

Perfluoroalkyl Derivatives of Sulphur. Part XI.¹ The Reaction of Polyfluoromonoiodoalkanes with Dimethyl Disulphide

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Photochemical reaction of a series of polyfluoromonoiodoalkanes with dimethyl disulphide gives high yields (80–93%) of the corresponding methyl polyfluoroalkyl sulphides together with lower yields (5–17%) of the corresponding *H*-polyfluoroalkanes. Thermal reaction of heptafluoro-1-iodopropane with dimethyl disulphide gives methyl heptafluoro-*n*-propyl sulphide (31%) and 1*H*-heptafluoropropane (61%). The results are interpreted in terms of a free-radical mechanism.

THE photochemical reaction of various polyfluoromonoiodoalkanes with dimethyl sulphide¹ gave the corresponding methyl polyfluoroalkyl sulphides, R_FSMe, in 30–65% yield, but formation of R_FH was often an important side reaction. The mechanism proposed for these interesting reactions, involving attack of the polyfluoroalkyl radical on sulphur, combined with the known susceptibility of the weak sulphur–sulphur bond in disulphides to free-radical attack,^{2–5} suggested that the reaction of polyfluoroalkyl radicals with dimethyl di-

sulphide might occur more readily. The results obtained from the photochemical reactions of a series of polyfluoromonoiodoalkanes with dimethyl disulphide, shown in the Table, amply justify this expectation.

The reactions were carried out for a period of 21 days using a disulphide:iodoalkane ratio varying between 2:1 and 8:1; the long and possibly excessive irradiation period ensured high conversions of the iodo-compound to product. The yields of the methyl polyfluoroalkyl sulphides are high, and the yields of the

¹ Part X, R. N. Haszeldine, B. Higginbottom, R. B. Rigby, and A. E. Tipping, preceding paper.

² W. A. Pryor, 'Mechanisms of Sulphur Reactions,' McGraw Book Co., New York, 1962, p. 42.

³ W. A. Pryor and H. Guard, *J. Amer. Chem. Soc.*, 1964, **86**, 1150.

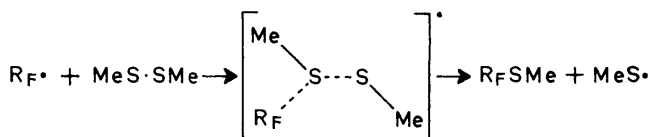
⁴ W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, 1965, **30**, 1375.

⁵ K. H. Buckel and A. Conte, *Chem. Ber.*, 1967, **100**, 1248.

H-polyfluoroalkanes are consequently relatively low. The lower polyfluoroalkyl sulphide : *H*-polyfluoroalkane ratios in the experiments in which both the gas and liquid phases were irradiated as compared with those in which only the liquid phase was irradiated is probably due to the more severe conditions used in the former experiments. It is also significant that by-product formation (methane, dimethyl sulphide, and methanethiol) was higher in the experiments in which both the liquid and gas phases were irradiated.

The major products, $R_F SMe$ and $R_F H$, are thought to

could also proceed by concomitant bond formation and bond breaking, *i.e.*



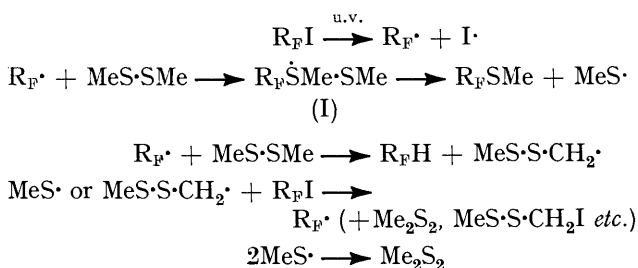
Reaction of heptafluoro-1-iodopropane with dimethyl disulphide at 150° gave methyl heptafluoro-*n*-propyl sulphide and 1*H*-heptafluoropropane in the ratio 31 : 61 (*cf.*

Reaction of polyfluoromonoiodoalkanes with dimethyl disulphide

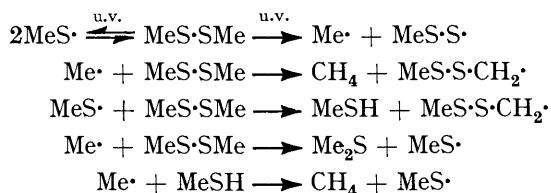
$R_F I$	Extent of reaction (%)	$R_F SMe$ †	$R_F H$	Products (%)			
				CH_4	Me_2S	$MeSH$	CS_2
$CF_3 I$ *	97	92	5	<1	1	<1	Trace
$CF_3 CF_2 CF_2 I$ *	92	93	6	<1	1	1	Trace
$(CF_2)_2 CFI$ †	100	83	12	2	4	2	Trace
$CF_2 Cl CF_2 I$ †	100	82	14	4	5	3	Trace
$(CF_2)_2 CF [CF_2]_4 I$ †	100	80	17	5	4	<1	Trace

* Liquid phase only irradiated. † Liquid and gas phases irradiated. ‡ See ref. 1 for identification.

arise by a mechanism similar to that postulated previously for the corresponding dimethyl sulphide reactions:



The by-products formed in the reaction probably arise, in part, by attack of polyfluoroalkyl radicals on the disulphide and, in part, by the independent photolytic decomposition of the disulphide.⁶



The methanethiol formed as a by-product probably contributed to the formation of the *H*-polyfluoroalkanes since separate experiments show⁷ that heptafluoro-*n*-propyl radicals react readily with methanethiol to give 1*H*-heptafluoropropane in high yield.

The mechanism of polyfluoroalkyl-radical attack on dimethyl disulphide could proceed *via* the formation of the expanded radical (I) as an intermediate, but it

⁶ P. M. Rao, J. A. Copeck, and A. R. Knight, *Canad. J. Chem.*, 1967, **45**, 1369.

⁷ R. N. Haszeldine, R. B. Rigby, and A. E. Tipping, unpublished results.

93 : 6 for the photochemical reaction). Appreciable breakdown of the disulphide also took place to give methanethiol (19%), dimethyl sulphide (42%), carbon disulphide (16%), and smaller quantities of hydrogen sulphide and carbonyl sulphide. Methanethiol was isolated in a much higher yield than in the corresponding photochemical reaction and it seems probable that the high yield of 1*H*-heptafluoropropane is due mainly to the hydrogen-abstraction reaction of the $n-C_3F_7 \cdot$ radicals with methanethiol.

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 S.500 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 (8 m) packed with Silicone M.S.550 oil (30%) on Celite] and were examined by i.r. spectroscopy (Perkin-Elmer 257 instrument with sodium chloride optics).

Dimethyl disulphide was a commercial sample which was purified before use.

Photochemical Reaction of Polyfluoromonoiodoalkanes with Dimethyl Disulphide.—The reactions using trifluoroiodomethane and heptafluoro-1-iodopropane were carried out with the reaction tube held in a vertical position and the liquid phase irradiated. The reactions involving the other polyfluoroiodoalkanes were carried out with the reaction tube held horizontally and both the gas and liquid phases irradiated.

The reaction with heptafluoro-1-iodopropane is described fully and the results of the other reactions are shown in the Table.

(a) *Heptafluoro-1-iodopropane.* A mixture of dimethyl disulphide (7.91 g, 84.3 mmol) and the iodoalkane (4.44 g, 15.0 mmol) was irradiated and gave (i) methane (trace), (ii) a mixture (0.155 g, 1.0 mmol; *M*, 155), shown by i.r.

spectroscopy and g.l.c. (column at 20°) to contain 1*H*-heptafluoropropane (0.15 g, 0.9 mmol, 6%) and methanethiol (0.005 g, 0.1 mmol, <1%), (iii) a mixture (3.22 g, 15.3 mmol; *M*, 210) separated by g.l.c. (column at 45°) into its four components identified as methyl heptafluoro-*n*-propyl sulphide (2.82 g, 13.0 mmol, 93%), unchanged iodoalkane (0.32 g, 1.1 mmol, 7% recovered), dimethyl sulphide (0.05 g, 0.8 mmol, 1%), and carbon disulphide (trace), (iv) a higher-boiling fraction (5.84 g) which on distillation through a Vigreux column (15 cm) afforded unchanged dimethyl disulphide (5.57 g, 59.3 mmol, 72% recovered), b.p. 107°, and (v) a black oily residue (*ca.* 3 g).

Further experiments with the reaction tube held horizontally and both the gas and liquid phases irradiated gave methyl heptafluoro-*n*-propyl sulphide (80–85%) and 1*H*-heptafluoropropane (13–18%).

(b) *Other polyfluoromonoiodoalkanes.* The amounts of reactants used in these experiments were as follows. (i) Trifluoroiodomethane (3.02 g, 15.4 mmol) and dimethyl disulphide (11.3 g, 120 mmol). (ii) Heptafluoro-2-iodopropane (8.45 g, 28.5 mmol) and dimethyl disulphide (11.5 g, 126 mmol). (iii) 1-Chloro-2-iodotetrafluoroethane (6.80 g, 25.9 mmol) and dimethyl disulphide (6.46 g, 68.7 mmol).

(iv) Pentadecafluoro-1-iodo-5-methylhexane (10.1 g, 20.3 mmol) and dimethyl disulphide (4.57 g, 48.6 mmol).

Thermal Reaction of Heptafluoro-1-iodopropane with Dimethyl Disulphide.—The iodoalkane (5.80 g, 19.6 mmol) and dimethyl disulphide (1.97 g, 21.0 mmol), sealed in a Pyrex tube (340 ml) and heated at 150° (72 h), gave (i) a mixture (1.7 mmol) shown by i.r. spectroscopy to contain carbonyl sulphide, silicon tetrafluoride, hydrogen sulphide, and an unidentified fluorocarbon, (ii) a mixture (1.20 g, 12.3 mmol; *M*, 98) shown by g.l.c. (column at 20°) to consist of 1*H*-heptafluoropropane (0.83 g, 4.9 mmol, 61%) and methanethiol (0.36 g, 7.4 mmol, 19%), (iii) a mixture (4.71 g) shown by g.l.c. (column at 40°) to consist of unchanged iodoalkane (3.40 g, 11.5 mmol, 59% recovered), dimethyl sulphide (0.51 g, 8.3 mmol, 42%), carbon disulphide (0.24 g, 3.2 mmol, 16%), methyl heptafluoro-*n*-propyl sulphide (0.54 g, 2.5 mmol, 31%), and trace quantities of two unidentified components, (iv) unchanged dimethyl disulphide (0.11 g, 1.2 mmol, 6% recovered), and (v) a black oily residue (*ca.* 1.4 g).

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