

Perfluoroalkyl Derivatives of Sulphur. Part XVI.¹ Photochemical Reactions of Trifluoroiodoethylene and Long-chain Polyfluoromonoiodoalkanes with Dimethyl Disulphide. Long-chain Polyfluoroalkanesulphonic Acids

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The photochemical reactions of trifluoroiodoethylene and long-chain polyfluoromonoiodoalkanes (C₆, C₈, and C₉) with dimethyl disulphide afford methyl trifluorovinyl sulphide (48%) and methyl polyfluoroalkyl sulphides (73–76%), respectively; oxidation of the latter gives sulphones and thence the corresponding polyfluoroalkanesulphonic acid salts in high yield. Methyl trifluoromethyl sulphide gives trifluoroiodomethane in a photochemical reaction with iodomethane.

THE photochemical reaction of dimethyl disulphide with various polyfluoromonoiodoalkanes to give the corresponding methyl polyfluoroalkyl sulphides in good yield has been described in an earlier paper.² This reaction has now been extended to a number of long-chain polyfluoromonoiodoalkanes and to an unsaturated iodo-compound, trifluoroiodoethylene. The results obtained are compared in Table 1 with some previous results.²

The results show that the reaction is general for a wide range of polyfluoromonoiodoalkanes. However, it appears that with the longer-chain polyfluoromonoiodo-

alkanes more of the hydrogen abstraction product R_FH is formed at the expense of the desired sulphide R_FSMe.

The photochemical reactions of trifluoroiodoethylene with nitric oxide in the presence of mercury to give trifluoronitrosoethylene³ and with olefins to give adducts⁴ are believed to involve the trifluorovinyl radical as an intermediate. It has now been shown that photochemical reaction of trifluoroiodoethylene with dimethyl disulphide rapidly (17 h) gives methyl trifluorovinyl sulphide (Table 1; *cf.* the *ca.* 21 days required for quantitative conversion of the saturated polyfluoroiodoalkanes into products). The relatively low yield of the un-

¹ Part XV, R. N. Haszeldine, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1973, 676.

² R. N. Haszeldine, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 159.

³ C. E. Griffin and R. N. Haszeldine, *J. Chem. Soc.*, 1960, 1398.

⁴ J. D. Park, R. J. Seffl, and J. R. Lacher, *J. Amer. Chem. Soc.*, 1956, **78**, 59 and references contained therein.

saturated sulphide (48%) is caused not by a parallel hydrogen abstraction reaction to give trifluoroethylene, only small amounts of which were formed, but by formation of a clear polymer film on the inside of the reaction tube. Since hexafluoro-4,4-di-iodobut-1-ene, $\text{CF}_2\cdot\text{CF}\cdot\text{CF}_2\cdot\text{CFI}_2$, the radical dimer of trifluoroiodoethylene,⁴

TABLE 1
Photochemical reactions with dimethyl disulphide

R_FI	Extent of reaction (%) *	Products (%) *	
		R_FSMe	R_FH
$\text{CF}_3\cdot[\text{CF}_2]_4\cdot\text{CF}_2\text{I}$	100	76	15
$\text{CF}_3\cdot[\text{CF}_2]_6\cdot\text{CF}_2\text{I}$	94	73	10
$(\text{CF}_3)_2\text{CF}\cdot[\text{CF}_2]_5\cdot\text{CF}_2\text{I}$	100	74	15
$\text{CF}_3\cdot\text{CF}_2\cdot\text{CF}_2\text{I}^\dagger$	92	93	6
$(\text{CF}_3)_2\text{CF}\cdot[\text{CF}_2]_3\cdot\text{CF}_2\text{I}^\dagger$	100	80	17
$\text{CF}_2\cdot\text{CFI}$	96	48	Trace

* Based on iodo-compound not recovered. † Ref. 2.

was not detected, the polymer probably arises mainly from methyl trifluorovinyl sulphide.

An attempt to extend the photochemical reaction of polyfluoroiodoalkanes with disulphides to bis-(2-chloroethyl) disulphide was unsuccessful; only complex mixtures of products including silicon tetrafluoride, ethane, and the polyfluoroalkanes R_FH and R_FCl ($\text{R}_F = \text{CF}_3$ or $n\text{-C}_3\text{F}_7$) were obtained. The yields of methyl perfluoroalkyl sulphides obtained by photochemical reaction of the long chain polyfluoroiodoalkanes with dimethyl disulphide were satisfactory however (Table 1), and the corresponding sulphones were formed in good yield by conventional oxidation with an excess of hydrogen peroxide in glacial acetic acid (Table 2).^{1,5-9} Treatment of the sulphones with aqueous potassium permanganate under reflux afforded the corresponding perfluoroalkane-sulphonates in good yield (Table 2).

TABLE 2
Oxidation reactions

Substrate	Reagent	Product	Yield (%)
$\text{CF}_3\cdot[\text{CF}_2]_4\cdot\text{CF}_2\cdot\text{SMe}$	$\text{H}_2\text{O}_2\text{-AcOH}$	$\text{R}_F\text{SO}_2\text{Me}$	89
$\text{CF}_3\cdot[\text{CF}_2]_6\cdot\text{CF}_2\cdot\text{SMe}$	$\text{H}_2\text{O}_2\text{-AcOH}$	$\text{R}_F\text{SO}_2\text{Me}$	79
$(\text{CF}_3)_2\text{CF}\cdot[\text{CF}_2]_5\cdot\text{CF}_2\cdot\text{SMe}$	$\text{H}_2\text{O}_2\text{-AcOH}$	$\text{R}_F\text{SO}_2\text{Me}$	89
$\text{CF}_3\cdot[\text{CF}_2]_4\cdot\text{CF}_2\cdot\text{SO}_2\text{Me}$	$\text{KMnO}_4\text{-H}_2\text{O}$	$\text{R}_F\text{SO}_3\text{K}$	74
$\text{CF}_3\cdot[\text{CF}_2]_6\cdot\text{CF}_2\cdot\text{SO}_2\text{Me}$	$\text{KMnO}_4\text{-H}_2\text{O}$	$\text{R}_F\text{SO}_3\text{K}$	68
$(\text{CF}_3)_2\text{CF}\cdot[\text{CF}_2]_5\cdot\text{CF}_2\cdot\text{SO}_2\text{Me}$	$\text{KMnO}_4\text{-H}_2\text{O}$	$\text{R}_F\text{SO}_3\text{K}$	81

An alternative pathway¹ for the conversion of long-chain polyfluoroiodoalkanes into the corresponding polyfluoroalkanesulphonic acids *via* the sulphide and sulphone is illustrated by the case of methyl tridecafluoro-*n*-hexyl sulphone, which was converted into its trichloromethyl analogue (78%) by reaction with aqueous sodium hypochlorite at room temperature. The trichloromethyl sulphone was hydrolysed with aqueous potassium hydr-

⁵ B.P. 896,373/1962.

⁶ K. Inukai, T. Veda, and H. Muramatsu, *Bull. Chem. Soc. Japan*, 1966, **39**, 2191.

⁷ R. B. Ward, *J. Org. Chem.*, 1965, **30**, 3009.

⁸ J. Hine and J. J. Porter, *J. Amer. Chem. Soc.*, 1960, **82**, 6118.

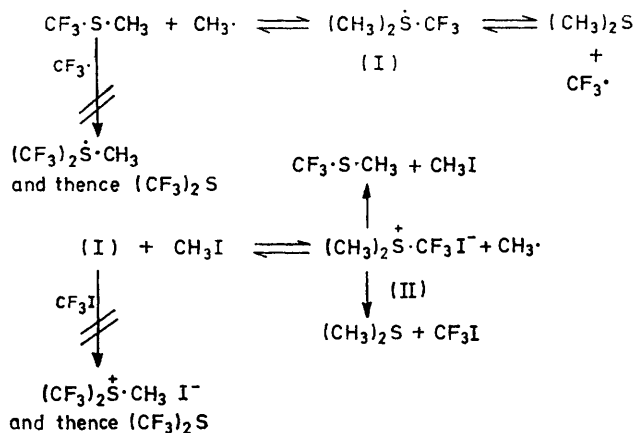
⁹ V. V. Orda, L. M. Yagupol'skii, V. F. Bystrov, and A. U. Stepanyants, *J. Gen. Chem. (U.S.S.R.)*, 1965, **35**, 1631.

¹⁰ R. N. Haszeldine, B. Higginbottom, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 155.

oxide in solvent dioxan to give potassium tridecafluoro-*n*-hexanesulphonate (75%) and 1*H*-tridecafluorohexane (13%).

These results thus extend the range of polyfluoroalkanesulphonic acids, prepared *via* the corresponding methyl polyfluoroalkyl sulphides, to a number which have potential industrial application.

The preparation of methyl trifluoromethyl sulphide in 63% yield by the photochemical reaction of trifluoroiodomethane with dimethyl sulphide has been described previously.¹⁰ It has now been shown that this reaction is reversible. Thus photochemical reaction (180 h) of a mixture of methyl trifluoromethyl sulphide and iodo-



SCHEME

methane (1:4 molar ratio) gave trifluoroiodomethane (54%), trifluoromethane (16%), and hexafluoroethane (17%) (see Scheme).

This reaction scheme, based on that proposed earlier,¹⁰ involves two key intermediates, (I) and (II). The sulphonium iodide (II) cannot be formed directly by reaction of iodomethane with methyl trifluoromethyl sulphide,^{11,12} nor presumably by reaction of trifluoroiodomethane with dimethyl sulphide since heptafluoro-1-iodopropane does not undergo thermal reaction at 100 °C with dimethyl sulphide.¹³ The absence of bis(trifluoromethyl) sulphide as a product suggests that neither methyl trifluoromethyl sulphide nor (I) reacts with trifluoromethyl radicals or trifluoroiodomethane, and is consistent with the observation¹⁴ that methyl heptafluoropropyl sulphide and not trifluoromethyl heptafluoropropyl sulphide is formed in the reaction of heptafluoro-1-iodopropane with methyl trifluoromethyl sulphide.

An attempted thermal reaction of iodomethane with methyl trifluoromethyl sulphide resulted in almost quantitative recovery of reactants.

¹¹ J. F. Harris, jun., *J. Org. Chem.*, 1967, **32**, 2063.

¹² K. E. Rapp, J. T. Barr, R. L. Pruett, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, jun., *J. Amer. Chem. Soc.*, 1952, **74**, 749.

¹³ R. N. Haszeldine, B. Hewitson, and A. E. Tipping, unpublished results.

¹⁴ R. N. Haszeldine, R. B. Rigby, and A. E. Tipping, *J.C.S. Perkin I*, 1972, 1506.

EXPERIMENTAL

Volatile materials were handled in a conventional vacuum system to avoid contamination with air or moisture. Pure products were separated by distillation at atmospheric or reduced pressure, by fractional condensation *in vacuo*, or by preparative-scale g.l.c. [Perkin-Elmer F21 or Pye 105 instrument with columns packed with Silicone SE30 oil (20%) on Celite unless stated to the contrary] and were examined by molecular weight determination (Regnault's method), i.r. spectroscopy (Perkin-Elmer 237 instrument with sodium chloride optics), n.m.r. spectroscopy, and mass spectrometry. For compounds marked with an asterisk, n.m.r. (^1H and ^{19}F) and/or mass spectral data are available as Supplementary Publication No. SUP 20999 (11 pp.).[†] Photochemical reactions were carried out in silica tubes (*ca.* 300 ml) *in vacuo* with the tubes shaken mechanically *ca.* 15 cm from a Hanovia S500 medium-pressure u.v. lamp.

Dimethyl disulphide was obtained commercially and was purified carefully before use. Bis-(2-chloroethyl) disulphide was prepared (67%) from the reaction of ethylene sulphide with sulphuryl chloride¹⁵ and methyl trifluoromethyl sulphide was obtained (86%) from the reaction of trifluoroiodomethane with sodium methanethiolate and dimethyl disulphide in solvent dimethyl sulphoxide.¹⁶ Trifluoroiodoethylene was prepared as reported⁴ and the polyfluoroiodoalkanes were either prepared by literature methods or were gifts from Pennwalt Corporation, or Uginé-Kuhlmann.

Photochemical Reactions with Dimethyl Disulphide.—(a) *Trifluoroiodoethylene.* A mixture of the iodoalkene (2.62 g, 12.5 mmol) and the disulphide (7.05 g, 75.0 mmol), irradiated for 17 h, gave (i) carbon dioxide (0.30 mmol) contaminated with a trace of trifluoroethylene, (ii) a mixture (1.11 g) which was shown by g.l.c. (2 m column at 60 °C) to consist of unchanged iodoalkene (0.10 g, 0.48 mmol, 4% recovered), unchanged dimethyl disulphide (0.42 g, 4.47 mmol, 6% recovered), and an unknown component (0.59 g), (iii) a mixture (4.25 g) of the same unknown component (0.14 g) and unchanged dimethyl disulphide (4.11 g, 43.72 mmol, 58% recovered), (iv) a purple oil which was shown (i.r.) to be mainly dimethyl disulphide contaminated with iodine, and (v) a clear polymeric film which coated the inside of the reaction tube and was not examined further.

The unknown component was isolated by g.l.c. (4 m column at 60 °C) and was identified as *methyl trifluorovinyl sulphide** (0.73 g, 5.72 mmol, 48%) (Found: C, 28.3; H, 2.3%; M^+ , 128. $\text{C}_3\text{H}_3\text{F}_3\text{S}$ requires C, 28.1; H, 2.3%; M , 128), b.p. (isoteniscope) 48 °C; λ_{max} 5.72s (C: C str.) μm .

(b) *Tridecafluoro-1-iodohexane.* A mixture of the iodo-compound (8.92 g, 20.0 mmol) and the disulphide (7.52 g, 80.0 mmol), irradiated for 21 days, gave (i) methane (trace), (ii) a mixture (0.33 g, 4.90 mmol; M , 68) of silicon tetrafluoride, dimethyl sulphide, carbonyl sulphide, and carbon dioxide, (iii) a two-phase liquid mixture (8.90 g), (iv) unchanged dimethyl disulphide (1.12 g, 11.90 mmol, 15% recovered), and (v) a black oil (*ca.* 4 g) which was not examined further.

The lower layer of the two-phase mixture was separated by g.l.c. (7.5 m column at 140 °C) into its components, unchanged dimethyl disulphide (0.51 g, 5.43 mmol, 7% recovered), 2,4-dithiapentane (0.48 g, 4.36 mmol), 1*H*-tridecafluoro-*n*-hexane* (0.98 g, 3.06 mmol, 15%), and *methyl*

*tridecafluoro-*n*-hexyl sulphide** (5.60 g, 15.30 mmol, 76%) (Found: C, 23.0; H, 0.9; F, 67.2%; M^+ , 366. $\text{C}_7\text{H}_3\text{F}_{13}\text{S}$ requires C, 23.0; H, 0.8; F, 67.5%; M , 366), b.p. (Siwoloboff) 131–132 °C.

The upper layer of the two-phase mixture was shown by i.r. spectroscopy and g.l.c. (as above) to be unchanged dimethyl disulphide (1.23 g, 13.1 mmol, 16% recovered) contaminated with a trace of methyl tridecafluoro-*n*-hexyl sulphide.

(c) *Heptadecafluoro-1-iodo-octane.* A mixture of the iodo-compound (10.92 g, 20.0 mmol) and the disulphide (7.52 g, 80.0 mmol), irradiated for 21 days, gave (i) methane (0.09 g, 5.8 mmol), (ii) a mixture (0.28 g, 3.0 mmol; M , 92) of silicon tetrafluoride, carbonyl sulphide, carbon disulphide, and methanethiol, (iii) a two-phase liquid mixture (7.70 g), and (iv) a black oil (*ca.* 10.2 g).

The upper layer (1.02 g) of the two-phase mixture was shown by i.r. spectroscopy and g.l.c. (2 m column at 80 °C) to be a mixture of dimethyl sulphide, carbon disulphide, and unchanged dimethyl disulphide. The lower layer (6.68 g) was separated by g.l.c. (7.5 m column at 130 °C) into its three components, unchanged heptadecafluoro-1-iodo-octane (0.65 g, 1.19 mmol, 6% recovered), 1*H*-heptadecafluoro-*n*-octane* (0.78 g, 1.80 mmol, 10%), and *methyl heptadecafluoro-*n*-octyl sulphide** (4.84 g, 10.39 mmol, 55%) (Found: C, 23.2; H, 0.8; S, 7.2%; M^+ , 466. $\text{C}_8\text{H}_3\text{F}_{17}\text{S}$ requires C, 23.2; H, 0.6; S, 6.9%; M , 466), b.p. 34 °C at 0.1 mmHg.

Distillation of the black oil gave a further quantity of methyl heptadecafluoro-*n*-octyl sulphide (1.58 g, 3.39 mmol, 18%) and a black tarry residue.

(d) *Nonadecafluoro-1-iodo-7-methyloctane.* A mixture of the iodo-compound (11.92 g, 20.0 mmol) and the disulphide (7.52 g, 80.0 mmol), irradiated for 21 days, gave (i) methane (trace), (ii) a mixture (1.79 mmol) of silicon tetrafluoride, carbon disulphide, and dimethyl sulphide, (iii) unchanged dimethyl disulphide (0.41 g, 4.36 mmol, 5% recovered), (iv) a two-phase liquid mixture (7.39 g), (v) *methyl nonadecafluoro-7-methyloctyl sulphide** (5.05 g, 9.79 mmol, 49%) (Found: C, 23.4; H, 0.6; S, 6.3; F, 69.7%; M^+ , 516. $\text{C}_{10}\text{H}_3\text{F}_{19}\text{S}$ requires C, 23.3; H, 0.6; S, 6.2; F, 69.9%; M , 516), b.p. (Siwoloboff) 185–186 °C, and (vi) a black tarry residue (5.34 g).

The upper layer (3.10 g) of the two-phase mixture was separated by g.l.c. (8 m Silicone MS 550 oil at 120 °C) into its components, unchanged dimethyl disulphide (2.67 g, 28.4 mmol, 36% recovered) and 2,4-dithiapentane (0.43 g, 3.9 mmol) and the lower layer (4.29 g) of the mixture was shown by i.r. spectroscopy and g.l.c. (as above) to consist of dimethyl sulphide (0.21 g, 3.45 mmol), methyl nonadecafluoro-7-methyloctyl sulphide (2.61 g, 5.06 mmol, 25%), and 1*H*-nonadecafluoro-7-methyloctane* (1.38 g, 2.93 mmol, 15%).

Oxidation of Methyl Polyfluoroalkyl Sulphides.—(a) *Methyl tridecafluoro-*n*-hexyl sulphide.* The sulphide (3.66 g, 10.0 mmol) was dissolved in glacial acetic acid (16 ml), hydrogen peroxide (16 ml; 27.5% soln.) was then added, and the mixture was stirred under reflux (24 h). Two further portions of hydrogen peroxide (2 \times 10 ml) were added during the reaction period; the first 3 h after the reaction commenced, the second after a further 3 h. The

¹⁵ G. Yu. Epshtein, I. A. Usov, and S. Z. Ivin, *J. Gen. Chem. (U.S.S.R.)*, 1964, **34**, 1961.

¹⁶ R. N. Haszeldine, B. Hewitson, B. Higginbottom, R. B. Rigby, and A. E. Tipping, *J.C.S. Chem. Comm.*, 1972, 249.

[†] For details of Supplementary Publications see Notice to Authors No. 7 (*J.C.S. Perkin I*, 1973, Index issue).

resultant solution was cooled, neutralised with aqueous sodium hydrogen carbonate, and extracted with ether (3 × 30 ml). The extract was dried (Na₂SO₄) and distilled. The residual white solid was sublimed twice *in vacuo* (40 °C) to give *methyl tridecafluoro-n-hexyl sulphone** (3.53 g, 8.87 mmol, 89%) (Found: C, 21.3; H, 0.8; S, 8.3; F, 62.4%; *M*⁺, 398. C₇H₃F₁₃O₂S requires C, 21.1; H, 0.8; S, 8.0; F, 62.1%; *M*, 398), m.p. 73–74 °C.

(b) *Methyl heptadecafluoro-n-octyl sulphide*. A solution of the sulphide (3.73 g, 8.00 mmol) in glacial acetic acid (16 ml), treated with hydrogen peroxide (36 ml; 27.5% solution) under the conditions described in the previous experiment, gave *methyl heptadecafluoro-n-octyl sulphone** (3.14 g, 6.31 mmol, 19%) (Found: C, 22.0; H, 0.6; S, 6.7; F, 64.4. C₉H₃F₁₇O₂S requires C, 21.7; H, 0.6; S, 6.4; F, 64.9%), m.p. 100.5–101.5 °C.

(c) *Methyl nonadecafluoro-7-methyloctyl sulphide*. A solution of the sulphide (3.61 g, 7.0 mmol) in glacial acetic acid (16 ml), treated with hydrogen peroxide (36 ml; 27.5% solution) under the conditions described in experiment (a), gave *methyl nonadecafluoro-7-methyloctyl sulphone** (3.42 g, 6.24 mmol, 89%) (Found: C, 22.2; H, 0.7; S, 5.9; F, 65.6. C₁₀H₃F₁₉O₂S requires C, 21.9; H, 0.5; S, 5.8; F, 65.9%), m.p. 84–85 °C.

Oxidation of Methyl Perfluoroalkyl Sulphones.—(a) *Methyl tridecafluoro-n-hexyl sulphone*. A mixture of the sulphone (1.39 g, 3.5 mmol), potassium permanganate (1.42 g, 9.0 mmol), and water (5 ml) was heated under reflux and vigorously stirred (20 h). The resultant mixture was filtered and the residue was extracted with ethanol (100 ml). The filtrate was neutralised with dilute hydrochloric acid, then evaporated to dryness and the residue was extracted with ethanol (20 ml). The combined ethanolic extracts were distilled and the residue was dissolved in acetone and reprecipitated with chloroform to afford potassium tridecafluoro-n-hexane-1-sulphonate* (1.13 g, 2.58 mmol, 74%) (Found: C, 16.5; S, 7.4; F, 55.9. Calc. for C₆F₁₃KO₃S: C, 16.4; S, 7.3; F, 56.4%), m.p. 272 °C.

(b) *Methyl heptadecafluoro-n-octyl sulphone*. A mixture of the sulphone (1.99 g, 4.0 mmol), potassium permanganate (3.16 g, 20.0 mmol), and water (5 ml) was heated under reflux and vigorously stirred (24 h). The excess of permanganate was destroyed with hydrogen peroxide (*ca.* 7 ml; 100 vol.) and the resultant material worked up as in the previous experiment to afford potassium heptadecafluoro-n-octane-1-sulphonate (1.47 g, 2.73 mmol, 68%) (Found: C, 18.1. Calc. for C₈F₁₇KO₃S: C, 17.8%), m.p. 284 °C (lit.¹⁷ 285 °C).

(c) *Methyl nonadecafluoro-7-methyloctyl sulphone*. A mixture of the sulphone (1.64 g, 3.00 mmol), potassium permanganate (1.42 g, 9.00 mmol), and water (5 ml), treated as described in experiment (a), gave *potassium nonadecafluoro-7-methyloctane-1-sulphonate** (1.42 g, 2.42 mmol, 81%) (Found: C, 18.4; S, 5.4; F, 61.4. C₉F₁₉KO₃S requires C, 18.2; S, 5.7; F, 61.4%), m.p. 248–249 °C.

Reaction of Methyl Tridecafluoro-n-hexyl Sulphone with Sodium Hypochlorite.—A mixture of the sulphone (1.00 g, 2.51 mmol) and aqueous sodium hypochlorite (50 ml; 14% available Cl) was stirred vigorously at room temperature (192 h; the long reaction time results from poor mixing of the solid sulphone and the aqueous solution) and the resultant material was extracted with ether (3 × 20 ml).

The extract was dried (Molecular Sieve Type 4A) and the ether was removed by distillation to afford a white solid which was sublimed twice *in vacuo* to give *trichloromethyl tridecafluoro-n-hexyl sulphone** (0.98 g, 1.95 mmol, 78%) (Found: C, 16.9; F, 49.0. C₇F₁₃Cl₃O₂S requires C, 16.8; F, 49.3%), m.p. 18–19 °C.

Hydrolysis of Trichloromethyl Tridecafluoro-n-hexyl Sulphone.—A mixture of the sulphone (0.60 g, 1.19 mmol), potassium hydroxide (0.28 g), and aqueous dioxan (6 ml; 60% v/v), sealed in a Pyrex tube (100 ml) and shaken at 100 °C (168 h), gave (i) carbon monoxide (0.02 g, 0.88 mmol), (ii) a two-phase liquid mixture of which the upper layer consisted of a mixture (6.83 g) of water and dioxan and the lower layer was shown by i.r. spectroscopy and g.l.c. (2 m column at 120 °C) to consist of 1*H*-tridecafluorohexane (0.05 g, 0.15 mmol, 13%) and dioxan (0.09 g), and (iii) a solid residue.

The residue was extracted with acetone (2 × 10 ml) and the acetone removed by distillation to afford a yellowish solid (0.44 g). This solid was purified by precipitation from an acetone solution with chloroform to give potassium tridecafluoro-n-hexane-1-sulphonate (0.39 g, 0.89 mmol, 75%), m.p. 274 °C.

Photochemical Reactions of Bis-(2-chloroethyl) Disulphide with Polyfluoromonoiodoalkanes.—Two photochemical reactions were investigated. The first reaction, with trifluoroiodomethane (117 h irradiation), gave (i) unchanged iodoalkane (46%), (ii) volatile products which included trifluoromethane, chlorotrifluoromethane, silicon tetrafluoride, ethane, and ethylene, and (iii) a black involatile oil which on distillation gave unchanged disulphide only. The second reaction, with heptafluoro-1-iodopropane (237 h irradiation), gave volatile products which included 1*H*-heptafluoropropane, 1-chloroheptafluoropropane, silicon tetrafluoride, chloroethane, and ethane and a black involatile oil from which only unchanged disulphide could be obtained on distillation.

Photochemical Reaction of Iodomethane with Methyl Trifluoromethyl Sulphide.—A mixture of iodomethane (0.55 g, 3.87 mmol) and methyl trifluoromethyl sulphide (0.11 g, 0.91 mmol) when irradiated for 180 h, gave (i) methane (0.009 g, 0.47 mmol; *M*, 19), (ii) a mixture (0.13 g, 0.78 mmol) which was shown by i.r. spectroscopy and g.l.c. (4 m dinonyl phthalate at 20 °C) to consist of trifluoroiodomethane (0.09 g, 0.44 mmol, 54%), trifluoromethane (0.01 g, 0.13 mmol, 16%), and hexafluoroethane (0.01 g, 0.07 mmol, 17%) together with traces of three unidentified components, (iii) unchanged methyl trifluoromethyl sulphide (0.01 g, 0.10 mmol, 12% recovered), (iv) unknown volatile material (0.15 mmol), and (v) a small amount of a black oil containing iodine.

An attempted thermal reaction of iodomethane (0.45 g, 3.17 mmol) with the sulphide (0.12 g, 1.03 mmol) at 168 °C (70 h) gave unchanged reactants (99%) only.

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¹⁷ T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 1957, 2640.