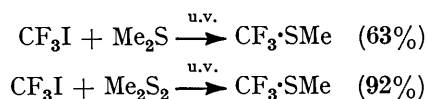


Perfluoroalkyl Derivatives of Sulphur. Part XIV.¹ The Reactions of Tetrafluoro-1,2-di-iodoethane and Octafluoro-1,4-di-iodobutane with Dimethyl Sulphide and Dimethyl Disulphide

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The photochemical reaction of tetrafluoro-1,2-di-iodoethane with dimethyl sulphide gives a high yield of tetrafluoroethylene, whereas reaction with dimethyl disulphide affords 1,2-bis(methylthio)tetrafluoroethane and 1,4-bis(methylthio)octafluorobutane as major products together with tetrafluoroethylene, methyl 1,1,2,2-tetrafluoroethyl sulphide, methyl tetrafluoro-2-iodoethyl sulphide, perfluorocyclopropane, and difluoromethane. Octafluoro-1,4-di-iodobutane and dimethyl sulphide give 1*H*-octafluoro-4-iodobutane, methyl octafluoro-4-iodobutyl sulphide, and trimethylsulphonium iodide as the major products with smaller amounts of 1*H*,4*H*-octafluorobutane, 1,4-bis(methylthio)octafluorobutane, and methyl 4*H*-octafluorobutyl sulphide.

THE reactions of polyfluoromonoiodoalkanes with dimethyl sulphide,² dimethyl disulphide,³ methyl ethyl sulphide,⁴ methyl trifluoromethyl sulphide,⁴ or diethyl disulphide¹ provide useful routes to alkyl polyfluoroalkyl sulphides, *e.g.*



The reactions of tetrafluoro-1,2-di-iodoethane with dimethyl sulphide and dimethyl disulphide and the reaction of octafluoro-1,4-di-iodobutane with dimethyl sulphide have now been investigated as possible routes to the $\alpha\omega$ -bis(methylthio)polyfluoroalkanes $\text{MeS}\cdot[\text{CF}_2\cdot\text{CF}_2]_n\cdot\text{SMe}$ ($n = 1$ or 2).

Reactions with Dimethyl Sulphide.—The two polyfluorodi-iodoalkanes showed a marked difference in reaction when irradiated in the presence of an excess of

dimethyl sulphide. The only product identified in the reaction of tetrafluoro-1,2-di-iodoethane was tetrafluoro-

TABLE I
Reaction of octafluoro-1,4-di-iodobutane with dimethyl sulphide

Product	Yield (%)	Product	Yield (%)
$\text{I}[\text{CF}_2\cdot\text{CF}_2]_2\cdot\text{SMe}$	44	$\text{Me}_3\text{S}^+\text{I}^-$	90
$\text{CHF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\text{I}$	42	$(\text{MeS})_2\text{CH}_2$	29
$\text{H}[\text{CF}_2\cdot\text{CF}_2]_2\cdot\text{SMe}$	6	C_2F_4 , CH_4 , CO , SiF_4	Traces
$\text{CHF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CHF}_2$	2	Tar	Large amount
$\text{MeS}\cdot[\text{CF}_2\cdot\text{CF}_2]_2\cdot\text{SMe}$	2		

Yields of $-\text{CF}_2\cdot\text{CF}_2-$ derivatives are based on the amount of $\text{I}[\text{CF}_2\cdot\text{CF}_2]_2\text{I}$ consumed. The yield of $\text{Me}_3\text{S}^+\text{I}^-$ is based on the amount of iodine consumed from the reactant $\text{I}[\text{CF}_2\cdot\text{CF}_2]_2\text{I}$. The yield of $(\text{MeS})_2\text{CH}_2$ is based on the amount of Me_2S consumed. The products thus account for 96% of the $-\text{CF}_2\cdot\text{CF}_2-$ and 90% of the iodine in the $\text{I}[\text{CF}_2\cdot\text{CF}_2]_2\text{I}$ consumed during the reaction.

ethylene (91%), whereas octafluoro-1,4-di-iodobutane gave a complex mixture of products as shown in Table I.

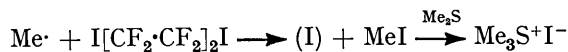
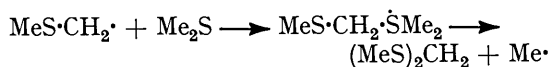
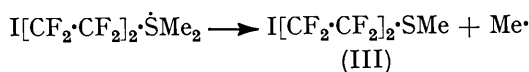
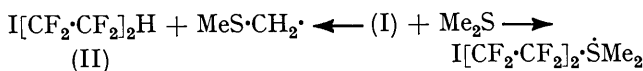
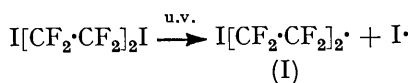
¹ Part XIII, R. N. Haszeldine, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 2180.

² R. N. Haszeldine, B. Higginbottom, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 155.

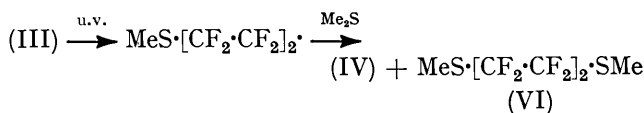
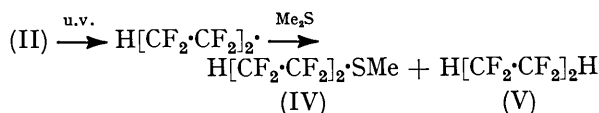
³ R. N. Haszeldine, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 159.

⁴ R. N. Haszeldine, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 1506.

A mechanism similar to that proposed earlier² accounts for these products:



followed by



The differences in the products obtained from the two reactions are attributed to the stabilities of the two intermediate radicals $\text{CF}_2\text{I}\cdot\text{CF}_2\cdot$ and $\text{I}[\text{CF}_2\cdot\text{CF}_2]_2\cdot$ (I) formed from the di-iodoethane and the di-iodobutane, respectively. The C-I bond in the di-iodoethane is cleaved photochemically more readily than that in the di-iodobutane, and the intermediate radical can form tetrafluoroethylene by loss of iodine more easily than it can attack dimethyl sulphide to give a mixture of the compounds $\text{CF}_2\text{I}\cdot\text{CF}_2\cdot\text{SMe}$ and $\text{CHF}_2\cdot\text{CF}_2\text{I}$ by cleavage of the relatively strong $\text{CH}_3\text{-S}$ or $\text{CH}_2\text{-H}$ bonds. The radical (I) cannot revert to olefins by elimination of an iodine atom, and although the presence of a small amount of tetrafluoroethylene in the products suggests that C-C fission has taken place to a small extent $[(\text{I}) \longrightarrow \text{C}_2\text{F}_4 + \text{CF}_2\text{I}\cdot\text{CF}_2\cdot \longrightarrow \text{C}_2\text{F}_4 + \text{I}\cdot]$, its main reaction is with the dimethyl sulphide.

The *ca.* 50 : 50 ratio observed for reduction : formation of methyl sulphides is in good agreement with the ratios obtained from the reaction of polyfluoromonoiodoalkanes with dimethyl sulphide,² *e.g.* CF_3I , ratio 33 : 63; $n\text{-C}_3\text{F}_7\text{I}$, 46 : 50; $\text{CF}_2\text{Cl}\cdot\text{CF}_2\text{I}$, 52 : 46; $(\text{CF}_3)_2\text{CF}\cdot(\text{CF}_2)_4\text{I}$, 45 : 46.

Reaction with Dimethyl Disulphide.—The reaction of tetrafluoro-1,2-di-iodoethane with dimethyl disulphide gave the satisfactory yields of methyl sulphides shown in Table 2.

Little reduction of the di-iodoethane has taken place, in agreement with the results obtained from the reaction of polyfluoromonoiodoalkanes with dimethyl

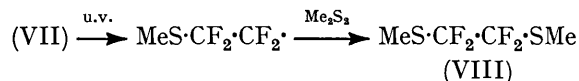
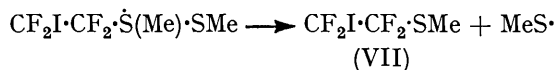
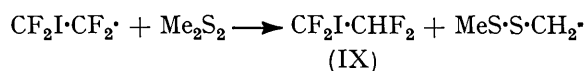
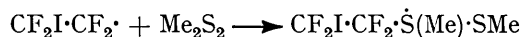
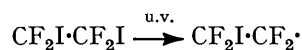
disulphide.³ An interesting feature of the reaction was the formation of methyl octafluoro-4-iodobutyl sulphide (III) and 1,4-bis(methylthio)octafluorobutane (VI), and the detection of small quantities of difluoromethane and perfluorocyclopropane.

TABLE 2

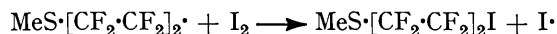
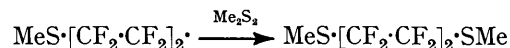
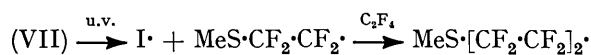
Reaction of tetrafluoro-1,2-di-iodoethane with dimethyl disulphide

Product	Yield (%)	Product	Yield (%)
$\text{MeS}\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{SMe}$	46	$\text{CF}_2\cdot\text{CF}_2$	5
$\text{MeS}\cdot[\text{CF}_2\cdot\text{CF}_2]_2\cdot\text{SMe}$	15	$\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2$	<i>ca.</i> 3
$\text{CHF}_2\cdot\text{CF}_2\cdot\text{SMe}$	8	$\text{I}[\text{CF}_2\cdot\text{CF}_2]_2\cdot\text{SMe}$	2
$\text{CF}_2\text{I}\cdot\text{CF}_2\cdot\text{SMe}$	6	$\text{CH}_2\text{F}_2, \text{SiF}_4, \text{CO}$	Traces

The products methyl tetrafluoro-2-iodoethyl sulphide (VII), 1,2-bis(methylthio)tetrafluoroethane (VIII), and methyl 1,1,2,2-tetrafluoroethyl sulphide (IX) can be explained by the sequence:

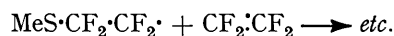
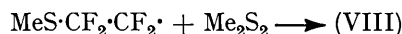
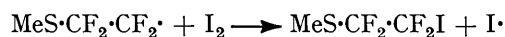
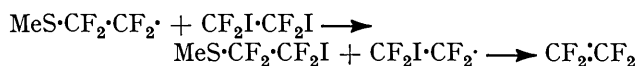
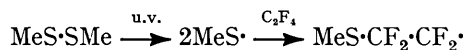


Attack of $\text{CF}_2\text{I}\cdot\text{CF}_2\cdot$ on dimethyl disulphide now appears to compete successfully with elimination of an iodine atom to give tetrafluoroethylene. Compounds (III) and (VI) are probably formed by further reaction of the iodo-compound (VII):



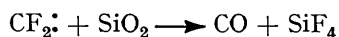
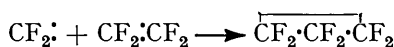
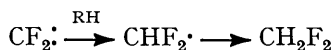
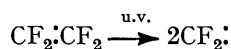
The thermal reaction of tetrafluoro-1,2-di-iodoethane with tetrafluoroethylene in the presence of iodine⁵ to form octafluoro-1,4-di-iodobutane and higher telomers takes place by a similar mechanism.

Photolytic breakdown of dimethyl disulphide followed by reaction of methanethiyl radicals with tetrafluoroethylene may also provide some of the product:



⁵ R. N. Haszeldine, *Nature*, 1951, **167**, 139; R. N. Haszeldine, A. E. Tipping, and F. Vennells, unpublished results.

The formation of small amounts of difluoromethane, carbon monoxide, and perfluorocyclopropane suggests that difluorocarbene may also play a minor role:



Iodine has been reported⁶ to catalyse ionic additions of disulphides to olefins. The attempted reaction of dimethyl disulphide with tetrafluoroethylene in the presence of iodine, however, gave only unchanged reactants.

EXPERIMENTAL

Volatile materials were handled in a conventional high-vacuum apparatus to avoid contact with air or moisture. Photochemical reactions were carried out in 300 ml silica tubes at a distance of 10 cm from a Hanovia S500 lamp. Pure products were separated either by repeated fractional condensation *in vacuo* or by g.l.c. [Perkin-Elmer 451 or 452 instruments using columns (2 m or 8 m) packed with Silicone MS 550 oil (30%) on Celite] and were examined by i.r. spectroscopy (Perkin-Elmer 257 instrument with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 machine operating at 60.00 MHz for ¹H and 56.46 MHz for ¹⁹F), and mass spectrometry (A.E.I. MS9 instrument). Molecular weights were determined by Regnault's method.

Dimethyl sulphide and dimethyl disulphide were commercial samples which were carefully purified before use. Tetrafluoro-1,2-di-iodoethane was prepared in 70% yield by the thermal reaction of tetrafluoroethylene with iodine,⁷ and further thermal reaction of the di-iodoethane with tetrafluoroethylene in the presence of iodine gave octafluoro-1,4-di-iodobutane.⁵

Reaction of ω -Di-iodopolyfluoroalkanes with Dimethyl Sulphide.—(a) *Tetrafluoro-1,2-di-iodoethane.* A mixture of dimethyl sulphide (13.95 g, 0.225 mol) and the di-iodoethane (8.50 g, 2.4 mmol), irradiated (14 days), gave (i) tetrafluoroethylene (2.01 g, 20.1 mmol, 91%) (Found: *M*, 100. Calc. for C_2F_4 : *M*, 100), (ii) unchanged dimethyl sulphide (13.3 g, 0.215 mol, 95% recovered), (iii) a higher-boiling fraction (1.02 g), and (iv) a tar containing a large amount of iodine (*ca.* 6 g).

The higher-boiling fraction was examined by g.l.c. (2 m column at 120°) and was shown to consist of five components, the major one of which was identified as unchanged tetrafluoro-1,2-di-iodoethane (*ca.* 0.75 g, *ca.* 2.1 mmol, *ca.* 9% recovered); the remaining four components were not identified.

(b) *Octafluoro-1,4-di-iodobutane.* A mixture of dimethyl sulphide (6.73 g, 0.108 mol) and the di-iodobutane (7.90 g, 17.4 mmol), irradiated (14 days), gave (i) a mixture (0.8 mmol) of methane and carbon monoxide, (ii) a mixture (trace) of tetrafluoroethylene and silicon tetrafluoride, (iii) a mixture (4.34 g, 69.4 mmol; *M*, 63), separated by

g.l.c. (8 m column at 60°) into its two components, 1*H*,4*H*-octafluorobutane (0.05 g, 0.25 mmol, 2%) and unchanged dimethyl sulphide (4.29 g, 69.2 mmol, 64% recovered), (iv) a higher-boiling fraction (7.11 g), and (v) a tarry residue (*ca.* 3 g) from which trimethylsulphonium iodide (2.03 g, 10.0 mmol, 90%) was obtained by extraction with water.

The higher-boiling fraction was separated by g.l.c. (8 m column at 160°) into its six components, unchanged octafluoro-1,4-di-iodobutane (3.16 g, 6.96 mmol, 40% recovered), bis(methylthio)methane (0.60 g, 5.58 mmol, 29%), and four compounds (A—D) in the ratio 44 : 7 : 47 : 2.

Component A was identified as 1*H*-octafluoro-4-iodobutane (1.42 g, 4.33 mmol, 42%) (Found: C, 14.6; H, 0.6%; *M*, 323. Calc. for $\text{C}_4\text{HF}_8\text{I}$: C, 14.6; H, 0.3%; *M*, 328), b.p. (Siwoloboff) 90° (lit.,⁸ 90—91°); *m/e* 328 (50%, *M*⁺), 239 (11%, $\text{C}_3\text{F}_4\text{I}^+$), 227 (8%, $\text{CF}_2\cdot\text{CF}_2\text{I}^+$), 201 [100%, (*M* - I)⁺], 177 (47%, CF_2I^+), 101 (18%, $\text{CF}_2\cdot\text{CHF}_2^+$), and 51 (65%, CHF_2^+).

Component B was not positively identified but its g.l.c. retention time suggested it was methyl 4*H*-octafluorobutyl sulphide (0.16 g, 0.65 mmol, 6%).

Component C was identified as *methyl octafluoro-4-iodobutyl sulphide* (1.71 g, 4.58 mmol, 44%) (Found: C, 16.3; H, 0.8; I, 34.3. $\text{C}_5\text{H}_3\text{F}_8\text{I}$ requires C, 16.1; H, 0.8; I, 34.0%); λ_{max} 3.39 μ (C-H str.), 6.95 m and 6.99 m (C-H bend), 8.42 vs, 8.86 vs, 9.15 s, 9.46 s, 10.25 m, 10.70 m, 11.14 m, 12.91 s, 14.96 s, 15.05 s, and 15.92 s μ m; *m/e* 374 (14%, *M*⁺), 247 [100%, (*M* - I)⁺], 227 (43%, $\text{CF}_2\cdot\text{CF}_2\text{I}^+$), 177 (16%, CF_2I^+), and 97 (53%, $\text{CF}_2\cdot\text{SMe}^+$); ¹H n.m.r. band for $\text{CF}_2\text{I}-\overset{2}{\text{C}}\text{F}_2-\overset{3}{\text{C}}\text{F}_2-\overset{4}{\text{C}}\text{F}_2-\text{SMe}$ at τ 7.65 (tt, Me, *J*_{5,4} 1.2, *J*_{5,3} 0.5 Hz) and ¹⁹F n.m.r. bands at -19.9 (ttt, F-1), 12.9 (ttq, F-4), 34.8 (ttt, F-2), and 41.2 p.p.m. (ttt, F-3) relative to external trifluoroacetic acid. The ¹⁹F spectrum was not first-order but the following approximate coupling constants were obtained: *J*_{1,2} 5.0, *J*_{1,3} 15.0, *J*_{1,4} 3.2, *J*_{2,3} 5.7, *J*_{2,4} 18.1, *J*_{3,4} 3.4 Hz.

Component D was identified as 1,4-bis(methylthio)octafluorobutane (0.06 g, 0.20 mmol, 2%) by its g.l.c. retention time (see later).

Reaction of Tetrafluoro-1,2-di-iodoethane with Dimethyl Disulphide.—A mixture of the di-iodoethane (10.36 g, 29.3 mmol) and dimethyl disulphide (11.23 g, 0.120 mol), irradiated (30 days), gave (i) a gas non-condensable at -196° (1.5 mmol), (ii) tetrafluoroethylene (0.15 g, 1.5 mmol, 5%) (Found: *M*, 98. Calc. for C_2F_4 : *M*, 100), shown by i.r. spectroscopy to be contaminated with small amounts of silicon tetrafluoride and difluoromethane, (iii) a mixture (0.22 g, 1.6 mmol; *M*, 138), shown by i.r. spectroscopy to be a mixture of carbon disulphide, perfluorocyclopropane, and an unidentified component(s) with main i.r. bands at λ_{max} 8.25 s and 10.05 s μ m, (iv) a mixture (0.41 g), shown by i.r. spectroscopy to contain small amounts of dimethyl disulphide and carbon disulphide and which, on shaking with mercury(II) chloride (15 h), afforded methyl 1,1,2,2-tetrafluoroethyl sulphide (0.36 g, 2.4 mmol, 8%) (Found: *M*, 146. Calc. for $\text{C}_2\text{H}_4\text{F}_4\text{S}$: *M*, 148), (v) a higher-boiling fraction (9.63 g), and (vi) a black obnoxious oil (*ca.* 11 g).

The higher boiling fraction was examined by i.r. spectroscopy and g.l.c. (8 m column at 160°) and shown to consist of unchanged dimethyl disulphide (5.14 g, 54.7 mmol,

⁷ K. Leedham and R. N. Haszeldine, *J. Chem. Soc.*, 1953, 1548.

⁸ C. G. Krespan, *J. Org. Chem.*, 1958, 23, 2016.

⁶ F. W. Stacey and J. F. Harris, jun., *Org. Reactions*, 1963, 13, 207.

46% recovered), bis(methylthio)methane (0.43 g, 4.0 mmol), methyl octafluoro-4-iodobutyl sulphide (0.10 g, 0.27 mmol, 2%) and three components (E—G) in the ratio 77 : 10 : 13; component G had the same retention time as component D in the previous experiment.

Component E was identified as 1,2-bis(methylthio)tetrafluoroethane (2.60 g, 13.4 mmol, 46%) (Found: C, 24.7; H, 3.3; S, 32.7. $C_4H_6F_4S_2$ requires C, 24.7; H, 3.3; S, 33.0%), b.p. (Siwoloboff) 150°; λ_{\max} 3.32w, 3.38m, and 3.52w (C—H str.), 6.94m and 6.99m (C—H bend), 7.53m, 8.12m, 8.20m, 8.33m, 8.93s, 9.26s, 9.66s, 10.26m, 11.01s, 11.24m, 12.32s, 13.19m, and 14.08m μm ; ^1H n.m.r. band $\overset{1}{\text{C}}-\overset{2}{\text{C}}-\overset{3}{\text{C}}-\overset{4}{\text{C}}$ for $\text{MeS}-\overset{1}{\text{C}}\text{F}_2-\overset{2}{\text{C}}\text{F}_2-\overset{3}{\text{C}}\text{F}_2-\overset{4}{\text{C}}\text{SMe}$ at τ 7.67 (quin, $J_{1,2} \approx J_{1,3}$ ca. 1.2 Hz) and ^{19}F n.m.r. band at 12.8 p.p.m. (broad) relative to external trifluoroacetic acid; m/e 194 (26%, M^+), 147 (5%, $\text{C}_2\text{F}_4\text{SMe}^+$), and 97 (100%, CF_2SMe^+).

Component F was identified as methyl tetrafluoro-2-iodoethyl sulphide (0.45 g, 1.64 mmol, 6%); λ_{\max} 3.44w and 3.50m (C—H str.), 6.94m and 6.99m (C—H bend), 8.15m, 8.26m, 8.44m, 8.77s, 9.13s, 9.62m, 9.85s, 10.26m, 11.63s,

and 13.16s μm ; m/e 274 (15%, M^+), 177 (4%, CF_2I^+), 147 (100%, $\text{C}_2\text{F}_4\text{SMe}^+$), and 97 (48%, CF_2SMe^+).

Component G was identified as 1,4-bis(methylthio)octafluorobutane (0.64 g, 2.18 mmol, 15%); λ_{\max} 3.34w, 3.44m, 3.52w, and 3.54w (C—H str.), 6.99m (C—H bend), 7.07m, 7.66m, 8.30m, 8.48s, 8.73m, 8.84s, 9.17s, 9.75m, 10.53m, 12.35m, 13.14m, 13.93m, and 14.39m μm ; m/e 294 (20%, M^+), 247 (4%, $\text{C}_4\text{F}_8\text{SMe}^+$), 147 (4%, $\text{C}_2\text{F}_4\text{SMe}^+$), and 97 (100%, CF_2SMe^+).

Attempted Ionic Reaction of Dimethyl Disulphide with Tetrafluoroethylene.—Dimethyl disulphide (11.10 g, 0.118 mol), iodine (7.61 g, 30.0 mmol), and tetrafluoroethylene (3.00 g, 30.0 mmol), sealed in a Pyrex tube (300 ml) and kept in the dark at room temperature (22 days), gave unchanged tetrafluoroethylene (3.00 g, 30.0 mmol, 100% recovered) and higher-boiling material presumed to be unchanged dimethyl disulphide and iodine.

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