup>4,5</sup> to hydrocarbon olefins or fluoro-olefins, nucleophilic addition of fluorinated or non-fluorinated thiols<sup>3,6</sup> and sulphenyl halides<sup>4,7</sup> to

<sup>1</sup> Part IX, R. E. Banks, R. N. Haszeldine, and W. D. Morton, *J. Chem. Soc. (C)*, 1969, 1947.

<sup>2</sup> F. W. Stacey and J. F. Harris, jun., 'Organic Reactions,' vol. 13, J. Wiley and Sons, New York, 1963; J. F. Harris, jun., and F. W. Stacey, *J. Amer. Chem. Soc.*, 1961, **83**, 840; K. Inukai, T. Ueda, and H. Murmatsu, *Bull. Chem. Soc. Japan*, 1966, **39**, 2191; J. F. Harris, jun., U.S.P. 3,326,867/1967.

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<sup>4</sup> J. F. Harris, jun., *J. Amer. Chem. Soc.*, 1962, **84**, 3148.

<sup>5</sup> W. S. Durrell, E. C. Stump, jun., G. Westmoreland, and C. D. Padgett, *J. Polymer Sci.*, 1965, **12A**, 4065.

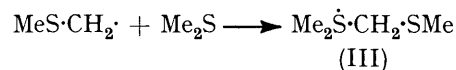
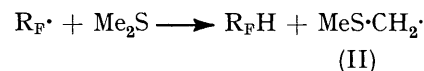
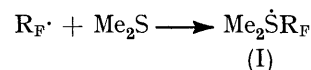
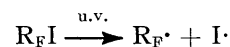
<sup>6</sup> K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, jun., *J. Amer. Chem. Soc.*, 1950, **72**, 3642; I. L. Knunyants, A. I. Schekotikin, and A. V. Fokin, *Izvest. Akad. Nauk S.S.R., Otdel. Khim. Nauk*, 1953, 282; U.S.P. 2,754,334/1956; D. C. England, L. R. Melby, M. A. Dietrich, and R. V. Lindsey, jun., *J. Amer. Chem. Soc.*, 1960, **82**, 5116; G.P. 1,069,143/1961; R. C. Terrell, R. Ucciardi, and J. F. Vitcha, *J. Org. Chem.*, 1965, **30**, 4011.

<sup>7</sup> I. L. Knunyants and E. G. Bykhovskaya, *Izvest. Akad. Nauk S.S.R., Otdel. Khim. Nauk*, 1955, 852; B.P. 926,573/1963; I. L. Knunyants, I. N. Rozhkov, A. M. Alexansdrov, and L. M. Yagupol'skii, *J. Gen. Chem. (U.S.S.R.)*, 1967, **37**, 1210.

fluoro-olefins, reaction of bis(trifluoromethylthio)mercury with polyhalogenoalkanes,<sup>8</sup> fluorination of polychloroalkyl sulphides with various fluorinating agents, *e.g.* anhydrous hydrogen fluoride,<sup>9,10</sup> mercuric fluoride,<sup>11</sup> and antimony fluorides,<sup>9,12</sup> and reaction of polyfluoromonoiodoalkanes with sulphur.<sup>13</sup>

During an investigation carried out in this department into the effect of solvents on the free-radical addition of trifluoroiodomethane to certain fluoro-olefins<sup>3</sup> it was observed that a photochemical reaction of the iodo-compound with trifluoroethylene which employed dimethyl sulphide as solvent gave products resulting from reaction with the solvent; the olefin was recovered unchanged. In view of this observation the reactions of a variety of polyfluoromonoiodoalkanes with dimethyl sulphide under photochemical (and in one instance thermal) conditions have been studied and found to

The major products can be explained by a free-radical mechanism which involves initial homolytic fission of the carbon-iodine bond in the iodoalkane.



The sulphur radicals (I) and (III) with expanded valence shells may then react further in two ways (Schemes I and 2),

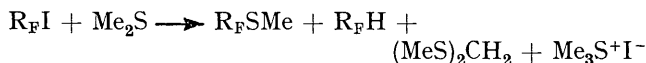
TABLE I

Photochemical reaction of polyfluoromonoiodoalkanes with dimethyl sulphide

R <sub>F</sub> I	Irradiation period (days)	Extent of reaction (%) *	Products (% yield) *			
			R <sub>F</sub> SMe	R <sub>F</sub> H	Me <sub>3</sub> S <sup>+</sup> I <sup>-</sup>	(MeS) <sub>2</sub> CH <sub>2</sub>
CF <sub>3</sub> I	14	100	63	33	87	24
CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> I	28	100	50	46	91	29
(CF <sub>3</sub> ) <sub>2</sub> CFI	24	78	32	66	92	53
CF <sub>2</sub> ClCF <sub>2</sub> I	28	100	45	52	86	25
(CF <sub>3</sub> ) <sub>2</sub> CF[CF <sub>2</sub> ] <sub>4</sub> I	28	83	46	45	83	15

\* Based on iodo-compound not recovered.

provide a useful route to methyl polyfluoroalkyl sulphides.

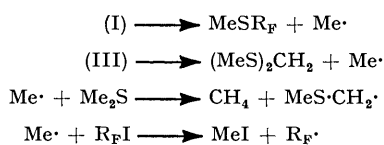


The reactions were carried out using a dimethyl sulphide : iodoalkane molar ratio of *ca.* 4 : 1 and the major products formed are shown in Table I. Attempted

The mechanism requires that hydrogen abstraction by the polyfluoroalkyl radical competes with attack on the sulphur atom of the sulphide to give radical (I). The 2-thiapropryl radical (II) formed by hydrogen abstraction then attacks a further molecule of sulphide to give radical (III).

Evidence for the ability of the sulphur atom to expand its valence octet has been reviewed.<sup>14</sup> Free-radical

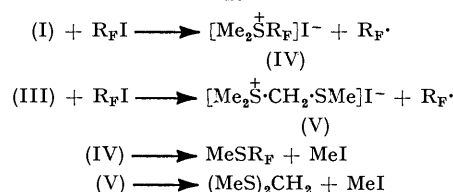
## SCHEME 1



followed by:



## SCHEME 2



reactions carried out in the dark at room temperature gave only unchanged reactants. In addition the minor products silicon tetrafluoride, carbon monoxide, and polyfluoroalkyl radical dimer were also formed.

<sup>8</sup> E. H. Man, D. D. Corrman, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 3575; J. F. Harris, jun., *J. Org. Chem.*, 1967, **32**, 2063.

<sup>9</sup> F. Boberg, G. Winter, and G. R. Schultze, *Annalen*, 1959, **621**, 8.

<sup>10</sup> K. Petrov and G. A. Sokol'skii, *J. Gen. Chem. (U.S.S.R.)*, 1957, **27**, 2751.

<sup>11</sup> C. T. Mason, U.S. Defence Doc., A.D. 419,526/1962.

<sup>12</sup> W. E. Truce, B. H. Birum, and E. T. McBee, *J. Amer. Chem. Soc.*, 1952, **74**, 3594.

displacements on disulphides are well known, but those on sulphides are rare; the first reported displacement involved the photolysis of 2-iodo-2'-methylthiobiphenyl which gave a quantitative yield of dibenzothiophen.<sup>15</sup>

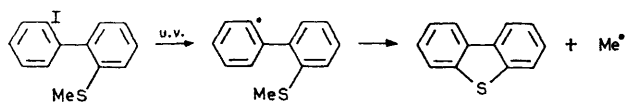
It is proposed that hydrogen abstraction occurs from

<sup>13</sup> G. A. R. Brandt, H. J. Emelús, and R. N. Haszeldine, *J. Chem. Soc.*, 1952, 2198; G. V. D. Tiers, *J. Org. Chem.*, 1961, **26**, 3515; P. D. Faurote and J. G. O'Rear, *J. Amer. Chem. Soc.*, 1956, **78**, 4999.

<sup>14</sup> S. Oae and G. C. Price, 'Sulphur Bonding', Ronald Press Co., New York, 1962; G. Cilento, *Chem. Rev.*, 1960, **60**, 147.

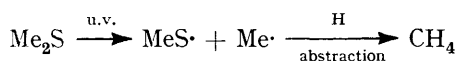
<sup>15</sup> J. A. Kampmeier and T. R. Evans, *J. Amer. Chem. Soc.*, 1966, **88**, 4096.

the dimethyl sulphide rather than from the methyl polyfluoroalkyl sulphide because (i) the total yields of *H*-polyfluoroalkane and methyl polyfluoroalkyl sulphide



are high (91–98%), (ii) the dimethyl sulphide is present in excess, and (iii) stabilisation of the radical  $R_F\dot{S}\cdot CH_2$  by  $\pi$ -bonding between the sulphur and carbon atoms would be less than for the radical  $MeS\cdot CH_2$  because of deactivation of the sulphur atom, in the former radical, by the  $-I$  effect of the  $R_F$  group.

On the present evidence it is not possible to distinguish between Schemes 1 and 2. Although the formation of methane could be cited as evidence for Scheme 1 rather than Scheme 2, the amount detected is only small (<5%) and methane is a known product from the photochemical decomposition of dimethyl sulphide.<sup>16</sup>



It is possible that a small amount of methyl polyfluoroalkyl sulphide arises by reaction of  $MeS\cdot$  radicals with polyfluoroalkyl radicals.

The proposed mechanism requires that (a) the only fluorine-containing products are the methyl polyfluoroalkyl sulphide and the *1H*-polyfluoroalkane, (b) the molar quantity of trimethylsulphonium iodide formed is equal to the molar quantity of polyfluoromonoiodoalkane reacted, and (c) the molar quantity of *1H*-polyfluoroalkane formed is equal to the molar quantity of 2,4-dithiapentane formed.

The results in Table 1 show that the first condition is largely satisfied. The second condition is also largely satisfied and the small differences may be explained by handling losses during the isolation of the trimethylsulphonium iodide.

The yield of *1H*-polyfluoroalkane does not parallel that of 2,4-dithiapentane possibly because some of the 2-thiapropryl radicals may react to give higher-boiling products other than 2,4-dithiapentane.

An accurate comparison of the reactivities of the various polyfluoromonoiodoalkanes towards dimethyl sulphide is not justified because the reactions were not all carried out for the same length of time. However, trifluoroiodomethane reacted faster than the other iodoalkanes and the yield of methyl trifluoromethyl sulphide was higher than those of the other fluoroalkyl sulphides.

The iodo-compound  $(CF_3)_2CFI$  gave the lowest yield of methyl polyfluoroalkyl sulphide, and it may be that the perfluoroisopropyl radical is more subject to steric interference than the primary fluorocarbon radicals, even  $(CF_3)_2CF\cdot[CF_2]_3\cdot CF_2\cdot$ .

Trimethylsulphonium iodide was the only salt isolated and the absence of dimethylpolyfluoroalkylsulphonium iodide is attributed to the low nucleophilicity of the

sulphur in the sulphide  $R_FSM_e$ . Iodomethane and dimethyl sulphide react immediately in the dark to give trimethylsulphonium iodide, but iodomethane and methyl trifluoromethyl sulphide do not react under the same conditions during a period of six months.

A thermal reaction of heptafluoro-1-iodopropane with dimethyl sulphide (1:3 ratio) at 170° gave methyl *n*-heptafluoropropyl sulphide in much reduced yield compared with the photochemical reaction (16%), *1H*-heptafluoropropane (69%), and trimethylsulphonium iodide (20%). That methyl *n*-heptafluoropropyl sulphide does not decompose to *1H*-heptafluoropropane under the reaction conditions was shown by a blank experiment.

The photochemical reaction of trifluoroiodomethane with bis(chloromethyl) sulphide did not yield chloromethyl trifluoromethyl sulphide, but only complex decomposition products.

TABLE 2

<sup>19</sup>F N.m.r. spectra of compounds containing the pentadecafluoro-5-methylhexane group

	$(CF_3)_2-CF-CF_2-CF_2-CF_2-CF_2X$					
	a	b	c	d	e	f
X = I	-5.4	110.8	37.8	43.0	35.6	-19.9
X = H	-4.2	112.2	39.1	46.7	54.2	62.6
X = SMe*	-6.0	111.1	38.9	43.6	43.6	14.1

\* <sup>1</sup>H N.m.r. band for methyl group at  $\tau$  7.62.

#### EXPERIMENTAL

Volatile materials were handled in a conventional high-vacuum apparatus to avoid contact with air or moisture. Photochemical reactions were carried out in silica tubes (*ca.* 300 ml.) at a distance of 15 cm from a medium-pressure Hanovia S.500 lamp. Pure products were separated either by repeated fractional condensation *in vacuo* or by g.l.c. [Perkin-Elmer 116, 451 or 452 instruments using columns packed with silicone M.S.550 oil (30%) on Celite] and were examined by i.r. spectroscopy (Perkin-Elmer 21 or 257 instruments with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 instrument operating at 60.00 MHz for <sup>1</sup>H and 56.46 MHz for <sup>19</sup>F, with internal tetramethylsilane and external trifluoroacetic acid as the respective references), and mass spectrometry (A.E.I. MS/2H or MS/9 instruments). Molecular-weight determinations were carried out by Regnault's method.

Bis(chloromethyl) sulphide was prepared in 69% yield by the reaction of thionyl chloride with *s*-trithian.<sup>12</sup> Dimethyl sulphide was a commercial sample which was carefully purified, and the polyfluoromonoiodoalkanes were prepared by literature methods or were gifts from Pennwalt Corporation.

*Photochemical Reactions of Polyfluoromonoiodoalkanes with Dimethyl Sulphide.*—The reaction tubes were shaken vigorously during irradiation; it was noted that satisfactory conversion to product was often obtained by irradiation until the reaction mixture became pale brown.

(a) *Trifluoroiodomethane.* Dimethyl sulphide (5.62 g, 90.7 mmol) and trifluoroiodomethane (4.25 g, 21.7 mmol), irradiated (14 days), gave (i) a mixture (0.046 g, 2.3 mmol; *M*, 20) of carbon monoxide and methane, (ii) trifluoromethane (0.51 g, 7.3 mmol, 34%) shown by i.r. spectroscopy to be

<sup>16</sup> L. Hörner and J. Drogos, *Tetrahedron Letters*, 1963, 757.

contaminated with traces of silicon tetrafluoride and hexafluoroethane, (iii) a mixture (3.93 g, 51.6 mmol;  $M$ , 76) which was separated by g.l.c. (8-m column at 20°) into its two components, unchanged dimethyl sulphide (2.34 g, 37.9 mmol, 42% recovered) and methyl trifluoromethyl sulphide (1.59 g, 13.7 mmol, 63%) (Found: C, 20.8; H, 2.6%;  $M$ , 116. Calc. for  $C_2H_3F_3S$ : C, 20.7; H, 2.6%;  $M$ , 116), b.p. (isoteniscope) 12.0° (lit.,<sup>12</sup> b.p. 11.5—11.7°/750 mm.), (iv) 2,4-dithiapentane (0.57 g, 5.3 mmol, 24%);  $m/e$  108 (82%,  $M^+$ ), 61 (100%,  $MeSCH_2^+$ ), 47 (7%,  $MeS^+$ ), 46 (8%,  $CH_2S^+$ ), 45 (22%,  $CHS^+$ ), 35 (19%,  $H_3S^+$ ), and 27 (8%,  $C_2H_3^+$ );  $\tau$  6.45 (s,  $CH_2$ ) and 7.90 (s,  $CH_3$ ), and (v) a solid, non-volatile tarry residue (4.7 g) which was extracted with water, evaporated to dryness, and the resultant material recrystallised from ethanol and identified as trimethylsulphonium iodide (3.79 g, 18.6 mmol, 86%), decomposition temp. 210—212° (lit.,<sup>17</sup> 215°).

(b) *Heptafluoro-1-iodopropane*. Dimethyl sulphide (5.74 g, 92.4 mmol) and heptafluoro-1-iodopropane (6.31 g, 21.3 mmol), irradiated (28 days), gave (i) a mixture (0.8 mmol) of carbon monoxide and methane, (ii) a mixture (1.82 g, 12.2 mmol;  $M$ , 149) separated by g.l.c. (8-m column at 20°) into its two components, unchanged dimethyl sulphide (0.15 g, 2.4 mmol, 3% recovered) and 1*H*-heptafluoropropane (1.67 g, 9.8 mmol, 46%), (iii) a mixture (4.98 g) separated by g.l.c. (8-m column at 40°) into its three components, unchanged dimethyl sulphide (2.65 g, 42.7 mmol, 46% recovered), a component (0.03 g) with an identical retention time to that of perfluoro-*n*-hexane, and *methyl n*-heptafluoropropyl sulphide (2.30 g, 10.7 mmol, 50%) (Found: C, 21.9; H, 1.4%;  $M$ , 215.  $C_4H_3F_7S$  requires C, 22.2; H, 1.4%;  $M$ , 216), b.p. (Siwoloboff) 61°;  $\lambda_{max}$  3.37m and 3.48m (C-H str.), 6.93m (C-H bend), and 13.41s ( $CF_3$  def.)  $\mu m$ ;  $m/e$  216 (79%,  $M^+$ ), 197 [12%, ( $M - F$ )<sup>+</sup>], 169 (20%,  $C_3F_7^+$ ), 147 (14%,  $C_2F_4 \cdot SMe^+$ ), 113 (9%,  $C_2F_3S^+$ ), 97 (100%,  $CF_2 \cdot SMe^+$ ), 69 (23%,  $CF_3^+$ ), 47 (69%,  $SMe^+$ ), 46 (33%,  $CH_2S^+$ ), 45 (37%,  $CHS^+$ ), and 15 (12%,  $Me^+$ );  $\tau$  7.60 [s(bd),  $CH_3$ ] and <sup>19</sup>F n.m.r. bands for  $CF_3 \cdot CF_2 \cdot CF_2 \cdot SMe$

at 3.6 (t, 3F,  $J_{a-c}$  9.4 Hz), 14.7 [qtq, 2F(c),  $J_{c-a}$  9.4,  $J_{c-b}$  3.3,  $J_{c-d}$  0.9 Hz] and 47.8 [t, 2F(b),  $J_{b-c}$  3.3 Hz] p.p.m. to high field of reference, (iv) 2,4-dithiapentane (0.72 g, 6.2 mmol, 29%), and (v) a residue (4.4 g), which when treated as in the previous experiment afforded trimethylsulphonium iodide (3.97 g, 19.4 mmol, 91%) and a small quantity of tar.

(c) *Heptafluoro-2-iodopropane*. Dimethyl sulphide (6.52 g, 0.105 mol) and heptafluoro-2-iodopropane (8.12 g, 27.4 mmol), irradiated (24 days), gave (i) a mixture (0.026 g, 1.3 mmol;  $M$ , 20) of carbon monoxide and methane, (ii) a mixture (2.53 g, 16.2 mmol;  $M$ , 157) separated by g.l.c. (8-m column at 20°) into its two components, 2*H*-heptafluoropropane (2.40 g, 14.1 mmol, 66%) and unchanged dimethyl sulphide (0.13 g, 2.1 mmol, 2% recovered), (iii) a mixture (6.28 g) separated by g.l.c. (8-m column at 50°) into its four components, unchanged heptafluoro-2-iodopropane (1.80 g, 6.1 mmol, 22% recovered), unchanged dimethyl sulphide (3.01 g, 48.6 mmol, 46% recovered), *methyl heptafluoroisopropyl sulphide* (1.47 g, 6.8 mmol, 32%) (Found: C, 22.4; H, 1.4%;  $M$ , 214.  $C_4H_3F_7S$  requires C, 22.2; H, 1.4%;  $M$ , 216), b.p. (Siwoloboff), 61°;  $\lambda_{max}$  3.39m (t) and 3.54m (C-H str.), 6.90m (C-H bend), and 13.76s and 13.89s ( $CF_3$  def.)  $\mu m$ ;  $m/e$  216 (68%,  $M^+$ ), 197 [14%, ( $M - F$ )<sup>+</sup>], 147 [100%, ( $M - CF_3$ )<sup>+</sup>], 113 (26%,  $C_2F_3S^+$ ), 97 (30%,  $CF_2 \cdot SMe^+$ ), 69 (24%,  $CF_3^+$ ), 63 (16%,  $CFS^+$ ), 47 (20%,  $SMe^+$ ), 46 (26%,  $CH_2S^+$ ), 45 (31%,  $CHS^+$ ),

and 15 (10%,  $Me^+$ );  $\tau$  7.60 (dsep,  $CH_3$ ) and <sup>19</sup>F n.m.r. bands for  $(CF_3)_2CF \cdot SMe$  at 1.5 p.p.m. [dq, 6F(a),  $J_{a-b}$  10.5,

$J_{a-H}$  1.0 Hz] to low field and 90.0 p.p.m. [sepg, 1F(b),  $J_{b-a}$  10.5,  $J_{b-H}$  2.4 Hz] to high field of reference, and an unknown compound (trace) possibly perfluoro(2,3-dimethylbutane), (iv) 2,4-dithiapentane (1.21 g, 11.2 mmol, 53%), and (v) a residue (ca. 4.5 g) which, when treated as in experiment (a), gave trimethylsulphonium iodide (4.00 g, 19.7 mmol, 92%) and a small quantity of tar.

(d) *1-Chlorotetrafluoro-2-iodoethane*. Dimethyl sulphide (5.42 g, 87.4 mmol) and the iodoalkane (6.24 g, 23.8 mmol), irradiated (28 days), gave (i) a mixture (2.00 g, 15.4 mmol;  $M$ , 130) of unchanged dimethyl sulphide and 2-chloro-1*H*-tetrafluoroethane which when treated with mercuric chloride afforded 2-chloro-1*H*-tetrafluoroethane (1.70 g, 12.5 mmol, 52%) (Found:  $M$ , 138. Calc. for  $C_2HClF_4$ :  $M$ , 136), (ii) a mixture (4.00 g) separated by g.l.c. (8-m column at 50°) into its two components, unchanged dimethyl sulphide (1.94 g, 31.3 mmol, 36% recovered) and *methyl 2-chlorotetrafluoroethyl sulphide* (1.96 g, 10.8 mmol, 45%) (Found: C, 19.8; H, 1.9; F, 42.0; S, 17.7%;  $M$ , 180.  $C_3H_2ClF_4S$  requires C, 19.7; H, 1.7; F, 41.6; S, 17.5%;  $M$ , 182), b.p. (Siwoloboff) 80°;  $\lambda_{max}$  3.39m (t) (C-H str.) and 6.92m (C-H bend)  $\mu m$ ;  $m/e$  184 and 182 (36%,  $M^+$ ), 169 and 167 [6% ( $M - Me$ )<sup>+</sup>], 147 (17% ( $M - Cl$ )<sup>+</sup>), 137 and 135 (5%,  $CF_2Cl \cdot CF_2^+$ ), 97 (100%,  $CF_2 \cdot SMe^+$ ), 87 and 85 (9%,  $CF_2Cl^+$ ), 77 (9%,  $CH_2S \cdot CF^+$ ), 63 (16%,  $CFS^+$ ), 47 (17%,  $SMe^+$ ), 46 (10%,  $CH_2S^+$ ), 45 (20%,  $CHS^+$ ), and 15 (5%,  $Me^+$ );  $\tau$  7.63 (tt,  $CH_3$ ) and <sup>19</sup>F n.m.r. bands at 8.9 p.p.m. [tq,  $CF_2Cl$ (a),  $J_{a-b}$  13.1 Hz,  $J_{a-H}$  0.7 Hz] to low field and 14.0 p.p.m. [tq,  $CF_2$ (b),  $J_{b-a}$  13.1 Hz,  $J_{b-H}$  1.3 Hz] to high field of reference, (iii) 2,4-dithiapentane (0.64 g, 5.9 mmol, 25%), and (iv) a residue (ca. 4.8 g) which when treated as in experiment (a) afforded trimethylsulphonium iodide (4.18 g, 20.3 mmol, 86%) and a small quantity of tar.

(e) *Pentadecafluoro-1-iodo-5-methylhexane*. Dimethyl sulphide (5.26 g, 84.9 mmol) and the iodoalkane (10.29 g, 20.7 mmol), irradiated (28 days), gave (i) a mixture (0.019 g, 1.0 mmol;  $M$ , 19) of carbon monoxide and methane, (ii) unchanged dimethyl sulphide (0.49 g, 7.9 mmol, 9% recovered), (iii) a mixture (3.69 g, 37.5 mmol;  $M$ , 98), shown by i.r. spectroscopy to contain dimethyl sulphide, which when treated with mercuric chloride afforded 1*H*-pentadecafluoro-5-methylhexane (2.84 g, 7.68 mmol, 45%) (Found: C, 22.4; H, 0.5%;  $M$  363.  $C_7HF_{15}$  requires C, 22.5; H, 0.3%;  $M$ , 370), b.p. (Siwoloboff) 90—92°;  $\lambda_{max}$  3.26w and 3.34w (C-H str.), and 13.87s ( $CF_3$  def.)  $\mu m$ ;  $m/e$  300 [1%, ( $M - CHF_3$ )<sup>+</sup>], 181 (7%,  $C_4F_7^+$ ), 131 (18%,  $C_3F_5^+$ ), 119 (6%,  $C_2F_5^+$ ), 101 (17%,  $CF_2 \cdot CHF_2^+$ ), 100 (7%,  $C_2F_4^+$ ), 69 (100%,  $CF_3^+$ ), and 31 (7%,  $CF^+$ ), (iv) a mixture (5.27 g) separated by g.l.c. (8-m column at 135°) into its three components, unchanged iodoalkane (1.72 g, 3.47 mmol, 17% recovered), 2,4-dithiapentane (0.27 g, 2.48 mmol, 15%), and *methyl pentadecafluoro-5-methylhexyl sulphide* (3.28 g, 7.97 mmol, 46%) (Found: C, 23.0; H, 1.0; F, 68.5; S, 7.9.  $C_8H_3F_{15}S$  requires C, 23.0; H, 0.7; F, 68.6; S, 7.7%), b.p. (Siwoloboff) 139°;  $\lambda_{max}$  3.39w (t) and 3.50w (C-H str.), and 6.90w and 6.94w (C-H bend)  $\mu m$ ;  $m/e$  416 (17%,  $M^+$ ), 397 [11%, ( $M - F$ )<sup>+</sup>], 364 (12%,  $C_7HF_{13}S^+$ ), 197 [12%, ( $M - C_4F_9$ )<sup>+</sup>], 128 (7%,  $C_2F_3 \cdot SMe^+$ ), 100 (7%,  $C_2F_4^+$ ), 97 (100%,  $CF_2 \cdot SMe^+$ ), 69 (29%,  $CF_3^+$ ), 47 (13%,  $SMe^+$ ), 46 (7%,  $CH_2S^+$ ), 45 (13%,  $CHS^+$ ), and 15 (7%,  $Me^+$ ), and (v) a residue (ca. 5.8 g) which, when treated

<sup>17</sup> W. Steinkopf and S. Muller, *Ber.*, 1923, **56**, 1928.

as in experiment (a), afforded trimethylsulphonium iodide (2.92 g, 14.3 mmol, 83%), an ether-soluble tar (0.41 g), and a solid black tarry residue.

*Thermal Reaction of Heptafluoro-1-iodopropane with Dimethyl Sulphide.*—A mixture of dimethyl sulphide (2.06 g, 33.2 mmol) and the iodoalkane (3.42 g, 11.5 mmol), sealed in a Pyrex ampoule (300 ml) and heated at 170° (72 h), gave (i) a noncondensable gas at -196° (0.9 mmol), (ii) silicon tetrafluoride (0.15 mmol), (iii) a mixture (1.00 g, 8.5 mmol; *M*, 118) containing dimethyl sulphide, which after treatment with mercuric chloride, afforded 1*H*-heptafluoropropane (0.74 g, 4.34 mmol, 69%) (Found: *M*, 167. Calc. for C<sub>3</sub>HF<sub>7</sub>: *M*, 170), (iv) a mixture (2.88 g) shown by g.l.c. (8-m column at 50°) to contain unchanged dimethyl sulphide (1.14 g, 18.4 mmol, 55% recovered), unchanged iodoalkane (1.52 g, 5.14 mmol, 45% recovered), and methyl *n*-heptafluoropropyl sulphide (0.22 g, 1.02 mmol, 16%), and (v) a residue (*ca.* 1.3 g) which, when treated as in experiment (a), afforded trimethylsulphonium iodide (0.26 g, 1.28 mmol, 20%), an ether-soluble tar (0.10 g) and a black, ether-insoluble solid.

*Photochemical Reaction of Bis(chloromethyl) Sulphide with Trifluoroiodomethane.*—The photochemical reaction of the sulphide with the iodoalkane (84 days), gave (i) unchanged iodoalkane (70%), (ii) volatile products which included trifluoromethane, hexafluoroethane, carbon disulphide, chlorotrifluoromethane, and hydrogen chloride, and (iii) a large amount of a black, tarry residue.

*N.m.r. Spectra.*—The spectra of all the compounds were in complete agreement with their respective structures but

the <sup>19</sup>F spectra of the pentadecafluoro-5-methylhexane derivatives shown in the Table were complex and the fine structure was poorly resolved. The bands were assigned on the following basis: (a) integrated band intensities; (b) the bands assigned to F<sub>a</sub>, F<sub>b</sub>, F<sub>c</sub>, and F<sub>d</sub> showed approximately the same chemical shift in the three compounds studied; (c) branching at the adjacent carbon atom causes F<sub>c</sub> to absorb at lower field than F<sub>d</sub>; (d) the chemical shift of F<sub>i</sub> is the most variable; (e) corresponding bands in the compounds have much fine structure in common.

In all three compounds the band system due to F<sub>a</sub> appeared as a triplet of triplets of doublets (*J*<sub>a-c</sub>, *ca.* 14.5; *J*<sub>a-d</sub>, *ca.* 8.9; *J*<sub>a-b</sub>, *ca.* 6.1 Hz.).

*Mass Spectral Data.*—All the methyl polyfluoroalkyl sulphides showed a strong parent peak in their spectra. Cleavage occurred at the CH<sub>3</sub>-S bond to give the CH<sub>3</sub><sup>+</sup> ion (*m/e* 15) and at the R<sub>F</sub>-S bond to give the CH<sub>3</sub>S<sup>+</sup> ion (*m/e* 47). The base peaks were observed from cleavage of the C<sub>α</sub>-C<sub>β</sub> bond of the polyfluoroalkyl chain. For compounds of type R<sub>F</sub>CF<sub>2</sub>SMe this peak occurred at *m/e* 97 (CF<sub>2</sub>·SMe<sup>+</sup>) and for the compound (CF<sub>3</sub>)<sub>2</sub>CF·SMe it occurred at *m/e* 147 (CF<sub>3</sub>·CF·SMe<sup>+</sup>). All the sulphide spectra also showed peaks arising from breakdown by loss of successive fluoroalkyl fragments while maintaining the integrity of the CH<sub>3</sub>·S group.

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