

## Perfluoroalkyl Derivatives of Sulphur. Part XIII.<sup>1</sup> The Reaction of Polyfluoromonoiodoalkanes with Diethyl Disulphide and of Pentafluoriodobenzene with Bis(trifluoromethyl) Disulphide

By R. N. Haszeldine,\* R. B. Rigby, and A. E. Tipping, Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Photochemical reactions of trifluoriodomethane and of heptafluoro-1-iodopropane with diethyl disulphide gives comparable yields (*ca.* 40%) of the corresponding ethyl polyfluoroalkyl sulphides and 1*H*-polyfluoroalkanes and lower yields of 1,1,1-trifluoropropane or 1,1,1,2,2,3,3-heptafluoropentane. Pentafluorophenyl trifluoromethyl sulphide, pentafluorophenyl trifluoromethyl disulphide, and trifluoriodomethane are formed in the photochemical reaction of pentafluoriodobenzene with bis(trifluoromethyl) disulphide.

IN previous papers in this series the photochemical reactions of various polyfluoromonoiodoalkanes with dimethyl sulphide,<sup>2</sup> dimethyl disulphide,<sup>3</sup> ethyl methyl sulphide,<sup>1</sup> methyl trifluoromethyl sulphide,<sup>1</sup> and methane-thiol<sup>1</sup> have been reported. Much higher yields of methyl polyfluoroalkyl sulphides were obtained from reactions with dimethyl disulphide than from those with dimethyl sulphide. In the latter reactions appreciable amounts of the corresponding mono-*H*-polyfluoroalkanes were formed.

The photochemical reactions of trifluoriodomethane and heptafluoro-1-iodopropane with diethyl disulphide have now been investigated as a possible general route

to the corresponding ethyl polyfluoroalkyl sulphides. The photochemical reaction of pentafluoriodobenzene with bis(trifluoromethyl) disulphide has also been studied in order to determine whether the scope of the reaction of polyfluoroiodo-compounds with dialkyl disulphides to form alkyl polyfluoroalkyl sulphides can be extended to the reaction of polyfluoroiodo-aromatic compounds with perfluorodialkyl disulphides.

The results of the reactions of the iodoalkanes with diethyl disulphide are compared in the Table with the results obtained of the corresponding reactions with dimethyl disulphide.<sup>3</sup> The products from the diethyl

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

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

<sup>1</sup> Part XII, R. N. Haszeldine, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 1506.

disulphide reactions also included appreciable amounts of ethylene and a black tar, lesser amounts of diethyl sulphide and ethane, and minor amounts of ethanethiol and hydrogen.

Reaction of polyfluoromonoiodoalkanes with diethyl and dimethyl disulphides

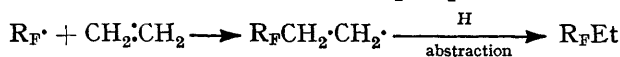
$R_F I$	$R_2 S_2$	Irradiation period (days)	Extent of reaction (%)	Products (%)			
				$R_F H$	$R_F S Et$	$R_F S Me$	$R_F Et$
$CF_3 I$	$Et_2 S_2$	48	100	40	43		7
$n-C_3 F_7 I$	$Et_2 S_2$	48	100	41	45		6
$CF_3 I$	$Me_2 S_2$	21	97	5		92	
$n-C_3 F_7 I$	$Me_2 S_2$	21	92	6		93	

The much higher yields of mono-*H*-polyfluoroalkanes obtained in the diethyl disulphide reactions, as compared with the dimethyl disulphide reactions, may be explained partly in terms of the larger number of hydrogen atoms available for abstraction by polyfluoroalkyl radicals and partly by the fact that diethyl disulphide contains four secondary carbon-hydrogen bonds.

The ethyl polyfluoroalkyl sulphides are considered to be formed by a similar mechanism to that postulated for attack of polyfluoroalkyl radicals on dimethyl sulphide<sup>2</sup> or dimethyl disulphide.<sup>3</sup>



Ethylene and compounds of the type  $R_F Et$  may arise by the routes put forward to explain the formation of 1,1,1,2,2,3,3-heptafluoropentane in the photochemical reaction of heptafluoro-1-iodopropane with ethyl methyl sulphide,<sup>1</sup> *i.e.*



The remaining observed volatile products, hydrogen, diethyl sulphide, and ethanethiol, are considered to arise by the independent photolytic decomposition of diethyl disulphide.

Since the reactants are readily available the foregoing reaction affords a reasonable route to ethyl polyfluoroalkyl sulphides even though the yields are not high. Ethyl trifluoromethyl sulphide has been reported<sup>4</sup> to be formed in much higher yield (*ca.* 80%) by the reaction of iodoethane with bis(trifluoromethylthio)mercury, but the difficulty in preparing higher molecular weight bis-(polyfluoroalkylthio)mercurials renders this type of reaction unsuitable as a general route to the ethyl polyfluoroalkyl sulphides.

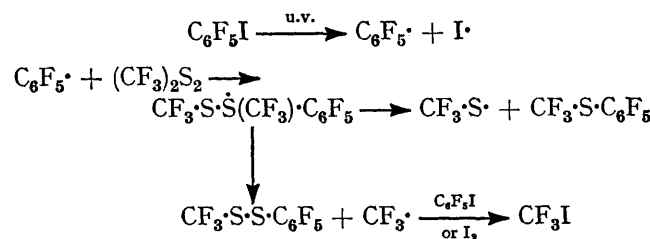
The photochemical reaction of pentafluoroiodobenzene

<sup>4</sup> J. F. Harris, jun., *J. Org. Chem.*, 1967, **32**, 2063.

<sup>5</sup> G. R. A. Brandt, H. J. Emel  us, and R. N. Haszeldine, *J. Chem. Soc.*, 1952, 2198.

with bis(trifluoromethyl) disulphide gave pentafluorophenyl trifluoromethyl sulphide (42%), pentafluorophenyl trifluoromethyl disulphide (13%), trifluoroiodomethane (44% based on iodine), unchanged pentafluoroiodobenzene (13%), a mixture of bis(trifluoromethyl) sulphide and unchanged bis(trifluoromethyl) disulphide, and a high-boiling residue.

The formation of pentafluorophenyl trifluoromethyl disulphide is in contrast to the reaction of polyfluoroalkyl radicals with dimethyl disulphide, in which methyl polyfluoroalkyl disulphides were not detected. It is possible that it is formed by attack of the pentafluorophenyl radical on bis(trifluoromethyl) disulphide, with displacement of a trifluoromethyl radical which abstracts iodine to afford trifluoroiodomethane.



#### EXPERIMENTAL

Techniques used were as described previously<sup>2,3</sup> [molecular weight determinations were carried out by Regnault's method; i.r. spectroscopy employed a Perkin-Elmer 257 instrument with sodium chloride optics, mass spectrometry employed an A.E.I. MS9 instrument, g.l.c. employed Perkin-Elmer 451 or 452 instruments with columns (8 m) packed with silicone MS 550 oil (30%) on Celite, and n.m.r. spectroscopy employed a 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]. Photochemical reactions were carried out in 300 ml silica tubes at a distance of 10 cm from a Hanovia S500 lamp with the tubes clamped horizontally above the lamp.

Diethyl disulphide was a commercial sample carefully purified and bis(trifluoromethyl) disulphide was made in 56% yield by the reaction of trifluoroiodomethane with sulphur<sup>6</sup> and in 83% yield by the reaction of bis(trifluoromethylthio)mercury<sup>6</sup> with iodine in tetrachloroethane as solvent.<sup>7</sup>

*Reactions of Polyfluoromonoiodoalkanes with Diethyl Disulphide.*—(a) *Trifluoroiodomethane.* A mixture of diethyl disulphide (9.75 g, 79.9 mmol) and trifluoroiodomethane (6.18 g, 31.5 mmol), irradiated (48 days), gave (i) a gas which did not condense at  $-196^\circ$  (trace), thought to be hydrogen, (ii) a mixture (24.1 mmol) shown by i.r. spectroscopy to contain ethane, ethylene, and trifluoromethane, which when treated with bromine afforded 1,2-dibromoethane (1.90 g, 10.1 mmol), and a mixture (0.925 g, 14.0 mmol; *M*, 66) of trifluoromethane (0.896 g, 12.8 mmol, 40%) and ethane (0.026 g, 1.2 mmol), (iii) 1,1,1-trifluoropropane (0.21 g, 2.1 mmol, 7%) (Found: *M*, 100. Calc. for  $C_3 H_5 F_3$ : *M*, 98), and (iv) a mixture (1.98 g), separated by g.l.c. (column at  $70^\circ$ ) into ethyl trifluoromethyl sulphide (1.76 g,

<sup>6</sup> E. H. Man, D. D. Coffman, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 3575.

<sup>7</sup> H. J. Emel  us and H. Pugh, *J. Chem. Soc.*, 1960, 1108.

13.5 mmol, 43%) which was identified by i.r. spectroscopy,<sup>4</sup> ethanethiol (0.02 g, 0.3 mmol), diethyl sulphide (0.14 g, 1.6 mmol), and an unidentified component (trace).

The higher-boiling material containing unchanged diethyl disulphide and black tar was not examined.

(b) *Heptafluoro-1-iodopropane*. A mixture of diethyl disulphide (9.92 g, 81.2 mmol) and the iodoalkane (7.90 g, 26.6 mmol), irradiated (48 days), gave (i) a gas which did not condense at  $-196^{\circ}$  (0.4 mmol), showed no i.r. absorption in the range 2.5–15  $\mu\text{m}$ , and was presumed to be hydrogen, (ii) a mixture (0.36 g, 12.0 mmol;  $M$ , 30) of ethane and ethylene, contaminated with a trace of silicon tetrafluoride, (iii) 1*H*-heptafluoropropane (1.86 g, 10.9 mmol, 41%) (Found:  $M$ , 168. Calc. for  $\text{C}_3\text{HF}_7$ :  $M$ , 170), (iv) a mixture (3.52 g) separated by g.l.c. (column at  $70^{\circ}$ ) into ethanethiol (0.03 g, 0.5 mmol), diethyl sulphide (0.22 g, 2.4 mmol), 1,1,1,2,2,3,3-heptafluoropentane (0.30 g, 1.5 mmol, 6%) (Found:  $M$ , 196. Calc. for  $\text{C}_5\text{H}_5\text{F}_7$ :  $M$ , 198), identified by its i.r. spectrum,<sup>1</sup> and ethyl heptafluoro-*n*-propyl sulphide (2.88 g, 12.5 mmol, 45%) (Found:  $M$ , 230. Calc. for  $\text{C}_5\text{H}_5\text{F}_7\text{S}$ :  $M$ , 230), identified by its i.r. spectrum,<sup>1</sup> (v) unchanged diethyl disulphide (4.09 g, 33.5 mmol, 40% recovered), and (vi) a black tar (ca. 11 g).

*Reaction of Pentafluoriodobenzene with Bis(trifluoromethyl) Disulphide*.—A mixture of pentafluoriodobenzene (5.20 g, 17.4 mmol) and bis(trifluoromethyl) disulphide (11.89 g, 58.6 mmol), irradiated (24 days), gave, as volatile products, (i) trifluoriodomethane (1.30 g, 6.6 mmol, 44% based on  $\text{C}_6\text{F}_5\text{I}$  converted) (Found:  $M$ , 196. Calc. for  $\text{CF}_3\text{I}$ :  $M$ , 196) and (ii) a mixture (8.08 g) of bis(trifluoromethyl) sulphide and unchanged bis(trifluoromethyl) disulphide.

The higher-boiling material (ca. 7.5 g) was extracted with ether ( $2 \times 25$  ml), washed with aqueous sodium thiosulphate to remove iodine, and dried over molecular sieves (type 4A); the ether was removed by distillation and the residue (5.3 g) was distilled from a microdistillation unit (5 ml) to give fraction A (1.74 g), b.p.  $120$ – $124^{\circ}$ , fraction B (1.28 g), b.p.  $130$ – $160^{\circ}$ , and a residue (2.01 g), b.p.  $>160^{\circ}$ , which was not examined further.

Fraction A was identified as *pentafluorophenyl trifluoromethyl sulphide* (1.74 g, 6.5 mmol, 42%) (Found: C, 31.5; F, 57.0; S, 11.8.  $\text{C}_7\text{F}_8\text{S}$  requires C, 31.4; F, 56.8; S, 11.9%);  $\lambda_{\text{max}}$  6.10s, 6.49s, 6.60s, 6.68s, 8.61s, 8.70s, 9.01s, 9.14s, 10.10s, 11.49s, and 13.16s  $\mu\text{m}$ ;  $^{19}\text{F}$  n.m.r. bands at  $-34.1$  (t, 3F,  $\text{CF}_3$ ,  $J_{\text{F}_0, \text{OF}_2}$  5.1 Hz), 54.6 (complex, 2F,  $\text{F}_0$ ), 72.6 (tt, 1F,  $\text{F}_p$ ,  $J_{\text{F}_m, \text{F}_p}$  19.3 Hz,  $J_{\text{F}_0, \text{F}_p}$  5.4 Hz), and 86.5 p.p.m. (complex, 2F,  $\text{F}_m$ ) relative to external trifluoroacetic acid (negative value to low field);  $m/e$  268 ( $M^+$ , 100%), 199 ( $\text{C}_6\text{F}_5\text{S}^+$ , 91), 155 ( $\text{C}_5\text{F}_5^+$ , 47), and 69 ( $\text{CF}_3^+$ , 91).

Fraction B was separated by g.l.c. (column at  $160^{\circ}$ ) into unchanged pentafluoriodobenzene (0.68 g, 2.3 mmol, 13% recovered) and *pentafluorophenyl trifluoromethyl disulphide* (0.60 g, 2.0 mmol, 13%) (Found: C, 28.4; F, 50.2; S, 21.1.  $\text{C}_7\text{F}_8\text{S}_2$  requires C, 28.0; F, 50.7; S, 21.3%);  $\lambda_{\text{max}}$  6.60s, 6.68s, 8.60s, 8.69s, 9.09s, and 10.15s  $\mu\text{m}$ ;  $^{19}\text{F}$  n.m.r. bands at  $-30.7$  (t, 3F,  $\text{CF}_3$ ,  $J_{\text{F}_0, \text{OF}_2}$  4.4 Hz), 55.7 (complex, 2F,  $\text{F}_0$ ), 71.5 (tt, 1F,  $\text{F}_p$ ,  $J_{\text{F}_m, \text{F}_p}$  19.6,  $J_{\text{F}_0, \text{F}_p}$  5.1 Hz), and 85.6 p.p.m. (complex, 2F,  $\text{F}_m$ ) relative to external trifluoroacetic acid;  $m/e$  300 ( $M^+$ , 61%), 231 ( $\text{C}_6\text{F}_5\text{S}_2^+$ , 18), 199 ( $\text{C}_6\text{F}_5\text{S}^+$ , 100), 155 ( $\text{C}_5\text{F}_5^+$ , 43), and 69 ( $\text{CF}_3^+$ , 63).

We thank Pennwalt Corporation for financial support.

[2/177 Received, 28th January, 1972]